Investigation and Engineering of the Homogeneity and Current Injection of Molecular Beam Epitaxy Grown III-Nitride Nanowire Ultraviolet Light Emitting Diodes

DISSERTATION

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Abstract

Self-assembled nanowires are attractive because of their innate ability to effectively strain relax without the creation of extended defects. This allows for interesting heteroepitaxial growths and extreme heterostructures. III-Nitride nanowires are of particular interest because of the wide range of direct bandgaps available in the material system, spanning from the infrared to the deep ultraviolet finding uses in sensors, photovoltaics, lasers and LEDs. The work presented here will be focused on nanowire LEDs with emission in the ultraviolet grown by molecular beam epitaxy. The first part of this work will discuss the possible inhomogeneities present in self-assembled nanowires and how these manifest themselves in ensemble devices. The effect of nonuniformities (specifically shorts) on the current spreading in devices where many individual diodes are wired in parallel is then addressed, and the use of a short-term-overload bias is shown as a way to reduce the presence of nonuniformities, increasing the efficiency of ensemble devices. Next, alternative substrates are investigated, with the growth of high-quality GaN nanowires being demonstrated on polycrystalline foils, the fabrication of the first UV LED grown directly on metal foil follows. The final portion of this work begins by addressing the grain-dependent uniformity issues present with growth on bulk polycrystalline foils through the use of thin nanocrystalline metal films and amorphous metals. Finally, a different nanowire LED structure is discussed in which the upper portion of the nanowires is coalesced to form a “thin-film” transparent conductive layer, enabling the substitution of the traditional fully conformal thin metal top contact with only a current spreading grid.
This work is dedicated to my parents and siblings for instilling and fostering the importance of knowledge and curiosity.
Acknowledgments

I would be nowhere close to where I am now without the help of many people. First, I must express my appreciation for all my group members, past and present. Dr. Thomas Kent and Dr. ATM Golam Sarwar for showing me not only how to operate MBE, but also the intricacies of device processing, and the ins and outs of the PINLED project. Sarwar really showed me the small things that are often overlooked in the world of MBE when it comes to making a working heterostructure. And although I didn’t share any specific projects with Dr. Zihao Yang or Dr. Brandon Giles, the work ethic and meticulousness of their work set the tone early on in my time here. When I came to OSU and joined the Myers group, I was accompanied by John Jamison. John has nearly single handedly kept the optics lab running in recent years and somehow managed to put up with sitting next to me for nearly our whole stay here. He has always been around to eagerly brainstorm ideas, which led to many (un)productive (un)scientific discussions, which always remind me that science doesn’t have to be serious, and can always be exciting.

The group added Elline Hettiaratchy last year, and I’ve had the pleasure of training her in the ways of MBE. For better or worse, she joined at a time where she very quickly realized what MBE actually stands for. She eagerly attacks every project, which is good, because there are a number of them that are very exciting right now. Darpan Verma is the newest member; he is a fast learner who is very gung-ho about the nanowire LED project. I’m excited to pass these projects on to a team of energetic hands.

I owe a great deal to my advisor, Prof. Roberto Myers. He brought me into his group when I arrived without an advisor. Since that day, he has only encouraged me, getting just as excited as me about some strange ideas, some of which turned into award winning conference talks. He didn’t
even hesitate when I proposed to leave for a summer internship in industry (something I came away from with a whole new outlook on research), showing that he cares about his students’ futures as much as their current state. I have learned a great deal from him, and will always be grateful.

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Fields of Study

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   Electronic Materials
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Chapter 1. Introduction and Overview

1.1 III-Nitrides for UV Optoelectronics

The material system of III-Nitrides has a wide range of applications spanning from high power/high frequency electronics because of the high dielectric breakdown voltage [1]–[4], electro-mechanical systems because of the piezoelectric properties [5]–[7]; and due to the wide range of bandgaps, they have shown applications in chemical sensors [8]–[11], photovoltaics [11]–[15], lasers [16]–[19] and LEDs [20]–[25] (Figure 1.1(a)). An abundance of optoelectronic applications are made possible because of the wide range of bandgaps, from ~0.7 eV (InN) [26]–[28] to 6 eV (AlN) [29]. With the ternary InGaN systems maintaining a direct bandgap from infrared (IR) to ultraviolet (UV), its adoption into solid state lighting is hopeful. Solid state lighting is of significant interest for general lighting applications as widespread implementation could result in drastic reductions in worldwide energy consumption [30]. The nitride system can also be pushed deep into the UV-C range by moving closer to AlN (Figure 1.1(b)).

The UV is of particular interest for III-Nitride optoelectronics, with various wavelengths in this range used for things such as curing of epoxies, photolithography, and germicidal disinfection [31]. Current UV technology is largely based on mercury halide lamps which are bulky, contain toxic mercury, and have limited wavelength selectivity due to relying solely on atomic energy transitions [32]. However, the efficiency of solid state UV devices drops exponentially as it is pushed deeper into the UV [33] (Figure 1.2). This is for a few different reasons. To get to the deeper wavelengths, higher Al compositions must be used, but efficient p-type doping becomes more difficult as the Al% is increased [34]–[36]. Also, at Al compositions as low as 25%, the polarization of the light switches from TE to TM polarized, which drastically
decreases the light extraction efficiency in top emitting devices [37], [38]. This can be pushed to higher Al% with the use of compressive strain [39], [40] but there are no reports yet of reaching beyond ~80%. Another issue with adding more Al is that the increased Al adds strain which can then generate threading dislocations which are non-radiative recombination centers and provide paths for shunt leakage [41], [42].

Figure 1.1: (a) Applications of III-Nitride materials, clockwise from top: high frequency HEMTs [2], electro-mechanical systems [7], sensors [8], photovoltaics [11], lasers [19], and general lighting [25]. (b) Band gap vs. lattice constant of the III-Nitride system
Advantages of Nanowires

Nanowires provide a unique solution to these aforementioned problems due to their ability to strain relax (Figure 1.3(a)). If the diameter can be thin, they are essentially able to be grown infinitely thick, on even a highly mismatched substrate, without formation of defects [43]. On top of this, due to the strain fields in the base of the nanowire, any threading dislocations that start in the substrate, or generated lower in the nanowire, tend to terminate at the sidewalls leaving a defect free upper section (Figure 1.4(b)) [44]–[46]. The excellent strain management allows for growth on a wide variety of substrates, with III-Nitride nanowires grown on materials such as Si, amorphous glass, and metal [47]–[56](Figure 1.4). Because they are essentially stand-alone structures and have great substrate versatility, they could also prove very promising for flexible electronics [57]–[64].

Figure 1.2: Chart of LED efficiencies in the UV wavelengths (from [32])
Another bonus of the ability of nanowires to efficiently strain relax is that it allows for huge flexibility in heterostructure engineering without the concern of lattice mismatch. One of the most effective ways of realizing doping (especially p-type) in these materials is through polarization doping [65]–[69]. Most nanowires grow along the (000\(\bar{1}\)) (or N-polar) direction [70], thus achieving p-type doping when grading from GaN to AlN. Polarization doping with steep gradients (~5%/nm) can result in compensation of the background donors and with the free hole density approaching the polarization charge [71], and even impurity-dopant free nanowire LEDs have been fabricated [72]. Nanowires have another advantage over their thin film counterparts when it comes to p-type doping, which is increased Mg incorporation [22], [73]–[75]. The strain fields in nanowires and the ability to grow structures laterally and radially could allow for tuning of the polarization fields in the heterostructure [23], [76]–[78], which can be used to increase electron-hole overlap in the active region, improving the light emission.
Besides the problem of p-type doping in III-Nitrides, and getting the electrons and holes to recombine and emit a photon, there is the added issue of light extraction efficiency (LEE), especially when pushing toward deeper UV wavelengths. The previously discussed change in emission polarization from top-emitting to side-emitting at higher Al% could be partially assuaged by the unique strain engineering opportunities in nanowires (core-shell structures). However, nanowires can also be thought of as a very short fiber optic cable, and if diameter and length are

![Figure 1.4: SEM images of MBE grown GaN nanowires grown on various substrates: (a) Si (from [47]), (b) SiOx (from [51]), (c.1) Ti and (c.2) Mo thin film on Si (from [55]) (d) different grains on a polycrystalline Ti foil and (e) a Ta foil (from [58])](image-url)
tuned correctly, there can be extraordinary potential gains in photonic extraction [79]–[84]. That being said, there is a reason that nanowire devices are still not up to par with thin film, with efficiencies only in the m% range.

1.3 Disadvantages of Nanowire Optoelectronics

1.3.1 Defects

One of the biggest advantages of nanowires is also possibly their biggest downfall. The same large surface area to volume ratio that allows for efficient strain relaxation and potential optical confinement is also a very large defect. The sidewalls result in radial discontinuities in the band diagram [23], [85], [86] leading to fermi level pinning and reduced electron hole overlap, both will reduce overall device efficiency. If the carriers are pushed toward the surface, they can non-radiatively recombine or overshoot the active region without combining radiatively. The effect of the surface related defects can be mediated using in-situ techniques such as passivating the surface by radially coating with a higher bandgap material (such as AlN) [21], [87], [88] or ex-situ techniques like planarization or oxidation [49], [89]–[91].

1.3.2 Nonuniformities

When looking at what would be a useful optoelectronic device, one would want a sizeable device area of at least a few microns by a few microns. However, each individual nanowire is an LED and they are typically only ~100 nm in diameter; this means that for a mesoscopic device many nanowires must be wired in parallel. Previous studies showed that the nonuniformities present in an ensemble device, i.e. one which has many nanowires wired in parallel, have a large effect on device efficiency. Figure 1.5 (a,b) show the IV curve of a mesoscopic InGaN based LED with a threshold voltage (V_{th}) of ~6 V [90]. This work essentially counted the number
of nanowire LEDs that were lighting up as the bias was increased, measuring \( \sim 10 \times 10^6 \) spots at \( V_{th} \) of the mesoscopic device. They saw that \( \sim 60\% \) of nanowires were observed to luminesce \( \sim 2 \) V prior to the \( V_{th} \) of the mesoscopic device. Even at 10 V, where the number of spots increases by another 10\%, the number of spots is still \( < 1\% \) of the number of nanowires present in the device. Thus, most of the nanowire devices, supposedly wired in parallel, are not luminescing at all under electrical injection. Another study by Bavencove et. al [92], used confocal microscopy (Figure 1.1(c-e)) to show that some nanowires begin luminescing early, and upon higher injection currents these continue to get brighter with very few additional nanowires beginning to emit light.

Figure 1.5: (a) IV curve of a nanowire LED with a contact area of 0.2 mm\(^2\) on a linear and (inset) logarithmic scale and (b) number density of electroluminescence spots as a function of the forward bias. The inset is a screen shot of a movie showing the EL during a ramp from 3 to 10 V forward bias. (from [90]). \( \mu \)-EL confocal mappings carried out under (c) 1 mA, (d) 50 mA and (e) 100 mA macroscopic injection CW-current (from [92])
Self-assembled nanowires have inherent nonuniformities with obvious differences in height and diameter observed in these systems. The distribution in diameter in particular is problematic as it results in different growth rates. Thinner nanowires have comparatively higher growth rates, as their growth front (top of the nanowire) is smaller, requiring fewer atoms to result in an increase in height. The differences in height can result in difficulties making a conformal top contact. Making good, and even, contact is essential to maximize the efficiency of a nanowire device, as the current must be spread evenly though all of the nanowires. If very uniform height was desired, a post-growth planarization and back etch could be done to trim any excessively tall nanowires.

![Figure 1.6: Variation in PL from InGaN with variation in NW diameter. Data from [93], [94]](image)

Another potentially more deleterious effect of diameter distribution is the resulting compositional nonuniformities. This has been controllably observed in InGaN nanowires through the use of patterned substrates with holes of different diameter and spacing (Figure 1.6) [93]–[96].
It was found that samples with a very low fill factor (FF), or the fractional area occupied by nanowires, there is a blueshift in the emission with increasing nanowire diameter. However, when the density of the nanowires is increased, increasing nanowire diameter resulted in a redshift in the emission.

These compositional nonuniformities arise because the supply of each atomic species is dependent on *directly impinging* atoms to the nanowire tops as well as the *diffusion* of adatoms to the column/top surface from sidewalls/substrate. The more diffusive species (In in InGaN or Ga in AlGaN) species is thought to only stick where they land, as their diffusion length at the growth temperature is limited by desorption. For instance, the work outlined in Figure 1.6 grew InGaN at 790-825°C, well beyond the desorption temperature of In, thus the diffusive contribution from adatoms of this species is ignored.

In most cases, the growth front is the most preferential location for adatom incorporation. At one extreme, a thin film would ideally give an equal concentration of the diffusive species everywhere (ignoring phase separation), as there is an equal likelihood of these atoms sticking everywhere. However, there are limited preferential sites for the short lifetime species to stick when dealing with nanowires.

The diameter dependence of the In composition for specific cases has been discussed briefly before [93], [94] but is illustrated in detail in Figure 1.7. There are two types of adatoms: species A (long lifetime) which can diffuse two grid spacings and species B (short lifetime) which incorporates only if it lands on a nanowire, otherwise it desorbs from the system. For the cases of low nanowire density (case 1 and case 2), the individual nanowire has only one B atom and each of the 5 A atoms in range has only one nanowire to migrate toward. With the small diameter of
case 1, one A atom lands on the nanowire, and 4 diffuse toward it, resulting in 83% A. As the nanowire diameter increases, it becomes able to gather more A atoms (from diagonal contributions in this schematic), increasing the A% to 90%. When the nanowire density is higher, each nanowire still gets only 1 B atom, and again, with the nanowire diameter being small, there is no contribution of A atoms from the diagonal locations. However, now with more nanowires present, each of the 5 A atoms can migrate toward 12 different places, thus case 3 would give 29% A. When the
nanowire diameter increases, (like case 2) 4 additional A atoms become in range. However, because the density of the nanowires is higher, there are now even more nanowires in range, resulting in 24 different locations for each A atom to move to, reducing the amount of A to 27%. In short, when the nanowire density is low, increasing the size decreases the amount of the more volatile species i.e. In, giving a blueshift in emission. But if the density is high, the concentration of the volatile species is proportional to nanowire size, thus giving a redshift in emission with increasing size.

1.4 Overview

This thesis will show the use of high throughput measuring techniques for measuring nonuniformities in nanowire devices and present ways to create a more homogenous distribution in an effort to achieve more efficient nanowire-based UV LEDs. Chapter 2 will discuss how the inhomogeneity in nanowire sizes effects device performance and although the use of InGaN tunnel junctions may yield lower threshold voltages, they also introduce a large amount of nonuniformity. Chapter 3 will look into the effect of these In% inhomogeneities in the tunnel junction as well as the identification and selective removal of nano-shorts using a reverse bias short-term-overload technique. Chapter 4 introduces a step toward a potential alternative to achieving efficient current injection without the use of an InGaN tunnel junction through direct growth of nanowire LEDs on polycrystalline metals. However, this method presents its own additional nonuniformities related to the underlying grain structure, which will be discussed. Chapter 5 will show work toward mitigating the non-uniformities observed in the previous chapter through the use of nanocrystalline metal films and amorphous metals. In conjunction with these explorations, the effect of a nanowire/metal/substrate interface on the current injection into the bottom of the nanowire is
investigated. Lastly the top portion of the nanowires is drastically redesigned, coalescing the nanowires at the top surface, allowing for an unconventional design using a non-conformal top contact, increasing the light extraction efficiency of nanowire UV LEDs. Some of these chapters have already been published by the author in peer reviewed journals [58], [97], [98] with some additional published work also present in appendices [99], [100].
Chapter 2. Measuring Nanowire Diode Uniformity at the Nano and Mesoscale

In order to develop efficient LEDs, the degree of nonuniformity among the nanowires must first be able to be quantified. A large degree of structural nonuniformity comes from the self-assembled growth process. At the nanoscale, the differences in sizes result in a distribution of electrical characteristics which then manifest as a distribution in characteristics in the fully processed ensemble devices. Some contents of the work in the following chapter were previously published by the author [98].

2.1 Material Synthesis

Nanowires are grown via plasma assisted molecular beam epitaxy (PAMBE) in a Veeco Gen930 system having a background pressure of \( \sim 5 \times 10^{-11} \) torr. The nitrogen plasma is provided by a Veeco nitrogen plasma source. Standard Knudsen effusion cells were used for Al, Ga, and In, and the fluxes measured via beam equivalent pressure (BEP). The growth temperatures of the substrate are measured using a calibrated pyrometer. A two-step method is used to separate control of nucleation density and vertical growth rate, where a brief nucleation period occurs at a relatively lower temperature than the bulk of the growth [101].

During the colder nucleation step, the impinging adatoms have relatively low surface mobility and form isolated GaN seeds. When the temperature is increased, the surface diffusion length of adatoms is increased. Then all impinging atoms will migrate to an existing GaN seed, and growth proceeds vertically, thus controlling the nanowire density. Nanowires can still be formed without a two-step approach [47], [102], [103], as when they reach a certain height, the
shadowing of existing nanowires prevents additional formation of GaN seeds. The two-step process allows growth to proceed in a more controlled self-assembled manner than a one-step approach and does not rely on the expensive and time-consuming process of patterned substrates. However, the disadvantage is that self-assembled methods will always rely solely on the stochastic motion of adatoms, resulting in higher degrees of nonuniformity than growth on a patterned substrate.
During the growth of GaN nanowires, the random impingement and movement of Ga and N adatoms results in a distribution of sizes, and location, of GaN seeds. In a random matrix, each nanowire will feel the shadowing effects of neighboring wires differently, resulting in uneven vertical growth rates. As previously discussed in section 1.3, the growth rate is also affected by the diameter of a nanowire, with the situation becoming even more complicated when discussing ternary materials such as (In or Al)GaN.

For this study, PAMBE was used to grow two different LED structures on Si. Figure 2.1 (a,b) shows the two structures, both grown on Si wafers with conductivity <0.005Ω·cm. The oxide from the surface of the Si was desorbed in-situ by heating to 1000°C for two minutes, at which point the reflection high energy electron diffraction (RHEED) pattern was observed to transition from cloudy to streaky. The fluxes of Al, Ga, and In, were of 3.85×10⁻⁸, 5.85×10⁻⁸, and 7.8×10⁻⁸, respectively. The nitrogen plasma was operated at 350 W, and a nitrogen over-pressure of ~3×10⁻⁵ was used, giving a growth rate of ~3 nm/min. Polarization grading is used to aid the doping of these structures using a sub monolayer (ML) shutter pulsing technique. Because >90% of the nanowires are known to grow N-face (000\textbar1) [70], grading from GaN to AlN will yield negative bound polarization charge, creating a repulsive Coulombic potential, resulting in effective p-type doping. In the same manner, n-type doping can be achieved by grading from AlN to GaN.

The first structure is grown directly on p-Si, having no tunnel junction (TJ) and consists of a 100 nm p-type section at 790°C, graded linearly from GaN to AlN co-doped with Mg. This is followed by a set of three 3 nm AlGaN quantum wells with 5 nm AlN barriers at (grown at 840°C), and then a 100nm n-type section graded from AlN to GaN co-doped with Si at 790°C. The high Al composition layers directly after the active region result in the formation of an Al-rich shell
which acts as effective surface passivation [21], [87], [88], [101]. However, in this structure, the p-Si/p-GaN interface has a large (~2 eV) valence band offset, which inhibits hole injection into the device.

The second structure removes this offset barrier by growing on n-Si and integrating an InGaN tunnel junction [104]–[106]. To investigate how nanowire diameter manifests at the mesoscopic level, the sample without a TJ is nucleated 35°C cooler, yielding smaller diameter nanowires (Figure 2.1(c-f)). The top part of the second structure is identical to the first, but the bottom section first consists of 110 nm of n-GaN grown at 790°C. The temperature is decreased to 700°C, and 15 nm of n++ GaN is grown, after which the temperature is dropped further to 600°C and ~2.5 nm of nominally 25% InGaN, followed by 15 nm of p++ GaN. The temperature is ramped back to 790°C before starting the p-type graded section. The integration of a polarization engineered TJ in nanowires was previously observed to decrease the threshold voltage by ~6V [106]. This resulted in decreased efficiency droop and doubled the amount of injection current sustainable prior to device failure, increasing the light output by 3.5×. However, this paper only investigated the mesoscopic characteristics of ensemble devices, and any information about the nanoscale characteristics were left unknown.
2.2 Nonuniformities at the Nanoscale

A first order approximation of one possible nonuniformity, resistance, can be made by treating nanowires like macroscopic wires which follow Pouillet’s law \( R = \rho l / A \). As seen in the previous SEM images (Figure 2.1(c-f)), there is a sizeable discrepancy in nanowire diameters between samples due to the different nucleation conditions, 85±17 nm without and 140±27 nm with a TJ. However, within each sample there are also the additional nonuniformities due to the self-assembled growth process, resulting in a ~±20% discrepancy in nanowire diameter in each individual sample. From cross-sectional SEM measurements, the nanowire heights without and with a TJ are ~220 nm and ~365 nm, respectively. The top section of the nanowire heterostructures are identical, thus the extra height in the TJ sample comes from the n-GaN and TJ region, as expected.

These inherent structural nonuniformities manifesting from the self-assembled growth, will then result in a distribution of resistances within an ensemble device. Figure 2.2(a) shows the

![Figure 2.2](image)

*Figure 2.2: (a) A plot of resistance \( R = \rho l / A \) vs diameter vs height of GaN nanowires using \( \rho = 2 \, \Omega \text{cm} \) [107], stars mark the average no TJ (blue) and TJ (red) nanowire sizes. (b) A zoomed in image of the plot of simple resistance as a function of nanowire diameter and height, showing the distribution in resistances resulting from a typical standard deviation in nanowire sizes.*
resistances of p-GaN nanowires (ρ= 2 Ωcm [107]) across a wide range of diameters and heights. Obviously, resistance increases linearly with increasing height and is inversely proportional to the square of nanowire diameter, but it can be seen that these discrepancies in size can result in huge differences. Assuming the resistance of the top portions are the same and that the TJ region contributes no resistance, if the nanowires in both samples follow Pouillet’s law, the TJ sample should be ×1.6 less resistive, simply due to the difference in size. Figure 2.2(b) shows a magnified portion, outlining the variation in resistances of GaN nanowires that have typical variations of ±10% in height and ±20% in diameter. The size distributions alone could result in nanowires with resistances >±70% away from the average for the TJ and nearly ±60% without the TJ.

This is a broad stroke example, and it is important to reiterate that these resistances are not actual resistance of these nanowire heterostructures, only a rough approximation to visualize the potential large effects of these nonuniformities. On top of this there are additional higher order effects not considered here. For instance, fermi level pinning at the surface [23], [85], [86] would reduce the effective conductive area of the nanowire to a small core region, giving extra diameter dependence. Perhaps most importantly pertaining to this investigation, is the additional diameter dependence of the In incorporation [93]–[96] which would be in the crucial TJ region; and for the same reasons there is also the additional possible change in AlGaN composition, which will be discussed more in chapter 3. All of these change the overall resistance, creating a very inhomogeneous system which is difficult to model.

2.3 Conductive AFM for Individual Nanowire Current-Voltage Curves

Conductive atomic force microscopy (cAFM) was done by Camelia M. Selcu in the NanoSystems Laboratory on a Bruker AXS Dimension Icon AFM system using a Bruker
SCM-PIT, platinum-iridium tip. The cantilever is grounded while the conductive tip is placed in contact with the top of the nanowire, typically with a force of ~100 nN. Because the samples in this study are grown on conductive Si, the bottom electrical contact is made by applying silver paste to the back of the Si wafer and mounting to the AFM stage. A bias is then applied across the sample and the current is measured (Figure 2.3).

Because the tip is smaller than the diameter of the nanowires, IV curves can be acquired by placing the tip over individual nanowires on both samples (Figure 2.4(a)). What is obvious at first glance is the reduction in $V_{th}$ of the nanowire diodes by ~2 V, to ~4.6 V from the tunnel junction (Figure 2.4(b)). The characteristics of the nanowires on p-Si were difficult to determine accurately via cAFM, as the maximum applied bias was limited by the equipment. Thus, it is not always possible to achieve full turn-on of a single nanowire device using cAFM. And even though the IV characteristics are measured from the region of the curve at the highest applied bias, $dI/dV$ can still be changing rapidly, leading to a skew of the $V_{th}^{nano}$ toward lower values and an underestimate of the single nanowire conductance ($G_{nano}$), compared to what would be measured at higher bias. The samples without the TJ also show higher leakage currents at -1 V. However, because of differences in nanowire diameter and coalescence, it is not possible to ascribe
this to the differences in heterostructure alone. The distribution of all measured characteristics are fit to Gaussian distribution curves. Despite having almost exclusively better device metrics, it is worth noting here that the TJ devices have a much wider distribution of characteristics than their non-TJ counterparts, which will be discussed more in the following chapter.

2.4 Conductive Atomic Force Microscopy for Areal Current Mapping

Conductive AFM is not limited to single point measurements, and in conjunction with typical AFM topography measurements can be used to take area maps of current under a specific bias using PeakForce-TUNA mode at a scan rate of 0.5 Hz. Figure 2.5 shows the AFM topography maps, revealing the tops of individual nanowires, with the same diameter variations that were observed via SEM discussed earlier, with their respective current maps for each sample at a +7 V bias below. The sample without the TJ has large areas passing less than 50 pA. The TJ clearly passes more than an order of magnitude higher current at the same bias, significantly more than
the ×1.6 difference estimated from size effects alone. Thus, the TJ must aid in the current injection for these devices.

To aid in a quantitative analysis of the current maps, histograms are made from each cAFM current map (Figure 2.6). These histograms provide statistics on individual pixels. To obtain statistics with respect to individual nanowires, the vertical axis is converted to “fraction of nanowires” by determining the number of pixels per nanowire from SEM measurements. Under +7 V bias, the histograms show average currents of 295 and 86 pA for the TJ and no TJ samples, respectively. This is a result of nearly 50% of the nanowires in the TJ sample yielding currents greater than 250 pA; whereas at the same bias, 95% of nanowires without a TJ pass less. Looking at the cumulative distribution of nanowire currents (inset Figure 2.6), the top 10% of the TJ sample passes more than ×3.5 the current than the top 10% of nanowires without a TJ. Another observation

![AFM height scans](image)

**Figure 2.5:** AFM height scans for samples (a) with no TJ and (b) with a TJ. cAFM images under +7 V bias for samples (c) with no TJ, and (d) with a TJ. Scale bars for all images are 1 μm (adapted from [98])
is that the integration of the TJ significantly increases the full width at half maximum (FWHM) of the current distribution from 87 to 227 pA. Now having insight into the nanoscale characteristics of the two types of nanowire LEDs, the distribution of device scale characteristics are investigated.

![Histogram of current distribution profiles at +7V from cAFM images for samples without a TJ (red) and with a TJ (blue). Inset shows the cumulative distribution profiles for each. (adapted from [98])](image)

**Figure 2.6:** Histogram of current distribution profiles at +7V from cAFM images for samples without a TJ (red) and with a TJ (blue). Inset shows the cumulative distribution profiles for each. (adapted from [98])

### 2.5 Manifestation of Nanoscale Uniformity at the Mesoscopic Scale

#### 2.5.1 Device Fabrication Procedure

Ensemble LED devices were made using standard cleanroom processing techniques (Figure 2.7). First the presence of any surface oxide was etched by dipping in concentrated HCl for 30 s. Then the deposition of a semi-transparent 10 nm Ti/ 20nm Au top contact was immediately done via e-beam evaporation. This was followed by the spin-on coating of a positive photoresist (S1813), and patterning of devices of various sizes via photolithography. The metal layer was removed using a wet etch consisting of TFA and HCl. Nanowire device mesas were then etched using a Cl₂/BCl₃/Ar reactive ion etch (RIE).
2.5.2 Ensemble Device Current-Voltage Curves and Electroluminescence

The electrical characteristics of ensemble devices were measured using a Keithley 2604B sourcemeter to collect IV curves. Figure 2.8(a) shows multiple curves collected from different 300×300 µm devices for samples both with (blue) and without (red) the integrated TJ. From the many ensemble devices tested, the addition of a TJ shows an average decrease in $V_{th}^{\text{meso}}$ by nearly 6 V (10.8 V to 4.9 V). The TJ sample shows a mesoscopic ensemble conductivity ($G^{\text{meso}}$) nearly $\times 1.6$ which could partly be attributed to the differences in nanowire geometry (larger
diameter). Combined with the average 5.5 V decrease in $V_{th}$, results in 2× reduction in power dissipation and a decrease in joule heating of nearly 70%. These predictions agree with the enhancement in electroluminescence and increased device lifetime observed in previous reports [106].

A small population of nano-shorts, nanowires with very high conductivity, was also revealed by cAFM, which will be discussed in detail in chapter 3. But now it is worth noting that these nearly-ohmic nano-shorts would result in a slight increase in $dI/dV$, especially at lower forward bias voltages, and also increase the reverse bias leakage current. The mesoscopic device leakage current ($I_{leak}^{meso}$) for both mesoscopic samples, mainly in the range of 100’s of pA, are far higher than those of the single nanowire measurements, which could be attributed to the presence of nano-shorts now being wired in parallel. The TJ sample exhibits a slightly lower leakage current on average. This cannot be solely ascribed to the difference in heterostructure (presence of TJ) because of the morphological differences between samples and the possible difference in the

Figure 2.8: (a) IV curves on mesoscale devices, the shaded regions represent the range of IV curves measured for devices without a TJ (red) and with a TJ (blue). The histograms of (b) threshold voltage (c) differential conductance, and (d) leakage current at -1 V from mesoscopic devices. (Adapted from [98])
number of shunt paths in the ensemble devices. Somewhat unsurprisingly, all the mesoscopic characteristics of the devices manifest as an amalgamation of the population of different types of nanowires wired in parallel. This validates the use of cAFM to acquire nanowire LED device properties without necessitating device processing.

Notably, there is again a much greater distribution of characteristics in the ensemble devices with the TJ than without. This is likely due to the addition of In inhomogeneities in the TJ. Figure 2.9 shows trends for three specific devices, over the distance of approximately 1.5 cm from the edge of the 3” Si substrate toward the center. The IV curves show that the threshold voltages for these devices also increases from 4 V to 5 V from the edge of the wafer toward the center, along with a slight decrease in the differential conductance. Aside from systematic trend toward more resistive devices at the edge, there are also discrepancies in emission wavelength between devices. The normalized EL spectra from the three devices on the same sample at injection current densities of 160 mA/cm² show an emission peak blueshift up to 7 nm moving toward the center of the wafer. The emission blueshift and trend toward higher \( V_{th} \) with a reduction in \( G \), point toward

![Figure 2.9: (a) IV curves trending from the edge of the Si wafer toward the center (b) Normalized EL spectra of three 250×250μm devices trending from edge to center under 1 mA of current injection.](image)
a decrease of the more volatile species (In in the TJ and Ga in the active region) when moving toward the center of the wafer. This is likely due to the temperature gradient across the wafer, with the center being slightly hotter. Thus, small variations within the same sample alone can present a challenge when comparing nanowire based devices.

2.6 Summary

In conclusion, this chapter discussed the nanoscale electrical characteristics of nanowire LED devices and how they manifest themselves in larger ensemble devices. Conductive AFM was proven to be a useful tool for investigating the nanowire ensembles, allowing current maps and distributions of nanowire populations to be acquired. Conductive AFM was also shown to have the ability to acquire single nanowire IV characteristics to compare different heterostructures. An improvement of the current injection for AlGaN based nanowire LEDs through integration of a tunnel junction was observed, namely a decrease of the threshold voltage of >3 V and an increase in the differential conductance. However, despite the increase in overall device performance provided by the tunnel junction, it also leads to increased device inhomogeneity. These results demonstrate the utility of cAFM to quantify the electrical inhomogeneity of as-grown nanowire ensembles. However, there are other nonuniformities that are not measured here such as the internal quantum efficiency or discrepancies in contact resistance with the conformal top contact between nanowires.
Chapter 3. Burn-In Conditioning of Nanowire LEDs

The nonuniformities that were discussed in the previous chapter can result in lower device efficiencies because of inhomogeneous current spreading. Ensemble devices contain hundreds of thousands of nanowire diodes wired in parallel. Ideally, each diode would be identical and receive the same current injection. Thus, the current would be spread throughout a mesoscopic device and each wire could luminesce equally. As discussed in previous papers [90], [92] this is not the case, and a small population of wires steal most of the current, leaving a large number of wires without sufficient current to reach threshold, let alone provide bright luminescence. This chapter discusses methods of dealing with some of these nonuniformities to improve current uniformity and was previously published [97].

3.1 How In% Nonuniformities Can Lower Device Efficiency

As shown in Section 2, there is a distribution of nanowire resistances in a given system. If the nanowire size, looking back at Figure 2.2 regarding the size dependent resistances, is taken to be represented as a Gaussian distribution about the average, the resistances can also be shown to be similarly distributed (Figure 3.1). This is calculated using a typical variation from the average height (diameter) of 10% (20%) and a standard deviation of 9 nm (4 nm). The resulting resistances then have a mean of nearly 530 kΩ and a standard deviation of 50 kΩ. The lower range of this distribution could explain what was observed in previous studies, which reported bright single nanowire luminesce under “even” current injection. Also present, but not discussed previously, are the presence of nano-shorts, which are even more detrimental to a device. These are not diodes, but semi-ohmic shorts that could arise from nanowire coalescence, surface shorts around the active
region, accidental top-contact metal deposition on nanowire sidewalls, etc. and would siphon off large portions of the current without providing luminescence at all.

Aside from the size dependent resistances from Pouillet’s law, there is also the aforementioned size dependence of In incorporation. Reviewing the information from the studies mentioned in Chapter 1 regarding PL shifts [93]–[96], the In concentration in InGaN nanowires can be calculated using a modified Vegard’s law with a bowing parameter \( b \) of 2.8 eV for relaxed InGaN [108], as shown in Equation 3.1.

\[
E_g^{InGaN} = x E_g^{InN} + (1 - x) E_g^{GaN} - bx(1 - x)
\]

Equation 3.1

This does not account for strain effects or quantum confinement, but the results are shown in Figure 3.2 and look (unsurprisingly) very similar to the plot in section 1.3.2. However, now we can see the typical amounts of In variation in our own TJ nanowires, based on the typical size distribution in self assembled nanowire ensembles. Judging by the samples with higher FF, which were
calculated knowing the nanowire diameter and pitch of the patterned substrate, over ranges of 
$\sim$55 nm ($\pm$20% the average diameter of 140 nm) the In% between nanowires could easily vary 
by 4% in a self-assembled system, and even beyond 10% if conditions allowed. Even these 
variations can have huge effects in the tunneling probability of the InGaN tunnel junction [105]. 
A total variation of 4% from the target value of 30% In, would result in a difference in the tunneling 
probability of nearly an order of magnitude, with the difference increasing quickly to $\sim$50x as the 
In inhomogeneity grows to 10%. This would ultimately manifest in the overall resistance of the 
TJ, which controls the hole injection into the LED.

The LEDs presented in this work all have a high FF and, for the reasons discussed in section 
1.3.2, we expect In to be favorably incorporated in larger diameter nanowires. These would then 
also have higher tunneling probability, resulting in a lower resistance of the tunnel junction and 
increase in differential conductance of the overall nanowire heterostructure. Following a similar 
argument, the incorporation of Ga would also be slightly higher with respect to Al in larger
diameter nanowires; resulting in increased effective p-type doping leading to lower differential resistance and lower Al composition in the active region and subsequent lower energy emission.

3.2 Theory of Burn-In

Burn-in is not a novel idea. Industry has been using pre-conditioning of devices, even outside of electronics [109], [110]. The idea is that when there are a multitude of components in a system, there are inevitably some that are weaker than others. Burn-in was developed to eliminate these weak components prior to distribution to customers. The system is subjected to conditions that are harsher than normal use for a certain period of time, causing the weak components to fail. The amount of time required for sufficient burn-in is dictated by the severity of the overload conditions and the failure rate of the weak components.

Here we demonstrate an alternative technique for increasing the degree of current spreading, specifically by the selective removal of nano-shorts and diodes with high leakage current, in nanowire ensemble devices through post-growth electronic conditioning. A short term overload voltage (high current density) is applied to the nano-shorts causing them to burn-out, becoming open circuits. This is shown schematically in Figure 3.3, where the nano-shorts (or low resistance diodes, dark green) which first pass the majority of the current, are broken. This would then allow current to pass through a larger population of nanowire LEDs, boosting the optical output. When multiple diodes and shorts are wired in parallel, current will preferentially flow through the shorts at low bias. But a high bias may be required to achieve sufficient current density through these shorts to render them open-circuit. At forward bias >Vth diodes will also begin to pass a large portion of the current and the current will be spread out. However, a high current density specifically to the nano-shorts is required, so as not to break working diode devices. If
reverse bias is used, much higher biases can be applied where current will flow primarily through
the nano-shorts and excessively leaky diodes, at least until the majority of the nanowire LEDs start
to experience breakdown.

![Diagram](image)

*Figure 3.3: Schematic diagram showing nanowire ensemble devices (a) with a single nanowire
short siphoning the current from the other nanowire diodes wired in parallel and (b) after burn-
in removal of the short, where the current now passes through the diodes, and light is able to be
emitted. (adapted from [97])*

### 3.3 Material and Device Synthesis

This study involves a detailed investigation of the same TJ integrated sample studied in
section 2. To reiterate, PAMBE was used to grow the TJ separate LED structures on Si. The
nitrogen plasma was operated at 350 W, and a pressure of $\sim 3 \times 10^{-5}$. The fluxes of Al, Ga, and In,
were of $3.85 \times 10^{-8}$, $5.85 \times 10^{-8}$, and $7.8 \times 10^{-8}$, respectively, giving a growth rate of $\sim 3$ nm/min.
Nucleation proceeded at 730°C followed by the polarization engineered TJ. This consists firstly of
110 nm of n-GaN grown at 790˚C. The temperature is decreased to 700˚C, after which 15 nm of n++ GaN is grown after which the temperature is dropped further to 600˚C and ~2.5 nm of nominally 25% InGaN, followed by 15 nm of p++ GaN. The temperature is ramped back to 790˚C before starting the 100 nm Mg-doped linearly graded region from GaN to AlN. The active region was grown at 840˚C, and consisted of three 3 nm AlGaN quantum wells with 5 nm AlN barriers, and then a 100nm Si-doped section graded from AlN back to GaN at 790˚C. The nanowire LED heterostructures examined in this study are close to fully dense (FF = 0.89, through image analysis in ImageJ), with diameters and heights of ~140 and ~365 nm.

3.4 Observation and Burn-In of Shorts at the Nanoscale Through Conductive-Atomic Force Microscopy

Conductive AFM again aids in the identification of nanoscale properties through the acquisition of areal maps as well as full voltage sweeps at discrete locations. The cAFM

![Figure 3.4: (a) IV curves taken by cAFM of two individual shorts, with solid (dotted) lines being prior to (post) burn-in. (b) shows the same curves but zoomed in, with a typical individual nanowire diode curve marked in green. (adapted from [97])](image-url)
measurements reveal the presence of a small population of nano-shorts with very high conductance. The solid lines in Figure 3.4 show two examples of these shorts the first time through a voltage sweep alongside a typical nanowire diode (green). Nanoscale current conditioning is demonstrated by taking multiple IVs out to high bias at such locations. After additional high bias sweeps, Short 1 (black solid line) is converted to an open-circuit (black dotted line). Short 2 (red line) is also rendered open-circuit relative to the operating voltage of the typical nanowire LEDs (green). However, at sufficiently high bias, Short 2 still displays diode-like characteristics with an on-state resistance almost the same as the before burn-in conditioning, but note that the typical nanowire diodes exhibit a far higher on-state conductance. Short 2 might be a parasitic current path that is only partially removed, but blocked by a large Schottky barrier.

The effect of nanoscale current conditioning can also be observed through large area cAFM scans. Current maps over increasingly larger areas at the same scan speed can give information on burn-in dose, rule out the possibility tip degradation and dislodgment or damage of nanowires by the cAFM tip, and also reveal the removal of high current pathways. Figure 3.5(a) shows a 5×5 μm area under zero bias. This obviously shows no current (<1 pA) for the entirety of the image. The tip bias is then increased to +7 V, which is slightly higher than V_{th} for the ensemble devices (discussed in section 1.3.2), thus the majority of the nanowire diodes should begin to turn-on. A subsequent 10×10 μm scan over the same area (Figure 3.5(b)) shows that the majority of nanowires do pass current, and that the center 5×5 μm area is relatively unchanged from the outer area. This shows that the degradation in current under the same bias is not due to damage from the tip, but from the electrical injection.
As biased cAFM images are acquired, the nanowires experience a burn-in dose proportional to the time a bias is applied across the individual nanowire. The scan rate is held at 0.5 Hz for each line scan in the acquisition of the image; the size of each scan increases with the dosage time being approximately 14, 7 and 3.5 ms for the 10×10, 20×20 and 30×30 µm images, respectively. Degradation is seen in Figure 3.5(c) from the previous 10×10 µm scan, marked by the red square, which after this scan had experienced burn-in for 21 ms. However, there is no additional degradation seen in the central 5×5 µm area, scanned without bias, observed in any of the subsequent images. The final image shows a 30×30 µm scan with two areas that were previously scanned at +7 V, with total accumulated burn-in times of 24.5 and 10.5 ms, marked with red and orange squares, respectively. What is seen, especially in the final two images, is that the high-current locations exist primarily in the region being scanned for the first time, outside the marked squares. Inside the marked squares, the population of high-current areas is much smaller with many replaced by low current.

Figure 3.5(c,d) can also be used to rule out the possibility of degradation of the cAFM tip upon subsequent imaging. Just outside the bottom left of the red 10×10 µm square, there are two locations in which high current is still seen in the 30×30 µm image. The values of these pixels

![Image](image.png)

*Figure 3.5: Sequence of CAFM scans showing a zero bias scan of (a) 5×5 µm and +7 V bias scans over the same areas of (b) 10×10 µm, (c) 20×20 µm, and (d) 30×30 µm. The red squares show the area of the 10×10 µm scan, and the orange square shows the 20×20 µm scan. Scale bars are 3 µm. (adapted from [97])*
from the 20×20 μm scan to the 30×30 μm are identical within the measurement error, 1.1-1.2 nA (first) to 1.07-1.13 nA (second) and 1.05-1.13 nA (first) to 1.07-1.08 nA (second) for the two points.

If the tip bias is variable between scans, it is more useful to view the maps as resistances, which can be done easily by dividing tip voltage by the measured current at each pixel. Multiple resistance maps are acquired of the same 10×10 μm area under different biases to explore the effect of burn-in (Figure 3.6). The first scan is at +3 V, a bias below the expected threshold of the typical nanowires, the average resistance is high (288 GΩ) due to the majority of nanowire diodes being sub-threshold. However, a few nano-shorts (black regions) are observed, exhibiting resistances around ×100 lower than the average (marked with white circles for clarity). The tip bias is then increased to +7 V, which then displays a drop in the average resistance to 45 GΩ. However, the nano-shorts still show a relatively lower resistance (~4× less than average). Given the cAFM scan speed, each nanowire receives the initial >V_th ~14 ms, apparently too short a time to cause observable changes in the resistance maps. However, after a second scan of the same area at +7V (Figure 3.6(c)), a local rise in the resistance of the former location of nano-shorts from

![Figure 3.6: Resistance maps taken by repeated cAFM over the same 10×10 μm area at (a) +3 V bias (b) +7 V bias, and (c) a repeated +7V bias. Scale bars are 2 μm. (adapted from [97])](image-url)
~11 to ~1400 GΩ is observed. There is an increase in the average device resistance from 45 to 140 GΩ, but notably, the median resistance is relatively unchanged (10-20 GΩ) after the second scan. The standard deviation of resistance also drops from 40.6 to 31.4 GΩ after the second scan. This signifies an increase in the electrical homogeneity of the ensemble. These results are consistent with the removal of nano-shorts, which formerly carried large amounts of current, observed also with the single nanowire measurements. If these are present underneath a conformal contact, these nano-shorts would steal current from nearby nanowires, so the removal of these shorts, and a subsequent increase in homogeneity should mean that the overall light output should increase under the same conditions.

3.5 Effects of Burn-In on Electroluminescence

Based on the observation of nano-shorts in the cAFM measurements, a method to systematically remove their impact in ensemble nanowire devices is proposed and demonstrated. Ensemble nanowire LED devices, (250×250 μm) containing ~3×10⁶ nanowires wired in parallel, were fabricated. Current-voltage measurements were done using a Keithley 2604B sourcemeter and the EL spectra acquired using a spectrometer with a CCD detector. A reverse bias DC voltage pulse is held for six seconds, to electrically condition an ensemble device. The reason for the use of a reverse bias scheme is explained in Section 3.2. EL spectra and IV curves are taken after each reverse bias voltage pulse, which is increased in magnitude from 0 to -20 V. To ensure minimal burn-in effects during acquisition of the EL spectra and IV curves a 100 Hz 4% duty cycle pulsed current was used, with the peak current limited to <1 mA.

Figure 3.7 shows the spectral characteristics under 0.2 mA pulsed injection as a function of increasing burn-in voltage. A remarkable increase in emission intensity is observed with
increasing burn-in. Beyond -20 V, a very sharp reduction in EL intensity was observed just prior to device failure. Failure occurred at lower voltages for some other devices measured. This failure voltage is likely limited by the breakdown of mesoscopic devices, where not only nano-shorts, but also a large number of diodes begin to break down and pass current. Further increase of burn-in bias leads to reduction in the total diode population, which upon subsequent bias yields a higher current density through each wire, which would then lead to failure.

Initially, the devices display a traditional burn-in behavior, where the EL intensity drops with increasing reverse DC bias, from 0 to -3 V, before achieving a stable baseline. This typical burn-in effect is ubiquitous to devices and used to eliminate early failing devices [109], [110]. However, once this initial burn-in behavior stabilizes, the devices begin to show an increase in performance upon increasing the magnitude of the reverse bias burn-in voltage. The peak EL intensity increases by 33× after reverse bias burn-in of -19.9 V (Figure 3.8(a)). A slight blueshift in the EL (320 nm to 314 nm) is also observed (Figure 3.8(b)) suggesting an increase in current

![Figure 3.7: EL spectra at 0.2 mA pulsed current injection as function of reverse bias burn-in voltage (adapted from [97])]
flow through wider bandgap (higher Al composition) nanowire LEDs due to burn-in conditioning. A similar trend is observed for the FWHM of the EL peak, decreasing by \(\sim 30\%\) at the same injection current, indicative of an improvement in the uniformity of the EL. Overall, the boost in EL intensity can be attributed to the elimination of nano-shorts by burn-in leading to increased current flow in the majority of the nanowire LEDs. This is further supported by the changes in IV characteristics, described in the next section.

Additional EL spectra were acquired at pulsed drive currents up to 1 mA at 100 Hz and 4% duty cycle. Similar trends for all drive currents are seen, an initial decrease in intensity, followed by a large increase in intensity (Figure 3.9). Only a slight shift in peak wavelength is seen with

\[
\text{Figure 3.8: (a) EL peak and (b) wavelength/FWHM as function of reverse bias burn-in voltage (adapted from [97])}
\]
burn-in at any drive current. Although, with increasing current, the emission intensity becomes brighter, and a slight blueshift is observed which can be attributed to the quantum-confined Stark effect.

Figure 3.9: Maps of EL intensity as a function of burn-in voltage and wavelength with corresponding peak intensity as a function of burn-in voltage for pulsed drive currents of (a) 0.2, (b) 0.4, (c) 0.6, (d) 0.8 and (e) 1.0 mA. (adapted from [97])
3.6 Effects of Burn-In on Current-Voltage Characteristics

Pulsed IV curves taken during burn-in conditioning are plotted in Figure 3.10. The IV curves were taken after each EL spectra, and used a 100 Hz 4% duty cycle pulsed voltage to ensure minimal burn-in effects during acquisition. The IV curve of the virgin device (green) has a $V_{th}$ of 5.07 V, decreasing to a stable baseline of 4.8 V during the initial burn-in from 0 to -3 V. However, upon increasing the magnitude of the reverse DC bias burn-in, $V_{th}$ increased to 5.4 V (Figure 3.11(a)). This is accompanied by a slight reduction in the differential conductance, which suggests that the current was re-routed to a larger fraction of nanowire LEDs which are slightly more resistive. A reduction in reverse bias leakage current at -5 V after burn-in reflects the elimination of nano-shorts in the ensemble device (Figure 3.11(b)). Additionally, looking at the IV curve at low currents (<0.1 mA) in Figure 3.10, the slight effect of a shunt current can be seen to reduce with increasing burn-in voltage. The changes in the ensemble IV curves are well correlated with

![Figure 3.10: Pulsed IV curves as function of burn-in voltage (black to red), original curve before any burn-in is marked in green. Inset shows reverse bias characteristics. (adapted from [97])](image-url)
what is observed in the cAFM and ensemble EL spectra. This overall increase in nanowire ensemble device resistance, concurrent with the EL intensity boost and blueshift, is consistent with the removal of nano-shorts and shift to high Al% nanowires by reverse bias burn-in.

### 3.7 Effects of Burn-In on Efficiency

The IV curves, in conjunction with EL spectra at various injection currents, are analyzed to calculate the overall device efficiency ($\eta$) at various injection currents (Figure 3.12). EL output power measurements are carried out using a power meter and a calibrated Si photodiode (Thorlabs PM100D and S120VC) placed above the devices. The previously discussed reduction in EL...
intensity at low reverse bias burn-in (<3 V) does not necessarily reduce $\eta$ since it coincides with a reduction in $V_{th}$. Similarly, the total 33$\times$ boost in EL output due to burn-in conditioning translates into more modest gains in $\eta$ since the rise in EL output overlaps with an increase in the operating voltage.

The trends in overall efficiency can be understood in terms of the interplay between the improvement in current uniformity by burn-in, and the non-uniform spread in threshold voltages of the nanowire LEDs [98]. As nano-shorts are removed by burn-in, one expects an increase in the average current density of nanowire LEDs at a given drive current, which leads to the observed large increase in EL. However, as shown in Figure 3.12, at low current injection (0.2 mA) $\eta$ increases by 5% (1.30 to 1.37 m%) during the initial burn-in (0 to -5 V) where the EL intensity is actually reduced, while conditioning out to -20 V actually leads to an overall efficiency decrease.

This counterintuitive behavior can be explained by consideration of the ensemble device in which nanowire LEDs are connected in parallel. At low drive currents (0.2 mA), the majority of the nanowires are at a sub-threshold bias and only a minority of the nanowire LEDs are carrying current, and are experiencing a disproportionately large current density. Thus, one expects the low current $\eta$ to be limited by loss mechanisms that come into play at high current densities, i.e. overshoot/droop. Only at high current injection, can we deconvolute the effect of burn-in from the nanowire LED non-uniformities, since at high drive current, the majority of nanowire LEDs are above threshold. Consequently, the largest increase in $\eta$ of 19% is observed under the highest current injection, 1.0 mA (0.27 to 0.32 m%). Before burn-in conditioning, efficiency drops by 4.50$\times$ (1.3 to 0.29 m%) as current increases from 0.2 to 1.0 mA. After burn-in conditioning this droop is slightly reduced to 4$\times$ (1.28 to 0.32 m%).
In an effort to elaborate on the effects of burn-in on device efficiency, we attempted to separate overall efficiency into quantum efficiency ($\eta_{qe}$), injection efficiency ($\eta_{inj}$), and photon extraction efficiency ($\eta_{ph}$). Assuming that burn-in could only make changes in current injection to the device, nothing physical is happening that would increase the $\eta_{qe}$ or $\eta_{ph}$. Of the current injected into the device, there would be current that contributes to recombination ($I_r$) and (due to shorts, overflow, etc.) some non-radiative portion current ($I_{nr}$). This would yield a system of equations such as the following:

$$I(V) = I_r(V) + I_{nr}(V), \quad \text{Equation 3.2}$$
$$I_r(V) = I(V)\eta_{qe}\eta_{inj}, \quad \text{Equation 3.3}$$
$$P(V) = I_r(V)V\eta_{ph}, \quad \text{Equation 3.4}$$

where P would be the measured output power and is related to the electroluminescence spectra by:

$$P = \int N_{ph}(E)dE = AZ_{int} \quad \text{Equation 3.5}$$

Figure 3.12: (a) Efficiency as a function of burn-in voltage at various pulsed injection current (adapted from [97]) (b) efficiency before and after burn-in as a function of injection current
Where \( N_{ph} \) is the number of photons, \( Z_{int} \) is the integrated EL spectra, and \( A \) is a correction factor to account for any collection inefficiencies in the spectrometer. However, the system of equations, as it stands now has too many unknowns, and while only being able to know the power of measured electroluminescence spectra, and IV curves, we were unable to find a way to elucidate specific values for \( I_{nr} \) and \( \eta_{inj} \) to see as a function of burn-in without knowing the other efficiencies.

### 3.8 Summary

In summary, the nonuniformities that can arise in nanowire-based ensemble devices were discussed. Reverse bias burn-in was shown as a method of removing one type of these nonuniformities, nano-shorts, showing increased efficiencies at higher injection currents due to fewer current sinks. From the existing ensemble EL spectra a reduction in FWHM from \(~30\) to \(~20\) nm is observed which is indicative of an improvement in EL uniformity, and would suggest current flow through a larger more homogenous population. However, without confocal EL maps, we cannot fully test this hypothesis. The effect of performing reverse bias burn-in on the lifetime and operational limits during typical forward bias operation has yet to be explored. Additional work is still needed to get quantitative numbers for the reduction of short current and to elucidate the physical phenomena that causes these nano-shorts. If the causes of these nano-shorts can be identified, additional burn-in schema can be developed to further increase the homogeneity of ensemble devices. Possibilities include much higher reverse bias voltages for shorter times for removal of more stubborn ohmic shorts, or low forward bias for long times to remove diodes that would have much lower \( V_{th} \) and still siphon current during normal operation. Because p-Si has a high valence band offset and the InGaN TJ could be one of the culprits of the high nonuniformity issues, there is still an issue with achieving high current injection and maintaining uniformity.
Chapter 4. AlGaN LEDs Directly on Flexible Polycrystalline Metal Foils

The removal of the valence band offset between p-GaN and substrate can be done in ways other than through use of a TJ. Traditionally, metals are used to make contact to semiconductors, so perhaps uniform injection can be achieved by growing directly on metal. By growing p-GaN directly on a high work function metal substrate, every wire should have approximately the same bottom contact, eliminating In segregation as one of the potential causes of nonuniformity. There are also bonus advantages for growing directly on large scale flexible substrates. These include: robust substrates which won’t shatter if dropped, inexpensive large area substrates, and if the bulk substrate is flexible there is an opportunity to move toward a high-throughput roll-to-roll style of fabrication. Nanowires from other material systems (Si, Ge, ZnO, CdS) have been fabricated on a wide variety metal substrates [60], [111]–[113], but here we will look at the first work of III-Nitride nanowires grown directly on polycrystalline metal foil [58].

4.1 Previous Work of III-Nitride Nanowires on Metal Substrates

III-Nitride nanowires have been grown on metal thin films deposited on single crystal Si or glass substrates [49], [50], [54], [55], [114]. Thin films of Mo or Ti were deposited on Si via e-beam evaporation, these metals were chosen due to their robust nature, and ability to withstand the temperatures of MBE growth without melting. Ti was a common choice because when it is exposed to a nitrogen plasma it forms TiN, which makes ohmic contact to n-GaN [115]–[117]. Very recently, growth on Al was reported [118] where they managed to overcome the issue of Al melting, which is extremely useful as Al reflects very well in the UV. Another group fabricated
InGaN-based red LEDs on a thick 500 nm Ti film deposited on a thick piece of polycrystalline Mo [56]. After the publication of the work contained in this chapter, demonstration of Nitride nanowires directly on metal has been shown by other groups [59], [119], [120]. However, at the time of publication there were no reports of growth of Nitride nanowires or working LEDs directly on polycrystalline metal foils.

4.2 Substrate Preparation and Synthesis

Ta and Ti metal foil substrates were chosen for this study because our group had previously grown on Ti thin films on Si, Ta was a similarly popular and inexpensive metal, and both could be purchased at high purity. The Ti and Ta foils were purchased from GalliumSource and the purities were >99.6% to maintain cleanliness of the chamber, but it is expected that less expensive foils would also work, at least structurally. At the time, we were looking to see if nanowires could be grown on these rather than for the achievement of efficient current injection, so higher work function metals weren’t looked into heavily; Ta and Ti have work functions (ϕ)

![EBSD maps of Ti foils](image)

*Figure 4.1: EBSD maps of Ti foils (a) as-received, (b) after anneal at 600°C for one hour*
of ~4.33 and 4.25-4.8 eV, respectively [121]. The metals with ϕ>5 eV (Au, Ni, Pd, Ir, Os, and Pt) are typically expensive and not readily available as foils, with the exception of Ni. They were chosen to be 100 µm thick so that they would maintain flexibility and then cut into 1 inch squares using electrical discharge machining (EDM). No surface preparation was done to the as-received foils other than a standard solvent degrease (acetone, methanol, and isopropyl alcohol) in an ultrasonic bath before introduction to vacuum. Prior to introduction to the growth chamber they are vacuum baked at 600°C for one hour. Electron backscatter diffraction (EBSD) images of the Ti foils reveal the polycrystalline nature (Figure 4.1). Ti is a hexagonal close packed structure, and the as received foils are textured towards the (0001) direction with grain sizes ~20 µm. After annealing at conditions that would replicate a typical buffer chamber bake for the foil samples (600°C for 1 hour under vacuum), the texturing remains, but the grain sizes increased to ~30-60 µm. This behavior is typical Ostwald ripening of polycrystalline materials [122].

GaN nanowires are grown on each type of foil via PAMBE in the same Veeco Gen 930 system equipped with a Riber N₂ plasma source. The Ga flux is 6.20×10⁻⁸ torr measured using a beam flux monitoring (BFM) ion gauge. A nitrogen flow rate of 7.5 sccm is used with a plasma power of 500 W, which gives a N-limited growth rate of ~11.2 nm/min. A III/V ratio of ~0.18 is used during growth. Care was taken to avoid nitridation of the surface by rotating the substrate away from the plasma source when striking plasma, and the sample only faced the plasma source (with the shutter closed) immediately prior to growth. The nanowires are grown employing the two-step growth method discussed previously [101]. GaN nanowires are first nucleated at 750°C for 5 minutes then growth proceeds at 800°C for 2 hours on both foils as well as a 3” Si substrate, which should yield wires around 1.34 µm tall. Reflection high energy electron diffraction
(RHEED) for the starting foils is difficult to obtain due to their unpolished, polycrystalline surface. However, after a few minutes of growth, RHEED begins to show a spotted ring pattern (Figure 4.2) that is similar to that of nanowires grown on single crystalline Si. This spotted ring configuration arises as a superposition of patterns from the single crystalline nature of the wires similar to a columnar film (spots) but with various azimuthal orientations to the substrate (rings).

4.3 GaN Nanowires on Bulk Metal Foils

Images of the flexible Ti and Ta foils after the deposition of the GaN nanowires are shown in Figure 4.3. The foils maintain their structural integrity, and there is obvious difference in the region where deposition occurred, as the shadow marks from the clips and faceplate of the quarter wafer holder are clearly evident. SEM measurements were carried out on a FEI/Philips Sirion for GaN nanowires grown on each substrate. The inset of Figure 4.4(a) shows the nanowires grown on a single crystalline Si substrate with the $c$-axis of the nanowires approximately perpendicular to the substrate. SEM images of wires grown on the Ti foil are shown in Figure 4.4(a-d). At the lower magnifications, a structure similar to what was observed via EBSD is observed. As the magnification is increased, it appears that the nanowires on metal foils are uniformly tilted with
respect to the surface normal within the individual grains of the foils. Despite the different growth
directions, throughout each region, the wires have similar heights and radii, and are evenly
distributed. However, between different grains, tilt direction is seen to vary greatly, which suggests
an epitaxial relationship with the crystallographic orientation of the grain directly below the
nanowire. The nanowire density between grains can also be very different, with some being nearly
devoid and others having a high degree of coalescence. In many cases, the boundaries between
these regions tend to have a very low number of nanowires. This could be due to local melting
[123]–[125] or just that grain boundaries are crystallographically complex. During the nucleation
step, adatoms will migrate toward a low energy location to form a seed, some grains will be low
in energy (close to (0001)), while others, further misoriented from the basal plane, could be very
high. Grain boundaries are necessarily two or more crystal orientations at the same point, so the
formation energy will be higher, and any adatoms that land there, will diffuse away toward the
center of the grain (or desorb) before forming a seed.

SEM images of the Ta foil (Figure 4.5) reveal individual regions larger than those
compared to the Ti foil, yet despite having a cubic structure, also show less variation between
regions. No EBSD was performed on the Ta foils, so exact orientations are unknown, but it can be inferred from the SEM images that while there are some small grains sizes around ~15 µm but others that are very large >100 µm. Increasing magnification SEM images of GaN nanowires on the Ta foil also reveal a lower degree of coalescence than the Ta foil. Although, that could just be a product of the presence of the larger grains, which have reasonable nanowire coalescence. There are still large regions where the nanowire denisty is low, with the nanowire growth direction being highly varied. The next step is verification of the crystal quality of these nanowires compared to nanowires on Si substrates.

Figure 4.4: Plan-view SEM images of GaN NWs on Ti foil under increasing from (a) low magnification, to (b) 1736× (c) 3472× to (d) 6447×. Inset of (a) shows tilt-view of nanowires on Si (adapted from [58])
Figure 4.5: SEM images of NWs on Ta foil at increasing magnifications of (a) 436×, (b) 873×, (c) 3491×, (d) 13965× and (e) 26850×.
4.4 Optical Characterization

Figure 4.6 shows normalized μ-PL spectra of the as-grown nanowires on Si (black), Ta (red), and Ti (blue) at 27.6 K on linear and semi-logarithmic scales. The nanowires were optically excited using a third harmonic (267 nm) of a mode-locked Ti:sapphire oscillator (Coherent Chameleon Ultra II) operating at 800 nm and 80 MHz. The laser had an average power of 125 µW at the sample and was focused on the surface through a 0.5 NA 36× reflective objective which results in a beam diameter of ~10 µm. The emission from the samples was collected through a 300 nm long pass filter and passed to a 0.5 m spectrometer (Princeton Instruments SP2500i) equipped with a UV–VIS CCD (Princeton Instruments PIXIS100) and a 1200 g/mm diffraction grating. All the samples show dominant ~358 nm (~3.472 eV) neutral donor bound A exciton (D0, X_A) recombination [54], [126]–[128]. A high energy shoulder is also observed at ~357.5 nm (~3.477 eV), attributed to free A exciton (X_A) recombination [54], [127]. A relatively broad and weak peak at ~362.7 nm (~3.427 eV) is observed. This peak has been previously attributed to

![Figure 4.6: (a) Micron resolution photoluminescence spectra and (b) time resolved photoluminescence on the 358 nm peak at 27.6 K (from [58]).](image)

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surface related excitons [129] or exciton bound to structural defects such as I\textsubscript{1} stacking faults in GaN nanowires [126], which could originate from sidewall coalescence of the nanowires [103], [127], [130] or from defects near the bottom surface of the nanowires. No long wavelength defect peaks (yellow luminescence) are observed in any of the samples.

Time-resolved PL was carried out using time-correlated single photon counting spectroscopy using a micro-channel plate (MCP) photomultiplier tube (PMT) detector coupled to a 0.15m spectrometer. Figure 4.6(b) shows the time-resolved PL at the 358 nm (D\textsuperscript{0}, X\textsubscript{A}) peak (data points) along with the instrument response function (IRF) (dashed line) to show the time resolution of our setup. The PL decay curves are well fitted to a biexponential model (solid lines) with a short lifetime and long lifetime component. For nanowires grown on Ta foil, both the short and long decay components are almost identical to those of nanowires grown on Si. On the other hand, the nanowires on Ti foil show a reduced short decay constant but enhanced long decay constant. Even with this variation, the relatively similar recombination characteristics for all the samples indicates that the nanowires grown on metal foils are of similar optical quality to those grown on single crystalline Si substrates.

### 4.5 First Ultraviolet LED Grown and Fabricated Directly on Metal Foil

Having established the high crystalline quality of GaN nanowires grown on metal foils, we grew an AlGaN LED on flexible Ta foil. The Ta foil was chosen due to the higher degree of uniformity compared to the Ti foil, as mentioned previously. Because the work function of Ta is reported to be ~4.8 eV [121], and the electron affinity of GaN is 4.1 eV [131], a simple p-down structure would have likely resulted in a larger (2.7 eV) offset. Therefore, the n-down TJ integrated structure was again chosen. The LED heterostructure follows the TJ integrated design that was
previously discussed in chapters 2 and 3. Additional SEM images of the as-grown LED structure are shown in Figure 4.7. A grain type structure is still observed, but the disparities between each grain is not as drastic as the previous images of GaN nanowires. This is because these nanowires are much shorter (~365 nm, compared to ~1.3 µm). Devices were fabricated using the same process as devices on Si outlined in section 2.5.1, using a semi-transparent top contact of 10/20 nm Ti/Au deposited by e-beam evaporation. A fully processed sample can be seen in the inset of Figure 4.7(c). The bottom contact was formed by mechanical removal of the nanowires and a diffused In dot soldered directly to the Ta.

The current-voltage curves (Figure 4.8) show good diode characteristics with threshold voltages ranging from 5-8 V; usually slightly worse, but in some cases better than the same heterostructure grown on n-Si. However, the leakage current of all tested devices on metal are >3 orders of magnitude higher. Looking at how closely the forward bias regime (prior to turn-on) matches the reverse bias, there is clearly a large amount of shunt current present in these devices.

The electroluminescence spectrum (Figure 4.9) shows ultraviolet emission with a peak at ~350 nm. The blue shift with increasing current injection in the EL is a result of the screening of
the quantum confined Stark effect by the polarization field in the QW [72]. It is noted that the EL intensity is about 16× lower compared to similar devices on Si at the same injection currents. Because the turn-on voltages observed were similar to values expected for growth on metal, the low EL intensity is likely the result of only a low number of nanowires contributing to the EL. In

Figure 4.8: IV curves of TJ LED devices on Si (black) and Ta (red) on (a) linear and (b) log scale (adapted from [58])

Figure 4.9: EL spectra of a LED on Ta foil (adapted from [58])
conjunction with the large leakage/shunt current present, this is likely from the inhomogeneous
distribution in nanowire tilt and density. Such variations could result in metal deposition on the
sidewalls of the nanowires and substrate during fabrication of the top contact. Consequently, a
leakage pathway is formed, reducing the number of active nanowires, and subsequently decreasing
the overall EL intensity.

4.6 Burn-In of Nanowire Ensemble Devices on Metal

Burn-in of the 250×250 µm devices on the LED on Ta foil was done. The procedure is
similar to that which is described in section 3.5, a reverse bias DC voltage is applied for six
seconds. After each burn-in event, an EL spectra was acquired using a pulsed current injection at
100 Hz and 20% duty cycle ranging from 0.2 to 1.0 mA. Subsequently, an IV curve was taken
using a pulsed voltage at 100 Hz and 4% duty cycle.

The effect of burn-in on the emission characteristics if a device on Ta are shown in Figure
4.10(a-d). The EL intensity at 1 mA dropped continuously up until failure after a burn-in pulse of
-7.8 V. The low peak intensity made peak fitting for an accurate FWHM difficult, but a general
trend of peak broadening is observed. Again, because the emission is relatively broad and the
intensity low, the precise peak wavelength was difficult to pin down, but shows no trend with
burn-in, hovering around 400 nm. The 400 nm peak was observed as the primary emission peak at
low injection currents (Figure 4.9), and the ~310 nm peak only begins to dominate at higher
injection currents. However, because analysis of burn-in requires “gentle” acquisition of the EL
characteristics, the use of high injection currents was avoided.

The electrical characteristics are also examined as a function of burn-in (Figure 4.10(e-h)).
The $V_{th}$ of the device shows a general increase over the course of burn-in, albeit only very slight
Figure 4.10: Burn-in characteristics on a 250×250 μm LED device on Ta. (a) EL spectra at 1mA pulsed injection before and after burn-in (b) Peak EL Intensity (c) Peak FHWM (d) Peak wavelength (e) IV curves as a function of burn-in (f) Threshold voltage (g) differential conductance and (h) leakage current at -5 V all as a function of burn-in voltage
(~0.1 V). The differential conductance also trends toward higher resistance. The leakage current at -5 V shows an increase until about -2V then begins to decrease again, reaching values close to the original. In the final measurements before device failure, the leakage current was actually observed to increase sharply. The electrical characteristics shows similar burn-in trends to the devices on Si discussed in the previous chapter, but an increase in emission intensity was never observed. When looking at the devices on Si, the emission increase didn’t begin until ~7V, and the samples on Ta would die prior to this.

4.7 Summary

This chapter focused on the growth of III-Nitride nanowires on polycrystalline metal. High quality GaN nanowires were demonstrated on bulk Ti and Ta foils, and was verified by PL and TRPL measurements. LED devices emitting in the UV were demonstrated, but the polycrystalline nature of the foils presented a whole host of new (and obvious) uniformity issues that previously investigated burn-in techniques alone were not able to remedy. This large degree of nonuniformity is detrimental not only to individual device performance but also yield, as few devices on the sample worked, with devices larger than 300×300 µm rarely able to handle any current. Work is still needed to understand the orientation between the nanowires and underlying grains. The following chapter will present ways of growing on metal, but maintaining the uniformity of nanowire ensembles.
Chapter 5. Engineering of the Bottom and Top Contacts for Improvement in Nanowire LED Homogeneity and Output Power

The previous chapters have discussed the need for nanowire ensembles with efficient carrier injection, but that homogeneity is also of key importance. If growth on large single crystal Si substrates requires complex tunnel junctions and shrinking the grains to the sizes typical in polycrystalline metals results in large scale nonuniformity what is left? If the orientation of the nanowires depends on the underlying grain and the grain size is much larger than the diameter of the nanowires, then one observes preferential orientation of the nanowires (Figure 5.1: (a)). If the grain size were to be made much smaller than the diameter of the nanowire (Figure 5.1: (b)), then the orientation preference due to the underlying microstructure disappears and the nanowires begin to grow along c-axis, due to low c-plane surface energy [132]. This has been seen previously on cold e-beam deposited metals, but delamination can be a problem when experiencing large thermal cycles that are sometimes necessary for an LED heterostructure, especially when trying to push AlGaN into the DUV [133].

As the grain size approaches zero, the material loses any long range structural order, and is classified as amorphous (Figure 5.1(c)), and for the same reason nano-crystalline films are expected to work, amorphous films should follow. GaN nanowires were previously demonstrated to grow preferentially along the (0001) axis on SiOx, [51] but insulating substrates are not useful for electronic devices, and silicates are not flexible. However, there are amorphous metals as well. These are commonly used outside of the nanoscale electronics as brazing foils, where the amorphous structure is key, as these are melted to join two pieces of materials and grain boundaries
provide sites for early melting. By using amorphous material, it is ensured that the foil melts completely evenly. Thus, multiple samples of different metallic glass foils (MGFs) were acquired (metallic brazing foils, MetGlas, USA) to test as substrates for nanowire growths.

This chapter will investigate the use of thin nanocrystalline Pt interlayers and MGFs as surfaces for formation of uniform nanowire ensembles on metal. After growth on these materials, techniques for improving the light extraction of top emitting DUV LED devices by removing emission-absorbing layers will be demonstrated.

Figure 5.1: Schematics of nanowires grown (a) on polycrystalline material with grains much larger than nanowire diameter and (b) grains smaller than nanowire diameter. (c) Nanowire arrays on amorphous (glass) substrate.
5.1 Use of Amorphous and Nanocrystalline Metal Substrates

5.1.1 GaN Nanowires on Thin Pt Films on Si

First, we studied the effect of thin (<5nm) Pt films on p-Si, to determine their impact on the electrical injection into p-GaN. The work function of Pt is \( \approx 5.65-6.1 \text{ eV} \) [121], [134], which should make efficient contact to p-GaN. Growth on metal could provide an efficient thermal transport pathway to mitigate heating effects and the use of metal at the interface acts as a hole reservoir for the polarization graded region [135]. The films are kept very thin to avoid any delamination that would result from the high temperature thermal cycling during growth of a DUV LED structure.

Prior to Pt deposition, an oxide removal of the p-Si wafers was performed using a ten minute piranha etch followed by a ten minute dip in dilute HF. They were then immediately loaded into the evaporation chamber, where they were coated with either 1, 2, or 5 nm of Pt at a rate of 0.1 Ås\(^{-1}\). The samples were loaded into a special substrate holder which can hold 4 substrates for simultaneous growth at separate temperatures [136], discussed in more detail in Appendix A. The multi-temperature nature of this block relies on different backing plates behind each substrate. However, if no backing plates are used, the four-fold symmetric faceplate is a good way to hold multiple substrates (that cannot be In bonded) under uniform conditions. An uncoated p-Si wafer, along with a 1, 2, and 5 nm Pt coated piece were loaded on the holder.

These samples were baked at 800°C in the buffer chamber for one hour prior to introduction into the main chamber. A Ga BEP of \( 6.20 \times 10^{-8} \text{ torr} \) was used, along with a Mg BEP of \( 3.7 \times 10^{-9} \text{ torr} \). A nitrogen plasma power of 400 W and flow rate of 4.75 sccm were used, giving a chamber background pressure of \( 2.61 \times 10^{-5} \text{ torr} \). The growth temperature was calibrated using a
pyrometer on the uncoated Si substrate present in the multi-wafer holder. To set the nanowire density, a 5 min p-GaN nucleation step was done at a colder temperature of 740˚C, followed by growth for 1 hour at 790˚C.

Plan-view SEM image of GaN nanowires on p-Si and Pt coated substrates are shown in Figure 5.2. The addition of 1 nm of Pt reduces the apparent large scale density of nanowires, growing in clumps that are similarly dense. This could be an effect of incomplete coverage of Pt, or ultrasonication of the substrates could have damaged such a thin film during cleaning. The 2 nm film shows structure remarkably similar to that of the bare Si wafer. However, if the thickness of the Pt is increased to 5 nm, GaN nanowire growth does not proceed at the same conditions.

This could be for two reasons, both involving inhibited nucleation of GaN seeds. The first being that a thicker layer of Pt, being a metal, will absorb more heat from the infrared radiation passing through the Si from the CAR, creating a slightly hotter surface than the bare Si wafer that was used for temperature calibration. This is very important during the temperature-critical nucleation step, if the temperature is too hot, nucleation will be inhibited, and then when the temperature is increased for the long growth section, there are no locations for growth to proceed. The second stems from previous discussion about nanocrystalline films. As evidenced in the previous chapter, nanowire growth does not proceed at grain boundaries as readily as bulk grains.
The energy barrier for formation of a single crystal on the boundary of two crystal rotations would be higher than that of a single crystal. Thus, if a single crystalline nanowire has a diameter that encompasses many different grain boundaries the energy barrier would be even higher, resulting in a lower nucleation density. It is possible that the 1 nm film had incomplete Pt coverage, resulting in the nanowire clumping. The 2 nm Pt film could be so similar to bare Si because it is too thin to absorb an appreciable amount of IR radiation, or to override the influence from the Si substrate. In either case, if one desires to grow on thicker nanocrystalline films, the problem can be solved by nucleating at a lower temperature.

5.1.2 GaN Nanowires on Amorphous Metal Foils

The metallic glass foils used here are alloys that are primarily Ni-based, which is thought to be beneficial as Ni-containing contacts are used for efficient contacts to p-type GaN [137], [138]. Many foils were tested (Table 5.1), only those that could handle temperatures of the current standard LED heterostructure growth (having solidus temperatures greater than the active region growth temperature of 850°C) were investigated. The as-received MGFs were cut into 2×2 cm squares and thoroughly cleaned with acetone before following the same cleaning procedure as the

Table 5.1: Different metallic glass foils tested, the solidus temperatures, compositions, and if they formed nanowires at the growth conditions tested

<table>
<thead>
<tr>
<th>Foil</th>
<th>Solidus Temp (˚C)</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Co</th>
<th>Nb</th>
<th>B</th>
<th>Si</th>
<th>P</th>
<th>NWs?</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBF-20</td>
<td>969</td>
<td>bal</td>
<td>7</td>
<td>4</td>
<td></td>
<td>3</td>
<td>4</td>
<td></td>
<td></td>
<td>Barely</td>
</tr>
<tr>
<td>MBF-30</td>
<td>984</td>
<td>bal</td>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>4</td>
<td></td>
<td></td>
<td>Barely</td>
</tr>
<tr>
<td>MBF-50</td>
<td>1052</td>
<td>bal</td>
<td>19</td>
<td></td>
<td>2</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td>Yes?</td>
</tr>
<tr>
<td>MBF-51</td>
<td>1030</td>
<td>bal</td>
<td>15</td>
<td></td>
<td>1</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td>No</td>
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<td>MBF-62</td>
<td>984</td>
<td>bal</td>
<td>20</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>7</td>
<td></td>
<td></td>
<td>Yes?</td>
</tr>
<tr>
<td>MBF-90</td>
<td>966</td>
<td>bal</td>
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<td>20</td>
<td>0</td>
<td>0</td>
<td>4</td>
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<td>Yes</td>
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<tr>
<td>MBF-91</td>
<td>1065</td>
<td>bal</td>
<td>14</td>
<td>9</td>
<td>4</td>
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<td>1064</td>
<td>bal</td>
<td>14</td>
<td>9</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td></td>
<td></td>
<td>Barely</td>
</tr>
</tbody>
</table>
bulk foils in section 4.2. They were loaded in the same multi-substrate holder discussed in the previous section along with a piece of bare Si to act as the temperature and growth reference. They were baked in the buffer chamber at 600°C, to stay well below the solidus temperature and attempt to minimize recrystallization. The growths were similar to those on the Pt films, p-GaN nanowires grown at 790°C for 1 hour. A range of temperatures from 740-760°C was used for the 5 minute nucleation period in an attempt to achieve uniform nanowires for different growths.

The different metallic glass foils resulted in a wide variety of morphologies (summarized in Table 5.1) varying from virtually no growth (MBF-51/92), to columnar lumps (MBF-50/62) of unknown composition/structure, to pockets of growth between very rough material (MBF-20/30/91/92), to extremely uniform over large areas (MBF-90). Selected representative SEM images for some of the different MGFs tested are shown in Figure 5.3. The reason for the large discrepancies in the ability to fabricate nanowires on some, but easily on others is not yet

![Figure 5.3: Plan-view SEM images of growths of GaN nanowires on (a) MBF-92 (with a nanowire circled in red), (b) MBF-20 (inset shows tilt view), and (c) MBF-90 (inset shows tilt view) (scale bars are all 1um). (d) Large area plan view image of GaN nanowires on MBF-90 showing large scale uniformity of nanowires (inset shows foil embrittlement post growth)]
understood. Figure 5.3(d) shows a large area plan-view image. The defect in the picture is the only sizeable defect seen in a 100×100 µm image and, as the uniformity rivals that of Si, was chosen to remain in the image for contrast. These are very promising results as this uniformity persists on length scales much larger than the size of typical devices.

5.2 Photoluminescence Measurements

Room temperature photoluminescence (PL) measurements were carried out using an excitation wavelength of 232 nm. (Figure 5.4). Band-to-band recombination was observed in samples grown both on Pt and MBF-90. There is a small but broad range of defect luminescence from ~475-625 nm [139]. Unfortunately several of the MGFs undergo embrittlement during the growth and become fragile (inset Figure 5.3(d)). This makes the foils unable to withstand the typical handling involved in the spin-on of photoresist and device patterning. However, other foils retained their flexibility after growth. Unfortunately, these foils didn’t grow nanowires uniformly enough
under these conditions to make mesoscopic devices, so future exploration will focus on developing nanowire devices on the more resilient MGFs.

### 5.3 Investigation of p-Type Electrical Contact to p-GaN Nanowires

At this point, we have come to an understanding that the bottom (p-type) portion of the nanowire and the current injection and uniformity are one of the limiting factors in the device performance. So, we again use cAFM to probe this at the nanoscale, but this time only looking at p-GaN nanowires, removing the complications of a full LED heterostructure. Conductive atomic force microscopy (cAFM) is used to probe the electrical characteristics of individual p-GaN nanowires on different substrates. It is worth noting that the cAFM tip/nanowire interface adds a Schottky barrier to the substrate/nanowire circuit during this measurement. Current-voltage (IV) curves were then taken on individual p-GaN nanowires directly on p-Si (blue) and on 2 nm Pt (red) (Figure 5.5(a)). The spread in color represents the distribution in characteristics. Nanowires on p-Si have a threshold voltages between 5-9 V and no notable current in reverse bias. However, upon the addition of a Pt interlayer, the current appears more ohmic, with some beginning to pass

![Figure 5.5: (a) cAFM curves of individual p-GaN nanowires on p-Si (black) and 2 nm Pt on p-Si (red) (b) Macroscopic p-device IV curves](image-url)

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current <4 V and also appearing more symmetric about 0 V, passing current in reverse bias. These results are consistent with the predicted reduction of the large Schottky barrier at the p-GaN/p-Si interface for p-GaN/Pt.

In addition to the cAFM measurements, mesoscopic devices were fabricated to test the effects of the Pt-interlayer on nanowire ensembles. A p-type top contact consisting of 20/30/80 nm of Pt/Ni/Au [140] was deposited using standard photolithography and liftoff techniques. Figure 5.5(b) shows the performance of mesoscopic devices on these two substrates. These measurements show that the Pt is indeed more conductive at low-bias. However, at these low biases, the injection current is ~1 mA, much lower than the operating current for the device. There seems to be a large series resistance in the thin Pt film devices, and at higher biases ~±1.5 V, the bare Si starts to be more conductive.

5.4 Light Emitting Diodes on Thin Pt Films

5.4.1 Removal of Reabsorbing Semiconductor Layers in LED Heterostructure

Now that GaN nanowires have been grown on Pt, the next step is fabrication of an LED. Up until now there has been a 100 nm graded section going all the way to GaN above the active region which, having below bandgap material, will absorb the emitted light. The new heterostructure design above the active region will primarily consist of AlGaN with a bandgap greater than that of the emission to avoid reabsorption (Figure 5.6) but will have a short 10 nm graded section from n-AlGaN to GaN so that good electrical contacts can be made.

The LED structure is grown on a p-Si wafer that had half coated with 2 nm of Pt using the methods described in section 5.1.1. The primary Al and Ga fluxes were $4.10 \times 10^{-8}$ torr and
6.20×10⁻⁸ torr. First, p-GaN nanowires were nucleated for 5 minutes at 730°C, the temperature was then increased to 770°C, and then a 100 nm linearly graded AlₓGa₁₋ₓN (x = 0 to 1) co-doped with Mg. The temperature was again increased to 850°C for the active region, consisting of 5 periods of 3 nm AlGaN QWs separated by 3 nm AlN barriers. After completion of the active region, the shutters for Si, and both Al and a separate Ga source with a BEP of 3.0×10⁻⁸ torr were immediately opened and the substrate temperature was cooled to 790°C at a rate of 25°C per minute. As the temperature cools, the amount of Ga incorporation increases, giving a composition gradient from pure AlN to AlGaN of a composition dictated by the relative Ga/Al fluxes and temperature. This section is roughly 190 nm, thus it is important that the bandgap of this region is larger than the emitted light, to avoid reabsorption. Then the high Al composition AlGaN is steeply graded back down to GaN over the course of 10 nm. A benefit of the p-down design is that grading composition this way in nanowires (which grow in the (0001) direction) gives further n-type

Figure 5.6: Band diagram of new long n-AlGaN, short top grade heterostructure on p-Si
polarization doping, which should enable easier electrical contact to the nanowire for device processing.

Deep UV reflectivity was used to check the composition of the long AlGaN section and explore the photonic impact of Pt films (Figure 5.7). The p-Si was slightly more reflective than Pt/p-Si at the deeper wavelengths, but they become similar around 300 nm, in agreement with previous reports [141]. Next, the substrates are examined with AlGaN nanowire devices on them. Unfortunately, transmission measurements are not possible with these samples being grown on Si as all UV light is absorbed. However, when using a steep angle for reflectance measurements, some light penetrates the material. Thus, if the light penetrating the material has an energy higher than that of the bandgap of the material, it can be absorbed. With nearly 200 nm AlGaN, Fabrey-Perot oscillations are observed down to ~220 nm for samples on both substrates. The disappearance of the oscillations coincides with the onset of absorption of the AlGaN at the bandgap of ~220 nm (5.64 eV). The addition of the nanowires also sees shifts in the peaks of the

![Figure 5.7: Reflectance of bare p-Si and p-Si coated with 2 nm of Pt with coalescence with and without the presence of AlGaN nanowire LEDs](image_url)
reflectance between the two substrates, showing that Pt/p-Si is more reflective than bare Si by >10% over select wavelength ranges. This highlights the importance of distinguishing between the AlGaN/substrate and air/substrate reflectivity spectra when evaluating substrates for DUV applications. Also worth noting at this point, is by reducing the top graded section to 10 nm, there are only ~3 nm of material with a lower bandgap than emission at 300 nm (4.1 eV), as opposed to ~27 nm when using the 100 nm graded section discussed in previous sections. However, if the target emission wavelength shifts deeper into the UV, such as 265 nm (4.7 eV, the ideal for germicidal applications), the amount of absorbing material is reduced from 50 to 6 nm.

### 5.4.2 Characterization of LEDs on Thin Pt Films

Typical mesa LEDs were then fabricated using the same procedure outlined in section 2.5.1 with heterostructure and processing details shown in Table 5.2. The EL spectra and IV curves for the devices on Pt are compared to devices on Si in Figure 5.8. Pulsed voltage IV curves were taken at 100 Hz and 4% duty cycle (Figure 5.8(b)). The black curve is the old standard.

**Table 5.2: The different devices grown and processed as well as the threshold voltage ($V_{th}$), output power ($P_{out}$) under an input power of 0.1 W, and maximum observed efficiency ($\eta$) * EL results for FG FC devices are not directly comparable**

<table>
<thead>
<tr>
<th>Device</th>
<th>Substrate</th>
<th>Bottom section</th>
<th>Top section</th>
<th>Top Contact</th>
<th>$V_{th}$ (V)</th>
<th>$P_{out}$ at 0.1W (nW)</th>
<th>Max $\eta$ (m%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FG on Si FC$_{Ti/Au}$</td>
<td>p-Si</td>
<td>100 nm grade</td>
<td>100 nm grade</td>
<td>10/20nm Ti/Au fully conformal</td>
<td>9.5</td>
<td>93*</td>
<td>0.26*</td>
</tr>
<tr>
<td>HG on Pt FC$_{Ti/Au}$</td>
<td>2nm Pt on p-Si</td>
<td>100 nm grade</td>
<td>190 nm AlGaN</td>
<td>10/20nm Ti/Au fully conformal</td>
<td>11.2</td>
<td>60</td>
<td>0.17</td>
</tr>
<tr>
<td>HG on Si FC$_{Ti/Au}$</td>
<td>p-Si</td>
<td>100 nm grade</td>
<td>190 nm AlGaN</td>
<td>10/20nm Ti/Au fully conformal</td>
<td>8.6</td>
<td>12</td>
<td>0.02</td>
</tr>
<tr>
<td>HG on Si GO$_{TV/Au}$</td>
<td>p-Si</td>
<td>100 nm grade</td>
<td>190 nm AlGaN</td>
<td>10/200nm Ti/Au grid</td>
<td>9.0</td>
<td>80</td>
<td>0.36</td>
</tr>
<tr>
<td>HG on Si GO$_{Al/Ni/Au/Ni}$</td>
<td>p-Si</td>
<td>100 nm grade</td>
<td>190 nm AlGaN</td>
<td>30/30/200/20nm Al/Ni/Au/Ni grid</td>
<td>8.5</td>
<td>191</td>
<td>0.54</td>
</tr>
</tbody>
</table>
heterostructure with the fully graded (FG) AlGaN regions on top and bottom, which shows a $V_{th}$ of 9.5 V. The devices with only the bottom half graded (HG) on Si (blue) shows a lower $V_{th}$ (8-9 V) and the devices Pt (red) curiously show the highest $V_{th}$ (11-12 V). The differential conductance for the different devices appear to be very similar under this voltage/current range. The leakage current of both of the devices on Si are very similar, but the device on Pt has ~10× and 1000× higher leakage currents at -10 V -4 V, respectively.

There are valid comparisons to be made regarding the electrical injection between the original FG and HG devices as we engineer the top contact region. However, it is worth noting that the structures for the old standard FG heterostructure is ~230 nm in height and the new HG nanowires are ~350 nm tall, and there are substantial height dependent photonic effects on EQE [81]. Attempting to extend the size of the top or bottom of the FG structure to match the height of the HG structure would change the effective polarization doping or amount of light reabsorption. And shrinking the top section of the nanowires would not allow for eventual nanowire coalescence.
(will be discussed more in the following section). Thus, the comparison of FG to HG is not as qualitative as one would want, and any comparison of light output between these devices are neglected in this chapter. The EL spectra of 250×250 µm devices shows significantly brighter emission on Pt-coated Si than identical devices on bare Si with the peak EL wavelength showing slight a blueshift with increasing injection current by 2.5 and 1 nm for devices on Si and Pt, respectively.

Extracted LED characteristics shown in Figure 5.9 show that the device on Pt is

![Figure 5.9 Device characteristics of 250×250 µm devices on p-Si (blue) and Pt (red). (a) EL spectra at 10 mA injection current (b) Peak EL intensity vs. drive current (c) Output power vs input power and (d) Efficiency vs. drive current](image-url)
approximately $29\times$ brighter than the identical device on p-Si at the points of max intensity. The output power of devices on Pt are $21\times$ higher than Si at 310 mW, and $35\times$ higher at lower input power. The efficiency of the devices on Si are lower, peaking around 0.02 m%. The efficiency of the device on Pt starts at $\sim 0.18$ m% but quickly decreases at higher injection currents, leveling off around 0.05 m%, due to the quick increase in operating voltage.

Operating voltages at different injection currents during acquisition of EL spectra are shown in Figure 5.10. The operating voltage of the device on Pt starts to increase quickly but appears to level off around 10 mA before increasing more quickly again prior to failure. Similar to what is observed in the pulsed IV curves, the device on Pt begins at higher voltages than the device on Si. It also begins to increase quickly but level off around 10 mA, before increasing more quickly again prior to failure. The device on Si has a lower operating voltage, which is relatively more constant, increasing $\sim 1.5$ V over the first 20 mA, compared to 5.9 V for Pt. The main difference in the early operating voltage is likely due to a difference in series resistances between

![Figure 5.10: Operating voltage as a function of drive current until device failure for the old standard fully graded sample (black), half graded samples on p-Si (blue) and Pt (red)](image-url)
the two devices. The operating voltage of the FG device (black) shows no dramatic increase or upturns during operation but lies between the two HG devices. The increased operating voltage for Pt could also result in increased joule heating, however the light output of the device doesn’t seem to dip, and the Pt should be better for thermal management.

5.4.3 Burn-in Characterization of LEDs on Thin Pt Films

The effect of reverse bias burn-in was also investigated on the new samples with thin metal interlayers. The burn-in procedure is similar to that which was described in Chapter 3, holding a reverse bias DC voltage for six seconds. After each burn-in pulse, an EL spectra is acquired using a pulsed current injection at 100 Hz and 20% duty cycle ranging from 0.2 to 1.0 mA. Subsequently an IV curve is taken using a pulsed voltage at 100Hz and 4% duty cycle. The burn-in characteristics of all samples that were measured this way are outlined in Table 5.3.

First looking at the EL characteristics at 1 mA injection as a function of burn-in (Figure 5.11(a-c)). Both devices show an initial reduction in EL intensity down to ~2 V of burn-

Table 5.3: Effects of reverse bias burn-in on characteristics of different devices including the maximum sustainable burn-in voltage before device failure and the percentage of the resulting changes in: EL intensity, full width half max, peak wavelength (\(\lambda\)), threshold voltage (\(V_{th}\)), differential conductance (\(dI/dV\)), leakage current at -5 V (\(I_{leak}\)), and efficiency (\(\eta\)). *EL comparisons for FG FC device are not directly comparable

<table>
<thead>
<tr>
<th>Device</th>
<th>Max B-I Voltage (V)</th>
<th>(\Delta EL) (%)</th>
<th>(\Delta FWHM) (nm)</th>
<th>(\Delta Peak \lambda) (nm)</th>
<th>(\Delta V_{th}) (V)</th>
<th>(\Delta (dI/dV)) (%)</th>
<th>(\Delta I_{leak}) (%)</th>
<th>(\Delta \eta) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FG on Si</td>
<td>-10.9</td>
<td>35%* -59%*</td>
<td>4.6%</td>
<td>-0.9%</td>
<td>10%</td>
<td>-10%</td>
<td>846% 27%</td>
<td>36%* -63%*</td>
</tr>
<tr>
<td>FC Ti/Au</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HG on Pt</td>
<td>-17.6</td>
<td>-138%</td>
<td>1.2%</td>
<td>1.0%</td>
<td>8%</td>
<td>-41%</td>
<td>-95%</td>
<td>-67%</td>
</tr>
<tr>
<td>FG Ti/Au</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HG on Si</td>
<td>-7.8</td>
<td>-25%</td>
<td>-13%</td>
<td>-1.2%</td>
<td>81%</td>
<td>-38%</td>
<td>-25%</td>
<td>-71%</td>
</tr>
<tr>
<td>FC Ti/Au</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HG on Si</td>
<td>-5.5</td>
<td>-5%</td>
<td>-6.6%</td>
<td>0.2%</td>
<td>60%</td>
<td>-96%</td>
<td>-99%</td>
<td>-87%</td>
</tr>
<tr>
<td>GO Al/Ni/Au/Ni</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Remarkably stable is the HG device on Pt, with constant intensity over a very large range of reverse bias burn-in voltages. After a reduction in the intensity early on, which also coincides with a slight redshift, the emission stabilizes at an intensity in but have a period of stable intensity after this. 

Figure 5.11: Burn-in characteristics on 250×250 μm LED devices on Si (blue) and Pt (red) as well as the old fully graded standard (black). (a) Peak EL Intensity at 1 mA pulsed injection (b) Peak FHWM (c) Peak wavelength (d) Threshold voltage (e) differential conductance and (f) leakage current at -5 V all as a function of burn-in voltage.
only slightly higher than its counterpart on Si before sudden device failure. Conversely, the HG device on Si shows an upturn in the peak intensity before device failure.

The effect of burn-in on the electrical characteristics is then examined (Figure 5.11 (d-f)). Prior to burn-in (at 0 V), the $V_{th}$ of all the devices are similar to what was observed in the full IV curves shown in the previous section, with the HG devices on Si being comparable to the FG sample. The devices on Pt have an apparently lower $V_{th}$ than observed previously but are still higher than the devices on bare Si.

For both HG samples, it appears the shift in $V_{th}$ is inversely proportional to the emission intensity, with increases in $V_{th}$ happening over the same ranges as the decreases in intensity. At the onset of burn-in, the HG devices quickly shift toward higher $V_{th}$ with the device on Si rising quickly from 7.25 to ~11 V at a burn-in of ~1 V, before continuously increasing at a comparatively slower rate to beyond 13 V at which point the device fails at a burn-in of ~6 V. The device on Pt has a $V_{th}$ that shifts slightly from 9 to about 9.5 V at the same rate that the GO device was increasing at, but then remains essentially constant over high burn-in voltages up to nearly -18 V. The slower increase of the devices on Pt, hints toward more device stability.

When looking at the differential conductance (Figure 5.11(e)) it is not surprising that the FG sample is the most conductive. The top region, being the 100 nm graded Si-doped AlGaN, has average of 50% GaN, compared to ~200nm of high Al% AlGaN. It also has nearly a decade of engineering that has gone into it. The trend of this follows $V_{th}$, becoming slightly more resistive overall as the burn-in voltage increases. With starting conductances only slightly lower than the FG device, the other HG devices follow a similar trend. Although, the device on Si has a sharp decrease prior to device failure.
The effect of burn-in on leakage current is also examined. The leakage current is measured from the IV curves at -5 V. The behavior of the FG sample stands in contrast with the other samples, having the lowest initial leakage currents, but then increasing by nearly an order of magnitude before dropping back down to levels comparable with the original. The HG device on Si has an initial reduction in leakage current, dropping quickly to fractions of a nA. But the device on Pt, has a high leakage current, starting in the µA range and decreasing over the initial ~6V of burn-in by slightly more than an order of magnitude before stabilizing at a level still ~100× higher than the other devices.

Lastly, the effect of reverse bias burn-in on the efficiency power of the devices under a pulsed current injection of 1 mA is calculated by combining the operating with the output power (Figure 5.12). Both devices follow trends similar to what was observed in the peak EL intensity, although, the higher operating voltage of the devices on Pt result in efficiencies (ƞ) that are a bit

Figure 5.12: Efficiency vs burn-in on a 250×250 µm LED for devices on Si and Pt
closer, both peaking at ~0.25 m% (with Pt being slightly higher) and showing overall reductions by ~70% (details listed in Table 5.3).

5.5 Removal of the Fully-Conformal Top Contact for Nanowire LEDs

Nanowire LEDs consist of a forest of individual nanowires, with each nanowire required to make direct metal contact in ensemble devices. Until now, we have been using a 10 nm Ti/20nm Au “semi-transparent” fully conformal (FC) top contact in an attempt to make contact to each nanowire, and also spread the current from the source (probe tip or wire) to each individual nanowire in the ensemble device. This has its own problems which have been touched on previously, such as needing to make identical contact to each nanowire to maintain as uniform as possible current injection, the possibility of making direct contact to the bottom substrate through gaps/low density locations, or unintentional coating of nanowire sidewalls. However, the “semi-transparent” claim of these contacts is generous, with the transparency of 300 nm (265 nm) light through 20 nm of Au being 20.6% (18.5%) and 10 nm of Ti 35.9% (38.3%). These numbers are accounting only for transmissive losses, and if one considers light lost to internal reflections, these quickly drop to <10% [141]. Thus, if the top contact can be thinned, or even better yet removed, there can be large gains to light extraction.

If the tops of the nanowires were to be coalesced material with a larger bandgap than the emission energy, they could act as a fully transparent current spreading layer, eliminating the need for a FC metal contact. There have been previous reports on coalesced GaN nanowires [142]–[146]. Thus, electrical contact could be fabricated with a grid only (GO) design having partial coverage and using the coalesced nanowire tops to spread the current away from the grid fingers. In one particular study, a visible LED was made through the use of a thick (>500nm) coalesced
p-GaN top contact [145]. However, for use in UV optoelectronics this still poses a few problems. Using GaN as the coalesced layer will absorb a great deal of emitted light, so high Al% AlGaN must be used in the coalesced layer. This would amplify the problem of p-type doping, so ideally the coalesced portion would also be n-type. All previously discussed heterostructures in this work have been n-up devices, and methods of increasing the hole injection into the p-type base of the nanowires has already been discussed, so these designs would yield themselves well to a coalesced design. Because nanowire growth proceeds both vertically and radially, even at elevated temperatures, if the original nanowire density is high enough, coalescence can be simply achieved by growing longer. Figure 5.13 shows SEM images of nanowires that have coalesced n-AlGaN top sections. The vertical/radial growth rate ratio is dependent on III/N flux ratios and substrate temperature [101], which when trending towards the thin film regime (colder, higher III/N) promotes radial growth and smoother surfaces; thus, a detailed study investigating the effects of a finely tuned coalesced layer with good surface morphology is eventually necessary.

A new processing strategy to take advantage of the coalesced nanowire tops (Figure 5.14) was adapted for GO devices using the coalesced top surface. The samples are first cleaned using acetone, methanol and isopropyl alcohol rinses, and dried by baking at 115°C for five minutes.
Then photoresist and patterning of mesas is done. A low power oxygen dry etch is done to remove any small amounts of photoresist that remained after developing. A reactive ion etch is done using Cl₂/BCl₃/Ar to etch the nanowires into mesa structures. The photoresist is then completely removed by soaking in acetone. The samples are again cleaned with fresh acetone and subsequent methanol and isopropyl alcohol rinses and dried at 115°C for five minutes. Photoresist is again applied, and grid structures patterned above the mesas. Another low power oxygen etch is used to remove any excess photoresist; this one is important because it involves preparing the
metal/semiconductor interface. Each sample was then placed in concentrated HCl at room temperature to remove any oxide that would have formed on the nanowire tops before placing in the e-beam deposition chamber. Lift-off by soaking in acetone was then used to remove the excess metal, leaving only the partial coverage top contact behind. Two types of GO contacts were examined, the first being a (10/200) nm Ti/Au contact to replicate the FC interface, and the other being a (30/30/200/20) nm Al/Ni/Au/Ni stack. The latter Al-containing contact was originally adopted for optional use as a hard mask if there was a desire to do a back etch of the short top graded region [147]. However, the dry etch seemed to degrade the contacts resulting in poorer overall performance, both electrically and optically, so this work will not focus on further discussion of back-etched devices.

5.5.1 Characterization of Grid-Only LEDs

Different device structures were fabricated and tested for comparison. Similar to Section 5.4.2, the same FG old standard sample with 100 nm graded bottom and top regions with FC Ti/Au contacts was used as a control for the electrical injection characteristics, but again no comparison between optical characteristics would be valid. There were no devices fabricated with FC thick (>200 nm) metal stacks, since it would not let any light out; and there is no coalesced layer for current spreading, so there is no need for a GO process with the uncoalesced samples. The HG samples with the top consisting of coalesced n-AlGaN were fabricated with semi-transparent Ti/Au contacts and with GO schemes using both Ti/Au and Al/Ni/Au/Ni metal stacks. The different devices grown and processed along with some of the LED characteristics for each are outlined in Table 5.2.
Pulsed voltage IV curves were taken at 100 Hz and 4% duty cycle (Figure 5.15). The FG sample showed a $V_{th}$ of 9.5 V. The coalesced samples show a slightly lower $V_{th}$, with the different contacts showing slightly varied on-state resistances with the GO devices being slightly more resistive than the FC contacts. This is likely due to the thick AlGaN section and the necessity of lateral current spreading in this more resistive coalesced layer compared to a FC metal contact.

The leakage current of the two FC devices are very similar, down to -10 V. The GO devices show a wider range of characteristics, with the GO$_{\text{Al/Ni/Au/Ni}}$ device (which also shows a higher shunt current in forward bias) having a ~10× larger leakage current at -10V than the FC devices. However, the GO$_{\text{Ti/Au}}$ device is exceptional with current in the nA range at -10 V, nearly 100× less than FC devices. The observation of lower leakage currents for GO devices is promising. An optimistic view attributes the reduction in leakage to the avoidance of direct wiring to nano-shorts (nanowire sidewalls/direct locations of coalescence). Whereas a more pessimistic option is that the coalesced region just isn’t spreading the current efficiently to the locations nano-shorts, and
improving the conductivity of the coalesced region will result in an increase in the leakage current again.

Unfortunately, despite having decent diode-like IV characteristics, no substantial light emission was observed for GO devices on Pt, so that will not be discussed here. This is could be because the samples were not fully coalesced and current was not being spread from the grid; despite electrically behaving like LEDs, the thick metal fingers would block all of the light. This idea is reinforced by the presence of a dim peak (>1000 time less intense than the other samples) which did not increase much, even at very high injection currents. The light that is being collected is likely leaking around the sides or from a very narrow region around the grid fingers. This is probably a result of the slightly lower nanowire density as described in section 5.1.1. This could be solved by implementing a slightly lower nucleation temperature, longer nucleation time, or longer growth time to encourage coalescence.

The EL spectra characteristics of 250×250 µm devices are shown in Figure 5.16. The removal of a conformal top contact drastically increases the peak EL at the same injection current. The GOAl/Ni/Au/Ni device on Si saturates the detector after 10 mA, where it shows 22× brighter peak EL than the FC device on Si, and 3.3× brighter emission than GOTi/Au. Even accounting for higher operating voltages (discussed later) the output power is still higher at the equal input power. The GO scheme shows efficiency increases up to 37× at the same input power and the highest observed overall device efficiency for the GO devices is 0.54m% compared to a peak efficiency of 0.02m% for the identical heterostructure with a FC contact.

Another promising result of coalesced top area and GO contacts, is the consistency of working large area devices. With self-assembled nanowire-based devices, getting a uniform area
as large as 2×2 mm working can be difficult using the FC contacts, with devices typically being short circuited. This could be because the odds of having (A) a single large short or (B) a single pocket devoid of nanowires in a 2×2 mm square is pretty high. However, by coalescing the tops and using grid only contacts, we significantly reduce the possibility of (B) and by only covering ~30% of the top with a contact, it greatly reduces the chance of direct contact to (A) shorts. The
inset of Figure 5.16(b) shows a 1×1 mm device in contact with the probe with grid fingers on the left side partially removed during the liftoff process. The inset in Figure 5.16(d) shows the same LED under operation; the section where the grid fingers are missing can still be seen in the camera image as an area without any emission, so the coalesced contact is not spreading current over those distances.

Operating voltages at different injection currents during acquisition of EL spectra are shown in Figure 5.17. Similar to the IV curves, the FC device shows the lowest voltages across the operating range. The GO devices have higher operating voltages, which both increase about at the same rate, but more quickly with increasing drive current than the previously shown IV curves would suggest. This points towards a higher series resistance or appreciable burn-in during forward bias operation, either could be a result of inefficient current spreading in the coalesced n-AlGaN layer. The inset in Figure 5.17 shows a 250×250 µm GO device on Si tested

![Figure 5.17](image)

Figure 5.17: Operating voltage as a function of drive current, until device failure for LEDs with fully conformal Ti/Au (solid circles), grid only Ti/Au (open circles), and grid only Al/Ni/Au/Ni contacts (open squares). Inset shows a 250×250 µm device on Si after operation until failure (left) and untested device (right)
until failure (left). When compared to the neighboring device, there is the obvious explosion and delamination of the of the top contact at the point of contact with the probe tip, but also large changes in color (purple to yellow) around the grid fingers where there is no metal. Under DC current injection the apparent change in color can be observed to creep outward from the grid fingers in real time. This could be evidence of a forward bias burn-in effect.

5.5.2 Burn-In Characterization of Grid-Only LEDs

The effect of reverse bias burn-in was also investigated on the new grid only devices structures. The burn-in procedure is identical to that discussed in the previous section with the characteristics summarized in Table 5.3. The FC samples discussed here (the full grade and half grade) both are again identical to the sample discussed in Section 5.4.3.

Because the GO devices with the Al containing contact were the brightest, only the burn-in characteristics of these are compared to FC contacts, as shown in Figure 5.18. But again, the optical properties of the FG devices are not comparable, so are not discussed. Both HG devices show an initial reduction in EL intensity, with the GO device steadily decreasing until ~2 V of burn-in, but have a period of stable intensity after this. The GO device showed very high initial intensity and after a 25% reduction in intensity, became stable with emission remaining ~9.5× higher than the FC device with very small changes in the FWHM (~6% reduction) and peak location (+0.2%).

The effect of burn-in on the electrical characteristics are also examined and again compared to the old standard (Figure 5.18(d-f)). Prior to burn-in (at 0 V), the $V_{th}$ of all devices are similar, and in agreement with the full IV curves. For all samples, it appears the increase of $V_{th}$ overlaps with the decrease in emission intensity. At the onset of burn-in, the $V_{th}$ of the HG FC rises very quickly from 7.25 V to ~11 V by ~1 V of burn-in, before continuously increasing at a slower rate
to beyond 13 V prior to device failure at a burn-in of -6 V. The $V_{th}$ of the GO sample also increases rapidly from 8.25 V to 12.75 V as the burn-in voltage is pushed to -2 V before then decreasing

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Figure 5.18: Comparison of burn-in characteristics of 250×250 μm devices (a) Peak EL Intensity (b) Peak FHWM (c) Peak wavelength (d) Threshold voltage (e) differential conductance and (f) leakage current at -5 V all as a function of burn-in voltage for the old standard fully graded (solid black circles) and the coalesced half graded LEDs with fully conformal (solid blue circles) and grid only (open blue squares) top contacts.
slightly prior to device failure at -5.5 V. The old standard device shows the smallest increase in $V_{th}$, as well as being able to endure the highest burn-in voltage. This could possibly be fixed by further engineering the conductivity of the coalesced AlGaN layer.

When looking at the differential conductance (Figure 5.18(e)) it is not surprising that both of the FC samples are more conductive overall, with the FG device being the highest. In the GO devices, the current must now be spread not just vertically through the nanowire from top contact to bottom contact, but also from the grid finger laterally throughout the coalesced region before passing through the active region. This is an obvious area of interest for future device engineering. There is also a quicker burn-in-voltage dependent decrease in differential conductance in the HG devices which could also be attributed to the current spreading in this top layer similar to what was shown in the inset of Figure 5.17.

The effect of burn-in on leakage current is also examined. The leakage current is measured at -5 V from the acquired IV curves. The HG FC device has a low starting leakage current and shows an initial reduction, dropping quickly to fractions of a nA. The GO device shows a high starting leakage current, but decreases by more than two orders of magnitude over the course of -6 V of burn-in. The strange increase between -2 and -4 V is a product of reverse bias negative differential resistance (NDR) which is not fully understood at this point. Also under current investigation, is the nearly three orders of magnitude difference in the starting leakage current, as it is expected that a GO design would reduce direct wiring to nanoshorts.

Lastly, the effect of reverse bias burn-in on the efficiency is again calculated by combining the operating power of the devices under a pulsed current injection of 1 mA with the output power (Figure 5.19). Prior to burn-in the GO device on Si has a much higher efficiency, but it
continuously drops as higher burn-in voltages are applied. The overall relative changes in efficiency are listed in Table 5.3, with the GO device on Si being the largest negative change observed. This large reduction in efficiency is likely due to the continuous decrease in differential conductance. Although the $V_{th}$ does not shift greatly, the increased resistance leads to higher operating voltages, thus continuously decreasing the efficiency. This could be the result of necessitating further lateral transport from the metallic grid fingers, similar to what was observed in the inset of Figure 5.17.

5.6 Summary

This chapter showed the growth of GaN nanowires on Pt films deposited on Si and on amorphous metallic glass foils. SEM images showed highly uniform growth of nanowires on 2 nm Pt thin films on Si under the same growth conditions as Si with no signs of film delamination. Thinner Pt films resulted in clusters of nanowires, and thicker films resulted in a dramatic decrease in nanowire nucleation density. The amorphous foils provided mixed results, with some devoid of
any nanowire nucleation sites, some forming small clumps of nanowires, and others showing remarkably uniform growth. More work is required to understand the reason behind the large disparity of these results. The high crystal quality of nanowires on the foil that provided uniform wires (MBF-92) as well as on 2 nm Pt films was verified by photoluminescence measurements. Processing of ensemble devices on MBF-92 foils was not achieved due to severe embrittlement post growth, thus more work is required to identify growth regimes on metals without embrittlement.

The Pt film yielded large gains in luminescence and efficiency increases of up to 35× over the identical devices on Si. The growth of a new LED structure with a coalesced top contact was also shown through utilizing the coalescence of the n-AlGaN nanowire tops. Thus enabling a grid-only top contact, with the current spreading taking place in the coalesced region rather than fully conformal thin metal contact. The utilization of a grid only contact resulted in a 9× increase in efficiency at high injection currents, and 37× increase at low injection currents. The grid only design also resulted in much better device yield, with devices up to 2×2 mm in size working much more consistently.

If the growth on Pt was to be combined with the grid-only scheme, efficiencies of up to 17m% could be seen. Also worth noting is that the coalesced layer in these devices are not optimized, and the current is likely not spreading fully, allowing dead spots, so more gains would be achieved by engineering the top section. Additionally, as it currently stands, the operating voltage for the grid-only devices is >6 V higher than similar devices with a fully conformal top contact. This could be attributed to the slightly higher V_th, but also to the decreased differential conductance which could be the result of less efficient current spreading in the coalesced layer.
Thus, some fine tuning of the top portion of the heterostructure (thickness, doping level, short-top grade) and device processing are needed to reduce this. If the operating voltage can be brought on par with the conformal devices, even further increases in efficiency could be achieved.
Chapter 6. Conclusions and Closing Remarks

In conclusion, the challenges of nonuniformity in self-assembled nanowire-based ensemble devices were investigated. The measurement of nonuniformities at the nanoscale through the use of conductive atomic force microscopy was shown as well as burn-in methods for increasing the homogeneity. Alternative substrates were investigated to achieve uniform contact at the backside of the nanowires by using polycrystalline metals, and the first LED devices directly on metal foil were achieved. However, polycrystalline metals provided a new set of uniformity issues due to underlying grains. The grain-induced nonuniformity issues were shown to be mitigated through growth on nanocrystalline films and amorphous foils. Although ensemble devices were unable to be fabricated on amorphous foils, devices with thin Pt films on Si showed efficiency increases of up to 32× compared to devices directly on Si. By coalescing the top n-AlGaN section of the nanowires, a grid-only device scheme was able to be achieved which avoids reabsorption by the top portion of nanowires as well as a conformal top contact which resulted in a 37× increase in light emission at constant input power. By combining the gains in efficiency demonstrated here, an efficiency of ~0.017% should be achievable, with additional improvements if the $V_{th}$ could be reduced to the values of the control samples on Si. The grid-only scheme also opens the door to new characterization of nanowire LEDs. For instance, cAFM was shown to be very useful for characterization of nanowire ensembles, but was never able to be used on devices after normal operation or burn-in because of the fully conformal metal top contact. However, now before and after cAFM area maps can be performed between the grid fingers to see how these ensemble devices evolve during operation and burn-in.
A detailed study of the nucleation conditions in an effort achieve a more uniform nanowires from the start could yield huge gains in uniformity of the overall device especially on the alternative substrates discussed here. A study specifically regarding engineering the uniformity of self-assembled nanowires during the nucleation step, even on the typically used Si substrates, could greatly benefit the field. The two-step approach used in our group yields itself nicely to this type of project, giving independent control of density and vertical growth rate. All samples discussed in this work were a flat 5 min nucleation before immediately proceeding with the growth of the remaining heterostructure, with the temperature of the nucleation set only by SEM characterization to ensure the density was sufficient for ensemble devices. However, the uniformity should be investigated using colder temperatures for shorter times as well as higher temperatures and longer times. The investigation at multiple temperatures could be done swiftly using the MTZ block discussed in Appendix A. There is also the option of adding an additional ripening step between nucleation and heterostructure growth. If short-time nucleation is done at a cooler temperature there should be a high density of tiny GaN islands. The substrate could then be heated and left at temperatures near the growth temperature for differing amounts of time while exposing only the N-plasma to the surface, allowing the GaN islands to coalesce into larger islands, similar to Ostwald ripening, in an effort to create a uniform distribution of islands to nucleate wires form.

A systematic study of the overall heterostructure density and height, is needed for enhanced photonic extraction, which is really where nanowires could have the potential advantage over their thin-film counterparts. The effect of nanowire density could be done in conjunction with the study of the nucleation conditions on uniformity. However, if the nanowire density is too low, the
formation of a coalesced layer could be difficult to achieve, and if the density is too high, the natural taper of the nanowires could result in premature coalescence, shorting the active region. Doing a more aggressive grade of the bottom nanowire section could yield better p-type doping and current injection into the bottom of the device, especially on metal substrates, which could act as a hole reservoir. With the new high Al% n-AlGaN top heterostructure, controlled investigation of the nanowire height is more achievable, since changing the height in earlier versions of the LED heterostructure would have involved changing the length of a graded region, also changing the effective doping. Work done in our group using a more aggressively graded p-graded region for the nanowire bottom section previously showed enhanced electrical characteristics, but the emission showed no trend. This is likely due to the change in the overall height between each heterostructure. A new set should be designed with p-type graded sections of different lengths (ex. 200, 100, 75, 50, 25 nm) but this time using the constant composition n-AlGaN layer to offset the reduction in height from the p-type section, keeping the overall height the same. Using the information gathered from this, the p-type section from the best performing device should be taken and then the overall height of the nanowire should be varied (using the n-AlGaN section). The effects of nanowire height on the emission, under the same current injection conditions, should be oscillatory, but the peaks of these oscillations will obviously depend on the substrate (Si, metal film, metal foil, etc.) that is used and the emission wavelength.

There are also additional active region/barrier designs that haven’t been explored such as the use of InAlN or BGaN for quantum wells, which could still emit in the DUV, and possibly avoid the polarization switch to side-emission as well as reduce the polarization of the QWs, reducing the quantum confined Stark effect. Since neither B or In are used in any other portion of
the p-down heterostructure, using different fluxes of these species for a growth set is trivial. For the case of incorporating B (which has a low vapor pressure) the active region could remain hot, and the Al shutter could be opened the whole time while opening the shutter for B to create a QW/barrier structure. The incorporation of In could be more difficult; as discussed in this work, In segregation is a large issue, and in the active region it could result in wide distribution of $V_{th}$ and increase of the FWHM of the emission. Besides this, using InAlN for DUV, would still require the use of AlN barriers, which would need to be grown hot (>800°C), and getting In to stick at these temperatures could be challenging. However, besides simply attempting the use of larger fluxes, by pulsing the Al/In shutters, some In may be trapped by impinging Al adatoms and buried before desorption could occur. When the desired QW structure/composition is found, structures with finely tuned AlGaN barrier compositions to reduce the polarization fields, and subsequently the quantum confined start effect, should be designed. An optimized electron blocking layer is also currently lacking.

There is still a lot of work to be done optimizing the top portion of the new HG heterostructure, but because it is an n-up device structure the problems should be solvable. Improving the sheet resistance of the coalesced layer is high on the list. For the samples discussed in Chapter 5, despite having ~190 nm of AlGaN to coalesce, the region of coalescence (and therefore current spreading) is still very thin. Thus, by growing thicker coalescence and subsequently the resistance could be improved, but this must be balanced with the photonic extraction discussed earlier. As the thickness is increased reabsorption of photons becomes increasingly important. For devices emitting at 300 nm, more Ga could be added to the coalesced layer before this occurs, but if samples with deeper UV emission is desired the amount of Ga that
can be added is only slight. The Si doping in this layer could also be increased. Growth conditions should be varied to approach that of thin film growth, dropping the III/N ratio, and even possibly going metal rich to see if smooth surfaces could be achieved. The contact resistance could also be improved through optimizing the growth of the aggressive grade to GaN. Using a 10 nm graded section minimizes absorption, but growth of this section takes only ~3 minutes, thus requiring fast shutter times (~6 seconds) and with the sample rotating at only 2 rpm, this is almost assuredly non-uniform. This section could be less aggressive, and any material that would absorb could be back-etched during processing. Another tangential route, involves the use of $\beta$-Ga$_2$O$_3$ for top contacts, as it is a wide bandgap semiconductor, and the nitride system is connected to an oxide system. Thus, it is possible to grow thick $\beta$-Ga$_2$O$_3 \textit{in-situ}$ on AlGaN in our facilities.

On the device processing side there is also more work to be done optimizing the grid contacts and spacing. The ideal metal stack for the grid should be investigated. Annealed contacts typically were not used for the nanowire devices for fear of spiking through the active region or creating unwanted surface effects. However, if the structures are coalesced, and can be essentially arbitrarily thick, these issues are now null, and structures can be designed following processing procedures previously developed for thin film technology. The grid will be thick metal, and will not transmit any light, thus the design must have grid fingers far enough apart to let out the most light, but close enough to achieve full current spreading through the coalesced layer. With the grid-only structure giving a high yield of working large-area devices, even larger devices should be designed to ultimately test the feasibility of roll-to-roll fabrication for nanowire-based optoelectronics.
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Appendix A. Substrate Holder for Simultaneous MBE Growth at Multiple Temperatures

When working to find the growth phase space for MoSe$_2$ essentially from scratch, I wanted to figure out a way to design a substrate holder that would allow me to cut my work in half by allowing simultaneous growth at different temperatures. Somewhere I heard the phrase “Laziness breeds ingenuity,” and that is part of what spurred this project. So I teamed up with Dennis Brandow at III-V Components and we came up with the idea of the multi-temperature zone (MTZ) block. Mark Brenner helped me set up a test vacuum chamber from old equipment in the lab where I did a lot of the preliminary tests before actually using it for growths. The results are explained in the following appendix and have been previously published elsewhere [100].

A.1 Benefits of Simultaneous Temperature Growth

Molecular beam epitaxy (MBE) allows atomically-precise control over the thickness, composition, and impurities within epitaxial layers through control of molecular beam fluxes and substrate temperature in order to obtain a desired growth mode resulting in a target film morphology or nanostructures [101], [148]–[150]. Typically when exploring new material systems, a growth map is created, which maps some material quality parameter, or heterostructure figure of merit [151]–[153] as a function of tunable variables during growth (Figure A.1). This quality parameter can be anything to compare sample quality i.e. XRD FWHM values, surface roughness, PL intensity, or even a heterostructure figure of merit. Two of the most easily tunable variables in this phase-space are substrate temperature and the flux ratio between atomic species. The central growth parameter of substrate temperature [154], [155], works generically by altering
the kinetic energy of adatoms. At relatively low temperatures, the adatom surface diffusion length is low resulting in statistically roughened thin films and the heterogeneous nucleation rate is high, leading to polycrystalline layers or very high nanostructure densities [156]. However, if the temperature is too high, the adatom surface desorption rate will exceed the epitaxial incorporation rate, and no growth will occur. Thus, a large range of intermediate temperatures must be explored in order to balance the adatom surface diffusion and desorption kinetics. Thus, to create a useful growth window, the parameters must be adequately sampled by performing many individual
growth runs. This is generally an inefficient process in terms of time and resources, as a typical day of growth usually yields no more than 3 distinctly different samples.

Due to the deliberately tedious nature of MBE, people have developed combinatorial techniques to speed things along. Knudsen cells, albeit designed to have a uniform flux profile, in many chambers are at an angle with respect to the substrate, thus the substrate must be rotated to keep the flux uniform across the sample during growth. However, if done carefully, the substrate can be left stagnant resulting in nonuniform flux profiles across a wafer/sample [157], [158]. This allows probing of multiple different flux ratios and compositions across the sample.

A similar method is utilized in our group with the AlGaN nanowire work. All substrate holders, in principle, contain some inherent degree of temperature variation; however this variation is typically uncalibrated and minimized by design to achieve uniform, large area deposition. Because we are growing on 3” Si wafers, the heater is not completely uniform across the whole wafer, different temperatures can be probed based on location of the wafer, center being ~10°C hotter than the edge. A simple approach might be to design a substrate holder to exploit this, i.e. a substrate holder with a large and continuous temperature gradient across the substrate. This approach however, like the previous flux-gradient method, would limit usability of the sample by prohibiting measurements requiring uniform regions, requiring any testable devices must be very short range to be self-consistent. Here we describe a new substrate holder that contains four distinct temperature zones to increase sample throughput and speed up growth phase-space sampling, while also producing uniform samples of practical dimensions. Instead, our current approach aims for a middle ground between increased throughput, and adequate uniform sample area for ex-situ materials characterization and processing.
A.2 How it Works

The substrate holder uses a multiple-temperature zone (MTZ) design where four samples can be grown simultaneously at different temperatures but under otherwise identical pressures and atomic fluxes. The parts are designed to be easily integrated into existing technology, and can be loaded into the current version of a three-inch substrate holder block. The full device can then be mounted on a continual azimuthal rotation (CAR) holder in an MBE growth chamber.

The method through which the device is able to maintain separate temperatures for individual substrates is shown in Figure A.2. Heat is supplied evenly from the CAR through a backing plate providing a uniform temperature across the back of the MTZ block \(T_b\). Inserts with different thermal resistances are placed between the backing plate and the substrates. The thermal resistances of the inserts are selected to be \(R_1 < R_2 < R_3 \approx R_4\) to achieve steady-state substrate temperatures of \(T_1 > T_2 > T_3 \approx T_4\). There is no theoretical limit on the maximum and minimum temperature differences other than the heater power. The temperature difference on the substrate is directly related to the thermal conductance of each zone (which is adjustable by changing the...
faceplate design), and the hot side (heater temperature) and cold side (radiative cooling, e.g. 77K cryo panel).

The MTZ device (Figure A.3) consists of a faceplate specifically designed to maximize the thermal resistance between the substrates ($R_f$) is used to hold the four substrates (intentionally left out in this image) firmly to the standard loading block, while maintaining thermal isolation between samples. A pyrolytic boron nitride (PBN) backing plate (seen through the substrate

Figure A.3: Photos of MTZ block (a) faceplate and windows and (b) back side shielding through the sapphire backing plate (from [100])

Figure A.4: Image of device in action (from [100])
windows) is then used to hold the samples in place. The backside of the backing plate (Figure A.3(b)) contains recessed space to hold the inserts, which are held in place by an ultra-thin quartz wafer and c-clip. To achieve the different temperatures in this study, zones 3 and 4 contained Ta foils with thicknesses of 25 μm and 127 μm, respectively. Zone 2 is a 127 μm thick Ta foil with 127 μm holes spaced 381 μm apart. Finally, zone 1 contains no insert to give the maximum achievable temperature. The radiation from each substrate (Q) is measured using a pyrometer to determine the temperature of each substrate zone. It can be seen in Figure A.4 that each zone is heated differently, as even by eye there is a difference in black body radiation.

### A.3 Testing of Prototype and Proof of Concept

The MTZ block was tested in a Veeco Gen930 system at a pressure of $3 \times 10^{-10}$ torr, and across a wide range of CAR temperatures. The temperature of the CAR is given by a thermocouple ($T_{TC}$), while the temperatures of the individual $1 \times 1$ inch Si (111) substrates are measured using a pyrometer at an emissivity of 0.16. The thermal resistances of the inserts are chosen to be $R_1 < R_2 < R_3 \approx R_4$, corresponding to zones 1-4, respectively. The inset of Figure 2 shows the four different zones at a $T_{TC}$ of 750˚C. The difference in blackbody radiation can be seen in each zone, and reflects the differences in the thermal resistances of the inserts. The block is rotated at a speed of 0.5 rpm such that every 30 s a substrate passes through the sensing area of the pyrometer. Figure A.5 shows the measured substrate temperature from the pyrometer ($T_{Pyro}$) as a function of time. The pyrometer temperature fluctuates on the expected 30 s time intervals, stabilizing for a few seconds as it measures the substrate. Over the 120 s period that is a full rotation, the highest of the minima is the temperature of zone 1 (black circle). As the separation in the faceplate crosses in front of the pyrometer, $T_{Pyro}$ spikes before falling and re-stabilizing over the next substrate. It can
be seen that at $T_{TC} = 780^\circ C$, zones 1, 2, 3, and 4 provide temperatures of 610, 581, 569, and 570$^\circ C$, respectively. The difference in temperature between $T_{TC}$ and $T_{Pyro}$ is due to the large thermal mass and resistance of the substrate block. The temperature difference between substrates is maintained during heating and cooling of the block and each stabilizes within a few seconds, as seen by the steps in Figure 2. Using this measurement method, the temperature variation of each zone as a function of $T_{TC}$ is acquired (Figure A.6).

Across all temperatures tested, zone 1 remains the hottest, with zones 3 or 4 being coolest, and zone 2 providing an intermediate temperature (Figure A.6(a)). This agrees with the thermal resistances for the inserts that were chosen for each zone. Upon subsequent sample loading, temperature differences between zones were found to be within $\pm 2^\circ C$ of the differences shown. However, a constant shift of $T_{Pyro}$ was observed in of $\pm 5^\circ C$. This is comparable to standard 3 inch substrate blocks, which can be attributed to variations in thermal contact between the substrates.
and the face/backing plates. As the $T_{TC}$ is increased, $T_{Pyro}$ for each zone rises linearly and the maximum temperature difference between the hottest and coolest substrates ($\Delta T_{\text{max}}$) increases, as shown in Figure A.6(b). The maximum observed temperature difference of 40°C is achieved at $T_{TC} = 780$°C. This trend should continue at even higher temperatures. At lower temperatures, the temperature variation decreases, and linear extrapolation predicts substrate temperature zones converge at $T_{TC} = 443$°C ($T_{Pyro} = 386$°C).

We demonstrate the utility of the MTZ block in growth phase space mapping in the case of MoSe$_2$ grown on Si [159]. Mo (purity 99.95%) is supplied by e-beam evaporation providing a beam equivalent pressure (BEP) of $2.08 \times 10^{-9}$ torr. Se (purity 6N) is supplied using a valved cracker sublimation source. The Se BEP is $\sim 2.08 \times 10^{-6}$ torr, giving a Se/Mo BEP ratio of $\sim 1000$. The Si (111) wafers are HF dipped to remove the native oxide after which a 7×7 pattern is observed prior to growth. MoSe$_2$ is deposited for 45 minutes after stabilizing $T_{TC}$ at 728°C. This results in temperatures for zones 1, 2, 3, and 4 of 584, 560, 551, and 552°C, respectively. Figure A.7 shows

![Figure A.6: (a) Zone temps as measured by a pyrometer vs thermocouple temperature and (b) the maximum temperature differences between zones as a function of thermocouple temperature (adapted from [100])](image-url)
wide angle, ω-2θ X-ray diffraction (XRD) scans of these samples after alignment to the Si wafer (111) diffraction peak. For the sample grown at 584°C (zone 1), there is no MoSe₂ (002) diffraction peak detected, however at 560°C (zone 2) a peak begins to emerge, and for zones 3 and 4 (~552°C) the peak becomes quite prominent. This high temperature limit of MoSe₂ is expected due to the low sticking coefficient and high desorption rate of Se adatoms at these temperatures [160], [161]. At the highest temperatures studied, the residence time of Se adatoms is too short to allow formation of MoSe₂. However, as the temperature of the substrate is decreased, the steady-state Se adatom concentration increases, enabling the formation of MoSe₂.

Figure A.7: XRD of MoSe₂ grown simultaneously at four different temperatures 584°C (black), 560°C (red), 551°C (blue), and 550°C (green). (from [100])

A.4 Summary

The MTZ substrate holder enables simultaneous growth at multiple distinct temperatures, increasing research throughput. In the first MTZ design discussed here, a maximum substrate temperature difference of 40°C is achieved between temperature zones at substrate temperatures near 590°C, and this temperature difference is expected to disappear below 390°C. However, the
temperature difference between zones can be altered through the choice of the thermal zone heat shielding to select the temperature difference and range of temperatures of interest for a particular material system. This holder can be used with many different material systems, and has been proven useful for exploring new material systems and substrates, such as, but not limited to those discussed in Chapter 5 as well.
Appendix B. Three-Dimensional Lattice Matching for Epitaxially Embedded Nanoparticles

B.1 History of Lattice Matching

Heteroepitaxy is a cornerstone of modern high performance electronics and photonics. With the continued downscaling of devices comes a drive to understand low dimensional structures, usually at the heart of such technologies. Low dimensional structures used in a variety of applications include quantum dots (QDs) or nanoparticles (NPs) embedded in a matrix of another material [162]–[164]. Metallic NPs provide a continuum of electron energy states in the semiconductor band gap [165], making them useful for improving tunnel junction conductivity [166]. Rare earth pnictide NPs embedded in IIIV semiconductors have been shown to exhibit picosecond photoconductance [167], enable reduction of the composite thermal conductivity,[168] and allow introduction of magnetic properties. Because of their heightened confinement, semiconductor NPs have been used as the emission centers in high efficiency LEDs [169], [170] and lasers [171]–[173]. The electronic and optical properties have been shown to be tunable by varying the particle size and strain state [174]–[179].

Epitaxial heterojunctions can generate internal strain energy that is alleviated by the introduction of crystalline line defects [180]. Such dislocations typically harm the performance of optoelectronic devices because they provide non-radiative traps, recombination centers, and short-circuit pathways. Previous models were developed to estimate the critical thickness at which dislocations form in planar thin films [181]–[183] and nanoislands on a surface [184]–[186] in order to relax the elastic energy arising from lattice mismatch at heterointerfaces. In these works,
it was found that for a prescribed lattice mismatch, there is a critical size above which defect formation becomes energetically favorable.

**B.2 In-Plane vs. Out-of-Plane Strain**

Thin films only experience a lattice matching constraint at the growth interface with the underlying substrate. Similarly, NPs that have not undergone overgrowth are also only constrained at the substrate interface but, unlike thin films, they substantially relax at the exposed surface and remain coherent with the substrate. However, if a particle is embedded within a matrix, shown schematically in Figure B.1, it can also be stressed in the out-of-plane (OP) direction in order to maintain coherency at the sidewalls. Eshelby [187], [188] studied the strain distribution around inclusions in a matrix in the late 1950s and showed that for the case of homogeneous ellipsoidal inclusions, the stress (and strain) within the inclusion is uniform. Eshelby noted that the strain is non-uniform in general for arbitrary shapes and that for an ellipsoidal inclusion, a tensor with components \( S_{ijkl}(x) \) can be used to determine the strain inside and outside of the inclusion. This method captures the attenuation of strain so that it is zero far from the inclusion. Eshelby’s model was later modified to enable the calculation of \( S_{ijkl}(x) \) for any arbitrarily faceted shape using the

![Figure B.1: Schematic of particle showing In-Plane and Out-of-Plane strain from overgrowth](image-url)
harmonic potential of a flat-faced volume [189]. Since then, analytical and finite element models have been developed and applied to find the strain state of semiconductor NPs of specific shapes and materials [179], [190], [199], [200], [191]–[198]. Although models have been used to estimate the strain distribution in some systems, to our knowledge, a generally applicable analytical model for the prediction of the onset of defects for epitaxially embedded NPs has not been developed.

In this study, we develop and apply a generic model to define the coherency limits of an arbitrarily-shaped 3D, epitaxial, embedded NP using the solution for $S_{ijkl}$ developed by Wal dovogel [189] and clarified by Rodin [201]. The strain energy of the system is first determined as a function of both the in-plane ($\epsilon_{IP}^*$) and out of plane ($\epsilon_{OP}^*$) mismatch strain. By comparing this to the formation energy of a dislocation loop, a critical particle size is determined above which defect formation is predicted. We find that defect formation is mitigated by tailoring the OP strain, providing another variable in the design of QDs and other embedded NPs.

**B.3 Calculation of Strain Energy Density**

Figure B.2 depicts an arbitrarily shaped NP with mismatch strains $\epsilon_{IP}^*$ and $\epsilon_{OP}^*$ in the in-plane and out-of-plane directions, relative to the surrounding matrix. $S_{ijkl}$ can be determined at spatial points inside and outside of the NP. For a cubic system, the indices 1, 2, and 3 are chosen to correspond to the [100], [010], and [001] crystallographic directions, respectively. The growth direction [001] is chosen as the OP direction. The strain at each respective point is found using the following equations:

$$\epsilon_{ij} = -S_{ijkl}\epsilon_{kl}^*$$  \hspace{1cm} \text{(B.1a)}

$$\epsilon_{ij} = \epsilon_{ij} - \epsilon_{ij}^*$$  \hspace{1cm} \text{(B.1b)}

$$e_{ij} = \epsilon_{ij}^* - S_{ijkl}\epsilon_{kl}^*$$  \hspace{1cm} \text{(B.1c)}
where $\epsilon_{ij}$ and $e_{ij}$ denote the components of total and elastic strain, respectively. $\epsilon_{ij}^*$ is the misfit (Eigen) strain arising from lattice mismatch so that the in-plane component $\epsilon_{IP}^*$ = $(a_{\text{matrix}} - a_{\text{particle}})/a_{\text{matrix}}$ and the out-of-plane component $\epsilon_{OP}^*$ = $(c_{\text{matrix}} - c_{\text{particle}})/c_{\text{matrix}}$ inside the particle and they are zero outside the particle. Here, $a$ and $c$ denote the natural (stress-free) lattice parameters along the in-plane and out-of-plane directions, respectively. The sign of these strains are opposite that which is defined by Eshelby, to follow the convention commonly used with epitaxial films. In conjunction with the calculated Eshelby tensor, Equation 1c allows calculation of $e_{ij}$.

The elastic strain energy density ($u$) at a material point is calculated from the stress ($\sigma_{ij}$) using the elastic constants ($c_{ijkl}$) and compliances ($s_{ijkl}$) at that point,

$$u = \frac{1}{2} \sigma_{ij} e_{ij} , \text{ where}$$

$$\sigma_{ij} = c_{ijkl} e_{kl} \quad \text{B.2a}$$

$$\text{B.2b}$$
\[ e_{ij} = s_{ijkl} \sigma_{kl} \]  

B.2c

The effect of insertion of a dislocation is to plastically strain the particle by average amount, \( e_{ij}^d \).

The total applied strain on the particle is now

\[ \epsilon_{ij}^t = \epsilon_{ij}^* + \epsilon_{ij}^d. \]  

3

The additional strain in i and j induced by the dislocation (\( \epsilon_{ij}^d \)) is dependent on the magnitude of the relative displacement in the directions of interest. The insertion of a dislocation loop produces a relative shear displacement of magnitude \( b \) and unit direction \( \mathbf{s} \) across a slip plane with normal \( \mathbf{n} \) and area \( A \), as shown in Figure B.2. The components of the slipped magnitude depend on the angle of the slip plane with respect to the growth plane, as well as on the angle between the i direction and the intersection of the slip plane with the growth plane. The plastic strain averaged over the particle of volume \( V \) is then

\[ \epsilon_{ij}^d = \frac{1}{2} \frac{A}{V} b (n_i s_j + n_j s_i), \]  

B.4

Particles have several slip systems in general. For example, a dislocation loop with \( \mathbf{s} = [110]/\sqrt{2} \) and \( \mathbf{n} = [\bar{1}11]/\sqrt{3} \) will impart a different plastic strain than a loop on different slip system, e.g., \( \mathbf{s} = [\bar{1}10]/\sqrt{2} \) and \( \mathbf{n} = [111]/\sqrt{3} \). The average plastic strain induced by all dislocation loops is the sum of the plastic strain from each loop,

\[ \epsilon_{ij}^d = \sum_a \epsilon_{ij a}^d (n_a), \]  

B.5

where \( n_a \) is the number of dislocation loops inserted on slip system \( a \).

The focus here is on the formation of symmetric arrangements of dislocations that produce only in-plane and out-of-plane strain and do not induce any shearing of the particle relative to the IP and OP directions. The rationale is that the modes that shear the particle break the IP-OP
symmetry are less likely because they store additional elastic energy associated with shear deformation. Setting $\epsilon_{ij}$ (in Eqs. B.1- B.2) equal to the $\epsilon_{ij}^t$, calculated from Eq. B.3 allows for the calculation of the strain energy density of the system before ($u^0$) and after ($u^d$) insertion of a

Figure B.3: Elastic strains and strain energy density for a truncated pyramidal InAs NP embedded in GaAs ($\epsilon_{OP}^* = \epsilon_{IP}^* = -0.072$). The $e_{IPx}$ at (a) the base of the particle (b) the top of the particle and (c) a cross section through the long edge along the <100>. The $e_{OP}$ at (d) the base of the particle (e) the top of the particle and (f) a cross section through the long edge along the <100>. The $u$ at (g) the base of the particle (h) the top of the particle and (i) a cross section through the long edge along the <100>. The particle edges are defined by the purple lines. (from [99])
dislocation. Therefore, the change in energy density, $\Delta u^e$, due to the insertion of dislocation loops is

$$\Delta u^e = u^d - u^o.$$  

The change in strain energy ($\Delta U_e$) due to insertion of dislocation loops is then determined by integrating $u$ over the volume of the entire system [202].

### B.4 Calculation of Dislocation Formation Energy

We now model the energy required to form a set of dislocations ($U^f$), which, to the first order, is proportional to the length of the dislocation loop. The length of the dislocation loop is the perimeter of the slipped area introduced by a slip of type a, which depends on the geometry of the plane within the particle.

$$U^f = C n_a$$  \hspace{1cm} B.7a

$$C = C_0 \ln \left( \frac{R_a}{r_0} \right).$$  \hspace{1cm} B.7b

$$C_0 = \frac{c_{44} b^2}{4\pi}$$  \hspace{1cm} B.7c

The energy of formation ($U^f$) is also dependent on the number of dislocations formed of each type (Eq. B.7a). The dislocation line energy ($C$) depends on the radius of the dislocation core ($r_0$) and the distance between loops of the type a ($R_a$), or the radius of the particle, whichever is smaller [203]. The dislocation line energy $C$ depends on the interaction between dislocation loops, the strength of the particle-matrix interface to opening and shearing [204], the effective anisotropic elastic constants of the phases, and the prismatic vs. shear nature of the loops. The line energy is typically 0.1 to 0.5 the value of the cost coefficient ($C_0$) outlined in Eq. B.7c.
There are multiple methods to estimate the dislocation line energy for a system. Method 1: Gram et. al measured the misfit dislocation line energy at interface of Cu/Ni multilayers to be \(C_{Cu,Ni} \approx 0.8\) nJ/m. This estimate is applied to other systems by normalizing by \(\mu b^2\), where \(\mu\) is the elastic shear modulus of the material. The result is \(C = 0.47\) nJ/m for InAs. Method 2: Another estimate for \(C\) is made by noting from Gram et. al that \(C_{Cu,Ni} \sim \) one-third the value for bulk Cu, Ni. Accordingly, 1/3 that of the bulk value calculated using \(1/2 c_{44} b^2\) gives \(C = 1.208\) nJ/m for InAs. Method 3: \(C = \mu b^2 / 4\pi(1 - \nu)\) for a prismatic loop with Burgers vector normal to the plane. For a shear loop, \(C\) above is multiplied by \((2 - \nu)/2\) [203].

The elastic energy of an embedded particle with in-plane and out-of-plane lattice mismatch is proportional to

\[
U_{elas} \propto \left[ M_{IP} (\epsilon_{IP} - \epsilon_{IP}^d)^2 + M_{OP} (\epsilon_{OP} - \epsilon_{OP}^d)^2 \right] V_p \quad B.8
\]

Where \(M\) is the appropriate anisotropic elastic modulus factor in the IP or OP direction, and \(V_p\) is the volume of the nanoparticle. This leaves the energy of formation of a dislocation to be simply the energy per unit length of dislocation (\(C\)) multiplied by the dislocation length.

\[
U_f \propto \left( \frac{\text{energy}}{\text{length}} \right)_d \text{length}_d \quad B.9
\]

For the critical particle size \(L_{c}\) associated with the first dislocation loop, there is a resulting change in strain from the first dislocation

\[
\Delta \epsilon^d \propto \frac{b A_{slip}}{V_p} \propto \frac{b l_{loop}^2}{V_p} \quad B.10
\]

This produces a change in elastic energy. This can be approximated by

\[
\Delta U_{elas} \propto \frac{dU_{elas}}{d \epsilon^d} \Delta \epsilon^d \quad B.11a
\]

\[
\Delta U_{elas} \propto M_{IP} (\epsilon_{IP} - \epsilon_{IP}^d)(-1) b L_d^2 \quad B.11b
\]
The energy of dislocation formation can be rewritten as

\[ \Delta U_f \propto A M d b^2 \ln \left( \frac{L_{\text{loop}}}{b} \right) L_d \]  

B.12

Where \( C = A M d b^2 \ln \left( \frac{L_d}{b} \right) \) is the energy per length of a dislocation loop of dimension \( L_d \), where \( M_d \) is an appropriate elastic modulus, \( b \) is the Burgers vector magnitude, and \( A = C_0 \).

Then set \( \Delta U_{\text{elas}} + \Delta U_f = 0 \) for moment when formation is favorable

\[ M_{\text{IP}} \epsilon_{\text{IP}} b L_d^2 = AM_d b^2 \ln \left( \frac{L_d}{b} \right) L_d \]  

B.13

\[ M_{\text{IP}} \epsilon_{\text{IP}} b^2 \frac{L_d}{b} = AM_d b^2 \ln \left( \frac{L_d}{b} \right) \]  

B.14

\[ \frac{L_d/b}{\ln(L_d/b)} \propto \frac{AM_d}{M_{\text{IP}} \epsilon_{\text{IP}}} \propto \frac{A}{\epsilon_{\text{IP}}} \]  

B.15

The elastic strain energy and dislocation formation energy scale differently with the size of the particle, \( \Delta U^e \propto -L^3 \) and \( U^f \propto L \ln(L) \). Dislocation formation is favorable when the reduction in strain energy exceeds the formation cost of a dislocation, yielding a lower energy system,

\[ \Delta U^e(L_c) + U^f(L_c) \leq 0, \]  

B.16

where \( L_c \) is the critical length. The critical length is determined as a function of \( \epsilon_{\text{IP}}^* \) and \( \epsilon_{\text{OP}}^* \) by solving Equations B.1-B.7 and B.16.

**B.5 Calculation of Critical Size of Embedded Nanoparticles**

We discuss solutions to Equation 8 for the specific case of the common truncated pyramidal InAs NP shape in GaAs, but ignoring the InAs wetting layer. This is rationalized because the thickness of the wetting layer is \( << \) scale of the particle. The top and bottom faces of the particle are (001) type and the sidewalls are \{111\} planes with a typical aspect ratio of 0.4 \( (f = h/0.5L) \).
The common slip system of \{111\}\langle110\rangle for InAs was used. The elastic constants for InAs were chosen to match those of the surrounding matrix (in this case GaAs), $c_{11} = 119$ GPa, $c_{12} = 53.4$ GPa, $c_{44} = 59.6$ GPa, and $\nu = 0.31$ [205]. It is has been shown that the elastic properties of a material are closely related to the lattice spacing, and if the particle is coherently strained, it can be assumed that elastic constants match that of the surroundings [192], [206]–[208]. The parameters used for the calculation are summarized in Table 1. Using these inputs, the critical length scales can be calculated for any applied strain case. Continuum methods were used to find the elastic strain state of an InAs NP in a matrix of GaAs by calculating the Eshelby tensor using Equation 1 at all points inside and outside the NP. Calculations of the Eshelby tensor proceeded using the technique of calculating the Newtonian potential of an arbitrary shaped polyhedral developed by Waldvogel [189] and refined by Rodin [201]. Once the Eshelby tensor is known, the elastic strain can be calculated for an applied lattice mismatch strain.

The misfit strain in the case of an InAs NP in a matrix of GaAs ($\varepsilon_{\text{OP}}^* = \varepsilon_{\text{IP}}^* = -0.072$) is of hydrostatic compression on the particle. The resulting elastic strains $e_{\text{IPx}}$ and $e_{\text{OP}}$ at different slices through the representative volume are given in Figure B.3, and videos of each are provided in the supplementary. The first, second and third columns show slices of the respective quantities at the base ($z=0$), the top ($z=f$), and through a center slice of the particle ($y=0$), respectively. The separate rows show the $e_{\text{IPx}}$ (Figure B.3(a-c)), $e_{\text{OP}}$ (Figure B.3(d-f)) and $u$ (Figure B.3(g-i)) at different slices through the representative volume. The $e_{\text{IPy}}$ (not shown here) is the same as the $e_{\text{IPx}}$ but rotated 90°, with the large compressive strain in the base instead lying along the $<010>$ and the large tensile strain at the top along the $<100>$. The edges of the particle are marked by the purple lines. Figure B.3(a-c) show that the largest $e_{\text{IP}}$ is ~-9% and occurs inside the particle at the
base, but positive $e_{IP}$ values occur in the surrounding matrix near the top of the particle. Conversely, Figure B.3(d-f) show that within the NP, $e_{OP}$ is small ($<\pm 4\%)$ compared to the matrix near the top and bottom facets ($\pm 9\%)$. The strain energy density ($u$) is then calculated at all points in the representative volume using Equation 2, as shown in Figure B.3(g-i). It is observed that almost 80% of the total $u$ in the system is from outside the particle itself (Figure B.3(i)), but $u$ subsides to 0 with increasing distance from the particle. This is due to the high strains outside the top and bottom interfaces.

The average strain energy density ($\bar{u}$) is calculated by multiplying each $u$ point by its specific volume, and summing the value of each of those points. Figure B.4 shows the $\bar{u}$ of the entire system as a function of $e_{IP}^t$ ($e_{IPx}^t = e_{IPy}^t$) and $e_{OP}^t$. It takes on the shape of an elliptical bowl centered on $e_{IP}^t = e_{OP}^t = 0$. Only half of the bowl is shown because only compressive strains ($e_{IP}^t < 0$) are considered. The long axis of the $\bar{u}$ ellipsoid (along line O-Y) follows a slope which is very close to the $-c_{11}/c_{12}$ ratio (-0.449). Beginning at the point O, movement to the right or left would impose a strain mismatch in the OP direction and the stored elastic energy would increase in a quadratic fashion with respect to $e_{IP}^t$. Movement downward from point O ($e_{IP}^t = 0$) to D ($e_{IP}^t = -0.072$), as in the case of InAs on GaAs, imposes a compressive elastic strain on the particle in the IP direction. The Poisson effect would attempt to elongate the particle in the OP direction. Capping with GaAs would move the strain state from point D to X ($e_{IP}^t = e_{OP}^t = -0.072$), increasing the total energy of the system. Capping with InSb would result in motion from point D to Z ($e_{OP}^t = +0.065$) resulting in a lower $\bar{u}$ because the OP expansion is somewhat compensated. Moving to point Y would decrease $\bar{u}$ to the minimum possible value (when $e_{IP}^t = -0.072$) because the Poisson expansion of the particle in the OP direction would furnish an OP
lattice parameter that exactly matches that of the surrounding matrix. The average strain energy density is observed to be $\sim 2.4 \times$ larger at point X than Y. More generally, movement away from O-Y will result in an increase in $\overline{u}$.

The elastic strain energy density after defect formation can be calculated using Equations 3-5. Figure B.4 shows the effective direction of movement in strain space, from point A to B, upon insertion of a dislocation pair. The values of $\epsilon_{IPx}^*, \epsilon_{IPy}^*$ and $\epsilon_{OP}^*$ shift by an amount defined by Equation 3. However, by restricting the strains to $\epsilon_{IPx}^* = \epsilon_{IPy}^*$, as would be the case for a combination of $\{111\} <110>$ slip systems that symmetrically distort the particle, the movement in strain space will follow a line with a slope $\Delta \epsilon_{IP}^*/\Delta \epsilon_{OP}^* = -1/2$. This path corresponds to zero volume change because the plastic strains induced by dislocations $\epsilon_{ij}^d$ correspond to shearing of

Figure B.4: The average strain energy density map for an InAs nanoparticle containing system as a function of both the total in-plane and out of plane strain ($\epsilon_{ij}^t$). The points X, Y and Z represent locations with the same $\epsilon_{IP}^t$ but X is hydrostatically strained, the most strain compensated point is given by Y, and the condition upon capping with InSb is given by Z. The points A and B represent theoretical locations in strain space before and after a dislocation is introduced, respectively. The red line represents the limit of coherency for a particle with base length of 16.3 nm (from [99])
atomic planes that render no change in volume. The magnitude of movement in Figure B.4 is proportional to the slipped area (Eqn. 4), which depends on both the location of the dislocation loop and the size of the particle. The movement in strain space can be computed for specific dislocation arrangements and the reduction in strain energy ($\Delta U^e$) can be computed, as described previously.

The reduction in strain energy is balanced by the formation energy ($U^f$) of a dislocation (Eq. 7). Because our study concerns the onset of the dislocation formation, $d_a$ is assumed to be the length of the in-plane edge of the particle ($L$). In principle, the location of the dislocation affects the length of the dislocation loop and therefore $U^f$. However, these NPs have a small aspect ratio and the dislocation loop is approximately parallel to the wall of the particle. Thus, there is a large central portion of the NP volume where the slipped areas are the same. We insert a pair of perpendicular dislocations, each of which intersect the top and bottoms facets of the NP. These slip planes are parallel to side facets and therefore they provide the largest slipped area. They thus provide the greatest reduction in strain energy ($\Delta U^e$) for a given increase in line length of dislocation or reduction in $U^f$. This should furnish the minimum conditions for relaxation. For simplicity, the energy per unit length of a dislocation loop is approximated by Eq. 7b where the prelogarithmic energy factor $C_0 = 1 \text{nJ/m}$ and $r_0 = b$ is chosen. Calculations for $C_0$ in an InAs/GaAs system vary from 0.47 to 1.59 nJ/m, which are marked in Figure B.5 by the dotted and dashed lines, respectively. More detailed information on the calculation of $C_0$ and the relationship to $L_c$ can be discussed in the next paragraph [209] [203].

Because $\Delta U^e \propto L^3$ and $\Delta U^f \propto L \ln(L)$ where in the latter case $C$ is just a constant, it is possible to use the following proportionality to calculate $L_c$ for arbitrary values of $C$. 

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\[
\frac{\ln(L_{c1})}{L_{c1}^2} C_1 \approx \frac{\ln(L_{c2})}{L_{c2}^2} C_2
\]

Thus, after calculation of \( L_c \) for a single case, such as \( C = 1 \) nJ/m (as shown in Figure B.5), it can easily be solved for graphically or numerically for any value of \( C \) (Figure B.6). This method was used to find the range of \( L_c \) for \( C_0 = 0.47 - 1.59 \) nJ/m that was mentioned in the text and is shown in supplementary 1b for comparison alongside the variation in \( L_c \) with \( \epsilon_{OP}^* \).

There is also a kinetic barrier that must be overcome prior to introduction of dislocations as well, but this is difficult to model generally as it is a function of temperature, deposition thickness, growth rate, III/V ratio, as well as other factors [163], but it would result in a higher than predicted value of \( L_c \) [183].

\[ \text{Figure B.5: Critical size as a function of out-of-plane strain with different cost coefficients. Experimental data from [175],[210] plotted alongside theory. (from [99])} \]

A variety of different initial strain states, \( \epsilon_{IP}^* \) and \( \epsilon_{OP}^* \), are considered, corresponding to different positions of point A in Figure B.4. Motion along the path \( \Delta \epsilon_{IP}^*/\Delta \epsilon_{OP}^* = -1/2 \) is
considered, corresponding to the injection of a symmetric array of dislocation loops. The reduction of energy is computed and the energy balance in Eq. 16 is assessed. Because the reduction $\Delta U^e \propto L^3$ and $\Delta U^f \propto L \ln(L)$, there exists a critical particle size ($L_c$, critical base length of the NP) at which Equation 8 is satisfied. Figure B.5 shows $L_c$ for truncated pyramidal InAs NPs grown on GaAs, keeping $\epsilon_{IP}$ constant at -0.072, but encapsulating the NPs with a different materials, such that the out of plane mismatch is varied, $-0.08 < \epsilon_{OP}^* < 0.08$. The largest attainable coherently strained particle has a base length of ~18.4 nm when $\epsilon_{OP}^* \sim 0.037$. This positive $\epsilon_{OP}^*$ completely stabilizes the OP Poisson expansion with the imposed $\epsilon_{IP} = -0.072$ and therefore $\Delta U^e$ is minimized.

Previous studies have reported on the growth of InAs NPs on GaAs capped with different In$_x$Ga$_{1-x}$As alloys, corresponding to $\epsilon_{OP}^* \approx -0.06$ [175], [210]. The particle sizes at which dislocations were observed are marked for comparison in Figure B.5. In these reports, measurements of the size of the dots were obtained using transmission electron microscopy.

Figure B.6: (a) Plot of $\ln(L)/L^2$ vs L (b) Plot of $\ln(L)/L^2$ vs $\epsilon_{OP}^*$ at $\epsilon_{IP} = 0.072$ along with the $L_c$ limits from the respective $C$ values from Figure B.5: Critical size as a function of out-of-plane strain with different cost coefficients. Experimental data from [175],[210] plotted alongside theory. (from [99])
(TEM). However, the onset of dislocation formation was measured by observing a saturation of the PL redshift using photoluminescence (PL). Maximov et al. [175] measured $L_c \sim 16$ nm when capped with $2.5$ nm of $\text{In}_{0.18}\text{Ga}_{0.82}\text{As}$, as marked by the red star in Figure B.5. Chen et al. [210] claimed that when capped with $6$ nm of $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$, the onset of dislocations happened with average base lengths between $20$ nm and $27$ nm, marked by open and filled blue stars in Figure B.5, respectively. TEM images of incoherent NPs with multiple dislocations were obtained, but not at the onset of dislocation formation. Therefore, only an upper bound on $L_c$ of $33$ nm can be inferred [210]. In the latter case, $L_c$ was measured to be larger despite being capped with a higher straining material. However, the capping was significantly thicker, allowing for more strain relief, before capping with GaAs. Additional complications involving phase segregation of In when using

Figure B.7: (a) Critical size of an InAs nanoparticle as a function of In-Plane and Out-Of-Plane strain (b) Dislocation regimes for particles with aspect ratio of $0.42$ and length of $16.3$ nm, dark regions represent strain cases that would be free of dislocations while, light regions would have defects (from [99])
In\textsubscript{x}Ga\textsubscript{1-x}As capping layers and deposition of capping material on the top facet of the particle are not considered in this study.

The same model described above is carried out at various $\epsilon^{*}\textsubscript{IP}$ and the resulting $L_c$ are plotted in Figure B.7(a). $L_c$ diverges when $\epsilon^{*}\textsubscript{IP}$ and $\epsilon^{*}\textsubscript{OP}$ are both zero and it quickly decreases with increasing applied strain. A coherency diagram for a particle of a given size can be obtained by taking a slice of Figure B.7(a). This is shown in Figure B.7(b) for the case, $L_c = 16.4$ nm. Regions in strain space can be seen where a NP of the specified base length is predicted to remain coherent (dark grey) or instead form dislocations (incoherent-light grey). The limit of coherency is shown as a red line in Figure B.7(b), which is also transposed onto Figure B.4. It is seen that this limit very closely follows the trend of the strain energy density of the system.

Based on this model, an epitaxially embedded particle can be put in the minimum energy state by engineering both $\epsilon^{*}\textsubscript{IP}$ and $\epsilon^{*}\textsubscript{OP}$. For example, InAs NPs with a base length of 16.4 nm, grown and capped with GaAs ($\epsilon^{*}\textsubscript{IP} = \epsilon^{*}\textsubscript{OP} = -0.072$, represented by point X in Figure B.4) corresponds to the incoherent region ($L_c = 15.3$ nm). However, if the same NP were capped with InSb $\epsilon^{*}\textsubscript{OP} = +0.065$ (point Z in Figure 3), then $L_c = 16.4$ nm is predicted and thus the particle remains coherent. This method of three-dimensional lattice matching can also be effective at avoiding alternative forms of strain relaxation, such as volume or shape change, activation of non-traditional slip planes, asymmetric introduction of dislocations, and atomic migration. By calculating the formation energy for these relaxation processes, similar to $U^{f}$, the corresponding energy reduction of the system, similar to $\Delta U^{e}$, can be obtained and the critical size/strain at which these energy reduction pathways activate can be identified.
B.6 Summary

An energy-based model is developed to predict the critical size at which dislocations form in a 3D epitaxial nanoparticle embedded in a matrix. For InAs NPs on GaAs, we predict InAs NPs to remain coherent up to a critical in-plane base length, $L_c = 18.4$ nm, if the out-of-plane lattice mismatch strain is tuned to $\epsilon_{OP}^* = +0.037$. This compensates for the induced Poisson expansion of the particle along the OP direction from the applied negative in-plane lattice mismatch ($\epsilon_{IP}^* = -0.072$). This reduces the overall strain energy density of the system so that a larger particle size must be attained before the onset of relaxation by dislocations. In principle, 3D Poisson-stabilization enables the creation of coherently strained nanoparticles in previously inaccessible strain states, thereby providing another means to controllably vary the strain-tunable band structure and associated optoelectronic properties.
Appendix C. Embedded Fe$_2$O$_3$ Layers in β-Ga$_2$O$_3$

C.1 Introduction

Wide bandgap semiconductors such as AlN, GaN and SiC have been the focus of recent major research. However, a new material β-Ga$_2$O$_3$ has been of increasing interest due to its stability in air, and as a result, availability of high quality bulk wafer made by crystal pulling [211], [212]. B-Ga$_2$O$_3$ has a larger breakdown voltage and bandgap ($V_{bd} = 8$ MV/cm, $E_g \approx 5$ eV [213], [214]) than both GaN and SiC giving better Johnson and Baliga figures of merit [215], [216] which means it could be very suitable for high-frequency applications and have fewer conduction losses.

It has been of great interest to add magnetic functionality to semiconductors for applications in multiferroics and spin-based research [217]. GaFeO$_3$ was the first known multiferroic material [218] and multiferroic materials tie together spin and charge transport. If

![Figure C.1](image-url)

*Figure C.1: Crystal structures of β- Ga$_2$O$_3$ layer showing the (a) (010) planes and the (b) (-201) planes marked with blue sheets. The octahedral GaO$_6$(red) and tetrahedral GaO$_4$(green) are also colored for clarity.*


β-Ga$_2$O$_3$ could be made magnetically functional it would be useful in spintronics because its wide
gap low spin-orbit coupling could give long spin lifetimes [219] and its high breakdown field
would allow use of large electric fields possibly enabling electric field controlled magnetism. The
lower thermal conductivity for β-Ga$_2$O$_3$ is often viewed as a negative, but it could be useful for
spin-caloritronics because it could hold large thermal gradients. The question becomes how to add
this magnetic functionality.

The unique monoclinic crystal structure of β-Ga$_2$O$_3$ offers a playground of facets for
epitaxial growth. Two of the more popular (2̅01) and (010) are already available as full 2-inch
wafers (Tamura Corp.). The (010) surface has an equal number of octahedral GaO$_6$ and tetrahedral
GaO$_4$ in the growth plane (Figure C.1(a)). However, the off-axis (2̅01) alternates between sheets
of octahedrals and tetrahedrals (Figure C.1(b)). If magnetic atoms were able to be placed
selectively in these locations it could lead to interesting ferroic properties.

In this study we look at the replacement of Ga with Fe atoms. The atomic radii of the two
atoms in either the octahedral or tetrahedral sites is only 4% [220]. Thus, if large amounts of iron
can be placed in very thin layers it could possibly adapt the underlying crystal structure. In this
study we show the growth of a new monoclinic phase of Fe$_2$O$_3$ (we will call µ-Fe$_2$O$_3$) which
matches the β-Ga$_2$O$_3$ lattice.

C.2 PAMBE Growth Details

First the deposition rate of Fe at a flux of 5.3×10$^{-8}$ was calibrated by simply depositing
opening the shutter on a cold Si wafer for 30 min at a pressure of 5×10$^{-9}$ torr. The thickness was
measured via SEM. Then assuming the Fe was fully dense BCC, as is the stable form of iron. The
density of Fe atoms is then converted to what it would be in the theoretical \( \mu\text{-Fe}_2\text{O}_3 \) crystal structure. This enables an estimate of the deposition rate of \( \mu\text{-Fe}_2\text{O}_3 \) of about 0.4 ML/s.

PAMBE was used to grow the (Fe,Ga)\(_2\)O\(_3\) structures in a MBE Control M7 system with a Veeco Oxygen plasma source. The growth conditions were chosen to match those for which high quality \( \beta\text{-Ga}_2\text{O}_3 \) growth occurs \[221\]. A (010) \( \beta\text{-Ga}_2\text{O}_3 \) substrate was used and the whole growth was done at a substrate temperature of 700°C. Gallium and iron fluxes were 8.6\( \times \)10\(^{-8}\) and 5.3\( \times \)10\(^{-8}\), respectively which gives a \( \beta\text{-Ga}_2\text{O}_3 \) growth rate of \(~3\text{nm/min} \). The films are grown in the oxygen rich regime with a chamber pressure of \(~1.5\times10^{-5}\) torr.

The structure of interest is a test to see how much Fe can be put into \( \beta\text{-Ga}_2\text{O}_3 \) before the growth degrades, so an increasing ML deposition structure was grown (Figure C.2(a)). First a 75 nm thick homoepitaxial of \( \beta\text{-Ga}_2\text{O}_3 \) was grown. Then a superlattice (SL) of varying thicknesses of \( \mu\text{-Fe}_2\text{O}_3 \) (increasing from 0.2 – 25 ML) with 15 nm Ga\(_2\)O\(_3\) buffer layers between each was grown. Detailed analysis of RHEED during the Fe deposition is difficult, because the shorter ML

![Figure C.2: (a) schematic of grown SL sample with increasing Fe containing layers and RHEED images (b) during Ga deposition and (c) during Fe deposition](image-url)
sections have shutter times of only ~1 s. Also, the magnetic actuator which closes the Ga shutter during the Fe deposition is next to the RHEED gun, so the beam is slightly moved back and forth every shutter sequence. However, the RHEED images did not change after subsequent layer depositions signaling a good surface remained throughout the growth (Figure C.2(b,c)).

C.3 Structural Characterization

C.3.1 X-Ray Diffraction

X-ray diffraction was done on a Rigaku Smartlab with a 4-bounce (220) Ge monochromator. A 2θ/ω scan was used to look for foreign phases, but no other naturally occurring phases of Fe₂O₃ were seen over a wide angle scan (Figure C.3). Looking closer at the substrate peak, SL peaks are observed. The position of the SL₀ peak indicates an average lattice constant of 3.044 Å for the entire SL structure, which is 91% β-Ga₂O₃, giving a lattice constant of 3.09 Å μ-Fe₂O₃.

![Figure C.3: HR-XRD of β-Ga₂O₃ substrate (black) and the Fe₂O₃/β-Ga₂O₃ superlattice structure (red) showing distinct superlattice fringes over (a) wide angle and (b) zoomed in over the substrate peak region](image)

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C.3.2 Scanning Transmission Electron Microscopy

A closer look at the SL was done using STEM (Figure C.4). Good crystalline quality is observed until >25 ML Fe. However, also at this point there was a brief growth interruption, but it is expected that thicker Fe regions can still be grown. Focusing on the region

![Figure C.4: STEM images of increasing ML superlattice under increasing magnification with an atomic resolution image of a Fe containing layer.](image)

![Figure C.5: STEM images showing (a) raw HAADF image and EDS images of (b) Gallium (c) Iron and (d) Oxygen](image)
below, there is no appearance of defects related to the SL. Atomic resolution images show that the monoclinic crystal structure of $\beta$-Ga$_2$O$_3$ persists entirely across the Fe layers. One can see the Fe regions (dark) appear wider than they were nominally deposited for.

To isolate where the Fe is, chemical mapping was done using EDS (Figure C.5). The raw HAADF image is shown on the left. It is observed that the Ga (red) spacer layers were ~17 nm. But what is enlightening is the Fe map (blue), showing that the Fe is well defined in the layers that it was deposited, in contrast to what was observed in the previous STEM images. The oxygen appears to be slightly higher in the Fe regions, this could be because Fe getters oxygen more readily.

![Figure C.6: EDS analysis showing (a) a linescan through multiple Fe containing layers and (b) the amount of Fe and FWHM of each layer.](image)

Figure C.6: EDS analysis showing (a) a linescan through multiple Fe containing layers and (b) the amount of Fe and FWHM of each layer.
than Ga. A line scan was also done on this area (Figure C.6), and again what is seen is a relative increase in the amount of Fe, as more was deposited but the FWHM is much lower than the dark regions in the previous STEM images. This would signify that the Fe is not out-diffusing from the growth location.

C.4 SQUID Measurements

Magnetic measurements up to 5 T were done on this sample using a superconducting quantum interference device (SQUID) at various temperatures (Figure C.7). The substrate shows a diamagnetic background and hysteresis of the pole piece of the magnet that has little temperature dependence, and is useful for elucidating the contribution from the SL. When looking at the μ-Fe₂O₃ containing sample, at 10 K it is very difficult to saturate at 50 kOe with magnetization already at ~1750 emu/cm³ and still increasing. There is no hysteresis in this portion of the curve signifying the presence of a paramagnetic component. The coercive field at 10K is ~300 Oe, and drops with increasing temperature, but persists up to 300 K signifying the presence of a ferro-(or ferri-) magnetic phase.
Figure C.7: SQUID Magnetization vs. applied field at various temperatures on (a) the substrate (b) zoomed in and (c) the Fe containing sample out to 5T and (d) a low field image to resolve coercive fields. (e) Coercive field as a function of temperature
C.5 Summary

In summary, the successful formation of $\mu$-Fe$_2$O$_3$ superlattices was shown on $\beta$-Ga$_2$O$_3$ without degrading subsequent material overgrowth. There does not appear to be significant Fe diffusion out of the layers, and the sample exhibits both paramagnetic and (ferro/ferri)magnetic behavior. Of course, being a calibration sample with many different ML thickness $\mu$-Fe$_2$O$_3$ layers, this sample is not ideal for detailed analysis. EDS data shows that Ga could be diffusing into the Fe layers as well. So the first order of business is to grow and measure superlattices with periods of equal thicknesses of $\mu$-Fe$_2$O$_3$. Along these lines, looking at the effects of increasing and decreasing the $\beta$-Ga$_2$O$_3$ spacer layer thickness on the structural, as well as magnetic properties. Growth on (012) $\beta$-Ga$_2$O$_3$ is also of interest because of the alternating (tetra/octa)hedra sites. In an attempt to specifically get the Fe or Ga species in the specific sheets, investigation of slower growth rates and lower temperatures to limit both Fe and Ga diffusion, will likely be of great importance. There is still substantial optical characterization such as absorption and transmission of these Fe containing films that needs to be done, as well as electrical characterization.
Appendix D.  Light Output from Mercury Bulb and 265 nm Emission from AlGaIN Nanowires

D.1 Germicidal wavelengths: LEDs versus Mercury Bulbs

One very large region of interest for solid state lighting is for germicidal applications, as mentioned in Chapter 1. When looking at device efficiencies as a function of wavelength, as in Figure 1.2, the device efficiencies at around 260 nm are notably higher than wavelengths slightly above and below. That is because this wavelength is at a peak in the absorption spectrum of many viruses (Figure D.1) and has been a major source of research, just look at the peak in efficiencies at ~260 nm in Figure 1.2). The four nucleotides of DNA have different absorption spectra, and it so happens that they happen to all have a peak around 260 nm. When exposed to light of the corresponding to the absorption wavelength, the nucleotide bases from opposing backbones break apart and re-bond to the same backbone forming a pyrimidine dimer [222]–[224]. If enough dimers are formed it can inhibit the reproduction of the DNA, and eventually the cell/virus dies. The current prevailing technology for UV based disinfection is mercury halide lamps which have emission based on the atomic transitions of the mercury ions. Thus, the efficiency of these devices is inherently limited. The emission spectrum of a typical UV bulb used for disinfection in industry (donated by UVConcepts) was tested on the probe station that the nanowire LEDs were also tested on (Figure D.2). An iris was used to limit the amount of light entering a solarized fiber optic cable which was then placed directly under the objective and sent to the spectrometer. Many peaks are observed across a wide range of wavelengths including the visible. These peaks have no germicidal effect, as they do not correspond with any primary absorption peaks.
The power of the 257 nm peak was measured using a Thorlabs PM100D and S120VC powermeter right at the opening of the iris at different iris openings (Figure D.2(c)). The power output is directly proportional to the iris opening size. As the powermeter is moved further from the bulb, the power drops (Figure D.2(d)). The reason for the slight increase in power for the small iris opening, is likely due to stray light, as the powermeter was moved away from the iris the holes for the wires to the bulb also came into view.

A power of 111 µW is seen at 0 distance from the iris at full open (5 mm) with an area of 0.196 cm². The entire area of the bulb is 448 cm². Thus, the entire 95 W bulb has an output power of estimated at ~253 mW at 257 nm, giving an efficiency of ~0.27%. However, because the emission of mercury is based on atomic transitions, the linewidth at 257 is extremely narrow, FWHM ~2 nm, and the resulting intensity at the peak DNA absorbance wavelength of 265 nm is nearly 1000× less. However, the absorbance of DNA ranges from ~235-290 nm, so it does work, the peaks just don’t line up perfectly.

Figure D.1: DNA absorption vs wavelength (from [224])
Figure D.2: (a) Spectra from UV bulb at different iris opening diameters. (b) Zoomed in on the spectra around the 257 nm peak of the UV bulb at different iris opening diameters. (c) Power of the 257 nm as a function of iris diameter and (d) power of the 257 nm peak at two different iris widths as a function of distance away from the bulb.

LEDs have great wavelength selectivity which would allow placement of the emission directly at the desired wavelength without wasting energy creating unusable light. This could also allow for things such as tuning of emission to be absorbed by certain viruses and not other cells, potentially avoiding some side effects of traditional UV radiation such as cancer.
D.2 Targeting 265nm Emission with AlGaN

We investigate emission in the germicidal range using AlGaN active regions with sub ML shutter pulsing. GaN nanowires were nucleated at 760°C for five minutes on Si, a GaN section was then grown at 790°C for 15 minutes before ramping the temperature to 850°C and growing AlN for 15 minutes. Then periods of five AlGaN/AlN quantum wells separated by AlN barriers. The AlGaN composition in the quantum wells was tuned using sub ML shutter pulsing. Shuttering times for the Ga and Al cells ranged from 2 to 9 s. The quantum wells were nominally grown at 850°C as calibrated at the center of the wafer, but there is a ~10°C temperature gradient across the 3” Si wafer. Photoluminescence measurements were done to check the emission of these quantum well structures (Figure D.3). It shows variation in peak wavelength from edge to center ranging

![PL spectra with edge to center variation targeting 265 nm](image)

*Figure D.3: PL spectra with edge to center variation targeting 265 nm*
from ~270 nm at the edge to beyond 265 nm, even below the 240 nm long pass filter cut off toward the center.

The growth of an LED was grown using shutter pulsing ratios of 2:3 Al:Ga for the active region. The heterostructure was similar to the half graded region structure, but this work was done prior to the work shown in Chapter 5, and has a long 450 nm n-AlGaN top region where the III/V ratio was increased by dropping the nitrogen flow to ~3 sccm, when the RHEED began to get bright and streaky. Device fabrication was done using the same procedure outlined in section 2.5.1 using a conformal 10/20nm Ti/Au top contact. Figure D.4 shows the electroluminescence spectra of a 100×100 μm device at an injection current of only 0.2 mA is shown in, with a narrow FWHM of only ~17 nm, but the output power is < 1 nW. Also, all the samples that had a drop in III/V ratio during coalescence were extremely resistive, and the operating current is very high at 39.6 V, resulting in an efficiency of < 0.01 m%. The limiting factor in these measurements is actually that the sourcemeter is limited to 40 V, not actually device failure. This is still promising, despite the

![Figure D.4: EL spectra of nanowire LED at a current density of 2 Acm⁻²](image)

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current low efficiency, as incorporating the changes in Chapter 5 (a working n-AlGaN coalesced layer and grid only contacts) the threshold voltage and light extraction can both be increased.

**D.3 Summary**

In summary, mercury lamps are still more efficient than solid state lighting and although thin film based UV devices are basically there, nanowire based UV devices still have a little catching up to do. However, 260 nm emission with a narrow FWHM is a promising start. As there are many things discussed in the main text that can be done using this active region to increase the efficiency of these devices. There is also the potential advantage of solid state over mercury if it can be pushed deeper into the UV, potentially through the use of AlN only structures, as the polynucleotide backbone of the DNA absorbs even more strongly than the nucleobase components in the DUV, < 210 nm.