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**Design, fabrication and characterisation of
ultraviolet light-emitting diodes for biomedical
applications**

Thesis presented by

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Declaration

This is to certify that the work I am submitting is my own and has not been submitted for another degree, either at University College Cork or elsewhere. All external references and sources are clearly acknowledged and identified within the contents. I have read and understood the regulations of University College Cork concerning plagiarism and intellectual property.

Signed: Peter Moroney

Date: 17/11/25

Abstract

The efficiencies of ultraviolet (UV) light-emitting diodes (LEDs) significantly lag behind those of their blue counterparts, owing to a variety of electrical and optical challenges. There is a marked dip in performance in the wavelength range $\sim 320 - 340$ nm, due to the difficulty in realising a high quality LED template at this composition range. This is precisely the target emission wavelength for LEDs developed in this project, with an application in fluorescence spectroscopy as part of a diagnostic endoscope. Thus, numerous strategies were investigated to improve the output power while eliminating parasitic emission.

A novel technique using patterning and overgrowth was built upon to realise a thicker LED template with increased crystal quality. This can result in a significant boost in device performance by improving the internal quantum efficiency and current spreading. Furthermore, by introducing interdigitated contacts and a reduced mesa size, fabricated μ LEDs demonstrated increased efficiency through enhanced current spreading. The first demonstration of a boron-containing UV LED was also presented, which indicated the potential benefits of small amounts of BN in the quantum wells. An increase in the wall plug efficiency was observed, although further work is required to understand the growth dynamics.

The p -type region of a UV LED was a large focus of this thesis, owing to its poor conductivity limiting device performance. Polarisation doping was investigated as a means to increase the hole concentration. LED structures with various p -type doping conditions were tested, with the best performance observed in an LED with *both* polarisation doping and impurity doping ('co-doped'). This is in contrast to studies of UVC LEDs, where polarisation doping *only* tends to result in the best performance. Additionally, long wavelength parasitic luminescence was eliminated without Mg doping, which is crucial for the biomedical application. A temperature-dependent study was also performed, which, along with room temperature simulations, offered insights into the device physics.

Temperature-dependent Hall effect measurements were performed on structures

with varied polarisation doping approaches (similar to the aforementioned LEDs) to gain a better understanding of the mechanisms at play. In a *p*-GaN reference sample, typical carrier freezeout was observed at lower temperatures. A detailed calculation of the carrier scattering mechanisms elucidated the temperature dependence of the mobility. However, polarisation doped structures (co-doped and polarisation doping only) exhibited more complex behaviours. While the samples' conductivity versus temperature generally agreed with the corresponding temperature dependent LED operating voltages, the co-doped sample exhibited mixed signs of hopping conduction at low temperatures. The presence of this transport mechanism would tend to agree with recent studies examining such effects.

Although there is still room for improvement in the output power of the UV LEDs realised in this work - thought to be mainly limited by the dislocation density - significant gains were made in LED performance. Narrow-linewidth UVA emission was achieved, along with the vital removal of parasitic long wavelength luminescence.

Dissemination of research

Publications

P. Milner (2022), “UV LEDs and their applications”, *The Boolean* 2022.

P. Milner, V. Z. Zubialevich, T. O’ Connor, S. M. Singh, D. Singh, B. Corbett, & P. J. Parbrook (2023), “BAIGaN light-emitting diode emitting at 350 nm”, *Electronics Letters*, 59(19), e12976.

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Conferences

P. Milner, S. M. Singh, R. Finn, V. Z. Zubialevich, B. Corbett, P. J. Parbrook, (2023), “UV-A Light Emitting Diode with Polarisation-enhanced $p\text{-Al}_x\text{Ga}_{1-x}\text{N}$ ” (Poster), *International Convention on UV LED Technology and Applications (ICULTA)*, Berlin, Germany.

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International Conference on Nitride Semiconductors (ICNS), Fukuoka, Japan.

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P. Milner, V. Z. Zubialevich, S. M. Singh, B. Corbett, P. J. Parbrook*, (2025), “Temperature-dependent investigation of polarisation doping in 330 nm ultraviolet light-emitting diodes” (Oral), *UK Nitride Consortium (UKNC)*, Cambridge, England.

P. Milner, V. Z. Zubialevich, S. M. Singh, P. Pampili, B. Corbett, P. J. Parbrook*, (2025), “Investigation of graded composition $p\text{-AlGa}\text{N}$ for improved 330 nm ultraviolet light emitting diode performance” (Poster), *International Conference on Nitride Semiconductors (ICNS)*, Malmö, Sweden.

*Presented by first author unless noted by **

Abbreviations

3DHG	3-dimensional hole gas
cTLM	circular Transmission line model
EBL	Electron blocking layer
EL	Electroluminescence
EQE	External quantum efficiency
ICP	Inductively coupled plasma
IE	Injection efficiency
IQE	Internal quantum efficiency
LEE	Light extraction efficiency
MOCVD	Metalorganic chemical vapour deposition
MQW	Multiple quantum wells
NUVL	Near-UV luminescence
PL	Photoluminescence
QCSE	Quantum confined Stark effect
QW	Quantum well
RSM	Reciprocal space map
RTA	Rapid thermal anneal
SEM	Scanning electron microscopy
SIMS	Secondary ion mass spectrometry
SPF	Semi-polar facet
SRH	Shockley-Read-Hall
TDD	Threading dislocation density
μ-HC	micro-honeycomb
WPE	Wall plug efficiency
XRD	X-ray diffraction

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Sir Isaac Newton famously said "If I have seen further, it is by standing on the shoulders of giants". This saying resonates with me especially now, as I have come to appreciate all of the scientific contributions made prior to me, allowing me to carry out my research. Special

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Lucky is he who has been able to understand the causes of things
- Virgil , 29 BC

1 Introduction

1.1 Ultraviolet light and its applications

In the electromagnetic spectrum, ultraviolet (UV) light exists at wavelengths shorter than those in the visible region - meaning the human eye is unable to see it. As illustrated in Figure 1.1, the UV region possesses wavelengths below 400 nm and is split into three discrete categories: UVA (400-315 nm), UVB (315-280 nm) and UVC (280-100 nm).

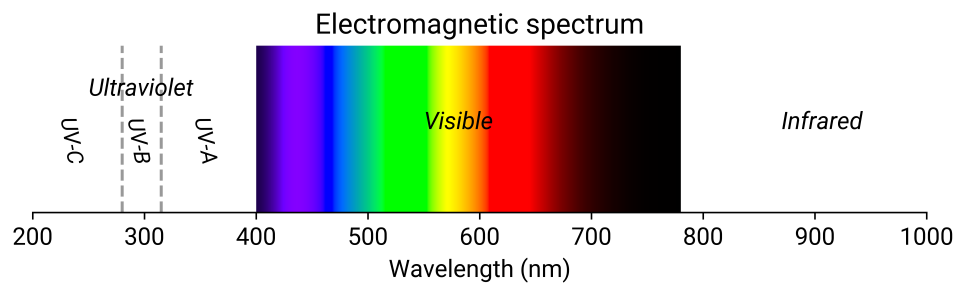


Figure 1.1: The electromagnetic spectrum showing the ultraviolet region relative to the visible light spectrum.

Conventionally, UV light was sourced from mercury-based lamps. By generating an arc in the mercury vapour, multiple discrete wavelengths are emitted in the UV from 254 nm to 405 nm. Mercury, however, is toxic to humans and managing the environmental impact poses serious challenges. Moreover, vapour lamps require high input power, offer limited and discrete wavelengths, are large and relatively immobile, and require a warm-up period. In 2013, the “Minamata Convention on Mercury” was held with regard to the environmental and health impacts of mercury. Article 4 of the text states that “each party shall not allow, by taking appropriate measures, the manufacture, import or export of mercury-added products listed in Part I of Annex A after the phasing-out date specified for these products...” [1]. Included in these products are mercury vapour lamps, with a phase-out date of 2020.

In contrast to lamps, light-emitting diodes (LEDs) offers continuous, tuneable wavelengths, significantly improved portability, and potentially greater efficiencies - all while being non-toxic to humans. The outcome from this convention will ultimately necessitate a transition towards a world in which the LED is the dominant UV light source, therefore it is important that the technology is ready. As of 2019, UV LEDs had captured almost 30% of the market share from UV lamps [2]. The UV LED market in general is expected to grow from

\$1.73B in 2024 to \$15.65B in 2034, currently dominated by Asia Pacific, with North America expected to grow the fastest (Figure 1.2).

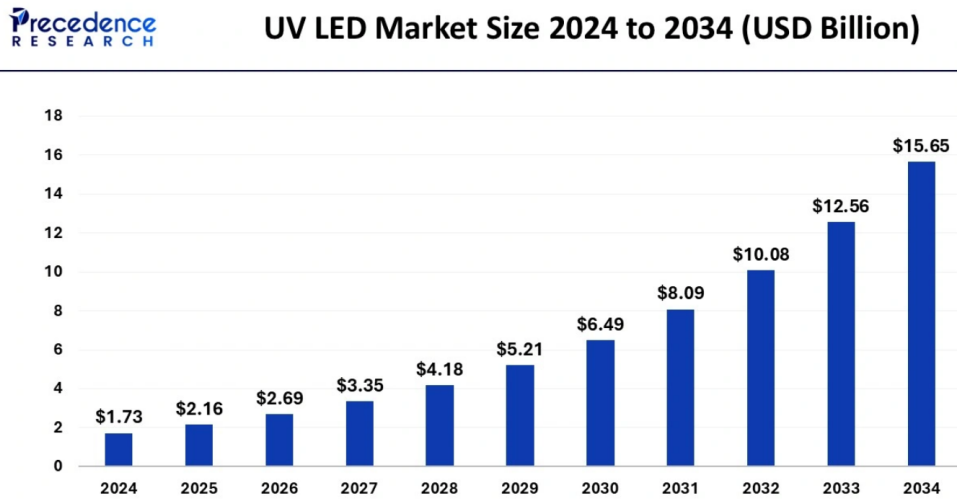


Figure 1.2: Predicted global UV LED market size from 2024 to 2034. Taken from [3] with permission from Precedence Research.

UV light has myriad applications spanning multiple industries and technologies [4–7]. The application is often specific to a certain wavelength range, as is illustrated in Figure 1.3. Originally, as longer wavelength UVA LEDs were developed, these dominated the market with applications in material curing, replacing bulky, costly mercury lamps [8]. The longer wavelength UVA light allows deeper penetration into the substrate materials. Examples of materials that undergo this polymerisation process include inks, fibre optic coatings and photoresists used in the processing of semiconductors [9]. LEDs also benefit from not generating large amounts of heat, as in lamps, allowing heat-sensitive materials to be cured.

In the UVB region, plant growth can benefit from LED irradiation. These wavelengths can modify the accumulation of certain metabolites in plants, which, after consumption by humans, have been shown to reduce the incidence of disease [10, 11]. Modules consisting of large arrays of UVB LEDs are available for plant growth applications, offering benefits such as controllable output power, the ability to be pulsed, and lack of heating effects. Phototherapy is another major application of UVB LEDs. Psoriasis is a debilitating skin disease that impacts over 100 million people worldwide. Targeted exposure of affected skin with UVB LEDs has been used to treat this disease [12], while other skin diseases such as atopic dermatitis, vitiligo, and pruritus, can also be treated with UVB light [5]. Small, portable modules with narrowband

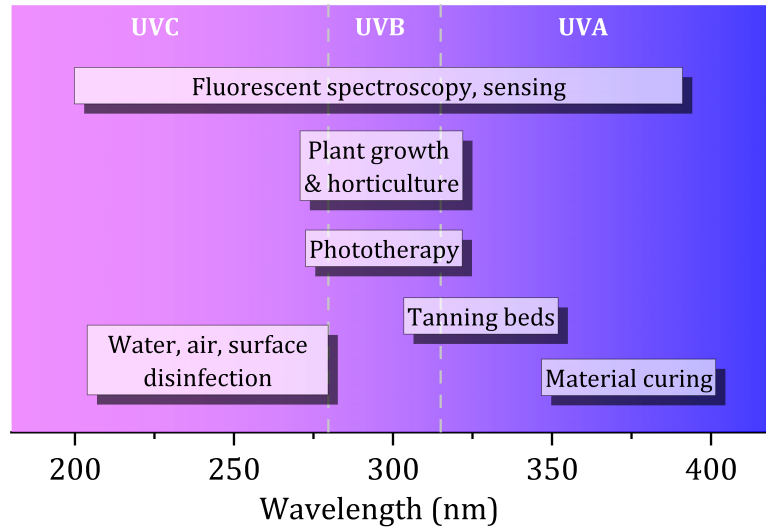


Figure 1.3: Examples of applications of UV LEDs with respect to their emission wavelengths.

UVB LEDs are now commercially available for these phototherapeutic uses [13].

Another use case which involves the irradiation of UV light on skin is tanning beds. This application is emerging with increasing LED output powers and efficiencies, realisable through powerful LED arrays. However, this light is typically a broad band of the UV spectrum, predominantly UVA at much higher doses [14], so it does not possess the same health benefits as those outlined from UVB light. Wavelength is inversely proportional to penetration depth, meaning UVA light can penetrate deeper into the tissue, while UVC is absorbed mainly in the outermost dead skin layer. Tanning fundamentally involves the damage of DNA, so is inherently carcinogenic [15]. A large body of literature has established the health risks associated with tanning bed usage, including increased risk of skin cancer, and recently, potential addiction [16–18]. As such, tanning beds remain a controversial application of UV LEDs.

The outermost layer of the skin, the stratum corneum, is composed mainly of dead skin cells and absorbs the majority of UVC radiation and protects the biologically active cells beneath [20]. This is of great importance as DNA/RNA begins to absorb light below approximately 300 nm, with its peak absorbance at approximately 265-270 nm [21]. The germicidal effect of UVC radiation is an established field, however, the COVID-19 pandemic has triggered a rapid surge in research (Figure 1.4). UVC light has been shown to break the adenine-thymine bonds in DNA, resulting in a covalent linkage between two adenine bonds [22]. This renders the cell unable to replicate. If this DNA belongs to a virus present in the air

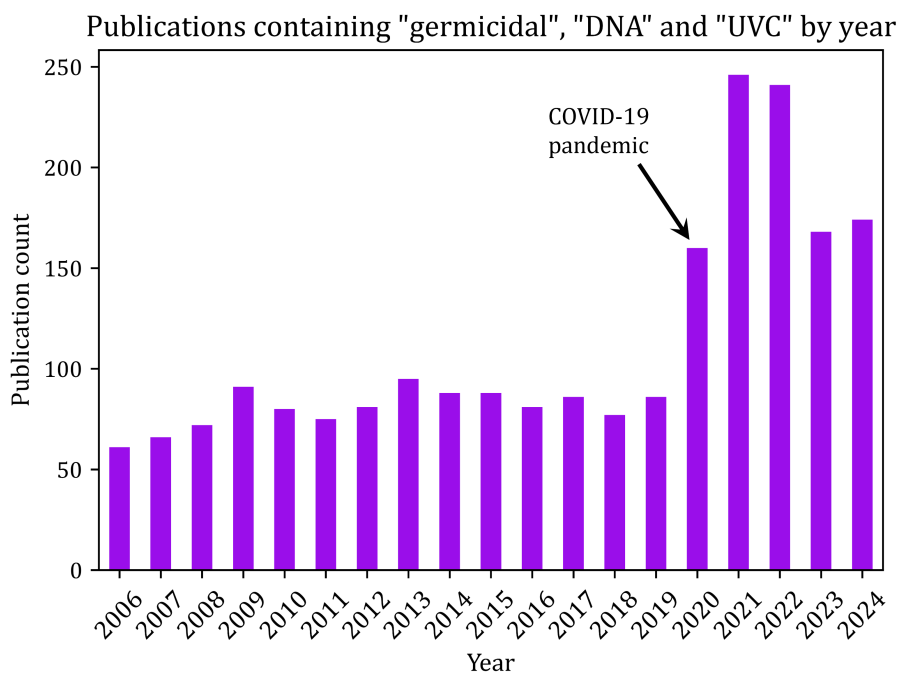


Figure 1.4: Research publications per year relating to the terms “UVC”, “germicidal” and “DNA”. Details on data acquisition can be found in Ref. [19].

or in water for example, then, with a sufficient dose, the virus will be inactivated. However, if this is the DNA cell of a human, it can be the first step in carcinogenesis. This emphasises the safety considerations necessary when dealing with UVC light from the perspective of human interaction. Otherwise, many novel techniques have been introduced for disinfection of air, water and surfaces utilising UVC LEDs [6, 23, 24]. More recently, with advances in technology, even shorter wavelength LEDs have been explored for inactivation of viruses and bacteria, while being safe for human exposure [25].

UV LEDs offer the significant advantage of wavelength tunability, which allows for targeted analysis of particular biological molecules with characteristic absorption wavelengths. A recent technique that makes use of the low penetration depth of UV light in tissue is microscopy using surface excitation (MUSE) [26]. Conventional histopathology methods for analysing tissue specimens are costly and time-consuming, involving specialist sectioning into slices and staining of the tissue. MUSE employs UV LEDs emitting around 265-280 nm so that the penetration depth into tissue is on the order of a few microns, which avoids the need for slide preparation [27]. Ultimately, lasers would be more suited as a near-monochromatic light source for this application, so the ongoing development of

solid-state UV lasers could allow for a major improvement in the quality of this research area.

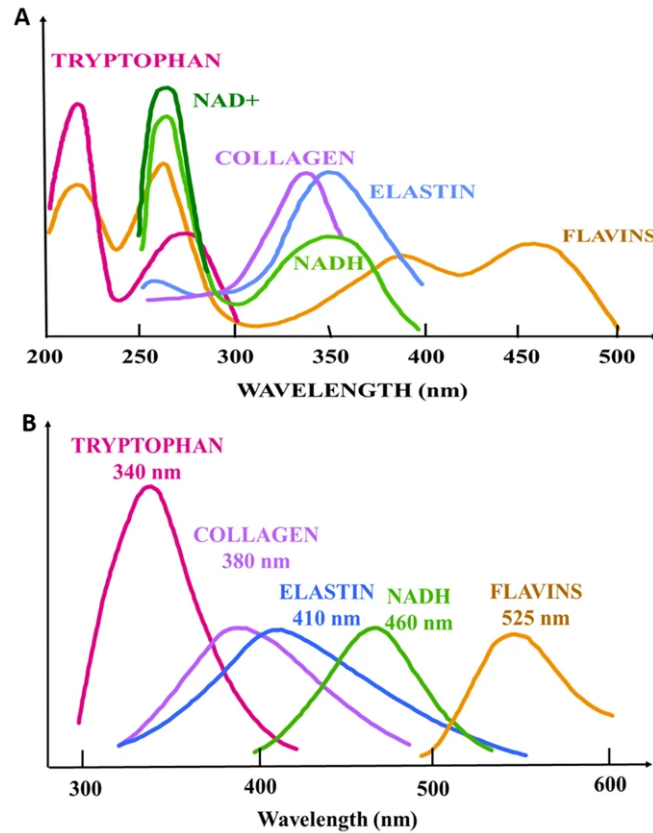


Figure 1.5: (a) Absorption and (b) emission spectra of various biological fluorophores from a mouse brain. Taken from [28] with permission.

Another area of application for UV light is fluorescent spectroscopy. This technique involves the photoexcitation of fluorophores (e.g. dyes or proteins in tissue), which allows for detection of their characteristic fluorescence. A prerequisite for this technique is an illumination source with a narrow emission linewidth at the excitation wavelength of the fluorophore, with sufficient output power. Conventionally, a broad-band mercury or deuterium lamp is used as a source, and the desired emission wavelength is filtered [29, 30]. As previously discussed, these lamps are inefficient. The majority of the generated spectrum is unused and some of the desired wavelength intensity is lost through the filtering. This inefficiency is also characterised by the generation of large amounts of heat, which can potentially damage the sample. Lamps are also typically costly, bulky and have limited lifetimes [31].

On the other hand, LEDs possess all the trademarks of an ideal light source for

fluorescence imaging: monochromatic with a customisable emission wavelength; long lifetimes; cheap costs; low power consumption and high efficiency, meaning little heat is generated; and small footprints. A comprehensive review on the use of LEDs in fluorescence-based analytical applications was carried out by Mukunda *et al.* [32]. Examples of biological molecules that show characteristic absorption in the UV include DNA (260 nm), collagen (290 nm, 320 nm), and elastin (325 nm) [33]. Figure 1.5 shows the corresponding excitation and emission spectra for various biological molecules.

As part of the Irish Photonics Integration Centre (IPIC) Biomedical theme [34], an advanced endoscope for surgical guidance and imaging is being developed (Figure 1.6) [35, 36]. Fluorescence spectroscopy is one such capability being incorporated into this system, requiring multi-wavelength sources (including UV) for different biomarker quantification. The application will require of the light source a narrow linewidth spectrum with low background spectral components. This is to prevent unwanted wavelengths from the LED overlapping the fluorophore emission spectra, which would hinder the sensitivity of detection. Sufficient dosage of UV light is required to excite the fluorophores, so a target output power specification of 1 mW was set. As seen in Figure 1.5, multiple biomarkers possess an excitation wavelength in the far-UVA, warranting an efficient light source with a clean, narrow spectrum.

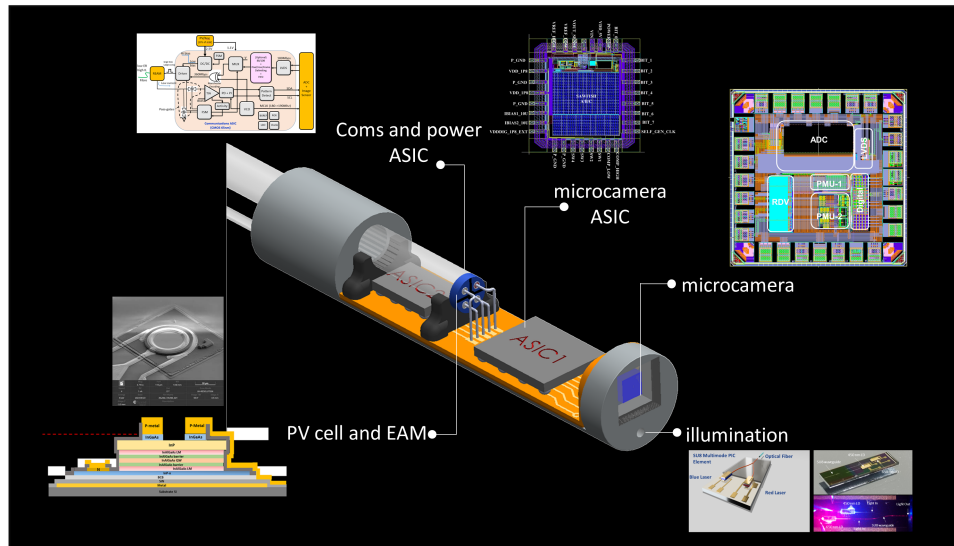


Figure 1.6: Computer graphic of the proposed surgical guidance endoscope, which will employ a UV light source for fluorescence imaging (in the illumination component). Courtesy of IPIC2 Biomedical Theme.

1.2 Light emitting diodes and the III-nitride material system

LEDs are a relatively mature technology since their emergence in the 1960s [37]. Blue LEDs, realised through collective efforts from Amano *et al.* [38, 39] and Nakamura *et al.* [40] in the late 1980s through to early 1990s, paved the way for more efficient lighting by employing phosphors to produce white light. These devices now demonstrate electrical-to-optical efficiencies of greater than 80% [41].

An LED consists of layers of specially engineered semiconductor materials. When an electrical current is passed through it, the material generates light at an energy commensurate with the bandgap. The bandgap is an intrinsic property of semiconductor materials with a periodic atomic structure. Semiconductor materials, by definition, have a non-zero bandgap. Certain semiconductors are ‘allowed’ to emit light (e.g. InP and GaN, but not Si), and it is the bandgap energy which determines the wavelength of light emitted. As UV light possesses shorter wavelengths (thus higher energies through Planck’s equation $E = hc/\lambda$), a semiconductor material system with a high bandgap energy is required for UV LEDs. The III-nitride semiconductor materials are binary or alloyed compounds consisting of a group III element from the periodic table and nitrogen. These primarily consist of aluminium nitride (AlN), gallium nitride (GaN) and indium nitride (InN) as well as their alloys. As evident in Figure 1.7, the bandgap of the material is a function of the alloy composition, x (e.g. $\text{Al}_x\text{Ga}_{1-x}\text{N}$).

During operation of an LED, negative charges (electrons) and positive charges (holes) recombine to generate photons of light, corresponding to the bandgap of the material. By forming quantum ‘wells’ in an engineered active region with reduced bandgap material, these charged carriers can be captured (and thereby generate light) more efficiently. Hence, the emission wavelength of the LED is tuned by varying the composition of material in the active region. Unlike conventional III-V materials emitting largely in the visible and infra-red (IR), the III-nitrides have a theoretical bandgap window from ~ 0.7 eV to ~ 6 eV (not considering BN), spanning the UV to the IR. This, along with its composition-independent direct (permitting light generation) bandgap, makes the material system attractive for many optoelectronic applications. III-nitride materials are also attractive for power electronics applications due to their large thermal conductivity and high voltage capabilities [42, 43].

For the synthesis of III-nitride crystals, a starting point is required to act as a ‘seed’

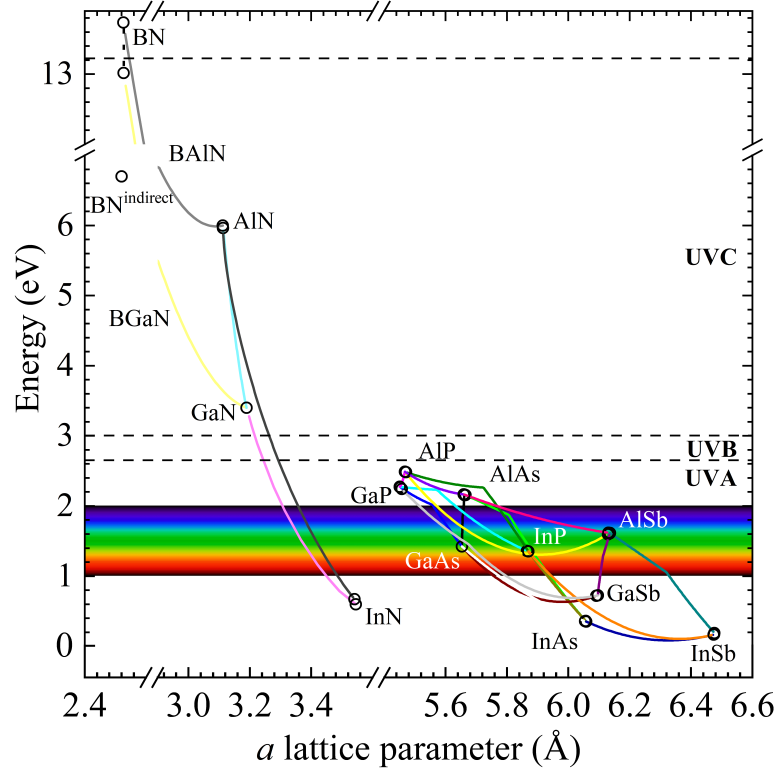


Figure 1.7: The III-V material system as a function of lattice constant and bandgap energy. The III-nitrides are seen on the left-hand side of the plot with smaller a lattice constants, spanning from the UV into the infra-red. Courtesy of Dr. Thomas O'Connor.

for the subsequent growth. While the same material as that to be grown would be an ideal candidate, III-nitrides unfortunately lack a readily-available homogeneous substrate. Single-crystal GaN is absorbing below approximately 360 nm, requiring intensive substrate removal processes. AlN substrates can be used to achieve transparent, ultra-high quality material [44, 45], however, this is costly to acquire. With high thermal conductivities, 4H- and 6H-SiC are popular but expensive substrate choices mainly for power electronics devices, where optical transparency is not of concern [46]. The most common substrate used for UV optoelectronic devices is sapphire, due to its low cost, wide availability, UV transparency, and similar crystallographic nature to III-nitride materials. Although treated as wurtzite in structure, there is a significant lattice mismatch between sapphire and AlN (13% after an in-plane lattice rotation), which, when combined with the thermal expansion coefficient mismatch, leads to wafer bowing and potentially cracking. Many techniques have been investigated to improve the quality of AlGaN on sapphire substrates such as patterning and regrowth, AlN connecting layers, and superlattice structures [47].

In spite of UV LEDs first being demonstrated around the same time as the first blue LEDs, their advancements have been significantly slower. There are numerous reasons for this which will be discussed in detail later in this thesis, but some main challenges in realising efficient UV LEDs include high internal absorption of the UV light and difficulties in the growth of the semiconductor materials. Device efficiencies for UV LEDs strongly depend on the wavelength region, but are usually in the single digits. A comprehensive overview of the technological status of UV LEDs can be found in Ref. [48].

1.3 The far-UVA gap

The UVA wavelength region ($400\text{ nm} > \lambda > 315\text{ nm}$) can informally be further split into two subregions: that of the (In)GaN-based material system for $400\text{ nm} > \lambda > \sim 365\text{ nm}$, sometimes referred to as ‘near-UV’; and the ‘far-UVA’ (Al)GaN-based material system for $315\text{ nm} < \lambda < \sim 365\text{ nm}$. The former sub-region benefits from adopted technology from blue LEDs, such as ITO current spreading layers [49], as well as the ability to realise coherently-grown high quality buffer layers on transparent GaN templates [50, 51]. This is reflected by the high EQE values observed at this wavelength region in Figure 1.8. Far-UVA LEDs, meanwhile, cannot utilise the same technological approaches. Both ITO and GaN become absorbing below $\sim 365\text{ nm}$. This means that GaN templates cannot be used. Instead, low Al content AlGaIn buffer layers are grown on AlN-on-sapphire templates with large lattice mismatches, resulting in relaxation through roughening and high dislocation density formation which can be catastrophic for performance [52]. This intensifies the dip in efficiencies observed at this wavelength range in Figure 1.8.

Moreover, a lack of mass market demand for applications at these wavelengths results in relatively less research pursuing their development. This can be observed in Figure 1.9, in which the number of commercially available UVC LEDs around 275 nm is significantly greater than those around 320 nm . Contrastingly, the high demand for LEDs around 275 nm compounds the “substrate sweet spot” at this composition (relatively less lattice mismatch) which is reflected in Figure 1.8 by the differing efficiencies between these wavelength ranges.

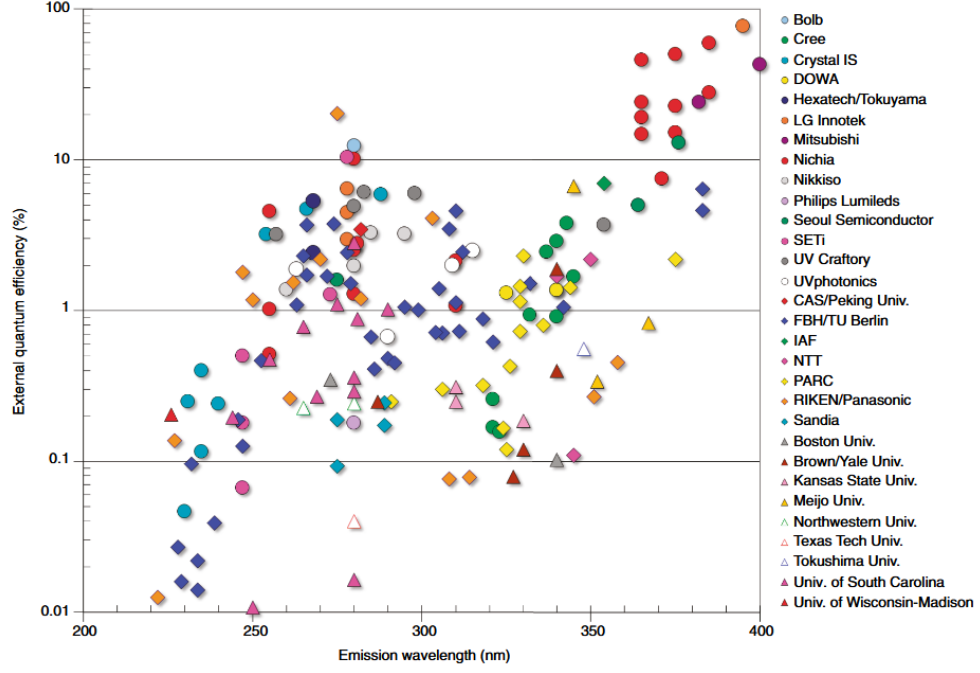


Figure 1.8: Reported EQE versus emission wavelength of commercially available UV LEDs. This data was taken immediately before the COVID-19 pandemic, so has since likely become further intensified. Taken from [53]. Reproduced with permission from Springer Nature.

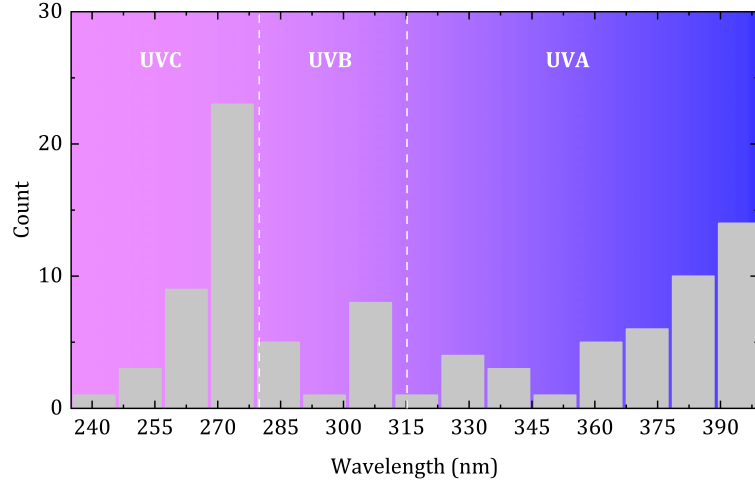


Figure 1.9: Non-exhaustive representation of commercially available UV LEDs, illustrating the frequency of available wavelengths.

1.4 LED efficiencies

Numerous efficiency metrics are referred to throughout this thesis, so for clarity an overview is presented here. In an ideal LED, every electron injected into the device will result in the emission of a photon (of energy $h\bar{\nu} \approx E_g$) into free space. In reality, this is not the case and

efficiencies are always less than 100%. Figure 1.10 illustrates various loss mechanisms, both electrical and optical, in an LED. Injected electrons may not reach the QWs, recombining *radiatively* ($h\nu \neq E_g$) or *non-radiatively* elsewhere in the device. The percentage of electrons that do reach the QWs is defined as the injection efficiency, η_{IE} . Of these, a further percentage may not recombine radiatively. The ratio of electrons that recombine radiatively (producing the desired emission wavelength) to those that reach the active region is referred to as the internal quantum efficiency, η_{IQE} .

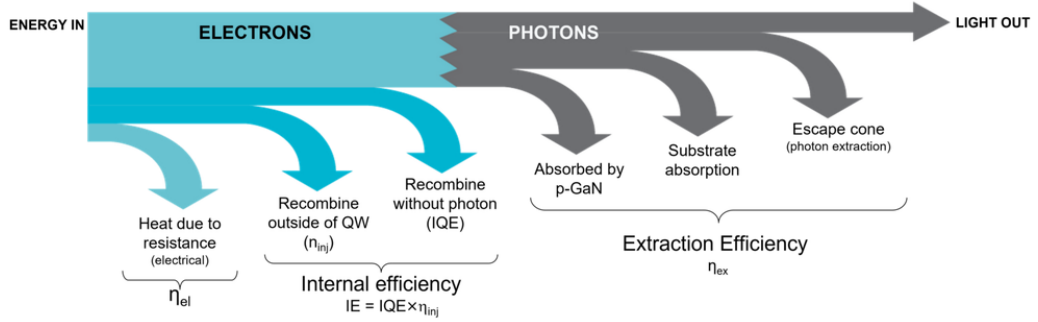


Figure 1.10: Schematic describing the different loss mechanisms in UV LEDs. Taken from [54].

Of the photons produced by radiative recombination in the QWs, a significant portion will not escape the structure, through a combination of total internal reflection and internal absorption. The light extraction efficiency, η_{LEE} , describes the ratio of photons emitted into free space to those emitted from the active region. These three efficiencies can be combined to express the external quantum efficiency, η_{EQE} :

$$\eta_{EQE} = \eta_{IE} \times \eta_{IQE} \times \eta_{LEE} = \frac{P_o/h\nu}{I/q} \quad (1)$$

The EQE can additionally be expressed by the second term in Equation 1 as the quantised output optical power, $P_o/h\nu$, divided by the injected charge. Additionally, an electrical efficiency, η_{ELE} , considers the mean energy of the emitted photons and the electron energy (qV). A general efficiency, referred to as the wall plug efficiency, η_{WPE} , simply considers the ratio of output optical power to input electrical power: $\eta_{WPE} = P_o/IV$. Table 1 summarises these different efficiencies.

Ultimately, all research towards the improvements of UV LEDs targets one of these efficiencies (and always the η_{WPE}). The injection efficiency of UV LEDs, a specific focus of this work (Chapter 4), suffers from the heavy effective mass of the hole in (Al)GaN, and the

Metric	Description
Injection efficiency (IE)	The percentage of electrons injected into a device that are injected into, and recombine in, the active region
Internal quantum efficiency (IQE)	The percentage of electron/hole pairs injected into the active region which result in the emission of a photon
External quantum efficiency (EQE)	The percentage of electrons injected into the device which result in the emission of a photon from the device
Light extraction efficiency (LEE)	The percentage of photons generated in the active region which are extracted from the device
Electrical efficiency (ELE)	The ratio of applied bias (qV) to the energy of the emitted photon ($h\nu$)
Wall plug efficiency (WPE)	The percentage of input electrical power converted into output photon power

Table 1: LED efficiency metrics.

asymmetry of conductivities between n - and p -type regions. The light extraction efficiency of UV LEDs is particularly poor due to the high energy of the photon ($E = hc/\lambda$) and the (necessary) presence of absorbing material.

Although the III-nitrides are remarkable in that they can operate so well in spite of high threading dislocation densities which would devastate devices of other material systems, these dislocations and other defect states limit the IQE to several percent. Threading dislocations (TDs) are structural defects in the semiconductor crystal which propagate throughout the subsequently grown layers. In III-nitride materials, these most commonly originate due to the lattice and thermal expansion coefficient mismatches involved with these materials. High densities of TDs deteriorate the efficiency of LEDs by numerous mechanisms, for example by providing non-radiative recombination centres, scattering carriers, and providing diffusion pathways for impurities.

The WPE - arguably the most pertinent efficiency for commercial use - is affected by all of these aforementioned effects and more, such as the typically high resistance of the material, increasing the drive voltage and worsening η_{ELE} . Thus, there are a plethora of avenues through which the performance of UV LEDs can be improved, some of which are pursued in this work.

1.5 Outline of thesis

The overarching theme of this thesis is the development of far-UVA LEDs with specifications of 1 mW output power and a clean, narrow emission spectrum. These devices are then to be integrated into a diagnostic endoscope, for the purpose of fluorescence imaging. With a range for the emission wavelength set in the range of 320 to 340 nm, various LED structures were investigated throughout the work with different peak wavelengths. The work discussed in this thesis spans from the design and simulation of the epitaxial structure, considerations around the growth strategies, fabrication of devices, and characterisation techniques to elucidate the device physics. A particular focus of the work was to improve the p -type conductivity in the LED to enhance the overall performance. This consisted of experiments revolving around a technique referred to as polarisation doping, attempting to address some hitherto undefined optimum conditions.

Chapters 1 and 2 introduce the general themes and give an overview of the experimental methods and theory used throughout the thesis, respectively. The research carried out towards general improvement of the LED performance are discussed in Chapter 3. This includes topics such as the use of a novel material used in the quantum wells, boron nitride, which has shown promise in improving the radiative efficiency of UV LEDs. This resulted in the first experimental demonstration of a B-containing UV LED, indicating potential benefits to its inclusion. Also, a novel strategy for the fabrication of an LED material with improved crystal quality through patterning and subsequent regrowth is revealed.

The optimisation of the p -type doping regime in far-UVA LEDs is discussed in Chapter 4. A technique which takes advantage of the built-in polarisation fields in III-nitride crystals, polarisation doping, was investigated. LEDs with varied p -doping approaches were compared and studied down to cryogenic temperatures. The concurrent use of polarisation doping with impurity doping exhibited an enhanced LED efficiency, and can additionally eliminate parasitic luminescence - a necessity for this LED's application - without impurity doping. With the aid of numerical simulations, some proposed explanations are discussed for the performance benefits.

Chapter 5 then takes a deeper dive into the physics involved in the polarisation doping. The Hall effect measurement is utilised to investigate the conduction mechanisms in p -type graded composition AlGaIn layers. Similar to the LED characterisation in Chapter 4,

these were carried out as a function of temperature. Specifically, the presence of hopping conduction - a phenomenon associated with heavy impurity doping - is analysed.

Finally, a conclusion summarises the main findings of the thesis and how the objectives were met. Additionally, areas of work for which there was not sufficient time or resources to study, but would be in the interest of future students to investigate, are explored.

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2 Experimental methods and theory

This chapter serves as a foundation and reference for the main simulation and experimental techniques used in this work, and the theory accompanying them. The growth of material in the AIXTRON metalorganic chemical vapour deposition system, used throughout this work, is addressed. I note here that while all of the fabrication, characterisation and simulations were carried out by me, the growth of materials for this project was carried out by either Dr. Sandeep M. Singh (another student on the project), Dr. Vitaly Z. Zubialevich, and occasionally Dr. Pietro Pampili. Regardless, the central role of growth in this body of work renders the inclusion of its explanation here essential.

An overview of concepts such as the physical properties of III-nitride materials as well as impurity doping are provided here. The fabrication process for the formation of individual LEDs, all of which was carried out in Tyndall National Institute’s III-V cleanroom, is outlined, with discussions surrounding particular aspects deemed central to this work.

The primary material and device characterisation techniques used throughout this thesis are also discussed, including the Hall effect measurement. Use of the LakeShore HMS 8404 occupied much of my final year, utilising the cryogenic measurement capabilities to explore some interesting physics. More on this work can be found in Chapter 5.

Finally, the framework underpinning Silvaco’s TCAD software is explained. Silvaco was employed to carry out simulations investigating device physics to complement the experimental work, the results from which can be found in Chapter 4.

2.1 Epitaxial growth of III-nitrides

The term *epitaxy* describes the growth of crystallographic materials. III-nitride materials are grown primarily by metalorganic chemical vapour deposition (MOCVD). Other techniques are also used, such as molecular beam epitaxy and hydride vapour phase epitaxy (which was arguably the method to launch the development of blue LEDs [1]). However, MOCVD is one of the most common techniques due to its suitability for mass production.

The growth reactor used to provide the material used in this work is an AIXTRON 3×2 inch close coupled showerhead-type reactor, seen in Figure 2.1a. The ‘showerhead’ refers to the lid of the reactor chamber through which the gases enter. It has multiple small input holes to allow for uniform distribution of the gases. A silicon carbide-coated graphite susceptor

(Figure 2.1b) holds up to three 2 inch wafers, under which is a tungsten heating element (Figure 2.1c), capable of heating the samples to 1300°C. A thermocouple presides underneath the surface of the susceptor to measure the temperature, and a pyrometer provides additional temperature metrology from the substrate surface. To further ensure uniform gas distribution, the susceptor also rotates during growth at 60 rpm.

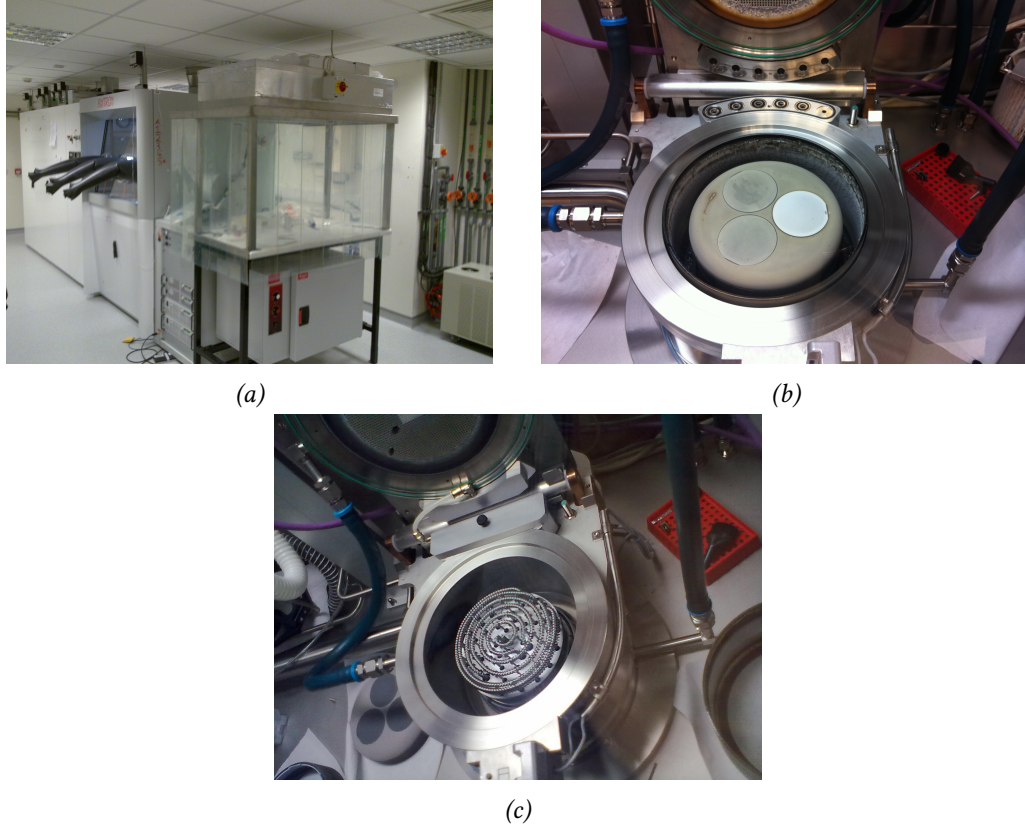


Figure 2.1: (a) The Aixtron MOCVD reactor used to grow the UV LED material for this thesis, (b) the susceptor, with its three 2 inch pockets, and (c) the tungsten heater underneath the susceptor.

The metals used in the synthesis of III-nitride compounds in this work (Ga, Al, B) are introduced to the reactor in the form of metalorganic precursors: trimethylgallium (TMGa), trimethylaluminium (TMAI), and triethylboron (TEB). The nitrogen is supplied in the form of ammonia (NH_3). These gas-phase precursors are flowed through the showerhead nozzles and into the reactor under hydrogen or nitrogen ambient. After diffusing and adsorbing onto a heated substrate surface, the precursors dissociate to metal atoms while ammonia cracks resulting in atomic nitrogen. The metal and nitrogen adatoms then undergo a kinetic ‘dance’ to find an appropriate lattice site for incorporation, thus forming the crystallographic epilayers.

2.1.1 LED structure

A typical III-nitride UV LED structure is depicted in Figure 2.2.

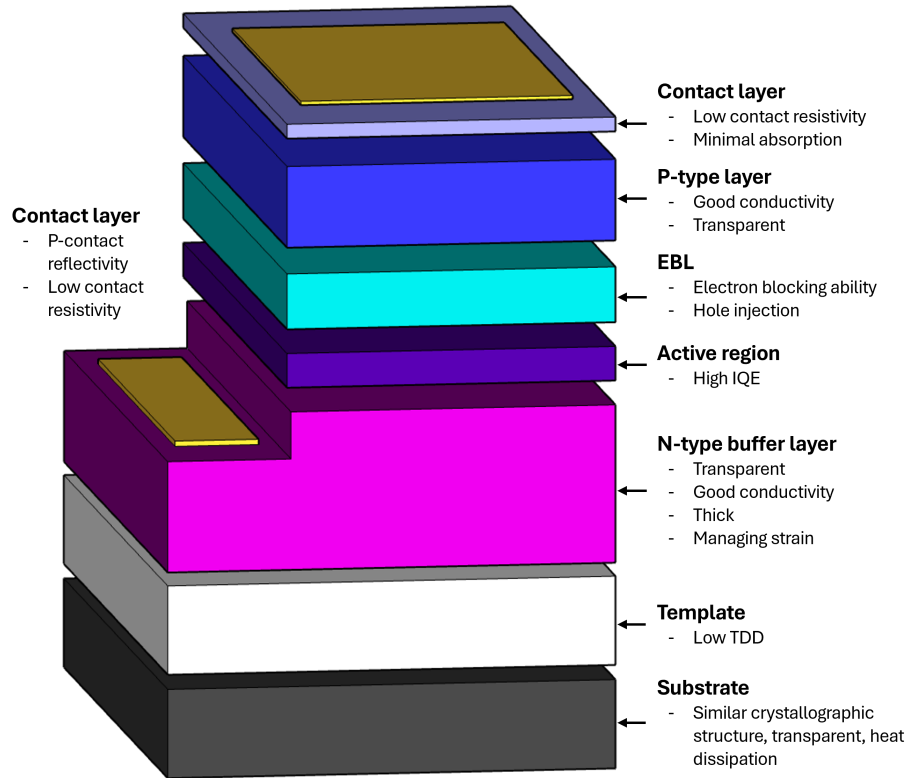


Figure 2.2: The requirements associated with each component in a typical UV LED structure.

First, a substrate must provide the ‘seed’ for subsequent growth of the LED structure; a template is then grown, and must be of good crystalline quality; an *n*-type layer must be transparent to the generated light, while being thick and conductive for good current spreading; the light-emitting active region, consisting of a series of narrower bandgap thin quantum wells (QWs) sandwiched between wider bandgap quantum barriers (QBs), must confine carriers and demonstrate good IQE; a higher bandgap layer follows the active region, commonly referred to as the electron blocking layer (EBL). This layer is especially vital in III-nitride LEDs in an attempt to prevent the overshoot of electrons from the active region into the *p*-type layers [2–4]. Next, a *p*-type layer should provide good conductivity, supplying holes into the active region. Finally, a thin *p*-type GaN layer is used to facilitate low resistivity electrical contact, while sacrificing on light extraction.

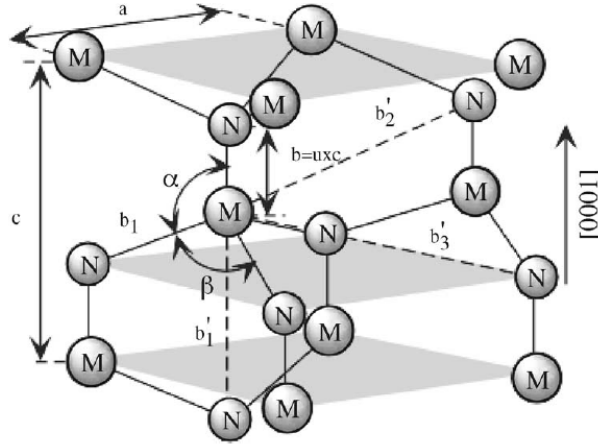


Figure 2.3: The generic metal (M)-polar III-nitride wurtzite crystal structure, illustrating the a and c plane lattice constants. Taken from [7] with permission.

2.1.2 Crystal structure and polarisation fields

The wurtzite phase is the most common form of III-nitride semiconductors because it is energetically favourable compared to zinc-blende. Figure 2.3 depicts the crystal structure of wurtzite III-nitride. Because the crystal structure lacks a centrosymmetric inversion plane, the crystal can be either in the form of metal-polar (metal atom-terminated) or N-polar (nitrogen atom-terminated). Aside from the orientation, the crystal structure is identical in both cases. However, both forms possess important distinctions in material properties, such as polarisation charge polarity and chemical stability. Conventionally, typical substrates lend to metal-polar nucleation, while as-grown metal-polar material is characterised by smooth surfaces, likely due to a higher adatom mobility. N-polar III-nitrides, on the other hand, require specific controlled procedures to ensure the growth of N-polar material, and have conventionally been characterised by high densities of hillocks on the surface. Although recent work has developed an understanding and solutions to such effects [5, 6], metal-polar is still the most common form of wurtzite III-nitrides. All material grown in this work is intended as and assumed to be metal-polar oriented, and is thus treated as such in all calculations relating to polarisation.

Wurtzite III-nitrides possess intrinsic, non-vanishing polarisation fields along the $[0001]$ axis. These are broken into two parts: spontaneous polarisation (P_{sp}) and piezoelectric polarisation (P_{pz}). Spontaneous polarisation originates from the lack of inversion symmetry in the wurtzite crystal structure, as well as the difference in electronegativity values between

the different atoms. The ideal ratio of the c to a lattice parameters in a wurtzite crystal structure is $\sqrt{8/3} \approx 1.633$, for all nearest neighbour bond lengths being equal [8]. Because of the large electronegativity of N, a strong ionicity in the bonds results in a deviation of the ideal c/a ratio, which significantly increases - but does not in itself result in [9] - the spontaneous polarisation. The electronegativity of N is significantly larger than that of other III-V semiconductors, leading to considerable non-zero dipole moments along the [0001] axis. For metal-polar III-nitrides, the P_{sp} field acts in the $[000\bar{1}]$ direction. To define the magnitude of the spontaneous polarisation, a reference crystal structure is required. The cubic zinc-blende system is employed as the reference structure due to its symmetry, and therefore zero P_{sp} term [10].

Strain present in electronegative III-nitride semiconductors results in piezoelectric polarisation fields. Strain, ϵ , can originate from mismatches in the a lattice parameter, through:

$$\epsilon = \frac{a_{sub} - a_0}{a_0}, \quad (2)$$

where a_{sub} and a_0 are the a lattice parameters of the substrate and epilayer, respectively. Strain can also arise from differences in the thermal expansion coefficients during cool-down after growth. The strain present in a layer will distort the c/a ratio: tensile strain reducing the ratio, worsening the non-ideality ($P_{pz} \parallel P_{sp}$); compressive strain bringing the ratio closer to the ideal (P_{pz} and P_{sp} acting anti-parallel). Because lattice mismatch is much more significant in In-containing alloys due to the large a lattice constant of InN, the piezoelectric component in $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys is dominant. Within the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloy, the lattice mismatch is relatively small ($\sim 2.5\%$) while the spontaneous polarisation of AlN is three times larger than that of GaN [11]. Therefore, the spontaneous polarisation dominates in AlGaIn alloys.

Polarisation fields, which can be on the order of MV/cm in wurtzite III-nitrides, will have significant effects on the band structure. The quantum confined Stark effect (QCSE) is a phenomenon which can occur in the quantum wells of III-nitride structures [12]. The fields across the QWs will act to bend the bands, from an ideal step-like shape to a ‘saw-tooth’ shape. This results in the electron and hole wavefunctions being spatially separated to either side of the wells, resulting in a reduced radiative recombination rate as well as a redshift in emission. The QCSE can therefore reduce the IQE of QWs.

2.1.3 Impurity doping

In an ideal case, a layer of undoped semiconductor should be electrically insulating, with all the electrons residing in the valence band. To realise conductive material, excess electrons (*n*-type) or holes (*p*-type) in the crystal need to be introduced. This is conventionally achieved by ‘doping’ the crystal with an impurity atom. For *n*-type (*p*-type) conductivity, Si (Mg) is the most common impurity atom for III-nitrides, where it sits on a Ga site to provide an excess electron (hole). The Si (Mg) atom becomes a ‘donor’ (‘acceptor’) atom, and once activated are positively (negatively) charged. These dopants are provided by the precursors disilane (Si_2H_6) for Si, and biscyclopentadienylmagnesium (Cp_2Mg) for Mg. Small amounts of these dopants are required for good conductivity ($\sim 0.01\%$), hence the name.

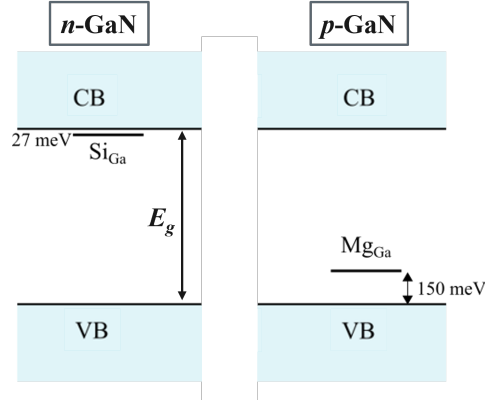


Figure 2.4: Band diagram illustrating the activation energy for the *n*-type dopant (Si) compared to *p*-type dopant (Mg) in GaN.

In the energy band structure (Figure 2.4), doping forms energy states close to the conduction band for *n*-type doping and the valence band for *p*-type doping. The energy required to excite a carrier from this donor (acceptor) state to the conduction (valence) band is referred to as the activation or ionisation energy (E_A). For Si-doped *n*-type III-nitrides, an activation energy on the order of thermal energy at room temperature ($kT/q \sim 25$ meV) is required, meaning for (almost) every Si atom incorporated into the crystal, a free electron is generated. Thus, excluding the case of high Al content AlGaN [13], *n*-type doping of III-nitrides is usually not an issue.

However, achieving *p*-type III-nitrides is not as straightforward. Unlike Si for *n*-type doping, Mg possesses a large activation energy in III-nitrides. The activation of the *p*-type dopant therefore requires more energy, and holes can remain localised to the acceptor atom

instead of contributing to band conduction. This deep acceptor effect is analogous to that in *p*-type oxides [14].

Additionally, native point defects (interruptions or distortions of bonds in a crystalline lattice) can compensate carriers. These can be categorised as vacancies (a missing atom in the lattice), interstitials (an extra atom in the lattice), and antisites (a cation and anion in reversed sites in a compound lattice). Defects can be characterised by their likelihood to form in a crystal lattice, quantified by their formation energy. A lower formation energy reflects an increased preference of a lattice to preserve energy through the formation of a certain defect. Figure 2.5 describes the formation energy of various point defects as a function of the Fermi level. The slope of the line corresponds to the charge state of the defect. The nitrogen vacancy, V_N , with a lower formation energy closer to the valence band, is therefore a bigger issue in *p*-type GaN, acting as a compensating centre (positive slope). During the growth of *p*-type III-nitrides, high ratios of NH_3 to the group III elements (termed the V/III ratio) are therefore employed to prevent the formation of nitrogen vacancies through depleted nitrogen on the surface.

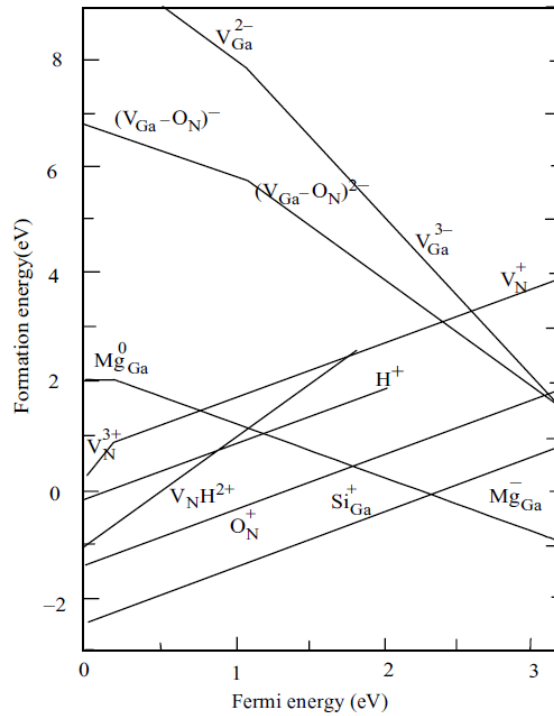


Figure 2.5: The formation energies of native point defects in GaN with respect to the position of the Fermi energy level. A positive slope corresponds to a positive charge state and vice versa.

Taken from [15]. Reproduced with permission from John Wiley and Sons.

During the growth of *p*-type III-nitrides, Mg forms a complex with H (which is always present due to cracked ammonia), passivating the Mg acceptor. Interestingly, this phenomenon is actually advantageous as it maintains the Fermi level closer to the mid-gap, allowing the Mg to be more preferentially incorporated (Figure 2.5) [16, 17]. After growth, however, the passivated Mg atoms need to be ‘activated’ by a thermal treatment ($T > \sim 700^\circ\text{C}$), during which the Mg-H complex is dissociated and hydrogen is out-diffused in a nitrogen ambient. These seminal discoveries were made in the early 1990s [18, 19], enabling the development of blue and UV LEDs. In this work, the activation of Mg-doped material was usually performed at 800°C for 30 minutes in N_2 .

2.2 Fabrication processes

The typical fabrication process flow employed for the realisation of LEDs in this work is shown in Figure 2.6. Some of these processes will be discussed in further detail in the following sections. After growing the material, a surface cleaning treatment is carried out, before lithography patterning and the *p*-metal deposition. Another lithography step defines the mesa pattern, which is formed by an inductively coupled plasma (ICP) dry etch. Next is the electron beam (e-beam) evaporation of the *n*-metal. In this work, a Ti/Al/Ti/Au (20/170/50/0 nm) stack is used. Due to the limited thermal budget with the *p*-metal present, the *n*-metal is not annealed. Nonetheless, it is Ohmic as-deposited.

A global sputtering of a dielectric material (usually SiO_2) passivates the surface, reducing non-radiative recombination on the surface and sidewalls. This step is especially important for smaller diameter devices (i.e. μLEDs) [20]. After patterning with lithography, selected areas of oxide are etched using ICP etching (SF_6 -based plasma) which exposes regions over the *p*- and *n*-metals, over which a final bondpad metal is deposited (Ti/Au 20/200 nm).

2.2.1 *p*-GaN surface clean treatment

The LED process flow begins with an initial chemical treatment to prepare the *p*-GaN surface for metal deposition. The formation of Ohmic contact to *p*-type GaN is known to be challenging, and is made worse by the presence of any oxide or contamination on the surface prior to metal evaporation. As such, a thorough wet-etch cleaning is required to prepare the surface immediately prior to this metal evaporation.

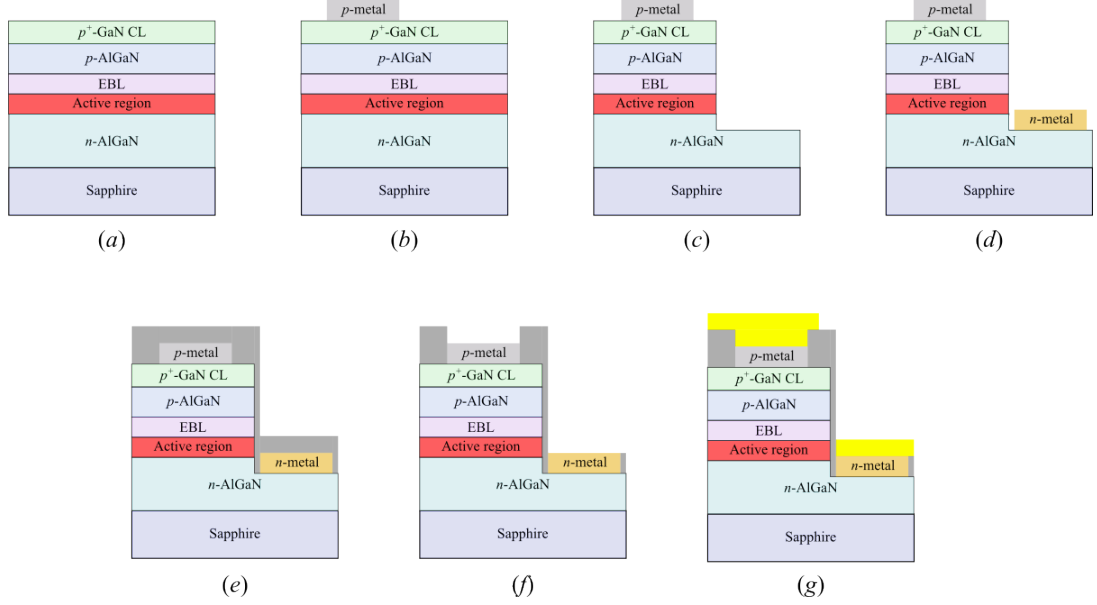


Figure 2.6: Typical fabrication flow of an LED starting from (a) the as-grown material. After preparing the surface and patterning by photolithography, the p-metal is evaporated (b). Following lift-off and further lithographic patterning, the mesa is formed by an ICP etch (c). After another round of lithography, n-metal evaporation occurs, followed by lift-off (d). A global SiO_2 desposition passivates the mesa sidewalls (e) and after optical lithography to define areas over the p- and n-metals, an ICP etch removes the oxide (f). A final round of lithography to define the bondpad positions is succeeded by the bondpad deposition and lift-off (g).

First, a 5 minute dip in buffered oxide etchant (low percentage of HF) is carried out, primarily for the removal of C [21]. Following a quick rinse in DI water, the sample is dipped in HCl:DI water (1:1) for 5 minutes primarily for oxygen removal [22]. Finally, a 30 second dip in 45% KOH at 100°C is performed, again for O removal [22]. After a final rinse in DI water and blow-dry under nitrogen air, photolithography is carried out to define the p-metal areas. A 30 second dip in aqua regia is performed immediately before loading the sample in the e-beam evaporator for the metal evaporation, which has been shown to potentially improve the electrical contact through modification of the GaN surface states [23].

2.2.2 Photolithography processes

Photolithography consists of forming patterns on a semiconductor's surface, which can be subsequently transferred into the material. Photosensitive polymers called photoresists are 'spun' onto the sample surface. The rate and time of spinning determines the thickness of resist, and for this work a rotational speed of 4000 rpm for 50 seconds was applied. The photoresist is then baked at a temperature and duration depending on the type of

resist. For better adhesion of the resist to the semiconductor surface, a monolayer of hexamethyldisilazane (HMDS) is usually first applied. A typical photoresist used in this work is Microposit S1813, which requires a bake at 115°C for 1 minute. The Karl-Suss MA6 mask aligner was used for the majority of mask alignment and exposures in this work, which employs a mercury arc lamp emitting at 365 nm. A dose of approximately 60 mJ/cm² was applied for most resists, which, considering the MA6 lamp power density of 10 mW/cm², corresponds to approximately 7 seconds exposure. After exposure, the material is then placed in a developer solution (TMAH-based Microposit MF319), which removes the exposed areas of resist. The sample is then ready to undergo subsequent processing such as an ICP etch, to transfer the developed resist pattern into the semiconductor material. After exposure to substantial heat in a plasma etch, the photoresist is usually severely cross-linked (polymer chains linked together) and requires repeated exposure to oxygen plasma along with prolonged dips in 90°C Microposit remover 1165 for successful removal.

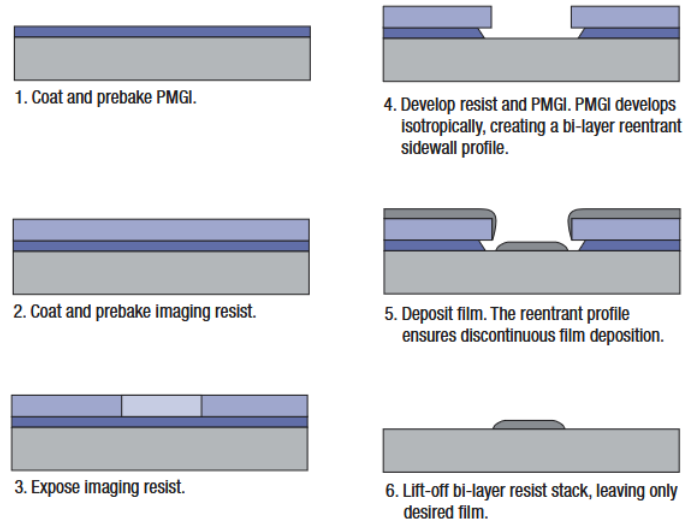


Figure 2.7: Process flow of a lift-off photoresist for a material deposition. The bi-layer process allows for a discontinuity in the deposited film, allowing the lift-off to occur without issue. Taken from [24].

A lift-off lithography process is employed for metal evaporations. This process, illustrated in Figure 2.7, involves initially the deposition of a pre-exposed resist (e.g. Microchem PMGI SF11), which is baked at 180°C for 3 minutes. This is followed by a standard resist and appropriate bake. After exposure and development of the bilayer of photoresists, an undercut is present in the sidewall profile, allowing the 1165 lift-off solution to contact the resist

through a discontinuity in the deposited film (step 5 in Figure 2.7).

2.2.3 Dry etching

Metal-polar III-nitrides boast an impressive resilience to wet etching by most chemicals, meaning dry etching is the go-to etching technique. An ICP dry etch, using the Oxford Cobra etcher, is employed for the formation of the LED mesas in this work. For etching of III-nitrides, Cl_2 and/or BCl_3 based gas mixes are usually employed due to the high volatility of the etch products [25]. These etches ideally result in fast, anisotropic etches with smooth surfaces [26]. The ICP etch utilises a physico-chemical etch to ablate the exposed material. The physical component is realised by the generation of high-energy ions produced by an RF field applied to the gas, which are accelerated at the sample surface, sputtering the material's surface. Meanwhile, a Cl reaction with surface Ga is understood to be the dominant mechanism in the chemical etching [27]. Generally, the vertical etch rate is greater than the lateral etch rate, however, anisotropy can be modified through optimisation of the process parameters. The main process parameters in the ICP etch to affect the etch rate and isotropy include the gas choice and flow ratios, RF power, ICP power, and pressure. Due to the wide range of available parameters, and access to an established GaN etch recipe, this recipe was used for the majority of etches carried out in this work: The process parameters consisted of a Cl_2 -based plasma, ICP power of 1200 W, RF power of 100 W, DC bias of 300 V, and pressure of 7.5 mT.

Considering the many layers in the LED structures with different Al compositions, a question may arise as to the selectivity of the etch process between AlGaIn alloys. A study by Buttari *et al.* [28] demonstrated no such selectivity between AlGaIn layers of different compositions, for Al content up to 35% - which is the highest Al content layer etched in this work.

The dry etching of *p*-type III-nitrides results in a significant deterioration of conductivity and makes difficult the formation of an Ohmic contact [29]. This has been explained by the formation of nitrogen vacancies during etching [30], and while some procedures have been shown to partly recover the conductivity of the etched *p*-GaN material [31, 32], it is generally avoided at all cost.

2.2.4 Metal contact deposition and Ohmic contact formation

To interface the device with the real world, metal contacts need to be deposited. The choice and thickness of the deposited metal are crucial choices determining the contact resistivity. The method used for depositing metal contacts is e-beam evaporation. Metal targets in a crucible are hit with a beam of electrons, after which the evaporated metal is deposited onto the substrate. This can be done in a (mostly) vertical deposition, or with additional angular rotation of the substrate ('360° rotation') to achieve more conformal deposition on patterned surfaces.

A stack of Ti/Al/Ti/Au (20/170/50/50 nm) is employed as the n -type contact for devices in this work. As deposited, the contact shows low resistivity Ohmic contact behaviour. The p -contact, however, is often not so straightforward and is a strong contributor to losses in UV LEDs. This is partly due to the low carrier concentrations achievable in p -GaN, although the choice of p -metal is also crucial. Figure 2.8 shows a simulated energy band diagram of a metal/ p -GaN interface. A Schottky barrier (ϕ_B) forms after metal/semiconductor contact owing to a metal work function ϕ_m being less than the semiconductor work function, ϕ_s (determined by the Fermi level, E_F). This corresponds to the condition: $\phi_m < E_g + \chi_s$, where χ_s is the electron affinity. Therefore, a metal with ϕ_m as large as or greater than ϕ_s should be chosen to reduce the barrier to hole injection. Unfortunately, no such metal exists.

The hole injection can be improved, however, through heavy p^+ -doping at the semiconductor surface. The dashed energy bands in Figure 2.8 illustrates the reduced surface depletion width with increased doping ($W_D \propto 1/\sqrt{N_A}$), increasing the probability of field emission of holes through this narrowed depletion region.

In reality, the situation is more complex: Due to the disruption of the periodic crystal structure at the surface, dangling bonds can result in surface states within the bandgap. These states can pin the Fermi level at the surface, and reduce the dependence of the metal work function on the Schottky barrier height [33, 34].

2.3 Material and device characterisation

2.3.1 Photoluminescence measurements

Photoluminescence (PL) consists of the photoexcitation of a material using high photon energy light, resulting in subsequent luminescence. This technique allows

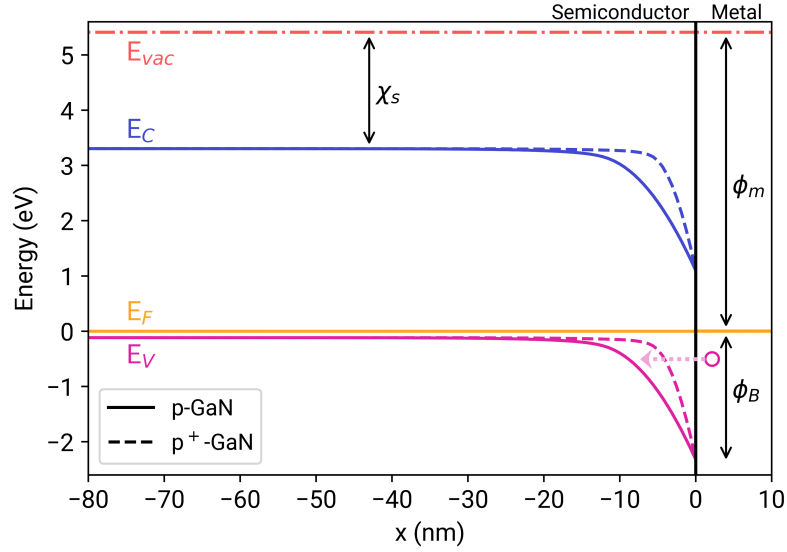


Figure 2.8: Simulated energy band diagram for a p-GaN/metal contact interface. The solid lines represent the energy bands of bulk p-GaN, while the dashed lines represent those of the same structure but with a 10 nm heavily doped layer at the surface. The following values were used in the simulation: $E_A = 200$ meV, $\phi_m = 5.41$ eV (Pd), $N_A(\text{p-GaN}) = 1 \times 10^{19} \text{ cm}^{-3}$, $N_A(\text{p}^+\text{-GaN}) = 5 \times 10^{19} \text{ cm}^{-3}$.

the characterisation of semiconductor material, offering insights into material quality, composition, and recombination dynamics. A light source is required, emitting photons with an energy greater than the bandgap of the material being studied. After absorption, generated carriers then recombine and emit light. The light source used in this work was primarily a continuous-wave frequency-doubled Ar⁺ ion laser, emitting at 244 nm. The incident beam was usually unfocused on the sample, with an approximate excitation power and spot size of 2 mW and 2 mm (32 mW/cm²), respectively. The concept is quite simple, however, in practice the results can be complex to fully understand.

A spectrometer is employed to capture the emission, which consists of an entrance slit where light enters the body, after which the light is filtered to restrict the wavelength range. The light is then focused onto a diffraction grating which breaks down the light into its constituent wavelengths, and is then focused onto a CCD detector for discrete wavelength measurements. Light was captured by a Horiba iHR320 imaging spectrometer equipped with a Synapse thermoelectrically-cooled CCD detector.

2.3.2 Hall effect measurements

When a current is passed through a material and an orthogonal magnetic field is applied, a voltage is produced due to the Lorentz force which is proportional to the current and magnetic field. This effect was experimentally discovered by Edwin Hall when he observed that a magnetic field applied to a current carrying wire resulted in “electricity pressing ... toward one side of the wire” [35]. The effect has since then been referred to as the Hall effect.

In the Hall effect measurement, the resistivity, ρ , of the material is initially measured. Then, using the measured Hall voltage, V_H , due to a known applied current (I) and magnetic field (B), material parameters can be calculated, such as the Hall sheet carrier density, n_H^{2D} , and Hall mobility, μ_H , from the relationships:

$$V_H = R_H IB , \quad (3)$$

$$\mu_H = R_H / \rho , \quad (4)$$

$$\rho = \frac{r_H}{qn_H \mu_H} , \quad (5)$$

where R_H is the Hall coefficient, r_H is the Hall scattering factor, and q is the charge on the electron. Knowing the thickness of the measured layer, the corresponding bulk Hall carrier concentration, n_H , can be obtained. The sign of V_H indicates the carrier type being measured, while the magnitude is proportional to the concentration. Although the Hall scattering factor, representing the scattering mechanisms at play, can be calculated, it is usually valid to assume a value of unity near room temperature. The value of r_H at lower temperatures is a complex matter which will be discussed in Chapter 5.

The sample preparation is an important factor for achieving valid measurements. Different sample geometries are viable, however, provided a sample is of homogeneous material with a uniform thickness and no holes, the shape of the sample should not impact the measurement. This principle is used in the van der Pauw geometry, and requires four small corner contacts on the samples [36]. In order to control errors due to finite contact sizes, uniform and repeatable geometries are commonly used. Chwang *et al.* [37] showed that the correction factor due to finite contact sizes, $\delta\rho/\rho$, is proportional to c/L (as defined in Figure 2.9a). For example, $c/L = 1/6$ corresponds to $\delta\rho/\rho = 2\%$ for square contacts and $\delta\rho/\rho < 1\%$ for triangular contacts. An Ohmic contact is prerequisite to ensure no effects from a potential barrier at the semiconductor/metal interface, thus ensuring a valid measurement.

All samples in this work were prepared by being scribed/diced into squares of approximately 10 mm x 10 mm. For p -type material, surface cleaning (as outlined in Section 2.2) was performed prior to a p -metal evaporation in which a 10 mm x 10 mm square piece of Si was placed on top and rotated at 45° to expose only the corner triangles (minimising the correction factor) of the sample. For n -type material, the same preparation was performed without the surface cleaning. Additionally, a small isolated drop of photoresist was often deposited on the contact corner and baked. A dip in aqua regia then removed excess metal to further improve the correction factor, as well as removing metal from the sidewalls to prevent any parallel conduction paths. Annealing was performed as required to ensure low resistivity, Ohmic contacts.

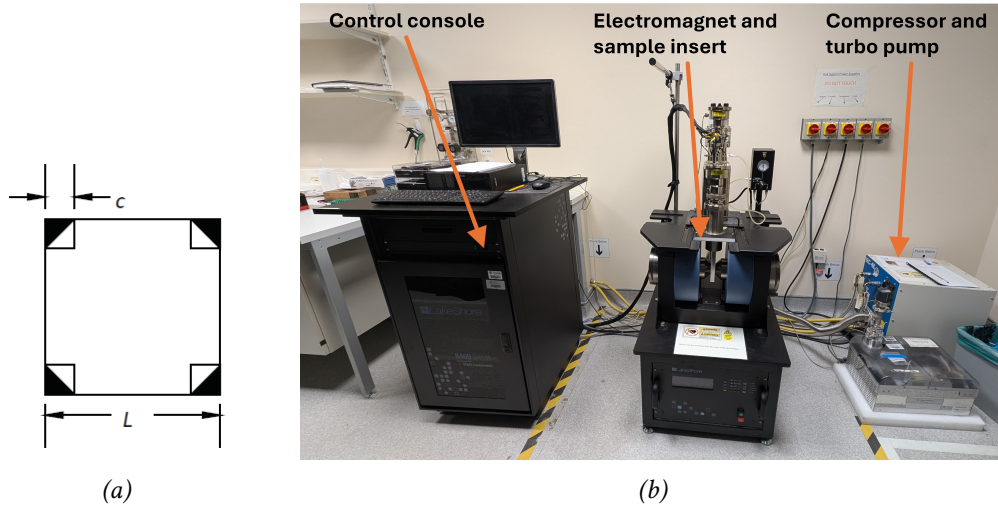


Figure 2.9: (a) Schematic of a square Hall sample with the black triangular areas representing the metal contacts. Taken from [38]. (b) The LakeShore 8404 Hall Effect Measurement System, used for all the work herein.

The Hall effect measurements in this work were carried out with a LakeShore 8404 Hall Effect Measurement System (Figure 2.9b). The electromagnet was set to the maximum deliverable field (1.7 T in DC operation, as well as 1.18 T RMS for AC measurements with variable frequency) for better signal to noise ratio (SNR).

Samples with low mobilities will have a correspondingly small Hall voltage, which can be difficult to measure accurately using a DC magnetic field due to poor SNR. AC Hall measurements with a magnetic field in the form $B\cos(\omega t)$ allow samples with low mobilities ($\mu_H < 1 \text{ cm}^2/\text{Vs}$) to be measured more accurately. The Hall voltage in this case is expressed

by:

$$V_H = R_H IB \cos(\omega t) - \beta B \omega \sin(\omega t) + \alpha \rho I + V_{te} , \quad (6)$$

where ω is the angular frequency of the time-varying field [39]. The second term is introduced to account for the inductance in the wires and sample, where β is a constant of proportionality. The third and fourth terms, representing the misalignment and thermal voltages (V_{te}), respectively, are still present as in the DC case, however, for AC measurements a capacitor removes these DC voltages. To remove the time-varying inductance voltage (-90 degrees out of phase with the magnetic field), a lock-in amplifier extracts the Hall voltage (in-phase with the magnetic field). The carrier type in this case is inferred from the phase of the measured voltage signal.

As discussed in Section 2.1.3, the role of compensating defects is of great interest especially in p -type III-nitrides. As the activation of carriers from their dopant atoms is a thermal process, one can investigate the activation energy, E_A , of the dopant by investigating the measured carrier concentration as a function of temperature. The LakeShore HMS 8404 is equipped with a closed cycle refrigeration (CCR) unit which is able to provide a temperature range of 10 K to 400 K. This allows for the measurement of a carrier concentration, p (n), as a function of temperature, T , and thus fitting the trend through the relationship [40]:

$$\frac{p(p + N_D) - n_i^2}{N_A - N_D - p + n_i^2/p} = \frac{N_V}{g} \exp\left(\frac{-E_A}{kT}\right) , \quad (7)$$

where N_D and N_A are the donor and acceptor concentrations, respectively, n_i is intrinsic carrier concentration, and g is the degeneracy factor. The effective density of states in the valence band, N_V , is expressed by:

$$N_V = 2 \left(\frac{2\pi m^* kT}{h^2} \right)^{3/2} , \quad (8)$$

where m^* is the effective mass of the carrier. Due to the large bandgap of III-nitride materials, the intrinsic carrier concentration is usually neglected, resulting in the following equation:

$$\frac{p(p + N_D)}{N_A - N_D - p} = \frac{N_V}{g} \exp\left(\frac{-E_A}{kT}\right) . \quad (9)$$

An effect sometimes referred to as the proximity effect in p -type III-nitrides was

excellently discussed by Brochen *et al.* in Ref. [41], and was also dealt with by Götz *et al.* in Ref. [42]. This phenomenon considers the dependence of the activation energy on the dopant concentration. The expression for the activation energy in equation 9 thus needs to be modified as being a function of the acceptor concentration, N_A :

$$E_A = E_{a0} - \gamma N_A^{1/3}, \quad (10)$$

where E_{a0} is the activation energy of an isolated Mg dopant atom, extrapolated to low concentrations of N_A . The constant γ describes the probability of finding an ionised acceptor in the vicinity of another ionised acceptor, and is expressed by:

$$\gamma = \Gamma(2/3)(4\pi/3)^{1/3} \left(\frac{q^2}{4\pi\epsilon} \right). \quad (11)$$

2.3.3 Contact resistivity characterisation

In optoelectronic devices, realising low resistance Ohmic contacts is fundamental in achieving high device efficiencies. To characterise the performance of these contacts, the transmission line model (TLM) is employed to quantify the specific contact resistivity, ρ_c . By forming a row of rectangular contacts on a semiconductor layer with varying gap spacings, a relationship between gap spacing and measured resistance can be formed and various parameters can be extracted. As with Hall effect measurements, a prerequisite for the TLM is that the metal contact I-V characteristic is linear. For a rectangular contact with width W , the sheet resistance, R_{sh} , can be extracted from the trend line with the slope equalling R_{sh}/W . Additionally, the y-intercept (resistor with length zero) equals twice the contact resistance R_c , while the x-intercept equals twice the current spreading length, L_s . The specific contact resistivity ($\Omega \text{ cm}^2$), can then be calculated from $L_s^2 R_{sh}$.

With this *linear* method, the efficacy of the measurement is limited by an effect known as current crowding [43]. As opposed to an idealised uniform current density across the contact, there is instead an exponential decrease in the current flow moving away from the contact edge. Instead, by using an annular structure, this effect is minimised due to the radial equipotential, but the calculations are further complicated due to the added geometric considerations [44]. Known as the *circular* TLM (cTLM) in this case, the point-point resistances are similarly measured for varying annular gap spaces.

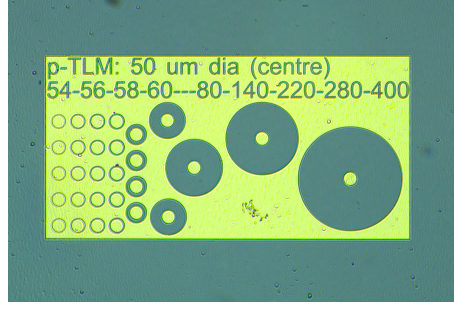


Figure 2.10: A cTLM pattern used in this work, with a Pd/Ni/Au contact.

To form the cTLM structure on the semiconductor, optical lithography with a cTLM pattern-containing mask is carried out, followed by a metal deposition and lift-off. The cTLM pattern can be seen in Figure 2.10, with the inner contact radius $r_1 = 50 \mu\text{m}$ in diameter, and the series of outer radii r_2 listed. The measurement is normally carried out with a current source range of -15 to $+15 \mu\text{A}$. This low current range is used to prevent the penetration of current into the lower layers of material while preserving the linear regime of the IV characteristic.

The measured point-point resistance, R_{pp} , can be expressed as the sum of the resistance contribution from the semiconductor material through which the current flows, and the resistance contribution from the inner and outer metal contacts:

$$R_{pp} = \frac{R_{sh}}{2\pi} \ln\left(\frac{r_o}{r_i}\right) + \frac{\rho_c}{2\pi L_s} \left(\frac{1}{r_i} + \frac{1}{r_o}\right), \quad (12)$$

where R_{sh} is the sheet resistance of the semiconductor material with thickness t . Using the measured values of R_{pp} for known r_i and r_o , a least squares fit is performed with equation 12. From this analysis, values for R_{sh} , ρ_c , L_s , and material resistivity, ρ_{mat} ($= R_{sh}t$), are obtained.

It is also important to consider the limitations of the cTLM measurement technique. In III-nitride devices, p -contacts have typical specific contact resistivities in the range $10^{-2} - 10^{-4} \Omega \text{ cm}^2$ [46, 47]. Lewis and Corbett [45] highlighted that it becomes very difficult to resolve the ρ_c of contacts to p -GaN with a value below approximately $10^{-3} \Omega \text{ cm}^2$. This is illustrated in Figure 2.11, in which the corresponding point-point resistance for varying values of ρ_c is plotted. For low values of ρ_c , the uncertainty increases as the contact resistance contribution to the measured resistance becomes relatively small compared to the high resistance from the p -type material (equation 12).

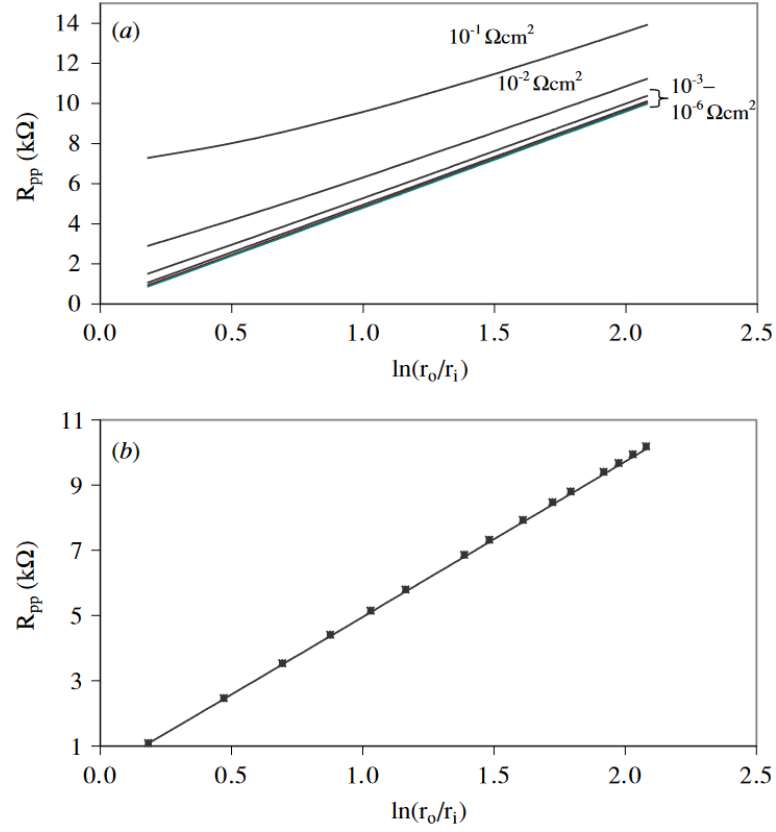


Figure 2.11: (a) cTLM data for varying specific contact resistivities, highlighting the lack of resolution below $10^{-3} \Omega \text{ cm}^2$. (b) Point-point resistance values from contacts with ρ_c of $10^{-4} \Omega \text{ cm}^2$ (solid line) and $10^{-6} \Omega \text{ cm}^2$ (data points). Taken from [45]. © IOP Publishing. Reproduced with permission. All rights reserved.

2.3.4 Current-voltage measurements

One of the most fundamental properties of any diode is the current-voltage (I-V) characteristic. One of the founding fathers of semiconductor theory, William Shockley, developed a theory to describe the current-voltage relationship of a p - n junction [48]:

$$I = I_0 \left[\exp \left(\frac{qV}{kT} \right) - 1 \right], \quad (13)$$

where I_0 is the theoretical reverse saturation current, q is the charge on the electron, k is Boltzmann's constant and T is the temperature. Soon after, work by Sah, Noyce and Shockley [49] introduced a term, n , in the denominator of the exponential term, now called the ideality factor, to describe the nature of recombination in the active region.

A typical I-V curve of a diode is plotted in Figure 2.12a. From this plot, the key

parameters of interest are the turn-on voltage and the series resistance, R_s . The turn-on voltage describes at what voltage the depletion width has been overcome and current begins to flow exponentially with the applied voltage. It is worth noting that there is no specific definition of a ‘turn-on voltage’: the ‘bend’ in the I-V curve can be changed by modifying the axes. Therefore, a voltage taken at a specific current is a more precise metric. This value should ideally equal the bandgap of the active region, in the context of an LED. The series resistance is given by the slope of the I-V curve at moderate voltages after turn-on, and represents primarily the resistivity of the material, and of the contacts. A lower turn-on voltage is desired as this will lead to reduced power consumption ($P_{elec} = IV$), and a lower R_s value will minimise self-heating ($P_{Joule} = I^2 R$).

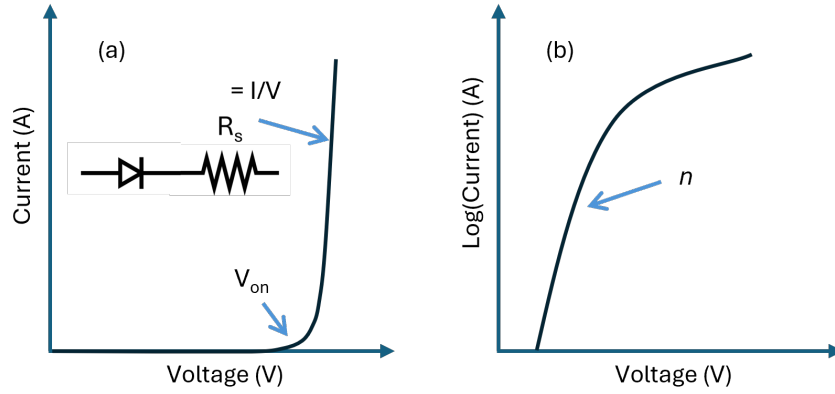


Figure 2.12: Typical I-V characteristic of a (non-ideal) diode (a) on a linear scale, illustrating the turn-on voltage and series resistance, and (b) a semi-log scale from which the ideality factor can be obtained.

When plotted on a semi-log scale, the carrier recombination dynamics can be better understood (Figure 2.12b). The ideality factor can be calculated by plotting $\ln(I)$ against voltage from the low voltage regime. The slope then equals q/nkT (from equation 13), from which n can be extracted. The ideality factor should exist between 1 and 2 for a mixture of minority carrier diffusion current and recombination in the depletion region [49]. In III-nitride LEDs, values for n are typically much greater than 2, which is usually attributed to tunnelling behaviour [50, 51], or multiple rectifying junctions within a device summing together [52].

A characteristic tunnelling energy, E_T , which represents the transparency of an energy

barrier to tunnelling, can be expressed as [50]:

$$E_T = \frac{4h}{\pi} \sqrt{\frac{N_I}{m^* \epsilon_r \epsilon_0}}, \quad (14)$$

where N_I is the ionised impurity concentration. The value as well as the temperature dependence of E_T can give insights into the carrier behaviour, with temperature independence indicating the presence of tunnelling. Additionally, the responsible tunnelling entity can be identified through its effective mass, m^* , by equation 14.

2.3.5 Electroluminescence measurements

While PL can offer important insights into the material properties, it is the electrically-driven performance which is of the greatest interest, as this is the condition in which the device will ultimately be operated. While the peak wavelength which the LED emits is obviously one of the most important metrics, the rest of the spectrum cannot be ignored. Upon injection into the active region, carriers recombine in the QWs to emit photons at approximately the bandgap of this material, producing the peak QW wavelength. However, the reality of the band structure is not as idealistic as Shockley once depicted it: “there is no mezzanine ... in the garage” [48]. Carriers can recombine radiatively through defect states within the bandgap (unfortunately, there can be many mezzanines in the garage). Additionally, unintended polarisation-induced band-bending resulting in effective wells for carriers can result in unwanted wavelength emission. As discussed in Chapter 1, parasitic luminescence at longer wavelengths can be detrimental to some applications. Therefore, analysing the EL spectrum is a high priority for this project.

The spatial emission can also offer insights into the device performance. By imaging a device during operation, the emission pattern can be captured by a CCD camera. This can provide information about the current distribution through a device, or lack thereof. Chapter 3 includes results using this technique to investigate the effect of current crowding.

For the majority of room temperature EL spectra measured in this work, an Ocean Optics USB2000 or HR4 spectrometer was used, in conjunction with a dedicated software (OceanView). The integration time can be adjusted to control the amount of light captured per unit time. Multiple scans can also be averaged to reduce the noise of the signal. Additionally, the background noise can be removed to create a dark reference point.

When coupled with a cryostat, temperature dependent EL measurements can allow further insight into the device physics. Many processes in a semiconductor are thermally activated, therefore varying the temperature allows one to investigate such mechanisms, such as the bandgap through the Varshni relationship [53]:

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{\beta + T} , \quad (15)$$

where $E_g(0)$ is the bandgap at 0 K, T is the lattice temperature, and α and β are material constants. In Chapter 4, temperature dependent EL spectra are measured and analysed. For this experiment, a cryostat usually used for PL measurements was modified to allow for the electrical connection of LEDs inside. Feedthrough wires were connected and devices were packaged to ensure secure connections to withstand thermal contraction/expansion. A Horiba iHR320 spectrometer was used to capture these spectra which is a stationary spectrometer with three different gratings on a rotating turret. Light enters through a slit entrance, the width of which can be controlled, allowing for greater resolution and adjustments for input light level.

2.4 Simulations using Silvaco TCAD

To support experimental investigations, complimentary modelling was performed to gain an insight into the theoretical device physics. Silvaco's technology computer-aided design (TCAD) software package was used for these simulations, specifically employing the device simulation software Atlas [54]. Atlas is a physically-based simulation tool which allows for the definition of a structure to be modelled, and solves carrier transport equations for discretised grid points based on pre-existing physical models. Other tools are available as part of the TCAD package which make for easier structure definitions (DeckBuild) and data visualisation (Tonyplot). This ecosystem of inputs and outputs is illustrated in Figure 2.13.

Atlas makes use of Blaze, a 2D device simulator for III-V materials and heterojunction devices. Blaze contains physical models for the various material systems. The bandgap, E_g , of the binary compounds are calculated from the Varshni equation (equation 15). Vegard's rule is then applied to calculate the bandgap of the alloyed material [55, 56]:

$$E_g(\text{Al}_x\text{Ga}_{1-x}\text{N}) = E_g(\text{AlN})x + E_g(\text{GaN})(1-x) - bx(1-x) , \quad (16)$$

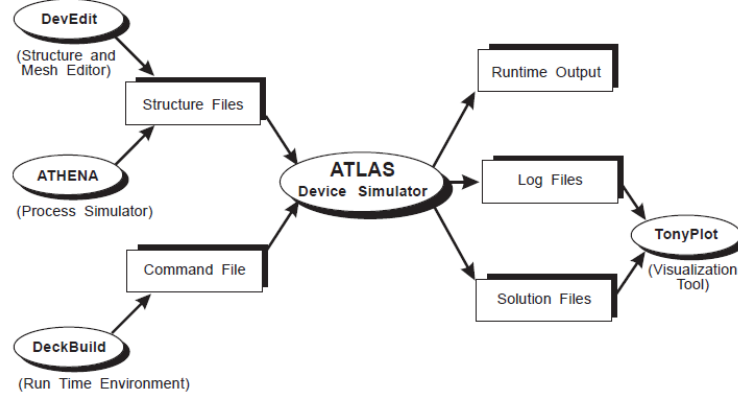


Figure 2.13: Schematic showing the inputs and outputs of Silvaco TCAD software [54].

where x is the mole fraction and the default bowing parameter b is 1.3 eV. All material constants are built into the Silvaco database for the binary compounds of GaN and AlN, and linear interpolations are usually used for alloyed materials. In reality, these relationships are rarely linear, and here lies a limitation of simulations with regard to predicting real world behaviour.

Simulations in Silvaco are based on the fundamental equations describing semiconductor physics, which are derived from Maxwell's equations. Poisson's equation correlates the electrostatic potential, ϕ , and charge density, ρ , through the permittivity, ϵ : $\nabla \cdot (\epsilon \nabla \phi) = -\rho$. The continuity equations determine the behaviour of time-sensitive charges (electrons, n , and holes, p) from the interplay of generation, $G_{n,p}$, and recombination, $R_{n,p}$, processes, and ensure charge neutrality.

$$\begin{aligned} \frac{\partial n}{\partial t} &= \frac{1}{q} \nabla \cdot \mathbf{J}_n + G_n - R_n, \\ \frac{\partial p}{\partial t} &= -\frac{1}{q} \nabla \cdot \mathbf{J}_p + G_p - R_p. \end{aligned} \quad (17)$$

Further to these equations, carrier transport models (mainly the drift-diffusion model) are employed to provide frameworks for the parameters in equation 17. In the drift-diffusion model, derived from Boltzmann transport theory, the current densities can be defined in terms of the quasi-Fermi levels E_n and E_p , the mobilities μ_n and μ_p , and the concentrations

of electrons and holes, respectively:

$$\begin{aligned}\mathbf{J}_n &= q\mu_n n \mathbf{E}_n + qD_n \nabla n, \\ \mathbf{J}_p &= q\mu_p p \mathbf{E}_p - qD_p \nabla p,\end{aligned}\tag{18}$$

where D_n and D_p are electron and hole diffusion coefficients, respectively.

The distribution of carriers with relation to an energy bandgap can be dealt with in Silvaco using the Fermi-Dirac statistics. The Fermi level E_F , defined as the probability $f(\varepsilon)$ of an electron occupying an available energy state, can be expressed as:

$$f(\varepsilon) = \frac{1}{1 + \exp\left(\frac{\varepsilon - E_F}{kT_L}\right)}.\tag{19}$$

Boltzmann's statistics make the assumption $\varepsilon - E_F \gg kT_L$ so that equation 19 simplifies to:

$$f(\varepsilon) = \exp\left(\frac{E_F - \varepsilon}{kT_L}\right).\tag{20}$$

While this approximation makes for much faster simulations, if a semiconductor is heavily (degenerately) doped where $\varepsilon - E_F \gg kT_L$, the Fermi-Dirac statistics model may be required. However, for simulations carried out in this work, the Boltzmann statistics were used.

Poisson's equation, as part of solving the electric field, incorporates a polarisation field, $\mathbf{P}$, through:

$$\mathbf{E} = \frac{\mathbf{D} - \mathbf{P}}{\varepsilon},\tag{21}$$

where $\mathbf{D}$ is the displacement field. When enabled through the `POLARIZATION` model statement, the polarisation term, P_t is a sum of the spontaneous (P_{sp}) and piezoelectric (P_{pz}) components: $P_t = P_{sp} + P_{pz}$. These polarisation fields are calculated independently in Silvaco as a function of the alloy composition, with both being independently switched on or off. The spontaneous polarisation is calculated simply by a linear interpolation of the spontaneous polarisation coefficients of AlN and GaN.

The strain, ε , of an epitaxial layer with an a lattice constant a_0 is calculated by equation 2, depending on the definition of the substrate to which other layers are strained. Through material-dependent piezoelectric coefficients e_{31} and e_{33} and elastic constants C_{13} and C_{33} ,

the strain-induced piezoelectric polarisation is calculated by:

$$P_{pz} = 2\varepsilon \left(e_{31} - e_{33} \frac{C_{13}}{C_{33}} \right) . \quad (22)$$

The strain (and therefore P_{pz}) can be switched on and off through the presence of the STRAIN model statement. The piezoelectric-related material constants used in this calculation are linearly interpolated for alloys.

The magnitude and sign of the implemented polarisation field can be modified through the POLAR . SCALE value, which was found to produce a polarisation charge concentration consistent with experiment (based on equation 25, discussed in Chapter 4) at a value of 0.5. These polarisation fields are applied in the solver in the form of sheet charges at the surfaces of material regions. The total polarisation field is then used to solve Poisson's equation (equation 21). Through this mechanism, polarisation charges are used to achieve charge neutrality in the system, paving the way for investigations into polarisation doping, which will be discussed in detail in Chapter 4.

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3 LED design and optimisation

This chapter explores the various efforts carried out towards the development of an efficient far-UVA LED. This includes a novel material for use as the p -contact and mitigating the current crowding in the mesa.

A recently established technique for the development of low Al content AlGaIn LED templates with improved crystal quality and reduced tensile strain, consisting of patterning and regrowth is presented. This addresses a major challenge present in the development of LEDs in this composition range. I would like to acknowledge Dr Pietro Pampili for performing the XRD RSM measurements. Additionally, an alternative use of the patterned template is attempted, to utilise the optoelectronic benefits of semi-polar planes.

Finally, the first demonstration of a boron-containing LED is discussed. Building on theoretical work indicating the potential of B in the active region of LEDs, and previous fundamental experimental work by Dr. Thomas O'Connor from our group on the growth of B-containing III-nitrides, this experimental realisation shows potential benefits to the wall plug efficiency, although better understanding of the mechanisms of B incorporation in the lattice structure would be required for future work. This section includes a published work [1], with additional discussion and analysis.

3.1 Alternative p -metal

The p -type contact is a main inhibitor of high efficiency UV LEDs, contributing to both the overall voltage drop, and the low light extraction efficiency. As UV LEDs are typically bottom emitting, a reflective top contact is desirable. However, few metals possess high reflectivity in the UV. Meanwhile, in order to obtain an Ohmic contact to p -GaIn with a work function of ~ 7 eV [2], a metal with a comparable work function is required. However, no metal possesses such a high work function, and although there are other effects at play in the formation of a metal-semiconductor contact (e.g. surface Fermi level-pinning), the contact resistivity to p -GaIn was shown to be correlated with the work function of the metal contact [3]. Table 2 summarises the work functions and reflectivity of some p -metal candidates.

As is evident from Table 2, a trade-off exists between low contact resistivity and high reflectivity. The most common contact approach is a thin layer of Ni followed by Au, which is then annealed in the presence of oxygen. In this scenario, NiO is formed which is believed

Metal	Work function (eV)	Reflectivity $\lambda = 320$ nm (%)
Ni	5.15 [4]	39 [5]
Au	~ 5.38 [5]	36 [5]
Al	~ 4.17 [5]	92 [5]
Mg	3.66 [5]	~ 94 [6]
Mo	~ 4.9 [5]	56 [5]
Ti	4.33 [5]	41 [5]
Rh	4.98 [5]	75 [5]
Pd	~ 5.41 [5]	55 [5]
ITO	$4.7^\dagger$ [7]	8 [8]

Table 2: Material parameters of various potential p-contact technologies. [†]Varies depending on doping level and deposition process. Reported to be between 3.3 eV and 5.7 eV [9].

to assist in the formation of Ohmic contact to *p*-GaN [10]. However, this approach results in a poor light extraction due to absorption in the metal contact. Adding a thin layer of Pd before the Ni (forming Pd/Ni/Au) can increase the reflectivity of the contact while maintaining relatively low contact resistivity.

A novel approach to the *p*-contact of UV LEDs was demonstrated utilising a stack of MoO_x/Al [11]. The reported advantage of MoO_x is its concurrent UV-transparency and Ohmic contact formation as a result of its large work function. This allows a high UV-reflective metal such as Al to be deposited on top to act as a mirror. An attempt was made to recreate this approach to utilise its benefits. For this experiment, blue commercial LED material with a *p*-GaN contact layer was used as a template. A surface cleaning (detailed in Chapter 2) was followed by a lithography step to define the cTLM test structure, and a 30 s dip in aqua regia was performed prior to evaporation. Using a solid molybdenum oxide source, 5 nm of MoO_x was deposited using electron-beam evaporation. Following this, the sample was moved to a different evaporator for 100 nm Al. Extra care had to be taken in the lift-off procedure due to the standard Microposit 1165 solution attacking MoO_x. As a result, a combination of a low adhesive tape and a dry CO₂ process was utilised to lift-off the metal and photoresist. Rapid thermal annealing was performed at temperatures of 200, 300 and 400°C in both nitrogen and air ambient, for 2 minutes. The cTLM measurement (outlined in Chapter 2) results are shown in Figure 3.1. As-deposited and all annealing conditions resulted in non-Ohmic contacts.

To understand the poor performance of the MoO_x/Al contact, the chemical properties of

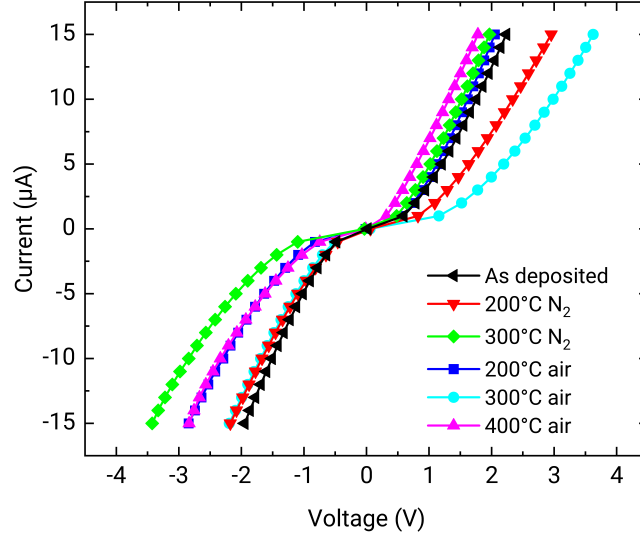


Figure 3.1: Results from cTLM measurements of MoO_x/Al contacts for an intermediate contact spacing. No Ohmic contact was obtained. The result from 400°C in nitrogen is not shown due to its rectifying behaviour.

MoO_x must be analysed. In its ‘pure’ stoichiometric state, molybdenum oxide forms MoO_3 . This oxide is a wide, indirect bandgap (3 eV) n -type semiconductor [12]. The reported work function values of MoO_x vary considerably, from 5.5 eV to 6.9 eV [13, 14]. The reason for the variability is in part due to a stoichiometric dependence on work function. Through the formation of oxygen vacancies, reduced oxides may exist in the form MoO_x where $2 < x < 3$. In particular, MoO_2 is semi-metallic in nature. In addition to possessing smaller work functions, reduced oxides become more absorbing due to the reduced bandgap [15], further diminishing their benefits as p -contacts in UV LEDs. The reduction from MoO_3 to MoO_x ($x < 3$) can occur, for instance, due to exposure to air [16, 17].

In the process of evaporating the MoO_x/Al contact stack for this experiment, the sample had to be transferred to a different tool for the Al evaporation which involved approximately 3 minutes exposure in air. It has been shown that the reduction of MoO_x , and therefore the work function, decreases with exposure time to air, and, in this case, can be calculated to have reduced by approximately 1 eV, potentially explaining the poor performance [17]. Unfortunately, due to the experimental setup in the facilities available for this work, it is not possible to realise a MoO_x/Al stack without exposure to air.

3.2 Current spreading and micro-LED arrays

III-nitride devices typically employ lateral device geometries due to the insulating sapphire substrate. This can lead to the current ‘crowding’ at the edge of a mesa on the side closer to the n -contact [18]. Poor current spreading can have detrimental effects on performance, such as increased self-heating through localised current densities, and enhanced efficiency droop [19]. The current spreading length, L_s , is defined as the distance from the mesa edge at which the current density has reduced by $1/e$ times, and is expressed as [20]:

$$L_s = \sqrt{(\rho_c + \rho_p t_p) \times \frac{1}{(\frac{\rho_n}{t_n} - \frac{\rho_t}{t_t})}} \quad (23)$$

where $\rho_p, t_p, \rho_t, t_t, \rho_n, t_n$ are the resistivities and thicknesses of the p -type layer, contact layer, and n -type layer, respectively [21]. For good current spreading, the n -type buffer layer should be as thick as possible.

Figure 3.2 shows the calculated current density as a function of distance from the mesa edge ($J[x] = J_0 \exp[-x/L_s]$). With increasing thickness of the n -type layer, the effect of current crowding is reduced, resulting in better current distribution throughout the device. Unfortunately, thick layers of $n\text{-Al}_x\text{Ga}_{1-x}\text{N}$ for low to moderate compositions of x are made difficult by the build-up of tensile strain in the film during growth, eventually leading to catastrophic cracks throughout the wafer. Current crowding in far-UVA LEDs is therefore a significant issue. Strategies to grow thicker $n\text{-Al}_x\text{Ga}_{1-x}\text{N}$ layers will be discussed further in Section 3.3.1.

In the interest of improving current spreading, micro-LED (μLED) arrays were investigated. Arrays of μLED s with interdigitated contacts can demonstrate improved current distribution between devices [22, 23], owing to shorter current paths from contacts as well as a lower required distribution of current in a smaller mesa.

LED material was grown by MOCVD with an active region designed for approximately 320 nm emission. Details on the epitaxial structure can be found in Section 3.3.1. Interdigitated arrays of μLED s were then fabricated with mesa diameters of 10, 20 and 30 μm . Due to the specifications outlined by the LED application, the overall active area was set as a $200 \times 200 \mu\text{m}^2$ window, therefore the number of devices in the array was scaled accordingly. SEM images of the fabricated arrays are shown in Figure 3.3. For comparison, a single device with mesa diameter 200 μm was also included in the mask design.

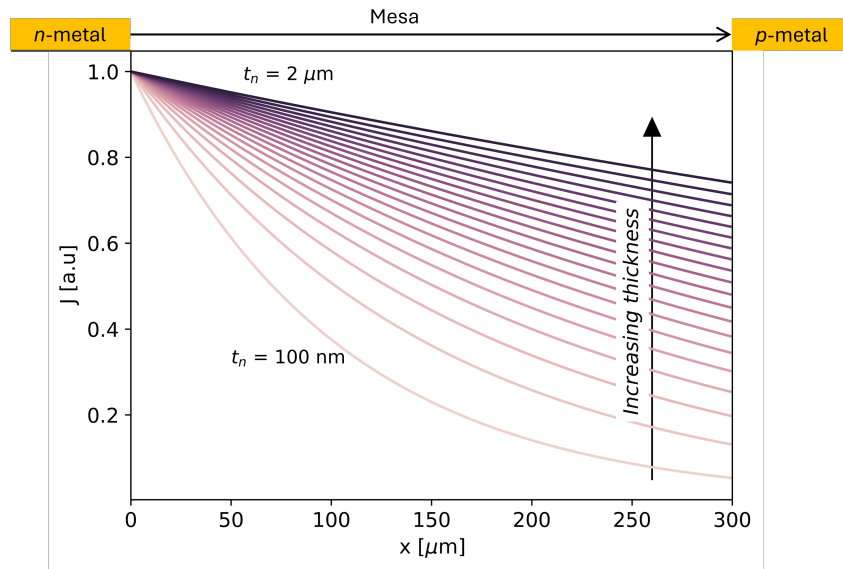


Figure 3.2: Effect of thickness of the n-AlGaIn buffer layer on current density as a function of distance from the n-contact for a lateral geometry LED design, from equation 3.2.

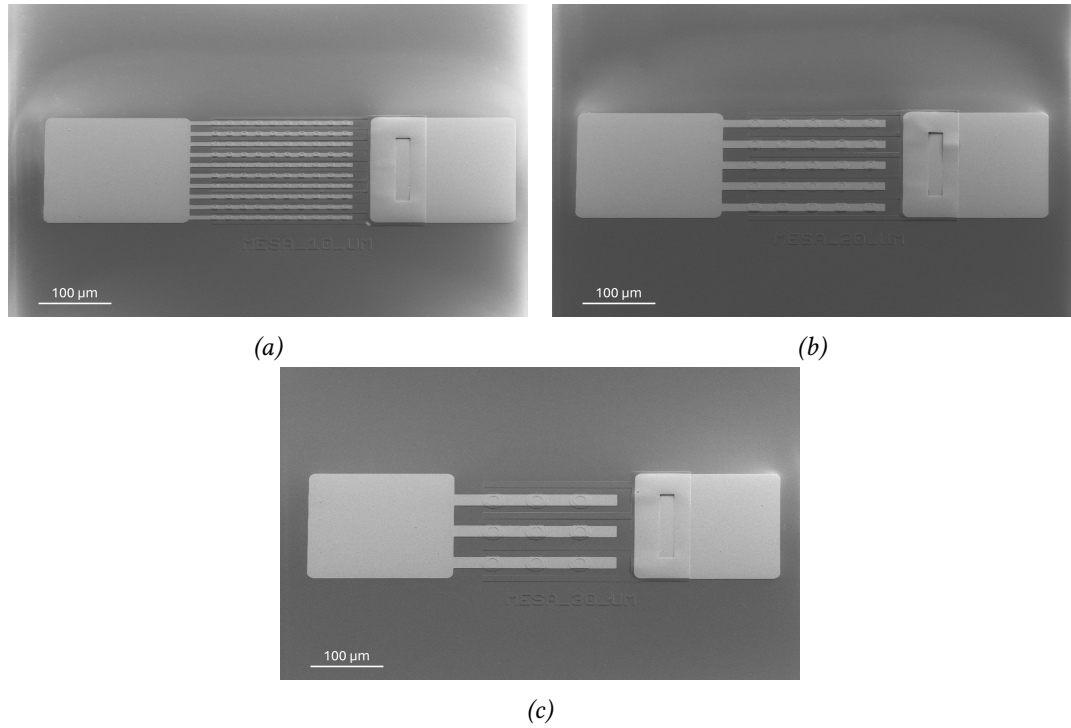


Figure 3.3: SEM images of the μ LED arrays with mesa size of (a) $10\text{ }\mu\text{m}$, (b) $20\text{ }\mu\text{m}$ and (c) $30\text{ }\mu\text{m}$.

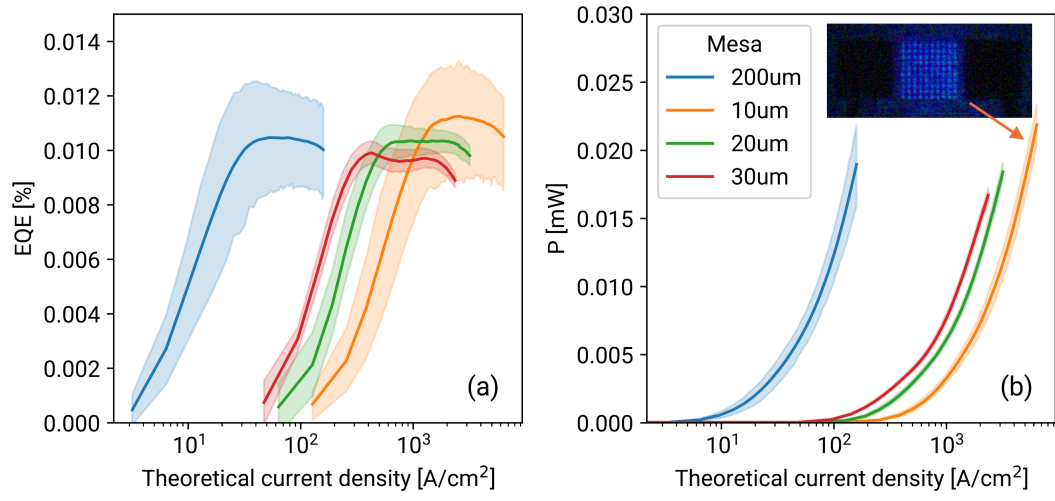


Figure 3.4: (a) EQE and (b) output power of μ LED arrays with varying mesa sizes. Inset is the 10 μ m diameter array imaged during operation.

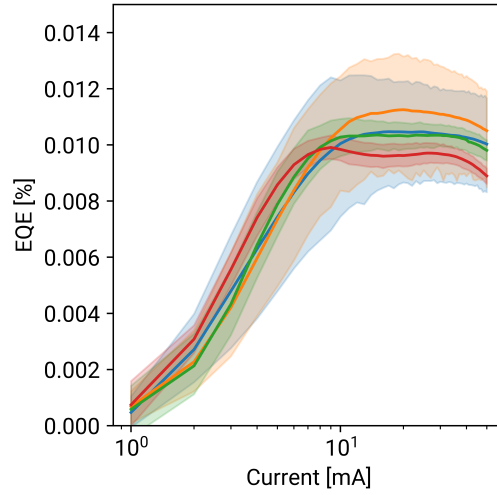


Figure 3.5: EQE plotted against the absolute current for the different device geometries.

The EQE and absolute output power of the arrays, as well as the single device, are plotted in Figure 3.4, measured under CW conditions. While the power density (mW/cm^2) may be more accurate in terms of the relative power between mesa sizes, it is the absolute power which is of interest for this thesis. Also, it is important to note that the calculated current density relative to the μLED mesas is the *theoretical* value: although the current should be divided equally between parallel rows ($J = \frac{I/A}{n_{\text{rows}}}$), devices with lower turn-on voltages will ‘steal’ current from other devices, distorting the actual distribution of current. Additionally, any dead devices (open circuit) will prevent current from reaching other devices along the row. The data plotted consists of multiple tested arrays (and in the case of the $200\ \mu\text{m}$ device, multiple devices) with the averages shown in a solid line. Inset in Figure 3.4b is an image of the $10\ \mu\text{m}$ mesa array during operation. Almost all devices are visibly operating, and this was the observed case for the majority of arrays. However, it is apparent in Figure 3.4a that with decreasing mesa size (and correspondingly increased rows in parallel and devices per row), the distribution of data increases, illustrating the challenge of uniform current distribution in arrays of parallel μLED s.

With decreasing mesa size, the peak EQE increases (Figure 3.4a, and 3.5). This can be attributed to better current spreading with smaller mesa size as well as the increased density of interdigitated contacts [24–26], while increased light extraction efficiency can also be a contributing factor [27]. However, the current density at which the peak EQE is reached increases with decreasing mesa size. The competing recombination mechanisms and their dependencies on carrier density can be expressed by the *ABC* model:

$$R = An + Bn^2 + Cn^3, \quad (24)$$

where R is the recombination rate, and A , B and C are constants representing (non-radiative) Shockley-Read-Hall (SRH) recombination, radiative recombination, and (non-radiative) Auger-Meitner recombination, respectively [28]. If the peak efficiency is delayed relative to the carrier density, it suggests that increased non-radiative recombination is dominating at lower currents. This is likely due to the increased effect of SRH recombination or leakage currents with decreasing mesa size. Dry etch-induced surface defects in the μLED sidewalls introduce non-radiative recombination pathways [23, 29]. Various solutions have been proposed to mitigate this effect [30, 31], however, in this work, no post-etch treatment was

performed as this was outside the scope of the investigation. As the mesa size is shrunk, the ratio of the carrier diffusion length to the mesa size reduces, worsening the effect of surface recombination. Although the large device will have a substantially lower contribution from non-radiative surface recombination, the impact of current crowding and heat dissipation offsets this, resulting in a similar EQE.

From this study, the need for improved current distribution in devices consisting of resistive materials (e.g. AlGaIn) is clear. Arrays of μ LEDs with interdigitated contacts can enhance the current spreading through reduced distances of current paths, although further work is required to reduce the surface damage from the mesa formation fabrication step.

3.3 Micro-honeycomb template for UV LED development

Conventionally, III-nitride-based LEDs are grown on the c -plane of the wurtzite crystal. This is due to a combination of the energetically favourable growth along this basal plane and ready availability of c -plane sapphire substrates. The c -plane of wurtzite III-nitride alloys is polar, meaning at each unit cell lies a dipole moment. As such, a polarisation field, P , exists perpendicular to this plane ($P \parallel [0001]$), the sign of which depends on the polarity of the crystal (metal- or nitrogen-polar). There also exists in the wurtzite structure, at alternative inclination angles relative to the c -plane, semi-polar and non-polar planes, exhibiting reduced, or no, net intrinsic polarisation fields. These planes are of interest, for example, in improving the ‘green gap’ with InGaIn-alloys, as their lack of polarisation can facilitate higher In content without inducing the QCSE [32]. For AlGaIn alloys, these planes can also be utilised, offering benefits such as: an increased carrier wavefunction overlap (improving recombination rates); smaller hole effective mass [33]; and improved thermal droop [34].

Recent work in our group investigated the development of a micro-honeycomb (μ -HC) shaped patterning of AlGaIn with epitaxial overgrowth for the formation of a semi-polar faceted morphology [35, 36]. This technique has the potential to improve the crystal quality through the removal of highly dislocated material, followed by bending and subsequent self-annihilation of threading dislocations (TDs). The understanding gained from this work is employed here for the development of a template for UV LEDs. Two distinct approaches are presented: the formation of a coalesced LED template with an improved crystal quality, and a semi-polar faceted LED on a non-coalesced template.

3.3.1 Coalesced micro-honeycomb LED template

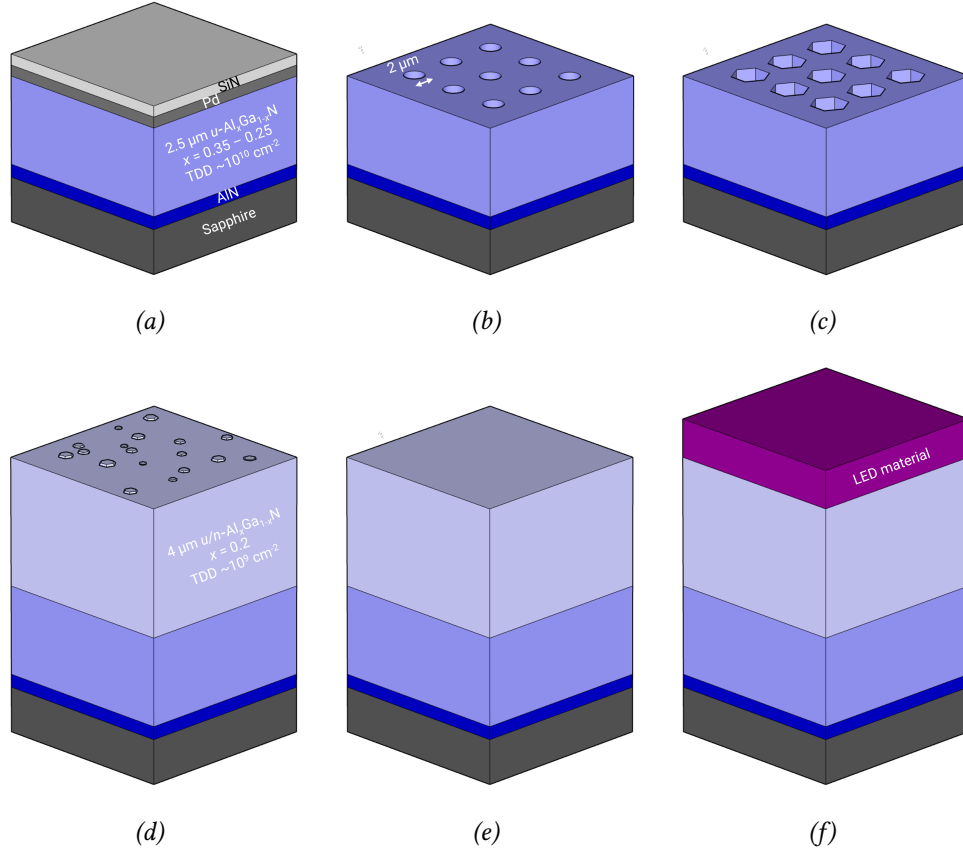


Figure 3.6: Simplified process flow of the μ -HC template development beginning with (a) the growth of $2.5 \mu\text{m}$ $\text{u-AlGa}_{1-x}\text{N}$ and deposition of Pd and SiN, (b) patterning and subsequent dry etching to form the holes, followed by removal of the SiN and Pd, (c) wet etching to expand the holes and form the crystallographic facets, (d) regrowth of AlGaIn, coalesced to a planar surface with some morphological defects, (e) reduction in surface features with CMP and wet etching, and finally (f) the growth of the LED structure.

Strain management in the composition range of interest ($\text{Al}_x\text{Ga}_{1-x}\text{N}$ with $x = 0 - 0.3$) is a major challenge. The TDD has a strong impact on the build-up of tensile strain in the Si-doped buffer layer, as well as significantly impacting the IQE [37]. The proposed mechanism of the μ -HC technique for an improved quality LED template is the removal of defective c -plane material, followed by the formation and expansion of faceted sidewalls (TDs self-annihilating in the process), and subsequent coalescence into an epi-ready c -plane surface with a reduced

TDD.

Figure 3.6 illustrates the simplified process flow for the development of a coalesced μ -HC template. This begins with the growth by MOCVD of $2.5\ \mu\text{m}$ of graded $u\text{-Al}_x\text{Ga}_{1-x}\text{N}$ ($x = 0.35 - 0.25$) on AlN/sapphire (Kyma Technology). The growth temperature was 1160°C , at 75 mbar, and a V/III ratio of 500. Further details on the growth conditions can be found in a detailed study by other members in our group on the morphological evolution of this approach with respect to facet expansion and coalescence [36]. Next, 70 nm of Pd is evaporated as a hard mask by e-beam evaporation, and SiN_x is deposited for a concurrent development process.

Photolithography was then performed using a mask consisting of $2\ \mu\text{m}$ diameter holes with a $3\ \mu\text{m}$ pitch, and the positive photoresist Microposit S1813. A dry etch is performed to remove the exposed SiN_x , and a 10 s dip in aqua regia removes the exposed Pd, after which the photoresist is then removed with Microposit 1165. A Cl_2 -based ICP etch was then carried out, etching the exposed area almost to the sapphire (Figure 3.6b, Figure 3.7a). Using 90°C AZ400K (KOH-based), a wet etch was carried out for approximately 12 hours to form crystallographic sidewalls, remove defective material and further expand the holes (Figure 3.6c, Figure 3.7b).

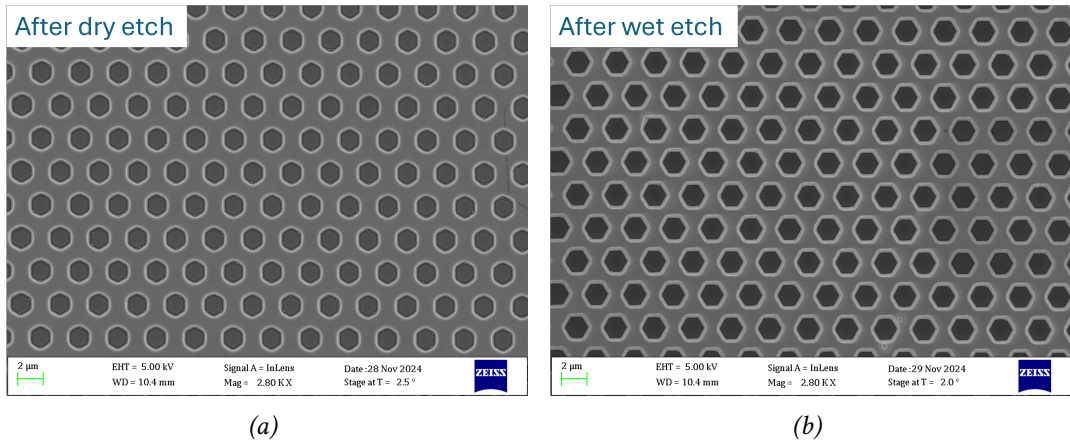


Figure 3.7: SEM image of the μ -HC template (a) after the dry etch to form the patterned holes and (b) after a wet etch to expand the holes and create the crystallographic sidewalls. It should be noted the hexagonal shape of the holes after dry etching in (a) is not necessarily crystallographic, but can be a result of diffraction during optical lithography and/or dry etch dynamics. The rotation of the hexagon after the crystallographic wet etch confirms that this initial hexagon is not crystallographic.

The wafer was then placed in the MOCVD reactor for a subsequent growth of $\sim 4\ \mu\text{m}$ $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ with the top $1\ \mu\text{m}$ n -doped. The growth conditions were optimised for minimal

expansion of the semi-polar planes with a preference for coalescence soon after. It is worth noting that during the growth of this final n -doped region, no significant increase in the *in situ* curvature was observed, indicating no significant increase in tensile strain which would have been expected in similar material with a higher TDD.

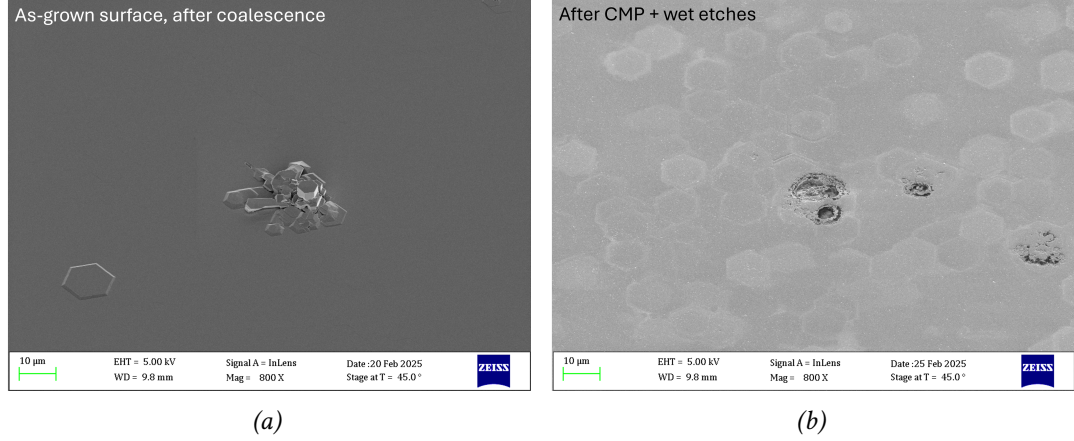


Figure 3.8: SEM images of the overgrown AlGaIn surface (a) immediately after growth showing an example of the hexagonal surface features and defective growth after coalescence. The hexagons have a vertical height of approximately several hundred nanometres. (b) A surface region after CMP and wet etching, which had a high density of hexagonal features post-growth. The hexagonal features are still visible but only as a compositional variation (thus conductivity variations seen in SEM). Their verticality has been eradicated following the treatments.

The surface morphology after coalescence exhibits hexagonal surface features (Figure 3.8a). These are undesirable in an LED template, potentially propagating through the structure causing challenges with the p -contact [38], or inhomogeneities in Al incorporation between the different crystal planes (broadening the LED linewidth) [39, 40]. Therefore, chemical-mechanical polishing (CMP) along with treatments using KOH- and HF-based solutions were carried out to remove such features from the surface (Figure 3.8b), and prepare it for the growth of the LED structure.

The μ -HC template was co-loaded in the reactor with a reference template (2.5 μ m graded $\text{Al}_x\text{Ga}_{1-x}\text{N}$ with $x = 0.35 - 0.2$ and the top 250 nm n -type) on Kyma/AlN connecting layer, for LED structure growth. Initially 600 nm $n\text{-Al}_{0.2}\text{Ga}_{0.8}\text{N}$ was grown, followed by the active region consisting five 2.5 nm $\text{Al}_{0.08}\text{Ga}_{0.92}\text{N}$ quantum wells with 10 nm $\text{Al}_{0.18}\text{Ga}_{0.82}\text{N}$ barriers. A 30 nm $\text{Al}_{0.35}\text{Ga}_{0.65}\text{N}$ electron blocking layer followed, with the top 20 nm p -doped. For the p -type region, polarisation doping was utilised through a linear grading of x to GaN over 80 nm, which was also doped with Mg. Finally, a 15 nm $p\text{-GaIn}$ layer topped the structure, and

in situ activation of Mg was performed at 820°C for 30 minutes in nitrogen.

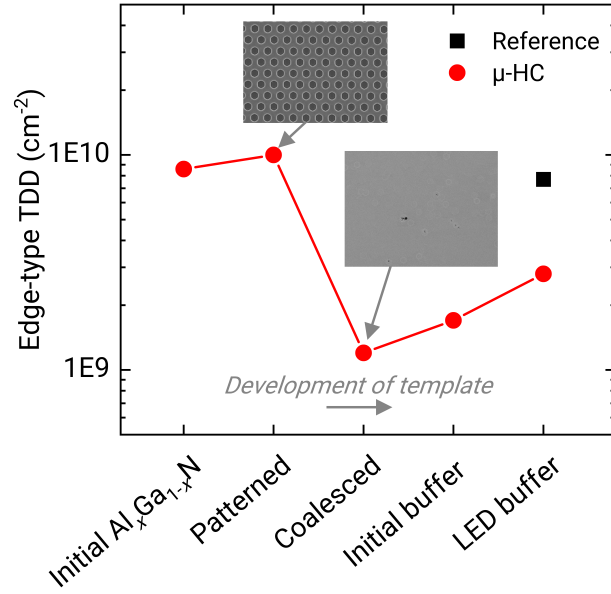


Figure 3.9: Edge-type dislocation density from the (101) XRD rocking curves of the μ -HC template during different stages in the development process. The measurement of the reference LED is also included, highlighting the improvement in quality achieved.

Figure 3.9 summarises the quality of the μ -HC template (determined by a (101) XRD rocking curve) at each stage of the development. After coalescence, a reduction in TDD of one order of magnitude was achieved, confirming the success of this approach in improving the LED template quality. However, subsequent growths showed gradual increases in the TDD, to almost three times higher than the lowest. It is proposed that after each regrowth, the formation of fissures during temperature ramping (associated with the presence of TDs [41, 42]) could facilitate the formation of new dislocations. Nonetheless, compared to the reference LED template, the TDD of the μ -HC LED template was still approximately three times lower.

Room temperature PL measurements were performed on the as-grown material (Figure 3.10). Despite the reduction in TDD of nearly 3 times, the PL QW intensity (~ 327 nm) of the μ -HC sample is approximately equal to that of the reference LED. The suppressed oscillations on the spectrum can be attributed to the increased surface roughness compared to the reference LED. The emission from the MQWs in the μ -HC LED is redshifted compared to the reference, in spite of both wafers' active regions being grown in the same growth run. Luminescence around 520 nm is thought to be analogous to the well known 'yellow

luminescence' in GaN, commonly attributed to Ga vacancies and complexes with oxygen [43, 44]. The intensity from this luminescence is stronger in the μ -HC LED, likely due to the greater thickness of the AlGaN template/buffer.

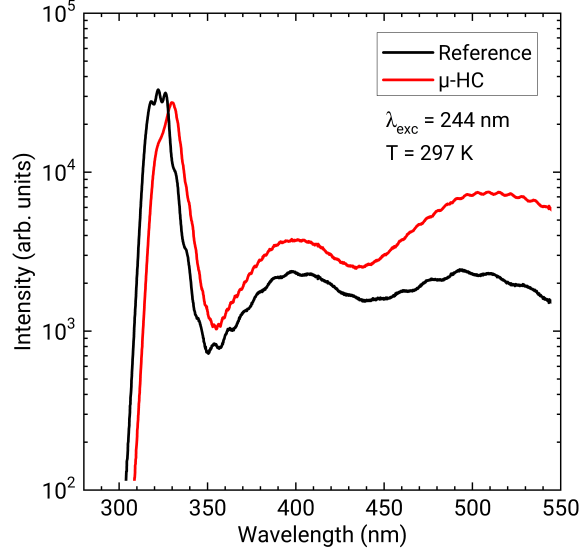


Figure 3.10: Room temperature PL spectra of the μ -HC template LED and reference LED. The excitation source was a 244 nm Ar⁺ ion laser.

The broad peak centred around 400 nm is attributed to recombination in the p -type layers [45]. Interestingly, this luminescence is increased in the μ -HC LED, suggesting enhanced Mg incorporation. The incorporation of Mg in III-nitrides has been strongly associated with the topology of the surface during growth [46–48]. It's possible that the increased surface roughness and presence of hexagonal features on the μ -HC template LEDs (although mostly removed) improved the incorporation of Mg during growth, but further investigations would be required to investigate this.

Fabrication into individual LEDs was performed, as previously described, with a Pd/Ni/Au p -metal stack. The EQE and output power of 200 μ m diameter LEDs are shown in Figure 3.11 as a function of current, measured using a calibrated Newport Si photodetector. By employing the μ -HC template for subsequent LED growth, an increase in EQE (and output power) of approximately two times is achieved. The lack of a pronounced peak in efficiency in the reference LED (in contrast to that of the μ -HC LED) indicates the suppression of the radiative recombination mechanism [49]. This improvement in performance is attributed primarily to the improvement in template quality.

The measured reduction of TDD should correspond to an approximate increase in IQE

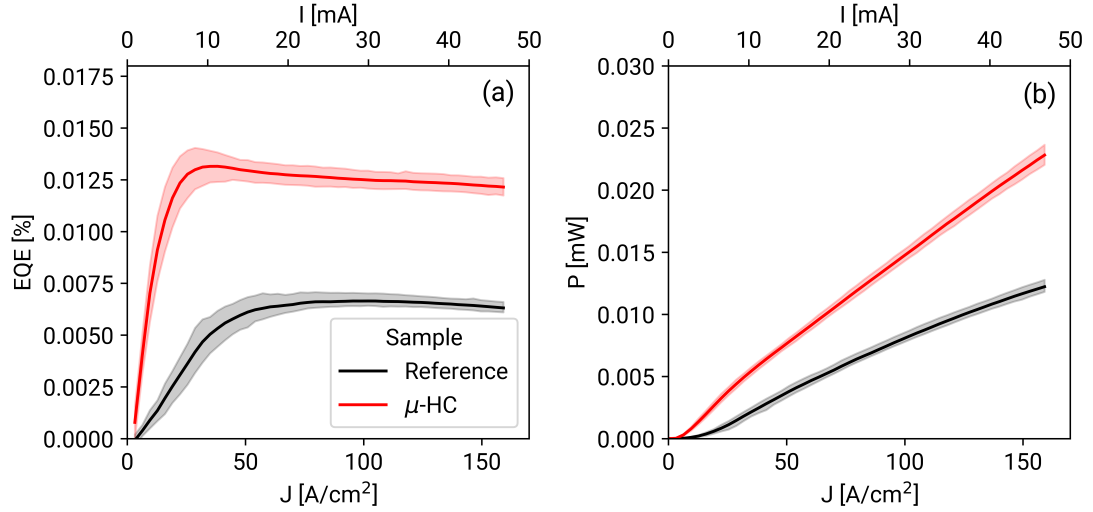


Figure 3.11: (a) EQE and (b) output power from the reference and μ -HC LEDs as a function of current density. Measured on 200 μ m diameter LEDs.

of almost three times [37]. The LEE of the μ -HC LED is, however, thought to be impacted due to Ga decomposition in the voids during template development. Therefore, the lack of a threefold enhancement in efficiency may be due to this loss in LEE. Conversely, there may be some beneficial effect of the voids in the template on the light scattering. Nonetheless, it is the reduction in TDD which is attributed to be the leading cause of the improvement in performance.

Normalised EL spectra of both LEDs are plotted in Figure 3.12, at an excitation current density of 200 A/cm². Despite the reference LED being approximately six times brighter, QW luminescence is observed around 330 nm in the μ -HC template LED, which is approximately 10 nm redshifted compared to the reference LED at $\sim$ 320 nm. The difference in emission wavelength may be related to a different strain state between the two LED structures.

Compositional pulling effects have been observed in III-nitrides, having been extensively studied in the InGaN system [50, 51]. It is relatively less researched in AlGaN alloys, however, its presence has also been indicated [52]. It is reported that compressive (tensile) strain enhances (reduces) the Al incorporation in AlGaN [53, 54]. Additionally, deformation of a crystal due to strain can affect the bandgap of a semiconductor [55]. In GaN, tensile strain reduces the bandgap, and compressive strain increases it [56, 57].

To investigate the strain state, reciprocal space maps (RSM) were obtained from both LED structures. Figure 3.13a shows the RSM of the reference LED, with the peak on the top right

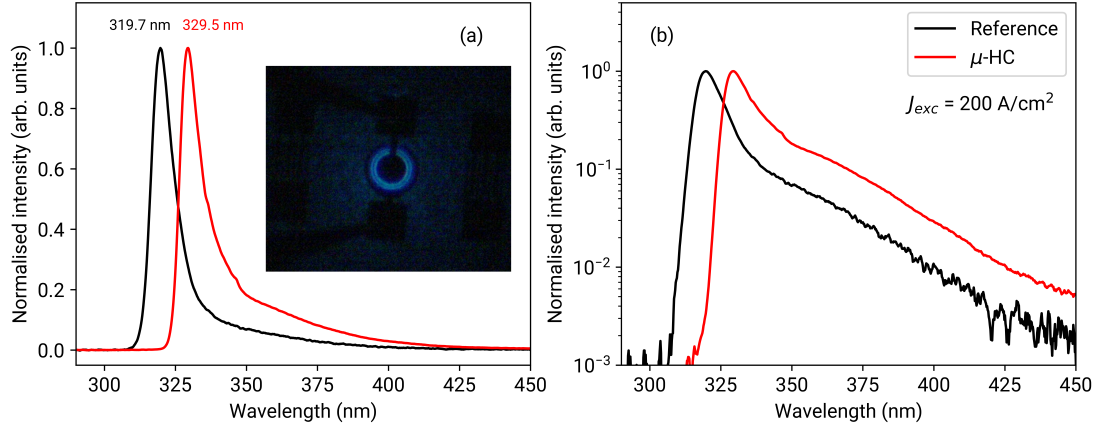


Figure 3.12: EL spectra of the reference LED and the μ -HC LED on a linear scale (a) and semi-log scale (b). A redshift of approximately 10 nm is observed in the latter compared to the reference. Inset in (a) is a top-down image of the device in operation.

of the map representing the AlN connecting layer (marked by an 'x'). Moving 'down' the map, the graded $\text{Al}_x\text{Ga}_{1-x}\text{N}$ buffer layer is observed (marked by a star), gradually relaxing slightly with growth. The lower peak (marked by a square) likely corresponds to the p -GaN layer. In Figure 3.13b, a markedly different behaviour is observed: a faint AlN peak is seen (attributed to the Kyma template), and the LED material then grows pseudomorphically to a more relaxed strain state compared to the reference LED. This is illustrated by the local maxima from the reference LED overlaid on the μ -HC LED map. The situation here is complicated by the dynamics of multi-directional growth (i.e. along different planes) during coalescence of the μ -HC template. The progression of the strain states of different planes within the stack during template development is ultimately outside the scope of this thesis. Nonetheless, the reference LED is confirmed to be more compressively strained, which can therefore result in the observed shorter wavelength LED emission, through a combination of deformation potential and higher Al composition owing to potentially compositional pulling effects.

3.3.2 Semi-polar faceted LED

Alternative to the coalescence approach of the μ -HC patterned template is the expansion of the μ -HC pattern into semi-polar planes. After patterning the initial AlGaN template and etching, altered growth conditions can result in the expansion of the semi-polar facets (SPFs) with well-defined hexagonal V-pits [35, 36]. An LED active region can be grown on such

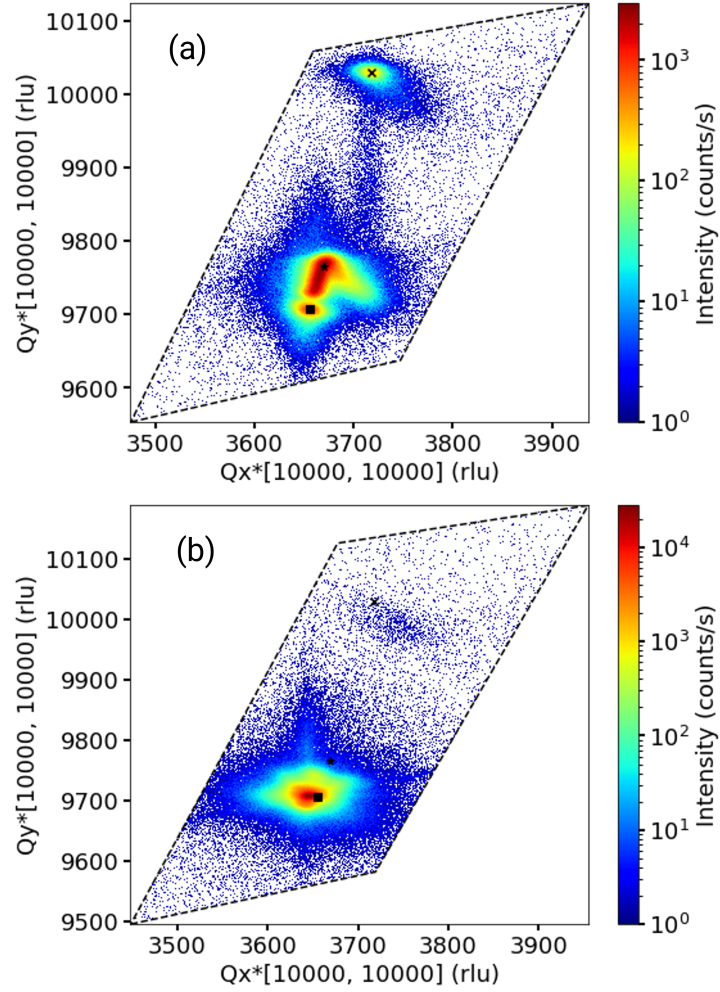


Figure 3.13: XRD RSMs of the (a) reference and (b) μ -HC LED material. The local maxima from the reference LED material are overlayed on the map of the μ -HC LED material, to highlight the difference in strain. A calibration procedure was performed to eliminate error in the tool's alignment, so that an absolute comparison could be carried out.

SPF, exploiting the aforementioned benefits of material grown on alternative crystallographic planes. Additionally, light extraction can be enhanced through increased scattering and reflection off adjacent angled facets [58].

Development of the μ -HC patterned template consisted of the same beginning as in Section 3.3.1, apart from the altered growth conditions for the overgrowth (i.e. after step (c) in Figure 3.6). A typical (for this project) UV LED was grown by MOCVD on this template, co-loaded with a conventional planar Kyma template. For this study, complete expansion of the SPFs on the overgrown template was not achieved, and some c -plane material still remained. This meant that LED material was also grown on the c -plane surface.

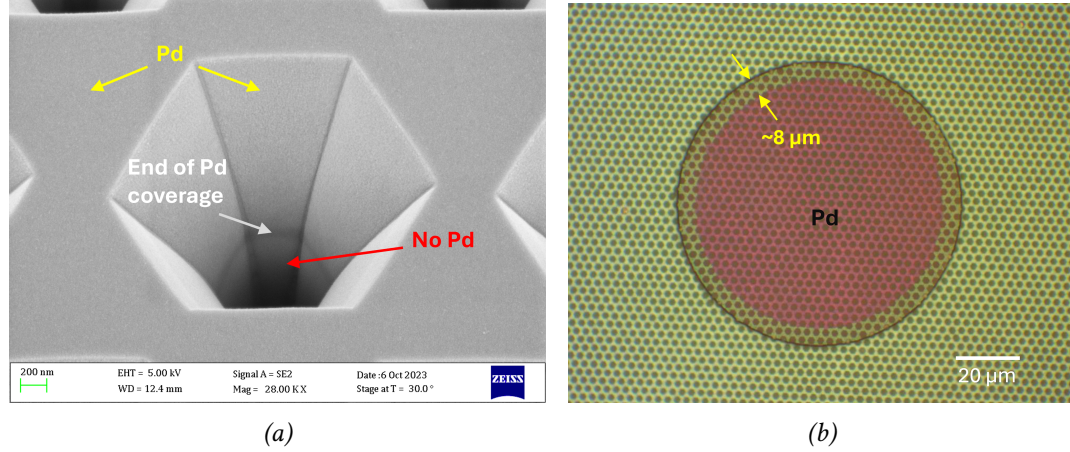


Figure 3.14: (a) SEM image after p-metal 360° evaporation, showing the successful prevention of the p-metal from entering the base of the pit. (b) Microscope image of the surface after undercut of the photoresist during wet etching of the Pd with aqua regia. A dry etch can then be performed to realise a mesa.

After growth, processing of the SPF wafer into LEDs consisted of a standard LED fabrication flow, with some modifications. First, in order to prevent potential wet etching of the facets by the hot KOH-based solution during the *p*-GaIn surface clean, a room temperature KOH-based treatment was instead carried out. Next, instead of the standard lift-off process after *p*-metal deposition, which may result in unintended behaviour of the photoresist with the facets/pits, a global evaporation was performed with subsequent wet etching. Additionally, in order to prevent metal from entering the base of the individual funnels and resulting in potential shorting to the *n*-type material, this evaporation was performed with samples angled at 45° to the source (360° evaporation). This was confirmed in SEM imaging (Figure 3.14a) showing the Pd coverage end before the pit opening, shadowed by the top edge of the facet.

A lithography step follows to define a *p*-metal contact area. For this step, a negative resist (AZ5214) was employed in order to protect a defined area, and after exposure, developing was performed using AZ400K:DI water (1:4). The exposed metal was then removed by aqua regia (3:1 HCl:HNO₃). One benefit of this approach is that it allows for self-alignment between the *p*-metal area definition and the mesa definition. By allowing an undercut during the Pd wet etch beneath the photoresist, a dry etch can then be performed on the already-defined mesa area. Figure 3.14b shows this undercut action in process, achieving a gap of ~ 8 μm. Next, an ICP-RIE etch was performed to expose the *n*-AlGaIn. The final step before testing consisted

of a lithography step to define the n -metal area and a subsequent Ti/Al/Ti/Au evaporation.

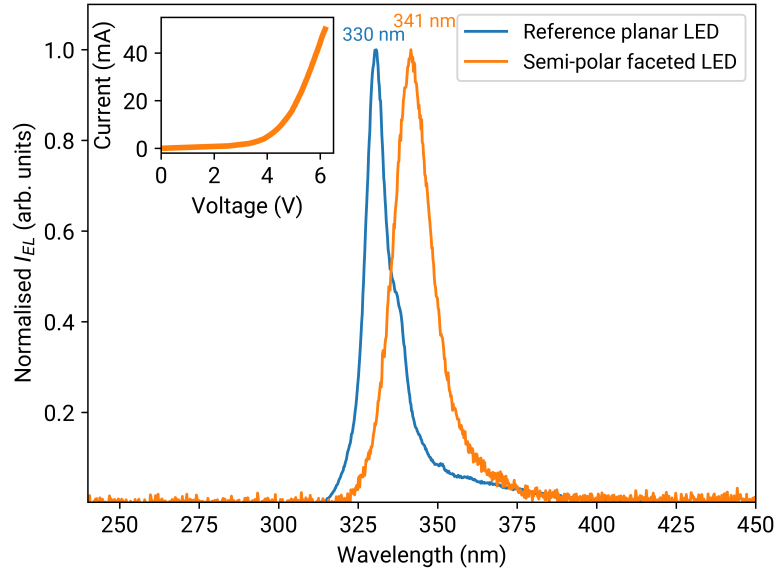


Figure 3.15: Normalised EL spectra of the SPF LED and a reference c -plane LED with nominally identical growth conditions. Emission from the SPF LED is observed at approximately 340 nm. Inset is the I-V characteristic of the SPF LED demonstrating diode-like behaviour.

Electroluminescence of the SPF LEDs is shown in Figure 3.15, along with a reference planar LED. As mentioned, some c -plane LED material was present on the surface. Due to the longer diffusion length of gallium adatoms compared to aluminium, Ga adatoms have a higher probability of diffusing to the SPF and incorporating there [40]. Indeed, μ -PL of similar structures has suggested increased Ga incorporation on the SPF when in competition with c -plane surfaces [35]. This indicates that the EL emission seen in Figure 3.15, which is redshifted relative to the emission from the reference planar LED, is from QWs on the SPFs. Meanwhile, an increased full width at half maximum of the SPF LED emission suggests a more inhomogeneous active region composition. Inset is the I-V characteristic for the SPF LED, demonstrating diode-like behaviour. No comparable I-V characteristic is shown for the reference LED here, as the exact current density of the SPF LED is not known owing to its localised recombination regions.

EL imaging of the SPF LED was carried out with a Basler scA1400 CCD camera, capturing emission from the top surface (through the Pd apertures at the base of the SPF pits). To confirm that the resolution of the camera is capable of resolving the pitch of the μ -HC pattern, a linescan of the intensity across the mesa under illumination was analysed. The

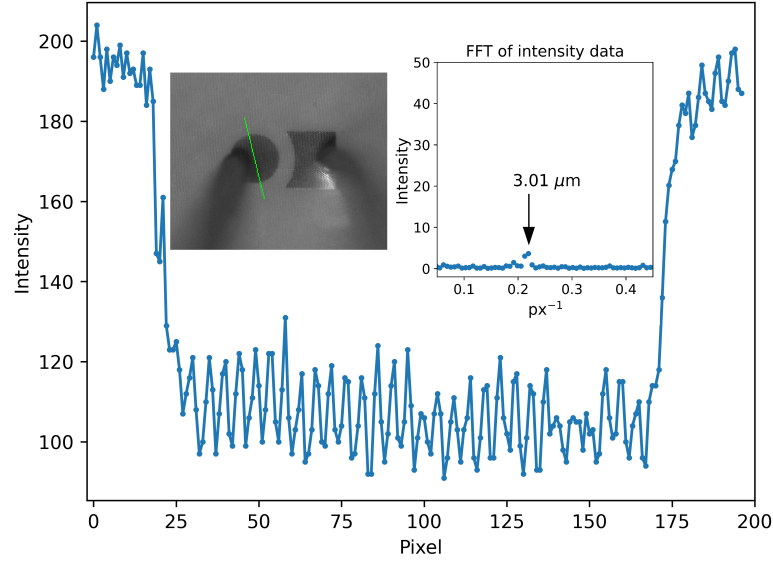


Figure 3.16: Intensity of a linescan across the mesa of the SPF LED. Inset is an image of the linescan location in green, and a Fourier transform of the intensity data showing a single frequency component, corresponding to the reflectance contrast from the μ -HC pitch.

pixel length was calibrated to the known length of the mesa and was found to equal approximately $0.67 \mu\text{m}$. Next, a discrete Fourier transform yielded a single frequency component corresponding to $3.01 \mu\text{m}$ (Figure 3.16), confirming the oscillations seen across the mesa are due to the reflectance of the μ -HC pattern.

Inset in Figure 3.17 shows a captured image of the LED operating at 9.25 V. Distinct isolated emitting areas are evident in the mesa area, indicative of the μ -HC pattern. A ring in the emission pattern tending towards the mesa side closer to the n -contact is clear, suggesting current crowding is an issue, which is to be expected given the lateral contact geometry. Additionally, the emission was captured as a function of applied bias, and the images were processed to extract information about the SPF pits. After converting each image to a greyscale and defining a binary threshold for each pixel, the percentage of ‘on’ pixels (proportional to the number of emitting SPF pits) was calculated as a function of applied bias (Figure 3.17). An increase in the number of emitting pits with increasing bias is evident, before the device dies after 9.5 V. Further quantifying the ratio of pits emitting should be possible, given the resolution of the image is sufficient. However, light leakage between pits (as well as light scattering within the structure and back-reflection through the holes) during electroluminescence introduces significant error. Nonetheless, visually there is only a small fraction of pits emitting, indicating a non-homogeneous distribution of current throughout

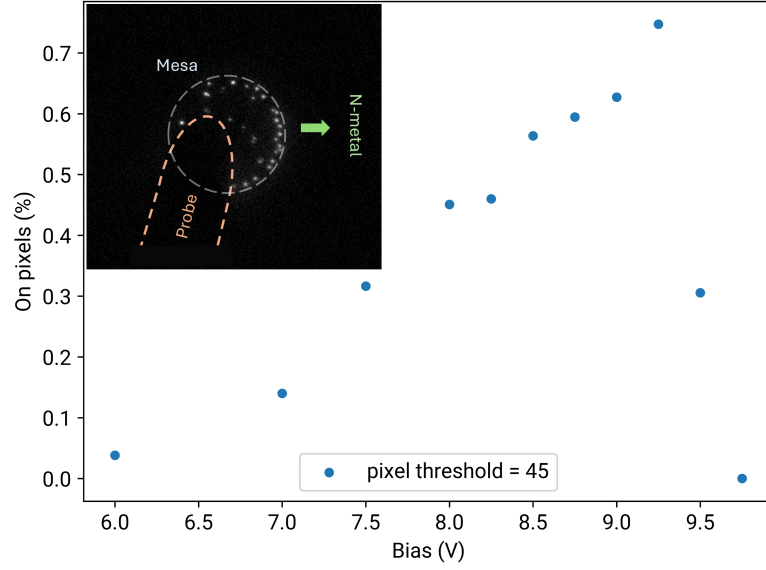


Figure 3.17: Percentage of ‘on’ pixels as a function of applied bias, proportional to the ratio of emitting SPF pits. Inset shows EL imaging of the SPF LED demonstrating light emitted from holes in the SPF pits. Due to the top-emitting setup and lack of bondpads, the camera had to be placed on top of the $100\ \mu\text{m}$ mesa, blocking part of the emission area. Nonetheless, emission is evident from isolated spots.

the device. Indeed, from the $\log(I)$ - V characteristic (not shown), significant sub-threshold leakage current is observed.

While this first attempt shows promise of such a topology, multiple areas for improvement exist here: reduction of the c -plane area for better current distribution and greater SPF emission area; optimisation of the growth conditions for enhanced carrier confinement; modified device (contact) geometry to enhance current spreading (and thus uniformity).

3.4 UV LED with boron-containing QWs

Large intrinsic polarisation fields across the active region, due to the much larger spontaneous polarisation component of AlN relative to GaN, severely limit the radiative recombination rate of UV LEDs [59]. These fields result in a separation of the electron and hole wavefunctions in the QWs, along with a redshift in the emission spectrum. This effect is known as the quantum confined Stark effect (QCSE) and is detrimental to the IQE of the device.

Wurtzite boron nitride is an ultra-wide indirect bandgap material with a bandgap of $\sim 6.7\ \text{eV}$, while the bandgap estimate for a direct transition is roughly $13\ \text{eV}$ [60, 61]. Numerical simulations have shown potential benefits to the spontaneous emission coefficient

in nitride-based QWs with small additions of BN [62]. The relatively small a lattice constant of 0.25 nm allows for the possibility of lattice-matching between well and barrier/buffer material [63]. Therefore, the addition of small amounts of BN to the (Al)GaN QWs has the potential to negate the polarisation field across the well and reduce the QCSE, thereby increasing the IQE. However, boron-containing QWs have to overcome many practical challenges in order to demonstrate experimentally their potential. Previous work in our group has investigated the growth of B-containing (Al)GaN [64], from which the work presented here is built on.

3.4.1 Experiment overview and material characterisation

A BAlGaN MQW UVA LED was grown by MOCVD. A 2 inch c -plane sapphire wafer with 25 nm sputtered AlN (Kyma Technologies) was used as the substrate, onto which a 200 nm AlN connecting layer was grown. This was followed by 400 nm u -Al_{0.35}Ga_{0.65}N, 1.8 μ m Al _{x} Ga_{1- x} N ($x = 0.35 \rightarrow 0.22$) (upper 0.9 μ m n -doped) graded composition layer to manage the tensile strain, five QW B _{x} (Al_{0.06}Ga_{0.94})_{1- x} N (3.5 nm)/Al_{0.16}Ga_{0.84}N (10 nm), 30 nm Al_{0.35}Ga_{0.65}N electron blocking layer (top 20 nm p -type doped), 50 nm p -Al _{x} Ga_{1- x} N ($x = 0.35 \rightarrow 0$), and 10 nm p -GaN contact layer. The growth temperature of the active region was 1160°C. Triethylboron (TEB) was used as the precursor for boron.

Test MQW stacks consisting of B _{x} (Al_{0.05}Ga_{0.95})_{1- x} N/Al_{0.15}Ga_{0.85}N with different TEB/III ratios were previously grown in our group by MOCVD, and TEM analysis (not shown) revealed the presence of nanope-shaped voids in the active region for a low TEB/III ratio ($< 1\%$) [64]. This effect has been attributed to surface segregation of boron during growth [65]. It is proposed that boron acts as a surfactant, reducing the surface energy of the semi-polar and nonpolar planes to below that of polar c -plane. In between the nanopepipes, the QWs are undisturbed and show high uniformity. For the sample prepared with a higher TEB/III ratio (3%), the QWs disappeared completely due to a high concentration of voids. Therefore, for this LED experiment the TEB/III ratio in the QWs was set to 1%. A reference LED was also grown, with an identical structure as above, but with no TEB flowing during QW growth.

To investigate the incorporation of B into the active region, the material was analysed using secondary ion mass spectrometry (SIMS). Figure 3.18 shows the SIMS depth profile of the boron-containing UV LED, showing Al, Ga, and B mole fractions. The B concentration is clearly correlated with the QW position at an initial concentration of 1% in the first grown well. An observable cumulative effect of the boron is present in subsequent QWs, rising

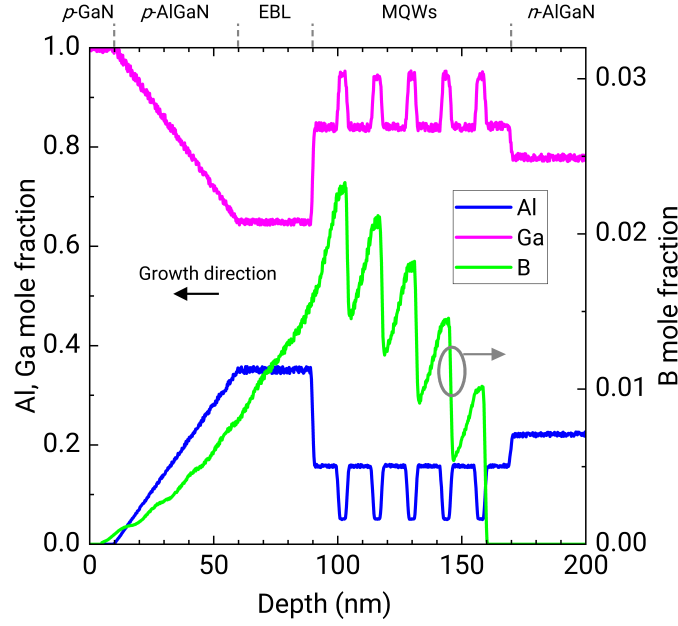


Figure 3.18: SIMS depth profile of the BAIGaN LED.

to approximately 2.3% in the final well. In the p -type region, the boron content decays slowly (despite TEB flowing only in QWs). These effects can be explained by increased surface accumulation of B with thickness during growth, reported in a study by Orsal *et al.* [66]. In this work, the authors found that for BGaN samples grown by MOCVD, the surface B composition increases with growth thickness, implying that boron accumulation on the surface is proportional to the growth thickness. In other words, as growth continues with TEB flowing, some of the B remains on the surface without incorporating, and continues to accumulate on the surface as long as more B is supplied. This is supported by the trend observed in the SIMS measurement of the B-containing LED in this study.

Another important observation from the SIMS result is the total concentration of Al, Ga and B. In a stoichiometric compound, the combined fraction of elements should sum to one. This can be seen in Figure 3.19 before the active region growth of the BAIGaN LED (right hand side of plot). However, once the B-containing QWs begin growth, the total summed mole fraction is found to rise to almost ~ 1.02 by the end of the active region. This suggests that either some of the B is sitting in interstitial sites in the lattice, or it accumulates on the surface during growth without incorporating (which also may be related to formation the voids). Moreover, applying Savistky-Golay filtering to the total mole fraction data shows the total mole fraction (and therefore formation of presumed interstitials) increasing at the onset

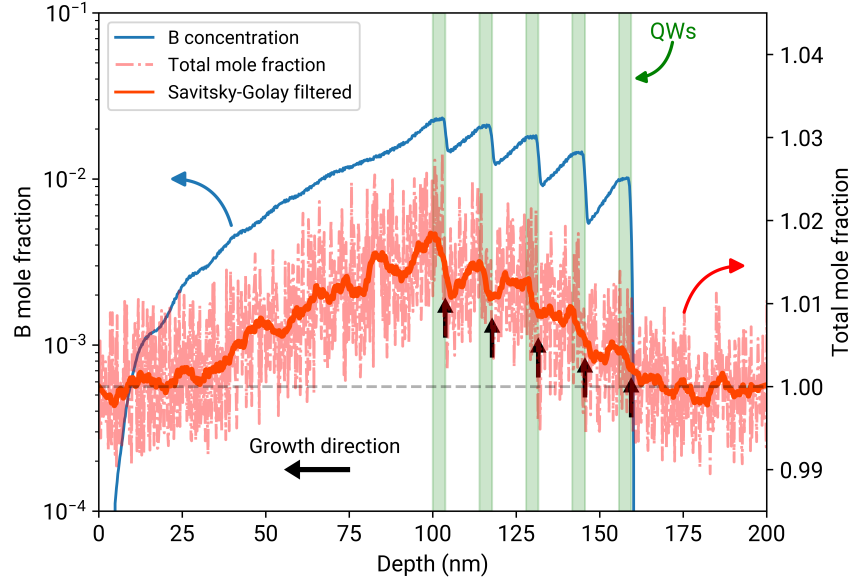


Figure 3.19: Total mole fraction (summed from B, Al, and Ga measured concentrations) from high resolution SIMS measurement of the BAIGaN LED. While the mole fraction is ~ 1 before the active region, it rises at the start of the TEB flow, indicating atoms are not incorporated into the crystal, but occupy interstitial positions. The black arrows highlight a spike in the total mole fraction at the beginning of each QW growth, corresponding to the B trace.

of each QW growth, when the TEB is introduced.

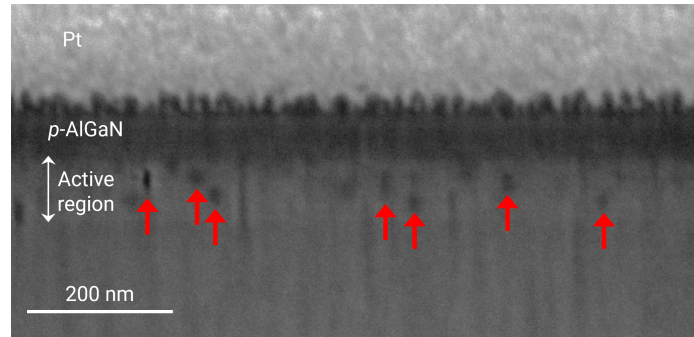


Figure 3.20: SEM image from FIB cut of BAIGaN LED material. Voids can be seen in the active region of the LED (some of them are highlighted by the red arrows), showing an effect of boron.

Figure 3.20 shows an SEM image of a focused ion beam (FIB) cross-section through the BAIGaN LED. The ‘jagged’ Pt interface is due to initial e-beam Pt evaporation and surface roughness. Voids can be seen in the active region of the LED, confirming the same mechanism of boron incorporation as observed in the BAIGaN test MQW sample preparation [8]. The AlGaIn reference LED showed no such disturbance of the active region (not shown).

These voids could explain the reduced peak intensity of the BAIGaN LED in the PL spectra

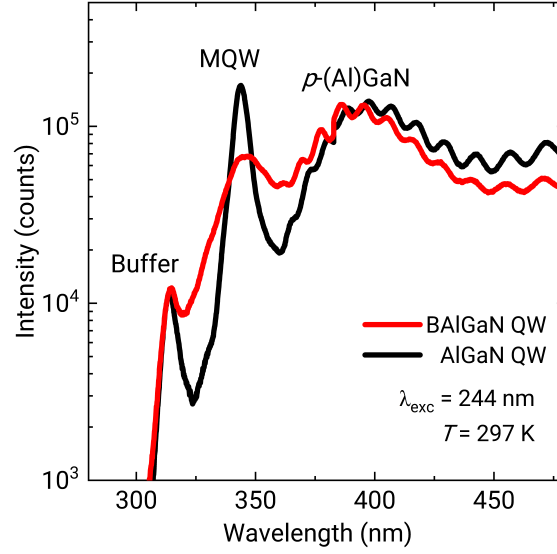


Figure 3.21: Room temperature PL of the LEDs. The BAlGaIn LED shows a reduction in intensity compared to the AlGaIn reference LED.

as seen in Figure 3.21. For these room temperature measurements, a frequency-doubled continuous wave Ar-ion 244 nm laser was used as the excitation source. The AlGaIn LED MQW emission has a peak at around 344 nm, and there is a slight redshift of 2 nm in the BAlGaIn LED. This is likely due to the significant bowing parameter of BGaN and BAlN alloys [60, 61]. The peak at 314 nm is attributed to emission from the buffer layer, while the broad peak centred around 400 nm is due to the p -type region. While the peak intensity is reduced with the addition of boron, the integrated intensity of the QW peak is approximately the same as that of the reference LED. It is possible that the proposed surfactant nature of the boron during active region growth affected the incorporation efficiencies of Al and Ga. This could then result in significant alloy fluctuations, especially in the vicinity of the observed voids.

3.4.2 Effects of boron incorporation on LED performance

After growth, both samples were processed into individual LEDs using previously described fabrication procedures. Figure 3.22a shows the I-V characteristics of the LEDs. Inset is the IV characteristic on a semi-log scale. One effect of the voids in the B-containing LED could be to provide a parasitic current path in the active region. Schubert describes the effect of a parasitic diode in an LED in Ref. [67], which can be due to leakage current through ‘defective regions’ in the active region. A parasitic diode demonstrates a turn-on voltage lower than that of the ‘main’ diode. The semi-log I-V of the BAlGaIn LED only is re-plotted in Figure 3.22b.

At around 5-6 V, such a ‘double-diode’ feature is apparent. By fitting two diode equations, it appears that two diodes are acting in parallel in the BAIGaN LED. The voids could be potentially providing recombination pathways through surface states on the sidewalls, with a lower turn-on voltage than the LED bandgap.

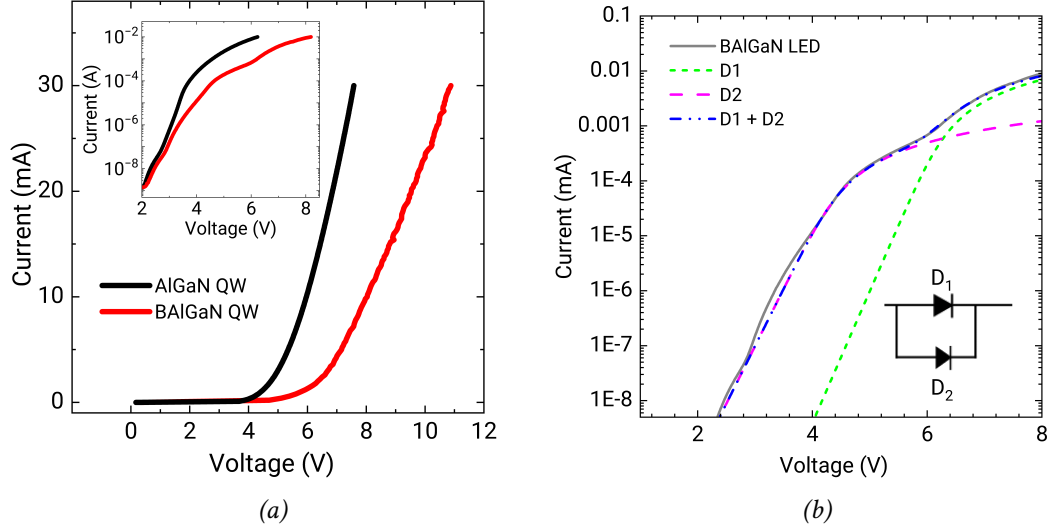


Figure 3.22: (a) I-V characteristic of the BAIGaN QW LED and AlGaIn QW reference LED. (b) Semi-log I-V plot of the experimental BAIGaN LED data (grey) and a SPICE simulation of the ‘real’ diode (D1) with a diode in parallel (D2), offering an explanation of the ‘double-diode’ feature in the BAIGaN LED.

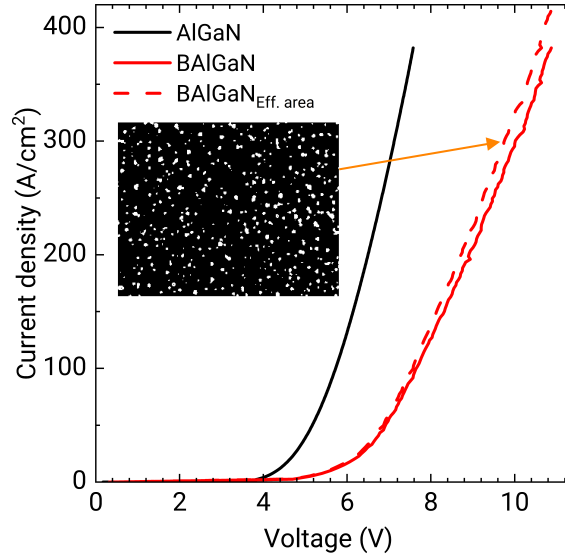


Figure 3.23: I-V characteristics from the BAIGaN and AlGaIn QW LEDs with an I-V curve (dashed) considering an 8% reduction in the active area of the BAIGaN LED. Inset is the processed image used for calculation of the density of voids from a top-view SEM image.

A noticeable increase in operating voltage upon addition of B in the QWs is clear, which could be due to the voids creating a more restricted path to carriers. This increase is not completely accounted for by just the increased current density, however. The density of voids in a BGaN/AlGaIn MQW stack was calculated to be approximately 10^{10} cm^{-2} , consuming about 8% of the LED area. Figure 3.23 illustrates how, when accounting for the 8% smaller area, the voltage is still higher than the AlGaIn reference LED. This indicates the presence of another mechanism at play contributing to the increased operating voltage. This will be discussed further later.

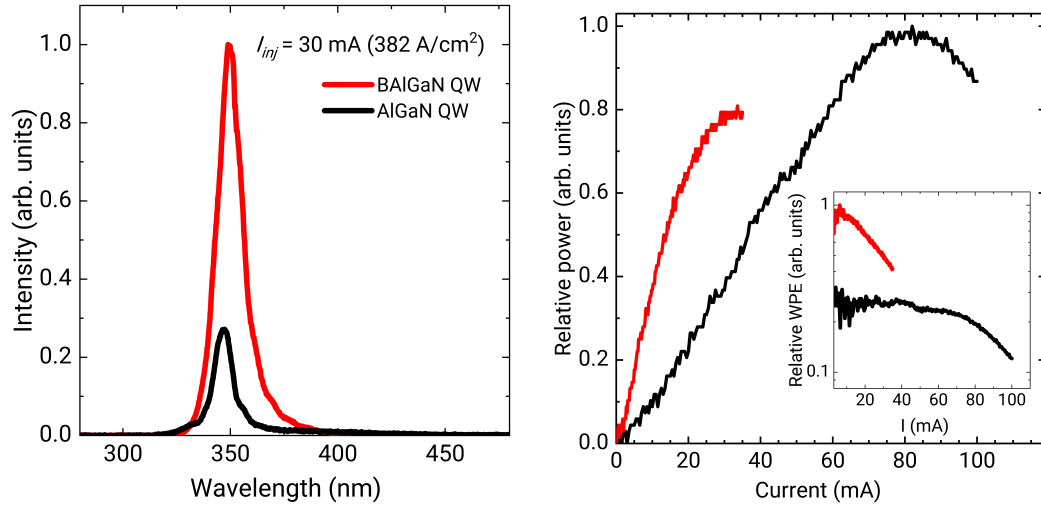


Figure 3.24: (a) EL characteristic of the BAIGaN QW LED and AlGaIn QW reference LED. Injection current was 30 mA for both samples. (b) LI characteristic of the BAIGaN QW LED and AlGaIn QW reference LED. Inset shows the relative WPE in arbitrary units versus current.

In the EL spectra shown in Figure 3.24a, contrary to the PL, the BAIGaN LED shows an integral intensity almost four times higher than that of the AlGaIn reference LED. This was consistent over multiple devices. The MQW peak from the BAIGaN LED (350 nm) shows a slight redshift compared to the AlGaIn LED (347 nm), similar to the PL. The exact reasons for this improvement in performance of the BAIGaN LED under electrical injection are not clear, but improved localisation of carriers due to the presence of boron, light scattering from voids, as well as higher current density in the BAIGaN LED are all possible contributing factors.

The increased current density theory would tend to support the enhancement in output power seen in the LI characteristic (Figure 3.24b). At lower currents, the BAIGaN LED has a higher output power, however it then shows an increased droop in output power at significantly lower injection currents than the AlGaIn reference LED. Pulsed measurements

have shown that this droop is largely due to increased Joule heating in the B-containing device. In addition, this droop could be related to non-radiative Auger recombination beginning to dominate with a higher current density (C term in the ‘ ABC ’ recombination model proportional to n^3) [49]. A relative WPE of the LEDs is plotted against current in the inset of Figure 3.24b. In spite of the higher operating voltage, the BAIGaN LED has a peak efficiency value approximately three times higher than that of the AlGaIn reference LED. This suggests that the IQE of the LED has been improved with the addition of small amounts of BN, although the potential effects of light scattering on extraction efficiency must be considered.

The increased operating voltage is now explored further. The p -contact resistivity and p -type series resistance are the main sources of increased voltage of UV LEDs [68]. The p -contacts in both LEDs show similar voltage drops from cTLM measurements (not shown), indicating it is the resistance of the p -type material that could be responsible for the increased operating voltage in the BAIGaN LED. This bulk resistance is largely a function of the hole concentration. The Mg concentration in both samples, measured by SIMS, is shown in Figure 3.25. The LED with boron in the QWs shows nearly half the Mg concentration compared to the reference, which will lead to a much reduced hole concentration in this LED. It is worth noting here that the growth conditions for the p -type material were nominally identical. The exact cause of this discrepancy in Mg concentrations is not fully understood, however the decay of B into the p -type region, as seen in Figure 3.25, is proposed to have some deleterious effect on Mg incorporation. The adverse effects of B on Mg incorporation is not something that has been reported before, although has been observed [69], so there is potential for future work in this area.

Figure 3.25 also shows an unintended spike in Mg concentration, evident in both LEDs at the onset of doping during growth, however, this spike consists of only one data point. An additional scan with a higher resolution capability was performed (on the boron containing LED only) which confirms the presence of this spike (inset Figure 3.25). The occurrence of this feature in both LEDs suggests it is not related to the presence of B. The same phenomenon has been reported previously in a SIMS measurement of Mg-doped (Al)GaIn [70]. Specifically at the onset of Mg doping, a ‘pile up’ in Mg concentration is observed. Additionally, they observe another Mg spike at the interface between $u\text{-Al}_x\text{Ga}_{1-x}\text{N}$ layers with different values of x . While the presence of Mg at this nominally undoped region is attributed to Mg diffusion through dislocation cores, the spike itself is suggested to be due to the interplay of Mg and

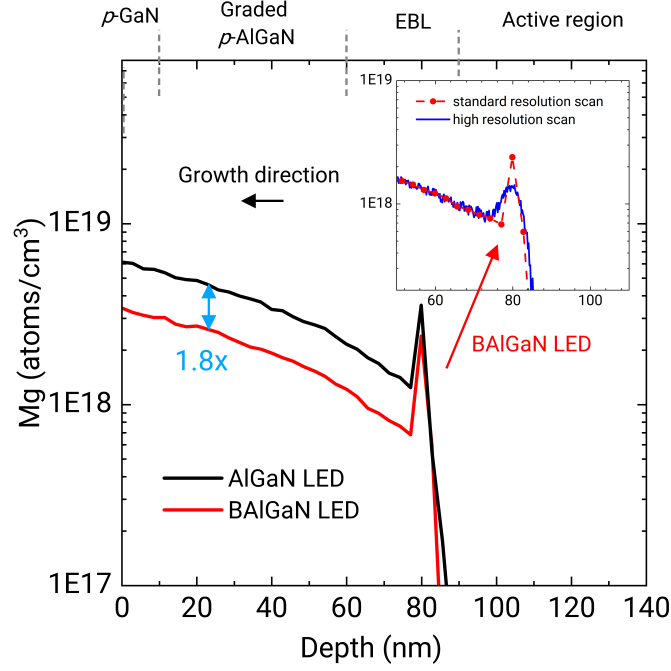


Figure 3.25: SIMS depth profile of Mg concentration in both LEDs. Inset: standard resolution scan versus high resolution scan of the Mg concentration in the BAIGaN LED, confirming the presence of the spike in the Mg concentration at the onset of Cp_2Mg flow.

dislocations at this interface (supported by transmission electron microscopy). Therefore, the spike present in this work could possibly be due to an interaction between Mg and the high density of dislocations near the compositional discontinuity of the EBL - although its position is not exactly at the compositional discontinuity. A p -GaN sample, also measured by SIMS, did not show such a spike at the u -GaN/ p -GaN interface, which would tend to support this theory.

One other possible explanation of this effect could be related to a specific step in the growth recipe. After growth of the first third of the EBL, a 10 s growth pause is implemented to allow a rebalancing of pressure in the gas lines before beginning the Mg flow. Studies have suggested prolonged exposure of GaN to high growth temperatures can result in the formation of ‘fissures’ due to Ga desorption - especially in the presence of tensile strain and TDs [42, 71, 72]. After the formation of the fissures, growth resumes with Mg now flowing, which could incorporate preferentially within the fissure regions, thus resulting in the observed spike in concentration at this depth in the LED. In the p -GaN sample where this effect was not observed, no such growth pause occurred, while the material is under less tensile strain. Nevertheless, further work would be required to confirm this effect.

3.5 Conclusion

In this chapter, the general design considerations for a far-UVA LED were explored. An alternative metal contact was attempted, consisting of a MoO_x/Al stack, potentially providing both Ohmic contact and high reflectivity. Although such a contact has previously been reported on p -GaN, a Schottky contact was observed in this work. After investigation, it was proposed that exposure of the MoO_x to air before Al deposition altered the stoichiometry of the MoO_x , such that its work function was much reduced.

Current crowding is another effect which can limit the efficiency of UV LEDs. To address this issue, micro-LED arrays were investigated, which boosted the efficiency compared to a larger device. Strain and current spreading are directly linked through the thickness of the n -type buffer layer: a thicker n -type layer reduces current crowding. Strain management at this composition range is a bottleneck in the development of far-UVA LEDs. Additionally, the threading dislocation density, impacting a multitude of device characteristics, is associated with the development of strain through the interaction of Si impurity atoms with the dislocation cores. Therefore, thicker, higher quality buffer layers are required to advance the device performance. A novel patterned template overgrowth approach was utilised, which, after coalescence, yielded an order of magnitude reduction in dislocation density. Use of this template allowed for improved device efficiencies. Additionally, the initial patterned template (before coalescence) can be employed as a *faceted* LED template, taking advantage of the optoelectronic properties of semi-polar planes. A novel demonstration of such a topology was presented, showing promise for further work.

Finally, to our knowledge, the first demonstration of a UV LED containing BAlGaIn QWs was presented. SIMS measurements confirmed the incorporation of B into the QWs, but showed a cumulative effect throughout the active region. Additionally, SEM images of a FIB cut into the as-grown LED revealed the presence of voids in the active region, as seen in previous test MQW samples. Despite the complexities with the growth of B, electroluminescence showed QW emission at around 350 nm with diode-like I-V behaviour, although the forward voltage is increased relative to the AlGaIn reference LED. A relative WPE plot shows that the B-containing LED is around three times more efficient, indicating potential beneficial effect of BN in the QWs. Further work is required to better understand the mechanism of these voids in the active region and how to control them with growth

conditions. This work demonstrates successful operation of a boron-containing LED, although the question of benefits in terms of mitigating QCSE in III-nitride based UV LEDs – or even boron incorporation in the undisturbed parts of BAlGa_N QWs remains open.

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4 P-type doping strategies for far-UVA LEDs

This chapter explores p -type doping strategies employed in far-UVA LEDs. Specifically, the technique known as polarisation doping is studied, and its interplay with impurity doping with regard to device performance. Numerical simulations support an experimental study of LEDs with varied p -type doping approaches, which additionally included low temperature characterisation of the LEDs, offering a rare insight into the device physics.

The content in this chapter is in part taken from a publication of this work [1], with additional supplementary analysis which was not included in the published work.

4.1 Challenges associated with Mg-doped (Al)GaN

The early work of Amano *et al.* [2] and Nakamura *et al.* [3] on the activation of Mg dopants in GaN contributed towards the Nobel prize for the realisation of blue LEDs, while propelling forward the III-nitrides field in the development of blue and ultraviolet semiconductor light sources. However, achieving high conductivity p -type (Al)GaN remains a challenge even today. It is often the limiting factor in UV LED WPE values, resulting in large operating voltages.

Few dopants have been successfully demonstrated to bring about a free hole concentration in GaN. Initial theoretical work showed beryllium to be promising as a p -type dopant with a potentially shallower acceptor level compared to Mg [4]. Like Mg, Be sits in the Ga site in the lattice and can form a shallow acceptor state at around 100 meV above the valence band [5]. However, the low formation energy of Be interstitials introduces double donor-type point defects [6], while Be also exhibits poor solubility in GaN due to the formation of beryllium nitride [4]. Beryllium is also highly toxic to humans, with exposure potentially leading to berylliosis [7]. While some recent work has shown promise for Be-doped p -type III-nitrides in MBE [8] and MOCVD [9, 10], Mg is still the most common dopant employed.

When doped in GaN, Mg atoms are initially passivated by H, forming a Mg-H complex. The as-grown material requires subsequent high temperature annealing ($> 700^\circ\text{C}$) in order to break the Mg-H bond and out-diffuse the H [11]. Mg substitutes a Ga atom in the lattice (Mg_{Ga}), forming an acceptor state with an activation energy of approximately 150 meV [12, 13]. For comparison, the Si donor atom in n -GaN is characterised by an activation energy

of 15 meV [14]. The activation energy of Mg in GaN is much greater than kT/q at room temperature meaning thermal activation of the Mg acceptor is poor.

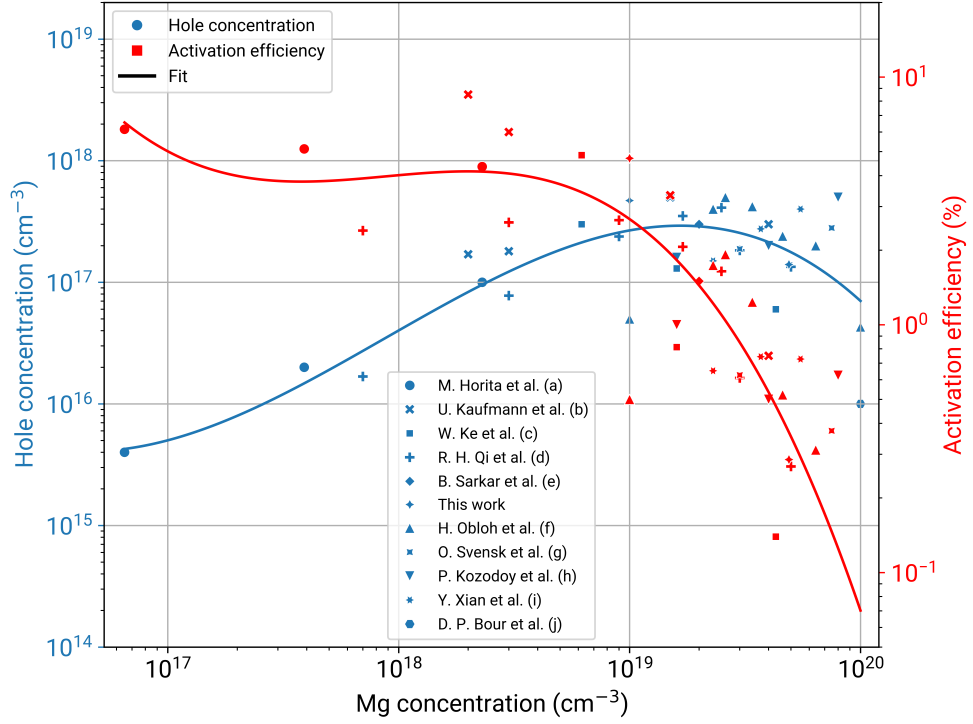


Figure 4.1: p-GaN data from the literature: Hole concentration measured by the Hall effect measurement versus the corresponding Mg concentration measured by secondary ion mass spectrometry (SIMS). The ratio of free hole concentration to acceptor concentration, termed ‘activation efficiency’, is also plotted. The solid lines offer a guide to the eye for the trends. A general increase in hole concentration with Mg concentration is observed, until the latter reaches approximately $2 \times 10^{19} \text{ cm}^{-3}$, at which point the activation efficiency also plummets. References: (a) Ref. [15]; (b) Ref. [16]; (c) Ref. [17]; (d) Ref. [18]; (e) Ref. [19]; (f) Ref. [20]; (g) Ref. [21]; (h) Ref. [22]; (i) Ref. [23]; (j) Ref. [24].

Figure 4.1 illustrates the challenge associated with *p*-type doping of GaN. Plotted is the free hole concentrations (*p*) measured by Hall effect measurements versus the corresponding Mg doping concentrations determined by SIMS measurements [15–24]. Also plotted is the activation efficiency, defined as the ratio of free holes to Mg atoms (p/N_A). With increasing Mg doping concentration, the hole concentration also increases, until low 10^{19} cm^{-3} and mid 10^{17} cm^{-3} , respectively. This maximum hole concentration corresponds to an activation efficiency of approximately 1%. The decrease in hole conductivity beyond a certain Mg concentration is attributed to increased self-compensation [16, 18, 20].

High Mg doping concentrations can also result in a degradation of the surface

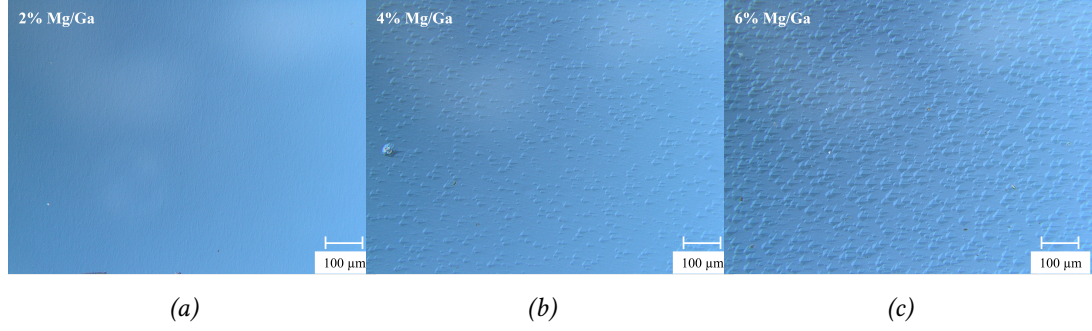


Figure 4.2: Nomarski images of the surface of p -Ga N grown using the same conditions, apart from a varying Mg/Ga ratio of (a) 2%, (b) 4% and (c) 6%.

morphology [22]. Figure 4.2 shows the surface of p -Ga N samples with varied Mg/Ga flow rates. At a Mg/Ga ratio of 2%, no observable degradation of the surface morphology is present. With increasing Mg flow, however, the concentration of hillocks or islands increases. This effect has been proposed to be due to a strain effect of Mg in Ga N . Tensile strain due to the large atomic size of the Mg atom can cause the material to relax through the formation of islands [17]. Another proposed explanation of these islands can be due to the interaction of threading dislocations with Mg. Usami *et al.* [25] suggest that the hillocks are formed by the spiral growth (enhanced by higher Mg concentrations) around nano-pipes resulting from electrically-inactive screw-type dislocations. Clustering of Mg around dislocation centres on the sidewalls of hillocks has also been observed in atom probe tomography [26]. The presence of these hillocks, although potentially providing improved light extraction efficiency through increased scattering [27], can compromise the p -contact [28].

As Al is introduced to the material, the activation energy of the Mg acceptor increases further [29, 30]. Doping of p -AlGa N is also made more challenging by the increased formation of compensating point defects. The positively charged nitrogen vacancy V_N is theoretically more energetically favourable in Al N than in Ga N [31], therefore leading to greater compensation of the hole concentration. While some have reported anomalously low activation energies of Mg in high Al composition p -AlGa N [32, 33], generally, the higher the Al composition, the more difficult p -type doping.

For the target application of diagnostic imaging, spectral purity of the UV LED is of high priority. The characteristic fluorescence wavelength of the excited fluorophore is only slightly longer than the excitation wavelength (e.g. collagen has an excitation wavelength of ~ 330 nm and a fluorescence wavelength of ~ 400 nm [34]). Thus it is vital that the spectrum of the LED

source should be spectrally clean with a narrow linewidth, to prevent the excitation source impacting the detection. An observed consequence of electron overflow in III-nitride LEDs is longer wavelength parasitic luminescence [35–37]. This is attributed to electron overflow into the Mg-doped p -(Al)GaN region, and subsequent recombination via deep-level states. Time-resolved electroluminescence (EL) measurements of a UV LED by Shatalov *et al.* [38] indicated the rise time of the parasitic peak to be associated with hole capture by acceptor states in the p -AlGaN. Such parasitic luminescence would be detrimental to the success of fluorescence spectroscopy. Although poor carrier confinement enables this recombination, it is ultimately the poor conductivity ratio (σ_p/σ_n) that enhances such electron overflow, further emphasising the importance of improving the hole concentration in p -AlGaN. This effect is usually not observed (at room temperature) in conventional III-V LEDs where the acceptor activation is not as challenging [39].

4.2 Carrier generation through polarisation field engineering: a solution

While p -GaN might be preferable in a UV LED for better conductivity, it is absorbing for wavelengths below ~ 360 nm, thus having deleterious effects on the light extraction efficiency. Wider bandgap AlGaN, therefore, is necessary. To overcome the challenge of the large activation energy in p -AlGaN, various strategies have been proposed. A doped short period superlattice (SPSL) - periodic structure consisting of thin layers of alternating bandgap materials - is one such technique aiming to improve the activation efficiency of p -AlGaN [40]. Through compositional variations in the valence band, effective wells are created where the hole quasi-Fermi level lies near or within the band edge, forming thin layers with high hole concentrations. While the SPSL has shown increased hole concentrations over conventional bulk doped material, the presence of lateral 2D hole gases (2DHGs) with repeated abrupt bandgap discontinuities limits the mobility in the direction of the current flow (along growth direction) in an LED [41].

Another technique involving periods of band engineering is delta doping (δ -doping), named after the mathematical representation of the one-dimensional doping profile achieved. This technique originally showed promise in II-VI technologies to achieve p -type conductivity in ZnSe [42]. In III-nitrides, it has similarly shown promise by increasing hole concentrations.

In this technique, the group-III precursor is paused while the nitrogen supply is continued to allow the surface to nitridise. Meanwhile, the dopant precursor is flowed for a set time (typically tens of seconds). The dopant precursor is then stopped and group-III precursor resumed to continue the epitaxial growth. This process constitutes one period, and the cycle is repeated to form a periodic structure of δ -profile doping distributions. A potential well is formed at the location of the δ -doping, brought about by the high concentration of localised impurity atoms. This method has been shown to increase the hole concentrations in p -(Al)GaN through a reduction in both the activation energy of Mg and in the presence of nitrogen vacancies [43, 44]. A combination of both SL and delta doping has also been reported, demonstrating improved hole concentrations and device performance [45]. Limiting the common use of this technique is the added cost of resources involved in the more complex and intensive growth run, and the need for optimisation of multiple parameters (e.g. period number, Mg precursor flow time).

A strategy referred to as polarisation doping or polarisation-enhanced doping, takes advantage of the intrinsic material properties of III-nitride crystals to produce high carrier concentrations. As previously discussed, polarisation fields exist in c -plane III-nitrides: spontaneous (P_{sp}), and piezoelectric (P_{pz}) polarisation. Because each unit cell in the crystal acts as a dipole, there exists a charge at each unit cell interface which is balanced by its neighbouring cell. If there is an abrupt discontinuity in the polarisation field, a 2D sheet charge will form due to the unbalanced charge at the discontinuity, with the polarity depending on whether the crystal is metal-polar or N-polar. Khan *et al.* [46] first realised this mechanism in 1992. This is the basis of operation for high electron mobility transistors (HEMTs) [47]. In a typical structure, a layer of GaN is followed by a layer of AlGaN, forming a positive sheet charge, resulting in a 2D electron gas (2DEG) at the interface. These 2DEGs have very high carrier densities with excellent lateral mobility at the heterointerface. However, in an LED, the carriers need to travel perpendicular to the interface, so a 2DEG is not very useful.

If, instead of an abrupt discontinuity of polarisation, the polarisation field is spread three-dimensionally via compositional grading along the growth direction, a 3D carrier gas can be realised [49]. Figure 4.3 illustrates the physics behind this linear compositional grade, and the corresponding polarisation charge that is produced, resulting in the field-ionised hole concentration. As opposed to the aforementioned complex doping techniques, this strategy

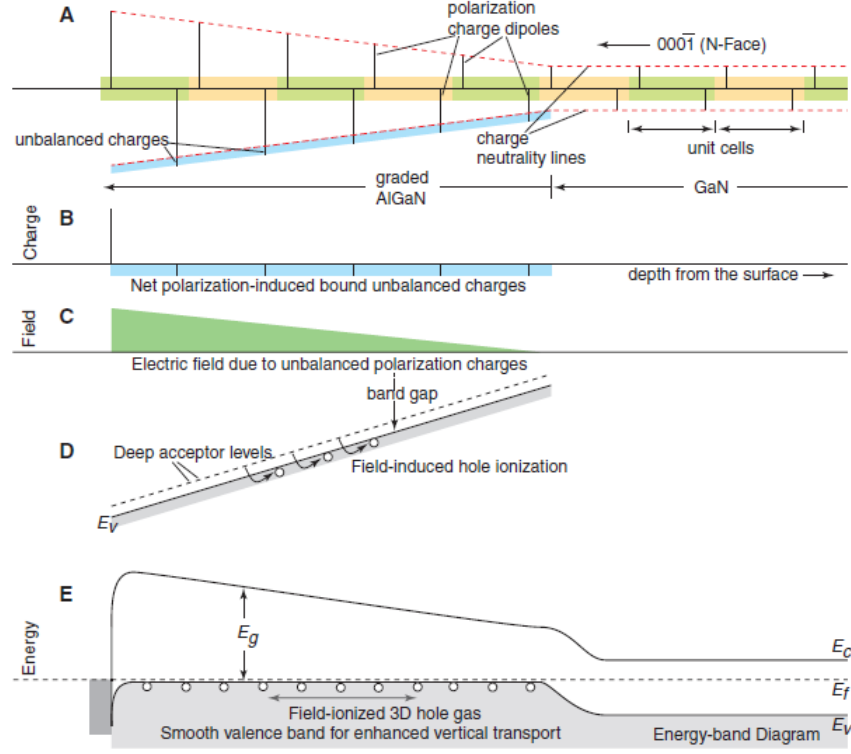


Figure 4.3: A. Schematic showing the unit cells of a N-polar GaN crystal (right side), followed by increasing Al incorporation. B. Corresponding charge due to unbalanced polarisation charge dipoles, which leads to the electric field in C. D. Valence band showing field-ionisation of holes, followed by the steady state energy band diagram in E. Taken from [48]. Reprinted with permission from AAAS.

requires three free parameters: a layer of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ linearly graded from x_1 to x_2 over a distance d can be approximated to possess a charge concentration, ρ_π , as per the expression [48]:

$$\rho_\pi = 5 \times 10^{13} \left(\frac{x_2 - x_1}{d} \right) \text{cm}^{-3}. \quad (25)$$

Polarisation doping, the technique of engineering the intrinsic polarisation fields in III-nitrides, has shown particular success in advancing this area through enhanced hole concentrations and mobilities [50–52]. Sato *et al.* [53] reported that for polarisation doped layers with higher Al compositions, it is beneficial to rely purely on polarisation doping, without impurity doping, due to the high concentration of compensating defects introduced by the Mg dopant. For lower Al compositions, in which the formation energies of compensating point defects are higher [31], it remains unclear whether concurrent Mg doping is beneficial to polarisation doped devices.

Furthermore, there presently exists little work exploring this mechanism in LED structures, particularly as a function of temperature. Whereas hole ionisation from impurity atoms is predominantly a thermally activated process, the field-ionised hole concentration is temperature independent. This warrants studying the temperature-dependent device characteristics to give insights into the device physics with polarisation doping. Ishii *et al.* [54] investigated the EL of a polarisation doped 265 nm UV LED grown on a low dislocation density bulk AlN substrate down to 6 K, concluding it is the injection efficiency that is the limiting factor of device performance at room temperature in DUV LEDs. Other groups have reported various other phenomena at low temperatures in conventionally doped UV LED EL measurements. In an early work, Chitnis *et al.* [55] reported an increase in EL intensity down to 10 K, which the authors attributed to deep-level states that provide tunnelling transport through the *p*-type layer. Grzanka *et al.* [56] observed quenching of the quantum well (QW) EL below 200 K, while photoluminescence (PL) monotonically increased down to 10 K. However, in a structure without an electron blocking layer (EBL), despite more than two orders of magnitude lower QW intensity, the EL monotonically increased down to 10 K (along with a stronger emission from *p*-type material). Based on these observations, the authors concluded that the hole injection is suppressed at lower temperatures by the valence band offset associated with the EBL. Conversely, Zhang *et al.* [57] reported a complete quenching of the QW EL at low temperatures, which was prevented by *inserting* a thin AlN EBL. Clearly, various manifestations of low hole concentrations, either through electron overflow or suppressed hole injection, appear consistently across these conclusions, suggesting it to be the dominant factor affecting EL behaviour at low temperatures.

It is worth acknowledging the pyroelectric nature of wurtzite III-nitrides [58]. With changing temperature, the deformation of the bands will alter the built-in polarisation charges. This opens up the possibility of interesting technology applications such as the use of $\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$ in infrared detector sensors [59]. As temperature dependent characterisation of pyroelectric $\text{Al}_x\text{Ga}_{1-x}\text{N}$ is performed here, this effect must be considered. However, given the small magnitude of the pyroelectric coefficient in AlN and GaN (approximately $10 \mu\text{C}/\text{m}^2\text{K}$ [60, 61]) relative to the induced polarisation field in graded $\text{Al}_x\text{Ga}_{1-x}\text{N}$ (orders of magnitude greater), this effect can be neglected in the analysis.

4.3 Polarisation-doped UV LEDs

4.3.1 Experimental details

To investigate the interplay of polarisation doping and impurity doping, three far-UVA LEDs were designed, grown, fabricated and characterised. The LED structures were grown using MOCVD, and the epitaxial structures are shown schematically in Figure 4.4. The structure of the three LEDs was nominally identical apart from the region between the active region and the top p -GaN layer. This consisted of a 200 nm AlN connecting layer on a 2-inch sapphire substrate with a commercially provided sputtered AlN layer. This was followed by 400 nm u -Al_{0.35}Ga_{0.65}N. Next, 1.8 μ m of Al_xGa_{1-x}N ($x = 0.35 - 0.22$) was then grown with the upper half n -doped to limit the doping-induced tensile strain. The buffer layers show a threading dislocation density (TDD) of approximately $3 \times 10^9 \text{ cm}^{-2}$ estimated from the full width at half maximum of x-ray diffraction (XRD) (002) and (101) measurements. The active region consisted of five 2.5 nm Al_{0.08}Ga_{0.92}N QWs with 10 nm Al_{0.18}Ga_{0.82}N barriers, at a growth temperature of 1160°C.

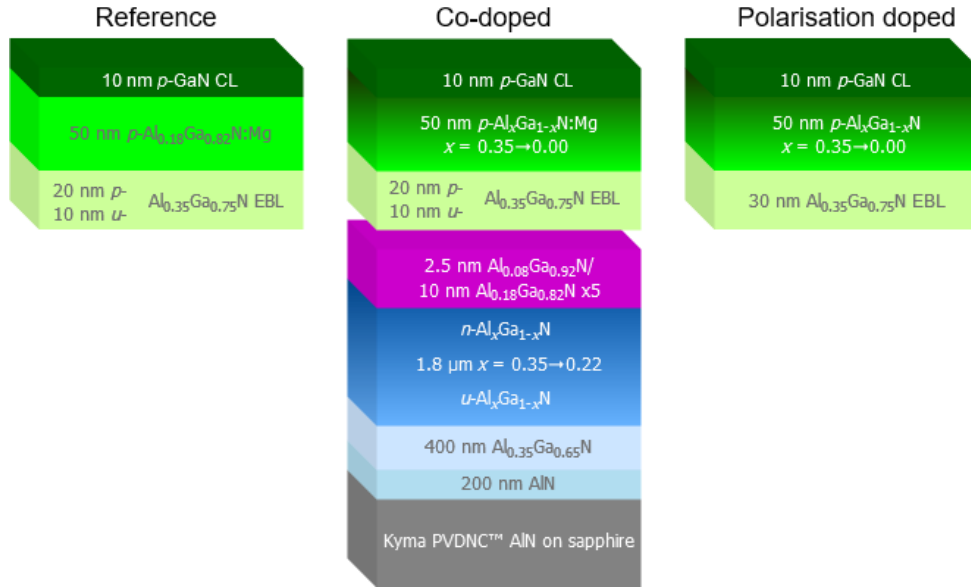


Figure 4.4: Schematic showing the three LED structures, which are identical except for variations in p -doping regimes.

The first (reference) LED, then had a 30 nm Al_{0.35}Ga_{0.65}N EBL with the upper two thirds Mg-doped. The decision to omit from the 10 nm adjacent to the active region was to prevent potential Mg diffusion, resulting in compensation and/or non-radiative

recombination [62, 63]. This was followed by 50 nm of Mg-doped $p\text{-Al}_{0.18}\text{Ga}_{0.82}\text{N}$. The second LED, labelled ‘co-doped’, possesses the same EBL as the reference LED but is followed by 50 nm Mg-doped $p\text{-Al}_x\text{Ga}_{1-x}\text{N}$ ($x = 0.35 - 0.00$). The final ‘polarisation doped’ LED has the same compositional structure as the co-doped LED, except no Cp_2Mg was supplied during EBL and $p\text{-Al}_x\text{Ga}_{1-x}\text{N}$ growth. The compositional grading in these $p\text{-Al}_x\text{Ga}_{1-x}\text{N}$ layers forms the negative (for metal-polar growth) polarisation charge concentration, which, according to equation 25, corresponds to approximately $3 \times 10^{18} \text{ cm}^{-3}$ of negative charges. SIMS measurements (not shown) of a similar structure confirmed the targeted Al compositions in this grading layer. The Mg doping concentration in the p -doped layers is approximately $5 \times 10^{18} \text{ cm}^{-3}$. All three structures were capped with 10 nm $p\text{-GaN:Mg}$ to minimise the contact resistivity, which were activated *in-situ* at 790°C in a nitrogen ambient for 20 minutes.

After growth, the samples were prepared for p -metal deposition using the procedure outlined in Chapter 2. Soon after, 30 nm Pd was evaporated, which was then annealed at 500°C in a nitrogen ambient. Next, an inductively-coupled Cl_2 -based plasma etch was used to define the $100 \mu\text{m}$ diameter circular mesas and a stack of Ti/Al/Ti/Au was then evaporated for the n -metal. SiO_2 passivation and Ti/Au bondpad deposition followed to complete the fabrication process.

Initial room temperature characterisation of the LEDs was carried out with an Ocean Insight HR4000 spectrometer and a Keithley 2400 sourcemeter. In each case, a number of individual devices were measured so as to identify a typical behaviour. For the temperature-dependent characterisation, further packaging of typical LEDs was carried out to allow for appropriate mounting. The LEDs were laser diced into smaller arrays and placed on aluminium nitride ceramic submounts. After wirebonding to individual devices and soldering of connections, the samples could be mounted to a closed cycle helium cryostat coldfinger with a thermal paste to ensure good thermal conductivity. Feedthrough wires in the cryostat allowed for the electrical characterisation with the Keithley 2400. Detection of the LED emission was carried out through the sapphire substrate and a small aperture in the ceramic submount using a Horiba iHR320 spectrometer with a Synapse thermoelectrically-cooled CCD detector. Pulsed current injection measurements (not shown) were performed at low temperatures. This confirmed that there was no observable redshift in emission wavelength, which may be indicative of Joule heating with increased duty cycle.

4.3.2 Room temperature characterisation and simulations

Figure 4.5 shows the room temperature EL spectra of the three LEDs, measured at 20 mA (approx. 250 A cm^{-2}). All LEDs show a distinct QW-related luminescence peak at 330 nm. When plotted on a semi-logarithmic scale (inset in Figure 4.5), it is evident that near-UV luminescence (NUVL) centred around 360 nm is present in both of the LEDs with Mg-doped AlGaIn, but is absent in the LED without. Based on this observation, we conclude that this NUVL band is a Mg-related defect peak similar to the blue luminescence in p -GaIn [16].

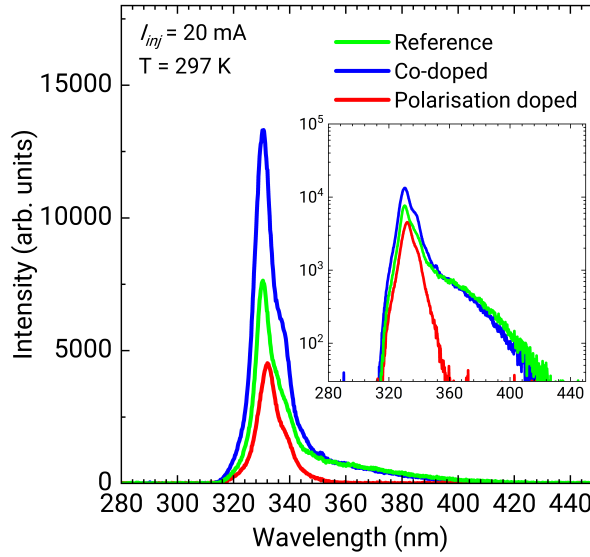


Figure 4.5: Room temperature EL spectra of the three LEDs. The co-doped LED shows the strongest intensity for the same injection current. Inset are the spectra on a semi-logarithmic scale highlighting the marked reduction of the long wavelength tail in the polarisation doped LED.

An improvement in EL intensity is observed in the co-doped LED compared to the reference LED. To examine this further, numerical simulations were performed with the TCAD package Silvaco. The LED structures were simulated at room temperature, as per the p -doping approaches in the three experimentally prepared LEDs except for two quantum wells instead of five. This is not expected to significantly impact the validity of the comparison to the experimental results, as the main changes are occurring in the p -type region. Moreover, this is constant between the three structures so a relative comparison between the three is reasonable. An acceptor concentration (N_A) of $1 \times 10^{18} \text{ cm}^{-3}$ was set in both the co-doped and reference p -AlGaIn regions. A polarisation-doped hole concentration was generated by the graded Al layers, if present, corresponding to the charge concentration from equation

25. Figure 4.6a shows the simulated band diagrams of the three structures at an applied bias of 3.9 V. The LEDs with graded p -AlGa $_x$ N layers show the band bending occurring mainly in the conduction band, to maintain the quasi-Fermi level position relative to the valence band. In the EBL region, the bands in the polarisation doped LED are reduced in energy by approximately 60 meV. The lack of Mg doping in the EBL forces the bands downward to accommodate a higher hole quasi-Fermi level. The resulting weaker barrier effect to electron overflow may partly explain the measured poorer EL performance from this LED [35]. Figure 4.6b in fact shows a lower radiative recombination rate from this simulated LED, which can be attributed to the reduced injection efficiency. Therefore, Mg doping of the EBL in UV LEDs is deemed to be important for efficient hole injection, which is supported by previous studies [64, 65].

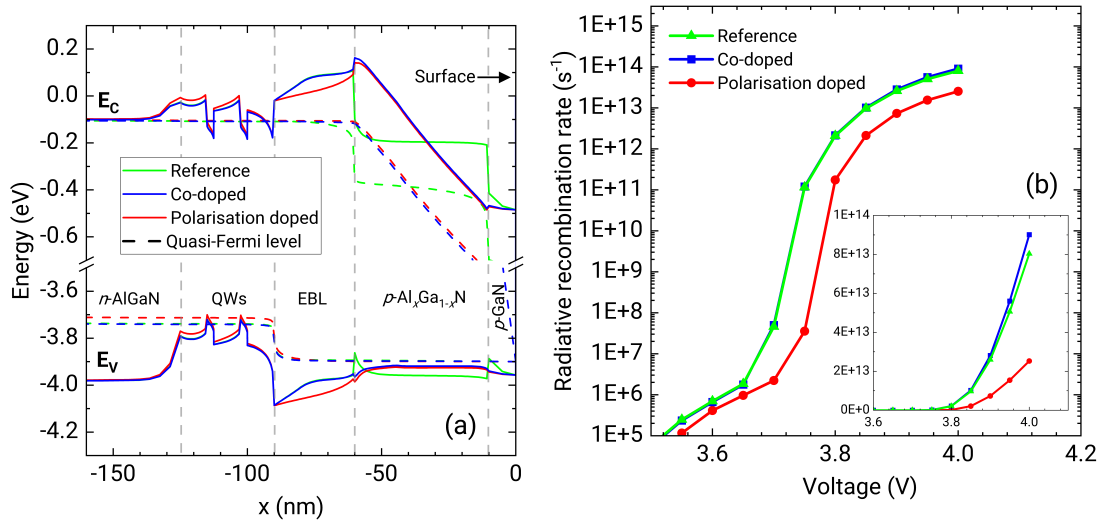


Figure 4.6: (a) Simulated band diagrams for the three LED structures at a bias of 3.9 V, and (b) the corresponding simulated radiative recombination rates as a function of bias.

A further feature of the simulation is that grading the p -Al $_x$ Ga $_{1-x}$ N region results in the elimination of the polarisation discontinuity at the p -AlGa $_x$ N/EBL interface, which prevents the formation of a two-dimensional hole gas (2DHG). The elimination of this discontinuity also enhances the hole injection into the active region [66]. However, it appears the EBL enhancement induced by the Mg doping is the dominant effect, as shown in Figure 4.6b, and consistent with the experimental observation. These results support the hypothesis that the injection efficiency is a significant factor governing the benefits reaped by polarisation doping [51, 54, 67].

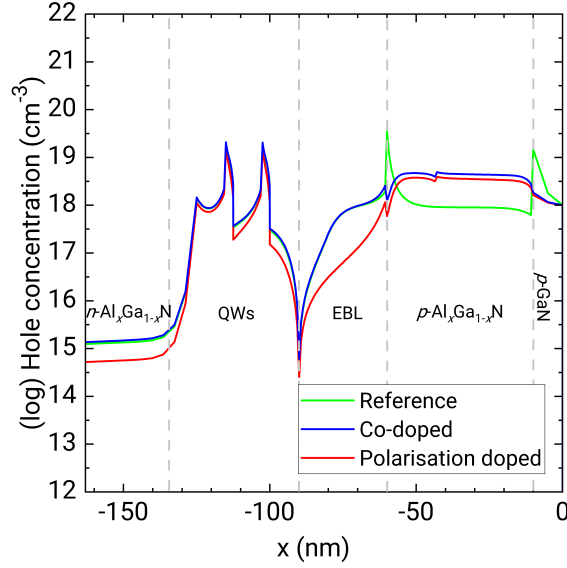


Figure 4.7: Simulated hole concentrations in the LED structures at a bias of 3.9 V. Increased hole concentrations are evident in the $p\text{-Al}_x\text{Ga}_{1-x}\text{N}$ layer with use of polarisation doping.

Additionally, the free hole concentrations from the simulated LED structures are plotted in Figure 4.7. In the $p\text{-Al}_x\text{Ga}_{1-x}\text{N}$ layer of the reference LED, the free hole concentration corresponds to the acceptor concentration (10^{18} cm^{-3}), in the case of complete activation. Meanwhile, in the polarisation doped LED, the free hole concentration corresponds to the polarisation charge concentration according to equation 25 (approximately $3 \times 10^{18} \text{ cm}^{-3}$). With both doping approaches combined then, the co-doped LED demonstrates a hole concentration equal to $\rho_\pi + N_A = 4 \times 10^{18} \text{ cm}^{-3}$.

A ‘kink’ is evident in the hole concentration of both structures with graded compositions (Figure 4.7). This is in fact an artefact relating to the effect of the compositional grading on the band structure. Three separate bands make up the valence band in wurtzite III-nitrides: heavy hole band (HH), light hole band (LH) and crystal field split-off band (CH). The energies for each band is a function of Al composition, as well as strain and polarisation. The ordering of these bands is different for AlN and GaN, so when the Al composition is graded between AlN and GaN, a change in the ordering of the bands occurs, resulting in a switching of the hole effective mass. While this crossover usually occurs at higher compositions in quantum systems (approximately $0.75 > x > 0.5$) [68, 69], it occurs at a lower composition for bulk $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($x \simeq 0.25$) [70]. The hole concentration from the co-doped LED along with the three valence bands, and aluminium composition are plotted in Figure 4.8a. Indeed, the

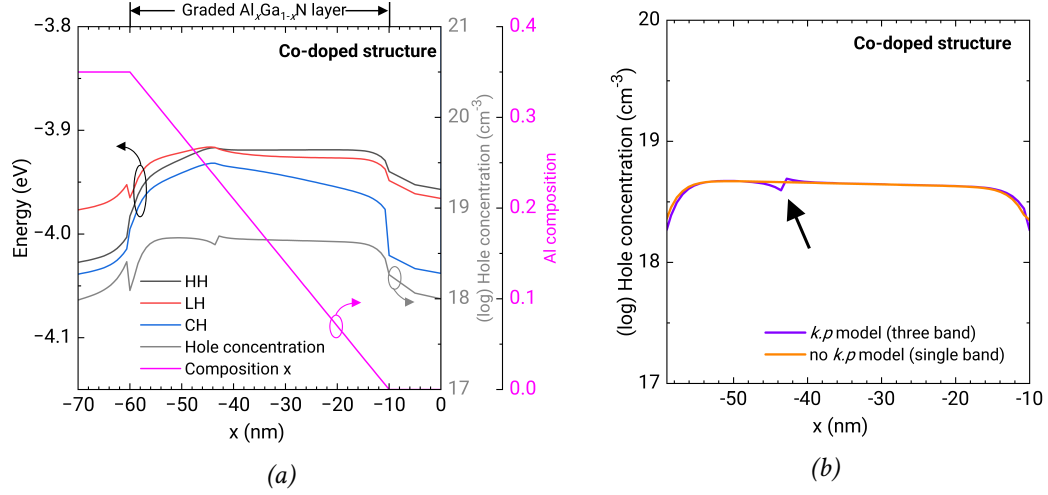


Figure 4.8: (a) Simulated valence band structure from the p-AlGaInN layer in the co-doped LED structure. The position of the crossover in bands occurs precisely at the perturbation in the hole concentration. (b) Simulated hole concentrations with and without the $k.p$ (three band) model.

observed crossover point in valence bands occurs at $x = 0.24$. Silvaco, by default, takes the minimum transition energy available for the bandgap (i.e. the energy difference between the conduction band and the topmost valence band in the three band $k.p$ model) which is then used for solving Poisson's equation [71]. Thus, this sudden change in the hole effective mass, or the different band filling effects, can lead to a perturbation in the calculated hole concentration at this crossover point. To confirm this, the co-doped structure was simulated without the $k.p$ model (single band approximation). The hole concentration in this case is plotted in Figure 4.8b, where no such 'kink' appears.

4.3.3 Temperature-dependent LED characterisation

The experimental LEDs were next characterised down to cryogenic temperatures. Figure 4.9 shows the measured LED voltage at a drive current of 5 mA as a function of temperature. At 300 K, there is no significant difference between the two LEDs with Mg doping, however, when the Mg is removed and only polarisation doping is relied upon, an increase of ~ 1 V is observed. At 12 K, the voltages corresponding to 5 mA increase by ~ 2 V and ~ 3 V for the co-doped and reference LEDs, respectively, while the polarisation doped LED shows almost no increase. The contrasting dependence of voltage on temperature between the three LEDs reveals the insensitivity of the field-ionised hole concentration to thermal energy.

There is no significant difference between the series resistances, R_s , of the LEDs, seen

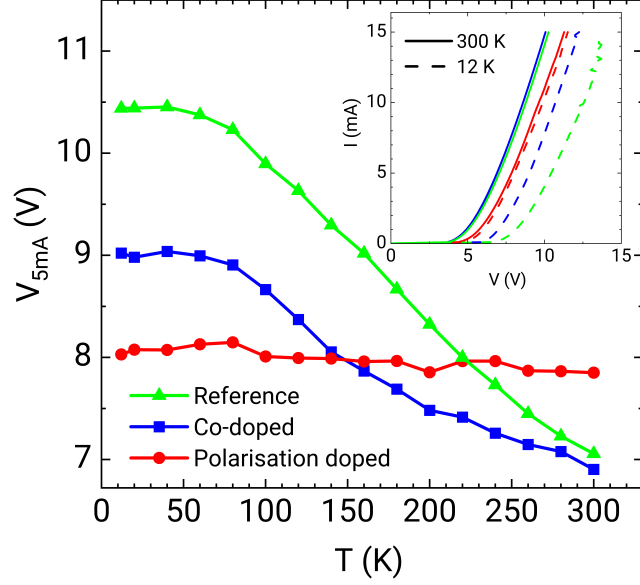


Figure 4.9: Voltage at 5 mA as a function temperature. Inset are the I-V characteristics at 300 K (solid) and 12 K (dashed).

in the current-voltage (I-V) characteristics inset in Figure 4.9. This can be understood by considering the small contribution to R_s from the thin p -region (the lateral resistance of the n -type current spreading layer likely dominates the overall R_s of the devices).

At low temperature, one might expect the co-doped LED to increase in operating voltage to the same value as the polarisation doped LED, as the hole concentrations in both should be created solely by field-ionisation. However, the voltage across the co-doped LED increases monotonically with decreasing temperature to 1 V higher than the polarisation doped LED. The reason for this behaviour is not clear, yet the presence of (non-activated) Mg impurity atoms may still have an impact on device performance. The energy barrier at the p -GaN/ p -metal interface has been proposed to be a contributing factor to the significantly increased operating voltage at low temperature [72]. However, whether this barrier is determined by the free hole concentration or the net $N_A - N_D$ concentration is not widely accepted. Degradation of the n -contact at low temperatures has also been suggested as a cause [55], yet from the temperature-independent voltage of the polarisation doped LED, this is unlikely to be the case.

The temperature-dependent EL spectra of the LEDs are plotted on a semi-logarithmic scale in Figure 4.10, normalised to their intensities at 12 K. The injection current was 5 mA (approx. 60 A cm^{-2}) for all temperature-dependent measurements, which is well below any

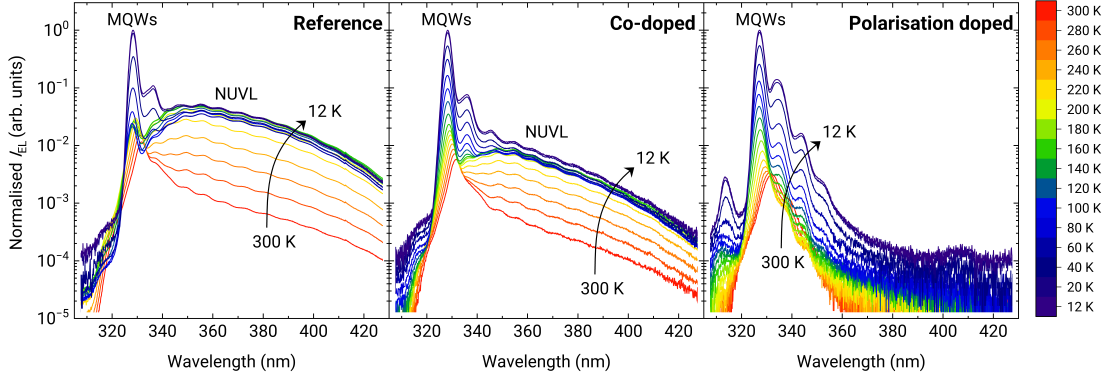


Figure 4.10: Temperature-dependent EL spectra of the LEDs, measured at an injection current of 5 mA.

observed droop in output power potentially stemming from thermal effects. Figure 4.11 shows the integrated intensities of the respective QW peaks versus temperature, calibrated based on their relative intensities at 300 K. The temperature dependence of the EL intensity of the reference LED is rather complicated (not monotonic): it has a local maximum at ~ 200 K and a local minimum at ~ 120 K. The internal quantum efficiency (IQE) is expected to only rise from high to low temperature, which is confirmed by the temperature-resolved PL for this sample (not shown). As such, the EL intensity initially rises with reducing temperature. However, with no polarisation doping to support hole conductivity at lower temperatures, a strong deterioration of injection efficiency (IE) is reflected by the degradation of EL intensity from 200 K to 120 K. This deterioration is accompanied by a larger voltage increase (to keep current at 5 mA).

The strong increase in EL intensity below 100 K for the reference LED is in contradiction to the expectation that the thermally-ionised hole concentration will freeze-out at low temperatures [73, 74]. It is clear that in our case, it is caused by a strong rise in IQE which is expected, but still leaves a question as to the origin of the holes at these extremely low temperatures. This ‘S’ shaped dependence of EL intensity on temperature has previously been observed by Lee *et al.* [75], but no explanation or speculations were provided by the authors for this effect.

One possible origin of holes at the lowest temperatures (< 100 K) is due to the large voltage drop across this LED, even though it is counter-intuitive at first glance. As thermally activated acceptors become frozen, fixed current excitation results in an increased voltage, for this LED especially (> 10 V at $T < 100$ K). The calculated effective field across the

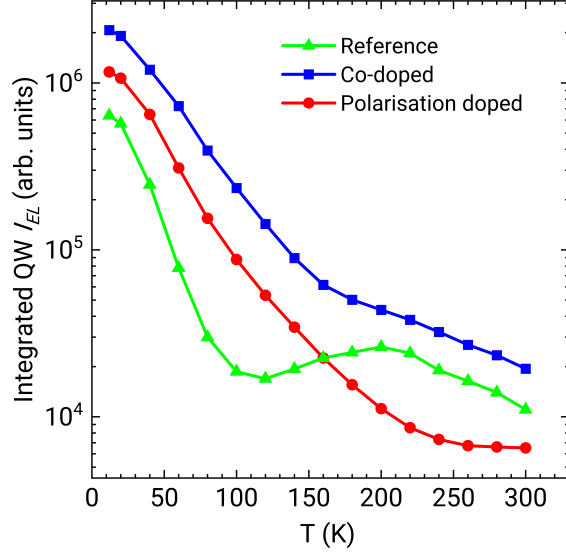


Figure 4.11: Integrated QW EL intensity as a function of temperature, calibrated based on their relative intensities at 300 K.

p -type region at this bias is on the order of 1 MV cm^{-1} , which is comparable to the field produced by polarisation doping [76]. At such a high electric field, there is sufficient energy to start field-ionising the holes from the now-frozen Mg acceptors, thus supplying a hole concentration to the active region. This might be the reason why the voltage does not rise further (it saturates at 10.5 V below 50 K as seen in Figure 4.9). As the V_{5mA} saturates at low temperature, so too does the IE. On the other hand, the IQE is expected to strongly increase in this temperature range (as seen also from both polarisation doped and co-doped LEDs). This apparent saturation in IE, coupled with the increasing IQE (towards 12 K), can explain the unexpected increase in EL intensity observed below 100 K.

The alternatives to the mechanism involving field-ionised holes (due to large bias) in the above explanation might be: the presence of a 2DHG at the EBL/ p -AlGaIn interface (Figure 4.6a); and nearest-neighbour hopping conduction between spatially adjacent Mg impurity atoms, previously reported for p -(Al)GaIn at low temperatures [77–79]. Further discussion about this effect can be found in Chapter 5.

As expected from the temperature-independence of a polarisation-doped carrier concentration, strong QW-related luminescence is observed at 12 K in both of the LEDs with graded Al p -type regions. From Figure 4.11, both of these LEDs show a general monotonic decrease in intensity with increasing temperature, presenting similar quenching behaviour up to approximately 150 K. At this temperature, the co-doped LED experiences a change in

slope, indicating a decrease in quenching. The behaviour of the co-doped LED just below room temperature is similar to that of the reference LED, which indicates that the electrical properties in this temperature range are dominated by the Mg acceptors. Meanwhile, above ~ 150 K, the polarisation doped LED continues an exponential decrease in intensity, until the temperature approaches 300 K at which point this quenching saturates.

The IE along with the IQE and the light extraction efficiency (LEE) determine the external quantum efficiency (EQE) of an LED, given by:

$$EQE = IE \times IQE \times LEE. \quad (26)$$

The LEE should remain approximately constant both across the temperature range and between LEDs. The integrated EL intensity in Figure 4.11 can therefore be used as a proxy for the trend in EQE with temperature.

The TDD is approximately equal between all templates. From equation 26, the temperature dependent behaviour of the polarisation doped LED should be mostly explainable in terms of IQE as its electrical properties are largely temperature-independent. The saturation in quenching towards 300 K would suggest that most of the defects that act as non-radiative recombination centres are already activated above ~ 260 K, and this seems to be the reason why no further EQE deterioration occurs above this temperature. Meanwhile, the presence of Mg can only have adverse or ideally no effects on IQE. Therefore, the slower EL quenching in the co-doped LED above 150 K is likely related to the unfreezing of Mg acceptors and a corresponding increase in p -type conductivity, which should contribute to an enhancement in IE.

4.3.4 Analysis of NUVL vs temperature

The rate at which electrons are captured by a trap state, R_n , can be expressed by:

$$R_n = C_n N_t [1 - f_F(E_t)] n, \quad (27)$$

where C_n is a constant proportional to the electron-capture cross section, N_t is the concentration of trap states, n is the concentration of electrons in the conduction band, and $f_F(E_t)$ is the probability that the trap contains an electron [80]. The rate at which

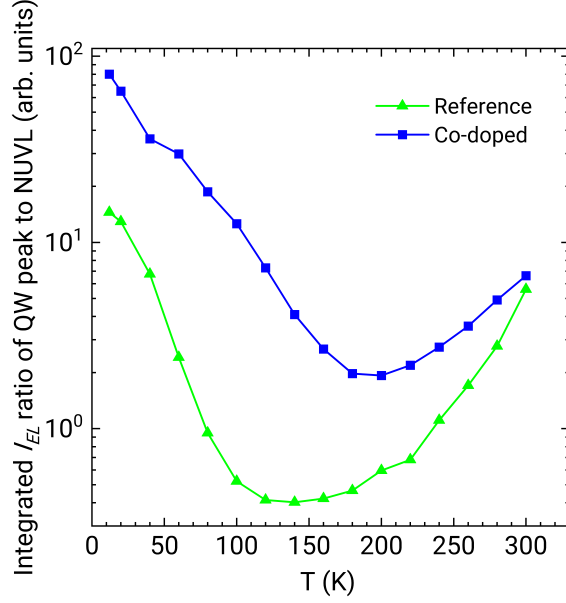


Figure 4.12: Ratio of QW peak and NUVL intensities. NUVL was not observed in the polarisation doped LED.

carriers are captured by the Mg-related defects is therefore proportional to the number of electrons in this region. Considering the recombination mechanism associated with this defect state and assuming N_t is roughly the same between LEDs due to nominally identical Mg concentrations, an increased number of electrons overflowing from the active region will result in an increased intensity of this NUVL band (inset Figure 4.5).

The evolution of the NUVL with temperature can also provide insight into the carrier dynamics. Figure 4.12 shows the ratio of the QW peak intensities to the NUVL intensities. No such peak is observed in the polarisation doped LED, hence its absence from this analysis. As was mentioned earlier, the origin of this broad peak is attributed to overflow of electrons into the p -type region and subsequent recombination involving Mg-related defect states [81–83]. In both of the Mg-containing LEDs, when the temperature is reduced, the intensity of this band increases, until about 180 K in the former and 120 K in the latter. The fact that the ratio of the reference LED presents a much larger drop with decreasing temperature indicates that the hole freezeout, and as a result electron overflow out of the active region is more severe without the aid of polarisation doping as was already alluded to above. The NUVL band is directly associated with recombination in Mg-doped regions and therefore is proportional to electron overflow. It is important to note that the efficiency of the transition associated with the NUVL should also increase with decreasing temperature, which would also act to

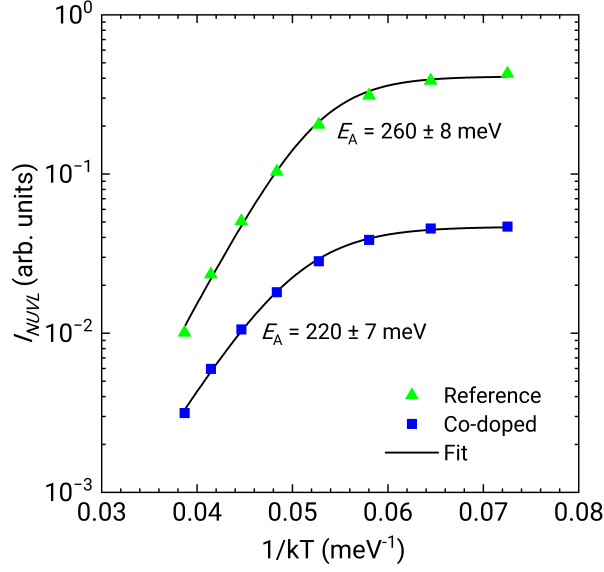


Figure 4.13: Arrhenius plot of the NUVL intensity for the two Mg-containing LEDs, using equation 28.

increase the NUVL intensity. Regardless, it is the relative behaviour between the two LEDs which supports the mechanism of enhanced IE resulting in the reduced rate of EQE quenching above 150 K.

To further investigate this, an Arrhenius plot of the integrated intensity of NUVL was plotted in Figure 4.13. The intensity, L , was fitted with the equation for a single quenching process with an activation energy E_A :

$$L = \frac{L_0}{1 + A \exp(-E_A/kT)}, \quad (28)$$

where L_0 is the light intensity extrapolated to 0 K, A is a constant and k is Boltzmann's constant. Activation energies of 220 meV and 260 meV were extracted for the co-doped and reference LEDs, respectively.

One interpretation of the fitted energy values could be as follows. When the temperature is reduced from 300 K, the number of inactivated Mg atoms increases due to its large activation energy. This increased concentration of non-ionised acceptor states leads to a rise in the transition between these acceptor states to deep-level donor point defects (and also conduction band edge), causing the initial increase in NUVL intensity. Thus the value of E_A associated with the reduced intensity of this peak can be interpreted as an insight into the activation energy of the Mg dopant, which is comparable to values reported in the

literature for this composition range [84, 85]. Therefore, the lower value of E_A in the LED with the graded Al layer compared to the LED with a uniform composition p -region indicates an increase in the activation efficiency of Mg. This can be understood by considering the effect of compositional grading on the valence band [86]. An enhanced activation of Mg could contribute towards the increased EL intensity observed in the co-doped LED, and the improved ratio of QW-related luminescence to NUVL.

It is again worth noting here that the behaviour of this NUVL as a function of temperature may also be affected by its varying efficiency as the recombination lifetimes associated with this transition change. It is important to focus here on the relative difference between the two Mg-containing LEDs, and not interpret this as a direct method for determining the dopant activation energy.

Ultimately, the device performance becomes less sensitive to temperature with the introduction of polarisation doping, as well as increased QW-related EL intensity across the temperature range. Sato *et al.* [53] propose that for p -type polarisation doping at higher Al compositions, the large activation energy of Mg leads to more compensating point defects which offset the polarisation doped hole concentration. The results presented here suggest that for lower Al compositions, Mg doping is beneficial alongside polarisation doping.

Finally, the weak emission at shorter wavelengths compared to the main QW-related peak is addressed. It appears at lowest temperatures as only a shoulder in the two Mg-doped LEDs, and it is visible as a distinct peak in the polarisation doped LED. Similar emission has already been observed in AlGaIn-based UV LEDs by De Santi *et al.* [87]. We attribute the origin of this peak to radiative recombination in the QBs. At low temperatures, the thermal energy is not enough to delocalise the carriers which happen to be trapped in shallow localised states in the barriers. On top of this, non-radiative centres also become inactive at low temperature. This explains why, in principle, this peak becomes visible at low temperature. Regarding its relatively increased intensity in the polarisation doped LED, we speculate that the suppression of this peak in the Mg-containing LEDs is related to Mg back-diffusion [62], allowing non-radiative recombination centres to suppress the luminescence even at low temperature. This suggests that this luminescence might be specifically from the final barrier, which experiences a large band-bending at the barrier/EBL interface, forming a quasi-well according to theoretical calculations using the classical drift-diffusion model [76].

4.4 Conclusion

In summary, distributed polarisation doping in far-UVA LEDs was investigated. UV LEDs emitting at 330 nm with varied p -doping approaches were grown and fabricated, and their electrical and luminescence behaviour was studied. At room temperature operation, it was found that an LED structure with both polarisation doping and Mg doping produces a higher EL intensity than polarisation doping only or impurity doping only. In the LED with only polarisation doping and no Mg, a cleaner spectrum was achieved due to the elimination of NUVL stemming from Mg-related defect states in the p -region. Numerical simulations indicate that both doping of the EBL, and grading of the p -AlGaIn layer enhance the hole injection and therefore device performance.

The LEDs were also characterised down to cryogenic temperatures, offering an insight into the temperature independence of a carrier concentration ionised through a polarisation field. The expected complete freeze-out of the holes at low temperature in the LED with only Mg doping was not observed, although it demonstrated a significantly increased forward bias to maintain fixed current injection. There was a complex progression of EL intensity with temperature, which may be due to an interplay between increasing IQE, decreasing IE, and another mechanism of hole conductivity at low temperatures (likely impurity band conduction). Meanwhile, both LEDs with polarisation doping showed a steady increase in EL intensity when the temperature was decreased from 300 K to 12 K, as expected from the increasing IQE along with the temperature-independent field-ionised hole concentration.

The overall improvement in performance with polarisation doping is attributed to both reduced electron overflow and increased hole injection, resulting in an improved IE. Rate equation analysis of the NUVL dependence on temperature suggests an enhanced Mg activation efficiency also contributes to the improved performance. Therefore, for lower Al compositions, we propose that (p -type) distributed polarisation doping benefits from co-doping with Mg. Further optimisation of the doping conditions could allow for increased EL intensity as well as a cleaner emission spectrum. For applications such as fluorescence imaging, removing long wavelength parasitic luminescence from the excitation light source (UV LED) is crucial to allow for the accurate detection of the fluorescence.

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5 Conduction mechanisms in *p*-type (Al)GaN

The temperature-dependent conduction mechanisms in *p*-type III-nitrides are studied in this chapter. There is a focus on the effect of compositionally graded AlGaN and the impact of polarisation doping on the carrier transport properties. The LakeShore 8404 Hall Measurement System was employed for the Hall effect measurements within a possible temperature range of 10-400 K.

I would like to acknowledge the insightful correspondences with Dr. Jeff Lindemuth from LakeShore Cryogenics, regarding the complex interpretation of these measurements and the intricacies (and limitations) of the instrumentation.

5.1 Carrier transport in doped semiconductor materials

In a conventional non-degenerate semiconductor, carriers are thermally excited from localised states within the bandgap to the ‘parent’ band (conduction or valence), to use the terminology employed by Seeger [1]. These localised states, formed by the presence of impurity atoms, exist at an energy level usually around tens of meV below and above the conduction and valence bands, respectively. The concentration of free carriers will have a dependence on temperature as illustrated qualitatively in Figure 5.1. At low temperatures, a lack of sufficient energy results in a ‘freeze-out’ of carriers, leaving them bound to the neutral impurity atom. Meanwhile, at higher temperatures, the intrinsic carrier concentration increases to greater than the donor or acceptor concentration.

If the doping concentration is large enough, the orbitals of the impurity atoms begin to interact and are no longer localised. Phonon-assisted ‘hopping conduction’ can then occur at lower temperatures. At still higher doping concentrations, the states begin to overlap and can result in the formation of an ‘impurity band’ at low temperatures. Carrier transport can occur solely in this impurity band. This is especially prevalent in *p*-type III-nitrides, where high doping concentrations are standard owing to the poor activation efficiency (see Chapter 4).

During conduction through a layer, the motion of carriers will be elastically and inelastically perturbed. Such a perturbation, otherwise referred to as scattering, will result in an associated time for the carrier to return to its equilibrium momentum state, referred to as the relaxation time, τ_m . The drift mobility, μ , of the carriers is related to the relaxation time

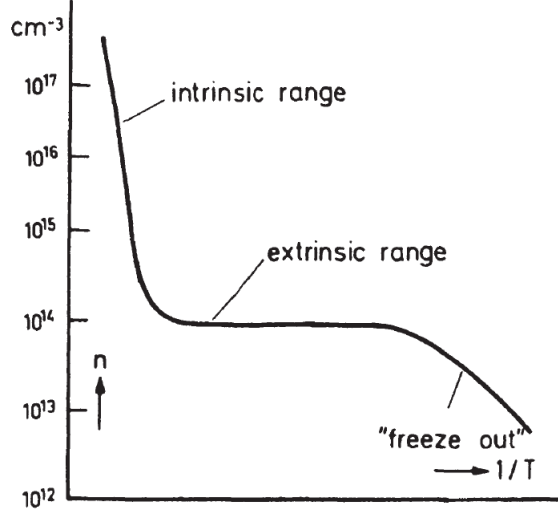


Figure 5.1: Semiconductor carrier concentration as a function of $1/T$. A ‘freeze-out’ of the free carrier concentration is observed at low temperatures. Taken from [1]. Reproduced with permission from Springer Nature.

by the Drude equation:

$$\mu = \frac{q\langle\tau_m\rangle}{m^*}, \quad (29)$$

where q is the elementary charge on the electron and m^* is the effective mass of the carrier. The averaged relaxation time is represented by $\langle\tau_m\rangle$. The conductivity, σ , is related to the mobility and carrier concentration, n , through $\sigma = qn\mu$, the inverse of which yields the resistivity, $\rho = 1/(qn\mu) = 1/\sigma$.

The Hall effect measurement can be used to characterise a layer of semiconductor material and extract electrical characteristics. The operation and procedure relating to the Hall effect measurement are outlined in Section 2. While a carrier concentration and mobility are extracted from the measurement, it is important to note that these are specifically the *Hall* carrier concentration, n_H , and *Hall* mobility, μ_H . These are related to the *true* carrier concentration, n , and *true* mobility, μ , through the Hall scattering factor r_H : $n = n_H r_H$ and $\mu_H = \mu r_H$. The Hall scattering factor accounts for the difference in energy dependences of the different scattering mechanisms between the drift mobility and the Hall mobility:

$$r_H = \frac{\langle\tau_m^2\rangle}{\langle\tau_m\rangle^2}. \quad (30)$$

The value of r_H in Hall effect measurements can be complex. The value of r_H is always close

to unity for traditional band transport when the effective-mass approximation holds, and it is always greater than 1 as $\langle \tau_m^2 \rangle > \langle \tau_m \rangle^2$. In the literature, its value is usually assumed to be unity [2–4]. In the presence of hopping conductivity, however, the effective-mass approximation is no longer valid, and r_H has been observed to be negative and its magnitude strongly temperature dependent.

Direct measurements of r_H are difficult and require high Hall signals for variable-field measurements. As such, analysis of this topic can be relatively complicated and assumptions (e.g. $r_H = 1$) are widespread to simplify calculations. For instance, the range of reported hole concentrations in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys as a function of x is far from consistent [5, 6]. With increasing x , it is expected that the activation energy of Mg in $\text{Al}_x\text{Ga}_{1-x}\text{N}:\text{Mg}$ increases, as predicted by a linear interpolation between the GaN and AlN activation energies. However, aforementioned heavy doping phenomena (to varying extents) can result in unusual results. In the following section, various scattering mechanisms and specifically their impact on graded p -AlGaN are discussed.

5.2 Carrier scattering mechanisms

The mobility due to carrier scattering is dominated by the scattering mechanism with the lowest associated mobility. Matthiessen’s rule expresses the total effective mobility, μ_{tot} , given i different mobility-limiting scattering mechanisms [7]:

$$\mu_{tot} = \left(\sum_{i=1}^i \frac{1}{\mu_i} \right)^{-1}. \quad (31)$$

It is important to note here some clarifications regarding calculations of mobilities and the application of Matthiessen’s rule. The calculations of mobilities here assume the relaxation time approximation. That is, the relaxation times of carriers owing to different scattering mechanisms are energy independent (i.e. scattering events are elastic and no energy is lost as a result of the scattering event). Additionally, an assumption is made when employing Matthiessen’s rule, in that the scattering mechanisms are independent of each other. In the following calculations, this is assumed to be the case, as an in-depth investigation into each scattering mechanism and their co-dependencies is outside the scope of this work. During similar investigations in the literature, the same assumption is usually made [4, 8, 9].

The expressions for scattering-limited mobilities have been taken from Ref. [10], unless otherwise stated. Some physical constants are repeated throughout these expressions and so are explained here for brevity: q is the charge on the electron, T is the temperature, k is Boltzmann's constant, h is Planck's constant, $\hbar$ is the reduced Planck's constant ($h/2\pi$), m^* is the effective mass of the carrier, and ϵ_s is the low-frequency dielectric constant.

5.2.1 Dislocation scattering

Threading dislocations (TDs) in III-nitrides can be electrically active [11, 12]. However, the matter is complicated, with screw type TDs suggested to contribute more towards leakage current, and edge type TDs responsible for carrier scattering [13]. Dangling bonds associated with edge type TDs can act as deep acceptors and thereby generate a space charge region around a dislocation core, scattering carriers. The electrical properties of dislocations in GaN have been extensively studied, with a focus on HEMT devices [14]. Leakage paths prevent a fully off state of the transistor. Although in the 'on' state, the high density of carriers should screen these charges (through the Debye screening length), alleviating the impact of dislocation scattering compared to bulk materials [15]. Still, charged dislocation scattering can become a contribution to the overall mobility for very high TDD, and necessitates the availability of high quality templates. This scattering-limited mobility can be expressed by:

$$\mu_{dis} = \frac{8\epsilon_s^2 2^{3/2} c^2 (kT)^{3/2}}{N_{dis} f^2 q^3 \sqrt{m^*} \lambda_D}, \quad (32)$$

where c is the c -plane lattice parameter, N_{dis} is the threading dislocation density (TDD), f is the occupation rate of the charge centres, and λ_D is the Debye screening length, given by:

$$\lambda_D = \sqrt{\epsilon_s kT / q^2 p'}, \quad (33)$$

where p' is the screening charge concentration, expressed by [16]:

$$p' = p + (p + N_D)[1 - (p + N_D)/N_A]. \quad (34)$$

5.2.2 Acoustic phonon scattering

Acoustic phonons are thermal lattice vibrations which propagate through a crystal as a wave. These vibrations can result in scattering of electrons in two ways: deformation potential scattering, and piezoelectric scattering. With deformation potential scattering, the vibrations in the lattice distort the periodic potential fluctuations (which are the foundational requirement for band transport in a semiconductor) thereby hindering carrier transport. The vibrations originating from thermal energy leads to a decrease of phonons at lower temperatures, and therefore a longer average time between scattering events. The mobility limited by deformation potential scattering, μ_{dp} , for a nondegenerate semiconductor with spherical bands can be expressed as:

$$\mu_{dp} = \frac{2\sqrt{2}\pi\rho s^2\hbar^4 q(kT)^{-3/2}}{3D_{ac}(m^*)^{5/2}}, \quad (35)$$

where ρ is the material density, s is the speed of sound, and D_{ac} is the deformation potential for acoustic phonon scattering.

As has been discussed in Chapter 4, the presence of strain in polar III-nitride crystals results in a piezoelectric field. Because the acoustic phonon has the ability to deform the lattice, piezoelectric fields can result from this localised strain. Through piezoelectric coupling with acoustic phonons, the interaction of electrons and holes with this field is referred to as piezoelectric scattering. This scattering mechanism is particularly important in III-nitrides due to their large piezoelectric coefficients, while it is relatively independent of T :

$$\mu_{pz} = \frac{16\sqrt{2}\pi\rho s^2\hbar^2 q(kT)^{-1/2}}{3(qh_{pz}/\epsilon_s)^2(m^*)^{3/2}}, \quad (36)$$

where h_{pz} is the piezoelectric coefficient.

5.2.3 Alloy scattering

An alloy consisting of 50% of two binary compounds (e.g. AlN and GaN) will ideally yield a scenario in which for every atom of Al, a Ga atom exists, and importantly, distributed equally across the lattice. In reality, however, this is not the case. Naturally-occurring random alloy disorder exists in quaternary alloys [17, 18]. The variations in composition result in fluctuations in the band-edge potential, thus scattering carriers. The mobility limited by alloy

scattering is given by:

$$\mu_{al} = \frac{q\pi\hbar^4(kT)^{-1/2}}{\sqrt{2}V_c x(1-x)\xi_{AB}^2(m^*)^{5/2}}, \quad (37)$$

where ξ_{AB} represents the scattering potential at the different binary sites (A and B), and V_c is the volume of the primitive unit cell. The scattering due to alloy disorder shows a small dependence on temperature, and is also a function of the ratio of the alloys ($x[1-x]$). The mobility is therefore lowest for the most severe alloy disorder, in the case of $x = 0.5$, all else being equal (e.g. m^*).

Interestingly, recent work has suggested that for hole transport in $\text{Al}_x\text{Ga}_{1-x}\text{N}$, alloy scattering could be negligible [4]. At the GaN/AlN heterojunction, $\Delta E_C : \Delta E_V$ is suggested to be 3:1 [19], meaning holes ‘see’ less of the alloy disorder compared to electrons. Additionally, at these lower Al compositions, the effect of alloy disorder should not be significant. For these reasons, alloy scattering was neglected in this analysis.

5.2.4 Optical phonon scattering

Similar to the lattice vibrations observed in acoustic phonons, optical phonons also describe the vibrational modes in a lattice, but with the optical mode. Optical phonon scattering can be divided into non-polar optical scattering and polar optical scattering. Non-polar optical phonon scattering is not well researched in III-nitrides. Regardless, polar optical phonons impact the carrier transport to a much stronger degree, so the latter will be focused on here.

As mentioned, the relaxation time approximation requires the scattering event to be elastic. In the case of electron-phonon interaction, this is not true. An accurate closed-form analytical expression for polar optical phonon scattering-limited mobility therefore is not available. Due to the high optical phonon energy in III-nitrides ($E_{LO}^{\text{GaN}} \approx 91$ meV), optical phonon scattering is dominant only at higher temperatures. Seeger [20] developed an expression for polar optical phonon scattering-limited mobility which matches well with experimental data for the higher temperatures of interest, and has been used by others for similar analysis of III-nitrides [21]:

$$\mu_{pop} = \frac{137q\exp(T_{LO}/T)}{2m^* \sqrt{\frac{m^* c_L^2}{2kT_{LO}}} (\epsilon_\infty^{-1} - \epsilon_s^{-1}) \omega_0}, \quad (38)$$

where T_{LO} is the polar optical phonon temperature, c_L is the speed of light in vacuum, ϵ_∞

is the high frequency dielectric constant, and ω_0 is the polar optical phonon frequency. The relaxation time approximation is often assumed while acknowledging the inelastic character of the optical phonon scattering [22].

5.2.5 Impurity scattering

Impurity scattering is an extrinsic scattering mechanism, brought about by adding impurity atoms to the lattice. It can be broken into two separate mechanisms: neutral impurity scattering and ionised impurity scattering. Neutral impurities consist of non-ionised impurity atoms, which for *p*-type III-nitrides, can be a non-negligible contribution. However, compared to other scattering mechanisms present, neutral impurity scattering is calculated to be multiple orders of magnitude greater, and so is deemed negligible for this analysis.

Ionised impurity scattering, on the other hand, is often the dominant scattering mechanism in doped III-nitrides, especially at low temperatures. Using the Brooks-Herring technique for scattering due to a singly charged ionised impurity concentration, N_I , its associated scattering-limited mobility is expressed by:

$$\mu_{imp} = \frac{128\sqrt{2\pi}\epsilon_s^2(kT)^{3/2}}{N_I q^3 \sqrt{m^*} [\ln(1+\gamma) - \gamma/(1+\gamma)]}, \quad (39)$$

where $\gamma = 24\epsilon_s m^* (kT)^2 / \hbar^2 q^2$.

5.2.6 Constants and material parameters used

Table 3 lists the various constants and material parameters used in the calculations. It is noted that there is a general uncertainty surrounding the value of the effective mass of the heavy hole in III-nitrides. Values can be found in the literature from $0.8m_0$ [23, 24] (even $0.3m_0$ for the purpose to fitting to PL data [25]) to $2.2m_0$ [26]. The impact of this will be discussed later. Moreover, the question of which effective mass with regard to direction (transverse or longitudinal) has not been clearly addressed in the literature. In a typical LED, transport is longitudinal. However, in the context of a Hall effect measurement, transport should be in-plane (i.e. transverse). The anisotropy of the GaN band structure is non-negligible: $m_{hh}^{long} = 1.10m_0$ and $m_{hh}^{tran} = 1.65m_0$ [27]. In the literature, the longitudinal mass is commonly used when dealing with Hall effect measurements, and so is applied here.

Constant	Symbol	Value		Reference
Physical constants				
Elementary charge	q [C]	1.60×10^{19}		
Free electron mass	m_0 [kg]	9.11×10^{-31}		
Boltzmann’s constant	k [JK ^{−1}]	1.38×10^{-23}		
Planck’s constant	h [Js]	6.63×10^{-34}		
Reduced Planck’s constant	$\hbar$ [Js]	1.06×10^{-34}		
Speed of light in vacuum	c_L [ms ^{−1}]	2.99×10^8		
Permittivity of free space	ϵ_0 [Fm ^{−1}]	8.85×10^{-12}		
Material parameters		GaN	AlN	
Low frequency dielectric constant	ϵ_s	8.9	8.5	[10]
High speed dielectric constant	ϵ_∞	5.5	4.77	[10]
Effective mass of hole	m^*	0.8–2.2	3.53	[†] , [27]
c lattice parameter (300 K)	c [nm]	0.5185	0.4982	[28]
Material density	ρ [kg m ^{−3}]	6150	3230	[10]
Speed of sound in material	s [ms ^{−1}]	6590	9060	[10]
Deformation potential for acoustic phonon scattering	D_{ac} [eV]	8.5	9.12	[29], [30]
Piezoelectric coefficient	h_{pz} [Cm ^{−2}]	0.5	0.56	[10]
Polar optical phonon temperature	T_{LO} [K]	1057	1310	[10], [31]
Polar optical phonon frequency (×10 ¹⁴)	ω_{LO} [s ^{−1}]	1.384	1.505	[10]
Threading dislocation density	N_{dis} [cm ^{−2}]	∼ 5 × 10 ⁹		Experiment

Table 3: The physical and material constants used in the calculations of temperature-dependent scattering mechanisms. [†] See discussion on effective hole mass of GaN.

5.3 Literature Review

Hopping conduction and its anomalous effect on Hall effect measurements was first identified in the 1960s by Friedman and Holstein [32], while a detailed understanding and theory was further developed into the 1970s by Emin [33] and Holstein [34]. Despite the time since its identification, the characteristics of hopping conduction in semiconductors is not widely accepted. Substantial decreases in mobility of p -GaN at low temperatures have been attributed to the onset of hopping conduction, although not investigated in detail [3, 35–38].

In recent years, studies have experimentally investigated the effect in III-nitride materials: Gunning *et al.* [2] demonstrated a switching in sign of the Hall coefficient of p -GaN at low temperatures, which they attributed to donor compensation. Another sample with higher Mg doping exhibited a lack of carrier freezeout due to impurity band conduction; Kajikawa [8] then analysed this same lower doped material using an analysis framework of hopping conduction. In this context, fitting procedures using nearest-neighbour hopping conduction models were consistent with the presence of such a transport mechanism at low temperatures. Conversely, Oh *et al.* [39] reported the occurrence of variable range hopping conduction in a sample of p -GaN based on the temperature dependence of the resistivity ($\rho \propto T^{-1/4}$).

Recently, Rathkanthiwar *et al.* [9] examined the conduction mechanisms in graded p -AlGaIn, where they reported the presence of nearest-neighbour hopping conduction at low temperatures, from the characteristic sign change of R_H . In a follow-up work, Rathkanthiwar *et al.* [40] investigated the effect of the compositional grading on the onset of hopping conduction, suggesting that an increased gradient enhanced the transition to hopping conduction. This was proposed to be a result of a perturbation of the acceptor wavefunction in the presence of the bulk polarisation field.

As is evident from the studies surrounding this phenomenon, depending on the methods employed to analyse a particular set of Hall effect measurements, interpretations can vary. A close investigation into the temperature-dependence of the conductivity in p -(Al)GaIn, especially in the presence of a compositional gradient, is thus warranted.

5.4 Experimental details

Three samples, comparable to the p -doping approaches in the UV LEDs in Chapter 4, were grown by MOCVD for the purpose of analysis with Hall effect measurements. Figure 5.2

illustrates the structural differences in the three samples. For a reference sample, 500 nm of p -GaN with a 3% Mg/Ga ratio was grown on 500 nm of undoped GaN, after 2 μm graded $u\text{-Al}_x\text{Ga}_{1-x}\text{N}$ ($x = 0.35 - 0.25$). The difference in electrical characteristics between a p -GaN sample and a $p\text{-Al}_x\text{Ga}_{1-x}\text{N}$ ($x = 0.18$) should not be significantly different. Two graded AlGaN samples were also grown, consisting of 100 nm graded $p\text{-Al}_x\text{Ga}_{1-x}\text{N}$ ($x = 0.35 - 0$) on a 1.1 μm $u\text{-Al}_{0.35}\text{Ga}_{0.65}\text{N}$ template. The ‘co-doped’ sample employed Mg doping (Mg/III = $\sim 2.5\%$) for the graded layer, while a ‘polarisation doped’ sample had no Mg doping. Both graded samples were capped with a 20 nm p^+ -GaN layer to facilitate the Ohmic contact required for the Hall effect measurement. As such, after growth, all samples underwent *in situ* Mg activation at 790°C in a nitrogen ambient for 30 mins. After a p -GaN surface clean, Pd (40 nm) was evaporated on the corners of approximately 10 cm $\times$ 10 cm square samples for van der Pauw geometry.

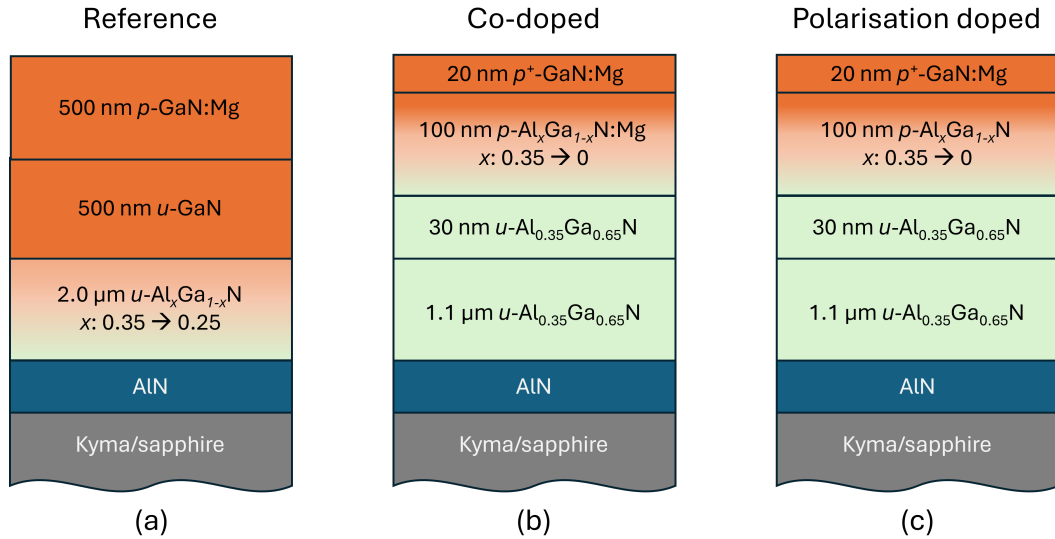


Figure 5.2: Overview of the three sample structures investigated in this work, including (a) a p -GaN reference layer, (b) a polarisation doped and Mg doped layer, and (c) polarisation doped only layer.

Temperature-dependent Hall effect measurements were carried out in the LakeShore 8404 HMS. With a closed cycle refrigerator (CCR) unit, a temperature range of $\sim 10\text{-}400\text{ K}$ is achievable. A DC magnetic field of magnitude 1.7 T can be applied to the sample. However, for samples with poor conductivity, it can become difficult to distinguish the Hall voltage from the noise present in the system (see Chapter 2). The AC field method makes it possible to access the lower mobility regime, although it employs a reduced magnetic field (0.91 T).

Given the low mobilities associated with p -type III-nitrides, the AC method was utilised for these measurements. A sufficiently high current was applied during measurements to maximise the signal to noise ratio, while maintaining a linear I-V characteristic from the contacts. For installation of the samples in the CCR insert, the samples had to be secured in place on the sample insert and electrically connected to avoid any effects from thermal contraction/expansion.

Although the cryostat in the system is capable of reaching 10 K, measurements in this study were carried out to a minimum temperature of ~ 100 K. This was in part due to the operating voltages becoming large owing to increased resistance in the contacts at lower temperatures, while needing to maintain the linear regime of the contact I-V characteristic. Additionally, below approximately 100 K, eddy currents generated in the material due to the AC magnetic field are known to cause heating effects [41]. This means the temperature in the sample may not be equal to the set temperature in the cryostat. Therefore, AC Hall effect measurements were ceased at 100 K.

SIMS measurements were carried out on both as-grown graded samples to confirm the compositional makeup of the structures, as well as the dopant profile. The results from these measurements (carried out externally) have been delayed slightly, but will be added here.

Ideally, no p -GaN contact layer would be employed to prevent any potential contribution of unwanted parallel conduction in this layer. However, attempts to make an acceptable Ohmic contact to graded AlGaN proved unsuccessful and the thin p -GaN contact layer was utilised. To see if there was any impact from the contact layer, identical samples were grown but with a 2 nm contact layer. The Hall effect measurement showed no significant change. Furthermore, the expected surface depletion width of a sample with a p -GaN contact layer would be on the order of 10 nm, therefore minimal conduction should be expected in this layer.

5.5 Strain and its effect on distributed polarisation doping

The induced polarisation charge due to compositional grading is due to both the spontaneous and piezoelectric polarisation components, of which the latter is dependent upon strain. For the purpose of distributed polarisation doping, the impact of strain on the polarisation field is crucial to understand its behaviour and ultimately that of the ionised carrier concentration.

Yasuda *et al.* [42] investigated the effects of lattice relaxation on the resulting polarisation field. In a graded $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layer intended for hole generation, they measured instead *n*-type conductivity. Further investigation revealed full relaxation *during* growth of the graded layer. Calculations of the polarisation charge considering relaxation supported the observed switch in polarity.

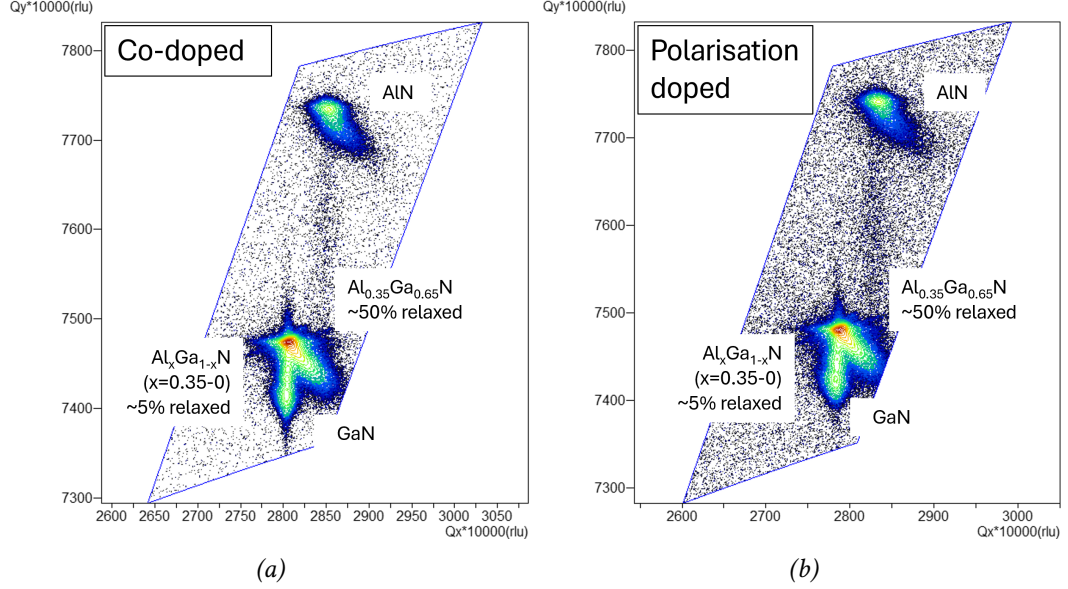


Figure 5.3: XRD RSM plots of the two graded Hall samples, (a) with and (b) without Mg doping. The $\text{Al}_{0.35}\text{Ga}_{0.65}\text{N}$ template is approx. 50% relaxed in both samples, while a minor relaxation of approx. 5% is observed in the graded $p\text{-Al}_x\text{Ga}_{1-x}\text{N}$ layer.

To confirm no such relaxation effects are present in these samples, x-ray diffraction reciprocal space map (RSM) measurements were performed to investigate the strain state of the graded layers. Figure 5.3 shows the RSM plots of the two graded structures. The $\text{Al}_{0.35}\text{Ga}_{0.65}\text{N}$ template is approximately 50% relaxed relative to the AlN connecting layer underneath. The $p\text{-Al}_x\text{Ga}_{1-x}\text{N}$ layer of interest in both samples then grows almost fully strained to the $\text{Al}_{0.35}\text{Ga}_{0.65}\text{N}$ template.

To quantify this relaxation with regards to its effect on the generated polarisation charge, the corresponding polarisation fields were calculated accounting for such a lattice relaxation. The piezoelectric and spontaneous polarisation charge components as a function of composition, x , in the layer are calculated by [43]:

$$P_{pz}(x) = 2\varepsilon(x) \left(E_{31}(x) - \frac{C_{13}(x)}{C_{33}(x)} E_{33}(x) \right) \quad (40)$$

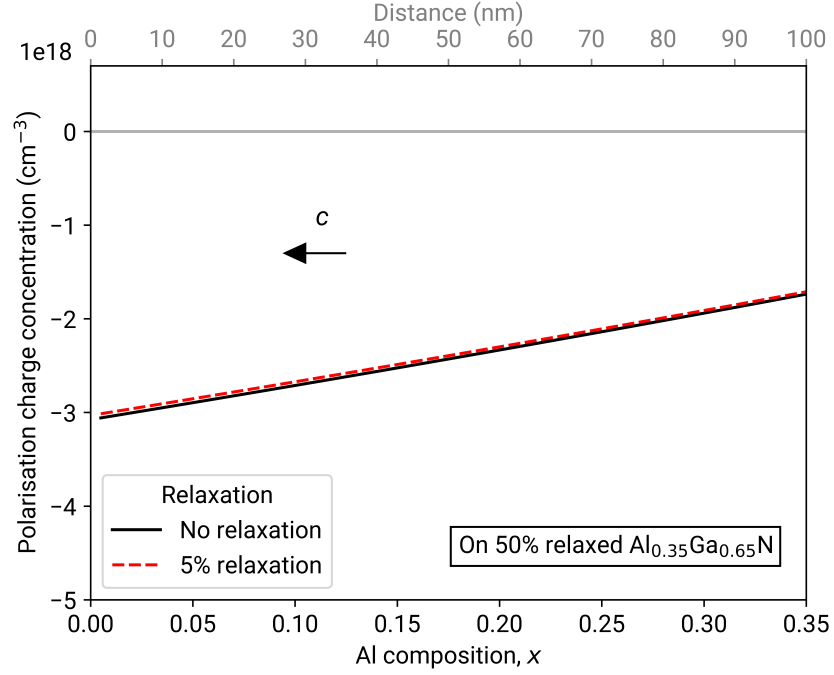


Figure 5.4: Calculated polarisation charge concentration in a 100 nm graded composition $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($x = 0.35 - 0.0$) layer, on 50% relaxed $\text{Al}_{0.35}\text{Ga}_{0.65}\text{N}$.

$$P_{sp}(x) = P_{sp}^{AlN}x + P_{sp}^{GaN}(1 - x) \quad (41)$$

where E_{31} and E_{33} are piezoelectric constants, C_{13} and C_{33} are elastic constants, ε is the strain, given by $\varepsilon = [a(x) - a_0]/a_0$ in which $a(x)$ and a_0 are the a lattice parameters at a composition x and the substrate ($\text{Al}_x\text{Ga}_{1-x}\text{N}$), respectively. The a lattice parameters were calculated from $a(x) = 0.31986 - 0.00891x$ [44], while the piezoelectric and elastic constants are taken from Ref. [45]. The net polarisation charge is then given by $P_{tot}(x) = P_{pz}(x) + P_{sp}(x)$. The three dimensional polarisation charge concentration can then be calculated by:

$$P_{tot}^{3D}(x) = \frac{\Delta P_{tot}^{2D}(x)}{\Delta d} \quad (42)$$

where Δd is the distance over which the layer is graded. The calculated polarisation charge concentration in a graded $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layer with no relaxation is plotted in Figure 5.4 (black line). The effect of a 5% gradual lattice relaxation is also calculated (dashed line). The strain state will only impact the piezoelectric polarisation component, and such a small relaxation over the thickness of the layer can be seen to have a negligible impact on the net

generated polarisation charge concentration. Therefore, we can be confident that the desired polarisation doping effect will not be effected by any significant relaxation.

5.6 Temperature-dependent Hall effect measurements

Figure 5.5a shows the conductivity, σ , of the three samples measured as a function of temperature. The p -GaN sample demonstrates a relatively stable conductivity down to approximately 250 K, after which there is a significant drop. The introduction of polarisation doping reduces the sensitivity of the conductivity to temperature, while the sample with polarisation doping only shows the most stable conductivity across the temperature range. Recalling the observations from Chapter 4, the LED with a co-doped approach demonstrated the best performance across the temperature range. The operating voltage of the polarisation doped LED (largely impacted by the p -type conductivity) did show the least dependence on temperature, similar to the conductivity of the polarisation doped structure here. There is a question about the validity of comparing a vertical transport scenario (as in the LED) with a lateral transport one (as in the Hall effect). As previously mentioned, the anisotropy of the III-nitride band structure yields different effective hole masses in the k_{xy} and k_z directions. The consequences of this have not been extensively studied. Nonetheless, with decreasing temperature, the increased operating voltages in the co-doped and reference LEDs are corroborated by the decreasing conductivities of the corresponding structures here.

Taking a closer look at the Hall mobility of the p -GaN sample, the mobility-limiting scattering mechanisms, as outlined in Section 5.2, can be calculated as a function of temperature. Figure 5.6 shows μ_H from the p -GaN sample, along with the mobility due to different carrier scattering mechanisms: ionised impurity scattering, μ_{imp} ; polar optical phonon scattering, μ_{imp} ; deformation potential scattering, μ_{dp} ; dislocation scattering, μ_{dis} ; and piezoelectric scattering, μ_{pz} . The net effect of these mobilities are represented by the total mobility, μ_{tot} , through the Matthiessen rule.

Considering the wide range of reported values for the effective mass of the heavy hole [46] and its significant impact on the different scattering mechanisms, the different mobilities have been calculated for the extreme reported values of m_{hh} ($0.8-2.2m_0$). The windows in Figure 5.6 correspond to the upper and lower bounds of m_{hh} . At higher temperatures, the mobility is dominated by polar optical phonon scattering, according to its temperature

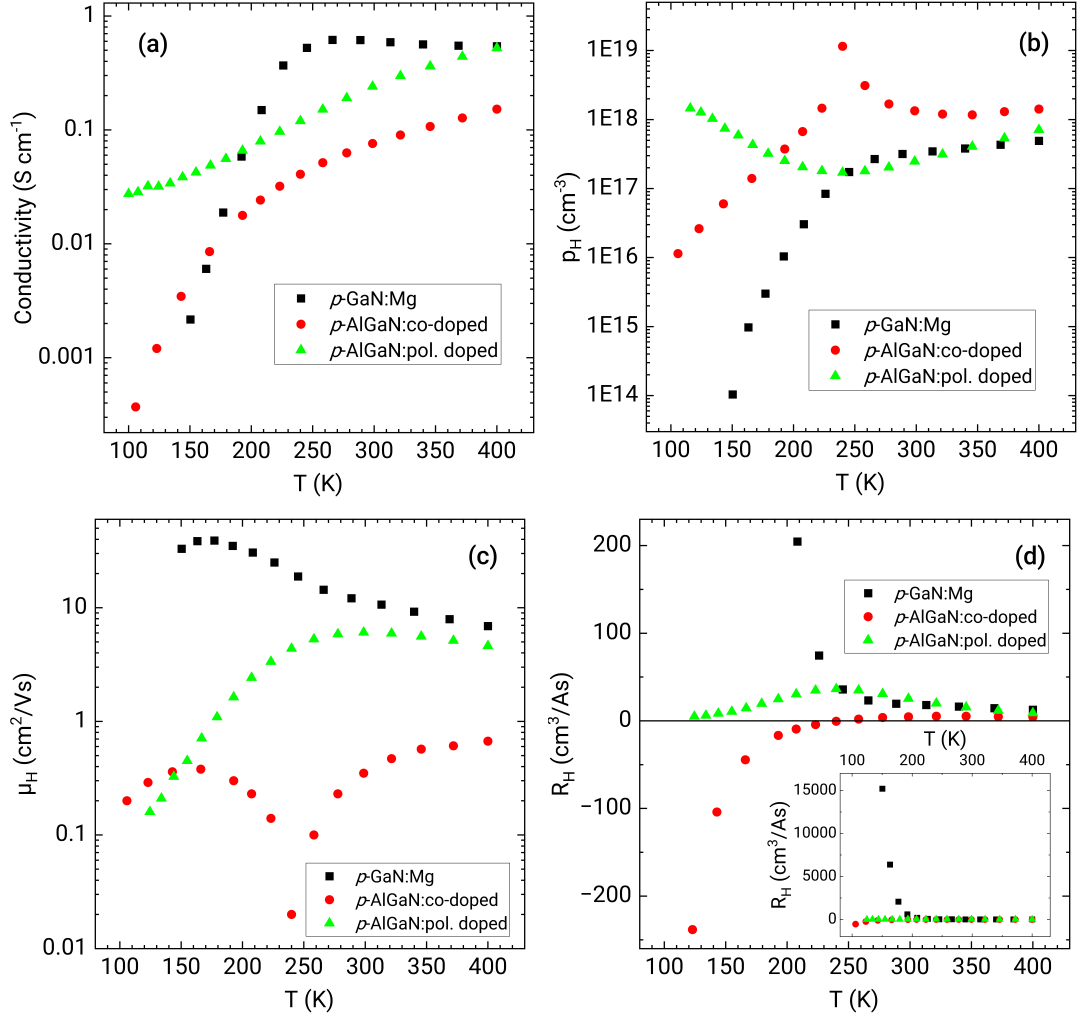


Figure 5.5: (a) Conductivity, (b) Hall hole concentration, p_H , (c) Hall mobility, μ_H , and (d) Hall coefficient, R_H , of the three p-type samples with varied doping approaches, measured as a function of temperature. Inset in (d) shows the full range of measured R_H values.

dependence of $T^{-3/2}$ (equation 38). Below ~ 200 K, ionised impurity scattering begins to dominate (equation 39). The calculated total mobility agrees well with the experimental Hall mobility for the measured temperature range, considering the range of values for m_{hh} . Although it was not possible to measure at lower temperatures, it is expected that ionised impurity scattering would further reduce the mobility. Furthermore, it is speculated that the experimental mobility may decrease even faster than the predicted mobility due to the onset of hopping conduction, frequently seen at low temperatures in p -GaN [2, 3, 8].

Further insights into the trends in the conductivity of the polarisation doped samples can be provided by considering the measured Hall hole concentrations, p_H , in conjunction with the Hall mobilities, μ_H , in Figures 5.5b and 5.5c, respectively. In the higher temperature

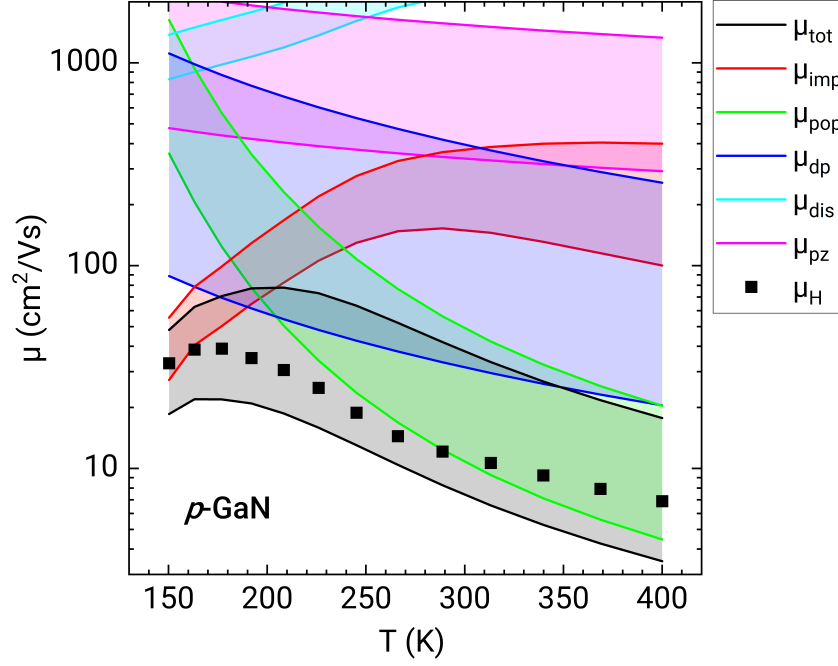


Figure 5.6: Measured Hall mobility of p-GaN plotted as a function of temperature, along with the various mobility-limiting scattering mechanisms. The upper and lower bounds of each calculated mobility correspond to an effective heavy hole mass of $0.8m_0$ and $2.2m_0$, respectively.

regime ($T > 300$ K), the co-doped sample shows the highest Hall hole concentration, with the polarisation doped and p-GaN samples exhibiting slightly lower values. Enhanced thermal activation of the acceptor combined with the polarisation doped hole concentration would agree with the observed highest hole concentration from the co-doped sample. With reducing temperature, p_H of the p-GaN sample gently decreases, before rapidly deteriorating after the onset of carrier freeze-out at around 250 K. Such a roll-off/saturation behaviour in the hole concentration at higher temperatures may suggest a relatively low Mg doping concentration ($N_A < 10^{19} \text{ cm}^{-3}$) [3, 47, 48]. Both graded samples show a more complex behaviour. The measured hole concentration of the polarisation doped sample slowly decreases to approximately 250 K, before increasing steadily at lower temperatures. The co-doped sample exhibits stable behaviour until the occurrence of a spike in p_H at around 250 K, after which it decreases.

The freezing out of holes in the p-GaN sample is accompanied by a rising Hall mobility with decreasing temperature. The Hall mobility of the polarisation doped sample exhibits a similar initial rise in mobility with decreasing temperature - likely due to freezing out of optical phonons as in Figure 5.6 - before decreasing rapidly below 250 K. The scattering

mechanism responsible for this decline at low temperatures is not clear, with none of the discussed candidates offering such a dependence of temperature (especially in the absence of μ_{imp}). The absence of ionised impurity scattering in this sample should not impact strongly the higher temperature regime ($\mu_{imp} \propto T^{3/2}$), but it does not account for this observed behaviour in polarisation doped AlGaN [4]. While it is important to consider the effect of the μ_H versus μ , the difference is on the order of one to two times, not an order of magnitude. As such, some other yet-unexplained mechanism is at play here. Alloy scattering, thought to be negligible in low Al content p -AlGaN, should otherwise have a low temperature dependence of $T^{-1/2}$. What is clear, as concluded by Kumabe *et al.* [4], is that the scattering mechanisms present in graded AlGaN differ from those in impurity doped p -GaN.

While the absence of impurity doping in the polarisation doped sample should limit the conductivity to band transport throughout the temperature range, the co-doped sample should be susceptible to hopping transport. The experimental conductivity data from the co-doped sample exhibits a linear trend when plotted against $1/T$ (Figure 5.7), with no obvious rise in conductivity towards the lower temperatures (right hand side of the plot). The activation energy associated with the conductivity is found to be ~ 74 meV. This value - notably smaller than the activation energy of Mg for this composition range - is similar in magnitude to other reports of Mg-doped p -AlGaN, which have been attributed to effects of heavy impurity doping on the carrier transport [9, 49, 50]. Hopping conduction exhibits increased conductivity at lower temperatures relative to the dominant band transport at higher temperatures. Conductivity due to hopping is calculated from $\sigma_{hop} = q\mu_{hop}p_{hop}$, where μ_{hop} (for nearest-neighbour hopping¹) is expressed by:

$$\mu_{hop} = \mu_{hop0} \left(\frac{T_3}{T} \right)^{3/2} \exp \left(\frac{T_3}{T} \right), \quad (43)$$

where μ_{hop0} and T_3 are constants. The hole concentration available for hopping transport is equivalent to the concentration of neutral impurity atoms (i.e. non-ionised carriers bound to localised acceptor atoms):

$$p_{hop} = N_A - N_A^- . \quad (44)$$

¹Variable-range hopping models also failed to provide a good fit to the experimental data. [8, 39]

The ionised impurity concentration, N_A^- , is calculated from:

$$N_A^- = \frac{N_A}{1 + \frac{g p}{N_V} \exp\left(\frac{E_A}{kT}\right)}, \quad (45)$$

where g is the degeneracy ($g = 4$), N_V is the density of states in the valence band ($N_V = 2 \left[\frac{2\pi m_{hh}^* kT}{h^2} \right]^{3/2}$), and E_A is the activation energy [3].

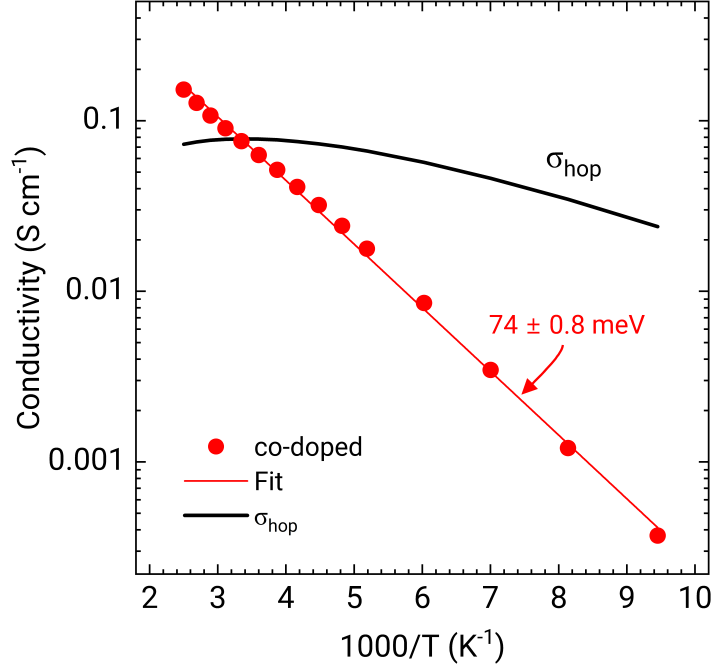


Figure 5.7: The experimental conductivity data of the co-doped sample (data points) shows a linear trend with $1/T$. An activation energy of this data is fitted to be 74 meV. Also plotted is a theoretical (from equations 43 and 44) conductivity due to hopping conduction, σ_{hop} , the values for which were taken from Table 3, as well as the following: $\mu_{hop0} = 0.03 \text{ cm}^2/\text{Vs}$, $T_3 = 450 \text{ K}$, $N_A \approx 4 \times 10^{19} \text{ cm}^{-3}$, $E_A = 250 \text{ meV}$.

The behaviour of the Hall coefficient with temperature, meanwhile, paints a clearer picture regarding hopping conduction. The definition of the Hall coefficient is recalled: the true hole concentration (mobility) and Hall hole concentration (mobility) are related through the Hall scattering factor, r_H . For valence band transport, $r_H \approx 1$ [9]. The Hall coefficient, extracted from the Hall effect measurement, offers an insight into the behaviour of r_H through the relationship:

$$R_H = r_H / qp. \quad (46)$$

In the p -GaN sample, a rapid rise in R_H below approximately 250 K (Figure 5.5d) can be

explained by a deteriorating hole concentration with no competing conduction mechanisms in this temperature range. In contrast, R_H of the co-doped sample undergoes a switch in sign at approximately 240 K, after which it reduces considerably. As discussed earlier, this phenomenon is attributed to the onset of hopping conduction. In the co-doped sample at this temperature, both p_H (Figure 5.5b) and μ_H (Figure 5.5c) experience a singularity, attributed to this switching in sign of R_H . This has similarly been observed by Kajikawa *et al.* [8] in heavily-doped p -GaN and was attributed to the transition between conduction mechanisms. The apparent enhancement in hopping conduction (from this metric) in the presence of graded Al composition has been suggested by Rathkanthiwar *et al.* [40] to be due to a spreading of the Mg acceptor state wavefunction by the induced polarisation field. However, the low Mg concentration in the p -GaN structure, hinted from the hole concentration behaviour in this sample (Figure 5.5b), may preclude this from occurring.

A possible explanation of the inconsistent signs of hopping conduction in this co-doped sample could be due to the low mobility exhibited at higher temperatures. A lower than expected conductivity at higher temperatures would render the transition to hopping conductivity invisible, as the Hall mobilities at low and high temperatures are not significantly different. There is a limited amount of data in the literature on the temperature dependent mobility of graded composition p -AlGaIn, but the room temperature conductivity here does appear to be lower compared to a similar structure [9]. As such, the conductivity switch between transport mechanisms may be ‘hidden’. One other possible explanation is the presence of a high concentration of compensating point defects in the material, interrupting the interatomic hopping motion [51]. Further detailed work would be required to gain an increased understanding of the phenomena observed here.

5.7 Conclusion

Three different p -type doping approaches have been investigated by means of temperature-dependent Hall effect measurements. Two samples employed polarisation doping through a compositional grading of Al, with one of these also having Mg doping present. A p -GaIn reference sample was also analysed for comparison. As a function of temperature, this reference sample exhibits a more ‘standard’ behaviour, with a freeze-out of carriers at low temperature. The mobility was also studied in detail, and calculations of

various mobility-limiting scattering mechanisms offered an insight into the temperature dependent behaviour. In particular, the consequence of the wide range of effective hole masses was highlighted, due to its strong influence on the mobility through $\mu \propto 1/m_{hh}^n$, where n is often greater than 1.

In contrast, the samples with polarisation doping exhibited a complex behaviour. The sample with polarisation doping only shows a more stable dependence of conductivity with reducing temperature compared to the p -GaN sample. The co-doped sample, although demonstrating a less severe decay of conductivity, still decreases below approximately 200 K. The LEDs in Chapter 4 with corresponding p -doping approaches demonstrated not dissimilar temperature dependences compared to these structures. A polarisation doping only approach yields the conductivity with the lowest temperature sensitivity.

Two exclusive metrics are generally investigated to detect for the presence of hopping transport at lower temperatures: a transition from the linear conductivity decay due to band transport (on a log scale versus $1/T$); and a switching in sign of the Hall scattering factor (and hence Hall coefficient). At lower temperatures, no apparent transition in the conductivity was observed in this co-doped sample, although a much reduced activation energy was noted suggesting some impurity band conduction mechanism.

The Hall coefficient of the co-doped sample, meanwhile, exhibited interesting behaviour, with a reversal in sign below 250 K. The contradictory indicators (Hall coefficient versus conductivity) of hopping transport in this sample could be due to an anomalously low mobility (hence conductivity) at higher temperatures, effectively hiding the transition expected from the conductivity due to valence band transport, to that of hopping transport at lower temperatures. That the graded sample showed signs of hopping conduction and the p -GaN sample did not, supports a recent study suggesting the effect of the polarisation field on the Mg wavefunction [50], although the Mg doping concentrations must also be considered.

The results from this study highlight the complexity involved when analysing Hall effect measurement results, particularly of heavily doped p -type III-nitride materials. Assumptions are regularly made during the interpretation (such as the effective mass of the carrier), and while some assumptions are necessary in order to initiate an analysis, in reality, care must be taken in the application of such assumptions. A single room-temperature result may paint a particular picture of the doping in a sample, however, as a function of temperature, an entirely different story may be revealed. Ultimately, the presence of the polarisation field has

significant impacts on the conduction mechanisms in graded Al AlGa_N:Mg.

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Conclusion and future work

Conclusion

The target outcome for this thesis was to realise UV LEDs emitting in the range of 320 to 340 nm for integration in a diagnostic endoscope for fluorescence spectroscopy. The requirements of the LED include a narrow linewidth and low background emission so as to be able to controllably target specific fluorophores, while not interfering with the detection at nearby wavelengths. An output power objective was set at 1 mW, to sufficiently excite the fluorophores. While UV LEDs generally struggle to match their blue counterparts in device performance, LEDs in this far-UVA wavelength range demonstrate especially poor efficiencies. This is largely due to challenges in the growth of thick, high quality templates. The context for this thesis was introduced in Chapter 1, describing such challenges and the need for more efficient UV LEDs. The methods and theory used in the analysis throughout the thesis are described in Chapter 2.

The difficulty in realising devices with thick *n*-type buffer layers at this Al composition range means current crowding is a prominent issue. Chapter 3 presents a study on arrays of μ LEDs with interdigitated contacts, which demonstrated improved efficiencies compared to standard device sizes. This was in part credited to an enhanced distribution of current with decreasing mesa diameter and increasing density of interdigitated contacts.

Building on previous work in our group, a novel template was utilised for LED growth, and this was detailed in Chapter 3. Thick *n*-type buffer layers at this composition range are challenging because of the build-up of tensile strain due to the interplay of the Si dopant and the high threading dislocation density stemming from the large lattice mismatch. A template development strategy - termed “micro-honeycomb” (μ -HC) - consisted of patterning and subsequent regrowth of AlGaIn, forming faceted sidewalls. Through the expansion of the facets (and elimination of the *c*-plane material), the threading dislocations are theorised to self-annihilate. After further growth, the patterned template was coalesced, ready for subsequent LED growth. An LED structure was grown on the μ -HC template, which, after fabrication, showed an increase in EQE of two times compared with a reference LED, co-loaded in the growth run. This was attributed to the decrease in the TDD, confirmed to be halved by XRD. This improvement was in spite of increased absorption in the template owing to Ga desorption during the template development, so the efficiency improvement can

be potentially greater.

The first experimental demonstration of a boron-containing UV LED was also presented in Chapter 3. Previous theoretical works have suggested the potential benefits to radiative recombination with the addition of small amounts of BN through lattice matching. A UV LED with nominally 1% B in the QWs was grown and fabricated alongside an identical LED without B. SIMS measurements confirmed the presence of B in the quantum wells, but with an unexpected cumulative behaviour with subsequent QWs. This can be explained by the reported surfactant nature of B in III-nitrides. Furthermore, voids were observed in the active region of the B containing LED, previously observed in B(Al)GaN QWs. Nonetheless, an increase in WPE was observed with the addition of B, with increased output powers at lower currents, demonstrating the promise of B-containing III-nitrides.

The work in this thesis explored different avenues towards pursuing the two primary metrics: output power and spectral purity. By reviewing UV LED challenges and obstacles to reaching the device objectives, the *p*-part of the LED was quickly identified as an area for potential improvement of both device specifications. The *p*-type doping of III-nitrides is characterised by relatively low hole concentrations and mobilities, which reduce the efficiency through inter-related effects such as electron overflow, reduced radiative recombination, poor hole injection and high operating voltages. Electron overflow is especially damaging as the electrons that have reached the *p*-region can recombine radiatively through defect states, producing unwanted long wavelength luminescence. Polarisation doping, a technique unique to III-nitrides, was investigated in Chapter 4 as a potential solution.

Three UV LED structures were grown, identical except for the *p*-doping technique. A ‘co-doped’ LED possessed both polarisation doping and impurity doping; a ‘polarisation doped’ LED relied solely on this technique; and a ‘reference’ LED utilised conventional impurity doping only. At room temperature, the co-doped LED demonstrated the highest output power, followed by the reference and then the polarisation doped LED. Numerical simulations supported this trend, with the co-doped approach showing an increased hole concentration, and improved electron blocking and hole injection. Significantly, it was found that in the absence of Mg, the parasitic luminescence band around 400 nm (present in both Mg-containing LEDs) was eliminated. This emission can be attributed to electron overflow and subsequent recombination through Mg-related defect states. Through further

optimisation, it is expected that a better trade-off between performance and reduced parasitic luminescence can be achieved.

Furthermore, the temperature-independent nature of polarisation doping warranted a temperature-dependent study. This revealed a temperature-insensitive operating voltage in the polarisation doped LED down to 12 K, while the others showed increased dependence on temperature. Additionally, analysis of the temperature dependence of the parasitic luminescence indicated enhanced activation of the Mg acceptors in the presence of polarisation doping.

Chapter 5 explores the temperature-dependent conduction mechanisms of *p*-type III-nitrides, with a specific focus on graded AlGaIn. Three different doping approaches were investigated: a reference *p*-GaIn:Mg sample; a ‘co-doped’ (polarisation doping and impurity doped) *p*-Al_xGa_{1-x}In:Mg ($x = 0.35 - 0$); and polarisation doping only sample *p*-Al_xGa_{1-x}In ($x = 0.35 - 0$). As a function of temperature, the reference *p*-GaIn sample showed a carrier freeze-out at around 250 K, with no signs of alternative conduction mechanisms to the lowest measured temperature. The mobility increased with decreasing temperature before beginning to drop off at low temperatures. This was explained through calculations of various scattering mechanisms to be the result of optical phonon scattering and ionised impurity scattering dominating at higher and lower temperatures, respectively.

The co-doped sample exhibited complex behaviour: the conductivity showed no signs of a transition in transport mechanisms at lower temperatures. However, the Hall coefficient showed a reversal in sign at around 250 K, which is characteristic of the onset of hopping conduction. The lack of an observed transition in conductivity could be due to an abnormally low mobility at higher temperatures effectively masking the transition. The polarisation doping only sample showed no such sign change in R_H , which is expected given the lack of impurity doping present. Despite the complicated results, the enhanced presence of a hopping conduction path in the presence of a polarisation field would tend to agree with recent studies on such effects.

In conclusion, while the target output power of 1 mW was not achieved, spectrally pure UV LEDs emitting in the target wavelength range were realised. The optimised *p*-doping technique exhibited much reduced parasitic wavelength emission, with increased efficiency. Improvements in crystal quality will certainly result in a boost in output power, although closing the gap to 1 mW would still require additional improvements. Moreover, the

characterisation carried out in this work was on-wafer: high-reflectivity packaging could boost the output power, although likely not by the orders of magnitude required to hit 1 mW.

Future work

Due to the finite time constituting a PhD, not all observations can be explored to the desired extent. One of the intrinsic ironies of a PhD is that with increasing knowledge and insights in one's latter years, one has increasingly-diminishing time to explore such gained knowledge. This section discusses some potentially interesting topics for which I had insufficient time to investigate, and may be worth the time of future researchers.

The work surrounding the μ -HC template in Chapter 3 provided a number of avenues of exploration: LED template development after coalescence, as well as a semi-polar facet LED topology. While both studies offered promising results, there is potential for improvement. With regard to the coalesced template, it was observed that with each subsequent growth during the development stages, the crystal quality deteriorated. In future, performing the development of the template in one to two growth runs should result in an order of magnitude reduction in TDD, as opposed to the achievement of a half presented here.

The SPF-LED approach has the potential for enhanced LEE owing to the angled sidewalls, as well as improved radiative recombination due to the reduced polarisation fields. However, further optimisation of the epitaxial structure is required, as Al incorporation can be different between competing crystal planes. With hindsight, the incorrect orientation of the starting pattern was employed. This resulted in the undesirable presence of (more defective) *c*-plane material. The rotation can be easily altered to result in a more preferable ratio of SPF to *c*-plane area, and should be employed for future experiments.

Also in Chapter 3, a SIMS measurement of the B-containing LED showed a marked reduction in Mg incorporation compared to the reference LED structure (despite identical *p*-type growth conditions). The reason for this is not understood, although the effect has previously been observed after correspondence with a SIMS expert². This should be of the utmost importance for future work on B-containing III-nitride structures, as *p*-type conductivity is already a crucial element of a device's efficacy.

Arrays of μ LEDs were investigated, and despite the improvements in efficiencies, the

²Private correspondence, September 2023

non-radiative recombination stemming from surface states is thought to be a limiting factor (which was indicated from the increasing current density at which the peak EQE occurred with decreasing mesa size). This effect must be mitigated if the μ LEDs are to be developed further.

The results from the experiments discussed in Chapter 4 indicated that polarisation doping in the presence of impurity doping resulted in enhanced device performance for low to medium Al compositions. This is in contrast to recent work suggesting that for higher Al compositions, impurity doping can degrade the benefits of polarisation doping. This result is attributed to the lower activation energy of Mg in this lower composition range, but further work could investigate this hypothesis by employing techniques such as deep-level trap spectroscopy.

Additionally, the LEDs with different p -type doping strategies could be studied with a focus on device lifetime and degradation. A large body of work by the group of Prof. Matteo Meneghini in University of Padua has indicated the link between the degradation of UV LEDs and Mg doping. The proposed mechanism is the diffusion of H from the p -type material into the active region during device operation, creating non-radiative recombination centres. Polarisation doping can potentially mitigate this effect through the reduced H incorporation without Mg doping. Furthermore, from simulations, grading of the composition in the p -type region should remove the presence of a 2DHG at the p -contact. This could reduce the effect of Auger recombination, which has also been shown to be a major contributing factor towards degradation of UV LEDs. Thus, device lifetime studies and associated analysis techniques could be of interest in relation to the p -type doping approaches.

Appendix

The TCAD package Silvaco was employed for the numerical simulations included in this thesis. The mesh is important factor to consider when defining the framework of a simulation. It determines how many spatial datapoints should be included in the calculations. A tighter mesh will results in a more accurate simulation, with the trade-off being a requirement of more compute. An appropriate mesh was therefore chosen to balance calculation time and accuracy. To maximise this performance trade-off, one can create finer meshing in the more critical areas of structure. The active region is a numerically taxing region of the LED structure: high carrier concentrations, carrier recombination, carrier scattering, and other phenomena over a small distance of under 100 nm demands fine meshing. However, the centre of a 1 μm layer $n\text{-AlGaIn}$ layer with contrastingly require little detail to ensure accurate calculations. As a result a region-dependent mesh was defined in the LED structure. Trial and error simulations were performed to identify the minimum grid spacings to ensure valid calculations, while minimising calculation time.

Similarly, the size of the simulated area will determine the compute required. There is no need to simulate the area of a real-life device ($>100\text{ }\mu\text{m}$) as we are dealing here with a quasi-one dimensional simulation on a much smaller scale. As a result, a 200 nm lateral dimension (x) was selected. For simplicity, a vertical structure was chosen, which neglects lateral effects stemming from current crowding. However, as the primary area of focus in these experiments is the relative carrier transport and device performance between doping regimes, the vertical structure was employed to simplify the calculations and interpretations.

Another area that requires careful consideration is the magnitude of the polarisation fields used in the calculation. The parameter `POLAR.SCALE` allows the user to apply a multiplier to the magnitude of the polarisation fields calculated in the models. A value of 0.5 was found to result in calculated hole concentrations corresponding to the expected values for such a compositional grading (equation 25). This has been found to be case anecdotally among researchers in the same area of research.

Below is code used in Silvaco DeckBuild version 5.2.29.R to simulate the UV LED structures with varied p -doping approaches.

Input deck

```
go devedit
work.area x1=0 y1=-2.1350 x2=0.2 y2=0.01
# devedit 2.8.5.R (Wed Mar 1 14:54:21 PST 2006)
# libMeshBuild 1.24.3 (Wed Mar 1 14:53:36 PST 2006)
# libSVC_Misc 1.28.0 (Tue Jan 31 20:56:53 PST 2006)
# libsflm 7.2.13 (Wed Feb 22 00:28:57 PST 2006)
# libSDB -0.005.3 (Tue Feb 21 23:41:46 PST 2006)
# libSvcFile 1.12.0 (Tue Jan 17 01:48:56 PST 2006)
# libDW_Version 3.2.0 (Mon Jan 16 23:45:02 PST 2006)

set file_name="file_name"
set variation="variation"
set voltage=3p9V

set Grading_Thick=0.05
set p_AlGaN_MF1=0.35
set p_AlGaN_MF2=0.0

set QW_comp=0.08
set QB_comp=0.18

set iter_id = 1
set grid_tolerance = 0.05

# =====
# SECTION: DEFINING STRUCTURE

# Top Electrode
region reg=12 name=anode mat=Nickel elec.id=1 work.func=0 \
color=0xfefe97 pattern=0xe
polygon="0.03,-2.125 0.03,-2.135 0.17,-2.135 0.17,-2.125"
constr.mesh region=12 default

# p-GaN 10nm
region reg=11 mat=GaN color=0xcba2a2 pattern=0xd \
polygon="0,-2.1150 0,-2.1250 0.2,-2.1250 0.2,-2.1150"
impurity id=1 region.id=11 imp=Acceptors peak.value=1e+18 \
ref.value=1e+16 #y1=-2.115 y2=-2.125 rolloff.y=none \
#conc.func.y=dist coef.y=$Grading_Thick conc.scale.y=1

# Graded p-AlGaN 50nm
#region reg=10 mat=AlGaN color=0xcba2a2 pattern=0xd \
polygon="0,-2.0650 0,-2.1150 0.2,-2.1150 0.2,-2.0650"
#impurity id=1 region.id=10 imp="Composition Fraction X" \
peak.value=$p_AlGaN_MF1 ref.value=$p_AlGaN_MF2 y1=-2.065 \
y2=-2.115 rolloff.y=low conc.func.y=dist coef.y=0.05 \
#conc.scale.y=0.5
#impurity id=2 region.id=10 imp=Acceptors peak.value=1e+18 \
ref.value=1e+16 #y1=-2.065 y2=-2.115 rolloff.y=none \
#conc.func.y=dist coef.y=$Grading_Thick conc.scale.y=1
```

```

# OR

# Uniform p-AlGaIn 50nm
region reg=10 mat=AlGaIn color=0xcba2a2 pattern=0xd \
polygon="0,-2.0650 0,-2.1150 0.2,-2.1150 0.2,-2.0650"
impurity id=1 region.id=10 imp="Composition Fraction X" \
peak.value=0.18 ref.value=0 # y1=-2.065 y2=-2.115 \
rolloff.y=low conc.func.y=dist coef.y=0.05 #conc.scale.y=0.5
impurity id=2 region.id=10 imp=Acceptors peak.value=1e+18 \
ref.value=1e+16 #y1=-2.065 y2=-2.115 rolloff.y=none \
#conc.func.y=dist coef.y=$Grading-Thick conc.scale.y=1

# EBL p-doped
region reg=9 mat=AlGaIn color=0xcba2a2 pattern=0xd \
polygon="0,-2.0450 0,-2.0650 0.2,-2.0650 0.2,-2.0450"
impurity id=1 region.id=9 imp="Composition Fraction X" \
peak.value=0.35 ref.value=0.35 #y1=-2.065 y2=-2.0350 \
rolloff.y=none conc.func.y=dist coef.y=0.03 conc.scale.y=1
impurity id=2 region.id=9 imp=Acceptors peak.value=1e+18 \
ref.value=1e+16 #y1=-2.045 y2=-2.125 rolloff.y=none \
#conc.func.y=dist coef.y=$Grading-Thick conc.scale.y=1

# EBL 1/3 undoped 10nm
region reg=8 mat=AlGaIn color=0xcba2a2 pattern=0xd \
polygon="0,-2.0350 0,-2.0450 0.2,-2.0450 0.2,-2.0350"
impurity id=1 region.id=8 imp="Composition Fraction X" \
peak.value=0.35 ref.value=0.35 #y1=-2.045 y2=-2.035 \
rolloff.y=none #conc.func.y=dist coef.y=$Grading-Thick/2 \
conc.scale.y=1

# QB #3 10nm
region reg=7 mat=AlGaIn color=0xcba2a2 pattern=0xd \
polygon="0,-2.025 0,-2.035 0.2,-2.035 0.2,-2.025"
impurity id=1 region.id=7 imp="Composition Fraction X" \
peak.value=$QB_comp ref.value=0.35 #rolloff.y=none \
#y1=-2.035 y2=-2.025 #conc.func.y=dist \
coef.y=$Grading-Thick/2 conc.scale.y=1

# QW #2 2.5nm
region reg=6 mat=AlGaIn color=0xcba2a2 pattern=0xd \
polygon="0,-2.0225 0,-2.0250 0.2,-2.0250 0.2,-2.0225"
impurity id=1 region.id=6 imp="Composition Fraction X" \
peak.value=$QW_comp ref.value=0 #y1=-2.0225 y2=-2.025 \
rolloff.y=none #conc.func.y=dist coef.y=$Grading-Thick/2 \
conc.scale.y=1

# QB #2 10nm
region reg=5 mat=AlGaIn color=0xcba2a2 pattern=0xd \
polygon="0,-2.0125 0,-2.0225 0.2,-2.0225 0.2,-2.0125"
impurity id=1 region.id=5 imp="Composition Fraction X" \
peak.value=$QB_comp ref.value=0 #y1=-2.0125 y2=-2.0225 \
rolloff.y=none #conc.func.y=dist coef.y=$Grading-Thick/2 \

```

```

conc.scale.y=1

# QW #1 2.5nm
region reg=4 mat=AlGaIn color=0xcba2a2 pattern=0xd \
polygon="0,-2.01 0,-2.0125 0.2,-2.0125 0.2,-2.01" \
impurity id=1 region.id=4 imp="Composition Fraction X" \
peak.value=$QW_comp ref.value=0 #y1=-2.01 y2=-2.0125 \
rolloff.y=none #conc.func.y=dist coef.y=$Grading_Thick/2 \
conc.scale.y=1

# QB #1 10nm
region reg=3 mat=AlGaIn color=0xcba2a2 pattern=0xd \
polygon="0,-2.0 0,-2.01 0.2,-2.01 0.2,-2.0" \
impurity id=1 region.id=3 imp="Composition Fraction X" \
peak.value=$QB_comp ref.value=0 #y1=-2.0 y2=-2.01 \
rolloff.y=none #conc.func.y=dist coef.y=$Grading_Thick/2 \
conc.scale.y=1

# n-AlGaIn 2000nm
region reg=2 mat=AlGaIn color=0xcba2a2 pattern=0xd \
polygon="0,0 0,-2.0 0.2,-2.0 0.2,0" \
impurity id=1 region.id=2 imp=Donors peak.value=2e+18 \
ref.value=0 # rolloff.y=none
impurity id=2 region.id=2 imp="Composition Fraction X" \
peak.value=0.35 ref.value=0.25 y1=0.0 y2=-2.0 \
rolloff.y=low conc.func.y=dist coef.y=2.0 # conc.scale.y=1

# Bottom Electrode
region reg=1 name=cathode mat=Aluminum elec.id=1 \
work.func=0 color=0xfefe97 pattern=0xe \
polygon="0.03,0.010 0.03,0 0.17,0 0.17,0.01" \
constr.mesh region=1 default

# =====
# SECTION: SET MESHING PARAMETERS

base.mesh height=0.1 width=0.1

bound.cond !apply max.slope=28 max.ratio=100 rnd.unit=0.0001 \
line.straightening=1 align.Points when=automatic

#
imp.refine min.spacing=0.02
#
constr.mesh max.angle=100 max.ratio=300 max.height=0.001 \
max.width=0.003 min.height=0.0001 min.width=0.0001

#
constr.mesh type=Semiconductor default
#
constr.mesh type=Insulator default
#
constr.mesh type=Metal default max.angle=180

```

```

#
constr.mesh type=Other default
#
constr.mesh type=Metal region=1 default max.angle=90 \
max.height=0.01
constr.mesh type=Semiconductor region=2 default \
max.height=0.02
constr.mesh type=Semiconductor region=3 default \
max.height=0.001
constr.mesh type=Semiconductor region=4 default \
max.height=0.0001
constr.mesh type=Semiconductor region=5 default \
max.height=0.001
constr.mesh type=Semiconductor region=6 default \
max.height=0.0001
constr.mesh type=Semiconductor region=7 default \
max.height=0.001
constr.mesh type=Semiconductor region=8 default \
max.height=0.001
constr.mesh type=Semiconductor region=9 default \
max.height=0.001
constr.mesh type=Semiconductor region=10 default \
max.height=0.001
constr.mesh type=Semiconductor region=11 default \
max.height=0.002
constr.mesh type=Metal region=12 default max.angle=90 \
max.height=0.01
Mesh Mode=MeshBuild

base.mesh height=0.1 width=0.1

bound.cond !apply max.slope=28 max.ratio=100 \
rnd.unit=0.0001 line.straightening=1 align.Points \
when=automatic

# =====

structure outfile="$file_name"_"variation".str
save outf="$file_name"_"variation"_0.str

#quit

go atlas simflags="-P 3"
#go atlas simflags="-V 5.36.0.R"

# 2 Dimensional Structure by DevEdit
# Expand 10 times to x-direction
mesh infile="$file_name"_"variation".str scale.x=1

save outf="$file_name"_"variation"_0.str

#quit

go atlas simflags="-P 4"

```

```

#go atlas simflags="-V 5.36.0.R"
mesh infile="$"file_name"$"variation"_0.str width=1

# =====
# SECTION: MATERIAL MODELS

region num=4 modify LED name=qwell
region num=6 modify LED name=qwell
#contact name=anode num=1 workfun=4.28

models polarization calc.strain polar.scale=0.5
#models incomplete
models SRH auger
model region=3 OPTR
model region=4 OPTR
model region=5 OPTR
model region=6 OPTR
model region=7 OPTR
model region=8 OPTR
model region=9 OPTR
model region=10 OPTR
model region=11 OPTR
model k.p
models chuang spontaneous

models print

mobility material=AlGaN mun0=100 mup0=10
mobility material=GaN mup0=10

# =====
# SECTION: OUTPUT FLAGS and METHOD

output con.band val.band band.param charge polar.charge e.mobility \
      h.mobility permi flowlines

METHOD NEWTON AUTONR GUMMEL climit=1e-6 maxtrap=7
# GUMMEL u.srh u.auger u.radiative las.loss las.refr

# =====
# SECTION: INITIAL SOLUTION AND SOLVING

solve init
output con.band val.band band.param charge polar.charge e.mobility \
      h.mobility permi flowlines
# Thermal equilibrium
save outf="$"file_name"$"variation"_therm-eq.str

#quit

```

```

# set probes for rad. recombination and tot. recombination in QWs
probe name="Recombination" recombination integrate rname=qwell
probe name="Radiative" Radiative integrate rname=qwell

log outf="$file_name"_"variation".log

#solve prev
solve v1=0.000001
solve v1=0.00001
solve v1=0.0001
solve v1=0.001
solve v1=0.01
solve v1=0.05
solve v1=0.1

# FOR FINE VOLTAGE SWEEP
solve vstep=0.1 vfinal=3.9 name=anode
save outf="$file_name"_"variation"_"voltage".str
save spectrum="$file_name"_"variation"_"voltage".spc \
lmin=0.28 lmax=0.380 nsamp=10000

# FOR COARSE VOLTAGE SWEEP TO 3.9 V
#solve vanode=1.0
#solve vanode=2.0
#solve vanode=3.0
#solve vanode=3.9
#save outf="$file_name"_"variation"_"voltage".str
#save spectrum="$file_name"_"variation"_"voltage".spc \
lmin=0.28 lmax=0.380 nsamp=10000

# =====
# SECTION: EXTRACT STATEMENTS

# Calc IQE [radiative recombination]/[recombination] in QWs
extract init infile="$file_name"_"variation".log"
extract name="IQE" curve(1e3*i."anode", \
100*probe."Radiative"/probe."Recombination") \
outfile="$file_name"_"variation"_IQE.dat"

# Calculate IE
# Procedure: Integrates carrier concentration in total \
structure & carrier concentration in active region
# 'x.val' sets cutline location
# n
extract init infile="$file_name"_"variation"_"voltage".str"
#extract name="n_depth" curve(depth,impurity="electron conc" \
x.val=0.1 material="All") outfile="n_depth.dat"
extract name="Total-electron" area from \
curve(depth,impurity="electron conc" x.val=0.1 material="All") \
where x.min=0.011 and x.max=2.01 \
outfile="$file_name"_"variation"_"voltage"_total_n.dat"
extract name="ActiveRegion-electron" area from \

```

```

curve(depth,impurity="electron conc" x.val=0.1 material="All") \
where x.min=2.01 and x.max=2.045 \
outfile="$file_name"_"variation"_"voltage"_activeRegion-n.dat"

# p
extract name="Total_hole" area from \
curve(depth,impurity="hole conc" x.val=0.1 material="All") \
where x.min=0.011 and x.max=2.01 \
outfile="$file_name"_"variation"_"voltage"_total-p.dat"
extract name="ActiveRegion_hole" area from \
curve(depth,impurity="hole conc" x.val=0.1 material="All")\
where x.min=2.01 and x.max=2.045 \
outfile="$file_name"_"variation"_"voltage"_activeRegion-p.dat"

set IE_n=$ActiveRegion_electron/$Total_electron
set IE_p=$ActiveRegion_hole/$Total_hole

quit

```