

Dynamics of Nanostructured Light Emitting Diodes



Christopher C. S. Chan
Department of Condensed Matter Physics
University of Oxford
Exeter College

A thesis submitted for the degree of
Doctor of Philosophy
2014 Hilary

Dynamics of nanostructured light emitting diodes

Christopher C. S. Chan

Exeter College

Thesis submitted for the degree of Doctor of Philosophy

Hilary Term 2014

Abstract

Experimental investigations of the optical properties of GaN nanostructured light emitting diode (LED) arrays are presented. Microphotoluminescence spectroscopy with pulsed and continuous wave lasers was used to probe the carrier dynamics and emission mechanisms of nanorod LED arrays fabricated by a top down etching method. Results show a possible reduction in internal electric field as nanorod diameter decreases. Localisation effects were also observed, affecting the spectral shape of the nanorod emission.

Under two-photon excitation, quantum dot-like sharp spectral peaks in the PL spectra are found to exist in abundance amongst all the nanorod samples. The optical properties of these localised states, which are shown to be associated with the nanorod free-surfaces, are characterised using non-linear and time resolved spectroscopy.

An investigation into spatially resolved single nanorods was also carried out. Single nanorods were isolated, and characterised using pulsed lasers. The etching is shown to increase the carrier decay life-time at extended intervals over several hundred ns. The temporal evolution and excitation power density dependence of the quantum dot-like states are also presented for the first time. The long lived localised states are thought to arise from surface effects, in particular Fermi-surface pinning, causing localisation and spatial separation of carriers.

Additional work on nano-pyramid array LEDs, with quantum wells on semi-polar surfaces is also presented. Optical properties using micro-photoluminescence are compared to cathodoluminescence studies. An uneven distribution of emission wavelengths across the pyramid facet is thought to lead to an emission mechanism involving carriers transferring between multiple spatially localised states.

Finally, experimental techniques and fabrication methods for future work are documented in detail.

To my grandparents

Acknowledgements

I first and foremost would like to express my deepest gratitude to my supervisor Professor Robert Taylor, for without his relentless support and encouragement, this Dphil would not have been made possible. Robert's enthusiasm for the subject is infectious, his love of personal involvement in the experiments along with his laser skills has helped me tremendously in obtaining my data. During the past four years, we have had many thought-provoking conversations about Physics and experimental techniques. I truly appreciate all his time, effort, and funding which has made which has made my Dphil experience most delightful and productive. Academic supervision aside, Robert has been very tolerant on our sometimes silly behaviour in our office. He leads the group in an easy-going atmosphere, encouraging group members to help each other not only in our academic studies such as practice viva questions and mock conference presentations, but also physical activities such as moving his garden shed.

I am extremely grateful for the guidance that Professor Duncan Allsopp and Dr. Philip Shields has given me, at the University of Bath. Duncan and Philip provided me with all the samples for my Dphil, and treated me as one of their students. Without their expertise and the many useful discussions, this thesis and my current publications would not have been made possible. I would also like to thank Dr. YiDing Zhuang for fabricating the Nanorod LEDs, Dr. Emmanuel Le Boulbar and Paolo Ki for showing me their lab and for the useful discussions I had in Bath. Many thanks also to my examiners Professor Michael Johnston and Dr. Paul Edwards for their time and their critical opinion and during my viva.

I am indebted to all the members of the Taylor group current and past: Dr. Mark Holmes (Mark-san), Dr. Tim Wong (Timsey), Dr. Daniel Collins, Dr. Anas Jarjour, Dr. Benjamin "P.L." Reid, Dr. Heedae Kim (Kimsey), Dr.

Youngsin Park, Nathaniel Read, Dr. Wei Jia, Shingo Nakazawa, Claudius Kocher, Dr. David Coles, Dr. Chunlin, and Luke Nuttall. The Taylor group members have contributed hugely to my project and also have been a large part of my life here at Oxford. Mark for showing me the many experimental techniques. He was always around to provide useful insights into my data. Tim provided me with knowledge of the drinking holes in Oxford, the journeys in his beloved Austin Metro were always thrilling. Benjamin has been providing me with very useful sporting facts since joining the group in 2010. His competitive attitude towards everything has seen us compete in the most obscure of ways, usually for seniority within the research group. I wish to thank Benjamin for his company, on our various adventures and for the numerous activities varying in levels of maturity. I really appreciate his time spent proof reading my work, and discussing presentation ideas such as how many lines I should spend on a point. Shingo for helping me print my conference poster in Japan. Youngsin for continuously providing me with exotic samples to experiment on, broadening my knowledge of semiconductors beyond III-nitride materials. Dave letting me stay over in his summertown dwellings on many occasions. It has been a pleasure to work with Dr. Haitham Al Ella, and Dr. Frederic Brossard, the late nights in the Clarendon were most memorable. I also wish to thank all the people I have shared office with: Chris Menelaou, Dr. Henning Urban, Christian Wehrenfennig, Dr. Harpal Baraj, and Dr. Huw Davies whom have all been greatly accommodating.

I must also thank Dr. Jack Alexander-Webber, Nathaniel Huang (Nate-dawg), who we consider to be part of the Taylor group family, most of all their help in the cleanroom. I wish to acknowledge the excellent support staff in the Clarendon, especially Robert Storey from the Cryogenic Facility. The staff at the workshop has been tremendously helpful, teaching me how to fabricate many apparatus for my experiments. Special thanks to Paul Pattinson for his helpful advice and excellent management of the cleanroom. I would like to acknowledge my past flatmates for being so accommodating, which has made my personal life in Oxford much rewarding. I would like to thank: Ren for the wine he shared and also the many discussions about

physics and wine tasting; Naoko Hosokawa, my dear flatmate in my fourth year, for the wonderful parties she organises, great pancakes, drinks and her one liner jokes; Benjamin Lok, my flatmate during my write-up period, for his support during this tough time has made my life much less stressful. I am also extremely grateful also for Aonghus Ryan and Kowcee, for their hospitality and for being the most wonderful hosts.

Dphil life in Oxford has been one of the most unique experiences, stretching me both personally and professionally. My time here would not have been as enjoyable without the many friends that I had had the joy to meet here. My friends from college: Eleanor Cooper, Henrick Indgard, Francisca Gale, Therese Fieler, for their sense of humour, eccentricity and banter in the MCR and at college formal dinners. My weightlifting bros: Christopher Wing Tai Chan (for introducing me to the sport, and being the best training buddy), Scott and Dom Manifold Manibros, John Liddon, Pirate Paul, Bacon, Dave, Martin Kendall, and Marcus, for it was with physical training and the gym that let my mind focus on something other than work and some of the emotional difficulties I have had. Friends I met through the Thursday night pub meets: Naoko Hosokawa, Tomoe Kumojima, Kimiko Kuga, Yuki Kawaguchi, Ken Chatfield (for real Chinese food), Aaron Lim (for the fried chicken), Tim Watts, Aonghus Ryan, Andrew Stewart, Aoi Watanabe (for all that junk food), Naz Ahmed, Francesca Williams (for the stoopid things we got up to). I especially wish to sincerely thank Hitomi Sato for her understanding, for her patience and the fun times we spent both here in Oxford and in Tokyo. I also would like to thank my friends Alfred Yu, Josh Levine, Emma Bradley (for her sardonic comments), Jasmeer Virdee, Divani Singh the “OP-crew” (for always having time for a cup of tea at the old parsonage), and Qiang Yi for his encouragement and time spent discussing the thesis with me. I would like to give special thanks to my Physics teacher, Chan Man Yiu, without his inspiration and contagious passion for Physics and natural philosophy, I would not have committed my past four years to the subject.

Finally, I would like to thank my parents, for their love and endless support. Throughout my academic pursuit, from graduating from Imperial College,

matriculating in Oxford, writing-up, preparing for my viva, my parents have never at any moment not been supportive. I have to thank Risa Wang Miemie sincerely and wholeheartedly, for her affection, her passion, and most of all her spiritual support that has motivated me throughout the process of writing this thesis. I am completely indebted to my grandfather John, who taught me the importance of hard work, modesty and independence in thinking. Most of all I wish to thank my grandmother Esther who encouraged my curiosity, and passion for knowledge from a young age. It is to my grandmother Esther and my grandfather John that this work is dedicated to.

Publications

Published peer review papers

1. *Optical studies of the surface effects from the luminescence of single GaN/InGaN nanorod light emitting diodes fabricated on a wafer scale*
Christopher C. S. Chan, Benjamin P. L. Reid, Wei Jia, Robert A. Taylor, YiDing Zhuang, Philip A. Shields and Duncan W. E. Allsopp. Applied Physics Letters **102**, 111906 (2013). [Chapter 6]
2. *High temperature stability in non-polar InGaN quantum dots: Exciton and biexciton dynamics*
Benjamin P. L. Reid, T. Zhu, F. Oehler, Christopher C. S. Chan, Claudius Kocker, M. J. Kappers, R. A. Oliver, and R. A. Taylor, to be published in Physica Status Solidi C (2013)
3. *Observations of Rabi oscillations in a non-polar InGaN quantum dot*
Benjamin P. L. Reid, Claudius Kocker, F. Oehler, T. Zhu, E. Robert, Christopher C. S. Chan, R. A. Oliver, and R. A. Taylor. Applied Physics Letter **104**, 263108 (2014).
4. *Photoluminescence of Single GaN/InGaN Nanorod Light Emitting Diode Fabricated on a Wafer Scale*
Christopher C. S. Chan, YiDing Zhuang, Benjamin P. L. Reid, Wei Jia, Mark J. Holmes, Jack A. Alexander-Webber, Shingo Nakazawa, Philip A. Shields Duncan W. E. Allsopp, and Robert A. Taylor. Japanese Journal of Applied Physics **52**, 08JE20 (2013). [Chapter 6]
5. *Origins of Spectral Diffusion in the Micro-Photoluminescence of Single InGaN Quantum Dots*
Benjamin P. L. Reid, Tongtong Zhu, Timothy J. Puchtler, Luke J. Fletcher,

Christopher C. S. Chan, Rachel A. Oliver, and Robert A. Taylor. Japanese Journal of Applied Physics **52**, 08JE01 (2013).

6. *Confocal microphotoluminescence mapping of coupled and detuned states in photonic molecules*

F. S. F. Brossard, Benjamin P. L. Reid, Christopher C. S. Chan, X. L. Xu, J. P. Griffiths, D. A. Williams, R. Murray, and Robert A. Taylor. Optics Express **21**, 16934 (2013).

7. *Optical studies of quantum dot-like emission from localisation centres in InGaN/GaN nanorod array LEDs*

Christopher C. S. Chan, Philip A. Shields, Mark J. Holmes, Yi Ding Zhuang, Xu Wang, Benjamin P. L. Reid, HeeDae Kim, Duncan W. E. Allsopp, and Robert A. Taylor. Physica Status Solidi C **9**, 635 (2012). [Chapter 5]

8. *Optical studies of GaN nanocolumns containing InGaN quantum disks and the effect of strain relaxation on the carrier distribution*

Mark J. Holmes, Young S. Park, Xu Wang, Christopher C. S. Chan, Benjamin P. L. Reid, HeeDae Kim, Jun Luo, Jamie H. Warner, and Robert A. Taylor. Physica Status Solidi C **9**, 712 (2012).

9. *Design and fabrication of optical filters with very large stopband (≈ 500 nm) and small passband (1 nm) in silicon-on-insulator*

Wei Jia, Jun Deng, Benjamin P. L. Reid, Xi Wang, Christopher C. S. Chan, Hong Wu, Robert A. Taylor, Aaron J. Danner. Photonics and Nanostructures-Fundamentals and Applications **10**, 447 (2012).

10. *Optical Studies on $In_xGa_{1-x}N$ quantum disks*

Mark J. Holmes, Young S. Park, Xu Wang, Christopher C. S. Chan, Anas F. Jarjour, Jun Luo, Jamie H. Warner, H. A. R. El-Ella, R. A. Oliver and Robert A. Taylor. Proc. SPIE **7937**, Ultrafast Phenomena in Semiconductors and Nanostructures Materials XV 793713 (2011).

11. *Carrier dynamics of $In_xGa_{1-x}N$ quantum disks embedded in GaN nanocolumns*

Mark J. Holmes, Young S. Park, Xu Wang, Christopher C. S. Chan, Anas F. Jar-

jour, Jun Luo, Jamie H, Warner, H. A. R. El-Ella, R. A. Oliver and Robert A. Taylor. Journal of Applied Physics **109**, 063515 (2011).

12. *Optical studies on a single GaN nanocolumn containing a single $In_xGa_{1-x}N$ quantum disk*

Mark J. Holmes, Young S. Park, Xu Wang, Christopher C. S. Chan, Benjamin P. L. Reid, Jun Luo, Jamie H, Warner, and Robert A. Taylor. Applied Physics Letters **98**, 251908 (2011).

Papers under review/in preparation

1. *Quantum dot-like excitonic behavior in individual single walled-carbon nanotubes*
Xu Wang, Jack A. Alexander-Webber, Wei Jia, Mark J. Holmes, Christopher C. S. Chan, Benjamin P. L. Reid, Robin J. Nicholas, C. Deng, and Robert A. Taylor. Manuscript prepared for submission
2. *Reduced Stark Shift in Three-dimensionally Confined GaN/AlGaN Asymmetric Multi-quantum Disks*
Young S. Park, Christopher C. S. Chan, Benjamin P. L. Reid, Mark J. Holmes, Seon H. Kim, Kwang S. Kim, Robert A. Taylor, Woo C. Yang, Hyunsik Im. Submitted to *Applied Physics Letters*
3. *Bandgap renormalization in valleytronics materials of single- and bi-layer MoS_2*
Young S. Park, Sang W. Han, Christopher C. S. Chan, Benjamin P. L. Reid, Robert A. Taylor, Seon H. Kim, Kwang S. Kim, Min G. Park, Sunmin Ryu, and Hyunsik Im.
4. *Nontrivial surface effects in semiconductor; Photoluminescence of a two-dimensional array of GaN nanotubes*
Young S. Park, Mark J. Holmes, Benjamin P. L. Reid, Christopher C. S. Chan, Robert A. Taylor, Kwang S. Kim, and Hyunsik Im. (2013)
5. *Optical anisotropy in mono- and bi-layer MoS_2*
Young S. Park, Christopher C. S. Chan, Sang W. Han, Benjamin P. L. Reid, Robert A. Taylor, Seon H. Kim, Kwang S. Kim, Min G. Park, Sunmin Ryu, and Hyunsik Im.

-
6. *Polarised emission from InGaN/GaN quantum discs embedded in GaN nanorods*
Young S. Park, Christopher C. S. Chan, Robert A. Taylor

Conference Presentations

1. *High Temperature Stability in Non-polar 11-20 InGaN Quantum Dots: Exciton and Biexciton Dynamics*
B. P. L. Reid, T. Zhu, C. C. S. Chan, C. Kocher, F. Oehler, M. J. Kappers, R. A. Oliver and R. A. Taylor. International Conference on Nitride Semiconductors, September 2013, Washington, USA
2. *Optical studies of Non-polar (11-20) InGaN Quantum Dots*
B. P. L. Reid, T. Zhu, C. C. S. Chan, C. Kocher, F. Oehler, R. Emery, M. J. Kappers, R. A. Oliver and R. A. Taylor. UK semiconductors July 2013, Sheffield, UK
3. *Carrier dynamics of single InGaN/GaN nano-LED fabricated on a wafer-scale nanorod array*
C. C. S. Chan B. P. L. Reid, M. J. Holmes, W. Jia, R. A. Taylor, S. Nakazawa, H. Kim, Y. Zhuang, P. A. Shields, D. W. E. Allsopp. International Workshop on Nitride Semiconductors October 2012, Sapporo, Japan
4. *Origins of spectral diffusion in the micro-photoluminescence of single InGaN quantum dots*
B. P. L. Reid, T. Zhu, T. J. Puchler, L. J. Fletchers, M. J. Kappers, C. C. S. Chan, R. A. Oliver, and R. A. Taylor. International Workshop on Nitride Semiconductors October 2012, Sapporo, Japan
5. *Mode mapping of coupled cavities in photonic crystal waveguides*
F. S. F. Brossard, B. P. L. Reid, C. C. S. Chan, D. A. Williams, R. Murray and R. A. Taylor. International Conference on Optical MEMS and Nanophotonics (OMN), Aug 2012, Banff, AB, Canada
6. *Single InGaN/GaN Nanorod luminescence from wafer scale nanorod array LED*
C. C. S. Chan, B. P. L. Reid, M. J. Holmes, R. A. Taylor, Y. Zhuang, P. A. Shields, D. W. E. Allsopp. UK Nitrides Consortium, January 2012, Bath, UK

-
7. *Evolution of quantum dot photoluminescence in GaN/InGaN nanorod LEDs*
C. C. S. Chan, R. A. Taylor, P. A. Shields, M. J. Holmes, Y. Zhuang, D. W. E. Allsopp. International Conference on Nitride Semiconductors, July 2012, Glasgow, Scotland
 8. *Optical Studies of GaN Nanocolumns Containing InGaN Quantum Disks and the Effect of Strain Relaxation on the Carrier Distribution*
M. J. Holmes, Y. S. Park, X. Wang, C. C. S. Chan, J. Luo, J. H. Warner, and R. A. Taylor. International Conference on Nitride Semiconductors, July 2012, Glasgow, Scotland
 9. *Optical Studies on $\text{In}_x\text{Ga}_{1-x}\text{N}$ Quantum Disks*
M. J. Holmes, Y. S. Park, X. Wang, C. C. S. Chan, A. F. Jarjour, J. Luo, J. H. Warner, H. A. R. El-Ella, R. A. Oliver and R. A. Taylor. SPIE Photonics West January 2011, San Francisco, CA, USA
 10. *Quantum Dot-like Emission Lines in Wet-etched Nano-rod Array GaN Based MQW LEDs*
C. C. S. Chan, M. J. Holmes, P. A. Shields, D. W. E. Allsopp and R. A. Taylor. UK Nitrides Consortium, January 2011, Manchester, UK
 11. *Carrier Dynamics in $\text{In}_x\text{Ga}_{1-x}\text{N}$ Quantum Disks Embedded in GaN Nanocolumns*
M. J. Holmes, Y. S. Park, X. Wang, C. C. S. Chan, A. F. Jarjour, J. H. Warner, J. Luo, H. A. R. El-Ella, R. A. Oliver and R. A. Taylor. UK Nitrides Consortium, January 2011, Manchester, UK
 12. *MOVPE Growth of InGaN Quantum Dots with AlGaN Barriers*
H. El-Ella, F. Christie, D. Collins, C. C. S. Chan, M. J. Kappers, R. A. Oliver and R. A. Taylor. International Workshop on Nitride Semiconductors, September 2010, Tampa, Florida, USA
 13. *Photoluminescence and Electroluminescence in InGaN/GaN Nano-rod Array LEDs Fabricated on a Wafer Scale*
P. A. Shields, C. Chan, N. Read, D. W. E. Allsopp, R. A. Taylor, and F. Causa. Solid-State and Organic Lighting, June 2010, Karlsruhe, Germany

Contents

Publications	vi
1 Introduction	1
1.1 Introduction and overview	1
1.1.1 Overview of LED research and development for lighting	2
1.1.2 Thesis outline	4
2 Properties of gallium nitride	7
2.1 Crystal structure of GaN	7
2.1.1 Polarisation	10
2.2 Band structure of GaN	10
2.3 Quantum confinement	11
2.3.1 Bandgap engineering	11
2.3.2 Quantum wells	11
2.4 Strain in InGaN epilayers	12
2.4.1 Piezoelectric effect	13
2.4.2 The quantum confined Stark effect	17
2.4.3 Polarity and wavefunctions	18
2.4.4 Carrier field screening	20
2.4.5 Phase separation	20
2.4.6 Localised states in InGaN quantum wells	21
2.4.7 Lifetime of a quantum system	23
3 Fabrication techniques	26
3.1 Introduction	26
3.2 Principles of nanoprocessing	27

3.2.1	Pattern transfer	27
3.2.2	Etching and deposition	28
3.2.3	Structural analysis	28
3.3	Nanorod array fabrication	29
3.3.1	Nanoimprint lithography	29
3.3.2	Nanorod array processing procedures	30
3.4	Grid fabrication	34
3.5	Nanorod masks of varying size	36
4	Experimental techniques	42
4.1	Introduction	42
4.2	Excitation sources	43
4.2.1	Ultrafast laser	43
4.2.2	Harmonic generation	44
4.2.2.1	INRAD ultrafast harmonic generation system	45
4.2.2.2	Two photon absorption	45
4.2.3	Continuous wave lasers	47
4.3	Optical setup	47
4.3.1	Confocal imaging	48
4.4	Time integrated photoluminescence spectroscopy	51
4.4.1	Cryogenics	52
4.4.2	Resolution	52
4.4.3	Resolving polarisation	55
4.4.4	Reflectivity measurements	58
4.5	Time resolved photoluminescence	59
4.5.1	Time correlated single photon counting	59
5	Spectroscopy of InGaN nanorod array LED fabricated on a wafer scale	61
5.1	GaN nanorods	61
5.2	Surface effects on InGaN	62
5.2.1	Strain relaxation	62
5.2.2	Fermi level pinning	63
5.2.3	Combination of strain relaxation and Fermi level pinning	64

5.3	Optical Properties of InGaN/GaN Nanorod LED Arrays	67
5.3.1	Design and fabrication of nanorod arrays	67
5.3.2	Time integrated photoluminescence	68
5.3.3	Quantum confined stark effect in etched nanorod array LEDs . .	72
5.3.4	Assessing relative strain relaxation of the different rods by photoluminescence	74
5.4	Evidence of other recombination mechanisms	76
5.4.1	Excitation power density revisited	77
5.4.2	Localisation in nanorods	78
5.5	Discovery of QD-like features	82
5.5.1	Two-photon excitation studies	85
5.6	Final remarks	88
6	Optical studies of single nanorod LEDs	89
6.1	Isolating single nanorod LEDs	89
6.2	Single QW LED initial optical characterisations	92
6.3	Initial optical studies on a single nanoLED	93
6.4	Low excitation power studies	99
6.5	Dynamics of single nanoLEDs	101
6.6	Final remarks	106
6.6.1	Future work and ideas	106
7	Semi-polar nano-LED	108
7.0.2	Surface morphology	109
7.1	Photoluminescence	110
7.2	High spatial resolution studies	112
7.3	The quantum well potential	113
7.4	Time evolution of photo emission	115
7.5	Chapter summary	122
8	Conclusion	124
A	Detailed fabrication information	127
A.1	Lift-off processing recipe and procedures	127
A.2	etch mask fabrication problems	130

B	Polarisation analysis	132
B.1	Instrument characterisation	132
B.2	MoS ₂ example	133
C	Poster presentations	136
	References	139

1

Introduction

1.1 Introduction and overview

The short history of semiconductor lighting traces its sources back to H. J. Round. In a short letter published in *Electrical World* in 1907, he reported an observation of light emission in silicon carbide *carborundum* on applying a potential between two points (1). In 1927, O. V. Losev reported emission of silicon carbide diodes and measured the I-V characteristics of the device and the thermal dependencies of emission (2). However practical uses of the LED as an alternative lighting device were not realised until 1962. In the paper published in Applied Physics Letters, N. Holonyak and S.G. Bevacqua (3) observed the first visible emission LED, centred at 710 nm (4). The first LED using GaN was reported in 1971 by Pankove *et al.* (5).

Since then, the LED industry has become one of the fastest growing areas in semiconductors in the past two decades. The world demand for lighting fixtures is in fact

projected to climb at $\sim 7\%$ annually through 2016 up to 153 billion USD (6). This growth is related to the expansion of the world's population combined with the needs of developing nations. The increasing appetite for artificial lighting has a tremendous impact on the demand of LEDs. The greatest demand remains in the domestic lighting market, competing against compact fluorescence lights which currently retail at much cheaper prices than LED bulbs. However, with both the decline in LED prices and increase in energy bills, payback time is increasingly shortened, and long-term forecasts of the LED's market penetration in fact reveals an estimated accelerated increase (7). Research in the field is therefore progressively expanding due to the financial benefits and also the increasing public awareness in the environment and energy conservation in addition to the many prospects of novel opto-electronic devices flourishing from the advance of semiconductor nanotechnology.

1.1.1 Overview of LED research and development for lighting

Bulk GaN is not widely available, nor are there suitable lattice-matched foreign substrates for growth. The relatively poor crystalline quality of GaN makes for defect abundant samples, compromising its light emission efficiency (8). It is therefore a surprise that under these circumstances, the GaN-based LED is still considered the most successful candidate for next generation ultra efficient lighting. To date, though the emission processes of InGaN devices have been under investigation and debate, they still remain poorly understood (9, 10, 11, 12). The current goals of GaN-based LED research remain focussed around: Achieving efficient emission in the whole visible spec-

trum range and beyond, the so called *Green Gap*, maintaining efficiency with higher and higher injection currents (i.e. high lumens/Watt), extraction efficiency photonics, and alternative materials.

For artificial lighting, colour balance is one of the most important aspects of design. The preferences for the colour of home lighting differ around the world (13). There is therefore much emphasis in producing the correct tone of white light. There are generally two ways of achieving a broad spectrum white light with LEDs. The first and most commonly used method is to have phosphor coated devices where the phosphor is excited by high energy blue photons emitted by a blue LED. The spectrum emitted is dependent on the phosphor used and can thus can be engineered to cover a wide spectral range, emitting close to the desired colour preferences. The use of phosphors is however lossy since each photon exciting the phosphor leads to a photon of lower energy leaving the system. This is inherently inefficient compared to direct emission of a broad spectrum. A phosphorless method of achieving the broad visible spectrum can also be obtained by physically combining bright LEDs emitting blue, green and red light. A desirable design would be to have a single LED chip which can emit a continuous composition of red, blue and green light (14). Not only would there be no loss of energy due to down conversion from the phosphor this technology, can also have tremendous impact on devices such as emissive display and projection technologies with a precise and wide colour space (15). A big obstacle in the development of this type of device is to overcome the *green gap*. Green and lower energy emission in GaN based LED systems requires a high level of indium incorporation in the active layer. This

gives rise to highly inefficient operation owing to strong piezoelectric and spontaneous polarisation fields which are particularly severe with high indium concentration InGaN heterostructures (16). Also, spinodal decomposition occurs due to the poor miscibility of InN and GaN at indium contents where the bandedge corresponds to the majority of the visible spectrum (17). Progress in nano-fabrication has recently allowed remarkable breakthroughs into the green by downsizing LED features, such as nanorod development (14, 18, 19, 20, 21). This type of nano-LED has drawn a considerable amount of attention in the research community as a hopeful candidate for the achievement of high efficiency broad spectral emission on a single chip. One other method to achieve this is to vary the composition and width of an InGaN quantum well particularly grown on facets of processed GaN strips and pyramids (22, 23). Reference (23) shows that varying indium content in the quantum well can be produced along these facets. Moreover, the facets of these pyramids and strips correspond different crystal planes than the conventional c-plane LEDs. This can result in reduced piezoelectric fields and better low photon energy emission efficiency.

Prices of LEDs depend largely on substrate, fabrication materials and packaging electronics. Raw material costs, for example the indium price, have seen a rising trend in the past 2 decades with an increasing demand in transparent electrodes in phones and mobile devices (24, 25). Limited by the efficiency droop (26, 27), the prices of LEDs in *cost per lm*, will have a dependence on the cost per unit area of the LED. By implementing nanostructured LEDs, such as nano-pyramids and core-shell nanorod structures (28), the surface area to volume ratio can increase dramatically, increas-

ing light output per manufactured wafer. Silicon substrates for GaN are also under development as a cheaper alternative to sapphire (29). A potential drawback to the continuous decrease in feature size is its effect on the emission and photonic properties of the LEDs resulting from strain relaxation, enhanced localisation, and surface effects (19, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40). Furthermore, since the high refractive index of GaN leads to a light extraction problem, the use of nanorods and photonic crystals in LEDs has been shown to increase the extraction efficiency (32, 41, 42).

Most of the recent developments in InGaN LEDs mentioned are aimed to bring down the price per lm of an LED. With the advances in nanoprocessing and fabrication, more and more possibilities can be conceived. Our understanding of the nanoscale material properties and physics of GaN is also becoming increasingly important.

A summary of the motivations, goals and strategies of LED research today is shown in Fig. 1.1

1.1.2 Thesis outline

In this thesis the optical properties of GaN/InGaN nanostructured LEDs with nanorod and nanopyramidal geometries are reported. These structures are both in current development for use in light emitting diodes to increase efficiency. Nanorods or nanocolumns have seen use not only in LEDs, but also in photonic crystals and sensor technology (43). Both GaN pyramids and nanocolumns have been reported to be used as seeds for quantum dot growth with site control (44, 45, 46, 47). Nanorod arrays have been shown to lase when arranged to tune the photonic bandgap of the periodic array to

	Efficiency	Colour	Lifetime	Initial Cost
	very low	Ideal CRI 100	very low few hours	low
	low	Ideal CRI 100	low few months	very low
	good	CRI 80	medium few years	low
	very good	CRI 95	extremely high decades	high
Research focus for LEDs	Non-Polar/Semi-polar materials, Growth of epilayers Phosphors Nanorods/pyramids photonic crystals		Manufacturing techniques packaging	Silicon/ alternative substrates

Figure 1.1: - Table comparing types of lighting and current strategies employed to solve the issues of LED lighting. The colour rendering index (CRI) is a measure of the ability of a light source faithfully reveal the colours of objects compared to a natural light source. The incandescent lamp and candle (fire) has a CRI of 100

the emission from the embedded quantum wells (48). A mass production method of nanorod array fabrication by nanoimprinting is introduced and the optical properties of the prototypes are investigated. Nanoimprinting was also used to make some of the smallest reported nanopyramidal arrays. These were also studied using photoluminescence experiments. In addition to the experimental results, the experimental methods and detailed sample preparation procedures performed during the course of the DPhil are detailed. These are included for future reference for pending spectrometry work in the research group.

In chapter 2 an overview of the properties of GaN with a brief discussion of internal electric fields and the effect of nanoprocessing on carrier distribution are presented.

Chapter 3 has a detailed summary of the nanoprocessing techniques used to fabricate the samples used studied in this thesis. Nanoimprint lithography, electron beam lithography along with a variety of clean room techniques for making grid structures for locating single structures and the designing tools are described.

In chapter 4 the experimental techniques employed to investigate the optical properties of the nanostructured LEDs are detailed. The investigations include time integrated and time resolved micro-photoluminescence techniques using time correlated single photon counting (TCSPC) with a pulsed Ti:sapphire laser system. A brief discussion on frequency doubling and tripling as well as two-photon absorption will be given. The resolution of the experimental setup as well as capabilities to perform micro-reflectivity and polarisation sensitivity will also be mentioned.

The core experimental data will be presented and discussed in chapters 5 and 6.

Microphotoluminescence was used to study the emission properties of the mass produced etched nanorods. A comparison of the optical properties of the nanorods which have undergone different etching times and temperatures is presented. Two-photon absorption studies on narrow spectral lines are carried out and reported. In chapter 6, single nanorods are studied from the top down using time resolved photoluminescence. The results summarised in this chapter have resulted in two peer review journal publications.

Chapter 7 summarises the experiments conducted to characterise semi-polar LEDs made using nanopylramids on templates created by nanoimprint lithography.

Following this will be the appendices which will include an in depth description of the fabrication methods. Also included are polarisation tests of the experimental setup and also a brief summary of the polarisation experiments currently being performed on MoS₂ monolayer samples.

Finally poster presentations that were given at the International Workshop on Nitride Semi-conductors (IWN2012) in Sapporo, Japan and UK nitrides consortium (UKNC) 2011 are presented.

2

Properties of gallium nitride

2.1 Crystal structure of GaN

Gallium nitride (GaN) is a III-V semiconductor with a tetrahedrally coordinated arrangement of atoms, it is naturally found crystallised in wurtzite and zinc blende forms. The wurtzite form of GaN is the most thermodynamically stable and is the most common form with each Ga atom covalently bonded with four N atoms at the corners of a tetrahedron. A schematic is shown in Fig. 2.1 plotted using freely available software¹. The unit cell in the wurtzite structure is characterised by two lattice constants: The edge length of the hexagonal base a and the height of the hexagonal prism c . Ga atoms are situated at two sites, $(0, 0, 0)$ and $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$, whereas the N atoms are at sites $(0,0,u)$ and $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2} + u)$, where u is an internal parameter defined as the length of the bond along the c -axis. The wurtzite structure is hence defined by the ratio of the parameters

¹Balls & Sticks <http://www.ccp14.ac.uk/ccp/web-mirrors/toycrate/bs/index.html>

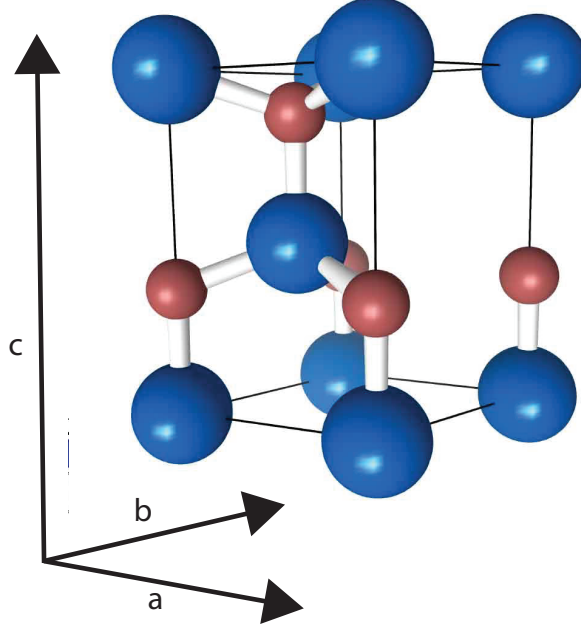


Figure 2.1: - Structure of wurtzite GaN unit cell, gallium atoms are in blue and nitrogen atoms in red

a , c and, u , where the ratio of $c/a = \sqrt{8/3} = 1.633$ and $u = 3/8 = 0.375$ in an ideal wurtzite crystal. However, the real values of u are found to differ from $\frac{3}{8}$. The measured values of a and c are approximately $3.188 \text{ \AA}$ and $5.186 \text{ \AA}$ at room temperature by X-ray diffraction (49). In this case $\frac{c}{a} = 1.626$ giving rise to a compressed unit cell in the $[0001]$ direction compared to the ideal crystal. The gallium atoms can be replaced by indium or aluminium atoms to form ternary/quaternary alloys which enables the engineering of crystals with a wide range of emission energies (50). A summary of typical experimentally determined lattice parameters of sapphire, AlN, GaN and InN is given in table 2.1. All of the work presented in this thesis was conducted on wurtzite GaN grown on sapphire by a commercial metal-organic chemical vapour deposition (MOCVD) procedure where typically, the substrate is heated to a temperature of up

2.1 Crystal structure of GaN

to 900 °C in the reactor. Subsequent cooling of the substrate gives rise to strain in the GaN layer due to difference in thermal expansion coefficients (51). The lattice and thermal mismatch in the of the substrate and epilayer gives rise to stress and strain, and thus a high degree of dislocations in GaN-based systems.

Typical Values			
	AlN	GaN	InN
$a(\text{\AA})$	3.112	3.188	3.544
$c(\text{\AA})$	4.982	5.185	5.718
u	0.390	0.378	0.384

Table 2.1: Typical experimental values of the lattice parameters of AlN, GaN, and InN (taken from references (52, 53, 54) . Table also shows the values of u compared to the ideal structure of $u = 0.375$

The effect of strain induced by lattice mismatch between layer and substrate alters the electronic properties of the epitaxially grown semiconductor. The growth of epitaxial layers within a certain thickness known as the critical thickness will take on the lattice constant of the substrate, resulting in strain. The lattice constant of the epitaxial layer perpendicular to the substrate, the c -axis in our common GaN c -plane growth, is forced to shrink or grow depending on the in plane lattice mismatch. Fig. 2.2 shows the two cases where the overlayer has lattice constant larger than the substrate, leading to an enlarged lattice constant in the growth direction and conversely a shrunken lattice constant perpendicular to the growth direction is seen when the lattice constant of the overlayer parallel to the interface is smaller than the substrate. This is known as pseudomorphic growth. Leyer *et al.* investigated the critical thickness of $\text{In}_{1-x}\text{Ga}_x\text{N}$ grown on [0001] GaN and found it to be ~ 7 to 10 nm for $x = 0.1 - 0.2$ (55).

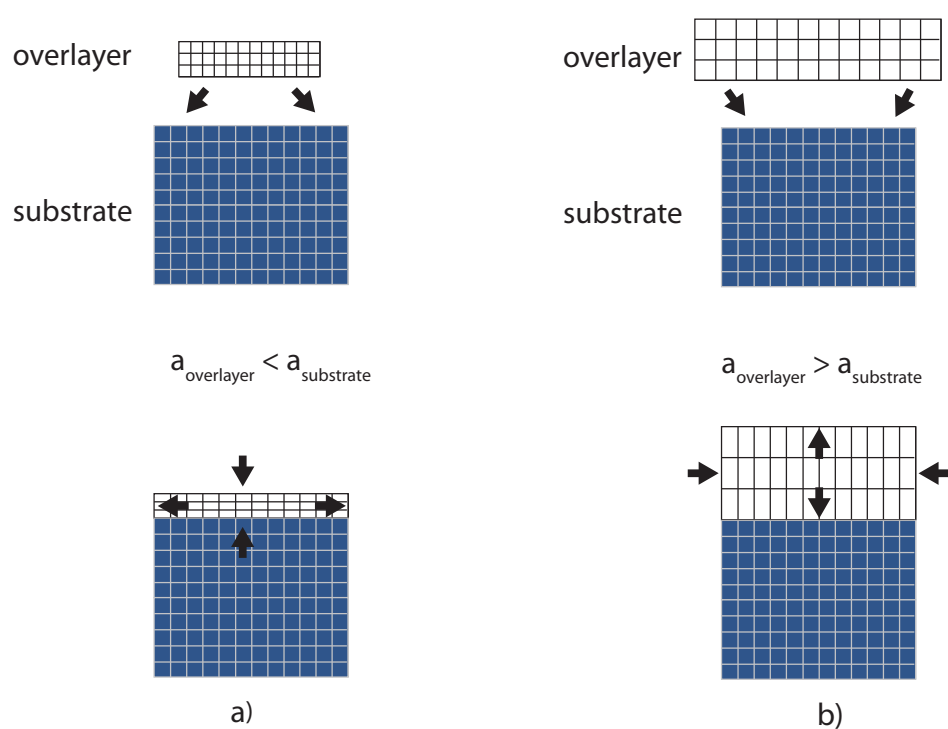


Figure 2.2: - Diagram of strained layer under pseudomorphic tensile and compressive strain. a) shows an overlayer of low lattice constant $a_{\text{overlayer}} < a_{\text{substrate}}$ under pseudomorphic tensile strain, the lattice parameter perpendicular to the boundary is shrunken. b) shows $a_{\text{overlayer}} > a_{\text{substrate}}$ under compressive strain, the lattice parameter perpendicular to the boundary is expanded

2.1.1 Polarisation

In group VI semiconductors such as silicon and germanium, the bonding is covalent and the shared electrons between the atoms have no preferential attraction to any site in particular. In the case of two different atoms such as GaN, the shared electron will in general be more strongly attracted to one of the atoms due to the difference in electronegativity. This results in a distortion of the electron cloud and is known as bond polarity. In the case of GaN, the high electronegativity of nitrogen (3.04) compared to gallium (1.81) creates a negatively charged nitrogen site and vice versa on the gallium sites. GaN crystallised in both zinc-blende and wurtzite forms has a polar axis. In wurtzite GaN, the bonds in the [0001] direction are aligned in the same direction of polarity giving a spontaneous polarisation to the unit cell.

The wurtzite space group $P6_3mc$, is non-centrosymmetric, and hence exhibits piezoelectric properties. The emergence of electric fields in response to strain has a great effect on the electronic properties of the system. Consequently, the combination of spontaneous and piezoelectric polarisation has a profound impact on the carrier recombination mechanisms in III-nitride devices.

2.2 Band structure of GaN

III-nitride semiconductors have a direct bandgap; in the case of GaN, this lies at 3.39 eV at the Γ point ($k = 0$) of the Brillouin zone. The concept of heavy hole, light hole and split-off band has limited validity to wurtzite structures. In wurtzite GaN, the

valence band near the Γ point are highly non-parabolic and single band effective mass approximations are no longer useful. The valence band is strongly affected by crystal field and the spin-orbit interaction, correspondingly a lifting of the degeneracy of the valence band splits it into three bands: (A), upper and lower (B) and (C) bands. The values of the energy splitting between the A and B bands is ~ 6 meV, and ~ 36 meV between the B and C bands (56).

2.3 Quantum confinement

2.3.1 Bandgap engineering

In common blue LEDs, a p-i-n structure is used, with an $\text{In}_x\text{Ga}_{1-x}\text{N}$ quantum well active layer sandwiched between p- and n- doped GaN. The quantum well confines the injected electron and holes spatially and by varying the indium content, the spectral range of emission can be altered. An important aspect of III-Nitride semiconductors for light emission devices is that by varying the composition x of the constituent atoms in the ternary alloys $\text{In}_x\text{Ga}_{1-x}\text{N}$ and $\text{Al}_x\text{Ga}_{1-x}\text{N}$, the emission wavelengths can be tuned in devices. Values for the bandgap of the ternary alloys are situated between the bandgaps for the pure forms of the two crystals bonded with nitrogen, that is, $E_{G\text{InN}} < E_{G\text{InGa}} < E_{G\text{Ga}}$, where E_G is the bandgap of the corresponding material. The dependence of bandgap of the ternary compound $\text{A}_x\text{B}_{1-x}\text{C}$ on its composition can be described by an almost linear relationship with the addition of a bowing parameter (b):

$$E_G^{A_x B_{1-x} C} = x E_G^{AC} + (1-x) E_G^{BC} - bx(1-x). \quad (2.1)$$

The values of E_G for InN vary widely in the literature as do the values of the bowing parameter (b). InN bandgaps have been reported to be as low as 0.7eV (57). As for AlN, a large bandgap of ~ 6.1 eV at room temperature (58) is generally accepted. This property combined with the relatively small lattice mismatch between GaN and AlN, makes AlGaN a frequent choice for use as a barrier material in nitride devices.

2.3.2 Quantum wells

Quantum wells (QW) can be realised by combining a thin layer of lower bandgap material with thickness comparable to the carrier's de Broglie wavelength, in between materials with higher bandgap acting as a barrier. This forms a 1D QW parallel to the direction of the interface. To understand the properties of a QW, the heterostructure can be treated as a 1D infinite QW resulting in a dispersion relation

$$E_n(k) = \frac{\hbar^2 \pi^2 n^2}{2m^* L} + \frac{\hbar^2}{2m^*} (k_x^2 + k_y^2) = \epsilon_n + \frac{\hbar^2}{2m^*} |\mathbf{k}|^2, \quad (2.2)$$

for quantum numbers n being positive integers and L is the well width. The first term, $\frac{\hbar^2 \pi^2 n^2}{2m^* L}$ corresponds to the quantisation of bound states by the infinite well and $\frac{\hbar^2 |\mathbf{k}|^2}{2m^*}$ term is the 2D free electron energy. The dispersion relation is parabolic for each n subband. The existence of these subbands gives rise to a step like density of states behaviour as opposed to the bulk structure where the density of states is a smooth continuous curve proportional to $E^{-\frac{1}{2}}$.

For a more realistic situation, the QW barriers need to be finite with a depth of V_0 . This problem can be solved by considering a trial wavefunction $\Psi(z)$ and considering that Ψ and its position derivative $\frac{\delta\Psi}{\delta z}$ remain continuous at the alloy interface. The solution Ψ and particle probability distribution Ψ^2 extends into the barrier regions; this is known as tunnelling. In practice, multiple quantum wells (MQW) are often used, and the tunnelling process plays a role when the MQW barriers are made sufficiently small; this leads to various optical phenomena being observed. Lee *et al.* gives an account of this in AlGaIn nanorods with thin GaN barriers (35). Tunnelling can also occur between localised states within the quantum well active layer. Brosseau *et al.* explains the long-lived, non-exponential carrier life-times in InGaIn QWs as the result of tunnelling between localised states formed from nanoscopic potential fluctuations (59)

2.4 Strain in InGaIn epilayers

The previous section greatly simplifies the actual InGaIn QW layers grown on GaIn. Strain, piezoelectric and spontaneous polarisation must be taken into account. Hooke's law relates the stress $\sigma = \frac{F}{A}$ and strain $\epsilon = \frac{\Delta L}{L}$ through the elastic modulus c ,

$$\sigma_{ij} = -c_{ijkl}\epsilon_{kl}. \quad (2.3)$$

Stress and strain are represented by rank 2 tensors hence the relationship mapping the two quantities is of rank 4 with a total of $3 \times 3 \times 3 \times 3 = 81$ components. However, in the absence of torque, the symmetry equates the shear components $\sigma_{xy} = \sigma_{yx}$ and we

can re-index the tensors using the Voigt notation:

$$\sigma_{ij} \Rightarrow \begin{pmatrix} \sigma_1 & \sigma_6 & \sigma_5 \\ \sigma_6 & \sigma_2 & \sigma_4 \\ \sigma_5 & \sigma_4 & \sigma_3 \end{pmatrix}. \quad (2.4)$$

This reduction in indices reduces the number of elements of the elastic modulus and it can be written as:

$$\sigma_i = c_{ij}\epsilon_j. \quad (2.5)$$

In the case of wurtzite structures, the stress-strain tensor can be written as:

$$\begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{xz} \\ \sigma_{xy} \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66} \end{pmatrix} \begin{pmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \epsilon_4 \\ \epsilon_5 \\ \epsilon_6 \end{pmatrix}. \quad (2.6)$$

This will be used in the following section to analyse the piezoelectric effect in wurtzite structures.

2.4.1 Piezoelectric effect

In addition to the spontaneous polarisation discussed in the previous section, piezoelectric polarisation needs to be taken into account in Wurtzite structures.

$$P_i = d_{ijk}\sigma_{jk}, \quad (2.7)$$

describes the relationship of the polarisation P_i induced by the stress tensor σ_{jk} , where d_{ijk} represents the piezoelectric tensor. With the symmetry of σ_{jk} , the number of independent elements of d_{ijk} is reduced such that:

$$d_{ijk} \Rightarrow \begin{pmatrix} d_{i1} & \frac{1}{2}d_{i6} & \frac{1}{2}d_{i5} \\ d_{i6} & d_{i2} & \frac{1}{2}d_{i4} \\ \frac{1}{2}d_{i5} & \frac{1}{2}d_{i4} & d_{i3} \end{pmatrix} \text{ and } P_i = d_{ij}\sigma_j. \quad (2.8)$$

For wurtzite symmetry, there only exist 3 components of d_{ij} , in full matrix notation P_i becomes:

$$\begin{pmatrix} P_1 \\ P_2 \\ P_3 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{pmatrix}. \quad (2.9)$$

Combining Hooke's law, $\sigma_i = c_{ij}\epsilon_j$, and the above equation, the piezoelectric polarisation can thus be written as:

$$P_i = d_{ik}(c_{kj}\epsilon_j) = e_{ij}\epsilon_j, \quad (2.10)$$

where

$$e_{ij} = d_{ik}c_{kj} \quad (2.11)$$

is the piezoelectric constant in the layer and consists of only 3 independent components. An in depth treatment is given in reference (60). Here, the relation between strain and piezoelectricity is established in the wurtzite structure. The typical values in III-nitrides for the piezoelectric constants have been determined by experiment and theory by many research groups. In the following section, an example of InGaN on GaN will be analysed to determine the degree of polarisation in the InGaN. In the c -axis growth direction (z in our representation), the polarisation is:

$$P_z = e_{31}(\epsilon_1 + \epsilon_2) + e_{33}\epsilon_3. \quad (2.12)$$

The strain of the system can be written as:

$$\epsilon_1 = \epsilon_2 = \frac{a - a_0}{a_0}, \quad (2.13)$$

and

$$\epsilon_3 = \frac{c - c_0}{c_0}, \quad (2.14)$$

where a_0 and c_0 are the lattice parameters in equilibrium. For InGaN layers, boundary conditions are of zero stress in the z direction (61), leading to $\sigma_3 = 0$. From Hooke's law, we can write:

$$\epsilon_3 = -2\epsilon_1 \frac{c_{13}}{c_{33}}. \quad (2.15)$$

The field due to the doped regions can be neglected as it is found at room temperature that this field is substantially smaller in magnitude than the polarisation fields (61). To calculate the piezoelectric potential P_{pz} , we can solve equation 2.9 which requires knowing piezoelectric tensor components and the stress of the system, or solving for equation 2.12, requiring knowledge of elastic modulus (stiffness) components and strain. We can use an interpolation method to approximate the physical properties of the ternary alloy $\text{In}_x\text{Ga}_{1-x}\text{N}$.

$$y(\text{In}_x\text{Ga}_{1-x}\text{N}) = xy(\text{InN}) + (1 - x)y(\text{GaN}). \quad (2.16)$$

Using parameters from Vurgaftman *et al.* (62) listed in table 2.2, we can interpolate

2.4 Strain in InGaN epilayers

the relevant parameters for $\text{In}_x\text{Ga}_{1-x}\text{N}$. Expanding equation 2.11 to a full matrix form,

Typical Values						
	d_{31} (pm/V)	d_{33} (pm/V)	c_{11} (GPa)	c_{13} (GPa)	c_{33} (GPa)	c_{12} (GPa)
GaN	-1.6	3.7	390	106	398	145
InN	-3.5	7.6	223	92	224	115

Table 2.2: Values of the dielectric tensor elements and elastic modulus elements for GaN and InN taken from Vurgaftman *et al.*

we have:

$$\begin{pmatrix} 0 & 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{15} & 0 & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66} \end{pmatrix}. \quad (2.17)$$

Thus, the values of the piezoelectric constants for indium concentration x can be determined after the interpolation of the InGaN parameters from table 2.2 and equation 2.16. e_{31} and e_{33} are found to be $\sim -0.52 \text{ Cm}^{-2}$ and $\sim 0.924 \text{ Cm}^{-2}$ respectively for an indium content of $x = 0.20$. Following the same type of interpolation, c_{13} , c_{33} , and the lattice constants of the InGaN layer with respect to x can be found. Using equation 2.12, the individuals components of the piezoelectric tensor can be filled out:

$$P_{\text{pz}} = \begin{pmatrix} 0 & 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{15} & 0 & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \epsilon_1 \\ \epsilon_1 \\ \epsilon_3 \\ 0 \\ 0 \\ 0 \end{pmatrix}. \quad (2.18)$$

Placing the e_{ij} elements in, we have:

$$P_{\text{pz}} = \begin{pmatrix} 0 & 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{15} & 0 & 0 \\ -0.52 & -0.52 & 0.924 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \frac{a_{\text{GaN}} - a_{\text{InGaN}}}{a_{\text{InGaN}}} \\ \frac{a_{\text{GaN}} - a_{\text{InGaN}}}{a_{\text{InGaN}}} \\ -2\epsilon_0 \frac{c_{13}}{c_{33}} \\ 0 \\ 0 \\ 0 \end{pmatrix}. \quad (2.19)$$

From the piezoelectric constant in the z -direction, the piezoelectric field across the boundary is simply given by:

$$E_{\text{pz}} = \frac{P_{\text{pz}}}{\epsilon_r \epsilon_0}. \quad (2.20)$$

The resultant electric field, E_{pz} due to the piezoelectric polarisation for a 20% ($x=0.2$) indium content QW is $\sim 3.7 \text{ MV cm}^{-1}$. The variation of E_{pz} with indium content x is plotted in figure 2.3, which shows the increase of the piezoelectric field with the increase in indium content of InGaN. This increase in the electric field has significant consequences in trying to achieve efficient light emitters of lower energy photons with InGaN quantum wells.

2.4.2 The quantum confined Stark effect

In the previous section lattice mismatch is shown to strain a thin film layer of InGaN. The non-centrosymmetric wurtzite crystal exhibits piezoelectric polarisation and it is shown by first principles that the resultant internal electric field in the ternary alloy layer is in the order of MV cm^{-1} . There is almost linear dependence on the incorporation content of the ternary compound. The presence of an internal electric field on quantum confined structures such as quantum wells, discs, wires, and dots is known as the quantum Stark effect (QCSE). This can be described by looking at a perturbation

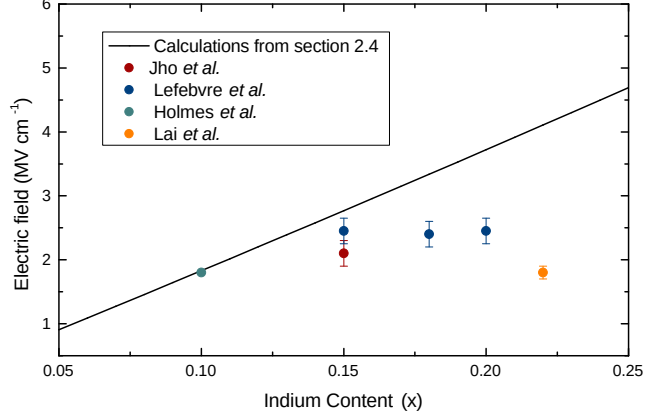


Figure 2.3: - Calculated piezoelectric field magnitude by first principles with respect to indium content compared to calculations and measurements reported in a few selected literature. Jho *et al.* has measured the field to be 2.1 MV cm^{-1} for $x = 0.15$.(63) Lefebvre *et al.* measurements are around 2.45 MV cm^{-1} for indium composition between $x = 0.15 - 2.0$ (64). Lai *et al.* (65) reported a lower 1.9 MV cm^{-1} for a $x = 0.22$ InGaN layer. Calculations performed by Holmes (66) reports a 1.8 MV cm^{-1} for $x = 10$

on the energy levels and wavefunctions of the QW due to an electric field acting perpendicular to the QW layer. As a result of the internal electric field, the band structure is modified and has two major consequences.

1. Reduction of effective bandgap leading to red-shift of the emission relative to an unstrained structure
2. Tilting of bands forces carriers to be distributed preferentially at opposite sides of the quantum well.

The band tilting effect is illustrated in figure 2.4, where a simulation was carried out on a 1 dimensional $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}$ QW of 2nm well width with GaN barriers using *nextnano*¹, a semiconductor nanodevice simulation package. Nextnano deals with the geometries and combination of materials in the device in one, two and three spatial dimensions

¹<http://www.nextnano.de/nextnano3/>

by defining a materials grid with the system parameters. The simulator minimises the strain in the system and solves for the band structure using a finite differences method, taking into account piezoelectric effects. The band diagram of a simple one-dimensional GaN/InGaN quantum well system has been calculated in Fig. 2.4. The effects of band gap reduction can be seen in the figure. The electric field perturbs the

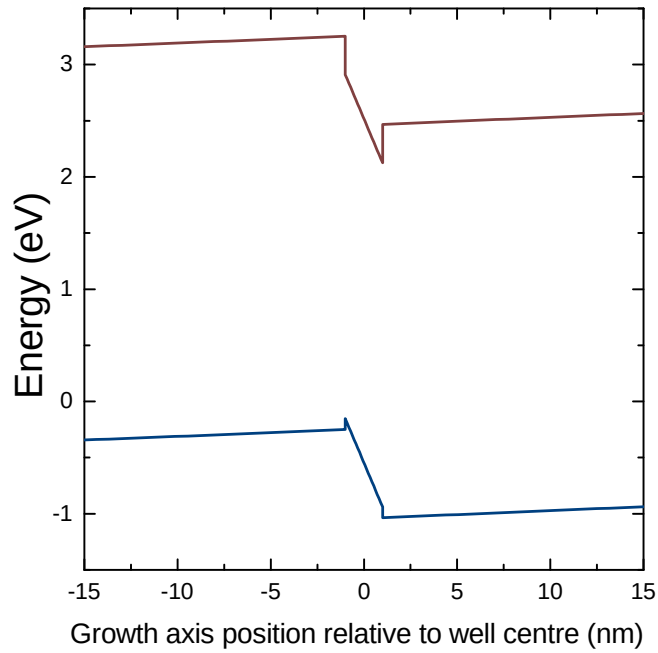


Figure 2.4: - Band structure of 2 nm $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}$ QW embedded in GaN. The strained QW tilts the band edges and reduces the apparent bandgap

ground state energy of the electron and hole wavefunctions in the QW. As a result, the carrier wavefunctions are spatially separated along the c-axis (perpendicular to the QW interfaces). A reduction in the overlap in the carrier wavefunctions causes a reduction in the rate of recombination.

Strain alone can also have a direct effect on the conduction and valence band edges through deformation potentials which describe the splitting of the band edges for tensile

	AlN	GaN	InN
$P_{\text{sp}} (\text{Cm}^{-2})$	-0.081	-0.029	-0.032

Table 2.3: Spontaneous polarisation constants of AlN, GaN and InN taken from calculations by Bernardini *et al.* (67)

or compressive strain along the [0001] axis. Hence, as a direct result of strain, the emission energy, line width, carrier recombination rate and probability of quantum confinement are greatly altered.

2.4.3 Polarity and wavefunctions

Accompanying the piezoelectric polarisation P_{pz} , we need to take into account the spontaneous polarisation P_{sp} due to the wurtzite symmetry as described in the previous section. In InGaN/GaN systems, piezoelectric polarisation is generally over an order of magnitude stronger than the effect of spontaneous polarisation. Nonetheless, the combined polarisation P_{total} can be written as:

$$P_{\text{total}} = P_{\text{pz}} + P_{\text{sp}}. \quad (2.21)$$

Spontaneous polarisation is parallel to the [0001] axis, and the constants for AlN, GaN and InN are given in table 2.3. Spontaneous polarisation constants for the ternary alloys of content x , can be approximated using the linear interpolation technique used in the previous calculations of the piezoelectric field. The effects of both spontaneous and piezoelectric polarisations on the carrier wavefunctions in an InGaN QW structure can be calculated and probability distributions visualised by using nextnano. Solving of the Poisson equation handles the spontaneous polarisation in the InGaN/GaN interface. In

addition, the piezoelectric polarisation is considered in the calculation by using a strain minimisation method employed by nextnano. The method is an iterative process that considers the overall strain energy and tries to minimise this by allowing relaxation and increase of strain in different areas of the user defined material grid. The self-consistent solution of the Schrödinger equation is determined for the wavefunctions. The resultant calculations for the carrier probability distributions are shown in Fig. 2.5. The hole wavefunction is marginally confined within the QW and a small overlap of the wavefunctions can be seen.

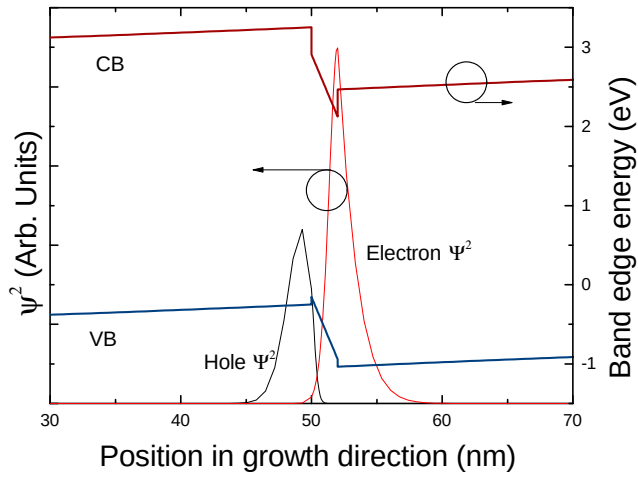


Figure 2.5: - Electron and hole wavefunctions (Ψ^2) with the corresponding calculated bands showing high spatial separation of the two carriers on opposite sides of the QW.

2.4.4 Carrier field screening

Photoluminescence of the strained QW photoemission will appear red-shifted because of the QCSE. However, an increase in the density of carriers generated by the excitation

source of the experiment leads to local screening of the electric field in the QW. The QCSE is therefore reduced and the tilted bandgap thus becomes flattened and recombination occurs at higher photon energies. The flattened bandgap means that the hole and electron probability wavefunction are now situated closer together in the centre of the QW, causing a larger carrier wavefunction overlap resulting in a higher oscillator strength of the exciton recombination transition (68). Experimentally, the increase in carrier density can almost always be seen to be accompanied by a shift in peak emission energy along with a decrease in recombination life-time in InGaN quantum wells. Although this is indicative of carrier screening of the internal field of the QW(69), it is rarely the sole effect. Localised states play an important role in the carrier dynamics of InGaN QWs. This added complication is responsible for giving InGaN QWs some very interesting optical characteristics.

2.4.5 Phase separation

The challenge of obtaining a full visible emission spectrum from InGaN is not only limited by the recombination inefficiencies with higher indium contents but also the difficulty in growing InGaN at different indium contents. Thermodynamically stable InGaN cannot be easily grown with high crystalline quality at different indium concentrations. There is a large difference in interatomic spacing between GaN and InN. In early studies, Ho and Stringfellow calculated a phase diagram of InGaN in their paper on miscibility of InGaN (17). Fig. 2.6 shows this phase diagram taken from their paper, showing a solid phase miscibility gap with a consolute temperature of approximately

1250 °C. Within the miscibility gap, the ternary alloy cannot exist in a single phase.

The arch-like curve shown is known as the coexistence curve.

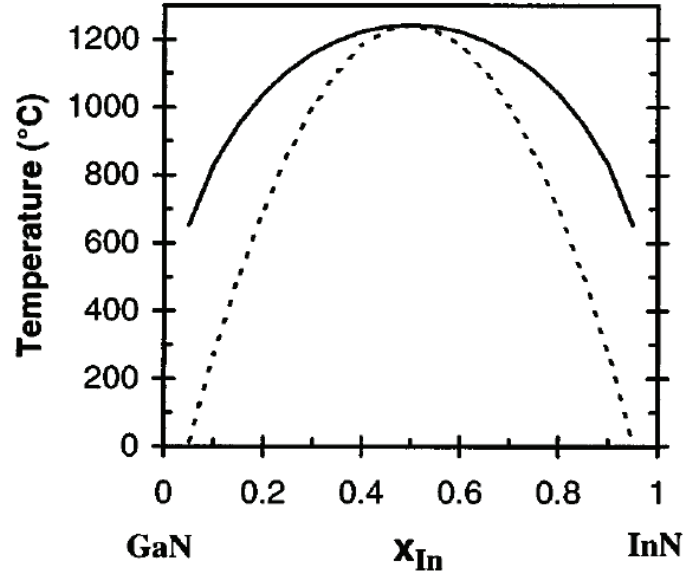


Figure 2.6: - Binodal (solid) and spinodal (dashed) curves for the $\text{Ga}_{1-x}\text{In}_x\text{N}$ system, taken from ref. (17) calculated by Ho and Stringfellow

Ho and Stringfellow went on to deduce that for temperatures of 800 °C, the solubility of In in GaN is calculated to be less than 6%. The spinodal composition is calculated to be 22%. Between the spinodal limit and the binodal curve, the system is known as being “metastable”. Phase separation into InN and GaN would occur and early metalorganic vapour phase epitaxy InGaN growth seemed to show evidence of this phase separation. This phase segregation is thought to form InN rich islands acting as deep traps, preventing carriers from recombining in dislocations (70). As shown earlier, InGaN quantum wells are typically under strain, whereas the calculations from Ho and Stringfellow considered relaxed InGaN. It has been shown that under strain, the phase separation can be suppressed (71). Karpov calculated a phase diagram for strained

InGaN. It shows that the spinode shifts to lower temperatures and towards the high In concentration side compared to that from Ho and Stringfellow (71). Strain engineering can thus lead to higher indium content quantum wells emitters (12). However, the insolubility of GaN and InN is still one of the big challenges preventing the continuous tuning of InGaN LED emission wavelength to span across the visible spectrum from UV-A to the near infra-red.

2.4.6 Localised states in InGaN quantum wells

Despite poor crystalline quality, early GaN based LEDs from Nichia achieved very high brightness, showing remarkably little sensitivity to structural dislocations (72). In fact, even dislocation densities of up to $2 \times 10^{10} \text{ cm}^{-2}$ do little to impede the blue LED's performance (73). Explanations of this exceptional behaviour suggested that some nano-scale structural features prevented non-radiative recombination of carriers. Initially, spatial distribution of indium was thought to vary over the $\text{In}_x\text{Ga}_{1-x}\text{N}$ layers. Gerthsen *et al.* reported indium segregation and measured lattice parameters with transmission electron microscopy (TEM), showing indium-rich agglomerates with sizes of a few nm. These suspected indium rich regions act as potential traps, creating localised energy states. Indeed, sharp emission lines were spatially resolved by photoluminescence spectroscopy using metal masks with small aperture openings on InGaN/GaN QW samples (74).

However, later studies have pointed out that the materials characterisation methods, in particular transmission electron microscopy (TEM) techniques used to directly

observe indium clustering were not entirely convincing (75). Smeeton *et al.* (76) demonstrated that the electron beam used in characterising the InGaN QWs were in fact damaging the active layer, giving apparent indium-rich regions. This finding invalidated a fundamental observation supporting the arguments for indium clustering, further opening up the debate on what accounts for the success of the blue LED in the mid-late 2000s.

An alternative school of thought on the localisation effect is fluctuations in QW width (12). Despite continual improvements in epitaxial techniques, these fluctuations are unavoidable (77). The quantisation energy depends on the width of QW, hence small changes in QW width can localise and trap carriers spatially across the plane. This results in quantum dot-like optical behaviour. In addition to the spatial fluctuation of potential, the thickness of the InGaN also affects the band due to the piezoelectric effect in the strained layer (78). It has also been shown that the degree of localisation or disorder increases for a greater indium content (79).

Localised states in InGaN QW structures can be demonstrated experimentally by an “S-shape” observed in the photoluminescence peak energy as the temperature of the sample is varied from cryogenic temperatures up to room temperature (80). The impact of localised states in QWs on the recombination dynamics have in the past decade been extensively studied by time resolved photoluminescence (81) and even direct observation of excitonic states in plane QWs (81).

Structural characterisations on the morphology of InGaN layers conducted by van der Laak *et al.* have shown QW width fluctuations and even discontinuity in the InGaN

layer. Interlinked strips of InGaN have been observed forming a complex network around dislocations (82). The extra confinement from these strips may indeed restrict carriers from recombining non-radiatively at these dislocations, accounting for the high efficiencies in the studied LEDs. But it is generally well accepted today that some form of localisation effect is what allows for the efficient radiative recombination of carriers despite the high density of defects.

2.4.7 Lifetime of a quantum system

For a two-level system with energy levels E_1 and E_2 (ground and excited states), when a photon of energy $h\nu$ is absorbed, the rate of absorption, promoting a charge carrier from E_1 to E_2 can be given by

$$R_{absorption} = B_{12}N_1\rho(\nu), \quad (2.22)$$

where $\rho(\nu)$ is the spectral energy density at frequency ν and B_{12} is the Einstein coefficient of absorption, and N_1 is the population of energy level E_1 . The rate of stimulated and spontaneous emission is given by

$$R_{stimulated} + R_{spontaneous} = A_{21}N_2 + B_{21}N_2\rho(\nu), \quad (2.23)$$

where A_{21} and B_{21} are the Einstein coefficients of spontaneous emission and stimulated emission respectively, and N_2 is the population of energy level E_2 . The rate equation for the change in population density of E_2 is thus given:

$$\frac{dN_2}{dt} = -A_{21}N_2 - B_{21}N_2\rho(\nu) + B_{12}N_1\rho(\nu), \quad (2.24)$$

For spontaneous emission, the rate equation yields:

$$N_2(t) = N_{20}e^{-A_{21}t}, \quad (2.25)$$

where N_{20} is the population density at time $t = 0$, and the spontaneous lifetime is given by $\frac{1}{A_{21}} = \tau$. The lifetime of the system is related to the transition rate between level 2 and level 1 which is the rate of change of the transition probability known as *Fermi's golden rule*

$$R = \frac{2\pi}{\hbar} |W_{12}|^2 D(E), \quad (2.26)$$

where $W_{12} = \langle 2|W|1 \rangle$ is the transition matrix element, W is the perturbation Hamiltonian, $D(E)$ is the density of the final states. In semiconductors, the transition between states 1 and 2 occurs between the conduction band and the valence band. For spontaneous emission, the transition matrix element is proportional to the overlap of the envelope electron and hole wavefunctions $\langle \Psi_e | \Psi_h \rangle$ (83). The spontaneous rate of recombination is thus proportional to the square of the electron and hole wavefunction overlap. In an InGaN QW system such as that shown in Fig. 2.5, the calculated wavefunction overlap is very small. The spatial separation causes a slow rate of recombination which can be measured by an extended decay rate of the QW emission.

Transition from level 2 to level 1 may go through intermediate states which may be non-radiative. In a simplified recombination process shown in Fig. 2.7, two paths are possible. The radiative process has a constant rate of decay, but the radiative lifetime τ_r is dependent on the number of carriers in level 2. The carriers in this level

also participate in the second recombination pathway (which we assume here is non-radiative). Hence the two decay processes compete and the effective life-time τ_{eff} in relation to τ_r and the non-radiative lifetime τ_{nr} is given as:

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_r} + \frac{1}{\tau_{\text{nr}}}. \quad (2.27)$$

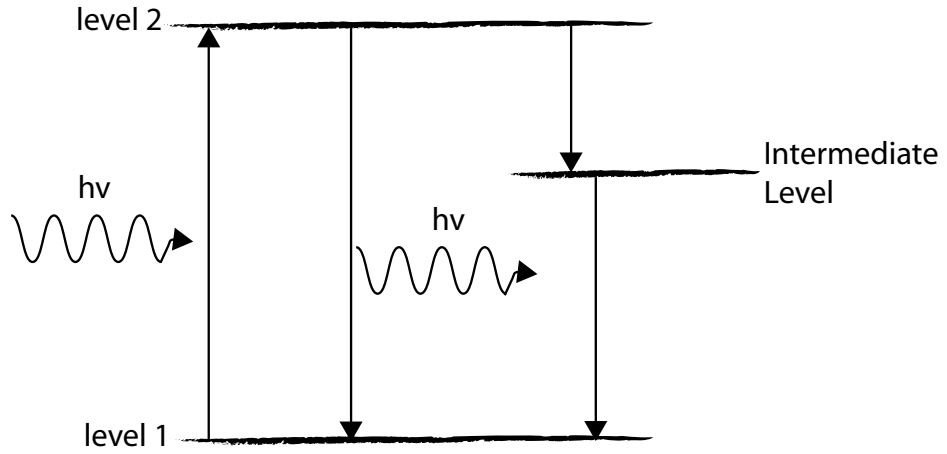


Figure 2.7: - Diagram of the interaction of a two-level system with a radiation field. A radiative process is shown giving a photon of energy $h\nu$ and a competing recombination process via an intermediate state

The lifetimes are inversely proportional to the recombination rates of the two processes. Radiative efficiency can thus be written as:

$$\eta = \frac{R_{\text{Rad}}}{R_{\text{total}}} = \frac{1}{1 + \frac{\tau_r}{\tau_{\text{nr}}}} = \frac{\tau_{\text{eff}}}{\tau_r}. \quad (2.28)$$

This gives a relationship between radiative (quantum) efficiency and measurable lifetimes of the system.

The simplified two-level system in Fig. 2.7 can be used to describe the effect of localised states on the emission dynamics of QWs, if we treat the intermediate energy

level as the localised state which recombines radiatively. Carriers are first generated in the QW (level 2) and a proportion of these carriers subsequently relax into localisation centres (intermediate level). Zhang *et al.* used this analysis to describe the interactions of InGaN QWs with localisation centres (84). The discussion on localisation effects is continued in the following chapters.

3

Fabrication techniques

3.1 Introduction

There are commonly two approaches to fabricate nanorod devices used for LED and photonic crystal applications.

1. Top down approach. Where the nanorods are etched into pre-existing GaN wafers (84)
2. Bottom up grown approach. Where the nanorods are grown by self assembly by precise reactor conditions (36, 40, 85, 86) or through selective area growth via masking (87)

While both these approaches have their advantages, there have been significant advances in the grown nanorods due to the high crystalline quality that can be achieved. The possible reduction of the internal piezo-electric field in active layers also leads to

the prospect of increased efficiency in high indium content InGaN QW LEDs prompting an abundance of research into the growth of nanorods resulting in very promising ideas for LED applications reported by Kishino *et al.* (21, 31, 44)

The top down etching approach, in contrast, relies on having suitably good wafer crystalline quality before nano-processing is performed. Current LED wafer growth, material properties and fabrication techniques are well understood and have been commercialised in the past decade. Low cost, *relatively* high quality wafers are available off the shelf. The top down etching approach can be an addition to the commercial process reducing the complications in acquiring new designated growth processes in production plants to realise photonic crystal LED based devices. The majority of this work focusses on the top down etched nanorods.

3.2 Principles of nanoprocessing

Nanoprocessing is a generalised term referring to miniaturisation of devices and circuit processing technologies and also atomic level manipulation such as crystal growth and epitaxial techniques. This chapter focusses on on miniaturisation processing technologies.

A series of different fabrication techniques were employed to produce etched nanorod samples, mostly: thin film deposition, lithography, resist technology, and thin film etching. The principle is to generate a pattern, which is then transferred onto a sample surface such that additional material can be deposited or removed according to the pattern on the sample. This is then repeated layer by layer and it is not uncommon

that a wafer would go through more than several tens of processing stages to produce commercial devices.

3.2.1 Pattern transfer

The pattern transfer principle draws parallels from traditional photographic film processing techniques. In film photography, a light sensitive emulsion is deposited onto acetate film. An image is projected onto the film through a camera and lens. Bright parts of the image expose the emulsion and change its chemical properties. By developing and fixing the film, the dark unexposed parts of the image get removed selectively due to the emulsion's light sensitivity. As a result, a negative of the image is left on the acetate. In nanoprocessing, the sample wafer replaces the acetate and the photographic emulsion is replaced by a resist. The image writing system can either be optical (mask aligner and stepper) like photography, by direct writing using electrons (electron beam lithography) or by applying pressure (imprint lithography). The pattern transferred to the resist is then developed. According to whether the resist is *positive* or *negative*, the exposed resist can be left behind or removed, leaving behind a positive or negative sample pattern covering the surface of the sample.

3.2.2 Etching and deposition

With the negative (positive) pattern formed on the sample surface with resist, material can be added by thin film deposition or removed by etching. Metal evaporation is a common thin film deposition technique used in making masks and electrical contacts.

Metal	Heater Source	Current
Al	Tungsten wire coil	45A
Au	Tungsten Boat	50A
Ni	Tungsten Dimple Boat	70A

Table 3.1: Metals evaporated in the *Edwards 306* with the boat type and current used

In this work, an *Edwards auto 306 evaporator* with a rotating turret boat holder for different metals in an evacuated bell jar is used. The thickness of the metal can be controlled via a crystal monitor. A brief summary of typical evaporation currents and heater sources (in which the metal is placed) is shown in table 3.1

Metals which are evaporated on to the sample will adhere to its surface as well as to the resist. The resist can then be washed off, leaving behind only the metal that was directly on the sample surface, hence creating a pattern of metal on the sample. This technique is called *lift-off* and is used to produce metal patterns in small areas of the sample.

Alternatively, a metal coated sample surface can be patterned with resist leaving exposed areas of metal. The sample can then be put in metal etcher which will selectively etch away parts of the exposed metal layer. Since the resist protects the metal underneath it, patterns can be made in the metal layer. This method is used to create small openings on metal masks and has been employed by our research group to isolate and register single quantum dots. (88, 89)

3.2.3 Structural analysis

The optical microscope provides a quick way to inspect the processing between steps. Despite being limited in resolution to features of $\sim$ few μm , the optical microscope is useful in looking at procedures such as resist development progress. When higher resolution images of the sample are required Scanning Electron Microscopy (SEM) is used to examine the nanostructures. A *Hitachi S-4300 SEM* is used for imaging structures down to $\sim 50\text{ nm}$. It is equipped with a rotating and tilt stage, and outputs images of 2560×1920 pixels. For non-conducting samples, electron accumulation causes charging on areas of the sample deflecting electrons. This is particularly serious when attempting to image resists, and very often a thin layer of metal can be deposited on top of these samples to obtain a clear image. In cases where thickness of a thin layer need to be measured, a *Dektak* profilometer can be used. The *Dektak* uses a low force stylus which is dragged across the sample surface to create a height profile such that nanometer vertical resolution can be achieved. If the sample requires even higher resolution, Atomic Force Microscopy (AFM) is employed to examine fine structural details in the three spatial dimensions.

3.3 Nanorod array fabrication

Nanorod array samples are fabricated by the Department of Electrical and Electronic Engineering at the University of Bath on commercially available LED wafers provided by OSRAM. The wafers consist of epitaxial grown GaN/InGaN P-i-N LED structure

on a sapphire substrate.

There are a multitude of available nanofabrication methods to create top down etched devices. The goal of the project in Bath was to create a photonic crystal array of nanorods which will provide advantages for light emitting diodes primarily for lighting. The design is a simple process of removing material from the wafer in a regular pattern with high precision. Common methods of patterning are: photolithography (mask aligner, stepper), electron beam lithography and nanoimprint lithography. Nanoimprint lithography was the preferred method due to the extremely low cost starting costs, high throughput, and low feature size (down to 20nm, (90, 91)) on large areas.

3.3.1 Nanoimprint lithography

Nanoimprint lithography (NIL) or hot embossing is a novel manufacturing technique pioneered by Chou (92) in 1996. NIL relies on mechanical deformation of resist by a master template for pattern transfer. It has been proven to achieve feature sizes which are beyond the resolution limits of optical lithography techniques at a relatively lower cost to mass produce. The resolution of NIL therefore depends primarily on the ability to fabricate fine featured master templates used to print the resist. These are currently made using electron-beam lithography methods to fabricate features down to 25 nm quite readily.

One major disadvantage of mechanical lithography is the difficulty of alignment. However, in fabrication of arrays of holes or rods with spatial translation symmetry across the whole wafer, such as preparation of large scale photonic crystals, alignment

is not particularly important. This makes NIL particularly interesting especially in the blue spectral region where short wavelengths require low feature sizes pushing manufacturing limits of conventional photo-lithography techniques.

Typically, nanoimprinting consists of two steps:

1. Imprinting of the mould by physically pressing it onto a substrate thinly coated with a liquid resist. The resist is hardened either thermally or by UV light exposure before removing the mould.
2. Pattern transfer onto the substrate surface by etching the thin residue layer of resist by reactive ion etching, creating the resist pattern on the substrate ready for further processing

There are many variations of nanoimprinting that have been developed in the past decade. Roller imprint process is chosen for the “*SMASH*” project at University of Bath as it offers a very high throughput and high wafer scale uniformity. The high throughput is achieved since the imprint process is continuous, the actual imprinting does not need to stop from wafer to wafer. The contact area of the mould and the substrate where pressure is applied is small and constant and hence evenness across the wafer is achievable. Roller nanoimprinting, as the name implies, is a roller-type continuous manufacturing method. There are two main approaches, the first of which is a roller mould, where the roller itself has embedded on it, a mould. A second approach is a flat mould and smooth roller type, where generally a flexible mould is used and the roller “irons” the pattern onto a soft resist surface. For development purposes,

the latter approach was taken upon since flat mould fabrication is much cheaper for prototyping and accuracy is very high.

3.3.2 Nanorod array processing procedures

An intricate series of etching processes are performed on the sample to produce nanorod arrays developed at the University of Bath. An outline of the process is given below:

1. Transfer of positive nanorod pattern onto resist spin onto substrate (nanoimprinting).
2. Preparation of GaN etch mask by nickel deposition and performing a liftoff.
3. Inductively coupled plasma reactive ion etching (ICP RIE) to form a nanorod array on the sample
4. Wet etching with potassium hydroxide (KOH).

The individual steps of the patterning are documented in Fig. 3.1 and the etching steps are shown in Fig. 3.2 Fig. 3.1(1) shows a 2 inch LED wafer prior to processing. A UV hardening resist is spin coated onto the wafer shown as the two shaded layers in 3.1(2). Subsequently a master mould is placed on top of the sample, mechanically imprinted on to the resist by a roller shown in 3.1(3). The resist is hardened by exposure to UV and the mould peeled off the sample 3.1(4).

The next step is to form a ICP RIE etch mask with nickel from the pattern using lift-off. This step is not straight-forward, since there is residual resist on the surface of the sample, which will have an effect on nickel adhesion and the sample uniformity. In

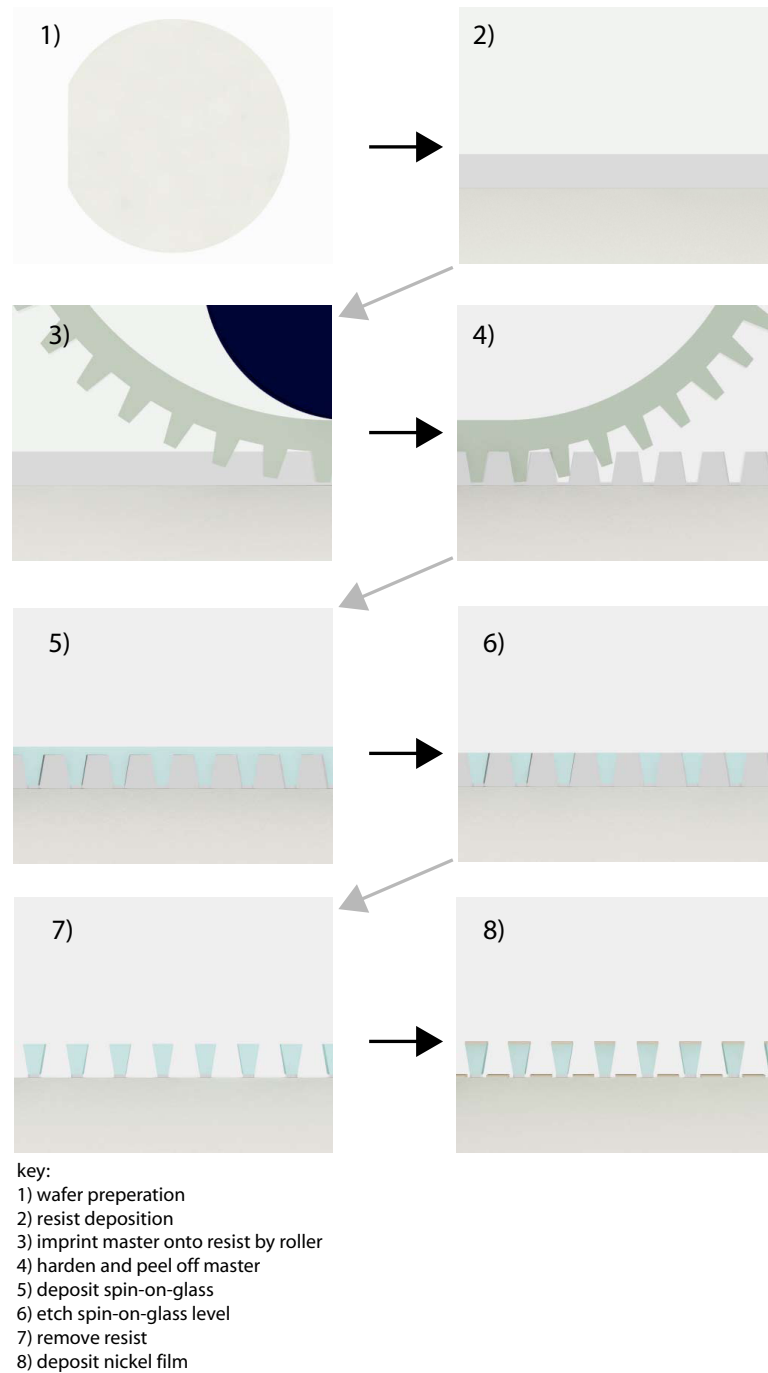
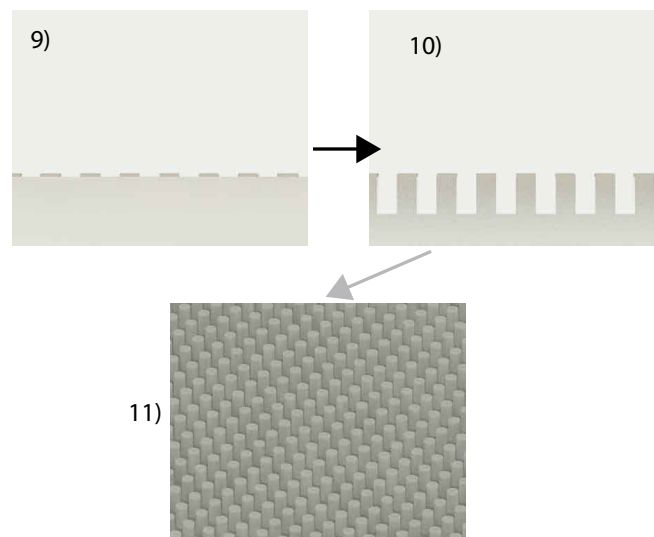


Figure 3.1: - Diagram showing the processes of nanoimprint lithography, steps are numbered and are briefly described in the key



key:
9) lift off resist, leaving nickel island mask
10) ICP etch, into the wafer structure
11) nanorod array formed

Figure 3.2: - Diagram showing the processes of ICP etching, steps are numbered and are briefly described in the key

3.3 Nanorod array fabrication

order to overcome this, a novel spin-on-glass (SOG) technique is employed, described in Fig. 3.1 (5-8). Upon removal of the imprinting mould, SOG is deposited on to the sample, covering the resist. The conformal deposition ensures that a thin layer of SOG covers all the resist pattern features. RIE is then used to etch down the SOG, exposing the resist on the surface, shown in 3.1(6). Next, the sample is washed in solvent to remove the nanoimprint resist through the gaps of the SOG, leaving a lattice of SOG with a positive pattern of the mould on the sample surface shown in 3.1(7). The sample is then mounted in an evaporator and a layer of nickel is deposited on top. The deposition is non-conformal meaning the nickel amongst the holes of the SOG lattice is isolated from the nickel which coats the top layer of the SOG, shown in 3.1(8).

Fig 3.2 (9) shows the lift-off procedure. Hydrofluoric acid (HF) is used to dissolve the SOG, leaving the isolated nickel on the surface of the wafer. The nickel acts as an ICP etch mask, which is highly resistant to the etching procedure. The ratio of the etching rates of GaN compared to nickel in our desired etching conditions is found to be around 30:1. Therefore the thickness deposited is dependent on the depth of the required etching. Finally ICP etching is carried out on the sample using chlorine and argon plasmas. The nickel etch mask prevents the underlying crystal from being attacked, allowing high aspect ratio nanorods to be formed as shown in 3.1(10, 11). Fig. 3.3 shows an SEM image of a nanorod array fabricated using this technique.

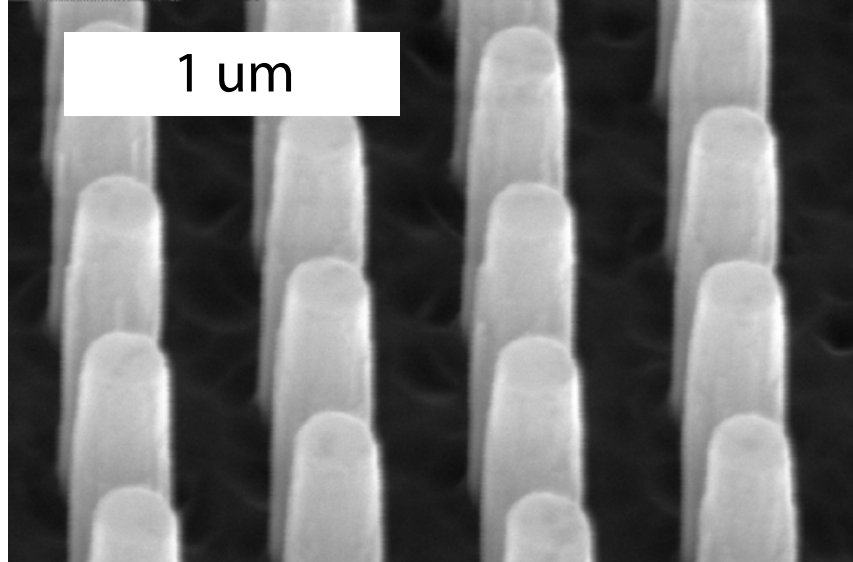


Figure 3.3: - SEM image showing nanorod arrays fabricated by nanoimprint lithography by YiDing Zhuang at the University of Bath

3.4 Grid fabrication

Reference grids have been fabricated on the samples used in this thesis in order to register individual nanoscopic features. Grids with numbered references were designed to give a clear image under our optical microscope. Previous reference systems were prepared using an etching method, gold layers were deposited and grid patterns were made by etching through the thin gold layer. The metal surface can be problematic in experiments when electronic contacts need to be used. An alternative method is to use lift-off to produce a metal reference pattern detailed below.

5 mm $\times$ 5 mm silicon wafers were used and patterned with an electron beam (e-beam) lithography system with a custom made grid. The grid design was made using *Autocad*, and the design is shown in Fig. 3.4 The large crosses are alignment markers

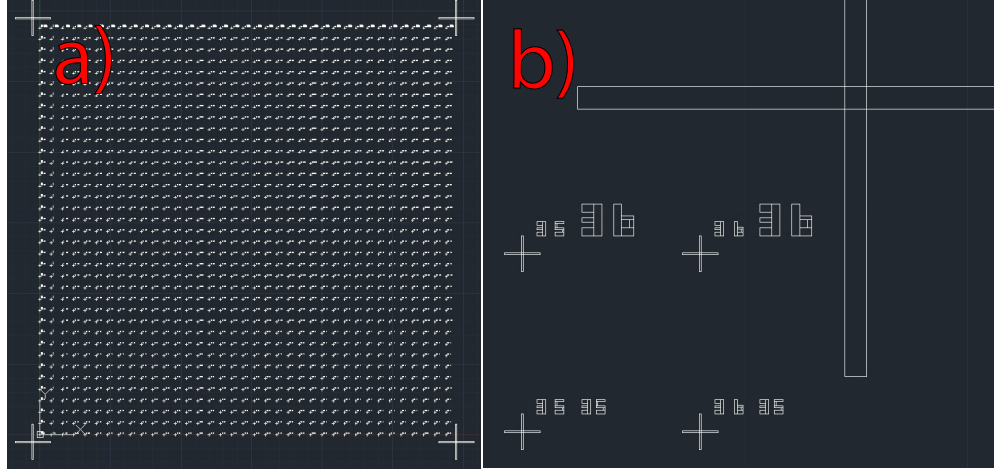


Figure 3.4: - CAD design of reference grids. a) shows the entire grid covering an area of 36 mm $\times$ 36 mm. b) an enlarged section of the grid showing the grid references.

such that the sample can be re-aligned allowing further processing such as fabrication of electric contacts on specified coordinates.

To perform a successful lift-off, two layers of resist of different exposure/development characteristics are typically used; this is known as a bi-layer resist. Upon electron beam exposure, both the resist layers are exposed with the desired pattern. The underlying resist is chosen to have a lower contrast and higher dissolution rate. After development, the underlying layer undercuts the top layer resist. This increases the separation of any subsequently deposited material between the resist and the sample surfaces, enabling a clean lift-off.

A layer of poly(methyl methacrylate) (PMMA) 495 A4 is spun on top of the surface of the wafer, subsequently PMMA 950 A8 is spun on as a top layer. The samples are exposed with the pattern in Fig. 3.4 by a *Jeol JBX-5500ZC* e-beam system and developed using a 1:3 methyl isobutyl ketone (MIBK) to isopropanol (IPA) ratio for

60 s. A post development optical microscope image is shown in Fig. 3.5 a). 50 nm of aluminium is then evaporated onto the surface of the developed resist; an SEM image is shown in Fig. 3.5b). A magnified SEM image of the number “9” in Fig. 3.5 c), clearly shows a thin layer of aluminium over the resist. The side profile shows that the aluminium on the resist layer is severed from the aluminium on the substrate with a clean edge. After lift-off with a solvent, the aluminium grid reference pattern is left on the wafer. Fig. 3.5 d) shows the reference grid with AlGaN nanocolumns dispersed on the surface. Single AlGaN nanocolumns can be seen to the left of the number “38” and to the bottom right of the alignment cross. The identified single nanocolumns can subsequently be examined with micro-photoluminescence and electrical contacts can also be made to an isolated nanocolumn.

3.5 Nanorod masks of varying size

For wafer scale fabrication by nanoimprinting, the original master moulds must be fabricated again each time a change is made to the dimensions, pitch and shape of the nanorod etch masks. Since NIL is a mass manufacturing technique this adds complications when it comes to making quick prototypes. Modifications to the master moulds are costly to make, and therefore electron beam lithography is generally used in the initial experimental developments where full wafer fabrication is not required.

For the purpose of studying nanorods of varying diameter, ideally the nanorods need to be fabricated on the same wafer to control the wafer variations. Etch masks with decreasing diameter from 5 μm micropillars to 50 nm nanorods were fabricated.

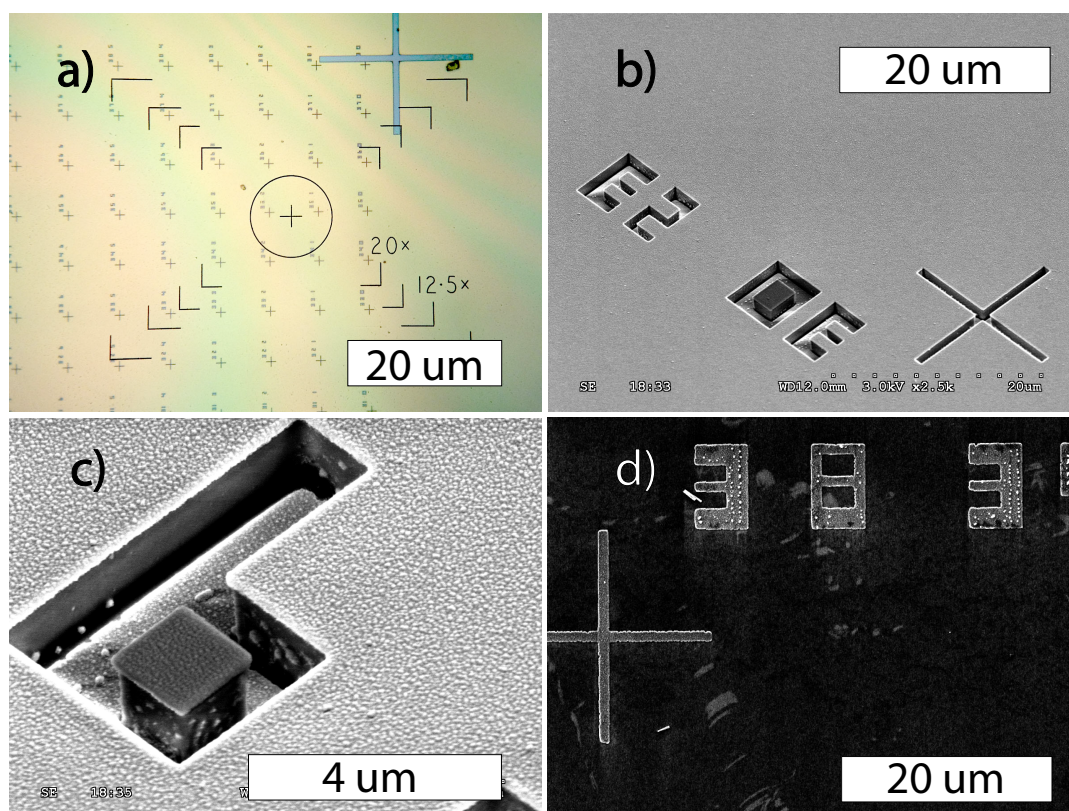


Figure 3.5: - Images of fabricated alignment reference grids. a) Optical microscope image of developed resist. b) SEM image of grid after aluminium coating. c) SEM image showing aluminium layer with slight overhang. d) SEM image showing AlGaIn nanorods scattered on the fabricated grid after lift-off

3.5 Nanorod masks of varying size

The micro pillars and the nanorods are to be made on the same wafer next to one another, but also to be far enough apart such that each can be separately resolved by our microscope. Fig. 3.7 shows the design used to fabricate the nanorod etch masks. A lift-off procedure shown in Fig. 3.6 was then used to perform the pattern transfer for the nickel etch mask.

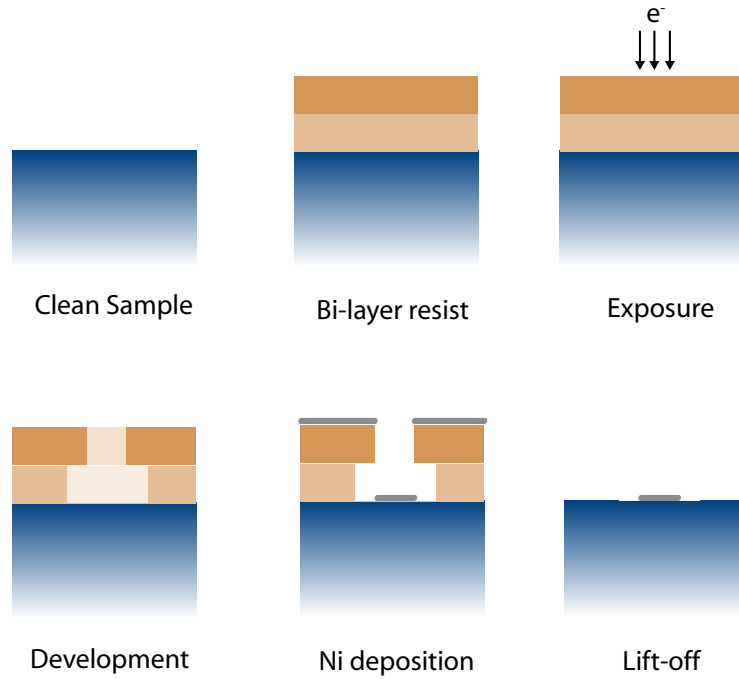


Figure 3.6: - Diagram showing the fabrication processes for the lift-off procedure used in making the nickel mask array. The sample is cleaned, then the resists are deposited. It is then exposed and developed, leaving a T-shaped cavity. The nickel is then deposited, and finally the resist is washed off leaving individual islands of nickel.

A suitable bi-layer resist recipe was found through a series of trial and error experiments. The underlayer was made using A4 495 PMMA spun at 4000 RPM for 40 s with a 500 RPM ramp, followed by a 90 s bake at 180 °C, giving a thickness of ~ 170 nm (93). The top layer was A4 950 PMMA span on at 4000RPM for 40 s with a 500 RPM

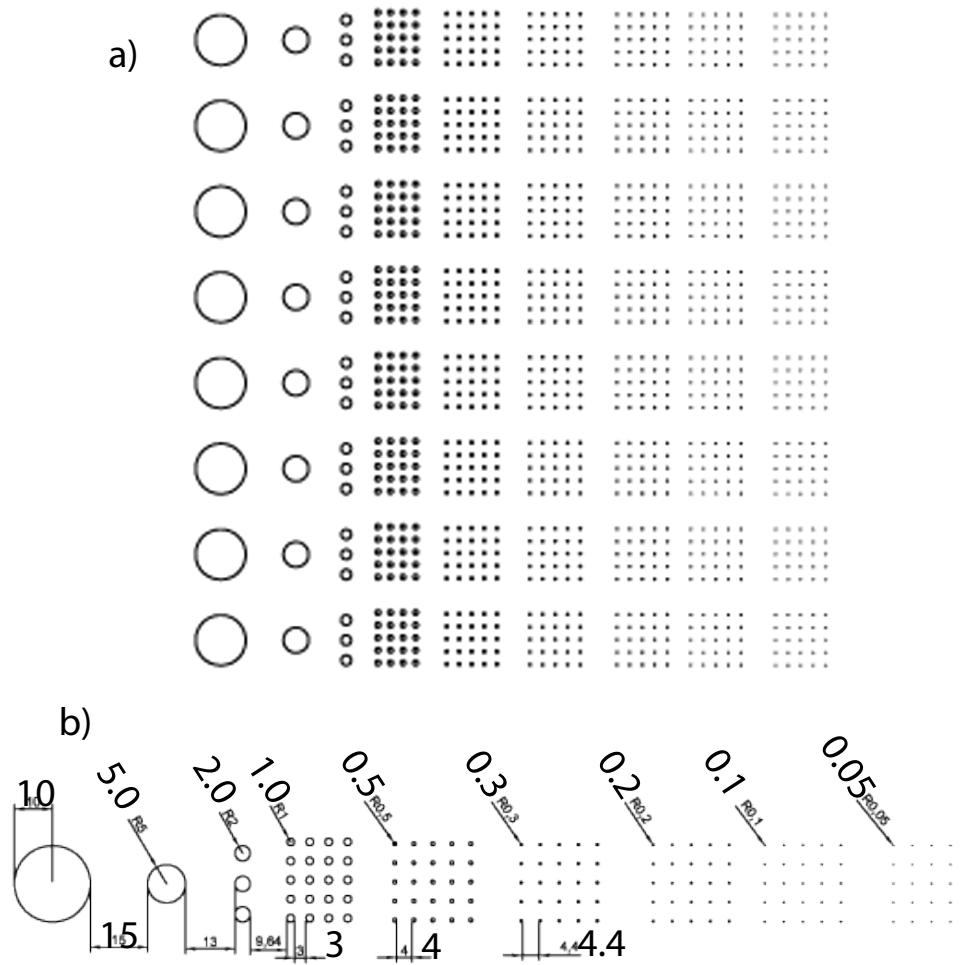


Figure 3.7: - Autocad design of the etch masks with varying diameter. a) shows the full pattern designed for a wafer of 1 mm $\times$ 1 mm in size. b) dimensions are shown for the masks of different sizes

ramp followed by a 90 s bake, giving a thickness of ~ 200 nm (93).

Evaporation of nickel is usually performed using electron beam evaporation. However, the only available evaporator to us is an *Edwards 306* thermal evaporator. Nickel has a relatively high evaporation temperature even at low pressures in the evacuated evaporation chamber. A small dimple tungsten boat *Kurt J. Lesker* part number *EVS9A005W* was used as the heater source with 1 g nickel pellets. Successful evaporation was achieved by carefully regulating the evaporation rate by means of manually controlling the current. Due to the high boat temperatures required, the evaporation of nickel is strikingly delicate. Fluctuations in current can cause the boat to snap spontaneously. On successful evaporation, a Dektak profilometer was used to measure the height profile of the across an edge of the nickel deposition. The profile of the nickel is shown in Fig. 3.8. it is relatively flat away from the edge at a height of ~ 50 nm. The edges are slightly lifted due to the removal of adhesive tape used to affix the sample inside the evaporation chamber. This data provides information on the positioning of

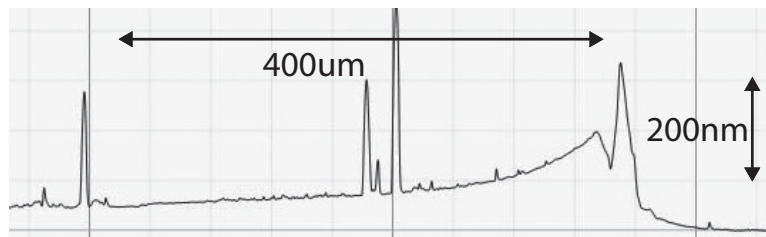


Figure 3.8: - Profile across an edge of the evaporated nickel measured by AFM. A rise of 200 nm along the edge can be seen, the metal is relatively flat $\sim 400 \mu\text{m}$ from the edge, with a height of ~ 50 nm.

the pattern.

Fig. 3.9 shows optical microscope images of the intermediate steps for the etch

3.5 Nanorod masks of varying size

mask fabrication. 3.9a) shows the developed resist. A bright pattern from the wafer surface can be seen, showing clean resist development. In b) the outline from the height difference of the pattern is shown after nickel deposition. c) shows the high contrast nickel masks after lift-off. A defected etch mask can be seen and a magnified image of the defected etch mask is shown in d). This could be due a locally incomplete development. The residual resist can result in risen areas of nickel inside the developed patterns, and therefore the etch masks may not be completely isolated from the nickel to be discarded in the lift-off. This results in rupture of the circular etch masks on lift-off. SEM images of the etch masks are shown in Fig. 3.10

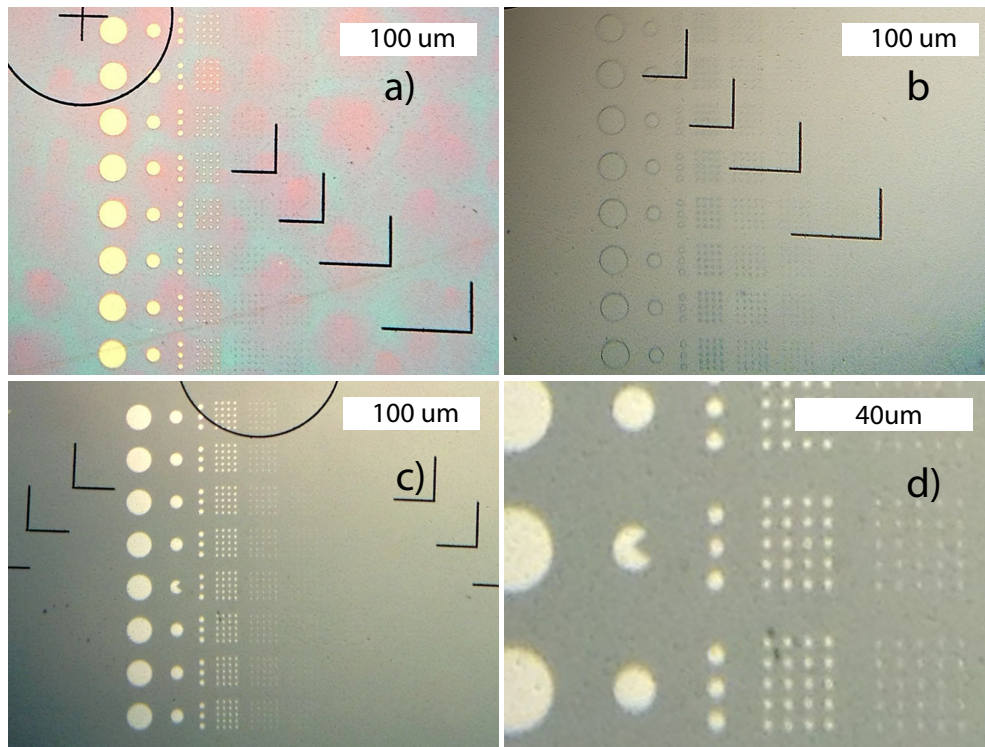


Figure 3.9: - a) Resist on sample after development. b) Sample after nickel deposition. c) Nickel masks after lift-off. d) Magnified image of c) showing a “pacman-like” defected etch mask.

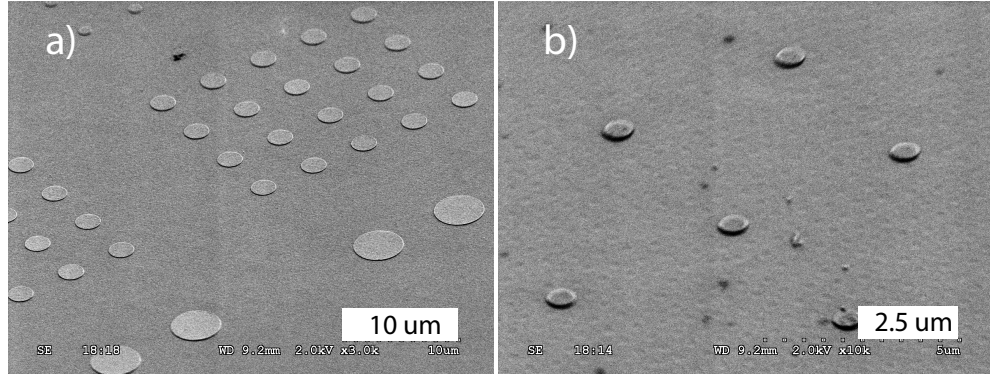


Figure 3.10: - a) SEM image showing circular etch masks on GaN LED surface. b) SEM image of 500 nm diameter etch masks on GaN LED surface

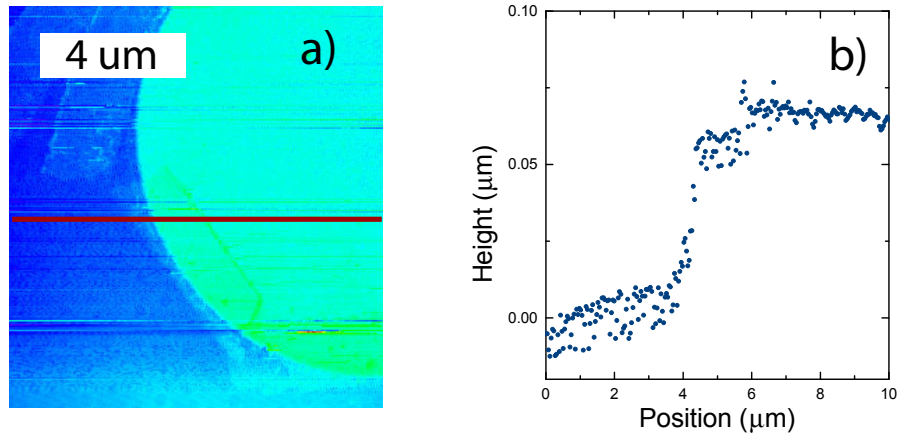


Figure 3.11: - AFM examination of a nickel etch mask on GaN LED wafer. a) shows the 2D height profile, the nickel circular mask is clearly seen. b) shows a line height profile across the position indicated by the red line in a).

AFM was performed on the etch masks to closely examine the thickness profile. Fig. 3.11a) shows a 2D surface profile across one of the larger etch masks. A line profile taken across the line marked in red through the image is shown in Fig. 3.11b). The data is relatively noisy, but is sufficient for the purpose of this characterisation. Approximately $5 \mu\text{m} \times 1 \mu\text{m}$ sized flakes can be seen in the height profile in Fig. 3.11a) around the etch mask. These are identified to be thin residual resist which was subsequently removed

3.5 Nanorod masks of varying size

by heated solvent. The average height across the measured etch mask is $62\text{ nm} \pm 5\text{ nm}$. Considering an etch mask redundancy of 30%, this gives a maximum GaN etch depth of $1.3\text{ }\mu\text{m}$ with a 30:1 etch ratio.

4

Experimental techniques

4.1 Introduction

The experimental apparatus used to perform experiments for this thesis is described in detail in the following sections. Photoluminescence (PL) is an important characterisation technique that allows us to probe material, electronic and optical properties of the sample under investigation. Two different types of PL measurements are performed in this work, namely: time integrated PL and time resolved PL. The principle of micro-PL is to selectively stimulate small areas of the sample optically, and collect the photons that the sample emits via PL through a spatial filter for analysis both spatially and spectrally. Combined with the ability to vary excitation power, energy and temperature and further modifications to measure polarisation enables us to obtain multi-dimensional data to perform in depth characterisation. The majority of the work was performed on a single optical setup consisting of a home-made microscope as the

backbone. Modifications and components are added to perform certain measurements. This chapter will commence with detailed description of excitation sources and followed by the optics and methods used to achieve the results. Finally, methods developed for polarisation detection are briefly discussed.

4.2 Excitation sources

4.2.1 Ultrafast laser

Mode-locked tunable Ti:sapphire laser systems are used to generate ultrafast pulsed emission. The active medium allows emission to be tuned in wavelength between 700 to 1000 nm in either continuous or mode-locked operation. There are two Ti:sapphire lasers used in this work:

- **Coherent Mira 900**
- **Spectra-Physics Mai Tai**

In the *Coherent Mira 900* system, the near infrared emission is obtained through several optical pump stages. The Ti:sapphire is pumped by a continuous wave laser system (*Coherent Verdi*) operating at 532 nm and 8 W. In the *Verdi* system, the 532 nm emission is achieved by second harmonic generation. A 1064 nm laser is frequency doubled through a lithium triborate (LBO) crystal. The 1064 nm beam is in turn generated by a diode pumped Nd:YVO₄ crystal inside the *Verdi*(94).

The *Mira 900* can have two operational modes, generating short femtosecond pulses of ~ 100 fs duration or picosecond pulses of ~ 1 ps. The spectral width of the laser is

inversely proportional to the temporal width by $\Delta t \Delta \nu \geq K$, where Δt and $\Delta \nu$ are the full width half maximum of the duration of the pulse and the bandwidth in frequency, and K is a parameter associated with the pulse shape which is generally modelled by a hyperbolic secant pulse ($K \sim 0.315$) (95). Therefore, for a 100 fs pulse $\Delta \nu = 3.15$ THz, corresponding to a $\Delta E \sim 13$ meV, and 1.3 meV for 1 ps pulses. This needs to be taken into account when choosing between the two laser modes especially for near band edge excitations and fine time resolution.

The normal mode-locked output produces a pulse repetition rate of 76 MHz, corresponding to a 13.2 ns time between pulses, at an average power of up to 1.5 W. In InGaN/GaN QW systems, typical QW lifetimes can easily exceed this (53, 69, 96), causing errors in photon statistics when carrying out time resolved measurements due to carriers unable to fully relax within the laser repetition time-frame. It is therefore necessary to reduce the repetition rate by utilising a pulse picker (*APE PulseSwitch*). The pulse picker works by modulating a crystal with a radio frequency creating periodicity in refractive index of the crystal. This enables the crystal to selectively deflect the beam in synchrony with the pulses, effectively creating a slower pulse repetition rate. The average power of the output decreases, but the signal of the photoluminescence scales with this reduction in average power only when the recombination lifetime is shorter than the repetition rate of the laser. The *Mai Tai* is a software controlled Ti:sapphire laser system with the same fundamental operation as the *Mira 900*, producing pulses of duration 100 fs at 80 MHz. The laser is tunable in a much narrower range between 795 nm and 805 nm with an average power of 800 mW.

4.2.2 Harmonic generation

It is necessary for excitation sources to be able to have an emission energy above the bandgap of the samples. Investigation of wide bandgap semiconductors such as III-nitrides with these lasers therefore requires either frequency up-conversion inside a birefringent non-linear crystal or non-linear two photon absorption of the sample.

The intensity of light is directly proportional to the square of the amplitude of the electromagnetic field. At low intensities, the displacement of the atoms in a solid has linear response with the electric field. With an increase in the intensity of electromagnetic fields, non-linear properties will show in materials on exposure. This non-linear relationship can be represented by an induced polarisation P which can be expanded as:(97)

$$P_i = \epsilon_0[\chi_{(1)}E_j + \chi_{(2)}E^2 + \chi_{(3)}E^3 + \dots] \quad (4.1)$$

The number in the parenthesis is the order of susceptibility where (1) is the linear, (2) and (3) being second- and third- order susceptibilities. Consider an incident field of frequency ω , and thus E can be written as $E = E_0e^{i\omega t}$, P is therefore:

$$P = \epsilon_0[\chi_{(1)}E_0e^{i\omega t} + \chi_{(2)}E_0^2e^{i2\omega t} + \chi_{(3)}E_0^3e^{i3\omega t} + \dots] \quad (4.2)$$

Polarisation is therefore written as a sum of terms containing higher order harmonics 2ω , 3ω , ... Higher order terms of P become more significant with higher E_0 of light. Hence, the intensity of incident light can induce higher order polarisation in the material.

In practice, the dispersion of the material will need to be taken into account. For

up-conversion to take place, the second harmonic has to propagate with matching phase velocity as the fundamental wave. The required condition can be achieved using birefringent crystals. By rotating the crystal relative to the incident beam, the two waves can be brought into phase; this is known as index matching.

4.2.2.1 INRAD ultrafast harmonic generation system

A commercially available *Inrad 5-050 ultrafast harmonic generation system* was used in our experiments to produce the 3rd harmonic from the Ti:sapphire laser system output. A lithium triborate (LiB_3O_5 or LBO) crystal was used for the second harmonic generation in the system. The crystal is positioned on multi-axis micrometer mounts such that phase matching conditions can be achieved. Output from the LBO crystal consists of the fundamental 800 nm beam and a frequency doubled 400 nm beam. Third harmonic generation made is possible by reintroducing the residual 800nm beam from the LBO crystal and combining this with the doubled 400nm beam via a delay arm to ensure correct temporal overlap in a beta-barium borate ($\beta\text{-BaB}_2\text{O}_4$ or BBO) crystal generating a 266nm ultraviolet beam.

For our experiments, a BBO crystal on a home built stage was used to frequency double the pulsed laser to 400nm. The layouts of the two excitation sources are shown schematically in Fig 4.1.

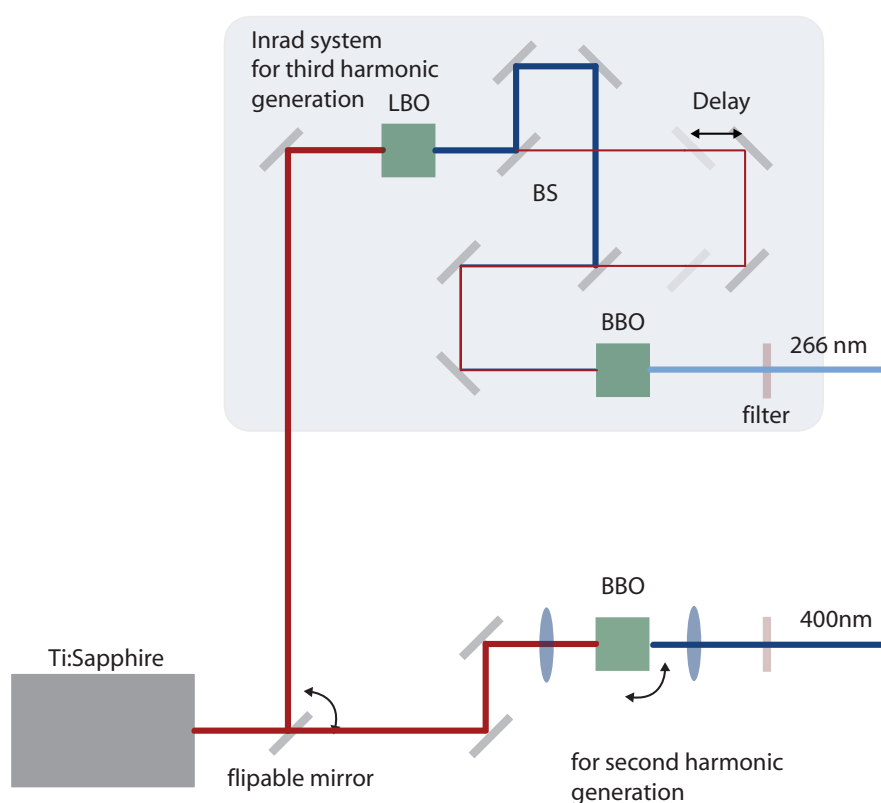


Figure 4.1: - Schematic showing our two laser excitation frequency schemes. The fundamental frequency is provided by a Ti:sapphire laser which has a flipable mirror in place to switch from the top (third harmonic) frequency tripled scheme by using the Inrad 5-050 Ultrafast Harmonic Generation System or the bottom simple BBO crystal doubling system.

4.2.2.2 Two photon absorption

Two photon absorption processes allow excitation of semiconductors below bandgap with high power pulses. The absorption process takes place via an intermediate virtual state shown in Fig. 4.2 Degenerate two photon absorption is achieved by using the

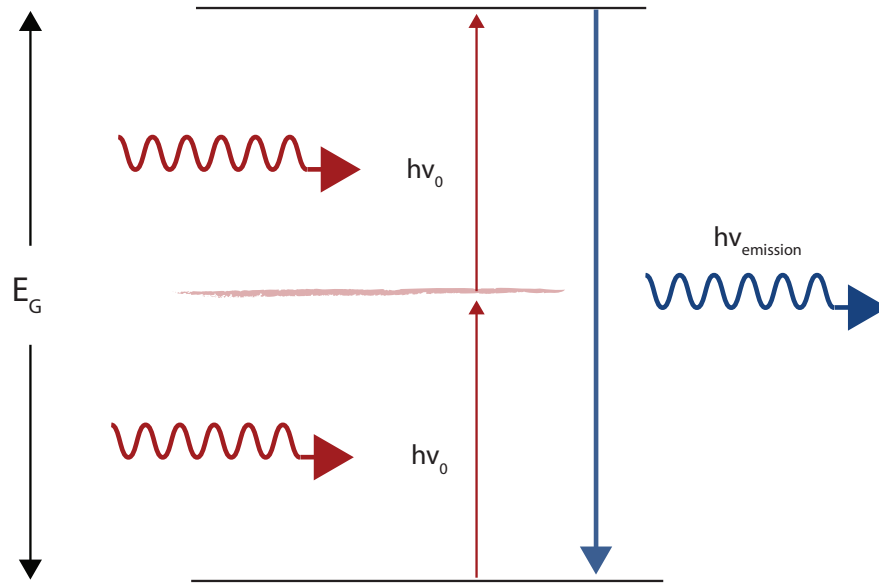


Figure 4.2: - Schematic of a degenerate two photon absorption. Two photons at the same energy arrives, and excites via a virtual state

picosecond mode on the *Mira 900* laser, directly exposing the sample to high the intensity laser, at peak power number of photons can reach up to 10^{18} over $1\mu\text{m}^2$. Intensity of emission is shown to have has a squared dependence on excitation power (98). Consequently, two photon absorption can provide superior spatial resolution to conventional single photon excitation techniques. It is also shown that the two photon absorption preferentially excites highly quantum confined structures such as quantum dots (98). The theoretical discussions of two photon absorption is outside the scope

of this thesis, since we only use this technique to reduce background emission when investigating sharp spectral features in samples as demonstrated in references (98, 99).

4.2.3 Continuous wave lasers

Alongside the pulsed laser systems, continuous wave laser systems are also used to investigate the samples. In this work, a 405 nm violet diode laser is used to excite directly into the bandedge of our InGaN systems. The diode laser is commercially available with an aluminium custom made holder and heat-sink. The violet laser is driven by a 12 V power supply producing up to 120mW of power. Stability of the laser in the home built holder and heatsink was measured and is shown to be reliably stable showing less than 1 mW of drift in power whilst operating at 120 mW over a period of 30 minutes measured. The laser is collimated and power is controlled by neutral density filters.

4.3 Optical setup

Central to the micro PL experiment is a far field confocal microscope. A schematic of the setup is shown in Fig. 4.3. For different wavelengths of laser, the optical setup needs to be modified slightly, which include mirrors, beam-splitters, neutral density gradient wheels, lenses, pin-holes, filters and also microscope objectives. A collimated white light source is available to illuminate the sample surface when identifying particular areas to excite. A slide in semi-transparent mirror is used to guide the collimated white light into the beam path when needed, also shown in figure.

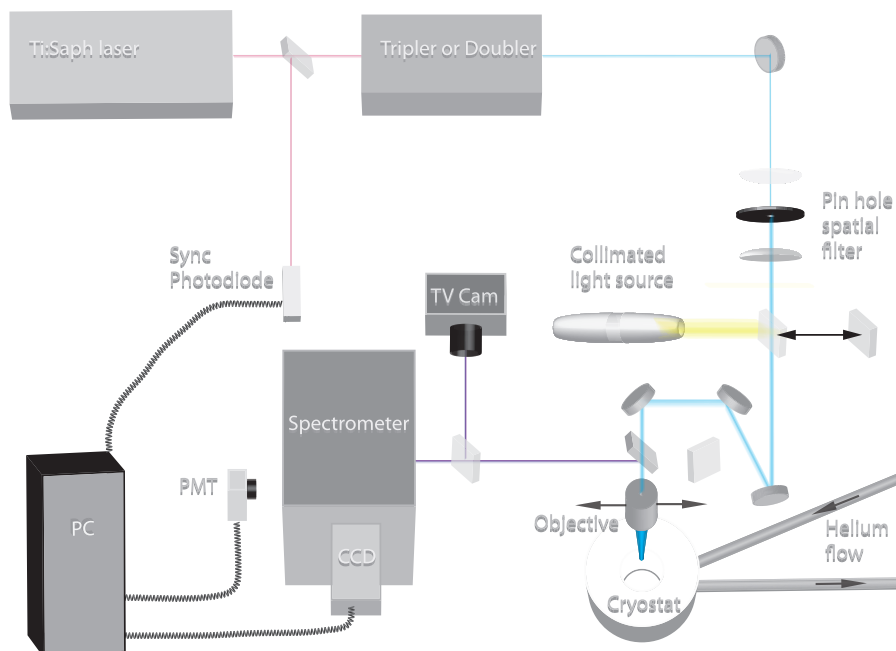


Figure 4.3: - Schematic showing the optical setup used in this work

The laser is focussed on the sample and luminescence is collected through the same objective. Due to the big differences in wavelengths between emission and excitation and the necessity of mounting the sample in a cryostat, long working distance achromatic/apochromatic/reflecting microscope objectives are used. Table 4.1 gives detailed information on the different objectives used for different laser excitation wavelengths.

4.3.1 Confocal imaging

The laser passed through a spatial filter, by focussing through a pin-hole and subsequently collimated. Since we are utilising a confocal geometry, collection of luminescence lies on the same beam path as the excitation beam through the same microscope objective. A dichroic mirror is therefore used as a beam splitter to separate the lu-

4.3 Optical setup

Specification	UV	Visible	Near Infra-red
Manufacturer	Techspec	Mitutoyo	Mitutoyo
Model	Adjustable RefleX	M Plan Apo	M Plan NIR
Magnification	36×	100×	100×
Numerical Aperture NA	0.5	0.7	0.5
Working distance (mm)	5.40	6.0	12.0
Focal length (mm)	5.4	2.0	2.0
Wavelength range (nm)	200-11000	330-700	380-1800

Table 4.1: List of objectives for different wavelength ranges used. Data is taken from Edmund Optics technical documentation (100)

minescence from the excitation beam. Previous measurements have used 50/50 beam splitters (33, 69, 101), but the dichroic mirror reduces the loss of excitation beam and also collected PL photons by half¹; since it reflects $\sim 99\%$ of the laser wavelength and has a sharp cut-off for transmitting PL wavelengths. A set of dichroic mirrors is available for different laser excitation wavelength.

The laser excitation spot can be seen as a relay image of the pin-hole shown in Fig.

4.4. Applying the simple magnification equation:

$$M = -\frac{f_c}{f_m} \quad (4.3)$$

For a typical 50 – 100mm collimating lens and a pin-hole of $25\mu\text{m}$, the relay image magnification typically is less than $\sim 1\mu\text{m}$ in diameter. Hence the excitation area is limited by the laser spot size, selectively exciting very small regions on the sample. For collection, since the same objective is used, the focal length must remain constant across the wavelengths used in both excitation and collection ranges. A farfield image

¹During UV excitation, the beam-splitter cubes were frequently damaged by the fs pulses. The damaged layer gives a broad luminescence around 430nm. For previous work, the luminescence of the QWs lay above this, and thus it did not effect the results obtained in (69)

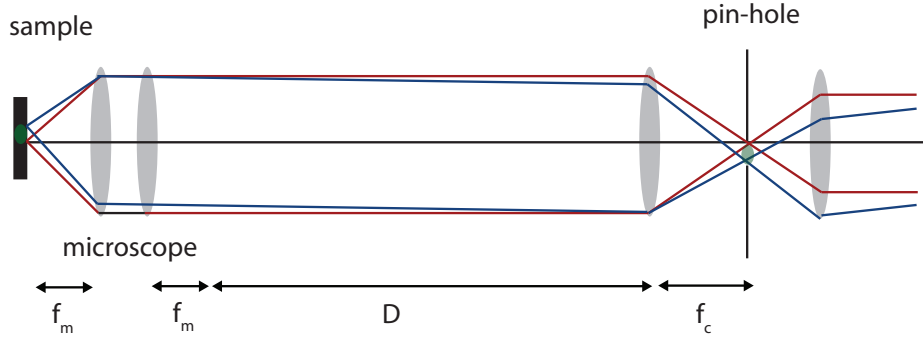


Figure 4.4: - Layout of infinite conjugate microscope, showing relay imaging of a pin-hole on the sample. f_m and the f_c are the focal length of the microscope objective and the focal length of the collimating lens

of the sample is formed on the plane of the spectrometer entry slit by a 50 mm lens on a 3-axis mount. The size of the farfield image of the excitation point is $\sim 25 \mu\text{m}$. By closing the entrance slit to $25 \mu\text{m}$ and aligning the laser reflection spot to coincide with the slit, we can essentially eliminate the scattered light from the out of focus regions, meaning PL from the excitation spot close to the focal plane can pass through the detector slit. The resolution is greatly improved in depth as well with the use of this configuration. Fig. 4.5 shows a schematic of the collection arm of the microscope setup. The sample can also be imaged on a CCD by diverting the parallel light with a mirror. In order to image, the illumination and collection point needs to perform a scan across the sample. Samples can also be scanned with variation of focal plane, thus obtaining a 3D image of the sample. In a conventional confocal system, a moving stage is used to perform the scans. However, for our work, the sample needs to be mounted in a cryostat with helium transfer tubes, hence instead the objective is held

4.4 Time integrated photoluminescence spectroscopy

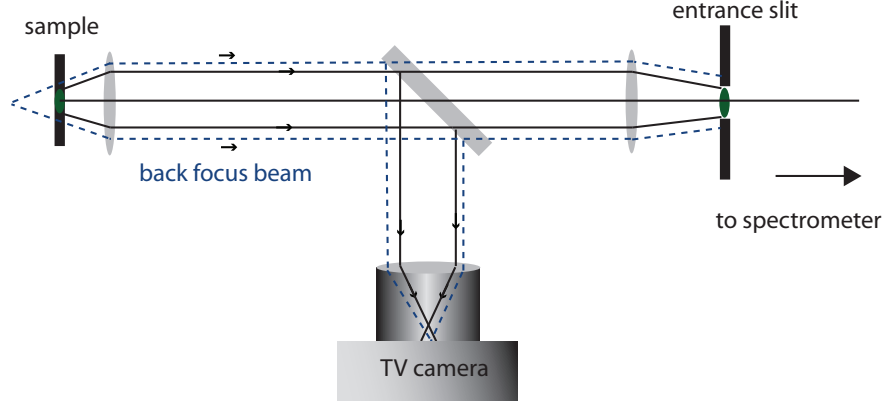


Figure 4.5: - Schematic showing the confocal imaging system with spatial filter blocking off beams which do not originate from the plane of the point illumination

in a nano-positioning modular stage to perform scans to position the laser spot with nm precision. The position module is the *Melles Griot NanoMax TS 3-Axis Flexure Stage* which contains piezoelectric crystals with a closed feedback loop control unit ensuring stability and absolute position readout. The positioning resolution is down to 5 nm in three directions. This unit can be controlled by computer to perform scans and for stabilisation of laser spot relative to sample used in experiments requiring long accumulation times.

4.4 Time integrated photoluminescence spectroscopy

Time integrated micro-PL allows the measurement of PL from a sub micron region of the sample. Using the confocal microscope described previously, a region of less than $1\mu\text{m}^2$ can be studied. PL collected through the slit depicted in Fig. 4.5 is passed into a spectrometer (*Andor Shamrock SR-303i*). The *SR-303i* is a 0.3 m imaging spectrometer. It has fully automated software control and is equipped with changeable reflecting

4.4 Time integrated photoluminescence spectroscopy

gratings mounted on a software controlled turret with absolute positioning. A choice of 1200 mm^{-1} , 600 mm^{-1} , and 300 mm^{-1} gratings are available. PL is dispersed on the grating and imaged onto a Peltier-cooled charge coupled device (CCD) (*Andor Technology DU420A-BV*). The CCD has an array of 1024×255 pixels with a pixel size of $26 \mu\text{m}$. It is possible to by-pass the dispersion grating and directly produce a 1:1 image of the slit onto the CCD for alignment purposes.

Use of higher resolution grating, despite being able to achieve a higher spectral resolution, comes at a cost of light throughput per channel on the CCD, meaning higher acquisition time. The dispersion of the spectrometer is given by:

$$\frac{d\lambda}{dx} = \frac{d}{f_L}, \quad (4.4)$$

where $d\lambda$ is a small change in wavelength, dx is the corresponding change in position x , d and f_L are the grating line spacing and the focal length of the spectrometer. (102) Applying this to our setup, a rough calculation gives us a dispersion of 2.78 nm mm^{-1} using the finest grating available. The combination of dispersion and ccd spatial resolution will therefore determine the lower limit of the spectral linewidth. Since the width of the slit is approximately equal to the width of each pixel. We can estimate this lowest limit of spectral linewidth by:

$$\delta_{\text{RES}} = 3 \times \text{dispersion}(\text{nm mm}^{-1}) \times \text{pixel width} \sim 0.21 \text{ nm}, \quad (4.5)$$

where the factor of three comes from the fact that the full width at half maximum of the raw data can only be obtained with at least 3 pixels. This corresponds to an energy

4.4 Time integrated photoluminescence spectroscopy

$\delta E = hc/\lambda^2 \times d\lambda \sim 1.6 \text{ meV}$ for wavelengths of 450 nm (2.76 eV).

4.4.1 Cryogenics

Measurements carried out at low temperatures used a liquid helium cooling system. The sample is mounted using silver conductive paint on a machined copper cold-finger in an evacuated cryostat. The cryostat used, *Janis ST-500*, was mounted on an $x - y$ micrometer stage to allow control of sample position. Liquid helium is transferred through to the cold finger from a liquid helium dewer. A pressure regulating system ensures stable helium flow to cool the sample, and the helium is subsequently returned through an helium cycle system. Mechanical stability and drift levels have been measured previously to be $\sim 60 \text{ nm}$ in 30 minutes (103).

4.4.2 Resolution

The spectral resolution and point illumination size were discussed previously. Here, the system resolution will be characterised experimentally. Light microscope resolution can generally be described by assessing the full width half maximum of the focal spot also known as the point spread function. The focus of a infinitesimally small point through an ideal lens on the image plane is represented by an Airy function intensity profile. By imaging fluorescent beads in solution, the emission can approximate small point-like objects.

Since our laser spot size and collection focal volume is not resolution limited (it was estimated in the previous section to be $\sim 1 \mu\text{m}$ in diameter), the measured apparent

4.4 Time integrated photoluminescence spectroscopy

size of small point sources will actually be a direct measurement of the excitation and collection spot size, as opposed to a point spread function.

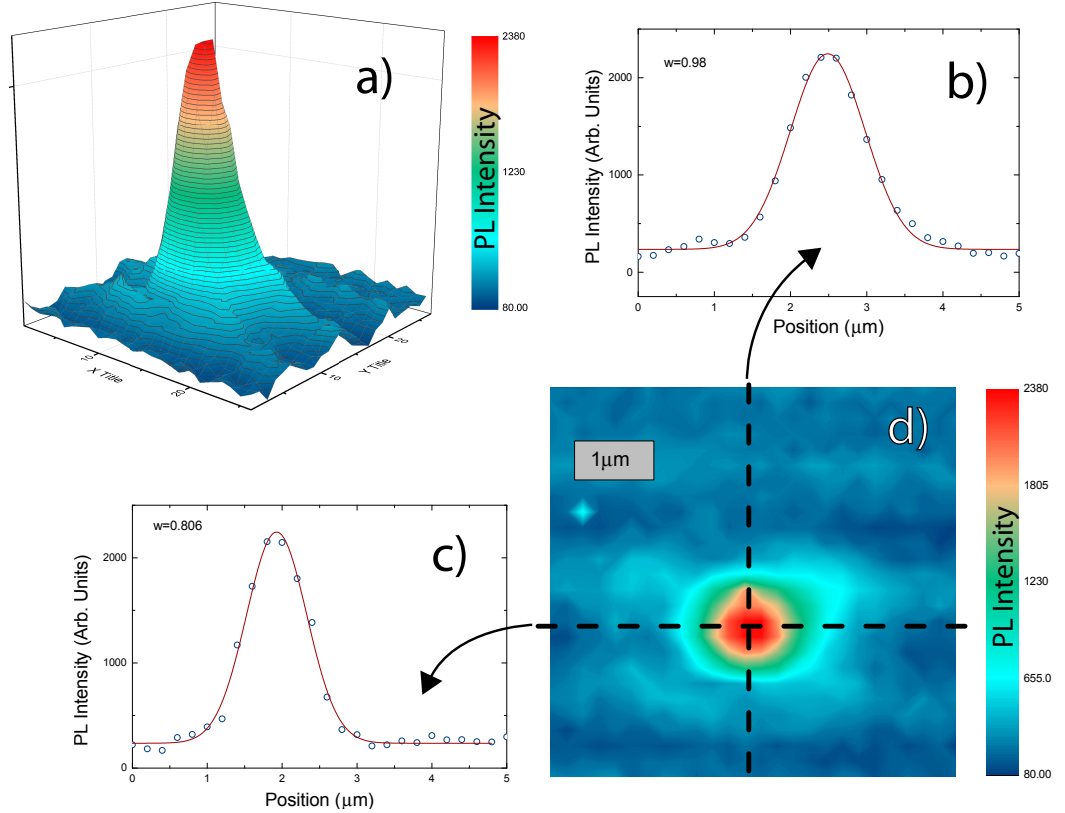


Figure 4.6: - Resolution test of a 2D scanned image of fluorescent beads. a) shows the intensity profile in 3D, b) and c) shows cross-section slice of the intensity profile along the dashed lines across the image shown in d)

Fig. 4.6 shows the integrated intensity plotted against position of a 2D scan using the piezo-controlled moving objective over a fluorescent bead excited with a 532 nm diode laser. 4.6 a) is a 3D plot of the intensity of the luminescence of the beads over the scan area. A clear sharp peak can be seen corresponding to the position of the fluorescent bead. 4.6 d) shows the contour plot of the same figure, showing imperfections of the setup. There is an asymmetry in the intensity profile between the vertical and

4.4 Time integrated photoluminescence spectroscopy

horizontal directions. There are also bands of varying high and low intensity across the horizontal direction only. It must be noted that the raster scanning is programmed to run horizontal line scans and increment the vertical position after the end of each horizontal line as depicted in Fig. 4.7, hence the vertical component of the image re-

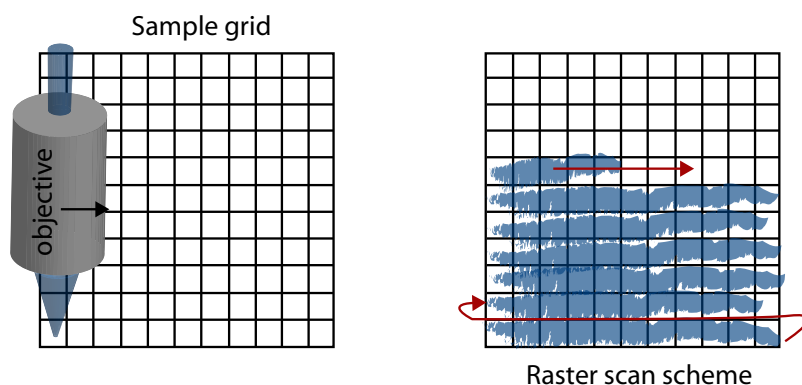


Figure 4.7: - Raster scanning scheme employed, the sample is split into a square grid and the objective moves to the start position to perform collection/excitation on the designated area defined by the spot size. The objective moves across the sample and collects in one horizontal direction only, before moving to the next horizontal line vertically above. The image is built up by integrating the intensity at each grid point and reforming the image in software

quires a much longer time to accumulate. In fact, the image shown in Fig. 4.6 took 20 minutes to acquire. During this time, any slow drift in the system will appear to distort the image in the vertical direction. The bands across the image are also an artefact of time dependent experimental conditions, in this case the temperature of the CCD. The CCD, despite being cooled, is still subject to room temperature change: as the room gets warmer, background counts increase. This periodic temperature fluctuation is clearly recorded here and was finally found to be due to the air-conditioning system in the laboratory.

4.4 Time integrated photoluminescence spectroscopy

The slight asymmetry in the shape of the intensity profile is analysed in 4.6 b) and c). Intensity data from the dashed lines are taken fitted with a Gaussian in the graphs shown. The horizontal slice gives a better fitting and a width of $\sim 0.8 \mu\text{m}$, with the vertical slice giving a width of $\sim 1 \mu\text{m}$. From 4.6 b), it can be seen that the fitting points slightly deviate from the fit towards the $3 \mu\text{m}$ position. A gradual stretch is probably due to drift over time, as each point is probably taken about 1 minute apart. However, overall the intensity profile shows that the laser spot or collection size is in fact only about $\sim 0.6 \mu\text{m}^2$ in area. This is an important characterisation, and must be taken into account and is used as a reference for the rest of the thesis. The components of the confocal microscope can be critically tuned to be diffraction limited by increasing the focal length of the collimator lens after the pinhole in the in the excitation arm. Also, the collection focal volume can be tuned to the limit of diffraction by using the same set of lenses and pinholes as in the excitation pathway in front of the spectrometer.

4.4.3 Resolving polarisation

Further modifications to the micro-PL apparatus to allow for the detection of polarisation of luminescence were performed. Polarisation sensitive measurements applied to micro-PL can be a very powerful tool in characterising nanostructures such as quantum dots where line splitting can be resolved by its polarised emission (45, 104, 105, 106, 107, 108). During the course of the experiments for this thesis, there have been continuous efforts to modify the micro-PL stage to enable polarisation studies. A brief account of the fundamentals are given below for reference to future polarisation related

4.4 Time integrated photoluminescence spectroscopy

work that will be carried out. The electric field can be written into linear orthonormal basis, X and Y. Circular polarisation can be viewed as the phase difference between the two basis. The Jones vector is a convenient way to view polarised light, writing the electric field as a vector we have:

$$\begin{pmatrix} E_X(t) \\ E_Y(t) \end{pmatrix} = \begin{pmatrix} E_X e^{i\phi_X} \\ E_Y e^{i\phi_Y} \end{pmatrix} e^{i(kZ - \omega t)} \quad (4.6)$$

Where ϕ is the retardation or increase in phase for a normalised amplitude. Hence linear polarised light along the X and Y directions can be represented as vectors:

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and } \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (4.7)$$

circular polarised light is simply a difference in phase of $\phi = \pi/2$, thus the corresponding Jones vector for the right handed and left handed circular polarised light is:

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix} \text{ and } \frac{1}{\sqrt{2}} \begin{pmatrix} i \\ 1 \end{pmatrix} \quad (4.8)$$

Optical elements can be represented by a set of transformation matrices called the Jones matrices. A list of common elements is found in table 4.2.

Considering a simple case: For a simple linear polariser in the X direction placed in the beam path of a polarised beam in the X direction, the output can be calculated by:

$$\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} E_X \\ 0 \end{pmatrix} = \begin{pmatrix} E_X \\ 0 \end{pmatrix} \quad (4.9)$$

The solution is trivial, the Jones vector remains unchanged. When we turn the polariser

4.4 Time integrated photoluminescence spectroscopy

Optical element	Jones Matrix
H. Polariser	$\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$
V. Polariser	$\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$
linear at $+45^\circ$	$\frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$
linear at -45°	$\frac{1}{2} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}$
Quarter wave plate	$e^{i\pi/4} \begin{pmatrix} 1 & 0 \\ 0 & -i \end{pmatrix}$

Table 4.2: List of Jones matrix of typical optical elements (97)

90° , we have:

$$\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} E_X \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \quad (4.10)$$

Hence linear polarised light can be detected simply by using a linear polariser in the beam path in front of a detector and rotating through 0 to 90° : the result should give a sinusoidal signal with polariser angle. For circular polarised light, a quarter waveplate can be used. It can be shown using the Jones matrices that the resultant light will be linear polarised 45° to the X axis as shown below:

$$e^{i\pi/4} \begin{pmatrix} 1 & 0 \\ 0 & i \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} E_X \\ E_Y e^{i\pi/2} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} E_X \\ -E_Y \end{pmatrix} \quad (4.11)$$

The linear polarised light can then be used in the measured $\pm 45^\circ$ position to measure the left and right handedness of the circular polarised light.

4.4 Time integrated photoluminescence spectroscopy

In our case, we need not only to be able to obtain the intensity of the different basis of polarisation but also spectral information. Since the *Andor* spectrometer uses a reflection grating which is polarisation sensitive, additional elements must be added to compensate for this added complication as shown in Fig. 4.8 To analyse the signal,

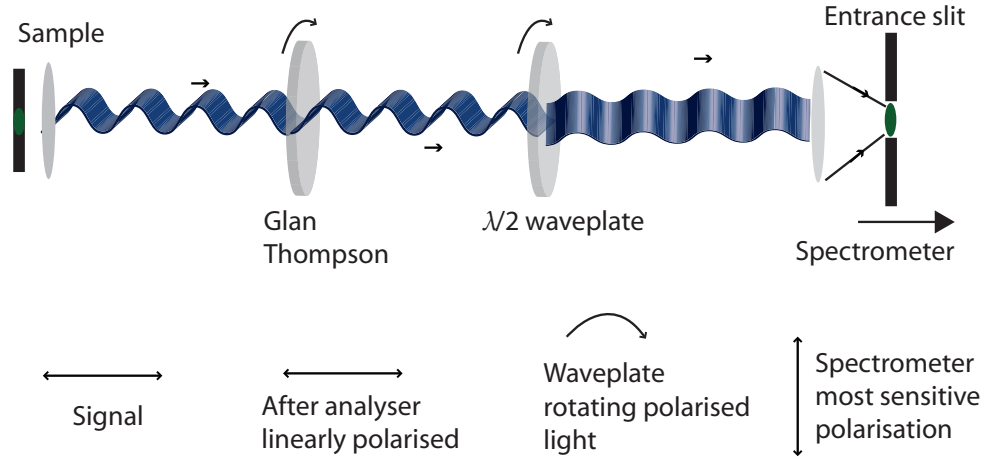


Figure 4.8: - Schematic of linear polarisation analyser employed in the micro-PL setup. PL is collected and analysed through a rotating Glan Thompson analyser. The polarised light output is then passed through a half wave plate to rotate (polarisation vector) signal through to an axis for which our spectrometer has a maximum sensitivity.

a Glan Thompson linear polariser is rotated along the beam path (rotating analyser) and passed to a rotating half wave plate which corrects for the detector's polarisation dependence by rotating the plane of linear polarisation from the analyser angle to the optical axis in which the spectrometer is most sensitive.

By adding in a quarter wave plate, and using the scheme described above, circular analysis is also possible. It is straight forward to determine whether the signal is completely linearly polarised or not, but in practice it is rare to have a fully polarised signal. Unpolarised and partially polarised light need to be taken into account but these require a more generalised form of vector analysis. The following section serves to outline

4.4 Time integrated photoluminescence spectroscopy

some theoretical background of polarimetry analysis. The experimental technique has yet to be fully implemented and is still under development stages.

Analysis of the polarisation information requires a deeper understanding of the data obtained by polarimetry. Stokes vectors provide an alternative representation of polarisation, spanning the space of unpolarised, partially polarised and fully polarised light. The basis of the Stokes vector were chosen for its ease in measurement. It is defined by:

$$\begin{pmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \end{pmatrix} = \begin{pmatrix} I_X + I_Y \\ I_X - I_Y \\ I_{+45^\circ} + I_{-45^\circ} \\ I_L + I_R \end{pmatrix} \quad (4.12)$$

where I_X and I_Y are the normalised intensities in the X and Y polarisation directions. I_{+45° and I_{-45° are the intensities linear to the $+/-45^\circ$ directions, while I_L and I_R are the left and right hand polarised light intensities. I is proportional to the product of the Jones vectors in equation 4.8 with its Hermitian adjoint. By definition, the representation can be directly measured and the axes are all defined by the apparatus. S_0 is obtained by measuring the intensity of light through a filter which passes half the incident light. S_1 is obtained by taking the intensity difference of the light passing through a linear polariser aligned to an axis X and of the same beam of light passing a linear polariser aligned to the Y axis, defined to be orthogonal to X . S_2 is the same, but the polarisers are now 45° rotated relative to the set used in obtaining S_1 . Similarly S_3 is obtained by measuring the difference of the intensity of the circular polarisation in the right handed direction to that of the left handed direction. The Stokes vector

4.4 Time integrated photoluminescence spectroscopy

obtained can then be analysed, and parameters such as the azimuth, ellipticity angles and degree of polarisation can be extracted.

This section lays down some of the theory behind building a polarisation detection add-on, to enable a more in depth analysis of the properties of light emitted from our samples. The full Stokes vector analysis provides all the information contained in the X-Y direction of light in the imaging plane. Partially polarised light can be analysed and represented graphically on a Poincaré sphere surface, enabling the ability to look at properties such as de-coherence, the reader is directed to references (109, 110) for further reading. The above scheme would be an exciting addition to the current apparatus, expanding measurement capabilities.

4.4.4 Reflectivity measurements

Micro-reflectivity measurements were carried out using a 12 V 100 W tungsten light source. As with Fig. 4.4, light from the lamp is passed through a pin-hole and relay imaged onto the sample. The 36 $\times$ achromatic UV-VIS reflecting microscope objective is used to provide the incident light. Collection of reflected light is through the same objective as depicted in Fig. 4.3. Broadband optics are used since the tungsten lamp is capable of producing near-UV light. The reflected light off the sample is analysed with the spectrometer. In order to normalise the signal to obtain the real reflectivity, a near perfect reflector (aluminium in our case) needs to be measured under the same experimental conditions. The two sets of data can then be combined to remove the system dependent factors.

4.5 Time resolved photoluminescence

As the name suggests, time resolved PL is a technique for obtaining information on the temporal evolution of the luminescence. In Fig. 4.3, the *PC*, *PMT* and *Sync Photodiode* on the left of the diagram form the time resolved arrangement used in this work. A small fraction of the pulsed Ti:sapphire laser beam is sent to a fast photodiode which generates a timing *clocking* signal to the computer from the laser pulse repetition rate. As described previously in the time-integrated PL section, the PL from the sample is dispersed by the spectrometer grating. As opposed to using the CCD a mirror can be flipped in place to divert the dispersed PL onto a second exit slit on the side of the spectrometer. The slit acts as a spectral filter with the same resolution as calculated by equation 4.4. The exit slit is controlled by a stepless micrometer manually and is typically set at $50 - 150 \mu\text{m}$. Spectral resolution is therefore at a cost of signal intensity. The selected wavelength to be measured is collected by a photomultiplier tube (PMT) and sent to a time correlated photon counting system.

In this work, a high speed PMT made by *Becker and Hickl* (*PMH-100-0*) is used. It has a large collection area (few mm) and a modest instrument response time of 150ps (111). The detection wavelength range covers the visible spectrum optimised for 300-650 nm. The fast photodiode used is the *Becker and Hickl* *PHD-400-N* and is optimised for 800 nm detection.

4.5.1 Time correlated single photon counting

Time correlated single photon counting (TCSPC) is used to perform the time resolved PL measurements. The basic working principle of TCSPC is the measurement of delay time of a single photon signal arriving at the PMT compared to the sync signal generated by the fast photodiode. A histogram of the delay times of each detected photon is built up over 1024 channels. The corresponding decay curve is generated by this histogram. A graphical description of this is shown in Fig. 4.9. It is important

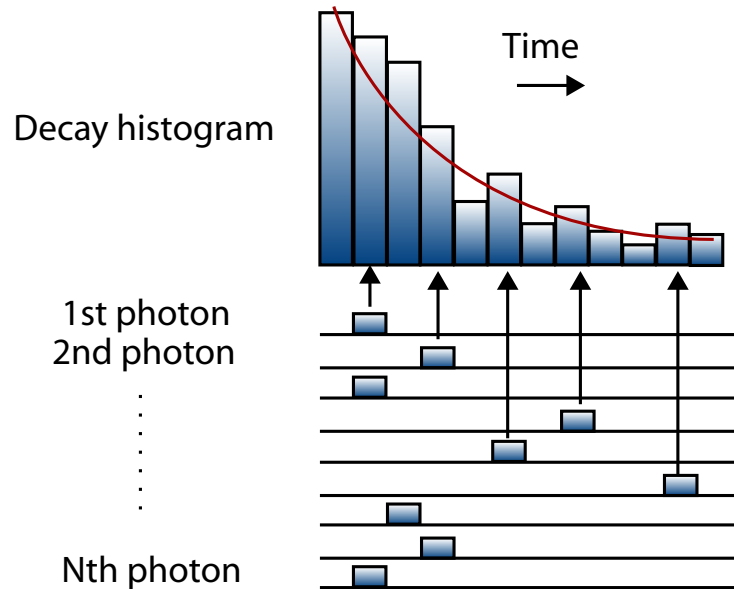


Figure 4.9: - Diagram of the measurement principle of TCSPC, histogram is created by individual photon signals binned to its delay time from timing pulse

that the intensity on the PMT is kept low enough, such that the probability of a single photon detection from each pulse is much less than one. Typically, the detection count rate will be set to around 1000 to 10000 counts per second by adjusting the slit width or using neutral density filters.

4.5 Time resolved photoluminescence

The signal measured is a convolution of the instrument response function (IRF, measured to be ~ 135 ps in our setup) with the real signal. It is necessary to perform deconvolution to the signal (or re-convolution of a fitted exponential decay with the measured IRF) when the measured decay time is close to the system's response time.

Spectroscopy of InGaN nanorod array LED fabricated on a wafer scale

5.1 GaN nanorods

GaN nanorod investigations began in the late 1990s with pioneering research focussing on self-organised growth of GaN nanorods by molecular beam epitaxy (MBE) (86, 112). The research initiated interesting studies in the semiconductor physics on scaling down of devices (37). This led to the successful demonstration of an InGaN/GaN quantum disk nanocolumn LED (31). However, for solid state lighting applications, a regular array of GaN vertically aligned nanorods provides significant benefits for device processing. Homogeneity in height is necessary, as it lends itself to more straightforward

methods to contact the nanorods with electrodes as well as further device processing. With these goals, the nanorod LED research community has fixated upon selective area growth techniques which can be utilised in fabricating controlled regular arrangements of nanorods. In 2009, Kishino *et al.* reported highly uniform arrays of GaN nanocolumns fabricated using selected area growth and rf-MBE (87). Subsequent work after the breakthrough in these high quality nanorod arrays demonstrated the multitude of possible devices that can be realised with nanorod LEDs. Two dimensional light confinement was confirmed with nanorod photonic crystals made in this manner (48). Furthermore, green stimulated emission was reported by the same type of nanorods (113) and recently, near infrared LEDs have been demonstrated operating at $1.46\mu\text{m}$ (21).

Although grown nanorods have shown a promising future for new generation ultra efficient artificial lighting, a top down etched approach can have significant advantages over the bottom-up approach in nanorod fabrication. In particular, the ability to fabricate arbitrary structures over well controlled arbitrary positions with homogeneous heights on well-established, highly commercialised, and high fabrication throughput *c*-plane GaN wafers. Furthermore, artificially controlling the diameter of an etched InGaN quantum disk in nanorods is speculated to be a highly effective method to enhance emission efficiency in higher indium content LEDs as described by Kawakami *et al.* (20, 114).

There are many schemes for fabricating nanorods from the top down. More industrial oriented methods for mass nanorod LED manufacturing commonly involve an etch

mask fabrication and a dry etching routine (115, 116, 117). Nanoimprint lithography provides an inexpensive, high throughput and high precision method to fabricate etch masks.

5.2 Surface effects on InGaN

The free surface around the nanorods are what gives the nanorod many of its unique properties. Understanding how this free surface affects the recombination mechanics allows us to harness the advantages of the nanostructured LED to increase the light output of these devices. As the diameters of nanorods decrease, surface effects from the sidewalls of nanorods become more and more apparent.

5.2.1 Strain relaxation

As explained in the previous chapters, strain has been one of the problems plaguing the III-nitrides devices and in terms of LEDs, generally considered a nuisance. Free surfaces on the sidewalls of nanorods can relax the strain in the GaN based structures. Both grown and top down etched nanostructures have reported decreases of strain (19, 20, 33, 37, 101, 113, 115, 116, 118, 119) . A truncation of the GaN crystal perpendicular to the $[0001]$ growth direction allows the strained GaN lattice sites to relax at the boundaries of the discontinuity. The compressive strain inherent within the GaN lattice for samples grown on sapphire can relax at these areas. Hence the side walls of any c -plane GaN crystal are typically strain free. This effect is indeed very small even if the artificially fabricated features are on the micron scale. However, downscaling these

features increases the free surface to emitter area ratio dramatically.

Nanorods which are grown typically have very high crystalline quality due to the strain being relaxed along the length of the nanorod as the GaN is formed during epilayer growth. One scheme to implement the nanorod LED is to embed the active layer (InGaN QW) within a GaN nanorod. Calculations on the strain distribution on a 2.5 nm thick $\text{In}_{0.1}\text{Ga}_{0.9}\text{N}$ quantum disk 140 nm in diameter in a GaN nanorod were performed in our group and published by Holmes *et al* (33). As expected, the quantum disk is under compressive strain in the xy -plane (plane of the quantum disk) and under tensile strain in the z -axis (growth) direction. Strain in the quantum disk plane is found to vary over 2 orders of magnitude from -1.1% at the centre of the disk to almost completely relaxed value of -0.05% at the edge of the nanorod (33).

The non-uniform strain distribution results in a corresponding non-uniform piezoelectric field across the plane of the quantum disk. This heavily reduces the quantum confined Stark effect and hence reduces the red shift in band edge around the perimeter of the quantum disk. The carrier separation is lower around the perimeter increasing the carrier overlap and recombination probability.

Furthermore, the change in strain will directly cause the conduction and valence bands to bend across the radius of the quantum disk described by deformation potential theory. A full account of this calculation can be found in Ref. (66). The effect of deformation will bend the conduction band edge downwards towards the edge of the quantum disk whereas the valence band edges have a slight upward bend at the very edge of the quantum disk (35, 120). A consequence of this band bending is that the

carriers will tend to distribute around the rim of the quantum disk.

5.2.2 Fermi level pinning

One further effect that must be taken into account in nanorod LEDs is Fermi-surface pinning. An upward or downwards bending in the conduction and valence band edges can arise due to the pinning of Fermi energy levels on semiconductor interfaces with surrounding materials.

Free dangling bonds on semiconductor surfaces lead to surface states being formed. Diffusion of charge from the bulk of the semiconductor to the surface states or vice versa results in an electron depleted (or accumulated) region near the surface. There exists a vast density of states on the surface of the semiconductor, proportional to the number of atoms. Carriers from the valence band fill these surface states to the extent that its Fermi energy levels coincides with the level where the surface states are filled, reaching thermal equilibrium and Fermi level is said to be *pinned*. The resultant change in Fermi energy relative to the conduction and valence bands causes the bands to bend into the semiconductor body. The separation between the conduction band minimum and the surface Fermi level is known as the barrier height Φ_B . This barrier can be positive or negative depending on the position of the surface Fermi level with respect to the conduction band edge.

In GaN surfaces the Fermi level is pinned within the band gap below the conduction band minimum and hence there is a electron depletion region beneath the surface (121). In GaN nanorods, this depletion region is located around the entire surface and thin

nanorods have been found to exhibit insulator properties at critical diameters below ~ 80 nm (122, 123). In InN, the surface Fermi level lies far above the conduction band edge (124), which is also found to be the case for $\text{In}_x\text{Ga}_{1-x}\text{N}$, with high In-content (125). As In-content decreases, Veal *et al* found that there is a transition of Φ_B from negative to positive with a relation to In-content estimated by the equation:

$$\Phi_B = 0.53 - 2.1x + 0.95x^2 \quad (5.1)$$

In the case of a typical $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}$ alloy, the Φ_B is positive, corresponding to the Fermi level lying below the conduction band minimum. Consequently an upwards bending of the conduction and valence is apparent at the surfaces of the alloy. In the case of a nanorod with an embedded InGaN quantum disk, the band bending leads to an inhomogeneous distribution of carriers across the plane of an InGaN quantum disk in a nanorod. Fig.5.1 shows a possible configuration of carriers due to Fermi level pinning.

5.2.3 Combination of strain relaxation and Fermi level pinning

The effects of side-wall strain relaxation and Fermi surface pinning individually affects the band structure around the perimeter of the nanorod. A full treatment of the potential in the quantum disk accounting for the combination of these effects requires complex calculations which are out of the scope of this thesis. A brief qualitative description of the carrier distribution in light of the the QCSE, deformation and Fermi surface pinning will however be outlined by considering the the effects laterally in the

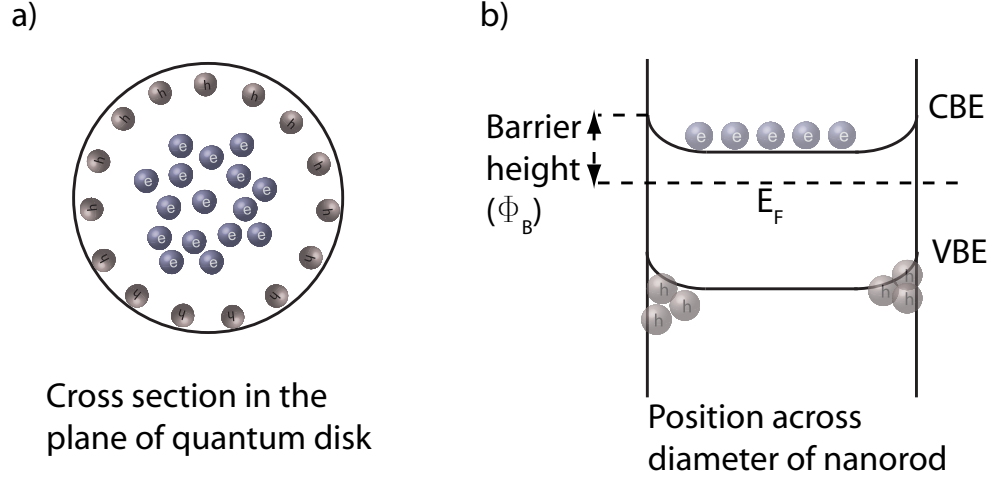


Figure 5.1: - Effect of Fermi surface pinning on carrier distribution of an InGaN quantum disk in GaN nanorod. a) Supposed carrier distribution in the quantum disk plane, showing lateral separation of electrons and holes. b) Band bending of $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}$ quantum disk due to Fermi surface pinning in nanorods leading to carrier separation

plane of the quantum disk and along the $[0001]$ axis, perpendicular to the quantum disk plane.

In the plane of the quantum disk, the piezoelectric field reduction tends to confine carriers in the centre of the nanorod and the deformation tends to confine carriers at the perimeter. The interplay between the effects therefore depends on the structural properties of the quantum disk such as the In-content and the thickness. Fermi surface pinning on the other hand separates the carriers in the plane of the disk.

For thicker quantum disks, the QCSE will be stronger in the centre of the nanorod, and it is likely to prevail over the deformation potential modifications to the band edge, whereas thinner quantum disks may favour carriers being confined at the perimeter as shown by Rivera *et al.*(126) and Holmes *et al.* (118). Analysis of higher In-content quantum disk system shows that electrons may be confined at the perimeter of the

nanorod and the holes confined to the centre (127). This is summarised in Fig. 5.2

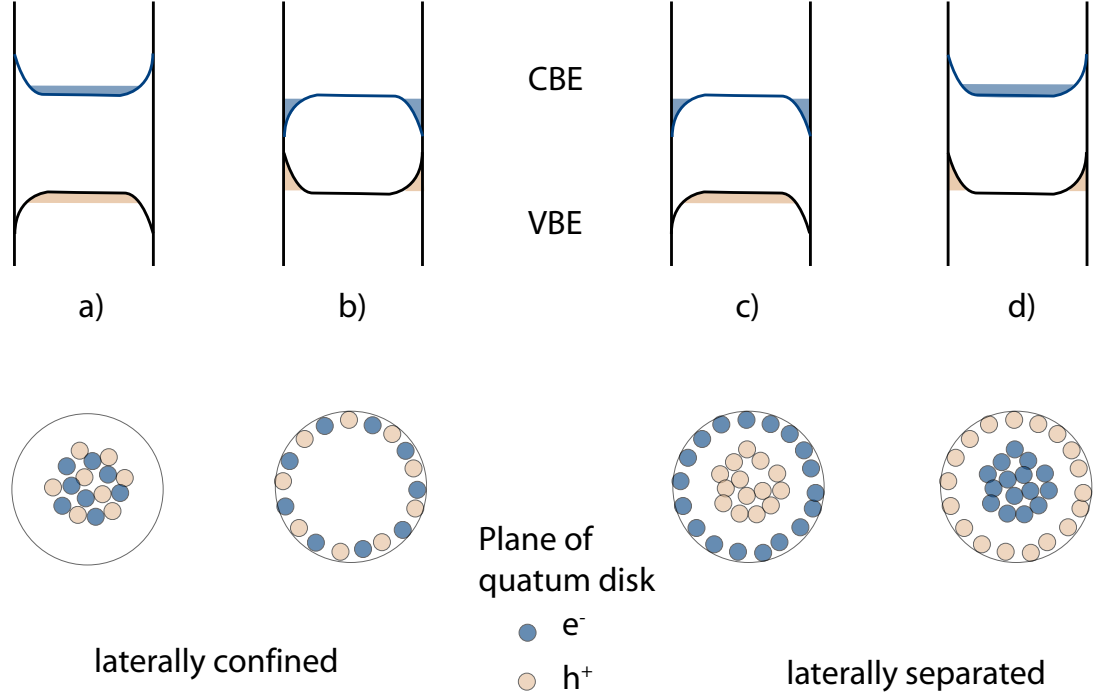


Figure 5.2: - Possible potential for in-plane directions of InGaN quantum disk. a) and b) are two confined configurations at the centre and at the perimeter respectively. c) and d) are the two laterally separated configurations. A graphical depiction of the carrier distributions on in the plane of the quantum disk is shown below

The side walls of the nanorod have less effect on the strain distribution along the growth $[0001]$ axis. Hence the strain related band bending is as calculated in section 2.4.3. The carrier wavefunctions are spatially separated along the $[0001]$ axis at either side of the interfaces of the quantum disk.

To date, a quantitative study on the distribution of carriers in relation to structural composition is still not a well published topic. Work by Bocklin *et al.*, Rivera *et al.*, and Holmes *et al.* all have pointed out that carrier separation due to the surface effects

are inevitable and must be taken into account when designing nanorod devices.

5.3 Optical Properties of InGaN/GaN Nanorod LED Arrays

rays

5.3.1 Design and fabrication of nanorod arrays

Nanorods were formed on a wafer-scale from a commercially available LED wafer by nanoimprint lithography. The LED wafer consisted of 6 pairs of 2.5 nm thick InGaN/GaN MQW layers. Initially nanorod array templates with a pitch of 450 nm were fabricated by ICP etching in Cl_2 and Ar. The resulting nanorods are of a truncated cone shape shown in Fig. 5.3 a). The nanocones have diameters ~ 230 nm at the top, with a base width of ~ 470 nm. It has been found that ICP etching can introduce a damaged layer extending up to ~ 50 nm beneath the etch surface (128). Subsequent wet etching with KOH was employed to further etch the nanocones in order to remove this damaged layer. KOH etching was performed at 40°C and 80°C to observe the effects hot KOH has on the nanocone structures. The KOH can create vertical sides on these structures since it is a facet sensitive etch. Thus this reduces the base width of the cone shape. The resultant nanorods with different etch parameters are shown in Fig 5.3 b)-e)

The nanorod diameter can be controlled using this wet-etching method. Initially, the KOH removes the ICP etch-damage layer, converting the nanocones into nanorods shown in Fig. 5.3c). Further etching in the 80°C solution starts to taper the base of

5.3 Optical Properties of InGaN/GaN Nanorod LED Arrays

the nanorod, showing a difference in etch rate of the n-type GaN as compared to the top p-type layer. This is shown in Fig. 5.3d). In fact, the nanorods can be etched even further to produce *top heavy* p-GaN structures standing freely on thin stems. The thinnest nanorods fabricated from this same ICP etch batch (pitch of 450 nm, 230 nm top and 470 nm base) gave a diameter of 50 nm from extensive KOH etching. Table 5.1 shows a summary of the etch time and temperature and corresponding nanorod diameter. For the more extreme etching conditions, the nanorods are very fragile and are prone to collapsing. This is shown in Fig. 5.4.

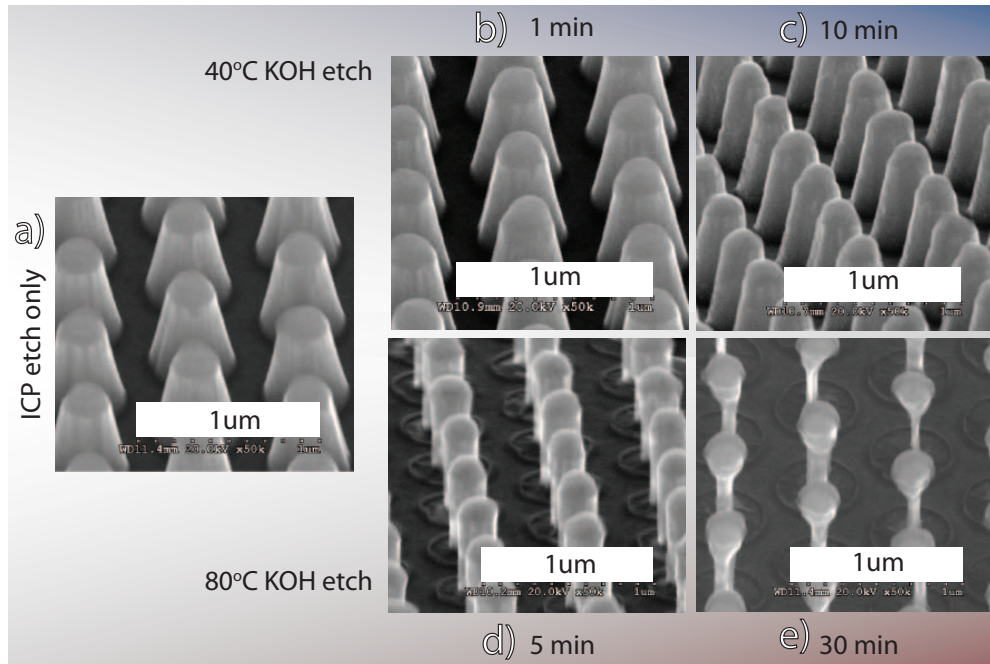


Figure 5.3: - Series of SEM images showing the effect of wet-etching on ICP etched nanorods. a) shows ICP etch only. b) 40°C for 1 minute, c) 40°C for 10 minutes. c) 80°C for 5 minutes, d) 80°C for 30 minutes

5.3 Optical Properties of InGaN/GaN Nanorod LED Arrays

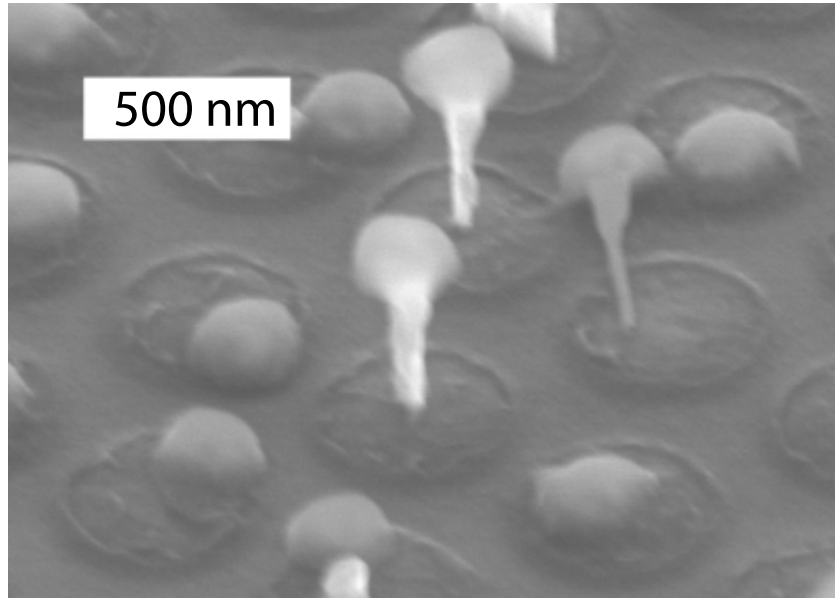


Figure 5.4: - SEM image of heavily etched samples in KOH. Many nanorods have collapsed during the etching process

Etching	ICP only	1 min 40°C	10 min 40°C	5 min 80°C	30 min 80°C
Average Di- ameter	370nm	340nm	320nm	230nm	80nm

Table 5.1: Average diameter of nanorods with etch time and temperature

5.3.2 Time integrated photoluminescence

The samples were mounted on a cryostat, cooled to 4.2 K and excited with a frequency tripled Ti:sapphire laser giving 100 fs pulses at 266 nm. A $36\times$ achromatic reflecting microscope objective was used to focus the laser to a spot of $\sim 1\mu\text{m}$ in diameter. This illuminates up to ~ 10 nanorods simultaneously. The laser power measured in the excitation beam before the microscope objective is $\sim 30\mu\text{W}$, giving an excitation power density on the sample of $\sim 1.9\text{kWcm}^{-2}$.

The time integrated PL spectra at 4.2 K of the different sized nanorods are shown in the insert of Fig. 5.5. The PL is centred around $\sim 2.79\text{eV}$. There is a variation in PL spectral shape between the samples which are more heavily etched. The variation of nano-rod diameter of the QW emission peak energy and intensity per unit emission area is shown in Fig. 5.5. With the 30min 80°C , ultra-thin sample aside, there is a trending blue shift in the QW emission with decreasing nanorod diameter excited with a constant excitation power of 1.9kWcm^{-2} . Similar effects have been observed in nanorod and nanohole structures investigated by Ramesh *et al.* (32), and are caused by a reduction in the piezoelectric contribution to the QCSE as the strain in the InGaN QWs relaxes at the surface of the nanorods.

The PL intensity per unit area is obtained by integrating the intensity of the PL over the entire MQW emission spectrum and dividing by the active area of the nanorods. It can be seen that this intensity increases with decreasing size down to the 5min 80°C sample, together with the increase in peak photon energy. With KOH etching of 30 minutes, the diameters of the nanorods reach 80 nm. At this diameter, the PL

5.3 Optical Properties of InGaN/GaN Nanorod LED Arrays

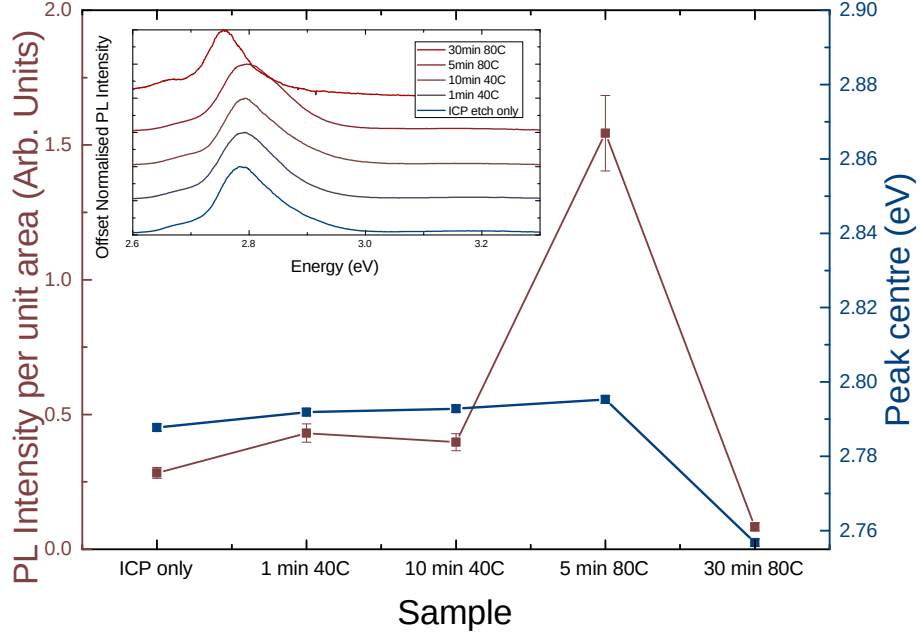


Figure 5.5: - Variation of PL peak emission energy and the intensity normalised by unit of emission area at 4.2K of InGaN MQW with different nanorod etch conditions. Insert shows the PL spectra of the different etch conditions on the nanorods

spectrum is found to change drastically, together with a decrease in intensity per unit area measured. This is most likely due to fewer nanorods being measured under the same size laser spot size, owing to copious numbers of collapsed nanorods shown in the SEM image in Fig. 5.4.

There are a few possible factors contributing to the increase in light output per unit area. Firstly an increase in electron and hole wavefunction overlap as the QCSE is reduced due to a reduction in strain on the sidewalls of the nanorod as its diameter is decreased. Secondly, a reduction in non-radiative recombination could arise when the nanorod diameter is comparable to the carrier diffusion length (typically 200 - 600 nm for InGaN/GaN (114)). Kawakami *et al.* describes how controlling the size of

5.3 Optical Properties of InGaN/GaN Nanorod LED Arrays

the nanorods can artificially restrain where the carriers recombine. Fast recombination may occur at the sidewalls of the nanorod due to the reduced QCSE as mentioned above. This can produce a radial distribution in carrier radiative lifetime which may allow carriers to diffuse from the centre of the nanorod radially to recombine closer to the perimeter (32). The overall effect is thus a reduction in carrier radiative recombination lifetime. Lastly, waveguiding effects such as lateral light confinement can have significant impact on the light output. Overall, the results in Fig. 5.5 show definite changes in carrier recombination on variation of etch conditions of nanorods, which are potentially advantageous to LED performance.

The spectral shape of the PL also shows changes when the diameter of the nanorod is etched down. Nanorods of diameter 370-320 nm show similar spectral shapes. At 230 nm diameter, there is a broadening towards the high energy side shown in the insert of Fig.5.5. The broadening appears as an extra feature in the spectrum on the high energy side resulting in an asymmetric spectral shape. On further etching, the 80 nm diameter nanorod shows a dramatic change in both peak photon energy and spectral width. The narrowing of the spectral width in the heavily etched sample could arise in two ways.

First of all, the number of nanorods excited under the laser spot is far fewer than that on the other samples since the thin nanorods are prone to collapsing hence have a much lower density, shown in Fig 5.4. The majority of the area on the surface of the 30 min 80°C sample does not actually give any luminescence; this seems to get worse with time, and can be due to damage from prolonged laser irradiation. The lower sample

5.3 Optical Properties of InGaN/GaN Nanorod LED Arrays

size measured on the 30 min 80°C nanorods will lead to inaccurate representation of the entire sample. We must take into account that there are extensive fluctuations in the potential of InGaN QW both locally and across the wafer. With a small sample area of one or two nanorods of 80 nm diameter, the peak width can misrepresent the average, explaining the slightly smaller and unexpectedly red-shifted peak in Fig. 5.5.

Secondly, the surface effects described in the previous section will have a much stronger influence in the smaller diameter sample. In fact, the free surface circumference to emission area ratio increases by a factor of 3 for the 230 nm diameter sample compared to the 80 nm diameter sample. On one hand, the strain relaxed side walls can lower the internal electric fields in the QW, leading to a reduction of QCSE giving a narrower line width as well as a blue shifted peak photon energy. On the other hand, the deformation potential contribution to the bandgap reduces as strain is relaxed towards the side-walls, red shifting emission. Other effects such as Fermi surface pinning can alter the band-profiles, lowering the effective band gap and separating carriers laterally across the QW layers as discussed in the previous section. The following work will be discussing the different effects

5.3.3 Quantum confined stark effect in etched nanorod array LEDs

The intensity of the excitation beam also affects the peak emission energy of the nanorods. Varying the laser excitation power density varies the carrier density in the sample. As carrier density increases, free carriers can screen the internal electric field in the QW, reducing the QCSE. An increase in PL emission photon energy is thus

5.3 Optical Properties of InGaN/GaN Nanorod LED Arrays

usually observed in InGaN QW systems when excitation power density is increased, and is evident in the presence of QCSE. Fig. 5.6 shows the excitation power density variation of the PL spectrum from the 370 nm nanorod (ICP only).

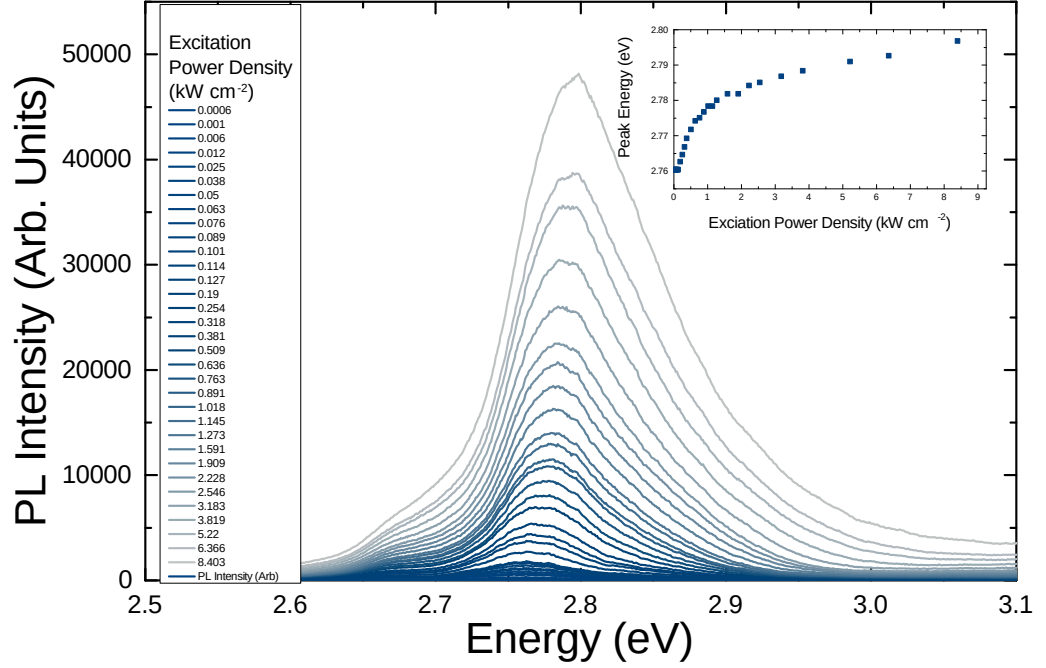


Figure 5.6: - Time integrated PL spectrum of InGaN emission as a function of excitation power density for 370 nm diameter nanorods. Insert shows MQW emission peak position with increasing excitation of the spectra shown

The peak position in photon energy is plotted against the excitation power density in the insert of Fig. 5.6. Peak energy centre positions can be roughly fitted with a parabolic curve for excitation power densities between 0.1-1.5 kW cm^{-2} . Robinson *et al* (129) showed that the electric field holds a quadratic relationship with energy shift. If we assume that the carrier density is proportional to the carrier field screening (130), we can infer from the relationship between the excitation power density and peak emission photon energy, that for this excitation range, the blue-shift is most likely due

5.3 Optical Properties of InGaN/GaN Nanorod LED Arrays

to carrier field screening of the QCSE.

Experiments on PL emission peak photon energy in relation to excitation power density were carried out systematically on the different nanorod arrays. Fig. 5.7 shows the change in peak photon energy with increasing excitation power densities over 3 orders of magnitude of the 5 different samples discussed. It can be seen clearly that there is an upwards shift in the peak photon energy for the entire excitation power series for decreasing diameters of nanorods apart from the most narrow sample (30 min 80°C).

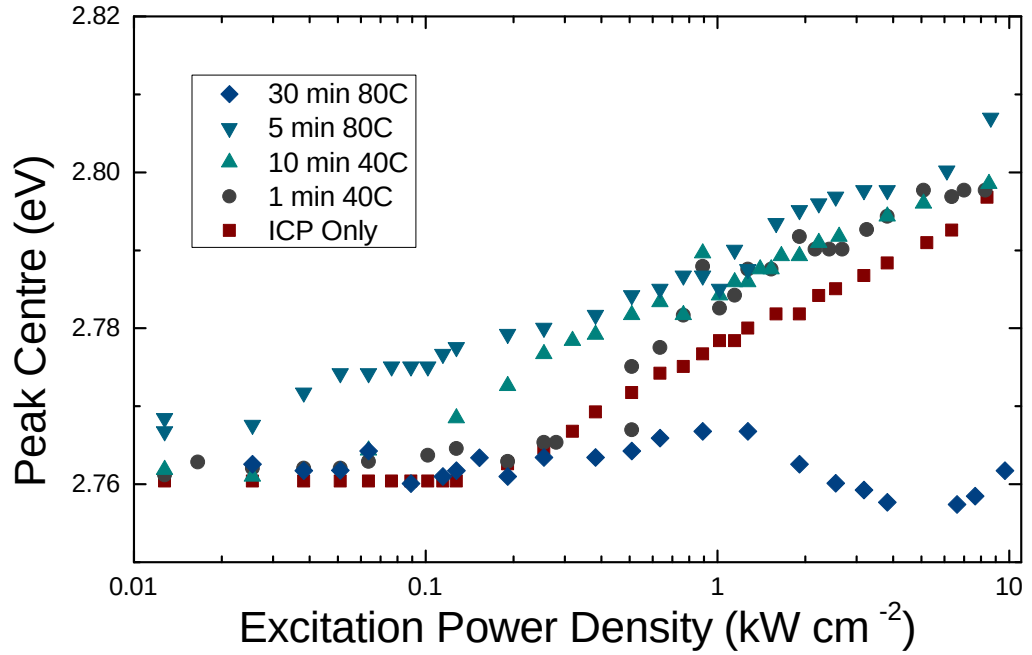


Figure 5.7: - Variation of PL emission peak photon energy with excitation power density for different nanorod samples

From the logarithmic plot of the shift in energy, we can see that the slope between 0.1-1.5 kW cm⁻² between the 4 larger diameter samples (370 nm to 230 nm) are similar, whereas the thinnest nanorod sample shows little change in peak photon energy as

5.3 Optical Properties of InGaN/GaN Nanorod LED Arrays

the excitation power is varied. As the excitation power is further increased, band tail state filling appears and becomes the dominant blue-shifting mechanism as described by Kuokstis *et al* (130). This can be seen by a logarithmic plot of the change in peak energy (shift) with excitation power density increase shown in Fig. 5.8. The gradient of the fitting decreases from 0.5 to a lower value above $\sim 1 \text{ kW cm}^{-2}$.

5.3.4 Assessing relative strain relaxation of the different rods by photoluminescence

By assuming a sheet charge, we can consider the carrier screening effect of the piezoelectric field to be proportional to the carrier density. The quadratic nature of the energy shift with internal field as described by Robinson *et al* (129), Fry *et al* (131) and Holmes *et al* (33) leads to a quadratic relationship between the shift in QW emission energy with the increase in carrier density. The increase in carrier density (carrier generation rate), which lessens the effective internal field strength, can be assumed to be proportional to the increase in excitation power density.

The magnitude of the internal field of each sample can therefore be roughly assessed relative to each other by looking at the overall absolute peak energy of the different samples *within* the limits of the quadratic excitation to peak energy regime shown in Fig 5.8. It is hence evident that despite having strain relaxed side-walls, the four thicker nanorods are still under the influence of the QCSE.

There is an overall decrease in the energy shift as diameters decrease summarised by table 5.2, where the energy shift is taken for the case when the *sensitivity* of the

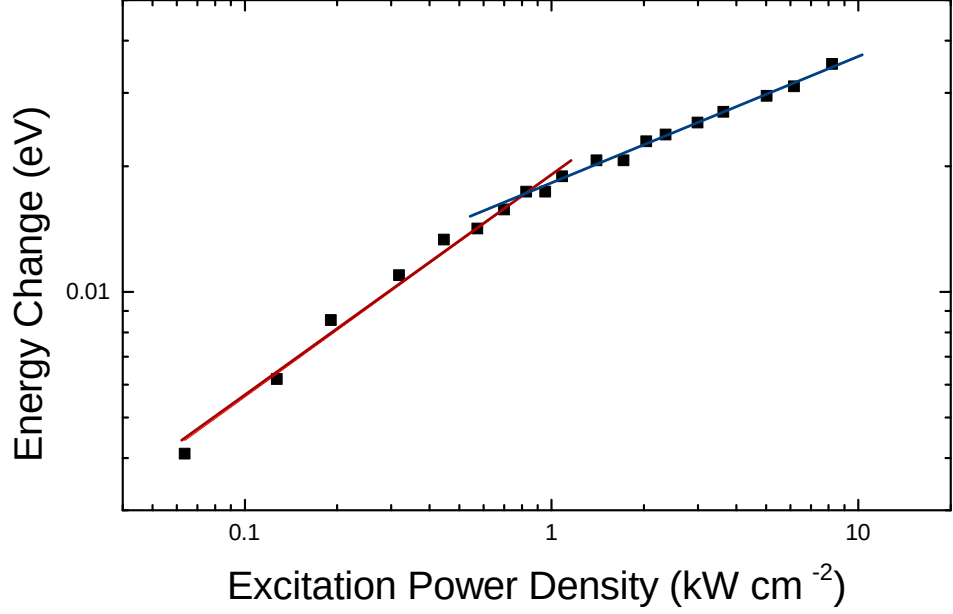


Figure 5.8: - Logarithmic plot of the change in peak energy and excitation power density in the ICP only sample. The blue shift across the excitation power range consists of two dominating mechanisms characterised by two rates of increase. The low limit has a slope of 0.5, which we assign to be due to carrier field screening of the QCSE.

	ICP only	1min40°C	10min40°C	5min80°C	30min80°C
Energy shift	~ 15 meV	~ 15 meV	~ 13 meV	~ 10 meV	N/A

Table 5.2: Blue shift in emission peak energy due to carrier field screening

5.3 Optical Properties of InGaN/GaN Nanorod LED Arrays

$\log \Delta E$ and $\log$ of the increase in excitation power density is quadratic. This is in good agreement with the assumption that as the surface to emission volume increases, the strain relaxation induced QCSE reduction from the side-walls of the nanorod has a larger effect on the overall emission properties.

Further evidence that the blue-shifted emission from the nanorods is due to a reduction in QCSE when its diameter is reduced can be found on examination of the time resolved PL (TRPL) data. Fig. 5.9 shows the time resolved decay trace of four of the nanorod samples. The data were taken at the photon energy corresponding to the peak intensity of each of the nanorod spectra. It can be seen clearly that the smallest diameter nanorod (5 min 80°C) shows a reduced lifetime compared to the other nanorods.

The lifetime of the InGaN QW system in nanorods was investigated extensively previously by Holmes *et al* (33). The study focussed on the carrier dynamics in quantum disks and revealed that despite suppressed by strain relaxation, the QCSE has a great impact on the emission of the nanorods. In particular, QCSE will tend to spatially separate carriers resulting in increased carrier recombination lifetime. Our initial TRPL study on wafer-scale fabricated nanorods shown in Fig. 5.9 complements the results presented in (69). For the smaller diameter nanorod we see a reduction in PL decay rate, indicating a better carrier wavefunction overlap in the smaller diameter system as a result of strain relaxation.

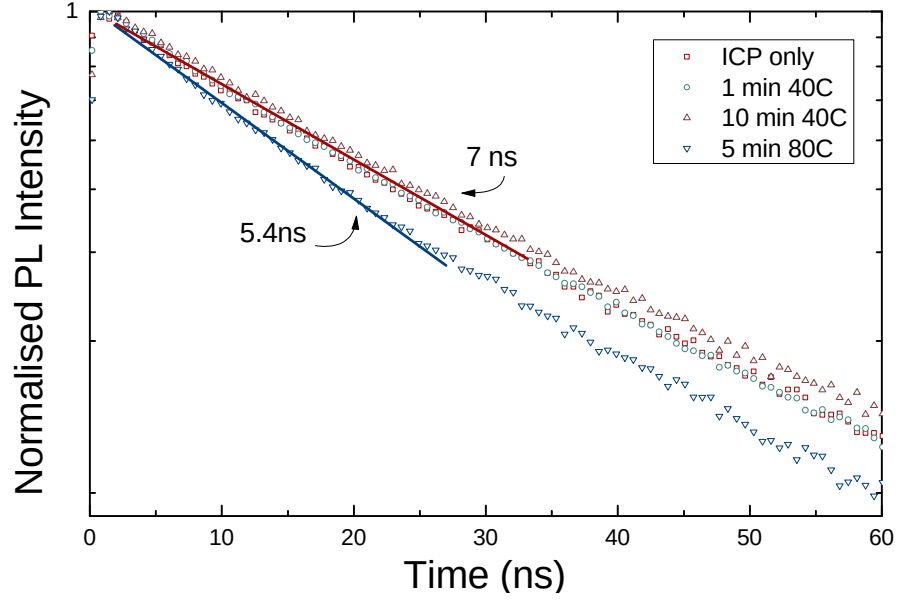


Figure 5.9: - Time resolved PL decay traces of four of the nanorod samples. The smaller diameter 5 min 80°C nanorod sample shows a lower lifetime than the other nanorods

5.4 Evidence of other recombination mechanisms

The peculiar broadened spectral shape from the 5 min 80°C sample, in the insert of Fig. 5.7, prompts the question of how other physical effects can be affecting the emission from etched nanorods and what the origins of the broadened emission can be.

5.4.1 Excitation power density revisited

Fig. 5.10 shows contour maps of the PL spectra plotted against excitation power density with normalised intensity to show the change in spectral shape and position. The FWHM is drawn on the plots and indicated by a dashed line as a guide to the eye. The larger samples, ICP only and 5 min 80°C show a broadening in line width as excitation power density increases. The smaller diameter sample shows a larger FWHM in the

5.4 Evidence of other recombination mechanisms

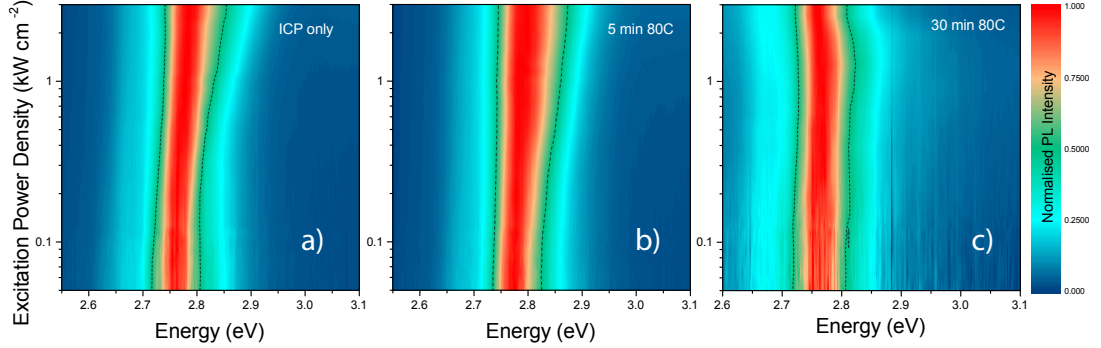


Figure 5.10: - Contour maps of the normalised PL spectra with variation of excitation power density for ICP only, 5 min 80°C and 30 min 80°C samples. The dashed lines in the three plots show the contour of the half maximum (50%).

emission energy than the larger diameter sample. For the 30 min 80°C sample, there is little broadening observed. The FWHM lines are almost parallel across the graph. On close examination of Fig. 5.10a) the low energy side of the normalised spectrum blue-shifts first followed by the broadening of the spectrum from $\sim 0.6 \text{ kW cm}^{-2}$. The 5 min 80°C sample in contrast, does not exhibit such a blue shift of the FWHM line on the low energy side. In a similar manner to the smallest diameter sample, the low energy side of the FWHM line remains straight across the excitation range. Broadening and blue shift occurs due to an asymmetric growth of the high energy side of the emission peak only.

This peculiar behaviour indicates that as the surface to emission volume ratio increases, there could be an additional emission path contributing to the broadening of the spectrum. This contribution does not undergo the usual blue shift exhibited by the larger nanorod, as shown in Fig. 5.10 a), suggesting that its emission mechanism is not greatly affected by the free carrier screening of the internal electric field and that

it can possibly be related to the free surface.

5.4.2 Localisation in nanorods

An S-shaped change in peak photon energy with temperature has been associated with localisation, first reported in InGaN/GaN QWs by Cho *et al.* Cho conducted a temperature dependent PL experiment and discovered a blue shift in peak emission energy followed by the conventional red shift according to the Varshni equation with the increase of sample temperature from 5K to 300K (80). This behaviour has been attributed to localisation in the InGaN QW due to potential fluctuations and is generally a well established and widely accepted phenomenon.

A temperature dependent study was carried out on sample 5 min 80°C to investigate the surface relaxation effect which is speculated to result in the small feature on the high energy side of its TIPL spectrum. Fig. 5.11 shows a compilation of the PL spectra taken at varying temperatures excited at 0.13 kW cm^{-2} laser power. The PL spectra of the InGaN QW can be seen as having a main low energy peak with a high energy shoulder. As the sample temperature is risen from 4.2 K to 300 K, a clear distinction can be seen between the two peaks as the intensity of the high energy side and the low energy side reaches a similar height. The overall effect from 4 K to 180 K is that the distribution of the emission shifts to a higher energy due to the intensity change between the peaks. Subsequent temperature increase causes band gap shrinkage due to lattice thermal expansion. A red-shift is thus observed as the sample temperature is increased to room temperature.

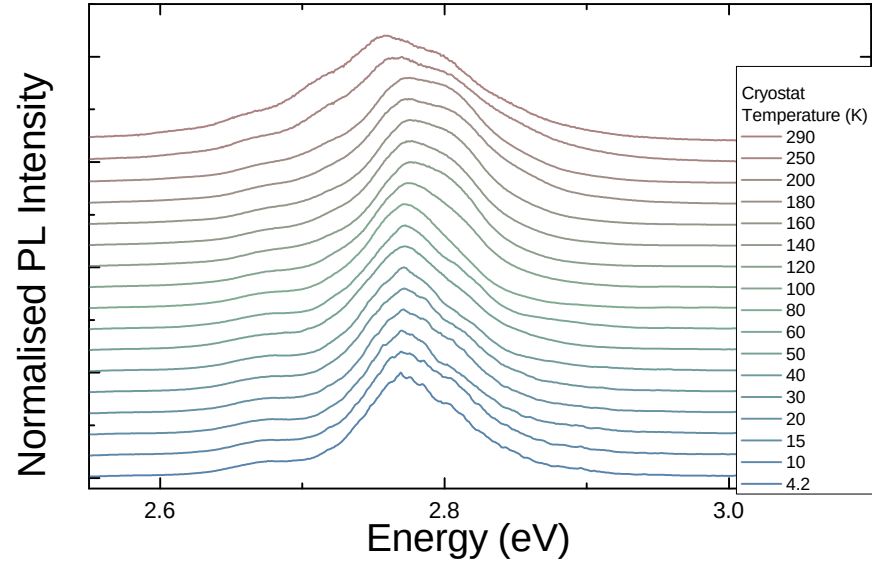


Figure 5.11: - Temperature dependent PL spectra of 5 min80°C sample

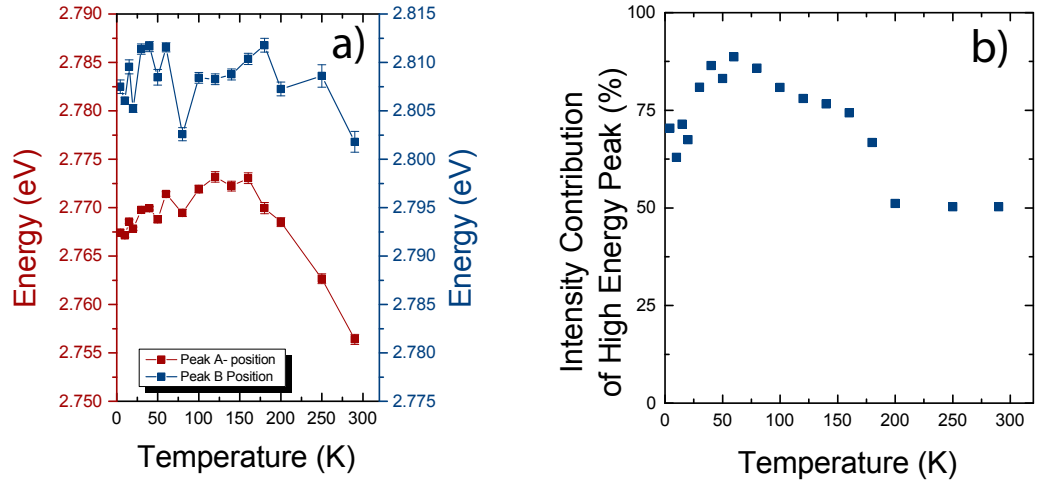


Figure 5.12: - Fitting of two peaks to the PL spectrum with varying temperature. a) shows the peak energies of the two fitted peaks. Peak A is the lower energy fitted peak and Peak B is the higher energy fitted peak. b) shows the intensity contribution ratios of the higher energy peak to the total integrated PL intensity.

5.4 Evidence of other recombination mechanisms

Fig. 5.12 shows the results of fitting two Lorentzian peaks to the PL spectral series. The double-peak fits very well with the PL spectrum throughout the temperature range. Fig. 5.12 a) shows the centre positions of the two fitted peaks. The lower energy peak (A) in red is shows a very slight blue shift followed by a red shift due to band gap shrinkage. The higher energy fitted peak (B) in blue shows a relatively stable peak energy as temperature rises from 4K to 200K. There is noticeable shift of B as the sample approaches room temperature. The two lines in Fig. 5.12 a) are plotted on the same scale. Hence the energy difference between the two peak has an increasing separation in energy from $\sim 160\text{K}$ to 300K . The intensity ratio of peak B with respect to the total integrated intensity ($A + B$) is shown in Fig. 5.12 b). As temperature rises, from 4K to 60K, the intensity of the higher energy peak dominates the PL spectrum and as temperature rises to room temperature, the intensity ratios for the two peaks becomes 1:1.

By normalising the spectral intensity for each individual temperature, contours of the normalised PL intensity are plotted in Fig. 5.13 a), showing very clearly the evolution of the PL spectrum following an “S-shape” shift. The broadening is shown as a contour line along the half maximum of the main peak, denoted by the dashed line in the figure. Broadening first occurs on the high energy side of the spectrum as temperature is raised to 100K before the whole spectrum is red shifted due to lattice thermal expansion.

Time resolved PL measurements were taken at three different photon energies throughout the temperature dependence investigations. Three different photon en-

5.4 Evidence of other recombination mechanisms

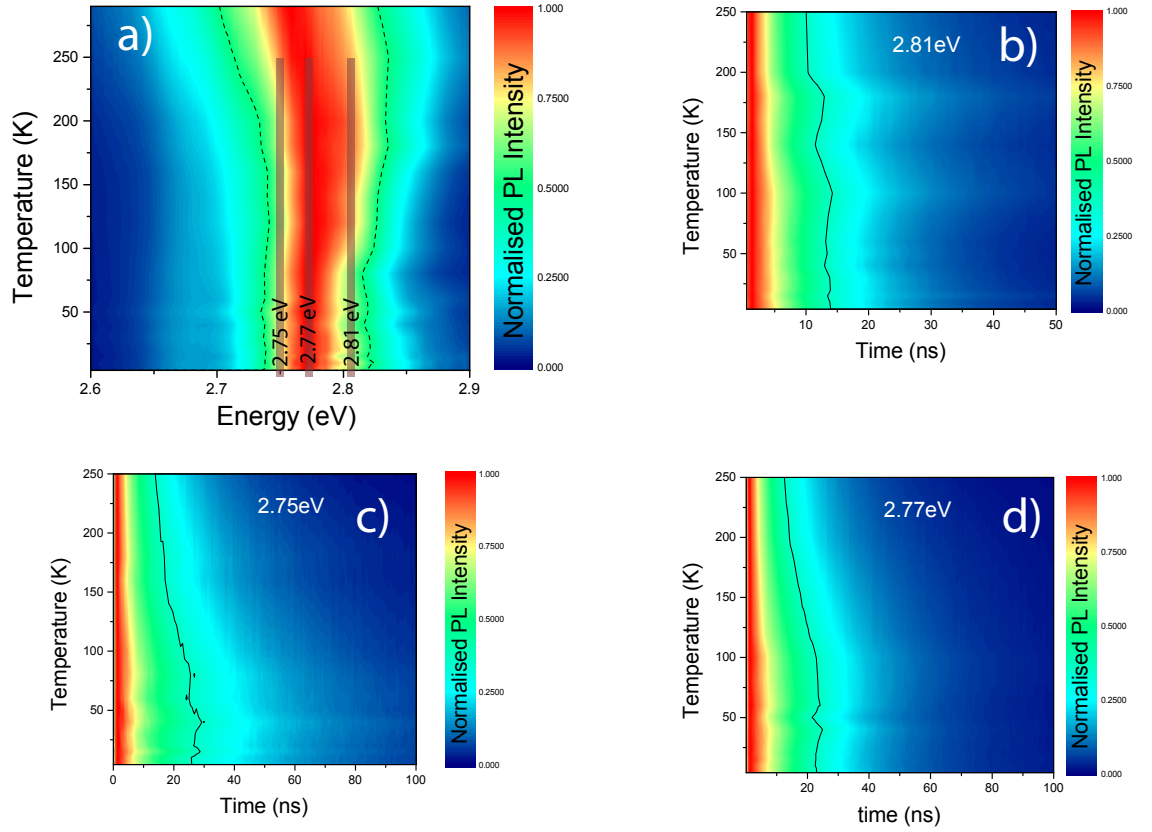


Figure 5.13: - Normalised intensity contour plots of time integrated and time resolved PL spectra with variation of temperature. a) Normalised PL intensity spectrum plotted with temperature showing broadening and an “S-Shape” shift in peak energy. Time resolved PL with normalised intensity at each temperature variation at photon energies of b) 2.81eV, c) 2.75eV, and d) 2.77eV are plotted with time after excitation pulse. These three photon energies are displayed by the three bars in a) as a guide to the eye.

5.4 Evidence of other recombination mechanisms

energies were examined, 2.75 eV, 2.77 eV, and 2.81 eV. 2.77 eV, and 2.81 eV correspond to the approximate energies of peak A and B in Fig. 5.12. The positions of these energies with respect to the TIPL spectrum are indicated by the red bars in Fig. 5.13 a). Contour plots of the TRPL taken at the three photon energies with intensities normalised at each temperature and stacked by time after excitation are shown in Fig. 5.13 b) c) and d). At the two lower energies, the temperature time resolved behaviour is comparable to that investigated by Holmes *et al.* on InGaN Quantum disks in nanorods. There is a decrease in decay rate as temperature is increased. The black line in the figure indicates the $1/e$ contour line. It is worth noting that the lifetime is non-exponential, hence the $1/e$ line is used as a comparison between the three sampled photon energies. At 2.75 eV and 2.77 eV, as temperature is increased from 4K, the decay rate remains unchanged (with even a slight increase at the lower temperatures) until ~ 100 K. The decay rate decreases with further increase in temperature and finally settling at a value of $1/e = 15$ ns. This effect is likely to be due to opening of nonradiative decay paths at increased temperatures. This is in stark contrast with the TRPL measured on the higher energy side of the spectrum (peak B) shown in Fig. 5.13 b). The decay rate here does not vary much with temperature increase though the rate is faster than the PL from lower energies.

The “S-shape” shift was investigated by Cho *et al* (80). Cho showed in their InGaN QW sample that as the temperature increased from 10K to 300K, a series of shifts in emission energy peak occurs. Time resolved studies provided Cho with clues about the interplay between radiative and non-radiative recombination alongside localisation

5.4 Evidence of other recombination mechanisms

from band-tail states with temperature variation. Photocarriers excited above bandgap recombine both at the bandedge and also at lower energy band-tail states, causing a red-shifted emission at low temperatures. As temperature increases non-radiative recombination paths start opening; this gives competition to the energy transfer of carriers to band tail localised states, resulting in an apparent blueshift in overall emission energy as explained in reference (80).

However, we speculate that the emission shift in the nanorod sample due to temperature is of a different nature to that reported by Cho mainly due to two reasons. Firstly, the 5 min 80°C sample clearly exhibits a two peak behaviour which experiences separation and change in intensities as temperature is varied. Secondly, the time resolved data shows that the decay rate of the high energy peak remains stable at $1/\tau \sim 13 - 11$ ns through temperature variation from 4 K to 250 K. Both these observations are different to the data presented in ref. (80). A possible explanation for the lack of decrease in decay rate for the high energy peak is due to the fact that the non-radiative recombination paths are suppressed due to localisation processes that are not present in plane unprocessed quantum wells. For nanorods, carriers can distribute in the quantum well unevenly and it is very likely that they can be localised around the periphery of the nanorod as a result of bandstructure modifications due to the free surface (33). Evidence from cathodoluminescence studies carried out by our collaborators Zhuang *et al* do indeed point out that there are two distinct regions in the quantum well of the etched nanorods emitting different wavelengths of light (132). Zhuang reported emission centred at 2.82eV for regions close to the surface of the nanorod, decreasing to 2.76eV at

5.4 Evidence of other recombination mechanisms

the centre of the nanorod. The high energy emission essentially forms a donut shape around the periphery of the quantum well in the nanorod. A donut shaped emission has also been observed by Kawakami *et al* in much lower energy nanorod array samples using high resolution fluorescent microscopy (133). In light of the results reported by Zhuang, we propose that the two peaks A and B, seen in Fig. 5.12 refers to emission from spatially separate regions of the nanorods. According to Zhuang's report, peak B comes from the periphery of nanorod whereas peak A comes mainly from the centre.

The PL from the periphery of the nanorod has a small decrease in decay rate as temperature rises from 4K to 250K as compared to that of the centre of the nanorod. This observation suggests that carriers recombining at the centre of the nanorod are more prone to non-radiative recombination that emerges at $\sim 100\text{K}$. Localisation of carriers at the periphery of the nanorod may be preventing some carriers from diffusing into non-radiative traps. This results in lowering of radiative recombination at the lower energies and hence the high energy peak appearing more dominant causing an apparent blue-shift in the normalised PL energy from 100K to 230K shown in Fig. 5.13. This strong localisation can lift the emission efficiency of nanorods at room temperature, providing a further explanation for the higher intensity per unit area of the etched nanorods demonstrated in Fig. 5.5.

5.5 Discovery of QD-like features

Thus far, discussion on the emission at low carrier density limits of the micro-PL experiment have yet to be discussed. With excitation power densities of a few W cm^{-2} , the PL spectra of nanorods are jagged despite long accumulation times. The jagged spectra are particularly apparent in samples which are etched heavily. These features are immediately washed out by the usual broad QW emission as excitation power is gradually increased. In this section, the emission mechanisms in the low carrier density regime in etched MQW nanorods are investigated using conventional one-photon excitation (OPE) and also non-linear two-photon excitation (TPE).

Under OPE, the normalised PL spectra of the smallest diameter sample 30 min 80°C are shown in Fig. 5.10c). At low power excitation densities below 0.2 kW cm^{-2} , the spectra show features which are above noise level. This phenomenon occurs across all the nanorod samples but is particularly pronounced in the narrowest sample. In this low excitation regime, the PL varies greatly with position. Fig. 5.14 shows a particular position on the sample where a narrow line in the spectrum can be isolated from the main emission peak. On the high energy side of the main emission, there is a narrow line of around 4 meV full width at half maximum. When the laser excitation power density is increased, the narrow line broadens and eventually merges into the background at 0.2 kW cm^{-2} . Above 0.6 kW cm^{-2} , fine features in the spectrum are no longer visible, the spectrum is smooth and blue-shift of the emission energy starts to occur with increasing excitation powers. A similar observation has also been made by

Kawakami *et al* (19). However, little was discussed about the peculiarity of the result. It was thought that the sharp peaks may have come from subband emissions which are only seen when the nanorod's PL is examined from the side and not top down. But this argument is contrary to our observations, since our nanorods are all free standing and micro-PL is conducted from the top-down.

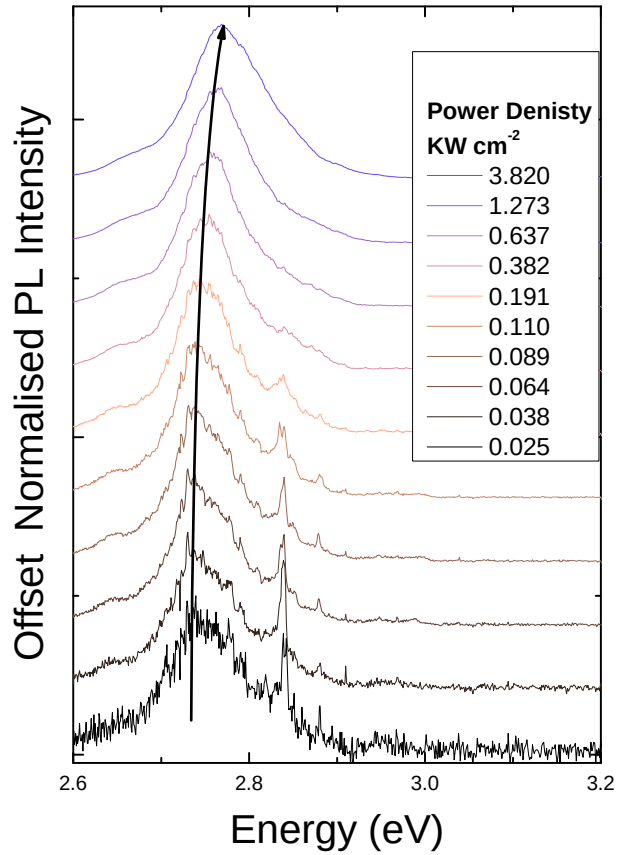


Figure 5.14: - Excitation power density dependence spectra from the 30 min 80°C sample. One photon above band-gap excitation is varied over 2 orders of magnitude at low power densities. Clear narrow lines can be seen.

Fig. 5.14 shows a detailed account of the evolution of these narrow emission lines with increasing excitation power density. Schömiig and Gotoh(74) (134) reported small features in the PL spectrum and argued that the origins of these states are due to

localisations in the InGaN well layer which can be resolved by high resolution micro-PL experiments. As more and more photocarriers are generated, they cease to be trapped in localised centres and recombination occurs over a larger area in the well. The localised centres are filled resulting in the spectrum gradually becoming smoother as these narrow line features are saturated. In contrast to the blue-shift of the broad main QW PL emission, the narrow lines remain at a fixed energy with variation of excitation power, similar to InGaN quantum dots (QD) (135).

5.5.1 Two-photon excitation studies

Two-photon excitation can be employed to suppress the background quantum well emission to study the narrow QD-like peaks arising from carrier localisation in the nanorods as demonstrated on InGaN QDs by Jarjour *et al* (98). It is necessary to use a high photon flux to excite the sample due to the two-photon absorption cross section being very small. Sample 1 min 40°C with base diameter ~ 340 nm showed very few narrow spectral features under OPE at 266 nm. Under TPE, spectral linewidths of less than 1 meV were observed with a highly suppressed background emission. Fig. 5.15 a) shows an excitation power density dependent study of the emission at ~ 2.705 eV at a sample temperature of 4.3K.

The spectrum at low excitation power density shows an isolated narrow QD-like peak on a low background. The increase in PL emission with excitation follows an $I \propto P^2$ relationship, indicative of excitonic emission under TPE. As excitation power increases, the QD-like line shows no energy shift. Instead, the increase in excitation

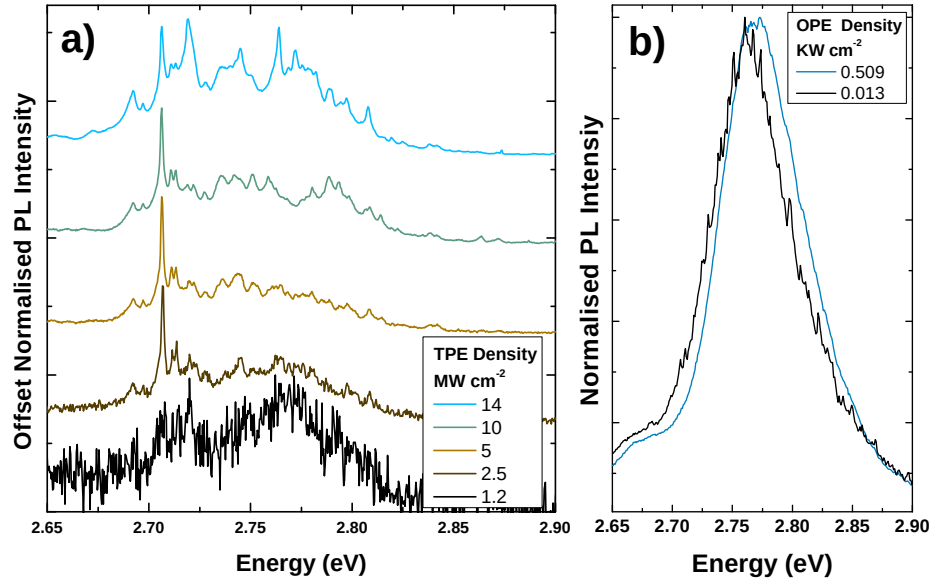


Figure 5.15: - Spectra showing a comparison of OPE and TPE on 1min 40C sample. a) Shows the TPE excitation power dependence results. There is no shift in energy in increasing excitation density for the narrow QW-like peak at 2.705 eV. b) Shows spectra for two-excitation power densities with a 266 nm laser OPE. The spectrum for 0.013 kW cm^{-2} excitation density has resolvable narrow features. For excitation density of 0.509 kW cm^{-2} , the peak has smoothed out.

power leads to the formation of new discrete peaks at the high energy side of the studied peak. The intensities of these higher energy peaks become increasingly pronounced. At 14 MW cm^{-2} , the high energy peaks are of a similar intensity as the studied QD-like peak 2.705 eV . Integration of these higher energy peaks which emerge with higher excitation density may be a contributing factor to the overall observed blue shift in the OPE PL when carrier density is increased.

Fig. 5.15 b) shows the OPE spectra for the 1 min 40°C sample at two excitation power densities. For the low excitation density, small features can clearly be seen within the main emission band. At 0.5 kW cm^{-2} excitation density, these features disappear to give a smoother emission band accompanied by a small blue-shift. The excitation density at which this shift occurs is approximately at the level where we would expect to begin to observe blue-shift due to piezoelectric field screening in InGaN QW samples. In light of the findings from TPE, we are lead to believe that as carrier density increases, higher energy localised states are filled. The resultant overall population of carriers moves towards a higher energy resulting in a blue-shift which is in addition to the carrier field screening of the QCSE.

The origins of these narrow QD-like peaks raise a considerable number of questions. Suggestions include charge-carrier localisation from QW thickness variations and composition fluctuations, carrier localisation due to strain relaxation, and Fermi-level pinning on the side walls of the nanorods. Furthermore, since the micro-PL area covers more than 10 nanorods, each with MQWs, the peaks could arise from individual QWs in the MQW structure. As excitation power increases, a wider area is excited due

to laser scatter. It is therefore possible that the rise of the higher energy peaks in Fig. 5.15 is due to excitation of additional nanorods.

A spatially dependent study of the sharp peak was performed by carrying out a raster scan and integrating 3 meV around the sharp emission line, shown in Fig. 5.16 b). The spot of the emission centre corresponds to the effective laser spot size for TPE, and hence is resolution limited. It can be seen that the studied peak is well isolated showing no emission in the 3 meV window over the $10 \mu\text{m}^{-2}$ scan, covering up to 70 nanorods. It is therefore unlikely that this QD-like peak originates from individual QWs in the nanorods, taking into account number of nanorods sampled. Temperature dependent studies were carried out on this QD-like peak. A scanning and remapping method was used to trace the position of the peak as temperature varied using a constant TPE power density of 2.5 MW cm^{-2}

Fig. 5.16 a) summarises the temperature dependent study at the same 2.705 eV emission peak. The temperature is gradually increased from 4.3 K. The signal of the peak is clearly detectable to 25 K. Beyond 25 K, spectral broadening and intensity decrease causes the investigated peak to be indistinguishable from background. No resolvable shift of emission energy can be seen in this temperature range. The linewidth broadening occurs asymmetrically towards the low energy side. Similar QD-like narrow peaks was studied by Schömig *et al.*, and it was thought that these peaks were localised states caused by indium fluctuations in planar 2-D InGaN/GaN QWs. Temperature studies conducted by Schömig found pronounced blue-shifts of $> 15 \text{ meV}$ when temperatures were raised from 10 K to 20 K (74). It was suggested that this

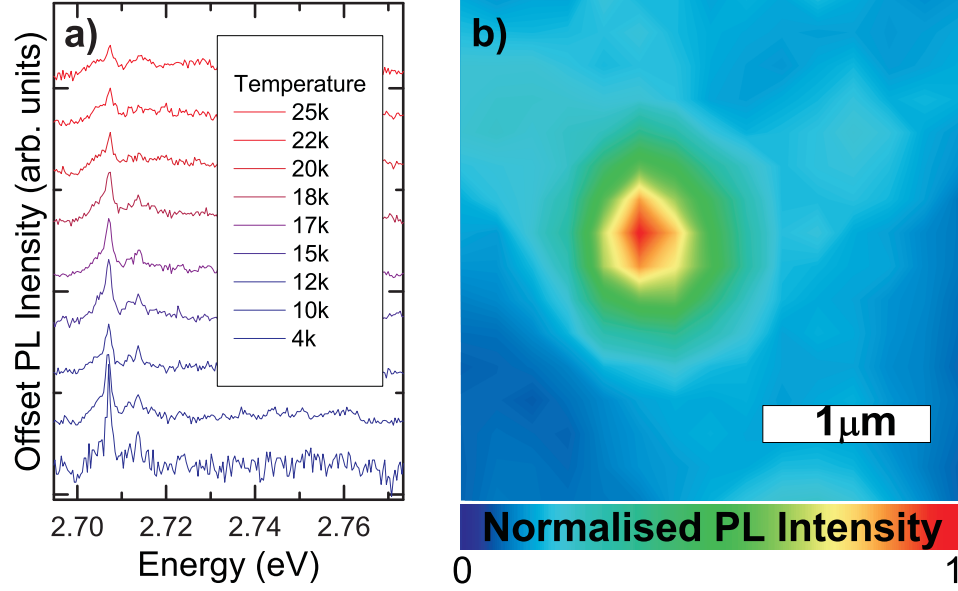


Figure 5.16: - a) Spectra showing the temperature dependence of a narrow QD-like peak. The QD-like peak starts to disappear at around 25 K. b) Spatial map of the studied QD-like peak showing a resolution limited spot.

observed blue-shift was due to temperature dependent screening of the internal electric field. There is however, no evidence of this temperature related field screening in our nanorod sample, questioning whether the origins of the peaks found in our sample are similar to those reported by Schömig.

5.6 Final remarks

Micro-PL with OPE and TPE was used to study carrier localisation in nanorod LED arrays made from top down processing of a commercial wafer. Narrow QD-like peaks with undetermined origins were discovered. Results using non-linear TPE spectroscopy are reported. There is no peak energy shift in either temperature or excitation density dependent TPE studies. This is indicative of carrier localisation.

Despite the numerous claims on GaN nanorods or nanocolumns being completely strain free, our position on this subject remains reserved. Both the work presented here and previous InGaN nanodiscs embedded in GaN nanorod work performed in our group (33, 69, 101) have shown that the optical properties may suggest otherwise. To interpret the unusual results from the optical studies carried out on wafer-scale fabricated nanorod LEDs, a more simplified system must be designed in order to isolate a single nanorod which fabricated in the same way in order to study, in isolation, from the top down, which leads to the work presented in the next chapter.

Recently, work on the fabrication of ICP etched nanopillars containing InGaN QDs has been carried out by our collaborators in Harvard University. In these samples, a higher than expected density of sharp peaks were observed under micro PL. It is believed that these observation are related to the etching induced localisations examined in this thesis.

6

Optical studies of single nanorod LEDs

Optical studies of nanorod LEDs are continued in this chapter. In the previous chapter, we saw that etched nanorod arrays gave rise to some interesting results. It is necessary to isolate a single nanorod fabricated using identical methods to be studied from the top down in order to further effects of downsizing of LEDs by means of ICP etching. The work detailed in this chapter has been presented in UKNC2012, IWN2012, and published in references (34, 39).

6.1 Isolating single nanorod LEDs

A simple single quantum well LED structure was used as the base wafer. The reason for this is to allow us to exclude possible complications arising from multiple quantum

wells in order to determine the origins of the QD-like peaks discovered in the previous chapter. The pattern was also designed such that the spacing between individual nanorods exceeded the laser spot size, making it possible to excite a single nanorod from the top down. Many previous studies have mechanically exfoliated the nanorods from their substrate and studied the emission from the side (19, 101). This method of removal can inflict damage to the nanorods. Whether or not this damage can affect emission characteristics of the nanorods is not within the scope of the thesis. We decided instead to isolate the nanorod and study it from the top down to keep the investigation as simple as possible.



Figure 6.1: - Diagram showing the bespoke LED with a exploded view showing the different layers. On etching, this results in nanorods with structure shown on the right.

Fig. 6.1 shows the structure of the LED wafer used for processing. The bespoke wafer was made by OSRAM, and is a functional commercial single QW LED. It consists of a 2 nm thick single $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}$ QW layer and a 20 nm AlGaIn electron blocking layer grown on top of 4 μm of GaN on a conventional sapphire substrate and capped with

6.2 Single QW LED initial optical characterisations

500 nm of p-doped GaN. Nanoimprint lithography was again used to define regular patterns on the surface of the LED and nickel etch masks deposited, under which the nanorods would be created. ICP was used to etch through the surface of the sample to reach the GaN layer with a diameter to etch depth aspect ratio of $\sim 1:3$.

The spacings of the nanorod array were designed such that only one nanorod would be illuminated under the laser spot. It was also necessary to resolve these individual rods by optical microscope. A pitch of $2\ \mu\text{m}$ was therefore selected with diameters of $\sim 400\ \text{nm}$. Fig. 6.2 shows a few SEM images of the nanorod array. An unprocessed wafer with an equivalent structure was also used as a control sample to compare the etching effects. However, since the processing is on a wafer scale and there is not only a degree of variation between manufactured wafers, but also variation across the surface of individual wafers, there exists a certain amount of variation in emission properties such as intensity and emission wavelength as a result.

6.2 Single QW LED initial optical characterisations

A high NA(0.7) objective was used to avoid excitation and collection of PL from more than one nanorod. The glass objective also proved to be much easier to align than the reflecting objectives used for UV excitation. A reflectivity study was carried out to give a brief assessment of the optical properties of the unprocessed SQW sample. under visible light excitation.

Fig. 6.3 shows the reflectivity spectrum of the SQW unprocessed sample superimposed with a corresponding PL spectrum. The reflectivity is taken using the method

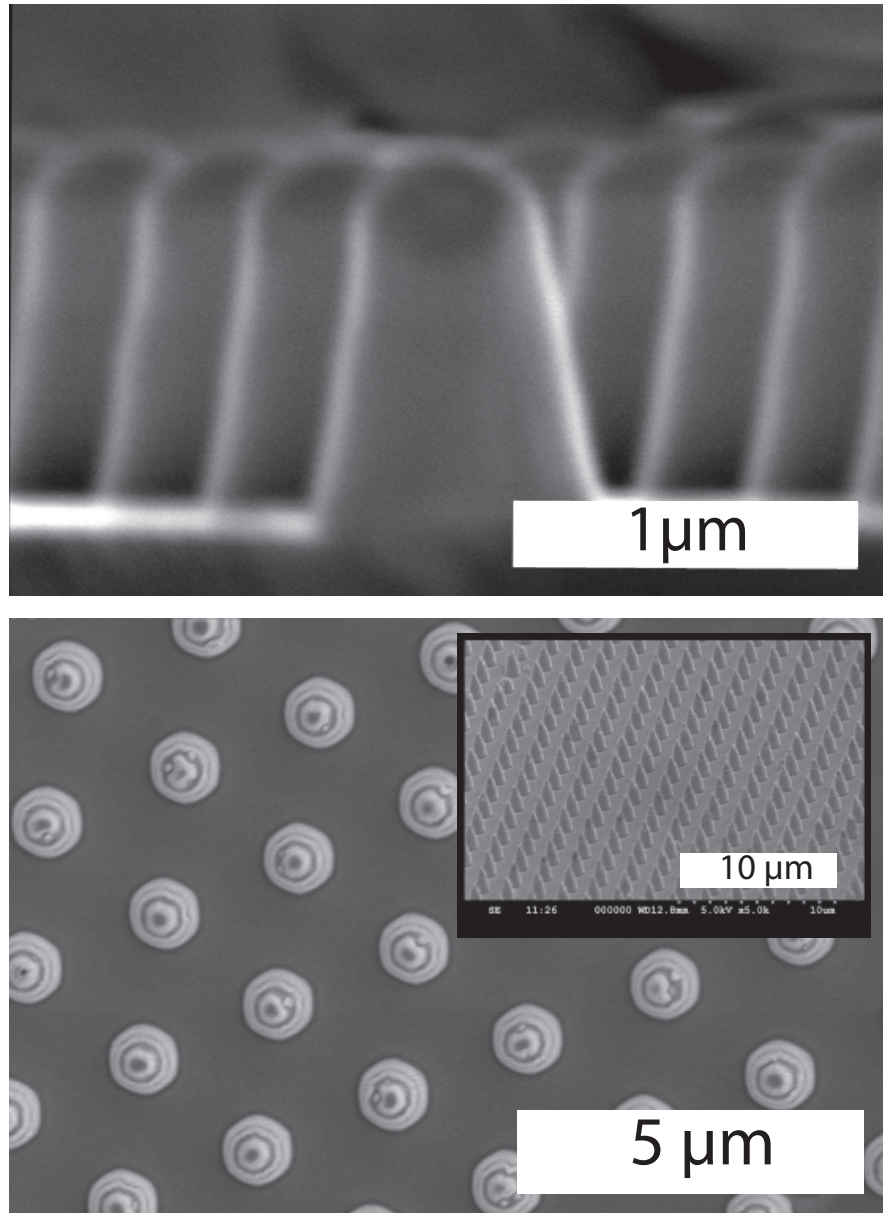


Figure 6.2: - Top shows a side view SEM image of the fabricated nanorods. Bottom SEM shows the nanorod array with an hexagonal pattern. Insert is an SEM showing a wider field of view of the nanorods.

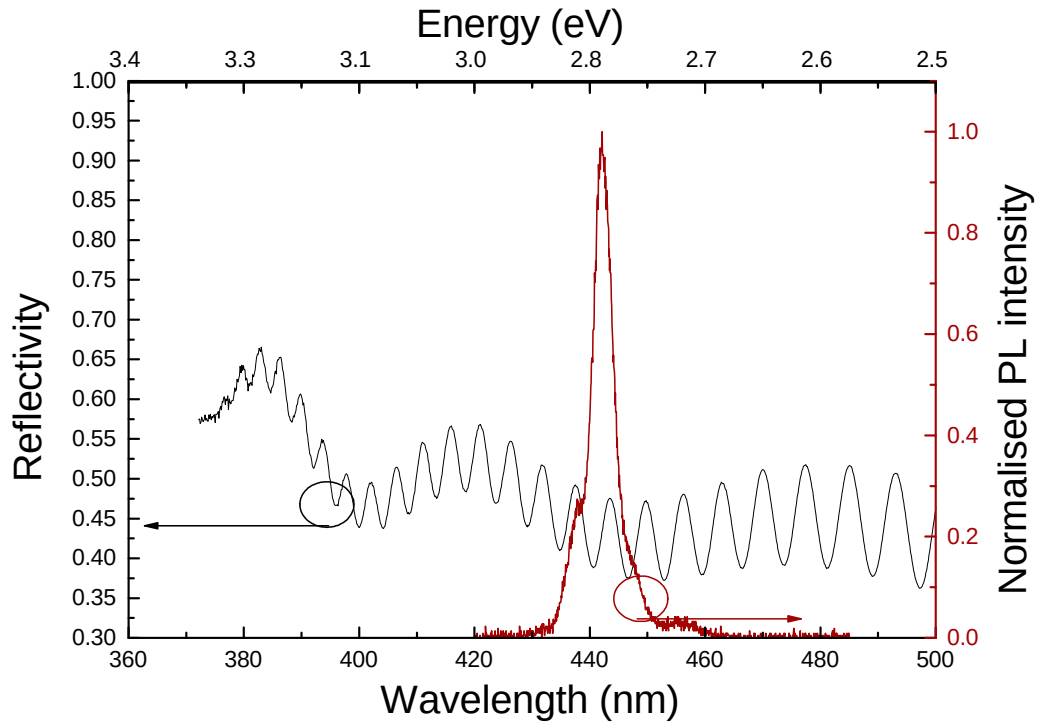


Figure 6.3: - Reflection spectrum normalised with aluminium mirror superimposed on top of the PL spectrum of the SQW unprocessed LED.

6.2 Single QW LED initial optical characterisations

described in section 4.4.4 and the spatial resolution is in the order of a few microns. Despite the study being very localised, the sample shows a similar characteristic in several randomly selected locations. The raw spectrum was normalised with a plain uncoated aluminium mirror, assuming a close to 100% flat band reflection of aluminium between 370 nm and 500 nm. The measurements give a close approximation of the reflectivity, since absolute reflectivity of the aluminium has not been recorded. Fringes are seen across the reflectivity spectrum corresponding to the optical modes between the sample substrate and surface interfaces, varying slightly across the wafer. The normalised PL intensity of the same sample within 1 mm vicinity of the reflection measurements is shown overlaid on the figure. The spot is excited with a 405 nm CW laser at very low excitation powers using a visible spectrum, $100\times$ 0.7 NA objective. The laser is able to excite the sample to give the QW luminescence, and hence in the following studies, the visible violet lasers are used as opposed to the tripled UV laser due to the smaller spot size and ease of alignment. Two shoulders can be seen approximately 30 meV on the high energy (low wavelength) side, and 30 meV lower in energy to the main PL spectrum. The periodicity in energy of the shoulders with the main peak coincides with that of the reflectivity spectrum. Concluding from this, the shoulders and the asymmetry in the PL spectrum are photonic effects modulated over the real PL rather than real luminescence properties.

Although the absorption behaviour of the sample requires knowledge of the transmission spectrum, the reflectivity spectra gives us an idea of the absorption edge, albeit only in a very general sense. There is a dip in the reflectivity spectrum at approxi-

mately 3.08 eV (403 nm), which is situated close to where we would expect the InGaN absorption to lie. Assuming that the detected reflectivity drop at 3.08 eV is due to the absorption edge, the Stokes shift is thus ~ 200 meV, typical of InGaN QW (81). In addition, the contrast of the fringes in the reflectivity decreases at high energies. The presence of these fringes is due to interfering reflected light from multiple surfaces of the sample. A decrease in contrast indicates an increased absorption, leading to a lower intensity of internal reflection. This is expected as the absorption of the InGaN QWs is found to increase rapidly above 3.2 eV (136). The increase in noise level is due to the intensity drop of the white light spectrum at higher photon energies.

6.3 Initial optical studies on a single nanoLED

Spatially resolved time integrated micro-PL was performed on the sample by exciting into the InGaN bandgap with a continuous wave solid state laser emitting at 405 nm. The laser was focussed to a spot size of $0.8 \mu\text{m}^2$ using a $100\times$ 0.7 NA visible objective (Mitutoyo M Plan Apo). The entrance slit to the spectrograph was kept at $25 \mu\text{m}$ and the luminescence was dispersed by a 1200 l mm^{-1} grating. Confocal PL imaging was performed by undertaking a raster scan using the piezo controlled microscope objective.

Fig. 6.4 shows a far field microscope image of a single nanorod under emission at room temperature. A nanorod is targeted with a the laser spot, and reflected laser is filtered out by a dichroic mirror in addition to a sharp edge filter. The far-field image is in real colour and is captured by a commercial colour CCD camera. The directly excited

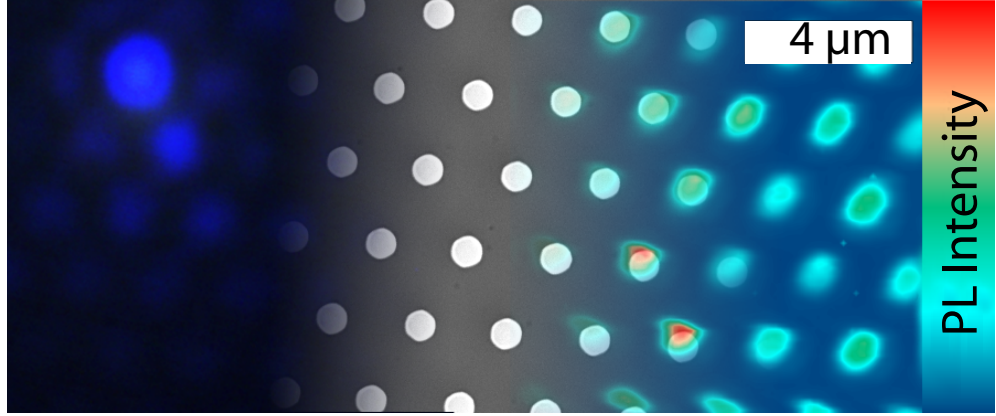


Figure 6.4: - Combined microscope images overlayed: *Left* Far-field PL image exciting a single nanorod and capturing the true colour image showing neighbouring nanorods excited due to scatter. *Centre* SEM image showing exact dimensions of the nanorods. *Right* Confocal microscope PL image made by raster scanning. Scale bar is shown in the corner

nanorod can be seen clearly as the brightest spot in the left of the figure. Adjacent nanorods can also be seen emitting weakly due to laser scatter. As a comparison between the the imaging methods, the far-field PL image is overlaid together with a scanning confocal image on top of the SEM. The right side of Fig. 6.4 shows a spatial map created by integrating the PL intensity from each step of a raster scan made on the sample in the confocal configuration. The PL is spatially filtered such that only luminescence from the confocal volume is collected by the CCD. It is clear from the image that there is negligible luminescence coming from the spacing between nanorods. The intensity contrast ratio between the nanorods and the surrounding space is up to 200:1.

There does however exist a certain degree a variation in intensity from rod to rod, albeit within a factor of 2 of each other. Fig. 6.5 shows a clearer PL intensity map with contours indicating intensity levels and a indication of the uniformity. A few nanorods

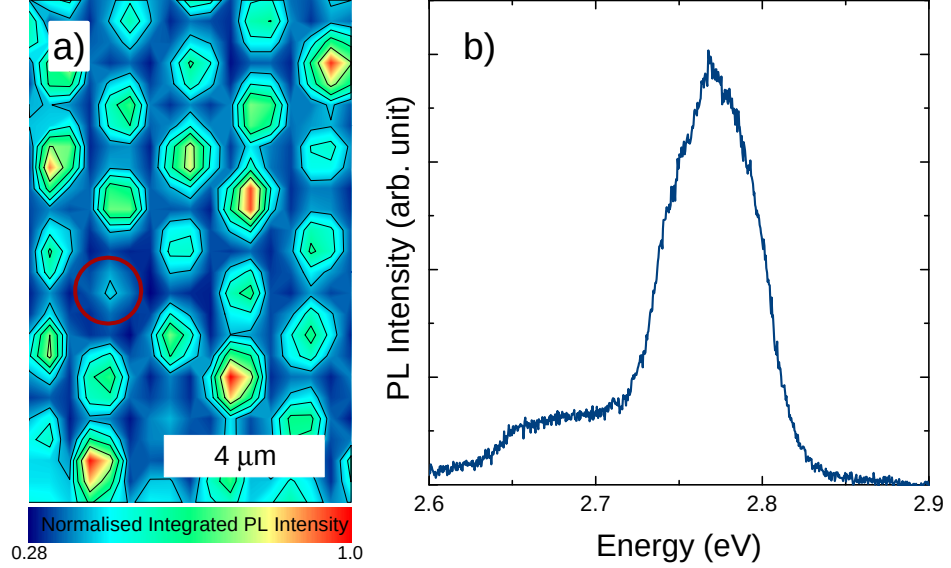


Figure 6.5: - a) $8 \times 12 \mu\text{m}$ PL map of the nanorod LED array. Normalised integrated intensity is indicated by the contours. b) PL spectrum of a single nanorod excited at 0.5 kW cm^{-2} at 4.2 K.

shown in Fig. 6.5 a) have degraded emission intensity (circled in the figure) due to previous laser irradiation damage when power reaches the MW cm^{-2} regime. A PL spectrum of a single nanorod at 4.2 K is shown in Fig. 6.5 b). It is excited at 0.5 kW cm^{-2} showing a shape similar to the nanorod PL presented in the previous chapter, centred at $\sim 2.76 \text{ eV}$. The PL emission energy, like the intensity, varies from rod to rod.

The room temperature PL spectrum from a single nanorod excited at 100 kW cm^{-2} is shown in Fig. 6.6. The emission is centred at $\sim 2.77 \text{ eV}$ broadened by a phonon replica towards the lower energy side of the main emission peak (130). The variation of peak energy between different rods forms a statistical mean of 2.81 eV and a rather large standard deviation of 22 meV . The spatially dependent spread in peak energy is

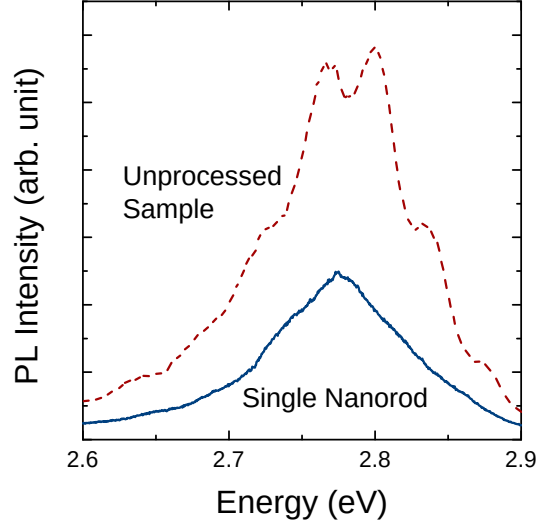


Figure 6.6: - Room Temperature PL spectrum of single nanorod (solid line) and of unprocessed sample (dashed line) excited at 100 kW cm^{-2}

much higher than that of the unprocessed control sample. The big spread in PL peak energies could be due to surface-irregularity related effects or effects which are related to the structure of the QW in the wafer. If the QW is uneven, etching small structures can cause an added degree of disorder as the single well is fragmented into quantum discs in the nanorods. The room temperature PL spectrum of the unprocessed sample from an equivalent wafer excited at the same laser power is also plotted in Fig. 6.6. The spectrum shows 4 to 5 peaks within the broad PL band which are identified as fringes due to optical resonator effects from the interfaces at the surface and substrate of the LED (137), these fringes are not present in the nanorod sample due to geometrical differences in light extraction. Reference (138) reports a detailed study of the modes associated with this type of nanorod array. The emission is centred at slightly higher energy than the nanorod; we suspect that this is mainly due to wafer variations as

6.3 Initial optical studies on a single nanoLED

discussed previously. The unprocessed sample exhibits a higher emission intensity than the single nanorod in Fig. 6.6. This arises since the emitting LED area under stimulation is smaller in the nanorod. Normalising the intensity with emission area for a rough comparison, i.e.,

$$\frac{\text{PL intensity of nanorod}}{\text{emission area of nanorod}} : \frac{\text{PL intensity of unprocessed sample}}{\text{collection spotsize of unprocessed sample}} \quad (6.1)$$

The ratio obtained is on average $\sim 2 \pm 1$ at an excitation power density of 100 kW cm^{-2} . Despite being a very rough estimate, this provides us with some additional information on the extent of actual damage on the nanorods from etching. Since the normalised intensity with emission area of the nanorod is higher than that of the unprocessed LED, we conclude that the damage caused by etching is not great. Light guiding effects together with increased recombination efficiency due to strain relaxation may also be contributing to the observed improvement in efficiency.

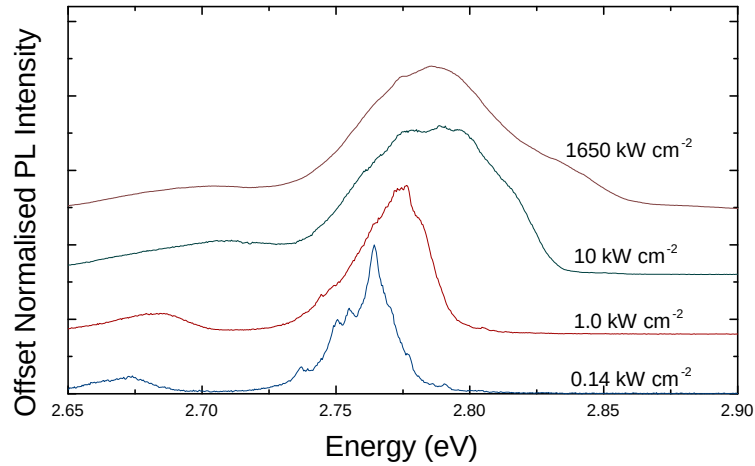


Figure 6.7: - Time integrated PL spectra taken from a single nanorod LED at 4.2 K under laser excitation powers of 0.1, 1, 10, and 1650 kW cm^{-2} .

On increasing the excitation power density at low temperatures (4.2 K), the PL

6.3 Initial optical studies on a single nanoLED

peak broadens asymmetrically with the majority of the carriers recombining at a higher energy. However there are major differences which occur pre- and post-etching. Fig. 6.7 shows a plot of the PL spectra of a single nanorod with increasing laser excitation power. The intensity of the spectra are normalised at each excitation power taken and the excitation power spans 4 orders of magnitude from 0.1 kW cm^{-2} to 1000 MW cm^{-2} . The power dependent PL can be separated roughly into three sections and subsequently explained by three effects that emerge from the observations similar to the investigations from the previous chapter ¹. At low excitation powers, the PL appears to be formed from multiple narrow peaks, which shows similarity to the peaks discovered and probed in section 5.5.1. At excitation power densities of 0.8 to 10 kW cm^{-2} , a smoother emission peak is formed and broadening to the high energy side occurs. This broadening is accompanied by a large increase in PL intensity and hence an apparent blue-shift is observed. On a normalised scale, the apparent shift can be seen as a high energy biased asymmetric broadening. The PL peak changes in shape drastically, and flattens out. This wide peak behaviour is found in section 5.4.2 on the prototype nanorod arrays, attributed to emission from the higher band gap at the side-walls, due to strain relaxation induced band tilt. Finally at excitation power densities of $> 10 \text{ kW cm}^{-2}$ the full width at half maximum (FWHM) linewidth of the emission stays at

¹The results presented in Fig. 6.7 and 6.8 are made by excitation using a CW laser. The excitation power density dependent PL emission is therefore different to that observed using pulsed sources. For pulsed excitation, after the sample is excited, carriers are generated in the sample and there is a dynamic decrease in carrier density as the carriers recombine before successive pulses arrive. The dynamical change is thus recorded and appears as a broadened peak integrated over a full range of internal field screening magnitudes in time-integrated PL (139). When CW excitation is employed, a constant carrier density can be maintained in the sample, meaning that the magnitude of the shielding of the internal field is kept constant in the QW through the time-integrated PL acquisition. The integrated peak will therefore appear narrower than using a pulsed laser.

6.3 Initial optical studies on a single nanoLED

~ 67 meV and does not increase further. This is more clear on a contour plot shown in Fig. 6.8 a), where the PL normalised PL spectra is plot on a contour map, combined using approximately 35 data sets.

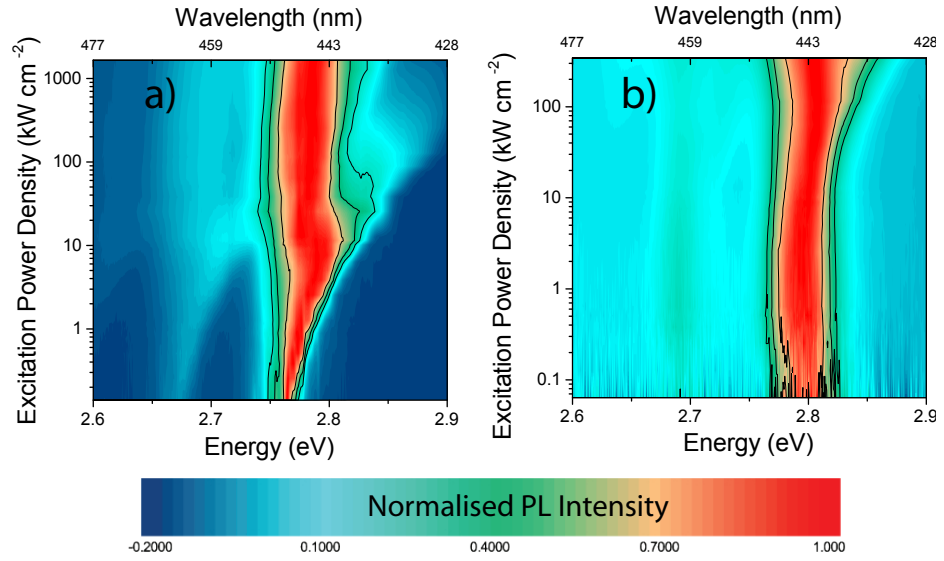


Figure 6.8: - Plot showing normalised PL spectral intensity with varying excitation power density from: a) a single nanorod and b) unprocessed control sample. Contour lines show $1/e$, 50% and 70% intensity levels.

The three stages of PL variation with excitation density in the nanorod shows a stark difference with that of the plain unprocessed sample shown in Fig. 6.8 b). The experimental parameters are the same for both samples in the figure. Emission energy is slightly higher in this sample due to the slight variations between wafers. For the unprocessed sample the following is observed: between 0 and 0.5 kW cm^{-2} excitation range, the quantum well emission spectrum smoothed out with increasing excitation power density due to an increase in signal to noise ratio. With increasing excitation power from 1 kW cm^{-2} to 100 kW cm^{-2} , there is a blue shift of approximately 20 meV

6.3 Initial optical studies on a single nanoLED

with an unchanged FWHM of ~ 50 meV, due to carrier screening of the QCSE under an increase in carrier density generated by CW laser excitation (140). This is followed by broadening accompanied by blue shift at excitation powers above 100 kW cm^{-2} , which can be attributed to filling of band tail states at high carrier densities (130).

In the single nanorods, the PL emission blue-shift and broadening saturates at 10 kW cm^{-2} , whereas in the unprocessed sample, the saturation does not occur in the excitation power range used. There are two possible reasons for the difference in saturation behaviour pre- and post-etching. For the unprocessed sample, full saturation cannot be fully achieved since for a Gaussian beam profile, areas on the edge of the excitation area are always partially screened. Whereas the reduction in size of the nanorod smaller than the size of the laser spot means the full active area is excited with a similar power, leading to difference in saturation behaviour (139). The side-walls on the nanorods relax the strain in the QW layer, which subsequently reduces the red-shifted emission due to band tilting (20, 116, 118, 141). Thus, the remaining QW layer which is strained or partially-strained is much smaller in comparison to the excited spot in the plane well. As a result, saturation to the blue-shift in emission energy will occur at much lower carrier densities, or in our case, laser excitation powers. This is also consistent with the observed change in spectral shape as excitation is increased from 1 kW cm^{-2} , where we see a drastic flattening to the tip of the emission peak.

6.4 Low excitation power studies

At low excitation powers, narrow spectral lines with a FWHM of less than 3 meV can be observed in the single nanorods. Fig. 6.9 shows a plot of 12 different nanorods at excitation power densities of below 0.1 kW cm^{-2} . There are an average of four such narrow lines per nanorod, giving a density of $\sim 5 \times 10^9 \text{ cm}^{-2}$. The behaviour of the forest of narrow peaks echoes closely the previously studied prototype samples in section 5.5.1. Recalling the previous chapter, various origins of the narrow peaks in the prototype nanorod arrays were proposed including: Individual quantum disc emission from the MQW in the nanorod array under the excitation spot, localisation due to variations in the QW thickness or indium content, as well as surface related effects were all suspected to be capable of causing the observed narrow peaks. Since multiple peaks are found at low excitation powers in a single nanrod with a single quantum well, it rules out that the narrow peaks reported in section 5.5.1 are individual QW emission from the MQW layers in the nanorod array. We also claim that both the narrow peaks discovered here and in the prototypes are alike, and arise from actual localisation effects within the quantum well in the nanorods.

As mentioned in section 5.5, these narrow lines resemble early studies on localised centres in InGa_N/Ga_N QWs by micro-PL (74). Previous observation of localised states from QWs was only possible by measuring the emission from a small area of the sample using holes in a metal mask generated by electron beam lithography and etching, creating apertures of a $1 \mu\text{m}$ to a few hundred nm in diameter (74). The unprocessed

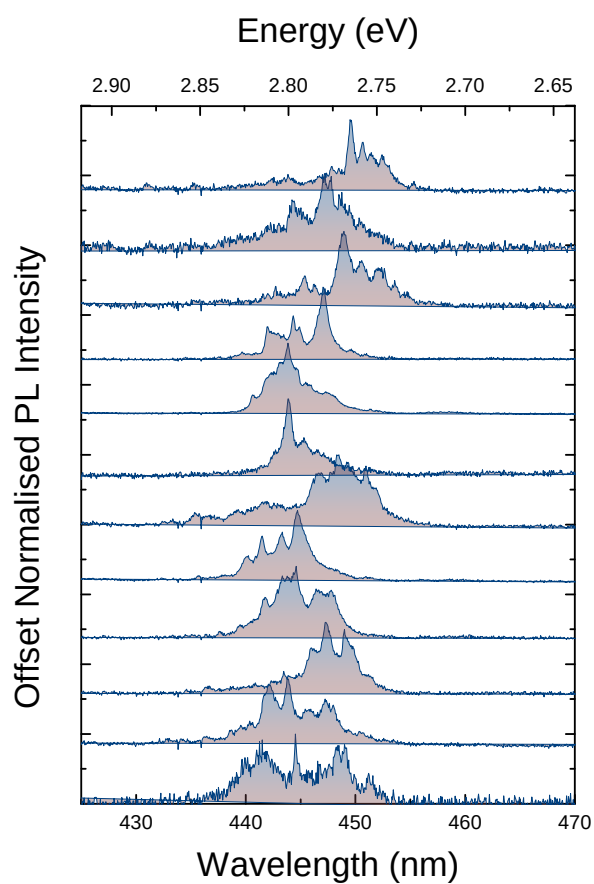


Figure 6.9: - Normalised PL spectra of 12 different nanorods at low excitation power densities. Excitation was carried out using a CW 405 nm laser

sample however does not exhibit any signs of these localised states with the low excitation powers under time-integrated micro-PL with a sub-micron excitation spot size.

6.5 Dynamics of single nanoLEDs

Time resolved PL studies were carried out on the single nanrods to further examine the effects of etching on SQW LEDs. A frequency doubled Ti:sapphire laser at 400 nm with 1ps pulses at a repetition rate of 2 MHz was used to excite into the InGaN bandgap. The optics used to carry out the time resolved PL is identical to that used in the previous section. Fig. 6.10 shows PL spectra from a single nanorod studied in

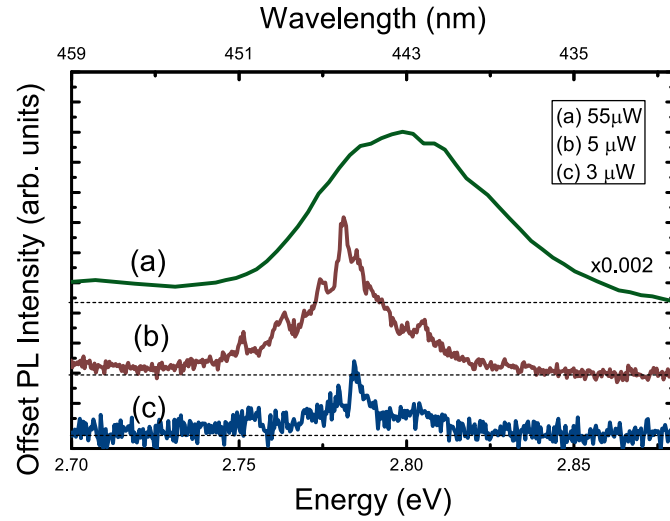


Figure 6.10: - TIPL spectra taken from a single nanorod LED at 4.2 K under a laser excitation power of (a) 55 μW , (b) 5 μW , and (c) 3 μW . A single sharp peak is seen in (c) at 2.785 eV.

this section excited at three different excitation powers with the pulsed laser showing familiar results to when the CW laser is used. No shift is seen in the spectral position of these sharp peaks with carrier density, showing similarity with InGaN quantum dot-like

emission (99). Traces from time-resolved PL studies of a single nanrod LED are shown in Fig. 6.11, where a comparison is made with emission from the unprocessed SQW wafer at 2.81 eV excited at the same high excitation power density. The TRPL decay traces of the InGaN QW are non-exponential for both samples; however, for rough quantification, we fit the curves using a bi-exponential decay for comparison purposes as used in reference (19):

$$I(t) = A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right) \quad (6.2)$$

The initial fast decay (labelled τ_1) is similar for both samples, with the single nanorod

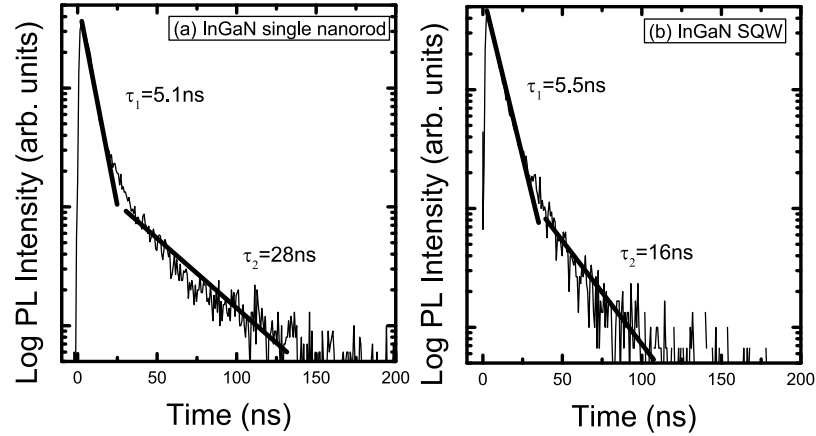


Figure 6.11: - Decay dynamics at 4.2 K of (a) a single nanorod LED and (b) a planar single quantum well LED both taken at emission photon energy of 2.81 eV

having a slightly shorter lifetime than the unprocessed SQW. This decay time encompasses the majority of the carriers recombining. However, for the long time portion of the decay, τ_2 , the single nanorod is consistently much longer lived than the unprocessed sample. In fact, we can see that τ_2 is an underestimate of the lifetime in the single nanorod, as the fitting is far from being ideal. The non-exponential decay is indica-

tive of the dynamic nature of the PL emission. The QCSE leads to reduced carrier wavefunction overlap, resulting in an increased lifetime and a redshift in the transition energies in InGaN QW epilayers (33)(142)(65). For pulsed laser excitation, the initial carrier density in the QW screens the QCSE leading to a blue shift in the emission. As excited carriers recombine, the screening effect decreases. This effect can be directly observed by combining the TCSPC decays taken at different photon energies. The dynamic picture of the emission spectrum of the single nanorod LED evolving with time is built using this method with a spectral resolution of ~ 0.5 nm (3meV) and a temporal resolution of 0.25 ns. Fig. 6.12 i) shows the time evolution of the PL spectrum of the single nanorod excited at a laser power of $55 \mu\text{W}$. The TRPL is performed on the same nanorod as with the TIPL spectra shown in Fig. 6.10, and the figure is normalised at each time interval to make apparent the spectral evolution. During the initial few ns, the majority of the carriers recombine at energies centred around 2.84eV, partially due to screening of the QCSE, and also due to excitation into higher energy localisation states. It can be clearly seen that as photocarriers recombine and decrease in population, a gradual red-shift in emission occurs. This effect can largely be due to the decrease in the screening effect and hence an increase in the magnitude of the QCSE induced band tilt with time. PL emission stays centred at 2.78 eV at 50 ns after the excitation, whence the spectrum evolves from a smooth Gaussian-like shape to reveal sharp features at times over 100 ns after excitation as the carrier density decreases further. At 200 ns, we find sharp features in the PL spectra at ~ 2.78 eV as shown in the foremost spectrum in Fig. 6.12i). The time-resolved PL from 50 ns to 200 ns

period taken at the PL emission energy of 2.78 eV is shown in Fig. 6.12ii). During this period, the decay of the unprocessed SQW wafer can be approximated by a single exponential with a straight line fit on the log-plot. The single nanorod on the other hand experiences a change in decay time at 100ns as indicated by the two straight lines in Fig. 6.12; coinciding with the formaion of the sharp peaks in Fig 6.12i).

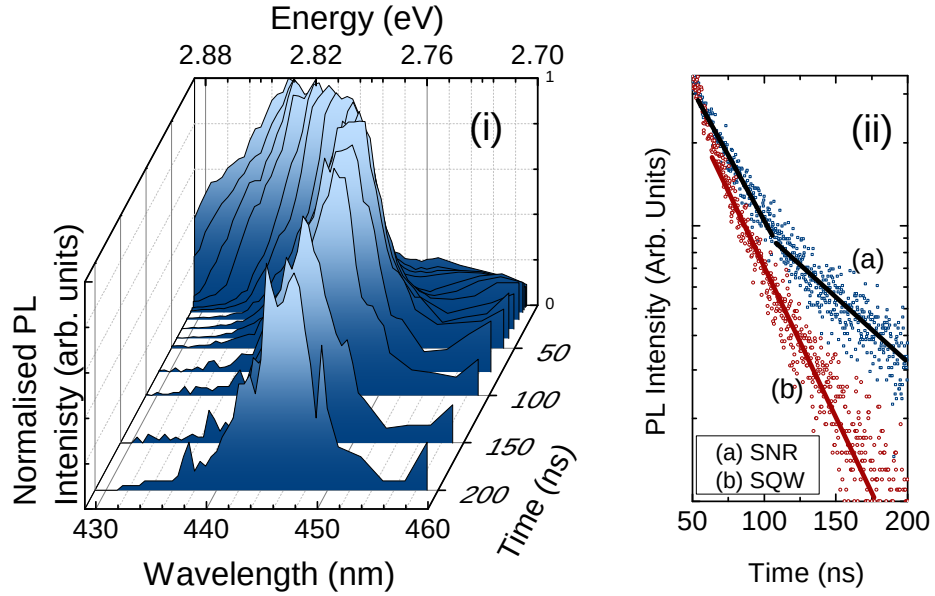


Figure 6.12: - i) Evolution of PL spectra with time at 4.2 K from a single nanorod LED under $55 \mu\text{W}$ excitation power showing a dynamic shift with time. ii) A decay trace showing a dynamic time-resolved PL at 2.78 eV from (a) a single nanorod and (b) a single QW unprocessed LED wafer, between 50 and 200 ns after excitation laser pulse

Fig. 6.13 shows a comparison of the low excitation power time-integrated PL spectrum with the time-resolved PL spectrum of a single nanorod at 230 ns after the excitation pulse. When superimposed upon the low excitation time-integrated PL spectrum, the peaks are aligned with surprisingly high accuracy confirming that the sharp peaks found in the time-integrated are the same peaks as those seen in the time-resolved spec-

trum at time segments above 100 ns. Hence, the sharp peaks in the time-integrated PL in Fig. 6.10 are long lived, and it is thus reasonable to believe that it is such features which cause the decay dynamics in the single nanrod to have a longer lived tail than that seen in the unprocessed SQW sample. At very low carrier densities, carriers recombine with long lifetimes in non-degenerate states that are populated preferentially. As carrier density increases, they *spill* into the SQW layer to recombine and the typical QW spectral peak emerges and starts to dominate the emission spectrum.

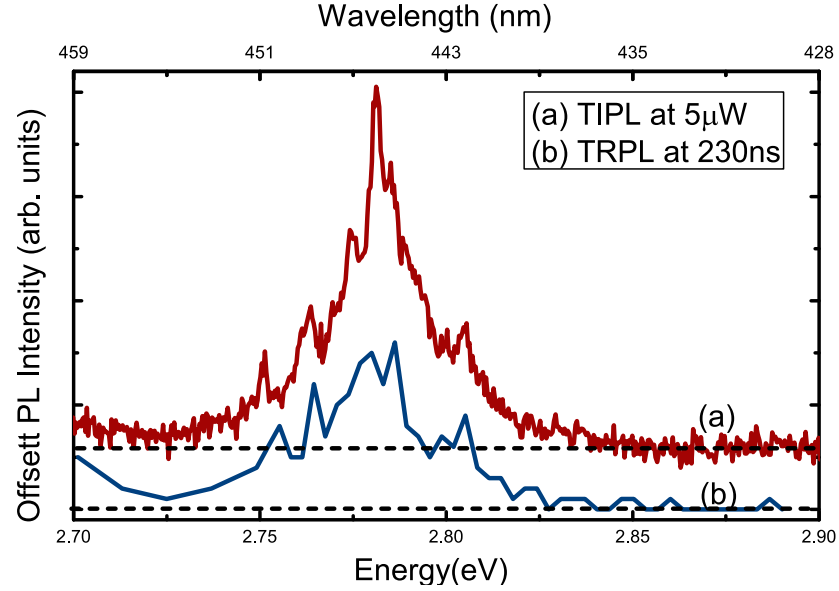


Figure 6.13: - Comparison of (a) the time-integrated PL spectrum of a single nanorod LED at low excitation power density and (b) the time-resolved PL spectrum of the same nanorod 230 ns after excitation, taken at 4.2 K.

The origins of sharp peaks in the PL spectrum of InGaN QWs have been well studied and often attributed to indium localisation (74) (143) (137). However, indium fluctuations or QW thickness variations in the InGaN epilayer are intrinsic to the growth of the LED wafer and therefore, we can assume the unprocessed SQW wafer

has similar fluctuations in potential in the quantum well to the nanorods. For a $1\ \mu\text{m}$ illumination and collection spot size, there appears to be no indication in the time-resolved or time-integrated PL spectra of the SQW of sharp peaks. This is evidence that the occurrences of such sharp long lived states observed in the single nanorod are mainly due to surface effects after sample processing.

Depending upon the position of the Fermi level and the charge neutrality level on the nanorod, the filling of surface states will lead to a charge depletion region close to the surface. This results in conduction and valence bands bending higher or lower into the semiconductor. Electrons or holes are, therefore, localised close to surface, with the recombining counterparts localised near the centre of the rod due to this band bending (125)(127). Slight variations of surface smoothness may cause fluctuations in the potential around the perimeter of the nanorod. Combined with the preferential distribution of carriers near the surface, localisation sites may therefore form at the side walls of the nanorod. These carriers trapped close to the surface can recombine with carriers localised in the centre of the nanorod at low carrier densities. With such a mechanism, there will be a large spatial separation between the recombining carriers, leading to very long lifetimes associated with this transition. Evidence of gaps forming in InGaN QW layers causing fragments of QW dispersed laterally has been a suggested cause for localisation. In addition, fluctuations in well thickness on the nanometre scale will also give rise to added disorder (12). Etching can cause further fragmenting of these QWs, producing a smaller average size of these fragments of QW across the sample.

These effects will also give rise to a similar PL spectrum, and it is possible that the observations are a combination of these. However, the majority of the lifetimes observed in these localised states are much higher than expected for indium rich clusters emitting at 450 nm (81). Comparison of the time-resolved data with that from the equivalent LED wafer shows that the PL lifetime in the quantum well of the unprocessed sample is much shorter than that measured for the nanorod, which is a further indication that the extended lifetimes arise from surface effects as discussed, related to the side-walls and possible surface roughness in the nanorods.

6.6 Final remarks

Concluding this chapter, we have extensively studied the optical properties of a single nanorod fabricated employing a mass production method from the top down. The results reveal that there could be surface trapping at low carrier densities, reducing the spatial overlap of recombining carriers at low temperatures. These features however disappear with increasing carrier density. The observation of highly localised states in InGaN QWs have been well reported over the last 15 years, and it has long been established that it is these localisations that give the blue LED its brilliance despite the high dislocation densities. Surface localisation in nano-LEDs has seldom been reported, though it has been recognised and discussed in literature briefly (120, 127). Reports of sharp peaks in single nanorod QW LEDs have been made before by Kawakami *et al.* (19), owing to the cross-sectional observation configuration in PL gathering, and not to extra localised states. It is uncertain whether or not that under high power and

room temperature operational regimes (such as in commercial lighting applications) that such localisation of carriers close to the surface will have much effect on light output. The surface roughness of mass produced nanorods by etching techniques may therefore not be too important a factor in room temperature lighting applications.

6.6.1 Future work and ideas

From an LED application perspective, the the results reported here may not ultimately be of much impact. However these results can cause severe difficulties in nanorod structures used for *site-controlled* quantum dot systems. Development of etched or ion-milled InGaN quantum dot wafers are of on-going interest especially in creating nanorods for light confinement and site-control for single photon sources. In these systems, typically small excitation powers are used to excite individual quantum dots. The large modifications to the optical properties of an etched InGaN QW leading to a quantum dot-like spectrum could potentially be parasitical in system such as ones prepared in references (144, 145).

Further work has been initiated to investigate if there exist any correlations between the density of narrow lines to size of nanorods. Larger nanorods have been designed and plans for the etch masks are to be made using electron beam lithography to investigate any carrier lifetime difference in the centre and near the edge of the rods. There are a variety of interesting experiments that can be carried out if a single nanorod can be contacted, including reverse bias measurements to measure the internal electric field and also EL experiments.

Semi-polar nano-LED

The internal piezo-electric field in GaN based light emitting devices is widely regarded as a detrimental effect especially to InGaN/GaN based LEDs emitting close to the green region of the spectrum. Controlling this material property is a key to achieving ultra bright, high efficiency devices. Almost all commercially available LEDs are grown on *c*-plane sapphire, and InGaN-based LEDs are constructed along the Ga-polar (0001) direction. InGaN heterostructures in this growth direction are susceptible to strong internal electric fields induced by spontaneous and piezoelectric polarisation. It has been demonstrated that the reduction of such an internal electric field by using non-polar and semi-polar material can lead to a reduced efficiency droop (146, 147). Furthermore, an improved efficiency of extended photon emission energy into the green band has also been reported (148, 149, 150). The limited availability of GaN substrates has been a major setback to the commercial realisation of non-polar and semi-polar devices and much research has been conducted in growth on foreign substrates. A scheme discussed

in this chapter is selected area growth (SAG) of semi-polar nano-pyramid devices by epitaxial layer overgrowth (ELOG) seeded from apertures in a mask made on conventional *c*-plane sapphire. This technique is capable of producing semi-polar LEDs with mass production techniques on readily available substrates. Dislocations are thought to be suppressed since the growth of the pyramids is only “seeded” from individual small areas of the *c*-plane GaN surface. There is also an additional advantage of active surface area increase due to the pyramidal geometry.

GaN nanopyramids were grown by MOVPE on a 100 nm thick SiO₂ SAG template deposited on a GaN layer on a *c*-plane sapphire substrate. Patterns in the SAG template were prepared using nanoimprint lithography and CHF₃ plasma etching (151). Apertures were made in an organised hexagonal array on the SiO₂, approximately 300 nm in diameter and separated by 450 nm. The difference in the growth rates of the {10 $\bar{1}$ 1} planes as compared to the {1000} leads to self-assembly behaviour. A reactor temperature of 1100 °C and a pressure of 200 mTorr was used in the growth of our n-GaN nanopyramids. Previous studies show that the sizes of the pyramids are determined entirely by aperture sizes of the SAG masks and are independent of pitch, or even symmetry of the aperture array (152). Reactor conditions were altered before merging of adjacent pyramids and a single InGaN QW layer is grown on the facets at a temperature of 825 °C, followed by growth of an Mg:GaN capping layer at 1070 °C and 100 mTorr. Scanning electron microscopy was used to study the morphology of the samples, and high spatial resolution cathodoluminescence and micro photoluminescence were employed to investigate the emission properties.

7.0.2 Surface morphology

SEM images of the nano-pyramids are shown in Fig. 7.1 and Fig. 7.2 The fig-

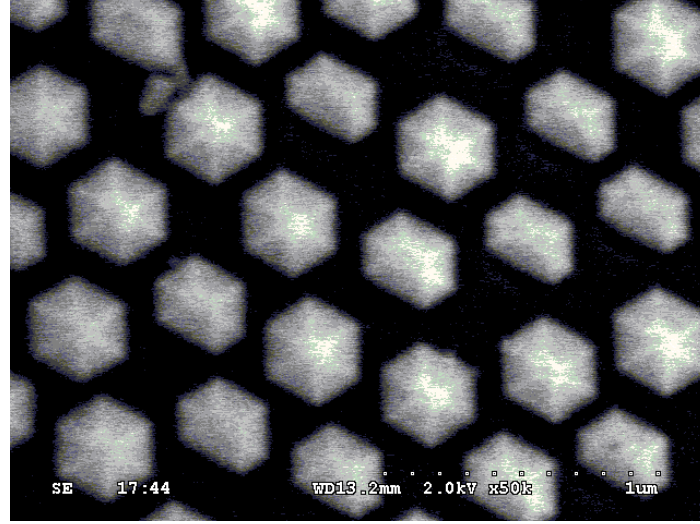


Figure 7.1: - Top down SEM image showing nano-pyramids with hexagonal symmetry amongst a number of asymmetric elongated pyramids

ures clearly show that there is still room for improvement in the uniformity of the nano-pyramids sizes. The spatial separation is however very uniform, showing good nanoimprint masking. The diameters of the hexagonal nano-pyramids are approximately 350 nm and are consistent throughout the sample. The density of the nano-pyramids is roughly $2 \times 10^9 \text{ cm}^{-2}$, implying that $\sim 50\%$ of the area of the sample is unused. The facets were grown making an angle of $\sim 62^\circ$ to the sample surface giving heights of around 310 nm. Therefore, the active layer area is approximately 9% larger than the surface area of the sample. With further tailoring by reducing the spacing between nano-pyramids, active area can be further increased. Growth of the nano-

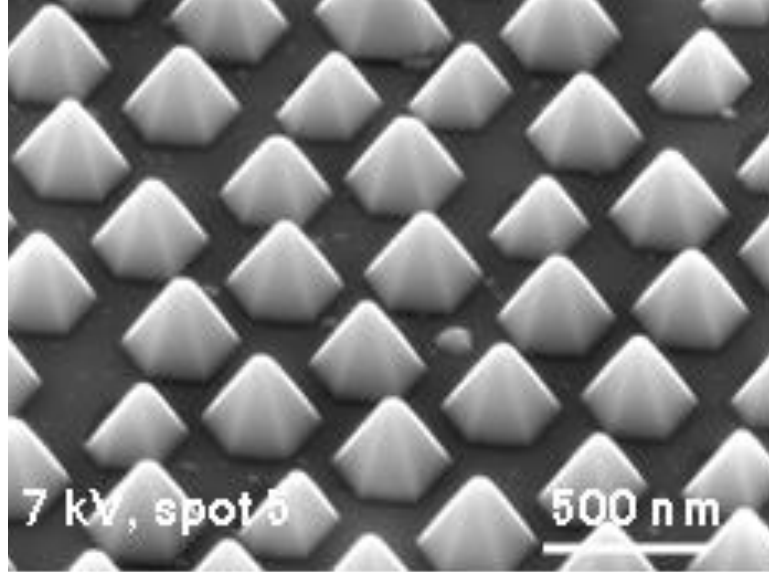


Figure 7.2: - SEM image taken at an angle from the surface, showing aspect ratio of the nano-pyramids and surface profile (image taken at University of Bath by P. Shields)

pyramids relied on ELOG employed on the apertures made from SiO_2 . Residual SiO_2 on the GaN surface within the apertures in the growth mask disrupts the growth of the pyramids. This can lead to the elongated pyramids seen in Fig. 7.2.

7.1 Photoluminescence

Micro-PL studies were conducted on the sample with a frequency doubled, pulsed picosecond Ti:Sapphire laser excitation source. Carriers are excited directly into the InGaN, avoiding emission from p-GaN impurities. A $100\times$ objective was used, giving a spot size which covers approximately 5 to 10 nano-pyramids. Fig. 7.3 insert shows the PL spectrum of the nano-pyramids with varying excitation power densities from 0.1 kW cm^{-2} to $\sim 100 \text{ kW cm}^{-2}$. The shape of the PL spectrum remains the same with increasing power. Fitting Gaussians to the spectra, a slight blue shift of the peak of

4.5 meV can be seen. This is comparable to other studies carried out on semi-polar InGaN QWs where around a $10 \mu\text{eV}$ shift at roughly similar emission wavelengths is found (153, 154). This shift is also accompanied by a slight broadening and is widely accepted to be caused by carrier screening of QCSE.

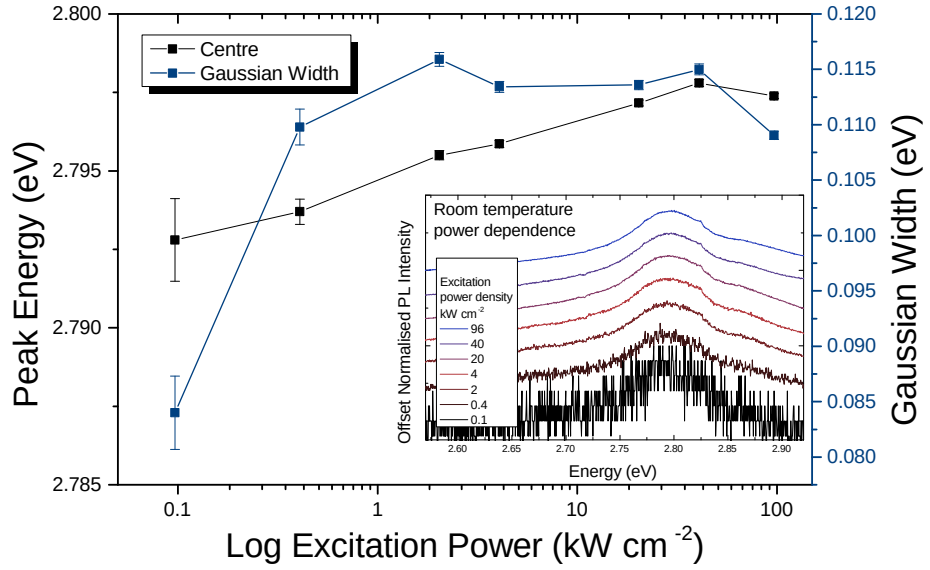


Figure 7.3: - Room temperature peak energy shift and variation of Gaussian width with different excitation power densities. Inset shows PL spectra series of normalised PL intensity for varying excitation powers

The evolution of the PL emission with varying excitation power density at 4.2 K, shown in Fig. 7.4, behaves very differently to that at room temperature. Although the population of carriers is largely recombining at higher energies as the density increases, the evolution does not preserve the shape of the spectrum. The spectrum is not a single gaussian-like curve, but has multiple shoulders, indicative of a possible inhomogeneous QW structure. A broadening towards the high energy side of the peak is found on increase of excitation power density. This broadening is accompanied by a change in the spectral shape at 0.13 kW cm^{-2} excitation power, a broad peak is seen ranging from

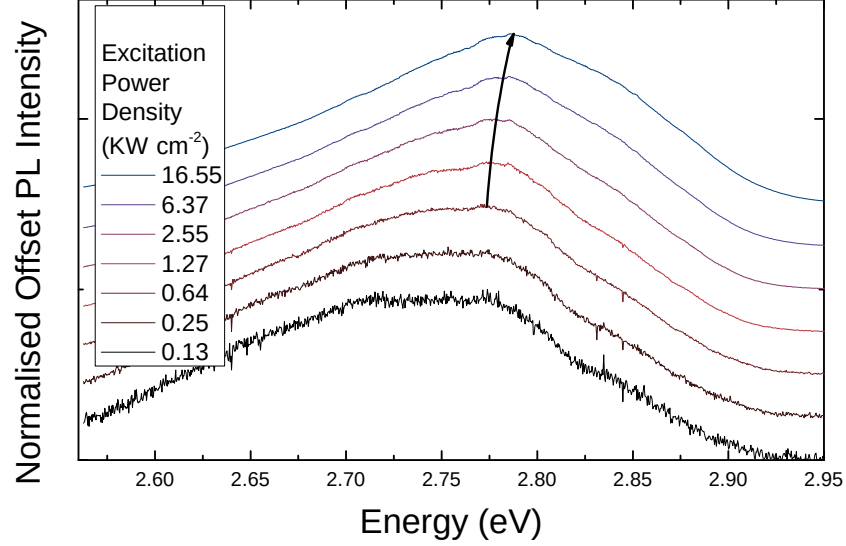


Figure 7.4: - 4.2 K PL spectra series of normalised PL intensity with different excitation power densities. At low excitation a broad flat peak is seen between 2.70 eV and 2.78 eV. An arrow shows the emergence of a dominant peak at 2.79 eV which undergoes a 10 meV blue shift when excited with high laser powers.

2.78 eV to 2.7 eV. On increasing excitation power, a peak emerges at 2.79 eV dominating the spectrum.

7.2 High spatial resolution studies

Since the pyramid spacing is much smaller than the laser excitation spot size in micro-PL experiments, CL can provide much more information revealing details regarding the emission homogeneity down the facets of the QWs. Room temperature CL measurements were carried out by K. J. Lethy at the University of Strathclyde on behalf of our collaborators at the University of Bath. The nano-pyramid samples were characterised using this technique in order to investigate the emission properties with very high spatial resolution.

Electrons are used to excite the sample in an electron microscope through impact ionisation. These energetic incoming electrons collide with the sample, creating electron-hole pairs as the electrons in the lattice are promoted to the valence band. The recombination of the generated carriers leads to photon emission which then can be collected and detected to analyse the optical properties.

Lethy *et al.* studied a sample with the same growth conditions as that studied in this chapter (sample name 2335), reported in Ref. (155). An emission peak centred around 2.8 eV is identified as the InGa_N peak from the QW layer. High resolution hyperspectral CL mapping was carried out, and a blueshift in QW emission peak energy from the base to the tip of the nanopylramids was reported (155). The emission from the PL studies summarised in the previous section corresponds to the quantum well emission on the facets of the nano-pylramids. The variation of emission energy down the facet of the pyramid indicates that either the QW may be tapering or that there is a variation of In_N fraction close to the tip of the pyramid. Both these effects will lead to higher photon energies being emitted. Previously published data on similar nano-pylramids grown with lower indium content and with the absence of doping suggest that the latter explanation is more viable due to the absence of QW emission from the nano-pylramid tip, and that the high number density and small size of the nano-pylramids will limit the the QW width variation (156).

7.3 The quantum well potential

Inhomogeneity of the QW emission along the facet of the nanopyramid cannot be resolved by micro-PL. The integrated effect however may be the cause of the non-Gaussian distribution of photon energy. On top of this unusual QW emission, we can comfortably deduce that the small blue shift seen by varying excitation power density at room temperature is due to a strongly suppressed piezo-electric field across the QW. At low temperatures, impurities and non-radiative recombination pathways are largely frozen out and carriers recombine largely radiatively, with photon energies centred around the InGaN QW bandgap. The blue-shift at low temperatures with increased excitation power density is caused by a combination of field screening and filling of localised states. From the CL analysis, a spatial distribution of indium is evident, with higher indium content close to the base of the pyramid. Combining these three effects, we have

1. A band tilt due to the quantum confined Stark effect across the entire QW layer
2. Localised energy states due to potential fluctuations in the QW layer
3. A trending decrease in potential down along the QW, from an average photon energy of 2.8 eV close to the tip to 2.6 eV near the base

A diagram of the proposed picture of this potential is shown in Fig. 7.5 c) The potential is sketched parallel to the facet from the base up to the tip of the nano-pyramid, and perpendicular to the facet across the QW layer at some arbitrary point. An increasing trend in the average recombination energy with position away from the base is

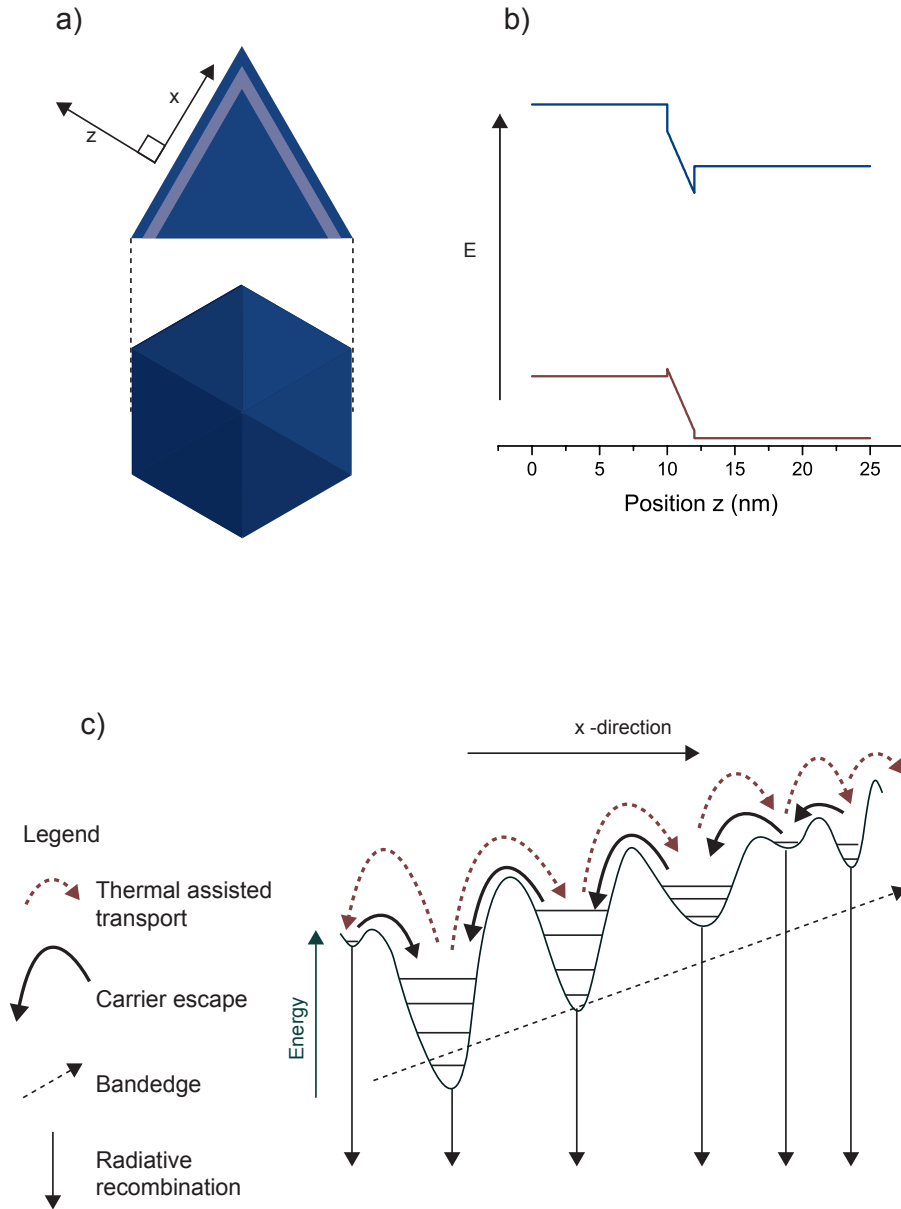


Figure 7.5: - Diagram showing the different effects on the potential of the QW. a) Schematic of a nano-pyramid showing directions in which the potentials are plotted against. b) Band diagram along the z -axis (perpendicular to the facet) across the QW. c) Diagram of proposed potential along the x -axis (facet) of the nano-pyramid.

shown overlayed by a potential fluctuation. Deeper, lower energy centres are associated with higher indium concentration. A high density of such localised states are located closer to the base of the nano-pyramid. Carriers captured by the shallower states with lower barriers will emit radiatively at higher energies but also escape over the barriers into neighbouring states with lower energies. An increase in sample temperature will enable carriers to overcome higher barriers and a larger proportion of carriers can now recombine at these these higher energy states. Such phenomena are typical of strong localisation in an InGaN QW often described by the S-shaped curve of emission peak energy with variation of temperature (80). On top of these potential fluctuation effects, there is the piezoelectric field acting perpendicular to the QW leading to the QCSE. A net piezoelectric field nonetheless will still exist in InGaN QWs despite being grown on semi-polar planes. This has an effect of separating the electron and hole wave functions perpendicular to the direction of the field by tilting the bands shown in Fig. 7.5 c). The band tilting takes effect along the nano-pyramid facet. The QW emission is thus red-shifted. This can be thought of as shifting Fig. 7.5 c) vertically in energy.

The dependence of emission spectrum with variation of excitation power in Fig. 7.4 can be explained by looking at the picture described by Fig. 7.5. At low excitations, carriers recombine in the localised states; the energy of these states are spread between 2.70 to 2.78 eV. As more and more carriers are generated the low energy states are filled, and there is an increasing likelihood that the carriers would recombine at the high emission energy tip of the pyramids which were identified by CL. We speculate that the high energy shoulder which becomes more prominent at high excitation power

is due to emission from the tip of the pyramid. There is also a slight $10\text{ }\mu\text{eV}$ shift of this peak with further increase in excitation power indicated by the arrow in Fig 7.4, which can be explained by carrier screening reducing the QCSE in the QW.

7.4 Time evolution of photo emission

Time resolved micro-photoluminescence was performed on the nano-pyramids to investigate their carrier dynamics. Fig 7.6 shows the decay traces taken at different photon energies accumulated for the same amount of time and excited with 16 kWcm^{-2} laser power density.

The decays are clearly not mono-exponential but can in general be fitted with a three part decay. There is clearly an initial fast component in the order of a few-hundred picoseconds followed by a second decay component of approximately 2 ns. Finally a long lived tail persists which is especially dominant close to the peak emission energy of the TIPL. Decay rates at lower photon energies are also longer. On lowering the excitation power density to 0.6 kWcm^{-2} , the decay trace still consists of three parts, but the decay constants in the fitting are comparably larger. The recombination rate is slower overall compared to that of the equivalent peak of the TIPL spectrum excited at a higher excitation power of 16 kWcm^{-2} . This decay behaviour deviates from a stretched exponential fitting (59, 157, 158) or a bi-exponential fitting (30, 32) which have both been used to fit the decay traces of InGaN QWs. The majority of the PL intensity is emitted within the first few ns, and the time constant associated with the first two decay fittings is much less than that of conventional *c*-plane QWs at similar

7.4 Time evolution of photo emission

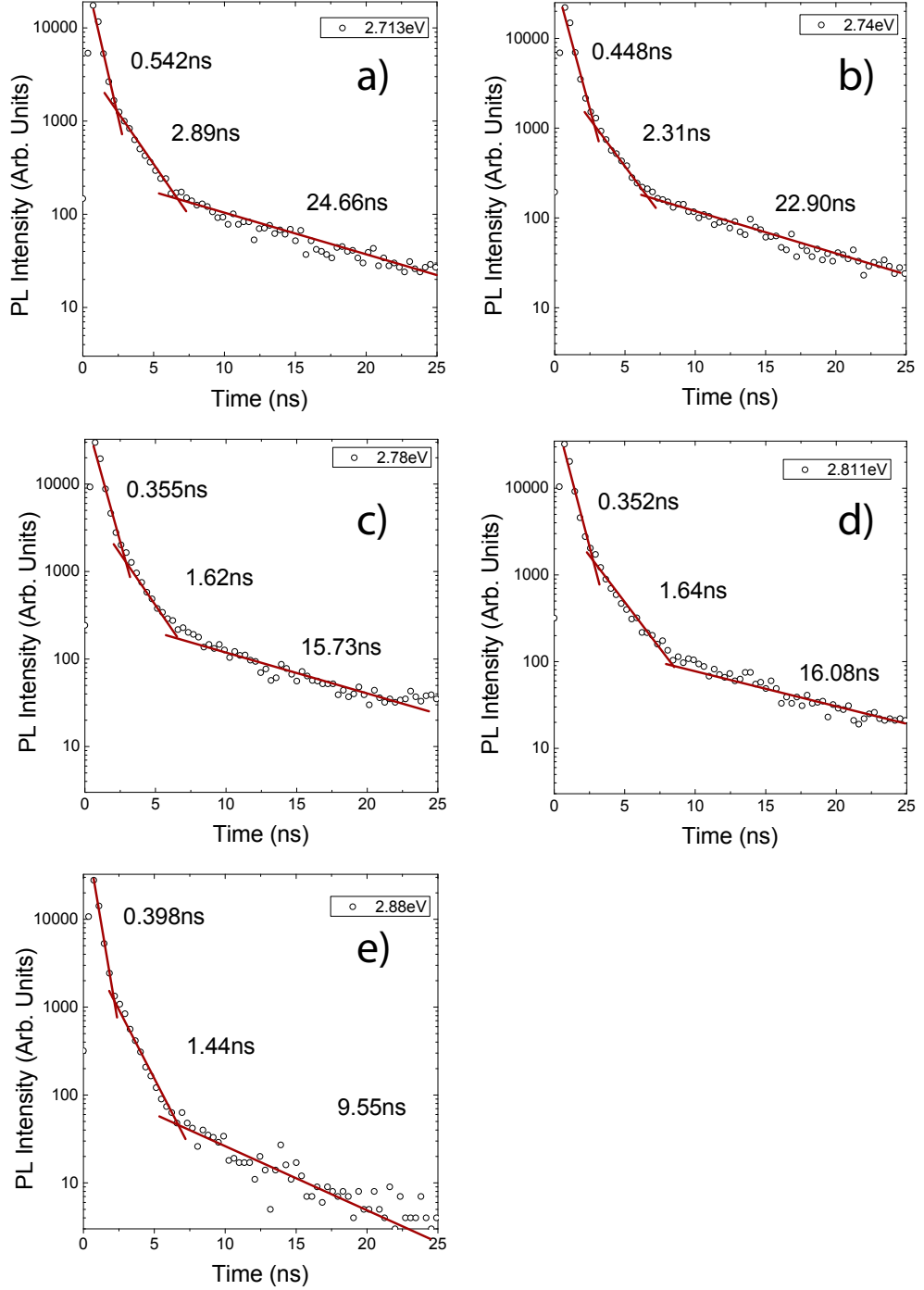


Figure 7.6: - a-e) decay traces of PL at different photon energies taken at 4.2K with an excitation power density of 16 kWcm^{-2} . Increasing photon energy shows a corresponding decrease in decay constant

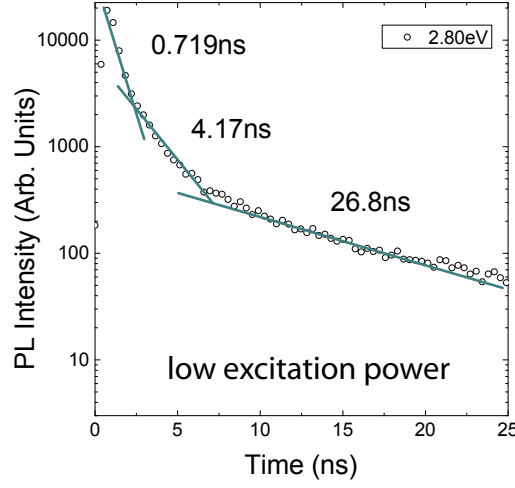


Figure 7.7: - Decay trace of PL at photon energy of peak spectral intensity (2.799 eV) with a low excitation power density of 0.6 kWcm^{-2}

wavelengths (69, 159). A lifetime reduction is indicative of an increase in oscillator strength and carrier wavefunction spatial overlap, as should be expected with QWs grown on semi-polar planes. The piezoelectric field in this case is however not fully diminished and this is demonstrated by the overall increase in carrier lifetime with the decrease of excitation power. Reduction of excitation power decreases the carrier density generated in the sample and in turn decreasing the carrier screening effect of the piezoelectric field increasing the carrier lifetime. The three part decay can be explained by considering the potential across the facet of the pyramid in Fig. 7.5. The initial fast part of the decay is due to the carrier escape from localisation at high energies. The two slower parts of the decay are the usual elongated exponential behaviour of InGa_N QWs which describe localisation and also carrier field screening (68, 160). The carrier field screening lifts the entire band such that all the localised recombination process is shifted to a higher energy. As carriers relax, screening has less of an effect

and the carriers relax in the long lived states red-shifted from the initial few ns. In Fig. 7.6, an decrease in measured decay rate in the fast part of the TRPL trace is seen with decreasing photon energy measured. This can be explained by a state filling and carrier escape mechanism. The fast part of the decay time measured is the combination of radiative recombination lifetime, carrier escape time, and carrier transport time from higher energy states as indicated in Fig 7.5. Carriers from high energy states escape over shallow barriers into deeper localisation states. As a result, lower energy states are fed more carriers than the higher energy states. Therefore, an increase is measured in the lifetime of the fast part of the decay. As for slow part of the decay, lower energy states have a stronger local piezoelectric field and thus a longer recombination time. Hence, a gradual increase in the lifetime of the extended slow part of decay is measured at lower emission energies. The full PL spectrum can be resolved in time by taking TCSPC traces at constant intervals in energy and subsequently recombining the data to extract the spectrum at particular times after excitation. Fig. 7.8 b) shows a series of spectra at different delay times after excitation with an excitation power density of 0.6 kWcm^{-2} . Fig. 7.8 c) is the same time series at the same position but excited by a higher power density of 16 kWcm^{-2} . The TIPL of the two excitation powers is shown in 7.8 a) for reference. Examining the low excitation power case, in the initial spectrum taken at 360ps after excitation, there is a clear non-symmetrical shape indicating a complex recombination. A particular shoulder is seen to the high energy side of the spectrum at 2.88 eV with a spectral peak at $\sim 2.80 \text{ eV}$. At $\sim 2 \text{ ns}$ delay, the high energy shoulder has disappeared with its peak situated at $\sim 2.80 \text{ eV}$. There is still a long tail towards

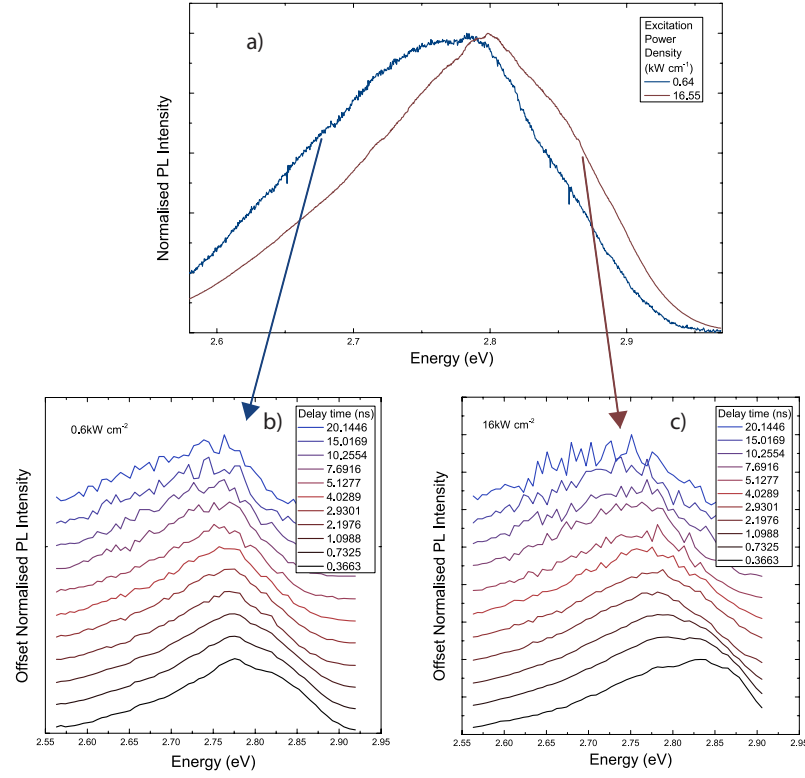


Figure 7.8: - a) Normalised time integrated 4.2K PL spectrum of the nanopyrramids excited at 16 kWcm⁻² (in red) and 0.6 kWcm⁻² (in black). b) Time resolved PL spectral series excited at 0.6 kWcm⁻². c) Time resolved PL spectral series excited at 16 kWcm⁻², showing a large shift in energy in the first nanosecond

the lower energy side of the peak. The peak energy gradually shifts to ~ 2.7 eV as the delay time exceeds 10 ns.

The shoulder in the initial few hundred ps after excitation originates from recombination of high energy states. Carriers at these energies relax by photo emission and transportation to lower energy states. These fast processes are assisted by carrier screening of the built in piezoelectric field, which also shifts the recombination to higher energies. After the first couple of ns, the carriers recombine with a largely unchanged spectral shape typical to QWs. From 2 ns to 10 ns, the red-shift of peak energy with increasing decay time is due a decrease in carrier density which gradually decreases the screening effect. Carrier separation increases and recombination occurs with the tilted band edges due to the QCSE.

At higher excitation powers the difference in the time evolution spectra is significant only in the initial nanosecond. At 360 ps delay time after excitation, the spectrum is now blue shifted to a peak at around 2.85 eV, with asymmetric tails elongating towards the low energy side. At 730 ps, a very broad peak is seen and at 2 ns and onwards the spectrum is the same as in the low excitation power density case in Fig. 7.8b). One other observation is that the slope of the low energy side of the peak at almost any given time in Fig. 7.8 b) and c) remains close to constant. This indicates that the recombination processes in the low energy states all undergo a similar change with increasing time. The carrier field screening of the QCSE for the low energy states manifests itself as a lateral red-shift with the increase in time, apparent in Fig. 7.8 c) which can be interpreted as a dynamic tilting of the band gap. This is consistent

7.4 Time evolution of photo emission

with the model in Fig. 7.5, where we suggest that the QCSE lowers the emission energy across the whole PL spectrum. The slope of the high energy side of the PL spectrum changes, unlike the low energy side. This is because the filled high energy band tail states are recombining very rapidly, producing the high energy photons as mentioned in experiments conducted by Eliseev *et al.* (80, 160, 161). As time lapses after the excitation pulse, the high energy states recombine the fastest and are no longer populated after a few ns. Hence the spectral shape on the high energy side of the spectra in Fig. 7.8 c) changes.

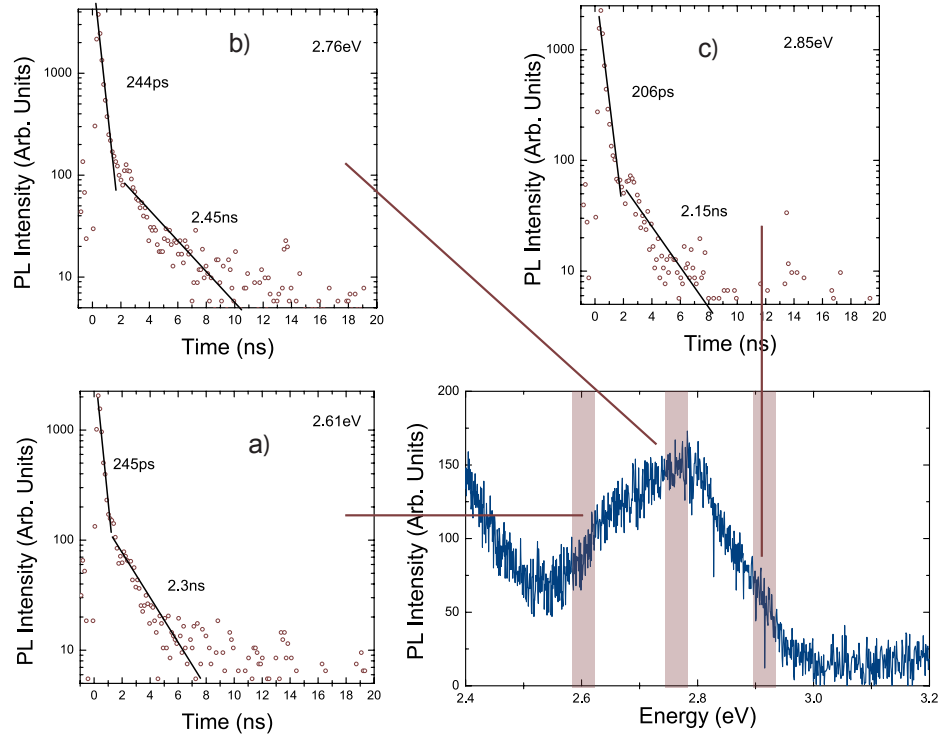


Figure 7.9: - Room temperature time resolved PL traces integrated at different parts of the spectrum fitted with bi-exponentials at: a) 2.61eV b) 2.76eV c) 2.85eV. The corresponding part of the TIPL spectrum is shown in the insert below

At room temperature, the decay rates are much shorter and of similar value across

the PL spectrum. Three decay traces at different parts of the spectrum excited with 1 kWcm^{-2} laser power density is shown in Fig. 7.9. There are three significant differences of the decay traces at room temperature. A bi-exponential fit is now employed, since the three-part decay used previously is over-parametrising as the decay reaches close to noise level by 10 ns. The initial fast recombining part of the TRPL traces have been reduced further close to the resolution limit of the detector. It is still evident that there is an increase in the decay rate for a decrease in measured photon energy. The lifetime has a spread of $\sim 40 \text{ ps}$ across the emission range from 2.6 eV to 2.85 eV whereas a similar comparison at 4.2 K gives a lifetime spread of $\sim 200 \text{ ps}$. In addition to the reduction in the spread of the lifetime across the PL spectrum, we also see a very small blue shift of the spectral peak with an increase in the excitation power density at room temperature.

As temperature is increased from 4.2 K, carriers are thermally assisted to overcome higher barriers in deep localisations in the vicinity of higher indium content areas. The enhanced carrier escape process can explain the similar rates of the fast decay part across different photon energies in Fig. 7.9 at room temperature. This enhancement together with activation of non-radiative recombination processes reduces the measured lifetime which is in good agreement with the proposed carrier recombination mechanism in Fig. 7.5c) in the previous section.

7.5 Chapter summary

GaN nanopylramids with a single InGaN quantum well grown on the facets of the inclined $\{10\bar{1}1\}$ semi-polar plane were characterised. The studied nanopylramids are some of the smallest nanopylramids and highest density to be fabricated by SAG and ELOG in a regular array, maximising active area of the LED. Growth of InGaN QWs on high density GaN has impacts on indium incorporation discussed by Liu *et al* (152, 156). Micro-PL experiments have been carried out to investigate the carrier dynamics and a recombination mechanism involving localisation along the QW and QCSE due to piezoelectric polarisation parallel to the QW has been proposed to describe the observations from the PL experiments.

- A lower recombination lifetime compared to conventional *c*-plane LEDs is due to reduction in internal electric field in quantum wells grown on the facets of nanopylramids.
- There is narrowing and blue shifting of the peak as excitation density is increased which is due to carrier field screening of the QCSE, showing that the piezoelectric field is still present, despite being suppressed.
- The time resolved studies reveal non-monoexponential decays. These cannot be easily fitted with conventional stretched and bi-exponentials commonly used in literature. The decay traces can be separated into three stages. This is explained in a model where we propose that the fast decay rates in the initial ns is due to a combination of carrier escape and capture from localisations, in addition to the

fast carrier recombination due to the screened piezoelectric field which gradually decreases with time. The extended lifetimes observed > 10 ns arise due to the deep localisation centres emitting in the lower energies.

- We observe that there is dynamical change of the time resolved PL spectrum. This is due to the difference in recombination rates of states localised at different energies as well as the decrease in carrier field screening as carrier density decreases.

In summary, the reduction of QCSE in the QW grown on semi-polar facets is shown through a reduced carrier lifetime. The inhomogeneity of the QW emission gives rise to some interesting effects which were investigated through time resolved PL studies. The selected area growth method for the fabrication of LEDs on semipolar planes shows great potential for an economical solution to the polarisation problem plaguing GaN based devices.

Conclusion

Novel methods in the fabrication and design of next generation LEDs by downsizing features to the nanoscale drastically modify their physical properties. The research presented in this thesis focusses on the optical properties of these nanostructured devices and also the development of further techniques to characterise and test the effects hypothesised for GaN based nanostructures.

Low temperature microphotoluminescence experiments were conducted on nanorod LED arrays fabricated on pre-existing off-the-shelf LEDs via nanoimprint lithography, a high throughput, low cost manufacturing technique, and reactive ion etching. This contact method is unlike optical fabrication techniques such as steppers which are expensive to implement and usually only used in complex nanoelectronics. The nanoimprinting gave very precise and high resolution etch masks and very good uniformity of nanorods.

Initial experiments were carried out on multi-quantum well samples with etched

nanorods of varying diameters with a pitch of approximately 400 nm. The emission was found to be modified by the nanoprocessing, with narrower rods emitting at higher energies as expected from the modifications of the strain in the active layer due to sidewall relaxation. However when the diameter of the nanorod LED was reduced down to less than 100 nm the fabrication regularity begins to deteriorate, and nanorods are easily broken. The emission spectrum also changes drastically, which we postulate to be due to surface states affecting the band structure of the quantum well in the thin nanorods.

Non-linear optical spectroscopy at low temperatures provided insight into a peculiar phenomenon which has rarely been reported in literature on InGaN/GaN quantum well nanorods. Spectrally narrow peaks were found over the InGaN spectrum which broadened and decreased in intensity considerably with increasing temperature. These peaks cannot be distinguished from the background emission at over 30 K. The peaks resembled the spectral characteristics of early InGaN quantum dot measurements. Further characterisation was carried out on samples which were structurally simpler and made with a wider pitch. This enabled us to experiment on a single nanorod from the top down. The study revealed that each nanorod had a unique spectral pattern dominated by the positions of the narrow peaks at low temperatures and low excitation powers. It was also shown by time resolved photoluminescence experiments that there was a dynamic shift in the spectrum as the carriers recombined. The temporal evolution of the emission of the sharp peaks was reported and thought to be a consequence of surface effects.

Experimental studies were carried out on the optical properties of GaN nanopyramid array LEDs with one of highest reported densities at the time. The quantum wells were grown on the facets of the nanopyramids which were naturally on the semi-polar crystal planes. Reduction in strain was shown by power dependent photoluminescence studies compared to conventional *c*-plane samples. The effect was further confirmed by the rapid decay rates observed in time-resolved photoluminescence experiments. The time-resolved results also showed varying decay rates with time which we concluded was due to a combination of: carrier transfer to and from localised states; field screening of the quantum confined Stark effect due to residual piezoelectric field; and also carriers recombining in lower energy parts of the quantum well which were shown to be near the base of the pyramid by cathodoluminescence.

This work also introduced a scheme for measuring polarisation of photoluminescence for the existing cryogenic microphotoluminescence experimental apparatus. Work has been carried out on MoS₂ flakes and also GaN nanorods, with very fascinating results. Comparing polarisation dependent excitation and polarised emission from samples will expand the capability of the system and lead to interesting studies of nanostructures in different materials.

The challenges that nitride based LEDs face are not easily solvable by a single solution in the near future. Strategies that introduce nanostructures, can for example improve the photonic properties but on the other hand often complicate the device physics significantly. Future experiments on the narrow spectral lines found in nanorod LEDs have already been planned and the initial fabrication design has been documented

in the thesis. We need to verify that the sidewall perimeter correlates with the number of observed localised states to confirm the surface effect that we hypothesised. Once this has been confirmed, this may have significant impact on the implementation of experimental InGaN based quantum systems relying on nanorod ion etching. In addition, recent change in the experimental setup has allowed us to see what we think may be lasing in the nanorod array system, but this is yet to be confirmed. Interesting studies on electroluminescence can also be made if the nanorods are cut off and scattered onto a reference grid to be contacted individually. The polarisation sensitivity can also be tested with different alignments of the nanorod which could potentially make way for novel designs in polarisation emitters. On top of that, with recent advances in the research group activity in optical cavity systems, coupling the nanorod emission to a tunable cavity would be a very interesting possibility.

Appendix A

Detailed fabrication information

A.1 Lift-off processing recipe and procedures

Process	Procedure
Sample preparation	• Cleave 5 mm $\times$ 5 mm Si sample • Clean sample wafer with acetone in ultrasonic cleaner for 5 mins, dry and repeat with IPA.
Resist Coating	• Load sample into spin coater and set resist recipe: 500 RPM ramp followed by 4000 RPM for 40 s • Use a pipette to place a drop of PMMA A4 495 onto the sample through a paper filter • Start the spin process • Place sample on hot plate set at 180°C for 90 s to evaporate solvent • Check to see if coating is even un optical microscope • Repeat the above process with PMMA A4 950 for the upper layer resist coating

A.1 Lift-off processing recipe and procedures

E-beam exposure	• Load sample into <i>Jeol 5500ZC</i> e-beam lithography system in the custom built sample holder and evacuate chamber • Set beam current to 1nA and proceed to calibrate the e-beam system • Load the <i>Autocad</i> .dwg file in the pattern designer to convert the file to .sdp file • switch to SE imaging mode to find sample coordinates and locate the sample centre in the custom holder • Expose the pattern in the centre of the sample setting the dose at $650 \mu\text{C}/\text{cm}^2$
Development	• Upon removal of sample from chip carrier, develop the exposed sample in MIBK: IPA (1:3) at room temperature for 15 s • Rinse in IPA • Check exposure and development under optical microscope • Repeat above steps until exposed PMMA is removed.
Metal evaporation	• Load sample into <i>Edwards a306</i> evaporator using tape • Load metal evaporation source with suitable crucible according to table 3.1 and proceed by following the <i>Edwards a306</i> user manual • On ramping the current, slowly increase the current until the metal pellet melts • Open the shutter and manually control the current dial to achieve a rate of 0.1 nm s^{-1} • Leave to cool and remove sample

A.1 Lift-off processing recipe and procedures

Inspection with SEM	• Load sample in <i>Hitachi S-4300</i> SEM to inspect the coated sample, checking for coating smoothness and good separation of metal layers in the pattern
Pattern lift-off	• Place sample in NMP solution on a hotplate set to 70°C • leave for 30 minutes agitate lightly for a few seconds • On successful lift-off a whole flake of metal will detach from the sample • Check under optical microscope to check complete resist removal. If not, repeat the above steps with more agitation and sonication
Removal of metal	• Nickel can be removed by using nitric acid • If nitric acid cannot fully remove the metal, aquaregis should be used

Design	Pitch	Diameter	Spacing
TM1	198nm	79nm	120nm
TM2	264nm	169nm	95nm

Table A.2: Table of design parameters used for fabricating etch mask arrays labelled *TM1* and *TM2*

A.2 etch mask fabrication problems

Many difficulties have been encountered in the course of fabrication of the etch masks. An attempt to fabricate etch masks for a narrow pitched prototype photonic crystal was carried out which revealed problems with E-beam lithography with writing closely neighbouring structures. The two designs used are *TM1* and *TM2* with design parameters listed in table: A.2

Electrons accumulating on the sample surface during e-beam writing causes complications when writing structures in close proximity to each other. If the electrons are not dissipated after exposing the resist, the local area becomes charged, resulting in deflection of the electron beam. GaN is prone to this charging effect, creating problems when fabricating closely packed structures such as photonic crystals.

FigA.1 shows SEM images of the two photonic crystal patterns on PMMA with 50 nm of nickel deposited on the surface. Despite *TM1* pattern having a smaller diameter holes, it was successfully written and developed on PMMA. However with smaller spacing between exposure areas, the proximity effect becomes significant as illustrated by the *TM2* pattern, where the spacing between exposure areas is 95 nm.

Another reason for the collapse of the *TM2* pattern could be due to a large difference in exposure/development between the two resist layers, causing a large undercut on development. If the undercut is too large, a large cavity is formed under the top layer of the resist. The resist therefore collapses near the centre of the structure. A combination of these two effects is likely to explain for the collapsed structure shown in Fig. A.1c) and d).

For the *TM1* pattern, lift-off was performed, however, the nickel islands were incomplete, the reason for this is still under investigation. SEM image of this is shown in Fig. A.2

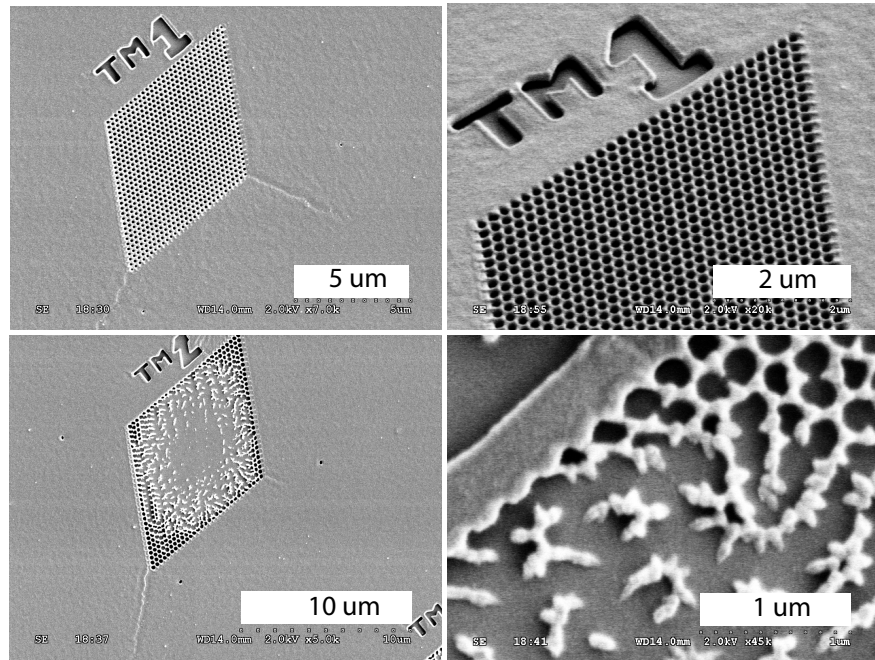


Figure A.1: - SEM images of *TM1* and *TM2* patterns. a) *TM1* pattern showing a clean exposure and development with regular holes created. b) angled view showing a magnified image of *TM1* pattern. c) *TM2* pattern showing a collapsed structure. d) Magnified image at the corner of the structure of the *TM2* pattern.

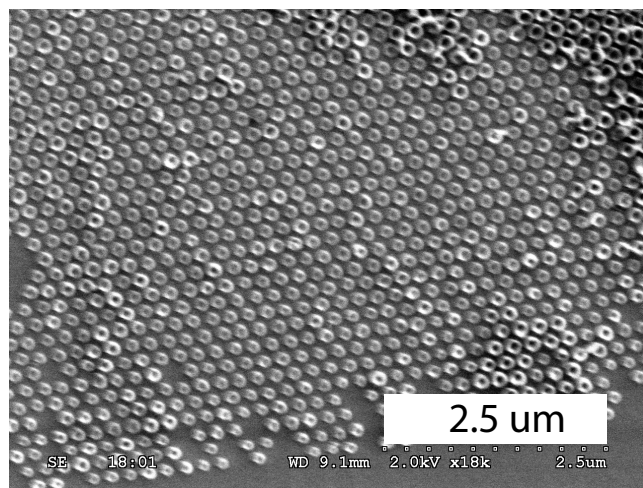


Figure A.2: - Incomplete array of nickel islands from the *TM1* pattern

Appendix B

Polarisation analysis

B.1 Instrument characterisation

A control (GaAs) quantum well in AlGaAs barriers emitting at 745nm was excited with a 532nm diode laser using a $100\times$ achromatic objective. The sample was grown in Cambridge by Paola Atkinson and used as a control non-polarising emitter for test. The PL was collected through the same objective and reflected into the polariser/analyser before being focussed onto the spectrometer slit. The analyser/polariser was turned through 360° and the intensity of the PL peak was recorded at every 10° intervals.

The alignment of the optics plays a crucial role in detecting polarisation with good spatial and spectral selectivity. Deviation of the beam by $10\text{ }\mu\text{m}$ can cause the PL to miss the entrance slit of the spectrometer entirely, resulting in inaccurate results. The alignment is therefore one of the main sources of error in the experiment. By increasing the entrance slit size, we can reduce the sensitivity of the experiment to misalignment, but at a cost of reduced spatial and spectral resolution.

Fig. B.1 shows the polarisation polar plot of the GaAs QW emission line. 0° is taken arbitrarily in the plot, and the PL is normalised to the PL at the angle with highest intensity. The entrance slit is at $100\mu\text{m}$, and it can be seen that the measurement exhibits a slight asymmetry mainly due to the instrument alignment errors. The maximum values are collected at 315° and 140° .

B.2 MoS₂ example

Mono-layer MoS₂ was chosen to be analysed in the polarisation study due to its interesting polarisation properties reported in recent literature. There is a growing interest

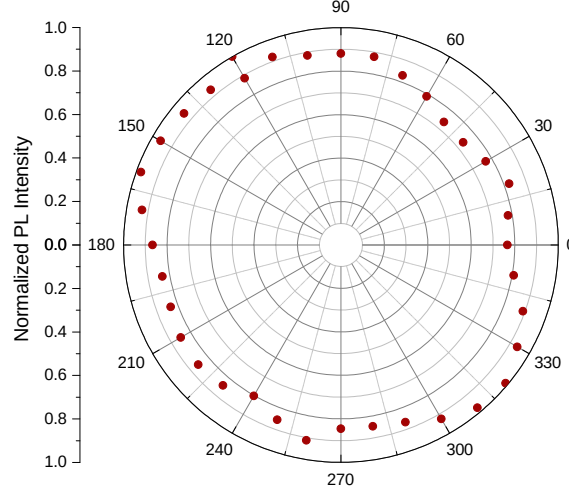


Figure B.1: - Polar plot of the intensity of the PL analysed at different polarisation angles

in MoS₂ due to the possibility of making devices utilising the degeneracies at the conduction band minima (valleytronics). The brief study was carried out to see if there is any differences in photoluminescence polarisation from bi-layer and mono-layer flakes at 4.2 K . The initial results are shown below. Mono-layer and bi-layer MoS₂ flakes were prepared on SiO₂ substrate by exfoliating bulk crystals of 2H-MoS₂. Micro-Raman experiments were conducted by Prof. Y. S. Park to verify monolayer and bi-layer flakes. Micro-PL mapping of the flake reveals differences in the optical behaviour of bi-layer and mono-layer, namely a double peak being observed in the mono-layer at 1.78eV and 1.88eV, whereas only a single peak at 1.88eV is observed in the bi-layer area. Spatially resolved polarisation studies of the PL were then carried out on the MoS₂ flake. The integrated intensity of the PL was taken at room temperature at every 20° intervals. The results are then normalised and divided by the control GaAs sample to obtain more reliable results.

Fig. B.2 shows the polar plot of the normalised PL intensity relative to the control GaAs sample for both mono- and bi-layer MoS₂ flakes taken at 4.2K. There is polarisation anisotropy for both samples, however, it is clearly visible that the mono-layer sample exhibits a higher degree of anisotropy, with a decrease of intensity at $\sim 240^\circ$ and $\sim 60^\circ$. The polarisation degree, P_d is defined as:

$$P_d = \frac{I_{max} - I_{min}}{I_{max} + I_{min}}, \quad (\text{B.1})$$

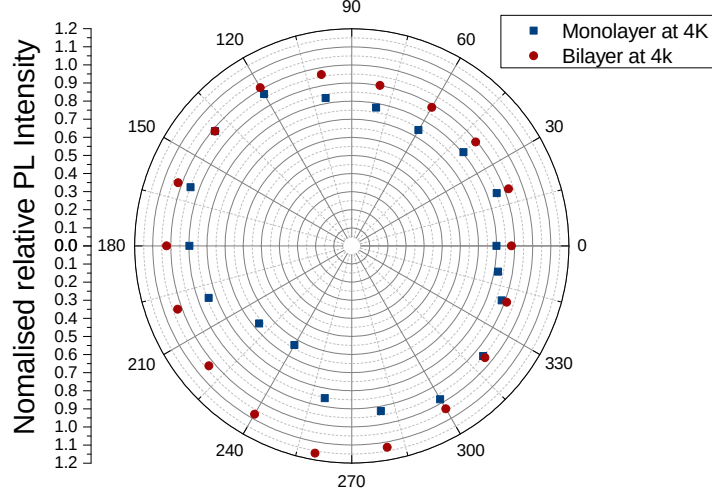


Figure B.2: - Polar plot of normalised PL intensity relative to control GaAs sample of bi-layer and mono-layer MoS₂ flakes at 4K

where I_{max} and I_{min} are the maximum and minimum measured intensities. The mono-layer sample measured above gives a degree of polarisation ~ 0.22 whereas the bi-layer gives a value of ~ 0.136 . The anisotropy gives rise to many questions with regards to its origins. Preliminary results also show that the degree of polarisation is also temperature dependent. Polarisation anisotropy of the bi-layer is found to be lifted when the sample is at room temperature. The discussion of this behaviour is still under-way and is a major topic of interest of our collaborators in Korea. It is initially thought that the polarisation anisotropy is caused by strain existing in the substrate to sample interface. This is however at very preliminary stages of experimentation and there has yet to be more research performed on the sample. Particularly on the verification the type of polarisation, for example whether the observed anisotropy is a result of partial polarisation, or elliptical polarisation. The need to further expand our experimental set-up to resolve left and right circularly polarised light is highlighted here.

Other experiments conducted by this set-up has shown promising results with quantum dot work given at by B. Ried at UKNC summer meet 2013. The results show good extinction ratios in linearly polarised light found in InGaN quantum dots grown on non-polar GaN.

Appendix C

Poster presentations

Quantum Dot-like Emission Lines in Wet-etched Nano-rod Array GAN Based MQW LEDs

Christopher C.S. Chan¹, Mark, J. Holmes¹, Philip A. Shields², Duncan W.E. Allsopp², and Robert A. Taylor¹

¹ Department of Physics, Clarendon Laboratory, University of Oxford, Oxford, UK OX1 3PU
² Department of Electronic and Electrical Engineering, University of Bath, Bath, UK BA27AY



LED nanorod arrays grown by University of Bath were Characterised optically using micro-Photoluminescence. Quantum Dot like features in the emission spectrum was observed and studied. Nanorod nano-rod arrays were made on a wafer-scale by from a commercial LED wafer by nanoimprint lithography[1]. The array was formed by ICP etching with ~450nm pitch. Subsequently the array is wet-etched and the effect of etching is shown in the SEM images in fig1.

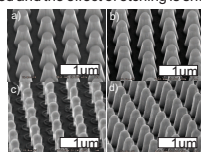


Fig.1 SEMs of columns a) shows ICP etch only columns before KOH etching. b) shows KOH etching for 1 minute at 40C. KOH etching for 5 minutes at 80C. d) shows KOH etching for 10 minutes at 40C

Wet-etching produces columns with progressively narrower bases (attachment to the bulk GaN). After a 30-minute etching in KOH, the columns thin to an extent that pod shaped structures are created. Many of these thinned down columns cannot support the GaN/InGaIn quantum well LED structure on the end, causing the whole pod like structure to topple. An SEM is shown in Fig 2a).

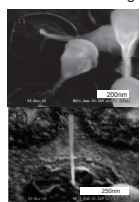
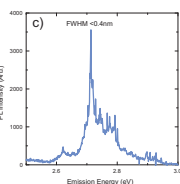


Fig. 2 a) SEM of pod-like structures studied. a) MQW structure on end of etched columns toppled over with tapering tails. b) In the middle of one of the nano-rod sites, the etching has left a thin column behind. c) micro-PL spectrum of a area on the sample



Micro-PL was carried out using a pulsed 266nm UV laser. Quantum Dot like emission spectra was observed at low excitation powers. Fig 2c) shows a single peak with a good background contrast, the FWHM of the peak is less than 0.4nm.

Excitation Power Dependent Study

Laser excitation power is changed to vary the carrier density. The peaks broaden and background states are filled with increasing power/carrier density. At higher excitation powers, the spectral shape of the normal LED array sample is recovered. Fig 3 shows an excitation power dependent spectrum of the sample. Some of the states visible at low excitation powers can be related to shoulders of the main peak at high powers. The main broad peak at high excitation is also seen to blue-shift with increasing excitation power. This blueshift can be a sign of QCSE in the GaN/InGaIn well structure[2], it may also be filling of the higher energy localised states. [3]

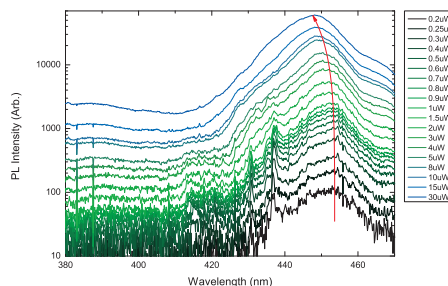


Fig. 3 Excitation power dependent spectra, red line shows shift in main broad peak. The peak shift measured ~6.5nm. Sharp peaks are seen on the Red side of the main peak

Fig. 4 shows an excitation power dependent series on a different area of the sample. The series shows the spectra in detail with progressive increase in excitation power until background states are filled. Seven sharp peaks can be identified in this area of the sample ranging from 380nm to 440nm emission range. Fig 4 insert shows the analysis of the peak wavelength and the width of the two peaks 1 and 2. Peak one shows a red-shift of around 1nm with increasing excitation power, and a FWHM increase. The rate of broadening of peak 2 is much higher than that of peak 1. Peak 1 shows very little broadening and a resolution limited blue shift is observed.

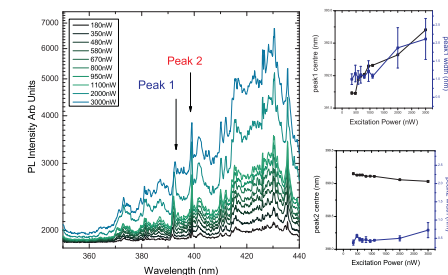


Fig. 4 LEFT: Excitation power dependent series spectra of pod like structure. Quantum dot-like features are shown. TOP RIGHT: Analysis of peak 1, graph showing change in peak emission centre and peak FWHM with increasing carrier density. BOTTOM RIGHT: Analysis of peak 2, showing a much less change in both peak centre and width with increasing carrier density.

Temperature Dependence

The sample temperature was varied from 4K to 60K and micro-PL was carried out to study the temperature dependence of the QD-like states with temperature. Fig. 5 shows the temperature dependent series of the sample. The effect of increasing temperature on individual peaks is similar to that of InGaIn QD.[4] The peaks broaden and disappear at around 45+K. The main peak broadens merging with the surrounding smaller peaks. However main peak intensity does not decrease within the 60K range.

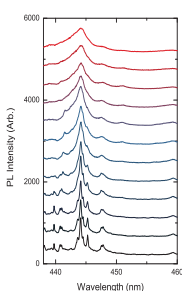


Fig.5 Spectra of pod like structure with increasing temperature

- Two peaks from the same confocal area (~micron) in the sample exhibits different responses to varying excitation powers, indicating two different types of structures
- Red Shift from peak 1 maybe due to local heating and lack of phonon heat dissipation at that specific area of structure.
- Narrow QD like states fill before the broad MQW states in the LED which forms the main broad peak seen in the other LED samples with less KOH etching.

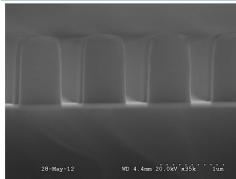
References

- G. Hubbard, S.J. Abbott, Q. Chen, D.W.E. Allsopp, W.N. Wang, C.R. Bowen, R. Stevens, A. Satka, D. Hasko, F. Uhrek, and J. Kovac, *Physica E*, **41**, 1118 (2009).
- Young S Park, mark holmes, Tae W Kang and Robert A Taylor 2010 *Nanotechnology* **21** 115401
- E. Kuokstis, J. W. Yang, G. Simin, M. Asif Khan, R. Gaska, and M. S. Shur, *Appl. Phys. Lett.* **80**, 977 (2002).
- Osamu Moriawaki, Takao Someya, Koichi Tachibana, Satomi Ishida, and Yasuhiko Arakawa, *Appl. Phys. Lett.* **76**, 2361 (2000)

Figure C.1: Poster for UKNC 2011, Manchester, UK

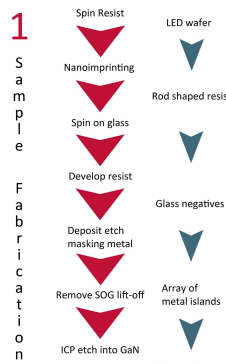
Carrier dynamics of single InGaN/GaN nano-LED fabricated on a wafer-scale nanorod array

Christopher C.S. Chan,^{1,*} Benjamin P.L. Reid,¹ Mark J. Holmes,¹ Wei Jia,¹ Robert A. Taylor,¹ Shingo Nakazawa,¹ Heedae Kim,¹ Yi Ding Zhuang,² Philip A. Shields,² Duncan W.E. Allsopp²
¹Department of Physics, University of Oxford, Clarendon Laboratory, Parks Rd, Oxford, UK
²Department of Electronic and Electrical Engineering, University of Bath, Bath, UK



Abstract

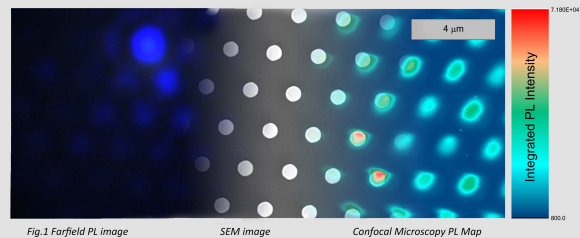
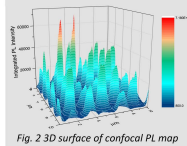
Single nanorods fabricated on a wafer scale on an LED wafer have been studied using micro-photoluminescence. Nanorods have been attracting great interest as a means to increase extraction efficiency and to reduce the effect of strain induced complex recombination dynamics, enhancing radiative recombination efficiencies in LEDs. Wafer-scale fabrication of these nanorod arrays on pre-existing LED wafers by using nanoimprint lithography means that the technology can be imported to pre-existing manufacturing methods at much lower costs than for grown nanorods. Specific patterns can be made repeatedly at a very precise level, realising cost effective photonic crystal based LEDs for future applications not only as energy efficient lighting, but light sources tailored for polarisation, and wavelength.



2 Micro-Photoluminescence (PL)

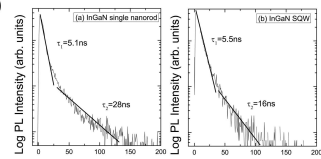
- 400nm doubled Ti:Sapphire laser
- 1/3m spectrograph, CCD collection
- Helium flow cryostat mounted T=4.2K
- 100x 0.7NA apochromatic objective
- Confocal PL collection
- Piezo mounted with 10nm precision

Raster scanning on sample
 Integrating PL generating spatial map
 High contrast ratio ~ 200:1
 Single nano-LED PL study is possible



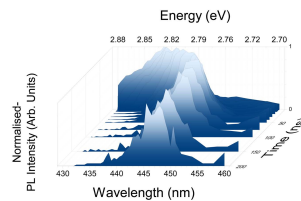
4 Time Resolved Photoluminescence (TRPL)

- Time correlated single photon counting (TCSPC)
- Carrier lifetime is longer in nanorod (Fig.4)
- Non-monoeponential dynamic decay



Carrier dynamics examined:

- 1) Red shift in carrier emission as delay time increases
- 2) Emission peak becomes non gaussian-like after 75ns
- 3) Sharp peaks apparent at times above 200ns



Effects in different stages of emission
 0-20ns: Dominated by main well emission with quantum confined stark screened giving the reduced lifetime

20-100ns Main well emission is only partially or even not screened. An increase in lifetime is observed in Fig 4. Red shifting of spectral peak ceases in Fig 5.

100ns+ Gaussian shape is due to degenerate states in 1d SQW, discrete peaks occur in this time regime due to localisation of carriers. Lifetimes of these states are long causing increase in lifetime for nanorod in figure 4

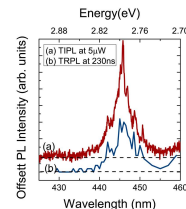
Similarities of spectrum at low carrier density

Spectrum at 230ns vs low excitation TIPL spectrum Fig.6

- Carriers deplete after pulse
- Recombination preferably in localised states
- Very long lived and only present in nanorods
- Indicates a high carrier spatial separation

Surface related localisation

- Band bending at semiconductor surfaces
- Fermi surface pinning causing the conduction/valence bands to bend at nanorod sidewalls.
- Carriers localised close to the rod perimeter
- Their recombining counterparts trapped in the centre
- High spatial separation for the recombining pairs
- States are filled with increasing carrier density lowering the lifetime

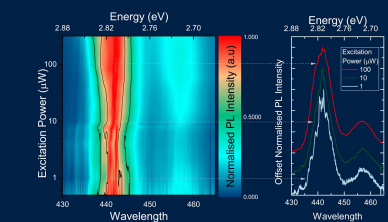


3 Excitation power dependence study

Excitation power varied over 3 orders of magnitude

Observations:

- 1) Slight blueshift and spectral broadening with carrier density increase
 - Quantum confined Stark effect from strain induced piezo electric field in QW layer screened by excess carriers
 - Shift is much less than plane unprocessed wafer
 - possible reduction of strain due to sidewall relaxation
- 2) At Low excitation power, sharp features observed in spectrum
 - Localised non-degenerate states filled at low carrier density
 - Carrier density increase, states fill, carriers spill into QW
 - Gaussian-like emission from InGaN QW at the higher excitations



5 Conclusions

Surface effects dominate at low carrier densities. Localisation effects can be related to surface roughness causing changes in local potentials around the perimeter of the nanorod. Top down processing issues are revealed optically in experiment. However, for lighting applications, high carrier densities are used and since these effects are only observable at low carrier density regimes. The importance, quantum mechanically, of surface roughness to the operation of nanorod LEDs may be further questioned.



To download poster use the QR code

Acknowledgements
 The authors would like to acknowledge Paul Pattinson, Robert Storey (University of Oxford), Sivapathasundaram Sivaraya, and Emmanuel Le Boulbar (University of Bath). This research was supported by the Engineering and Physical Sciences Research Council (EPSRC) U.K. (Grant No. EP047816) and the European Union (FP6-Contract No. 017461, "N2T2", and FP7 Contract No. 228999, "SMASH").

Christopher Chan c.chan1@physics.ox.ac.uk

Figure C.2: - Poster for IWN2012, Sapporo, Japan

References

- [1] HJ ROUND. **A note on carborundum.** *Electrical world*, 1907. 1
- [2] OV LOSSEV. **CII. Luminous carborundum detector and detection effect and oscillations with crystals.** *Philosophical Magazine*, **6**(39):1024, 1928. 1
- [3] NICK HOLONYAK AND S. F. BEVACQUA. **COHERENT (VISIBLE) LIGHT EMISSION FROM Ga(As_{1-x}P_x) JUNCTIONS.** *Applied Physics Letters*, **1**(4):82, 1962. 1
- [4] NIKOLAY ZHELUDEV. **The life and times of the LEDa 100-year history.** *Nature Photonics*, **1**(April):189–192, 2007. 1
- [5] JI PANKOVE AND EA MILLER. **Electroluminescence in GaN.** *Journal of luminescence*, **4**:63–66, 1971. 1
- [6] FREEDONIA. **World Lighting: Lamps & LEDs - Market Size, Market Share, Market Leaders, Demand Forecast, Sales, Company Profiles, Market Research, Industry Trends and Companies**, 2013. 1
- [7] MCKINSEY&COMPANY. **Lighting the way: Perspectives on the global lighting market.** Technical report, 2013. 1
- [8] AKIO KANETA, MITSURU FUNATO, YUKIO NARUKAWA, TAKASHI MUKAI, AND YOICHI KAWAKAMI. **Direct correlation between nonradiative recombination centers and threading dislocations in InGaN quantum wells by near-field photoluminescence spectroscopy.** *Physica Status Solidi (C)*, **3**(6):1897–1901, June 2006. 2
- [9] L. BELLAICHE, T. MATTILA, L.-W. WANG, S.-H. WEI, AND A. ZUNGER. **Resonant hole localization and anomalous optical bowing in InGaN alloys.** *Applied Physics Letters*, **74**(13):1842, 1999. 2

-
- [10] YUKIO NARUKAWA, YOICHI KAWAKAMI, MITSURU FUNATO, SHIZUO SHIGEO FUJITA, SHIZUO SHIGEO FUJITA, AND SHUJI NAKAMURA. **Role of self-formed InGaN quantum dots for exciton localization in the purple laser diode emitting at 420 nm.** *Applied Physics Letters*, **70**(8):981–983, 1997. 2
- [11] SHIGEFUSA F CHICHIBU, AKIRA UEDONO, TAKEYOSHI ONUMA, BENJAMIN A HASKELL, ARPAN CHAKRABORTY, TAKAHIRO KOYAMA, PAUL T FINI, STACIA KELLER, STEVEN P DENBAARS, JAMES S SPECK, UMESH K MISHRA, SHUJI NAKAMURA, SHIGEO YAMAGUCHI, SATOSHI KAMIYAMA, HIROSHI AMANO, ISAMU AKASAKI, JUNG HAN, AND TAKAYUKI SOTA. **Origin of defect-insensitive emission probability in In-containing (Al,In,Ga)N alloy semiconductors.** *Nature materials*, **5**(10):810–6, October 2006. 2
- [12] R A OLIVER, S E BENNETT, T ZHU, D J BEESLEY, M J KAPPERS, D W SAXEY, A CEREZO, AND C J HUMPHREYS. **Microstructural origins of localization in InGaN quantum wells.** *Journal of Physics D: Applied Physics*, **43**(35):354003, September 2010. 2, 21, 22, 105
- [13] HAPPEK UWA. **Basics of lighting: Efficacy, Color Rendering and Color Temperautre.** *The electrochemical society Interface*, (Winter):29–30, 2009. 2
- [14] ANDREAS WAAG, XUE WANG, SÖNKE FÜNDLING, JOHANNES LEDIG, MILENA ERENBURG, RICHARD NEUMANN, MOHAMED AL SULEIMAN, STEPHAN MERZSCH, JIANDONG WEI, SHUNFENG LI, HERGO H. WEHMANN, WERNER BERGBAUER, MARTIN STRASS BURG, ACHIM TRAMPERT, UWE JAHN, AND HENNING RIECHERT. **The nanorod approach: GaN NanoLEDs for solid state lighting.** *Physica Status Solidi (C)*, **8**(7-8):2296–2301, July 2011. 2, 3
- [15] J. DAY, J. LI, D. Y. C. LIE, C. BRADFORD, J. Y. LIN, AND H. X. JIANG. **Full-Scale Self-Emissive Blue and Green Microdisplays Based on GaN Micro-LED Arrays.** In MANIJEH RAZEGHI, ERIC TOURNIE, AND GAIL J. BROWN, editors, *Proc. of SPIE*, **8268**, pages 82681X–82681X–8, January 2012. 2
- [16] S.F. CHICHIBU, T. SOTA, K. WADA, O. BRANDT, K.H. PLOOG, S.P. DENBAARS, AND S. NAKAMURA. **Impact of Internal Electric Field and Localization Effect on Quantum Well Excitons in AlGaIn/GaN/InGaIn Light Emitting Diodes.** *Physica Status Solidi (a)*, **183**(1):91–98, January 2001. 3

-
- [17] I-HSIU HO AND G. B. STRINGFELLOW. **Solid phase immiscibility in GaInN.** *Applied Physics Letters*, **69**(18):2701, 1996. 3, 20, 21
- [18] K. KISHINO, A. KIKUCHI, H. SEKIGUCHI, AND S. ISHIZAWA. **InGaN/GaN Nanocolumn LEDs Emitting from Blue to Red.** *Proc. of SPIE*, **6473**:64730T–64730T–12, February 2007. 3
- [19] Y. KAWAKAMI, S. SUZUKI, A. KANETA, M. FUNATO, A. KIKUCHI, AND K. KISHINO. **Origin of high oscillator strength in green-emitting In-GaN/GaN nanocolumns.** *Applied Physics Letters*, **89**(16):163124, 2006. 3, 62, 83, 89, 101, 106
- [20] H J CHANG, Y P HSIEH, T T CHEN, Y F CHEN, C-T LIANG, T Y LIN, S C TSENG, AND L C CHEN. **Strong luminescence from strain relaxed InGaN/GaN nanotips for highly efficient light emitters.** *Optics express*, **15**(15):9357–65, July 2007. 3, 62, 99
- [21] KATSUMI KISHINO, JUMPEI KAMIMURA, AND KOUICHI KAMIYAMA. **Near-Infrared InGaN Nanocolumn Light-Emitting Diodes Operated at 1.46 um.** *Applied Physics Express*, **5**(3):031001, February 2012. 3, 26, 62
- [22] S. SRINIVASAN, M. STEVENS, F. A. PONCE, AND T. MUKAI. **Polychromatic light emission from single InGaN quantum wells grown on pyramidal GaN facets.** *Applied Physics Letters*, **87**(13):131911, 2005. 3
- [23] K. NISHIZUKA, M. FUNATO, Y. KAWAKAMI, Y. NARUKAWA, AND T. MUKAI. **Efficient rainbow color luminescence from In_xGa_{1-x}N single quantum wells fabricated on {1122} microfacets.** *Applied Physics Letters*, **87**(23):231901, 2005. 3
- [24] SMG INDIUM RESOURCES LTD. **Historical Indium Prices (2002 2012) Indium - 10 Year Price History**, 2013. 3
- [25] GEOLOGY.COM. **Indium Price Supported by LCD Demand and New Uses for the Metal**, 2009. 3
- [26] JOACHIM PIPREK. **Efficiency droop in nitride-based light-emitting diodes.** *Physica Status Solidi (a)*, **207**(10):2217–2225, October 2010. 3
- [27] JUSTIN IVELAND, LUCIO MARTINELLI, JACQUES PERETTI, JAMES S. SPECK, AND CLAUDE WEISBUCH. **Direct Measurement of Auger Electrons Emit-**

- ted from a Semiconductor Light-Emitting Diode under Electrical Injection: Identification of the Dominant Mechanism for Efficiency Droop.** *Physical Review Letters*, **110**(17):177406, April 2013. 3
- [28] A.-L. BAVENCOVE, P. GILET, A. DUSSAIGNE, LE SI DANG, B. MARTIN, P. FERRET, J. EYMERY, C. DURAND, M. LAFOSSAS, D. SALOMON, B. ANDRÉ, AND F. LEVY. **Light emitting diodes based on GaN core/shell wires grown by MOVPE on n-type Si substrate.** *Electronics Letters*, **47**(13):765–767, June 2011. 3
- [29] D ZHU AND CJ HUMPHREYS. **Low-cost high-efficiency GaN LED on large-area Si substrate.** In *CS Mantech conference*, pages 269–272, 2013. 3
- [30] Y. KAWAKAMI, A. KANETA, L. SU, Y. ZHU, K. OKAMOTO, M. FUNATO, A. KIKUCHI, AND K. KISHINO. **Optical properties of InGaN/GaN nanopillars fabricated by postgrowth chemically assisted ion beam etching.** *Journal of Applied Physics*, **107**(2):023522, 2010. 3, 116
- [31] AKIHIKO KIKUCHI, MIZUE KAWAI, MAKOTO TADA, AND KATSUMI KISHINO. **InGaN/GaN Multiple Quantum Disk Nanocolumn Light-Emitting Diodes Grown on (111) Si Substrate.** *Japanese Journal of Applied Physics*, **43**(No. 12A):L1524–L1526, November 2004. 3, 26, 61
- [32] V. RAMESH, A. KIKUCHI, K. KISHINO, M. FUNATO, AND Y. KAWAKAMI. **Strain relaxation effect by nanotexturing InGaN/GaN multiple quantum well.** *Journal of Applied Physics*, **107**(11):114303, 2010. 3, 69, 70, 116
- [33] MARK J. HOLMES, YOUNG S. PARK, XU WANG, CHRISTOPHER C. S. CHAN, ANAS F. JARJOUR, ROBERT A. TAYLOR, JAMIE H. WARNER, JUN LUO, H. A. R. EL-ELLA, AND R. A. OLIVER. **Carrier dynamics of $\text{In}_x\text{Ga}_{1-x}\text{N}$ quantum disks embedded in GaN nanocolumns.** *Journal of Applied Physics*, **109**(6):063515, March 2011. 3, 49, 62, 63, 74, 76, 82, 88, 102
- [34] CCS CHAN, YD ZHUANG, AND BPL REID. **Photoluminescence of Single GaN/InGaN Nanorod Light Emitting Diode Fabricated on a Wafer Scale.** *Japanese Journal of Applied Physics*, **52**:10–13, 2013. 3, 89
- [35] KWAN H. LEE, JONG H. NA, ROBERT A. TAYLOR, SAM N. YI, STEFAN BIRNER, YOUNG S. PARK, CHANG M. PARK, AND TAE W. KANG. **Enhancement of free-carrier screening due to tunneling in coupled asymmetric**

- GaNAlGaN quantum discs.** *Applied Physics Letters*, **89**(2):023103, 2006. 3, 12, 63
- [36] Y S PARK, J H NA, R A TAYLOR, C M PARK, K H LEE, AND T W KANG. **The recombination mechanism of Mg-doped GaN nanorods grown by plasma-assisted molecular-beam epitaxy.** *Nanotechnology*, **17**(3):913–916, February 2006. 3, 26
- [37] Y. S. PARK, C. M. PARK, D. J. FU, T. W. KANG, AND J. E. OH. **Photoluminescence studies of GaN nanorods on Si (111) substrates grown by molecular-beam epitaxy.** *Applied Physics Letters*, **85**(23):5718, 2004. 3, 61, 62
- [38] C CHAN AND PA SHIELDS. **Optical studies of quantum dotlike emission from localisation centres in InGaN/GaN nanorod array LEDs.** *Physica Status Solidi (C)*, **638**(3):635–638, 2012. 3
- [39] CHRISTOPHER C. S. CHAN, BENJAMIN P. L. REID, ROBERT A. TAYLOR, YI-DING ZHUANG, PHILIP A. SHIELDS, DUNCAN W. E. ALLSOPP, AND WEI JIA. **Optical studies of the surface effects from the luminescence of single GaN/InGaN nanorod light emitting diodes fabricated on a wafer scale.** *Applied Physics Letters*, **102**(11):111906, 2013. 3, 89
- [40] S. N. YI, JONG H. NA, KWAN H. LEE, ANAS F. JARJOUR, ROBERT A. TAYLOR, Y. S. PARK, T. W. KANG, S. KIM, D. H. HA, G. ANDREW, AND D. BRIGGS. **Photoluminescence properties of a single GaN nanorod with GaNAl-GaN multilayer quantum disks.** *Applied Physics Letters*, **90**(10):101901, 2007. 3, 26
- [41] MIN-KI KWON, JA-YEON KIM, IL-KYU PARK, KI SEOK KIM, GUN-YOUNG JUNG, SEONG-JU PARK, JE WON KIM, AND YONG CHUN KIM. **Enhanced emission efficiency of GaNInGaN multiple quantum well light-emitting diode with an embedded photonic crystal.** *Applied Physics Letters*, **92**(25):251110, June 2008. 3
- [42] HWA-MOK KIM, YONG-HOON CHO, HOSANG LEE, SUK IL KIM, SUNG RYONG RYU, DEUK YOUNG KIM, TAE WON KANG, AND KWAN SOO CHUNG. **High-Brightness Light Emitting Diodes Using Dislocation-Free Indium Gallium Nitride/Gallium Nitride Multiquantum-Well Nanorod Arrays.** *Nano Letters*, **4**(6):1059–1062, June 2004. 3

-
- [43] JAE-WOONG LEE, KYEONG-JU MOON, MOON-HO HAM, AND JAE-MIN MYOUNG. **Dielectrophoretic assembly of GaN nanowires for UV sensor applications.** *Solid State Communications*, **148**(5-6):194–198, November 2008. 5
 - [44] HIROTO SEKIGUCHI, KATSUMI KISHINO, AND AKIHIKO KIKUCHI. **Formation of InGaN quantum dots in regularly arranged GaN nanocolumns grown by rf-plasma-assisted molecular-beam epitaxy.** *Physica Status Solidi (C)*, **7**(10):2374–2377, October 2010. 5, 26
 - [45] CHIH-WEI HSU, ANDERS LUNDSKOG, K FREDRIK KARLSSON, URBAN FORSBERG, ERIK JANZÉN, AND PER OLOF HOLTZ. **Single excitons in InGaN quantum dots on GaN pyramid arrays.** *Nano letters*, **11**(6):2415–8, June 2011. 5, 55
 - [46] M. JETTER, V. PÉREZ-SOLÓRZANO, A. GRÖNING, H. GRÄBELDINGER, M. UBL, AND H. SCHWEIZER. **Carrier dynamics in site-controlled Ga_{1-x}In_xN quantum dots.** *Physica Status Solidi (C)*, **3**(6):2060–2064, June 2006. 5
 - [47] P. R. EDWARDS, R. W. MARTIN, I. M. WATSON, C. LIU, R. A. TAYLOR, J. H. RICE, J. H. NA, J. W. ROBINSON, AND J. D. SMITH. **Quantum dot emission from site-controlled InGaNGaN micropylramid arrays.** *Applied Physics Letters*, **85**(19):4281, 2004. 5
 - [48] TETSUYA KOUNO, KATSUMI KISHINO, KOUJI YAMANO, AND AKIHIKO KIKUCHI. **Two-dimensional light confinement in periodic InGaN/GaN nanocolumn arrays and optically pumped blue stimulated emission.** *Optics express*, **17**(22):20440–7, October 2009. 5, 61
 - [49] THEERADETCH DETCHPROHM, KAZUMASA HIRAMATSU, KENJI ITOH, AND ISAMU AKASAKI. **Relaxation Process of the Thermal Strain in the GaN/ α -Al₂O₃ Heterostructure and Determination of the Intrinsic Lattice Constants of GaN Free from the Strain.** *Japanese Journal of Applied Physics*, **31**(Part 2, No. 10B):L1454–L1456, October 1992. 7
 - [50] W. SHAN, W. WALUKIEWICZ, E. E. HALLER, B. D. LITTLE, J. J. SONG, M. D. MCCLUSKEY, N. M. JOHNSON, Z. C. FENG, M. SCHURMAN, AND R. A. STALL. **Optical properties of In_xGa_{1-x}N alloys grown by metalor-**

- ganic chemical vapor deposition.** *Journal of Applied Physics*, **84**(8):4452, October 1998. 7
- [51] M LESZCZYNSKI AND T SUSKI. **Thermal expansion of gallium nitride.** *Journal of Applied Physics*, **76**(May 2004):4909–4911, 1994. 8
- [52] M. LESZCZYNSKI, T. SUSKI, H. TEISSEYRE, P. PERLIN, I. GRZEGORY, J. JUN, S. POROWSKI, AND T. D. MOUSTAKAS. **Thermal expansion of gallium nitride.** *Journal of Applied Physics*, **76**(8):4909, 1994. 8
- [53] R. OLIVER. **Growth and characterisation of nitride nanostructures.** *Materials Science and Technology*, **18**(11):1257–1271, November 2002. 8, 43
- [54] O AMBACHER. **Growth and applications of group III-nitrides.** *Journal of Physics D: Applied Physics*, **31**:2653–2710, 1998. 8
- [55] M. LEYER, J. STELLMACH, CH. MEISSNER, M. PRISTOVSEK, AND M. KNEISL. **The critical thickness of InGaN on (0001)GaN.** *Journal of Crystal Growth*, **310**(23):4913–4915, November 2008. 9
- [56] G. D. CHEN, M. SMITH, J. Y. LIN, H. X. JIANG, SU-HUAI WEI, M. ASIF KHAN, AND C. J. SUN. **Fundamental optical transitions in GaN.** *Applied Physics Letters*, **68**(20):2784, 1996. 10
- [57] T. SHUBINA, S. IVANOV, V. JMERIK, D. SOLNYSHKOV, V. VEKSHIN, P. KOPEV, A. VASSON, J. LEYMARIE, A. KAVOKIN, H. AMANO, K. SHIMONO, A. KASIC, AND B. MONEMAR. **Mie Resonances, Infrared Emission, and the Band Gap of InN.** *Physical Review Letters*, **92**(11):117407, March 2004. 11
- [58] H. YAMASHITA, K. FUKUI, S. MISAWA, AND S. YOSHIDA. **Optical properties of AlN epitaxial thin films in the vacuum ultraviolet region.** *Journal of Applied Physics*, **50**(2):896, February 1979. 11
- [59] COLIN-N. BROUSSEAU, MATHIEU PERRIN, CARLOS SILVA, AND RICHARD LEONELLI. **Carrier recombination dynamics in In- $\{x\}$ Ga- $\{1x\}$ N/GaN multiple quantum wells.** *Physical Review B*, **82**(8):085305, August 2010. 12, 116
- [60] J. F. NYE. *Physical Properties of Crystals: Their Representation by Tensors and Matrices.* Oxford University Press, 1985. 14

-
- [61] URSULA M. E. CHRISTMAS, A. D. ANDREEV, AND D. A. FAUX. **Calculation of electric field and optical transitions in InGaNGaN quantum wells.** *Journal of Applied Physics*, **98**(7):073522, 2005. 14
 - [62] I. VURGAFTMAN AND J. R. MEYER. **Band parameters for nitrogen-containing semiconductors.** *Journal of Applied Physics*, **94**(6):3675, 2003. 15
 - [63] Y. D. JHO, J. S. YAHNG, E. OH, AND D. S. KIM. **Measurement of piezoelectric field and tunneling times in strongly biased InGaN/GaN quantum wells.** *Applied Physics Letters*, **79**(8):1130, 2001. 16
 - [64] P. LEFEBVRE, A. MOREL, M. GALLART, T. TALIERCIO, J. ALLEGRE, B. GIL, H. MATHIEU, B. DAMILANO, N. GRANDJEAN, AND J. MASSIES. **High internal electric field in a graded-width InGaN/GaN quantum well: Accurate determination by time-resolved photoluminescence spectroscopy.** *Applied Physics Letters*, **78**(9):1252, 2001. 16
 - [65] C. Y. LAI, T. M. HSU, W.-H. CHANG, K.U. TSENG, C.M. LEE, C.C. CHUO, AND J.-I. CHYI. **Direct measurement of piezoelectric field in In[0.23]Ga[0.77]N/GaN multiple quantum wells by electrotransmission spectroscopy.** *Journal of Applied Physics*, **91**(1):531, January 2002. 16, 102
 - [66] MARK J. HOLMES. *Optical Spectroscopy of Wide-bandgap Semiconductors*. PhD thesis, University of Oxford, 2011. 16, 63
 - [67] FABIO BERNARDINI, VINCENZO FIORENTINI, AND DAVID VANDERBILT. **Spontaneous polarization and piezoelectric constants of III-V nitrides.** *Physical Review B*, **56**(16):R10024–R10027, October 1997. 19
 - [68] C. R. HALL, L. DAO, K. KOIKE, S. SASA, H. H. TAN, M. INOUE, M. YANO, P. HANNAFORD, C. JAGADISH, AND J. A. DAVIS. **Recombination dynamics and screening of the internal electric field in ZnO/Zn- $\{x\}$ Mg- $\{1x\}$ O multiple quantum wells.** *Physical Review B*, **80**(23):235316, December 2009. 20, 116
 - [69] MARK J. HOLMES, YOUNG S. PARK, JAMIE H. WARNER, AND ROBERT A. TAYLOR. **Quantum confined Stark effect and corresponding lifetime reduction in a single In_xGa_{1-x}N quantum disk.** *Applied Physics Letters*, **95**(18):181910, 2009. 20, 43, 49, 76, 88, 116

-
- [70] V. KACHKANOV, K. P. O'DONNELL, S. PEREIRA, AND R. W. MARTIN. **Localization of excitation in InGaN epilayers.** *Philosophical Magazine*, **87**(13):1999–2017, May 2007. 21
- [71] S. YU. KARPOV. **Suppression of phase separation in InGaN due to elastic strain.** *MRS Internet Journal of Nitride Semiconductor Research*, **3**:Art. 16, 1998. 21
- [72] SHUJI NAKAMURA, MASAYUKI SENOH, NARUHITO IWASA, AND SHIN-ICHI NAGAHAMA. **High-Brightness InGaN Blue, Green and Yellow Light-Emitting Diodes with Quantum Well Structures.** *Japanese Journal of Applied Physics*, **34**(Part 2, No. 7A):L797–L799, July 1995. 21
- [73] S. D. LESTER, F. A. PONCE, M. G. CRAFT, AND D. A. STEIGERWALD. **High dislocation densities in high efficiency GaN-based light-emitting diodes.** *Applied Physics Letters*, **66**(10):1249, 1995. 21
- [74] H. SCHÖMIG, S. HALM, A. FORCHEL, G. BACHER, J. OFF, AND F. SCHOLZ. **Probing Individual Localization Centers in an InGaN/GaN Quantum Well.** *Physical Review Letters*, **92**(10):106802, March 2004. 22, 83, 87, 100, 104
- [75] T. M. SMEETON, M. J. KAPPERS, J. S. BARNARD, M. E. VICKERS, AND C. J. HUMPHREYS. **Electron-beam-induced strain within InGaN quantum wells: False indium cluster detection in the transmission electron microscope.** *Applied Physics Letters*, **83**(26):5419, 2003. 22
- [76] T. M. SMEETON, C. J. HUMPHREYS, J. S. BARNARD, AND M. J. KAPPERS. **The impact of electron beam damage on the detection of indium-rich localisation centres in InGaN quantum wells using transmission electron microscopy.** *Journal of Materials Science*, **41**(9):2729–2737, April 2006. 22
- [77] N. K. VAN DER LAAK, R. A. OLIVER, M. J. KAPPERS, AND C. J. HUMPHREYS. **Characterization of InGaN quantum wells with gross fluctuations in width.** *Journal of Applied Physics*, **102**(1):013513, July 2007. 22
- [78] D. M. GRAHAM, A. SOLTANI-VALA, P. DAWSON, M. J. GODFREY, T. M. SMEETON, J. S. BARNARD, M. J. KAPPERS, C. J. HUMPHREYS, AND E. J. THRUSH. **Optical and microstructural studies of InGaNGaN single-quantum-well structures.** *Journal of Applied Physics*, **97**(10):103508, April 2005. 22

-
- [79] T. J. BADCOCK, R. HAO, M. A. MORAM, P. DAWSON, M. J. KAPPERS, AND C. J. HUMPHREYS. **The effect of indium concentration on the optical properties of a-plane InGaN/GaN quantum wells grown on r-plane sapphire substrates.** *physica status solidi (a)*, **208**(7):1529–1531, July 2011. 22
- [80] YONG-HOON CHO, G. H. GAINER, A. J. FISCHER, J. J. SONG, S. KELLER, U. K. MISHRA, AND S. P. DENBAARS. **S-shaped temperature-dependent emission shift and carrier dynamics in InGaN/GaN multiple quantum wells.** *Applied Physics Letters*, **73**(10):1370, 1998. 22, 78, 81, 115, 120
- [81] SHIH-WEI FENG, YUNG-CHEN CHENG, YI-YIN CHUNG, C. C. YANG, YEN-SHENG LIN, CHEN HSU, KUNG-JENG MA, AND JEN-INN CHYI. **Impact of localized states on the recombination dynamics in InGaN/GaN quantum well structures.** *Journal of Applied Physics*, **92**(8):4441, 2002. 22, 93, 105
- [82] NICOLE K. VAN DER LAAK, RACHEL A. OLIVER, MENNO J. KAPPERS, AND COLIN J. HUMPHREYS. **Role of gross well-width fluctuations in bright, green-emitting single InGaNGaN quantum well structures.** *Applied Physics Letters*, **90**(12):121911, 2007. 23
- [83] RA ARIF, HONGPING ZHAO, YK EE, AND NELSON TANSU. **Spontaneous Emission and Characteristics of Staggered InGaN Quantum-Well Light-Emitting Diodes.** *Quantum Electronics, IEEE Journal of*, **44**(6):573–580, 2008. 24
- [84] SHAOFEI ZHANG, YUKUN LI, SAEED FATHOLOLOUMI, HIEU PHAM TRUNG NGUYEN, QI WANG, ZETIAN MI, QIMING LI, AND GEORGE T. WANG. **On the efficiency droop of top-down etched InGaNGaN nanorod light emitting diodes under optical pumping.** *AIP Advances*, **3**(8):082103, August 2013. 25, 26
- [85] L. W. TU, C. L. HSIAO, T. W. CHI, I. LO, AND K. Y. HSIEH. **Self-assembled vertical GaN nanorods grown by molecular-beam epitaxy.** *Applied Physics Letters*, **82**(10):1601, 2003. 26
- [86] M YOSHIKAWA, A KIKUCHI, AND M MORI. **Growth of Self-Organized GaN Nanostructures on 1 (0001) by RF-Radical Source Molecular Beam Epitaxy.** *Japanese Journal of Applied Physics*, **36**:459–462, 1997. 26, 61

-
- [87] KATSUMI KISHINO, HIROTO SEKIGUCHI, AND AKIHIKO KIKUCHI. **Improved Ti-mask selective-area growth (SAG) by rf-plasma-assisted molecular beam epitaxy demonstrating extremely uniform GaN nanocolumn arrays.** *Journal of Crystal Growth*, **311**(7):2063–2068, March 2009. 26, 61
- [88] S YASIN. **Sub-wavelength Al mask apertures for addressing individual InGaN quantum dots.** *Microelectronic Engineering*, **73-74**(null):762–766, June 2004. 28
- [89] JAMES W. ROBINSON, JAMES H. RICE, ANAS JARJOUR, JONATHAN D. SMITH, ROBERT A. TAYLOR, RACHEL A. OLIVER, G. ANDREW D. BRIGGS, MENNO J. KAPPERS, COLIN J. HUMPHREYS, AND YASUHIKO ARAKAWA. **Time-resolved dynamics in single InGaN quantum dots.** *Applied Physics Letters*, **83**(13):2674, September 2003. 28
- [90] STEPHEN Y. CHOU AND PETER R. KRAUSS. **Imprint lithography with sub-10 nm feature size and high throughput.** *Microelectronic Engineering*, **35**(1-4):237–240, February 1997. 29
- [91] MINGTAO LI, JIAN WANG, LEI ZHUANG, AND STEPHEN Y. CHOU. **Fabrication of circular optical structures with a 20 nm minimum feature size using nanoimprint lithography.** *Applied Physics Letters*, **76**(6):673, 2000. 29
- [92] SY CHOU. **Nanoimprint lithography.** *Journal of Vacuum Science & Technology B*, **14**(June):4129–4133, 1996. 29
- [93] MICROCHEM CORP. **NANO PMMA and Copolymer data sheet.** Technical report, 2001. 37
- [94] COHERENT. **Verdi V-8/V-10 Diode Pumped Lasers, Operator’s Manual.** 43
- [95] CLAUDE RULLIERE. *Femtosecond Laser Pulses: Principles and Experiments.* Springer, 2005. 43
- [96] CK SUN, S KELLER, AND G WANG. **Radiative recombination lifetime measurements of InGaN single quantum well.** *Applied Physics Letters*, **69**:1936–1938, 1996. 43
- [97] EUGENE HECHT. *Optics.* Addison-Wesley Longman, Incorporated, 2002. 44, 56

-
- [98] ANAS F. JARJOUR, ALEX M. GREEN, TIM J. PARKER, ROBERT A. TAYLOR, RACHEL A. OLIVER, G. ANDREW D. BRIGGS, MENNO J. KAPPERS, COLIN J. HUMPHREYS, ROBERT W. MARTIN, AND IAN M. WATSON. **Two-photon absorption from single InGaN/GaN quantum dots.** *Physica E: Low-dimensional Systems and Nanostructures*, **32**(1-2):119–122, May 2006. 45, 85
- [99] ANAS JARJOUR, RACHEL OLIVER, ABBES TAHRAOUI, MENNO KAPPERS, COLIN HUMPHREYS, AND ROBERT TAYLOR. **Control of the Oscillator Strength of the Exciton in a Single InGaN-GaN Quantum Dot.** *Physical Review Letters*, **99**(19):197403, November 2007. 45, 101
- [100] EDMUND OPTICS. **Edmund Optics Mitutoyo Infinity Corrected Long Working Distance Objectives Technical Specifications**, 2013. 49
- [101] MARK J. HOLMES, YOUNG S. PARK, XU WANG, CHRISTOPHER C. S. CHAN, BENJAMIN P. L. REID, HEEDAE KIM, ROBERT A. TAYLOR, JAMIE H. WARNER, AND JUN LUO. **Optical studies on a single GaN nanocolumn containing a single In_xGa_{1-x}N quantum disk.** *Applied Physics Letters*, **98**(25):251908, June 2011. 49, 62, 88, 89
- [102] W. DEMTRÖDER. *Laser Spectroscopy: Basic Concepts and Instrumentation*. Springer-Verlag, 2001. 52
- [103] KWAN H. LEE, ALEX M. GREEN, ROBERT A. TAYLOR, DAVID N. SHARP, JAN SCRIMGEOUR, OLIVIA M. ROCHE, JONG H. NA, ANAS F. JARJOUR, ANDREW J. TURBERFIELD, FREDERIC S. F. BROSSARD, DAVID A. WILLIAMS, AND G. ANDREW D. BRIGGS. **Registration of single quantum dots using cryogenic laser photolithography.** *Applied Physics Letters*, **88**(19):193106, May 2006. 52
- [104] SANIYA DESHPANDE, JUNSEOK HEO, AYAN DAS, AND PALLAB BHATTACHARYA. **Electrically driven polarized single-photon emission from an InGaN quantum dot in a GaN nanowire.** *Nature communications*, **4**:1675, January 2013. 55
- [105] R. BARDOUX, T. GUILLET, B. GIL, P. LEFEBVRE, T. BRETAGNON, T. TALIERCIO, S. ROUSSET, AND F. SEMOND. **Polarized emission from GaN/AlN quantum dots: Single-dot spectroscopy and symmetry-based theory.** *Physical Review B*, **77**(23):235315, June 2008. 55

-
- [106] K.F. KARLSSON, S. AMLOY, Y.T. CHEN, K.H. CHEN, H.C. HSU, C.L. HSIAO, L.C. CHEN, AND P.O. HOLTZ. **Polarized emission and excitonic fine structure energies of InGaN quantum dots.** *Physica B: Condensed Matter*, **407**(10):1553–1555, May 2012. 55
- [107] V D KULAKOVSKII, G BACHER, R WEIGAND, T KÜMMELL, AND A FORCHEL. **Fine Structure of Biexciton Emission in Symmetric and Asymmetric CdSe /ZnSe Single Quantum Dots.** *Physical Review Letters*, **82**(8):1780, 1999. 55
- [108] S. AMLOY, K. F. KARLSSON, T. G. ANDERSSON, AND P. O. HOLTZ. **On the polarized emission from exciton complexes in GaN quantum dots.** *Applied Physics Letters*, **100**(2):021901, 2012. 55
- [109] AZZAM. *Principles and Applications of Optical Polarimetry.* Wiley-Blackwell, 1988. 58
- [110] MAX BORN AND EMIL WOLF. *Principles of Optics: Electromagnetic Theory of Propagation, Interference and Diffraction of Light.* Cambridge University Press, 1999. 58
- [111] BECKER AND HECKL. *High Speed PMT Detector Head for Photon Counting specifications.* 59
- [112] M.A. SANCHEZ-GARCIA, E. CALLEJA, E. MONROY, F.J. SANCHEZ, F. CALLE, E. MUÑOZ, AND R. BERESFORD. **The effect of the III/V ratio and substrate temperature on the morphology and properties of GaN- and AlN-layers grown by molecular beam epitaxy on Si(1 1 1).** *Journal of Crystal Growth*, **183**(1-2):23–30, January 1998. 61
- [113] SHUSUKE ISHIZAWA, KATSUMI KISHINO, RYUICHI ARAKI, AKIHIKO KIKUCHI, AND SHUICHI SUGIMOTO. **Optically Pumped Green (530560 nm) Stimulated Emissions from InGaN/GaN Multiple-Quantum-Well Triangular-Lattice Nanocolumn Arrays.** *Applied Physics Express*, **4**(5):055001, April 2011. 62
- [114] KOICHI OKAMOTO, AKIO KANETA, YOICHI KAWAKAMI, SHIGEO FUJITA, JUNGKWON CHOI, MASAHIDE TERAZIMA, AND TAKASHI MUKAI. **Confocal microphotoluminescence of InGaN-based light-emitting diodes.** *Journal of Applied Physics*, **98**(6):064503, 2005. 62, 70

-
- [115] CHENG-YIN WANG, LIANG-YI CHEN, CHENG-PIN CHEN, YUN-WEI CHENG, MIN-YUNG KE, MIN-YANN HSIEH, HAN-MING WU, LUNG-HAN PENG, AND JIANJANG HUANG. **GaN nanorod light emitting diode arrays with a nearly constant electroluminescent peak wavelength.** *Optics express*, **16**(14):10549–56, July 2008. 62
- [116] YR WU, CHINGHUA CHIU, AND CY CHANG. **Size-dependent strain relaxation and optical characteristics of InGaN/GaN nanorod LEDs.** *Selected Topics in Quantum Electronics*, **15**(4):1226–1233, 2009. 62, 99
- [117] TAO-HUNG HSUEH, HUNG-WEN HUANG, CHIH-CHIANG KAO, YA-HSIEN CHANG, MIAO-CHIA OU-YANG, HAO-CHUNG KUO, AND SHING-CHUNG WANG. **Characterization of InGaN/GaN Multiple Quantum Well Nanorods Fabricated by Plasma Etching with Self-Assembled Nickel Metal Nanomasks.** *Japanese Journal of Applied Physics*, **44**(4B):2661–2663, April 2005. 62
- [118] MJ HOLMES, YS PARK, AND XU WANG. **Optical studies of GaN nanocolumns containing InGaN quantum disks and the effect of strain relaxation on the carrier distribution.** *Physica Status Solidi (C)*, **714**(3):712–714, 2012. 62, 65, 99
- [119] HORNG-SHYANG CHEN, DONG-MING YEH, YEN-CHENG LU, CHENG-YEN CHEN, CHI-FENG HUANG, TSUNG-YI TANG, C C YANG, CEN-SHAWN WU, AND CHII-DONG CHEN. **Strain relaxation and quantum confinement in InGaN/GaN nanoposts.** *Nanotechnology*, **17**(5):1454–1458, March 2006. 62
- [120] MARK J HOLMES, YOUNG S PARK, XU WANG, CHRISTOPHER C S CHAN, ANAS F JARJOUR, JUN LUO, JAMIE H WARNER, H A R EL-ELLA, R A OLIVER, AND ROBERT A TAYLOR. **Optical Studies on InGaN quantum disks.** *Proceedings of SPIE*, **1**:7937, 2011. 63, 106
- [121] M. NIEBELSCHÜTZ, V. CIMALLA, O. AMBACHER, T. MACHLEIDT, K.-H. FRANKE, J. RISTIC, J. GRANDAL, M. A. SÁNCHEZ-GARCÍA, AND E. CALLEJA. **Space charged region in GaN and InN nanocolumns investigated by atomic force microscopy.** *Physica Status Solidi (C)*, **5**(6):1609–1611, May 2008. 64

-
- [122] L. POLENTA, M. ROSSI, A. CAVALLINI, R. CALARCO, M. MARSO, R. MEIJERS, T. RICHTER, T. STOICA, AND H. LÜTH. **Investigation on Localized States in GaN Nanowires.** *ACS Nano*, **2**(2):287–292, 2008. 64
- [123] RAFFAELLA CALARCO, MICHEL MARSO, THOMAS RICHTER, ALI I. AYKANAT, RALPH MEIJERS, TOMA STOICA, AND HANS LU. **Size-dependent Photoconductivity in MBE-Grown GaN-Nanowires.** *Nano letters*, **5**:981, 2005. 64
- [124] I. MAHBOOB, T. VEAL, C. McCONVILLE, H. LU, AND W. SCHAFF. **Intrinsic Electron Accumulation at Clean InN Surfaces.** *Physical Review Letters*, **92**(3):036804, January 2004. 64
- [125] T. D. VEAL, P. H. JEFFERSON, L. F. J. PIPER, C. F. McCONVILLE, T. B. JOYCE, P. R. CHALKER, L. CONSIDINE, HAI LU, AND W. J. SCHAFF. **Transition from electron accumulation to depletion at InGaN surfaces.** *Applied Physics Letters*, **89**(20):202110, November 2006. 64, 105
- [126] C. RIVERA, U. JAHN, T. FLISSIKOWSKI, J. PAU, E. MUÑOZ, AND H. T. GRAHN. **Strain-confinement mechanism in mesoscopic quantum disks based on piezoelectric materials.** *Physical Review B*, **75**(4):045316, January 2007. 65
- [127] CHRISTOPH BÖCKLIN, RATKO G. VEPREK, SEBASTIAN STEIGER, AND BERND WITZIGMANN. **Computational study of an InGaN/GaN nanocolumn light-emitting diode.** *Physical Review B*, **81**(15):155306, April 2010. 65, 105, 106
- [128] X. A. CAO, H. CHO, S. J. PEARTON, G. T. DANG, A. P. ZHANG, F. REN, R. J. SHUL, L. ZHANG, R. HICKMAN, AND J. M. VAN HOVE. **Depth and thermal stability of dry etch damage in GaN Schottky diodes.** *Applied Physics Letters*, **75**(2):232, 1999. 67
- [129] JAMES W. ROBINSON, JAMES H. RICE, KWAN H. LEE, JONG H. NA, ROBERT A. TAYLOR, DAVID G. HASKO, RACHEL A. OLIVER, MENNO J. KAPPERS, COLIN J. HUMPHREYS, AND G. ANDREW D. BRIGGS. **Quantum-confined Stark effect in a single InGaN quantum dot under a lateral electric field.** *Applied Physics Letters*, **86**(21):213103, 2005. 72, 74
- [130] E. KUOKSTIS, J. W. YANG, G. SIMIN, M. ASIF KHAN, R. GASKA, AND M. S. SHUR. **Two mechanisms of blueshift of edge emission in InGaN-based**

- epilayers and multiple quantum wells. *Applied Physics Letters*, **80**(6):977, 2002. 72, 73, 95, 99
- [131] P W FRY, I E ITSKEVICH, D J MOWBRAY, M S SKOLNICK, J J FINLEY, J A BARKER, E P O'REILLY, L R WILSON, I A LARKIN, P A MAKSYM, M HOPKINSON, M AL-KHAFAJI, J P DAVID, A G CULLIS, G HILL, AND J C CLARK. **Inverted electron-hole alignment in InAs-GaAs self-assembled quantum dots.** *Physical review letters*, **84**(4):733–6, January 2000. 74
- [132] YD ZHUANG AND SZYMON LIS. **Optical properties of GaN nanorods containing a single or multiple InGaN quantum wells.** *Japanese Journal of applied physics*, **52**:1–5, 2013. 82
- [133] Y KAWAKAMI, A KANETA, AND L SU. **Optical properties of InGaN/GaN nanopillars fabricated by postgrowth chemically assisted ion beam etching.** *Journal of Applied Physics*, **107**:023522, 2010. 82
- [134] H. GOTOH, T. AKASAKA, T. TAWARA, Y. KOBAYASHI, T. MAKIMOTO, AND H. NAKANO. **Detecting spatially localized excitons in InGaN quantum well structures with a micro-photoluminescence technique.** *Solid State Communications*, **138**(12):590–593, June 2006. 83
- [135] R. W. MARTIN, P. R. EDWARDS, R. A. TAYLOR, J. H. RICE, J. H. NA, J. W. ROBINSON, J. D. SMITH, C. LIU, AND I. M. WATSON. **Luminescence properties of isolated InGaN/GaN quantum dots.** *physica status solidi (a)*, **202**(3):372–376, February 2005. 83
- [136] J. KVIETKOVA, L. SIOZADE, P. DISSEIX, A. VASSON, J. LEYMARIE, B. DAMILANO, N. GRANDJEAN, AND J. MASSIES. **Optical Investigations and Absorption Coefficient Determination of InGaN/GaN Quantum Wells.** *Physica Status Solidi (a)*, **190**(1):135–140, March 2002. 93
- [137] SHIGEFUSA CHICHIBU, TAKAYUKI SOTA, KAZUMI WADA, AND SHUJI NAKAMURA. **Exciton localization in InGaN quantum well devices.** *Journal of Vacuum Science & Technology B*, **16**:2204–2214, 1998. 96, 104
- [138] C. J. LEWINS, D. W. E. ALLSOPP, P. A. SHIELDS, X. GAO, B. HUMPHREYS, AND W. N. WANG. **Light Extracting Properties of Buried Photonic Quasi-Crystal Slabs in InGaN/GaN LEDs.** *Journal of Display Technology*, **9**(5):333–338, May 2013. 96

-
- [139] D. TURCHINOVICH, P. UHD JEPSEN, B. MONOZON, M. KOCH, S. LAHMANN, U. ROSSOW, AND A. HANGLEITER. **Ultrafast polarization dynamics in bi-ased quantum wells under strong femtosecond optical excitation.** *Physical Review B*, **68**(24):241307, December 2003. 97, 99
- [140] X.H ZHANG, W LIU, AND S.J CHUA. **Optical transitions in InGaN/GaN quantum wells: effects of the piezoelectric field.** *Journal of Crystal Growth*, **268**(3-4):521–526, August 2004. 99
- [141] PEICHEN YU, C. H. CHIU, YUH-RENN WU, H. H. YEN, J. R. CHEN, C. C. KAO, HAN-WEI YANG, H. C. KUO, T. C. LU, W. Y. YEH, AND S. C. WANG. **Strain relaxation induced microphotoluminescence characteristics of a single InGaN-based nanopillar fabricated by focused ion beam milling.** *Applied Physics Letters*, **93**(8):081110, 2008. 99
- [142] M. LEROUX, N. GRANDJEAN, M. LAÜGT, J. MASSIES, B. GIL, P. LEFEBVRE, AND P. BIGENWALD. **Quantum confined Stark effect due to built-in internal polarization fields in (Al,Ga)N/GaN quantum wells.** *Physical Review B*, **58**(20):R13371–R13374, November 1998. 102
- [143] K. P. O'DONNELL, R. W. MARTIN, AND P. MIDDLETON. **Origin of Luminescence from InGaN Diodes.** *Physical Review Letters*, **82**(1):237–240, January 1999. 104
- [144] HAITHAM A. R. EL-ELLA, DANIEL P. COLLINS, MENNO J. KAPPERS, ROBERT A. TAYLOR, AND RACHEL A. OLIVER. **Optical cavity efficacy and lasing of focused ion beam milled GaN/InGaN micropillars.** *Journal of Applied Physics*, **112**(11):113516, 2012. 106
- [145] LEI ZHANG, CHU-HSIANG TENG, TYLER A. HILL, LEUNG-KWAY LEE, PEI-CHENG KU, AND HUI DENG. **Single photon emission from site-controlled InGaN/GaN quantum dots.** *Applied Physics Letters*, **103**(19):192114, 2013. 106
- [146] JUN HO SON AND JONG-LAM LEE. **Strain engineering for the solution of efficiency droop in InGaN/GaN light-emitting diodes.** *Optics express*, **18**(6):5466–71, March 2010. 108
- [147] J S SPECK, S F CHICHIBU, AND GUEST EDITORS. **Nonpolar and Semipolar Group III Materials.** *MRS Bulletin*, **34**(05):304, 2009. 108

-
- [148] S. SRINIVASAN, M. STEVENS, F. A. PONCE, H. OMIYA, AND T. MUKAI. **Carrier dynamics and electrostatic potential variation in InGaN quantum wells grown on {1122} GaN pyramidal planes.** *Applied Physics Letters*, **89**(23):231908, 2006. 108
- [149] ANDRÉ STRITTMATTER, JOHN E. NORTHRUP, NOBLE M. JOHNSON, MIKHAIL V. KISIN, PHILIPPE SPIBERG, HUSSEIN EL-GHOROURY, ALEXANDER USIKOV, AND ALEXANDER SYRKIN. **Semi-polar nitride surfaces and heterostructures.** *Physica Status Solidi (B)*, **248**(3):561–573, March 2011. 108
- [150] HITOSHI SATO, ANURAG TYAGI, HONG ZHONG, NATALIE FELLOWS, ROY B. CHUNG, MAKOTO SAITO, KENJI FUJITO, JAMES S. SPECK, STEVEN P. DENBAARS, AND SHUJI NAKAMURA. **High power and high efficiency green light emitting diode on free-standing semipolar (112) bulk GaN substrate.** *physica status solidi (RRL) Rapid Research Letters*, **1**(4):162–164, July 2007. 108
- [151] G. HUBBARD, S.J. ABBOTT, Q. CHEN, D.W.E. ALLSOPP, W.N. WANG, C.R. BOWEN, R. STEVENS, A. ŠATKA, D. HAŠKO, F. UHEREK, AND J. KOVÁČ. **Wafer-scale transfer of nanoimprinted patterns into silicon substrates.** *Physica E: Low-dimensional Systems and Nanostructures*, **41**(6):1118–1121, May 2009. 109
- [152] CHAOWANG LIU, PHILIP A. SHIELDS, QIN CHEN, DUNCAN W. E. ALLSOPP, WANG NANG WANG, CHRIS R. BOWEN, T.-L. PHAN, AND DAVID CHERNS. **Variations in mechanisms of selective area growth of GaN on nano-patterned substrates by MOVPE.** *Physica Status Solidi (C)*, **7**(1):32–35, January 2010. 109, 122
- [153] HONGBO YU, L. K. LEE, TAEIL JUNG, AND P. C. KU. **Photoluminescence study of semipolar {1011} InGaNGaN multiple quantum wells grown by selective area epitaxy.** *Applied Physics Letters*, **90**(14):141906, 2007. 111
- [154] THOMAS WUNDERER, PETER BRUCKNER, BARBARA NEUBERT, FERDINAND SCHOLZ, MARTIN FENEBERG, FRANK LIPSKI, MARTIN SCHIRRA, AND KLAUS THONKE. **Bright semipolar GaInNGaN blue light emitting diode on side facets of selectively grown GaN stripes.** *Applied Physics Letters*, **89**(4):041121, 2006. 111

-
- [155] LETHY KRISHNAN JAGADAMMA. *Characterisation of nanostructured light emitters*. PhD thesis, University of Strathclyde, 2012. 112, 113
- [156] CHAOWANG LIU, ALEXANDER ŠATKA, LETHY KRISHNAN JAGADAMMA, PAUL R. EDWARDS, DUNCAN ALLSOPP, ROBERT W. MARTIN, PHILIP SHIELDS, JAROSLAV KOVAC, FRANTISEK UHEREK, AND WANG WANG. **Light Emission from InGaN Quantum Wells Grown on the Facets of Closely Spaced GaN Nano-Pyramids Formed by Nano-Imprinting**. *Applied Physics Express*, **2**(12):121002, December 2009. 113, 122
- [157] A. MOREL, P. LEFEBVRE, S. KALLIAKOS, T. TALIERCIO, T. BRETAGNON, AND B. GIL. **Donor-acceptor-like behavior of electron-hole pair recombinations in low-dimensional (Ga,In)N/GaN systems**. *Physical Review B*, **68**(4):045331, July 2003. 116
- [158] M POPHRISTIC, F H LONG, C TRAN, I T FERGUSON, AND R F KARLICEK. **Time-resolved photoluminescence measurements of quantum dots in InGaN multiple quantum wells and light-emitting diodes** Time-resolved photoluminescence measurements of quantum dots in InGaN multiple quantum wells and light-emitting diodes. *Journal of Applied Physics*, **86**:1114, 1999. 116
- [159] TAKAMASA KURODA, ATSUSHI TACKEUCHI, AND TAKAYUKI SOTA. **Luminescence energy shift and carrier lifetime change dependence on carrier density in In[sub 0.12]Ga[sub 0.88]N/In[sub 0.03]Ga[sub 0.97]N quantum wells**. *Applied Physics Letters*, **76**(25):3753, 2000. 116
- [160] GUAN SUN, GUIBAO XU, YUJIE J. DING, HONGPING ZHAO, GUANGYU LIU, JING ZHANG, AND NELSON TANSU. **Investigation of fast and slow decays in InGaN/GaN quantum wells**. *Applied Physics Letters*, **99**(8):081104, 2011. 116, 120
- [161] PETR G ELISEEV, PIOTR PERLIN, JINHYUN LEE, AND MAREK OSISKI. **Blue temperature-induced shift and band-tail emission in InGaN-based light sources**. *Applied Physics Letters*, **569**:5–8, 1997. 120