Optical Studies of Polar InGaN/GaN Quantum Well Structures

A thesis submitted to The University of Manchester for the degree of Doctor of Philosophy in the Faculty of Engineering and Physical Sciences

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1T single temperature
2T two temperature
BL blue luminescence
Ce:YαG cerium doped yttrium aluminium garnet
CFD constant fraction discriminator
CFL compact fluorescent lamp
CW continuous wave
DAP donor-acceptor pair
DH double heterostructure
DOS density of states
DVD digital versatile disc
EBL electron blocking layer
ELOG epitaxial lateral overgrowth
EQE external quantum efficiency
FWHM full width at half maximum
GWWF gross well width fluctuation
HEMT high electron mobility transistor
HVPE hydride vapour phase epitaxy
II/P integrated intensity per unit excitation power
IQE internal quantum efficiency
IR infra-red
LD laser diode
LED light emitting diode
LEEBI low energy electron beam irradiation
LO longitudinal optical
MBE molecular beam epitaxy
MCA multichannel analyser
MOCVD metal organic chemical vapour deposition
OWC optical wireless communication
PC personal computer
PL photoluminescence
PMT photomultiplier tube
PSB phonon sideband
Q2T quasi-two temperature
QCSE quantum confined Stark effect
QW quantum well
RT-IQE room temperature internal quantum efficiency
STEM-HAADF scanning transmission electron microscopy-high angle annular dark field
TAC time to amplitude converter
T-bounced temperature bounced
TCSPC time correlated single photon counting
TD  threading dislocation
TEM  transmission electron microscopy
TMA  trimethylaluminium
TMG  trimethylgallium
TMI  trimethylindium
UV  ultra-violet
VLC  visible light communication
WWF  well width fluctuation
XRD  x-ray diffraction
YL  yellow luminescence
Abstract

The work in this thesis was submitted to The University of Manchester for the degree of Doctor of Philosophy in April 2016 by William Eric Blenkhorn and is entitled “Optical Studies of Polar InGaN/GaN Quantum Well Structures”.

In this thesis, I will present and discuss research performed on InGaN/GaN multiple quantum well (QW) structures. The results of which were taken using photoluminescence (PL) spectroscopy and PL time decay spectroscopy.

In the first two experimental chapters, I report on the effects of QW growth methodology on the optical properties of c-plane InGaN/GaN QWs. I compare structures grown using the single temperature (1T), quasi-two temperature (Q2T), temperature bounced (T-bounced) and two temperature (2T) QW growth methodologies. The T-bounced and 2T structures are observed to have gross well width fluctuations (GWWF), where the QW width varies from 0 to 100% created when the QWs are exposed to a temperature ramp. Whereas, the 1T and Q2T structures have continuous QWs with only one or two monolayer well width fluctuations. The structures with GWWFs are observed to have a larger room temperature internal quantum efficiency (RT-IQE) at low excitation conditions i.e. below efficiency droop compared to those without. The larger RT-IQE is ascribed to several factors which include an increased radiative recombination rate, increased thermal activation energy of non-radiative recombination and reduced defect density of the QWs. The effect of barrier growth temperature is also investigated. No clear trend is observed between barrier growth temperature and RT-IQE.

In the last experimental chapter I report on studies of carrier localisation in InGaN/GaN QWs using resonant PL spectroscopy. The effect of carrier localisation on the independently localised electrons and holes are investigated and the resonant PL spectrum is studied in detail. The InGaN/GaN QW structure is observed to exhibit an effective mobility edge at 12 K where delocalised carriers are created above a particular excitation energy. The emission from the resonantly excited localised states which are accompanied by the emission of a longitudinal optical phonon (resonant LO feature) is investigated as a function of temperature and excitation energy. The integrated PL intensity of the resonant LO feature is observed to quench rapidly with temperature up to around 45 K, independent of excitation energy. The integrated PL intensity of the resonant LO feature is fitted to an Arrhenius model and a thermal activation energy of $\sim 1(\pm 1)$ meV is extracted. This activation energy is speculated to be consistent with the localisation energy of electrons.
Declaration

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I would like to thank my supervisor Prof. Philip Dawson and the Photon Physics group for the opportunity to complete my doctorate at The University of Manchester. I would also like to thank the EPSRC for funding my research under grant code EP/I012591/1 entitled “Lighting the Future”. Special thanks must go to my supervisor for the support and guidance over these many years, for which I am truly grateful. I would like to acknowledge Dr. Thomas Badcock, Dr. Matthew Davies and Dr. Simon Hammersley for their support, guidance and patience throughout my doctorate. Furthermore, for the countless helpful discussions over the course of my doctorate. I would also like to thank the Department of Material Science and Metallurgy at the University of Cambridge for providing the sample structures I studied. Specifically, I’d like to acknowledge Sir. Prof. Colin Humphreys, Dr. Rachel Oliver, Dr. Menno Kappers, Dr. Fabien Massabuau and Dr. Suman-Lata Sahonta for their support, helpful discussions and contributions to this work over the last few years.

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List of Publications


If you always put limit on everything you do, physical or anything else. It will spread into your work and into your life. There are no limits. There are only plateaus, and you must not stay there, you must go beyond them.

Bruce Lee
CHAPTER 1

Introduction

The group III-nitride semiconductors InN, GaN and AlN are a group of direct bandgap semiconductors. They, along with their ternary and quaternary alloys have a broad range of bandgaps, ranging from 0.76 eV for InN to 6.2 eV for AlN at room temperature. This broad range of bandgaps allows III-nitride semiconductor devices to detect and emit light from the infra-red (IR) to the deep ultra-violet (UV), encompassing the entire visible spectrum.

A large amount of research has been conducted into III-nitrides due to their broad range of emission energies and potential applications in devices. Most notably III-nitride semiconductors have been used to create white light emitting diodes (LEDs). Solid state lighting has been the subject of a vast amount of research due to the large potential energy savings compared to other lighting sources. III-nitride semiconductors have also been widely used in the production of laser diodes (LDs) for short range optical communications, water sterilisation and data storage. Further understanding of III-nitride semiconductor systems is of great importance due to their potential energy saving and wide range of applications.
1.1 Applications

III-nitride semiconductor devices are extensively used commercially, with one of the largest applications being in solid state lighting for homes, offices, street lighting etc. (see Figure 1.1). White light emission from LEDs is currently produced in two main ways. Firstly, by combining blue LEDs with a wavelength converting yellow phosphor such as cerium doped yttrium aluminium garnet (Ce:YaG). Alternatively, by combining a UV LED with different colour phosphors mainly red, blue and green. The latter method is preferred for general purpose lighting due to its improved colour temperature. Though the first method is preferred for lighting exhibits in galleries and museums due to the lack of UV radiation (when using blue LEDs) which can degrade objects and paintings. Other methods of producing white light emission involve combining several colours of LEDs mainly red, blue and green. Furthermore, LEDs which contain quantum dots of different shapes and sizes that emit over the visible spectrum can also produce white light.

![Commercially available white, blue, green and red LEDs](image)

Figure 1.1: Commercially available white, blue, green and red LEDs, taken from [14].

White LEDs are preferred for general lighting purposes because of their higher luminous efficacies typically around 100 lmW\(^{-1}\). These figures surpass compact fluorescent lamps (CFLs) and high-intensity discharge lamps which have efficacies in the range of 60 to 90 lmW\(^{-1}\), as well as incandescent light bulbs which range from 15 to 20 lmW\(^{-1}\). The lighting sector according to the International Energy Agency accounts for almost 20% of global electricity consumption. Thus energy saving in the lighting sector will have a significant impact on energy consumption and pollution.
Along with the energy saving benefits white LEDs also have superior lifetimes, with commercially-available LEDs rated for around 15,000 hours [17] compared with 10,000 hours for CFLs [18]. Furthermore LEDs offer superior durability with the number of switch cycles before failure, rated at 50,000 [17] compared with 10,000 for CFLs [18]. This dramatic increase in switch cycles along with their near instantaneous full light output means that LEDs are also preferred for smart lighting systems in offices and factories.

III-nitride LEDs or LDs have been shown to be a suitable material system for optical wireless communications (OWCs). This involves the transfer of data through a modulated optical signal, which is detected and converted back into an electrical signal by a receiver. LEDs and LDs can be used as the optical source with LEDs being preferred for indoor applications due to their low cost, high reliability and reduced health hazard. The development of visible light communication (VLC) devices such as white LEDs have been the subject of a large amount of research recently due to the fact that they can provide lighting and data transfer simultaneously [19]. Harnessing visible light as a communication medium can provide a secure broadband network as visible light cannot penetrate through walls. OWCs devices can also provide high data transfer rates with a recent study [20] reporting a rate of 224 Gbs$^{-1}$ over a $\sim 3$ m distance, which is comparable to current wired ethernet connections of 100 Gbs$^{-1}$.

UV emitting AlN devices are currently being used to purify water and for sterilisation in the food and medical industries [21]. This is because UV radiation can cause damage to living organisms, with DNA having an absorption peak between 4.1 and 6.2 eV [22]. UV LEDs are replacing mercury lamps for sterilisation purposes due to fact that mercury lamps are highly toxic, consume a large amount of power and have a poor device lifetime of around 10,000 hours. Whereas LEDs are environmentally safe, energy efficient and have longer device lifetimes of around 25,000 hours. LEDs also have the added advantages of being a small compact device and more importantly wavelength tunable so the efficiency of killing bacteria can be maximised [23].

Blue emitting (405 nm) InGaN LDs have found commercial success in data storage for reading high density disks which can store around 25 GB of data [24]. This is a dramatic improvement over previous digital versatile disc (DVD) technology which could store 4.7 GB of data on a 120 mm disc. The improvement in data density was achieved in part by lowering the diffraction-limited spot size which is approximately given by $\lambda/NA$, where $\lambda$ is the wavelength of light and $NA$ is the
1.1 Applications

Numerical aperture of an objective lens. By replacing the 650 nm emitting AlGaInP LD used in DVD players \[25\] with the 405 nm emitting InGaN LD and changing the numerical aperture from 0.6 to 0.85, amongst other improvements; resulted in an increase in data density from 3.3 Gbit/in$^2$ to 16.5 Gbit/in$^2$ \[26\].

III-nitride semiconductors have been proven to be a good material system for fabricating high electron mobility transistors (HEMTs). GaN based HEMTs are currently being used for solid state power amplification of microwave and millimetre waves for military and aerospace applications due to the high breakdown voltage, good thermal conductivity, durability and low noise \[27, 28\]. III-nitride semiconductors are also being developed to harness the power of the Sun as a renewable energy source in solar cells, due to their broad energy bandgap and high efficiencies. Typically devices consist of several layers with different energy bandgaps to extract the most energy from the solar spectrum which ranges from $\sim 0.6$ eV to $\sim 4.1$ eV with a peak at around 2.3 eV \[29, 30\].
1.2 History and Development

One of the first reported III-nitrides to be synthesized was AlN in 1907 by Fichter [31]. Followed by GaN in 1932 by Johnson et al. [32] and then InN in 1938 by Juza and Hahn [33]. The growth of a crystalline GaN film by hydride vapour phase epitaxy (HVPE) on a 2 cm² sapphire substrate was first reported by Maruska and Tietjen in 1969 [34]. Maruska and Tietjen reported that the GaN films were n-type with a very high electron concentration of $\sim 10^{19}$ cm$^{-3}$ which they attributed to a high density of nitrogen vacancies which act as donors. Maruska and Tietjen also reported that GaN had a direct bandgap of 3.39 eV from room temperature optical-absorption measurements.

The first III-nitride based LED was reported by Pankove et al. [35] in 1971, some 43 years after the creation of the first LED by Russian scientist Oleg Losev in 1928 [36]. The LED was of the metal-insulator type which consisted of an undoped n-type layer grown on a sapphire substrate, followed by a Zn doped insulating GaN layer connected to indium electrodes. The Zn doping acted to compensate for the inherent n-type characteristic of the undoped GaN. The device had an external quantum efficiency (EQE) of 1 % and glowed green at room temperature due to the deep acceptor level at 1.1 eV above the valence band. The following year, a blue emitting LED using Zn doping [37] and violet LED using Mg doping [38] were produced.

In 1971, significant advancement in GaN growth was made by Manasevit et al. [39], who were the first to produce GaN by metal organic chemical vapour deposition (MOCVD) on silicon carbide and sapphire substrates. Further advancement came in 1974 by Akasaki, who was able to grow a single crystal of GaN using molecular beam epitaxy (MBE) for the first time. Though there had been significant advancement in GaN growth, the quality of the GaN was still poor due to the large lattice and thermal expansion mismatches between GaN and sapphire [40]. This problem was overcome by Yoshida et al. [41] in 1983, who inserted a AlN layer between the GaN layer and sapphire substrate using MBE; this is referred to as two-step growth. The reduced lattice and thermal mismatch between AlN and GaN resulted in improved crystalline, electrical and optical properties compared with GaN grown directly on sapphire. Further development of the use of AlN buffer layers was achieved in 1986 by Amano et al. [42] who successfully grew high quality GaN on AlN buffer layers using MOCVD. Even further improvement in electrical and crystalline quality of GaN was
achieved by Nakamura \[43\] in 1991, who grew GaN on top of a low temperature GaN buffer layer.

The first p-type doping of GaN was achieved by Amano et al. in 1989 by exposing Mg-doped GaN to a post growth \textit{low energy electron beam irradiation (LEEBI)} treatment at room temperature \[44\]. Though Amano et al. did not understand why they had achieved p-type doping. The \textit{LEEBI} treatment reduced the resistivity by more than 5 orders of magnitude from \(> 10^8\) to \(\sim 35\ \Omega\text{cm}\) and achieved hole concentrations of \(10^{16}\ \text{cm}^{-3}\). This achievement allowed Amano et al. to report on the first p-n junction UV LED, which consisted of undoped n-type GaN grown on a sapphire-AlN pseudo-substrate followed by a Mg-doped GaN layer which was exposed to \textit{LEEBI} treatment and connected with aluminium electrodes. Later in 1992, Nakamura et al. \[45\] also achieved p-type doping of GaN films but using \(\text{N}_2\) ambient thermal anneal treatment at temperatures above 700 °C. Nakamura et al. were able to achieve hole concentrations of \(10^{17}\ \text{cm}^{-3}\) and speculated that the thermal anneal effects during the \textit{LEEBI} process caused the p-type doping. Later that year, Nakamura et al. \[46\] solved the p-type doping mystery. Nakamura et al. proposed that during growth, ammonia (\(\text{NH}_3\)) dissociates into \(\text{H}_2\) and \(\text{N}_2\) and the hydrogen passivates the GaN creating acceptor-hydrogen complexes. On thermally annealing the GaN layer, the hydrogen dissociates from the complex leaving behind an acceptor and thus leading to p-type behaviour.

Growth of the ternary alloys started in 1972 with InGaN films grown by electron beam plasma technique \[47\]. Followed by AlGaN in 1978 grown by \textit{HVPE} \[48\] and then AlInN in 1981 by RF sputtering \[49\]. Significant developments in the production of InGaN came in 1989, when Nagatomo et al. were able grow InGaN films on sapphire substrates using \textit{MOCVD} \[50\]. Nagatomo et al. were able to achieve relatively high indium concentrations of 42 % at a growth temperature of \(\sim 500\ ^\circ\text{C}\). Nagatomo et al. found the incorporation of indium into InGaN layers was highly affected by the substrate growth temperature, with structures grown at lower temperatures incorporating more indium due to the weak In-N bond which sublimes around 550 °C \[51\]. Growth of InGaN films at high temperatures was first achieved by Yoshimoto et al. \[52\] in 1991, who grew InGaN films on sapphire at 800 °C using \textit{MOCVD}. Yoshimoto et al. were able to achieve an indium incorporation of 23 % and were the first to observe \textit{photoluminescence (PL)} from InGaN films. Yoshimoto et al. compared the structural and optical properties of InGaN films grown at 500 °C to those grown at 800 °C. They observed that the crystalline quality and \textit{PL} emission
1.2 History and Development

from the higher temperature structures were superior to those grown using lower temperatures. Although there had been significant advancement in InGaN quality it was still inadequate for LED and LD applications. The breakthrough in crystal quality came in 1992 by Nakamura et al. \cite{53}, who grew high quality InGaN films on GaN-sapphire pseudo-substrates by MOCVD using the two step growth method employed for high quality GaN growth a year earlier \cite{43}. Nakamura et al. were the first to observe band to band emission in the UV and blue region of the spectrum depending on composition from InGaN layers.

Taking advantage of the improved crystalline quality of InGaN films and the ability to p-type dope GaN. Nakamura et al. \cite{54} created the first InGaN double heterostructure (DH) blue LEDs in 1992. The DH consisted of a p-GaN/n-InGaN/n-GaN structure deposited on a GaN-sapphire pseudo-substrate by MOCVD with a gold contact on the p-type GaN and aluminium on the n-type GaN. The device emitted at 440 nm with an output power of 125 µW and an EQE of 0.22 %. Soon after the first commercially available blue LED was reported by Nakamura et al. \cite{55}. The device consisted of an InGaN/AlGaN DH which emitted at 450 nm with an output power of 1500 µW and an EQE of 2.7 %. The EQE of devices were significantly improved in 1995 with the use of QW active regions instead of DHs \cite{56, 57}. The use of InGaN as an active region for LDs was first demonstrated by Nakamura et al. for pulsed operation in 1996 \cite{58} and for continuous operation in 1997 \cite{4}. Further development of LDs has resulted in the fabrication of LDs which emit from 1.84 eV in the red \cite{59} to 3.63 eV in the UV \cite{6}.

Since these early devices a vast amount of research has been undertaken with the aim of further developing both the performance of the devices and understanding of the underlying physical processes. Recent advancements have seen white LEDs with EQEs in excess of 80 % \cite{60}. Even with recent advancements, a huge amount of knowledge has yet to be gathered about III-nitride semiconductors.
1.3 Growth Techniques

Several techniques have been used for the growth of III-nitride semiconductors, they include HVPE, MBE, MOCVD and boule growth. The structures in this work are all grown by MOCVD using a Thomas Swan close coupled showerhead reactor (Figure 1.2), capable of growing six 2 in wafers or one 6 in wafer. The structures were grown by colleagues in the Department of Material Science and Metallurgy at the University of Cambridge.

MOCVD growth involves building up layers of atoms on a substrate through chemical reaction. To achieve this, precursor gases flow over a heated substrate such as sapphire. The heated gases undergo a chemical reaction on the substrate surface to create atomic layers. Some of the precursor chemicals used for III-nitride semiconductors are trimethylindium (TMI), trimethylgallium (TMG), trimethylaluminium (TMA) and ammonia which are carried by hydrogen or nitrogen gas. n-type doping can be achieved with the addition of silane as a source of silicon to the mix of precursor chemicals. Similarly, p-type doping can be achieved with the addition of bis-cyclopentadienyl magnesium as a source of magnesium. The concentrations of the precursor chemicals in the carrier gas determine the composition of the alloy deposited.

The typical growth sequence for the InGaN multiple QW structures grown in this work involved the growth a 30 nm GaN nucleation layer at 540 °C on low defect density c-plane (0001) sapphire with a nominal 0.25° miscut toward (1120). Following that, an approximately 5 μm thick layer of GaN was grown at 1020 °C to create a GaN pseudo-substrate. The QW stacks were grown on top of the sapphire-GaN pseudo-substrates and consisted of alternating layers of InGaN QWs and GaN barriers.
Figure 1.2: Thomas-Swan close coupled showerhead MOCVD reactor [64].
1.3 Growth Techniques

1.3.1 QW Growth Methodologies

One of the growth methodologies used for InGaN/GaN QWs is single temperature (1T) growth. 1T growth involves the growth of InGaN QW layers below 800 °C, which is necessary to achieve good indium incorporation (> 20 %) \[65\], due to the low desorption temperature of InN at around 600 °C \[51\]. Following the InGaN QW growth, the GaN barrier is grown at the same temperature as the InGaN QW layer with no pause in the growth. The optimal growth temperature of GaN to achieve a low defect density is \( \sim 1000 \) °C \[66\]. Therefore the GaN grown in the 1T growth methodology has a high density of defects which can act as non-radiative centres and dramatically affect the recombination efficiency of InGaN/GaN QWs \[42, 67\].

To overcome this problem InGaN/GaN QWs can be grown using a two temperature (2T) growth methodology, where the InGaN QWs are grown below 800 °C and the GaN barriers are grown at \( \sim 860 \) °C with the growth being interrupted while the temperature is adjusted \[68\]. To note, the growth of the GaN barrier in the 2T methodology starts before the maximum barrier growth temperature is achieved. The exposure of the InGaN QW layer to a growth interruption \[69\] and/or a temperature ramp \[68, 70–72\] can result in the desorption of indium from the InGaN QW layer due to its poor thermal stability. The desorption of indium from the InGaN QW layer can result in the formation of gross well width fluctuations (GWWFs).

The desorption of indium caused by the 2T growth methodology is a real problem for the production of high indium content InGaN/GaN QW devices. One of the ways to overcome this problem is to grow a thin layer of material, typically around 1 nm thick on top of the InGaN QW; this is grown at the QW growth temperature to protect it from being exposed to a growth interruption or temperature ramp. This low temperature QW cap has been shown to result in the reduction of the amount of indium desorbed during a growth interruption or temperature ramp and is sometimes referred to as a low temperature QW cap \[73\]. QWs caps are employed in the quasi-two temperature (Q2T) growth methodology of InGaN/GaN QWs which reduces the indium desorption. Q2T growth involves InGaN QW layers being capped by a low temperature QW cap of GaN. After the QW cap, growth of the GaN barrier is continued during the temperature ramp to the normal high temperature growth conditions. Growth of the GaN barrier continues at high temperature until the desired thickness is achieved.
Another way to grow InGaN/GaN QW structures is referred to as temperature bounced (T-bounced) which involves the growth of InGaN QW below 800 °C. Following that, the growth is paused and the temperature is ramped up to the normal growth temperature of the GaN barriers around 860 °C resulting in the formation of GWWFs. The temperature is then lowered back to the QW growth temperature for the growth of the GaN barrier. A diagram of the temperature profiles used in all the above mentioned growth methodologies are shown in Figure 1.3. The specific growth conditions of each multiple QW structure used in this work is discussed in more detail in Section 4.2, 5.2 and 6.2.

Figure 1.3: Temperature profiles for the growth of the (a) 1T, (b) Q2T, (c) T-Bounced and (d) 2T structures. The InGaN growth is represented by the blue box and the GaN by the yellow.
1.4 Thesis Outline

In Chapter 2 of this work the fundamental properties of InGaN/GaN QWs will be discussed. This will include a description of the QW and its effect on the density of states. Moreover, the band and crystal structure of III-nitride semiconductors and their consequences on the structural and optical properties will be discussed. The luminescence properties of undoped GaN are also discussed.

In Chapter 3 the experimental techniques used in this work will be described in detail, these include PL spectroscopy and PL time decay spectroscopy.

In Chapter 4 the effects of a Q2T growth methodology on the properties of InGaN/GaN multiple QWs are investigated. The Q2T grown structures are compared to structures grown using a 2T methodology, with conclusions being drawn on which methodology is most efficient in terms of the room temperature internal quantum efficiency (RT-IQE) under certain excitation conditions and possible reasons why.

In Chapter 5 the effects of GWWFs and barrier growth temperature on the properties of InGaN/GaN multiple QWs are investigated. The properties of structures grown using a 1T, Q2T, T-bounced and 2T methodology are compared mainly in terms of their optical efficiency under various excitation conditions.

In Chapter 6 resonant PL spectroscopy is utilised to study the effects of carrier localisation on the independently localised electrons and holes of InGaN/GaN QW structures. The resonant PL spectrum is also investigated in detail as a function of both temperature and excitation energy.

In Chapter 7 conclusions from the previous chapters are summarised and potential further work is discussed.
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1.5 References


References


1.5 References


1.5 References


CHAPTER 2

Properties of InGaN/GaN Quantum Wells

In this chapter, the properties of InGaN/GaN QWs relevant to all the subsequent chapters of this thesis will be discussed in detail. The properties discussed will include; quantum wells, crystal and band structure, polarisation fields, carrier localisation, QW decay dynamics and QW efficiency.
2.1 Band Structure

The binary III-nitrides GaN, InN and AlN can be combined to produce ternary and quaternary alloys. The bandgaps of the binary alloys are fixed but the ternary and quaternary alloys have variable bandgaps depending on composition. The composition dependence of the bandgap for the ternary alloys AlGaN, InGaN and AlInN follow a quadratic form as shown in Figure 2.1 given by

\[ E_{\text{gap}}(A_xB_{1-x}C) = xE_{\text{gap}}(AC) + (1-x)E_{\text{gap}}(BC) - bx(1-x), \]  

(2.1)

where \( E_{\text{gap}}(A_xB_{1-x}C) \) is the energy bandgap of the ternary alloy, \( E_{\text{gap}}(AC) \) and \( E_{\text{gap}}(BC) \) are the bandgaps for the binary alloys, \( x \) is the composition of material A and \( b \) is the bowing parameter.

![Figure 2.1: Bandgap energy of the III-nitride alloys at 12 K as a function of lattice constant. The lattice constant of sapphire and the spacing between oxygen atoms of sapphire are also shown.](image)

The bandgaps of GaN, InN and AlN at 12 K in wurtzite form are presented in Table 2.1. Estimates of the bowing parameters for InGaN, AlGaN and AlInN are 1.4 eV, 0.7 eV [1] and 3.0 eV [2] respectively. The bandgap of III-nitrides also have a temperature dependence which is described by the Varshni formula given in
Equation (2.2),

\[ E_{\text{gap}}(T) = E_{\text{gap}}(0) - \frac{\alpha T^2}{\beta + T} \]  

(2.2)

where \( E_{\text{gap}}(T) \) is the energy bandgap at temperature \( T \), \( \alpha \) and \( \beta \) are Varshni fitting parameters which are shown in Table 2.1 [3].

The most important part of the band structure of wurtzite III-nitrides consists of a single conduction band and 3 separate valence bands. The conduction band originates from the s-like subshell of the electron orbitals. The s-type subshell has a single spherical orbit and thus consists of a single band. The valence band originates from the p-like subshell, which has 3 dumbbell shape orbitals. Hence the valence band has 3 bands, which are referred to as the heavy hole, light hole and split off bands. The heavy hole has an orbital in the x-direction \([1\bar{1}20]\) and the light hole in the y direction \([1\bar{1}00]\), both with \(|X \pm iY\rangle\) symmetry. Whereas, the split-off band has an orbital in the z-direction \([0001]\) with \(|z\rangle\) symmetry [4–6].

The valence band degeneracy is lifted mainly due to the crystal field created by the surrounding ions and partially due to the spin-orbit interaction. The energy separation between the heavy hole and light hole valence band has been measured to be \(\sim 7\) meV in unstrained GaN. Whereas, the energy separation between the light hole and split off valence band has been measured to be \(\sim 22\) meV [7–9]. Each band has a different effective mass along the c-axis and perpendicular to the c-axis, these are listed in Table 2.1 for the binary III-nitrides.

### Table 2.1

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Bandgap energy at 12 K (eV)</td>
<td>3.510</td>
<td>0.78</td>
<td>6.25 [1]</td>
</tr>
<tr>
<td>( \alpha ) (meV/K)</td>
<td>0.909</td>
<td>0.245</td>
<td>1.799 [1]</td>
</tr>
<tr>
<td>( \beta ) (K)</td>
<td>830</td>
<td>624</td>
<td>1462 [1]</td>
</tr>
<tr>
<td>( m_e^\parallel (m_0))</td>
<td>0.20</td>
<td>0.07</td>
<td>0.32 [5]</td>
</tr>
<tr>
<td>( m_e^\perp (m_0))</td>
<td>0.20</td>
<td>0.07</td>
<td>0.30 [5]</td>
</tr>
<tr>
<td>( m_{hh}^\parallel (m_0))</td>
<td>1.96</td>
<td>1.67</td>
<td>3.68 [5]</td>
</tr>
<tr>
<td>( m_{hh}^\perp (m_0))</td>
<td>1.87</td>
<td>1.61</td>
<td>6.33 [5]</td>
</tr>
<tr>
<td>( m_{lh}^\parallel (m_0))</td>
<td>1.96</td>
<td>1.67</td>
<td>3.68 [5]</td>
</tr>
<tr>
<td>( m_{lh}^\perp (m_0))</td>
<td>0.14</td>
<td>0.11</td>
<td>0.25 [5]</td>
</tr>
<tr>
<td>( m_{so}^\parallel (m_0))</td>
<td>0.14</td>
<td>0.10</td>
<td>0.25 [5]</td>
</tr>
<tr>
<td>( m_{so}^\perp (m_0))</td>
<td>1.96</td>
<td>1.67</td>
<td>3.68 [5]</td>
</tr>
</tbody>
</table>

**Table 2.1**: Table lists the bandgap at 12 K, Varshni parameters and effective mass of electrons and holes \((m_e/h)\) in the parallel/perpendicular orientation to the c-axis of the binary III-nitrides.
2.2 The Quantum Well

One of the first major developments in light emitting semiconductor devices was the proposal of the double heterostructure (DH) laser in 1963 by Alferov and Kazarinov \[10\] and also by Kroemer \[11\]. Alferov and Kroemer’s proposal of the DH led them to be awarded the Nobel Prize for Physics in 2000. A DH is a structure where a semiconductor is grown between two layers of another semiconductor which have a larger bandgap (e.g. AlGaAs sandwiched between layers of GaAs) creating a potential well. Electrons can become confined by this potential well when the width of the potential well becomes smaller than the de Broglie wavelength and the DH is then referred to as a QW. Quantum confinement in one direction results in the electron energy levels in that direction becoming discrete and dependent on the size of the potential well \[12\]. The QWs studied in this work consist of InGaN QWs sandwiched between GaN barriers.

The effects of a QW can be best described by considering the energy of the electron. The kinetic energy, $KE$ of an electron in free space is given by the following relationship,

$$KE = \frac{p^2}{2m_0}$$  \hspace{1cm} (2.3)

where $p$ is the electron’s momentum and $m_0$ is the free electron mass. The electron momentum is related to its wavevector, $k$ by the de Broglie relation

$$p = \hbar k,$$  \hspace{1cm} (2.4)

where $\hbar$ is the reduced Planck constant. The kinetic energy can now be rewritten in terms of the wavevector to give,

$$KE = \frac{\hbar^2 k^2}{2m_0}$$  \hspace{1cm} (2.5)

which describes the energy dispersion of a free electron. The motion of an electron in a lattice is not free however and the effects of the crystal potential need to be taken into consideration. The electron moves in a periodic potential resulting in the electron having an effective mass, $m^*$. The periodic potential depends on the crystallographic direction and thus the kinetic energy is given by,

$$KE = \frac{\hbar^2 k_x^2}{2m^*_x} + \frac{\hbar^2 k_y^2}{2m^*_y} + \frac{\hbar^2 k_z^2}{2m^*_z}$$  \hspace{1cm} (2.6)
where $x, y$ and $z$ define directions in 3 dimensional space. Quantum confinement of the electron in one dimension restricts the energy states that it can occupy to specific values in that dimension. The confined electron energy levels in a QW of width $L$ can be described by a particle in a one dimensional infinite potential well of the same width. These energy states can be calculated by solving the time independent Schrödinger equation given by Equation (2.7),

$$-\frac{\hbar^2}{2m^*_z} \frac{d\psi^2(z)}{dz^2} = [E_n - V_0]\psi(z) \quad (2.7)$$

where $\psi$ is the carrier wavefunction, $m^*$ is the effective mass of the carrier, $z$ is the direction the carrier is confined, $E_n$ is the energy state of the carrier and $V_0$ is the confining potential. Inside the QW, $V_0 = 0$, thus the Schrödinger equation reduces to the following expression,

$$-\frac{\hbar^2}{2m^*_z} \frac{d\psi^2(z)}{dz^2} = [E_n]\psi(z). \quad (2.8)$$

The wavevector, $k_z$ can be expressed as follows,

$$k_z = \sqrt{\frac{2m^*_zE}{\hbar}} \quad (2.9)$$

then the Schrödinger equation reduces to,

$$\frac{d\psi^2(z)}{dz^2} = -k_z^2\psi(z). \quad (2.10)$$

The wavefunction in the QW takes the general form,

$$\psi(z) = A \sin(k_zz) + B \cos(k_zz). \quad (2.11)$$

Given the boundary conditions that $\psi(0) = \psi(L) = 0$ for an infinite potential well, the wavefunction at the boundaries can be written as follows,

$$\psi(0) = A \sin(k_z[0]) + B \cos(k_z[0]) = 0 \quad (2.12)$$
$$\psi(L) = A \sin(k_z[L]) + B \cos(k_z[L]) = 0. \quad (2.13)$$

The $B$ term and $\sin(k_zL)$ must equal zero to satisfy the boundary conditions. Hence the wavevector must be given by the following relation to satisfy the boundary
2.2 The Quantum Well

conditions,

\[ k_z = \frac{n\pi}{L} \]  

(2.14)

where \( n \) is an integer. The energy of the confined state in the quantum well (QW) is then given by the following,

\[ E = \frac{\hbar^2 n^2\pi^2}{2m_z^* L^2}. \]

(2.15)

The electron energy is thus discrete in the \( z \) direction and depends on the QW width as shown in Figure 2.2. Though the energy levels are discrete in the \( z \) direction due to quantum confinement, in the \( x \) and \( y \) directions the energy is continuous. The total energy of the carrier in the QW is now given by Equation 2.16.

\[ E = \frac{\hbar^2 n^2\pi^2}{2m_z^* L^2} + \frac{\hbar^2 k_x^2}{2m_x^*} + \frac{\hbar^2 k_y^2}{2m_y^*}. \]

(2.16)

Figure 2.2: Schematic diagram showing a quantum well of width \( L \) with discrete energy levels and wavefunctions.

The density of states, \( Z(E) \) i.e, the number of states per unit area, \( A(= L^2) \) per energy interval for a quantum well (QW) (2D) can be calculated by evaluating the number of states in \( k \)-space. The area of \( k \)-space between \( k \) and \( k + dk \) is \( 2\pi kdk \), and using the \( k \) space area per state of \( (2\pi/L)^2 \), the number of electron states, \( N(k) \) between \( k \) and \( k + dk \) is given by,

\[ N(k) = \frac{\text{Area of } k \text{ space}}{k \text{ space area per state}} = \frac{2\pi kdk}{(\frac{2\pi}{L})^2}. \]

(2.17)
The total number of states is multiplied by two to account for the two different spins of the electron. Therefore the density of states between $k$ and $k + dk$, is given by,

$$Z(k) = \frac{kdk}{\pi}. \quad (2.18)$$

The wavevector can be rewritten in terms of energy using Equation 2.5 but using an effective mass $m_{QW}^\ast$. Thus the density of states of a QW (2D) in terms of energy, can be given by the following relation;

$$Z_{QW}(E_n) = \frac{nm_{QW}^\ast}{\pi\hbar^2}. \quad (2.19)$$

The density of states is a constant for the $n^{th}$ energy state of the QW and is independent of energy. A comparison of the density of states of 3D bulk material and a 2D QW can be seen in Figure 2.3.

![Graph of the density of states](image)

**Figure 2.3:** Graph of the density of states, $Z(E)$ as a function of energy, $E$ for bulk material (3D) and a QW (2D).
2.3 Crystal Structure

Group III-nitrides can exist in both wurtzite (hexagonal closed packed) and zincblende (cubic) form depending on the symmetry of the substrate. Both wurtzite and zincblende have tetrahedral coordination, which means that each atom’s nearest neighbours consists of four atoms of a different type. The InGaN/GaN QW structures studied in this work are all of wurtzite form, an example of which can be seen in Figure 2.4. The wurtzite structure of group III-nitrides consists of alternating layers of N atoms and group III elements arranged as shown in Figure 2.4.

![Diagram of wurtzite GaN crystal structure](image)

**Figure 2.4:** Diagram of wurtzite GaN crystal structure, where \( a \) is the lattice constant of the hexagonal plane and \( c \) is the spacing of the hexagonal planes [13].

The hexagonal plane is referred to as the c or basal plane (0001) and the distance between these planes is defined as the \( c \) lattice constant. The distance between atoms in the c plane is defined as lattice constant \( a \). The lattice constants of GaN, InN and AlN are summarised in Table 2.2. The lattice constant \( a \) of the ternary alloys, can be calculated using Vegard’s law given by Equation (2.20).

\[
d_{\text{alloy}}(A_xB_{1-x}C) = x a_{(AC)} + (1 - x) a_{(BC)}.
\] (2.20)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>GaN</th>
<th>InN</th>
<th>AlN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant, ( a ) (Å)</td>
<td>3.189</td>
<td>3.545</td>
<td>3.112</td>
</tr>
<tr>
<td>Lattice constant, ( c ) (Å)</td>
<td>5.185</td>
<td>5.703</td>
<td>4.982</td>
</tr>
</tbody>
</table>

**Table 2.2:** Summary of the lattice constants of III-nitrides [1].

Group III-nitrides are most commonly grown on sapphire (\( \alpha-Al_2O_3 \)) substrates due to their thermal and chemical stability at high growth temperatures along with
excellent structural and surface morphology. Furthermore sapphire is commercially available in large good quality wafers [14]. The InGaN/GaN QW structures grown for this work are deposited on sapphire-GaN pseudo-substrates. For GaN to be grown on sapphire, the hexagonal plane of the GaN structure rotates by 30° with respect to the underlying sapphire substrate. This results in the group III atoms aligning with the oxygen atoms of the sapphire substrate as shown in Figure 2.5. The oxygen atoms have a lattice constant $a_{\text{sapphire}}$ of $\frac{a_{\text{sapphire}}}{\sqrt{3}}$ (2.747 Å [15]), resulting in a lattice mismatch of $\sim 14\%$ with GaN. This lattice mismatch results in the GaN layers being compressively strained to the underlying sapphire substrate. The InGaN QW layers grown on the sapphire-GaN pseudo-substrates are also under compressive strain due to the lattice mismatch between GaN and InGaN. The amount of compressive strain depends on the lattice constant of the alloy. For example In$_{0.25}$Ga$_{0.75}$N grown on GaN is under more compressive strain than In$_{0.15}$Ga$_{0.85}$N, as the lattice constant $a$ of In$_{0.25}$Ga$_{0.75}$N is significantly larger than In$_{0.15}$Ga$_{0.85}$N as shown in Figure 2.1. Above a critical layer thickness, the compressively strained layers can relax and form defects [16].

![Diagonal View of GaInN Structure](image)

**Figure 2.5:** Schematic diagram showing the GaN hexagonal plane rotated by 30° to align with the oxygen atoms of the underlying sapphire substrate.

Typically GaN grown on sapphire has a [threading dislocation (TD)] density on the order of $10^8$ to $10^{12}$ cm$^{-2}$ [17-20]. Defects can have a significant impact on
device performance acting as non-radiative recombination centres \[^{21,23}\] and lead to unwanted radiative recombination such as the yellow and blue defect luminescence bands \[^{24}\]. Thus a vast amount of research has been devoted to growth techniques to reduce the defect density. These include buffer layers \[^{25}\] , epitaxial lateral overgrowth (ELOG) using SiO\(_2\) masks \[^{26}\] , Pendeo-Epitaxy \[^{27}\] , ELOG using 3D islands \[^{28}\] , grooved substrates \[^{29}\] and textured substrates \[^{30}\] . ELOG growth involves the growth of GaN through a dielectric mask such as SiO\(_2\) , which results in the formation of islands which later coalesce. Pendeo-Epitaxy involves the growth of GaN from etched GaN seed layers. The growth of the GaN layer occurs both vertically and laterally for Pendeo-Epitaxy. The best achieved TD density is on the order of \(\sim 10^7\) cm\(^{-2}\) using Pendeo-Epitaxy and ELOG with grooved substrates; which is still large. Thus recently bulk GaN and AlN have been used as substrates, leading to improved lattice and thermal expansion mismatch and TD densities of \(\sim 10^5\) cm\(^{-2}\) for device structures. The widespread use of bulk GaN and AlN substrates for devices is currently limited by size restraints as well as high costs \[^{31}\] .

The effects of TD density on the RT-IQE of InGaN/GaN QWs is unclear. Some authors \[^{32,33}\] report a decrease in the RT-IQE with increasing TD density, whereas some authors \[^{34,35}\] observe no systematic effect on the RT-IQE. The insensitivity of the RT-IQE to TD density is attributed to the effects of carrier localisation \[^{34,35}\] , which is discussed in more detail in Section \(\ref{sec:2.5}\). Both authors \[^{34,35}\] suggest that the RT-IQE is insensitive to TD density, so long as the diffusion length of the carriers are less than the spacing of the TDs. Thus suggesting that other defects such as point defects play a more significant role in non-radiative recombination.

\section*{2.3.1 Lattice Defects and Impurities}

The crystal structure of III-nitride structures have a variety of defects. The main defect types of interest are:

1. Point defects e.g. interstitial, substitutional, vacancies, antisites and complexes

2. Linear defects e.g. dislocations

which will be discussed in Section \(\ref{subsec:2.3.1.1}\) and \(\ref{subsec:2.3.1.2}\) respectively.

\subsection*{2.3.1.1 Point Defects}

Point defects can be caused by impurities, vacancy defects, interstitial defects and substitutional defects. Vacancy defects are caused by the absence of atoms at a
particular atom site, for example the absence of a gallium atom in GaN. Interstitial defects are caused by the insertion of an atom where there usually is not an atom site, whereas substitutional defects are the placement of different atoms at a normal atom site. An example of a substitutional defect is an antisite, caused when the arrangement of atoms breaks down and for example a gallium atom occupies a nitrogen site in the case of GaN. Complexes form when two or more defects bind together.

Nitrogen vacancies act as donors and have a transition level around $0.5 \pm 0.2 \text{ eV}$ above the valence band edge \[36\]. Gallium vacancies act as acceptor-like and introduce 3 defect transition levels at around 1.1, 0.64 and 0.25 eV above the valence band edge \[37\]. These deep acceptor levels are expected to play a key role in the emission of yellow luminescence (YL) in GaN which will be further discussed in Section 2.3.2.1

Interstitials and antisites can act as both donors and acceptors depending on their charge state.

Impurities can play a key role in the properties of GaN, mainly to achieve n- and p-type doping. Donor impurities include mainly oxygen, silicon, and germanium whereas acceptor impurities include magnesium and carbon. Unintentional doping of interest in undoped InGaN/GaN MQWs are mainly oxygen from the atmosphere along with carbon and hydrogen from the trimethyl [(CH\(_3\))\(_3\)] precursors used during MOCVD growth. Oxygen impurities are of particular interest concerning GaN as they have been shown to be the cause of the unintentionally doped n-type behaviour \[38\]. Complexes of hydrogen with gallium vacancies along with carbon and oxygen are also of interest as they can contribute to YL emission \[24\, 36\, 39\, 40\].

### 2.3.1.2 Dislocations

Dislocations are formed due to stress on the crystal and hence strain. The strain causes displacement of atoms from their equilibrium position and this displacement can be described by the Burgers vector. The Burgers vector, \( \mathbf{b} \) is the vector which would have to be applied to the crystal in order to restore it to its equilibrium position. There are two main types of dislocations: edge and screw type (see Figure 2.6). Edge type dislocations involve the insertion of an extra half plane into the lattice structure. The insertion of the plane causes compression of the lattice for atoms in-line with the plane and extension for atoms not in-line with the extra plane. Edge dislocations form perpendicular to the displacement of the atoms around the inserted plane.

Screw type dislocations form parallel to the displacement of the atoms instead of
2.3 Crystal Structure

Figure 2.6: Schematic showing the displacement of the lattice to form a edge (top) and screw (bottom) type dislocations.

perpendicular like edge dislocations. Screw type dislocations can be considered as being produced by cutting the crystal partway through and then pushing one of the cut halves one lattice space over. The displacement of atoms from their equilibrium position causes the areas around dislocations to be highly strained. Dislocations can also be mixed type with a combination of both edge and screw [41].

2.3.2 Defect Luminescence Bands

Lattice defects can contribute to the luminescence properties of III-nitride structures, leading to both sharp and broad emission features. A typical low temperature PL spectrum of a undoped c-plane GaN template is shown in Figure 2.7. The spectrum consists of a blue and yellow defect luminescence band, donor-acceptor pair (DAP) emission and exciton emission.

Excitons form when the motion of an electron and hole pair become correlated due to the Coulomb interaction between the two oppositely charged particles. At low temperatures, excitons can become bound to neutral donor or acceptor states via the Coulomb interaction. Neutral impurities are efficient at trapping excitons as the attraction lowers the recombination energy with respect to free excitons. Emission
from these states typically occurs between 3.35 and 3.5 eV in c-plane GaN.

Recombination between donor electrons and acceptor holes gives rise to the DAP emission at 3.28 eV in Figure 2.7. The series of peaks separated by \( \sim 91 \text{ meV} \) on the lower energy side of the DAP emission is attributed to the longitudinal optical (LO) phonon replicas of the DAP emission [43]. The recombination energy, \( \hbar \omega \) of the DAP emission is given by,

\[
\hbar \omega = E_{\text{gap}} - E_A - E_D + \frac{e^2}{4\pi\epsilon_\epsilon_0 R}
\]  

(2.21)

where \( E_{\text{gap}} \) is the bandgap energy, \( E_A \) is the acceptor binding energy, \( E_D \) is the donor binding energy, \( e \) is the electron charge, \( R \) is the distance between the donor and acceptor pair, \( \epsilon_0 \) is the dielectric constant and \( \epsilon_r \) is the relative permittivity. The last term in Equation (2.21) accounts for the Coulomb interaction between the donor electron and acceptor hole. Thus the recombination energy depends on the binding energies and the pair separation, with closer pairs recombining at higher energy. The variation in the DAP separation leads to the inherent non-exponential form of the PL decay transients, with closer pairs recombining faster due to the increased wavefunction overlap [44].
The blue luminescence (BL) band observed between 2.7 and 3.0 eV with a peak around 2.9 eV is commonly observed in undoped, Mg-doped and Zn-doped GaN. In undoped GaN, the BL band is attributed to the transitions from shallow donors (at low temperature) or the conduction band (at elevated temperatures) to a relatively deep acceptor, which has an ionisation energy of around 0.34 to 0.40 eV. The BL band has fine structure at low temperatures in high quality GaN. This fine structure leads to a set of peaks on top of the broad band spaced by 36 ± 1 meV, along with their phonon replicas. These sharp peaks along with the broad band are observed to shift to higher energies on increasing the excitation power. The PL intensity of the BL band is fairly temperature independent up to around 200 K. Above which, the BL band quenches with increasing temperature due to the escape of holes to the valence band [45]. The PL decay transients of the BL band are non-exponential at low temperatures due to the recombination of DAPs. On increasing the temperature, the non-exponential decay is replaced by a nearly exponential decay, as the recombination mechanism changes from DAPs to electron-acceptor transitions [46].

### 2.3.2.1 Yellow Luminescence Band

The YL band, is a broad structureless band commonly observed in undoped GaN which peaks at around 2.2 eV and has a full width at half maximum (FWHM) of around 350 to 450 meV as shown in Figure 2.7 Though the exact shape and position of the YL band has been found to be sample dependent. The YL band is commonly accepted to originate from complexes of hydrogen with gallium vacancies [24] and complexes of oxygen with carbon (C$_{\text{N}}$-O$_{\text{N}}$) [40].

The PL intensity of the YL band has been observed to be temperature dependent. On increasing the temperature from 12 K, the PL intensity of the YL band remains fairly constant up to a temperature of around 200 K. The PL intensity is observed to increase and then decrease slightly between temperatures of 200 to 300 K, which is attributed to the thermal activation of carriers to defects associated with the YL band and variations in hole capture respectively. The PL intensity remains fairly constant on increasing the temperature up to around 450 K. Above this temperature the luminescence quenches rapidly on increasing the temperature further due to the ionisation of an acceptor with an activation energy of about 0.85 ± 0.2 eV [24]. The peak of the YL band remains fairly constant to within an accuracy of 20 to 40 meV with increasing temperature up to around 600 K [47, 48], though the GaN bandgap reduces by around 230 meV over this temperature range.
The reported PL decay time of the YL band varies dramatically from 20 ps \cite{49} up to 300 ms \cite{50}. The PL decay transient is non-exponential at low temperatures characteristic of DAP transitions. On increasing the temperature the decay becomes nearly exponential at 150 K as the DAP transitions are replaced by electron-acceptor transitions at elevated temperatures.

The PL intensity of the YL band is observed to increase linearly with excitation power at low carrier densities up to a critical value. Above the critical power density the PL intensity increases sub linearly with excitation power and eventually has a square root dependence. The observed power dependence of the PL intensity is attributed to the saturation of sites associated with the YL band \cite{51, 52}. The square root dependence of the YL band PL intensity with excitation power has been attributed to a variety of factors which include; the concentration of deep donors near the surface \cite{51}, geometrical factors, photon recycling \cite{24} and the interaction of band to band recombination with the YL band \cite{52}.
2.4 Polarisation Fields

Group III-nitrides structures grown in the wurtzite form exhibit strong spontaneous polarisation fields and they can also exhibit strong strain-induced piezoelectric fields [53–56]. The spontaneous polarisation arises from the arrangement of the atoms in the wurtzite form as shown in Figure 2.8. A polarisation exists across the bond of the group V nitrogen atoms and the group III gallium and indium atoms. The bonding of III-nitrides is a mixture of covalent and ionic. The electrons in the covalent bond are shared between the group III and nitrogen atoms, though the electrons are attracted more strongly to the nitrogen atoms due to their higher electronegativity. This results in a shift of the charge distribution and a polarisation field across the bond. Furthermore in the case of ionic bonds, group III atoms can be positively charged after donating their electrons to group V nitrogen atoms, which become negatively charged. This also leads to a polarisation field acting toward the group III atoms.

![Schematic diagram showing the tetrahedron arrangement of atoms for MOCVD grown III-nitrides in wurtzite crystal form in a unstrained and compressively strained state.](image)

Each group III-nitrogen bond has a polarisation associated with it, in the case that all the bonds are of equal length (denoted by $d_A$ and $d_B$ in Figure 2.8) and the all the bond angles are the same (denoted by $\Theta$ and $\Phi$ in Figure 2.8), the polarisation would sum to 0. In unstrained wurtzite crystals, the bond lengths and angles are not
2.4 Polarisation Fields

equal and hence there is a net polarisation across the tetrahedron structure parallel with the c axis. The wurtzite structure can be polar in the [0001] or [000\bar{1}] direction, depending on whether the wurtzite structure is gallium or nitrogen faced as shown in Figure 2.9 [14]. Typically high quality GaN grown by MOCVD is gallium terminated at the surface, whereas GaN grown by MBE is nitrogen terminated [14].

![Figure 2.9](image.png)

**Figure 2.9:** Diagram of Ga- and N-faced Wurtzite GaN, resulting in polarisation fields in the [0001] and [000\bar{1}] directions respectively. Adapted from [14].

The direction of the spontaneous fields can either be along the [0001] or [000\bar{1}] direction depending on whether the structure is terminated by a nitrogen atom or a group III atom respectively. The spontaneous field for the binary III-nitrides are summarised in Table 2.3. The spontaneous field, $P_{SP}$ for the ternary III-nitride alloys can be calculated using Equation (2.22):

$$P_{SP}(A_xB_{1-x}C) = xP_{SP}(AC) + (1 - x)P_{SP}(BC) - b_{AB}x(1 - x), \quad (2.22)$$

where $x$ is the composition fraction and $b$ is the bowing parameter. Fiorentini et al. [57] investigated the non-linear dependence of the spontaneous field of III-nitride alloys and calculated bowing parameters of 0.038, 0.019 and 0.071 Cm$^{-2}$ for InGaN, AlGaN and AlInN respectively.

The piezoelectric polarisation field is the polarisation created due to tensile or compressive strain on the crystal structure. The application of strain to the crystal structure results in changes to the bond angles and lengths. This results in a change of the overall polarisation field. In the case of InGaN/GaN QWs the InGaN layers
Table 2.3: Table summarising the spontaneous polarisation, elastic and piezoelectric constants of III-V Nitrides.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>GaN</th>
<th>InN</th>
<th>AlN</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{SP}$ (C/m²)</td>
<td>-0.034</td>
<td>-0.042</td>
<td>-0.090</td>
</tr>
<tr>
<td>$C_{13}$ (GPa)</td>
<td>106</td>
<td>92</td>
<td>108</td>
</tr>
<tr>
<td>$C_{33}$ (GPa)</td>
<td>398</td>
<td>224</td>
<td>373</td>
</tr>
<tr>
<td>$e_{31}$ (C/m²)</td>
<td>53</td>
<td>-0.49</td>
<td>-0.57</td>
</tr>
<tr>
<td>$e_{33}$ (C/m²)</td>
<td>53</td>
<td>0.73</td>
<td>0.97</td>
</tr>
</tbody>
</table>

are compressively strained to the lattice constant $a$ of the GaN layers, an example of which can be seen in Figure 2.8. The piezoelectric field, $P_{PZ}$ can be calculated using Equation (2.23):

$$P_{PZ} = \varepsilon \cdot \varepsilon,$$

(2.23)

where $\varepsilon$ is the piezoelectric tensor and $\varepsilon$ is the strain tensor. For InGaN/GaN QWs grown along the [0001] direction under biaxial stress in the c-plane, the piezoelectric polarisation can be expressed as the following [58]:

$$P_{PZ} = 2e_{31}\varepsilon_{xx} + e_{33}\varepsilon_{zz},$$

(2.24)

where $e_{ij}$ are piezoelectric matrix elements of the piezoelectric tensor (shown in Table 2.3) and $\varepsilon_{xx/zz}$ are the strain fields in the c-plane and c-axis respectively. The strain field along the c-axis can be expressed in terms of the in-plane strain by the following [58]:

$$\varepsilon_{zz} = \frac{2\varepsilon_{xx}C_{13}}{C_{33}},$$

(2.25)

where $C_{13/33}$ are matrix elements of the elasticity (shown in Table 2.3). Furthermore, the strain in the c-plane can be written in terms of the lattice constant $a$ by the following [58]:

$$\varepsilon_{xx} = \frac{a_B - a_{QW}}{a_{QW}},$$

(2.26)

where $a_{B/QW}$ is the lattice constant $a$ of the barrier and quantum well respectively. The piezoelectric field for an InGaN/GaN QW under biaxial strain, can thus be expressed as follows [55, 58]:

$$P_{PZ} = 2\left[\frac{a_B - a_{QW}}{a_{QW}}\right] \left(e_{31} - e_{33} - \frac{C_{13}}{C_{33}}\right).$$

(2.27)

The components of the elasticity and piezoelectric tensor for the ternary III-nitride
alloys can be extracted by a linear interpolation between the values of the two binary III-nitrides, which make up the alloy. Abrupt changes to the polarisation at sample surfaces or QW interfaces can result in the accumulation of charge in these regions and the creation of electric fields. For the InGaN/GaN QW structures in this work, which are group III atom terminated; the electric field acts across the QW along the the [0001] direction. The electric field strength, $F_{QW}$ can be calculated using Equation (2.28) \[59\],

$$F_{QW} = \frac{L_{\text{barrier}} (P_{\text{Total\ barrier}} - P_{\text{Total\ QW}})}{\epsilon_0 (L_{\text{QW}} \epsilon_{\text{barrier}} + L_{\text{barrier}} \epsilon_{\text{QW}})}$$ (2.28)

where $\epsilon_{0/\text{QW/barrier}}$ are the dielectric constants of free space, the QW and barrier material respectively; $L_{\text{QW/barrier}}$ are the thickness of the QW and barrier layers respectively and $P_{\text{Total\ barrier/QW}}$ are the total nett polarisation of the barrier and QW layer. The electric field across the QW can cause a potential drop, $V_{\text{well}}$ across it which can be calculated using Equation (2.29),

$$V_{\text{well}} = F_{QW} L_{\text{QW}}.$$ (2.29)

The potential drop has been suggested by Bernardini and Fiorentini \[60\] to be limited to the bandgap energy of the QW.

### 2.4.1 Quantum Confined Stark Effect

The large electric fields across the QW, typically on the order of $10^6$ Vcm\(^{-1}\) \[58, 61\], can induce tilting of the potential profile of the QW and barrier regions as shown in Figure 2.10. This tilting, induces a large potential drop across the QW which acts to force the electrons and holes to opposite sides of the QW. This causes a reduction in electron and hole wavefunction overlap, which in turn reduces the probability of radiative recombination. The tilting of the potential profile also reduces the ground state recombination energy of the QW as shown in Figure 2.10, which is known as the quantum confined Stark effect (QCSE) \[62–64\].

The initially square potential is converted into a triangular potential. The effect of the triangular potential has been investigated by Bonfiglio et al. \[59\] using perturbation theory. Bonfiglio et al. determined the energy difference of the lowest confined electron and hole states in a triangular potential well to be given by the
2.4 Polarisation Fields

Figure 2.10: Schematic showing the wavefunctions (red curves) of the lowest confined states of (a) a finite square QW and (b) a finite square QW with an applied electric field.

The following relation,

\[ E = E_{\text{gap}} - F_{\text{QW}} L_{\text{QW}} + \left( \frac{9\pi\hbar e F_{\text{QW}}}{8\sqrt{2}} \right)^{\frac{2}{3}} \left[ \frac{1}{m_e^*} + \frac{1}{m_h^*} \right]^{\frac{1}{3}} \]  

(2.30)

where \( E_{\text{gap}} \) is the bandgap energy of the III-nitride alloy, \( e \) is the electron charge and \( m_{e/h}^* \) are the effective masses of the electron and the hole in the QW respectively.

The electron and hole populations which accumulate on opposite sides of the QW can act as additional sources of charge at the interfaces. The polarisation created by the electrons and holes acts to oppose the total polarisation due to both the spontaneous and piezoelectric contribution. At sufficiently high carrier densities screening of the electric field can occur. Several authors have modelled total screening of the electric field to occur at carrier densities of \( \sim 10^{13}\text{cm}^{-2} \) \[58, 65, 66\] for an electric field on the order \( 10^6 \text{Vcm}^{-1} \). The screening of the electric field leads to a reduction in the potential drop across the QW which results in a blueshift of the PL emission energy and an increase in the wavefunction overlap of the electrons and holes.
2.5 Carrier Localisation

The RT-IQE of a multiple QW structure depends on both the radiative and non-radiative recombination rate. At 10 K the recombination is assumed to be 100% radiative, whereas at 300 K its a combination of both radiative and non-radiative [67].

The internal quantum efficiency (IQE) $\eta_{IQE}$ of a MQW structure can be calculated using the following relation,

$$\eta_{IQE} = \frac{\Gamma_R}{\Gamma_R + \Gamma_{NR}} \times 100\%$$  \hspace{1cm} (2.31)

where $\Gamma_R/NR$ are the radiative and non-radiative recombination rate respectively. InGaN multiple QWs can achieve significantly high RT-IQE ($\sim 60\%$) [33] despite the high density of defects which can occur due to growth of structures on foreign substrates such as sapphire. This insensitivity to the defects which can cause non-radiative recombination is mainly attributed to the effects of carrier localisation [34].

The localised states are created due to local disorder induced alloy fluctuations [68, 69] and well width fluctuations [61] in InGaN/GaN QW structures.

A localised state is a state occupied by either an electron or hole which is restricted to a particular region of space and is unable to contribute to transport at absolute zero. Localisation was first discussed by Anderson [70] in 1958. Anderson proposed a model in which transport in a random lattice occurred via quantum jumps between localised states. Furthermore his model estimated the strength of the random potential necessary for the absence of diffusion in a disordered lattice. Mott [71] later described the relationship between transport and localisation in terms of the mobility edge. Mott defined the mobility edge as a particular energy which separates the localised states from the extended states [72].

The large localisation energy created by disorder is assumed to give a distribution of localised states which have a Gaussian [69, 73] or exponential [74, 75] form. In this work a stretched exponential density of localised states is assumed. The localised density of states (DOS) function, $\rho_{e,h}$ can be calculated using Equation (2.32),

$$\rho_{e,h}(E) \approx \rho_{e,h} \exp \left[ - \left( \frac{E - E_{e,h}}{\sigma_{e,h}} \right)^{a_{e,h}} \right]$$  \hspace{1cm} (2.32)

where $E$ is the energy, $\sigma_{e,h}$ is the energy parameter of the distribution (for electrons and holes respectively), $a$ is the exponent (for the electrons and holes respectively)
2.5 Carrier Localisation

and \( E_{e,h} \) is the centre of the distribution for the conduction and valence bands respectively. Electrons and holes occupy the lowest energy states (band tail) of the localised electron and hole distributions respectively [76].

There have been a number of proposed mechanisms for the localisation of carriers which include indium clustering [77–79], alloy fluctuations [80–82] and well width fluctuations [61, 75, 83]. Local fluctuations in indium content and well width result in local modifications to the effective energy bandgap. These variations in the local potential can be sufficient to localise carriers.

The localisation of carriers at non-random clusters of high indium content was first proposed by Narukawa et al. [77]. The authors observed indium clustering using transmission electron microscopy (TEM) and energy dispersive x-ray measurements on a purple \( \text{In}_{0.2}\text{Ga}_{0.8}\text{N/In}_{0.05}\text{Ga}_{0.95}\text{N} \) laser diode. Furthermore, the authors speculated that the indium rich regions act as quantum dots localising the carriers away from non-radiative recombination sites. The formation of these indium rich regions was originally believed to be due to spinodal decomposition [79, 84] resulting in In-rich and In-poor phases. This conclusion was backed by theoretically modelling reported by Ho and Stringfellow [85].

The observation of indium clustering through TEM was later disputed by Smeeton et al. [86] and O’Neill et al. [87]. Both groups reported on the effect of exposure of the \( \text{InGaN QWs} \) to an electron beam as a function of time prior to TEM image being recorded. They reported that the wells were uniform before exposure to an electron beam. On exposure to the electron beam, the groups observed indium rich regions in the \( \text{QWs} \) through TEM contrast images. Recent work by Galtrey et al. [88] concluded that indium clustering was not needed for high brightness \( \text{InGaN/GaN QW} \) structures and that the indium was deposited in a way that expected from a random alloy distribution.

The effects of local alloy fluctuations on the localisation energy of carriers has been modelled by Watson-Parris [89]. Watson-Parris define the localisation energy to be the \( \sigma \) value in Equation 2.32. The model predicts that local fluctuations in indium composition mainly localise the holes with localisation energies varying from \( \sim 20 \) to \( \sim 50 \) meV with varying indium composition from 5 to 25 %, resulting in localisation lengths of 0.2 to 3 nm. The electrons on the other hand were calculated to have a localisation energy of \( \sim 10 \) meV independent of indium content, with localisation lengths varying from 5 to 12 nm. Watson-Parris also commented on the effects of well width fluctuations (WWFs) on the localisation energy of electrons.
and holes. Reporting that a 10 nm diameter disk WWF can result in an electron localisation energy of \(~\sim 10\) meV. The hole localisation energy is unaffected by the WWFs due to its small localisation length (0 to 3 nm), which is much smaller than the diameter of the WWFs that are typically around 5 to 10 nm wide [90].

The localisation lengths predicted from Watson-Parris’ [89] model fit well with values extracted by Graham et al. [61]. Graham et al. [61] investigated the coupling strength of electron and hole pairs with LO phonon modes for a series of single InGaN/GaN QW structures with varying average indium content and well width at 6 K. The extracted values of the Huang-Rhys factor which describe the coupling strength, were compared to a theoretical model and a localisation length was extracted. The localisation length was observed to decrease from around 3 nm to approximately 1 nm on increasing the average indium composition of the InGaN/GaN QW from 5 % to 15 % (Correlated well width change from 2.5 nm to 2.9 nm). The localisation length remained constant at around 1 nm on increasing the average indium composition up to 25 % (Well width increased up to 3.3 nm from 2.9 nm).

The effects of alloy and WWFs on the localisation energy have also been reported recently by Schulz et al. [91] using an atomistic tight binding model. Schulz et al. modelled the effects of 2 monolayer WWFs with a diameter of 5 nm and alloy fluctuations on a 3.5 nm wide In_{0.25}Ga_{0.75}N/GaN QW. The model predicts that the holes are strongly localised by the random alloy distribution and the electrons are weakly localised. Furthermore, the electrons are localised by the WWFs consistent with the model by Watson-Parris [89]. Schulz et al. report that the ground state energy of the electrons varies in a range from 2 to 45 meV, whereas the holes varies from 10 to 150 meV. The large difference between the electron and hole energies is attributed to the much higher hole effective mass compared to the electron effective mass. Schulz et al. also modelled the effects of the addition of the Coulomb interaction between the electrons and holes on the system. The wavefunction overlap was only slightly increased compared to the system without the Coulomb interaction. Indicating that the spatial separation of the electron and hole wavefunction due to the presence of the electric field and the effects of localisation are much stronger than the attractive Coulomb interaction.

2.5.1 Optical Signatures of Localisation

Localisation of carriers not only has a profound effect on the IQE of InGaN/GaN MQWs, but also on the characteristic optical properties. Some of these characteristic
properties include:

1. Large inhomogeneous PL linewidths due to disorder.

2. Strong longitudinal optical (LO) phonon coupling.

3. The “S”-shape temperature dependence of the PL peak emission energy.

4. Non-exponential decay dynamics.

2.5.1.1 LO Phonon Coupling

Strong coupling of charge carriers to LO phonon modes of the crystal occurs via the electrostatic Fröhlich interaction. The Fröhlich interaction occurs due to a Coulomb interaction between the charge carriers and the crystalline lattice. On excitation the electrons and holes become spatially separated which creates a dipole moment, which interacts with the crystal lattice. When the electron and hole recombine, the dipole moment is removed and the potential energy stored in the crystal is dissipated via an LO phonon[92]. The phonon–charge carrier coupling gives rise to LO phonon replicas in the PL spectra of InGaN/GaN structures (see Figure 2.11). The energy separation between the LO phonon replicas for polar InGaN/GaN QW structures is typically around 91 meV [75, 93–95]. LO phonon replicas are predominately seen as the Fröhlich interaction is the strongest, compared with the deformation potential interaction with optical and acoustic phonons and the piezoelectric interaction with acoustic phonons [96]. The coupling strength can be determined from the Huang-Rhys factor, $S$. The relationship between the intensity of the $n$th phonon replica, $I_n$, and the main emission peak, $I_0$ is given by Equation (2.33) [97].

$$I_n = I_0 \frac{S^n}{n!} \quad \text{for } n = 0, 1, 2, \ldots$$

Kalliakos et al. [93] studied the variation of the Huang-Rhys factor of InGaN/GaN QWS and quantum boxes as a function of well width and box size. The authors observed that on increasing the well width or the box size the Huang-Rhys factor increased up to around 0.45 for a QW of width 5.5 nm. This increase was attributed to the effects of the electric field which acts to force the electrons and holes toward opposite sides of the well or box. The Huang-Rhys factor is strongly dependent on pair separation and hence it increases on increasing the structure size. The Huang-Rhys factor was observed to decrease for thick QWS attributed to the spreading...
2.5 Carrier Localisation

Figure 2.11: Low temperature (12 K) PL spectra for a InGaN/GaN multiple QW structure, showing the main emission peak $I_0$ and its LO phonon replicas $I_1$ and $I_2$.

of the wavefunction in the plane of the QW. This variation in the Huang-Rhys was determined to be best described by independently localised electron and hole distributions on opposite sides of the structure. The variation of the Huang-Rhys factor of InGaN/GaN QWs as a function of indium composition has been studied by Graham et al. [61]. The authors observed an increase in Huang-Rhys factor on increasing the indium composition. They attributed this increase to the effects of the electric field across the QW similarly to Kalliakos et al. [98].

2.5.1.2 “S”-Shape Temperature Dependence of the PL Peak Emission Energy

Another major fingerprint of localisation is the “S”-shape temperature dependence of the PL peak emission energy. This phenomenon describes the variation in the PL peak energy with temperature from the predicted variation of the bandgap energy with temperature, given by the Varshni formula in Equation 2.2. An example of the “S”-shape temperature dependence of the PL peak emission energy for an InGaN/GaN multiple QW structure is shown in Figure 2.12. Typically up to a temperature of $\sim 70$ K, the PL peak energy is observed to red shift. The PL peak
2.5 Carrier Localisation

Energy is then observed to blue shift up to a temperature of $\sim 200$ K. On increasing the temperature further, it is observed to red shift again.

**Figure 2.12:** PL peak position of an $\text{In}_{0.18}\text{Ga}_{0.82}\text{N}/\text{GaN}$ QW structure as a function of temperature (black), showing its deviation from the predicted change in bandgap energy (red) calculated from Equation (2.2) using Varshni parameters $\alpha = 0.805 \text{ meVK}^{-1}$ and $\beta = 798$ K.

The “S”-shape of the PL peak emission is attributed to the thermal redistribution of carriers amongst the distribution of localised states \[74, 99-101\]. At low temperatures ($\leq 10$ K), carriers occupy the distribution of localised states randomly. On increasing the temperature up to around 70 K, weakly localised (in energy) carriers are able to thermally redistribute amongst the distribution of localised states. The redistributed carriers tend to occupy more deeply localised states, which results in a red shift of the PL peak emission energy with $\sim 4$ meV of this red shift due to the temperature dependence of the bandgap. Above $\sim 70$ K, more deeply localised carriers are able to thermally redistribute amongst the localised states. The probability of the redistributed carrier occupying a relatively weaker localised state with a higher emission energy now becomes significant which results in a blue shift of the PL peak emission energy up to a temperature of around 200 K. Above 200 K, even more deeply localised states are able to thermally redistribute and the probability of the redistributed carrier occupying relatively weaker localised state increases further.
Though the temperature dependent shift of the bandgap becomes significantly large so as to pull the PL peak emission energy down resulting in a red shift.

The characteristic “S”-shape of the PL peak energy is also accompanied by a “W”-shape temperature dependence of the FWHM. On increasing the temperature from 0 K, the FWHM is observed to increase, followed by a decrease and then an increase. These characteristic temperature dependent behaviour have been modelled by Rubel et al. [74] for disordered (GaIn)(NAs) QWs. They assumed that the QW had an exponential distribution of localised states, \( g(E) \) given by,

\[
g(E) = \frac{N_0}{E_0} \exp \left( \frac{E}{E_0} \right)
\]

where \( E_0 \) is some characteristic energy scale and \( N_0 \) is the concentration of localised states. The results from their model suggest that on increasing the temperature from 0 K, the PL peak energy red shifts up to a temperature given by \((0.6 - 0.8)E_0/k_B\). Whereas the FWHM increases up to a temperature of \((1.0 - 1.2)E_0/k_B\) before decreasing and increasing again. Thus they concluded that the temperature dependent behaviour was strongly related to the distribution of localised states.

The “S”-shape temperature dependent behaviour of the PL peak emission has been observed to reduce on increasing the carrier density [100, 102, 103]. Hammersley et al. [100] reported on this reduction in “S”-shape for a 5 period InGaN/GaN QW structure as a function of excitation power density. At low excitation power densities (<10 Wcm\(^{-2}\)), no reduction in “S”-shape was observed. On increasing the power density above 10 Wcm\(^{-2}\), a steady reduction in “S”-shape was observed. This reduction correlated with the onset of the reduction in integrated PL intensity per unit excitation power i.e. efficiency droop. The results suggest that the reduction in “S”-shape was caused by the saturation of the localised hole states, with the localised electron states saturating at an excitation power density of around 10 Wcm\(^{-2}\) i.e. the onset of efficiency droop.

### 2.5.1.3 Non-Exponential Decay Dynamics

The PL decay transients of InGaN/GaN QWs excited at low carrier density (i.e. below efficiency droop) and temperature (<12 K) are observed to have a characteristic non-exponential form [104, 105] as can be seen in Figure 2.13. The non-exponential PL decay transients are typically characterised by their \( \tau_{1\text{PL}} \) or \( \tau_{2\text{PL}} \) decay time, which is the time taken for the PL intensity to drop by a factor of 10 or \( e \) respectively.
The non-exponential form of the PL decay has been studied by Lefebvre et al. [105] and Morel et al. [106]. Lefebvre et al. [105] reported on the effect of well width on the PL decay time for InGaN/GaN QWs at 8 K. Lefebvre et al. observed that the decay had a non-exponential form and that on increasing the well width the PL decay time was observed to increase.

Morel et al. [106] modelled this behaviour for InGaN/GaN QWs using a DAP model introduced by Thomas et al. [44], referring to the recombination as a two dimensional “Pseudo DAP” like recombination. The model describes electrons and holes which are independently localised and spatially separated. A larger spatial separation of the localised electrons and holes results in a reduction of wavefunction overlap and hence a reduced radiative rate. The non-exponential form of the PL decay arises from the large number of permutations of the separation of the localised electrons and holes caused by the random nature of the local well and indium fluctuations.
2.6 PL Decay Dynamics

The PL decay transients of InGaN/GaN QW structures have a non-exponential form due to the effects of carrier localisation as described previously in Section 2.5.1.3. The $\tau_{10}$ PL decay time is observed to increase on reducing the detection energy from the high energy side over the main PL emission spectrum ($I_0$) as shown in Figure 2.14. Furthermore, on plotting the decay curves on a reduced time base (i.e. time/$\tau$ PL decay time), all the decays have a universal shape across the PL emission spectrum [105, 106].

Figure 2.14: $\tau_{10}$ PL decay time for a In$_{0.17}$Ga$_{0.83}$N/GaN QW structure at 10 K across the PL emission spectrum under low injection conditions.

The variation in the PL decay time with detection energy is believed to arise from the variation in radiative decay time due to variations in the average indium composition [75] and well width [107, 108]. At low temperatures ($\leq$ 10 K), carriers are localised and spatially separated due to the effects of localisation [82, 91, 109]. Areas of higher average indium content result in regions of higher piezoelectric electric field, which acts to force the electron and hole wavefunctions toward opposite sides of the QW. A decrease in the wavefunction overlap results in a decrease in the radiative rate. Given that the variation in recombination energy across the spectrum is mainly determined by the distribution of hole localisation energies with local average indium
composition \cite{81, 82}. The variation in average indium content across the PL emission spectrum and subsequent variation in electric field, can thus account for the variation in PL decay time.

The PL decay dynamics of InGaN/GaN QWs has been modelled by Morel et al. \cite{106} in terms of a two dimensional “Pseudo DAP” like recombination as mentioned in Section 2.5.1.3. The spatial separation of the localised electrons and holes is mainly controlled by the electric field which forces the electrons and holes to opposite sides of the QW. Thus the decay time is mainly controlled by the local indium composition and resultant electric field strength. The electric field dependence can be removed by plotting the decay transient on a reduced time base. The observed universal decay shape, arises from the large number of permutations of the in-plane separation of the electrons and holes caused by the random nature of the local well and indium fluctuations. The PL decay dynamics of the InGaN/GaN QWs studied in this work are assumed to be “Pseudo DAP” like recombination \cite{106}. 

2.7 QW Efficiency Vs. Power Density

The IQE of III-nitride based QWs is well known to depend on carrier density at room temperature. Typically at low carrier densities the IQE is observed to increase with increasing carrier density up to a peak efficiency at room temperature as shown in Figure 2.15. This peak efficiency is typically around 10 to 100 Wcm$^{-2}$ for c-plane blue emitting InGaN/GaN multiple QW structures and a few Acm$^{-2}$ for III-nitride based LEDs. Increasing the carrier density further, results in a decrease in the IQE which is the well known phenomenon referred to as efficiency droop [110]. The drop in IQE at high carrier densities is a real issue for the realisation of efficient high current and brightness LED devices such as car headlamps [111], micro-projectors and solid state lighting for homes, offices, etc. [112]. Efficiency droop will be discussed in more detail in section 2.7.1.

![Figure 2.15: Typical PL efficiency response of an InGaN/GaN QW structure at room temperature.](image)

The initial increase in IQE with increasing carrier density is mainly attributed [113-117] to the saturation of non-radiative pathways. Saturation can occur, as defects which cause non-radiative recombination and unwanted radiative recombination such as the YL band; have a finite density of states which can become filled. The filling of the defect states, reduces the probability of carrier capture into...
2.7 QW Efficiency Vs. Power Density

these states and hence reduces the non-radiative rate. Thus resulting in an increase in the IQE [113][117]. The relative importance of the radiative and non-radiative processes at low carrier density can be described by the following relation,

\[ II = kP^i \]  

(2.35)

where \( II \) is the integrated PL intensity, \( P \) is the excitation power density, \( i \) is the exponent of \( P \) and \( k \) is a constant. If \( i > 1 \), then non-radiative recombination dominates the emission. Whereas, if \( i \approx 1 \) then the recombination process is dominated by radiative emission. Furthermore, if \( i < 1 \) the non-radiative processes become sufficiently high that the efficiency drops with increasing carrier density [115][117].

2.7.1 Efficiency Droop

The drop in IQE with increasing carrier density or the efficiency droop phenomenon has been observed in PL [100][118][119] and electroluminescence [120][122] experiments. Efficiency droop has been proposed to occur due to a variety of different mechanisms which include; non-radiative Auger recombination [123][125]. poor hole injection efficiency [121][126][127], modification or occupation of the localised states of the QW [128][132] and a variety of other carrier leakage mechanisms [110].

2.7.1.1 Auger Recombination

The effects of Auger recombination was first investigated in semiconductors by Beattie and Landsberg [133]. Auger recombination has been investigated both experimentally [124][134] and theoretically [135][137] in a variety of different material systems. Auger recombination is a 3 particle process, in which an electron and hole recombine and energy from the recombination is transferred to either an electron (ehe) or a hole (ehh). There are 2 main types of Auger recombination, direct and indirect; where indirect Auger recombination involves phonon interactions as shown in Figure 2.16. Auger recombination can result in the liberation of a carrier within the same band or to a higher energy band known as intra-band and inter-band Auger recombination respectively.

The efficiency response of an InGaN QW structure has been described by an empirical rate equation model [123]. The model describes the different recombination mechanisms in the structure. Assuming the electron density is equal to the hole...
2.7 QW Efficiency Vs. Power Density

Figure 2.16: Schematic showing the 2 main Auger recombination mechanisms, (a) direct and (b) indirect.

density. The rate of change of carrier density is described by the following relation,

$$\frac{dn}{dt} = -An - Bn^2 - Cn^3 + G$$  \hspace{1cm} (2.36)

where \(n\) is the carrier density, \(A\) is the Shockley-Read-Hall non-radiative recombination, \(B\) is the bimolecular radiative recombination, \(C\) is the Auger recombination rate and \(G\) is the carrier generation rate. In LED devices the generation rate is given by,

$$G = \frac{n_i J}{qd}$$  \hspace{1cm} (2.37)

where \(n_i\) is the carrier injection efficiency, \(J\) is the injected current density, \(q\) is the electron charge and \(d\) is the width of the QW. Substituting Equation (2.37) into Equation 2.36 and considering the equilibrium condition (i.e. \(\frac{dn}{dt} = 0\)), gives the following relation,

$$\frac{n_i J}{qd} = An + Bn^2 + Cn^3.$$  \hspace{1cm} (2.38)

The IQE \(\eta_{IQE}\) is defined as the fraction of carriers which recombine radiatively compared with the total recombination rate of the structure. Thus the efficiency can be calculated by

$$\eta_{IQE} = \frac{Bn^2}{An + Bn^2 + Cn^3}.$$  \hspace{1cm} (2.39)

where \(Bn^2\) represents the radiative recombination rate in the QW and \(An + Bn^2 + Cn^3\)
represents the total recombination rate, incorporating the non-radiative Shockley-Read-Hall, radiative and Auger recombination. The empirical rate equation model has been used to determine estimates of the Auger recombination coefficient, $C$ varying in order from $10^{-34}$ to $10^{-29}$ cm$^6$s$^{-1}$. Some of the theoretical work suggests that Auger recombination cannot solely be responsible for efficiency droop.

### 2.7.1.2 Hole Injection Efficiency

Carrier injection efficiency is defined as the fraction of injected carriers which are captured within the active region of the structure. In LEDs, electrons and holes are injected into the active regions from the n-type and p-type layers on opposite sides of the structure respectively. Drift-diffusion models which only consider the capture of carriers into the QWs suggest that the electrons are fairly evenly distributed amongst the QWs once captured. Whereas, the holes tend to be captured by the first few QWs due to their large effective mass and low diffusivity. There has been some experimental evidence to confirm these conclusions by David et al. who used angle resolved far field measurements to determine that only the QW nearest the p-layer emits light; regardless of how many QWs are grown.

The carrier injection efficiency, $\eta_{INJ}$ can have a significant impact on the measured EQE of LEDs given that the EQE can be calculated using the following relation,

$$\eta_{EQE} = \eta_{IQE} \times \eta_{INJ} \times \eta_{EXT}$$

(2.40)

where $\eta_{IQE}$ is the internal quantum efficiency and $\eta_{EXT}$ is the light extraction efficiency of the LED. The poor hole injection efficiency has thus been suggested to be the cause of efficiency droop at high carrier densities for LED structures. Though poor hole injection efficiency does not explain the efficiency droop observed in optical experiments, where the QWs are excited directly with a laser; creating an electron and hole pair in the same QW.

In a recent report by Hammersley et al., they improved on the drift-diffusion model by taking into consideration the redistribution of carriers due to thermally driven escape and recapture processes once captured. The authors determined that even if the holes are captured into the first few QWs redistribution of carriers amongst the QWs can result in a fairly uniform hole distribution across the LED structure. Thus redistribution processes are very important when considering carrier
2.7 QW Efficiency Vs. Power Density

distributions in LEDs.

2.7.1.3 Modification or Occupation of the Localised States

The high efficiencies observed in III-nitride based QWs are mainly attributed to carrier localisation, preventing carriers from reaching defects and recombining non-radiatively; as discussed in Section 2.5. Changes to carrier localisation and/or the saturation of the localised states have been suggested to result in efficiency droop by many authors [23, 100, 119, 128–130, 150]. Cao et al. [129] and Yang et al. [128] investigated efficiency droop in a range of AlInGaN-based LEDs on sapphire and bulk GaN substrates under both continuous and pulsed excitation. Cao et al. and Yang et al. reported that efficiency droop must be a non-thermal process and could not be explained by Auger recombination as the peak efficiency occurred at a current density of 1.4 A cm\(^{-2}\) for a green LED. Moreover, an Auger coefficient as high as \(10^{-30}\) cm\(^{6}\)s\(^{-1}\) could not account for the droop behaviour. Cao et al. and Yang et al. explained efficiency droop in terms of carrier overflow from localised states, which then undergo non-radiative recombination. They based this on the observed blue shift in the electroluminescence spectra with increasing current density for the green LED consistent with filling of the localised states.

Shatalov et al. [150] reported on efficiency droop in AlGaN UV LED at 12 K and 300 K. The peak of efficiency occurred at a similar power density for both temperatures. The PL peak energy is also observed to blueshift with increasing power density. Shatalov et al. described efficiency droop in terms of the saturation of localised states, whereby the lower energy states become filled and the carriers begin to occupy higher energy states which are more weakly localised or even free. Thus the higher energy states are more susceptible to non-radiative recombination and cause efficiency droop.

Efficiency droop was modelled by Hader et al. [130] in terms of a density activated defect recombination for GaN based LDs. In this model, at low carrier densities electrons and holes are localised by fluctuations in composition and/or well width. These fluctuations are assumed to have varying potential depth and spatial separation. These regions of local potential minima are relatively defect free and separate from regions of high defect density. On increasing the carrier density, the local potential minima states become filled and carriers are free to move around in regions of high defect density where they are susceptible to non-radiative recombination. Hader et al. described the loss of carriers from the QW structure, \(J_{\text{loss}}\), by the following
relation,

\[ J_{\text{loss}} = J_{\text{defect}} + J_{\text{rad}} + J_{\text{DADR}} \]  (2.41)

where \( J_{\text{defect}} \) represents the loss of carriers due to non-radiative recombination in the potential minima, \( J_{\text{rad}} \) is the radiative loss of carriers and \( J_{\text{DADR}} \) represents the density activated defect recombination loss. Auger recombination is not included in the loss current as it was previously determined [141] that the Auger coefficient was too small to explain efficiency droop. The density activated defect recombination loss was described to take the form,

\[ J_{\text{DADR}} = \begin{cases} 
0, & \text{for } N < N_0 \\
\frac{e n_w (N-N_0)^2}{\tau_{\text{DADR}} 2N_0}, & \text{for } N > N_0 
\end{cases} \]  (2.42)

where \( e \) is the electron charge, \( n_w \) is the number of wells, \( \tau_{\text{DADR}} \) is the defect recombination lifetime, \( N \) is the sheet carrier density per well and \( N_0 \) is related to the density of localised states. Hader et al. were successfully able to model the efficiency droop behaviour of a 410 nm and a 530 nm emitting LED structure using the model.

Hammersley et al. [100] reported on the effects of carrier density on the temperature dependent behaviour of InGaN/GaN QWs. Hammersley et al. observed a reduction in “S”-shape temperature dependent behaviour of the PL peak emission with increasing carrier density. The reduction occurred above power densities required to achieve efficiency droop at 10 K. The effects of increasing the carrier density were modelled using an effective mass approximation to solve the Schrödinger equations. The combined theoretical and experimental results suggested that the reduction in “S”-shape of the PL peak emission was attributed to the change in occupation factor of the localised states with increasing carrier density. This change in occupation results in efficiency droop, consistent with the density activated defect recombination model proposed by Hader et al. [130].

Bochkareva et al. [23] reported on the effects of current density on a commercially available InGaN/GaN white light emitting LED structure. On increasing the current density above 1 Acm\(^{-2}\), the LED was observed to droop. This droop was accompanied by a significant broadening on the high energy side of the emission spectrum, with little change to the low energy side of the spectrum. Bochkareva et al. suggested that at low current densities the injected carriers occupy the localised states uniformly. The carriers trapped in shallow local potential can relax down to deeper localised
states via phonon-assisted tunneling and then recombine radiatively. At high carrier densities, the deeper localised states become filled and the carriers begin to occupy higher energy states which are less weakly localised resulting in a broadening of the emission spectrum. Furthermore, the thermalisation of carriers to the mobility edge begins to dominate over the relaxation process to deeper localised states. Carriers at the mobility edge are more prone to non-radiative recombination, which results in efficiency droop.

Similar broadening of the high energy side of the PL spectrum at high carrier densities was observed by Davies et al. [119] for blue emitting InGaN/GaN QW structures in the droop regime. The broadening of the emission was also accompanied by a fast decay transient in the decay dynamics of the high energy side of spectrum. Davies et al. attributed this fast initial decay to the emission of weakly localised or delocalised carriers, consistent with the model of carrier loss mechanism associated with the reduction of carrier localisation or saturation of the localised states [23, 100, 130, 150].

### 2.7.1.4 Other Carrier Leakage Mechanisms

The other main carrier leakage mechanisms include: carrier overflow [151, 152], thermionic emission [153, 154] and quantum tunnelling [155, 156]. Carrier overflow refers to electrons which overshoot the QW region without being captured into the QW. This is a problem for LED structures and results in less electrons recombining in the active region of the LED. Thermionic emission can occur due to the thermal distribution of carriers in the system. A small fraction of the carriers can escape the confining potential of the QW into the barriers. Quantum tunnelling involves the direct transport of carriers through the confining potential of the QW into the barrier regions.

Carrier overflow in LED structures can be reduced by the insertion of an electron blocking layer (EBL) between the active region and the p-type side of the LED. EBLs are typically just layers of higher electronic potential than the barriers. For example, InGaN/GaN LEDs typically have AlGaN EBLs [152] or even superlattices of AlGaN/GaN [157]. Direct evidence of carrier overflow has been reported by Vampola et al. [152]. The authors studied the effect of current density on an InGaN/GaN LED with an extra p-type QW after the EBL. No emission was observed from the extra QW at low carrier densities. On increasing the carrier density, emission from the extra QW was observed due to recombination of electrons which had overflowed...
On increasing the carrier density further the LED began to droop.

Hurst et al. investigated the effect of thermionic emission on the PL intensity and decay time of a series of InGaN/GaN QW structures with 2, 3, 5, 10 and 18 QWs. Hurst et al. reported that the reduction in integrated PL intensity as a function of temperature was reduced on increasing the number of QWs. Furthermore, the PL decay time as a function of temperature was observed to reduce at different rates dependent on the number of QWs, with the onset of the reduction at higher temperatures for larger numbers of QWs. Hurst et al. modelled the effect of thermionic emission on the PL decay time using rate equations which considered the loss and recapture of carriers into the active regions of the structure. Hurst et al. found a reasonable agreement between the calculated and measured decay times as a function of temperature. Therefore they concluded that the effects of thermionic emission were a significant loss process, which could be negated by increasing the number of QWs in the structure. Thus increasing the probability of recapture into the active regions of the structure and hence PL intensity.

Bochkareva et al. investigated the effect of carrier density and temperature on the efficiency droop on a In$_{0.20}$Ga$_{0.8}$N/GaN LED structure. Bochkareva et al. observed that the peak of efficiency occurred at decreasing forward current with decreasing temperature. Furthermore, the peak of efficiency occurred at the same diode forward voltage independent of temperature. The efficiency droop behaviour was determined to be consistent with a tunnelling loss process to defects in the barriers.
2.8 References


2.8 References


References


2.8 References


2.8 References


2.8 References


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2.8 References


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3.1 Photoluminescence Spectroscopy

PL is a non-destructive technique widely used to investigate the optical properties of semiconducting material systems. PL involves the generation of electrons and holes within the sample by the absorption of photons from a light source. The photoexcited carriers can recombine non-radiatively with the emission of one or several phonons, or radiatively with the emission of a photon which can be accompanied by one or several phonons. The emitted luminescence from the sample structure can be detected and measured providing information about the recombination mechanisms.

A schematic diagram of a typical PL setup is shown in Figure 3.1.

Several excitation sources were used in this work which included a continuous wave (CW) HeCd laser (plasma filtered) emitting photons at 3.815 eV, a CW dye laser (Stilbene 420) emitting photons ranging from 2.661 to 2.973 eV and a frequency doubled mode-locked Ti:sapphire laser system which produces \( \sim \) 100 fs photon pulses ranging in energy from 2.610 to 3.542 eV. The sample under investigation was mounted on the cold finger of a high vacuum closed-cycle helium cryostat, which allowed the temperature of the sample to be varied from 6 K to 300 K. The sample was illuminated by a focused excitation source, which had passed through a chopper that modulated the light source at a user defined frequency. The power of the excitation source could be controlled using neutral density filters. The luminescence from the sample was collected by a lens and focused through a polariser onto the entrance slits of a single- or double-grating spectrometer. Double spectrometers were used when stray light was an issue as they have increased rejection over single gratings. The spectrometers used in this work are summarised in Table 3.1. Their
3.1 Photoluminescence Spectroscopy

Figure 3.1: Schematic diagram of a typical PL Spectroscopy setup.

resolution depends on the grating dispersion, the focal length of the spectrometer and the width of the slits.

The incident light on the spectrometer is dispersed inside the spectrometer and detected by a Peltier cooled GaAs or multi-alkali (S20) photomultiplier tube (PMT). The photocathode type was chosen based on spectral response and the detection energy ranges of interest. Cooling the PMT improves the signal to noise ratio by minimising the effects of thermal noise. The PMT converts the incident photons into a small electrical signal with an amplitude dependent on the incident photon intensity and the acceleration voltage in the PMT. The sensitivity of the PMT

<table>
<thead>
<tr>
<th>Spectrometer model</th>
<th>Number of gratings</th>
<th>Dispersion (Å/mm)</th>
<th>PMT type</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPEX 1404 0.85 m</td>
<td>Double</td>
<td>8</td>
<td>GaAs</td>
</tr>
<tr>
<td>SPEX 1403 0.85 m</td>
<td>Double</td>
<td>8</td>
<td>Multi-Alkali</td>
</tr>
<tr>
<td>SPEX 1702/1704 0.75 m</td>
<td>Single</td>
<td>16</td>
<td>GaAs</td>
</tr>
</tbody>
</table>

Table 3.1: Summary of the spectrometers used, their dispersion and the photomultiplier attached to them.
3.1 Photoluminescence Spectroscopy

can be adjusted by changing the acceleration voltage, with higher voltages having a greater sensitivity. The output signal from the PMT is connected to a lock-in amplifier and an oscilloscope, so the signal can be monitored over the course of the experiment. A reference signal from the chopper is also connected to the lock-in amplifier. The lock-in amplifier will only amplify the output signal from the PMT which is modulated at the same frequency and phase as the reference signal from the chopper. The amplified signal is then integrated over a time period set by the user. The output signal from the lock-in amplifier is then recorded using data-logging software on a personal computer (PC). The detection wavelength of the spectrometer can be controlled via a PC. A typical PL scan involves the luminescence intensity of the sample being recorded as a function of wavelength.
3.2 Fabry-Pérot Etalon Interference

Most InGaN/GaN QW structures are grown on GaN buffer layers which have been deposited on sapphire substrates. The refractive index of sapphire is $\sim 1.77$ [1] and that of GaN is $\sim 2.45$ [2] for photon energies in the range of 2.2 to 2.8 eV at room temperature. The change in refractive index at the sapphire/GaN and the GaN/air interfaces creates an optical cavity inside the sample. PL emitted inside the sample may undergo multiple reflections at these interfaces resulting in Fabry-Pérot etalon interference which leads to a transmittance from the GaN/air interface which depends on the energy of the incoming photons. The transmittance becomes a periodic function of period, $\nu_F$ which can be calculated using the following

$$\nu_F = \frac{c}{2nd}, \quad (3.1)$$

where $c$ is the speed of light in a vacuum, $n$ is the refractive index of the medium between the interfaces and $d$ is the distance between the sapphire/GaN and GaN/air interfaces. Typically $d$ is measured to be around $5 \mu m$ which means the transmittance maxima are spaced around $100$ meV apart in detection energy. These large variations in transmittance result in PL spectra with large modulations of the intensity.

The effects of Fabry-Pérot interference can be suppressed by using the Brewster angle geometry [3] which is shown in Figure 3.2. Light incident at the GaN/air interface contains both horizontal (electric field out of plane of the page) and vertical (electric field in the plane of the page) polarisation components. When light is incident at Brewster’s angle ($\theta_B$), the vertical component of the light is not reflected at the GaN/air interface. Thus the transmitted vertical component of light has not undergone multiple reflections inside the sample and is free from Fabry-Pérot etalon interference. The detection of the vertical component of light which has been incident on the GaN/air interface at Brewster’s angle gives PL spectra free from Fabry-Pérot etalon interference. The Brewster angle, $\theta_B$ can be calculated using the following

$$\theta_B = \tan^{-1}\left(\frac{n_{air}}{n_{GaN}}\right), \quad (3.2)$$

and is $\sim 22^\circ$ at room temperature for photon energies in the range of 2.2 to 2.8 eV. The corresponding angle from the sample normal, $\beta$ in Figure 3.2 can be calculated

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by the following

\[ \beta = \sin^{-1} \left( \frac{n_{GaN} \sin(\theta_B)}{n_{air}} \right) \]  

(3.3)

and is \( \sim 68^\circ \). The Brewster angle geometry has been used for all the PL measurements taken in this work.

**Figure 3.2:** Diagram representing the Brewster angle setup. \( \theta_B \) is the Brewster angle between the GaN/air interface, \( \alpha \) is the angle the light is transmitted from the sample surface and \( \beta \) is the angle the light is transmitted from the sample normal.
3.3 Photoluminescence Time Decay Spectroscopy

Photoluminescence time decay spectroscopy is a very powerful optical technique which can be used to investigate the recombination dynamics of carriers in semiconducting systems. PL time decay involves correlating the initial excitation of electron and hole populations and the time delay between their subsequent decay using time correlated single photon counting (TCSPC). To achieve this correlation the excitation source is pulsed at a repetition rate such that all the carriers have recombined before the next pulse is incident on the sample. A schematic of the PL time decay system used in this report is shown in Figure 3.3.

The excitation source was a mode locked Ti:sapphire laser pumped by a CW diode pumped solid state laser. The Ti:sapphire laser produces pulses with a width of \( \sim 100 \) fs at a repetition rate of 80 MHz and the output photon energy can be tuned from 1.305 eV to 1.771 eV. The pulse train from the Ti:sapphire laser is passed through a pulse picker which reduces the repetition rate by a particular division ratio set by the user. The pulse picker also sends a \textit{START} signal to the time to amplitude converter (TAC). The \textit{START} signal is synchronised to arrive at the TAC at the same time as the laser pulse at the sample. The \textit{START} signal starts a linear voltage ramp inside the TAC. The linear voltage ramp can be adjusted by the user so that it takes between 50 ns and 2 ms for the voltage to reach a maximum. The selected laser pulses are then frequency doubled by a non-linear crystal in the second harmonic generator to achieve output energies in the range of 2.610 eV to 3.542 eV. The laser is then focused onto a sample which was mounted on the cold finger of a high vacuum closed cycle helium cryostat which can be temperature controlled between 6 K and 300 K.

A pulse from the laser creates electron and hole pairs in the sample, at the same time the TAC starts a linear voltage ramp. The luminescence from the sample is collected by a lens and focused through a long pass filter and polariser onto the entrance slits of a spectrometer. The long pass filter is selected so as to block the laser light from entering the spectrometer. The incident photons are dispersed inside the spectrometer and are incident on the photocathode of a cooled PMT with a fixed acceleration voltage. The absorption of photons at the photocathode results in the emission of electrons due to the photoelectric effect. The emitted electrons are electrostatically accelerated onto the first dynode. The impact of the
3.3 Photoluminescence Time Decay Spectroscopy

Figure 3.3: Schematic diagram of the PL time decay system.

Electrons onto the dynode liberates multiple electrons. The liberated electrons are then electrostatically accelerated to the next dynode and this electron multiplication process occurs over several dynodes. The electrons from the last dynode are collected at the anode which creates an electric signal pulse. The electrons can traverse the PMT along multiple paths which results in a distribution of times that the electrons arrive at the anode. This variation in arrival time is known as the transit time.
spread. The transit time spread can be reduced by reducing the distance between the photocathode and the first dynode. The transit time spread can also be reduced by making the dynodes a curved shape and increasing the electric field between them. Thus typically the voltage in the PMT is set to the maximum.

The signal pulse from the PMT is then passed through an amplifier into a constant fraction discriminator (CFD). The CFD has two major functions, first to improve signal to noise ratio and secondly to improve timing errors which can occur using leading edge detection on signals of different amplitudes. The signal entering the CFD is split up into two parts. The first part of the circuit involves the signal being split into two components which pass through two different delay lines. The two components which are delayed from each other are feed into the inputs of a comparator. The effective input signal to the comparator is the difference between the two components, when the voltage level transitions through a set baseline the comparator outputs a positive signal. The second part of the circuit involves the signal pulse being compared with a user set threshold level. When the pulse amplitude is above the user set threshold level the comparator outputs a positive signal which improves the signal to noise ratio. The output from the two comparators are used as the inputs of an AND logic gate, which outputs a positive signal only if both inputs are positive. A positive signal from the AND logic gate triggers the CFD to output a STOP signal to the TAC which stops the linear voltage ramp. The output from the CFD is also connected to a counter which displays how many photons have been detected per second for the user to monitor over the course of the experiment. The TAC then outputs a pulse to a multichannel analyser (MCA) connected to a PC, the amplitude of which correlates with the amount of time which has passed between the START pulse and the STOP pulse. The MCA has a number of channels (up to 8192), each of which represents a small range of voltages that correlate with a particular time segment. For example a 50 ns time window for the voltage ramp, divided into 8192 voltage channels results in time segments of 6 ps. The incoming pulse to the MCA is sorted by voltage amplitude into the correct channel, which adds one count into that particular channel. This process is repeated until typically 1000 counts have been collected in a single MCA channel. This produces a histogram of counts (or intensity) versus time and is referred to as a PL decay transient.

Theoretically a count could be detected for every pulse that is incident on the sample structure. Though this leads to a distorted signal from the TAC and a well known problem called pulse pile up. Pulse pile up occurs due to the fact that
only the first detected photon results in a count in the MCA and thus any other photons detected before the next pulse are not recorded. The loss of these photons is more probable to occur for photons which are detected at longer times after the initial START pulse. Thus it becomes artificially more probable to detect photons at shorter time scales after the initial START pulse resulting in a shortening of the decay transient. To circumvent this problem the number of counts detected is reduced to 1 % of the repetition rate of the laser [4]. The PL decay transient can also be artificially shortened if the electron and hole populations have not completely decayed in the time between excitation pulses. The probability of detecting photons at shorter time scales becomes artificially higher due to long lived carriers from the preceding pulse. To overcome this problem a repetition rate is chosen, such that all the carriers have decayed before the next excitation pulse.

The PL time decay system has an associated system response or temporal resolution which is the fastest time that it can respond. The system response is defined as the time taken for the signal level to increase from 10 % of its maximum to its maximum as shown in Figure 3.4. The system response is affected by several factors which include the transit time spread of the detector, the detection energy and the multipath dispersion associated with the spectrometer and the collection geometry. The temporal resolution of the system used in this work is on the order of 400 ps.
3.3 Photoluminescence Time Decay Spectroscopy

Figure 3.4: A typical time decay system response curve using scattered laser light.
3.4 References


CHAPTER 4

Comparison of the Two-Temperature and Quasi-Two Temperature Growth Methodologies

4.1 Introduction

One of the key issues with the growth of high quality InGaN/GaN QWs is indium incorporation. This is due to the low miscibility of InN in GaN [1] and the low desorption temperature of InN of around 600 °C [2]. The indium content of InGaN films is mainly controlled by the growth temperature [3]. To achieve high indium content (> 20 %) InGaN layers, growth temperatures are generally kept below 800 °C [4]. One of the growth methodologies used for InGaN/GaN QWs is 1T growth. 1T growth involves the growth of the InGaN QW layer at low temperatures required for good indium incorporation. Following the InGaN growth, the GaN barrier is grown at the same temperature as the InGaN QW layer with no growth pause in-between. The optimal growth temperature of GaN to achieve a low defect density is ~ 1000 °C [5]. Therefore the GaN grown in the 1T growth methodology is sub-optimal. The growth of GaN at low temperatures results in layers with a high density of defects which can act as non-radiative centres and dramatically affect the recombination efficiency of InGaNS/GaN QWs [6] [7].

To overcome this problem InGaN/GaN QWs can be grown using a 2T growth methodology, where by the QW and barriers are grown at different temperatures with the growth being interrupted while the temperature is adjusted [8]. The exposure of the InGaN QW layer to a growth interruption [9] [11] and/or a temperature ramp [8] [12] [14] can result in the desorption of indium from the InGaN QW layer. The desorption of indium from the InGaN QW layer can result in GWWWFs, where the well width varies by more than two monolayers [15].
4.1.1 Gross Well Width Fluctuations

The desorption of indium during a temperature ramp/growth interruption can be so severe that the InGaN layer is desorbed completely, in some areas leaving behind troughs which create a network of InGaN strips as shown in Figure 4.1. The InGaN strips tend to align with the direction of the step edges of the underlying GaN pseudo-substrate surface [16]. The correlation between the spacing of bilayer atomic steps at the surface of a GaN pseudo-substrate and the trough spacing of an InGaN epilayer exposed to a thermal anneal process was established by Jouvet et al. [17]. These authors suggested that the double step edges preferentially incorporate indium and that these indium-rich regions are less stable to the thermal anneal process than the surrounding material and decompose creating the trough regions. Later work by Massabauau et al. [18] suggested that even a single layer atomic step can contribute to trough production, with single atomic steps being more frequent than double or triple layer steps. Furthermore Massabauau et al. determined that the distance between step edges depends on the substrate miscut, with a larger miscut resulting in a shorter distance between step edges and thus troughs. The average indium content has been observed to vary across an InGaN strip between trough regions with the highest indium content in the centre of the strip using energy dispersive x-ray measurements [19]. The large variation in well width and average indium content across the InGaN QW strip creates large variations in the effective bandgap of the QW thus GWWFs have been proposed as a means of carrier localisation preventing carriers from being captured by non-radiative sites [19].

![Atomic force microscope images of an InGaN layer produced by the University of Cambridge, showing the InGaN strip network (grey) with troughs (black) in-between which tend to align parallel to the [11\(\bar{2}0\)] direction, adapted from [18].](image)

**Figure 4.1:** Atomic force microscope images of an InGaN layer produced by the University of Cambridge, showing the InGaN strip network (grey) with troughs (black) in-between which tend to align parallel to the [11\(\bar{2}0\)] direction, adapted from [18].
4.1.2 Comparison of Single and Two Temperature Growth

The structural and optical properties of InGaN/GaN QW structures grown using the 2T growth methodology have been compared to those grown using the 1T methodology by several authors [7, 8, 13, 14]. Structures grown using the 2T methodology were observed to have blue shifted PL emission peaks compared with their 1T counterparts, which was attributed to the desorption of indium from the QW and to the reduction in well width during the growth interruption and temperature ramp. The PL linewidths of structures grown using the 2T method were observed to be larger than the equivalent 1T structure, this was attributed to the larger intra and inter-well width variations in the 2T growth methodology [8, 14].

The room temperature PL intensity [7] and RT-IQE [8] of InGaN/GaN QWs are observed to be larger for the 2T grown structures under certain excitation conditions not stated by the authors. This increase in PL intensity and RT-IQE is ascribed to a reduction in the density of defects in the GaN barriers when the GaN is grown at high temperatures. The reduction in defect density was determined from the reduction in the defect YL band compared to the QW emission [7]. The PL intensity and RT-IQE of the QWs are also thought to be increased due to the observed reduction of the 4 K PL decay time, which implies the radiative rate has increased and thus the efficiency of the QW. This reduction in decay time was determined to be consistent with the reduction in indium content and resulting electric field strength in the wells, in the 2T growth method [8]. The surface morphology of samples grown using the 2T growth methodology were observed to have an improved surface morphology, but with an increase in pit formation. The increase in pit formation was attributed to the GWWFs produced in the 2T growth method [7, 13].

4.1.3 Quasi-Two Temperature Growth

The desorption of indium caused by the 2T growth methodology is a real problem for the production of high indium content InGaN/GaN QW devices. One of the ways to overcome this problem is to grow a thin layer of material, typically around 1 nm on top of the InGaN QW at the QW growth temperature to protect it from being exposed to a growth interruption or temperature ramp. This low temperature QW cap has been shown to result in the reduction of the amount of indium desorbed during a growth interruption or temperature ramp [20]. QW caps are employed in the Q2T growth methodology of InGaN/GaN QWs to reduce indium desorption.
4.1 Introduction

**Q2T** growth involves the InGaN **QW** layers being capped by a low temperature **QW** cap of GaN. After the **QW** cap, growth of the GaN barrier is continued during the temperature ramp to the normal high temperature growth conditions. Growth of the GaN barrier continues at high temperature until the desired thickness is achieved.

Several materials have been used for low temperature **QW** caps which include GaN, AlGaN [21, 22], low indium content (2%) InGaN and AlInGaN [23]. Here we focus on the effects of the inclusion of GaN **QW** caps on the structural and optical properties of InGaN/GaN **QW** structures, which have been reported by many authors [7, 12, 20, 21, 24–29].

Massabuau et al. [29] reported on the effects of a **Q2T** growth methodology on the structural properties of InGaN/GaN **QWs**. These authors reported that a significant amount of indium is incorporated into the GaN barrier grown after the **QW**, due to the indium surfactant layer on top of the InGaN **QW**. Furthermore, the **Q2T** structure was measured to incorporate more indium than the **2T** structure due to the absence of a temperature ramp before the growth of the GaN barrier, resulting in more indium coverage before the growth of the GaN barrier. The incorporation of indium into the GaN barriers results in the degradation of the **QW** interfaces and was simulated to result in a reduction in the wavefunction overlap.

The rest of the literature in this section compare structures grown using a **2T** growth methodology with those grown using a variant of the **Q2T** growth methodology. The thickness of the **QW** cap has been shown to affect the amount of indium desorbed from the **QW** with larger thickness **QWs** caps resulting in less indium desorbed [20, 24]. Furthermore a single monolayer of **QW** cap has been shown to be effective in reducing the amount of indium desorbed from the **QW** [20]. The surface quality has been shown to generally improve with the inclusion of a **QW** cap due to a reduction in the size and density of ‘V-defects’ [30]. The interface quality between the **QW** and barrier is also observed to improve with **QWs** caps [7]. The **QW** thickness generally increases with a **QW** cap due to the reduction in indium desorption [21]. Although Ju et al. [27] found no difference in the **QW** and barrier periodicities determined by high resolution x-ray diffraction and Ivaldi et al. [28] observed that the periodicity worsened on the insertion of a **QW** cap. Ivaldi et al. suggests that the uncontrolled growth rate of the **QW** cap leads to local differences in the growth speed and results in a stepped growth front.

The effect of the inclusion of a GaN **QW** cap on the optical properties of InGaN/GaN **QWs** is to introduce a red shift in the PL emission energy compared with
4.1 Introduction

an equivalent sample without a QW cap. The red shift in the PL emission energy is ascribed to a reduction in the amount of indium desorbed from the QW during the temperature ramp and growth interruption. The thickness of the QW cap has been observed to affect the FWHM of the PL emission with varying results reported. Pendlebury et al. [20] reported that a monolayer thick QW cap results in an increase in the FWHM, whereas a 0.75 nm and 1.5 nm thick QW cap resulted in a decrease, compared to the structure without a QW cap. Moreover these authors report that a 3 nm thick QW cap had negligible impact on the FWHM in comparison to the structure without a QW cap. The initial increase in FWHM for the 1 monolayer thick QW cap is thought to be due to the increased retention of indium in the QW. Leem et al. [24] also reported on the effect of QW cap thickness, with a 2 nm thick QW cap resulting in an increase in FWHM over the structure without. Furthermore a 5 and 7 nm thick QW cap resulted in a decrease in the FWHM compared with the structure without, with the 5 nm QW cap having a larger decrease. Ju et al. [27] noted that a 1 nm QW cap had a negligible effect on the FWHM, whereas Ivaldi et al. [28] observed an increase in FWHM for a structure with a QW cap of the same thickness. The varying results suggest that the effect of the GaN QW cap on the FWHM is not general and depends on the specific growth conditions of the structure.

The effect of a QW cap on the PL intensity of the QW at room temperature has also been investigated, with authors reporting a variety of results. Pendlebury et al. [20] reported that the PL intensity of the QW reduced with increasing thickness of the QW cap up to 3 nm, when the structures were excited at $\sim 2 \text{ Wcm}^{-2}$ with a CW HeCd laser. They attribute this reduction in PL intensity to an increase in defect density from the increased thickness of the QW cap, which is situated next to the QW. The quality of the barriers is very important as the electron and hole wavefunctions penetrate into them [29, 31, 32]. They rule out the effect of increased indium content with increasing QW cap thickness changing the emission energy and thus the radiative rate; by comparing the samples with QW cap with structures without the QW cap which emit at the same energy by varying the indium content (QW growth temperature). They observed that the structures without QW caps had slightly improved PL intensity emitting at a similar energy. They also comment on the reduction in PL intensity not being linked to an increase in the electric field and thus a reduction in the electron and hole wavefunction overlap; because they believe the wells were too thin (3 nm) and no increase in the electric field was observed in the reference structures without QW caps.
Ishikawa et al. [25] also reported on the effect of increasing the QW cap thickness, when the structures were excited at \( \sim 1.4 \) Wcm\(^{-2}\) with a CW HeCd laser. They observed a negligible increase in the peak PL intensity of the QW on the insertion of a 1 nm thick QW cap with respect to the structure without. Moreover, a relative decrease was observed for a 2 nm thick QW cap. They suggest that the decrease in the peak PL intensity is a result of the 2 nm thick QW cap not being effective enough at stopping indium evaporation. Kim et al. [7] observed an increase in the relative PL intensity of the QW on the insertion of a 2 to 4 monolayer QW cap, when the structures were excited with a CW HeCd laser. No mention was made by the authors as to what power density was used. They suggest that the increase in PL intensity results from the reduction in pit formation and the improved interface between the InGaN QW and the GaN barrier. The improved interface is thought to improve the quantum confinement and prevents the formation of defects resulting in a larger PL intensity.

Leem et al. [24] investigated the effect of increasing the QW cap thickness on the PL intensity from the QW, when the structures were excited with a CW HeCd laser. No mention of the excitation power density was made by the authors. On the insertion of a 2 nm thick QW cap the PL intensity was improved slightly, with a further improvement coming when the QW cap was increased to 5 nm. Increasing the QW cap thickness yet further to 7 nm resulted in a drop in the PL intensity but the PL intensity was still larger than the structure without a QW cap. Ivaldi et al. [28] also observed an increase in the PL intensity of the QW on the insertion of a 1 nm thick QW cap on samples grown on free standing GaN, though no mention was made of the excitation conditions. They attribute the increase in PL intensity to a reduction in well width fluctuations and increased indium content.

To summarise, both an increase and decrease in PL intensity have been reported on the insertion of a QW cap of various thickness. The increase in PL intensity was attributed to the reduction in pit formation and improved interface quality between the InGaN and GaN. The improved interface is thought to improve the quantum confinement and prevent the formation of defects resulting in a larger PL intensity. The decrease in PL intensity was attributed to high defect density of the low temperature QW cap situated next to the QW. The carrier wavefunctions can penetrate into the GaN barriers and an increase in the defect density will result in a increase in non-radiative recombination. From the varying conclusions on the effects of including a QW cap on the properties of InGaN/GaN QWs, it is evident that a
full and detailed investigation is required. The aim of this work is to determine what effects the inclusion of a QW cap has on the properties of InGaN/GaN QWs. In this study the properties of InGaN/GaN QWs grown using the 2T methodology are compared to those grown using a Q2T methodology.
4.2 Sample Details and Structural Properties

Two 10 period polar In$_{0.16}$Ga$_{0.84}$N (2.5 nm)/GaN (7.5 nm) QW structures were grown by MOVPE in a Thomas Swan 6 × 2 in showerhead reactor; one was grown using the Q2T (C4815A) methodology and the other the 2T (C4825A). The structures were grown on low defect density c-plane sapphire/GaN pseudo-substrates with a nominal 0.25° miscut toward (1120). For the Q2T sample, following the growth of a QW at 740 °C, a ∼ 1 nm GaN QW cap is grown. Afterwards the temperature was ramped up to 860 °C during which growth continued and then the rest of the barrier was grown. For the 2T sample, to compensate for any loss of indium during the temperature ramp, the QW was grown at 725 °C. The growth was then paused and the temperature was ramped up to a maximum of 860 °C. The growth of the GaN barrier began just before the maximum temperature was reached, for which the rest of the GaN was grown. Scanning transmission electron microscopy-high angle annular dark field (STEM-HAADF) images produced by the University of Cambridge, of the Q2T and 2T structures are shown in Figures 4.2a and 4.2b respectively.

(a) Q2T.  
(b) 2T.

**Figure 4.2:** Scanning transmission electron microscopy-high angle annular dark field images taken along the ⟨11\(\overline{2}0⟩\rangle zone axis for the (a) Q2T and (b) 2T structures.

The Q2T structure is observed to have smooth continuous wells whereas GWWFs are present in the 2T structure. In the 2T structure the lower interface of the QW as can be seen in Figure 4.2b is smooth while the upper interface is rough. Though no GWWFs are present in the Q2T structure, it still exhibits one or two monolayer fluctuations in well width. The smooth continuous wells of the Q2T structure suggests
that this growth methodology helps to prevent the desorption of indium from the QW, resulting in the reduction of well width fluctuations. The GWWFs observed in the STEM-HAADF images of the 2T structure were analysed to determine their dimensions by Cambridge University. A substantial WWF defined as when the local QW thickness is less than half the maximum thickness, was measured to occur once every $\sim 100$ nm \[33\].

The sample details are summarised in Table 4.1, where the well and barrier thickness along with the average indium content were determined by STEM-HAADF images and x-ray diffraction (XRD) at the University of Cambridge. The GWWFs in the 2T structure, unfortunately hinder the determination of these properties by XRD and thus only its well and barrier thickness can be determined using the STEM-HAADF images.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Growth method</th>
<th>QW thickness (nm)</th>
<th>Barrier thickness (nm)</th>
<th>Average indium content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4815A</td>
<td>Q2T</td>
<td>2.4 $\pm$ 0.1</td>
<td>7.3 $\pm$ 0.1</td>
<td>16 $\pm$ 1</td>
</tr>
<tr>
<td>C4825A</td>
<td>2T</td>
<td>0 to 2.5 $\pm$ 0.1</td>
<td>7.5 $\pm$ 0.2</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.1: Summary of sample details.
4.3 Results and Discussion

A series of experiments were performed to compare the optical properties of the structures, which included PL spectroscopy and PL decay time measurements as a function of both temperature and excitation power density.

4.3.1 Temperature Dependent PL

The RT-IQE of InGaN/GaN QW structures is well known to depend on the excitation power density [34], with the efficiency increasing on increasing the power density at low carrier densities. On increasing the power density further the efficiency begins to plateau and eventually decreases at high carrier density, which is the well known phenomenon of efficiency droop [35]. Initially the samples were compared using temperature dependent PL measurements at a constant excitation power density to determine their spectral behaviour and RT-IQE. The structures were excited using a power density of 2 W cm$^{-2}$ with a CW HeCd laser of photon energy 3.815 eV, which is well below the carrier densities required to achieve efficiency droop. The normalised 12 K PL spectra for the Q2T and 2T structures are shown in Figure 4.3. The PL peak energies of the Q2T and 2T structures were measured to be 2.755(±0.001) eV and 2.728(±0.001) eV respectively. The oscillations in the PL spectra are caused by two main effects. Firstly due to the LO phonon replica [36] which results in oscillations spaced at around 91 meV below the main emission peak. Secondly due to Fabry-Pérot etalon interference effects even though attempts were made to reduce them using the Brewster angle setup. The Fabry-Pérot etalon peaks are separated by around 100 meV and occur across the whole spectrum.

The FWHM values at 12 K for the Q2T and 2T structures were measured to be 94(±6) and 162(±8) meV respectively. The large FWHM values of InGaN/GaN QWs are attributed to large variations in both the hole and electron energy. The hole energy varies due to intra- and inter-well local alloy fluctuations. Whereas the electron energy varies due to intra- and inter-well fluctuations in alloy composition and well width [37, 38]. The holes are not affected by fluctuations in well width due to the strong localisation effects. Holes are estimated to be strongly localised by local alloy fluctuations on a length scale of ~1 to 3 nm [37, 38] compared to WWFs which have a diameter of around 5 to 10 nm [39].

The effects of both alloy and well width fluctuations on the electron and hole energy have been modelled by both Watson-Parris [40] and Schulz et al. [38]. Watson-
4.3 Results and Discussion

Figure 4.3: Normalised 12 K PL spectra for the Q2T and 2T sample structures.

Parris modelled a 3 nm thick In$_{0.25}$Ga$_{0.75}$N/GaN QW with a randomly distributed alloy composition. The localisation energy ($\sigma$ in Equation (2.32)) of the holes was calculated to be $\sim 55$ meV and that of the electrons to be $\sim 11$ meV, due to the effects of alloy fluctuations alone. Furthermore, the electrons were calculated to have localisation energies of $\sim 10$ meV due to the effects of the WWFs. Watson-Parris also investigated the effects of indium composition on the localisation energy of both the electrons and holes. The electrons were found to have a constant localisation energy with indium composition of $\sim 10$ meV. This was attributed to the relatively small effective mass of the electron which results in a weak localisation in terms of energy depth. Whereas the hole localisation energy increases with indium composition as $\sqrt{x(1-x)}$, due to the large effective mass and small localisation length.

Schulz et al. [38] modelled a 3.5 nm thick In$_{0.25}$Ga$_{0.75}$N/GaN QW with a randomly distributed alloy composition. The authors reported on the combined effects of alloy fluctuations and two monolayer WWFs with a diameter of 5 nm. They reported that the variation in the hole ground state energies varied from 10 to 150 meV. Whereas for the electron, they varied from 2 to 45 meV. Thus the majority of the PL FWHM is attributed to the variation in the hole localisation energy.

The main difference between the Q2T and 2T structures is the presence of GWWFs in the 2T structure. The presence of GWWFs has two main effects, which
are to vary the \( QW \) width from 0 to 100 % and to vary the measured average indium content across the strip \[19\]. The large variation in \( QW \) width leads to large variations in the confined electron energy. Furthermore, the large variation in \( QW \) width will also result in variations to the electric field across the \( QW \) and the associated QCSE \[41\]. The effect of reducing the \( QW \) width on the recombination energy has been modelled using a commercially available Schrödinger-Poisson solver (nextnano\(^3\) \[42\]). A reduction in \( QW \) width has been simulated to result in an increase to the recombination energy. Thus the reduction in \( QW \) width leads to broadening on the high energy side of the PL emission spectrum.

The variation in average indium content across the InGaN \( QW \) strip, results in large variations to the bandgap of the \( QW \). This is because for a random distribution of indium atoms, the distribution of local indium compositions depends on the average indium composition. The standard deviation of the local indium composition distribution is proportional to \( \sqrt{x(1-x)} \), where \( x \) is the average indium composition \[40\]. In other words, the amount of disorder increases as the average indium composition increases. The average indium content is a minimum at the edges of the \( QW \) strips and a maximum at the centre. The total distribution of local indium contents is now a convolution of several local indium distributions from different regions of the \( QW \) strip. The resultant distribution has significant broadening on the high local indium content side as the amount of disorder increases with increasing indium content. This results in asymmetric broadening of the PL emission spectrum with the half width at half maximum of the low emission energy side of the spectrum being larger than the high energy side. The large variation in both the well width and average indium composition across the \( QW \) in the 2T structure, thus leads to a fairly symmetrical broadening of the FWHM of the PL spectra compared to the Q2T structure.

The temperature dependent PL spectra, measured between 12 and 300 K, are shown for the Q2T and 2T structures in Figures 4.4 and 4.5 respectively. The spectra are found to be prone to interference oscillations, with the 2T structure being particularly susceptible. The Fabry-Pérot interference fringes reduce as a function of temperature. This maybe in part due to the change in refractive index of the GaN \[43\] as a function of temperature. The refractive index of GaN is expected to increase by 0.01 for photons in the range 2.2 to 2.8 eV, on increasing the temperature from 0 to 300 K. This results in a change in the Brewster angle calculated using Equation 3.2. Furthermore, this changes the angle, \( \beta \) in Figure 3.2 for which the
vertical polarisation component of light exits the structure that has not undergone reflections inside the structure; which can be calculated using Equation 3.3. The refractive index changes from $\sim 2.44$ to $\sim 2.45$ on increasing the temperature from 0 to 300 K, which results in a change in $\beta$ from $68.4^\circ$ to $67.8^\circ$ for photons in the range 2.2 to 2.8 eV. Thus this change in $\beta$ with temperature may result in a more optimal Brewster angle setup. The integrated PL intensities are shown as a function of temperature in Figure 4.6 with the 10 K value being normalised to 1 for comparison. The integrated PL intensity is observed to decrease as a function of temperature, with the rate of decrease being significantly larger for the Q2T compared with the 2T structure. The quenching of the PL intensity with temperature has been in part attributed to the thermal activation of carriers to defects where they can recombine non-radiatively [44, 45]. The RT-IQE was calculated for each structure by comparing the 300 K integrated PL intensity value with that measured at 12 K. The RT-IQE values of the Q2T and 2T structures were calculated to be $9 \pm 1$ % and $30 \pm 2$ % respectively.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.4.png}
\caption{PL spectra for the Q2T structure as a function of temperature, ranging from 10 to 300 K. The spectra are offset for clarity.}
\end{figure}

The PL peak emission energy shift from the 12 K value was measured as a function of temperature for each structure and a comparison is shown in Figure 4.7, with corrections being made for the temperature dependent shift in the bandgap
4.3 Results and Discussion

Figure 4.5: PL spectra for the 2T structure as a function of temperature, ranging from 10 to 300 K. The spectra are offset for clarity.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>PL Intensity (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td></td>
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<tr>
<td>2.6</td>
<td></td>
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<td>2.7</td>
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<td>2.8</td>
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<td>2.9</td>
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<td>3.0</td>
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<td>3.1</td>
<td></td>
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<tr>
<td>3.2</td>
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</table>

Figure 4.5: PL spectra for the 2T structure as a function of temperature, ranging from 10 to 300 K. The spectra are offset for clarity.

energy using the Varshni Equation. The Varshni parameters for each structure were obtained by a linear interpolation between the GaN and InN values, using an indium content of 16 % for the Q2T structure and the 2T structure is estimated to have the same indium content. The $\alpha$ and $\beta$ parameters used for both structures were 0.805 meVK$^{-1}$ and 798 K respectively. The PL peak energy shift of both structures follows the well known “S”-shape temperature dependence behaviour [46]. The initial redshift for the Q2T and 2T structures are measured to be 21(±2) and 5(±2) meV respectively. The blueshift for the Q2T and 2T structures was measured to be 60(±6) and 44(±6) meV. The “S”-shape temperature dependence of the PL peak energy is attributed to redistribution of the most weakly localised holes amongst all the localised hole states [47]. This redistribution is reflected in a change to the PL linewidth of the spectrum given that it is mainly determined by fluctuations in the hole localisation energy. The change in PL linewidth results in a shift in the peak energy position. The large FWHM of the 2T structure may mask the change in PL linewidth and resultant change in peak energy position. This would explain the reduced “S”-shape behaviour of the PL peak energy observed for the 2T structure.
4.3 Results and Discussion

Figure 4.6: Comparison of the normalised integrated PL intensity for both Q2T and 2T structures; as a function of temperature, ranging from 10 to 300 K. The 10 K value has been normalised to 1 for each structure, for comparison purposes.

Figure 4.7: Measured PL peak emission energy shift from its position at 12 K as a function of temperature for each structure after correction for the temperature dependent shift in the bandgap.
4.3 Results and Discussion

4.3.2 Temperature and Power Dependent PL

The 2T structure was determined to have a larger RT-IQE than the Q2T structure at an excitation power density of 2 W cm\(^{-2}\). The RT-IQE of InGaN/GaN QW structures are well known to depend on the excitation power density [34], as mentioned previously, and thus the RT-IQE of both structures were investigated as a function of excitation power density. To do this the structures were excited as a function of both excitation power density and temperature. The integrated intensity per unit excitation power (II/P) was calculated as a function of power density and temperature for the Q2T and 2T structure and the results are shown in Figures 4.8 and 4.9 respectively.

![Figure 4.8: Integrated intensity per unit excitation power for the Q2T structure as a function of excitation power density and temperature.](image)

Over the excitation power density range used for both structures, the II/P is observed to be constant with excitation power at 12 K. For both structures, the II/P is observed to decrease as the temperature is increased from 12 K; with a larger decrease in II/P observed for lower excitation power densities. Thus the RT-IQE of both structures are increasing with increasing power density for the power range used. This behaviour is typical of InGaN/GaN QWs at low carrier densities and is attributed to the saturation of non-radiative centres [48, 49]. The RT-IQE values for both structures were calculated using the II/P values as a function of temperature.
4.3 Results and Discussion

Figure 4.9: Integrated intensity per unit excitation power for the 2T structure as a function of excitation power density and temperature.

at a constant excitation power density. The RT-IQE of the Q2T structure varied from 6 ± 2 to 23 ± 3 % with a variation of excitation power density from 0.2 to 9 Wcm⁻², whereas that of the 2T structure varied from 32 ± 5 to 56 ± 8 % with a varying excitation power density of 0.5 to 22 Wcm⁻². Thus over the power density range used, the 2T structure is more efficient than the Q2T structure. These results are consistent with the observations made by Pendlebury et al. [20] and Ishikawa et al. [25] at low power densities when comparing structures with and without QW caps. Pendlebury et al. attribute the reduction in PL intensity to an increase in the defect density in the GaN barriers which are grown at sub-optimal temperatures. This leads to an increase in the non-radiative recombination rate and a decrease in RT-IQE.

The RT-IQE depends on both the radiative and non-radiative rate, hence the larger RT-IQE of the 2T structure could be due to a change in one or both of these rates. An increase in the radiative rate would result in an increase in the RT-IQE. Furthermore a decrease in the non-radiative rate would also result in an increase of the RT-IQE. To investigate this further, initially the radiative rate of both structures were compared. To do this the 12 K PL decay times were compared. At 12 K, the recombination of carriers is assumed to be 100 % radiative and thus the radiative
4.3 Results and Discussion

decay time can be directly extracted.

4.3.3 12 K PL Decay Time Measurements

The 12 K PL time decay measurements were performed on both structures with an excitation energy of 3.179 eV (below the GaN bandgap energy), at a repetition rate of 398950 Hz and a peak power density which varied from 7 to 270 MWcm$^{-2}$pulse$^{-1}$. The decay transients at various detection energies across the PL linewidth at peak power density of 7 MWcm$^{-2}$pulse$^{-1}$ for the Q2T and 2T structure are shown in Figures 4.10 and 4.11 respectively. The decay transients of both structures exhibit non-exponential behaviour typical of InGaN/GaN QWs, this is discussed in detail in Section 2.6. The PL decay transients can therefore not be described by a single decay constant. Typically the decay time, $\tau_{\text{PL}}$, is described by the time taken for the number of counts to drop to 1/10 of its maximum value, which is used as a guide to the decay time.

Figure 4.10: Decay transients at various detection energies across the PL spectrum at 12 K for the Q2T structure excited with a power density of 7 MWcm$^{-2}$pulse$^{-1}$.

The decay time for both structures as a function of detection energy and excitation power are shown in Figure 4.12. Note the figure only shows the minimum and maximum excitation power densities as the PL decay time does not change within
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Figure 4.11: Decay transients at various detection energies across the PL spectrum at 12 K for the 2T structure excited with a power density of 7 MWcm$^{-2}$ pulse$^{-1}$.

the error over the excitation power range used. The decay time is measured to generally increase with decreasing detection energy as expected of InGaN/GaN QWs. This increase is attributed to the detection of photons which originate from areas of higher indium content, that have a larger piezoelectric field. The increased electric field acts to further separate the electrons and holes along the c-axis, resulting in a reduced wavefunction overlap and increased decay time. At some of the lowest detection energies, the decay time is observed to decrease with decreasing excitation energy. This behaviour is due to the detection of photons from the LO phonon replica, which has been reported by Graham et al. [36].

The PL decay time is measured to be constant at any given excitation energy over the power density range used. These results correlate with the constant efficiency of the QW at 12 K for both structures measured in Section 4.3.2.

The decay times for the 2T are generally lower at the same detection energy than the Q2T structure. Thus the radiative rate of the 2T structure is larger than that of the Q2T structure by around a factor of 2. The increased radiative rate of the 2T structure allows it to compete with non-radiative processes to a higher degree, which results in an increased RT-IQE for the 2T structure; as measured in Section 4.3.2.

The improved radiative rate of the 2T structure is partly consistent with the around
4.3 Results and Discussion

Figure 4.12: $\tau_{100}$ PL decay time at 12 K as a function of detection energy and excitation power density for the Q2T and 2T structures.

10\% increase in wavefunction overlap for the 2T structure compared with the Q2T structure simulated by Massabuau et al. [29]. The increase in wavefunction overlap was attributed to the reduction in indium incorporation in the GaN barrier grown after the InGaN QW. The improved radiative rate of the 2T structure could also be due to the presence of GWWFs. Several authors [50, 51] have shown that on decreasing the well width, the radiative rate is observed to increase. The authors attribute this increase, to a reduction in electron hole pair separation along the c-axis. The electric field over the QW acts to force mainly the electron wavefunction to the upper rough interface of the QW and only slightly affects the hole wavefunction which is tightly bound around local indium fluctuations. Therefore a reduction in the well width results in an increase in wavefunction overlap of the electrons and holes along the c-axis and hence an increase in the radiative rate.

4.3.4 Non-Radiative Recombination Model

The radiative rate of the 2T structure has been shown to be larger at 12 K and may in part explain the increased RT-IQE in comparison to the Q2T. The RT-IQE also depends on the non-radiative rate. To investigate the thermal activation of non-radiative recombination further, the temperature and power density dependent
data in Section 4.3.2 was analysed using an Arrhenius model fit described by Leroux et al. [44].

This simple model describes a two level system in which, the presence of defects result in deformations to the band structure [52, 53]. These deformations to the band structure with the addition of localisation effects create a potential barrier, $\Delta E$; which localised carriers need to overcome to recombine non-radiatively at defects as shown in Figure 4.13. The potential barrier includes an average localisation energy of the carrier. All excited carriers are assumed to be captured into the QWs and recombine either radiatively in the QW or non-radiatively at a non-radiative site.

![Figure 4.13: Schematic of the thermal activation of non-radiative recombination model.](image)

The PL emission efficiency, $\eta$ is given by Equation (4.1),

$$\eta = \frac{P_R}{P_R + P_{NR}}$$  \hspace{1cm} (4.1)

where $P_{R/NR}$ is the probability of radiative/non-radiative recombination. $P_{NR}$ is temperature dependent and calculated using Equation (4.2),

$$P_{NR} = P_{NR0} \exp \left( \frac{-\Delta E}{k_B T} \right)$$  \hspace{1cm} (4.2)

where $P_{NR0}$ is a coefficient independent of temperature. $P_{NR0}$ is assumed to be proportional to the density of non-radiative centres and constant for a given ex-
4.3 Results and Discussion

citation power density. In this simple model, the radiative rate is assumed to be independent of temperature and recombination energy. Substituting Equation (4.2) into Equation (4.1), the temperature dependence of the PL emission efficiency can be calculated using Equation (4.3),

\[ \eta(T) = \frac{1}{1 + Ce^{\frac{\Delta E}{k_BT}}} \]  

(4.3)

where \( C = \frac{P_{NR}}{P_R} \). Assuming the efficiency at 12 K is 100 %, Equation (4.3) can be written in terms of the \( \frac{I}{P} \) and can be calculated using Equation (4.4).

\[ \frac{I}{P}(T) = \frac{\frac{I}{P}(12 \text{ K})}{1 + Ce^{\frac{\Delta E}{k_BT}}} \]  

(4.4)

The \( \frac{I}{P} \) as a function of temperature was analysed using a fit to the model for both structures. The fit was used to extract values of \( \Delta E \) and \( C \) as a function of power density. Fits of the model to the \( \frac{I}{P} \) at a power density of 0.6 Wcm\(^{-2} \) for the Q2T and 2T structures are shown in Figures 4.14 and 4.15 respectively. A reasonable fit to the model was achieved for the Q2T structure with a reduced chi squared, \( \chi_{RED}^2 \) of 1.8 using the following fitting parameters: \( \frac{I}{P}(12 \text{ K}) \) of 304 ± 17 a.u., \( \Delta E \) of 30 ± 2 meV and a \( C \) of 31 ± 5. A good fit to the model was achieved for the 2T structure with a \( \chi_{RED}^2 \) of 1.0 using the following fitting parameters: \( \frac{I}{P}(12 \text{ K}) \) of 132 ± 4 a.u., \( \Delta E \) of 44 ± 7 meV and a \( C \) of 9 ± 3. The rest of the fitting of the \( \frac{I}{P} \) data can be found in Appendix A.1. The extracted values of \( \Delta E \) and \( C \) as a function of power density for both structures are plotted in Figures 4.16 and 4.17 respectively.

\( \Delta E \) is observed to reduce from 31.4(±2.5) to 21.5(±2.8) meV on increasing the power density from 0.2 to 9 Wcm\(^{-2} \) for the Q2T structure. Whereas it reduces from 45.0(±7.7) to 29.9(±4.4) meV on increasing the power density from 0.5 to 22 Wcm\(^{-2} \) for the 2T structure. This corresponds to a reduction of 9.9(±5.3) and 15.1(±12.1) meV for the Q2T and 2T structures respectively. Therefore within the error of the experiment, \( \Delta E \) hardly varies with power density. \( \Delta E \) is observed to be \( \sim 10 \) meV larger for the 2T than the Q2T structure over a power density range of 0.5 to 9 Wcm\(^{-2} \). The increase in activation energy between the Q2T to the 2T structure, in this simple model would be equivalent to an increase in the average localisation energy and/or the energy barrier to reach the non-radiative centre.

The localisation energy of the electrons as previously mentioned is estimated to
4.3 Results and Discussion

Figure 4.14: Fit of the thermal activation of non-radiative recombination model (red line) to the II/P as a function of temperature, for the Q2T structure at an excitation power density of 0.6 Wcm$^{-2}$.

be around 10 meV independent of indium composition for a constant well width. Furthermore, the electron localisation due to monolayer fluctuations in well width is also estimated to be around 10 meV. Whereas, the localisation energy of the holes is around $\sim$ 40 meV due to inter-well variations in indium composition for a In$_{0.16}$Ga$_{0.84}$N/GaN QW\textsuperscript{40}. Therefore at room temperature (i.e. $k_B T \approx 26$ meV), the majority of the electrons are expected to be delocalised. Whereas, the majority of the holes are expected to be localised. Hence the electrons are anticipated to be most susceptible to non-radiative recombination. Thus, it is expected that a possible increase in localisation energy would be attributed to the electrons. Though the localisation energy of the electrons is determined by the local region that the electron experiences. The InGaN QW strips of the 2T structure have large fluctuations in width over 10’s to 100’s of nanometres\textsuperscript{18}. On the local scale of the electrons $\sim$ 10 nm, both the 2T and the Q2T structure are susceptible to monolayer fluctuations. Thus it is believed that the localisation energy of the electrons are the same in both the Q2T and 2T structures.

An increase in energy barrier to reach the non-radiative centre could be due to the energy barrier created by the GWWFs of the 2T structure. The QW width
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**Figure 4.15**: Fit of the thermal activation of non-radiative recombination model (red line) to the II/P as a function of temperature, for the 2T structure at an excitation power density of 0.6 Wcm\(^{-2}\).

**Figure 4.16**: Activation energy as a function of power density for both structures.
in 2T grown structures can vary significantly from 0 to 100 % width. These large variations in QW width lead to large fluctuations in potential in the plane of the QW. This would create a broad scale potential barrier which inhibits the diffusion of electrons in the plane of the QW. The effect of QW interface roughness on the diffusion length of carriers has been modelled using a Monte Carlo simulation by Lu et al. [54]. The authors report a reduction in carrier diffusion with an increase in QW interface roughness. This leads to a slight improvement of the IQE due to the reduced probability of non-radiative recombination. Thus the activation energy may be slightly larger in the 2T compared to the Q2T structure due to the broad scale potential barrier created by the GWWFs.

$C$ is observed to reduce from $56.4(\pm 9.0)$ to $6.6(\pm 1.0)$ on increasing the power density from 0.2 to 9 Wcm$^{-2}$ for the Q2T structure. Whereas it reduces from $9.8(\pm 3.4)$ to $2.1(\pm 0.4)$ meV on increasing the power density from 0.5 to 22 Wcm$^{-2}$ for the 2T structure. $C$ is observed to be larger for the Q2T compared to the 2T structure over an equivalent power range. The decrease in $C$ with increasing power density could be due to a reduction in the coefficient of non-radiative recombination or an increase in the radiative rate and a combination of the two. A reduction in the probability of non-radiative recombination can occur due to the saturation of

**Figure 4.17:** $C$ as a function of excitation power density for both structures.
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non-radiative pathways on increasing the power density. Saturation occurs due to the fact that non-radiative centres have a finite density and long lifetimes \[55\]. An increase in the radiative rate can occur on increasing the power density due to free carrier screening of the electric field resulting in an increase in the wavefunction overlap \[56\]. Though no evidence of free carrier screening was observed as the efficiency of both structures are constant at 12 K over the power range used. Hence the reduction in \(C\) with increasing power density is attributed to the saturation of non-radiative pathways.

The larger extracted value of \(C\) for the \(Q2T\) structure could be due to the difference in radiative rate, with the \(2T\) structure having a radiative rate around a factor of 2 larger than the \(Q2T\) which was determined in Section 4.3.3. The coefficient of non-radiative recombination which is assumed to be proportional to the number of defects, maybe larger in the \(Q2T\) structure due to the sub-optimal growth temperatures of the GaN barriers which results in larger defect densities compared to optimal growth temperatures. Furthermore the exposure of the \(QW\) to a temperature ramp in the \(2T\) growth process may anneal out defects in the \(QW\) which act as non-radiative recombination centres. Thermal anneal processes have been shown \[57, 58\] to reduce the defect density of GaN films. This reduction in defect density was based on the dramatic reduction in yellow luminescence of the films, which arise from native defects and complexes with carbon and hydrogen impurities in GaN. The YL band is discussed in more detail in Section 2.3.2.1.

The difference in RT-IQE between the \(Q2T\) and \(2T\) structures is mainly determined by the difference in \(C\). Thus the speculated difference in defect density was further investigated. Initially the effect of the sub-optimal GaN barriers of the \(Q2T\) structure on the RT-IQE was investigated. To do this, the ratio of the integrated intensity of the YL band to QW emission was compared at room temperature as a function of power density. The ratio of the emission components has widely been used as an approximation of the relative defect densities in GaN by several authors \[5, 55, 59\].

4.3.5 Comparison of the YL Emission to the QW

The \(PL\) measurements were performed on both structures using a pulsed frequency doubled Ti:Sapphire laser with a photon energy of 3.179 eV at a repetition rate of 398950 Hz. The excitation energy is below the GaN bandgap, which excites the QWs more strongly than the GaN barriers. A pulsed laser was used so that \(PL\) decay time
measurements could be taken simultaneously with the PL measurements. The room
temperature time integrated PL spectra for the Q2T and 2T structures as a function
of excitation power density are shown in Figures 4.18 and 4.19 respectively.

**Figure 4.18:** PL spectra for the Q2T structure as a function of excitation power
density at room temperature.

Both structures have QW peak emission energies around 2.7 eV and a broad
yellow luminescence band centred around 2.2 eV. The QW and YL emission for the
Q2T and 2T structures have been integrated and plotted as a function of power
density in Figures 4.20 and 4.21 respectively.

The integrated PL intensity of the QW and YL band are observed to increase on
increasing the power density for both structures. The integrated intensity of the QW
and YL band were fitted (green line) using a power law dependence \[60\] given by
Equation (2.35). The integrated PL intensity of the QW increases super-linearly with
increasing excitation power density for both structures, therefore the overall efficiency
of the QW is increasing. A super-linear increase suggests that the recombination is
dominated by non-radiative recombination \([61, 62]\). The exponent in Equation (2.35)
for the QW emission of the Q2T structure (1.60 ± 0.02) is larger than the exponent
of the 2T structure (1.25 ± 0.01), suggesting that the non-radiative component is
more dominant in the Q2T structure; consistent with the RT-IQE measurements
in Section 4.3.2. The integrated PL intensity of the YL increases sub-linearly with
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**Figure 4.19:** PL spectra for the 2T structure as a function of excitation power density at room temperature.

**Figure 4.20:** Integrated PL intensity for the Q2T structure as a function of excitation power density at room temperature. The green line denotes linear fits to both the QW and YL PL integrated intensity.
4.3 Results and Discussion

Figure 4.21: Integrated PL intensity for the 2T structure as a function of excitation power density at room temperature. The green line denotes linear fits to both the QW and YL PL integrated intensity.

Increasing excitation power density for both structures. Therefore the YL is becoming saturated due to the finite density of defects associated with it. The ratio of the integrated PL intensity of the YL to the QW emission is plotted in Figure 4.22.

The ratio of the integrated PL intensity of the YL to the QW is observed to be generally much larger in the Q2T than the 2T structure with increasing excitation power density. At the lowest excitation power density 3 MW cm$^{-2}$ pulse$^{-1}$, the QW and YL have the same integrated PL intensity for the Q2T structure whereas the YL is 5(±3) % of the QW emission for the 2T structure. At the highest excitation power density $\sim$ 400 MW cm$^{-2}$ pulse$^{-1}$, the ratio of the integrated PL intensities of the YL compared to the QW are around 1 % for both structures. This suggests that the YL band is a significant emission component in both structures and more significant in the Q2T structure.

The structures are excited below the GaN bandgap energy, under these excitation conditions the QWs are more strongly excited over the GaN barriers; given the large difference in absorption coefficients between GaN (1 $\times$ 10$^3$ cm$^{-1}$ to 4 $\times$ 10$^4$ cm$^{-1}$) and InGaN QWs (1 $\times$ 10$^5$ cm$^{-1}$) at $\sim$ 3.18 eV. The YL band can be directly excited through the excitation of defect states in the GaN barriers,
4.3 Results and Discussion

Figure 4.22: Ratio of the integrated PL intensity of the YL to the QW for both structures as a function of excitation power density at room temperature.

though the strength of the absorption is relatively weak compared to the absorption into the QWs. Therefore to have a significant emission from the YL band which originates from defects in the GaN barriers, a significant amount of carriers must transfer from the QW to the GaN barriers.

4.3.5.1 Carrier Transfer

Several authors [67–69] have observed direct experimental evidence of carrier loss from QWs. The escape of carriers from the QW can occur via 2 main mechanisms, which are thermionic emission [70, 71] and quantum tunnelling [68, 72].

Thermionic emission is the process where carriers are thermally ejected from the QW to the barrier. Carriers have a finite probability given by the Fermi-Dirac distribution to occupy an energy state higher than the potential barrier. Carriers ejected into the barrier can then be recaptured by the same or a different QW; or occupy states in the barrier. Carriers in the barrier can then relax into defect states e.g. those associated with the YL band. These carriers can then recombine to emit YL. The importance of thermionic emission on the optical properties of InGaN/GaN QW has been reported by Hurst et al. [70]. They modelled the effects of thermionic
emission on the PL decay time using rate equations on a series of structures with varying numbers of QWs. A reasonable agreement was found between the model and the experimental data, thus leading the authors to conclude that thermionic emission was a significant loss process for holes.

Quantum tunnelling is the process of carrier transport through a potential barrier. The lowest confined electron and hole wavefunctions in an InGaN/GaN QW can penetrate into the barrier regions [29, 32]. Therefore the carrier wavefunctions can have a considerable overlap with defect states in the GaN barrier; leading to quantum tunnelling of carriers into defect states [31, 68, 72]. Carriers occupying defect states associated with the YL band can then recombine to emit YL. Thermally assisted tunnelling can also occur, which is the tunnelling of higher order states of the QW. At elevated temperatures, the occupation of the higher order confined states is increased. These higher order states can have significantly increased wavefunction extent in the GaN barriers and even into adjacent QW compared to the lowest confined states [32]. Thus the wavefunction overlap of the higher order states with defects can be even larger than the lowest confined state.

Radiative recombination in the QW requires both electrons and holes, thus the loss of one or both of these carrier species from the QW is equivalent to a non-radiative process. Thus, the transfer of carriers to the GaN barriers is a non-radiative process of the QW and must affect the decay rate of carriers which depend on both the radiative and non-radiative rate. The transfer of carriers is expected to be most significant for the electrons at room temperature, as they are less localised compared to the holes as discussed previously. To investigate the transfer of carriers further, the PL decay transients of the structures were measured at room temperature as a function of excitation power density. The decay transients for the Q2T and 2T structures are shown in Figures 4.23 and 4.24 respectively.

The Q2T structure at an excitation power density of 3 MWcm\(^{-2}\) pulse\(^{-1}\), exhibits a non-exponential form with what appears to be a two decay component behaviour with a fast and slow decay. The initial fast decay appears to become slower with increasing excitation power density, whereas the slow decay becomes faster. The 2T structure appears to have a non-exponential form also and does not vary much with excitation power density. The extracted \(\tau_{1/10}\) \(\text{PL}\) decay times at the QW peak energy as a function of power density for the two structures are plotted in Figure 4.25.

The \(\tau_{10}\) decay time of the 2T structure was measured to increase slightly from 48(±3) to 57(±3) ns over an excitation range of 7 to 270 MWcm\(^{-2}\) pulse\(^{-1}\).
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Figure 4.23: Decay transients at the QW peak energy as a function of excitation power density at room temperature for the Q2T structure.

Figure 4.24: Decay transients at the QW peak energy as a function of excitation power density at room temperature for the 2T structure.

Whereas for the the Q2T structure, it was measured to increase dramatically from 23(±2) to 80(±5) ns over an excitation range of 3 to 458 MWcm$^{-2}$pulse$^{-1}$. Above
4.3 Results and Discussion

Figure 4.25: $\tau_{1/10}$ PL decay times at the QW peak energy as a function of excitation power density for the Q2T and 2T structures at room temperature.

100 MW/cm$^2$ pulse$^{-1}$, the decay time of the Q2T structure is observed to be constant around 80 ns. This reflects the saturation of the YL band on increasing the power density due to the finite density of the defect states associated with the YL band. Therefore the increase in decay time is due to the saturation of the YL band and an increase in the non-radiative decay time.

4.3.5.2 Competition Between the QW and the YL Band

Given the YL band is a significant emission component in both structures, it suggests the transfer of carriers to defects associated with the YL band is significant. On increasing the power density, the defects associated with the YL band become saturated due to their very long recombination time of several microseconds as shown in Figure 4.26. Similar saturation effects have been observed for GaN by Grieshaber et al. [60].

The saturation of the YL band results in less carriers being transferred into the GaN barriers as the defect states become filled. Moreover, more carriers being recaptured into the QWs after being transferred into the GaN barriers as they are less likely to occupy the defect states, if a larger proportion of the defect states are
filled. This results in a decrease in the non-radiative rate which correlates with the increase in decay time of the QW with increasing power density. Furthermore, it correlates with the increase in the efficiency of the QW on increasing the power density. Therefore the reduced defect density of the GaN barriers in the 2T growth methodology, results in less carriers being transferred to defect states in the barriers and a larger RT-IQE compared to the Q2T structure.

Figure 4.26: Decay transients as a function of excitation power density at room temperature for the YL band of the Q2T structure at a detection energy of 2.206 eV.
4.4 Summary

The effects of including a low temperature QW cap on the properties of InGaN/GaN QW structures were investigated under low excitation conditions (i.e. below efficiency droop). Two 10 period polar In$_{0.16}$Ga$_{0.84}$N (2.5 nm)/GaN (7.5 nm) QW structures were investigated, with one grown using the 2T growth methodology and the other Q2T. The Q2T structure with the QW cap was observed to have a reduction in well width fluctuations, with no GWWFs.

The RT-IQE of the 2T structure was measured to be larger than the Q2T structure for power densities less than 20 Wcm$^{-2}$. The larger RT-IQE was attributed to an increase in the radiative rate and a reduction in competition between the QW and defects mainly in the GaN barriers. The increase in radiative rate was ascribed partly to the reduction of indium incorporation into the GaN barrier grown after the InGaN QW, which results in an increase in the wavefunction overlap. The increase in radiative rate was also speculated to be due to the reduction in the well width of the QW, resulting in an increase in the wavefunction overlap. A reduction in the competition between the QW and defects mainly in the GaN barriers was determined from the reduction in the ratio of the integrated PL intensity of the YL band to QW for the 2T structure. This reduction in competition was ascribed to, firstly the reduction of defects in the QW due to the thermal anneal process in the 2T growth methodology. Moreover, the reduction in defect density in the GaN barriers due to the optimal growth temperature of the barriers in the 2T growth methodology. Secondly, due to the increase in radiative rate of the QW allowing the QW to compete to a higher degree with the transfer of carriers to the GaN barriers. Thirdly, due to an increase in the thermal activation energy of non-radiative recombination of the QW, which results in less carriers thermally lost to non-radiative centres mainly in the GaN barriers. This increase in thermal activation energy was assigned to an increase in the potential barrier to the reach the non-radiative centre caused by the presence of GWWFs.
4.5 References


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The Effects of Gross Well Width Fluctuations and Barrier Growth Temperature

5.1 Introduction

In Chapter 4, it was determined that the RT-IQE of the InGaN/GaN QW structure grown by a 2T growth methodology was significantly larger than the equivalent Q2T grown structure for power densities less than 20 Wcm$^{-2}$. This increase in RT-IQE was ascribed to several factors. The increase in RT-IQE was in part ascribed to an increase in the radiative rate for the 2T structure, determined from the difference in 12 K $\tau_{1/10}$ PL decay time where the decay of carriers is assumed to be 100% radiative. This increase in radiative rate was assigned in part to the effects of the reduction in the incorporation of indium in the GaN barrier grown after the QW which has been shown by Massabuau et al. [1] to result in an increase in the wavefunction overlap. Furthermore, GWWFs were speculated to result in an increase in the wavefunction overlap along the growth direction of the QW due to the reduced QW width and increased confinement.

The increase in RT-IQE was also attributed to a reduction in the competition between the QW and defects, mainly in the GaN barriers. This reduction in competition was ascribed to a reduction in defect density within the QW due to the thermal anneal process in the 2T growth methodology. Moreover, the competition between the QW and defects was further increased due to a reduction in the density of defects in the GaN barriers due to the optimal growth temperature of the barriers. The increase in radiative rate of the QW was also believed to allow the QW to compete to a higher degree with the capture of carriers at non-radiative centres mainly in the GaN barriers. Furthermore, the RT-IQE was also further increased...
due to an increase in the thermal activation energy of non-radiative recombination of the QW, which results in less carriers thermally lost to non-radiative centres mainly in the GaN barriers. This increase was attributed to an increase in the energy barrier to reach the non-radiative centre created by a broad scale potential caused by the GWWFs.

In this chapter, the effects of defect density in the GaN barriers and GWWFs on InGaN/GaN QWs are investigated independently, to determine which effect dominates the RT-IQE of InGaN/GaN QWs. To do this equivalent pairs of structures are grown with and without GWWFs. Each pair of structures has one structure grown using the optimal GaN barrier growth temperature and the other sub-optimal. For the pair of structures without GWWFs, a comparison is made between 1T and Q2T growth methodologies, where the majority of the GaN barrier is grown at high temperature. For the pair with GWWFs, a comparison between structures grown using a T-bounced and 2T growth methodology are made. The T-bounced growth methodology is very similar to the 1T method except the growth is paused after the QW and the temperature is ramped up to around the optimal growth temperature of the barrier. Following that the temperature is lowered to the QW growth temperature for the growth of the barrier. The exposure of the QW to the temperature ramp results in the formation of GWWFs and the barriers are grown at sub-optimal temperatures.
5.2 Sample Details and Structural Properties

Four 10 period polar In$_{0.16}$Ga$_{0.84}$N (2.5 nm)/GaN (7.3 nm) QW structures were grown in a Thomas Swan 6 × 2 in showerhead reactor by MOVPE. The structures were grown on low defect density c-plane sapphire/GaN pseudo-substrates with a nominal 0.25° miscut toward (1120). Each structure was grown using either a 1T, Q2T, 2T or T-bounced methodology. For the 1T structure, the QW and GaN barrier were grown continuously with no growth pause, at a constant temperature of 756 °C. For the Q2T sample, directly following the growth of the QW at 756 °C, a ∼ 1 nm GaN QW cap was grown. Afterwards the temperature was ramped up to 860 °C during which growth continued and then the rest of the barrier was grown. For the T-bounced sample, following the growth of the QW at 756 °C, growth was paused and the temperature was ramped up to 803 °C. The temperature was then lowered to the QW growth temperature for the growth of the GaN barrier. For the 2T sample, to compensate for any loss of indium during the temperature ramp, the QW was grown at 725 °C. The growth was then paused and the temperature was ramped up to a maximum of 860 °C. The growth of the GaN barrier began just before the maximum temperature was reached, for which the rest of the GaN was grown.

STEM-HAADF images produced by Cambridge University of the structures are shown in Figure 5.1. The 1T and Q2T structures are observed to have smooth continuous wells, whereas the T-bounced and 2T structures are subject to GWWFs as expected. To note, though the Q2T and 1T structures have smooth continuous wells, they still exhibit one or two monolayer well width fluctuations. The GWWFs of the T-bounced and 2T structures were analysed by Cambridge University to determine their dimensions. The average width of the trough regions defined as the distance over which the QW is half the maximum QW width, were measured to be 54(±4) nm and 31(±2) nm for the T-bounced and 2T structure respectively. The distance between trough regions was measured for the 2T structure to be 80(±5) nm. The average width of the QWs for the T-bounced and 2T structures was determined to be reduced by a factor of around 1.4 to 1.7 due to the GWWFs. Thus leading to a reduction in the volume of InGaN layers for the structures with GWWFs, which were determined to have a volume of around 60 to 70 % of those with continuous wells.

The sample details are summarised in Table 5.1 where the well and barrier thickness, repeat distance (QW and barrier) and the average indium content were
5.2 Sample Details and Structural Properties

Figure 5.1: STEM-HAADF images taken along the $\langle 11 \overline{2} 0 \rangle$ zone axis for the (a) 1T, (b) Q2T, (c) T-Bounced and (d) 2T structures.

determined by XRD at the University of Cambridge. The GWWFs in the 2T and T-bounced structure, unfortunately hinder the determination of their properties by XRD. Though the repeat distance was determined for both structures.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Growth method</th>
<th>QW thickness (nm)</th>
<th>Barrier thickness (nm)</th>
<th>Repeat distance (nm)</th>
<th>Average indium content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5249C</td>
<td>1T</td>
<td>2.6 ± 0.1</td>
<td>7.1 ± 0.1</td>
<td>9.7 ± 0.1</td>
<td>19 ± 1</td>
</tr>
<tr>
<td>C5244C</td>
<td>Q2T</td>
<td>2.4 ± 0.1</td>
<td>7.4 ± 0.1</td>
<td>9.8 ± 0.1</td>
<td>17 ± 1</td>
</tr>
<tr>
<td>C5246C</td>
<td>T-bounced</td>
<td>-</td>
<td>-</td>
<td>9.4 ± 0.2</td>
<td>-</td>
</tr>
<tr>
<td>C5248D</td>
<td>2T</td>
<td>-</td>
<td>-</td>
<td>9.5 ± 0.1</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5.1: Summary of sample details.
5.3 Results and Discussion

A series of experiments were performed to compare the optical properties of the structures, which include PL spectroscopy and PL decay time measurements as a function of both temperature and excitation power density.

5.3.1 RT-IQE Comparison

Initially the samples were compared via temperature dependent PL measurements performed at a constant excitation power density to determine their RT-IQE. The structures were excited at low power density using a power density of 6 W cm$^{-2}$ with a CW HeCd laser of photon energy 3.815 eV. The normalised 12 K PL spectra for the structures are shown in Figure 5.2.

![Figure 5.2: Normalised 12 K PL spectra for the 1T, Q2T, T-Bounced and 2T sample structures.](image)

The LO phonon replica of the QW can be observed clearly for the 1T and Q2T structures, spaced at around 91 meV below the main emission peak. The LO phonon replica of the T-bounced and 2T structure are not seen due to the large FWHM of the spectra. The other oscillations in the PL spectra mainly observed in the structures with GWWFs are due to the Fabry Pérot etalon interference, which are spaced by
Results and Discussion

The peak energies and FWHM for the structures at 12 K were measured and are summarised in Table 5.2. The samples observed to have GWWFs have spectra with larger FWHMs at 12 K compared to those without. The T-bounced and 2T structures will be subject to the linewidth broadening mechanisms due to the GWWFs as discussed in Section 4.3.1. The GWWFs are expected to result in a larger variation in the confined electron energy and the QCSE, resulting in a larger FWHM. Furthermore, the average indium composition across the InGaN QW strips created in the growth methodologies with GWWFs has been shown to vary significantly. This variation is expected to result in a broadening of the distribution of local indium fractions, resulting in a broadening of the FWHM of the PL spectra of the structures with GWWFs.

The temperature dependent PL spectra, measured between 12 and 300 K, for the 1T, Q2T, T-bounced and 2T structures are shown in Figures 5.3, 5.4, 5.5 and 5.6 respectively.

Figure 5.3: PL spectra for the 1T structure as a function of temperature, ranging from 10 to 300 K. The spectra are offset for clarity.

The PL intensity for each structure has been integrated and the integrated PL intensity is shown as a function of temperature in Figure 5.7, with the 10 K value being normalised to 1 for comparison. The integrated PL intensity is observed to decrease as a function of temperature, with the rate of decrease being larger for...
5.3 Results and Discussion

Figure 5.4: PL spectra for the Q2T structure as a function of temperature, ranging from 10 to 300 K. The spectra are offset for clarity.

Figure 5.5: PL spectra for the T-bounced structure as a function of temperature, ranging from 10 to 300 K. The spectra are offset for clarity.
the structures without GWWFs. The RT-IQE of the 1T, Q2T, T-bounced and 2T structures are 25(±2) %, 12(±2) %, 35(±3) % and 45(±4) % respectively. The structures with GWWFs have larger RT-IQEs than those without. The 2T structure has a larger RT-IQE than the T-bounced structure as expected from the optimal barrier growth temperature. Though the 1T structure has a larger RT-IQE than the Q2T, which is the opposite of what is expected from the barrier growth temperature. Thus the results in terms of barrier growth temperature are conflicting.

The peak PL emission energy and FWHM at 12 K, along with the RT-IQE at ∼ 6 Wcm⁻² for the structures in Chapters 4 and 5 are summarised in Table 5.2 for comparative purposes. Generally samples with GWWFs have a larger FWHMs and RT-IQE. The peak PL emission energy and the FWHM of the two sets of Q2T and 2T samples cannot be compared as both the peak energy and FWHM of the structures depend on the specific area of the sample which is excited. The RT-IQE of the Q2T structures are different between sample sets. This difference may arise from differences in impurity incorporation and related defect density during growth. However, the RT-IQE of the 2T samples are the same within the error. Further work on a series of Q2T and 2T samples is needed to determine their typical RT-IQE at a given excitation power density.
### 5.3 Results and Discussion

#### Table 5.2: Summary of the PL peak emission energy and FWHM for the structures, along with their RT-IQEs at a power density of $\sim 6 \text{ Wcm}^{-2}$.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Growth method</th>
<th>Peak emission energy at 12 K (eV)</th>
<th>Full width at half maximum at 12 K (meV)</th>
<th>Room temperature IQE at $\sim 6 \text{ Wcm}^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5249C</td>
<td>1T</td>
<td>2.796±0.001</td>
<td>61±3</td>
<td>25±2</td>
</tr>
<tr>
<td>C5244C</td>
<td>Q2T</td>
<td>2.771±0.001</td>
<td>77±3</td>
<td>12±2</td>
</tr>
<tr>
<td>C4815A</td>
<td>Q2T (Chap. 4)</td>
<td>2.749±0.001</td>
<td>97±6</td>
<td>21±4</td>
</tr>
<tr>
<td>C5246C</td>
<td>T-Bounced</td>
<td>2.751±0.001</td>
<td>105±6</td>
<td>35±3</td>
</tr>
<tr>
<td>C5248D</td>
<td>2T</td>
<td>2.768±0.001</td>
<td>108±8</td>
<td>45±4</td>
</tr>
<tr>
<td>C4825A</td>
<td>2T (Chap. 4)</td>
<td>2.719±0.001</td>
<td>157±8</td>
<td>48±7</td>
</tr>
</tbody>
</table>

#### Figure 5.7: Comparison of the normalised integrated PL intensity for the structures; as a function of temperature, ranging from 10 to 300 K. The 10 K value has been normalised to 1 for each structure, for comparison purposes.

The PL peak emission energy shift from the 12 K value was determined as a function of temperature for each structure and a comparison is shown in Figure 5.8, with corrections being made for the temperature dependent shift in the bandgap energy using the Varshni equation (Equation 2.2). The Varshni parameters for
5.3 Results and Discussion

each structure were obtained by a linear interpolation between GaN and InN, using an indium content of 19 % for the $\text{1T}$ structure and 17 % for the others. The $\alpha$ and $\beta$ parameters used were 0.783 meVK$^{-1}$ and 791 K for the $\text{1T}$ structure respectively. The $\alpha$ and $\beta$ parameters used for the other structures were 0.796 meVK$^{-1}$ and 795 K respectively. All structures are observed to follow the well known "S"-shape temperature dependence of the PL peak energy. The initial redshifts are measured to be 8($\pm$2), 12($\pm$2), 7($\pm$2) and 6($\pm$2) meV for the $\text{1T}$, $\text{Q2T}$, T-Bounced and 2T structure respectively. The corresponding blue shifts were measured to be 57($\pm$6), 59($\pm$6), 46($\pm$6) and 50($\pm$6) meV respectively. The “S”-shape behaviour of the $\text{1T}$ and $\text{Q2T}$ structure can be directly compared as the FWHM is narrow enough not to mask the behaviour as with the T-bounced and 2T structures. The redshift and blueshift of the two structures are the same within error. Furthermore, the maximum redshift for the $\text{1T}$ and $\text{Q2T}$ structures occurs at 50($\pm$10) K and 60($\pm$10) K respectively. The temperature at which the maximum redshift occurs has been modelled by Rubel et al. $^2$ to be related to the distribution of localised states given by Equation (2.34). The maximum redshift was modelled to occur at a temperature given by $(0.6 - 0.8)E_0/k_B$, where $E_0$ is some characteristic energy scale related to the width of the localised states. Therefore the results suggest that the width of the distribution of localised electron and hole states of $\text{1T}$ and $\text{Q2T}$ structures are similar.
5.3 Results and Discussion

Figure 5.8: Measured PL peak emission energy shift from its position at 12 K as a function of temperature for each structure after correction for the temperature dependent shift in the bandgap.

5.3.2 Power Dependent Efficiency Comparison

As stated previously, the RT-IQE of InGaN/GaN QW structures depends on the excitation power density. Thus to fully compare the structures, power dependent PL measurements were performed at room temperature. The II/P was calculated as a function of excitation power density for each structure and are plotted in Figure 5.9.

The II/P for each structure has been corrected using the RT-IQE at 6 Wcm$^{-2}$ calculated previously, for comparative purposes. The structures with GWWFs have a larger II/P up to around 100 Wcm$^{-2}$. Furthermore below 100 Wcm$^{-2}$, the 2T structure has the largest II/P followed by the T-bounced, 1T and Q2T structures in descending order. The 2T structure has the largest II/P over all excitation power densities, with the Q2T having the smallest. Above 100 Wcm$^{-2}$ the T-bounced structure is observed to droop by 10 % to the same efficiency as the Q2T structure. Moreover, the 2T structure was observed to droop by 5 %. Also the 1T structure becomes more efficient than the T-bounced structure above 100 Wcm$^{-2}$.

Efficiency droop is a carrier density effect [3–5] and thus would be effected by the reduction in volume of the InGaN layers. As stated previously, the volume
5.3 Results and Discussion

Figure 5.9: Comparison of the room temperature integrated PL intensity per unit excitation power as a function of excitation power density for each structure.

of the structures with GWWFs are estimated to have around 60 to 70 % of the volume of the structures without GWWFs. This reduction in volume is estimated to increase the carrier density by a factor of 1.4 to 1.7 [6]. This change in carrier density is not sufficient to explain the observed change of around an order of magnitude difference between the peak II/P. Hence the competition between the radiative and non-radiative rates must be significantly different between the structures.

5.3.3 Radiative Rate Comparison

To compare the radiative rates of the structures, the $\tau_{1/10}$ PL decay times of the structures were compared at 12 K, where the recombination is assumed to be 100 % radiative. To do this, the structures were excited with an excitation energy of 3.179 eV, at a repetition rate of 398950 Hz and a power density of 13 MWcm$^{-2}$pulse$^{-1}$. The decay transients at various detection energies across the PL spectrum for the IT, Q2T, T-bounced and 2T are shown in Figures 5.10, 5.11, 5.12 and 5.13 respectively.

The decay transients of all structures exhibit non-exponential decays, typical of InGaN/GaN QWs. The $\tau_{1/10}$PL decay times were measured and plotted as a function of detection energy in Figure 5.14. The $\tau_{1/10}$PL decay time generally increases with
5.3 Results and Discussion

Figure 5.10: Decay transients at various detection energies across the PL spectrum at 12 K for the 1T structure excited with a power density of 13 MWcm$^{-2}$pulse$^{-1}$.

Figure 5.11: Decay transients at various detection energies across the PL spectrum at 12 K for the Q2T structure excited with a power density of 13 MWcm$^{-2}$pulse$^{-1}$.
5.3 Results and Discussion

Figure 5.12: Decay transients at various detection energies across the PL spectrum at 12 K for the T-bounced structure excited with a power density of 13 MWcm$^{-2}$pulse$^{-1}$.

decreasing detection energy for all structures. Detection of the lowest energies of the spectrum result in a reduction of the $\tau_{1/10}$ PL decay time due to the detection of photons from the LO phonon replica [7]. The $\tau_{1/10}$ PL decay times measured at the QW peak for the T, Q2T, T-bounced and 2T structures were measured to be $46\pm 4$ ns (2.728 eV), $50\pm 2$ ns (2.761 eV), $31\pm 3$ ns (2.731 eV) and $26\pm 1$ ns (2.743 eV) respectively. On increasing the power density to 269 MWcm$^{-2}$pulse$^{-1}$, the $\tau_{1/10}$ PL decay time at the QW peak did not change within the error (see Appendix B.1). Thus the radiative rate is constant with increasing power density for all structures.

The structures with GWWFs are observed to have lower $\tau_{1/10}$ PL decay times at the QW peak compared to structures without. Furthermore the structures with GWWFs are observed to have lower $\tau_{1/10}$ PL decay times by around a factor of 2 at the same detection energies across the spectrum. This is consistent with the reduced average QW width for the structures with GWWFs, which has been shown by several authors [8, 9] to result in an increase the wavefunction overlap between the localised electrons and holes. These results are in line with the presence of GWWFs act to increase the wavefunction overlap and increase the radiative rate of the QW.
5.3 Results and Discussion

Figure 5.13: Decay transients at various detection energies across the PL spectrum at 12 K for the 2T structure excited with a power density of 13 MW cm\(^{-2}\) pulse\(^{-1}\).

Figure 5.14: \(\tau_{1,0}\) PL decay time at 12 K as a function of detection energy for all structures at a power density of 13 MW cm\(^{-2}\) pulse\(^{-1}\).
5.3.4 Non-Radiative Recombination Model

The radiative rate at 12 K of the 2T and T-bounced structures which have GWWFs were measured to be same within the error over the zero LO phonon PL linewidth, though the measured RT-IQE of the 2T and T-bounced structures are different. Assuming any change in radiative rate as a function of temperature for the 2T and T-bounced structures are the same, it suggests that the non-radiative rate of the structures are different. A similar statement can be made about the structures without GWWFs. To further investigate the difference in non-radiative rate, initially the temperature dependent PL spectra in Section 5.3.1 was analysed using the thermal activation of non-radiative recombination model (Section 4.3.4). The fit of the integrated PL intensity as a function of temperature to the model for the 1T, Q2T, T-bounced and 2T structures are shown in Figures 5.15, 5.16, 5.17 and 5.18 respectively.

![Figure 5.15: Fit of the thermal activation of non-radiative recombination model (red line) to the integrated PL intensity as a function of temperature, for the 1T structure at an excitation power density of 6 Wcm$^{-2}$.](image)

A poor fit to the model was achieved for the 1T structure with a $\chi^2_{RED}$ of 4.84, therefore no conclusions could be made from the fit. Reasonable fits to the model were achieved for the rest of the structures with $\chi^2_{RED}$ between 0.25 to
5.3 Results and Discussion

Figure 5.16: Fit of the thermal activation of non-radiative recombination model (red line) to the integrated PL intensity as a function of temperature, for the Q2T structure at an excitation power density of 6 Wcm$^{-2}$.

4. The activation energy of the T-bounced and 2T structure were determined to be 56.7(±3.6) and 50.7(±9.5) meV respectively. These activation energies of the structures with GWWFs are around a factor of 2 larger than the Q2T structure (23.2(±1.1) meV). This suggests that the GWWFs are the cause of the increased activation energies. The extracted activation energies of the Q2T and 2T structures fit with the extracted values for the equivalent samples in Chapter 4 of ∼25(±2) and ∼40(±5) meV respectively (see Section 4.3.4).

The prefactor $C$ for the Q2T, T-bounced and 2T structures were determined to be 17.8(±1.2), 15.1(±2.4) and 5.7(±2.4) respectively. The extracted $C$ values for the Q2T and 2T structures fit with the extracted values for the equivalent samples in Chapter 4 of ∼9(±3) and ∼4(±1) respectively (see Section 4.3.4). The $C$ value determined for the T-bounced and 2T structure are dramatically different, given their radiative rates are very similar, this suggests that the non-radiative rate is significantly different between the two structures. This difference may reflect the difference in GaN barrier growth temperature between the two structures and the resultant defect density. The $C$ value extracted for the Q2T and T-bounced structures are the same within error which may reflect mainly the low growth temperature of
5.3 Results and Discussion

**Figure 5.17:** Fit of the thermal activation of non-radiative recombination model (red line) to the integrated PL intensity as a function of temperature, for the T-Bounced structure at an excitation power density of 6 Wcm$^{-2}$.

the GaN barriers and resultant defect density.

Structures with GWWFs are exposed to a temperature ramp in the growth process to create the GWWFs. Exposure of GaN to high temperatures typically around 800 °C, has been shown to reduce the defect density of the exposed layers [10] and subsequent layers grown on top [11–14]. The reduced defect density was determined from the reduction in ratio of the PL intensity of the YL emission compared to the near band edge emission in GaN layers [11, 13, 14]. Annealing above around 950 °C, has been shown [11] to result in evaporation of the exposed layer and degradation of the crystal structure at the nucleation sites. The thermal anneal process essentially allows the disordered atoms to rearrange and form an improved crystal structure, with less defects [15]. Therefore the exposure of the InGaN layers to high temperatures during the temperature ramp for the 2T and T-bounced growth methodologies, can anneal out defects in the QW. This will result in a reduction in defect density of the QW, leading to a reduction in non-radiative recombination and improving the RT-IQE of the 2T and T-bounced structures.

The results suggest that the main difference in RT-IQE between structures with and without GWWFs is the increased activation energy for non-radiative
5.3 Results and Discussion

Figure 5.18: Fit of the thermal activation of non-radiative recombination model (red line) to the integrated PL intensity as a function of temperature, for the 2T structure at an excitation power density of 6 W cm$^{-2}$.

recombination and the improved defect density of the QW for the structures with GWWFs. Furthermore, the difference in RT-IQE between structures with GWWFs is the difference in defect density of the GaN barriers.

5.3.5 Yellow Luminescence Comparison

To further investigate the differences in defect density of the GaN barriers and their effect on the RT-IQE, the relative YL to QW emission of the structures are compared. The YL band was determined in Chapter 4 to compete with the QW, with a significant amount of carriers which transfer out of the QW recombining to emit YL. The saturation of these defects with increasing power density led to an increase in the efficiency of the structure. Thus the competition between the QW and the YL band was investigated by comparing the ratio of their emissions at room temperature as a function of power density. To do this the structures were excited using a pulsed frequency doubled Ti:Sapphire laser of photon energy of 3.179 eV at a repetition rate of 400 kHz. The PL spectra were integrated and the ratio of the integrated PL intensity of the YL band to the QW for the structures are plotted in
Figure 5.19: Ratio of the integrated PL intensity of the YL to the QW for all structures as a function of excitation power density at room temperature.

The Q2T structure is observed to have the largest ratio of the integrated PL intensity of the YL band to the QW at 13 MWcm$^{-2}$pulse$^{-1}$, followed by the 1T, T-bounced and 2T structures. The structures with the larger ratio of YL band emission are observed to have lower RT-IQE. Thus the relative YL to QW emission reflects the overall efficiency of the structure. The T-bounced and 1T structure are expected to have a similar relative YL to QW emission, considering the low growth temperature of the GaN barriers and resultant increase in defect density. The reduced ratio of YL to QW emission for the T-bounced structure is ascribed to the increased activation energy of non-radiative recombination caused by the GWWFs, reducing the amount of mainly electrons which transfer to the GaN barriers. Furthermore, to the increased radiative rate of the QW. This results in an increase in radiative recombination in the QW which reduces the probability that mainly electrons are thermal activated to defect states in the GaN barrier, allowing the QW to compete to a higher degree with defects mainly in the GaN barriers. The results confirm that the RT-IQE is mainly determined by the effects of the GWWFs and not the barrier growth temperature.
5.4 Summary

The effects of GWWFs and barrier growth temperature on the properties of In-GaN/GaN QWs were independently investigated. This was achieved by comparing pairs of structures with and without GWWFs. Each pair had one structure grown using the optimal growth temperature for the GaN barriers (or at least the majority of the barrier) and the other sub-optimal growth temperature. For the pair of structures with GWWFs, a comparison was made between a structure grown using a T-bounced and 2T growth methodology. For the pair of structures without GWWFs, a comparison was made between a structure grown using a 1T and Q2T growth methodology.

The RT-IQE of structures with GWWFs were determined to be larger than the structures without, at an excitation power density of 6 Wcm$^{-2}$. Furthermore, structures with GWWFs were determined to be more efficient than those without, at low carrier densities below 100 Wcm$^{-2}$. This increase in efficiency was ascribed to three main factors. Firstly, an increase in the radiative rate of the QW due to a reduction in the well width and increase in the wavefunction overlap. Secondly, to an increase in the thermal activation energy of non-radiative recombination caused by the GWWFs ascribed to an increase in the energy barrier to reach non-radiative centres. Thirdly, to the reduced defect density of the QWs caused by the exposure of the structures to a temperature ramp during growth which anneals out defects in the QW.

The RT-IQE results in terms of barrier growth temperature are conflicting, with the 2T being more efficient than the T-bounced structure as expected from the difference in defect density in the GaN barriers. Though the 1T was more efficient than the Q2T structure, which was the opposite of what was expected from the barrier growth temperature. The results show that the RT-IQE of InGaN/GaN QWs are mainly determined by the presence of GWWFs and the effects of the thermal anneal process. Further work is needed to determine why the 1T was more efficient than the Q2T structure.
5.5 References


CHAPTER 6

Studies of Carrier Localisation using Resonant Photoluminescence Spectroscopy

6.1 Introduction

The growth of InGaN/GaN QW structures on substrates such as sapphire, is difficult because of the large lattice mismatch (14 %). The initial GaN is strained but rapid relaxation occurs above a critical layer thickness (∼ 30 Å for GaN on AlN [1]). The relaxation of this strain when the layer is grown thicker than the critical layer thickness leads to the formation of layers with a high density of TD and point defects [2-4]. Typically InGaN/GaN QWs can have TD densities of 10⁸ to 10¹² cm⁻² [5-8]. Despite these high density of defects which can cause non-radiative recombination, InGaN/GaN QW LEDs are able to achieve high RT-IQEs up to ∼ 90 % [9, 10]. These results are in stark contrast to other material systems such as GaP [11], where TD densities of 10⁵ cm⁻² are sufficient to quench the luminescence significantly [12]. This apparent insensitivity to high defect densities is attributed to the effects of carrier localisation [13-15], which prevents the diffusion of carriers to the defects where they can recombine non-radiatively. This restriction of carrier diffusion results in a reduction in the non-radiative rate, allowing InGaN/GaN QWs to exhibit high RT-IQEs [13].

Carrier localisation is widely accepted to occur due to monolayer fluctuations in well width [16-20] and local fluctuations in alloy composition [19-22]. The effects of monolayer WWFs and local fluctuations in alloy composition for polar InGaN/GaN QWs have been modelled by Watson-Parris [23] and Schulz et al. [20], using an effective mass approximation and atomistic description respectively. Watson-Parris [23] modelled the effects a single monolayer WWF of diameter 10 nm on
a set of samples with varying average indium content from 5 % to 25 % for an InGaN/GaN QW of width varying from 2.5 nm to 3.3 nm. Whereas, Schulz et al. modelled the effects of 2 monolayer WWFs with a diameter of 5 nm on a 3.5 nm wide In$_{0.25}$Ga$_{0.75}$N/GaN QW. Both authors consider the InGaN QWs to have a distribution of local alloy compositions which can be considered to be of random form and ignore the effects of the Coulomb interaction between the electrons and holes. The results of both models suggest that the holes are strongly localised around local fluctuations in indium content on the few nanometre scale. Whereas, the electrons are more weakly localised mainly by monolayer WWF on a length scale comparable with the diameter of the WWF.

Watson-Parris [23] was able to extract a localisation energy for both the electrons and holes. Watson-Parris defined the localisation energy as $\sigma$ in Equation (2.32). For a InGaN/GaN QW with no WWFs, Watson-Parris calculated the localisation energy of the holes to vary as $\sqrt{x(1-x)}$ from $\sim 20$ to $\sim 50$ meV with increasing average indium content, $x$ of the InGaN QW from 0.05 to 0.25. Whereas, the localisation energy of the electrons was calculated to be constant with average indium content at $\sim 10$ meV. Monolayer WWFs were observed to localise the electrons by $\sim 10$ meV. Schulz et al. [20] did not calculate a localisation energy but rather commented on the variation in the calculated ground state energies of the electrons and holes. The ground state energy of the electrons varied from 2 to 45 meV for 10 different atom configurations, whereas that of the holes varied from 10 to 150 meV. The standard deviation of the distribution of electron energies was calculated to be 14.23 meV and that of the holes to be 48.08 meV.

Schulz et al. [20] extended their atomistic description to include the Coulomb interaction between the localised electrons and holes. The results of the improved model suggest that the Coulomb interaction mainly introduces an energetic shift of the whole emission spectrum and that the wavefunction overlap between the electrons and holes is only slightly increased. Thus the electrons and holes can be treated as independently localised carriers.

The independent localisation and spatial separation of carriers in InGaN/GaN QWs has been used to explain some of the optical characteristics of these material systems, such as the strong coupling of carriers to LO phonons [17, 24] and the luminescence recombination dynamics [25]. The aim of this work is to further understand carrier localisation and its effect on the independent charge carriers. A powerful technique which has been used in the past to investigate systems with
6.1 Introduction

localised states is resonant PL spectroscopy [26–32]. This technique involves the direct excitation of subsets of the localised electron and hole states. This is achieved by exciting within the emission spectrum using a laser source. The form of the resonant PL spectrum can depend strongly on the coupling of electron and hole pairs to phonons [26, 27, 32].

6.1.1 Carrier-Phonon Coupling

Phonons are waves of vibrations of atoms in condensed matter. When the vibrational wave propagates, entire planes of atoms move either perpendicular or parallel to the direction of the wavevector, $k$ and are referred to as transverse or longitudinal waves respectively. The frequency, $\omega$ of the wave depends on the wavevector which is known as the dispersion relation. The dispersion relation can be calculated through the equations of motion of the atoms in the structure.

Figure 6.1: Schematic diagram illustrating optical and acoustic phonon modes for longitudinal and transverse waves in a diatomic linear lattice. The blue and red balls represent atoms with different masses with the faint balls representing the equilibrium positions.

In the linear chain model where planes of atoms with different masses given by $M_1$ and $m_2$ are repeated over a distance given by $a$ (see Figure 6.1). The force on the planes of atoms is assumed to be proportional to the difference in the displacement of the atoms. The displacement of the plane of atoms with mass $M_1$ about its equilibrium position is given by $u_s$ and similarly mass $m_2$ by $v_s$. Assuming that each
plane only interacts with its nearest neighbour planes and that the force constants are identical between all pairs of nearest neighbour planes. The equations of motion for masses $M_1$ and $m_2$ are given by Equation (6.1) and (6.2) respectively, assuming that the elastic response of the crystal is a linear function of the forces.

\[ M_1 \frac{d^2 u_s}{dt^2} = C(v_s - u_s) + C(v_{s-1} - u_s) \]  \hspace{1cm} (6.1)

\[ m_2 \frac{d^2 v_s}{dt^2} = C(u_{s+1} - v_s) + C(u_s - v_s), \]  \hspace{1cm} (6.2)

where $C$ is the force constant and is different for longitudinal and transverse waves. Solutions to the equations of motion for the mass $M_1$ take the general form,

\[ u_s = u \exp(iska) \exp(-i\omega t) \]  \hspace{1cm} (6.3)

where $s$ is a integer value greater than zero. Similarly the solutions for mass $m_2$ take the general form,

\[ v_s = v \exp(iska) \exp(-i\omega t). \]  \hspace{1cm} (6.4)

Substituting the general solutions into Equations (6.1) and (6.2), then gives

\[ -\omega^2 M_1 u = Cv[1 + \exp(-ika)] - 2Cu \]  \hspace{1cm} (6.5)

and

\[ -\omega^2 m_2 v = Cu[\exp(ika) + 1] - 2Cv. \]  \hspace{1cm} (6.6)

The homogenous linear Equations (6.5) and (6.6), have a solution only if the determinant of the coefficients of the equations is equal to zero, i.e.

\[ \begin{vmatrix} 2C - M_1 \omega^2 & -C[1 + \exp(ika)] \\ -C[1 + \exp(ika)] & 2C - m_2 \omega^2 \end{vmatrix} = 0, \]  \hspace{1cm} (6.7)

or

\[ M_1 m_2 \omega^4 - 2C(M_1 + m_2)\omega^2 + 2C^2(1 - \cos ka) = 0. \]  \hspace{1cm} (6.8)

Solving Equation (6.8) for $\omega^2$ gives the dispersion relation,

\[ \omega^2 = \frac{C(M_1 + m_2)}{M_1 m_2} \pm C \left[ \left( \frac{M_1 + m_2}{M_1 m_2} \right)^2 - \frac{2(1 - \cos ka)}{M_1 m_2} \right]^{\frac{1}{2}}. \]  \hspace{1cm} (6.9)
Each value of the wavevector has two solutions or phonon branches, referred to as the optical and acoustic branches corresponding to the + and − sign in Equation (6.9) respectively (see Figure 6.2). For the optical branch, the atoms oscillate in opposing directions such that their centre of mass is fixed. Whereas for the acoustic branch, the atoms oscillate such that the atoms and centre of mass move together.

![Figure 6.2: Illustration of the phonon dispersion relation for a diatomic structure.](image)

Wurtzite structures have eight normal phonon modes, of which two are acoustic ($A_1$ and $E_1$) and six are optical ($A_1$, $E_1$, $2 \times B_1$ and $2 \times E_2$). The atomic displacements for each of the optical phonon modes are shown in Figure 6.3. The atomic displacements of the $A_1$ and $B_1$ modes are along the c-axis. Whereas, the $E_1$ and $E_2$ modes have atomic displacement perpendicular to the c-axis. Quasi-phonon modes can also be excited when the atomic displacement is a mixture of phonon modes e.g. mixture of $A_1(LO)$ and $E_1(LO)$ [33, 34].

The phonon energies for unstrained III-nitride semiconductors determined by Raman scattering are shown in Table 6.1 at both 6 K and 300 K. The phonon energies are observed to reduce on increasing the temperature due to the thermal expansion of the lattice [35]. The phonon energies of ternary III-nitride alloys have also been investigated by Raman spectroscopy. The phonon energies for unstrained ternary alloys vary with alloy composition, between the phonon energies of the binary III-nitrides which constitute the alloy [36–38]. For example, the phonon energy of the $A_1(LO)$ mode of InGaN has been observed to decrease by $\sim 1.2$ cm$^{-1}$ for every 0.01 increase in indium fraction [36, 39]. The phonon energy has also been shown to
be dependent on strain \cite{40, 41}. The strain induced shift, $\Delta \omega$ of the $A_1(LO)$ phonon mode can be calculated using the following relation,

$$\Delta \omega = 2 \left( a_\lambda - \frac{C_{13}}{C_{33}} b_\lambda \right) \left[ \frac{a_{\text{Unstrained}} - a_{\text{Strained}}}{a_{\text{Unstrained}}} \right] \quad (6.10)$$

where $C_{13/33}$ are the elastic constants of InGaN, $a_\lambda$ and $b_\lambda$ are the phonon deformation potentials, $a_{\text{Unstrained/Strained}}$ are the lattice constant $a$ of the unstrained and strained material respectively \cite{41}.

Coupling of electrons and holes to phonons can have a significant impact on the properties of InGaN/GaN multiple QWs, which include carrier cooling \cite{44}, LO phonon replicas \cite{45}, acoustic phonon sidebands \cite{46} and acoustic phonon assisted hopping \cite{47}. These interactions can occur in a variety of ways which include deformation potential interactions with optical (non-polar) and acoustic phonons, piezoelectric interactions with acoustic phonons and the Fröhlich interaction \cite{48}.  

<table>
<thead>
<tr>
<th>Mode</th>
<th>GaN 6 K \cite{42}</th>
<th>GaN 300 K \cite{42}</th>
<th>InN 6 K</th>
<th>InN 300 K \cite{43}</th>
<th>AlN 6 K \cite{42}</th>
<th>AlN 300 K \cite{42}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1(LO)$</td>
<td>91.1</td>
<td>91.0</td>
<td>-</td>
<td>71.9</td>
<td>110.8</td>
<td>110.3</td>
</tr>
<tr>
<td>$A_1(TO)$</td>
<td>66.2</td>
<td>65.9</td>
<td>-</td>
<td>59.5</td>
<td>76.0</td>
<td>75.8</td>
</tr>
<tr>
<td>$E_1(LO)$</td>
<td>92.2</td>
<td>91.9</td>
<td>-</td>
<td>70.7</td>
<td>113.7</td>
<td>113.1</td>
</tr>
<tr>
<td>$E_1(TO)$</td>
<td>69.5</td>
<td>69.3</td>
<td>-</td>
<td>59.0</td>
<td>83.5</td>
<td>83.2</td>
</tr>
<tr>
<td>$E_{2}^{L}$</td>
<td>17.8</td>
<td>17.9</td>
<td>-</td>
<td>10.8</td>
<td>30.8</td>
<td>30.8</td>
</tr>
<tr>
<td>$E_{2}^{H}$</td>
<td>70.5</td>
<td>70.4</td>
<td>-</td>
<td>60.5</td>
<td>81.5</td>
<td>81.8</td>
</tr>
</tbody>
</table>

Table 6.1: Summary of optical phonon energies (meV) of III-nitride semiconductors.
6.1 Introduction

with LO phonons. The deformation potential arises from macroscopic distortions of the lattice (acoustic) or microscopic distortions of the unit cell (optical). These deformations of the structure change the carrier energies at different points in the Brillouin zone. The piezoelectric coupling occurs due to strain which induces an electric field. Carriers in the presence of this field have a reduced energy which is proportional to the piezoelectric potential. The Fröhlich interaction occurs due to a Coulomb interaction between the carriers and oscillations of positive and negative ions of the lattice. The oscillating charges, create an oscillating macroscopic polarisation creating an electric field, which carriers can interact with [49].

Coupling of electrons and holes to acoustic phonons can result in the appearance of acoustic phonon sidebands in QWs and quantum dots [32, 46, 50]. Electron and hole pairs can couple to a distribution of acoustic phonons in both the absorption and emission of a photon [27, 32] which can lead to the appearance of broad emission bands above and below the emission spectrum of, for example quantum dots [51, 52]. At low temperatures the density of phonons is very low and therefore the probability of absorbing a phonon is very low. Thus typically at low temperatures (∼12 K) phonon sidebands are observed at lower energy below the zero phonon line of the quantum dot where an acoustic phonon is emitted. The appearance of the phonon sideband above the zero phonon line of the quantum dot does not occur until elevated temperatures where the probability of absorbing a phonon becomes significant.

Coupling of electrons and holes to acoustic phonons can also result in acoustic phonon assisted hopping resulting in redistribution of carriers amongst the localised states in the lifetime of the carrier given sufficient wavefunction overlap between the states. The temperature dependence of the FWHM and PL peak energy in disordered (GaIn)(NAs) quantum wells has been modelled via kinetic Monte Carlo simulations in terms of acoustic phonon assisted hopping for excitons [47, 53]. In the model, an exponential density of states is assumed and the energies of the localised states do not depend on their spatial position. Furthermore, low excitation conditions are assumed such that the excitons relax independent from each other. The hopping transition rate, \( \nu_{ij} \) from an occupied state \( i \) to an empty state \( j \) over a distance \( r_{ij} \) is described by the Miller-Abrahams relation,

\[
\nu_{ij} = \nu_0 \exp \left( -\frac{2r_{ij}}{\alpha} - \frac{\epsilon_j - \epsilon_i + |\epsilon_j - \epsilon_i|}{2k_B T} \right)
\]

where \( \nu_0 \) is the attempt to escape frequency, \( \epsilon_{i/j} \) are the energy of states \( i \) and \( j \).
respectively, \( \alpha \) is the decay length of the exciton centre of mass wavefunction in the localised states, \( k_B \) is the Boltzmann constant and \( T \) is temperature. The tunnelling rate between initial and final states is a sensitive function of the separation between the states and hence the energy dependent DOS. For example, low energy states which have a low density of states and thus large average pair separation between the states; have a very low hopping rate and vice versa for high energy states.

The acoustic phonon assisted hopping process has recently been used by Badcock et al. [54] to explain the low temperature (\( \leq 100 \) K) carrier redistribution dynamics in InGaN/GaN QWs. The authors reported on the decay transients detected across the PL spectrum at 12 K under low injection conditions. They observed that the decay transients detected at lower energy had an increasing plateau or constant intensity region in time with decreasing detection energy. This was attributed to carriers undergoing hopping to lower energy states resulting in the lower energy states becoming refilled and creating the plateau in the decay transient.

Badcock et al. [54] also reported on the variation in the time-integrated PL intensity and decay time with increasing temperature (\( \leq 100 \) K) for a given detection energy. Below a temperature of 50 K, for a detection energy above the PL peak energy at 10 K, the time integrated PL intensity and decay time are observed to decrease with increasing temperature. Whereas for a detection energy below the PL peak energy at 10 K, the time integrated PL intensity and decay time are observed to increase with increasing temperature. The authors attribute this behaviour to the energy dependent hopping rate, with lower energy (more localised) states having a reduced energy loss hopping rate compared to higher energy (less localised) states. Above a temperature of 50 K, the behaviour of the time integrated PL and decay time reverse. In this temperature region the hopping of carriers to higher (less localised) states becomes significant. Badcock et al. also investigated the effects of excitation density on the shift in time integrated PL and decay time at detections energies across the PL peak. Similar behaviour was observed to that of the low injection conditions but the relative shifts in time-integrated PL intensity and decay time were reduced. The authors attributed this behaviour to the reduction in available unoccupied localised states. Thus leading to an increase in the average separation of an unoccupied localised state and hence a reduction in the hopping rate.
6.1.2 Resonant Photoluminescence Spectroscopy

Resonant PL spectroscopy has been used to investigate several materials systems which exhibit localised states. For example, Cohen and Sturge \cite{26} investigated exciton localisation in $100 - 200 \, \mu m$ thick CdS$_x$Se$_{1-x}$ platelets ($x = 0.29, 0.53, 0.9$) using resonant PL spectroscopy as a function of both excitation energy and temperature. On resonant excitation at 2 K sharp lines were observed around 0.44 meV wide, with sidebands on the low energy side with a width of $\sim 4$ meV. The sharp lines were attributed to LO accompanied emission from the resonantly excited subset of the localised states. The broad sidebands are observed to become broader on increasing the excitation energy above a particular energy within the non-resonant emission. Cohen and Sturge attributed the sidebands to the transfer of the resonantly excited localised states to lower energy localised states via acoustic phonon assisted hopping within the lifetime of the excitons. The sharp lines were observed to disappear above a certain excitation energy which Cohen and Sturge suggest may indicate an effective mobility edge where carriers are delocalised above this excitation energy. The sharp lines are also observed to quench rapidly with increasing temperature and disappear at a temperature of around 16 K for the CdS$_{0.53}$Se$_{0.47}$ sample.

Similar experiments have also been performed by Permogorov et al. \cite{27} on excitons in CdS$_{1-x}$Se$_x$ with $x \leq 0.3$. The authors investigated the effect of both excitation energy and temperature on the resonant PL spectrum. On resonant excitation of the CdS$_{1-x}$Se$_x$ at 2 K, sharp emission lines with low energy tails were observed at LO phonon energies away from the excitation energy. The LO phonon energies were close to those of pure CdS, CdSe and a combination of the two. Though no low energy tail was observed for the sharp line attributed to the LO phonon energy of CdSe, this was ascribed by the authors to the peculiarities of the vibrations. The authors attributed the sharp emission lines to emission from the resonantly excited localised states which had been accompanied by an LO phonon. The width of the sharp emission lines were attributed to the spread of the emitted LO phonon energies. The broad bands were attributed to acoustic phonon assisted absorption and emission along with phonon-assisted tunnelling between the localised states within the carriers lifetime.

Permogorov et al. observed that the total emission intensity of the resonant PL decreased on decreasing the excitation energy through the non-resonant PL spectrum. They attribute this decrease in PL intensity to the reduction in the density of
localised states. Furthermore, they observed that the PL emission spectrum does not depend upon excitation energy when exciting the sample above the high energy edge of the non-resonant PL spectrum. The authors described this behaviour in terms of exciton mobility, with the high energy edge being an effective mobility edge where delocalised carriers are excited. Exciting below the high energy mobility edge, resonant excitation of weakly localised states occurs resulting in a narrowing of the PL emission band and the appearance of the sharp emission features. The relative intensity of the sharp emission lines to the total emission intensity increased on decreasing the excitation energy up to the peak of the non-resonant PL spectrum. The broad emission band was also observed to narrow on decreasing the excitation energy. The authors attributed this narrowing to the excitation of deeper localised states which have a reduced probability of acoustic-phonon tunnelling between the localised states. The relative intensity of the sharp emission line to the total emission did not decrease further, when decreasing the excitation energy past the non-resonant PL peak. On decreasing the excitation further, the resonant PL emission becomes very weak and the sharp emission features are replaced by Raman lines.

Permogorov et al. \cite{27} also investigated the temperature dependence of the resonant PL spectrum. The sharp emission lines were observed to quench with increasing temperature and disappear almost completely at a temperature of around 10 K for the CdS\textsubscript{0.05}Se\textsubscript{0.95} sample; independent of excitation energy. The temperature dependence of the sharp lines were speculated to be consistent with the interaction of the resonantly excited states with low energy acoustic phonons. Thus resulting in a change to the carriers energy and a loss of the emission from the resonantly excited localised states.

Mariette et al. \cite{28} report on the resonant excitation of Hg\textsubscript{1-x}Zn\textsubscript{x}Te alloys with \(x > 0.9\). The resonant 2 K PL spectrum consisted a sharp line always at 26 meV below the excitation energy and a broad band at lower energy. These features were interpreted to the same features observed by Permogorov et al. \cite{27} in CdS\textsubscript{1-x}Se\textsubscript{x} solid solutions. The sharp line was observed to be temperature dependent, with the PL intensity quenching significantly by a temperature of around 17 K for an excitation energy of 573 nm in the Hg\textsubscript{0.06}Zn\textsubscript{0.94}Te sample.

Resonant excitation of InGaN/GaN QWs has previously been studied by Graham et al. \cite{32} on a pair of single InGaN/GaN QWs with indium fractions of 0.15 and 0.25. The low temperature (6 K) PL spectrum of the In\textsubscript{0.15}Ga\textsubscript{0.85}N/GaN single QW excited non-resonantly with an excitation of 3.408 eV is shown in Figure 6.4(b).
Exciting within the emission spectrum at an excitation of 2.602 eV, produced the resonant PL spectrum shown in Figure 6.4(a). The resonant PL spectrum has three main features. Feature A is ascribed to acoustic-phonon assisted emission from localised states which have been excited via acoustic-phonon assisted absorption. The resonantly excited localised electron and hole pairs can couple to a broad distribution of acoustic phonons via mainly the deformation potential [46]. Feature B is attributed to emission from the resonantly excited localised states which are accompanied by the emission of an LO phonon. Feature C is ascribed to the LO phonon replica of feature A.

Of particular interest here is B, which allows the directly excited states to be monitored without running into experimental detection issues concerning scattered laser light. Feature B was observed by Graham et al. [32] to be temperature dependent, with the emission being completely quenched when the sample structure was heated to a temperature of around 40 K for an excitation energy of 2.602 eV. Graham et al. attributed the temperature dependence of B to the thermal redistribution of carriers amongst the localised states, which is the process that governs the “S”-shape temperature dependent behaviour of the PL peak energy [55, 56]. They proposed that at higher temperatures the resonantly excited localised electrons and/or holes are able to thermally redistribute amongst their respective localised state distribution.
thus negating the initial resonant excitation process.

In this chapter, the effect of the thermal redistribution process on the independently localised electrons and holes in InGaN/GaN QWs is studied in greater detail. The loss of either the localised electron or hole from the resonantly excited states would result in the reduction of the PL intensity of B with increasing temperature. Localised holes are known to thermally redistribute with increasing temperature which results in the “S”-shape temperature dependence of the PL peak energy in InGaN/GaN QWs \cite{56}. The broad FWHM of the PL spectra of InGaN/GaN QWs is mainly attributed to the variation in hole localisation energy, hence the hole localisation energy is predicted to be a function of excitation energy across the PL spectrum \cite{19}. Therefore the thermal activation of holes from the resonantly excited states maybe dependent on the excitation energy. To investigate this, the temperature dependence of the PL intensity of B is studied as a function of excitation energy. To determine whether the loss of B is due to the loss of the localised electrons or holes from the resonantly excited state and thus gather more information about their respective localisation energies.
A 10 period polar In$_{0.16}$Ga$_{0.84}$N (2.5 nm)/GaN (7.3 nm) QW structure was grown by the University of Cambridge using the Q2T growth methodology. The structure was grown on a low defect density c-plane sapphire/GaN pseudo-substrate with a nominal 0.25° miscut toward (1120). The sample details are summarised in Table 6.2, where the well and barrier thickness, repeat distance (QW and barrier) and the average indium content were determined by XRD at the University of Cambridge. A more detailed description of the sample structure can be found in Section 5.2.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Growth method</th>
<th>QW thickness (nm)</th>
<th>Barrier thickness (nm)</th>
<th>Repeat distance (nm)</th>
<th>Average indium content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5244C</td>
<td>Q2T</td>
<td>2.4 ± 0.1</td>
<td>7.4 ± 0.1</td>
<td>9.8 ± 0.1</td>
<td>17 ± 1</td>
</tr>
</tbody>
</table>

Table 6.2: Summary of sample details.
6.3 Results and Discussion

Both resonant and non-resonant PL measurements were performed on the Q2T structure with a CW dye (Stilbene 420) laser using a power density of 250 W cm\(^{-2}\). The 12 K non-resonant PL spectrum excited with a photon energy of 2.973 eV is shown by the black curve in Figure 6.5. The PL peak emission energy and FWHM of the main emission line were measured to be 2.774(±0.001) eV and 67(±2) meV respectively. The 12 K resonant PL spectrum excited with a photon energy of 2.783 eV is shown by the red curve in Figure 6.5.

![Figure 6.5: 12 K PL spectra using a non-resonant excitation energy of 2.973 eV (black) and a resonant excitation energy of 2.783 eV (red) for the Q2T structure. The red arrow denotes the resonant excitation energy. The curves are offset for clarity.](image)

The resonant PL spectrum for the Q2T structure exhibits the same 3 features observed by Graham et al. [32] on resonant excitation of a single In\(_{0.15}\)Ga\(_{0.85}\)N/GaN QW. Feature A being a broad emission ascribed to the acoustic phonon sideband (PSB), feature B being due to emission from the resonantly excited states which are accompanied by the emission of an LO phonon and feature C being the LO phonon replica of feature A. Feature B will now be referred to as the resonant LO feature for convenience. A was attributed by Graham et al. [32] to acoustic-phonon assisted emission from resonantly states which had been excited via acoustic-phonon
assisted absorption. Recently reported evidence by Badcock et al. [54] suggested that acoustic phonon assisted hopping can occur resulting in the redistribution of carriers amongst the localised states in InGaN/GaN QWs even at 12 K as mentioned previously. Therefore it is believed that localised electrons and/or holes can undergo acoustic phonon assisted hopping during the carriers lifetime before recombination via phonon assisted emission.

The resonant LO feature can be extracted from the resonant PL spectra by removing the background luminescence from the other features in the spectrum. To do this, narrow scans were taken over the resonant LO feature, a typical spectra is shown by the black curve in Figure 6.6. The background luminescence from the acoustic PSB and its LO phonon replica were approximated by Gaussian functions with the same width. The tail of the Gaussian fits to the acoustic PSB and its LO phonon replica are shown by the red and green curves in Figure 6.6 respectively. These are summed to give the total background luminescence (blue curve) which is subtracted from the resonant PL spectrum (black curve) to give the PL intensity of the resonant LO feature represented by the magenta curve in Figure 6.6. The resonant LO feature has an asymmetric lineshape with a broad tail for larger energy shifts from the excitation energy. The FWHM of the resonant LO feature is $\sim 3$ meV at an excitation energy of 2.724 eV. The resonant LO feature is observed to have a peak at an energy shift of 91.5(±0.2) meV from the excitation energy. The peak of the resonant LO feature occurs at an LO phonon energy consistent with a quasi-LO phonon of the $A_1$ (91.1 meV) and $E_1$ (92.2 meV) phonon modes of GaN at 6 K [33].

The LO phonon replicas of InGaN/GaN QWs have previously been investigated by several authors [17, 32, 45]. Kalliakos et al. [45] investigated the LO phonon replicas of a series of InGaN/GaN QWs with varying QW width from 1 to 3 nm at 10 K. The authors report that the 1LO and 2LO phonon replicas of all the structures in the series were separated by 91 meV from the zero phonon emission, which is close to the GaN LO phonon energy at 6 K. Graham et al. [17] investigated the change in LO phonon energy with indium composition for a series of single InGaN/GaN QWs. The authors observed that the LO phonon energy was constant with indium composition at the GaN LO phonon energy of 91(±1) meV. The authors suggested this maybe due to the competing effects of composition and strain. Graham et al. [32] also investigated the LO phonon energy of the resonant LO feature for an In$_{0.15}$Ga$_{0.85}$N/GaN single QW under resonant excitation (2.602 eV) at 10 K. The authors report an LO phonon energy of 91 meV for the resonant LO feature,
Figure 6.6: Resonant PL intensity (black) for the Q2T structure with an excitation energy of 2.724 eV at 12 K. The background luminescence from the acoustic PSB (red) and its LO phonon replica (green) have been summed (blue) and subtracted from the resonant PL spectrum to extract the resonant LO feature (magenta).

consistent with the measured LO phonon energy here.
6.3 Results and Discussion

6.3.1 Excitation Energy Dependence at 12 K

The resonant LO feature was investigated as a function of excitation energy and the resonant PL spectra are shown in Figure 6.7. On increasing the excitation energy toward the high energy side of the non-resonant PL emission spectrum, the resonant LO feature disappears. This behaviour is consistent with observations of the resonant LO feature in CdS$_{1-x}$Se$_x$ [26, 57]. The peak energy of the acoustic PSB is observed to increase with increasing excitation energy across the non-resonant PL emission spectrum up to an excitation energy of 2.82 eV as shown in Figure 6.8. On increasing the excitation energy past 2.82 eV, the peak of the spectra remains constant at the non-resonant PL peak energy of 2.774(±0.002) eV. The energy at which the acoustic PSB peak energy becomes constant coincides with the energy at which the resonant LO feature cannot be observed.

![Figure 6.7: Normalised resonant 12 K PL spectra for the Q2T structure as a function of excitation energy. The curves are offset for clarity.](image)

Similar observations were made by Permogorov et al. [57] on CdS$_{1-x}$Se$_x$ solid solutions. Permogorov et al. explained this behaviour in terms of an effective mobility edge. Above a particular excitation energy (2.82 eV in this case) the vast majority of excited carriers are delocalised and quickly relax randomly amongst the localised state distribution. The relaxation process is expected to occur on the 10’s to 100’s
6.3 Results and Discussion

Figure 6.8: Phonon side band peak energy position (feature A) as a function of excitation energy, along with the non-resonant 12 K PL spectra for the Q2T structure.

fs time scale by carrier-carrier and carrier-phonon scattering \[58, 59\]. Exciting at excitation energies below the effective mobility edge at 2.82 eV, resonant excitation of localised electrons and holes occurs which results in the appearance of the acoustic PSB and the resonant LO feature.

The extracted normalised PL intensity of the resonant LO feature taken at various excitation energies across the non-resonant PL spectrum are shown in Figure 6.9. The peak of the resonant LO feature remains constant within the error at 91.6(±0.2) meV. The FWHM is observed to increase from ~ 3 meV to ~ 4.5 meV on decreasing the excitation energy from 2.792 to 2.731 eV. The tail on the higher energy shift side of the PL peak also becomes longer.

The form of the resonant LO feature reflects mainly the coupling between the electron-hole pairs and the phonons \[57, 60\]. The broad tail on the high energy shift side equivalent to higher LO phonon energy, reflects a distribution of LO phonon energies which the resonantly excited localised states can couple to. The coupling of electron-hole pairs to LO phonons of varying energy can occur in disordered semiconductors when the translational symmetry of the crystal is broken by impurities and defects etc; which results in the breakdown of the wavevector, \(\Delta k = 0\) selection

\[\begin{align*}
\text{PL Intensity (a.u.)} \\
\text{Excitation Energy (eV)}
\end{align*}\]
6.3 Results and Discussion

Figure 6.9: Normalised PL intensity of the resonant LO feature as a function of excitation energy for the Q2T structure at 12 K.

rule for direct bandgap semiconductors \[61\]. Electrons and holes can therefore couple to a range of LO phonons with different energies depending on the wavevector of the phonon.

Kraus et al. \[62\] observed the breakdown of the $\Delta k = 0$ selection rule for direct bandgap semiconductors when investigating Raman signals of resonantly excited DAP recombination in p-doped CdTe and ZnSe. Under resonant excitation of the DAPs, Kraus et al. observed two extra Raman peaks below the LO($\Delta k = 0$) phonon energy for ZnSe:N and a single peak for all other p-doped samples which were not observed when exciting the samples under non-resonant conditions. The phonon energies of these extra peaks were measured to decrease with increasing the excitation energy. The authors attributed these extra peaks below the LO($\Delta k = 0$) phonon energy to phonons where $\Delta k \neq 0$. Furthermore, the authors describe the variation in peak phonon energy in terms of a model in which the wavevector, $k$ is related to the DAP separation, $R_{DA}$ by the following relation,

$$k = \frac{m\pi}{R_{DA}} \quad (6.12)$$

which fulfils the condition that the separation between $m + 1$ nodes ($m$ is a positive


6.3 Results and Discussion

integer) of the mode is equal to the DAP separation. Resonant excitation of DAPs creates DAPs with a fixed pair separation which can be calculated using Equation (2.21). The corresponding fixed wavevector can be calculated by Equation (6.12). This fixed wavevector corresponds to a phonon mode with a specific energy given by the phonon dispersion relation. The variation in the phonon energy with excitation energy was explained as follows. On increasing the excitation energy, DAPs with a relatively shorter pair separation are created, which in turn leads to a larger wavevector from Equation (6.12). This results in a relatively lower phonon energy as can be seen from the phonon dispersion relation in Figure 6.2.

Drawing analogies from this model may explain in part the form of the resonant LO feature. In the case of resonantly excited localised electron and hole pairs, a range of pair separations are created for any one given excitation energy. This results in a range of wavevectors calculated using Equation (6.12) but replacing the DAP separation discussed above with that of the localised electrons and holes. The range of wavevectors results in a range of phonon energies, which the localised electron and hole pairs can couple to. The Huang-Rhys factor increases for larger localised electron and hole pair separation, $R_{eh}$ [7, 24]. Therefore as $R_{eh} \rightarrow \infty$, $\Delta k \rightarrow 0$; hence the peak of the resonant LO feature is for larger localised electron and hole pair separation. Taking into consideration the dispersion curve of the LO phonon modes for GaN [42], it is expected that the phonon energy decreases with increasing $\Delta k$ (smaller $R_{eh}$) from the $\Delta k = 0$ point. Though this decrease in phonon energy is negligible close to $\Delta k = 0$ for the LO phonon modes of GaN. Thus it is expected that the resonant LO feature would have a symmetric shape.

The variation between what is expected and what is observed may be explained by taking into consideration the Coulomb interaction between the localised electrons and holes. The recombination energy, $E_{\text{photon}}$, would now be given by the following relation,

$$E_{\text{photon}} = E_{\text{Exc}} - E_{\text{phonon}} - \frac{e^2}{4\pi\epsilon_0\epsilon_r R_{eh}} \quad (6.13)$$

where $E_{\text{Exc}}$ is the excitation energy, $E_{\text{phonon}}$ is the LO phonon energy, $e$ is the electron charge, $R_{eh}$ is the electron-hole pair separation, $\epsilon_0$ is the permittivity of free space and $\epsilon_r$ is the relative permittivity. The dispersion curve for the LO phonon modes of GaN are essentially flat close to $\Delta k = 0$ as mentioned previously. Thus the change in phonon energy with $\Delta k$ can be treated as negligible. Therefore the change in recombination energy in Equation (6.13), depends on the change in the Coulomb term. On decreasing the pair separation the Coulomb term increases, which in turn
results in a reduction in the recombination energy leading to a broad tail on the higher energy shift (from the excitation energy) side of the resonant LO feature. The variation in the lineshape of the resonant LO feature with excitation energy could be explained in terms of the change in the distribution of the localised electron and hole pair separations with excitation energy. On decreasing the excitation energy through the non-resonant PL spectrum, electron and hole pairs are excited in areas of higher local indium composition and hence electric field strength. This increase in electric field strength leads to an increase in the average electron and hole pair separation, a reduction in the Coulomb term and an increase in the recombination energy. Thus an increasing number of localised electron and hole pairs recombine at a higher energy with increasing electric field strength resulting in the apparent broadening of the resonant LO feature lineshape with decreasing excitation energy.

The integrated PL intensity of the resonant LO feature as a function of excitation energy is shown in Figure 6.10. The integrated PL intensity of the resonant LO feature is observed to increase with increasing excitation energy across the PL emission spectrum. The increase in integrated PL intensity with increasing excitation energy is attributed to an increase in the DOS and reduction in the local electric field strength. This results in an increase in wavefunction overlap and absorption strength of the resonant excited states and hence an increase in the integrated PL intensity of the resonant LO feature.
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Figure 6.10: Integrated PL intensity of the resonant LO feature as a function of excitation energy at 12 K.

6.3.2 Temperature Dependence

To investigate the effect of thermal redistribution processes on the independently localised electrons and holes, the temperature dependence of the resonant LO feature was studied as a function of excitation energy. The Q2T structure was excited with a power density of 250 W cm$^{-2}$. A typical set of temperature dependent PL spectra for the resonant LO feature is shown in Figure 6.11 at an excitation energy of 2.777 eV. The resonant LO feature quenches rapidly with temperature and is completely quenched at a temperature of around 45 K, independent of excitation energy. The peak of the resonant LO feature remains constant with temperature at 91.6(±0.3) meV.

The temperature dependent data was analysed in order to extract a thermal activation energy, $E_A$ for the thermal redistribution process. To do this the temperature dependence of the integrated PL intensity of the resonant LO feature was fitted to an Arrhenius model. The integrated PL intensity, $II$ of the resonant LO feature at a given temperature, $T$ was described by the following relation,

$$II(T) = II(0) \left(1 - \exp \left[\frac{-\Delta E_A}{k_B T}\right]\right)$$

(6.14)
where $k_B$ is the Boltzmann constant. A typical Arrhenius fit of the integrated PL intensity of the resonant LO feature at an excitation energy of 2.754 eV is shown in Figure 6.12. Fits to the temperature dependence of the integrated PL intensity of the resonant LO feature for the other excitation energies can be found in Appendix C.1. Reasonable fits to the model were achieved with the adjusted coefficient of determination, $R^2_{\text{ADJ}}$ varying between 0.73 to 0.97. The extracted activation energy as a function of excitation energy is shown in Figure 6.13. The activation energy is observed to be constant within the error at $\sim 1(\pm 1)$ meV with varying excitation energy.

This simple model is a dramatic over simplification of a very complex model. In reality, for any one given excitation energy; a range of localised electrons and holes are excited with different localisation energies which recombine at the same energy as shown in Figure 6.14. The difference in the width of the localised electron and hole distributions in Figure 6.14 are estimated from the calculated localisation energies by Watson-Parris [23] of $\sim 10$ meV and $\sim 40$ meV for a In$_{0.17}$Ga$_{0.83}$N/GaN QW structure respectively. The localisation energy probed is an average of the range of localisation energies excited for the electrons and holes respectively. It can be seen that for a given excitation energy a band of localised holes are excited, whereas the
6.3 Results and Discussion

Figure 6.12: A typical fit of the integrated PL intensity of the resonant LO feature to the simple two level model system. Here shows a fit of the Q2T structure at an excitation energy of 2.754 eV.

The vast majority of the localised electron distribution is excited. Thus mainly the hole localisation energy is changed when exciting at different regions of the non-resonant PL spectrum.

The extracted activation energy is expected to reflect the localisation energy of the localised electrons or holes, where the localisation energy is the difference in energy between the resonantly excited localised state and a higher energy state in which thermal redistribution amongst the localised states is possible. The higher energy state could be some effective mobility edge. In this case, the results measured in Figure 6.8 suggest that the localisation energy of the holes is on average around \( \sim 50 \) meV; which is the energy difference from the effective mobility edge at 2.82 eV to the peak of the non-resonant PL spectrum at 2.774(\( \pm 0.001 \)) eV. The activation energy (\( \sim 1(\pm 1) \) meV) is thus much smaller than the expected localisation energy of the localised holes. This may suggest that the loss of the resonant LO feature is due to the thermal redistribution of the localised electrons from the resonantly excited states. Furthermore, the lack of excitation energy dependence of the activation energy is also consist with the loss the localised electrons from the resonantly excited states. This fits with a model in which electrons are more weakly localised in energy.
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Figure 6.13: Extracted electron localisation energies from the Arrhenius fit for the Q2T structure.

compared to the holes, consistent with the work by Watson-Parris et al. [19] and Schulz et al. [20].
Figure 6.14: Schematic of the variation in localisation energy of the localised electrons and holes for any one given excitation energy. Three different excitation energies are shown by the solid red, blue and magenta lines.
6.4 Summary

The effects of carrier localisation on the independently localised electrons and holes was investigated using resonant PL spectroscopy. A 10 period polar In$_{0.17}$Ga$_{0.83}$N (2.5 nm)/GaN (7.5 nm) QW structure grown using a Q2T methodology was investigated. Three main features were observed in the resonant PL spectroscopy. These included an acoustic PSB excited via acoustic phonon assisted absorption and its LO phonon replica, along with emission from the resonantly excited localised states which are accompanied by the emission of a LO phonon (resonant LO feature).

The resonant LO feature was extracted from the background luminescence and studied as a function of excitation energy at a temperature of 12 K. The resonant LO feature was observed to have an asymmetric lineshape, with a broad tail for larger energy shift from the excitation energy. The peak of the resonant LO feature was found to be constant with excitation energy at the quasi-LO phonon mode of $A_1$ and $E_1$ of GaN. This was attributed to the effects of strain and composition on the InGaN QWs and the oscillations of the phonon being mainly in the GaN. On increasing the excitation energy the high energy shift tail became broader and the relatively lower energy shift tail remained unchanged. This increase in the broad tail resulted in an increase of the FWHM from $\sim$ 3 to $\sim$ 4.5 meV on decreasing the energy from 2.792 to 2.731 eV. The form of the resonant LO feature was tentatively explained by a model in which the wavevector of the phonon is inversely proportional to the localised electron and hole pair separation and the recombination energy of the resonantly excited localised electron and hole pairs which couple to LO phonons in the emission process are determined by the Coulomb interaction. Furthermore, the broadening of the resonant LO feature with decreasing excitation energy was attributed to the variation in the distribution of the localised electron and hole pair separations due to the excitation of regions with increasing higher electric field strength.

The integrated PL intensity of the resonant LO feature was found to increase with increasing excitation energy at 12 K. This was attributed to an increase in the DOS and absorption strength. The increase in absorption was ascribed to the increase in wavefunction overlap caused by the reduction in electric field over the QW at higher excitation energy. Above an excitation energy of 2.82 eV, the resonant LO feature became indistinguishable from the background luminescence and the PL peak energy of the acoustic PSB becomes that of the non-resonant PL spectrum. This behaviour
was attributed to an effective mobility edge, in which the vast majority of carriers are delocalised when excited above this energy. Carriers excited above the effective mobility edge quickly relax into the localised states resulting in a loss of the resonant LO feature.

The temperature dependence of the resonant LO feature was also investigated as a function of excitation energy. The resonant LO feature was observed to quench rapidly with temperature up to around 45 K, independent of excitation energy. A thermal activation energy equivalent to a localisation energy was extracted by fitting the integrated intensity of the resonant LO feature to an Arrhenius model. The activation energy was observed to be $\sim 1(\pm 1)$ meV, independent of excitation energy. The activation energy was found to be consistent with the localisation energy of the electrons. Furthermore, the activation energy was consistent with a model in which the electrons are more weakly localised in energy depth compared with holes.
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In Chapter 4 and 5, the effect of QW growth methodology on the optical properties of InGaN/GaN multiple QWs was reported. The effects of GWWFs and barrier growth temperature were independently investigated. The QW structures with GWWFs were observed to have a much larger RT-IQE regardless of barrier growth temperature for excitation power densities less than 100 Wcm$^{-2}$. The production of GWWFs during a temperature ramp is believed to have 3 main effects which are to thermally anneal out defects in the QW [1, 2], produce a broad scale potential barrier which restricts carrier diffusion in the plane of the QW and reduce the amount of indium incorporation into the barriers increasing the wavefunction overlap of the localised electrons and holes [3]. Furthermore, the GWWFs reduced the QW width by a factor of 1.4 to 1.7, which results in an increase in the wavefunction overlap.

The formation of point defects which can act as non-radiative recombination centres [4, 5], have been shown to be dependent on the growth temperature with higher growth temperatures leading to reduced point defect density [6, 7]. Therefore the effect of QW growth temperature on the RT-IQE of InGaN/GaN QWs would be of interest for further research. Higher QW growth temperatures may lead to a reduction in point defect density and an increase in RT-IQE of InGaN/GaN QWs. Further work would also be to investigate and identify which point defects contributed to non-radiative recombination.

The effects of barrier growth temperature on the RT-IQE had conflicting results in Chapter 5. Higher barrier growth temperatures are expected to result in a reduction in defect density [8, 9]. A reduction in defect density of the barriers should result in less non-radiative recombination in the barriers and an increase in RT-IQE. The 2T structure with the higher barrier growth temperature had a larger RT-IQE than the
structure with a relatively lower barrier growth temperature; following the expected trend. Though, the 1T structure with the relatively lower barrier growth temperature compared to the Q2T structure had a larger RT-IQE. Therefore further research is needed to determine the correlation between barrier growth temperature and RT-IQE. A comparison of the structural defect properties of the samples may explain this behaviour, if for example the 1T structure had less point defects than the Q2T sample. Furthermore, a full systematic investigation into the effect of barrier growth temperature on the RT-IQE and defect density would also be of interest.

In Chapter 6, the effects of carrier localisation on the independently localised electrons and holes in InGaN/GaN QWs was investigated using resonant PL spectroscopy. The majority of the work involved investigating the emission from the resonantly excited localised electron and hole states which had been accompanied by the emission of an LO phonon (resonant LO feature) as a function of both temperature and excitation energy. The form of the resonant LO feature was tentatively described in terms of a model in which the wavevector of the LO phonon is inversely proportional to the localised electron and hole pair separation and the recombination energy of the resonantly exited localised electron and hole pairs which couple the LO phonons in the emission process are determined by the Coulomb interaction. Further work is needed to prove the model accurately describes the form of the resonant LO feature. This would involve extensive theoretical work to determine things such as the density of phonon states and the coupling between the localised electron and holes with the distribution of phonon states.

The resonant LO feature was observed to have an asymmetric PL lineshape with a broad tail to larger energy shifts from the excitation energy. The broad tail was observed to become longer on reducing the excitation energy across the non-resonant PL emission spectrum. This was tentatively described to be a result of the variation in the distribution of localised electron and hole pair separations caused by the excitation of regions with increasing electric field strength. A larger pair separation reduces the Coulomb term in Equation (6.14), which results in a larger recombination energy assuming the change in LO phonon energy is negligible. Further work would be to investigate the lineshape of the resonant LO feature of higher average indium content InGaN/GaN QW structures. The lineshape of the resonant LO feature would be expected to be broader as the pair separation increases with electric field strength. The results from this may help to determine whether the model used to describe the form of the resonant LO feature is correct.
The resonant $^{\text{LO}}$ feature was observed to quench rapidly with temperature at around 45 K, independent of excitation energy. The thermally driven loss of the resonant $^{\text{LO}}$ feature is attributed to the thermal redistribution of either the localised electrons or holes amongst the localised states. A thermal activation energy of $\sim 1(\pm 1) \text{ meV}$ was extracted from the temperature dependence of the integrated $^{\text{PL}}$ intensity of the resonant $^{\text{LO}}$ feature, independent of excitation energy. The extracted activation energy was consistent with an average localisation energy of electrons $^{[10, 11]}$. Further work is needed to prove this is the case. Such as investigating a sample with a much higher average indium content. The localisation energy of holes depends strongly on the average indium content of the $^{\text{QW}}$ structure, with increasing average indium content resulting in an increase in the localisation energy $^{[12]}$. Thus it maybe expected that the localisation energy of the holes would increase with a higher average indium content sample. The results from this may shed some light on whether the loss of the resonant $^{\text{LO}}$ feature is due to the loss of the localised electrons or holes.

The resonant $^{\text{LO}}$ feature was observed to become indistinguishable from the background resonant $^{\text{PL}}$ spectrum above a particular excitation energy. Furthermore, the resonant $^{\text{PL}}$ spectrum peaked at the non-resonant $^{\text{PL}}$ peak energy above the same excitation energy. This behaviour was ascribed to an effective mobility edge and the transition from resonant $^{\text{PL}}$ to non-resonant $^{\text{PL}}$. Further work would be to investigate this mobility edge behaviour and the thermal redistribution of carriers amongst the localised states. The difference between the effective mobility edge and the non-resonant $^{\text{PL}}$ would be expected to increase for a sample with a higher average indium composition which has a larger localisation energy. Thus the investigation of samples with higher average indium content would be of interest for further research.
7.1 References


A.1 Fitting of the Thermal Activation of Non-Radiative Recombination Model

The plots in this appendix are the Arrhenius model fits to the integrated PL intensity referred to in Section 4.3.4 for the Q2T (C4815A) and 2T (C4825A) structures.

Figure A.1: $I_{II}/P$ as a function of temperature for the Q2T structure at an excitation power density of 0.2 Wcm$^{-2}$. The red line denotes a fit to the thermal activation of non-radiative recombination model.
Appendix A.1

Figure A.2: II/P as a function of temperature for the Q2T structure at an excitation power density of 0.4 Wcm\(^{-2}\). The red line denotes a fit to the thermal activation of non-radiative recombination model.

![Graph](image)

Figure A.3: II/P as a function of temperature for the Q2T structure at an excitation power density of 1 Wcm\(^{-2}\). The red line denotes a fit to the thermal activation of non-radiative recombination model.

![Graph](image)
Figure A.4: $I_{\text{II}}/P$ as a function of temperature for the Q2T structure at an excitation power density of $2 \text{ Wcm}^{-2}$. The red line denotes a fit to the thermal activation of non-radiative recombination model.

Figure A.5: $I_{\text{II}}/P$ as a function of temperature for the Q2T structure at an excitation power density of $3 \text{ Wcm}^{-2}$. The red line denotes a fit to the thermal activation of non-radiative recombination model.
Figure A.6: II/P as a function of temperature for the Q2T structure at an excitation power density of 5 Wcm$^{-2}$. The red line denotes a fit to the thermal activation of non-radiative recombination model.

Figure A.7: II/P as a function of temperature for the Q2T structure at an excitation power density of 7 Wcm$^{-2}$. The red line denotes a fit to the thermal activation of non-radiative recombination model.
Figure A.8: II/P as a function of temperature for the Q2T structure at an excitation power density of 9 Wcm$^{-2}$. The red line denotes a fit to the thermal activation of non-radiative recombination model.

Figure A.9: II/P as a function of temperature for the 2T structure at an excitation power density of 0.5 Wcm$^{-2}$. The red line denotes a fit to the thermal activation of non-radiative recombination model.
Figure A.10: $\Pi/P$ as a function of temperature for the 2T structure at an excitation power density of 0.8 $\text{Wcm}^{-2}$. The red line denotes a fit to the thermal activation of non-radiative recombination model.

Figure A.11: $\Pi/P$ as a function of temperature for the 2T structure at an excitation power density of 1 $\text{Wcm}^{-2}$. The red line denotes a fit to the thermal activation of non-radiative recombination model.
Figure A.12: II/P as a function of temperature for the 2T structure at an excitation power density of 2 Wcm$^{-2}$. The red line denotes a fit to the thermal activation of non-radiative recombination model.

Figure A.13: II/P as a function of temperature for the 2T structure at an excitation power density of 3 Wcm$^{-2}$. The red line denotes a fit to the thermal activation of non-radiative recombination model.
Figure A.14: $\Pi/\mathcal{P}$ as a function of temperature for the 2T structure at an excitation power density of $7 \text{ Wcm}^{-2}$. The red line denotes a fit to the thermal activation of non-radiative recombination model.

Figure A.15: $\Pi/\mathcal{P}$ as a function of temperature for the 2T structure at an excitation power density of $14 \text{ Wcm}^{-2}$. The red line denotes a fit to the thermal activation of non-radiative recombination model.
Figure A.16: II/P as a function of temperature for the 2T structure at an excitation power density of 22 Wcm$^{-2}$. The red line denotes a fit to the thermal activation of non-radiative recombination model.
APPENDIX B

Additional Data for Chapter 5

B.1 12 K PL Decay Time Measurements

The plots in this appendix refer to the 12 K PL decay transients of the 1T, Q2T, T-bounced and 2T structures taken in Section 5.3.3.

**Figure B.1:** $\tau_{10}$ PL decay time at 12 K of the 1T structure as a function of detection energy at power densities of 13 and 269 MWcm$^{-2}$/pulse$^{-1}$.
Appendix B.1

Figure B.2: \( \tau_{1_{10}} \) PL decay time at 12 K of the Q2T structure as a function of detection energy at power densities of 13 and 269 MW cm\(^{-2}\) pulse\(^{-1}\).

Figure B.3: \( \tau_{1_{10}} \) PL decay time at 12 K of the T-Bounced structure as a function of detection energy at power densities of 13 and 269 MW cm\(^{-2}\) pulse\(^{-1}\).
Figure B.4: $\tau_{110}$ PL decay time at 12 K of the 2T structure as a function of detection energy at power densities of 13 and 269 MWcm$^{-2}$pulse$^{-1}$.
APPENDIX C

Additional Data for Chapter 6

C.1 Temperature Dependence of the Resonant LO Feature

The plots in this appendix are the Arrhenius fits to the integrated PL intensity referred to in Section 4.3.4 for the Q2T (C5244C) structure.

Figure C.1: Integrated PL intensity as a function of temperature for the Q2T structure at an excitation energy of 2.800 eV. The red line denotes the Arrhenius fit.
Figure C.2: Integrated PL intensity as a function of temperature for the Q2T structure at an excitation energy of 2.792 eV. The red line denotes the Arrhenius fit.

Figure C.3: Integrated PL intensity as a function of temperature for the Q2T structure at an excitation energy of 2.785 eV. The red line denotes the Arrhenius fit.
Figure C.4: Integrated PL intensity as a function of temperature for the Q2T structure at an excitation energy of 2.777 eV. The red line denotes the Arrhenius fit.

Figure C.5: Integrated PL intensity as a function of temperature for the Q2T structure at an excitation energy of 2.769 eV. The red line denotes the Arrhenius fit.
Figure C.6: Integrated PL intensity as a function of temperature for the Q2T structure at an excitation energy of 2.746 eV. The red line denotes the Arrhenius fit.