Optical Characterisation of Group III – Nitride Semiconductors

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Catherine Ann Othick

School of Physics and Astronomy
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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>2T</td>
<td>2-temperature [growth method]</td>
</tr>
<tr>
<td>BBO</td>
<td>Beta barium borate</td>
</tr>
<tr>
<td>BL</td>
<td>Blue Luminescence [band]</td>
</tr>
<tr>
<td>CL</td>
<td>Cathodoluminescence</td>
</tr>
<tr>
<td>CW</td>
<td>Continuous wavelength</td>
</tr>
<tr>
<td>DAP</td>
<td>Donor acceptor pair</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive x-ray</td>
</tr>
<tr>
<td>EL</td>
<td>Electroluminescence</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>HR-TEM</td>
<td>High resolution transmission electron microscopy</td>
</tr>
<tr>
<td>HR-XRD</td>
<td>High resolution X-ray diffraction</td>
</tr>
<tr>
<td>h-ScN</td>
<td>Hexagonal phase scandium nitride</td>
</tr>
<tr>
<td>IQE</td>
<td>Internal Quantum Efficiency</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann’s constant</td>
</tr>
<tr>
<td>LED</td>
<td>Light emitting diode</td>
</tr>
<tr>
<td>LD</td>
<td>Laser diode</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular beam epitaxy</td>
</tr>
<tr>
<td>ML</td>
<td>Mono-layer</td>
</tr>
<tr>
<td>MOCVD</td>
<td>Metalorganic chemical vapour deposition</td>
</tr>
<tr>
<td>MOVPE</td>
<td>Metalorganic vapour phase epitaxy</td>
</tr>
<tr>
<td>MQW</td>
<td>Multiple quantum wells</td>
</tr>
<tr>
<td>$P_{\pi}$</td>
<td>Piezoelectric polaisation</td>
</tr>
<tr>
<td>$P_{\phi}$</td>
<td>Spontaneous polarisation</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PLE</td>
<td>Photoluminescence excitation</td>
</tr>
<tr>
<td>PMT</td>
<td>Photomultiplier tube</td>
</tr>
<tr>
<td>QD</td>
<td>Quantum dot</td>
</tr>
<tr>
<td>QW</td>
<td>Quantum Well</td>
</tr>
<tr>
<td>RGB</td>
<td>Red-green-blue</td>
</tr>
<tr>
<td>RHEED</td>
<td>Reflection high energy electron diffraction</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>rf</td>
<td>Radio frequency</td>
</tr>
<tr>
<td>RL</td>
<td>Red luminescence [band]</td>
</tr>
<tr>
<td>RSM</td>
<td>Reciprocal space map</td>
</tr>
<tr>
<td>SEM-CL</td>
<td>Scanning Electron Microscopy – Cathodoluminescence</td>
</tr>
<tr>
<td>SHG</td>
<td>Second harmonic generator</td>
</tr>
<tr>
<td>STEM-HAADF</td>
<td>Scanning transmission electron microscopy – high-angle angular dark field transmission electron microscopy</td>
</tr>
<tr>
<td>SQW</td>
<td>Single quantum well</td>
</tr>
<tr>
<td>$T_{gw}$</td>
<td>Temperature of quantum well growth</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>VASP</td>
<td>Vienna \textit{ab initio} simulation package</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>YL</td>
<td>Yellow luminescence [band]</td>
</tr>
</tbody>
</table>
Abstract

Optical Characterisation of Group III – Nitride Semiconductors
Catherine Ann Othick, Ph.D., The University of Manchester, 2011

Research presented in this thesis focuses on the optical characterisation of InGaN/GaN quantum well (QW) and quantum dot (QD) structures and ScGaN epilayers, supported by microscopy results from the University of Cambridge.

Reported in the first part of this thesis are the optical properties of sets of high In fraction (~25%) multiple QW structures designed to emit in the green part of the spectrum. Sets of InGaN/GaN QW structures were investigated which were grown using traditional methods but by varying QW growth temperature. These samples were found to have very broad photoluminescence linewidths and 1 – 10 % room temperature IQE. Changes to the growth procedures had little effect on the improvement of the samples’ luminescence properties. It was found that the first two wells of these samples were thicker and/or contained more indium than subsequent wells grown in the stack. The added thickness and/or indium content of these InGaN/GaN QWs resulted in lower energy emission than the rest of the QW stack, broadening the photoluminescence linewidth and decreasing the IQE.

A modification of the growth procedures was developed to ensure that the individual QWs have as similar properties as possible so that the contribution to the PL linewidth due to well-to-well variations was significantly reduced. These modified procedures were used to produce new sets of InGaN/GaN 10 QW structures. These new structures showed a marked increase (~30%) in IQE and a significant decrease in PL linewidth. Furthermore, a set of 1, 3, 5 and 10 QW structures grown under modified growth procedures were investigated to determine the optimum number of QWs needed. It was found that 3 QWs provided a significant improvement to the IQE over the 1 QW samples; however, no additional improvements were realised by growing additional QWs.

The second part of this thesis explores the use macroscopic optical spectroscopy methods to study the properties of QDs. InGaN QDs are typically studied using spatially resolved techniques which allow for the study of individual dots in a structure. A sample which was known to contain InGaN QDs was investigated; however, it was determined that macroscopic spectroscopic techniques were unable to determine the existence of QDs in the structure.

Difficulties creating highly efficient green or near-UV light emitting InGaN semiconductors have lead to an interest in alternative material structures. One suggested alternative is to replace indium with the Group IIIB transition metal, scandium. The final part of this thesis explores a series of ~ 260 µm thick MBE-grown ScGaN layers on 500 µm thick MOCVD-grown GaN templates. It was found that these materials, believed to contain up to 8% scandium, emit a broad spectrum violet luminescence. This broad luminescence spectrum resolves into multiple, narrower features with either increased substrate temperature during growth or by decreasing the scandium effusion cell temperature. The absorption spectrum, on the other hand, only shows evidence of GaN and samples grown at the highest substrate temperature revealed an exciton absorption feature near the band edge of GaN, a sign of increased crystal quality. These results have lead to questions as to whether the violet luminescence is due to the ternary alloy ScGaN or rather from shallow, radiative defects in the material.
Declaration

No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.
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Fluctuat nec mergitur
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Chapter 1: Introduction

1.1 Introduction to Nitrides

Group III-nitride semiconductors such as GaN, InN, and AlN are of particular interest in optoelectronics due to their large, direct bandgaps which range at room temperature from 0.7 eV to 6.2 eV [1]. This ability to span the infrared (IR) to ultraviolet (UV) spectrum makes them ideal for optical devices and nitride semiconductors have been successfully used in light emitting diodes (LEDs) and laser diodes (LDs) [2].

There are many types of semiconductor devices on the market today; however, none of them promise to reduce our energy consumption as much as the ones based on the nitrides. Group III-V semiconductors such as GaAs, InP, and GaInP have direct bandgaps, but their functionality is limited to the emission of light in the red and IR part of the spectrum. Other III-V semiconductors such as GaP, AlAs, and AlP have indirect bandgaps which are unsuitable for LEDs as they have low efficiency for light emission. GaP:N based structures can be used to create green emitting LEDs; however InGaN green LEDs surpass their brightness by a factor of 60 [3]. The group IV compound, SiC, can be fabricated into blue emitting LEDs; however manufacturers such as Cree discontinued their SiC program and converted to fabricating InGaN LEDs which are 100 times brighter [3,4]. Group II-VI semiconductors such as ZnSe can emit light in the range of 480 to 520 nm, making them suitable for short-wavelength devices [5]. However, p-type doping is very difficult in the II-VI compounds due to an abundance of native n-type impurities which compensate p-type dopants [6]. This makes it difficult to produce a p/n junction. Furthermore, the lifetime of ZnSe LEDs is no more than 100 hours [7], whereas violet nitride LEDs have lifetimes in excess of 50,000 hours [8]. The high brightness and longer lifetimes of the nitride semiconductors make them a better alternative for optoelectronic devices.

The nitride semiconductors do have their problems as well. Nitrides contain an incredibly large amount of structural and point defects and can have defect densities on the order of $10^9$ cm$^{-2}$ [9]. This large density of defects is mainly due to a lattice mismatch with the commonly used substrate, sapphire, which will be discussed further in Section 1.3. Yet what makes the nitrides remarkable is that
despite these large defect densities, optical devices continue to have high internal quantum efficiencies, which is uncommon in III-V semiconductor materials.

1.2 Developments in III-Nitride Materials

Much of the research involving III-nitride technology has happened in the last 20 years; however the first synthesis of GaN occurred in 1938 when Juza and Hahn [10, 11] synthesized the first needles and platelets of the material by passing ammonia through hot gallium. Approximately 30 years later, the first large-area GaN was epitaxially grown on a sapphire substrate by Maruska and Tietjen using halide vapour phase epitaxy [12]. The ability to grow large-area GaN led to the first nitride-based devices. In 1971, Pankove et al. [13] fabricated the first blue GaN-based metal-insulator-semiconductor LED. In 1972, Maruska et al. [14] fabricated a violet electroluminescent diode. Despite these achievements, poor quality epilayers hindered the progress of GaN devices as many of the optical and electrical results were not reproducible [15].

Modern growth techniques such as molecular beam epitaxy (MBE) and metal-organic chemical vapour deposition (MOCVD) allowed further development and progress to be made. Efforts to optimise growth conditions included the introduction of buffer layers and in 1983, Yoshida et al. [16] added an AlN layer grown at low temperature between the sapphire substrate and the GaN using MBE. This two-step method for growing GaN films on sapphire was later improved using MOVCD by Amano et al. in the late 1980’s where they showed that an AlN layer grown at 500 °C, followed by GaN growth at 1050 °C resulted in smooth surfaces with low background carrier density and high room temperature photoluminescence (PL) intensity [17].

Early GaN films were unintentionally doped n-type and p-type doping was difficult to achieve; however Yoshida et al. [18] and Akasaki et al. [19] were the first to realise p-type doping in GaN. They did this by doping with magnesium (Mg) during GaN growth and then activating the acceptors via electron beam irradiation. Nakamura et al. [20] later showed that acceptor activation also occurred after thermal annealing. The understanding of p-type growth then quickly led to the first p-n junction LED in 1989 [21].

In the early 1990’s, ternary alloys were finally realised, allowing for heterojunctions to be created. Matsuoka et al. [22] grew In$_x$Ga$_{1-x}$N on sapphire with different values of $x$, and later Nakamura et al. [23] created InGaN/GaN
heterostructures. Khan et al. [24] and Itoh et al. [25] were the first to grow AlGaN on GaN.

These developments lead to a boom in GaN research in the mid-to-late 1990’s. Green and blue LEDs soon became commercially available from Nichia Laboratories [26,27]. Research on GaN-based lasers also progressed rapidly with reports on surface mode emission [28], optical gain [29], optically pumped lasers [30,31,32], and injection lasers [33]. In addition, the fabrication of field effect transistors using GaN was realised in 1993 [34].

1.3 Growth of III-Nitride Semiconductors

Substrate Materials

The first large area GaN was grown on a c-plane (0001) sapphire substrate. Sapphire was, and still is, commonly used as a substrate because of its low cost, stability at high temperatures, and transmittance in the visible region. Figure 1.1 shows a representation of the c-plane atomic arrangement of GaN superimposed on sapphire. The crystal orientation of c-plane sapphire is similar to GaN, but its unit cell is rotated by 30° and its lattice constant is about 15% greater than that of GaN [35,36]. The lattice constant of GaN is 3.189 Å, whereas for sapphire it is 2.75 Å. This large difference in lattice constant means that GaN grown directly on sapphire is under considerable compressive strain.

Figure 1.1. Schematic diagram of (0001) plane of GaN superimposed on sapphire. The group III-nitride axis is rotated 30° to the sapphire axis.

In addition to sapphire, 6H-SiC and Si substrates have been investigated as alternative substrate materials. The advantages of 6H-SiC are that the lattice mismatch is only about 3.5%, the electrical and thermal conductivity are very good,
and good quality wafers are readily available. The disadvantage is the high cost of 6H-SiC wafers [37]. Silicon is an extremely cheap substrate from which many semiconductor devices are already fabricated. Silicon is cubic and GaN grown on (100) Si is predominantly cubic [38]; however growth on (111) Si leads to the growth of wurtzite GaN and GaN-based LEDs have recently been grown on (111) Si [39]. Nonetheless, growth on sapphire is a more mature growth method and is the substrate of choice in this research.

**MOCVD growth of high quality GaN**

Metal organic chemical vapour deposition (MOCVD) is a common growth method for nitride semiconductors and is the technique used to grow the structures discussed in this thesis. High quality GaN epilayers have been achievable using this method since the late 1980s and the technology is now relatively well established [38]. MOCVD is the dominant process for the commercial production of group III-nitride semiconductors.

MOCVD is a growth technique whereby the compounds are formed by a surface reaction between metalorganics and a hydride. The substrates are placed on a heated susceptor which acts like a catalyst for the thermal decomposition of the gaseous species. The metalorganic and hydride subspecies react on the surface at lattice step edges and form the semiconductor compound. By-products from the reaction (e.g. CH₄) are then safely expelled from the system.

The structures discussed in this thesis were grown in a Thomas Swan 6x2” Close Coupled Showerhead ® MOCVD reactor at the University of Cambridge (see Figure 1.2). The metalorganic precursors are trimethylgallium (TMGa), trimethylindium (TMIn), and trimethylaluminium (TMAI). Ammonia (NH₃) is used as the nitrogen source. Up to six 2 inch wafers can be placed on the heated graphite supseptor. A quartz liner prevents reactions with the interior surface of the reactor. Water flows through the showerhead and the reactor walls to prevent overheating.

The substrate material for the samples in this thesis is sapphire. The ~15% difference in lattice constant between sapphire and Group III-nitrides means that epilayers grown directly onto sapphire are under considerable compressive strain. The calculated critical thickness of GaN on sapphire is less than one monolayer so the strain is relieved via the formation of misfit dislocations [40]. However, good
quality epilayers can be achieved by growing a lower temperature buffer layer before the epilayer growth.

A two-step growth method described by Nakamura et al [42] is used during the growth process to reduce defects due to the large lattice mismatch between the $c$-plane sapphire substrate and the nitride system. A GaN nucleation layer is deposited at low temperature ($\sim 530 \degree C$) onto the sapphire before a $\sim 4.5 \mu m$ thick higher temperature ($\sim 1060 \degree C$) GaN layer is grown. This allows the in-plane lattice parameter of the semiconductor structure to be matched to the GaN buffer layer.
instead of the sapphire substrate. The density of dislocations achieved with this method is typically $10^9$ cm$^{-2}$ [9].

1.4 Thesis outline

The work contained in this thesis is concentrated on the optical properties of group III-nitride semiconductors, particularly indium gallium nitride and scandium gallium nitride. The InGaN/GaN system is of great importance as it is the basis for the group III-nitride UV – green LD and LED applications. The InGaN/GaN system is more complex than other III-nitride systems and despite all the recent progress, the fundamental physics of InGaN is far from being understood.

An introduction to the material and optical properties of the group III-nitride semiconductors is discussed in Chapter 2. Particular attention is paid to GaN as it is used as a template structure in all samples discussed in this thesis work and furthermore is the barrier material for the InGaN QW structures. In addition, properties of InGaN are also discussed as well as the effects of forming heterostructures with GaN. These effects include strain due to lattice mismatch of InGaN and GaN and polarisation fields.

The experimental techniques employed to perform the research discussed in this thesis work are discussed in Chapter 3. Optical techniques such as photoluminescence spectroscopy, photoluminescence excitation spectroscopy, photoluminescence time decay measurements and transmission spectroscopy are described as well as a discussion of some of the underlying principles involved.

The aim of the research in Chapter 4 is to investigate the physics and materials issues which determine quantum efficiency of light emitting structures. The structures investigated are high indium content (~25 %) InGaN/GaN quantum well structures which emit light at a wavelength of around 540 nm. This particular work has revealed new information on growth procedures necessary to ensure that the contribution to the photoluminescence linewidth due to well-to-well fluctuations are reduced, increasing room temperature internal quantum efficiency.

The research discussed in Chapter 5 examines the use of macroscopic optical spectroscopy techniques in attempts to observe InGaN quantum dots (QDs) in a semiconductor sample. InGaN QDs are typically investigated using
microscopic techniques which explore the characteristics of single QDs. This study explores the possibility of macroscopically observing collections of QDs.

The aim of the research in Chapter 6 is to investigate the optical properties of ScGaN. Few reports on this material exist in the literature and there are no known reports on the luminescence properties of ScGaN. This particular work explores the optical emission and absorption properties of this novel material.

References


Chapter 2: Properties of III-nitrides

2.1 Introduction

This chapter describes the basic properties of Group III-nitrides. Section 2.2 focuses on properties of GaN, including crystal structure, band structure and radiative recombination. Section 2.3 explores the properties of InGaN/GaN QW structures, in particular the material properties, effects of polarisation and carrier localisation.

2.2 Material & Optical Properties of GaN

2.2.1. Crystal Structure

Group III-nitride semiconductors are thermodynamically most stable in the wurtzite structure, the unit cell of which is displayed in Figure 2.1a. The wurtzite structure can be described as two interpenetrating hexagonal close packed sublattices (Figure 2.1b) in which each plane of the tetrahedra are mirror images of each other. For GaN, this requires each Ga atom to be surrounded by four N atoms and visa versa.

![Figure 2.1](image)

(a) (b)

Figure 2.1 Crystal structure of Group III-nitrides. (a) Wurtzite unit cell, highlighting the mirroring tetragonal bonds. (b) Hexagonal representation of wurtzite crystal structure.

2.2.2. Band Structure

Group III-nitrides and their alloys have direct bandgaps. The conduction band can be approximated by a parabolic dispersion relation whereas the valence band is non-parabolic and split into 3 bands at the Γ-point (Brillouin zone centre)
due to crystal field and spin-orbit coupling [1]. Crystal field splitting occurs due to the lower symmetry of the wurtzite phase. Displayed in Figure 2.2 is the valence band structure of GaN which has been calculated by Ren et al. using k·p theory [2]. The valence bands are commonly referred to as the $A$, $B$, and $C$ bands in descending order. Ren et al. calculated the energy difference between the $A$ and $B$ bands to be 6 meV and between the $B$ and $C$ bands to be 20 meV.

![Figure 2.2. Calculated valence band structure of GaN [2].](image)

### 2.2.3. Radiative Recombination

The process of radiative emission in a semiconductor leads to spectral features which are the result of various recombination mechanisms. An example low temperature (6 K) photoluminescence (PL) spectrum of a GaN epilayer is shown below in Figure 2.3. The spectrum consists of four radiative recombination features: excitonic emission, donor-acceptor pair (DAP) emission, and emission from the blue luminescence (BL) and yellow luminescence (YL) bands.
The emission feature observed at about 3.48 eV in Figure 2.3 is due to the zero-phonon recombination of excitons. As GaN is unintentionally n-type, this emission feature is likely due to excitons bound to neutral donors; however in some emission spectra, free excitons associated with the A, B, and C valence bands can be observed [3,4]. A low intensity feature observed in the spectrum at 3.39 eV is due to bound exciton recombination accompanied by a longitudinal-optical (LO) phonon, which for GaN is reported to have an energy of 91 meV [5,6,7]. Excitons are able to couple to the polar LO phonon modes of the crystal lattice due to the Fröhlich interaction [8]. This results in phonon replicas of the zero-phonon emission which are spaced at integers of the phonon energy, that is

$$h\nu = E_0 - nE_{\text{ph}},$$  \hspace{1cm} 2-1$$

where $E_0$ is the zero-phonon emission energy, $n$ is an integer, and $E_{\text{ph}}$ is the phonon energy.

The DAP emission feature observed at 3.28 eV in Figure 2.3 is due to the zero-phonon recombination of electrons bound to donors and holes bound to acceptors [9,10,11]. The ionized donor and acceptor final states also undergo
Coulomb attraction which is dependent upon the separation distance of the pair. Therefore, the emission energy of a DAP transition is

\[ h\nu = E_g - E_A - E_D + \frac{e^2}{4\pi\varepsilon\varepsilon_0 r}, \]

where \( E_g \) is the bandgap energy, \( E_A \) is the acceptor binding energy, \( E_D \) is the donor binding energy, \( e \) is the charge of an electron, \( \varepsilon \) is the relative dielectric constant, \( \varepsilon_0 \) is the permittivity constant, and \( r \) is the distance between the pair. The series of peaks on the low energy side of the DAP feature, which are separated by 91 meV, are attributed to LO phonon replicas of the zero-phonon DAP feature [5,6,7].

The broad band centred about 2.86 eV in the PL spectrum displayed in Figure 2.3 is known as the BL band. The exact nature of the recombining centres is still a matter of debate. The BL band is observed in undoped, Zn-doped, Mg-doped, and C-doped GaN. Reschikov et al. [3,12] believe the BL band involves zinc acceptors and they have shown similarities in the emission spectra between unintentionally doped and low Zn doping (<10^{18} \text{ cm}^{-3}) of GaN. Kaufmann et al. [13,14] have shown that the BL band is related Mg concentrations of around \( 1 \times 10^{19} \text{ cm}^{-3} \) and attribute it to a Mg atom located at a Ga site and a vacancy at a N site (Mg_{Ga}-V_{N} complex). Seager et al. [15,16], on the other hand, have shown the BL feature is observed when carbon doping exceeds \( 1 \times 10^{17} \text{ cm}^{-3} \) and attributed the emission to C atoms situated at a Ga and a N site (C_{Ga}-C_{N} complex). Regardless of the exact impurities involved, this band is attributed to the recombination of an electron bound to a shallow donor and a hole bound to a deep acceptor.

The broad band centred about 2.25 eV is known as the YL band. The nature of this broad, defect-related luminescence band is also a matter of debate. The YL band is attributed to shallow donor to deep acceptor transitions. It is often believed to be due to the V_{Ga}-O_{N} complex (where there is a vacancy at a Ga site and an O atom at a N site) in undoped GaN [3,17]. Nevertheless, the YL band has also been observed to increase in intensity with increasing carbon concentration and for carbon-doped samples, the YL is attributed to the V_{Ga}-C_{N} complex [18,19].

2.3 Properties of InGaN/GaN QWs

2.3.1 Material Properties

Although the various properties of GaN have been well documented for years, the properties of InN are less well known. For many years, the low
temperature bandgap of InN was thought to be 1.9 eV; however recent experiments have shown the bandgap to be 0.7 eV [20,21,22,23]. This new value of the InN bandgap further complicates the understanding of InGaN and requires careful consideration of research published before 2002.

The compositional dependence of bandgap energy for ternary alloys follows a quadratic form,

\[ E_{gA,B} = xE_{gA} + (1-x)E_{gB} - x(1-x)b_{AB}, \]  

where \( E_{gA} \) and \( E_{gB} \) correspond to two binary bandgap energies, \( x \) is the composition, and \( b_{AB} \) is a bowing parameter relating to the nonlinearity of the interpolation [1]. Displayed in Figure 2.4 is the bandgap energy versus lattice constants for the group III-nitride system which was calculated from Equation 2-3 using the binary constants and bowing parameters proposed by Vurgaftman and Meyer [1].

![Figure 2.4. Calculated bandgap energy versus lattice constant for the group III-nitride system.](image)

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**2.3.2. Polarisation Effects**

Wurtzite heterostructures are strongly influenced by polarisation due to the tetrahedral bonding of the crystal structure. A distortion of the crystal lattice creates
molecular dipoles in the material which set up macroscopic polarisation fields. Group III-nitrides experience strong spontaneous and piezoelectric fields.

The spontaneous polarisation \( P_{sp} \) is a result of the reduced symmetry of the wurtzite structure, and occurs along the (0001) direction of the wurtzite lattice. The strength of \( P_{sp} \) is highly dependent on alloy structure; the spontaneous polarisation constant of GaN is \(-0.029\) C/m\(^2\) and of InN is \(-0.042\) C/m\(^2\) [1]. These values are considerable in strength, being only about three times smaller than spontaneous polarisation constants of ferroelectric materials [24]. Bernadini and Fiorentini [25] have shown that the spontaneous polarisation for ternary III-nitride materials follow a Vergard-like relationship, and for In\(_x\)Ga\(_{1-x}\)N spontaneous polarisation is described as

\[
P_{sp, In_{x}Ga_{1-x}N} = xP_{sp, InN} + (1-x)P_{sp, GaN} \times b_{sp, InGa},
\]

where \( b_{sp, InGa} \) is a bowing parameter describing the nonlinear relationship between the spontaneous polarisation constants of InN and GaN.

Piezoelectric polarisation \( P_{pz} \) is a result of strain in the material. Strain is present in group III-nitride heterostructures due to the mismatched lattice constants between the layers [26]. When a thin layer of In\(_x\)Ga\(_{1-x}\)N is grown on a GaN template, the In\(_x\)Ga\(_{1-x}\)N lattice will be compressed to match the GaN lattice. This compression leads to biaxial strain within the (0001) growth plane, setting up a polarisation in the material. The relationship between piezoelectric polarisation and strain is given by Bernadini and Fiorentini [25] as

\[
P_{pz} = 2 \left( \frac{d_{33 \text{GaN}}}{d_{33 \text{InN}}} \right) \left( \varepsilon_{33 \text{GaN}} \frac{C_{13}}{C_{33}} \right),
\]

where \( a \) is the lattice constant of In\(_x\)Ga\(_{1-x}\)N, \( a_{\text{GaN}} \) is the lattice constant of the GaN template, \( \varepsilon_{31} \) and \( \varepsilon_{33} \) are piezoelectric constants of In\(_x\)Ga\(_{1-x}\)N, and \( C_{13} \) and \( C_{33} \) are the elastic constants of In\(_x\)Ga\(_{1-x}\)N.

Discontinuities of the polarisation charges at heterointerfaces result in electrostatic fields. In the case of a quantum well (QW) structure, the two interfaces will have opposite charges and thus set up an electric field in the material. Bonfiglio et al. [27] have shown that for a QW structure, the electric field in the well is described as

\[
F_x = -\frac{L_x (P_x^{\text{GaN}} - P_x^{\text{InN}})}{\varepsilon_0 (L_x \varepsilon_0 + L_y \varepsilon_y)},
\]
where $L_{b,w}$ corresponds to the layer thickness, $P_{b,w}^{\text{tot}}$ to the total polarisation charge and $\varepsilon_{b,w}$ to the relative dielectric constant of the barrier or well, respectively, and $\varepsilon_0$ to the permittivity constant. Shown in Figure 2.5 is the calculated reduction in QW potential due to the electric field described in Equation 2-5 for a 2 nm InGaN/GaN QW as a function of indium concentration. This reduction in potential becomes more severe with increasing indium content and has a profound effect on the optical properties of the QW.

![Figure 2.5](image)

Figure 2.5. Calculated reduction of potential energy across a 2 nm InGaN/GaN QW as a function of indium concentration in the well.

This electric field strongly modifies the band structure by tilting the potential across the QW, creating a triangular-shaped well. In Figure 2.6 is a schematic diagram of (a) a QW with no electric field effects and (b) a QW under a polarisation induced electric field. The significant tilt of the potential results in a reduction of the ground state within the well, relative to the unperturbed state. This polarisation-induced effect is called the quantum confined Stark effect. In addition, the electron and hole wavefunctions within the well become spatially separated. Spatial separation of the wavefunctions reduces the radiative recombination rate, leading to longer recombination lifetimes.
As was shown in Figure 2.5, InGaN/GaN quantum wells with higher indium concentrations will have greater band tilting and this greater tilt will further reduce the ground state transition energy and, more importantly, decrease the overlap of electron and hole wavefunctions. This results in longer radiative lifetimes for higher indium concentrations.

The large internal electric field in III-nitrides spatially separates electrons and holes along the growth axis and this significantly reduces the overlap integral for wider QW widths. This reduced oscillator strength increases radiative lifetime which allows non-radiative centres, such as those at dislocations, to become a more competitive process of recombination [28]. Long radiative recombination lifetimes are undesirable in quantum well structures as they can reduce the internal quantum efficiency of the material.

### 2.3.3. Carrier Localisation

Despite the longer radiative lifetimes experienced by InGaN/GaN QWs, it is widely believed that nano-scale confinement of carriers due to carrier localisation prohibits non-radiative recombination of electron-hole pairs at dislocations [29]. It is this carrier confinement that allows blue emitting InGaN/GaN QW structures to emit such bright light, despite the materials containing dislocation densities on the order of $10^9$ cm$^{-2}$ which would normally quench the light emission [30]. It has been proposed that the localising centres are caused by fluctuations in indium concentration [31], In-N-In chains [32], indium clustering [33,34], and fluctuations in well-width [35].
Spatially resolved cathodoluminescence (CL) [36] and PL [37] measurements have shown the existence of localised states in InGaN/GaN QW structures and that the recombination at low temperature is dominated by these localised states. Furthermore, a study by Graham et al. [38] in which the strength of phonon coupling measured from PL spectra of samples with indium concentrations ranging from 5 % to 25 % was compared to a theoretical model estimated the carrier localisation length in the plane of the QWs to be about 2 nm.

Until recently, it was thought that the localising centres were due to thermodynamic instability of InGaN. Calculations have shown there is a miscibility gap for InGaN which results in decomposition of the material into indium-rich and indium-poor regions [39]. Furthermore, prolonged annealing has also been shown to separate InGaN epilayers into indium-rich and indium-poor regions [40].

The regions of higher indium concentration locally reduce the bandgap of the QW material, further confining carriers and thus act like quantum dots (QDs) in the material [4]. As an increase in indium concentration reduces the bandgap of InGaN, it was believed that electron-hole pairs become spatially localised in these nanometre-scale, indium-rich regions. The average threading dislocation spacing is about 300 nm, therefore very few dislocations would pass through the indium-rich regions [30]. This would result in carriers being localised away from the majority of dislocations where they could potentially recombine nonradiatively.

The explanation that localisation is due to indium clustering comes from observations in transmission electron microscopy (TEM) images. Differences in strain show up as variations in the contrast of the TEM images and are very similar to those of legitimate QD-like nanometre-scale changes in material composition. The TEM images apparently show indium-rich regions in the plane of the QW with a size of about 3 nm [41,42]. Recently, however, it was shown that the electron beam used in TEM measurements can induce inhomogeneous strain in InGaN QW structures; however, when a lower intensity electron beam is used, there is no evidence of indium clustering [43,44]. Measurements using a 3-dimensional atom probe have also confirmed that indium atoms in InGaN/GaN QWs are randomly distributed throughout the QW layer, disproving the existence of indium clusters [45].

Another mechanism proposed as the cause of carrier localisation in InGaN/GaN QW structures is variations in QW thickness. High resolution TEM
images have shown that although the lower (GaN/InGaN) interface is atomically abrupt, the upper interface (InGaN/GaN) contains monolayer steps which extend 1-2 nm in length [38]. This type of mechanism is attributed to the localisation of excitons in GaAs/AlGaAs QW structures [46,47,48]; however, this effect is only observed in GaAs/AlGaAs QWs at low temperatures as the localising potential due to monolayer fluctuations is only a few meV. In InGaN/GaN QWs, the effect of a single monolayer variation is greatly enhanced due to the strong piezoelectric-induced electric field. For example, a single monolayer increase to a nominally 3.3 nm thick In$_{0.25}$Ga$_{0.75}$N/GaN QW will result in approximately 60 meV reduction of the energy separation of the electron and hole ground states within the QW which is sufficient to confine carriers at room temperature [38].

Watson-Parris et al. [49,50] predicted the ground-state hole localisation length is approximately 1-2 nm, regardless of the existence or absence of monolayer well-width fluctuations. In their calculations, they investigated the effects of disc-like monolayer increases in QW thickness on localisation length scale of a 3.3 nm thick In$_{0.25}$Ga$_{0.75}$N single QW with statistically random distribution of indium. They proposed the effect of well-width fluctuations on hole localisation length scale is negligible due to the electric field localising the holes on the smoother surface of the QW and that they are strongly localised by statistical fluctuations of indium concentration. On the other hand, the electron localisation length scale, which is inherently longer due to their smaller effective mass, was proposed to be affected by the well-width fluctuations in addition to the statistical fluctuations of indium concentration. Watson-Parris et al. simulated the PL spectrum of a 3.3 nm thick In$_{0.25}$Ga$_{0.75}$N single QW both with and without monolayer well-width fluctuations and found that including the effect of well-width fluctuations will broaden the spectral linewidth, however, not to the same extent as the effect of the strong hole localisation. Therefore, they propose that carrier localisation is defined by the random distribution of indium atoms but monolayer fluctuations have the ability to further localise carriers.
References


Chapter 3: Experimental Techniques

3.1 Introduction

This chapter describes the experimental techniques employed during the work for this thesis and discusses some of the underlying principles involved. Probably the most important experimental technique discussed is photoluminescence spectroscopy. This non-destructive technique provides insight into the energy states in a semiconductor material by observing the process of emission. Photoluminescence excitation spectroscopy further clarifies the nature of the energy states by observing the processes of absorption and carrier transfer. Photoluminescence time decay measurements give information about the lifetime of excited carriers. Another technique that is briefly discussed is transmission spectroscopy.

3.2 Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy is an essential non-destructive optical tool for understanding the energy band structure and quality of Group III-nitride semiconductors. The experimental setup consists of a monochromatic excitation source (typically a laser) that gives a large enough photon energy to excite electrons in the material from the valence band states to the conduction band states. This creates electron-hole pairs that, when they recombine, give off energy in some form. Radiative recombination occurs when the energy given off is in the form of a photon. Recombination processes resulting in radiative recombination can include band-to-band, free and bound excitons, donor bound electrons to free holes in the valence band, free electrons in the conduction band to acceptor bound holes and donor-acceptor pairs. The radiative emission intensity is measured as a function of detection energy.

A schematic diagram of the photoluminescence experimental setup is shown below in Figure 3.1. Various excitation sources and spectrometers were used which are described below.
Excitation Sources

The choice of excitation source for a PL experiment depends upon the band structure of the sample. For quantum well structures studied here, the excitation photon energy chosen is greater than the bandgap of the QW barrier; however, in some experiments, an excitation photon energy less than the QW barrier is used to investigate the QW directly.

The most common excitation source employed for the PL experiments was a continuous wave (CW) Kimmon-Koha helium-cadmium (He-Cd) laser [1] which emits at 3.815 eV (325 nm). Various Coherent argon ion (Ar+) lasers [2] are also used. These CW lasers can be tuned to emit at a choice of energies, both visible and UV, including 3.408 eV (363.8 nm), 2.708 eV (457.9 nm) and 2.602 eV (476.5 nm). A Spectra-Physics Ti:Sapphire laser [3], which is optically pumped by all lines of a CW Ar+ laser, can be tuned to emit in the range of 1.476 eV (840 nm) to 1.722 eV (720 nm). A fourth type of laser excitation source used during this work consists of an optically pumped Coherent Rhodamine 6G dye laser [4] whose output is frequency-doubled to emit light at a wavelength of 290 nm which was pumped by the 514.5 nm line of a mode-locked Ar+ laser.
Light from the gas laser sources was filtered to reduce the effect of plasma lines. The excitation beam was chopped using a mechanical chopper and then focused onto the sample using a quartz lens.

**Sample Mounting**

Samples were mounted on either a block at room temperature or a Leybold closed-cycle refrigerator cryostat, model RDK 6-320 [5]. This cryogenic system uses Joule-Thompson cooling of compressed helium gas to reach temperatures as low as 6 K. An external Leybold LTC 60 low temperature controller [6] allows the sample temperature to be set in the range of 6 K to 300 K using a resistive heater.

In some cases, Fabry-Pérot interference within the sample is severe enough that it can be difficult to distinguish between interference fringes and features of the true luminescent spectra. To reduce the effect of Fabry-Pérot interference on emission spectra, samples are mounted at their Brewster angle. The benefit of mounting samples at their Brewster angle relative to the spectrometer is that light which is polarized parallel to the GaN/air interface has no reflection at that angle. With zero reflection at the Brewster angle, the possibility of multiple reflections resulting as interference becomes negligible. Inserting a polarizer in front of the spectrometer (as shown in Figure 3.1) which is oriented to transmit only light parallel to the GaN/air interface allows only photoluminescence to pass into the spectrometer. This reduces the amount of light collected into the spectrometer, but greatly reduces the effects of the interference fringes.

**Collection of Luminescence**

A quartz lens collects luminescence from the sample and focuses it onto the entrance slit of the spectrometer. Two spectrometers were used for the PL experiments: a single-grating SPEX 1702/04 0.75 m monochromator (16 Å/mm resolution) [7] and a double-grating SPEX 1404 0.85 m spectrometer (8 Å/mm resolution) [8]. Both spectrometers analyse emitted light and are controlled externally by a computer. The benefit of the double-grating spectrometer is its ability to reject stray light. A double-grating spectrometer is essentially two single-grating spectrometers in series. The second monochromator acts as a very narrow filter, further rejecting stray light which has passed into the first monochromator [9].
This allows for the detection of emission nearer to the energy of the excitation source.

A cooled (-30 °C) RCA C31034 GaAs photomultiplier tube (PMT) [10] is located at the exit slit of the spectrometer. The resulting signal is amplified using a Stanford Research Systems SR510 phase-sensitive (lock-in) detector [11], referenced to the frequency of the mechanical chopper. The signal voltage and corresponding wavelength are then recorded by the computer.

3.3 Photoluminescence Excitation Spectroscopy

Photoluminescence excitation (PLE) spectroscopy is an optical characterisation technique used to give information on the absorption spectrum and also the processes which occur between absorption and emission. In PLE experiments, the spectrometer is set to detect a particular wavelength of light emitted from the sample. A tuneable wavelength source excites the sample and the emission intensity is recorded as a function of source wavelength. The emission intensity is dependent upon the probability of an incident photon being absorbed, the probability that carriers will relax to a particular emitting state, the probability of radiative recombination from that state and the excitation intensity [12]. Therefore, in addition to the absorption spectrum, PLE experiments provide information on possible transitions in the band structure.

A schematic diagram of a PLE system is shown in Figure 3.2. The excitation source for PLE experiments in this thesis is a 300 W Thermo Oriel xenon arc lamp whose output is dispersed with a SPEX Minimate 0.25 m monochromator. Light exiting the Minimate is focused onto samples which are mounted in the cryogenic refrigerator. Luminescence is collected and focused onto the entrance slit of the SPEX 1404 0.85 m double-grating spectrometer. The double-grating spectrometer is needed for this experiment in order to scan the source as close to the detection wavelength as possible without scattered light overwhelming the detector. The double-grating spectrometer is set to transmit a desired wavelength to the cooled (-30 °C) RCA C31034 GaAs PMT and then the excitation source is scanned across a range of desired wavelengths. The resulting signal is amplified using a phase-sensitive (lock-in) detector, referenced to the frequency of the mechanical chopper. The signal voltage and corresponding excitation wavelength are then recorded by the computer.
3.4 Time Correlated Single Photon Counting Measurements

Time correlated single photon counting (TCSPC) is an optical characterisation technique used to gain information about carrier recombination dynamics. In TCSPC experiments, an ultra-short laser pulse excites the sample, creating an excited carrier population. The intensity of the resulting photoluminescence is proportional to this excess carrier concentration and follows the same temporal dependence. The time difference between the laser pulse and the detection of an emitted photon from the semiconductor is recorded. Repeating this measurement many times results in a histogram which is representative of the probability distribution of the detection of a photon and, hence, the decay of the photoluminescence intensity as a function of time. A schematic diagram of the time-correlated single photon counting system is shown in Figure 3.3.

The ultra-fast laser pulses come from a frequency-doubled Coherent 702 Rhodamine 6G dye laser which is optically pumped by the 514.5 nm line of a mode-locked Coherent 100 Ar+ laser. Mode locking is achieved by a Coherent 468-AS Mode Locker Driver and a Coherent 7220 cavity dumper reduces the repetition rate of the output laser pulses.
Mode-Locking

Mode locking is a technique which can create powerful, ultra-short pulses of laser light. In this technique, the phases of the longitudinal modes of the laser cavity are fixed, leading to a train of pulses separated by a time, $t_p$, such that

$$ t_p = \frac{2L}{c}, \quad 3.1 $$

where $L$ is the length of the cavity and $c$ is the speed of light. The temporal duration of each pulse is

$$ \tau_N = \frac{2L}{cN}, \quad 3.2 $$

where $N$ is the number of modes within the cavity. The phases of the longitudinal modes can be ‘locked’ by periodically modulating the mode amplitudes with a frequency $c/2L$. Modulating the amplitude is achieved by modulating the cavity loss.

The Coherent 468-AS Mode Locker Driver uses acoustic loss modulation to achieve mode locking of the Coherent 100 Ar+ laser. The method by which it does this is by diffraction of light by sound waves. An acousto-optic modulator
consisting of a fused silica prism bonded to a piezoelectric transducer is placed within the cavity of the laser. A radio frequency (rf) signal from the external unit generates standing sound waves, and hence density variations, within the prism. The variation in index of refraction, $\Delta n$, in the prism due to acoustic standing waves along $x$ is of the form [13],

$$\Delta n(x, t) = a \sin(\omega_s t + \theta) \sin \frac{2\pi x}{\lambda_s}, \quad 3-3$$

where $a$ is a constant dependent on the material constants of the prism and the intensity of the sound wave, $\omega_s$ is the temporal oscillation frequency, $\theta$ is the diffraction angle and $\lambda_s$ is wavelength of the sound wave. It follows that maximum (or minimum) diffraction will occur periodically in time with a frequency $2\omega_s$ and when this occurs at the mode frequency spacing, $c/2L$, mode locking is achieved.

In this system, mode locking of the 514.5 nm line results in a train of pulses separated by $t_p = 13$ ns, having a temporal duration of $\tau_N \approx 170$ ps.

The mode locked Ar$^+$ beam is then used to optically pump the Coherent 702 Rhodamine 6G dye laser. Synchronous mode locking of the dye laser is achieved by setting the length of the cavity equal to that of the Ar$^+$ laser and by using a dye which has a recovery time of less than the pulse rate of the Ar$^+$ laser. The resulting pulse rate is equal to that of the Ar$^+$ laser (13 ns); however the duration of the pulses is narrowed to only a few picoseconds due to the larger gain linewidth which increases the number of longitudinal modes oscillating in the cavity. Following Equation 3-2, increasing the number of modes significantly decreases $\tau_N$.

The use of a cavity dumper allows the separation time of the pulses to increase in multiples of $t_p$, increasing the separation from 13 ns up to 6.5 $\mu$s. This is done using a Coherent 7220 Dye Cavity Dumper. An acousto-optic modulator in the cavity dumper head replaces the output coupler of the dye laser to deflect out certain light pulses travelling within the laser cavity. It is driven at an integer division of the mode locker frequency in order to obtain selectable pulse repetition rates.

Light diffracted by an optical phase grating is typically spread amongst many diffraction orders [14]. Although this is satisfactory for mode-locking systems where the diffracted beam is exhausted, the diffracted beam of a cavity-dumped system is the output of the laser system and therefore needs to be confined in one diffraction order.
In order to achieve this, the fused silica prism is oriented at the Bragg angle with respect to the incident beam, resulting in as much diffracted light as possible being diffracted into only one of the first two diffraction orders [15]. This system also uses a double pass configuration to maximise the extinction ratio and can achieve an extinction ratio of up to 2,000:1 [14]. The cavity dumper driver also sends an electronic ‘start pulse’ each time a laser pulse is transmitted from the dumper head.

**Second Harmonic Generation**

The light from the dye laser is then sent through an Inrad 5-035C second harmonic generation system [16] which uses a beta barium borate (BBO) crystal to double the frequency, reducing the wavelength from 580 nm to 290 nm. Frequency doubling is a non-linear optical effect which occurs in certain materials where there exists a non-linear relationship between an applied electric field and the electrical polarisation in the material. An incident electromagnetic wave creates an oscillating electric field within the material. This induces an oscillating electrical polarisation which consists of multiple components: one at the incident frequency, a second at twice that frequency, and so on.

The generation of the second harmonic is typically not a very efficient conversion. The difference in index of refraction for the first and second harmonics leads to two waves travelling at different speeds through the crystal and causes a spatial interference effect. The power conversion efficiency for second harmonic generation is defined by the proportionality,

\[
\eta_{\text{SHG}} \propto \sin^2 \left( \frac{\Delta n}{2} \right),
\]

where \( \Delta n \) is the difference in index of refraction of the two harmonics and \( L \) is the length of the non-linear crystal.

Angle phase matching is one way to reduce \( \Delta n \) and increase the conversion efficiency. This method requires a birefringent crystal, such as BBO, where the index of refraction depends upon the polarisation direction of light travelling within the crystal. At an angle, \( \theta_p \), with respect to the optical axis, the index of refraction for both harmonics is the same, resulting in large \( \eta_{\text{SHG}} \). Rotating the BBO crystal so that the pump beam from the dye laser is incident at \( \theta_p \) with respect to its optical axis, yields a time-averaged power of around 2 mW for the second harmonic,
compared to the incident 150 mW power of the dye laser. A bandpass filter is used after the Inrad 5-035C in order to remove the fundamental.

**Detection and Photon Counting**

Light pulses transmitted through the bandpass filter are then focused onto the sample which is mounted in the cryogenic refrigerator. Photoluminescence emission from the sample is collected and focused onto the entrance slit of the SPEX 1702/04 0.75 m monochromator. Located at the exit slit of the spectrometer is a cooled (-30 °C) Burle C31034A02 GaAs PMT [17] which has system response of ~300 ps and dark count of ~10 per second when an accelerating voltage of 2.0 kV is applied. The pulsed signal from the PMT is then amplified using a Stanford Research Systems SR445 fast preamplifier. The amplified signal is then passed to the timing electronics.

A Tennelec TC454 constant fraction discriminator [18] is used to significantly reduce the detection of non-photonic signals and, more importantly, to reduce timing errors. The PMT will output a broad distribution of electrical pulse amplitudes due to noise, single photon and multiple photon events. With leading-edge detection, simultaneous pulses of different amplitudes can erroneously appear to arrive at different times. To resolve these problems, a user-defined threshold is set to reject any noise-related electronic pulses with amplitude less than the reference level. Signals above the discriminator level are then normalised so that they arrive at the same time. This is done by splitting the signal into two parts. One signal is delayed and then subtracted from a percentage of the other. The resulting bipolar signal has a zero crossing point which is a fraction of the original signal amplitude. Provided the pulse shape is constant, this fraction will not vary with respect to amplitude. In this manner, the problem with leading edge detection is controlled.

The precisely timed, constant amplitude electrical pulses are then output to an Ortec 567 time-to-amplitude converter [19]. The converter measures the time difference between a laser pulse and detection of an emitted photon. The timing process is electrically triggered by the cavity dumper when it allows a laser pulse to be transmitted from the dye laser cavity. A potential difference is then linearly increased until the time is stopped by an electrical pulse from the constant fraction discriminator. The time scale over which the voltage increases between 0 and 1 V
can be set by the user in increments between 50 ns and 2 ms. Therefore, the voltage is proportional to elapsed time between laser emission and sample emission. With every subsequent start/stop pulse, a voltage pulse of magnitude proportional to elapsed time is sent to an Ortec TRUMP-PCI multi-channel analyser (MCA) card fitted in a personal computer.

The MCA consists of $2^n$ channels, where $n$ is a user-defined integer between 8 and 13. Each channel corresponds to a voltage representing a time in the range of the converter. The MCA receives a string of voltage pulses from the converter and assigns a pulse to a channel, depending on the pulse’s voltage. Each pulse which is assigned to a particular channel is counted. The channels count their assigned pulses over a period of time, building up a histogram of counts versus channel. As the channel is representative of the time delay between laser excitation and emission of a photon, the histogram is representative of the probability of detecting a photon at a particular time after laser excitation. In this work, the first channel is allowed to accumulate 1000 counts in order to achieve a high-quality signal to noise ratio.

Counting the first photon to reach the detector after an excitation pulse and ignoring any subsequent photons created from the same pulse can lead to a shorter PL decay time than the true value. If a slow photon from a previous pulse reaches the detector before a photon from the current pulse, the arrival time will be erroneously recorded as fast. This type of error is called pulse pile-up and it can be corrected by reducing the photon count rate to less than one detected photon per laser pulse. Reducing the ratio of photon count rate to laser pulse repetition rate to 0.01 has been shown to minimise this error [20,21]. For this reason, a Philips PM6650 counter [22] was connected to the output of the discriminator to monitor the count rate and maintain a level of <1 kHz, which results in the ratio of photon count rate to laser pulse repetition rate to be about 0.007, assuming a constant repetition rate of the laser.

### 3.5 Transmission Spectroscopy

For transmission measurements, a light source with a broad spectrum is normally incident upon a sample. Wavelengths corresponding to allowed energy transitions are absorbed. Wavelengths not absorbed by the sample pass through the sample and are recorded by the detector. By taking the ratios of the incident and
transmitted intensities as a function of wavelength, one can conclude which wavelengths were absorbed to obtain an absorption spectrum of the sample.

The transmission source is a 12 W tungsten filament bulb which is focused onto the back (substrate side) of the sample. Light which is transmitted through the sample is collected and focused onto the entrance slit of a SPEX 1404 0.85 m double-grating spectrometer (resolution of 8 Å/mm). A cooled (-30 °C) RCA C31034 GaAs photomultiplier tube (PMT) is located at the exit slit of the spectrometer. The resulting signal is amplified using a Stanford Research Systems SR510 phase-sensitive (lock-in) detector, referenced to the frequency of the mechanical chopper. The signal voltage and corresponding wavelength are then recorded by the computer. A schematic diagram of the transmission spectroscopy equipment set-up is shown in Figure 3.4.

Figure 3.4. Schematic Diagram of a Transmission Spectroscopy Experiment
References


Chapter 4: Green Emitting InGaN/GaN QWs

4.1 Introduction

Optoelectronic devices based on InGaN/GaN multiple quantum wells (MQWs) have been developed to emit light at wavelengths across the visible spectrum and into the near-ultraviolet (UV). This remarkable ability to span the entire visible spectrum is achievable owing to the variation of the low temperature bandgap energy of $\text{In}_x\text{Ga}_{1-x}\text{N}$ which ranges from 0.7 eV at $x = 1$ to 3.5 eV at $x = 0$. Nevertheless, one of the biggest problems preventing the full exploitation of nitride semiconductors across the visible spectrum is the relatively poor room temperature internal quantum efficiency (IQE) of InGaN/GaN quantum well (QW) structures emitting in the red-to-green part of the spectrum.

The InGaAlP material system is well-established in the LED industry for red emission; however, the Group III-phosphide material system is not a suitable alternative for green light as the material becomes indirect, resulting in a dramatic reduction of IQE. For green emission, InGaN/GaN QWs are 60 times more efficient than Group III-phosphides [1].

The reduction of IQE at green wavelengths for both the Group III-nitride system and the Group III-phosphide system is known in the industry as the ‘green gap’. Global companies such as Philips Lumileds and Osram Opto-Semiconductor in addition to governments such as those of Japan, Korea, Taiwan and the USA sponsor research programmes as part of an effort to reduce the so-called ‘green gap’. The United States Department of Energy consider increasing the efficiency of green light emitting diodes (LEDs) to be a ‘high priority’ research area [2].

Strong global interest exists in improving the efficiency of green emitting LEDs because they are paramount to achieving efficient white light LEDs via red-green-blue (RGB) colour mixing. RGB colour mixing is the method by which televisions and computer monitors, for example, create millions of colours without each pixel consisting of millions of single wavelength sources. By varying the individual intensities of a red, green, and blue triad source, virtually any colour can be seen by the eye. A high intensity of all three colours can yield white light. To achieve RGB colour mixing from an LED triad source, a brighter, more efficient green source is needed.
Figure 4.1 shows a survey of reported room temperature IQE obtained by PL and electroluminescence (EL) measurements for InGaN/GaN QW structures plotted against their respective peak PL/EL emission energy [3,4,5,6,7,8]. IQE is shown to be about 70% in the blue to violet range, but quickly drops off for shorter peak emission energies. The cause of this IQE reduction is not completely understood.

\[ \text{Room Temperature IQE (\%)} \]
\[ \text{PL Peak Energy (eV)} \]

Hangleiter et al. [3]
Sun et al. [4]
Fuchsmann et al. [5]
Graham et al. [6]
Kunzer et al. [7]
Jeong et al. [8]

Figure 4.1. A survey of reported room temperature IQE values from InGaN/GaN QW structures as a function of their PL peak energy [3,4,5,6,7,8].

It is widely believed that nano-scale confinement of carriers due to localisation prohibits non-radiative recombination of electron-hole pairs at dislocations [9]. It is this carrier confinement that allows blue-violet InGaN/GaN QW structures to emit such bright light, despite containing dislocation densities on the order of $10^9 \text{ cm}^{-2}$ [10].

There are a number of material issues which are thought to restrict the IQE for InGaN/GaN QW structures designed to emit at lower energies. One problem
relating to these structures is the increased strain in the QWs due to the lattice mismatch with GaN. As the indium concentration is increased, the lattice constant increases relative to the GaN barriers. This causes strain in the QW which in turn increases the piezoelectric polarisation in the wells [11]. Discontinuities of the polarisation charges at the well/barrier interfaces result in electrostatic fields [12]. The field causes band tilting which reduces the electron-hole energy but also separates them in space (See Figure 2.6). The separation in space reduces the electron-hole wavefunction overlap resulting in longer radiative lifetime. These longer radiative lifetimes allow for better competition with other non-radiative recombination mechanisms which result in lower IQE.

Furthermore, if the strain in the InGaN QW reaches a critical level, it becomes energetically favourable for the strained crystal lattice to relax via the formation of misfit dislocations [13,14]. Strain can build up not only in each individual QW, but also throughout the stack of QWs [15,16,17]. Therefore, strain relaxation is more likely to occur when many QWs are grown. It is believed that the introduction of strain relaxation decreases the effects of exciton localisation due to the addition of dislocations [15,17]. This can be detrimental to the IQE of a group III-nitride light emitting device as the dislocations act as effective non-radiative recombination routes for excited carriers.

Additionally, the process of increasing indium content, whilst maintaining reasonable quality InGaN material, is difficult. This is because InN has a low melting point of 1100°C (resulting in thermal instability above 500 °C) and ammonia is difficult to crack below 1000 °C [18]. The consequence is that growth at higher temperatures yields higher crystal quality, but lower temperatures are required to increase indium content by reducing indium desorption. Compounding this problem is the fact that GaN requires much higher temperatures for growth. The optimum growth temperature of MOCVD-grown GaN is 1040 °C [19]. Using a two-temperature (2T) growth method, where the InGaN QWs are grown at a lower temperature (680-690 °C) and the GaN barriers are grown at a higher temperature (860 °C) has been shown to improve room temperature IQE for higher indium content QWs over their single temperature counterparts [20]. These materials, however, were shown to contain large variations in QW thickness [20,21,22,23].
Understanding the mechanisms limiting IQE requires knowledge of the optical and micro-structural properties of these materials. This chapter reports on the optical properties and microstructure of sets of high indium fraction (~25%) QW structures designed to emit in the green part of the spectrum. In particular, the growth procedures are discussed which are necessary to ensure that the individual QWs have as similar properties as possible, ensuring that contribution to the photoluminescence linewidth due to well-to-well variations is reduced.

The research discussed in this chapter is separated into two main sections. Section 4.2 discusses optical properties of samples grown under the conventional 2T growth method. Section 4.3 discusses the optical properties of samples grown under modified growth procedures, which were based on the findings of the study presented in Section 4.2.

### 4.2 Conventional Growth Methods

#### 4.2.1. Sample Growth

To achieve green emission the concentration of indium must be of the order of 25 %, which on c-plane sapphire substrates leads to a large degree of strain in the quantum well which in turn leads to a large internal electric field. This electric field leads to a reduction of the electron/hole wavefunction overlap and, where there is a competing non-radiative pathway, low values of IQE. To counteract these effects, InGaN/GaN QWs were designed to have small (2 nm) QW thicknesses which maximises the wavefunction overlap.

The QW structures were grown at the University of Cambridge by Kappers [24] on (0001) sapphire substrates in a Thomas Swan 6 x 2” Close Coupled Showerhead® MOCVD reactor using a 2T growth method in which the wells were grown at a low (650-700 °C) temperature and the barriers at a higher (860 °C) temperature. The QW structures consist of nominally 2 nm thick In$_x$Ga$_{1-x}$N quantum wells with 9 nm thick GaN barriers. The indium concentration in the QWs was approximately 25 %. The number of QWs in the structure was also varied from a single QW to 10 QWs in the stack.
4.2.2. Effects of QW Growth Temperature

4.2.2.1. Sample Details

The set of samples discussed in this section consist of a series of samples each containing 10 QWs. The $\text{In}_x\text{Ga}_{1-x}\text{N}$ growth temperature was varied between 650°C and 700 °C. For the samples with higher QW growth temperatures, the ramp time (i.e. the time duration of the temperature change from the low temperature $\text{In}_x\text{Ga}_{1-x}\text{N}$ QW growth to the high temperature GaN barrier growth) is 60 s; however, for lowest QW growth temperatures, the ramp time was increased to 90 s due to the larger difference between QW growth temperature and the high temperature of the GaN barrier growth. These samples and their growth details are listed in Table 4.1 below.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ramp Time (s)</th>
<th>QW growth temperature (°C)</th>
<th>Number of QWs</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3692</td>
<td>90</td>
<td>650</td>
<td>10</td>
</tr>
<tr>
<td>C3693</td>
<td>90</td>
<td>670</td>
<td>10</td>
</tr>
<tr>
<td>C3613</td>
<td>60</td>
<td>680</td>
<td>10</td>
</tr>
<tr>
<td>C3396</td>
<td>60</td>
<td>690</td>
<td>10</td>
</tr>
<tr>
<td>C3694</td>
<td>60</td>
<td>700</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 4.1. Growth parameters of a series of $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$ 10 QW samples.

4.2.2.2. Experimental Results

**Low Temperature PL Spectroscopy**

Low temperature (6 K) photoluminescence spectroscopy was performed on the set of 10 QW samples grown using various QW growth temperatures. For these measurements, the excitation photon energy used was 2.708 eV (457.9 nm), which is an energy less than the bandgap of the GaN barriers (below gap excitation). This excitation photon energy allows the QWs to be directly excited, instead of the QWs capturing excited carriers from the barriers. This method in particular does not result in excitation of luminescence due to native defects in the GaN barriers. The resultant low temperature below-barrier PL spectra are shown in Figure 4.2.

Although these measurements were taken in a Brewster angle geometry, there does appear to be some Fabry-Pérot interference on the spectra. Interference fringe spacing for this nitride material system is calculated to be about 35 meV, which is consistent with the interference fringes observed in these spectra.
Figure 4.2. Low temperature (6 K) PL spectra for the set of 10 QW samples with QW growth temperatures of 650 °C (C3692, cyan line), 670 °C (C3693, blue line), 680 °C (C3613, green line), 690 °C (C3396, red line) and 700 °C (C3694, black line).
In addition to the interference fringes, these spectra appear to consist of at least two overlapping luminescence bands: an intense band due to QW emission and a less intense band due an unknown emission mechanism. The QWs grown at 650 °C (C3692) emit at 2.265 eV with a broader, less intense feature centred about 2.10 eV. The QWs grown at 670 °C (C3693) emit at 2.200 eV with a broader, less intense feature centred about 2.020 eV. The QWs grown at 680 °C (C3613) emit at 2.348 eV with a broader, less intense feature centred about 2.149 eV. The QWs grown at 690 °C (C3396) emit at 2.313 eV with a less intense feature centred about 2.216 eV. The QWs grown at 700 °C (C3694) emit at 2.307 eV with a less intense feature centred about 2.214 eV.

The two samples with lowest QW growth temperatures emit at lower energies and have more pronounced secondary luminescence than the samples grown with higher QW growth temperatures. Growth temperature affects the efficiency of indium incorporation in In$_x$Ga$_{1-x}$N [25,26,27]. Lower temperature In$_x$Ga$_{1-x}$N growth results in higher concentrations of indium which result in lower emission energy. Therefore, the samples grown at lower QW growth temperature could possibly contain a larger concentration of indium, and hence have lower emission energies.

The QWs grown with the lowest two growth temperatures also had ramp times 30 seconds longer than the other samples. Ramp time can also have an effect on the growth of In$_x$Ga$_{1-x}$N and it has been found that longer ramp times result in higher energy QW emission due to indium desorption occurring between the time the In$_x$Ga$_{1-x}$N QW is grown and when the GaN barrier is deposited [28]. Nevertheless, the samples grown with 90 second ramp times do not follow this trend so it is believed that the effect of increasing the ramp time from 60 seconds is negligible.

The secondary luminescence requires further investigation to understand the origin of the recombination mechanism. Previous results by Graham [20] on samples grown via a similar method have shown a single PL spectral feature when excited by a 2.708 eV (457.9 nm) beam; however, when those samples were excited at energies greater than the GaN bandgap, low intensity yellow defect-related luminescence was observed.
The so-called ‘yellow luminescence (YL) band’ typically peaks at about 2.25 eV [29]. This broad defect luminescence band is the result of the $V_{Ga\text{O}_N}$ (gallium vacancy – oxygen acceptor) complex which is a shallow donor to deep acceptor radiative transition [30]. Although commonly observed when exciting at energies above the bandgap of GaN, it is not usually observed when exciting at energies less than the bandgap of GaN.

To test the likelihood of observing this defect band when exciting at energies less than the GaN bandgap, the PL spectrum of a GaN epilayer, known to exhibit YL when excited at higher energy [31], was measured at 6 K using an excitation photon energy of 2.708 eV (457.9 nm). The PL spectrum is shown in Figure 4.3. Two features are observed in the spectrum: the YL band which is centred about 2.25 eV, and the so-called ‘Red Luminescence’ (RL) band which is centred about 1.65 eV and 14 times more intense than the YL. The RL band is attributed to shallow donor to deep acceptor transitions in GaN and is not commonly observed in PL spectra when exciting at energies above the GaN bandgap [29]. It should also be pointed out that the RL band is not observed in any of the PL spectra of the InGaN/GaN QW structures shown in Figure 4.2.

![Figure 4.3. Low temperature PL spectra of a GaN epilayer, excited using 2.708 eV (457.9 nm), which is less than the GaN bandgap energy.](image)
The PL spectra in Figure 4.3 proves that although direct excitation of the $V_{Ga}O_N$ complex is possible, the contribution to PL intensity is negligible at low temperature. This makes it highly unlikely that the secondary luminescence is due to direct excitation of GaN defects.

**Photoluminescence Excitation Spectroscopy**

In order to further explore the nature of the secondary luminescence feature of the higher QW growth temperature samples, low temperature PLE spectra were measured on sample C3396 ($T_{QW} = 690 \, ^\circ C$). The PLE spectra, monitoring both the main QW emission peak at 2.335 eV (red line) and the secondary feature emission at 2.141 eV (green line), are shown in Figure 4.4. A PL spectra of the sample taken under 2.708 eV (457.9 nm) excitation from the Xe lamp/Minimate monochromator system is also displayed in black for reference. The maximum intensity of each spectra are normalised to 1 to highlight their differences.

The basic shape of the two PLE spectra in Figure 4.4 is essentially the same, whether detecting at an energy within the QW PL peak or at an energy of the secondary luminescence feature. Both PLE spectra show a sharp edge at about 3.5 eV which corresponds to the GaN absorption edge and also a lower intensity broad band which extends to about 2.4 eV which corresponds to absorption in the InGaN QWs. The narrow fluctuations in the spectra are due to Fabry-Pérot interference fringes caused by multiple reflections of the excitation light within the sample and have a spacing of 35 meV. The strength of the PL intensity due to InGaN absorption, relative to GaN absorption, is stronger when detecting at the QW peak than at the secondary feature.

The PLE spectrum obtained when monitoring the 2.335 eV QW emission peak (red line) indicates the GaN absorption edge is broadened, compared to when detecting the secondary luminescence feature. The PLE spectra monitored at 2.141 eV in the secondary luminescence band (green line) shows an abrupt absorption edge with a GaN exciton feature resolved at 3.48 eV.

Broadening of the GaN exciton state is a sign of increased defect density or disorder in the GaN material [32,33]. Strain builds up throughout a stack of QWs and relaxation (which introduces defects) is more likely to occur in the upper QWs in a stack [15,16,17]. This implies that the secondary luminescence feature could be
originating deeper within the structure. Deeper QW periods will have fewer relaxation-induced defects than the later grown, upper QW periods in the stack and, hence, there will be less broadening of the exciton feature of the GaN absorption edge.

Figure 4.4. Low temperature (6 K) PL spectra using and excitation photon energy of 2.708 eV (black line) and low temperature PLE spectra detected at the peak of the QW emission (2.335 eV, red line) and in the region of the secondary feature (2.141 eV, green line) of sample C3396 ($T_{QW} = 690 \, ^\circC$).

The shape of the PLE spectra when detecting on either the QW peak or the secondary luminescence indicate that the electron and hole states are populated when exciting both the GaN barriers and the QWs. This phenomenon is expected from the QW peak as photo-excited carriers generated in the barrier region can be captured by the QWs adding to the QW emission intensity, but this implies that the secondary luminescence is also populated through the excitation of InGaN QWs.
The $V_{Ga,N}$ complex results in trap states located deep within the GaN bandgap \cite{30}. Correia et al. \cite{34} have shown that when monitoring the YL band using PLE spectroscopy, there is virtually no contribution to the PL intensity when exciting with a photon energy below the GaN absorption edge. Therefore, if the secondary luminescence feature is due to YL, then the PL intensity should contain minimal evidence of InGaN absorption. However, this is not the case for sample C3396, indicating the secondary luminescence band is not likely due to the $V_{Ga,N}$ complex in the GaN barriers.

**Low Temperature Above-Gap Excitation PL Spectroscopy**

To further investigate the differences in absorption from excitation photon energies greater than the GaN barrier bandgap (above-gap) compared to photon energies which are less than the GaN bandgap but greater than the QW bandgap (below-gap), low temperature (6 K) PL spectroscopy was performed on sample C3396 ($T_{QW} = 690 \, ^\circ\text{C}$) using an above-gap excitation source of 3.815 eV (325 nm) from a HeCd laser. The spectrum is shown in Figure 4.5 (red line). For comparison, a spectrum taken under 2.708 eV (457.9 nm) below-gap excitation is also shown (black line). Both spectra are normalised to highlight the relative changes in PL line shape.

The PL intensity of the spectrum acquired using above-gap excitation peaks at 2.317 eV, in agreement with the PL peak of the QWs observed using below-gap excitation. The intensity and form of the secondary feature, on the other hand, is significantly reduced.

As the YL band is due to recombination involving $V_{Ga,N}$ defects in GaN, one would expect that exciting the sample with an energy greater than the bandgap of the GaN barriers would enhance the probability of defect recombination occurring and, hence, increase the intensity of the YL band. On the contrary, the PL spectra shown in Figure 4.5 reveal the opposite effect. Exciting with a photon energy above the GaN bandgap energy effectively reduces the secondary luminescence. This further indicates that the secondary luminescence feature is not due to YL defect states.
Figure 4.5. Low temperature (6 K) normalised PL spectra of the sample with QWs grown at 690 °C, under excitation from a 2.708 eV (457.9 nm, less than the GaN bandgap) source and 3.815 eV (325 nm), greater than the GaN barrier bandgap) shown by the black line and red line, respectively.
**Low Temperature Time-Decay Spectroscopy**

Time decay measurements were recorded at low temperature (6 K) for the samples with QWs grown at 670 °C (C3693) and 690 °C (C3396). Samples were excited with a photon energy of 4.275 eV (290 nm) and measurements were taken whilst detecting at energies spanning the QW emission peak and extending across the secondary luminescence feature.

Figure 4.6 shows the emission strength as a function of time for a selection of four of the detection energies measured across the PL emission spectrum of the sample with QWs grown at 690 °C (C3396). Not all of the decay time measurements taken across the PL spectrum are shown here for reasons of clarity.

Furthermore, the emission strength as a function of time for a selection four of the detection energies measured across the PL emission spectrum of the sample with QWs grown at 670 °C (C3693) is shown in Figure 4.7. Again, only selections of the decay curves are shown here for clarity.

The decay curves shown in Figure 4.6 and in Figure 4.7 are non-exponential in shape and faster with increasing emission energy. Decay curves for these materials are typically non-exponential and is due to the DAP-nature of the localising states [35,36,37,38]. For an InGaN/GaN QW structure, the large polarisation-induced electric field separates electrons and holes across the plane of the well towards the interfaces. In-plane fluctuations of the potential, due to randomly located indium atoms, act as isoelectronic traps, capturing electrons near one interface and holes near the other interface [39]. The result is a separation of electrons and holes within the plane of the well, in addition to the field-induced well-width separation. The rate of radiative recombination is exponentially dependent on the electron-hole separation [40,41,42]. Therefore, electrons and holes which have smaller in-plane separations will have shorter recombination lifetimes, whereas electrons and holes with larger in-plane separations will have longer recombination lifetimes and the result of all of the possibilities is non-exponential decay shapes [39,43,44].

The non-exponential shape of the PL decay makes it impossible to quote a single time constant. Therefore, the lifetime is defined as the time it takes for the initial PL intensity to drop by 1/e of its original value [36]. Although this time is of no theoretical significance, it provides a useful measure of differences across the PL spectra and between samples.
Figure 4.6. Decay curves detected at various PL emission energies for the sample with QWs grown at 690 °C (C3396).
Figure 4.7. PL decay curves measured at various detection energies of the sample with QWs grown at 670 °C (C3693).
Figure 4.8 shows the 1/e lifetime (red squares) calculated for emission energies detected across the PL spectra (black line) of the sample with QWs grown at 690 °C (C3396). The PL spectra shown were measured using a pulsed excitation beam of 4.275 eV (290 nm) which was also used for the decay measurements. The lifetime, as measured from the decay curves, decreases from 46 ns at 2.12 eV to 12 ns at 2.41 eV. Furthermore, Figure 4.9 shows the corresponding 1/e lifetime (red squares) measured of the sample with QWs grown at 670 °C (C3693) for various detection energies across the PL emission spectra (black line). The lifetime decreases from 71 ns at 1.98 eV to 2 ns at 2.41 eV.

Both samples exhibit a similar trend of decreasing lifetime with increasing emission energy. This general trend (observed not only in the group III-nitrides) is a characteristic of a localised electronic system which assumes the presence of an exponential-type density of tail states [43, 45, 46, 47, 48]. As the measured lifetime is due to both radiative recombination lifetime and to the transfer process to the tail states, the result is an exponential-type change in measured lifetime.

As emission energy decreases, the lifetime observed from both samples steadily increases from across the PL spectra. Although this is expected across the QW PL peak, there is no significant difference in the lifetime between the QW luminescence feature and the secondary luminescence feature. The decay time of the secondary luminescence feature almost appears to be a continuation of the QW lifetime curve.

Yellow defect luminescence is known to have a decay lifetime on the order of microseconds [49, 50]. The relatively short lifetimes recorded in the region of the secondary luminescence rule out this feature being assigned as “yellow defect luminescence.” These lifetime measurements agree with the PLE spectra of Figure 4.4 which indicate that the secondary luminescence feature may be associated with recombination in the QWs.
Figure 4.8. Measured $1/e$ lifetime (red squares) for decay times measured at different energies across the PL spectra (black line) of the sample with QWs grown at 690 °C. Energy resolution is 18 meV.

Figure 4.9. Measured $1/e$ lifetime (red squares) for decay times measured at different energies across the PL spectra (black line) of the sample with QWs grown at 670 °C. Energy resolution is 18 meV.
Variable Temperature PL Spectroscopy

PL spectroscopy was performed at temperatures ranging from 6 K to 300 K using a below-barrier excitation photon energy of 2.708 eV (457.9 nm). The spectra are shown on a log scale in order to observe the full temperature range for each sample. As was the case for the spectra observed in Figure 4.2, not all of the Fabry-Pérot interference fringes have been suppressed despite the use of a Brewster Angle geometry in the experimental set-up.

The PL spectra shown in Figure 4.10 are of sample C3692, which has QWs grown at 650 °C. The main peak, observed at 2.265 eV at 6 K, reduces just over one order of magnitude by 300 K. The secondary feature, observed at about 2.10 eV at 6 K disappears by 160 K.

The PL spectra of sample C3693 (TQW = 670 °C) are shown in Figure 4.11. The main peak, observed at 2.200 eV at 6 K, reduces just over one order of magnitude by 300 K. The secondary feature, observed at 2.02 eV at 6 K disappears by 200 K.

The PL spectra of sample C3693 (TQW = 680 °C) is shown in Figure 4.12. The main peak at 2.348 eV reduces in intensity by over 2 orders of magnitude from 6 K to 300 K. The secondary feature, observed at 2.149 eV at 6 K disappears by 160 K, at which point a third, lower energy emission becomes apparent in the spectra up to 300 K.

The PL spectra of C3396 (TQW = 690 °C) is observed in Figure 4.13. As temperature is increased, the intensity of the QW feature reduces over 2 orders of magnitude between 6 K and 300 K. By 80 K, the secondary luminescence becomes the dominant feature and remains so until the measurement temperature reaches 260 K, after which the QW feature dominates again.

In the PL spectra shown in Figure 4.14 of sample C3694 (TQW = 700 °C), the secondary luminescence is notable in that its emission spectrum is very close in energy to the main QW feature and has largely disappeared at temperatures above 180 K. Intensity of the main QW peak decreases about 1 order of magnitude between 6 K and 300 K.
Figure 4.10. PL spectra of sample C3692, which has 10 QWs grown at 650 °C, measured at temperatures ranging between 6 K and 300 K.
Figure 4.11. PL spectra of sample C3693, which has 10 QWs grown at 670 °C, measured at temperatures ranging between 6 K and 300 K.
Figure 4.12. PL spectra of sample C3613, which has 10 QWs grown at 680 °C, measured at temperatures ranging between 6 K and 300 K.
Figure 4.13. PL spectra of sample C3396, which has 10 QWs grown at 690 °C, measured at temperatures ranging between 6 K and 300 K.
Figure 4.14. PL spectra of sample C3694, which has 10 QWs grown at 700 °C, measured at temperatures ranging between 6 K and 300 K.
The QW samples grown at 680 °C and 690 °C (C3613 and C3396) have lower energy luminescence bands which are not fully quenched at higher temperatures. These two samples also both show a greater reduction of PL intensity with increasing temperature. To exemplify the thermal quenching of PL intensity for the 10 QW samples, integrated PL intensity of the whole spectrum as a function of measurement temperature is shown in Figure 4.15.

Figure 4.15. Normalised integrated PL intensity as a function of temperature for QW growth temperatures of 650 °C (black squares), 670 °C (red dots), 680 °C (green upright triangles), 690 °C (blue downward triangles), and 700 °C (cyan diamonds).

For InGaN/GaN QW structures, the low temperature recombination is assumed to be purely radiative due to the small (around a factor of 2) change of integrated PL intensity compared to the large (around a factor of 16) variations in the rate of decay [20,36]. Therefore, normalising the integrated intensity at 6 K to 100 %, the room temperature internal quantum efficiency (IQE) can be determined
from the 300 K value [51]. Using this method, the QWs grown at 680 °C and 690 °C have a very low IQE of 1 %. The QWs grown at 670 °C and 650 °C have an IQE of 6 % and 9 %, respectively. The QW grown at 700 °C has an IQE of 14 %.

Although these values imply that the lowest and highest QW growth temperatures result in the highest IQE, their respective PL peak emission energies need to taken into consideration in order to fully understand the effect of QW growth temperature on overcoming the limits of the ‘green gap’. Figure 4.16 shows the IQE of these samples versus their respective PL peak energy. In addition, IQE of the state-of-the-art samples [4,5,6,8] are also shown in grey to illustrate the limiting factor of the so-called ‘green gap’ on IQE.

![Graph showing IQE vs. PL peak energy](image)

**Figure 4.16.** IQE of C3692, C3693, C3613 and C3694 (red triangles), compared to the ‘state-of-the-art’ IQE as reported by several authors [4,5,6,8] (black shapes).

When IQE is put into context of emission energy, sample C3694, which had the highest QW growth temperature (700 °C) and highest IQE (14 %), is actually performing about 1/3 of the maximum IQE reported at about that emission energy. This is in contrast to sample C3693 (\(T_{\text{QW}} = 670 \, ^\circ\text{C}\)) which performs with an IQE of
6% yet appears to be pushing the boundaries of the ‘green gap’ at 2.20 eV. Samples C3613 ($T_{QW} = 680 \degree C$) and C3396 ($T_{QW} = 690 \degree C$) fall well below the state-of-the-art curve and this is likely due to the additional luminescence bands contributing to luminescence at higher temperatures. Nevertheless, when comparing IQE of the variable QW growth temperature samples, the samples grown with the lowest QW growth temperatures appear to be the best performers, relative to the state-of-the-art samples.

### 4.2.2.3. Summary of Varying QW Growth Temperature Results

Low temperature PL spectroscopy indicates that regardless of QW growth temperature, these samples have emission spectra consisting of a strong high energy feature and a secondary lower energy feature. The primary, higher energy luminescence feature is ascribed to the recombination of electrons and holes in the InGaN QWs; however the cause of the secondary, lower energy luminescence feature is not fully understood. It is believed that the secondary emission may be due to QW emission and not YL band.

Photoluminescence excitation spectroscopy results cast doubt on the secondary luminescence feature being due to the $V_{GaO_N}$ defect complex. When monitoring the secondary luminescence feature, the PLE spectrum (shown in Figure 4.4) showed strong contribution to the PL intensity from absorption of the InGaN QWs. This implies that the secondary luminescence feature is either due to emission from the InGaN QWs or by carrier relaxation from the InGaN QWs into a radiative defect state. The only known radiative defect which emits around 2.25 eV is the $V_{GaO_N}$ defect complex of GaN [29,30], but it has been shown there is virtually no contribution to the PL intensity when exciting with a photon energy below the GaN absorption edge [34].

Furthermore, the PL spectrum which was measured using above-gap excitation shows a decrease in the secondary luminescence relative to the primary, higher energy QW emission when compared to the spectrum measured using below-gap excitation. This characteristic is the opposite of what one would expect if the luminescence was originating from $V_{GaO_N}$ defects in the GaN barriers.

Both PLE spectroscopy and above-gap excitation PL spectroscopy show different trends than what would be expected for the YL band. Therefore, the
secondary luminescence band is not ascribed to yellow defect luminescence caused by the $V_{Ga}\text{O}_{N}$ complex in the barriers.

Photoluminescence excitation spectroscopy results also imply that the secondary luminescence originates deeper within the sample. The GaN exciton feature observed in the PLE spectra becomes resolved when detecting on the secondary luminescence which is known to be a sign of increased crystal quality, compared to the higher energy emission feature [32,33]. Crystal quality of the GaN is known to degrade with increased thickness [17]. Therefore, it would be expected that fewer defects exist in the crystal structure for the lowest lying QWs. This would result in better resolved GaN exciton spectra, which is what is observed when monitoring the secondary luminescence feature.

This could also imply the secondary luminescence is originating deeper in the QW stack. One additional consequence of changing the excitation photon energy in a PL experiment is the resulting difference in the penetration depth. The penetration depth is dependent on the wavelength of the light being absorbed as it is a function of the absorption coefficient. As light passes through the material, a percentage of the incident light is absorbed according to the Beer-Lambert law, that is

$$I_{\text{transmitted}}(\lambda, \xi) = I_{\text{incident}} e^{-\alpha(\lambda)\xi},$$

where $\alpha(\lambda)$ is the absorption coefficient of the absorbing material and $\xi$ is distance travelled. The extinction coefficient or penetration depth is defined as the distance it takes for the incident intensity to reduce by $1/e$ of its original value [52]. From Equation 5-1, this occurs when $\xi = 1/\alpha(\lambda)$.

The absorption coefficient of GaN at 3.815 eV (325 nm) is $11.9 \times 10^4$ cm$^{-1}$ and at 2.708 eV (457.9 nm) is virtually zero [53]. These values result in a penetration depth of 83 nm for 3.815 eV (325 nm) excitation and no absorption for 2.708 eV (457.9 nm) excitation. By just considering the absorption of GaN, the penetration depth of a 3.815 eV (325 nm) excitation source is equivalent to about 9 GaN barriers in this system. This means that most of the light would be absorbed before it reached the bottom 2 QWs, the first GaN barrier, and the buffer layers. On the other hand, light from 2.708 eV (457.9 nm) excitation would penetrate further into the sample.

Therefore, the reduction in PL intensity of the secondary luminescence when increasing the excitation photon energy could be a result of the difference in
penetration depth. If the secondary luminescence is in fact originating in the lowest QWs/barriers (as is suggested by the PLE spectra) and the HeCd laser light is unable to efficiently penetrate to the lowest lying QWs/barriers, then there would clearly be a reduction in PL intensity from these layers as is observed in Figure 4.5.

These results imply that the secondary luminescence originates from the lowest lying QWs of the stack. Further information is required, however, to understand why the lower lying QWs are contributing to lower energy PL emission.

4.2.3. Varying the Number of QWs

In section 4.2.2, it was found that the traditional 2T growth method for high indium content (~25%) InGaN/GaN 10 QW structures results in multiple luminescence features, regardless of QW growth temperature. Above-gap excitation PL and PLE measurements indicate that the secondary luminescence band originates deep in the sample, possibly in the first few QWs. As PLE spectra of the secondary luminescence indicate a difference in the crystal quality, it is possible that the critical thickness is being exceeded for these high concentration InGaN QWs. The increase in the number of misfit dislocations as a result of exceeding the critical thickness will have a detrimental effect on the IQE of the material. To further investigate the origin of the secondary luminescence and the reduced IQE for higher QW growth temperatures, a series of QW structures were investigated in which the QWs were grown at the same temperature but consisted of a single QW and stacks of 3, 5 and 10 QWs.

4.2.3.1. Sample Details

The series of samples discussed in this section consist of a set of four samples where the In$_x$Ga$_{1-x}$N QW growth temperature remained constant at 690 °C, the ramp time remained constant at 60 s, whilst the number of QWs grown varied between 1 and 10. Sample C3396 (10QWs) was discussed in the previous section and is included here for completeness. The details of this sample set are described in Table 4.2 below.
Table 4.2. Sample growth parameters of a set of varying number of In$_x$Ga$_{1-x}$N QWs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ramp Time (s)</th>
<th>QW growth temperature (°C)</th>
<th>Number of QWs</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3389</td>
<td>60</td>
<td>690</td>
<td>1</td>
</tr>
<tr>
<td>C3997</td>
<td>60</td>
<td>690</td>
<td>3</td>
</tr>
<tr>
<td>C3395</td>
<td>60</td>
<td>690</td>
<td>5</td>
</tr>
<tr>
<td>C3396</td>
<td>60</td>
<td>690</td>
<td>10</td>
</tr>
</tbody>
</table>

4.2.3.2. Experimental Details

**Low Temperature PL Spectroscopy**

This sample series was investigated using low temperature (6 K) PL spectroscopy. The excitation source was the 2.708 eV (457.9 nm) line of an Ar$^+$ laser which excites carriers in the QWs, but not in the GaN barriers. The PL spectra of the 10 QW (black line), 5 QW (red line), 3 QW (green line), and 1QW (blue line) samples are shown in Figure 4.17.

Figure 4.17. Low temperature (6 K) PL spectra of QW samples where the 1 (C3398, blue line), 3 (C3397, green line), 5 (C3395, red line) or 10 (C3396, black line) QWs were grown at 690 °C.
The PL spectrum of the single quantum well structure (sample C3398) consists of a narrow, asymmetric feature, which peaks at 2.164 eV. The spectrum of the 3 QW structure (sample C3397) is much broader, centred about 2.208 eV, and appears to have a shoulder on the high energy side, around 2.33 eV. Also, the low energy side of the spectrum follows the shape of the single QW spectra. This indicates that the PL spectrum of the 3 QW structure may consist of overlapping QW emission features. The PL spectra of the 5 QW structure (sample C3395) and 10 QW structure (sample C3396) have a similar shape and appear to have two distinct features: an intense QW emission at 2.327 eV and a less-intense, broad band which is centred about 2.260 eV. This lower energy PL band is similar in shape to the PL spectrum of the 3 QW structure.

These results support the suggestion from Section 4.2.2 that the first few QWs contribute to lower energy emission and later grown QWs contribute to the higher energy emission. The broad nature of the PL emission of the 3 QW structure (sample C3397) compared to that of the single QW structure (sample C3398) imply that the second and third QWs emit at higher energy than the first QW. As there is little change between the PL line-shape of the 5 and 10 QW structures (samples C3395 and C3396), it is likely that the emission energy does not shift further after the 5th QW is grown.

**Variable Temperature PL Spectroscopy**

PL spectra of the samples with different numbers of QWs were measured at temperatures ranging between 6 K and 300 K. The spectra contain strong Fabry-Pérot interference fringes despite the use of a Brewster angle geometry in the experimental set-up.

The temperature dependent PL spectra of sample C3396 (10 QWs) are shown in Figure 4.13 of the previous section and are therefore not shown again here. As a reminder, the 6 K PL spectrum contains a high energy feature at 2.313 eV with a less intense, broad, lower energy feature at about 2.216 eV. The intensity of the secondary luminescence feature (which is now believed to be due to emission from the first few QWs) becomes dominant by 80 K and remains so until 260 K, after which the high energy QW feature (due to the later grown QWs) becomes dominant again. The overall PL intensity reduces by about 2 orders of magnitude.
The temperature dependent PL spectra of sample C3395 (5 QW) are shown in Figure 4.18 and are very similar in shape to that of the 10 QW sample, with the exception of the contribution to the PL intensity from the later grown wells is reduced, relative to the contribution from the first few wells. Furthermore, like the 10 QW spectra, the PL contribution of secondary feature of the 5 QW sample becomes the dominant feature in the spectra by 100 K. It remains dominant until 300 K. The overall PL intensity also reduces by about 2 orders of magnitude to room temperature.

The temperature dependent PL spectra of sample C3397 (3 QW) are shown in Figure 4.19. The contribution to the PL intensity from what may be the first two QWs is dominant at 6 K and remains so until 220 K when the intensity of the higher energy feature, possibly due to the third QW, becomes dominant. The overall PL intensity reduces by over 2 orders of magnitude between 6 K and 300 K.

The temperature dependent PL spectra of sample C3398 (1 QW) are shown in Figure 4.20. The spectra consist of a single PL feature at all temperatures. The intensities of this sample, similar to the multiple QW samples, reduce by about two orders of magnitude between 6 K and 300 K.

The higher energy luminescence feature, which may be due to the third through tenth QWs, quenches faster than PL intensity of the first two QWs in the stack at low temperatures (up to about 100 K). For higher temperatures, the PL contribution from the first two QWs of the multiple QW structures is nearly fully quenched by room temperature.

The integrated PL intensities for these QW structures as a function of measurement temperature are shown in Figure 4.21. Assuming the low temperature PL emission is purely due to radiative recombination in the QWs (i.e. 100 %) [20,36], room temperature IQE can be determined from the ratio of the integrated PL intensity at 300 K to integrated PL intensity at 6 K.

From the integrated intensities shown in Figure 4.21, the 5 and 10 QW structures (samples C3395 and C3396, respectively) have a room temperature IQE of about 1 %. The triple QW structure (sample C3397) has the poorest room temperature IQE of 0.2 %. The single QW structure (sample C3398) has an IQE of about 0.7 %.
Figure 4.18. PL spectra of C3395 (5 QWs) measured at temperatures between 10 K and 300 K.
Figure 4.19. PL spectra of C3397 (3 QWs) measured at temperatures between 6 K and 300 K.
Figure 4.20. PL spectra of C3398 (1 QW) measured at temperatures between 6 K and 300 K.
4.2.4. Microscopy Results

Microscopy measurements were taken by colleagues at the University of Cambridge to further understand the findings of the optical measurements discussed in Sections 4.2.2 and 4.2.3. Measurements reported in this section include scanning transmission electron microscopy high-angle angular dark field transmission electron microscopy (STEM-HAADF) and high resolution x-ray diffraction (HR-XRD).

STEM-HAADF microscopy yields information on the total thickness of a QW period and also information of the QW, itself. Additionally, it shows Z-contrast which results in the InGaN QWs appearing to have a lighter colour than GaN barriers in the images. The contrast acts as an indication of the amount of indium present; however, brightness cannot be taken as an absolute measure of indium concentration as these values are averaged through the thickness of the specimen.
High resolution X-ray diffraction (HR-XRD) measurements of MQW samples can yield information on indium content and layer thickness of InGaN QWs. By modelling the measured HR-XRD rocking curves, the thickness of the QWs and barriers can be estimated, as well as the average indium concentration.

Scanning Transmission Electron Microscopy

STEM-HAADF microscopy was performed by D. V. Sridhara-Rao [54] of the University of Cambridge on sample C3693 (10 QWs grown at 690 °C). Shown in Figure 4.22 is a STEM-HAADF image of the first five QWs obtained along the [012\bar{1}] axis. The darker regions correspond to GaN buffer/barrier layers and the thin bright stripes correspond to the InGaN QWs. The substrate would lie to the left of the images and the QWs are numbered according to the order in which they were grown on the substrate, that is, QW “1” was the first to be grown, QW “2” was the second, and so on.

It is clear from Figure 4.22 that higher numbered wells have significantly less contrast than the lower numbered wells (that is, they appear darker relative to the lower QWs). Furthermore, there is a decrease in thickness uniformity in the plane of QWs as well number increases. The yellow arrows in the image point out two regions, in particular, which have much thinner regions within the plane of the wells.

Figure 4.23 shows an enhanced image of the first three wells. Here the individual 0.519 nm thick \(c\)-planes can be observed more clearly. Sridhara-Rao measured the average thickness of the GaN barriers to be 8.83 nm and the average thickness of first three QWs to be 3.17 nm. The 4th QW through to the 10th QW contained many more variations across each of the wells and were therefore too difficult to determine an average QW thickness for each of these wells.

These STEM-HAADF images show that the first few wells are indeed significantly different from the rest of the QW stack. The first 2 or 3 wells are more uniform than wells 4 – 10. The images also show the larger numbered QWs appear much fainter which may be an indication that these QWs contain less indium. Nevertheless, the results confirm that the wells are not uniform throughout the 10 QW stack.
Figure 4.22. STEM-HAADF image obtained along the $[\{11\bar{2}0\}]$ axis of the first five QWs of the sample with a 690 °C QW growth temperature [54]. The substrate would lie to the left of the image.

Figure 4.23. STEM-HAADF image obtained along the $[\{11\bar{2}0\}]$ axis of the first three QWs of the sample with a 690 °C QW growth temperature [54]. A c-plane is defined as 0.519 nm thick.
**High Resolution X-Ray Diffraction**

McAleese [55] performed HR-XRD measurements on the 10 QW samples C3692 \( (T_{QW} = 650 \, ^\circ C) \), C3693 \( (T_{QW} = 670 \, ^\circ C) \), C3613 \( (T_{QW} = 680 \, ^\circ C) \), C3396 \( (T_{QW} = 690 \, ^\circ C) \) and C3694 \( (T_{QW} = 700 \, ^\circ C) \). Measurements were recorded in both open detector and triple axis \( \omega/2\theta \) (0002) scans. The spacing of the narrow fringes is related to the total thickness of the QW structure, whereas the wider, more intense fringe spacing is related to the thickness of the QW periods.

Measurements confirm that the QW stacks may not be completely ideal. Many of the scans contained no distinct minimum of the satellite peak intensity, indicating that there exist well-to-well fluctuations in the QW stacks. The satellite peak intensity allows for a simulation to approximate the well and barrier widths and indium concentration of the wells. Simulations of the measured scans typically assume an ideal stack, i.e. assuming all 10 QWs are identical. Therefore ideal simulations resulted in poor fits to the measured scans.

McAleese found that sample C3694 \( (T_{QW} = 700 \, ^\circ C) \) is the closest of all 10 QW samples to conform to an ideal stack. Nonetheless, as QW growth temperature is reduced, there is no longer a distinct minimum of the satellite peak observed in the reflection scans. Without distinct minima, simulations are not reliable and in sample C3692 \( (T_{QW} = 650 \, ^\circ C) \), for example, no reliable simulation could be carried out, indicating that this sample is a highly non-ideal QW stack.

The HR-XRD triple-scan measurement of sample C3694 \( (T_{QW} = 700 \, ^\circ C) \) is shown below in Figure 4.24. The blue line represents the experimentally measured rocking curves of the triple axis scan. The red curve is a ‘best fit’ simulation, based on an ideal structure, of the experimental data. This measurement reveals that the QW stack may not be completely ideal, but the distinct minimum in the satellite peak intensity allows for the ideal simulation to approximate the well and barrier widths and also the indium concentration of the wells. For this sample, McAleese calculated the GaN barrier thickness to be 9.2 nm ± 0.1 nm, the InGaN QW thickness to be 2.1 nm ± 0.1 nm, and the indium concentration to be 25.3 % ± 1.2 %. McAleese noted that these values will be an average across the entire structure and the indium content will be an underestimate of the true value.
Results from the HR-XRD measurements of sample C3693 ($T_{\text{eff}} = 670 \, ^\circ \text{C}$) are shown in Figure 4.25. The scan contained no distinct minimum of the satellite peak intensity, indicating that the well-to-well fluctuations are greater in this sample. For this reason, the ideal simulation shown in Figure 4.25 is a very poor fit to the measured data.
Therefore, McAleese adjusted the ideal simulation to account for two QWs being equally different from the other 8 QWs. He adjusted the parameters of the simulation to either a) assume 2 QWs have different thickness; or b) to assume that the 2 QWs contain different indium content from the other 8 QWs in the stack. For each of these simulations, the GaN barrier width was assumed to be ideal and identical to the values obtained from the simulation of sample C3693 (QWs grown at 700 °C).

McAleese’s simulations of the HR-XRD rocking curves for sample C3693 are presented in Figure 4.26. Here, the blue line represents the experimentally acquired HR-XRD rocking curve. The magenta line is a simulation which assumes all 10 QWs are identical. In this case, the ‘best fit’ was obtained for 2.2 nm thick wells containing In$_{0.22}$Ga$_{0.78}$N. The red line represents a simulation based on two wells having an increased thickness. For this case, a ‘best fit’ was obtained assuming 8 QWs had the ‘ideal’ parameters but the thickness of the 2 QWs was increased to 2.8 nm. The green line represents a simulation in which two wells contained greater indium content. For this situation, a ‘best fit’ was obtained assuming the 8 QWs had the ‘ideal’ parameters but the 2 QWs contained 28% indium.

Figure 4.26. HR-XRD rocking curve of sample C3693, QW growth temperature of 670 °C (blue line) and simulations based on an ideal 10 QW structure (magenta line), thicker initial two wells (red line), and higher indium content in first two wells (green line) [55].
Both of the simulations of the measured HR-XRD rocking curves which were adjusted for a difference in 2 of the 10 QWs show a significant improvement on the fit of the model to the experimental data. This implies that the structure does indeed have variation between the QWs, such that there exist 2 QWs in the stack that either contain more indium or have thicker well-widths. Both of these situations would result in lower bandgap energy of the QWs, in agreement with the optical measurements discussed in Sections 4.2.2 and 4.2.3. However, it is not clear from the simulations whether the difference is a thickness variation or an indium concentration variation. It could also be a combination of both, but HR-XRD measurements alone are unable to clarify this.

4.2.5. Summary on Conventional Growth Methods

PL spectroscopy discussed in Section 4.2 has shown there exist two distinct luminescence features for high indium content InGaN/GaN QW structures grown using the conventional 2T growth method. These features are ascribed to two distinct regions of the QW stack: the lower energy, lower intensity, broad feature is ascribed to the first 2 or 3 QWs which have thicker well-widths and/or greater indium content than the rest of the stack; the higher energy, higher intensity, narrow feature is ascribed to the third or fourth through tenth QWs.

The microscopy results in Section 4.2.4 confirm the suggestion made in Section 4.2.3.2 that the first 2 or 3 (lowest lying) QWs in the stack are thicker and/or contain more indium than the rest of the QW stack. Furthermore, STEM-HAADF microscopy confirms the suggestion that the crystal quality of the lower QWs is better than the upper QWs. STEM-HAADF measurements reveal that the first 2 or 3 QWs grown are fairly uniform in thickness, but further QWs contain inter- and intra-well thickness fluctuations. The change in contrast of the first few QWs, relative to later QWs suggests that a reduction in indium concentration might also occur in these samples. HR-XRD measurements support the suggestion that a reduction of indium concentration in later grown QWs could, in addition to thickness variations, contribute to the observance of at least two luminescence features.

The optical and microscopy measurements discussed in this section are unable to confirm whether the secondary luminescence is solely a result of thickness variations between the first few wells or whether it is due to a combination of
thickness and indium concentration. What is certain, however, is that the first few QWs have the least well-to-well variations, compared to the rest of the QWs in the stack. Minimising these well-to-well variations could result in narrower emission spectra. Therefore, it was proposed that the growth process for multiple In$_x$Ga$_{1-x}$N quantum wells grown with high (~25%) indium concentration should be modified on a well-to-well basis in order to minimise well-to-well variations.

4.3 Modified Growth Methods

4.3.1. Introduction

In the previous section, it was determined that for high indium content In$_x$Ga$_{1-x}$N/GaN multiple quantum wells (x ~ 0.25), traditional 2T growth methods resulted in variations between the quantum wells grown within a stack. Increasing the temperature of the QW growth was found to reduce the energy separation of the two luminescence features. The first two wells (at least) had more indium, were thicker, or possibly a combination of both. In this section, the conventional 700 °C 2T growth parameters were slightly varied on a well-to-well basis in order to reduce the variations between wells. It was predicted that reducing these variations would result in a single PL feature from the quantum wells and increase the internal quantum efficiency.

4.3.2. Sample Details

The samples to be discussed in this section include two series of 4 samples each and a 10 QW control sample. Each series contained a single quantum well, and a 3, 5, and 10 quantum well stack. The ramp time for all samples was 60 s. The control sample is C3694, a 10 QW sample where all wells were grown at 700 °C with a growth time of 190 s.

The Time-Adjusted series had adjustments to the QW growth time to compensate for a thickness variation. All wells had a 700 °C growth temperature; however, the first well growth time was 164 s, and the second well was grown for 177 s. All further wells were grown for 190 s. The Time-Adjusted series samples and their growth parameters are listed in Table 4.3.
Table 4.3. Sample parameters of the Time-Adjusted In$_x$Ga$_{1-x}$N/GaN 10 QW structures

The Temperature-Adjusted series had adjustments to the growth temperature to compensate for an indium variation. All wells had a 190 s growth time. The first well was grown at 710 °C, the second at 705 °C, and the rest at 700 °C. The Time-Adjusted series samples are described in Table 4.4.

Table 4.4. Sample parameters of the Temperature-Adjusted In$_x$Ga$_{1-x}$N/GaN 10 QW structures.

4.3.3. Experimental Results

Low Temperature PL Spectroscopy

Low temperature (6 K) photoluminescence measurements were performed on the Time-Adjusted and Temperature-Adjusted samples. The samples were mounted in a closed cycle helium cryostat horizontally rotated to the Brewster angle for a GaN/air interface. Samples were excited using the 2.586 eV (479.5 nm) line from the Ar$^+$ laser.

Low temperature photoluminescence spectra of the 10 QW structures, including the control sample, are presented in Figure 4.27. The low temperature PL spectrum of control sample C3694 (black line) has a very broad emission band with a FWHM of 211 meV which consists of at least 2 overlapping features: a high energy feature at 2.307 eV and a low energy feature at 2.214 eV. The PL spectrum of the time-adjusted 10QW sample (C3865, red line) has a much narrower FWHM of 135 meV and appears to consist of a feature at 2.389 eV. Similarly, the PL spectrum of the temperature-adjusted 10QW sample (C3862, green line) has a narrower FWHM of 125 meV and consists of a single feature at 2.393 eV.
Figure 4.27. PL spectra of the 10 QW structures which were grown via conventional methods (C3694, black line), by adjusting the individual QW growth time (C3865, red line), and by adjusting the individual QW growth temperature (C3862, green line).
Changing the growth parameters of the first two wells by either adjusting the growth time or the growth temperature has a similar, dramatic effect on the PL spectra of the 10 QW samples, as displayed in Figure 4.27. The secondary luminescence virtually disappears and the result is a 40% reduction of the PL linewidth compared to that of the non-adjusted, standard sample.

Low temperature PL spectroscopy of the Time-Adjusted QW series is shown in Figure 4.28. The PL peak energy of the samples increases with increasing number of QWs. The FWHM obtained from these spectra are 85 meV for the single QW (C3858), 130 meV for the 3 QW (C3863), 129 meV for the 5 QW (C3864) and 135 meV for the 10 QW (C3865). The 3 and 5 QW structures are 1.5 times broader than the single QW. This indicates that although the growth time has been adjusted to correct for well-to-well variations in thickness, further adjustments to either the thickness or indium content may be required to achieve better uniformity through the QW stack.

Low temperature PL spectra of the Temperature-Adjusted series are shown in Figure 4.29. The PL peak energy of the samples increases with increasing number of QWs, similar to as was observed by the traditionally grown samples in Figure 4.17. This indicates that although the temperature has been adjusted to correct for well-to-well variations in the indium content, further adjustments to either the indium content or thickness are required to achieve uniformity across all wells.

The low temperature PL spectra of the Time- and Temperature-Adjusted single QW samples (C3858 and C3859, respectively) contain multiple, low intensity features on both the low and high energy sides of the main PL peak. The PL spectra of these samples were measured in a Brewster angle geometry to reduce the effects of Fabry-Pérot interference. Kappers [56] used reflectivity to measure the spacing of Fabry-Pérot interference fringes for these samples and found a spacing of about 35 meV. This spacing is much less than the spacing of the features observed in the PL spectrum and therefore the features are not believed to be due to Fabry-Pérot interference.
Figure 4.28. Low temperature PL spectra of the Time-Adjusted series: 10 QW (C3865, black line), 5 QW (C3864, red line), 3 QW (C3863, green line), and 1 QW (C3858, blue line).
Figure 4.29. Low temperature PL spectra of the Temperature-Adjusted 10 QW (C3862, black line),
5 QW (C3861, red line), 3 QW (C3860, green line) and 1 QW (C3859, blue line) samples.
On the low energy side of the QW PL peak, the features are equally spaced at about 91 meV apart. For InGaN QW structures, longitudinal-optical (LO) phonon replicas are spaced about 91 meV apart on the low energy side of the zero-phonon emission line [57,58,59,60]. Therefore, the lower energy, evenly spaced features are likely due to LO-phonon replicas.

The features on the high energy side of the main emission line are not evenly spaced. Furthermore, LO phonon replicas are only observed at energies lower than the zero-phonon emission energy. Therefore, there must be a different explanation for the features observed on the higher energy side of the PL spectra.

The spectrum of the Temperature-Adjusted single QW sample (C3859) in Figure 4.29 shows a particularly intense shoulder on the high energy side of the QW PL peak and upon further inspection a second, very low intensity function at higher energy. The features on the high energy side of the QW recombination peak are not evenly spaced. In fact, the first feature is spaced about 64 meV above the QW recombination peak and the second is about 100 meV above the first feature. With this being a single QW structure, the spectra should not suffer from the effects of inter-well variations of thickness or indium content and so do not correspond to the additional PL features observed in the non-adjusted, standard QW structures.

One thought is that these features could be due to ‘network structures’. Van der Laak et al. reported [21,22] that InGaN epilayers which were grown using the 2T growth method contain gross well-width fluctuations consisting of a brain-like network of interlinking InGaN strips, as shown in the STEM-HAADF image shown in Figure 4.30 [21]. These strips contained indium-rich centres and are divided by troughs of GaN which were thought to be formed from decomposition of the InGaN layer during the temperature ramp of the 2T growth process. The size of these network structures is on a lateral length scale of tens of nanometres. The centres of the strips were found to be indium rich and the edges were found to be indium deficient.

The low temperature PL spectrum of the single QW structure grown by the temperature-adjusted method (Figure 4.29) has a peak at 2.344 eV with two higher energy features at 2.412 eV and 2.510 eV. Using the program BluCalc [61] to estimate QW confined states by effectively solving the Schrödinger equation whilst taking into account electric field effects, the high energy features would require the
indium concentration to decrease from 25% to 24% and 20% for the 2.412 eV and 2.510 eV features, respectively.

![STEM-HAADF image of an uncapped InGaN QW in plan-view](image)

Figure 4.30. STEM-HAADF image of an uncapped InGaN QW in plan-view [21].

Although the InGaN strips shown in Figure 4.30 have, on average, a higher indium concentration centre and lower indium concentration at the edges, the indium distribution is not a discrete step. Also, the strips are not all identical. A typical laser spot size used in the PL experiments discussed this thesis is about 200 µm in diameter. This would span across many InGaN strips which all have random indium fluctuations across the strip. The indium content would thus average out to some extent across the laser spot size. The PL features observed in the PL spectra of the single QWs may be too discrete for such distributions.

An alternate suggestion for the higher energy PL features is fluctuations of the QW thickness. Decreasing the QW thickness of an InGaN QW can have a profound effect on the QW confined states. In addition to increasing the quantum confinement on electron-hole energy levels, reducing the QW thickness reduces the impact of band-bending which is due to the strain-induced piezoelectric constants of InGaN. STEM-HAADF images of InGaN/GaN QWs have been shown to contain monolayer variations in well thickness [27,62,63]. Furthermore, Graham et al. [27] showed that the lateral extent of these fluctuations was 1-2 nm in the plane of the well.

An extensive search of the literature provided no references for observing monolayer fluctuations in PL spectra of InGaN/GaN QW structures, though monolayer fluctuations have been proposed as causing broadening of PL spectra.
A monolayer for the nitrides consists of 0.259 nm [71,72]. Using BluCalc [61] to estimate transition energies, a monolayer decrease in QW thickness would result in an energy increase of 78 meV. A second monolayer decrease would correspond to a further 111 meV increase above the single monolayer emission. These energy separations are approximately what are observed in the PL spectra of sample C3859. Therefore, it is proposed that these high energy features are due to discrete thickness fluctuations in the QW.

**Temperature Dependent Photoluminescence Results**

Temperature dependent photoluminescence measurements were taken of the samples in the Time- and Temperature-Adjusted series. The temperature dependent PL spectra of the control sample, C3694, can be found in Figure 4.14 in Section 4.2.2.2 and is therefore not shown again here.

The PL spectra of the Time-Adjusted 10 QW sample (C3865) are shown in Figure 4.31. There appears to be some Fabry-Pérot interference in the spectra, despite the Brewster angle experimental set-up. There is no secondary luminescence feature in the 2.2 – 2.3 eV range for any temperature. The spectra reduce in intensity less than one order of magnitude between 6 K and 300 K.

Figure 4.32 displays the PL spectra of the Temperature-Adjusted 10QW sample over the range of 6 – 300 K. Again, the spectra exhibits a single, narrow feature and there is no observable spectral feature in the 2.2 – 2.3 eV range for all temperatures. Furthermore, the spectra reduce less than an order of magnitude in intensity between 6 K and 300 K, similar to what was observed for the Time-Adjusted 10 QW sample.

These spectra are significantly improved compared to the control sample (C3694) which exhibited a secondary feature at about 2.2 eV. This feature was barely distinguishable by 180 K, but the result was a severe reduction in intensity at room temperature.
Figure 4.31. PL spectra of the Time-Adjusted 10 QW sample (C3865) measured at temperatures ranging between 6 K and 300 K.
Figure 4.32. PL spectra of the Temperature-Adjusted 10 QW (C3862) sample measured at temperatures ranging between 6 K and 300 K.
The integrated intensity of the PL spectra at each measurement temperature for the 10 QW samples is shown in Figure 4.33. The integrated intensity of the Time-Adjusted sample (C3865) is shown in red circles, the Temperature-Adjusted sample (C3862) is shown in black squares and the control sample (C3694) is shown in green triangles. Internal quantum efficiency is calculated assuming the emission is completely radiative at low temperature. This yields an IQE for the Time-Adjusted sample as 33% and for the Temperature-Adjusted sample as 38%. These are huge improvements in IQE over the samples grown using traditional methods such as the control sample which was found to have an IQE of 14%.

![Figure 4.33](image.png)

**Figure 4.33.** Normalised integrated intensity as a function of measurement temperature for the Time-Adjusted sample (C3865, red circles), the Temperature-Adjusted sample (C3862, black squares) and the control sample (C3694, green triangles).

Temperature dependent PL spectra of the Time-Adjusted 5 QW (C3864), 3 QW (C3863), and 1 QW (C3858) samples are shown in Figure 4.34, Figure 4.35, and Figure 4.36, respectively. As the number of QWs is reduced, LO phonon replicas become more pronounced on the lower energy side of the main luminescence peak. The PL spectra from these samples also indicate that a high
energy feature may be present up to about 80 K. The PL spectra of the single QW sample (C3858) shows these monolayer features quite distinctly and two features are clearly visible in the spectra below 80 K. This sample also exhibits Fabry-Pérot interference in the PL spectra with narrow energetic spacing corresponding to the fringe spacing determined from reflectivity measurements [56].

Temperature dependent PL spectra of the Temperature-Adjusted 5 QW (C3861), 3 QW (C3860), and 1 QW (C3859) samples are shown in Figure 4.37, Figure 4.38, Figure 4.39, respectively. The PL spectra of these samples also indicate a high energy monolayer feature which is present up to 80 K. The single QW PL spectra contain two of these features.

The internal quantum efficiency was determined for all samples from the room temperature value of normalised integrated PL intensity of all samples, as discussed previously. For the Time-Adjusted series, the 10, 5, 3 and 1 QW samples had IQE values of 33 %, 34 %, 25 %, and 3 %, respectively. The Temperature-Adjusted series 10, 5, 3, and 1 QW samples had IQE values of 38 %, 31 %, 20 %, and 2 %, respectively. The IQE for both the Time- and Temperature-Adjusted series are plotted against their low temperature (6 K) PL peak energy in Figure 4.40. The Time-Adjusted samples are displayed as red triangles and the Temperature-Adjusted samples are displayed as green triangles. For comparison, the IQE values of ‘state-of-the-art’ samples [4,5,6,8] are also displayed using grey symbols.

The room temperature IQE of the single quantum well samples from the Time- and Temperature-Adjusted series are both significantly less than the multiple QW samples. This is expected because these samples do not have any other wells which could participate in carrier recapture. For single QWs, carriers which are thermally excited out of the well will only add to the QW PL intensity if they are subsequently recaptured by the same well. The multiple QW structures may have an IQE greater than the single QW structures because photo-excited carriers which are thermally excited out of a well have the added probability of being captured by another well. Increasing the number of QWs has been shown to reduce the thermal quenching of the PL intensity of lower indium content QW structures [73]. Clearly from the IQE values displayed in Figure 4.40, growing three or more QWs greatly enhances room temperature PL intensity by suppressing the optical quenching effect at higher temperature.
Figure 4.34. PL spectra of the Time-Adjusted 5 QW sample (C3864) measured at temperatures ranging between 6 K and 300 K.
Figure 4.35. PL spectra of the Time-Adjusted 3 QW sample (C3863) measured at temperatures ranging between 6 K and 300 K.
Figure 4.36. PL spectra of the Time-Adjusted 1 QW sample (C3858) measured at temperatures ranging between 6 K and 300 K.
Figure 4.37. PL spectra of the Temperature-Adjusted 5 QW sample (C3861) measured at temperatures ranging between 6 K and 300 K.
Figure 4.38. PL spectra of the Temperature-Adjusted 3 QW sample (C3860) measured at temperatures ranging between 6 K and 300 K.
Figure 4.39. PL spectra of the Temperature-Adjusted 1 QW sample (C3859) measured at temperatures ranging between 6 K and 300 K.
The room temperature IQE of 3, 5, and 10 QW samples, follow the ‘state-of-the-art’ IQE values more closely. This implies that only 3 QWs are needed to achieve state-of-the-art room temperature IQE. There is little improvement by adding two extra QWs and adding an extra seven QWs appears to begin affecting the IQE by reducing it, relative to the ‘state-of-the-art’ IQE values. It could be argued that according to Figure 4.40, the 10 QW samples might be suffering from exceeding critical thickness or some other feature which is beginning to reduce the IQE, relative to the ‘state-of-the-art’ curve.

To further investigate the thermal quenching of the PL intensity, the integrated intensities calculated from the Time- and Temperature-Adjusted PL spectra are plotted as a function of $1/k_BT$ (see Figure 4.41 and Figure 4.42, respectively). From these Arrhenius plots, an activation energy for the thermal quenching process can be determined.

The temperature dependence of the integrated PL intensity for InGaN/GaN QWs is relatively constant in the 6 K to 20 K range due to carriers being localised at such low temperatures [74,75]. In the higher temperature region, however, PL intensity decreases exponentially due to thermally activated non-radiative recombination mechanisms [76,77]. This high temperature quenching of the PL intensity can be explored by solving the Arrhenius equation, i.e.

$$I(T) = A e^{E_a/k_BT},$$

where $A$ is a constant, $E_a$ is the activation energy, $k_B$ is Boltzmann’s constant, and $T$ is temperature. Taking the natural logarithm of this equation yields

$$\ln(I(T)) = -E_a/k_BT + \ln(A),$$

which describes a straight line where the slope is defined by the activation energy.

The activation energies calculated for the Time-Adjusted and Temperature-Adjusted series which were determined from solving the Arrhenius equation for higher temperatures are plotted in Figure 4.43. The activation energies of the single QW samples are 64 meV and 78 meV for the Time- and Temperature-Adjusted samples, respectively. The activation energies of the 3 QW samples are 27 meV for both the Time- and Temperature-Adjusted samples. The activation energies of the 5 QW samples are 20 meV and 22 meV for the Time- and Temperature-Adjusted samples, respectively. Finally, the activation energies of the 10 QW samples are 23 meV and 20 meV for the Time- and Temperature-Adjusted samples, respectively.
Figure 4.40. IQE of the Time- and Temperature-Adjusted sample series (red and green triangles, respectively) as a function of low temperature PL emission energy. Also included are 'state-of-the-art' IQE values collected from the literature [4,5,6,8].
Figure 4.41. Arrhenius plots of integrated intensity for the Time-Adjusted QW series.

Figure 4.42. Arrhenius plots of integrated intensity for the Temperature-Adjusted QW series.
The activation energies for the single QW structures are very different from the multiple QW structures. The single QW structures have large activation energies around 70 meV whereas the multiple QW structures have activation energies around 23 meV. The difference of these activation energies corresponds with the relationship between sample IQE and the ‘state-of-the-art’ curve shown in Figure 4.40. The single QW samples were found to have an IQE much less than the state-of-the-art samples at similar emission wavelength; however the IQE of the multiple QW structures become less dissimilar from the state-of-the-art IQE values.

![Activation Energy Determined from Integrated PL Intensity for the Time- and Temperature-Adjusted Sample Series](image)

Figure 4.43. Activation energy determined from integrated PL intensity for the Time- and Temperature-Adjusted sample series.

The activation energy of the Temperature-Adjusted single quantum well is 78 meV. This energy corresponds very well to the depth of the electron ground state for a 2 nm In_{0.25}Ga_{0.75}N QW, which using BluCalc [61], is estimated at 77 meV. Therefore, for the single QW structures, the PL intensity quenching could be due to electrons thermally escaping from the InGaN QW to the GaN barrier and the activation energy of this process is that of the electron confinement energy.
For multiple QWs, the activation energy reduces to between 20 – 30 meV. For these materials, the reduction in luminescence intensity could be due to a dissociation of excitons. Hangleiter et al. have shown that free excitons in group III-nitride QWs dissociate at higher temperatures [78,79]. Vurgaftman and Meyer predict the theoretical range for the free exciton binding energy of group III-nitrides is in the range of 23 – 28 meV [80]. Furthermore, Viswanath et al. have experimentally shown the free exciton binding energy in group III-nitrides is approximately 26 meV [81,82]. This exciton binding energy could therefore explain the activation energy observed for the multiple QW structures.

4.3.4. Microscopy Results

STEM-HAADF images and analysis were provided by Zhang [83] at the University of Cambridge. Images of the Temperature-Adjusted and Time-Adjusted 10 QW samples (C3862 and C3865, respectively) are shown in Figure 4.44. The GaN buffer layer is located on the left side of the images and therefore the QW growth order goes from left to right. Zhang measured thicknesses by taking an average of 20 points across the well or barrier being investigated and his per-well thickness measurements for the Time- and Temperature-Adjusted 10 QW samples are plotted in Figure 4.45.

Zhang’s measurements show that the first few QWs of the Temperature-Adjusted sample are thicker than the rest of the QWs in the stack, as was the trend observed previously for the 10 QW sample grown using the conventional 2T growth method (see Figure 4.22). This decrease in thickness is somewhat expected as the temperature adjustment of the first two wells during growth would affect the indium content and not necessarily the thickness of the well. Alternatively, Zhang’s measurements of the Time-Adjusted 10 QW sample show a decrease to the inter- and intra-well thickness variations.
Figure 4.44. STEM-HAADF images of the 10 QW structures C3862 and C3865 which were grown using Temperature-Adjusted and Time-Adjusted techniques [83]. The substrate is located towards the left side of the images and the wells were grown in an order from left to right.

Figure 4.45. Individual QW thickness measured at 20 points across each well [83].
4.3.5. Summary of Modified Growth Methods

Modifying the growth conditions on a well-to-well basis has a very positive effect on the luminescence spectra and IQE of high indium content InGaN/GaN QW structures. The adjustments to growth time and the adjustments to growth temperature have a very similar effect on improving PL linewidth and IQE. The secondary luminescence feature is eliminated. For the 10 QW structures, this leads to a 40% reduction in PL linewidth at low temperatures. Furthermore, the IQE of the modified 10 QW structures is over twice that of the unmodified structure.

The single QW structures performed poorly, relative to the other modified samples. The activation energy of the thermal quenching of the PL intensity for these samples is dominated by the energy required for a hole to escape from the ground state of the QW. The multiple QW structures, on the other hand, have an IQE on a level with 'state-of-the-art' samples which have been reported in the literature [4,5,6,8]. The activation energy of the thermal quenching of the PL intensity for these samples appears to be limited by the exciton binding energy.

STEM-HAADF images show that adjustments to the growth time of sample C3865 (10 QWs) successfully reduce the QW thickness of the first two wells, relative to the rest of the QWs in the structure. For this structure, the growth time of the first well was 164 s, the second well was grown for 177 s, and the third through tenth wells were grown for 190 s. It may be necessary to adjust the growth time of the third well to reduce the thickness and possibly further reduce the PL linewidth.

The STEM-HAADF image of the Time-Adjusted sample follows the QW thickness trend observed in the corresponding data for unmodified structures. This sample reduced over 3 Å in thickness over the first 5 QWs, but remarkably this change in thickness does not appear to affect the PL linewidth or IQE of these samples. The huge improvements in linewidth and IQE for this sample are clearly from adjustments in the indium content from adjusting the growth temperature from 710 °C for the first well, 705 °C for the second well, and 700 °C for all further wells.

It is believed that the secondary luminescence observed in unmodified QW structures may be due to a combination of changes in both the indium concentration and the thickness of the first few QWs. Adjustments to both the thickness and of the indium content make significant improvements to sample
performance and it cannot be concluded that one type of adjustment is more effective than the other type.

4.4 Discussion and Conclusions

The modified growth conditions successfully reduce PL line-width and enhance room temperature IQE, as compared to the traditional 2T growth methods. It is not clear why these QWs change on a well-to-well basis. STEM-HAADF results from the Section 4.2 indicate that after 3 wells were grown, further wells had diminished uniformity across each well and also between wells. Significant well-width fluctuations are observed beginning with well number 3 (see Figure 4.22) and the indium content starts to lose consistency, too.

Larger indium concentrations not only affect the bandgap of In$_x$Ga$_{1-x}$N, but lead to a larger amount of lattice mismatch between In$_x$Ga$_{1-x}$N and GaN. In a QW stack, the In$_x$Ga$_{1-x}$N will be strained to the lattice of the GaN barriers and buffer layer. The greater the indium concentration is, the greater the strain in the wells will be. A 24% indium concentration will, for example, create a 2.6% lattice mismatch with GaN. This added strain induces lattice relaxation via misfit dislocations in the crystal lattice.

One possibility for the reduction of uniformity of the wells is the introduction of strain relaxation in the QW stack. Strain relaxation is known to occur with increasing number of QWs \[15,16,17\]. Relaxing the crystal lattice will have two effects: it will increase the number of defects and reduce the strain-induced piezoelectric field. A reduction of the piezoelectric field will reduce the localisation of carriers and their activation energy.

The critical thickness of In$_{0.25}$Ga$_{0.75}$N is considered to be quite low, and theoretical models have shown this thickness to be about 2 nm for such high indium concentrations \[84,85,86\]. This would imply that the critical thickness could be reached by the first or second well. Hence wells 3-10 are not as uniform and this would affect the luminescence properties of the sample.

Others have observed the effects of strain relaxation on the luminescence of InGaN/GaN QWs. Bai \textit{et al.} \[87\] investigated the effect of strain relaxation on InGaN/GaN QWs. They studied the PL spectra and XRD rocking curves of 2, 3, 5, and 10 QW structures. They found the peak of the 10 K PL spectra for these structures shifts to higher energy with increasing number of QWs. The extent of
the shift decreases with increasing QW number such that there is a large shift (~70 meV) between the 2 and 3 QW structures, yet a small shift (~10 meV) between the 5 and 10 QW structures. Their XRD measurements show the 2 QW structure is fully strained (100%) to the GaN barriers and that the 3, 5 and 10 QW structures contain residual strain of 51%, 46% and 40 %, respectively. They attribute their observed PL shifts to strain relaxation.

Similarly, Wu et al. [88] investigated the strength of the piezoelectric field across a green emitting InGaN 5 QW stack using cathodoluminescence (CL). By tuning the electron beam voltage, they were able to probe through the depth of the structure in order to investigate the effects on each individual well. The acceleration voltages used were found not to cause a significant screening effect of the piezoelectric fields. They observed an increase in CL peak energy with increasing QW number. They suggested this shift could be due to the first 3 QWs remaining fully strained whilst the fourth and fifth QWs undergo strain relaxation, resulting in a reduction of piezoelectric field and, hence, an increase in the emission energy.

It is highly likely that the critical thickness is exceeded by the growth of the third well. STEM-HAADF images indicate a significant change occurs in the thickness uniformity from at least the third QW. However, the PL linewidth and IQE of the structure as a whole can be significantly improved by modifying the growth of further wells in order to compensate for the changes in PL emission energy from exceeding critical thickness.

Although these changes to growth can significantly improve performance, as shown by the optical spectroscopy discussed in Section 4.3.3, their improvements only follow IQE results of other state-of-the-art QW samples. There is no further improvement beyond the limitations of the ‘green gap’. From these results, it is recommended that only 3 QWs need to be grown in order to achieve state-of-the-art performance of high indium content InGaN/GaN QW structures. The growth of 3 QWs allows for carrier recapture to increase overall PL intensity, but does not detrimentally exceed the critical thickness.

In addition to material parameters, the research discussed in this chapter has shown that care should be taken when choosing an excitation photon energy for PL measurements of thicker InGaN/GaN QW stacks. The most common laser excitation source for PL measurements of group III-nitride semiconductors reported in the literature is a HeCd laser which emits at an energy of 3.815 eV
This laser is popular because the emission energy is great enough to excite carriers in the GaN barriers which are then captured by the InGaN QWs; however, the penetration depth of that energy limits its ability to successfully probe beyond 83 nm of GaN. The 10 QW stacks investigated in this chapter exceeded this thickness and it was found that using a HeCd laser skewed the PL spectra by probing mainly the upper QWs of the stacks. Furthermore, the laser excitation photon energy used in the time decay measurements is of an even higher energy and would therefore penetrate even shallower in the stack. It is highly likely that the time decay spectra do not provide a full depiction of the lifetime of the lowest QWs.

This research has shown that as many as 10 QWs are not needed to achieve state-of-the-art green emitting InGaN QW structures and therefore use of a HeCd laser should not be a problem for future research on these materials; however, for lower indium content QWs where 18 periods have proven to be highly efficient at room temperature [73], a HeCd or higher energy laser should not be used for the purpose of probing the entire QW stack.

References


Chapter 5: Macroscopic Spectroscopy of InGaN Quantum Dots

5.1 Introduction

The ability of InGaN/GaN quantum well (QW) structures to emit bright light despite the large density of defects present in the material has been a matter of debate for years. The defects are formed as a result of the difference in lattice constant between the InGaN/GaN and the commonly used substrate, sapphire. Defect densities are typically on the order of $10^9 \text{ cm}^{-2}$ [1]. This high level of defects present would cause other III-V semiconductors to not emit light efficiently. Yet what makes the group III-nitrides remarkable is that despite these large defect densities, optical devices have high internal quantum efficiencies (IQE). It would be advantageous to understand the emission mechanism of InGaN/GaN QWs to further improve device performance.

The reason behind the high IQE in InGaN/GaN QWs is generally attributed to minor fluctuations in the bandgap which cause localised energy states. These localisation centres are thought to keep carriers from diffusing towards defects such as threading dislocations where the carriers could recombine non-radiatively. Depending on the lateral size and the severity of the localising potential, these localising centres can be described as segmented QWs, quantum disks, or QDs [2].

Intentionally fabricating localisation centres, such as QDs, can provide insight to their optical properties, and have been shown to significantly enhance the efficacy of laser diodes (LDs) [3]. In the case of InGaN-based LDs, this effect is at least 10 times greater than when QDs are used in laser diodes based on other III-V materials [4].

One method of intentionally fabricating QDs is by Modified Droplet Epitaxy. This method involves the MOCVD growth of a thin InGaN epilayer on a GaN template commonly referred to as the ‘wetting layer’. The structure is then annealed in $\text{N}_2$ at the same temperature as the InGaN growth before a GaN cap is grown at the same temperature.

Annealing in $\text{N}_2$ is believed to decompose the InGaN layer forming pits at what were indium-rich regions of the epilayer and generating metallic indium droplets on the surface, including the surface of the pits [5]. Figure 5.1 [6] is an AFM image at this stage of the growth process. The dark regions represent pits in
the film and the bright dot-shaped regions are nanometre-sized droplets on top of the epilayer. The nanostructures in this image have an average height of 0.93 ± 0.1 nm and a density of 1 x 10^{10} cm^{-2}.

![AFM image of InGaN epilayer after annealing in N\textsubscript{2} for 30 s after growth. Image size is 1.8 µm x 1.8 µm with an image height of 5.82 nm][6].

When a capping layer of GaN is subsequently grown on top of the InGaN epilayer, the metallic droplets then re-react with the ammonia (NH\textsubscript{3}) and inter-diffuse within the capping layer, forming In\textsubscript{x}Ga\textsubscript{1-x}N QDs. These QDs are of varying sizes and furthermore some QDs are located on the surface of the InGaN epilayer whereas other QDs are surrounded by GaN. Decreasing the indium concentration in the QDs will result in larger bandgaps. Decreasing QD size increases confinement, also resulting in greater bandgap energy. Furthermore, the formation of InGaN QDs is generally thought to accompany strain relaxation of the wetting layer [7,8,9]. A reduction of strain in a QD results in reductions of the piezoelectric field, band bending, and electron-hole separation. Therefore, with variations in indium concentration, size and strain, the emission from the QDs may be at a higher or lower energy than the emission from the wetting layer [5]. This distribution results in inhomogeneous broadening which broadens the delta-like density of states [10,11].

In order to limit the distribution of QD sizes, spectroscopy which probes single or very small quantities of QDs in a structure is often studied instead of
macroscopic techniques. Spatially resolved photoluminescence (micro-PL) experiments allow for the investigation of optical properties of individual QDs. Spatial resolution can be achieved by evaporating a metal (typically aluminium) mask which has nanometre-scale apertures onto the sample. Alternatively, the sample can be etched, forming nanometre-scale mesas which contain about one QD.

Although these studies have proved useful to investigate the characteristics of single dots, the samples become damaged in the process. It would be useful to have a non-destructive, contact-less method to study the optical properties of QDs. With this in mind, a sample which is known [5,6,12] to contain InGaN QDs was used to test various experimental methods.

5.2 Sample Details

The quantum dot sample discussed in this chapter was grown by Oliver et al. at the University of Cambridge using the Modified Droplet Epitaxy method [13]. The sample consists of a 30 nm GaN buffer layer grown at 540 °C on a c-plane sapphire substrate, followed by the growth of a 2.8 µm GaN template grown at 1020 °C. An additional 500 nm GaN ‘connecting layer’ was grown to provide a clean, flat surface for the 10 mono-layers (ML) of InGaN growth at 700 °C. After InGaN growth, the sample was annealed in N₂ for 30 s. The sample was finally capped with 7 nm of GaN at 700 °C.

The existence of QDs was determined from a different piece of the wafer by Rice et al. [6] at the University of Oxford using micro-PL measurements. For these measurements, 100 nm of aluminium was evaporated onto the surface, a mask pattern was fabricated using electron-beam lithography, and square apertures were produced using reactive ion etching. The aperture size was varied between 2 µm and 100 nm.

Rice et al. took micro-PL spectra at 4.2 K using the excitation of a frequency-tripled titanium-doped sapphire (Ti:Sapphire) laser emitting at 4.66 eV (266 nm) and collecting luminescence via a 25 cm monochromator with spectral resolution of ~700 µeV. Figure 5.2 shows the micro-PL spectrum of the QD sample recorded using a 2 µm aperture. Also displayed in this figure is the a micro-PL spectrum (2 µm aperture) of an InGaN QW which was grown to have the same thickness as the InGaN ‘wetting layer’ of the QD sample (in red). The spectra both show significant Fabry-Pérot interference fringes. The micro-PL spectrum of the
QD sample consists of a single feature centred about 2.695 eV (460 nm) and delta-like functions on the high energy (low wavelength) side of the broad PL feature. Rice et al. attributed the high energy side of the peak to QD luminescence and the centre of the peak to the ‘wetting layer’.

Figure 5.2. Low temperature micro-PL using a 2 µm aperture of the QD sample and a single QW of the same width as the wetting layer. The inset shows more clearly the QDs observed in the spectra around 415 nm [6].

Rice et al. also took micro-PL spectra using smaller apertures to limit the number of QDs probed by the excitation light. Figure 5.3 shows their micro-PL spectra of the QD sample taken using (a) a 2 µm aperture, (b) a 500 nm aperture, and (c) a 200 nm aperture. Significant Fabry-Pérot interference fringes are observed in spectrum (a), but are less noticeable in the spectra taken with smaller aperture sizes as the background signal is reduced. The sharp peaks in the spectra were attributed to the recombination of excitons strongly confined in single QDs.
5.3 Experimental Results

Low temperature Photoluminescence Spectroscopy

Low temperature (6 K) photoluminescence spectroscopy was performed on the QD sample using a 3.815 eV (325 nm) excitation source and 200 µm spot size. As the density of QDs for this sample is $1 \times 10^{10}$ cm$^{-2}$, the laser should excite approximately $1.24 \times 10^{13}$ dots. The sample was mounted in a Brewster angle geometry to reduce the effects of Fabry-Pérot interference. The measured spectrum is shown in Figure 5.4.

This spectrum reveals an intense feature which peaks at 2.66 eV (466 nm) and has a full width at half-maximum (FWHM) of 209 meV. Close inspection of the high energy side of the 2.66 eV feature reveals very low intensity features. Figure 5.5 shows the low temperature PL spectra on a much smaller scale which reveals these features at 3.48 eV, 3.39 eV, and 3.29 eV. The feature at 3.48 eV corresponds to the bulk GaN exciton and its observation was also reported by Oliver et al. The feature at 3.39 eV is 90 meV less than the GaN exciton feature and corresponds to the LO-phonon replica of the GaN exciton transition. The feature at 3.29 eV is possibly due to donor-acceptor pair transitions. Although not mentioned by Rice et al., this feature can be seen in their micro-PL spectra shown in Figure 5.2 at about 380 nm.
Figure 5.4. Low temperature (6 K) PL spectra of the QD sample.

Figure 5.5. Low temperature (6 K) PL spectra of the QD sample.
**Power Dependent PL spectra**

Excitation power dependent PL measurements were taken at low temperature (6 K) of the QD sample. Normalised PL spectra shown in Figure 5.6. The ‘dips’ in the PL intensity at 2.616 eV and 2.681 eV are due to unsuppressed Fabry-Pérot interference fringes which were confirmed by repeating the measurement without the Brewster angle setup. As excitation power increases above 0.112 W/cm², the width of the PL peak narrows and the peak centre shifts to higher energy.

This type of shift is commonly observed in InGaN/GaN QWs excited at higher excitation densities and is due to the screening of the piezoelectric fields [14,15,16]. In a QW, the confinement is in 1-dimension; therefore a continuum of states exists within the plane of the well for further electron-hole pairs to populate. This effect, however, is not possible in a QD because once 2 electron-hole pairs are created in a 3-dimensionally confined QD energy state, no further population is allowed in that state, the result of which is that screening of the piezoelectric fields is not possible for an InGaN QD [17,18,19]. Consequently, the peak shift observed in Figure 5.6 is ascribed to QW luminescence, not QD luminescence.

![Excitation Power Density (W/cm²)]

**Figure 5.6.** Normalised low temperature (6 K) PL spectra of the QD sample measured under different excitation powers.
Excitation power dependent PL spectra of the low intensity, high energy features are shown in Figure 5.7 on a log10 intensity scale to highlight the differences with excitation power. The GaN exciton feature at 3.48 eV and the LO-phonon replica of that transition at 3.39 eV do not significantly shift with excitation power. The feature at 3.29 eV shifts to higher energy with increasing excitation power.

Peak energy of the 3.29 eV feature and GaN exciton feature versus excitation power are shown in Figure 5.8. The shift to higher peak energy with higher excitation power confirm the 3.29 eV feature is due to donor-acceptor pair (DAP) emission, as distant pairs become saturated with increasing excitation power. The feature located about 90 meV below the DAP feature shifts in a similar fashion and is therefore believed to be the LO-phonon replica of that DAP transition. No QD-like emission was detected using these macroscopic PL measurements.
Figure 5.8. Low temperature PL peak energy versus excitation power of the GaN exciton feature and the DAP feature.
Photoluminescence excitation spectroscopy was also performed on the QD sample to investigate the absorption and possible carrier transfer processes of the QDs, wetting layer, and GaN template/cap layers. The PL emission was detected for several energies across the PL emission spectrum. Displayed in Figure 5.9 are the PLE spectra detected at the PL peak energy (black line) and an example of the PL emission detected on the high energy side of the PL peak (red line), in the region where Rice et al. [6] observed a large number of QD emission peaks in their micro-PL spectrum.

Both spectra exhibit a sharp absorption edge at 3.48 eV which is due to the creation of carriers which are excited in the GaN which subsequently relax into the InGaN wetting layer and cause an increase in the PL emission intensity at the energy being detected. The narrow oscillations in the InGaN absorption band are due to Fabry-Pérot interference fringes caused by multiple reflections of the excitation light within the sample.
The PLE spectra, whether detecting at the PL peak (wetting layer) or when
detecting on the high energy side of the PL peak (where Rice et al. observed QD
emission), are essentially the same. The slight difference in slope of the low energy
tail is a consequence of the detection energy. Therefore, macroscopic PLE
measurements are unable to detect QDs in this sample.

**Nonlinear PL Spectroscopy**

The PL spectra examined thus far are dominated by what appears to be
QW-like luminescence which is due to the 2-dimensional ‘wetting layer’ on which
the QDs are grown. Nonlinear excitation spectroscopy using a micro-PL setup has
been shown by Jarjour et al. [20,21] to successfully reduce the background (wetting
layer) luminescence, revealing the underlying luminescence of the QDs. Nonlinear
PL spectroscopy uses an excitation photon energy which is less than the bandgap of
the structure. This allows only transitions by multiple photon absorption to occur
because the zero-dimensional confinement of QDs enhances the nonlinear
absorption cross-section, relative to that of the QWs [19].

Therefore, macroscopic nonlinear PL spectroscopy was performed on the
QD sample and, for comparison, a GaN template sample. The excitation source
was a tuneable Ti:Sapphire laser and the excitation photon energy was tuned across
several wavelengths in the region where 2-photon absorption would occur in
InGaN.

Figure 5.10 shows the nonlinear PL spectra of the QD sample and a GaN
template (which contains no InGaN). The nonlinear PL spectra from both the QD
sample and the GaN template sample are identical. All of the delta-like features
observed from the QD sample are observed in the template spectra as well.
Therefore, macroscopic PL spectra measured using 2-photon absorption processes
are unable to detect the spectra of the QDs in the sample.
Figure 5.10. Two-photon PL spectra of the QD sample (black line) and a GaN template (Red line).
5.4 Discussion

The macroscopic experimental methods investigated in this chapter failed to provide any evidence for the existence of QDs in this sample. Low temperature PL spectroscopy showed a QW-like emission feature which is due to the wetting layer. In addition to the wetting layer emission feature, DAP, GaN exciton, and LO-phonon replicas of those transitions were also observed. Photoluminescence excitation spectroscopy also indicated only QW-like absorption. Nonlinear excitation spectroscopy showed multiple delta-function-like features across the spectrum; however these nearly identical lines were also seen in the spectrum obtained from a GaN template. Therefore, it is concluded that the QDs in this sample cannot be determined from the macroscopic optical spectroscopy techniques explored in this chapter.

Concurrent with this research, Davies et al. reported observing QD-like behaviour from macroscopic PL and PLE [22]. They discuss samples grown using an interrupted growth method where InGaN is grown on GaN for a time, $t$, then growth is paused for 20 s before a second InGaN growth of time, $t$. Their QDs grown by this method were measured via AFM to average 7 nm in height and 30 nm across, before a GaN capping layer was applied.

The PL spectra recorded by Davies et al. (see Figure 5.11) shows a reduction in peak wavelength with increasing growth time, $t$. They suggested this reduction in wavelength is due to a greater dot height, an increase in indium concentration within the dots, or a combination of both. They report that their QDs lie on a two-dimensional InGaN wetting layer, but they report they are unable to measure how this layer changes in thickness with added growth time. This information would be vital to fully understanding their PL spectra. Although greater QD height or increased indium in their QDs could be an accurate description of their observed reduction in PL peak emission energy, an increase in growth time of an InGaN QW (here, the ‘wetting layer’) would also increase the QW thickness, resulting in a reduction of QW emission energy.

They calculate that a 2 nm increase in height for a 15% indium concentration QD would decrease the emission energy by 300 meV. This energy shift is approximately 100 meV less than what they observed for the difference in emission energy between their $t = 12$ s sample and their $t = 18$ s sample. However, according to their HAADF image, the wetting layer thickness of the $t = 15$ s sample
is approximately 6 nm. As the total growth time is $2t$, the growth rate is estimated at about 1 nm per 5 s of growth, assuming a constant growth rate throughout. Using this assumption, the $t = 12$ s sample would then have a 5 nm wetting layer and the $t = 18$ s sample would have a 7 nm wetting layer, which is in agreement with the 2 nm increase in dot height assumed by Davies et al. Now if, for example, their InGaN wetting layer had about 15 % indium content (which is a reasonable guess based on their $t = 12$ s sample emits at about 2.6 eV and is said to only contain QW emission) and if the thickness of this layer increases from 5 nm to 7 nm, then the peak emission energy would decrease by 418 meV. This energy difference is approximately the same amount as the observed decrease in peak PL emission energy between the $t = 12$ s sample and the $t = 18$ s sample. Hence, the approximately 400 meV decrease of emission energy can also be explained by possible differences in QW thickness.

![Figure 5.11. Normalised PL intensity for the QD samples with varying growth time, $t$ [22].](image)

In addition to the macroscopic PL data, Davies et al. also measured the macroscopic PLE spectra of the $t = 13.5$ s sample (see Figure 5.12). The PLE spectra, as monitored at different energies across the emission spectrum, show the GaN absorption edge at about 3.5 eV and a less intense InGaN absorption feature which decreases with decreasing excitation photon energy towards the emission peak. The increase in absorption between about 2.65 eV and the sudden increase caused by the detector picking up stray source light is claimed to be due to QD excited state absorption. The feature at about 2.8 eV is said to be due to an artefact of the measurement system.
Figure 5.12. Normalised PL (black line) and PLE detected at several energies across the emission spectrum (coloured lines) of the QD sample with a growth time of $t = 13.5$ s [22].

The arguments put forward by Davies et al. regarding the observed PLE spectra being due to QDs are a) the lack of GaN exciton features at the absorption edge, b) the lack of a constant intensity immediately below the GaN band edge on a log$_{10}$ plot, and c) the existence of the ‘excited state absorption’ below 2.645 eV; however, this claim was later retracted as being due to background signal [23]. Nevertheless, the first two arguments for observing QDs in macroscopic PLE spectra can easily be countered as being due to QW effects.

The first argument put forward by Davies et al. claims a symptom of dot-like behaviour is the lack of GaN exciton features in their PLE spectra. As was reported in Section 4.2.2.2, the GaN absorption edge for InGaN QWs does not always show a defined excitonic feature at the band edge. This feature is easily broadened by defects and disorder in the material [24,25]. Therefore the lack of GaN excitonic features in the PLE spectra does not necessarily denote the existence of QDs but could describe a disordered QW.

Secondly, the ‘constant intensity’ of the InGaN QW absorption edge just below the GaN absorption edge on a log$_{10}$ plot which Davies et al. claimed was a key sign of QD absorption has been observed within the context of this thesis research to occur only for higher content InGaN QWs. Figure 5.13 shows example PLE spectra previously obtained for In$_{0.06}$Ga$_{0.94}$N and In$_{0.25}$Ga$_{0.75}$N QWs. These spectra show the same form of absorption edge for the lower indium content QWs as Davies et al. reported for their QD spectra. The higher content QW PLE spectrum,
on the other hand, displays the ‘constant intensity’ InGaN absorption in the region just below the GaN absorption edge. Davies et al. suggest their QDs may have up to 15% indium concentration, which would result in absorption spectra closer in shape to the bottom spectra of Figure 5.13 than to the top spectra. Hence, the argument of observing a ‘constant’ intensity in a log10 plot of PLE may not even be valid for their sample.

Therefore, the PLE spectra of a QD sample measured by Davies et al. can also be plausibly described as being due to low indium content InGaN QWs. The PLE spectra do not exhibit behaviour which is special to the existence of QDs, but is also seen by QW structures.

![Figure 5.13. PLE spectra of In0.06Ga0.94N (blue line) and In0.25Ga0.75N (green line) MQWs.](image)

There is no doubt that the InGaN QDs investigated by Davies et al. exist in their samples. Both their AFM measurements and micro-PL measurements confirm the existence of QDs in their samples. Nevertheless, the AFM measurements can only be recorded before the top layer of GaN is grown and the micro-PL measurements require either etching or an aluminium mask to be applied after sample growth. Non-destructive measurements by Davies et al., however, can be
plausibly argued to be due to QWs. Their HAADF images were unable to resolve the dots. Their macroscopic PL and PLE measurements could not prove on their own, without a doubt, the existence of QDs in their materials. Plausible alternative arguments can be made to describe the macroscopic optical spectra based on a QW model.

Therefore, the question still remains whether non-destructive macroscopic optical measurements can, on their own, confirm or deny the existence of InGaN QDs in a group III-nitride material. The research methods discussed in this chapter were unable to observe specifically dot-like characteristics from a sample which is known to contain InGaN QDs. It is likely that because the emission energy of individual InGaN QDs span across the emission spectrum of the wetting layer, they are spectrally too similar to distinguish from the wetting layer emission and this may be why Davies et al. are the only other known authors to study InGaN QDs macroscopically. Indeed, the non-destructive macroscopic optical measurements by Davies et al. could be easily argued to be due to QW characteristics instead of QD characteristics. Consequently, without destructive tests on a sample which is claimed to contain QDs, the research methods discussed in this chapter would be unable to conclude whether the sample really contained QDs.

References


Chapter 6: Optical Spectroscopy of ScGaN

6.1 Introduction

Difficulties creating highly efficient green or UV light emitting Group III-nitride heterostructures have lead to interest in alternative material structures. Also the low melting point of InN (1100 °C) [1] and thermal instability of InGaN, which leads to indium decomposition [2,3,4], limits its potential for applications in optoelectronic devices operating at high-temperatures. As an alternative, it has been suggested to alloy ScN with GaN [5].

Scandium is a transition metal from Group IIIb. Transition metal nitrides are of interest in a variety of applications due to their high melting point, hardness and mechanical strength [6]. They are used for such things as rocket nozzles, golf spikes, cutting/drilling tools and snow tyre studs [7]. Typically, these compounds crystallise in the NaCl (rocksalt) structure and can act as either a metal or as a semiconductor.

ScN is of additional interest as it is a semiconductor with a wide bandgap (2 – 2.4 eV) [8]. It has a high melting point (> 2,600 °C) and could be used for high temperature Ohmic contacts for traditional Group III-nitrides [9] and as an optical coating [10]. Its lattice constant in the stable rocksalt structure is 4.50 Å which is a close match to zinc-blende GaN (4.54 Å), making it suitable as a buffer layer or even a substrate material for cubic GaN structures [11].

Traditional group III-nitrides, such as GaN, are more stable in the wurtzite structure and the growth technology is more mature for wurtzite nitrides. Although it is possible to grow rocksalt GaN under very high pressures, this phase has a cohesion energy approximately 887 meV/2 atoms larger than the wurtzite phase [12]. To grow true ScGaN alloys, it would be advantageous to have a stable hexagonal phase of ScN in order to avoid a mixture of phases within the structure.

Takeuchi [13] used total energy calculations to explore the possibility and stability of ScN in structures other than rocksalt. Crystal structures explored included rocksalt, CsCl, NiAs, zinc-blende and wurtzite. Although Takeuchi confirmed rocksalt as the lowest energy structure for ScN, he predicted a metastable wurtzite structure with a lattice constant of 3.49 Å, which is 0.06 Å less than the lattice constant of InN.
Farrer and Bellaiche [14] used local density approximation calculations to investigate the hexagonal phases of ScN, including the wurtzite phase. They determined that wurtzite ScN would in fact be an unstable phase; however there is an alternative hexagonal ScN phase which they predicted would be stable. Its primitive cell is 15% larger than wurtzite GaN and 17% smaller than wurtzite InN. The most significant difference between this stable phase hexagonal ScN (denoted hereafter as $h$-ScN) and wurtzite GaN or InN is the number of nearest neighbour bonds. The wurtzite structures have 4 nearest neighbours, yet $h$-ScN has 5; each Sc atom has three short bonds with N atoms within the same basal plane and 2 longer bonds with N atoms in the plane above and the plane below it (See Figure 6.1). This structure, they pointed out, is non-polar, unlike the wurtzite structures. Farrer and Bellaiche predicted that Sc$_x$Ga$_{1-x}$N alloys of low and intermediate concentration of Sc would crystallise in the $h$-ScN phase, whereas the highest concentrations would result in rocksalt structures.

![Figure 6.1. Hexagonal h-ScN crystal structure as shown by Farrer and Bellaiche [14]. Sc atoms indicated by black balls and N atoms indicated by grey. Nearest neighbour distances are $d_{nn1}$=2.11 Å and $d_{nn2}$=2.21 Å.](image)

Further work from Ranjan, Bellaiche and Walter [12] investigated the effect of compressive strain on the $h$-ScN structure. They used local density approximation calculations to investigate the changes in the piezoelectric coefficient and optical transitions resulting from compressive strain along the $a$-axis. Such compressive strain would allow the ScN lattice ($a_{\text{h-ScN}}$ = 3.66 Å) to fit the wurtzite GaN lattice ($a_{\text{GaN}}$ = 3.189 Å). Ranjan et al. discussed three strain regimes. The first
regime occurs for strain between 0 and 3.4%, where the hexagonal lattice is non-polar (as in Figure 6.1). In the second regime (3.4% - 6.4%), the lattice becomes polar, but not yet wurtzite. In the final regime (strain greater than 6.4%), the lattice becomes wurtzite. They found that in the first regime, ScN is an indirect semiconductor where the valence band maximum is located at the $\Gamma$-point and the conduction band minimum is located at the $K$-point (see the Brillouin zone diagram in Figure 6.2). In this first regime, the bandgap is relatively constant at about 1.5 eV for strain up to 3.4%. In the second regime, they calculated that the bandgap dramatically increases with strain, shifting across the spectrum, from 1.5 eV at 3.4% to 4 eV at 6.4%. For the highest strain regime (i.e. wurtzite configurations), they determined the bandgap to be stable around 4 eV and indirect, but with a conduction band minimum along the $\Sigma$-line and valence band maximum at the $M$-point.

![Figure 6.2. Diagram of a hexagonal crystal lattice (black) and the corresponding first Brillouin zone in reciprocal lattice space (red).](image)

Moreno-Armenta et al. [15] used total energy calculations to theoretically study Sc$_x$Ga$_{1-x}$N in both the rocksalt and wurzite phases with varying $x$. They confirmed previous calculations that the most stable ScN structure is rocksalt and the most stable GaN structure is wurtzite, but found that as $x$ increases in Sc$_x$Ga$_{1-x}$N, the lowest energy structure changes from wurtzite to rocksalt at about $x = 0.65$. Moreno-Armenta et al. then calculated band structures for Sc$_x$Ga$_{1-x}$N in their theoretically equilibrium crystal structures. They found that for high Sc concentration rocksalt phases, an indirect bandgap occurs and a larger, direct bandgap also forms as $x$ decreases. Conversely, the lower Sc concentrations, which
are more stable in the wurtzite-like phase, were calculated to have a direct bandgap. In all cases, they found the bandgap to decrease as Sc content increases.

Despite the theoretical work on ScGaN, few experimental studies have been reported to date. Little and Kordesch [16] grew thin films of Sc\(_x\)Ga\(_{1-x}\)N using reactive sputtering on quartz substrates. Scandium concentrations, determined from scanning electron microscopy measurements, ranged from \(x = 0.2\) to 0.7. They performed optical absorption measurements in the range of 190 – 820 nm and compared their results to pure ScN and GaN samples. They found the absorption edge to decrease linearly with increasing Sc concentration, shifting from 3.5 eV for GaN to 2.0 eV for ScN. X-ray diffraction (XRD) measurements, however, showed weak or no structure, meaning these samples were likely amorphous or microcrystalline at best.

Constantin et al. [17,18] have also reported experimental studies on Sc\(_x\)Ga\(_{1-x}\)N. In their work, they grew Sc\(_x\)Ga\(_{1-x}\)N for \(0 < x < 1\) using radio frequency (rf) molecular beam epitaxy (MBE) on GaN templates grown on sapphire substrates, during which in situ reflection high energy electron diffraction (RHEED) was used to determine the crystal structure. They found that Sc concentrations up to 17 % yielded wurtzite-like, hexagonal structures. Higher concentrations (\(<54\ %\)) resulted in rocksalt crystal structures. Concentrations between 17 % and 54 % resulted in a crystallographic mix between the hexagonal and rocksalt phases. Optical absorption measurements showed the absorption edge to decrease with increasing Sc concentration in three different regimes, shifting from 3.37 eV for GaN to 2.15 eV for ScN. The absorption edge in both the low Sc regime (\(0 < x < 0.3\)) and the highest Sc regime (\(0.54 < x < 1\)) decreased monotonically with increasing \(x\). The middle regime showed large variations, consistent with the mix of crystal structures present. Furthermore, they determined from XRD measurements that in the wurtzite-like regime (\(0 < x < 0.17\)), the Sc\(_x\)Ga\(_{1-x}\)N lattice flattens out with increasing \(x\), becoming more like the hexagonal 5-fold coordinated lattice.

There have yet to be any reports of luminescence from Sc\(_x\)Ga\(_{1-x}\)N thin films. For ScGaN to be a viable candidate for replacing InGaN in applications such as in light emitting diodes, it needs to exhibit efficient radiative recombination. In this chapter, variable temperature photoluminescence (PL) spectroscopy, photoluminescence excitation (PLE) spectroscopy, and transmission spectroscopy are used to investigate a series of Sc\(_x\)Ga\(_{1-x}\)N thin films grown on GaN.
6.2 Sample Growth

The samples studied consist of an MBE-grown $\text{Sc}_x\text{Ga}_{1-x}\text{N}$ layer on top of semi-insulating MOVPE-grown GaN template layer on sapphire substrates. The 500 nm thick GaN templates were grown at the University of Cambridge by MOVPE on 2 inch diameter $c$-plane sapphire substrates and have threading dislocation densities of around $6 \times 10^9 \text{ cm}^{-2}$ [19]. MBE growth of the ~270 nm thick $\text{Sc}_x\text{Ga}_{1-x}\text{N}$ film was performed at the University of Liverpool [19].

The Sc concentration in the samples was controlled by varying the temperature of the Sc and Ga effusion cells. The nitrogen source used was NH$_3$. The Sc mole fractions were estimated using energy dispersive x-ray (EDX) spectroscopy of pure ScN and GaN samples grown in the same MBE system. The samples discussed in this chapter are estimated to have Sc mole fractions between 2% and 8%.

The experimental results and discussion sections of this chapter are separated into two sections. In Section 6.3, the effects of substrate temperature during MBE growth is discussed. Substrate temperature has a great effect on the growth rate, and single crystal growth requires high substrate temperatures; however too high substrate temperatures during growth can be detrimental to crystal quality [20].

In addition to investigating the effect of substrate temperature on the optical properties of ScGaN, the effect of increasing the Sc effusion cell temperature is discussed in Section 6.4. Increasing the temperature of the effusion cell in MBE growth increases the amount of that element deposited in the semiconductor. For an alloy material, it can effectively increase the fractional content of that element in the alloy material.

6.3 Effects of Varying Substrate Temperature

6.3.1 Sample Details

For the samples discussed in this section, the temperature of the substrate during MBE film growth varied in the range of 650 °C to 900 °C. The Sc effusion cell temperature remained constant at 1400 °C and Ga effusion cell temperature was 940 °C. Growth details and microscopy data for these samples are outlined in Table 6.1 below.
Table 6.1. Growth Details of Variable Substrate Temperature MBE Films

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Substrate Temperature (°C)</th>
<th>Ga Cell Temperature (°C)</th>
<th>Sc Cell Temperature (°C)</th>
<th>MBE Film Growth Time</th>
<th>ScGaN Film Thickness – HRXRD (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBE 51</td>
<td>650</td>
<td>940</td>
<td>1400</td>
<td>135 min</td>
<td>267 ± 10</td>
</tr>
<tr>
<td>MBE 52</td>
<td>725</td>
<td>940</td>
<td>1400</td>
<td>130 min</td>
<td>260 ± 10</td>
</tr>
<tr>
<td>MBE 45</td>
<td>800</td>
<td>940</td>
<td>1400</td>
<td>90 min</td>
<td>264 ± 10</td>
</tr>
<tr>
<td>MBE 50</td>
<td>900</td>
<td>940</td>
<td>1400</td>
<td>135 min</td>
<td>267 ± 10</td>
</tr>
</tbody>
</table>

6.3.2. Experimental Results

**Low Temperature PL Spectroscopy**

Low temperature (6 K) photoluminescence measurements using the 3.815 eV (325 nm) line of a HeCd laser were performed on the Sc$_x$Ga$_{1-x}$N samples grown with substrate temperatures of 650 °C, 725 °C, 800 °C and 900 °C and the spectra are shown in Figure 6.3.

All four PL spectra of the Sc$_x$Ga$_{1-x}$N films exhibit a broad asymmetric feature which peaks in the violet, around 3.15 eV. In addition to the violet feature are features commonly observed from GaN [21]: the GaN exciton luminescence at 3.48 eV, and for samples MBE 45 and MBE 50, the so-called yellow luminescence (YL) band centred at 2.25 eV.

The violet PL feature is very broad, with the full width at half maximum ranging from 350 - 450 meV between samples. The shape of the violet feature is asymmetric with a tail forming on the low energy side. Some structure is also observed in the violet band of the PL spectra of all four samples.

The fluctuations in the broad violet feature are not due to Fabry-Pérot interference fringes as they were measured (see later in Figure 6.9) to have a spacing of 161 meV. This fringe spacing does not correspond to the spacing observed in the spectra of Figure 6.3, nor does it explain the narrow feature on the high energy side of the violet luminescence feature in the spectrum of MBE 50. Furthermore, the energy spacing of the fluctuations does not allow for the assignment of phonon replicas. For low concentration GaN-alloys, longitudinal-optical (LO) phonon replicas are spaced about 91 meV apart and are relatively weak in intensity, compared to the zero-phonon emission [22,23,24,25]. The features observed in the violet emission band do not follow this trend and therefore cannot be described as phonon replicas.
Figure 6.3. Low Temperature (6 K) PL spectra of samples MBE 51 (blue line), MBE 52 (red line), MBE 45 (green line), and MBE 50 (black line) which were grown at substrate temperatures 650 °C, 725 °C, 800 °C and 900 °C, respectively.
For comparison, a low temperature photoluminescence spectrum of a sample consisting of only the GaN template (sample C3536) was measured under identical conditions as the Sc$_x$Ga$_{1-x}$N film samples. The emission spectrum of the template sample is shown in Figure 6.4. Features commonly observed in bulk GaN [21] are observed in the template spectra: the GaN near-band-edge feature at 3.48 eV, its LO-phonon replica at 3.39 eV, the so-called ‘blue-luminescence (BL) band’ at 2.95 eV and the so-called ‘yellow-luminescence (YL) band’ at 2.2 eV. There is no violet luminescence observed in the PL spectrum of the template sample.

![Figure 6.4. Low Temperature (6 K) PL spectrum of the GaN template, sample C3536.](image)

The violet luminescence, therefore, does not originate from the GaN template underneath the Sc$_x$Ga$_{1-x}$N films. Furthermore, changing the substrate temperature during MBE growth affects the shape of the PL spectra as follows: with increasing the substrate temperature, the broad violet luminescence feature is resolved into a series of overlapping, narrower features. This becomes most
apparent in the PL spectra of MBE 50 where a distinct feature appears on the high energy side of the violet band.

To further understand the nature of the violet luminescence band, a model of multiple, overlapping Gaussian line-shape functions was applied to the 6 K PL spectra of sample MBE 50. Features observed in the template sample (the YL, BL, and GaN exciton features) were included to fully understand the nature of the violet luminescence features. A 'best-fit' solution was obtained in OriginPro® using a model consisting of a summation of Gaussian functions. In addition to the YL, BL, and GaN exciton features, 3 Gaussian functions were found to best describe the violet band (See Figure 6.5). These functions include a narrow feature at 3.278 ± 0.0002 eV (labelled A), a more intense feature at 3.192 ± 0.002 eV (labelled B), and a broader feature at 3.075 ± 0.022 eV (labelled C). The square of the correlation coefficient (i.e. $R^2$) between the model and experiment was 0.99948. The emission energies of these 3 violet features do not correspond to commonly observed [21] luminescence lines in GaN, including common donor- and defect-related luminescence.

![Figure 6.5. Deconvolution of the 6 K PL spectrum of sample MBE 50 using the Gaussian line-shape functional form and the comparison of their sum (“Model”).](image-url)
**Power Dependent PL Spectroscopy**

Excitation power dependent PL measurements were taken at low temperature (6 K) of sample MBE 50. The samples grown at lower substrate temperatures were not measured against excitation power as the individual features were not as resolved, even at higher excitation powers. The excitation power dependent spectra of sample MBE 50 are shown in Figure 6.6, overlayed with the Gaussian models described previously. As excitation power decreases, the intensity of the high energy violet feature at 3.278 eV decreases rapidly with respect to the other violet features. The violet feature at 3.192 eV also decreases at a faster rate than the 3.075 eV feature so that at an excitation power of 0.003 mW, it is no longer the dominant violet feature. The BL band also becomes more prominent in the spectra as excitation power and ensuing intensities of the violet features decrease. The differing rates of decreasing PL intensity with respect to decreasing excitation power indicate that the individual features of the model shown in Figure 6.5 may be an accurate representation of the violet luminescence band.

**Temperature Dependent PL Spectroscopy**

Temperature dependent PL spectra were recorded of the Sc$_x$Ga$_{1-x}$N film samples and GaN template sample. Figure 6.7 shows the PL spectra of MBE 50 taken at temperatures ranging from 6 K to 300 K. The PL intensity is shown on a log$_{10}$ scale for the spectra to be shown over the full range of temperature. PL spectra of the samples grown with lower substrate temperatures are not presented here due to a lack of details in the spectra, as compared to the PL spectra for MBE 50.

As the temperature is increased, the exciton feature shifts with the GaN bandgap. The YL band shifts with the GaN bandgap and decreases in intensity until about 240 K after which it remains at a constant intensity. The violet feature “A” at 3.278 eV does not shift with temperature and is largely disappeared by 300 K. Features “B” (3.192 eV) and “C” (3.075 eV) also do not appear to shift with temperature. Both “A” and “B” features thermally quench at a faster rate than either “A” or the BL band. At 300 K, they are barely detectable. Feature “B” thermally quenches at a faster rate than “C” such that at 180 K, “B” is no longer the dominant feature of the violet band. By 240 K, the BL band becomes more dominant in the spectra than “C”.

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Figure 6.6. Excitation power dependent PL spectra of MBE 50, the sample with an MBE growth substrate temperature of 900 °C.
Figure 6.7. Temperature dependent PL spectra of MBE 50, the sample with an MBE growth substrate temperature of 900 °C.
Low Temperature PLE Spectroscopy

In order to understand the recombination processes, low temperature (6 K) photoluminescence excitation spectroscopy (PLE) was performed on the Sc\textsubscript{x}Ga\textsubscript{1-x}N samples. Low temperature PLE spectra for each ScGaN sample are shown in Figure 6.8. These spectra were recorded at the peak of the low excitation power PL peak of the violet luminescence band; however, similar shaped spectra were obtained for each sample, regardless of detection energy across the violet luminescence band.

The onset of absorption for all four samples occurs at about the same energy with increased broadening of the absorption edge as the substrate temperature decreases. The PLE spectra of the sample grown with the highest substrate temperature of 900 °C (black line) also exhibits an exciton peak at 3.48 eV. Below the fundamental absorption edge, the PL intensity quickly diminishes and no other absorption features are observable at lower excitation energies.

An absorption edge at 3.50 eV corresponds to the creation of carriers that are excited in GaN and which relax to the emitting state, contributing to the violet PL intensity. The feature at 3.48 eV corresponds exactly to the absorption energy of excitons occurring just below the fundamental absorption edge of GaN. The exciton feature of GaN not resolved for substrate temperatures below 900 °C. Additionally, the GaN absorption edge significantly broadens with decreasing substrate temperature. This broadening may reflect the quality of the material improving with increasing substrate temperature.

As there are no other absorption features besides that of GaN observed in the spectra of the four ScGaN samples, it raises the question as to what the mechanism is behind the violet luminescence band. The absorption edge of low concentration Sc\textsubscript{x}Ga\textsubscript{1-x}N was observed by Little and Kordesch [16] and Constantin \textit{et al.} [17,18] to linearly decrease with increasing \( x \). Furthermore, theoretical calculations by Moreno-Armenta \textit{et al.} [15] predict the bandgap of Sc\textsubscript{x}Ga\textsubscript{1-x}N to decrease from the GaN value with increasing \( x \). Yet in the PLE spectra of Figure 6.8 there is no observable absorption edge below that of GaN.
Figure 6.8. Low temperature (6 K) PLE spectra of samples MBE 51 (blue line), MBE 52 (red line), MBE 45 (green line), and MBE 50 (black line) which were grown at substrate temperatures 650 °C, 725 °C, 800 °C and 900 °C, respectively.
**Room Temperature Transmission Spectroscopy**

Room temperature transmission measurements were performed on the $\text{Sc}_x\text{Ga}_{1-x}\text{N}$ sample grown with a substrate temperature of 800 °C (MBE 45) and on the GaN template sample. The room temperature transmission spectra were converted into absorbance spectra using the Beer-Lambert law, i.e.

$$A(\lambda) = \log_{10}\frac{I_{\text{incident}}(\lambda)}{I_{\text{transmitted}}(\lambda)}, \quad \text{Eq. 6-1}$$

where $I_{\text{incident}}(\lambda)$ is the spectral response of the lamp and $I_{\text{transmitted}}(\lambda)$ is the spectrum of the transmitted beam.

The absorbance spectra are presented in Figure 6.9. The spectra both exhibit a sharp exciton feature at the absorption edge. The oscillations below the absorption edge are due to multiple reflections of light within the samples. The different spacing of the oscillations is a direct result of the additional thickness of the MBE film on a template, as compared to the template-only sample.

The exciton feature of the template absorbance spectra peaks at 3.431 eV and corresponds to the combination of the spectrally overlapping GaN $A$ and $B$ excitons [26,27]. The small feature, about 3.456 eV corresponds to the $C$ exciton of GaN [26,27]. The broad peak at about 3.52 eV may be due to phonon assisted absorption as it is about 90 meV above the $A$ and $B$ exciton line [28,29,26].

The absorbance spectra of sample MBE 45 also has a sharp feature at the absorption edge which peaks at 3.434 eV. A broad feature is also observed about 90 meV above the sharp feature. The energy of the sharp feature is within the measurable uncertainty of the GaN $A$ and $B$ exciton feature observed in the absorbance spectra of the template sample. Additionally, the broad feature at about 3.52 eV is also observed at the same energy as the phonon-assisted absorption of the GaN template. The $C$ exciton of GaN, as observed in the template sample, is not observed in the absorbance spectra of MBE 45, although this is likely due to the fact that the $C$ exciton is more sensitive to strain than the $A$ and $B$ excitons and it is often not resolved in absorbance spectra of GaN [30,31]. Therefore, it is unsurprising that it is not observed in the absorbance spectra of MBE 45 in Figure 6.9.
Figure 6.9. Absorbance spectra of sample MBE 45 which was grown with a substrate temperature of 800 °C (red line) and GaN template sample C3536 (black line). The dotted line is a guide for the eye.
6.3.3. Summary of the Effects of Substrate Temperature

There are strong indications that the PL spectra of ScGaN are made up of multiple features which merge to form the broad (~400 meV) violet spectral component centred at about 3.16 eV. As substrate temperature during MBE growth is increased, the broad violet luminescence band begins to resolve into multiple narrower, overlapping features. Interference fringes and phonon replicas were ruled out as possible causes for the features. Excitation power dependent PL measurements imply the individual violet features react differently with respect to excitation power, lending support to the model of 3 individual features. Moreover, the features are affected differently by the temperature at which the PL spectra are recorded. This implies that the features involve different processes further supporting the model consisting of 3 violet features.

Photoluminescence excitation spectroscopy indicates that the violet luminescence observed in the PL spectra of the ScGaN samples are a direct result of absorption of light in GaN. The PLE spectra of the four ScGaN samples show an absorption edge corresponding to the absorption edge of GaN. Theory predicts the bandgap of Sc\textsubscript{x}Ga\textsubscript{1-x}N to occur at an energy lower than GaN [15] and others have experimentally shown Sc\textsubscript{x}Ga\textsubscript{1-x}N absorption occurs at energies lower than GaN [16,17]. In these experiments, however, there is no sign of a ScGaN absorption band below the GaN band edge.

Room temperature transmission spectroscopy corroborates the PLE spectroscopy. The absorbance spectrum of MBE 45 shows evidence of the A and B excitons of GaN and related phonon-assisted absorption. Once more, no clear sign of a ScGaN absorption band is observed below the GaN band edge. This raises questions about whether absorption of the MBE-grown films is due to the ternary alloy, ScGaN, or if it is from GaN alone.

As the temperature of the substrate during MBE growth decreases, the GaN exciton feature in the PLE spectra reduces and the absorption edge broadens. One possibility for this broadening is that the scandium layer acts as a defective GaN layer instead of as a ternary alloy. Trautman et al. [32] recorded room temperature optical absorption spectra for GaN films grown via MOVPE at different temperatures on sapphire substrates. They found that the absorption spectra of the sample grown at 1075 °C showed a sharp exciton edge at 3.5 eV. As the growth temperature was reduced to 800 °C, this exciton feature broadened and became less
pronounced. As the growth temperature was reduced further to 500 °C, the absorption spectra broadened to such an extent that there was no longer a well-defined absorption edge at 3.5 eV and the absorption tail extended to 2.8 eV. This broadening of the absorption edge for lower growth temperatures was suggested to be a result of increased dislocation densities at lower GaN growth temperatures.

Additionally, doping has also been shown to broaden the GaN exciton absorption. Zhao et al. [33] have studied the effect of silicon doping on the absorption spectra of GaN at room temperature. They observed that increasing the doping concentration from $10^{18}$ cm$^{-3}$ to $10^{19}$ cm$^{-3}$ reduced the GaN exciton absorption feature and significantly broadened the absorption edge.

Therefore, the reduction of the exciton absorption feature and consequent broadening of the absorption edge, as observed in both the PLE (Figure 6.8) and absorbance spectra (Figure 6.9), could be the result of decreased crystal quality in the MBE-grown films.

A further indication of a decrease in crystal quality of the MBE-grown layer with decreasing substrate temperature is that the features forming the violet luminescence band are less resolved when the layer is grown at lower substrate temperatures. It is well known that the crystalline quality of GaN when grown by MBE improves with higher substrate temperatures [34,35,36,37]. The same effect could be happening with the ScGaN layers. As substrate temperature increases, crystal quality of the ScGaN layer could be improving.

Both the PL spectroscopy and absorption spectroscopy (via PLE and transmission measurements) appear to show an increase in crystal quality of the MBE-grown layer with increasing substrate temperature during the growth process. The photoluminescence of samples containing a ScGaN layer results in multiple violet luminescence features; however, it is important to note that there is no clear sign of a ScGaN absorption edge. Without an apparent ScGaN absorption edge, it cannot be concluded that the MBE-grown layer is truly a ternary alloy. More information is required to understand the origin of the violet luminescence.
6.4 Varying Sc Effusion Cell Temperature

6.4.1. Sample Details

An additional set of ScGaN samples were grown in which the temperature of the Sc effusion cell was 1380 °C and 1400 °C. The Ga effusion cell temperature remained constant at 950 °C and the substrate temperature was 800 °C. Table 6.2 shows the growth parameters and results from x-ray measurements for this pair of samples.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Substrate Temperature (°C)</th>
<th>Ga cell Temperature (°C)</th>
<th>Sc cell Temperature (°C)</th>
<th>ScGaN Film Growth Time</th>
<th>ScGaN film thickness – HRXRD (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBE 47</td>
<td>800</td>
<td>950</td>
<td>1380</td>
<td>120 min</td>
<td>289 ± 10</td>
</tr>
<tr>
<td>MBE 43</td>
<td>800</td>
<td>950</td>
<td>1400</td>
<td>90 min</td>
<td>276 ± 10</td>
</tr>
</tbody>
</table>

Table 6.2. Growth Details of Variable Sc Effusion Cell Temperature MBE Films

6.4.2. Experimental Results

Low Temperature PL Spectroscopy

Low temperature (6 K) photoluminescence measurements were performed on the Sc$_x$Ga$_{1-x}$N film samples grown with scandium effusion cell temperatures of 1380 °C and 1400 °C and are presented in Figure 6.10. Both spectra exhibit the GaN exciton feature at 3.48 eV and the broad asymmetric feature which peaks in the violet, centred around 3.15 eV. The spectra of sample MBE 47 has overlapping features in the violet band and shows signs of the yellow luminescence band, centred about 2.16 eV.

As the Sc effusion cell temperature during MBE growth increases, the broad violet luminescence feature resolves into a series of narrower features. These features are centred at 3.20 eV, 3.01 eV, and 2.77 eV. A shoulder on the high energy side of the violet band occurs at about 3.25 eV. The shoulder and highest energy resolved peak occur at very similar energies to the “A” and “B” peaks of the modelled PL spectra of sample MBE 50, the sample grown with a substrate temperature of 900 °C.
Figure 6.10. Low Temperature (6 K) PL spectra of samples MBE 47 (black line) and MBE 43 (red line) which were grown with an MBE Sc effusion cell temperature of 1380 °C and 1400 °C, respectively.
Low Temperature PLE Spectroscopy

Low temperature (6K) photoluminescence excitation spectroscopy was performed on the Sc$_x$Ga$_{1-x}$N samples grown with varying Sc effusion cell temperatures. Typical low temperature PLE spectra for both samples are shown in Figure 6.11. The onset of absorption for both samples occurs at about the same energy. An exciton peak at 3.488 eV is observed in the PLE spectra of sample MBE 47. This corresponds to the low temperature exciton absorption of GaN [21]. The spectrum of MBE 43, which was grown with a higher Sc effusion cell temperature, does not contain this exciton feature. Instead, the absorption edge is broadened and the exciton feature is no longer resolved. No other distinct absorption features are detected in the PLE spectra of either sample, as was observed for samples grown with varying substrate temperature as discussed in Section 6.3.1.

![Figure 6.11. Low temperature (6 K) PLE spectrum of MBE 47 and MBE 43, grown with Sc effusion cell temperature of 1380 °C and 1400 °C, respectively.](image)
6.4.3. Microscopy Results

This section details additional results of measurements on the variable Sc effusion cell temperature samples described in Table 6.2 which were taken by Moram et al. at the University of Cambridge [38]. These results are discussed in support of the optical measurements discussed in Section 6.4.2.

**Cathodoluminescence**

A comparison of the PL spectra of the GaN template and of all the ScGaN film samples discussed in this chapter indicates that the violet luminescence band is a result of the MBE-grown ScGaN film. The PL spectrum of the template, as shown in Figure 6.4, does not contain a violet luminescence band; however the PL spectra of all ScGaN layer samples contain a broad violet band. Furthermore, modifying the film’s growth parameters results in changes to the characteristics of the PL spectra of those samples. Yet the lack of evidence for an absorption edge other than that of GaN raises questions about whether the luminescence is actually from the ScGaN layer. The light penetration depth for a 325 nm wavelength beam would exceed the thickness of the ~200µm MBE-grown layer. This opens up the possibility that the luminescence could originate from the GaN template or even at the interface between the film and the template.

To further investigate the origin of the luminescence, scanning electron microscope cathodoluminescence (SEM-CL) was performed on MBE 47 by Moram et al. at the University of Cambridge [38] using a Philips XL30 field-emission gun scanning electron microscope and Gatan MonoCL4 detection system. Measurements were taken in both plan view and cross-section. A transmission electron micrograph was also taken to characterise the structure. Figure 6.12 shows (a) the transmission electron micrograph, (b) cross sectional view SEM-CL at 93 K, and (c) typical CL spectra obtained from an area of the GaN (dotted line) and an area of the ScGaN layer (solid line).

The brighter areas of Figure 6.12(b) indicate a greater integrated CL intensity. It is clear from the figure that the entire region of the ScGaN film is showing a much greater integrated intensity than the GaN template. This supports the suggestion that the luminescence is coming from the ScGaN layer and not the GaN template or interface. Furthermore, the bright area is uniform throughout the
film and not just at the interface, implying that the luminescence is indeed originating in the film region.

The SEM-CL spectra shown in Figure 6.12(c) are very similar to PL spectra observed in Figure 6.4 (template) and Figure 6.10 (MBE 43). The SEM-CL spectrum taken from the template region (dotted line) shows the well-known exciton feature, BL band and YL band emission of GaN [21]. The spectrum taken from the ScGaN film region (solid line) shows a broad violet feature peaking at 392 nm (3.163 eV) which is not much different to the PL spectrum of MBE 43 taken at a similar temperature.

To confirm this, Figure 6.13 shows a PL spectrum of MBE 47 taken at 80 K on the same wavelength scale and normalised to the maximum intensity of the SEM-CL spectrum of the ScGaN region MBE 47. The two spectra have comparable FWHM, though the “B” peak seems to be dominant in the CL spectra, whereas the “C” peak is dominant in the PL spectra. This difference could be due to the much greater carrier generation rates of CL, as compared to optical excitation. Nevertheless, the violet luminescence bands observed in the SEM-CL spectra and the PL spectra are essentially the same. This confirms that the violet luminescence observed in the PL spectra is originating in the ScGaN layer and not from the GaN template below.
Reciprocal Space Maps

High resolution x-ray diffraction (HRXRD) measurements were performed on samples MBE 43, MBE 47, and C3536 (the GaN template) by Moram et al. at the University of Cambridge using ω-2θ scans [38]. Their measurements confirmed that the MBE films are [0001]-orientated and that only a single crystalline phase is present. Reciprocal space maps (RSM) of the 10T5 reflection, which they obtained in the asymmetric geometry, are plotted in Figure 6.14. The top diagram is the RSM of the GaN template, the middle figure is the RSM of the sample grown with a Sc effusion cell temperature of 1380 °C (MBE47), and the bottom figure is the RSM of the sample grown with a Sc effusion cell temperature of 1400 °C (MBE 43). The RSM of sample C3536 shows a single large elliptical feature, which is the reflection from the GaN template layer. Group III-nitride RSMs often occur in an elliptical shape with their major axis along the ω-direction [39]. The middle and bottom diagrams show the reflection of the samples which have a ScGaN layer grown on a GaN template. The GaN elliptical reflection feature is observed (as expected due to the thick template below the ScGaN) in addition to another elliptical feature. The centre of the second feature shifts down and to the left as the Sc effusion cell temperature increases. The ellipse is also rotated in orientation to the GaN feature.
The shift of the secondary ellipse in reciprocal space is a direct indication of a difference in lattice parameter between the ScGaN layer and the GaN template which it is grown upon. In the case of increasing Sc effusion cell temperature (thus increasing Sc content in the MBE-grown layer), Moram et al. found the lattice of the ScGaN layer is expanding in both the $a$- and $c$-planes, relative to the GaN template on which it is grown. Furthermore, they reported that the broadening of the ScGaN RSM peak with increasing Sc effusion cell temperature suggests a progressive decrease in the crystalline quality of that layer.

Figure 6.14. Reciprocal space contour maps of the $10\overline{1}5$ reflection for ScGaN films grown with varying Sc cell effusion temperature [38].
6.4.4. Summary of the Effects of Sc Effusion Cell Temperature

Increasing an effusion cell temperature during MBE growth should increase its concentration within the grown material. In the case of sample MBE 47 (Sc effusion cell temperature = 1380 °C) and sample MBE 43 (Sc effusion cell temperature = 1400 °C), increasing the scandium effusion cell temperature whilst keeping the Ga effusion cell temperature constant appears to decrease the crystal quality. The violet luminescence features in the low temperature PL spectra observed in Figure 6.10 become less resolved with increasing Sc effusion cell temperature. Furthermore, the GaN band edge of the PLE spectra of Figure 6.11 broadens with increasing Sc effusion cell temperature. The broadening ScGaN reflection features of the RSMs in Figure 6.14 confirm the optical spectroscopy results, pointing towards a decrease in crystal quality with increasing Sc effusion cell temperature.

It is important to note that increasing the Sc effusion cell temperature, and hence, the concentration of Sc in the Sc\textsubscript{x}Ga\textsubscript{1-x}N layer does not provide any further indication of an absorption edge other than that of GaN. When detecting across the violet PL band, only a GaN band edge is observed in the PLE spectra. This implies that there is no direct absorption which leads to the violet emission other than from a direct absorption of GaN.

The SEM-CL data in Figure 6.12 show that the violet emission does not originate from the GaN template layer, but uniformly from the ScGaN layer. Without an observable bandgap, it cannot be confirmed that the Sc atoms have formed a true ternary alloy with GaN. The SEM-CL data confirms the notion that the luminescence is from the MBE-grown layer; however it does not fully explain the nature of the luminescence.

6.5 Discussion

Not much is experimentally known about the ternary alloy Sc\textsubscript{x}Ga\textsubscript{1-x}N and its bandgap. To date, there are no reports on Sc\textsubscript{x}Ga\textsubscript{1-x}N emission spectra; however there have been some experimental reports on absorption spectra. Little and Kordesch [16] found the energy of the absorption edge to decrease linearly with increasing Sc concentration; however it should be noted that these samples were suggested to be either amorphous or microcrystalline. They reported the bandgap
varied from 3.5 eV at $x = 0$ to 2.0 eV at $x = 1$. Using this linear interpolation of the bandgap, a sample containing 5% Sc would have an absorption edge of 3.43 eV which is a 2% reduction from the GaN absorption value. Additionally, Constantin et al. [17,18] studied absorption of $b$-Sc$_x$Ga$_{1-x}$N and found that for $0 < x < 0.3$, the absorption edge decreases monotonically with increasing $x$. Using their linear model which varies from 3.37 eV at $x = 0$ to their extrapolated value of 2.3 eV at $x = 1$, a sample containing 5% Sc would have an absorption edge of 3.35 eV. This value is a 2% reduction of the value of the GaN absorption edge, in agreement with the model by Little and Kordesch [16].

The GaN absorption edge, as observed from room temperature transmission measurements (shown in Figure 6.9), is 3.43 eV. Following the linear models proposed for absorption edge energy shift as observed by Little and Kordesch [16] and Constantin et al. [17,18], a 2% reduction of the absorption edge of GaN observed in this work would occur at 3.36 eV. This would mean that a sample containing 5% Sc would result in a 70 meV reduction in energy from the GaN value. The Sc$_x$Ga$_{1-x}$N layers in this work have been reported [19] to contain as much as 8% Sc. Yet no measurable shift in absorption edge has been detected for any of these samples.

The violet luminescence is clearly originating from the ScGaN layer. Still, without an observable bandgap from absorption measurements, there is no conclusive evidence that the recombination is due to a band-to-band transition. Other emission mechanisms must be explored in order to explain the origin of the violet light.

One possible explanation is that the bandgap of ScGaN could be indirect for these films. Optical transitions across an indirect bandgap require the additional participation of a phonon in order to satisfy conservation of momentum. The probability of two such processes happening simultaneously is much smaller than the probability of a direct transition [40]. This would significantly reduce the absorption coefficient of the material.

Ranjan et al. [41] investigated the theoretical electronic band structure of ordered (GaN)$_m$/ScN$_n$ systems. They found that in the systems having a Sc concentration of less than or equal to 50%, the valence band significantly flattens along the $\Gamma$-to-$\Lambda$ line in the Brillouin zone. They determined from their calculations
that the difference in valence maxima between the \( \Gamma \) - and \( \Lambda \)-point is small, i.e. -10 meV for 50% Sc and -12 meV for 25% Sc.

The theoretical work by Moreno-Armenta et al. [15] investigated band structure of disordered Sc\(_x\)Ga\(_{1-x}\)N alloys. They determined the fundamental gap for low concentration Sc alloys was direct; however, upon closer inspection of their band diagram for 25% Sc (see Figure 6.15), the flat nature of the valence band between the \( \Gamma \)- and \( \Lambda \)-point is clear, though this feature of the valence band is not discussed by the authors.

![Figure 6.15. Band structures of Sc\(_{0.25}\)Ga\(_{0.75}\)N and GaN, as calculated by Moreno-Armenta et al. [15].](image)

Furthermore, band structure simulations performed by D. Holeč [38] using the Vienna \textit{ab initio} simulation package (VASP) [42,43,44] also appear to indicate that the valence band maximum of Sc\(_{0.06}\)Ga\(_{0.94}\)N is rather flat, extending from the \( \Gamma \)-point towards the \( \Lambda \)-point. The results of those simulations are shown in Figure 6.16 below. This calculation is for a much lower Sc content, yet the valence band still shows a marked increase in energy at the \( \Lambda \)-point, as compared to the valence
band of the GaN. Holeč predicts the bandgap of $\text{Sc}_{0.06}\text{Ga}_{0.94}\text{N}$ to be direct, but does not further discuss this feature of the valence band.

It is important to note that the band structure calculations by Moreno-Armenta et al. [15] and D. Holeč [38] are for fully relaxed systems; however the MBE-grown layers experimentally investigated in this chapter are thought to be partially strained. High resolution transmission electron microscopy (HRTEM) of sample MBE 43 (Sc cell temperature 1400 °C) reported by Moram et al. [19] shows that although some stress relaxation has occurred in this sample (believed to contain 8% Sc), it is not completely relaxed. In fact, the $a/c$ ratios reported by Moram et al. remain relatively constant with increasing Sc concentration, whereas Constantin et al. [17,18] report an increase in the $a/c$ ratio with increasing Sc concentration.

Figure 6.16. Band structure diagram of $\text{Sc}_{0.0625}\text{Ga}_{0.9375}\text{N}$ and GaN, as calculated by Holeč [38]. The valence band of $\text{Sc}_{0.0625}\text{Ga}_{0.9375}\text{N}$ between the $\Gamma$- and $A$-point is circled in red for the eye.

Strain in GaN is well known to affect the in-plane and out-of-plane band structures differently due to the asymmetry of the hexagonal crystal structure [45,46]. In crystal structures where there is a secondary band valley of similar energy to the primary valley (such as GaAs, GaSb InP, or AlGaAs), strain can have such an effect on the band structure that it can cause a change to the bandgap resulting in a transition between a direct and indirect bandgap [47,48,49,50]. Ranjan, Bellaiche and Walter [12] also reported that when a thermodynamically stable $b$-ScN
lattice is compressed to fit the wurtzite GaN lattice, the bandgap transitions from direct to indirect.

Possibly the stress of ScGaN grown on GaN could have a similar effect. If the difference between the Γ- and Α-point valence band energy is only on the order of 10 meV, it could potentially have a significant effect under strain. It would be advantageous to understand the effect of strain on the band structure of ScGaN in order to validate the hypothesis that the ScGaN layers discussed in this chapter could have an indirect bandgap.

Another possible explanation for the violet luminescence reported in this chapter is that the ScGaN layers are simply GaN doped with Sc. Carrier mobility and electrical resistivity measurements performed by J. Durrell [38] using in-plane Hall measurements in the van der Pauw configuration [51] confirm the ScGaN thick films discussed in this chapter to all be highly n-type. Sample MBE 43 (Sc cell temperature 1400 °C) was reported to have a room temperature n-type carrier concentration of 1.35×10¹⁹ cm⁻³ whereas the GaN template had less than 10¹⁷ cm⁻³. Furthermore, Durrell found the Hall voltage of the Sc films to decrease as temperature increased, which is a characteristic of carrier transport in both the conduction band and an additional, shallow impurity band [52, 53].

This shallow impurity band could be due to Sc atoms acting like donor atoms in the GaN. Despite having 3 valence electrons, Sc has been shown to be an effective shallow donor in the III-V semiconductor, InAs [54,55]. Furthermore, isoelectronic impurities including As and P have been known to form defects in neutral, +, and 2+ oxidation states in GaN [56,57,58]. As was established by Durrell’s Hall measurements, the MBE-grown layers have two orders of magnitude greater room temperature n-type carrier concentration, compared to the GaN template. Possibly the Sc in these samples is not forming a true alloy but effective shallow donors instead.

To investigate this possibility, it is advantageous to further consider Durell’s electrical measurements. For doped semiconductors, conductivity is related to carrier concentration and mobility by

\[ \sigma = q(n_\text{c} \mu_\text{c} + n_\text{D} \mu_\text{D}), \]

where \( q \) is the electron charge, \( n_\text{c,D} \) are electron concentration in the conduction band and donor band, respectively and \( \mu_\text{c,D} \) are the corresponding carrier mobilities [52]. At low temperatures, electron concentration in the conduction band is
reduced so that the number of electrons in the donor states becomes much greater than those in the conduction states. Therefore, Equation 6-2 reduces to

$$\sigma = qn_D \mu_D.$$  

6-3

Mobility measurements from Durrell demonstrate a linear increase with temperature. Therefore, the conductivity can be modeled as

$$\sigma = A \exp\left(\frac{E_D}{k_B T}\right),$$  

6-4

where $A$ is a constant and $E_D$ is the donor energy [59].

Using this equation to model Durrell’s resistivity measurements as a function of inverse $k_B T$ yields an activation energy of 26 ± 2 meV (See Figure 6.17). This energy is comparable with donor levels of the common shallow dopants of GaN, such as silicon (30 meV) [60] and oxygen (33 meV) [60]. Therefore, the Sc atoms could be acting like shallow donors in GaN.

![Figure 6.17. Durrell’s resistivity measurements (as their inverse, i.e. conductivity) [38] as a function of inverse $k_B T$ and a basic model of his measured data.](image)

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It could also be that the presence of Sc during MBE growth is enhancing or activating other common shallow dopants such as oxygen. ScN and GaN are prone to oxygen impurities [19, 21] and the increase in donors such as O\textsubscript{N} forms V\textsubscript{Ga} due to self-compensation [61]. The resulting V\textsubscript{Ga}O\textsubscript{N} pair is widely accepted as one of the main causes of the YL band, which is observed in the PL spectra of the samples which were grown with the highest substrate temperature or Sc effusion cell temperature, both cases in which we would expect more Sc present in the sample.

More information is needed on the actual content of the MBE-grown film in order to better identify the true nature of the violet luminescence. Recently, it was suggested that the samples discussed in this work may have less Sc content than previously thought [62]. Accurately knowing the content of Sc and/or any unintentional dopants would provide more insight towards the understanding of the observed violet luminescence band and the narrow features which make up that band. Without further microscopy on these ScGaN films, the true nature of the violet luminescence will remain inconclusive.

References


Chapter 7: Conclusions

Research presented in this thesis focused on the optical characterisation of InGaN/GaN QW and QD structures and ScGaN epilayers, supported by microscopy results from the University of Cambridge.

Reported in Chapter 4 were the optical properties of sets of high indium fraction (~25%) multiple QW structures designed to emit in the green part of the spectrum. Sets of InGaN/GaN QW structures were investigated which were grown using traditional methods but by varying QW growth temperature. These samples were found to have two PL emission bands and low (1-10 %) room temperature IQE. Changes to the QW growth temperature had little effect on the improvement of the samples’ luminescence properties.

It was found that uniformity of the QWs degraded after the first few wells were grown, resulting in reductions of the average well thickness and indium content of the third through tenth QWs. The consequence of a reduction of thickness and/or indium is lower energy emission than the first few QWs, thus broadening the photoluminescence linewidth and decreasing the IQE.

A modification of the growth procedures was developed to ensure that the individual QWs have as similar properties as possible so that the contribution to the PL linewidth due to well-to-well variations was significantly reduced. These modified procedures were used to produce new sets of InGaN/GaN 10 QW structures. These new structures showed a significant decrease (~40%) in PL linewidth and a marked increase (~30%) in IQE.

Furthermore, a set of 1, 3, 5 and 10 QW structures grown under modified growth procedures were investigated to determine the optimum number of QWs needed. It was found that 3 QWs provided a significant improvement to the IQE over the 1 QW samples; however, no additional improvements were realised by growing additional QWs.

Reported in Chapter 5 were the use macroscopic optical spectroscopy methods to study the properties of QDs. InGaN QDs are typically studied using spatially resolved techniques which allow for the study of individual dots in a structure. A sample which was known to contain InGaN QDs was investigated; however it was determined that macroscopic spectroscopic techniques were unable to determine the existence of QDs in the structure.
The research discussed in Chapter 6 explored a series of ~ 260 µm thick MBE-grown ScGaN layers on 500 µm thick MOCVD-grown GaN templates. It was found that these materials, believed to contain up to 8% scandium, emit a broad spectrum violet luminescence. This broad luminescence spectrum resolves into multiple, narrower features with either increased substrate temperature during growth or by decreasing the scandium effusion cell temperature. The absorption spectrum, on the other hand, only shows evidence of GaN and samples grown at the highest substrate temperature revealed an exciton absorption feature near the band edge of GaN, a sign of increased crystal quality. These results have lead to questions as to whether the violet luminescence is due to the ternary alloy ScGaN or rather from shallow, radiative defects in the material.
Acta est fibula.