

Microstructural Characterisation of Novel Nitride Nanostructures using Electron Microscopy

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Abstract

Novel semiconductor nanostructures possess a range of notable properties that have the potential to be harnessed in the next generation of optical devices. Electron microscopy is uniquely suited to characterising the complex microstructure, the results of which may be related to the growth conditions and optical properties. This thesis investigates three such novel materials: (1) GaN/InGaN core/shell nanowires, (2) n-GaN/InGaN/p-GaN core/multi-shell microrods and (3) Zn₃N₂ nanoparticles, all of which were grown at Sharp Laboratories of Europe.

GaN nanowires were grown by a Ni-catalysed VLS process and were characterised by various techniques before and after InGaN shells were deposited by MOCVD. The majority of the core wires were found to have the expected wurtzite structure and completely defect free – reflected in the strong strain-free photoluminescence peak –with *a*- and *m*- axis orientations identified with shadow imaging. A small component, <5%, were found to have the cubic zinc-blende phase and a high density of planar faults running the length of the wires. The deposited shells were highly polycrystalline, partially attributed to a layer of silicon at the core shell interface identified through FIB lift-out of cross section samples, and accordingly the PL was very broad likely due to recombination at defects and grain boundaries. A high throughput method of identifying the core size indirectly via the catalyst particle EDX signal is described which may be used to link the shell microstructure to core size in further studies.

An n-GaN/InGaN/p-GaN shell structure was deposited by MOCVD on the side walls of microrods etched from *c*-axis GaN film on sapphire, which offers the possibility of achieving non-polar junctions without the issues due to non-uniformity found in nanowires. Threading dislocations within the core related to the initial growth on sapphire were shown to be confined to this region, therefore avoiding any harmful effect on the junction microstructure. The shell defect density showed a surprising relationship to core size with the smaller diameter rods having a high density of unusual ‘flag’ defects in the junction region whereas the larger diameter sample shells appeared largely defect free, suggesting the geometry of the etched core has an impact on the strain in the shell layers. The structure of unusual ‘flag’ defects in the *m*-plane junctions was characterised via diffraction contrast TEM, weak beam and atomic resolution ADF STEM and were shown to consist of a basal plane stacking faults meeting a perfect or partial dislocation loop on a pyramidal plane, the latter likely gliding in to resolve residual strain due to the fault formed during growth.

Zn₃N₂ has the required bandgap energy to be utilised as a phosphor with the additional advantage over conventional materials of its constituent elements not being toxic or scarce. The first successful synthesis of Zn₃N₂ nanoparticles appropriate to this application was confirmed via SAD, EDX and HRTEM, with software developed to fit experimental polycrystalline diffraction patterns to simulated components suggesting a maximum Zn₃N₂ composition of ~30%. There was an apparent decrease in crystallinity with decreasing particle size evidenced in radial distribution function studies with the smallest particles appearing completely amorphous in 80kV HRTEM images. A rapid change in the particles under the electron beam was observed, characterised by growth of large grains of Zn₃N₂ and ZnO which increased with increasing acceleration voltage suggesting knock-on effects driving the change. PL data was consistent with the bandgap of Zn₃N₂ blue shifted from 1.1eV to around 1.8eV, confirming the potential of the material for application as a phosphor.

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List of Abbreviations

ADF	Annular Dark Field
BF	Bright Field
BSF	Basal Stacking Fault
CBED	Convergent Beam Electron Diffraction
CS	Core Shell
DF	Dark Field
DP	Diffraction Pattern
ECR	Electron Cyclotron Resonance
EDX	Energy Dispersive X-ray Spectroscopy
EELS	Electron Energy Loss Spectroscopy
EQE	External Quantum Efficiency
FFT	Fast Fourier Transform
FIB	Focussed Ion Beam
FWHM	Full Width Half Maximum
GaN	Gallium Nitride
HAADF	High Angle Annular Dark Field
HRTEM	High Resolution Transmission Electron Microscopy
III-N	Three Nitride
InGaN	Indium Gallium Nitride
IQE	Internal Quantum Efficiency
LED	Light Emitting Diode
MOCVD	Metalorganic Chemical Vapour Deposition
NW	Nanowire
PL	Photoluminescence
PLA	Pulsed Laser Ablation
QCSE	Quantum Confined Stark Effect
RDF	Radial Distribution Function
RMS	Route Mean Squared
ROI	Region of Interest

SAD	Selected Area Diffraction
SEM	Scanning Electron Microscopy
SLE	Sharp Laboratories of Europe
STEM	Scanning Transmission Electron Microscopy
TEM	Transmission Electron Microscopy
VLS	Vapour-Liquid-Solid
VSS	Vapour-Solid-Solid
WPOA	Weak Phase Object Approximation
XRD	X-ray Diffraction
ZB	Zinc Blende
Zn(NH₂)₂	Zinc Amide
Zn₃N₂	Zinc Nitride
ZnO	Zinc Oxide

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Chapter 1

Introduction and Research Objectives

1.1 The Wider Motivations

There is a wide recognition that a substantial change in the global approach to energy policy is required as a matter of urgency. The reasons are threefold: firstly, even optimistic predictions expect peaking of oil production to occur within thirty years [5], meaning cheap oil and gas could run out within our lifetime. The second is the issue of security of supply, with many countries reliant on a few which control the majority of fossil fuel reserves [6]. The final factor is the growing acceptance that the greenhouse gases produced in the burning of fossil fuels are changing the climate, with many models projecting that continued energy production at the current level is likely to bring changes in the global temperature associated with catastrophic effects [7].

The precise strategy required is much debated but it must be a broad approach, addressing energy production and consumption. The following work is broadly motivated by a need to improve perhaps the most wasteful example of the latter – lighting.

Electric lighting consumes 19% of total global energy production and uses as much energy as that produced by all gas-fired generation – greater than 2200 TWh/year. [8] This equates to greenhouse gas emissions of 1900 megatonnes of CO₂ per year and estimates of artificial lighting demand project an increase between 80-300% by 2030, meaning emissions from lighting will soon overtake that from all of the world's cars [9]. Not only does lighting consume a vast amount of energy but it is also incredibly inefficient with the dominant technology still incandescent bulbs with an energy conversion to visible light of just 5%. While 'energy-efficient' compact fluorescents are marginally better at 20%, they still compare extremely poorly to that of other household device components such as electric heaters and motors (70 and 90% respectively). It is this striking combination of rapidly increasing energy consumption and poor efficiency that means that there is probably greater potential for energy savings in this area than any other, providing the broader motivation for the following work.

1.2 Background

This project aims to make progress on this front by using electron microscopy to understand the microstructure of novel semiconductor nanomaterials, the properties of which make them attractive for use in LEDs. The following work therefore sits at a point in which three important areas of technological development of the last century overlap.

1.2.1 Solid state lighting

An LED harnesses the phenomenon of electroluminescence – first described in 1907 [10] – and consists of a junction between two classes of semiconductor material, an electron carrying n-type layer and a hole carrying p-type layer. When a forward voltage is applied, the recombination of

these charge carriers across the junction may result in radiative emission with wavelength related to the characteristic energy bandgap of the semiconductor or non-radiative emission via mechanisms involving interaction with defects, surface states and interaction of the lattice [11]. LED device design seeks to promote the former and reduce the latter and has advanced rapidly since the first true LED was made in 1962 at General Electric [12]. New colours became available via the development of the GaAlInP system by Toshiba [13] and HP [14] and, with particular relevance to this project, the pioneering work of Shuji Nakamura at Nichia in the development of the GaInN system allowing for the fabrication of blue LEDs [15]. Nakamura went on to demonstrate the feasibility of semiconductor-derived white light generation [16] using their InGaN blue chip to pump a yellow phosphor and advanced the potential application of LEDs beyond that of indicators to a realistic alternative lighting technology[17] [18].

Despite progress in III-nitride blue pump efficiency and adapting phosphor technologies resulting in efficacy values in the range 100-120 lm/W for cool white and 80-100 lm/W for warm white light [18], there are still a number of sticking points in the ongoing development of white light sources for illumination. Although these efficiency values are impressive, they only apply to relatively low operating currents and temperatures whereas at more realistic operation values they rapidly decrease [19]. The efficiency loss is the cumulative effect of a number of loss channels including the phosphor, light extraction from the package and effects reducing the internal quantum efficiency (IQE) of the III-nitride blue pump itself [20]. A number of groups have recognised the possibility of making progress on all three of these problem areas by utilising the potential of another rapidly developing field of research – nanotechnology.

1.2.2 Nanotechnology

Three years before the first true LED was produced at General Electric, Richard Feynman gave his often-cited talk, 'There's plenty of room at the bottom', in which he described 'a new field of physics' aimed at harnessing matter at progressively smaller length scales and foresaw many of the

technological developments in this area with striking accuracy [21]. This new field, first termed nanotechnology by Norio Taniguchi [22] and later defined as the manipulation of matter with at least one dimension sized from 1 to 100 nanometres, has had no larger influence than that on the transformation of semiconductor devices. Initially driven by the increasing miniaturisation of microelectronics[23], semiconductor nanostructures were later recognised to offer benefits across a wide range of technologies due to novel properties such as quantum confinement, allowing bandgap tuning [24], mechanical and thermal stability due to the surface/volume ratio [25] and possible quantised electrical conductance leading to high carrier mobility[26]. Many research groups are now using careful control of the size, shape and composition of semiconductor nanostructures, as Feynman suggested, to tailor these properties in order to tackle the ongoing issues of LED efficiency. To illustrate the potential of these materials in terms of the three loss channels noted above, specific examples are: the use of nanoparticles in place of conventional phosphors with the bandgap tuneable by their size to improve conversion efficiency; enhancing light extraction efficiency by employing nanostructures which have an increased surface area [27]; and one method of increasing IQE of the III-nitride pump is to use nanowires which may be grown dislocation free and therefore have a reduced non-radiative recombination channel.

1.2.3 Electron microscopy

Feynman also acknowledged in his talk, that the electron microscope, first constructed by Knoll and Ruska in 1931[28], was the tool necessary to observe this new field at the nanoscale but also recognised that in its existing form, it did not have the resolution necessary to image individual atoms. This led him to question ‘why must the lenses be axially symmetrical?’, echoing the idea originally proposed by Scherzer in 1947 [29] of the possibility of correcting for the aberrations inherent to such lenses. Aberration corrected electron microscopy has indeed since allowed routine imaging on the atomic scale, facilitating the careful control of size, shape and composition of nanomaterials described above.

Nanomaterials by definition have dimensional limits in 1D, 2D or 3D and it is because of these limits, and that they are therefore electron transparent in at least one direction, that the TEM is so suited to observing them. All of the processes outlined in the definition of nanotechnology – ‘involving imaging, measuring, modelling and manipulating matter at this length scale’[30] – may be achieved with one of the many branches of electron microscopy, several of which are utilised in the following work to probe the properties of novel nanomaterials and assess their potential use in the next generation of optical devices.

1.3 Research Objectives

The broad aim of this project is to make use of several electron microscopy techniques to explore the links between the growth, microstructure and optical properties of GaN/InGaN core/shell nanowires, n-GaN/InGaN/p-GaN core/multi-shell microrods and Zn₃N₂ nanoparticles. The materials have been grown at Sharp Laboratories of Europe (SLE) where their optical properties have also been investigated and these results will be related to the electron microscopy characterisation work described in this thesis. Within this broad aim, several specific questions are considered, including:

- i. How does the GaN nanowire core size and crystallography impact upon the morphology of the deposited InGaN shell;
- ii. How can the core sizes of individual core/shell nanowires be straightforwardly determined to allow question i to be studied;
- iii. Are the misfit dislocations associated with the initial growth of the c-axis GaN, comprising the GaN microrod cores, confined to this region or do they reach the active area within the shells;
- iv. What is the density and character of unusual defects found in the non-polar junctions deposited on the etched core/shell microrods;
- v. Can the synthesis of zinc nitride nanoparticles be successfully confirmed;

- vi. What is the quantity of impurities and degree of crystallinity within the zinc nitride nanoparticle sample and how does this vary with size and use of capping agent;
- vii. What is the nature of the rapid change under the electron beam observed in these nanoparticles;
- viii. Finally, relating to all three of the materials studied: how does the observed microstructure relate to the results of optical studies carried out at SLE?

The literature review of the following chapter will summarise existing reports of work in this field to place these specific questions in context.

Chapter 2

A Review of the Literature

2.1 Introduction

The following is a summary of the reports in the literature of growth and characterisation of semiconductor nanomaterials relevant to those investigated in this thesis, namely GaN nanowires, GaN/InGaN core/shell wires, n-GaN/InGaN/p-GaN core/multi-shell microrods and zinc nitride nanoparticles. An overview of nitride semiconductors is given, summarising the wealth of information available on the III-nitrides and the comparatively scarce reports on zinc nitride. Section 3 contains a summary of the various types of extended defects found in these semiconductors to provide a reference for the microstructural characterisation work, particularly of Chapters 4 and 6. The remainder of this chapter focuses on reports of the specific materials studied in this thesis including: an outline of the advantages over conventional semiconductor materials for application in

optoelectronic devices; description of the various growth methods and their relationship to the morphology observed; and a summary of the characterisation of the microstructure with a focus on electron microscopy in particular.

2.2 Nitride Semiconductors

2.2.1 The III-nitrides

In the years since Nakamura first demonstrated high brightness blue InGaN LEDs suitable for commercial applications [15], the III-nitride material system has become the dominant technology in solid state lighting development. GaN was not a new material first being described in 1907 [31], with the crystal structure analysed in 1937 and the first growth reported in 1969 [32] but several technological developments were required in terms of smooth film growth via MOCVD [33] and activation and density control of p-type doping [34][35] before commercial optoelectronic devices could be fabricated. GaN, like all the III-nitrides, may have zinc-blende, rock salt or wurtzite crystal structures but the latter is the thermodynamically stable structure under ambient conditions and is illustrated, with conventions for labelling planes, in the figure below[1]. The *m*- and *a*-planes are often referred to as the prismatic planes, whereas those inclined to the *c*-axis such as the $\{11\bar{2}\bar{2}\}$ planes shown below are described as pyramidal.

The first attempts to synthesise InN and examine the crystal structure were in 1938 [36], around the same time as that of GaN, although the first successful growth of material with good electrical properties was not until 1972 [37]. This is illustrative of the difficulties involved in growth of single crystal InN due to the high equilibrium vapour pressure over the InN[38]and low InN dissociation temperature[39] necessitating a low growth temperature which results in a reduced decomposition rate of NH₃ and reduced migration of deposited materials [40]. Despite high quality crystalline films now routinely achievable [41][42][43], difficulties with doping, high lattice mismatch and it's small bandgap energy thus far preclude its use in optical device structures studied here and it is its

incorporation into the ternary alloy InGaN, the most important optoelectronic material along with GaN, in which it is most often employed.

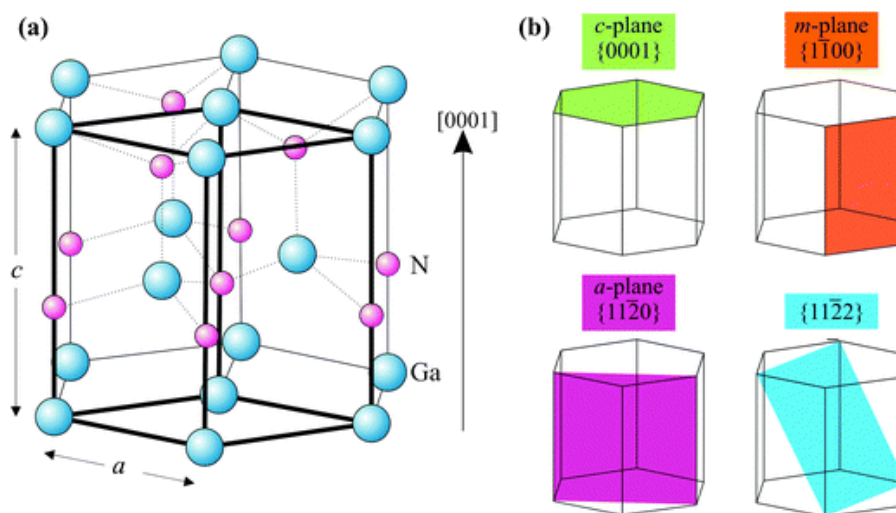


Figure 2.1 Crystal structure of GaN. The hexagonal unit cell is highlighted with bold lines, whilst adjacent atoms are included to highlight the overall hexagonal nature of the structure. Ga–N bonds are shown as dashed lines. Within the hexagonal structure, (b) highlights the polar c-plane, the non polar a- and m-planes and the semi-polar $\{11\bar{2}2\}$ plane. Reproduced from [1].

2.2.2 Zinc nitride

In stark contrast to the body of literature focussed on group III nitrides, there is very little reported of the growth and characterisation of group II nitrides and so their properties remain largely unknown. The experimental work of Chapter 7 focuses on the characterisation of zinc nitride nanoparticles which, with a bandgap energy of around 1.0-1.3eV[44][45], are being explored as a non-toxic alternative to CdTe nanoparticle phosphors. The limited reports of the growth and properties of this material are outlined in section 7, whereas the following sections focus mainly on the more understood III-nitride system.

2.2.3 Attractive properties of the III-nitrides

There are two main reasons for the majority of solid state lighting research and development focussing on the III-nitrides. Firstly, they form a continuous alloy system with the possibility of preparing alloys with band gaps spanning a huge range of energies from infrared to deep UV shown

in Fig. 2.2 below [2]. The second factor is the strong chemical bond making the material very stable and resistant to degradation, even when exposed to high current density and intense illumination as found in the active region of an LED. This also accounts for the difficulty in introducing dislocations once the material is grown – the main mechanism of degradation in other III-V materials[46].

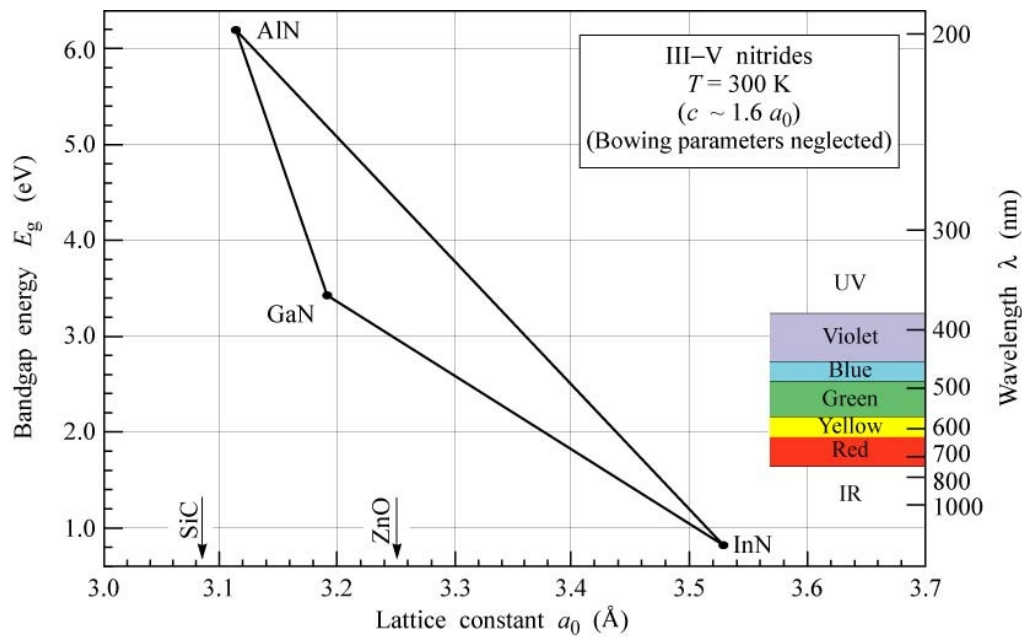


Figure 2.2 Band gap energies versus lattice constant for the III-nitride materials at room temperature. Reproduced from [2].

They also have reasonably high electron mobilities with $900 \text{ cm}^2/\text{V s}$ and $1700 \text{ cm}^2/\text{V s}$ being reported in GaN epilayer and AlGaN/GaN heterostructures respectively as well as good thermal conductivity meaning that III-nitride devices can work at high temperatures as well as hostile environments [47].

2.2.4 Growth and Substrates

The obvious disadvantage with the III-nitride system is the lack of suitable substrates for thin film growth as the large bond energy limits the choice of substrates to materials that can sustain the required elevated growth temperatures. The most commonly used are sapphire ($\alpha\text{-Al}_2\text{O}_3$) and silicon carbide (6H-SiC) but these both have a number of unfavourable properties which limit the quality of III-N films. Sapphire has an extremely large lattice mismatch of around 15% which results in a high

density of threading dislocations – around 10^{10}cm^{-2} [48]. TEM diffraction contrast characterisation has shown these to be mostly of edge character with the most common Burgers vector being $1/3[11\bar{2}0]$ [49] as will be discussed in more detail in section 2. The thermal conductivity of sapphire is low - around 0.25 W/cm K at 100°C – and therefore it is poor at dissipating heat [50], it has a higher thermal expansion coefficient than GaN meaning the growth of thick films is restricted by cracking of the films and substrate [51] and there is evidence that oxygen from sapphire is responsible for unintentional doping, raising background electron concentrations [52].

Silicon carbide has several advantages over sapphire in that it has a smaller lattice mismatch of 3.5%, a high thermal conductivity of 3.8 W/cm K and is available with both carbon and silicon polarities, aiding in control of the GaN film polarity [50]. However the lattice mismatch is still sufficient to cause a large dislocation density in the GaN films of $10^9\text{-}10^{10}\text{ cm}^{-2}$ [52] and the higher surface roughness of SiC substrates – 1nm RMS – is also a source of defect formation.

2.2.5 Polarisation

The wurtzite crystal structure of the III-nitrides provides for both spontaneous and piezoelectric polarisation, with coefficients greater in magnitude than any of the other III-V materials, thus creating large ($>1\text{ MV/cm}$) electric fields along the c -axis [53] – the preferred growth orientation of III-N films. This can complicate device fabrication as these fields cause a spatial separation of the electron and hole wavefunctions in the active area of LEDs [54] and reduce the electron capture probability in the quantum wells [55], reducing radiative recombination rates. The emission from an LED is red shifted and the stability of the emission wavelength with current is also reduced. The combination of these effects is referred to as the quantum-confined stark effect (QCSE) [56]. In order to avoid these issues, significant effort has been invested in growing GaN films in non-polar, such as m -axis, or semi-polar, such as $\{11\bar{2}2\}$, orientations [57]. However the viability of non-polar GaN grown by conventional techniques on different orientations of sapphire is diminished by a very high density of defects [58]. Greatly increased external quantum efficiencies (EQEs) have been

reported for non-polar GaN grown on *m*-plane GaN substrates, cleaved from extremely high quality *c*-axis GaN but apart from being more costly, indium incorporation is 2-3× less efficient in non-polar orientations [59]. Characterisation of non- and semi-polar junctions grown on the exposed facets of novel nano- and micro- structures is an alternative solution and described in the experimental work of Chapters 4-6.

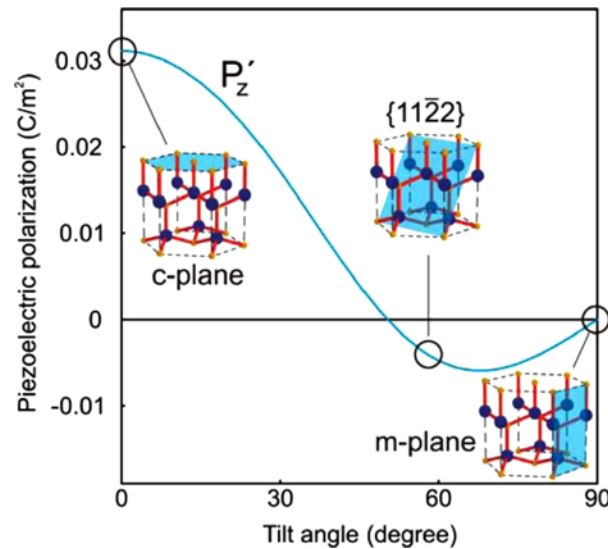


Figure 2.3 The polarisation coefficients of different crystal orientations of GaN. Reproduced from [41].

2.2.6 Alloying

$\text{In}_x\text{Ga}_{1-x}\text{N}$ is the primary alloy of interest for visible spectrum LEDs as the variation of the InN mole fraction, x , decreases the emission band gap from 3.4eV (365nm, UV-A) at $x=0$ (GaN), to, in principle 0.7eV (1800nm, infrared) at $x=1$ – maintaining a direct bandgap across the entire compositional range [20]. However the controlled growth of InGaN has proven to be extremely challenging as the large lattice mismatch between GaN and InN – 11% - means InGaN epilayer microstructure deteriorates by strain relaxation when its thickness exceeds a critical value. This process can occur via three different routes – phase separation, plastic relaxation and elastic relaxation. Phase separation was predicted from thermodynamic theory as a result of the large atomic spacing giving rise to a solid phase miscibility gap [60] which may result in ‘up-hill’ diffusion of the indium to form

regions of different equilibrium compositions [61] and eventual breakdown of crystallographic structure [20]. This has been experimentally observed as broadening and splitting of luminescence peaks [62] and as periodic compositional modulation in TEM images [63]. Plastic relaxation occurs when new dislocations – in addition to existing substrate-derived misfit dislocations – are generated as the InGa_N layers exceed a critical thickness [64]. Finally, elastic relaxation may occur in which InGa_N growth becomes three-dimensional [65]. All of these relaxation processes prevent the desired growth of planar InGa_N epilayers with both high indium composition and low defect densities.

This trade-off between higher crystal quality and increased In_N incorporation is made more difficult as, at the high temperatures required for good crystal quality, In_N incorporation is suppressed due to the high equilibrium vapour pressure of N over In_N [66]. So as well as the thickness of an InGa_N layer being restrained by the critical thickness, the amount of indium that can be incorporated in a given layer is also restricted. At a typical growth temperature of 800°C the equilibrium indium mole fraction is less than 6% indicating InGa_N alloys are unstable over most of the compositional range [60].

The severity of this effect is diminished in LED structures as phase separation in InGa_N quantum wells is suppressed by the external strain from the mismatch with the Ga_N layers lowering the critical temperature [67] [68]. Unfortunately this strain also limits further indium incorporation itself at a given temperature in an InGa_N quantum well [69] which can be observed as ‘composition piling’ where the indium content in the InGa_N well varies with the distance from the mismatched Ga_N underlying layer [70].

The need to employ lower growth temperatures combined with increasing strain with increased In_N mole fraction, promotes the formation of defects with a corresponding degradation in optical efficiency at higher indium content and therefore longer wavelengths [54]. The possibility of employing nanostructures having novel geometry which has strain relieving properties is one of the motivations in utilising nanowires, as explored in Chapter 4 and discussed in the following sections.

2.3 Defects in nitride semiconductors

The high density of defects derived from the substrate misfit is an important issue as dislocations are widely recognised as non-radiative recombination centres in semiconductors [71][72]. For other III-V compounds, for example GaP, dislocations densities of the order of 10^7 cm^{-2} are sufficient to completely quench the luminescence [73]. However examination of Nichia's high brightness LEDs showed that even though the density of dislocations was extremely high, the efficiency of radiative recombination was still good, leading to the conclusion that dislocations in GaN are not strong recombination centres unlike other III-V compounds [48]. This was later shown to be incorrect by showing correlations in cathodoluminescence inhomogeneity and the positions of defects [74] indicating that defects in GaN do act as nonradiative recombination centres. The careful characterisation of the defects is therefore crucial in determining the potential of the materials in optoelectronic devices and forms a central theme in the following work. The common types of extended defects found in the III-nitrides are summarised briefly below and will be referred to in the experimental work of Chapters 4-6.

2.3.1 Perfect dislocations

The smallest translation vectors in the wurzite lattice are $\mathbf{a} = \frac{1}{3}\langle 11\bar{2}0 \rangle$ and $\mathbf{c} = \langle 0001 \rangle$ and therefore the possible Burgers vectors of perfect dislocations are $\mathbf{a}$, $\mathbf{c}$ and $\mathbf{a}+\mathbf{c}$ with the character of the dislocation given by the relative orientation of its Burgers vector and line direction[75]. Therefore in the most common c -axis growth direction, threading dislocations running along the c -axis with burgers vectors $\mathbf{a}$, $\mathbf{c}$, or $\mathbf{a}+\mathbf{c}$ refer to edge, screw or mixed character [76]. All of these types are commonly observed with edge generally reported as being the most numerous with pure screw the rarest[77]. Care needs to be taken when considering dislocations in films grown in other directions, such as the non-polar junctions of Chapters 4-6, since the same Burgers vectors refer to different dislocation types in different orientations and the reduced symmetry complicates the analysis[78].

2.3.2 Stacking faults

Stacking faults are also commonly observed in the III-nitrides in which the small difference of $\sim 10\text{meV/atom}$ between formation energies of the wurtzite and zinc-blende crystalline phases favours a reversal between phases during most growth techniques. This is observed as change in the ABAB stacking of the (0001) wurtzite planes to the ABCABC stacking of the (111) cubic planes. There are several types of basal plane stacking fault, characterised by the number of violations of this stacking rule as illustrated in Fig. 2.4 below [79].

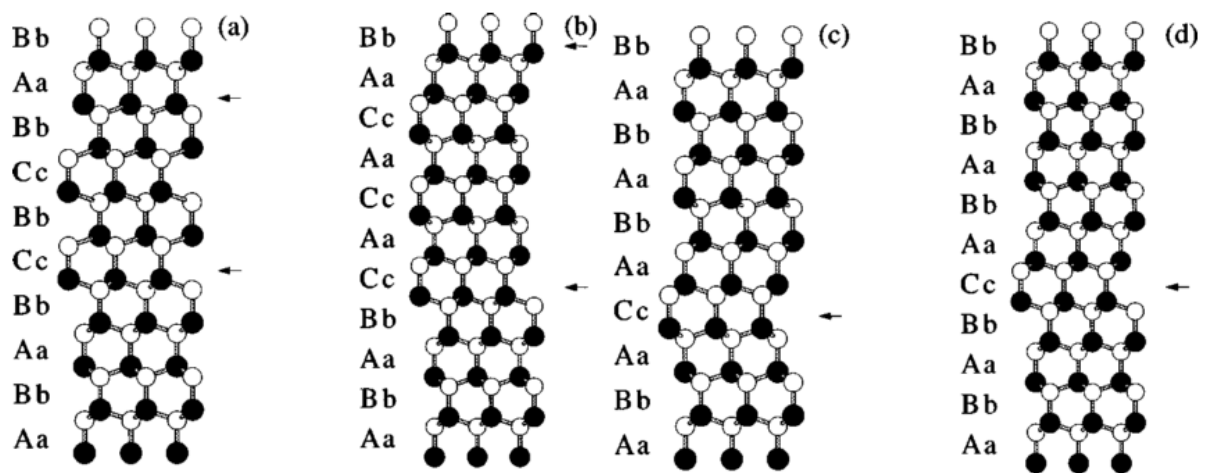


Figure 2.4 Types of basal plane stacking fault found in the III-nitrides: (a) Intrinsic type 1, (b) type 2, (c) type 3 and (d) extrinsic. The capital and lowercase letters refer to the group III and N atom positions respectively. Diagram adapted from [80].

Intrinsic type I_1 BSFs contain just one violation or one cubic layer comprising ...ABABCBC... and have the lowest formation energy; I_2 have two violations ... ABABCABAB... and have the second lowest energy; type 3 faults have one of the A or B layers in the wrong C position i.e. ... ABACABAB... and are rarely observed; and finally extrinsic have an additional C layer inserted in the middle of the normal wurtzite stacking sequence.. ABCABAB... and have the largest formation energy. These stacking faults have fault vectors equal to the Burgers vector of their associated bounding partial dislocations which are given below. Although I_1 type stacking faults have the lowest energy, their formation requires removal of a basal bilayer in addition to a shear of $\frac{1}{3}\langle 10\bar{1}0 \rangle$ and therefore they are likely to be formed during growth whereas I_2 BSFs are caused by stress during or after growth by movement

of a glissile Shockley partial in the basal plane. The high energy extrinsic BSFs are formed by precipitation of point defects on the basal plane [81].

In addition to basal plane stacking faults, stacking faults on the prismatic planes, which have a fault vector of $\frac{1}{2}\langle 10\bar{1}1 \rangle$ are also occasionally observed – particularly in non-polar *a*- or *m*-plane nitrides[82][83].

Stacking faults introduce additional electronic states above the valence band maximum observable in photoluminescence experiments [3]. In addition, the differing band gaps of the two phases means stacking faults can bound quantum well-like regions of zinc-blende material surrounded by the wurtzite phase. Such areas give rise to a luminescence line below the band gap of wurtzite GaN [84].

2.3.3 Partial dislocations

The common perfect dislocation types are those that cause the close packed planes to slip over one another. However, direct slip corresponding to atoms moving from one corresponding position (A or B) to another requires a significant amount of energy since it involves atoms passing directly over one another. The slip may therefore also be accomplished by two sequential steps, which circumvent the atom between the two corresponding positions. For example the atoms may slip from an 'A' position to a C then back to an A. Such a slip may be accomplished by the sequential passage of two dislocations with Burgers' vectors which are not whole lattice vectors. Such dislocations are examples of partial dislocations, the Burgers vectors of which sum to give the perfect dislocation Burgers vector. It is not uncommon to find a perfect dislocation in the wurtzite lattice dissociated locally into a configuration that can be described as two parallel partial dislocations connected by a stacking fault on the glide plane of the dislocation.

The types of partials dislocations found in the wurtzite lattice include: sessile Frank-Shockley dislocations which have a Burgers vector $\frac{1}{6}\langle 20\bar{2}3 \rangle$ and bound type I₁ stacking faults; Shockley partials which bound I₂ stacking faults with $\mathbf{b} = \frac{1}{2}\langle 10\bar{1}0 \rangle$ and may be formed via the disassociation of

a perfect dislocation with $\mathbf{b} = \mathbf{a}$; and Frank partial dislocations which have $\mathbf{b} = \frac{1}{2}\langle 0001 \rangle$ and bound extrinsic basal plane stacking faults[85].

The limited reports of structural TEM studies of non-polar III-nitride layers suggest partial dislocations are particularly prevalent [81][86] and are of particular interest due to the reports of specific luminescence signals from these defects [87].

2.4 GaN Nanowires

A new class of structure has emerged since the early 1990's, with cross sections on the nanometer scale and lengths up to several microns, they were initially called 'nanowhiskers' [88] and later 'nanowires' [89]. These structures exhibit novel properties such as quantum confinement which allows bandgap tuning with the radius of the wire, mechanical and thermal stability due to the surface/volume ratio and possible quantised electrical conductance leading to high carrier mobility [26]. Applications being researched include nanoscale laser diodes [90][91], field effect transistors [92], sensors [93], photovoltaics [94], photonic circuit elements [95] as well as various kinds of LEDs [27], [96], [97] – the latter being described in greater detail below.

2.4.1 Advantages of nanowires in LEDs

There are a number of benefits to using nanowire material in LEDs. The primary impetus is the fact that the misfit dislocations found in GaN films, thought to be directly or indirectly responsible for reduced efficiency, are not generally observed in nanowires [29]. The misfit strain can be accommodated coherently rather than releasing strain with a structural defect due to the small cross sectional interface [98]. This results in greater luminescence intensity due to the reduced rate of nonradiative recombination [29] which increases the maximum efficiency of devices fabricated from these materials [99].

In addition to relieving interfacial strain, the nanowire geometry has also been shown theoretically to reduce alloying strain from the large lattice mismatch between InN and GaN [100]. This has been demonstrated in the fabrication of the full compositional range of InGaN nanowires [101] as well as InGaN nanowires of greater thickness than the usual critical thickness for InGaN films [102]. This means that nanowires offer a way of overcoming the well documented reduction in efficiency at green and longer wavelengths. There is also evidence that the reduction in strain also reduces the piezoelectric polarisation component and therefore reduces the magnitude of the QCSE [103].

Another advantage is the increased light extraction efficiency due to the greater surface area of nanowires compared to conventional LEDs in which it is only a few percent owing to the total internal reflection occurring at the LED/air interface [27]. Finally, there are few surface states acting as recombination centres in the band gap of GaN unlike other III-V materials for which such states can dominate the observed behaviour [104]. This makes GaN an attractive material for preparing nanoscale devices such as nanowire LEDs for which the surface-to-volume ratio is large.

2.4.2 Nanowire growth

The vapour-liquid-solid (VLS) process is generally employed in the growth of semiconductor nanowires. The method involves heating catalytic particles in the form of metal nanoclusters above the eutectic temperature of the metal–semiconductor system of choice in the presence of a vapour-phase source of the semiconductor. This results in many liquid metal-semiconductor alloy droplets which, via continuous delivery of the semiconductor reactant, become supersaturated leading to nucleation of the solid semiconductor. It was first proposed by Wagner to explain silicon whisker growth [105] and was primarily based on the appearance of the nanowires after growth with the catalyst particle clearly visible on the nanowire tip (although metal droplets may not necessarily remain on the wire tip due to interfacial dewetting and large interfacial expansion differences which may dislodge them [26]). The VLS process has now been confirmed by direct observation in an *in-situ* high temperature TEM [106]. The gaseous semiconductor may be generated via physical

techniques such as pulsed laser ablation [107] or molecular beam epitaxy [108] but the most regularly used technique is the decomposition of precursors in chemical vapour deposition. For compound semiconductors such as the III-nitrides, chemical vapour transport [91] and PLA [109] are often used but MOCVD now appears to be the most popular with Ni, Fe or Au used as the catalyst [110].

There are two competing interfaces during nanowire growth – the liquid/solid interface between the eutectic particle and the nanowire and the gas/solid interface between the reactants and the exposed surface of the growing nanowire. The former results in VLS elongation of the nanowire and the latter the radial thickening. Either mechanism can dominate depending on the specific growth conditions such as temperature, pressure, flow rate and reactant species [4].

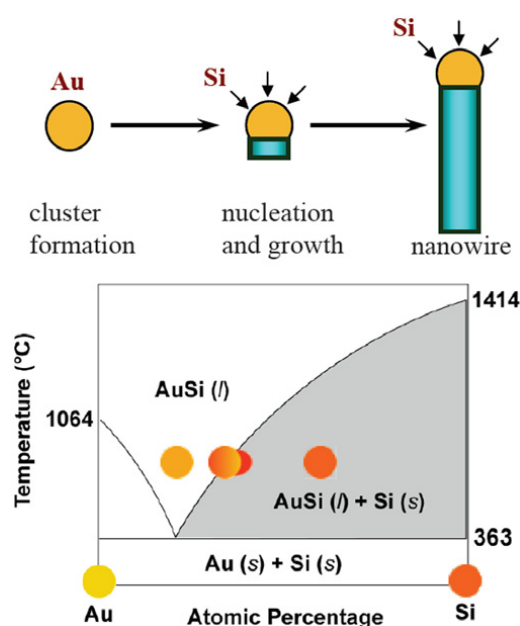


Figure 2.5 A schematic illustration of the VLS growth of gold catalysed silicon nanowires with the corresponding phase diagram showing the 1D growth driven by continuous Si vapour delivery. From [4].

2.4.3 Possible deviation from VLS growth to VSS

Several reports have pointed out that the Ga-N phase diagrams [111] indicate that normal GaN NW growth temperatures are far below ($\sim 300^\circ\text{C}$ less than) that of the lowest eutectic temperature,

contradicting the usual description of VLS growth. This suggests either a reduction in melting point due to the increasing surface energy component at smaller particle sizes, resulting in a reduced cohesion between atoms (the Gibbs-Thomson effect) or that the catalyst particle remains a solid during the growth process. Observed catalyst particles at the end of GaN NWs often appear faceted in contrast to the spherical particles usually reported for the VLS process which has been cited as evidence supporting the hypothesis that wires grow via a vapour-solid-solid (VSS) process [112]. Experiments into the size-dependent reduction in melting point of Ni suggest that a ~2nm particle will have a reduction in melting point of 10% [113] and therefore is unlikely to account for the change in melting point needed of a typical catalyst particle ~10s nm in diameter. There have been confirmations of a VSS process for other III-IV and III-V materials which also show the catalyst particle is an alloy of the metal and group III element only [114]. There is little work on the impact on GaN nanowire morphology of the catalyst particle remaining solid although work on other materials has reported increased kinking and variation of growth orientation[115] and more pronounced tapering [116] for wires grown via a VSS process.

2.4.4 Control of morphology and growth orientation

Control of growth temperature and pressure has been shown to change the morphology of GaN nanowires from tapered structures – resulting from simultaneous axial and radial growth - to highly uniform aligned arrays which are more desirable for most device applications [117].

Because, under the right growth conditions, the diameter of the nanowire is largely determined by the size of the catalyst particle, it has been demonstrated that nanowires of any specific size can be obtained by controlling the diameter of the monodispersed catalyst particles and the growth time for the diameter and length respectively [118]. The ability to choose the crystallographic growth direction is more difficult and much sought after as it would allow tuning of anisotropic properties such as spontaneous piezoelectric polarisation, thermal and electric conductivity, dielectric constant, lattice strain and bandgap [90]. For example the growth direction of the semiconductor nanowires

has been shown to influence the optical properties of the material [119] [120] and III-V semiconductor nanowires in particular, often have a much higher density of stacking faults in certain growth orientations [121] and photoluminescence measurements of GaN nanowires have revealed a blue shift of ~100 meV in the spectra of [11-20] orientated wires from that of [0001] wires [110].

The growth orientation is usually chosen to minimise the total free energy which includes the ‘bulk’ energy of the NW, the semiconductor/vacuum energy and the semiconductor/catalyst energy, with the latter usually being the dominant term. Studies on Si NWs have shown that different growth directions may dominate at different diameters as the semiconductor/vacuum energy term begins to dominate at low radii where the surface/volume ratio is large[122]. Nanowires with a wurtzite crystal structure are usually found to be preferentially orientated along the [0001] *c*-axis, however the III-nitrides actually seem to show less preference to a particular direction [121] and growth axes perpendicular to the *a*-, *m*- and *c*-planes have been observed – see table below.

Orientation	Cross section	Polarity	Reference
[0001] <i>c</i> -axis		Polar direction	[123] [124]
$\langle 10\bar{1}0 \rangle$ <i>m</i> -axis		Non-polar direction	[125] [123][126]
$\langle 11\bar{2}0 \rangle$ <i>a</i> -axis		Non-polar direction	[126] [110]

Table 2.1 The observed growth orientations of III-nitride nanowires with corresponding cross section and polarity.

One method of controlling the orientation of GaN NWs involves selecting specific substrates with lattice constants matching different planes of wurtzite GaN to selectively grow *m*- and *a*-axis wires 100) γ -LiAlO₂ and (111) MgO single-crystal substrates respectively [123].

2.4.5 Microstructure of III-nitride nanowires

As outlined previously, dislocations are very rarely observed in GaN nanowires and the most frequently observed planar defects are stacking faults. HRTEM has been used to image stacking faults dividing regions of hexagonal and cubic GaN which are often observed to run the entire length of both *a*- and *m*- orientated nanowires parallel to the (0001) planes of the wurtzite GaN [126] [127]. Recent work has suggested the likelihood of stacking faults occurring is increased by the use of a metal catalyst particle as in the VLS process and reports weaker photoluminescence from these wires [128]. It has also been suggested that Mg doping (frequently used for p-type doping of GaN required for device fabrication) can induce formation of Zincblende regions in GaN nanowires [129].

An important consideration in employing the VLS growth method is the possibility that the metal catalyst may introduce impurities into the nanowire, unintentionally doping the semiconductor. Since even small amounts of impurities can significantly affect the physical and optical properties of a semiconductor, it is important to characterise the levels of impurities introduced by the catalyst. HAADF STEM has been used to image single Au catalyst-derived atom impurities in Silicon nanowires [130] and put an upper bound on impurity concentration. The same report concludes that the catalyst impurities are incorporated into the nanowire during growth. This technique has yet to be applied to Ni-catalysed GaN nanowires and obtaining results is likely to be difficult due to the similarity in atomic number of Ga and Ni giving minimal Z-contrast. Optical characterisation methods such as photoluminescent spectroscopy have been used to analyse radiative defects in GaN nanowires. Reports using this technique have identified near band emission peaks in the PL spectra and attributed them to Ni impurities acting as acceptors above the valence band in GaN nanowires [84].

Finally, with respect to alloying, HRTEM images show no large variations in indium concentration within the nanowire up to In concentrations of 70-90% at which point some compositional modulation and texturing is observed [101]

2.5 Heterostructured Core/Shell Nanowires

An important breakthrough in the synthesis of novel nanostructures is the controlled growth of heterostructures since LEDs require at least a connection between p- and n-doped regions but a major objective is to realise the more complex heterostructures that have been successful in planar devices for increased efficiency [131]. This has been achieved by depositing p- and n-type nanowires on a substrate in a 'crossed-nanowire' architecture using directed fluidic assembly [97] and by modulating the vapour phase semiconductor reactants during the growth process to produce axial heterostructured nanowires containing p- and n-type regions [132]. However, both of these methods suffer from reduced light output due to limited charge injection through the nanoscale p-n junction interfaces [133] and therefore a significant research effort has focussed on core/shell nanowires.

2.5.1 Growth of Core-Shell Nanowires

Such structures are fabricated by firstly growing the core as described by the VLS method above, before altering the growth conditions to favour homogeneous vapour-phase deposition on the nanowires surface [134], giving an increased area junction interface. By modulating the vapour-phase semiconductor reactants, multiple shells of chosen thickness can be deposited on the nanowires surface and more complex heterojunctions can be fabricated. This technique has been used to fabricate core/multi-shell nanowire LEDs using heterostructures commonly employed in conventional LEDs, as illustrated in Fig. 2.6 below[99], which use single or multi-quantum wells with a AlGa_N electron blocking layer to confine electrons for efficient recombination.

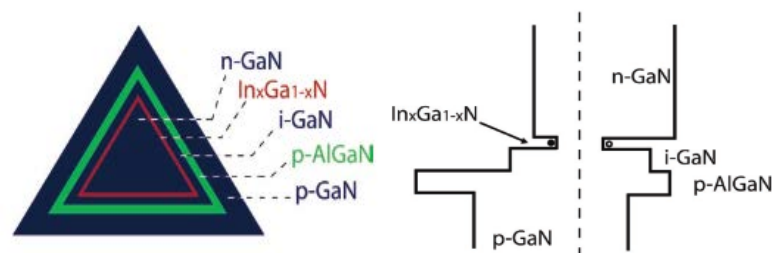


Figure 2.6 An example core/multi-shell nanowire heterostructure and the corresponding band diagram. Reproduced from [99]

2.5.2 Advantages of core/shell nanowires

Core-shell nanowires offer a number of other advantages including the possibility of interfacing materials to produce structures not possible in planar devices, avoiding interfacial polarisation charges and improvements in alloying ranges possible. As explained in section 2.5, attempts to fabricate non-polar III-N heterostructures to overcome the QCSE met with difficulties due to the quality of the material in these orientations. C/S nanowire structures are seen as a way round this as the material can be grown in the common polar directions which mean the side facet interfaces between the core and shells are actually non-polar or semi-polar [135]. This may help to reduce the QCSE and also carrier leakage out of the active region because of the effects of the polar interfaces on the band structure. The non-polar interfaced heterostructures may partially explain the high efficiencies observed in initial testing of core-shell nanowire LEDs.

2.5.3 Strain and critical dimensions in core shell nanowires

One important consideration in the design and fabrication of core shell heterostructures is the strain that arises due to the lattice mismatch between materials. Such strain affects the electronic and optical properties of the materials and also determines the device dimensions at which coherence is lost and dislocations form, which are likely to significantly degrade performance.

The first attempt to analyse theoretical coherency limits used a much earlier model for coherency in epitaxial films [136] and applied it to 1D heterostructures [98]. The authors found that, for a given lattice mismatch, the critical radius of a nanowire heterostructure is approximately an order of magnitude larger than the critical thickness of the equivalent planar heteroepitaxial system. This would allow integration of classes of material into heterostructures that are not realisable in planar systems. A development of this theory was applied to III-nitride heterostructures to show there is a material-dependent critical core thickness below which any thickness of core may be accommodated

coherently [137]. The results found for GaN cores with different $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy shells are shown in Fig. 2.7 below, where the curve shows the combination of core-shell dimensions that will yield coherent structures, above which a line dislocation will form along the length of the wire. The critical core radius is the minimum of the curve and this value decreases for increasing indium composition due to the increased strain in the system.

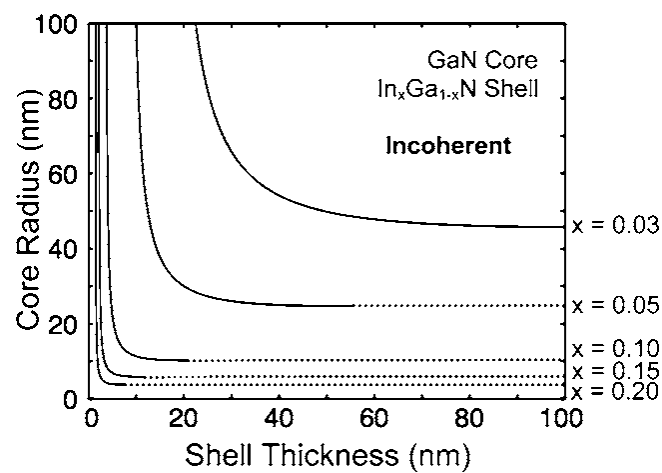


Figure 2.7 The theoretical allowed geometries of GaN/ $\text{In}_x\text{Ga}_{1-x}\text{N}$ core/shell nanowires for a range of x . The area above the curve indicates geometries for which plastic relaxation via dislocation formation will occur. From [137].

2.5.4 Microstructure and defects in core/shell nanowires

In experimental reports of these systems[99] [138][133], the radius of the core and shell often exceed the critical geometries predicted and yet the heterostructures appear coherently strained with no relaxation via dislocation formation observed [139]. This may be partially due to the difficulty in observing such dislocations, the most common of which are line dislocations running down the length of the core-shell interface and also the fact that many InGaN NWs reported are m -axis orientated so may deviate from the theory applied to c -axis oriented wires above. There are some reports of threading dislocations in InGaN layers on GaN cores [102] where the core/shell ratio far exceeds the allowed geometries in Fig. 2.7. Other reports [140] explicitly state that the morphology of their core shell wires exceed the critical geometry in the theory [137] and yet they are unable to observe any dislocations at the interface although they do suggest their existence

could account for the GaN in-plane relaxation implied by their XRD data. Dislocation loops running around the interface have also been observed in GaN-GaP CS wires [141] which were predicted to be the second most favourable plastic relaxation mechanism for strained core shell nanowires.

It is important to note the significance of the defects of the GaN core described in section 4 on the overall morphology of a core/shell structure. A study using three dimensional visualisation showed surface defects of the GaN core derived from the VLS growth propagating through to the surface of the deposited AlGaIn shell [142].

One commonly observed feature in III-nitride core/shell nanowires is the asymmetry in shell growth on different facets of the core. GaN NWs with a $\langle 10\bar{1}0 \rangle$ *m*-axis orientation are usually reported as bounded by the *c*-plane and two equivalent $\{1\bar{1}01\}$ semipolar planes [133] [143] and InGaIn shell growth is observed to be much greater on the latter, resulting in asymmetric shells [102] [99]. Qian et al. found no detectable In signal from the thin shell on the (0001) plane and explored this using CBED to show the *c*-plane was the N-polar face [138] which has previously been reported to have a much slower growth rate [144] due to the lower surface energy compared to the $\{1\bar{1}01\}$ planes. It was also shown that In-rich nanowires exhibit spontaneous bending attributed to the different strain placed on the facets by the non-symmetrical shell coating, which is likely to have implications in device fabrication [138]. In addition to this asymmetry in coating between shells of differing polarity, a difference in thickness has been observed between the identical $\{1\bar{1}01\}$ planes [102]. These facets have identical surface energy so the difference in shell growth was attributed – via finite element analysis - to the tendency of the nanowire to minimise its total strain energy. Stacking faults have also been observed at the intersection of the $\{1\bar{1}01\}$ planes with HRTEM [138] and asymmetrical shells in [0001] orientated GaN/AlGaIn nanowires have been shown to lead to dislocations at the core-shell interface [140].

Although the strain-relieving geometry of core/shell nanowires aids in stabilising the alloying process, indium-rich clusters on a scale of 10 to 50 nm have been observed in thicker InGaIn shells

[99] and InGaN NWs [145]. Also the 'composition pulling' effect has been observed to produce a graded In composition in NW shells from ~20% at the interface to ~40% at shell surface due to strain [102].

There is also evidence of the influence of the shell on the optical properties of the core. The large external surface area of nanowires may introduce a high density of surface-trap states which is detrimental for light emission [146]. Investigations into GaN/AlGaIn core/shell nanowires have shown that the growth of a shell leads to passivation of surface state luminescence seen in pure GaN nanowires. The same report described a progressive blue shift with increasing shell thickness attributed to increasing strain on the GaN core[147].

2.6 Etched Core/shell Microrods

2.6.1 Top-down approach

The vapour-liquid-solid mechanism is an example of a 'bottom-up' approach which has been very successful in the synthesis of semiconductor nanowires. However, it may be possible to preserve many of these advantageous features, outlined in section 2.5, but reap additional benefits by moving to a so-called 'top-down' approach. This refers to the synthesis of GaN nano- or microstructures in which the structures are defined using lithography [148] before selective etching of the material [149]. Firstly, bottom-up growth of nanowires is only possible within a very narrow region of growth conditions which relates to lower than optimal growth temperature and III to V ratio[150]. Such growth parameters may introduce an increased density of point defects [151] and impurities [152] relative to those optimised for planar films for LEDs and allow less flexibility for adjusting to favourable conditions for doping. In contrast top-down technique utilise established techniques in thin film growth for precise control of the doping level [153]. They may also be better suited to large scale processing due to uniformity of cross section, length and spacing in comparison to bottom-up nanowires which exhibit a much greater degree of tapering and morphological variation [154]. Top-

down fabrication techniques are now capable of producing nanostructures with dimensions <20nm [155] and facet-dependant etch rates mean that pre-defined shapes have been observed for compound semiconductors [156].

These advantages of top-down structures come at the cost of (1) limitations associated with the dislocation density of the thin film from which they are etched and (2) etch-related surface damage – both of which will be described in more detail below.

2.6.2 Etching of GaN

Historically, the most important top-down process for fabricating 1D structures is wet chemical etching which has been applied to a wide range of semiconductors [149] [157] but generally only produces slow and anisotropic etching in III-nitrides [158] due to the high chemical stability of the material [159]. Such processes also suffer from poor accuracy and reproducibility [160] however they can often be used to identify defects [161], polarity [162] or to compliment dry etching techniques [150] when applied to the III-nitrides.

The four primary dry etch techniques employed to the III-nitrides are reactive ion etching [163], electron cyclotron resonance etching [164], magnetron reactive ion etching [165], and inductively coupled plasma etching [166]. Reactive ion etching generally gives the lowest degree of anisotropy and slowest etch rates with ECR producing the fastest [167]. Such techniques give vastly increased etch rates [168], material selectivity and controlled anisotropy [167] but suffer from a number of potential difficulties such as surface damage in the form of introduction of defects, introduction of contaminants and changes in stoichiometry [169] leading to degradation of the internal quantum efficiency [170] and electrical properties [171]. There have been several reports of methods to avoid these difficulties such as: chemical vapour-phase etching [172]; using a N₂ plasma treatment to restore stoichiometry [173]; using a two-step process in which an anisotropic wet etch is applied to remove the initial dry etch damage [174]; and repairing of the damaged *m*-plane facets via subsequent GaN re-growth [175] as is used in the microrods studied in Chapter 5.

The precise etch method and chemistry also has an impact of the morphology of the remaining structure, including the aspect ratio and degree of tapering [176] – the latter also being affected by the size of the mask pattern as illustrated in Fig. 2.8 below [177].

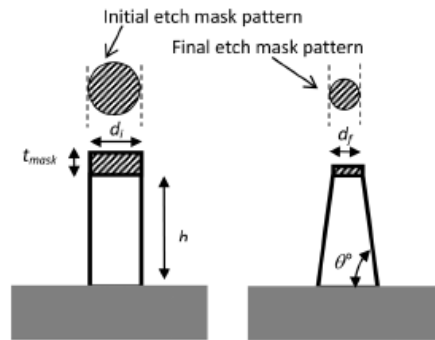


Figure 2.8 An illustration of how etching of the mask pattern can lead to tapering of the final etched structure[177]

2.6.3 Core/Shell structure

After top-down growth of the GaN core structures, shells may be deposited on the non-polar side walls via MOCVD similarly to the nanowires described in section 4 in order to gain the associated advantages of junctions free from QCSE. This technique was originally employed to utilise the etched side walls of [0001]-grown GaN bars to provide the crystallographic template for non-polar growth of nitride material [178] and later adapted to GaN columns rather than bars to give an increased surface area [179]. CVD deposited InGaN shells on the latter tend to form *m*-plane facets on the side walls and often semipolar $\{1\bar{1}01\}$ facets on the top of the underlying core forming a hexagonal pyramid. The InN fraction varies considerably over the structure, attributed to facet-dependant indium incorporation and less available indium able to reach the lower portion of the core structure[180].

2.6.4 Defects in etched core/shell structures

In addition to many of the considerations relating to core/shell nanowires described in section 2.5, utilising a top-down fabricated core introduces a number of other questions to be answered in the characterisation process – many of which there is little report of in the literature. Importantly, the

use of cores derived from conventionally grown films implies a significant density of dislocations in this region and raises the question of whether these propagate to the shells or are confined to the core given they are predominantly aligned with the c-axis[181]. There is also the possibility that, for small diameter core-rods, many will be dislocation free. For example, if the dislocation density of the original GaN film is $\sim 5/\mu\text{m}^2$, the vast majority ($\sim 90\%$) of $\sim 150\text{nm}$ diameter rods etched from it will be dislocation free[150]. The implications of the etch damage on the shell microstructure and therefore the optical properties of the material is also a feature which needs to be understood.

The early work on GaN ‘bars’ reported dislocation density in the side wall-grown material of 4-5 magnitudes lower than the core [178] whereas reports of growth on GaN column structures described dislocations bending through 90° at the $\{1\bar{1}01\}$ facet interface to follow a low energy propagation direction parallel to the basal plane [179]. Other than these few reports there is very little in the literature concerning the detailed microstructure and particularly characterisation of defects in GaN and InGaN shells deposited on top-down fabricated cores and this will be the primary aim of the experimental work of Chapter 6.

2.7 Zn₃N₂ nanoparticles

2.7.1 Nanoparticle phosphors

There has been a strong interest in 0D semiconductor nanoparticles or quantum dots over the last 30 years, largely due to the possibility of tuning a number of properties through control of the size of the crystals and the corresponding quantum confinement [182]. A wide variety of semiconductors have been synthesised in nanocrystal form - including II-IV[183][184], III-V [157][158] and IV-VI materials [187][188] – utilising a diverse range of techniques such as sol-gel [189], chemical precipitation [190], hydrothermal synthesis [191], pyrolysis [192] and vapour phase methods [193]. Such nanoparticles are often stabilised during growth via surface modification with organic ligands in order to prevent aggregation and precipitation of the nanocrystals[194][195]. The size-dependent

optical properties mean they are potential candidates for converting the blue/UV light of a III-nitride LED to longer wavelengths as a nanoparticle phosphor [196] which have an advantage over conventional phosphors. Although there is the potential for surface states and lower crystallinity to decrease the quantum efficiency of nanoparticle phosphors compared to conventional phosphors [197] they have a number of other advantages in addition to emission wavelength tuning, such as improved photometric performance, avoiding colour change with angle found in large grain phosphors [198] and may be easily printed onto the desired substrate[199]. There are also political issues associated with a reliance on a small number of countries for the supply of the rare earth minerals required in conventional phosphor materials [200]. In addition, there are very few conventional red phosphors (required in combination with a green phosphor to convert blue/UV to warm white light) that can be excited by low wavelengths and the few examples exhibit low efficiencies and broad emissions[201]. In comparison, red and green tuned CdSe–ZnSe quantum dots provide vastly improved colour rendering and efficacy when applied to a blue InGaN LED [202].

There are however motivations to investigate more unusual materials to employ in quantum dot phosphors , the main factor being that many of the constituent materials of existing QDs are highly toxic. Cadmium and Selenium for example, two of the most widely used constituent metals are known to cause acute and chronic toxicities and are of considerable human health and environmental concern [203]. One such material, which has thus far attracted very little attention, is zinc nitride.

2.7.2 Zinc nitride

There is relatively little work reported on the growth and characterisation of Zn_3N_2 which is a group II-V semiconducting compound that was first investigated in the 1940s when it was shown to have the *anti*-bixbyite crystal structure in which the metal atoms are in tetrahedral sites of an approximately cubic close packed array of nitrogen atoms.[204]. However it has begun to attract greater interest due to its promising electrical properties [205] and the low cost of its constituent

elements[206]. There has been a large degree of variation in the reported value of the bandgap with figures ranging from 1.01eV[207] to 3.2eV[208] but the majority place it in the near infrared or visible regions and *ab initio* electronic structure calculations suggest a fundamental gap of 1.17eV[209]. This uncertainty in the optical bandgap measured is likely due to the role of structural defects, the formation of which is linked to the growth conditions[210], and the incorporation of impurities, related to the specific growth technique and post growth storage conditions [211]. In particular oxygen is a common impurity in nitride layers, with theoretical studies suggesting it is responsible for the n-type conductivity [211], which may be introduced during exposure to air after growth. Zn_3N_2 films have been shown to rapidly oxidise in air, with rates of 20-36nm a day at growth temperatures of 298 and 473 K respectively, with the oxide layers blue-shifting the emission [206].

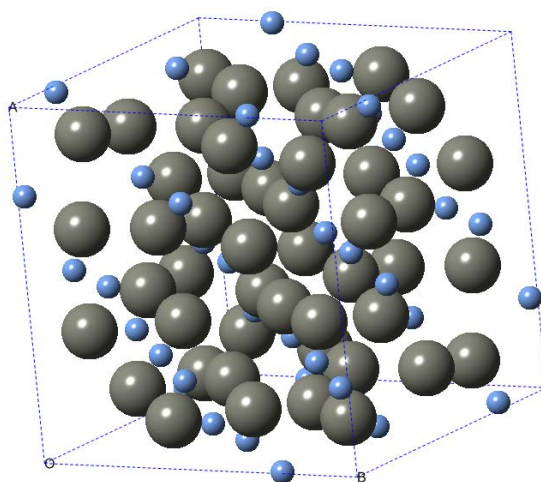


Figure 2.9 The anti-bixbyite structure of Zn_3N_2

Zn_3N_2 has been grown via a number of methods giving varying morphologies: Zn_3N_2 powder has been synthesised via the nitridation reaction of Zn powder with NH_3 gas [212]; polycrystalline films have been grown by reactive radio frequency magnetron sputtering [213] and annealing zinc metal films in ammonia [214]; and more unusual morphologies have been observed such as empty spheres [215]. In addition, a number of nanostructures have been synthesised including nanoneedles [216] and nanowires [45][217] with the growth of the latter being via a vapour-solid mechanism

[218]. There was, however, no report anywhere in the literature of OD Zn_3N_2 nanocrystals relevant to the application of nanophosphors before the recent successful synthesis at SLE of the material discussed in Chapter 7[219].

2.8 Summary

The above review outlines relevant work on the growth and characterisation of the novel semiconductor nano- and micro-materials studied in this thesis, with particular focus on their microstructure and the associated relationship to their potential application in optoelectronic devices. It also allows for identification of those areas which require further investigation and form the basis of the experimental work described in Chapters 4-7. These include: (1) The relationship between GaN nanowire core morphology and crystallography on the InGaN shell microstructure; (2) the impact of misfit dislocations in GaN microrod cores on the microstructure of the non-polar junctions comprising the shells; (3) a detailed structural study of the defects found in the non-polar junctions deposited on etched microrods; (4) the confirmation of successful synthesis of Zn_3N_2 nanoparticles and the relationship between the morphology and optical properties. These areas reflect the primary questions tackled in Chapters 4-7 respectively, each of which have a range of secondary questions which are described in detail in the corresponding introductions.

Chapter 3

Experimental Techniques

3.1 Introduction

The broad aim of this work, as outlined in first chapter, is to gain an understanding of the microstructure of the novel semiconductor nanostructures of interest in order to link these properties to the growth process and the optical properties. In order to achieve this aim, a wide range of characterisation techniques have been employed, the majority of which are connected to the various branches of electron microscopy. This chapter therefore aims to present the practical principles and theory behind the techniques, with particular reference to their application to semiconductor nanostructures, to provide a basis for the description of the applications and analysis of the following experimental chapters.

3.2 The Transmission Electron Microscope

The transmission electron microscope (TEM) has become the principal tool in nanoscale material characterisation as it enables the collection of both quantitative structural and chemical information at resolutions beyond any other one technique. The first TEM was constructed by Knoll and Ruska [28] with the goal of overcoming the limited resolution in visible-light microscopes by utilising the smaller wavelength of electrons compared to light. The basis of the technique involves accelerating electrons through a thin sample and magnifying and refocusing the diffracted and transmitted beams to form an image on a viewing screen. In simple terms a TEM consists of an illumination system, a specimen stage, an objective lens system, the magnification system, the data recording system(s), plus an optional chemical analysis system – illustrated schematically in Fig. 3.1 below which includes deflection coils and an annular detector for scanning TEM imaging. These elements may be combined in a number of different operational modes to collect different sample information. The principles of these techniques are described in the following sections with emphasis on the specific applications used in the following work.

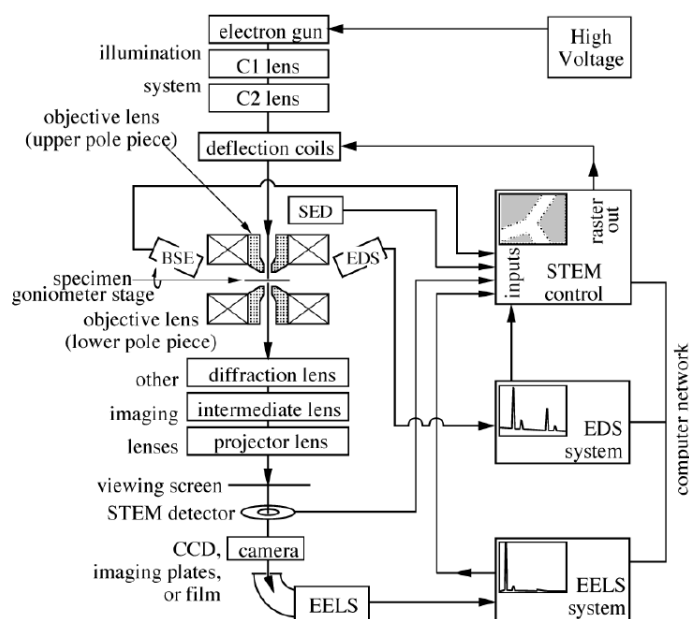


Figure 3.1 Schematic of a (S)TEM consisting of five primary systems: the illumination, specimen stage, imaging, magnification and data recording systems plus the chemical analysis systems such as EDX and EELS and additional control for raster scanning of the probe and detection for STEM capability. Reproduced from [79].

3.3 Diffraction

Electron diffraction was first demonstrated from thin crystals of nickel [220] before being performed in a TEM for the first time in 1939[221]. It is hugely important since it allows the determination of crystal structures and orientations but also is the basis for diffraction contrast imaging in which the contrast arises due to the variation in intensity of diffracted beams across the specimen.

Electrons scatter strongly from a crystalline specimen when the Bragg condition is satisfied:

$$2d \sin \theta_B = n\lambda \quad (3.1)$$

That is, the electron waves interfere constructively at the Bragg angle θ_B for a specific lattice spacing, d , and electron wavelength λ to give the resultant diffraction spots. $\dots G, 2G, 3G \dots$ illustrated in the figure below.

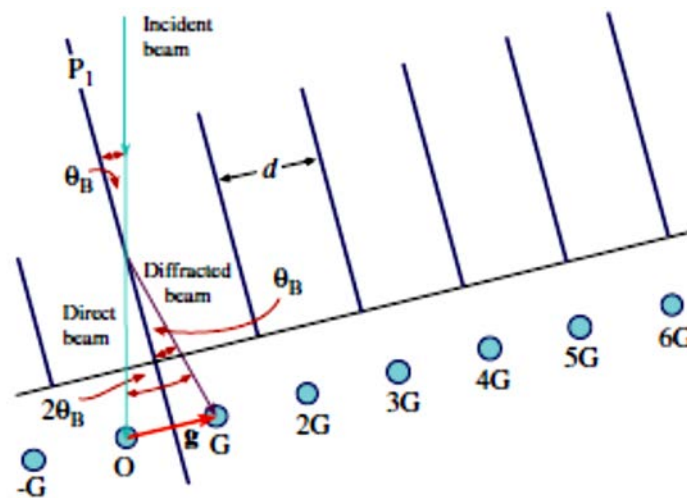


Figure 3.2 Schematic illustration of diffraction from a set of crystal planes separated by distance d . The crystal has been orientated to the Bragg diffraction condition to give diffraction spots G , $2G$ etc. The reciprocal lattice vector g is the distance from the origin O (representing the direct transmitted beam) to the first diffraction spot G , normal to the diffracting planes. This figure was reproduced from reference [30]

The formation of a diffraction pattern is often easiest to visualise in reciprocal space in which the Ewald sphere construction [222] may be used to show the conditions at which the Bragg equation is satisfied. Often shown in 2D for clarity, as in figure below, the reciprocal lattice is really a 3D array of points, each of which represents a family of crystal planes in real space. The Bragg condition is

satisfied and diffraction occurs when the Ewald sphere, of radius $1/\lambda$, intersects one of the reciprocal lattice points. In other words diffraction occurs when, the change due to diffraction $\mathbf{K} = \mathbf{k}_D - \mathbf{k}_I$, illustrated in Fig. 3.3 below, is equal to $\mathbf{g}$. The reciprocal lattice vector $\mathbf{g}_{hkl}$ is the inverse of the real space planar spacings d_{hkl} and will often be referred to when considering specific diffracted beams in the forthcoming theory and experimental work of the proceeding chapters.

The change in the diffraction pattern with tilt of the sample or beam can then be visualised by the change of intersection with the tilt about the origin, O, of the reciprocal lattice or Ewald sphere respectively.

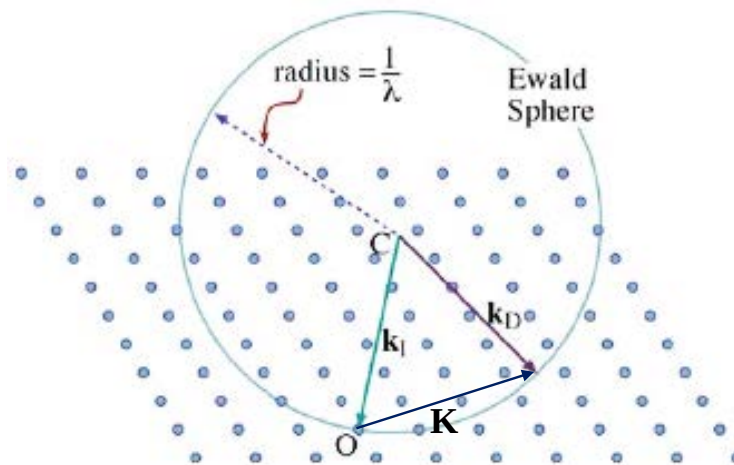


Figure 3.3 The Ewald sphere construction allows for visualisation of the conditions leading to diffraction in reciprocal space. The vector CO is the wave vector of the incident wave $\mathbf{k}_I$ with $\mathbf{k}_D$ that of the diffracted wave. Diffraction occurs when the Ewald sphere of radius $1/\lambda$ intersects the reciprocal lattice so that $\mathbf{K}=\mathbf{g}$. Figure adapted from[30]

3.3.1 Selected area diffraction and shadow imaging

The selected area diffraction technique first developed by LePoole in 1947 [223] has now become an indispensable tool for characterising nanomaterials where an understanding of crystal structure and defects is essential in controlling properties. The practical steps involve inserting a selected area aperture in an imaging plane to isolate electrons from the region of interest and adjusting the imaging-system lenses so that the back focal plane of the objective lens acts as the object plane for intermediate lens and the DP is projected onto the viewing screen[30], illustrated in Fig. 3.4 below.

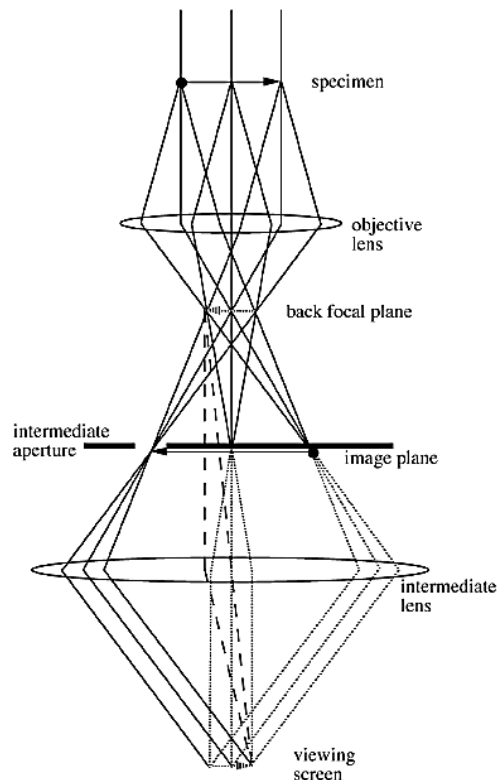


Figure 3.4 Selected area diffraction mode. The SA aperture in the imaging plane provides a sampling off all diffracted beams from the chosen area of the sample

Careful combination of the DP and the image can give structural and orientation information of a nanostructure, however, this process is made more complicated by difficulties in ensuring the electron beam is perpendicular to the sample and the existence of an instrument defined rotation between the image and diffraction pattern due to the Lorentz force. Calibrating for this rotation is often achieved by careful analysis of samples which have a high aspect ratio where the orientation of the longer dimension is known such as MoO_3 [224]. However since nanowires have a high aspect ratio themselves it is possible to measure the growth orientation directly by using the shadow imaging technique in which the image and diffraction pattern may be captured simultaneously in diffraction mode. This involves changing the beam convergence and adjusting the brightness to bring the beam cross over under or over the nanowire as illustrated in Fig. 3.5 below. The growth direction is then given by the index of the diffraction spot parallel to the nanowire image – provided the beam is perpendicular to the growth direction. There is no guarantee that a nanowire will be lying flat on the substrate so this is best overcome statistically by examining a large number of wires [225].

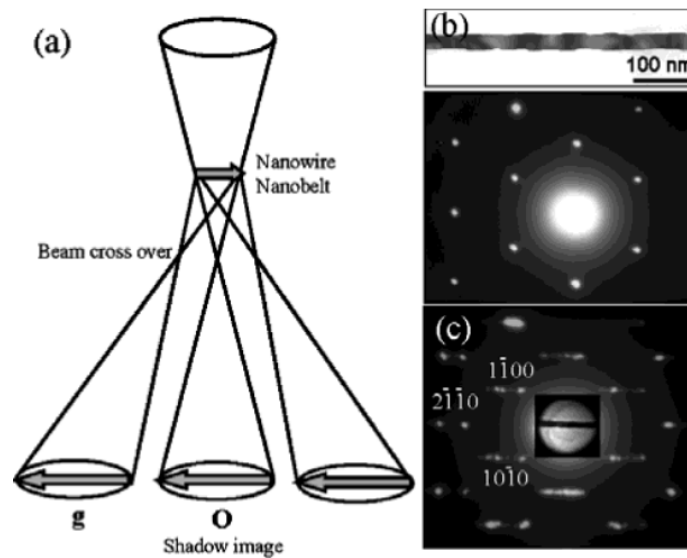


Figure 3.5 Shadow imaging technique: a) Optics of the technique, b) TEM image and SADP and c) combined shadow image. Image reproduced from [225].

3.3.2 Integrated diffraction patterns

In the application of selected area diffraction to polycrystalline or nanoparticle specimens, it may of interest to rotationally average the intensity in the pattern to determine the predominant phases in the sample and allow easy comparison to other techniques such as X-ray diffraction. Mitchell has created a script for Digital Micrograph to achieve this [226] by employing a method to accurately find the centre of the diffraction pattern before calculating an azimuthal average presented as a line plot in which the predominant intensity peaks relating to the rings in the pattern, may be identified and indexed. This also allows for easy comparison to simulated polycrystalline diffraction data – approximated by a sum of Gaussians of area proportional to the calculated intensities. Using this technique, the diffraction is assumed to be kinematic and the Bragg scattering intensities are calculated from the square of the structure factors which can be thought of as the scattering

amplitude due to the unit cell. They depend on the type of lattice and group of atoms associated with each lattice point and are calculated according to:

$$F_{hkl} = \sum_i^{atoms} f_i e^{2\pi i(hx_i + ky_i + lz_i)} \quad (3.2)$$

where f_i is the atomic scattering factor for atom i with atomic coordinates x_i, y_i, z_i . There are a number of different methods to calculate the f_i factors, a description of which has been given by Kirkland [227].

This comparison between experimental azimuthally averaged diffraction data and similar simulated data is utilised in Chapter 7 to obtain compositional information from the diffraction data.

3.4 Diffraction contrast imaging

3.4.1 Conventional Bright and Dark Field Imaging

In conventional TEM imaging mode, an image of the specimen may be projected onto the viewing screen by adjusting the intermediate lens so that its object plane is in the image plane of the objective lens. Such images, however, will have poor contrast as the scattered and transmitted beam intensities – which vary in intensity from different regions of the sample - recombine at the viewing screen [79]. Determining crystallographic information – and particularly the presence of defects – requires imaging the intensity variation of specific diffracted beams to give diffraction contrast. This is achieved by inserting an objective aperture in the back focal plane to select either the transmitted beam for BF images or one of the diffracted beams to form DF images where the electrons forming the image have been scattered by a specific set of planes – see Fig. 3.6. This technique can therefore be used to image dislocations and other defects in crystals where the strain in the vicinity of a dislocation can bend the planes into or away from the Bragg condition. The theory of diffraction contrast imaging of defects was developed by Howie, Whelan and Hirsch [228][229] who showed

that, by analysing intensity distributions for different reflections, the type of dislocation and its Burgers vector can be determined [230].

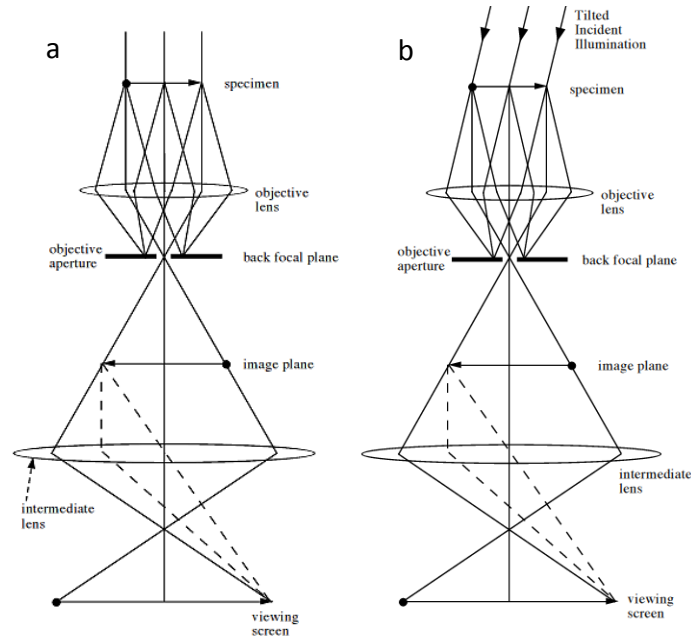


Figure 3.6 Ray diagrams for bright field (a) and dark field (b) imaging modes in the TEM. Reproduced from reference[79]

3.4.2 Burgers vectors determination via $g \cdot b$ analysis

When studying an individual dislocation the main parameters to be determined are the Burgers vector, defined by the magnitude and direction of lattice distortion resulting from the dislocation, and the line direction. These can then be used to determine the character of the dislocation as edge (Burgers vector perpendicular to line direction), screw (parallel to line direction) or mixed (components of each).

The displacement field $\mathbf{R}$ around a dislocation in an isotropic solid for the general (mixed dislocation) case is given by

$$\mathbf{R} = \frac{1}{2\pi} \left(\mathbf{b}\phi + \frac{1}{4(1-\nu)} \{ \mathbf{b}_e + \mathbf{b} \times \mathbf{u} (2(1-2\nu) \ln r + \cos 2\phi) \} \right) \quad (3.3)$$

in polar coordinates r and ϕ , where $\mathbf{b}$ is the Burgers vector, $\mathbf{b}_e$ the edge component of the Burgers vector, $\mathbf{u}$ the unit vector along the dislocation line and ν is Poisson's ratio.

If only one diffracted beam is considered, i.e. we make a 'two-beam approximation' (approached when the crystal is tilted such that only one diffracted beam is strong), the intensity in the direct beam ϕ_0 and diffracted beam ϕ_g , are given by the Howie-Whelan equations[228][229]

$$\begin{aligned}\frac{d\phi_g}{dz} &= \frac{\pi i}{\xi_g} \phi_0 e^{-2\pi i s z} + \frac{\pi i}{\xi_0} \phi_g, \\ \frac{d\phi_0}{dz} &= \frac{\pi i}{\xi_0} + \frac{\pi i}{\xi_g} \phi_g e^{2\pi i s z}.\end{aligned}\tag{3.4}$$

In the case of the imperfect crystal which includes a lattice distortion $\mathbf{R}$, the intensity in the diffracted beam can be expressed as

$$\frac{d\phi_g}{dz} = \frac{\pi i}{\xi_g} \phi_0 e^{-2\pi i (s z + \mathbf{g} \cdot \mathbf{R})} + \frac{\pi i}{\xi_0} \phi_g.\tag{3.5}$$

Since the intensity given by the Howie-Whelan equations is proportional to $\mathbf{g} \cdot \mathbf{R}$, it can be seen from equation 3.3 that for the screw case, when $\mathbf{b}_e=0$ and therefore $\mathbf{R} \propto \mathbf{b}$, that the intensity depends on $\mathbf{g} \cdot \mathbf{b}$. The case is complicated somewhat when the dislocation has an edge component as the contrast from the dislocation then depends on two terms $\mathbf{g} \cdot \mathbf{b}$ and $\mathbf{g} \cdot \mathbf{b} \times \mathbf{u}$. In general, if $\mathbf{g} \cdot \mathbf{b}=0$ then no contrast will be observed as the diffracting planes are parallel to $\mathbf{R}$ – the so-called invisibility criterion.

Therefore, by identifying two reflections $\mathbf{g}_1$ and $\mathbf{g}_2$ for which $\mathbf{g} \cdot \mathbf{b}=0$, the direction of the Burgers vector may then be calculated from $\mathbf{g}_1 \times \mathbf{g}_2$.

This process is less-straightforward experimentally as dislocations appear out of contrast when $\mathbf{g} \cdot \mathbf{b} < 1/3$ in addition to the issue mentioned above concerning dislocations not appearing invisible even if

$\mathbf{g} \cdot \mathbf{b} = 0$, when $\mathbf{g} \cdot \mathbf{b} \times \mathbf{u} \neq 0$. However if a dislocation is imaged under a range of diffraction conditions by tilting to strong two beam conditions and selecting appropriate $\mathbf{g}$ vectors, the Burgers vector can usually be determined.

3.4.3 Weak beam imaging

A useful branch of diffraction contrast imaging involves forming a dark field image with weakly excited beams and facilitates the study of individual lattice defects at a higher resolution than that possible with conventional BF/DF imaging but without requiring the *a priori* knowledge that may be necessary when using HRTEM [231]. First described fully in 1969 [232], the technique involves firstly tilting the crystal far from the Bragg condition for given set of planes corresponding to a specific $\mathbf{g}$. In such an orientation, since the planes of the perfect crystal do not satisfy the Bragg condition they will only very weakly scatter into the chosen $\mathbf{g}$ and therefore this region of the crystal will appear dark. However in the vicinity of a defect, where there is sufficient strain to bend the planes back into the Bragg condition, the planes will scatter strongly into $\mathbf{g}$. Therefore this region around the defect will appear bright in the image allowing the defect to be imaged. Because the crystal is tilted a long way from the Bragg condition, a large strain is required to bend the planes sufficiently to produce contrast in the image and therefore the contrast is limited to a very localised region around the defect (as illustrated in Fig. 3.7 below) and a greater resolution may be achieved than that of standard diffraction contrast imaging.

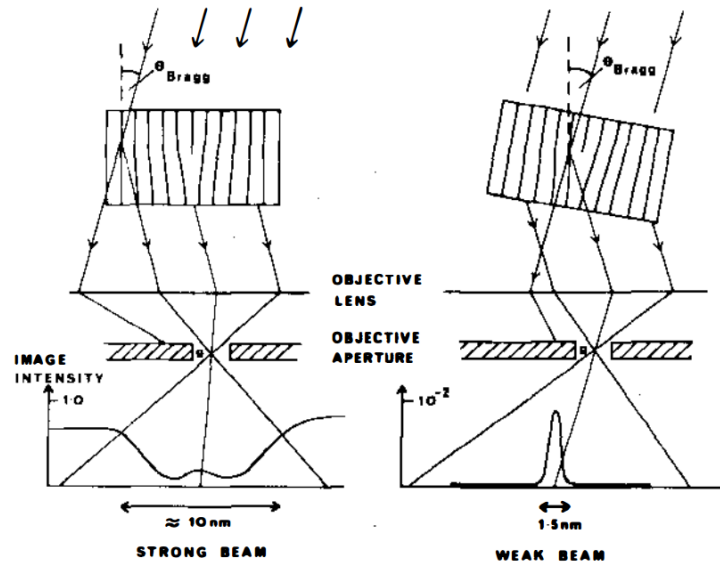


Figure 3.7 Comparison of strong beam and weak beam conditions with corresponding image intensity profiles.
Reproduced from reference [231]

Experimentally, this first involves selecting a particular $\mathbf{g}$ and bringing it onto the optical axis to form a conventional on-axis DF image but then tilting the specimen away from the Bragg condition to make the excitation error $s_{\mathbf{g}}$ (a measure of the deviation from the exact Bragg condition) large and imaging with the weak reflection $\mathbf{g}$. If a dislocation is present, the diffracting planes may be bent back to the Bragg condition locally to the core to give intensity in the image at this area, as illustrated in Fig. 3.7 above. The contrast is heavily dependent on the excitation error, which is set by viewing the Kikuchi map whilst tilting the specimen to position the $n\mathbf{g}$ Kikuchi line just outside the $n\mathbf{g}$ reflection on the $\mathbf{g}$ -systematic row, where the excitation error may be calculated from

$$s = \frac{1}{2}(n - 1)|\mathbf{g}|^2\lambda. \quad (3.6)$$

The case for $n=3$, a so called $\mathbf{g}(3\mathbf{g})$ condition is illustrated in Fig. 3.8 below. By choosing the diffraction condition so that the 'weak beam criterion', $s_{\mathbf{g}}=0.2\text{nm}^{-1}$, is satisfied, ensures that the image will have a narrow width, high contrast between the defect and background and the image peak will correspond closely to the core position [30].

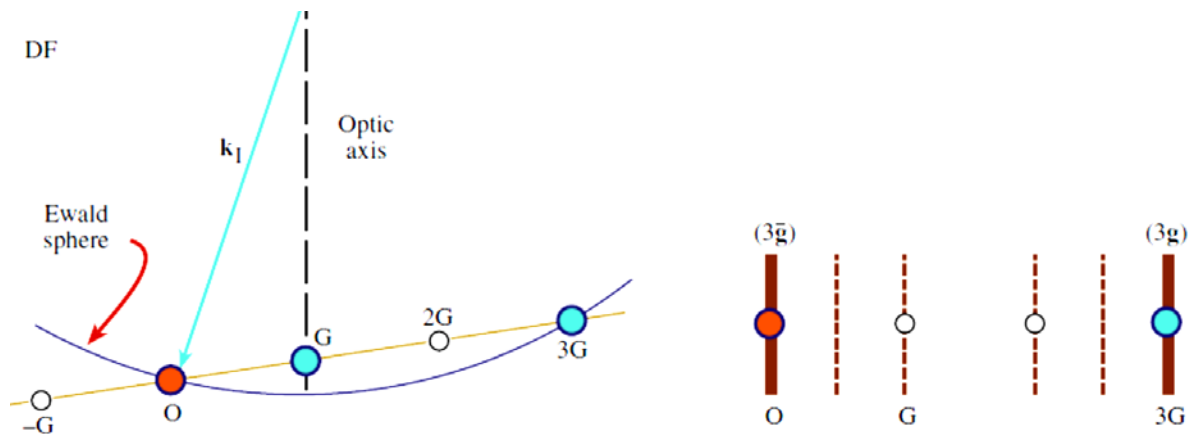


Figure 3.8 A Schematic illustration of the relationship between the orientation of the Ewald sphere and the position of the Kikuchi lines on the systematic row of diffraction spots for the chosen g . The correct tilt conditions are set by viewing the Kikuchi map (right hand side) to position the $3G$ Kikuchi line just outside the $3g$ reflection to give a $g(3g)$ weak beam condition. Reproduced from [30]

3.5 Radial Distribution function

When studying amorphous materials, which have short range order but lack significant long range structure, a real space approach is often favoured over the reciprocal space diffraction method. The most common way of describing their structure is using distribution functions which describe the average number of atoms within a spherical shell dr at a radius r from a central atom [233].

Distributions of atoms are commonly investigated by scattering experiments with the structure of amorphous materials typically studied by neutron and x-ray diffraction. In the case of amorphous nanoparticles, such as those studied in Chapter 7, the scattering cross sections for these radiations are too small and electron diffraction in the electron microscope is preferable. Early work by Debye described the mathematical conversion of such diffraction patterns into information about the structure [234] and was the basis for more recent development and application to electron diffraction from nanoscale amorphous materials [235].

The scattered intensity at given scattering angle $\mathbf{q}$ from an atom i at $\mathbf{r}_i$, with associated atomic scattering factor $f(\mathbf{q})$ is given by the Debye formula ,

$$I(\mathbf{q}) = Nf^2(\mathbf{q}) + \sum_{i \neq j} \sum_j f^2(\mathbf{q}) \sin(qr_{ij}) / (qr_{ij}), \quad (3.7)$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and an isotropic distribution has been assumed.

Because $g(\mathbf{r})$

is directly

related to

the local

average

density,

when

discounting

small

scattering
$$I(\mathbf{q}) = Nf^2(\mathbf{q}) + 4\pi Nf^2(\mathbf{q}) \int_0^\infty [g(r) - \rho_0] \frac{r}{q} \sin(\mathbf{q}\mathbf{r}) dr. \quad (3.8)$$

angles, the

above

equation can

be

integrated

over the

sample

volume to

give

This equation describes how the intensity deviates from the mean intensity $Nf^2(\mathbf{q})$, arising from atoms scattering independently, when the local density at $\mathbf{r}$ deviates from the mean density ρ_0 . By defining the reduced intensity function

$$\varphi(\mathbf{q}) = \left[\frac{I(\mathbf{q}) - Nf^2(\mathbf{q})}{Nf^2(\mathbf{q})} \right] \mathbf{q}, \quad (3.9)$$

the reduced density function $G(\mathbf{r})$ may be obtained by substitution into equation 3.8, given by

$$G(\mathbf{r}) = 4 \int_0^\infty \phi(\mathbf{q}) \sin(\mathbf{qr}) d\mathbf{q} = 4\pi r[g(\mathbf{r}) - \rho_0] = J(\mathbf{r})/r - 4\pi r\rho_0. \quad (3.10)$$

Using this equation, $G(\mathbf{r})$, the radial distribution function $J(\mathbf{r})$ and the pair distribution $g(\mathbf{r})$ can all be extracted from an experimental diffraction pattern by straightforward mathematical manipulation.

This is achieved by forming $\phi(\mathbf{q})$ from the experimental intensity $I(\mathbf{q})$ by fitting to the background mean scattering intensity $Nf^2(\mathbf{q})$. $G(\mathbf{r})$ may then be calculated from the Fourier transformation of $\phi(\mathbf{q})$.

$G(\mathbf{r})$ may then be plotted and maxima in the function give the most probable distances between specific atom types which, using prior knowledge about the types of material within the sample, may be related to specific bonds.

In practice, software is used to fit $Nf^2(\mathbf{q})$ to the experimental data using a combination of knowledge about the atom types in the sample to produce a model followed by a Monte Carlo fitting procedure to reconfigure the model and improve the fit. Fitting may be improved by fitting at large q where there are fewer features and subtracting to provide $I(\mathbf{q})$. An example of fitting $Nf^2(\mathbf{q})$ to experimental data) is shown in Fig. 3.9(a) below.

This is subtracted to give the reduced intensity function which is then converted to the real space reduced density function, as shown in Fig. 3.9(b). The software also allows for the experimental data to be compared to a model crystal, built in CrystalMaker, so that the function can be compared to simulated data based on potential candidate crystals of varying size. Using this technique therefore, gives an idea of the type of bonds in addition to an idea of the range of order within the sample.

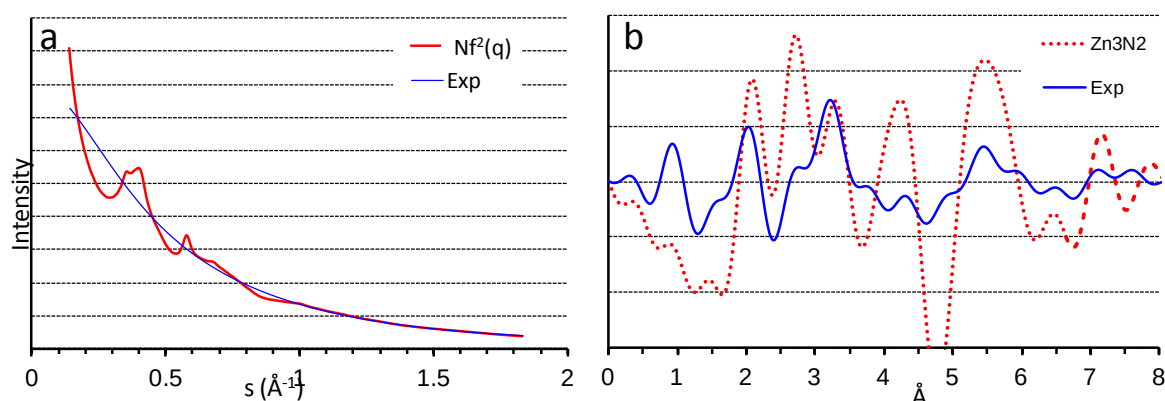


Figure 3.9 Illustration of the use of the radial distribution function software to (a) fit and subtract the intensity from independent atom scattering $Nf^2(q)$ and (b) convert to $G(r)$ to compare the spacings within the sample to that of a model of possible candidate material crystals.

3.6 High resolution transmission electron microscopy

Due to the high sensitivity of semiconductor nanostructures to their microstructure, characterisation of defects and interfaces at the atomic scale is often necessary which cannot be achieved in TEM diffraction contrasts images. Phase contrast is the primary contrast mechanism of HRTEM images which arises due to the differences in phase of electron waves scattered through a thin specimen. The fundamental practical difference in forming phase contrast images compared with that of diffraction contrast is the number of beams selected with the objective aperture. The contrast then results from the interference between the transmitted and diffracted beam to produce lattice fringes, with, in general, the resolution of the image increasing with the number of beams. This contrast mechanism is highly sensitive to a large number of microscope and sample variables making it difficult to interpret and often needs to be complimented with simulations.

HRTEM theory is usually developed in terms of Fourier transforms [236], where the spatial frequencies of the sample, $\mathbf{u}$, are transformed to the diffraction pattern on the back focal plane and back again to the image with the aim being to preserve the maximum amount of useful information transferred. The information is carried by the phase of the electron wave and relies on the sample being thin enough that it imparts only phase changes on the incoming coherent electron wave and very small changes of amplitude – the so called weak phase object approximation (WPOA).

A mathematical expression of the weak phase object approximation can be derived starting from a general model for the specimen function $f(\mathbf{r})$

$$f(x, y) = A(x, y) \exp(-i\phi_t(x, y)), \quad (3.10)$$

Where $A(x, y)$ is the amplitude function and $\phi_t(x, y)$ is the phase which depends on the thickness of the specimen. This may be simplified further by setting the incident wave amplitude to unity $A(x, y) = 1$. It can then be assumed that the specimen is so thin that we can write down a projected potential $V_t(x, y)$ as

$$V_t(x, y) = \int_0^t V(x, y, z) dz, \quad (3.11)$$

Thus creating a two dimensional projection of the crystal where the total phase shift is dependent only on $V(x, y, z)$ where

$$d\phi = \sigma V_t(x, y), \quad (3.12)$$

σ being the interaction constant. The effects of absorption can be accounted for by including a further function $\mu(x, y)$ so that the specimen transfer function becomes

$$f(x, y) = \exp[-i\sigma V_t(x, y) - \mu(x, y)], \quad (3.13)$$

known as the phase-object approximation. Finally if the specimen is very thin so that $V_t(x, y) \ll 1$, we can expand this expression to arrive at the weak phase-object approximation,

$$f(x, y) = 1 - i\sigma V_t(x, y). \quad (3.14)$$

The aberrations in the magnetic lenses mean that the relationship between the image wave and the sample exit wave is highly non-linear and also depends on defocus and electron wavelength – the details of which are contained in the contrast transfer function. In the case where the WPOA holds this may be expressed as

$$T(\mathbf{u}) = A(\mathbf{u})E(\mathbf{u})2 \sin \chi(\mathbf{u}) \quad (3.15)$$

where $A(\mathbf{u})$ is the aperture function – a step function representing the cut off at higher frequencies due to the objective aperture; $E(\mathbf{u})$ is the envelope function representing the attenuation of the electron wave at higher scattering angles due to the spatial coherence of the source and chromatic aberration; and $\chi(\mathbf{u})$ describes the aberrations of the lens. The latter can be written in terms of defocus Δf , spherical aberration C_s and electron wavelength λ as

$$\chi(\mathbf{u}) = \pi \Delta f \lambda u^2 + \frac{1}{2} \pi C_s \lambda^3 u^4 \quad (3.16)$$

Collecting interpretable HRTEM images therefore relies on knowledge of the contrast transfer function of the microscope used so that defocus may be varied to maximise the amount of interpretable information transferred – minimising the number of zeros in the function which represent gaps in the output spectrum. In 1949 Scherzer described the optimum relationship between defocus and spherical aberrations [237] which balances their effects. The extended Scherzer defocus can be written as

$$\Delta f_{Sch} = -1.2(C_s \lambda)^2 \quad (3.17)$$

and means all beams have nearly constant phase out to the first crossover of the zero axis, meaning the contrast can be interpreted intuitively. It is however important to note that many samples are too thick for the WPOA to hold, which results in contrast reversal with thickness and associated difficulties in image interpretation. In the work of this thesis, HRTEM has been carried out with a JEOL 3000F and 2200MCO and is used to identify the presence of defects such as dislocations and stacking faults in III-nitride nanowires and microrods in addition to helping in confirming the crystal structure of zinc nitride nanoparticles.

3.7 Scanning transmission electron microscopy

STEM involves raster scanning a fine ($1\text{-}10\text{\AA}$) probe perpendicular to the sample to build up an image by collecting the chosen signal in series. Changing the camera length and the detector is analogous to changing the illumination conditions in TEM - electrons scattered through particular angular ranges may be collected to give differing sample information as illustrated in the figure below.

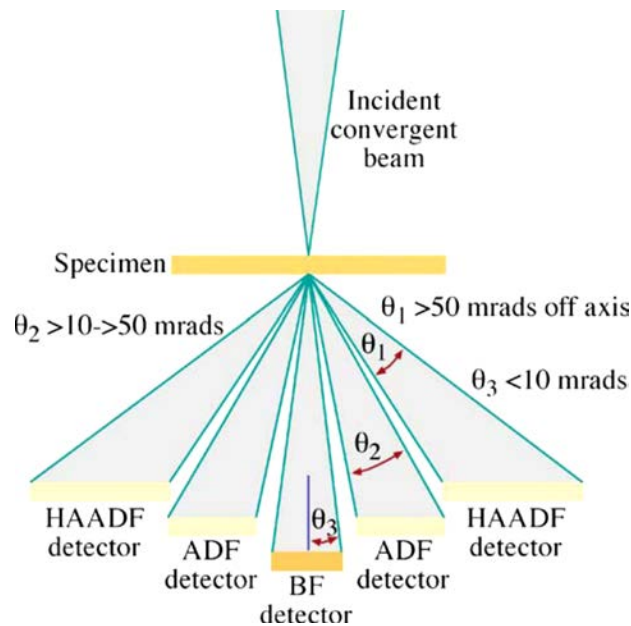


Figure 3.10 Schematic illustration of the detector set up for different electron scattering angle ranges in a STEM.
Reproduced from [30]

Diffraction contrast STEM images can be understood the principle of reciprocity [238] which states that, for elastic scattering, as long as the electron ray paths contain equivalent angles of convergence and collection the contrast will be identical to that of a TEM. This also helps to understand why good diffraction contrast STEM images are inherently noisy as when the collection angle is reduced towards the TEM illumination angle the signal falling on the detector becomes extremely small.

ADF STEM imaging (the primary STEM mode used in the following work) is fundamentally different to DF TEM as images are formed via collection of the majority of scattered electrons in an annular dark field (ADF) detector in contrast to the fraction that are selected with the objective aperture in

TEM. This means they are less noisy as well as being unaffected by the spherical aberrations that inhibit off axis DF TEM images. By selecting angles out to even higher angles with a high angle ADF (HAADF) detector, Bragg scattered electrons are effectively removed, leaving those due to Rutherford-like scattering (a mechanism dependent on atomic number)so chemical information is obtainable.

A benefit of using high angle incoherent scattering to form images is that there is no phase effect which is involved in the summing of electron wave amplitudes in HRTEM, instead the image intensity is given by a simple convolution between the scattering power of the specimen and the probe intensity profile [239]. Each atom may be considered an independent scatterer meaning HAADF images are more directly interpretable in terms of atom types and positions with contrast that is unaffected by small changes in defocus and thickness unlike HRTEM [240].

Because of these advantages it is primarily ADF STEM that is employed in the following work with the JEOL 3000F used for lower magnification imaging and EDX mapping and a JEOL 2200MCO for high resolution imaging in which aberration correction allows for a smaller probe to be formed to achieve greater resolution.

3.8 Spectroscopy

In addition to diffraction and imaging, the high-energy electrons in a TEM cause electronic excitations of the atoms in the specimen, from which the corresponding signals may be studied under the broad term of analytical TEM. It is important to note that such inelastic processes deposit energy in the sample which may have unwanted or damaging effects [241] as observed in the characterisation work of zinc nitride nanoparticles described in Chapter 7.

3.8.1 Energy dispersive X-ray analysis

The most important secondary signal generated in the specimen are the characteristic X-rays of the sample atoms which are analysed in energy dispersive X-ray spectroscopy (EDX) [242]. Such signals are produced when a high energy electron interacts with the core-electrons of an atom, ejecting one leaving the atom in an excited state. An X-ray of characteristic energy unique to that element is emitted when an outer shell electron drops into the vacated state and therefore these signals give compositional information. There are several different types of EDX detector available [243] but all rely on generating a charge pulse proportional to the X-ray energy which may be processed and binned according to energy range. This technique has been used in STEM mode to determine the composition changes and interfaces in cross sections of the materials studied.

The quantification of the detected elements may either be performed by using a standard or standardless analysis. The following work uses the latter in which the software quantifies the elements detected by calculating the area under each peak and, accounting for the acceleration voltage of the electrons used to produce the spectrum, calculates sensitivity factors or k factors to convert the area under the peak into a weight or atomic percentage.

3.8.2 Electron energy-loss spectroscopy

The analysis of the energy distribution of electrons after they have traversed the specimen, originally developed by Hillier and Baker [244], predates EDX but was relatively slow to develop although it is now perhaps the dominant STEM spectroscopy technique. It has certain advantages over EDX in that it can be used to detect light elements which have X-ray emission of too low energy to be detected, it has greater spatial resolution and analytical sensitivity and gives a wealth of additional chemical information including the bonding and valence state, dielectric response, free-electron density, bandgap and specimen thickness [245]. The technique involves dispersing the electrons by using a magnetic prism which allows resolution of energy differences <1 eV. The spectra produced include information from the plasmon interactions with the weakly bound conduction and valence band

electrons and elemental information from interactions with the more tightly bound core-shell electrons. This technique has been applied to determine the lighter elements present in the nanoparticles described in Chapter 7.

3.9 Scanning electron microscopy

An SEM uses a demagnified electron beam to scan across a sample whilst collecting various types of signals produced by the incident electrons. The first precursor to the modern SEM was developed by Knoll four years after the TEM[246] with Von Ardenne the first to implement scan coils to achieve electromagnetic scanning of a focussed probe[247] while the later development of the Everhart-Thornley detector allowed for the first commercialisation[248].

SEM offers advantages over transmission microscopy in certain applications since it does not require extensive sample preparation and therefore may preserve morphological and surface information that TEM sample preparation may destroy. It also retains a larger depth of field allowing a large amount of structural data to be collected and it is particularly suited to collecting surface topological information.

The collected signals may include secondary electrons (generally with energy $<50\text{eV}$), backscattered electrons (incident electrons scattered with energies $>50\text{eV}$), characteristic X-rays, light (cathodoluminescence) and specimen current.

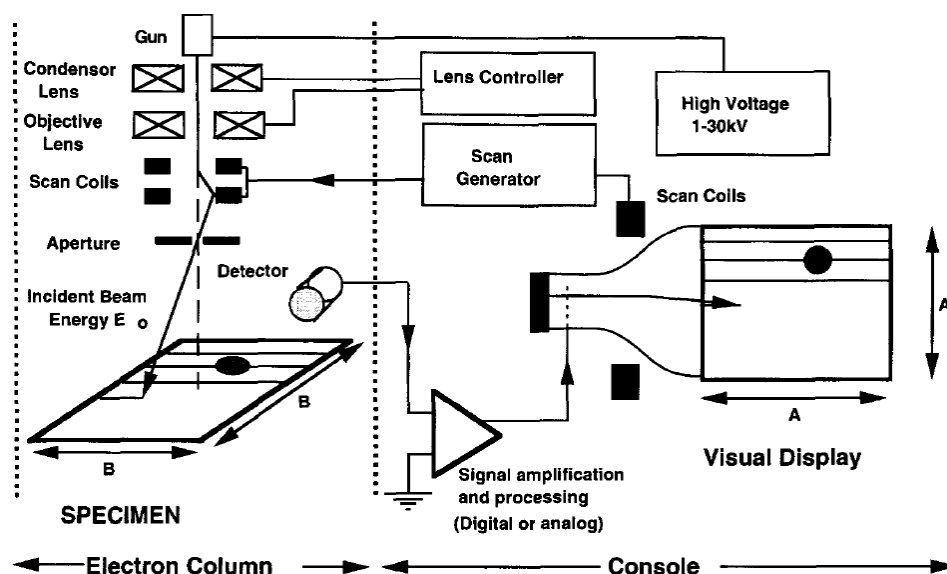


Figure 3.11 Basic components of the scanning electron microscope. Reproduced from reference [249]

Since secondary electrons have very low energies, they emerge from a shallow escape region near the surface and therefore may be used to reveal the surface properties of nanoscale materials. This imaging mode is implemented in this work to characterise the surface topology of core/shell nanowires and in combination with the focussed ion beam in a Zeiss Nvision 40 to survey the morphology of cross section samples prepared from core shell wires and rods.

3.10 Specimen preparation

The general requirements for specimen preparation in TEM are for electron transparency, robustness in order to handle the specimen and for it to be representative of the sample as a whole. The method chosen to prepare the specimen depends on the specific sample and several are employed in the following experimental work.

3.10.1 Drop-casting

As described in Chapter 1, the dimensions of semiconductor nanostructures mean they are often by definition electron transparent in at least one direction. For these materials, such as the nanowires of Chapter 4 and the nanoparticles of Chapter 7, all that is required is to suspend them in a solvent

and place a drop of the solution onto an amorphous carbon film-coated TEM grid. The amorphous carbon film supports the nanoparticles but has low contrast in the TEM so as not to obscure contrast arising from the specimen. The nanowires first require removal from the growth substrate which is achieved via sonication in a solvent to dislodge the attached nanowires. The nanoparticles simply require diluting to an appropriate concentration for the right level of dispersion when dropped on to the grid. However since the zinc nitride nanoparticles are highly sensitive to oxidation, in this case the entire process from dilution to drop-casting to loading into the microscope was performed under a nitrogen environment, as is discussed in more detail in Chapter 7.

3.10.2 FIB cross section lift out

In order to study the cross section structure of the core/shell nanowires and microrods (and in the case of the latter to reach electron transparency for which the whole structures are too large) it was necessary to prepare slices through the structures. This is achieved within a Zeiss NVision dual-beam FIB which combines various elements including: an electron column with a focussed ion beam aligned at 54° to the electron beam for simultaneous viewing and milling; a gas injection system to facilitate deposition of various materials with the ion beam; and a micromanipulator to lift out the prepared specimen and attach to a TEM grid. The FIB therefore offers a method of preparing specimens from precise locations, not possible with other techniques.

Care needs to be taken in using this technique since the FIB may introduce artefacts into the specimen including a change in the microstructure such as amorphous regions and the introduction of defects plus possible changes in the composition due to gallium implantation. Awareness of such artefacts is important in order to ensure the defects and gallium composition observed are intrinsic to the growth process rather than the result of FIB-related damage. With appropriate precautions good quality specimens may be prepared for high resolution imaging with minimal artefacts introduced [250].

Taking into account these considerations, the first step, illustrated in Fig. 3.12(a), is to deposit platinum with the electron beam which is much less damaging than the FIB and provides an initial layer of protection. An initial carbon layer is then deposited with the e^- -beam before a thicker layer is then applied with the FIB beam, as shown in (b), which provides more protection against gallium implantation and damage and holds the chosen structure to the substrate surface. Trenches are then milled either side of the section with the FIB, as illustrated in (c), before the micromanipulator is moved in and attached to the corner of the section with carbon deposited with the FIB as shown in (d). The section is then cut free of the substrate with the FIB before lifting out by moving the stage away and attaching to the TEM grid using further carbon deposition (e-f). The section may then be tilted 1-2° away from the FIB beam before thinning progressively by gradually reducing the beam current and polishing to electron transparency as shown in Fig. 3.12 (g-h).

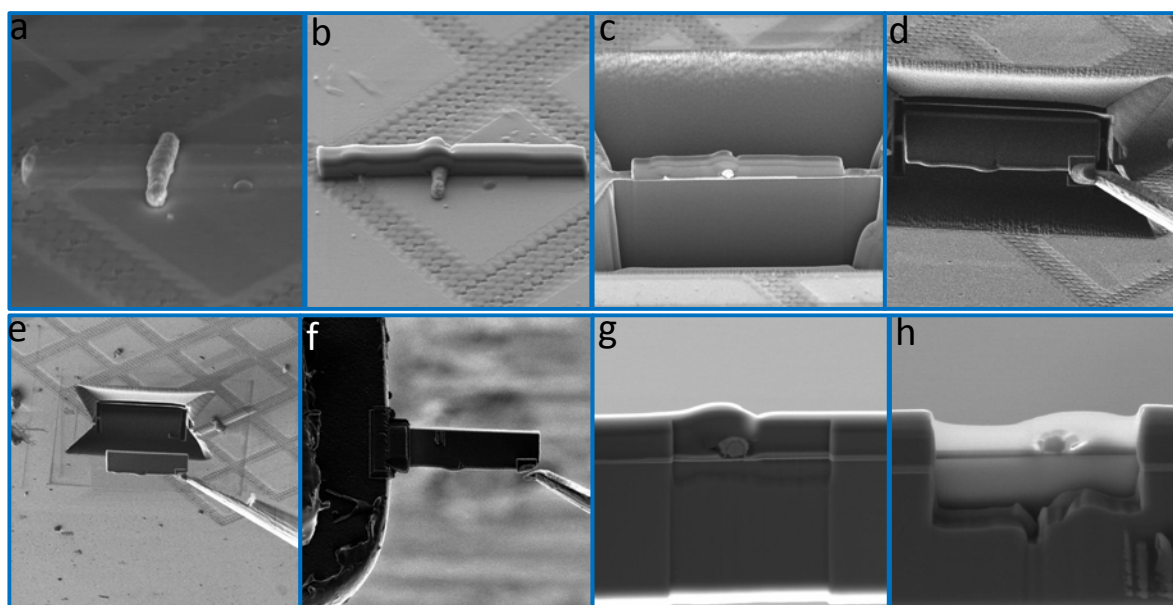


Figure 3.12 The cross section lift out procedure of a core shell nanowire deposited on a silicon wafer by deposition of (a) tungsten and (b) carbon straps, (c) milling of trenches, (d,e) lift out with micromanipulator, (f) attaching to a grid and (g,h) milling to electron transparency

In this thesis several methods were explored for achieving this including progressively thinning the section towards the far edge from the grid and thinning a specific region of interest in order to give the sample better stability and also leaving a thicker region which may be beneficial in EDX analysis.

3.10.3 Ultramicrotomy

Ultramicrotomy is an alternative technique used to prepare cross section samples which operates by moving a sample back and forth past a sharp diamond blade to produce thin (<100nm thick) sections which are collected on the surface of a water-filled trough and transferred to a grid. In order to section particles such as those studied in this work, they must be embedded in resin which is attached to the end of the sample arm as illustrated in the diagram of Fig. 3.13.

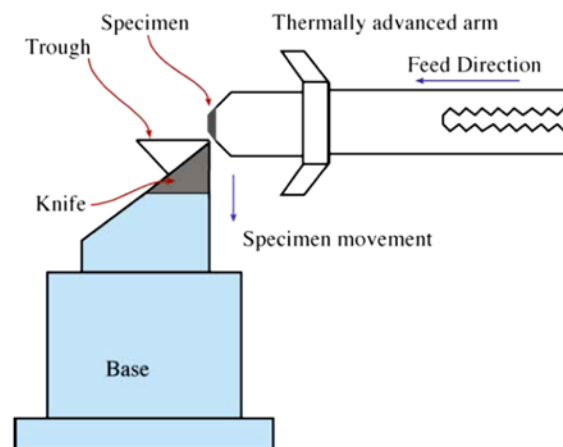


Figure 3.13 Schematic illustration of a microtome taken from [30]

This technique offers the potential advantage of the FIB method in that it leaves the chemistry unchanged as it avoids detrimental gallium implantation. However the sectioning of hard materials such as GaN is really one of (partly) controlled fracturing which can introduce further defects into the material so often a compromise must be reached.

3.11 Summary

The characterisation tools used in the experimental work of Chapters 5-7 have been described with a very brief overview of the basic theory in order to provide a foundation for the experimental discussions.

After introducing the (scanning) transmission electron microscope, the diffraction techniques used have been described, including selected area, convergent beam and integrated polycrystalline

diffraction. A wide range of imaging techniques are presented including conventional bright and dark field, weak beam, HRTEM and ADF STEM in addition to the primary spectroscopy techniques of EDX and EELS. The theoretical background to the radial distribution function was introduced as a basis to the investigation of order in nanoparticles. The mechanism and advantages of SEM were discussed which is relevant to the study of core/shell microrods in Chapters 5 and 6. Finally, three specimen preparation techniques used are outlined with their various advantages and drawbacks highlighted.

Chapter 4

Core/Shell GaN/InGaN Nanowires

4.1 Introduction

The III-nitride family of semiconductors are firmly established as the primary material system of interest in the development of short wavelength LEDs for solid state lighting. The favourable properties include the possibility of tuning the bandgap over a wide range of energies from infrared to deep UV via alloying and the strong chemical stability giving a reduced rate of degradation in comparison to other candidate materials. There are however, well-documented development difficulties including the high dislocation densities associated with a lack of suitable growth substrates and the strong polarisation fields along the *c*-axis, the predominant growth direction - both of which are believed to reduce the efficiency of devices based upon these materials. The former is believed to lead to non-radiative recombination reducing emission intensity although the exact role the defects play in the luminescence from these materials is still under debate. The effect

of the piezoelectric fields across the junctions is to spatially separate the electron and hole wavefunctions, limiting the efficiency of radiative recombination, and to introduce a current-dependent red-shift in wavelength referred to as the quantum confined stark effect (QCSE).

Core-shell GaN/InGaN nanowires offer a potential solution to both of these issues. Firstly, the misfit strain with mismatched substrates may be accommodated coherently in nanowires due to the small cross sectional interface with the substrate and large surface area, meaning they may be grown completely dislocation free [29], [143], [146], [251]. Secondly, the core-shell geometry allows for junctions to be grown on the non- and semi-polar side facets of the nanowires, avoiding the detrimental effects of QCSE on the radiative recombination efficiency across polar junctions[252]. In addition, research suggests the strain-relieving nanowire geometry means that, for a given lattice mismatch, the critical radius of a nanowire heterostructure is approximately an order of magnitude larger than the critical thickness of the equivalent planar heteroepitaxial system[98], allowing for growth of coherent heterostructures not possible in planar systems.

Despite these promising features there is still a large amount of work required in order to fully understand the link between the optical properties and microstructure of these novel structures and to develop and optimise the material towards application in future optoelectronic devices. One of the primary questions is the link between the core nanowire size, crystallography and faceting and the overgrown shell morphology with previous theoretical studies suggesting there is a material-dependent critical core thickness below which any thickness of core may be accommodated coherently [137] and others indicating that growth rate is very dependent on specific core facets[102] [99]. In particular, since the size of the nanowire core is believed to play a significant role in determining whether the shell grows coherently, an accurate way to determine the core size within the core shell structure is desired. Another question is linked to the metallic catalyst particle used to grow the core and whether it remains embedded within the shell where it may affect the electronic properties of the structures.

The aims of this chapter are therefore as follows: (1) to first characterise the nanowires comprising the core including their crystallography and growth orientation; (2) to study the relationship between core size and crystallography and the shell quality and (3) to determine a reliable way to measure the core size within core-shell structures of varying size and shell thickness.

4.2 GaN Nanowire cores

4.2.1 General morphology

The GaN nanowires, upon which the InGaN shells would later be deposited, were grown at SLE via the vapour-liquid-solid mechanism, described in Chapter 3. In this case a growth temperature of 920°C was used, with Ni clusters as the catalyst on an α -plane sapphire substrate. In practice however, the straight forward description of the VLS growth process is not fully sufficient, since, rather than individual Ni droplets guiding the growth of single nanowires, a range of structures are observed to grow on the metal droplets, as can be observed in the SEM image of the growth substrate in Fig. 4.1(a) below.

There are clearly a range of large plate-like structures in addition to the intended 1-D nanowires and the large size of the clusters means that the idea of an interface between the GaN NWs and the sapphire substrate is really not accurate but rather the semiconductor grows atop the nickel islands. Figure 4.1(b) includes a BFTEM image of a typical large GaN nanowire with accompanying characteristic HRTEM image of the defect free wurtzite structure along the c -axis. A wide range of nanowire sizes were observed from 8nm – >200nm diameter, with lengths of 1-5 μ m, but all shared similar morphological characteristics of being very straight with a Ni catalyst particle, still attached at one end, as shown in the ADF STEM image of (c).

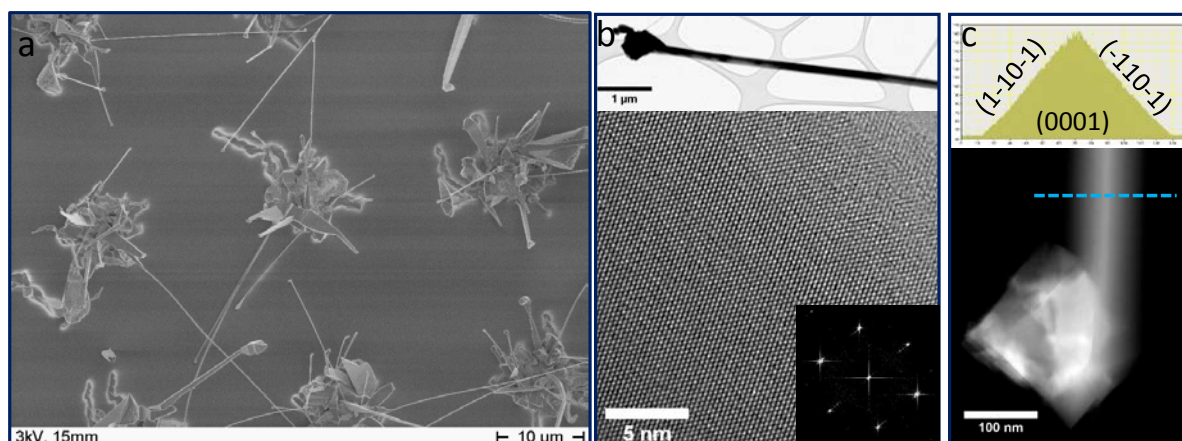


Figure 4.1 (a) SEM image of the nanowire growth substrate indicating growth of a range of GaN nanostructure morphologies from the nickel islands. (b) BFTEM image of an individual GaN nanowire with accompanying characteristic HRTEM image showing that the wires are generally defect free. (c) ADF STEM image of the end of the nanowire showing the faceted structure of the catalyst particle with accompanying intensity profile indicating the triangular shape of the cross section.

The catalyst particle at the end of the wire often appears faceted, as can be seen in Fig. 4.1(c) above, which has previously been cited as evidence that the catalyst particle remains solid during a vapour-solid-solid process. Although it is difficult to determine the cross section of the wires in conventional imaging of the wires dispersed on a grid, strong evidence of a triangular cross section – which has often been observed in the literature – is provided from ADF STEM line profiles. Since the ADF STEM intensity is approximately proportional to the thickness of the wire here, the intensity line profile across the wires (the blue dashed line in Fig. 4.1(c)) gives an idea of the cross section and clearly suggests a triangular shape. The facets bounding the triangle will depend on the growth direction – with the expected facets of an *a*-axis wire given in (c) - and will be returned to in the direct cross section imaging of the lift out work of Section 4.

4.2.2 Crystallography and growth direction

The vast majority of the nanowires had the expected wurtzite crystal structure and appeared completely dislocation free. This is illustrated in the data of Fig. 4.2(a) which includes an SAD pattern along the *c* axis inset and corresponding bright field image. By defocusing the diffraction pattern to combine the diffraction and image data in a shadow image, the growth orientation may be

determined. Both m -axis and a -axis orientated wires were observed in roughly equal proportion with the example of Fig. 4.2(a) clearly being an $\{1\bar{1}00\}$ m -axis orientated wire and (b) showing an $\{11\bar{2}0\}$ a -axis wire. ADF STEM profiles indicated triangular cross sections for both orientations and previous reports in the literature suggest the triangular cross section is formed by a c -plane and the $\{11\bar{2}2\}/\{1\bar{1}01\}$ pyramidal planes for a/m - axis orientated wires respectively. The presence of these lowest-energy pyramidal planes forming the triangular shape is confirmed in the FIB cross section work presented in Section 4.4.

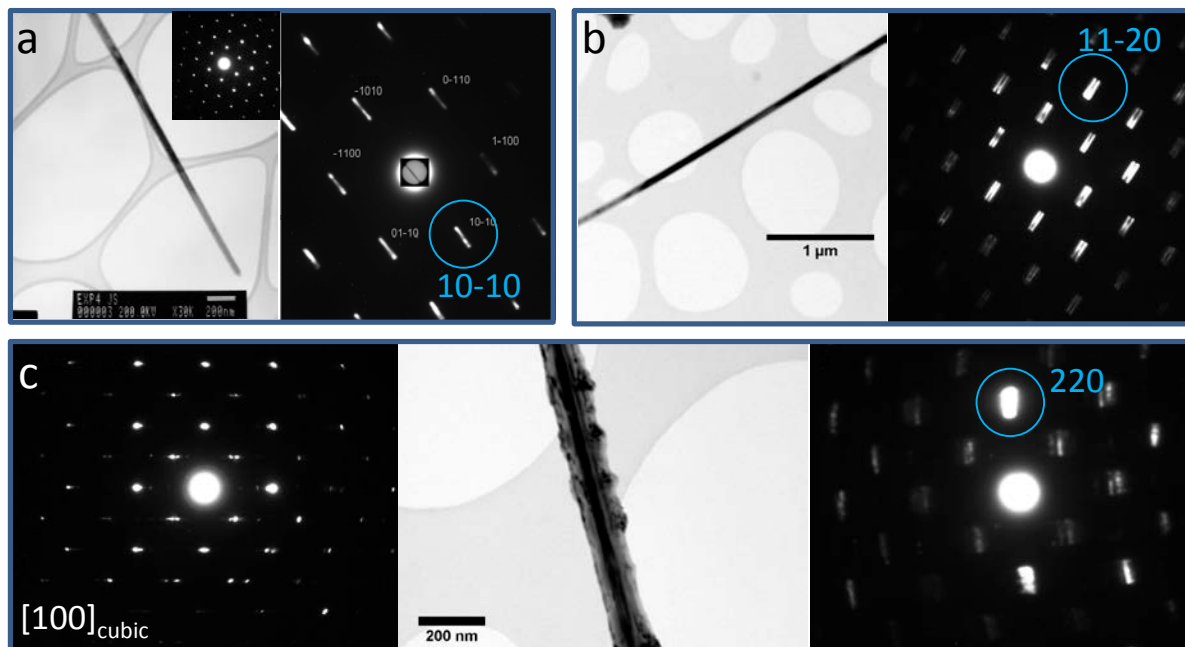


Figure 4.2 Crystallography of GaN nanowires comprising the cores. Most nanowires were wurtzite structure as expected for GaN with shadow imaging suggesting growth directions along the (a) $[1-100]$ m and (b) $[11-20]$ a directions. (c) Evidence of cubic wires was also present with growth along the $[220]$ direction

Unusually, there was also some evidence of the cubic zinc blende phase in a small proportion of wires, an example of which is provided in Fig. 4.2(c) which includes an SAD pattern indexed as $[100]_{\text{zb}}$. These cubic wires had $[220]$ growth orientations and, unlike the wurtzite wires, often had less uniform morphologies with rough surfaces and defects present – illustrated in the BFTEM image of the figure. The SADP shows prominent streaking which was often observed perpendicular to the growth direction, indicative of planar defects such as stacking faults and regions of differing

crystallographic phase [253] running along the axis of the cubic wires. The intensity in diffraction patterns from heavily faulted fcc crystals is known to redistribute to the hcp and twin positions as faulting increases [253]. If the pattern in Fig. 4.2(c) is analysed, the additional small spots can all be seen to be on the streaks running in the 220 direction. Electron diffraction theory explains that continuous streaks in the diffraction pattern from one point to the next indicate the zones bordered by stacking faults are only a few atoms thick. However as the size of the zones increase the streaks in the diffraction pattern shorten and become discrete spots as seen in this pattern suggesting the presence of larger regions of hexagonal material as well as cubic in these defected nanowires[253][254].

There is very little report of cubic GaN wires in the literature and they may have some advantages if their growth could be reliably controlled due to a higher mobility, p-type conductivity plus the advantages of being non-polar and easier to integrate with other (predominantly cubic) semiconductor technologies [255][256].

4.3 Core Shell nanowires

4.3.1 General morphology

InGaN shells were deposited on the GaN nanowires by MOCVD before removal from the growth substrate by sonication and drop casting onto TEM grids for analysis. EDX analysis suggested the indium content was lower than the intended value of 10% at around 1-5%. This low value was initially attributed to an unintentional contribution from the GaN core but this was ruled out by the cross section work described in the following section and so may be explained by known issues with indium incorporation in growth of InGaN described in Section 2.2.6.

The shells were also extremely rough with a range of morphologies observed, examples of which are provided in Fig. 4.3 below. The smallest wires appeared to have incomplete shells with islands of

InGaN attached to the core as seen in (a). The larger wires with complete shells showed a degree of variation in morphology with some having apparently fairly regular faceting and a strong recognisable single crystal SADP like that of (b) whereas others seemed to have less regular faceting and a stronger polycrystalline component in the diffraction pattern.

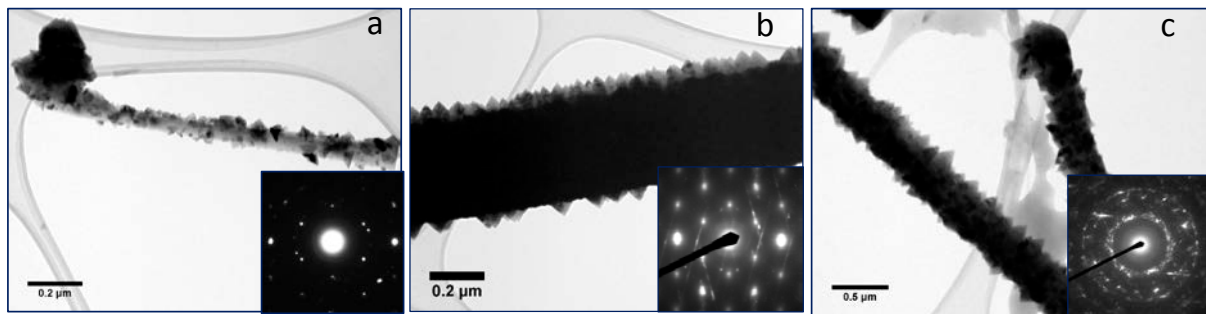


Figure 4.3 Example of the range of sizes and morphologies of the rough shells deposited on the GaN nanowire cores

It is not immediately clear from studying image and diffraction data to differentiate between the core and shell contributions so it is for example difficult to determine whether there is epitaxial, single crystal shell material on the large wire in Fig. 4.3(b) or whether the data is actually reflective of a large GaN core wire which gives the contribution in the diffraction pattern. Similarly it is not immediately obvious whether the more uniform faceting of the shell in (b) compared to (c) is simply related to the viewing orientation of the wire as opposed to any difference in crystallography.

To explore these questions further, in particular whether there is any dependence of the shell morphology on the underlying core diameter, it is desirable to find a quick method to determine the core size within the shell.

4.3.2 Identifying core size in conventional TEM

For the smallest wires with incomplete shells the core measurement is trivial but with the larger complete shells it is not straightforward to determine the core thickness. Due to the large variation in size and morphology of the wires there is no one method that allows for a quick measure of the core size but instead several methods must be employed. In the case of small wires with thin

complete shells it is often possible to tilt to a strong two beam condition using a core reflection in the SADP, if it can be identified, to form a DF image to reveal the core size, as illustrated in Fig. 4 (a) and (b) below.

In the case of large wires with thick shells such as that of Fig. 4.4(c), an EDX line scan may be used to identify the core shell structure and gain a measurement of the core as shown in (d). However, due to the low indium content and corresponding weak EDX signal, this technique is not applicable to all wires and requires a certain thickness of InGaN shell in order to identify the core. These two methods therefore cover the two morphological extremes – small wires with thin shells and large wires with thick shells but it is of interest to determine a technique to apply to a wider range.

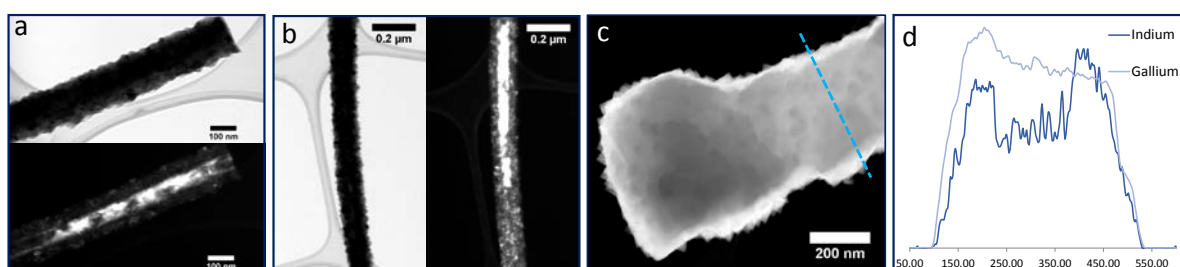
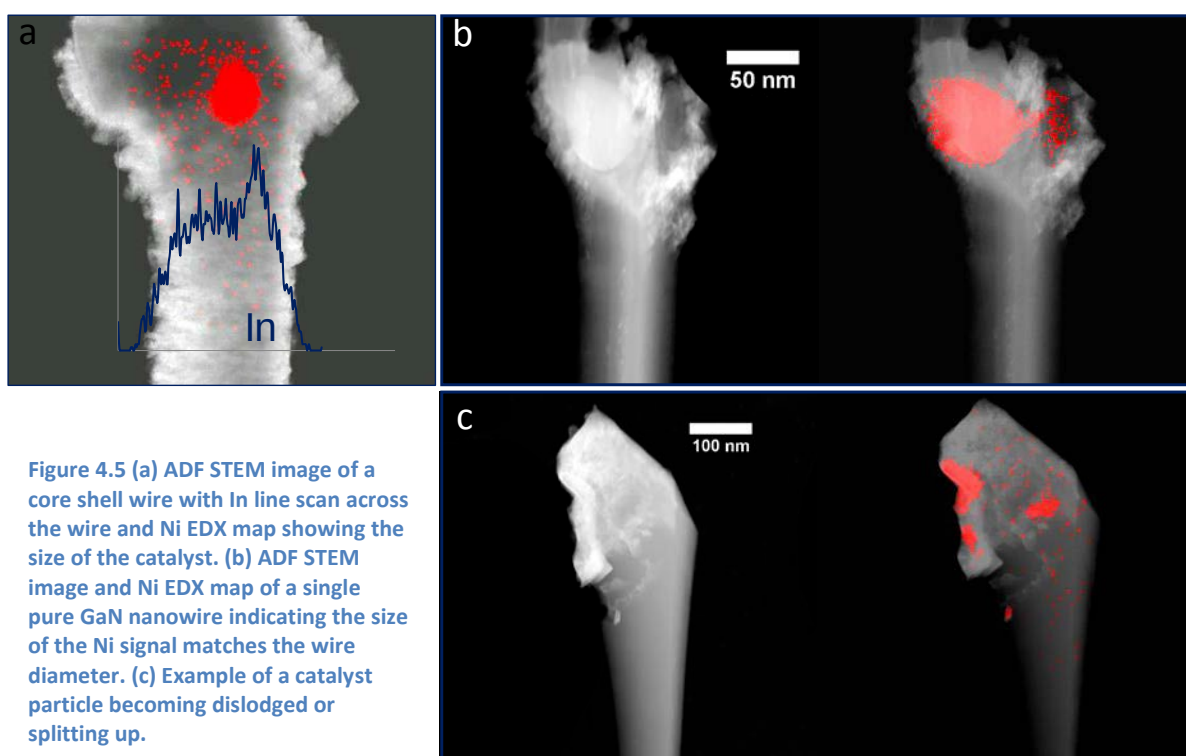


Figure 4.4 Methods of measuring the core size in complete shell CS nanowires: (a-b) DF imaging using strong reflection from core. (c-d) Determining core size of thick-shelled wires from the indium EDX line profile.

Another technique which has the potential to be applied to a wide range of the morphological variety observed uses knowledge of the VLS growth process and EDX signal from the nickel catalyst particle. The VLS process describes the size of the metal catalyst particle governing the diameter of the wires and since the nickel signal is much stronger than that of the indium, the diameter of the core can potentially be inferred from this signal. Figure 4.5(a) shows a wire for which the indium signal (blue line trace) does not give a clear impression of the core shell structure but the nickel catalyst is clearly identifiable from the Ni EDX signal (red).

Figure 4.5(b) includes an ADF STEM image of the end of a pure GaN nanowire of the type shelled in (a), with accompanying nickel EDX map in which the catalyst particle is visible within a surrounding

GaN layer in both the ADF and EDX signals. There is a fairly good match between the size of the catalyst particle and the diameter of the wire, with an error of around $\pm 15\%$, indicating that this method of determining the core size via the catalyst particle EDX signal provides a useful indicator. Unfortunately in a few cases the catalyst particle may become dislodged, likely due to interfacial dewetting and large interfacial expansion differences, with an example being 4.5(c) below, although this a small minority.



There is also some potential uncertainty over whether the size of the Ni signal from the region embedded at the end of the wire is representative of the alloy catalyst particle during growth. Since the liquid alloy droplet contains GaN in addition to Ni, this is likely expelled from the catalyst particle during cooling. This is almost certainly why a large amount of nonuniform GaN is seen encasing the Ni region at the end of the wire in the vast majority of cases. This leads to two questions of uncertainty, specifically; whether the Ni region can truly be related to the size of the alloy droplet and also whether all of the nickel involved in the growth is left within the tip of the wire or whether some of this is expelled, the latter being a possible explanation for the multiple nickel regions seen in

Fig. 4.5(c). Despite these issues, in the majority of single GaN nanowires studied, the Ni signal matches the diameter of the wire fairly well and therefore may be used as an indicator of core size in core/shell wires in which the core cannot be measured directly.

Although the Ni appears fairly localised and contained at the end of the wire in the majority of cases, the observations of a less localised Ni signal in (a) and the broken up catalyst particle in (c) suggest that there is a possibility of unintentional doping due to the catalyst particle having an impact on the materials properties in a small fraction of wires.

Using this technique on a range of core-shell wires to link the core size to the shell morphology it appeared that the large core shell wire of Fig. 4.3(b), which has a mainly single crystal SADP, actually was shown to have a large core GaN NW which could account for the main contribution to the DP rather than it being indicative of a single crystalline shell as was suggested. In order to obtain more direct evidence it was necessary to prepare cross sections, allowing for direct measurement of the core size and characterisation of the shell including indexing of the core facets to analyse the growth on different facets.

4.4 Core shell nanowire cross sections

Core/shell nanowire cross sections were prepared using the dual-beam FIB following the procedure outlined in Section 3.11.2. Due to the issues with the possible introduction of artefacts due to gallium implantation, the wires were also embedded in resin and ultramicrotomy was attempted to allow for a comparison. Unfortunately the latter technique was unsuccessful as no wire sections could be located in the resin sections and the only GaN pieces found were large and non-uniform. These issues may be due to the low density of the wires placed in the resin and also potential problems with the wires being pulled out of the resin by the blade during sectioning. For this reason, the following results are based on the FIB lift-out method in which extra care has been taken to

minimise the introduction of artefacts by depositing thick protective layers with the less damaging electron beam only after which the FIB is used to deposit additional protective layers.

4.4.1 SEM imaging

The core shell wires were firstly analysed via secondary electron imaging in the SEM which allowed for a better understanding of the surface features, in addition to study of a range of core sizes. The secondary electron image of Fig. 4.6(a), clearly illustrates the topography of the rough surface, which is likely indicative of three dimensional growth of the InGaN shell. While the head of the wire appears to be covered with randomly orientated pyramidal grains, the main body of the nanowire has a more preferential orientation with ridges running down the length of the nanowire which appear to be made of smaller, similarly orientated thin grains. These features can be seen in cross section in (b), which is prepared from the nanowire in (a), showing the trapezoidal shape of the ridge on the top left side of the wire cross section. The milled sections in (b) and (c) (the latter being a different wire with larger core) provide the first direct confirmation of the triangular cross section of the cores which was suggested by the ADF STEM intensity profile in Fig. 1(c).

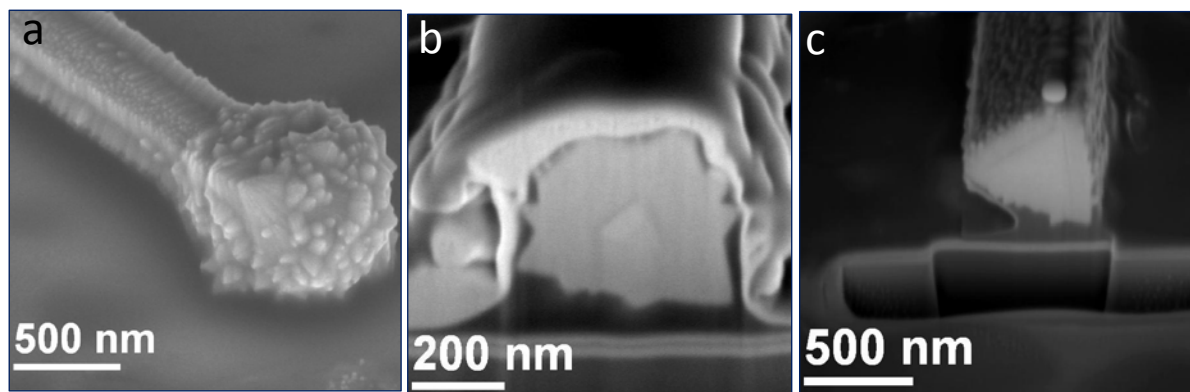


Figure 4.6 Secondary electron images showing (a) the tip of a core/shell wire and the core shell structure of wires with (b) smaller and (c) larger core diameter.

One feature of note is the dark region at the core shell interface possibly due to a differing chemical composition in this region forming at some stage of the fabrication process or alternatively it may

derived from the potential of the heterojunction at the core shell interface giving voltage contrast. This is explored more fully in the analysis of the TEM lift out specimen below.

The shells appear to follow the triangular shape of the core with uniform growth on all facets; in contrast to reports in the literature. Despite the triangular shape of the shell growth it is of course not certain whether this material is single crystal, representing coherent epitaxial growth of the shell and the large protruding grains, particularly those of (b) perhaps suggest polycrystalline material in agreement with diffraction work. In order to confirm this diffraction contrast work was performed on cross sections lifted out using the technique described above.

4.4.2 Diffraction contrast

Diffraction contrast work, such as the example given in Fig. 4.7 below, revealed the polycrystalline nature of the shells. Using SAD the core nanowire was identified as *m*-axis orientated and the facets of the core were indexed as (0001) and two $\{2\bar{1}\bar{1}2\}$ -type pyramidal planes, illustrated in (c), which was achieved using the shadow imaging process shown in (d) and (e).

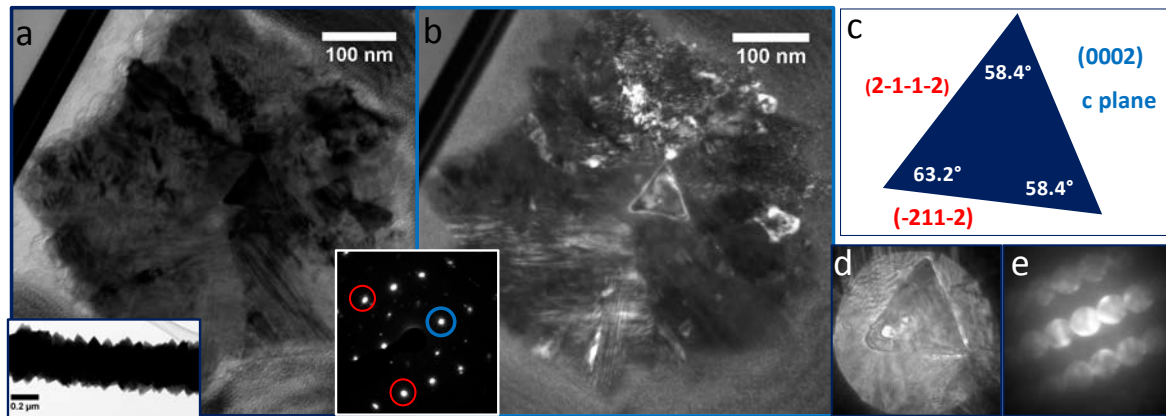
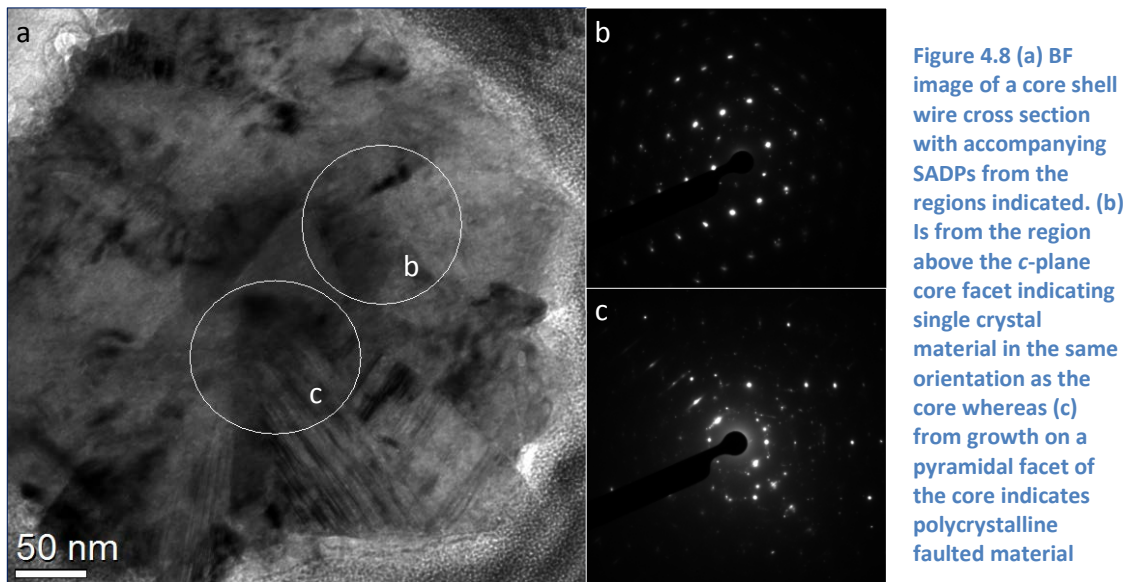


Figure 4.7 BF (a) and DF with $g=c$ (b) images of core shell nanowire cross sections showing the polycrystalline shells and confirming the triangular cross section of the GaN nanowires (c). The Shadow image of (d) and (e) confirm the crystal facets as indexed in (c).

The morphology observed here appears to be a further advanced stage of the incomplete islands observed, for example, in Fig. 4.3(a), in which the islands have coalesced to form the thick polycrystalline material observed.

There appears to be a greater degree of coherent orientated growth the c -plane facet, which gives a clear m -axis SADP from this region as indicated in Fig. 4.8. In contrast, the diffraction pattern from the material immediately surrounding one of the $\{2\bar{1}\bar{1}2\}$ -planes suggests it is very polycrystalline with several grains of differing orientation. This may reflect the faster growth rate on this surface as reported in the literature in which asymmetric shells are often observed[99][138]. There is also a very high density of stacking faults in these grains, clearly visible in the BFTEM image below and also indicated by the streaking in the diffraction pattern from this region.



4.4.3 STEM EDX of cross sections

Another difficulty in 'plan-view' analysis of the complete nanowires was the difficulty in obtaining reliable values for the indium composition due to uncertainties in thickness variation and the unintentional contribution of the pure GaN core. Although the difficulty with the low indium EDX signal remains, working on a cross section avoids the possibility of a contribution from the core and also gives a relatively uniform thickness. It also provides the possibility for studying the variation of the indium composition across the shell. Although such variations could not be identified in EDX maps, analysing the indium ratio at certain fixed points showed a degree of variation as illustrated in the STEM image of Fig. 4.9 below in which the indium ratio varies from 0-4%. Similarly low values as

those seen in plan-view work were observed suggesting that these values are accurate and are not an artefact produced by an unintentional contribution of the core as previously considered. The variation suggests a degree of clustering of the indium and there also seems to be a possible trend showing a decrease in indium composition from the region near the core to the edge, suggesting strain may play a role in indium incorporation as previously reported in the literature[70].

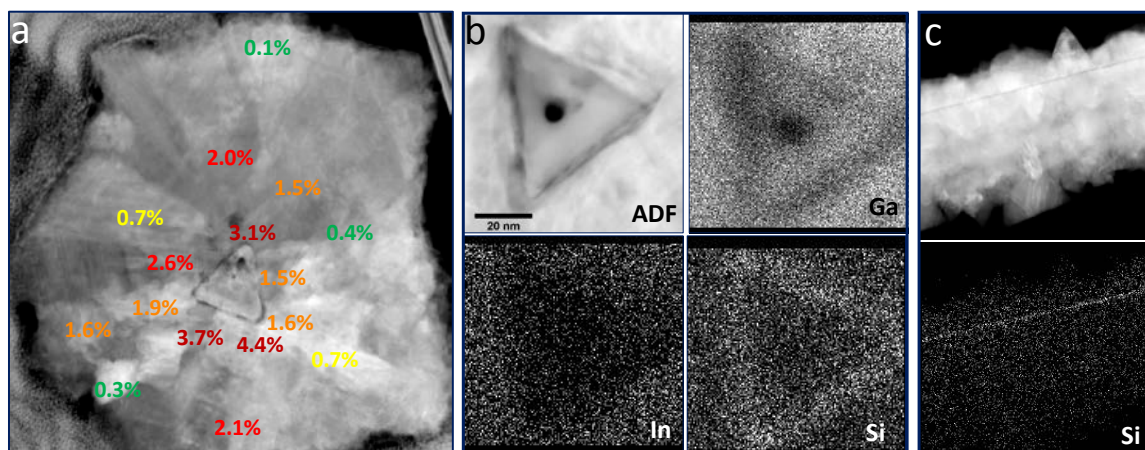


Figure 4.9 EDX analysis of core shell wires. (a) Indium composition variation in shell. (b) Ga, In and Si EDX maps around core indicating possible layer of Si contamination. (c) Similar Si layer observed in plan-view imaging of core shell wire.

STEM EDX analysis of the core region, presented in Fig. 4.9(b), shows the expected reduction in the indium signal from this region but also an unexpected decrease in gallium counts around the interface with the core and shell. This area was found to be associated with a high silicon EDX signal suggesting potential contamination between the core wire grown and shell overgrowth. Similar observations had been made in the plan view analysis, such as that of Fig. 4.9(c), but the origin of the extended line of Si counts was not clear. It now can be assumed that this line in the EDX and STEM map is a core facet, contaminated with Si, aligned parallel to the imaging direction. This result emphasises the importance of cross section analysis to avoid ambiguity in the interpretation of complex structures in the TEM.

This apparent, relatively thick silicon interface region, which has been observed in many of the wires is likely to have a detrimental impact on the quality of the overgrown shells and may be a contributing factor to the polycrystalline shells observed.

4.5 Optical properties

Photoluminescence and electroluminescence measurements of the GaN nanowires and core/shell GaN/InGaN nanowires were carried out at SLE and the results are given in Fig. 4.10 (a) and (b) respectively.

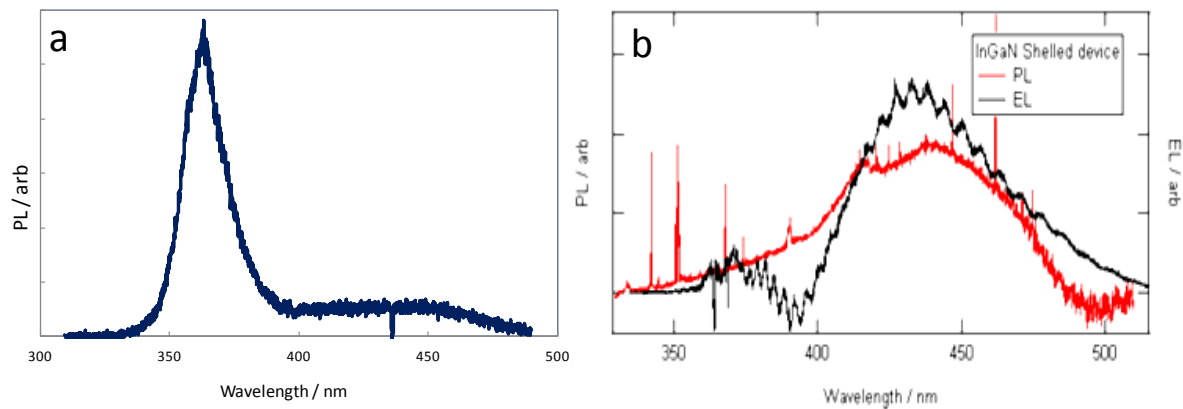


Figure 4.10 (a) Photoluminescence data from a pure GaN nanowire and (b) photoluminescence and electroluminescence data from a core shell structure.

The pure GaN sample has a sharp peak at 362nm, consistent with band edge emission from GaN [257], at a very slightly higher wavelength than the generally accepted strain and defect-free value of 355-360nm[258]. This illustrates that the pure GaN nanowires are free from strain since the effect of any compressive or tensile strain would be to significantly shift the PL to higher or lower energies respectively [259][260]. The fact that the emission is at slightly lower energy than the nominal strain free value shows that there is no compressive strain due to the sapphire substrate but there perhaps may be some small tensile effect due to growth on the nickel clusters. The position, sharpness and absence of longer wavelength emission are in good agreement with the observed good crystal quality of the pure GaN nanowires.

In contrast the emission from shelled wires is extremely broad and of significantly reduced intensity. There are likely to be several contributing factors to this result including recombination at grain boundaries, defects such as dislocations and stacking faults within the grains [261][262][87] and indium composition fluctuation [263]. The relationship between the indium composition and bandgap of InGaN is non-linear and still under active investigation [264]. Using a suggested formula[265], $E_G(x) = 3.42x + 0.77(1-x) - 1.43x(1-x)$ (including the values 3.42eV and 0.77eV for the bandgaps for GaN and In respectively and bowing parameter of $b=1.43$ eV), the observed peak value of $\sim 440\text{nm}$ would correspond to an indium composition of 15% which is much higher than the observed values in EDX results of 1-5% suggesting strain and defects play a significant role in increasing the peak emission wavelength.

4.6 Discussion

4.6.1 Shell morphology and core size

Since there have been initial reports on links between the core nanowire size[137], crystallography [102] [99] and microstructure[142] and the overlying shell, one of the primary aims of this chapter was to explore these relationships more thoroughly. Although all of the shells had very rough surfaces, there was evidence in some; particularly the larger wires such as Fig. 4.3(b), that there may be single crystal material with the same orientation as the core. Specifically, the main component of the SADP was a clear single crystal diffraction pattern, with some other smaller spots and streaking, which would be interpreted as a coherent shell with some island growth on the surface. This diffraction data was in clear contrast to other wires, such as Fig. 4.3(c), in which the main component of the diffraction pattern was clearly polycrystalline and so the clear question is whether some shells are coherent single crystal shells and whether this is related to the core diameter.

Several techniques were used to determine core diameter measurements in an effort to relate core size to the over grown shell morphology. In particular, a method of inferring the core size from the

Ni catalyst EDX signal was identified and verified as a high turnover way of measuring the core size in a range of core shell morphologies. Applying this technique, it appeared that wires with single crystal SADPs appeared to have large cores and therefore it seemed likely that the core was contributing to the diffraction pattern and the additional spots and streaking in the pattern were related to the grains of a polycrystalline shell. Combining this with the direct evidence of polycrystalline shells, from the successful FIB lift outs (Fig. 4.7), it can be concluded that the vast majority, if not all, the wires studied had polycrystalline shells and therefore any effect of core size on shell morphology is likely being outweighed by a more significant factor.

4.6.2 Origins of polycrystalline shell

The data suggests that the deposition of the InGaN shells progresses via initial growth of islands, as observed in Fig. 4.3(a) before coalescing into the polycrystalline shells observed in Fig. 4.7. The large lattice mismatch of around 11% between InN and GaN means that InGaN grown on GaN suffers compressive strain, increasing with film thickness and indium composition, until the stress is relaxed via dislocation formation or three dimensional growth. Recent theoretical work comparing the strain energy associated with each relaxation mechanism [266] suggests that three dimensional growth is favoured above dislocation formation for indium composition below 27% [266] as is the case for the material studied here.

Theoretical work has been carried out to determine the critical GaN core radius that can support a coherent InGaN shell of given thickness [137]. Although the majority of the wires exceed this critical geometry that can support the strain coherently, many examples of small wires have been identified which should be within these limits and yet still polycrystalline (partial) shells are observed. This observation, combined with the fact that coherent shells have been reported for wires exceeding these geometries [99], [133], [138], suggests that strain related to growth of InGaN on the GaN core surface cannot be the primary reason for the polycrystalline morphology observed.

A transition from 2D layer growth to 3D island growth of InGaN on GaN, has also been observed under various changes of growth conditions, particularly high reactor pressures and growth rates [267] and so the observation of this kind of growth mode may simply be linked to the specific InGaN growth conditions used. The fact that the growth rate is reportedly slower on the *c*-plane[99][138] may explain why the material around this region in Fig. 4.8 appears to be single crystal and oriented to the underlying core facet.

Another possible factor may be the silicon layer identified in the STEM EDX work of Fig. 4.9, upon which the InGaN shells grow. The origin of this substantial layer is not clear, although Si is used as an n-type dopant in GaN it is generally regarded as very thermally stable and therefore redistribution of Si to the surface of the GaN nanowire is unlikely[268]. It therefore may originate from contamination of the CVD chamber itself, perhaps from alternative use in Si-based material growth. A thin layer of a few nm's, believed to be this silicon region, was identified in HRTEM images of the surface of a partially shelled wire, as illustrated in Fig. 4.11 below. The layer seemed to grow epitaxially with the GaN core with evidence of dislocations observed as evidenced in image (c) below. Epitaxy of III-nitrides on silicon is often reported to lead to polycrystalline, columnar material[269][270] similar to that which is observed here and therefore this Si layer may contribute to the shell morphology.

The InGaN grains are often highly faulted as observed in Fig. 4.11(d) below which is likely to broaden the PL due to optical transitions associated with stacking faults and is likely to contribute to the broad peak in the optical emission as shown in Fig. 4.10(b).

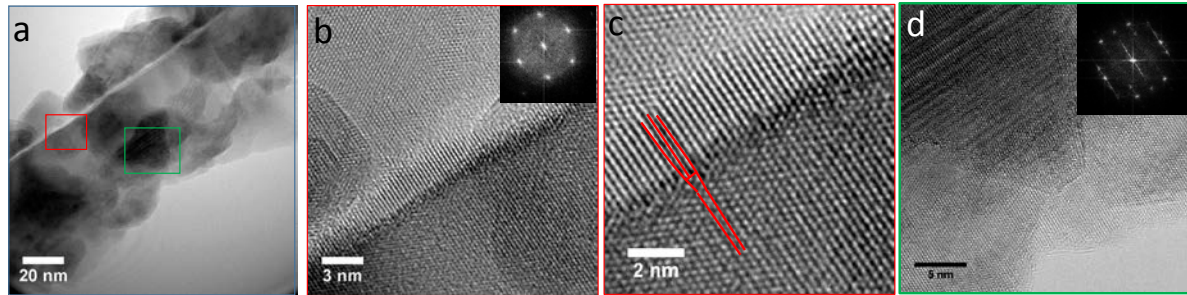


Figure 4.11(a) BF TEM image of a small wire with incomplete shell. (b) The silicon layer is observed at the surface which appears to have an epitaxial relationship with the GaN core with (c) possible misfit dislocation identified. (d) High density of stacking faults in overgrown islands

4.7 Conclusions

GaN nanowires and core/shell GaN/InGaN nanowires have been characterised using a variety of structural and optical characterisation techniques.

Ni catalysed GaN nanowires were found to be of high crystal quality with the majority having the expected wurtzite crystal structure but a small proportion having the cubic zinc blende phase. The former were shown to be completely defect free with diffraction contrast and HR TEM but the latter had a high density of defects which were mainly planar faults running along the wire axis. The hexagonal wires had both *m*- and *a*-axis orientations whereas the ZB wires grew along the *a* {220} direction. The fraction of cubic wires observed may be due to GaN wires growing upon the Ni clusters rather than having an epitaxial relationship with the sapphire substrate. The pure GaN wires had a narrow PL emission peak close to the strain free value for GaN confirming the large surface area aids in accommodating any strain from the mismatch with the substrate or nickel catalyst clusters.

The InGaN shells deposited via MOCVD on the GaN nanowires described above were extremely rough and are believed to be fully polycrystalline in all cases. Although there was some evidence for single crystal shells in the form of strong single crystal SADPs, this was believed to originate from the contribution from the large GaN cores in these cases. In order to identify the core size in completely shelled wires a technique was developed in which the EDX signal from the Ni catalyst, still embedded

with the wire, is used to infer the size of the core since it governs the initial wire diameter during VLS growth.

Cross sections were lifted out using a dual beam FIB which allowed for diffraction contrast work to confirm the polycrystalline shells and reveal a higher indium composition nearer the core suggesting strain plays a role in the variation of the In fraction. This work also revealed a silicon layer between the core and shell which may play a role in the formation of polycrystalline shells. The broad PL peak observed in the shelled structures was likely related to the observed variation in composition and defect related transitions with the intensity reduced due to non-radiative recombination at defects and grain boundaries.

Chapter 5

Core/Shell Etched Microrods

5.1 Introduction

Core/shell structures fabricated via deposition of shells onto the non-polar facets of etched GaN microrods are being explored as a potential alternative to GaN core/shell nanowires whereby many of the advantageous properties of the latter are maintained but the problems due to non-uniformity and sub-optimum growth conditions are avoided.

Despite the promising properties of core/shell nanowires described in Chapters 2 and 4, there are difficulties involved in their large scale processing and integration in devices due to non-uniformity and morphological variation. Bottom-up growth also necessitates a specific, narrow region of growth conditions which are related to sub-optimal growth temperature and III to V ratio[150]. Such growth parameters may introduce an increased density of point defects [151] and impurities [152] relative

to those optimised for planar films for LEDs and allow less flexibility for adjusting to favourable conditions for doping. There is therefore a motivation to look to top-down structures prepared from conventionally grown GaN films which utilise established techniques in thin film growth for precise control of the doping level [153] and display a greater uniformity of cross section, length and spacing[154]. Shells may then be deposited on the exposed non-polar facets, as with the nanowires, to harness the beneficial properties of non-polar junctions and homoepitaxial growth. However, since the core structures are prepared from conventionally grown *c*-axis GaN on sapphire substrates they are likely to have the high dislocation densities in the core region common to such material. Whether these dislocations reach the active, junction area on the side walls and whether other dislocations form during growth of these shells is unknown and a detailed understanding of the defects present in non-polar nitride junctions is necessary due to the impact of the microstructure on the optical properties of the material [2].

The work of the next two chapters therefore looks to answer the following questions: (1) are the dislocations associated with the initial growth of the *c*-axis GaN comprising the core confined to this area or do they reach the active region?; (2) does a difference in core morphology have an influence on the microstructure of the deposited shells; and (3) what is the density and character of defects in the junction region? This chapter primarily deals with the first and second of these questions whereas the in-depth characterisation of the shell defects is presented in the following chapter.

5.2 Growth

Initially, conventional *c*-axis oriented GaN films were deposited on sapphire substrates via MOCVD, before a novel, proprietary mask and dry etch method was used to leave a uniform array of free standing microrods with diameters dependent on the initial mask. MOCVD was then used to deposit a series of shells upon these core structures as follows: firstly, approximately 50nm of n-GaN was deposited with the intention of smoothing and repairing the etch damage; 50nm InGaIn was then

applied to act as the active layer; finally a layer of p-GaN, doped with magnesium, with a thickness of approximately 100nm was deposited.

This series of shells were deposited on two differing core structures, sample A being longer, and narrower, sample B shorter and wider, the details of which are provided in table 5.1 below. This was carried out simultaneously so that the growth conditions of the shells were exactly the same. Fig. 5.1(a) is an SEM image of an interface between the etched and non-etched, intact region of the GaN film after shell deposition has taken place while (b) and (c) illustrate the difference in morphology between sample A and B rods respectively, after they have been removed from the growth substrate via sonication and drop cast onto a silicon wafer.

	Sample A	Sample B
Thickness of initial GaN wafer	20 μ m	10 μ m
Diameter	1.5-3 μ	4 μ m
Comments	Some variation in length with degree of tapering observed	Uniform dimensions across sample

Table 5.1 The differing morphologies of shelled microrod sample A and B

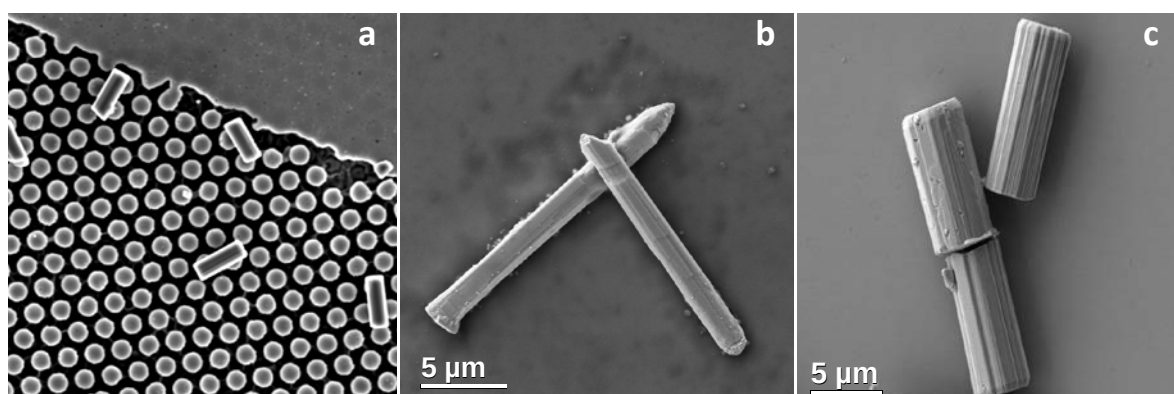


Figure 5.1 SEM images of (a) shelled sample B rods attached to the growth substrate, (b) shelled sample A and (c) sample B rods removed from the growth substrate and deposited on an Si substrate

5.3 Cross section preparation

Clearly, these materials are too large to image in the TEM as whole structures and therefore, in order to answer the questions relating to the presence of defects within the microrods defined above, sections through the structures have to be prepared. This was achieved using an NVision dual beam FIB by milling and lifting-out longitudinal and radial cross sections through the microrods as illustrated schematically below. Again, microtoming was attempted to compare results but was unsuccessful, likely due to the blade pulling the rods out of the resin or fracturing them non-uniformly as suggested in the previous chapter.

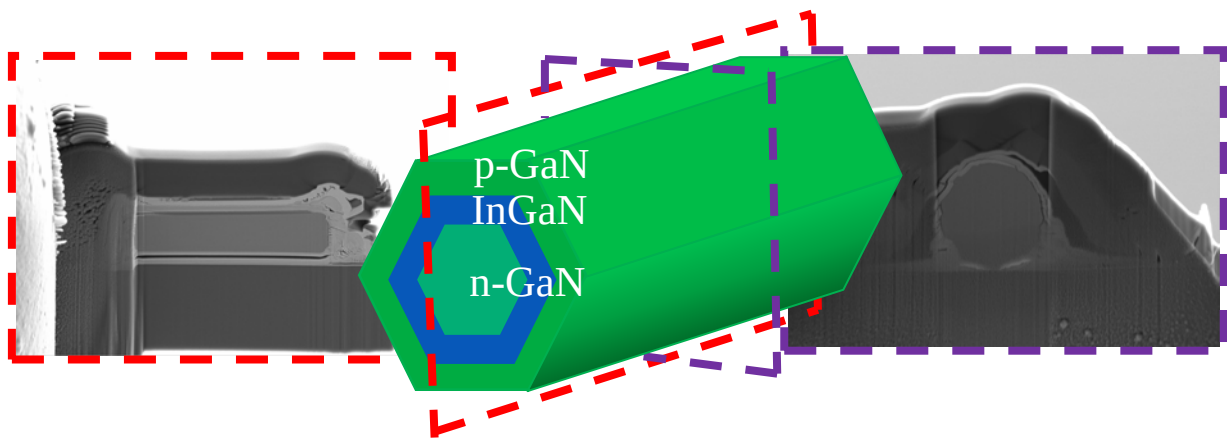


Figure 5.2 An illustration of the geometry of the longitudinal and radial cross sections taken from core/shell microrods

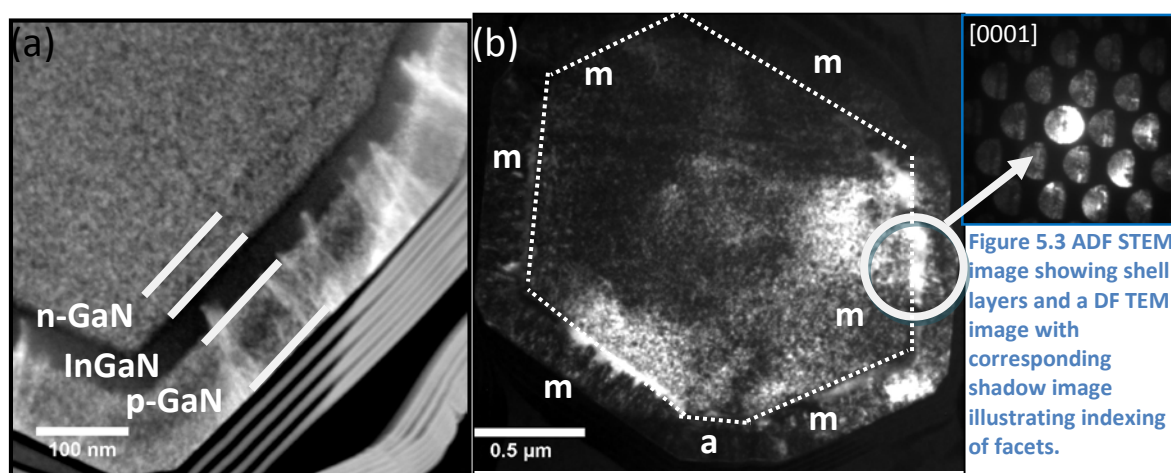
The lift-out procedure is described in detail in Chapter 3 but since these structures are much larger than the nanowires documented in the previous chapter, there is the additional consideration of gaps between the rods, substrate and protective layers forming which could make the sections unstable and liable to loss during the process of lifting-out, thinning and transferring to a TEM grid. Therefore, an additional first step was used, involving depositing material along the side of the microrods from 54° to prevent any gaps developing between the rods and substrate. Again, deposition of the protective layer was always first carried out with the electron beam to minimise exposure to the high energy gallium ions and the possibility of introducing defects.

5.4 Results and Discussion

5.4.1 General morphology

The shell layers are clearly visible in *c*-plane cross sections through the microrods, as illustrated in the ADF STEM image of Fig. 5.3(a) in the case of a sample A microrod with the layer thicknesses approximately equal to the intended values as given in table 5.1. In some cases the interface between the original etched core and the deposited n-GaN layer is visible suggesting that the intended repairing of the etch damage was not wholly successful and there is some change in composition or microstructure in this interface region in some cases.

The facets defining the outer shape of the *c*-plane cross section were indexed using the shadow image technique in which the selected area aperture is used to select one of the planes, as indicated in the DF TEM image of Fig. 5.3(b), and a defocused diffraction pattern is obtained. Using this combination of imaging and diffraction it was determined that the larger facets are *m*-planes connected in some cases by smaller *a*-plane facets at the corners, illustrated in the aforementioned figure below. Since the rods will often rest upon these larger facets when drop cast onto a Si wafer for sectioning, the prepared longitudinal sections – examples of which are given in Fig. 5.5 - tend to be approximately $\{11\bar{2}0\}$ *a*-plane sections.



5.4.2 Composition

The composition of the shell regions was analysed via energy dispersive x-ray analysis and typical data acquired in the JEOL 2000FX for both samples is compared in Fig. 5.4 below. As with the core/shell nanowires described in the previous chapter, there was a lower indium signal than expected in the InGaN shell, with a standardless quantification calculation using INCA software giving values in the range 2-5%, as opposed to the intended value of 10%. This may be due to the known issues with indium incorporation in epitaxy on nonpolar facets, with the *m*-plane in particular having the lowest indium uptake [271][272]. There was no clear difference between the indium compositions of the InGaN layers in the two samples with significant variation in repeat measurements, perhaps suggesting the possibility of compositional variation within individual shells.

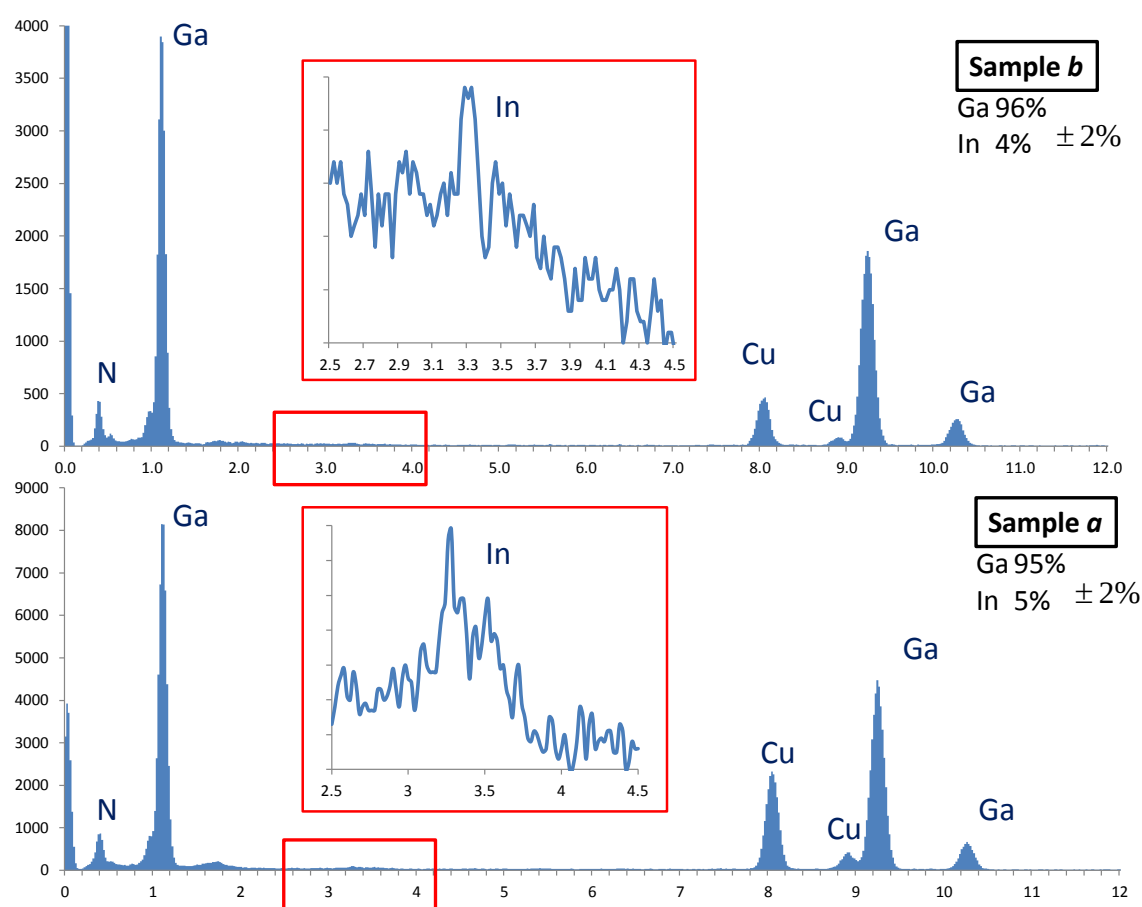


Figure 5.4 Typical EDX spectra from the larger aspect ratio sample B rods and the small aspect ratio sample A rods with an enlarged version of the indium peak inset.

5.4.3 Core dislocations

As expected, dislocations were observed in the cores of both varieties of microrod as is clear from the STEM image of a longitudinal sample A section and the DF TEM image of a sample B section in Fig. 5.5 (a) and (b) respectively. The dislocations, originating from the high degree of misfit with the sapphire substrate, thread along the long axis of the nanowire in the *c* direction. From counting dislocations observed end-on in diffraction contrast TEM images of *c*-axis sections, the estimated density of threading misfit dislocation in the core regions is 10^8 - 10^9 cm⁻².

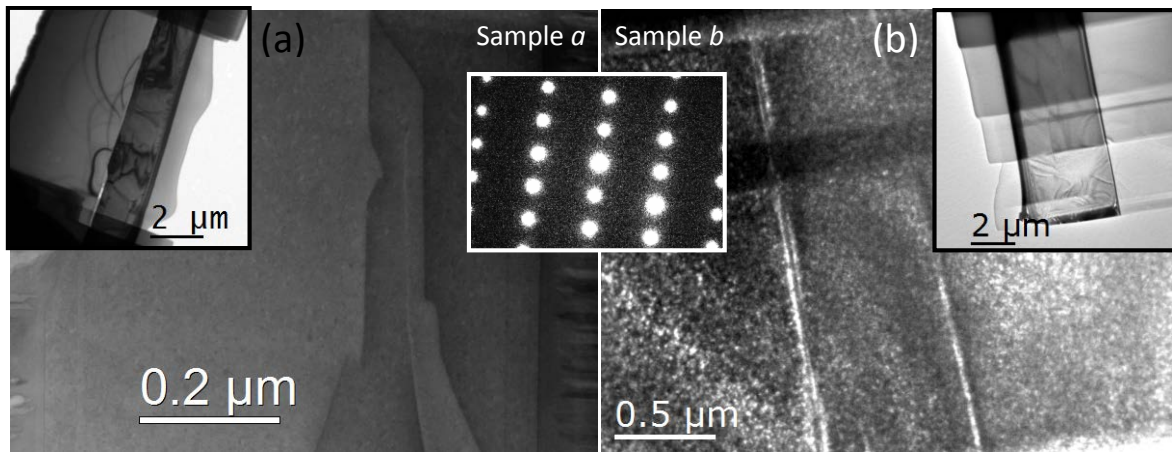


Figure 5.5 Examples of *c*-axis oriented dislocations in longitudinal *a*-plane cross sections of sample A and B microrods respectively. The inset BFTEM images show low magnification images of the full prepared FIB sections.

These core dislocations were characterised in conventional diffraction contrast studies using $\mathbf{g} \cdot \mathbf{b}$ analysis to determine the burgers vectors. Using the usual invisibility criterion, i.e. when $\mathbf{g} \cdot \mathbf{b} = 0$ the dislocation is 'out of contrast', the burgers vector, $\mathbf{b}$, and therefore the character of the dislocations can be determined. The analysis shows that the left hand dislocation in Fig. 5.6 below is of mixed character ($\mathbf{b} = \mathbf{a} + \mathbf{c}$) since it is visible for both $\mathbf{g}=\mathbf{m}$ and $\mathbf{g}=\mathbf{c}$ whereas the right hand dislocation is pure edge ($\mathbf{b} = \mathbf{a}$) since it is invisible when viewed under $\mathbf{g}=\mathbf{c}$ diffraction conditions. These are the common dislocation types for *c*-axis GaN films [273].

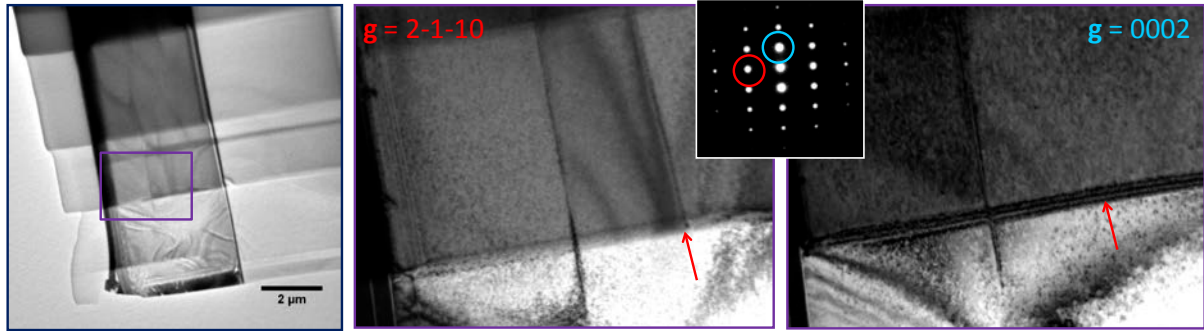


Figure 5.6 Low magnification image of a sample B rod with accompanying BF images where the sample has been tilted to strong two beam conditions near the $[10\text{-}10]$ m-axis to excite the $2\text{-}1\text{-}10$ a-planes (centre) and 0002 c-planes (right).

One of the unknowns concerning the growth of non-polar junctions in this way was the impact, if any, of the core dislocations, derived from the initial c -axis growth on sapphire, on the junction region. In the vast majority of cross sections prepared, the observed misfit dislocations, deriving from the interface with the substrate, were seen to be confined to the core region away from the surrounding junction. However this was not always the case as certain dislocations were observed to kink at the interface with the first, n -Ga N layer and propagate into the shell series as highlighted in both c -axis and a -axis sections of a type A microrods in Fig. 5.7 below. This may be explained by considering a threading dislocation which passes through the original Ga N film into a region removed during the etch process and thus terminates at the core boundary which then propagates through the shell layers during their growth.

Although this could be considered detrimental to potential device performance, the minimal instances that such an effect was observed suggests that it is likely to be insignificant compared to the independent nucleation of junction defects which appear much more numerous -even in sample B which has a greatly reduced defect density of shell defects compared to A, as explained below.

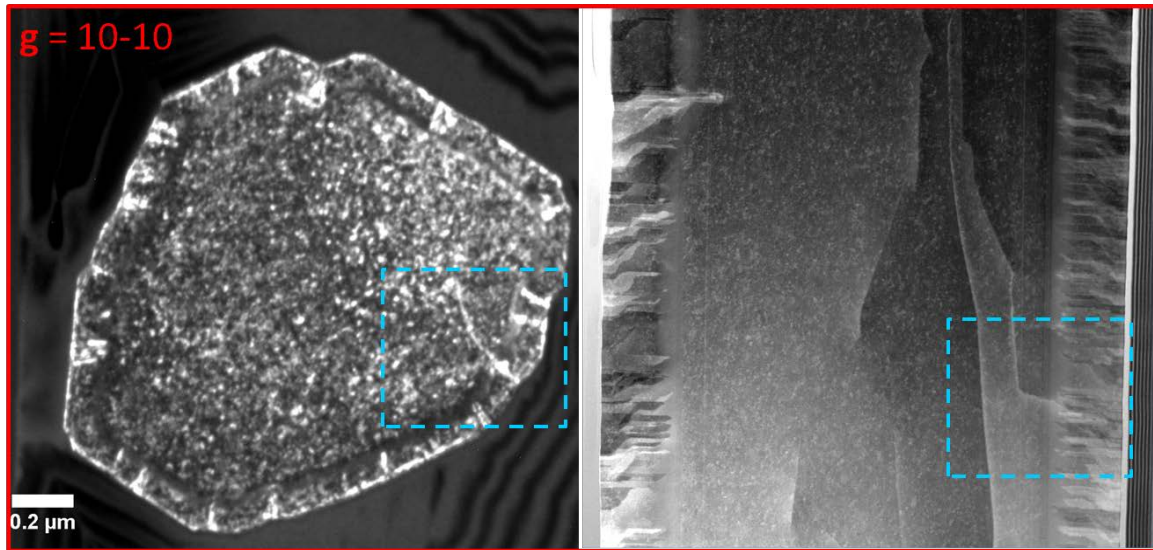


Figure 5.7 Evidence of misfit dislocations in sample A rods originating from the growth of the GaN film on sapphire reaching the interface with the shell layers and propagating through the junction.

5.4.4 Differing shell defect density between samples

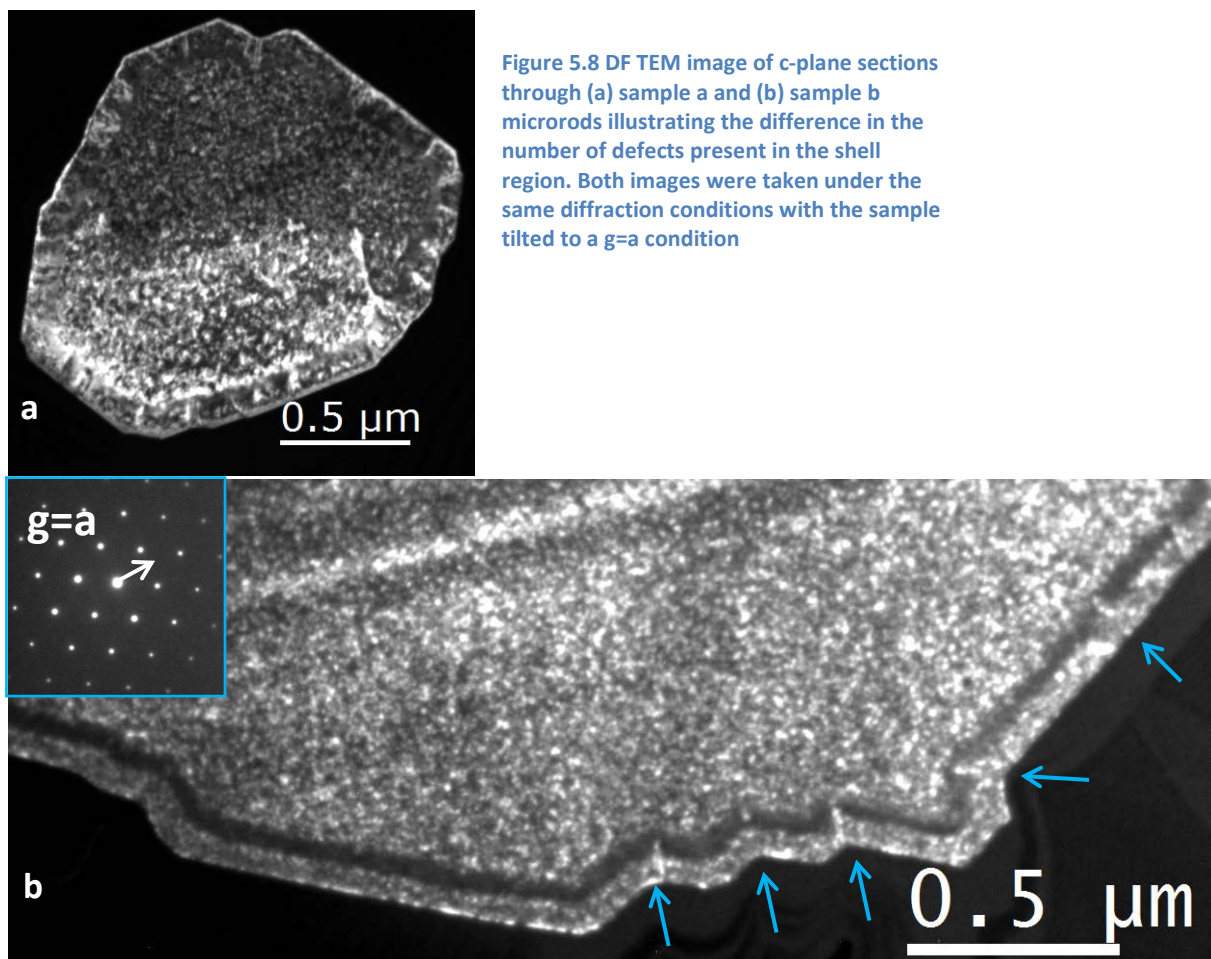
As described above, two samples were investigated during this work, with the difference being solely due to preparation of the underlying core, sample A having been etched from 20 μm GaN film with a diameter of around 2 μm whilst sample B was etched from 10 μm wafer with a diameter of around 4 μm , with both shelled simultaneously. It was perhaps surprising then that there was a marked difference in the appearance of the shell region.

The major difference between samples was the number of defects visible in the shell region; with a much higher density visible in the smaller diameter sample A microrods. On average, there were around 1-2 defects per μm of interface in the larger diameter sample B rods whereas 8-12 μm^{-1} in the small diameter sample A rods. This contrast is presented in the DF TEM images of Fig. 5.8 which were both taken under equivalent imaging conditions with the sample tilted to a $\mathbf{g}=\mathbf{a}$ condition. Both sample cross sections show contrast from defects which begin in the InGa N layer and extend to the outer surface of the rods. However, in the case of sample A they are much more numerous and appear to form equally on all facets defining the outer walls of the core, whereas in the case of sample B they are limited to a few cases, forming primarily at the inward-facing corners of the core

which form the grooves running along the length of the microrods, visible for example in Fig. 5.1(c).

Apart from the dislocations visible in these areas there are large stretches of interface across individual facets having uniform contrast, suggesting coherent growth of the shell layers in these regions.

The presence of dislocations at these corner regions, which are indicated by arrows in Fig. 5.8(b) below, may be explained considering the increased compressive strain in these regions deriving from the increased lattice spacing of the InGa_N layer compressed across the curved surface of the underlying GaN core which has a smaller lattice parameter .



Apart from the formation of dislocations at these isolated regions, much of the interface is dislocation free in this sample and compares favourably to data reported in the literature for conventional growth of non-polar GaN/InGaN junctions. This is promising for the potential of such materials being utilised in optoelectronic devices as these results suggest junctions can be grown largely dislocation free on the side walls of free standing microrods.

The reasons behind the contrasting defect density of the shell regions between the two samples must lie in the properties of the core due to the simultaneous deposition of the shell layers. Several explanations might be offered, linking the observations to the core morphology such as: (1) Differences in the growth parameters and therefore the properties of the initial GaN film from which the cores are etched; (2) geometrical effects on the strain due to the difference in curvature and length of the cores; and (3) a greater degree of etch damage to the surfaces of the sample A rods than the sample B rods.

The first possibility may be ruled out as there was no known difference in the growth parameters of the initial wafers in either case other than the duration of growth. The second suggestion relates to the impact of the differing curvature of the cores on the strain in the shell regions which has been shown theoretically to be an important factor in coaxial heterostructured nanowires [137] in which it plays a role in determining the critical thickness of the shell layers. However the structures studied here are much larger than the nanowires considered in the aforementioned reports and, while the curvature of the core may play a role in the shell growth around the corners as suggested in the explanation of the few defects observed in the sample B rods, it might seem unlikely to explain the presence of defects along the extended *m*-plane facets forming the majority of the microrod side-walls. In addition, it might be expected that the biaxial compressive strain relating to growth on the sapphire substrate, would be more fully relaxed in the larger surface area sample A rods and therefore there should be a closer lattice match between the core and InGaN layers, in contradiction to the greater observed defect density.

In terms of the etch damage, again there was no known difference in the process used for each sample, however, it has been shown that mask erosion is more dominant in smaller diameter structures [177] where it can lead to side-wall damage and a greater degree of tapering – the latter being a feature of sample A microrods. There was some further evidence for a greater degree of etch damage in the smaller rods in that the interface between the core and first n-GaN layer was much more often visible in (S)TEM images of this sample compared to the larger rods, for example in Fig's 5.4(a) and 5.7. Since etch damage may take the form of a loss of crystallinity, introduction of contaminants and a change in stoichiometry [169], this could explain the observed change in contrast at this interface region. This layer of etch damage may then have a resulting impact on the quality of the over grown shell layers in the form of an increased dislocation density and is therefore perhaps a possible explanation for the difference in quality of the shell layers between the samples. The structure of the defects in the sample A rods are examined in detail in the following chapter with possible formation mechanisms discussed in order to shed further light on the observed differences in the shell regions of the two samples.

5.4.5 Photoluminescence

Photoluminescence data was collected from the two samples by Dr S Hooper at Sharp Laboratories of Europe and is displayed below in Fig. 5.9. There are several notable differences between the two PL spectra including: (1) a blue shift in the main peak position in the smaller diameter sample a rods compared with sample b; (2) a broader main peak in the sample A spectrum; and (3) a secondary peak around 565nm in the sample A spectrum. Reasons for these differences, in addition to the common features of the spectra, will be discussed with reference to the observed differences in the microstructure.

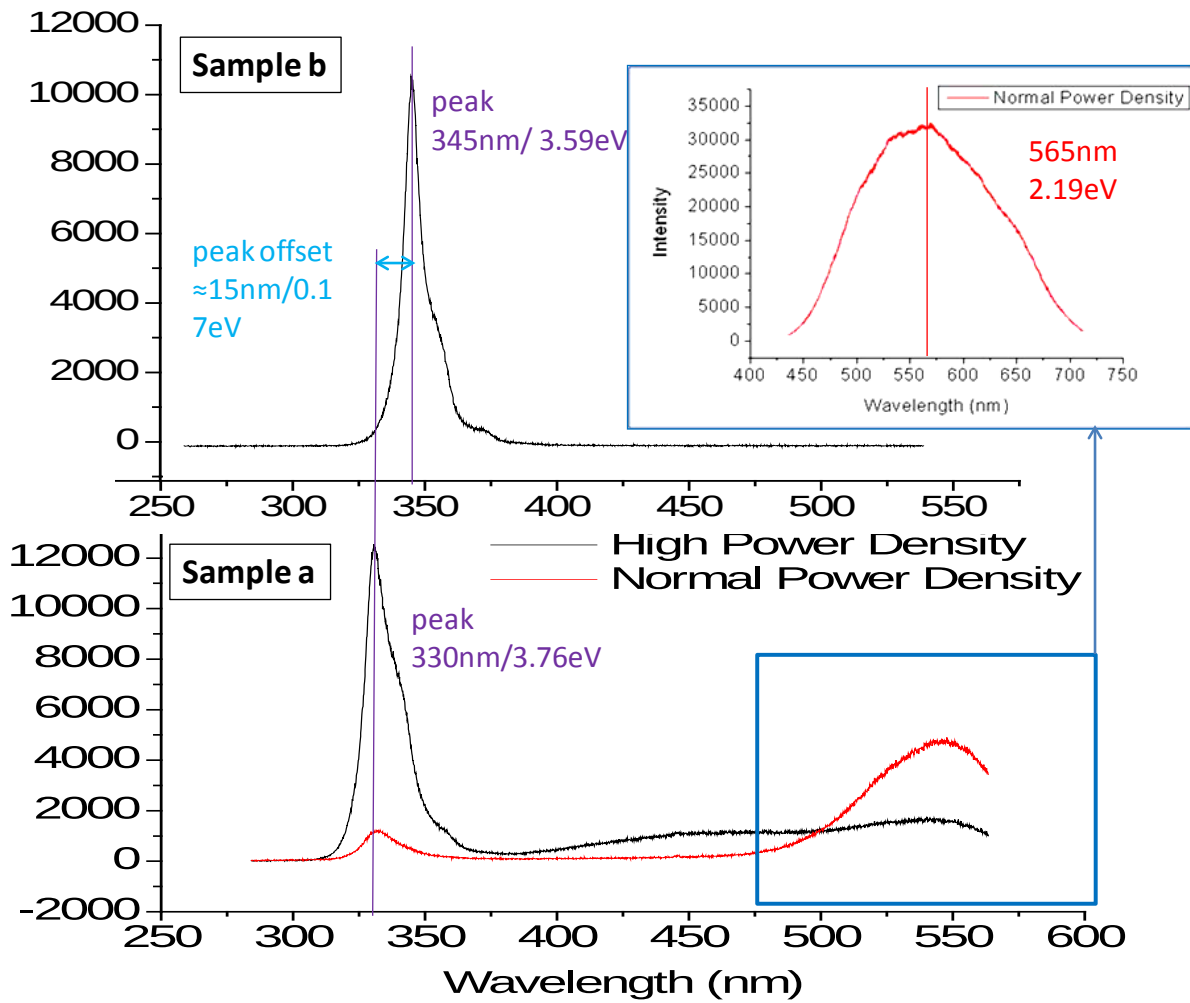


Figure 5.9 A comparison of photoluminescence data collected from the two shell microrod samples

5.4.5.1 Primary peak

The dominant PL line in GaN grown by any technique on any substrate is commonly the D^0X_A peak due to excitons bound to neutral donors [258]. The energy position of the luminescence lines and bands may depend on strain in thin GaN layers, temperature, and excitation intensity with the strain-free value in high quality GaN samples with a low concentration of defects around 3.471 eV[258]. Strain has a significant effect on the value however, with thin GaN films on sapphire experiencing a biaxial compressive strain shifting the PL lines to higher energies whereas a tensile

strain, such as that due to growth on SiC, shifts the PL to lower photon energies[259][260]. In addition to this principal peak (which itself may have a finer structure in high quality samples [274]) there are often other lines relating to excited states, satellite transitions and phonon replicas related to the shallow donor-bound excitons, such as those visible in Fig. 5.10 below, which shows a typical low-temperature PL spectrum of a high quality free standing GaN template [275]. The primary peak in the data presented above has a FWHM of over 0.1eV and is therefore likely to include several such transitions with the finer structure not clear with the experimental energy resolution achieved. Dislocations are known to introduce numerous energy levels in the gap[261][262] and may be responsible here for both reducing the intensity and broadening the peak. The data from both samples has two shoulders on the low energy side of the primary peak which may relate to unresolved transitions such as those relating to acceptor bound excitons or the two electron satellite peaks in the figure below.

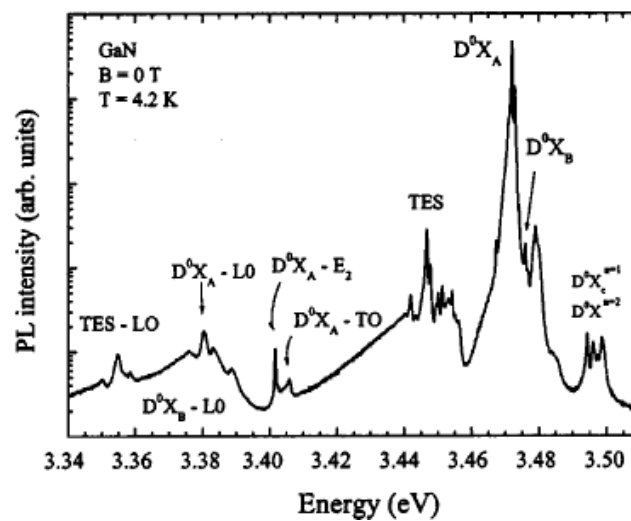


Figure 5.10 Low temperature PL spectrum of free standing GaN template – reproduced from Wysmolek *et al* [275]

In both samples the peak emission is at shorter wavelengths than expected for GaN, which is normally in the range 355-360nm. Assuming the detection system was accurately calibrated; this shift may be explained by a compressive biaxial strain, associated with growth on sapphire, which blue-shifts the emission wavelength. As described above, the indium composition was very low so

any emission from this region would only be expected to be at slightly longer wavelengths than the emission from the GaN and may explain the prominent shoulder on the long wavelength side of the primary peak.

5.4.5.2 Blue shift in peak position in sample A rods

Comparing the spectra, there is a clear blue shift of around 0.15 eV in the peak of sample A compared to that of sample B. This could be explained by better indium incorporation in this sample, shifting the emission to longer wavelengths from the junction region. Although the EDX experiments did not reveal a significant difference in indium composition, it could be that the wider sampling technique of this PL experiment exposed a trend not seen in the relatively few rods sampled via FIB sectioning and EDX analysis in the microscope.

As mentioned above, compressive strain is also a cause of blue shift in the emission spectrum, so it may be that the sample B rods display a greater degree of strain relaxation back to the nominal value. As mentioned above, this seems unusual, since it might be expected that the greater surface area of the sample A rods would mean they relax more easily after etching and removal from the sapphire substrate. One further explanation might be that the shells apply a compressive strain on the core which has been shown to affect the luminescence in core/shell nanowires [147] which would have a larger effect in the smaller diameter sample A rods in which the shells are relatively thicker.

Although a satisfactory explanation is difficult to determine, an increased compressive strain in the core of sample A rods compared to sample B, is consistent with a higher density of defects in the InGaN layer of the former in addition to the PL peak, due to a greater lattice mismatch.

5.4.5.3 Broader peak in sample A rods

In addition to the blue shift the luminescence peak of the higher aspect ratio sample A rods, they also displayed a broader peak than that of sample B, for which there may be several contributing

factors. As described above the etch damage was not fully repaired by the deposition of an initial n-GaN layer on the rods, as an interface region was still visible as an area of differing contrast in TEM and STEM images. This change in contrast may be due to a change in stoichiometry which is a demonstrated effect of etch damage as the surface N atoms are preferentially removed and may be replaced with O atoms [276]. These bonds may lead to additional transitions around the band gap in addition to increased non-radiative recombination and associated degradation of photoluminescence. Since the sample A rods have an increased surface area and corresponding region of etch damage this may contribute towards the broader peak in the PL. In addition, the high density of stacking faults, described in detail in the following chapter, may play a role since BSFs and their terminating partials are known to produce a range of strong luminescence peaks around the D^0X_A peak [87].

5.4.5.4 Broad 2.2eV peak

In addition to the strong, near band edge peak, the Sample A spectrum also contained a broad peak centred on 2.2eV which became more pronounced at reduced excitation power density. This feature is commonly seen in n-type GaN samples grown by all techniques and is generally characterised by a broad, nearly Gaussian shape, peaking at 2.2-2.25eV, which is structureless even at the lowest measurement temperatures [258]. This so-called YL band has been the subject of a huge number of publications, with many suggested theories on its origin. The YL band appears when a wide range of elements are implanted into GaN [277], meaning it is not related to a specific impurity but a native defect, with the Ga vacancy often cited as being involved either independently[278][279] or forming a complex[280][281]. These point defects may be trapped at structural defects [282][283] (the exact type of which may have an effect on the exact form of the luminescence [258]) and therefore the YL band intensity may be correlated with the density of such defects in the material.

The appearance of the YL band in the luminescence spectrum of sample A may then be attributed to the increased density of structural defects in the shell region, which trap the point defects related to

the yellow emission. Similarly, the increased proportion of etch damage due to the smaller diameter and greater surface area of these rods may play a role since such dry etch damage has been shown to promote the YL band in top-down prepared samples [150]. The increased intensity of the YL band at lower pump power may be explained by the fact that high and even moderate excitation power can saturate the defect-related PL as the defect concentration and lifetime are finite [258]. It has been demonstrated in several publications that the deleterious effects of the dry etch damage can be removed with a subsequent wet etch [150] or anneal in NH_3/N_2 [284], significantly reducing the YL band luminescence, so it is clear that this kind of processing step prior to the shell deposition would be advantageous in the development of these materials.

5.5 Conclusions

The above-documented work, describes the characterisation of novel core/shell GaN/InGaN microrods, which have potential for application in optoelectronic devices due to the growth of junctions along nonpolar directions; avoiding the detrimental effects to efficiency related to the polarisation fields across junction in conventional *c*-axis devices. Two varieties of microrod with differing aspect ratios, were investigated by preparing cross sections through the samples with a dual beam FIB and lifting out to analyse via TEM and STEM. Threading dislocations in the core region were identified via diffraction contrast TEM and were confirmed to be mostly of edge and mixed character, in agreement with reports of GaN growth on sapphire. Although occurrences of these core dislocations reaching the shell region were identified the vast majority remain confined to the core and are unlikely to have a detrimental effect on the junction microstructure and therefore optical properties.

Despite attempts to heal the etch damage via deposition of an initial GaN shell, residual damage, likely in the form of altered stoichiometry and crystallinity, was identified as a region of differing contrast in (S)TEM images, particularly in the case of the smaller diameter sample. The major

difference between the two samples however, was the presence of a high density of defects in the shell region of the smaller diameter sample. These defects likely contribute to a broader near band edge luminescence and emergence of a yellow band in the photoluminescence data of this sample.

The higher energy band edge luminescence peak in the higher aspect ratio/smaller diameter sample is consistent with a greater degree of compressive strain in the core of this sample, the reason for which is unknown, but a greater degree of strain in this sample would also perhaps explain the higher density of defects in the InGaN layer due to an increased lattice mismatch. Increased etch damage to the smaller rods may also be a factor in the greater defect density in the shells of this sample. The structure of these defects are analysed in detail in the following chapter. The successful growth of largely coherent nonpolar GaN/InGaN junctions on the larger diameter rods is promising for their ongoing development as active materials in optoelectronic devices.

Chapter 6

Characterisation of defects in non-polar GaN/InGaN junctions on microrods

6.1 Introduction

As described in Chapter 2, there is a currently a strong research effort into optimising the growth of non-polar GaN/InGaN junctions to exploit potential efficiency gains derived from the absence of polarisation fields across the junctions[252]. Unfortunately, thus far any potential gains from these effects have been to some extent nullified by a high density of extended defects , particularly in the case of heteroepitaxially grown materials[58], [81], [83], [86], [285], [286]. Such defects include high densities of basal plane stacking faults[287]–[289], prismatic stacking faults lying on the a -planes [4][11][12], inversion domain boundaries [58][291] and perfect and partial dislocations [58][286][292]. Such defects will almost certainly have an impact on the viability of utilising these novel materials in devices due to associated effects on the growth morphology and optical

properties. For example, implications include: the documented correlation between threading dislocations in *m*-plane GaN and pyramidal ‘hillocks’ forming at the sample surface[293]; specific peaks in luminescence data attributed to particular types of defect [87] and the high density of defects often cited as the limiting factor in the power output of LEDs based on nonpolar materials[294][295].

The above results however, predominantly refer to planar non-polar films, grown heteroepitaxially or on non-polar GaN substrates cleaved from larger *c*-axis grown material. Therefore it is the subject of the current work, to determine the structure of the defects observed in non-polar junctions grown on the etched side walls of free standing GaN microrods. Such materials are likely to benefit from reduced strain associated with homoepitaxy on the non-polar GaN side walls but the extent to which the etch damage could affect the above grown layers is not well understood. As presented in the previous chapter, there was a marked difference in the defect density observed in the junction regions of the two differing core/shell microrod samples with the smaller sample A rods having a large number of unusual defects present in this region. The work presented in this chapter documents the effort to characterise these defects in the sample A rods, which have an unusual structure, unlike that of those commonly observed in conventionally grown non-polar GaN/InGaN material.

6.2 Flag defects

In addition to large numbers of individual basal plane stacking faults (BSFs), as widely reported for non-polar nitride material, the *m*-plane junctions contained a high density of unusual defects which were identifiable by their ‘flag’ shape when viewed along the *a*-axis in the longitudinal cross sections. Fig. 6.1 illustrates the geometry of the *a*-plane and *c*-plane sections, prepared from the rods using the Zeiss NVision dual beam FIB, which will be referred to throughout this chapter. The flag-shaped defects are clearly visible in the junction region of the ADF STEM image of the *a*-plane

section in Fig. 6.1(a) with a selected region shown enlarged and rotated by 90° in (c) showing the distinctive flag shape. This shape is not visible in *c*-plane images although the presence of defects is clear from the areas of bright strain contrast in the DF TEM image of Fig. 6.1(b). The defects usually start in the InGaN layer nearer the p-GaN interface and propagate through to the free surface of the shelled rods. The defects are comprised of straight sections lying in the basal *c*-plane and sections inclined at fairly regular angles appearing to match those of certain pyramidal planes, which together bound the distinctive flag shape. The inclined side of the defects always point in the same *c*-axis direction which may be related to the polarity of the material as has been confirmed in the case of pyramidal defects in p-GaN [296]. The following work documents the attempt to determine the geometry of these defects using a number of electron microscopy techniques.

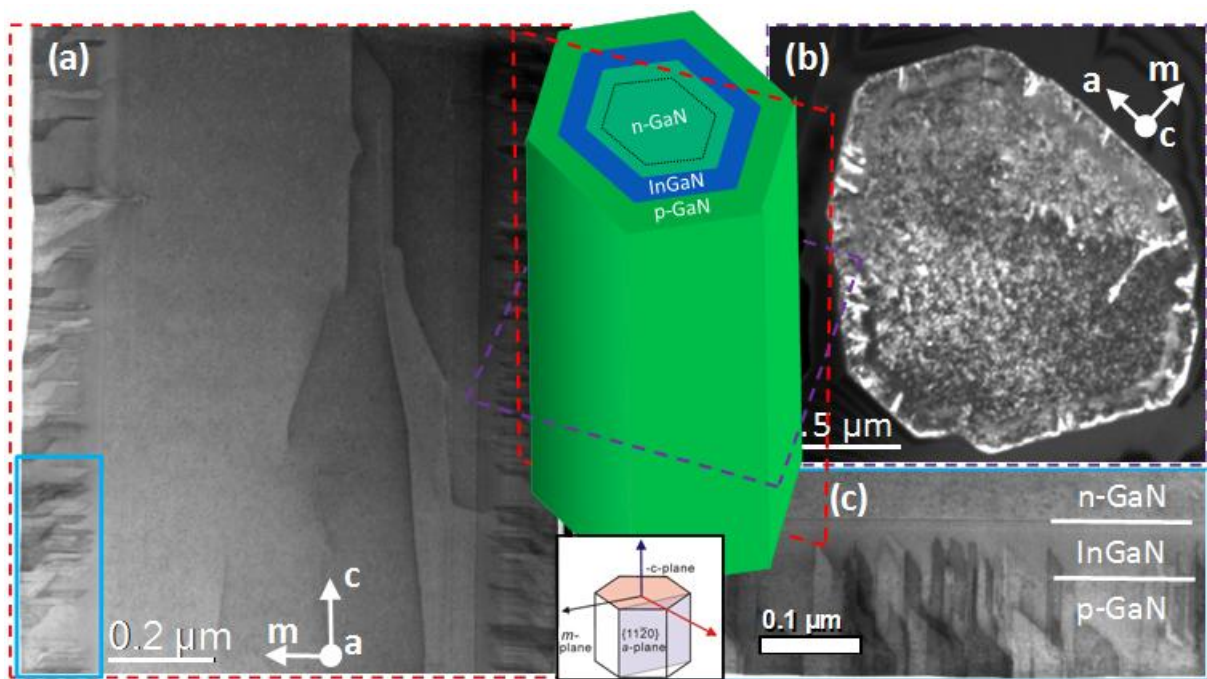


Figure 6.1 A schematic illustration of the geometry of the a-plane and m-plane sections through the core/shell microrods which will be referred to throughout this chapter. The indicated region in the ADF STEM image (a) of the a-plane section is rotated and enlarged in (c), clearly showing the ‘flag’ shape of the defects through the junction region. (b) shows a DF TEM image of a *c*-plane cross section in which the defects are clearly visible around the perimeter but have a less well defined shape.

6.3 Diffraction contrast analysis

In order to understand the geometry and character of the defects, diffraction contrast was firstly used to help determine whether they were formed from stacking faults, perfect or partial dislocations and what the corresponding fault or Burgers vectors might be. A full discussion of this experimental technique in addition to a description of the common defect types found in the III-nitrides can be found in Chapter 2.

Two flag defects were selected that could be easily re-identified so that this data may later be compared to high resolution and weak beam images. The defects were imaged under a wide range of diffraction conditions over several zone axes, a selection of which are shown in Fig. 6.2 below. A schematic diagram of the defects is also included, showing the labelling which will be used to refer to the individual constituent elements of the defects, with the upper flag termed defect 1 and the lower defect 2. Since the parts of the defect lying parallel to the basal plane and those lying at inclined angles often displayed differing contrast variations – for example, under the $g=c$ condition in the figure below, only the inclined section of defect 2 is visible – these sections were given an additional label so that they may be referred to individually. Therefore the basal plane elements are given the additional suffix ‘a’ and the inclined, pyramidal plane pieces ‘b’ so that, for example, flag defect 1 is formed from element 1a and 1b.

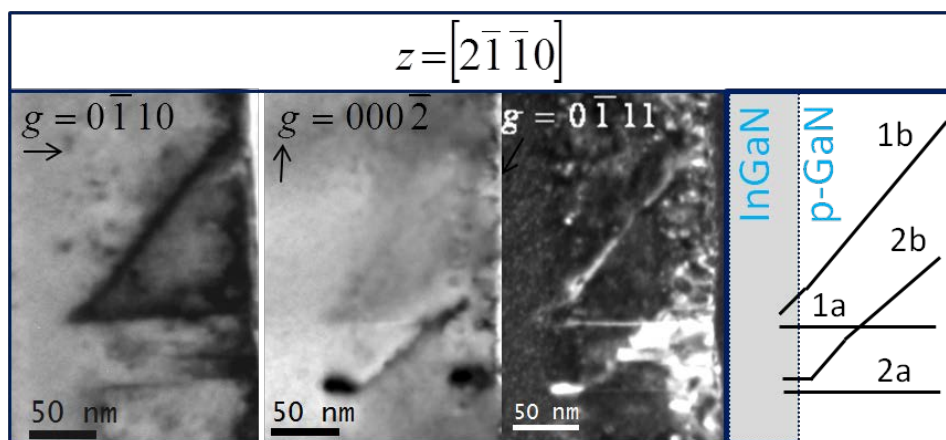


Figure 6.2 Two chosen flag defects, imaged along the a -axis under three different diffraction conditions with a schematic illustration of their structure. The upper flag defect will be referred to as defect 1 and the lower defect 2 with the basal plane elements of the flags given the additional suffix ‘a’ and the pyramidal plane elements given ‘b’ so that for example, defect 1 is formed from 1a and 1b.

The contrast of the individual defect elements in each image was defined as strong, weak or invisible and the data compiled so that it could be compared to calculated $\mathbf{g} \cdot \mathbf{b}$ values. As described in the diffraction contrast theory presented in Chapter 3, there is some uncertainty in interpreting the contrast due the possibility of defects appearing invisible when $\mathbf{g} \cdot \mathbf{b} < 1/3$ and the presence of residual contrast such as the case when $\mathbf{g} \cdot \mathbf{b} \times \mathbf{u} \neq 0$. The defects were therefore imaged under a wide range of imaging conditions so the contrast changes could be compared to the theoretical values for a number of defect types and the best fit for each chosen. A small subsection of this data is presented in table 1 below, in which the upper portion of the table gives the calculated $\mathbf{g} \cdot \mathbf{b}$ values for the perfect and partial dislocation types (the latter given in the left hand column) under the diffraction conditions utilised experimentally, with zone axes and $\mathbf{g}$ vectors given in the top and second to top rows respectively. For example, the upper left (shaded) cell of the table indicates that a perfect dislocation with $\mathbf{b}=[0001]$ appears invisible ($\mathbf{g} \cdot \mathbf{b}=0$) when viewed along the $[2\bar{1}\bar{1}0]$ zone axis and tilted to a $\mathbf{g}=0\bar{1}10$ two beam condition. All perfect dislocation types; $\mathbf{b}=\mathbf{c}$, $\mathbf{a}$ and $\mathbf{a}+\mathbf{c}$, are included in addition to Frank-Shockley ($\mathbf{b}=\pm \frac{1}{6} \langle 20\bar{2}3 \rangle$) and Shockley ($\mathbf{b}=\pm \frac{1}{3} \langle 1\bar{1}00 \rangle$) partial dislocations. Frank partials with $\mathbf{b}=\pm \frac{1}{2} \langle 0001 \rangle$ are omitted since they would show similar contrast variations as a $\mathbf{b}=\mathbf{c}$ perfect dislocation so may be identified by the presence of a stacking fault with partials showing contrast variations as given in this top row.

The most commonly observed basal plane stacking faults, type I_1 and I_2 , are also included, with the vectors given in the 'b' column corresponding to their fault vector. Stacking faults are invisible when $\mathbf{g} \cdot \mathbf{R}$ has an integer value and therefore I_1 or I_2 type basal plane stacking fault may be identified by invisible contrast under these diffraction conditions, which are shaded blue in the corresponding cells of the table.

The lower, separated portion of the table gives the experimentally observed contrast of the constituent defect elements 1a, 1b, 2a and 2b as invisible, weak or visible. The cells which indicate theoretical invisible contrast in the upper, calculated portion of the table are shaded, as are the

experimentally observed invisible contrast cells in the lower table, for ease of comparison. These contrast changes will be referred to in the following discussion which will deal first with data relating to defect 2, followed by that of defect 1.

		g	[2-1-10]			[-211-1]		[10-10]	[1-100]
			0-110	0002	0-111	-110-3	10-13	-12-10	-1-120
Perfect dislocations	$\pm <0001>$	0001	0	0	1	-3	3	0	0
		2-1-10	0	0	0	1	1	1/3	1/3
	$\pm 1/3 <11-20>$	1-210	1/3	0	1/3	1	0	2/3	1/3
		11-20	1/3	0	1/3	0	1	1/3	2/3
	$\pm 1/3 <11-23>$	11-23	1	2	0 or 2	3	2	1	2
		1-213	1	2	2 or 0	2	3	2	2
Partial dislocations (or corresponding SF)		-2113	0	2	1	2	2	2	1
	Shockley partial	1-100	1/3	0	1/3	2/3	1/3	1	0
	$\pm 1/3 <1-100>$	10-10	1/3	0	1/3	1/3	2/3	0	1
		01-10	1/3	0	2/3	1/3	1/3	1	1
	Frank-Shockley	20-23	1/3	1	1/6 or 5/6	7/6 or 11/6	13/6 or 5/6	0	1
	$\pm 1/6 <20-23>$	2-203	1/3	1	5/6 or 1/6	5/6 or 13/6	11/6 or 7/6	1	0
Basal plane stacking faults		02-23	2/3	1	1/6 or 7/6	7/6 or 11/6	11/6 or 7/6	1	1
	I_1 -type BSF	20-23	1/3	1	1/6 or 5/6	7/6 or 11/6	13/6 or 5/6	0	1
	$R=\pm 1/6 <20-23>$	2-203	1/3	1	5/6 or 1/6	5/6 or 13/6	11/6 or 7/6	1	0
		02-23	2/3	1	1/6 or 7/6	7/6 or 11/6	11/6 or 7/6	1	1
	I_2 -type BSF	1-100	1/3	0	1/3	2/3	1/3	1	0
	$R=\pm 1/3 <1-100>$	10-10	1/3	0	1/3	1/3	2/3	0	1
		01-10	1/3	0	2/3	1/3	1/3	1	1

Experimentally
observed contrast:

I = invisible

W = weak

V = visible

d1a	V	I	V	W	I	I	I	BSF
d1b	V	I	W	V	I	V	W	[1-210]
d2a	V	I	W	W	I	I	I	BSF
d2b	W	V	V	V/W	V	I/W	W	[20-23]

Table 6.1 The upper portion of the table gives calculated $g \cdot b$ values for perfect dislocations and partials (and their corresponding stacking faults) in the wurtzite lattice. The expected contrast variations are shown for a range of zone axis and diffraction conditions which were used experimentally. The lower portion of the table indicates the contrast variations which were actually observed for the four constituent parts of defects 1 and 2, under the diffraction conditions given in the top two rows.

6.4 Structural analysis of flag defect 2

6.4.1 Basal plane element 2a

Considering first the basal plane defect element 2a, the contrast changes described in table 1 above do not show an exact match to any of the wurtzite defects given but most closely follow those of

either an I_1 or I_2 basal plane stacking fault. Defect 2a appears invisible under $\mathbf{g}=0002, \bar{1}2\bar{1}0$ and $\bar{1}\bar{1}20$ as expected but there is a discrepancy for $\mathbf{g}=10\bar{1}3$ in which the defect also appeared invisible despite $\mathbf{g}\cdot\mathbf{R} \neq \text{integer}$. Despite this inconsistency, a basal plane stacking fault appeared the most likely candidate when all the diffraction conditions used are considered in addition to the appearance of the defect as a very thin straight line parallel to the basal plane and indeed this was confirmed in the HRSTEM data described below. This discrepancy may possibly be explained by the very small deviation from an integer value of $\mathbf{g}\cdot\mathbf{R}$ in the case of an I_1 type fault or the tilt conditions used deviating slightly from those intended. Since both I_1 and I_2 type BSFs are invisible for the same $\mathbf{g}$ conditions, it is not straightforward to distinguish between them purely based on the contrast study. There are likely to be differences between the two due to the difference in the exact values of the non-integer $\mathbf{g}\cdot\mathbf{R}$ conditions (e.g. $\mathbf{g}\cdot\mathbf{R}=1/6$ rather than $1/3$) but it would be extremely difficult to reliably distinguish between them.

High resolution ADF STEM was collected using an aberration corrected JEOL 2200MCO, from the regions around the defects which could be used to identify the exact change in stacking and therefore the type of BSF. Figure 6.3 below shows that defect 2 bounds a region of brighter contrast, with element 2a comprising an atomically flat interface between this brighter region and that of the darker bulk. It should be noted that the detector angles were such that there is likely to be a significant degree of Bragg scattering included in the image, which likely explains the bright contrast visible within defect 2, as will be discussed in the following sections. High resolution data collected from this region shows a clear change in stacking across the interface comprising ABABABCBCBC, corresponding to an I_1 type BSF with fault vector $\mathbf{R}=1/6[20\bar{2}3]$ which agrees with the diffraction contrast data presented above. Given this result, it is tempting to suggest that the change in intensity across 2a (which is often seen within the regions defined by the flags as evident in Fig. 6.1(c)) derives from this observed change in stacking, an idea which will be expanded upon in the following sections.

In order to explore this possibility, it is firstly necessary to return to the $\mathbf{g} \cdot \mathbf{b}$ analysis to determine potential burgers vectors of the inclined, pyramidal element of the defect, 2b.

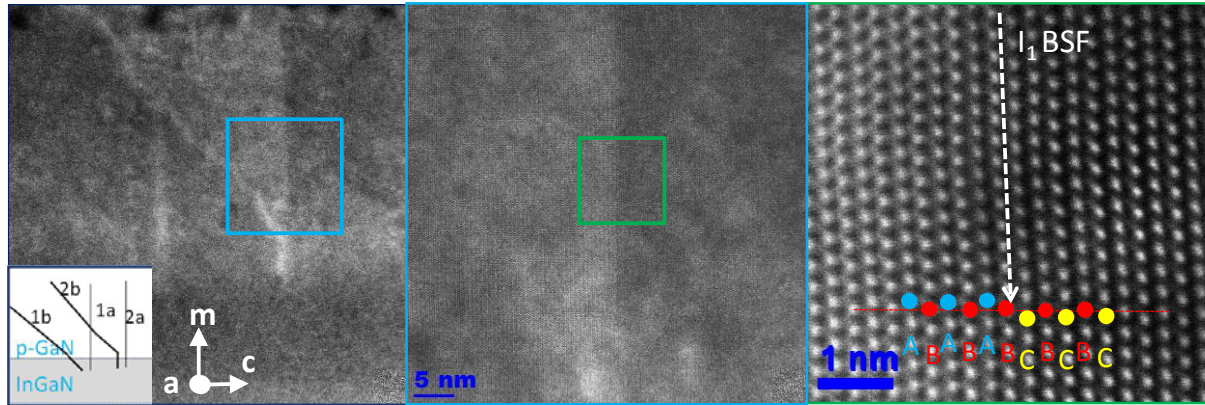


Figure 6.3 A series of ADF STEM images of defect element 2a at increasing magnification showing the atomically flat interface between a region of brighter contrast bounded by the defect and the darker contrast of the bulk. High resolution data shows a change of stacking across this interface comprising ABABCBC relating to a type I_1 basal plane stacking fault.

6.4.2 Inclined element 2b

With reference to table 1, it is clear that 2b displays contrast changes with diffraction conditions matching that of a Frank-Shockley partial dislocation since it only appeared invisible under a $\mathbf{g} = \bar{1}2\bar{1}0$ condition when tilted near the $[10\bar{1}0]$ axis. It is interesting to note that such a defect has a Burgers vector $\mathbf{b} = 1/6[20\bar{2}3]$ matching that of the fault vector of the corresponding I_1 BSF and therefore supports the theory that the contrast, contained within the area defined by the defect, is derived from a change in stacking sequence.

Again, high resolution ADF STEM was used to compare to the diffraction contrast work and, although perhaps not as clear as the change in stacking sequence observed across the BSF of 2a, there was evidence in the data, presented in Fig. 6.4, that there was a similar change in stacking – namely ABABABCBCBC – across this dislocation 2b. The red line in Fig. 6.4(c) provides a guide for the eye across the red ‘B’-position c-planes which stay constant and the change in stacking may be observed as the change in positioning of the A/C columns in between these B positions relative to this guide

line. Although it is difficult to determine an abrupt change in stacking at a certain position, the change in positioning from one side to the other is emphasised by the comparison between two neighbouring B columns (marked with blue circles) on the left and two C columns (marked with yellow circles) on the right. It is clear the position of these two columns relative to the guide line is shifted on the right hand side of the image in comparison with the left, suggesting a change in stacking configuration. The fact that more of a gradual change in stacking rather than an abrupt change is observed may be due to 2b actually being a partial dislocation loop, an idea explored in more detail below.

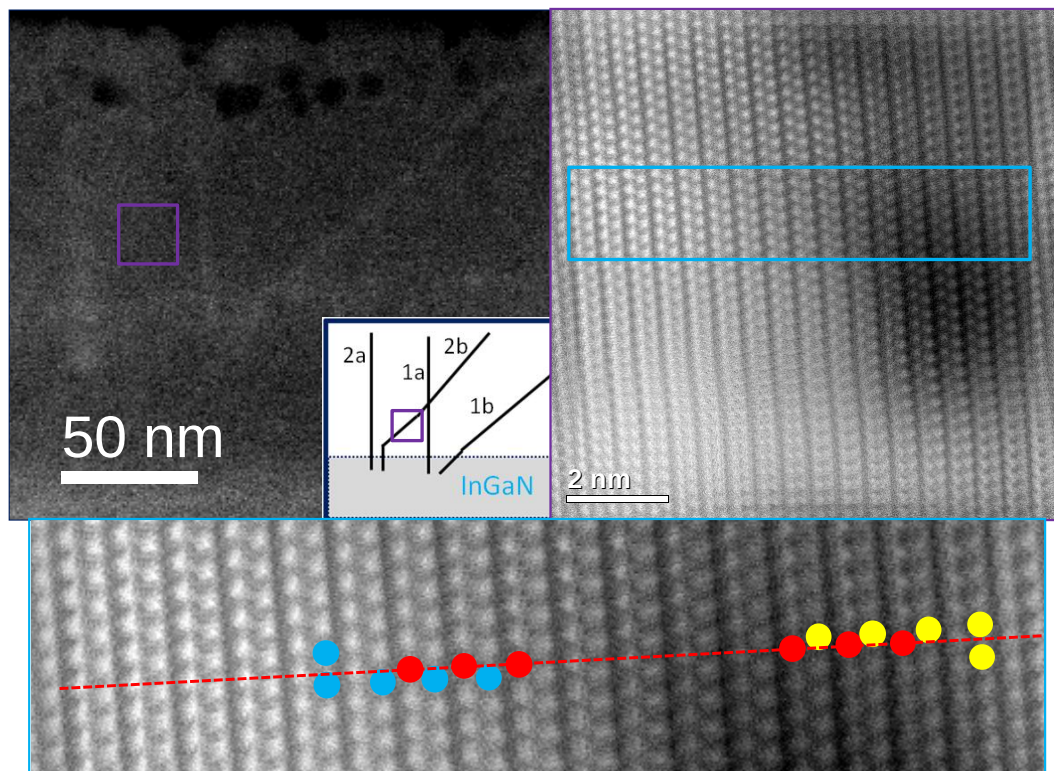


Figure 6.4 High resolution STEM data from an area around inclined defect 2b showing an apparent change in stacking sequence comprising ABABCBC consistent with the partial dislocation assigned in the diffraction contrast work.

This change in stacking sequence observed above could be achieved by a Frank-Shockley partial dislocation loop (of the type suggested by the diffraction contrast work) lying on a pyramidal plane. If such loops are present they should be visible in *c*-axis diffraction contrast images on *c*-plane sections so the data was reviewed and further weak beam data collected in order to get clearer

contrast in the images. Fig. 6.5 consists of two $g(3g)$ weak beam images with $g = \{11\bar{2}0\}$ and appears to show loops as predicted in the junction region which are invisible under one of the $g=a$ conditions, consistent with the Burgers vectors of Frank-Shockley partial dislocation.

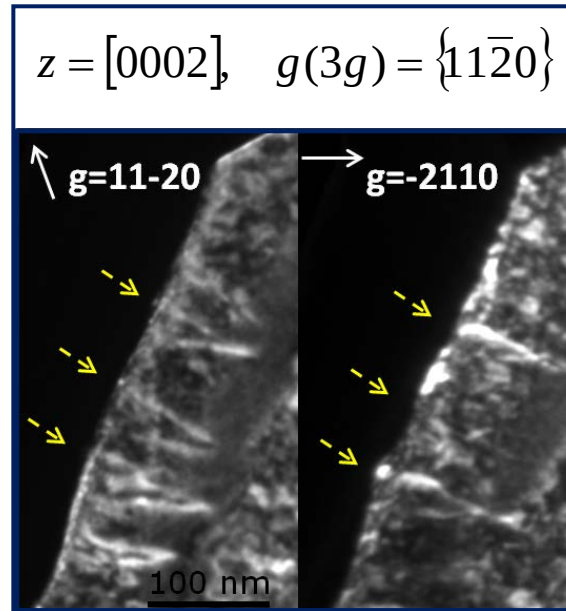


Figure 6.5 weak beam images under $g(3g)$ conditions with $g = \{11\bar{2}0\}$ of c-plane cross section showing loops in the junctions which show contrast changes consistent with Frank-Shockley partial dislocations

6.4.3 Model structure of defect 2

Summarising the data on defect 2, the high resolution data shows with certainty that the basal plane element 2a is a type I_1 basal plane stacking fault and the diffraction contrast and weak beam studies suggest that the inclined element 2b has a Burgers vector matching that of a Frank-Shockley partial dislocation on a pyramidal plane which was supported by additional high resolution ADF STEM data. The defects enclose a region bearing differing contrast to that of the surrounding material in ADF STEM and diffraction contrast TEM images and, since both defects have equal fault vectors, it is tempting to suggest that they form a domain of differing stacking to the surrounding material which leads to differing contrast in this area. A Frank-Shockley partial dislocation loop on the pyramidal plane, as illustrated in Fig. 6.6 below, would achieve such a domain of differing stacking. This may also explain the difficulty in observing an abrupt change in stacking across 2b as, if the plane of the

loop is slightly inclined to the viewing direction; two regions of differing stacking are being imaged in projection near the defect making it difficult to determine a clear interface.

Since these two defects have equal Burgers vectors it is possible that sections where the defects meet, indicated by the yellow arrow in the diagram of Fig. 6.6, may annihilate leaving two dislocation dipoles bounding the domain of differing stacking.

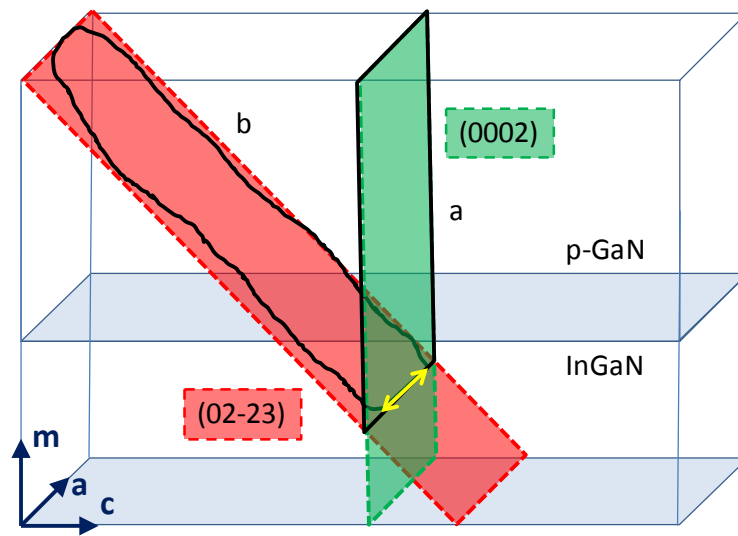


Figure 6.6 Schematic illustration of a flag defect consisting of a partial dislocation loop on a pyramidal plane and a basal plane stacking fault

6.5 Structural analysis of flag defect 1

6.5.1 Basal plane element 1a

Returning to the diffraction contrast work presented in table 1, the element of defect 1 lying in the basal plane, 1a, displayed very similar contrast changes to those of 2a, matching a basal plane stacking fault. Again, the discrepancy of this part of the defect appearing invisible under a $\mathbf{g}=10\bar{1}3$ two beam condition was also observed so this may be related to the very small deviation from $\mathbf{g}\cdot\mathbf{b}=\text{integer}$ in the case of a Frank-Shockley dislocation as suggested above. Unfortunately, unlike the case of defect 2, it was not possible to acquire supporting HRSTEM images around this defect in order to determine unquestionably the exact type and therefore the following deduction is based on

the other data available. The appearance of the defect as a thin line in diffraction contrast images parallel to the basal plane and contrast changes matching those of 2a suggest very strongly that it is a basal plane stacking fault. Furthermore, due to the close match in diffraction contrast changes to those of 2a (including the fact it appears invisible for $\mathbf{g}=10\bar{1}3$) it is very likely that it is also an I_1 type stacking fault. This type of stacking fault was identified as the basal plane element of every other flag defect for which HRSTEM was successfully obtained so it seems likely that this is the case.

Furthermore, I_1 stacking faults also have a different formation mechanism to I_2 , forming during growth rather than a result of lattice slip, and therefore, due to the similar morphology of these defects, it is unlikely that they form by differing mechanisms, which perhaps adds further weight to the argument that defect 1a is of the same type to 2a.

6.5.2 Dislocation 1b

Conversely, the inclined element associated with defect 1, 1b, did not match those of defect 2 but rather had contrast changes matching that of a perfect dislocation with Burgers vector type $\mathbf{b}=1/3[1\bar{2}10]$. It is interesting to note that this defect does not display the contrast changes within the flag shape which might be linked to the fact that such a perfect dislocation would not change the stacking sequence.

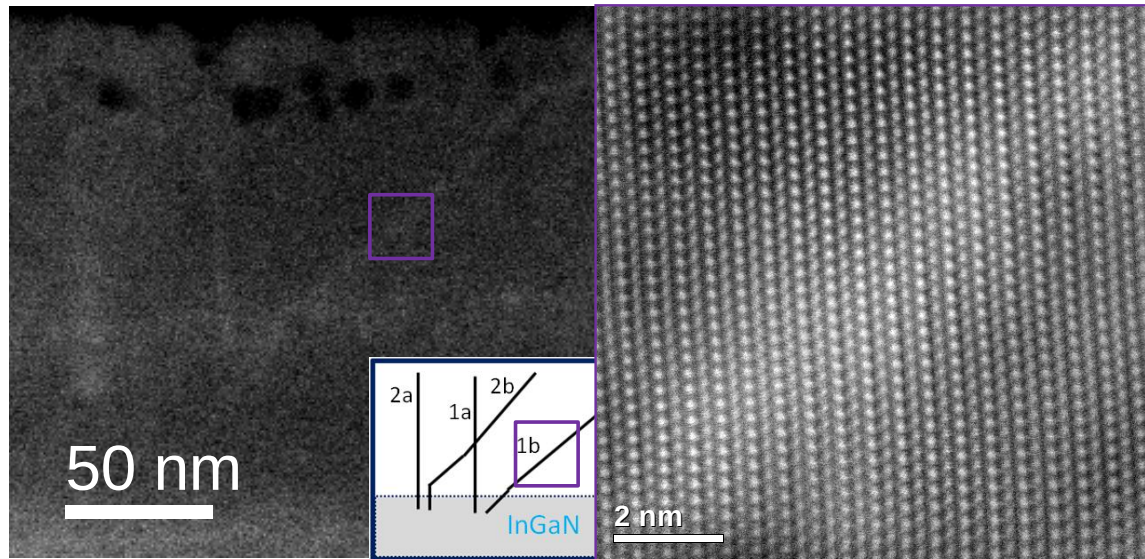


Figure 6.7 High resolution data acquired from the indicated region around 1b with no discernible change in stacking observed, consistent with a perfect dislocation as ascribed via the diffraction contrast study.

Again, high resolution STEM was used to image the area around the apparent perfect dislocation comprising defect 1b and, as might be expected, there was no observable change in stacking sequence across the dislocation. As before, the detector angles were such that there is likely to be a significant fraction of Bragg scattering included, which must be taken into account in analysing the contrast changes. Fig. 6.7(a) indicates the region around dislocation 1b from which the high resolution data was acquired and, while 6.7(b) clearly shows the contrast deriving from the dislocation strain field passing diagonally through the image, there is no discernible change in stacking across it.

6.5.3 Inclined defects in c-plane sections

Due to the unexpected result of the inclined edges of the flag defects 1 and 2 having differing dislocation types this diffraction contrast work was also repeated on the *c*-axis cross sections with images taken under various diffraction conditions. Given that all types of basal plane stacking faults appear invisible under $\mathbf{g} = \mathbf{m}$ and $\mathbf{a}$ conditions, they will not be observed in these images taken along the *c*-axis and it can therefore be assumed that the defects observed in Fig. 6.8 below are the inclined pyramidal parts of the flag. Clearly it was not possible to study the same two defects chosen

in the a -axis section studied above but it was useful to determine whether the contrast changes observed for similar defects were, in general, consistent with the Burgers vectors assigned to the specific inclined defect elements above.

Fig. 6.8 below contains examples of diffraction contrast images taken near the c -axis on c -plane sections of the defects visible in the shell regions, assumed to be the pyramidal dislocations identified in the $\mathbf{g} \cdot \mathbf{b}$ work above. Figure 6.8(a) shows two such defects, each of which is invisible for one of the three $\mathbf{g} = \mathbf{m} = \{1\bar{1}00\}$ vectors, consistent with a Burgers vector of type $\mathbf{b} = \mathbf{a} = \frac{1}{3}\{11\bar{2}0\}$, corresponding to a perfect dislocation as assigned to dislocation 1b. Figure 6.8(b) shows two defects (marked by red arrows) which each appear invisible for certain $\mathbf{g} = \mathbf{a} = \{11\bar{2}0\}$ conditions, consistent with a Burgers vector of type $\mathbf{b} = \frac{1}{6}\{20\bar{2}3\}$ corresponding to a partial dislocation of the type assigned to defect element 2b.

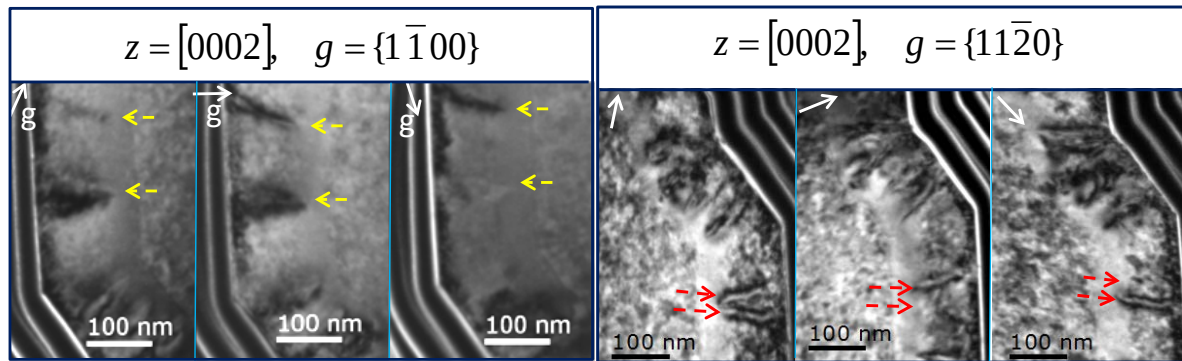


Figure 6.8 BF TEM images of c -axis sections taken near to the c -axis with $\mathbf{g}$ vectors equal to each of the 3 independent $\mathbf{m}$ -planes in (a) and $\mathbf{a}$ -planes in (b). Dashed arrows indicate the dislocations whereas the solid arrows in the top left corner show the diffraction condition. It is clear that in each case certain defects appear invisible for one of these three vectors consistent with the Burgers vectors assigned to the pyramidal dislocations in the diffraction contrast work on the a -plane section above.

6.5.4 Weak beam imaging of 1b

As noted above, the inclined sides of the defects appear to follow fairly regular angles when viewed in the a -axis sections. This was investigated further by employing weak beam imaging of the inclined defect elements 1b and 2b from different zone axes and studying the change of geometry of the dislocation lines. As described in Chapter 2, the weak beam criterion states that if the excitation

error $s_g \geq 0.2\text{nm}^{-1}$, then the peak in the weak beam image should correspond fairly closely to the dislocation core position. Values of s_g , given below in table 1, were therefore calculated for various g in GaN so that the approximate diffraction condition could be chosen to ensure the position of the image peak could be directly related to the dislocation core.

g	n $d_{hkl}(\text{nm})$	$s_g (\text{nm}^{-1})$									
		1	2	3	4	5	6	7	8	9	10
0002	0.260	0.000	0.019	0.037	0.056	0.074	0.093	0.112	0.130	0.149	0.167
11-20	0.160	0.000	0.049	0.099	0.148	0.197	0.247	0.296	0.345	0.395	0.444
1-100	0.274	0.000	0.017	0.033	0.050	0.067	0.084	0.100	0.117	0.134	0.151
10-11	0.242	0.000	0.021	0.043	0.064	0.086	0.107	0.129	0.150	0.171	0.193
10-12	0.019	0.000	0.036	0.071	0.107	0.143	0.179	0.214	0.250	0.286	0.322
11-21	0.151	0.000	0.055	0.110	0.165	0.220	0.275	0.330	0.385	0.440	0.495

Table 6.2 Values of s_g in nm^{-1} for various n and g in GaN

In practice however this was not always possible as the contrast became too weak when tilting to the large values of n necessary to satisfy the weak beam criterion $s_g \geq 0.2\text{nm}^{-1}$. This is likely due to the fact that the average intensity decreases as $1/s^2$ and the required sample thickness to give the Kikuchi lines needed to set up the required conditions often resulted in a loss of contrast. In the case of the pyramidal dislocations of defects 1 and 2, it was possible to satisfy the criterion using $g = a = \{11\bar{2}0\}$ with $n \approx 5.1$ and give good contrast in the image but with $g = m = \{1\bar{1}00\}$, a value of $s \approx 1.2$ by using $n \approx 8.1$ was the best possible.

By measuring the length and angle of inclination of the dislocation from a number of zone axes, as illustrated in Fig. 6.9 below, it was possible to determine which plane the dislocation lay on. As expected, the angles matched those of several pyramidal planes with the specific case of the dislocation 1b shown below, lying on a $\{02\bar{2}\bar{3}\}$ plane.

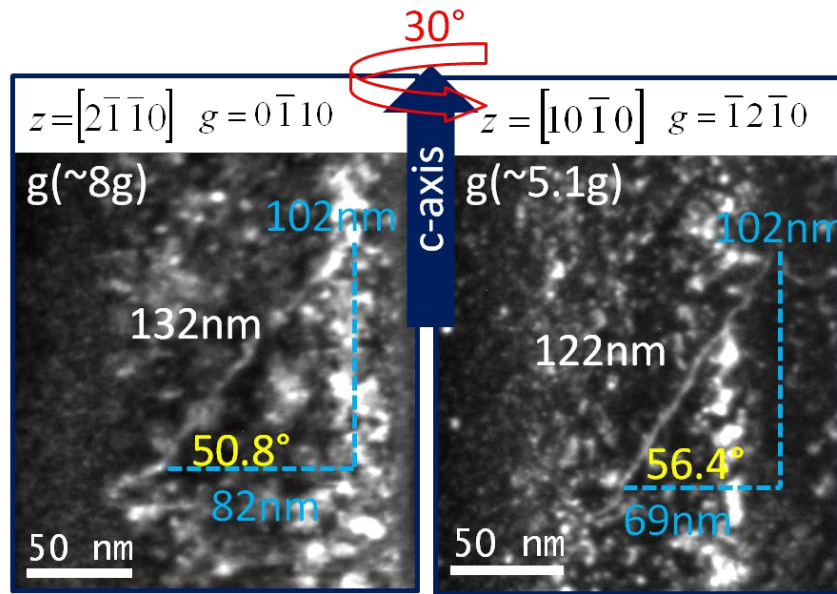


Figure 6.9 An example of the use of weak beam imaging from multiple zone axes to determine the plane which the inclines dislocations lay on. The projection of the dislocation geometry was measured from close to the $[a]$ and $[m]$ axes, with the changes consistent with the dislocation core on a $\{02\bar{2}3\}$ plane

6.5.5 Model structure of the flag defect 1

To summarise the data relating to defect 1, the diffraction contrast work suggests the pyramidal dislocation is a perfect $\mathbf{b}=\mathbf{a}$ type which was supported by the high resolution STEM data in which there was no observable change in stacking across the defect. Although no high resolution data could be obtained across the basal plane element 1a, the similarity of appearance and contrast variation with 2a strongly suggest it is also a basal plane stacking fault, most likely also type I_1 which was observed for all stacking faults for which HRSTEM images could be obtained. The structure of this defect may then be similar to that proposed in Fig. 6.6 for defect 2, but with a perfect dislocation loop lying on a pyramidal plane which approaches the BSF. A high number of loops were observed in c -plane sections, such as the example given in Fig. 6.8(a), which displayed invisibility for one of the three $\mathbf{g} = \mathbf{m} = \{1\bar{1}00\}$ conditions, an observation only consistent with perfect $\mathbf{b}=\mathbf{a}$ or $\mathbf{b}=\mathbf{a}+\mathbf{c}$ type dislocations suggesting that such defects are common in these materials. Such a configuration would not enclose a domain of differing stacking to that of the surrounding material, as suggested for defect 2 and therefore this difference could explain the fact that defect 1 did not show the enclosed region of brighter contrast observed in TEM and STEM images of defect 2.

6.6 Discussion of possible formation mechanism

Since such defects, in particular the partial dislocations that bound I_1 type BSFs, are believed to act as nonradiative recombination centres in non-polar InGaN/GaN junctions [271], the reason and mechanism by which they nucleate in the materials studied here is of significant interest. The following discussion first considers the I_1 BSFs, which are found primarily as components of the flag defects analysed in detail above but also individually as will be shown below, before considering the pyramidal perfect and partial dislocations. Similar observations previously reported in the literature are reviewed briefly to aid in discussing the possible reasons for the nucleation of these defects and suggest reasons for their association in the flag shape arrangement observed.

6.6.1 Basal plane stacking faults

The I_1 type BSFs that are prevalent in the m -plane junctions and form part of the flag defects have a very low formation energy[3][80] and can only be formed during growth rather than being generated as a result of lattice slip during strain relaxation [297]. They have previously been observed perpendicular to m -plane GaN/InGaN junctions and since the bounding partials have a component of the Burgers vector along the c -axis, the net effect of I_1 BSF formation may be to reduce compressive stress [298].

There are various mechanisms reported describing the formation of stacking faults during the growth of non-polar GaN/InGaN. A number of researchers cite the morphology of the underlying substrate surface as an important factor in their formation, with the appearance of bundles of BSFs correlated with undulations of the substrate surface, thermally induced substrate roughening [299] or incorporation of impurities during substrate heating [300]. Other reports suggest that the difference in growth characteristics of the $(000\bar{2})$ N-face and the (0002) Ga-face normal to the non-polar substrate surface are a possible cause of BSF generation[301]. In particular, it is argued that, since the N-face has a much lower growth rate than that of the Ga-face, islands that may form during initial three-dimensional growth are likely to have primarily N-face side facets which also

have a low formation energy of stacking faults[302] and therefore produce the high densities of BSFs when the islands coalesce[303][301].

It might be expected that, if either of the above described formation mechanisms –either roughness/damage to the underlying microrod side walls, or coalescing of islands during growth - were responsible for the BSFs comprising part of the flag defects, they would likely be observed to begin near to the initial etched surface in the initial n-GaN layer. The impact of the etch damage on the growth surface has been considered in Chapter 5 as a potential reason for the defect formation and there certainly are occurrences of bundles of defects starting at or near the core surface. Such examples, potentially derived from the initial etch damage to the core surface, are indicated with yellow arrows in Fig. 6.10 below. However such observations are relatively uncommon, as the majority of BSFs, whether individual or forming the sides of flag defects, usually start some distance into the InGaN layer. Examples of individual BSFs and those relating to flag defects are indicated by green and blue arrows respectively, in Fig. 6.10 below.

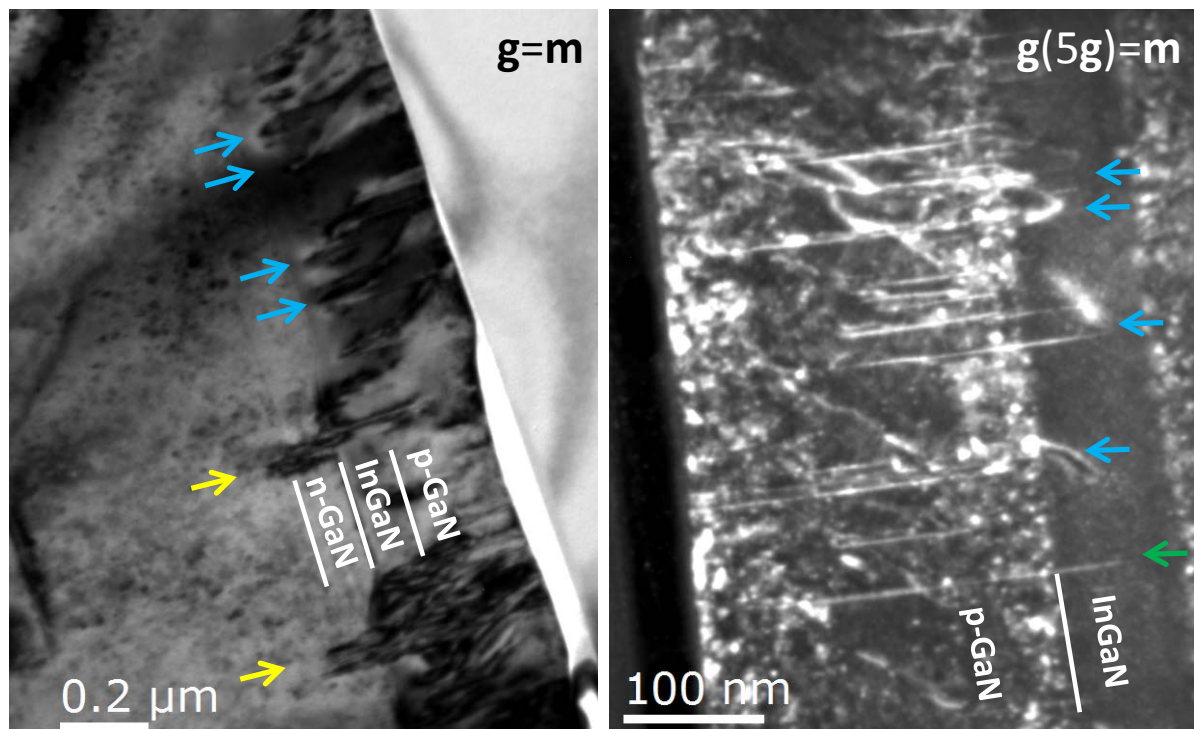


Figure 6.10 Bright field and weak beam image with $g=m$, showing both the possibility of stacking faults forming at the core surface and within the InGaN layer – the latter being more numerous

Although it cannot be ruled out that the damage to the initial core initiates a delayed effect in the overlying layers with perhaps the increasing strain only leading to the formation of the defects after some critical thickness, it might more likely suggest a formation mechanism related to the growth of the InGaN layer. A relationship between the onset of BSF formation and a critical thickness and indium content of the InGaN layer has been suggested previously [304] and, although this was observed with much higher indium content films (the InGaN layers here appear to only be ~2-5% indium) the thickness of the InGaN layer in the work here is much greater. Another known issue is that the *m*-plane exhibits the lowest indium uptake in the growth of InGaN films which may make them more prone to growth errors at the low temperatures required for growth [271][272].

Considering all of these factors, it could be concluded that although damage to the underlying core is responsible for a certain fraction of the defects observed, the majority appear to be related to the growth of the InGaN layer, with both the accumulation of strain due to the lattice mismatch and growth errors due to the low temperature and lack of indium incorporation responsible for the nucleation of stacking faults.

6.6.2 Dislocations and the flag configuration

The unusual aspect to the defects observed here is the association of the BSFs with an adjacent dislocation loop, forming the characteristic flag shape. Although such a configuration has not been reported in the literature, there is discussion of almost periodic arrays of pairs of BSFs which enclose regions of differing stacking and have the net effect of relaxing misfit strain along the *c*-axis by the removal of a basal plane [305]. Since the formation of BSFs may only reduce misfit strain along the *c*-axis it may be possible that the perfect and partial dislocations glide in along the pyramidal planes identified to reduce the misfit strain within the basal plane. A similar situation has been observed in ZnO/ZnMgO core-shell structures[306] with strain released in the non-polar shell regions by dislocations lying in pyramidal planes with Burgers vectors having components along the *c*-axis and within the *c*-plane. Similarly, mixed dislocations have been observed to glide in on pyramidal planes

from the free surfaces of *c*-plane GaN/InGaN/AlGaIn multilayers to relieve strain once the films exceed a critical thickness and have also been shown to accompany neighbouring basal plane dislocations [307]. In addition, dislocations have also been shown to form and move so as to relieve local stresses due to stacking faults formed during the growth of *c*-plane GaN films [308].

Considering these reports in the context of the observations described here, a possible explanation may be that the stacking faults are formed via growth errors during the growth of the InGaIn layer as described above whilst the perfect and partial dislocation loops glide in from the free surface on the pyramidal planes to form the flag configuration, illustrated in Fig. 6.6. This process may be driven by the accumulation of strain associated with the growth of the InGaIn layer but also that associated with the stacking faults themselves with the proximity of the dislocation loop to the stacking fault governed by energy equilibrium considerations. The Burgers vectors identified would be able to reduce misfit strain in the growth plane and in the case of the partial dislocation loops which have Burgers vectors equal to the fault vector of the BSFs, there is the possibility of annihilation with the bounding partial of the BSF leaving the domain of differing stacking with respect to the surrounding material. The flags displaying enclosed regions of contrast would then be those which involve a partial dislocation loop forming the domain of differing stacking with the BSF, with the contrast derived from slight mistilts of these domains with respect to the bulk which result in brighter or darker contrast depending on whether they are more or less strongly scattering under the diffraction conditions used.

6.7 Conclusions

Non-polar junctions deposited on the exposed *m*-planes of etched GaN microrods are free from the spontaneous and piezoelectric fields which are detrimental to the efficiency of conventional *c*-plane devices and are therefore of interest in the development of next generation optical devices. Using a dual-beam FIB to prepare various cross sections through these materials, it was found that growth

on smaller diameter rods results in a high density of unusual defects which are identifiable by their characteristic flag shape when viewed along the a -axis. These defects were characterised in detail using conventional diffraction contrast TEM to perform a $\mathbf{g} \cdot \mathbf{b}$ analysis, high resolution STEM and weak beam imaging. It was found that the defects were comprised of type I₁ basal plane stacking faults and both perfect and partial dislocation loops lying on pyramidal planes. Using the data and reference to previous work in the literature it was suggested that a proportion of the basal plane stacking faults are formed due to etch damage on the core surface but the majority are formed via growth errors relating to the low temperatures required to grow InGaN films and the very low indium incorporation into m -plane material. The dislocation loops are believed to glide in from the free surface to relieve lattice mismatch strain and possibly stress relating to the stacking faults themselves leading them to approach the stacking faults to a certain distance to neutralise the stress related to these BSFs. In the case of the partial dislocation loops, domains of differing stacking sequence may form which can have slight mistilts with respect to the surrounding material which result in the flag bounding regions of differing contrast in diffraction contrast TEM and ADF STEM images. These defects are likely to explain the broader near band edge peak and the yellow band in the photoluminescence data presented in the previous chapter. The comparison between samples of differing core radius suggests that these issues may be overcome by using larger diameter microrods which allow for the non-polar shells to be grown largely defect free and therefore offer a promising candidate material in future optical devices.

Chapter 7

Zinc Nitride Nanoparticles

7.1 Introduction

7.1.1 Background

Zinc nitride (Zn_3N_2) nanoparticles have the potential to be utilised in phosphors to profit from the advantageous properties common to semiconductor nanocrystals such as size tuning of emission, improved photometric performance[198] and ease of integration[199] but without the toxicity or scarcity associated with conventional quantum dot phosphor materials [203]. There have been many conflicting reports of the bandgap in zinc nitride with values stated between 1.01eV[207] and 3.2eV[208] but the majority place it in the near infrared or visible regions, in agreement with the theoretical result of 1.17eV[209], suitable for size tuning over the long wavelength range of the visible spectrum.

The, thus-far limited, reports of this material have become more frequent due to a growing recognition of its promising electrical properties [205] and the low cost of its constituent elements[206]. Several different morphologies have now been described, including polycrystalline films[213], hollow micro spheres[215] and nano-needles [216] and wires [45][217]. However there has been no report of 0-dimensional Zn_3N_2 nanoparticles suitable for nanophosphors before the growth at SLE of the material studied here[219] and therefore this work represents the first attempt to characterise such structures.

7.1.2 Aims

The primary aim of the work presented in this chapter is therefore to confirm the presence of Zn_3N_2 in a range of nanoparticle samples and therefore verify the first successful growth of these materials. This task is made significantly more complicated by two factors: firstly, Zn_3N_2 is extremely sensitive to oxidation in air or the presence of water, with which it reacts rapidly to form ZnO [206]; secondly, initial experiments indicated that all samples changed rapidly under the electron beam in the microscope. Therefore one of the major challenges of the work is differentiating between the structure and properties of the material 'as grown' and those after oxidation and/or exposure to the electron beam.

The work of this chapter therefore involves applying a wide range of techniques in order to (1) firstly confirm the presence of Zn_3N_2 in the samples; (2) analyse the compositional and structural differences in samples of differing particle size and with/without organic capping agents; and (3) study the changes in the material under the electron beam and after exposure to air.

7.2 Samples

A range of nanocrystal samples have been investigated, with three selected to illustrate the general trends observed, the details of which are given in table 1 below.

The nanocrystals were prepared by Dr Peter Taylor at SLE following a procedure outlined in a recent publication [219] by bubbling ammonia through 1-octadecene heated to 225°C before periodically injecting diethylzinc into the reaction mixture at regular intervals with the continued addition of diethylzinc leading to larger nanocrystals such as those of sample 1 relative to sample 2. Sample 3 was prepared by a similar method but with the addition of a capping agent oleyamine in the reaction mixture intended to further control the size of the nanocrystals and improve their optical properties through the passivation of surface states.

Sample	Description	Morphology
1	Large uncapped nanoparticles	Large circular clusters with average particle/grain size of 7-8nm. Also a variety of rod/wire morphologies
2	Small uncapped nanoparticles	Tend to form large clusters with average particle/grain size from HRTEM of ~4-5nm
3	Small capped nanoparticles	Small clusters of a few particles with average size of ~3-4nm

Table 7.1 Description of the three samples investigated in the following work, with an outline of the differences in general morphology

As described above, Zn_3N_2 is extremely prone to rapid oxidation and therefore several steps were taken during the sample preparation process to minimise the exposure to air. The nanoparticle suspensions in anhydrous toluene were stored in sealed vials under nitrogen in a glove box. Grids were prepared shortly before analysis by drop-casting a suitable dilution of the suspensions onto a holey carbon TEM grid within the nitrogen atmosphere of the glove box. The grids were then sealed in a nitrogen-containing jar which had previously been carefully cleaned and dried in order to transport to the microscope. The prepared nanoparticle grids were loaded into the sample holder in the microscope room within a glove bag which had first been evacuated and filled with N_2 several times, before placing the air-tight protective cap over the end of the sample holder to preserve the N_2 atmosphere around the sample after removing from the glove bag. It was only at the last moment, before putting the specimen holder into the microscope and starting to pump down, that

the air-tight protective capping tube was removed from the end of the specimen holder. Throughout the sample preparation process the exposure to air was therefore minimised to 1-2 seconds whilst removing the protective tube from the holder and inserting into the microscope plus the short additional time whilst the specimen exchange chamber was pumped down. The effect of this short exposure to air was investigated by a series of control experiments in which this length of time was varied before the composition was measured - the results of which are described in Section 7.10.3.

7.3 General Morphology

The prepared grids were firstly imaged using conventional diffraction contrast TEM indicating the samples had a range of morphologies. In particular sample 1 contained a variety of structures with large circular clusters composed of grains with average size of around 7-8nm, pictured in Fig. 7.1(a) with size analysis in (e), which appeared the most likely candidates for the Zn_3N_2 nanocrystals from initial EDX and diffraction studies, in addition to a range of nanorod and wire morphologies such as those of Fig. 7.1(b). The latter were mostly single crystal and careful indexing of the selected area diffraction patterns suggested they were mostly zinc amide, as shown in Fig. 7.1(b), although there was also some evidence for ZnO and metallic zinc present in the sample.

The uncapped smaller sample 2 nanoparticles similarly formed large agglomerates, pictured in Fig. 7.1(c), and the continuous polycrystalline diffraction rings indicate a smaller crystallite size than that of sample 1, with an estimated average of 4-5nm from HRTEM as shown in Fig. 7.1(f). This trend continued in sample 3, in which the capping agent likely controlled the size of the particle further to an estimated 3-4nm average giving extremely diffuse diffraction. DF TEM imaging showed much smaller agglomerates of just a few particles when appropriately diluted - and it was therefore more straightforward to measure the sizes, indicating that the capping helps to minimise agglomeration of the nanoparticles seen in the uncapped samples.

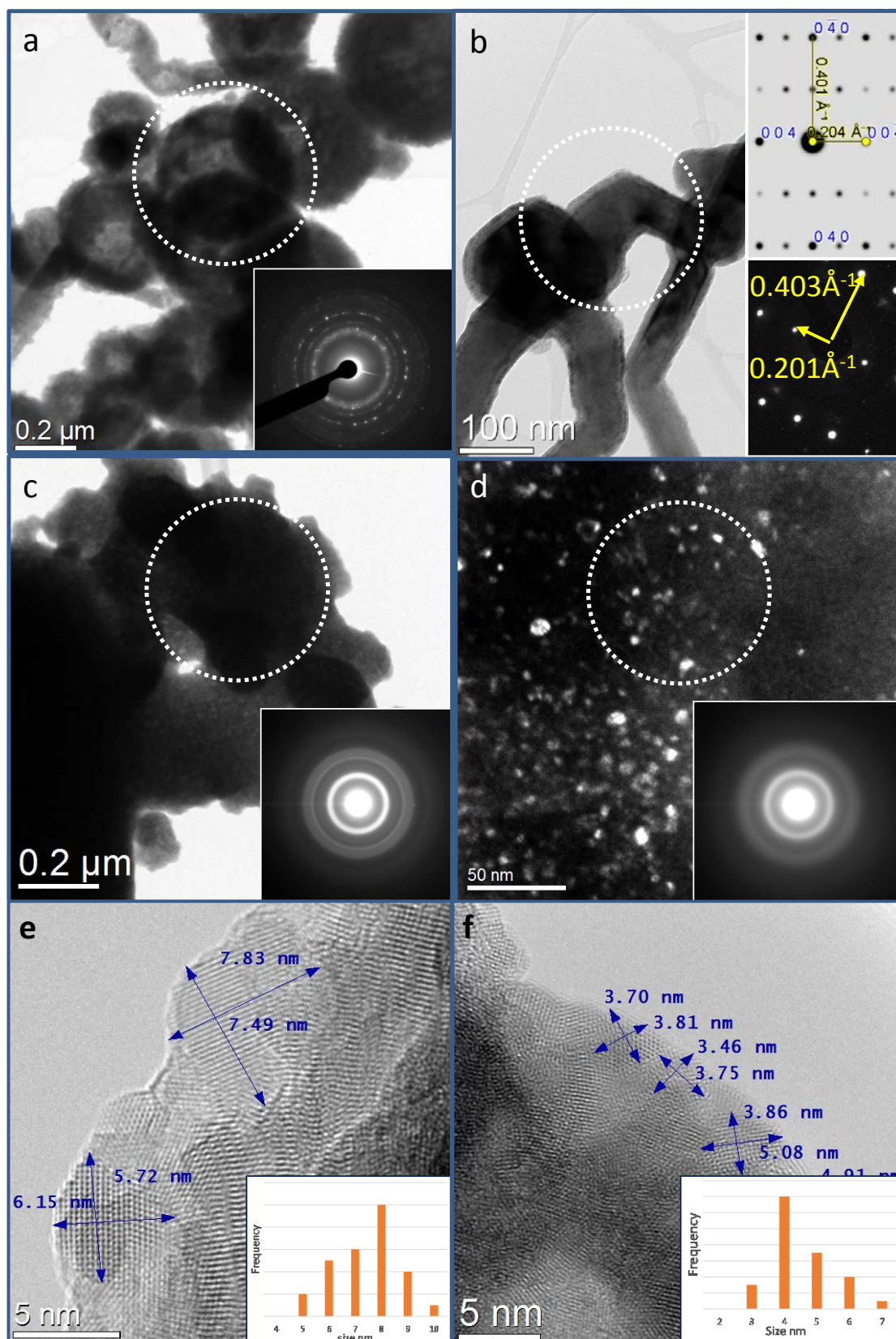


Figure 7.1 BF (a-c) and DF (d) TEM images illustrating the morphology of the samples with corresponding SAD patterns from areas indicated. Sample 1 had a varied morphology with: (a) the large uncapped nanoparticles clustering into large spherical objects and (b) single crystal $\text{Zn}(\text{NH}_2)_2$ rods and wires also present. The inset diffraction data was indexed as the $\{10\bar{1}0\}$ axis of zinc amide as shown. (c) Sample 2 small uncapped nanoparticles forming large agglomerates on the grid and (d) sample 3 small capped nanoparticles forming smaller agglomerates. (e) and (f) are HRTEM images of sample 1 and 2 respectively showing measurements of approximate grain size.

7.4 Composition

The materials were analysed via EDX spectroscopy in order to gain an understanding of the composition of the materials. The results appeared to vary across different regions of the sample which may be in part due to different materials being present but also the rapid onset of beam damage, which is analysed in more detail in Section 7.6. Despite these difficulties, typical quantification data is presented for samples 1 and 2 in Fig. 7.2 below with errors in the values of $\pm 5\%$ due to the reasons given above. Unfortunately the signal from the smallest capped nanoparticles was too weak and they damaged too quickly to be able to extract meaningful EDX analysis from this sample.

The standardless quantification calculation of Fig. 7.2(a) relating to sample 1 gives a ratio consistent with a majority of zinc nitride with a small ZnO component, whereas the larger zinc composition calculated for sample 2 in (b) is too large for it all to be bound in ZnO and Zn_3N_2 , perhaps suggesting a greater composition of metallic zinc. In addition there is likely to be a significant zinc signal contribution from the zinc amide component as identified in the diffraction analysis of the following section.

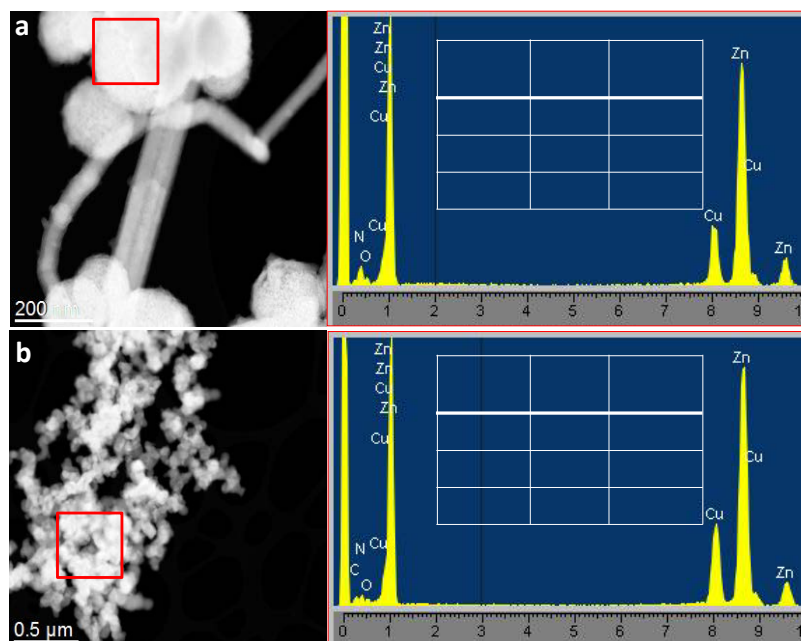


Figure 7.2 ADF STEM images with EDX spectra from the indicated regions of interest in (a) sample 1 and (b) sample 2 nanocrystals. Weight and atomic percentages were calculated using the quantification feature of the INCA software package. As described above, it was not possible to obtain a strong enough signal from the small capped nanoparticles to conduct this analysis.

The small capped particles of sample 3 were further investigated with EELS using a VG HB 501 STEM in an attempt to gain compositional information that was hampered by rapid beam damage and a weak signal in the EDX analysis. Typical data is provided in Fig. 7.3 below, collected from a large agglomerate of particles within the capping agent such as that pictured in (a) with the full spectrum given in (b), including the background subtracted edges inset, and the output of a quantification calculation on this data provided in the table in (c). As above there was significant variation in the precise values with similar magnitude of error however these results did indicate a majority of zinc, as seen in the EDX data of the other two samples, but with a greatly increased oxygen fraction observed which, although EELS is more sensitive to lighter elements, suggests an increased zinc oxide fraction in sample 3, a result reflected in the following diffraction work.

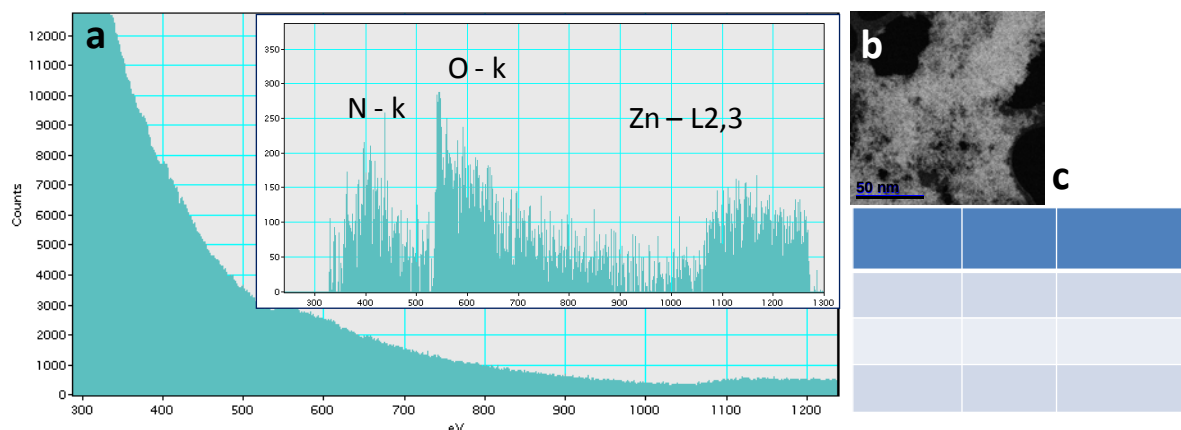


Figure 7.3 (a) EELS data from the a cluster of small capped nanoparticles in sample 3 with background-subtracted edges inset (b) an ADF STEM image indicating the ROI, (b) the EELS spectra and (c) a table indicating the results of a quantification calculation.

7.5 Integrated polycrystalline diffraction

Initially, the samples were analysed via selected area diffraction with the intention of identifying the presence of the zinc nitride *anti-bixbyite* crystal structure. Due to the random orientation of the small particles or crystal domains, selected area patterns generally produce polycrystalline ring patterns with the 'spottiness'/completeness of the rings linked to the crystallite size in the sample. These patterns were rotationally averaged following the method outlined in Section 3.3.2, which provides a number of advantages to the analysis. The initial motivation was that the data may be directly compared to X-ray diffraction data acquired at SLE from the samples in solution before they were analysed in the microscope, as discussed in Section 7.10.5. By using broad area diffraction the beam intensity incident on the sample may also be minimised to mitigate beam damage effects which were often observed when the beam was focussed onto a smaller area. Finally, this method allows for a strong visual, qualitative comparison to the spacings of various candidate materials as illustrated below.

7.5.1 Comparison to candidate materials

The latter point above was achieved via the extraction of structure factors and diffraction spacing information using the CrystalMaker SingleCrystal software which could then be plotted as markers on the experimental intensity line plots to aid in identifying the peaks. Possible candidate materials

in the samples, in addition to the intended Zn_3N_2 were identified from knowledge of the synthesis process and earlier diffraction work and include ZnO , metallic Zn and zinc amide ($\text{Zn}(\text{NH}_2)_2$). The hexagonal structures of the first two are well understood and were therefore straightforward to import into SingleCrystal in order to output the planar spacings and associated structure factors. The crystal structures of zinc nitride and zinc amide were built with CrystalMaker following the results of neutron diffraction work by D.E. Partin et al [309] and X-ray diffraction work of B. Fröhling et al respectively[310], before the simulated structure factors were calculated using SingleCrystal.

Fig. 7.4(a) below illustrates the comparison between rotationally integrated diffraction data from sample 1 material and markers indicating the major reflections from Zn_3N_2 , ZnO , Zn and $\text{Zn}(\text{NH}_2)_2$. The experimental data was collected in the form of selected area diffraction in (c) from the circular objects in (b).

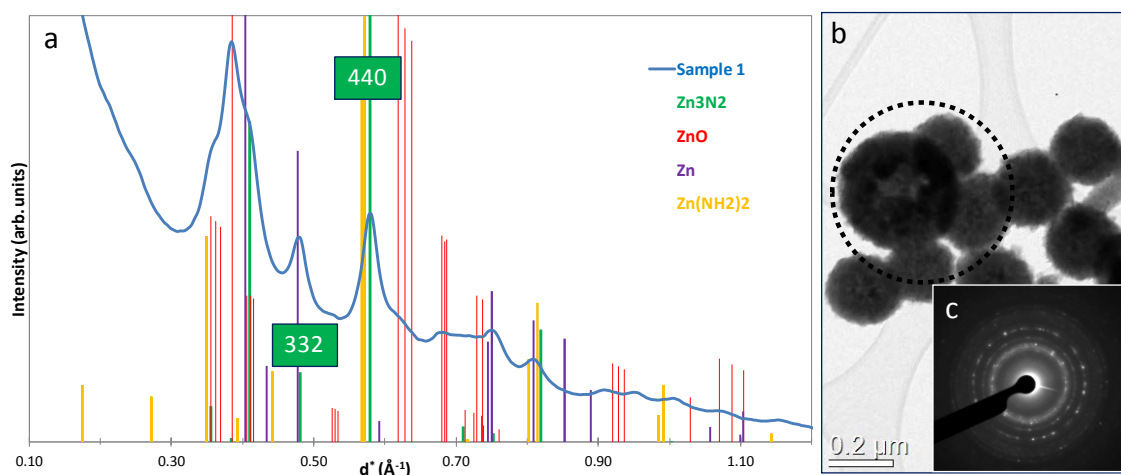


Figure 7.4 (a) An azimuthally averaged diffraction intensity plot with markers indicating the major reflections of Zn_3N_2 , ZnO , Zn and $\text{Zn}(\text{NH}_2)_2$ with the 332 and 440 reflections, which may be used to identify the presence of Zn_3N_2 . The plot was processed from diffraction data(c) from spherical clusters (b) in sample 1.

This technique therefore allows for a qualitative determination of the presence of Zn_3N_2 by comparison to the solid, green markers in Fig. 7.4(a) above. In particular, the appearance of the strong $332_{\text{Zn}_3\text{N}_2}$ (at $0.480 \text{ \AA}^{-1}$) and $440_{\text{Zn}_3\text{N}_2}$ ($0.579 \text{ \AA}^{-1}$) peaks (marked in the figure) was noted as a good indicator of the material being present. This judgement is hampered slightly by the nearby 101_{Zn} ($0.478 \text{ \AA}^{-1}$) and $408_{\text{Zn}(\text{NH}_2)_2}$ ($0.571 \text{ \AA}^{-1}$) peaks but the appearance of both Zn_3N_2 peaks with the

correct relative intensities in addition to the absence of expected peaks for the other noted materials meant that this technique could be used to determine the presence of Zn_3N_2 with a good degree of confidence.

Characteristic results for the three samples are displayed in Fig. 7.5 below with markers for the spacings of Zn_3N_2 with the heights proportional to the expected intensity per unit volume from those reflections, calculated as described in Section 3.3.2.

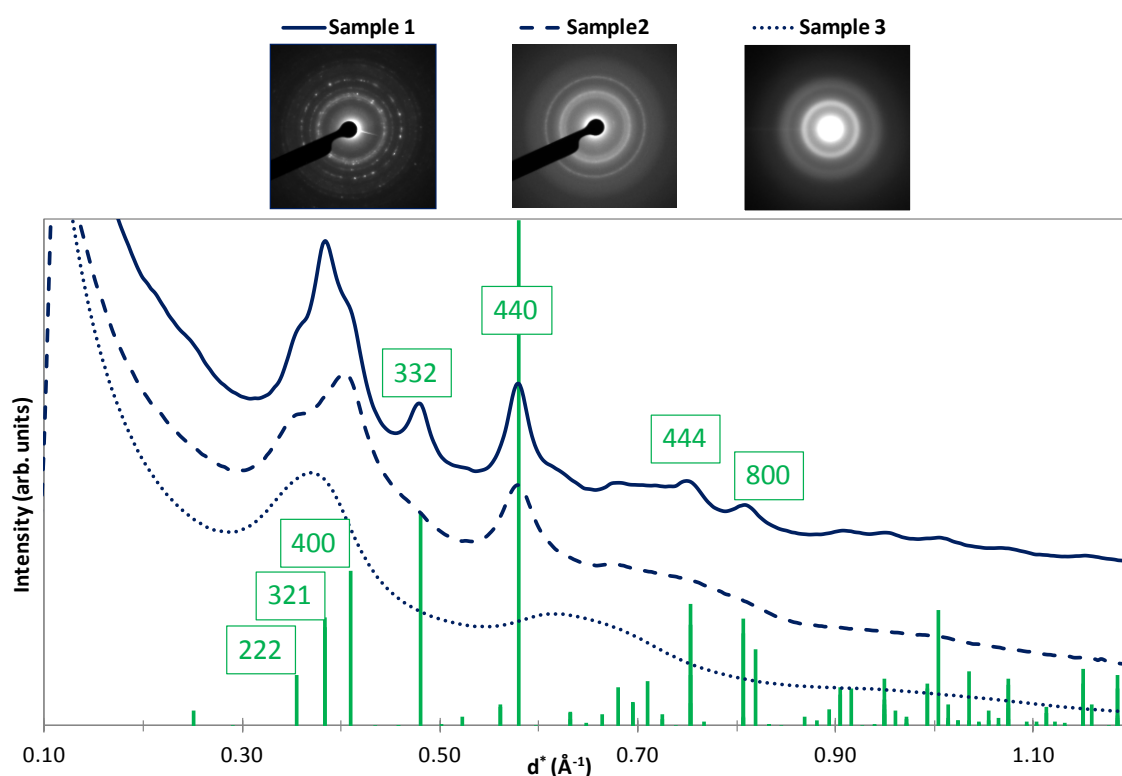


Figure 7.5 Azimuthally averaged diffraction profiles with samples 1, 2 and 3 shown with solid, dashed and dotted lines respectively with markers indicating the diffracting planes of Zn_3N_2 .

The results suggest, certainly for samples 1 and 2, the presence of Zn_3N_2 in the samples while the diffuse pattern observed from sample 3 is more ambiguous. There is a clear broadening of peaks with decreasing particle size as expected, although some peaks – in particular the 332 peak – appear to reduce in intensity more than others which hint at a reduced crystallinity or preferential orientation in the smaller particles, an idea that is discussed in Section 7.10.

7.5.2 Least squares fitting

In order to go beyond the qualitative comparison approach of the above analysis, a linear least squares fitting script was developed in Matlab in order to find the ratios of possible candidate materials that most closely matched the experimental data. The script first produced a simulated azimuthally integrated diffraction pattern for each of the candidate materials defined above, following the procedure outlined in Section 3.3.2, then performed a least squares fit between the experimental data and a linear combination of these components to give the ratio of the materials that gave the closest fit. The script could also vary the Gaussian width, σ , independently for each material to find the best fit, allowing for material-dependent broadening of the diffraction peaks relating to differing particle sizes. The attenuation of the diffraction intensity with increasing scattering angle was accounted for by including Debye-Waller factors where possible[309]–[312], but it was found that a much improved fit could be achieved by including an additional, increased damping factor. In order to perform the fit, the background had to first be subtracted from the experimental intensity. Various background models were implemented but it was found that a power law form allowed for the best empirical fit.

Fig. 7.6(a) below illustrates the process of combining Gaussians at the appropriate reciprocal lattice spacings and also the effect of changing σ – the latter by the difference between the red and blue curves. Graphs (b) and (c) show the background-subtracted experimental intensity in dashed red against the least squares fit in blue for samples 1 and 2 respectively. The inset table indicates the composition and the individual Gaussian width, sigma, of each component materials required to give this best fit. The errors in the composition figures are estimated to be fairly large at approximately $\pm 7\%$, judged from repeats runs of the code with slightly differing input data and parameters. The reasons for which will be discussed in more detail in Section 7.10.2.

Both sample 1 and 2 indicate a significant Zn_3N_2 component in the broad area diffraction patterns before any influence of beam damage but also a considerable amount of zinc oxide and zinc amide.

As suggested from the qualitative comparison of Fig. 7.5 above, the fitting implies a greater component of Zn_3N_2 in the larger sample 1 nanoparticle samples compared with sample 2 and the sigma values confirm the difference in particles size, the narrower peaks of the Zn_3N_2 component in sample 1 being indicative of larger particles. In each case the zinc amide component has a sigma value very close to that of the nitride component, suggesting particles of similar size, whereas the zinc and zinc oxide diffraction components are extremely broad, the reasons for which are discussed in Section 7.10, along with issues and drawbacks to the analysis.

The graphs of Fig. 7.6 (d) and (e) show the data from the same area of each sample after extended exposure to the electron beam and therefore the possible change in composition brought about by this interaction and will be referred to in the analysis of the beam damage in the following section.

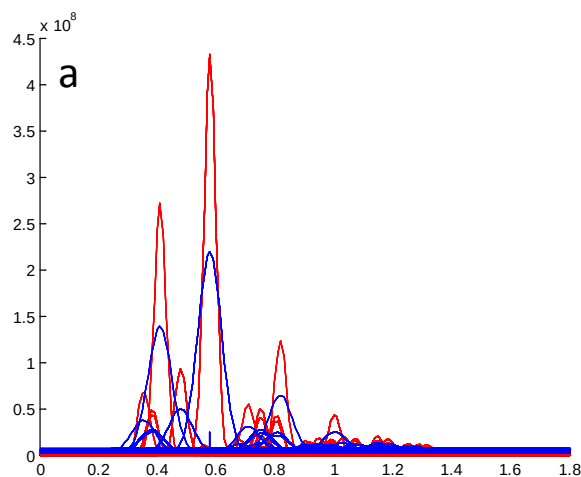
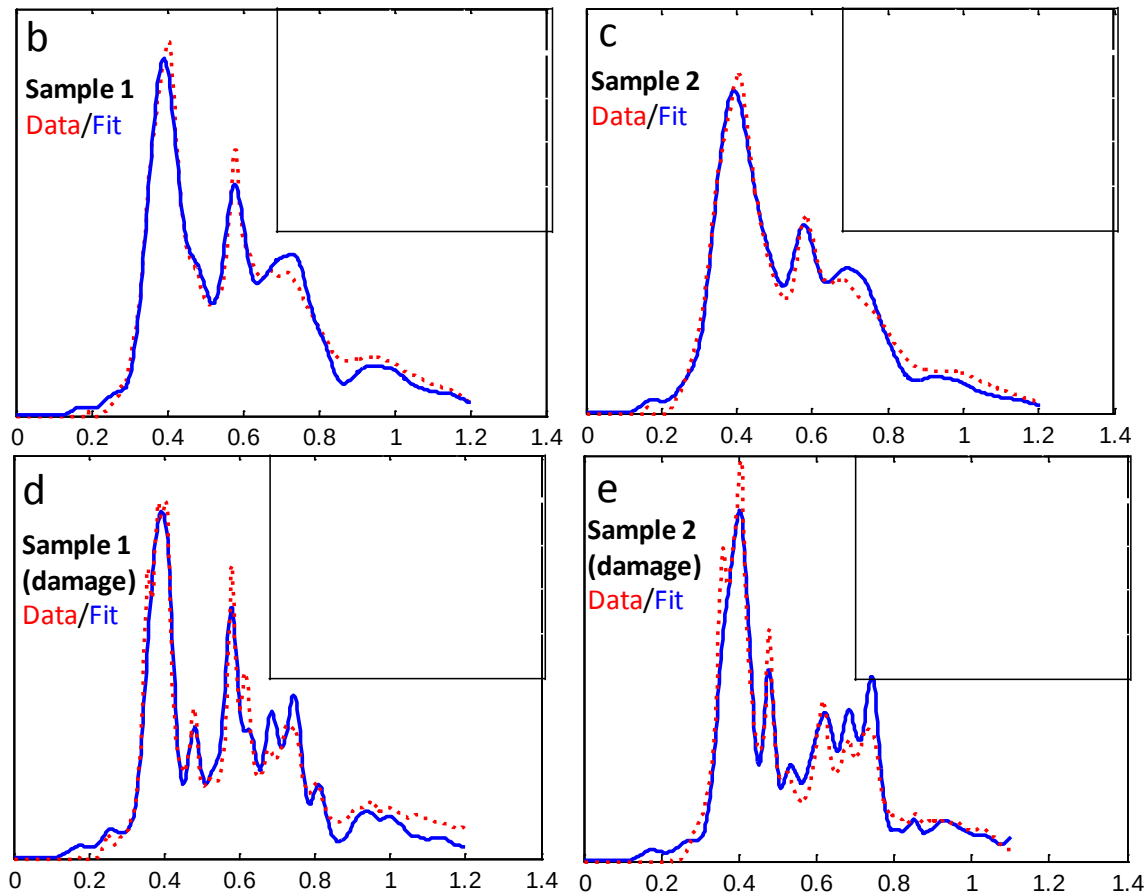


Figure 7.6 Least squares fitting to experimental diffraction data. (a) Illustration of the summation of Gaussians method with the difference between the red and blue curves due to changing the value of sigma. (b-c) Sample 1 and 2 experimental (red) and fitted diffraction data respectively, with inset composition and sigma details relating to the fit. (c-d) Experimental and fitted data from the same regions after extended exposure to the electron beam. All horizontal axis units are $\text{\AA}^{-1}$



7.6 Change under the electron beam

As touched upon above, it was noted early on that there was an observable change in morphology of all of the samples studied under the electron beam, the rate of which increased if the beam was focussed on a smaller area. The smooth, uniform contrast observed on the sample 2 small uncapped nanoparticle clusters in Fig. 7.7(a) breaks up into the patchy contrast observed in (b) after extended

beam exposure. The polycrystalline SAD patterns also show a change from smooth continuous rings into spotty broken rings indicative of a coalescing and growing of crystal grains under the beam. In order to understand this process more thoroughly, image, EDX and diffraction data was collected before and after, intentionally exposing a region to the focussed beam for varying amounts of time.

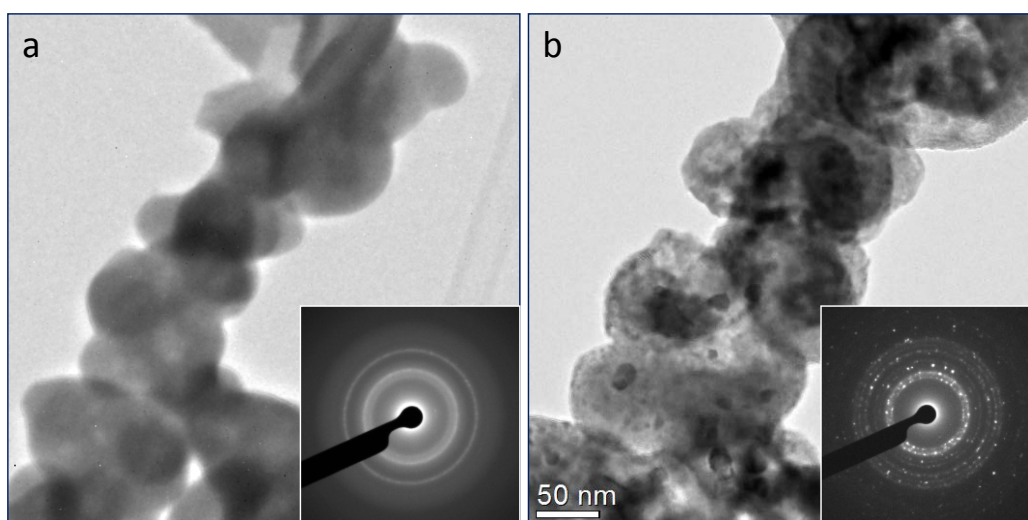


Figure 7.7 The effect of electron beam exposure on sample 2 material. The initially uniform smooth contrast before any extended beam exposure (a) becomes mottled with larger grains forming after the electron beam has been focussed down onto this region (b).

Typical STEM images, EDX spectra and processed diffraction data from the same regions of sample 1 nanoparticle clusters are shown in Fig. 7.8. Similar changes in the diffraction data to those of sample 2 were observed, again suggesting that the, initially relatively small, grains coalesce and crystallise under the beam to form extended crystallites. The extracts from EDX spectra taken from the region of interest show an apparent decrease in nitrogen signal in these regions and increase in the oxygen signal. The heavily reducing environment of the electron beam is unlikely to promote oxidation of the metallic zinc in the material suggesting that the influence of the beam is to encourage ripening and growth of existing zinc oxide crystallites. However, the azimuthally averaged diffraction data shows that, in addition to ZnO peaks the Zn_3N_2 peaks also become more pronounced suggesting the growth of larger Zn_3N_2 grains under the beam in addition to ZnO.

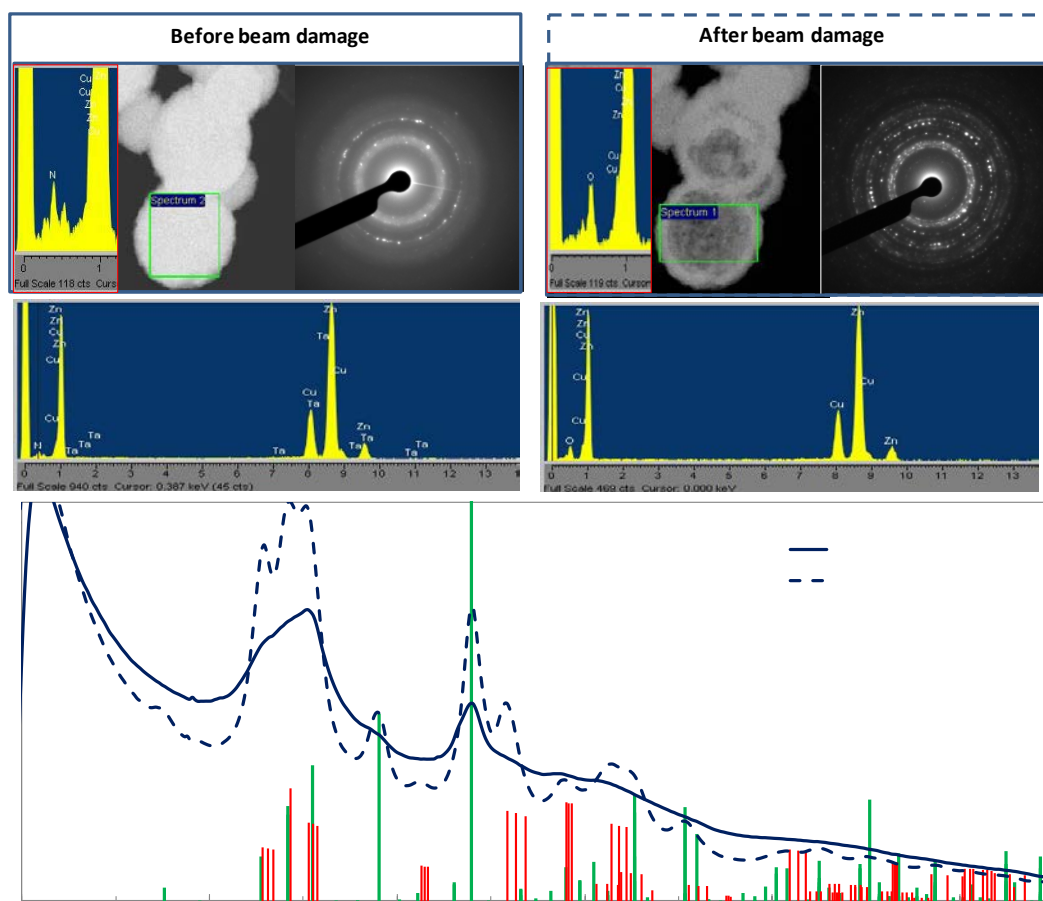


Figure 7.8 EDX, STEM and diffraction data, before and after extended electron beam illumination of a sample 1 nanoparticle cluster. The apparent effect of the beam is to cause ripening of the Zn_3N_2 nanocrystals with additional growth of ZnO which is evidence by the increase in the oxygen EDX signal and the appearance of peaks in the diffracted intensity at scattering angles relating to the planar spacings of ZnO – marked with red lines.

The quantitative diffraction analysis of samples 1 and 2 before and after beam damage presented in Fig. 7.6(d) and (e) reveals a slightly differing process of change under the beam between the two samples. Sample 1 suggests a growth of both Zn_3N_2 and ZnO grains under the beam, supporting the data presented in Fig. 7.8, with the peak widths, σ , decreasing significantly. In contrast to the EDX data, the outcome of the fitting procedure suggests the composition of the nanoparticle clusters remains fairly constant, with a slight increase in Zn_3N_2 . The effect of the beam on the smaller sample 2 however, appears to be consistent with its EDX data, which followed the trend of sample 1 above, showing a process of growth and ripening of ZnO crystals and a decomposition of the Zn_3N_2 component. In both samples the metallic zinc and zinc amide fractions appear to be fairly constant

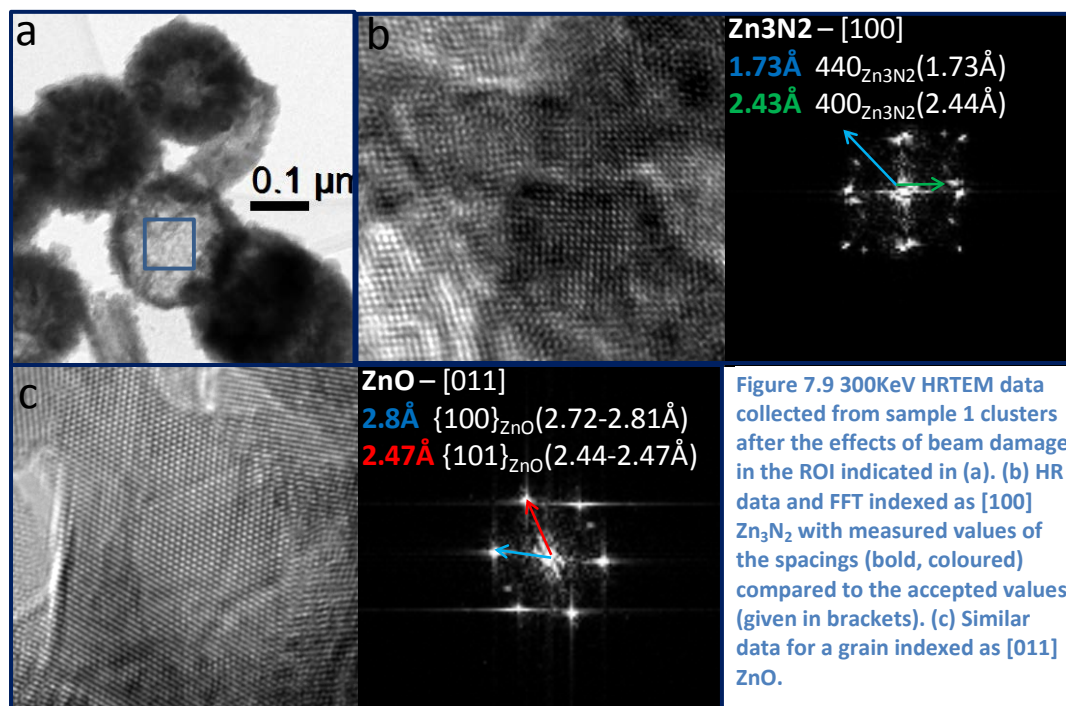
with the sigma values for the latter also not changing, suggesting the size of these particles remains the same. The mechanism behind these changes is likely to be knock-on effects, due to an increasing rate of change with acceleration voltage, and is discussed with reference to the discrepancy between EDX and diffraction data for sample 1, in Section 7.10.6.

7.7 HRTEM

7.7.1 300 kV data

In an effort to support the evidence in the diffraction data, HRTEM images were obtained in order to unequivocally confirm the presence of Zn_3N_2 in the samples. In practice however, the acquisition of this data (collected with a JEOL 3000F) was severely obstructed by the rapid changes in the material under the focussed beam necessary to obtain the required image intensity for HRTEM imaging. In addition, the agglomerated nature of the samples meant that it was difficult to find lone particles to image but rather it was necessary to image many overlapping crystallites simultaneously which reduced the image quality and hampered interpretation. It was found that if, to overcome the latter issue, the protruding grains at the side of clusters were imaged, they were found to be predominantly ZnO , likely due to these exposed areas more rapidly oxidising.

Despite these difficulties, evidence for the cubic Zn_3N_2 structure was identified, with typical data shown in Fig. 7.9 below. Most success was found through imaging the centre of the clusters, which would eventually stabilise after several minutes of beam exposure and large grains of Zn_3N_2 and ZnO were observed, in agreement with the quantitative diffraction results above.



Having observed some evidence for a slightly slower rate of change under a 200kV beam to that of 300kV, further high resolution imaging was carried out with the JEOL 2200MCO at 80kV in order to study the process further and with the hope of obtaining data before the onset of the beam-induced change.

7.7.2 80 kV data

Moving to lower voltages did indeed appear to allow for observation of a reduced rate of change under the beam at high resolution. Since this process of change under the beam can be observed clearly at 80kV, in collecting data after only a brief exposure to the beam, the structures observed may be assumed to be the original structures with some confidence. Examples of such images, taken immediately before the onset of change in the material, are shown in Fig. 7.10 below, in which every effort was made to increase the dispersion on the grid via sonication and to locate lone particles to facilitate HR imaging. Fig. 7.10 (a-c) are various 80keV HRTEM images of sample 2 particles which showed significant variation in their structures. A number of larger particles were identified that appeared to have unusual single crystal structures such as that of (a), which could not be readily

identified as any clear zone axis of the candidate materials. Although often some spacings within these particles appeared to match Zn_3N_2 the associated symmetries did not, perhaps suggesting either an unknown contaminant or an alternative zinc nitride phase to that of the usual anti-bixbyite structure. However, a small number of small grains, such as those in (b), were indexed as the expected Zn_3N_2 structure as shown. Other areas appeared to be mostly amorphous, such as that pictured in Fig. 7.10(c), which sometimes had small regions with crystalline fringes present which may be identified in the figure from the associated spots in the FT.

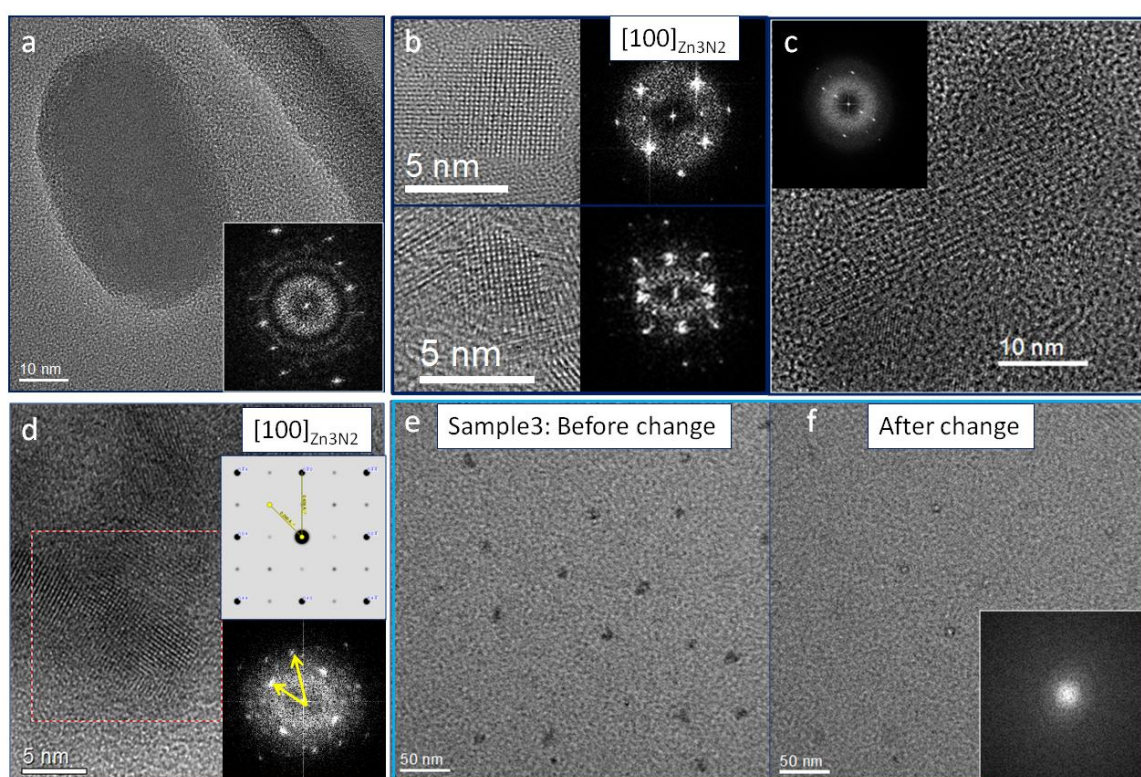


Figure 7.10 80keV TEM images of the zinc nitride nanocrystals before any change under the beam. (a-c) Images of uncapped small sample 2 nanoparticles showing a varying degree of crystallinity. (d) HR image from a [100] orientated grain on the edge of a cluster. (e-f) Sample 3 particles before and after change under the beam indicating that the particles are amorphous before and after the change.

This difficulty in finding and indexing nitride grains before change under the beam may be somewhat expected if the Zn_3N_2 composition is as low as 18% in sample 2 as suggested by the diffraction fitting work. Indeed, Zn_3N_2 grains were more easily identified in the larger uncapped sample 1 material (see Fig. 7.10(d)) but the small capped sample 3 particles appeared completely amorphous before and

after exposure to the beam, as is clear from (e) and (f) respectively. In this case, with the particles well dispersed on the grid, the effect of the beam damage was not to cause further crystallisation but rather the small particles seemed to lose mass and contrast and remain amorphous, with no discernible change in the FFT as discussed in Section 1.10.6.

In summary, this high resolution data on the nanoparticles before the effect of the beam, appears to agree with the diffraction work, that there is a decrease in crystallinity with size through samples 1-3, with the smallest sample 3 particles appearing completely amorphous whereas sample 1 contain clear crystal grains. Although the limited sampling of HRTEM must be noted, Sample 2 appears to be an intermediary stage, with single crystal particles identified but also amorphous material surrounding partially crystalline areas.

In order to study the range of order, or the lack thereof, in the materials, further analysis of the diffraction data was carried out by employing radial distribution function analysis.

7.8 Radial distribution function

As described in detail in the description of experimental techniques in Chapter 3, this approach allows the experimental diffraction data to be converted to the reduced density function $G(r)$, the maxima of which relate to the most probable distances between atoms in the sample. These distances may be related to specific bonds between atom types using knowledge of the relevant crystal structures likely to be present. Importantly to this application, the experimental $G(r)$ calculated from the diffracted intensity data may be compared to model crystallites, the size of which may be varied - to give an idea of the range of crystalline order within the sample.

$G(r)$ from broad area diffraction data collected from sample 1 is plotted against that of a model $2 \times 2 \times 2$ supercell of Zn_3N_2 with a volume of about 8nm^3 in Fig. 7.11(a) below. This comparison indicates that all of the inter-atomic distances associated with the Zn_3N_2 structure are present and the maxima continue out to $20\text{\AA}$ suggesting long range order indicative of crystal grains of at least

comparable size to the model. The lesser intensity of the maxima compared to that of the model is almost certainly due to the fact the thickness of the clusters studied leads to significant multiple scattering – not accounted for by the Debye scattering equation which assumes purely kinematic scattering from a thin film. Large specimen thickness and the corresponding breakdown of this approximation can lead to suppressed maxima in the calculated $G(r)$. Another factor is the assumption of the model $G(r)$ calculation of a thin film consisting of random orientations of particles purely of the size specified, $8\text{nm}^3 \text{Zn}_3\text{N}_2$ grains in the case of Fig. 7.11(a). The fact that in reality there is likely to be a distribution of particle sizes would change the relative heights of peaks at different atomic distances, r , so taking this into account in the model would likely give a better fit to the experimental $G(r)$.

This level of agreement with the distribution of atomic distances in Zn_3N_2 is clearly not seen in the small uncapped sample 2 in Fig. 7.11(b) in which some of the maxima are significantly reduced or missing and there appear to be some peaks, such as those around 3.7 and $5.8\text{\AA}$, which appear to more closely fit those of ZnO . A second notable feature is the reduced range of order with the maxima no longer identifiable after $7\text{--}8\text{\AA}$ which is in clear contrast to the $G(r)$ for models of Zn_3N_2 and ZnO with crystal sizes of around 1nm^3 in which the maxima persist over a much longer range. This lack of long range order is still more apparent in the smallest capped particles and is clearly observed in the comparison of the experimental $G(f)$ compared to those of the $\sim 1\text{nm}$ model crystals, given in Fig. 7.11(c). There is only one clear peak at $3\text{--}3.5\text{\AA}$ corresponding to N-N and Zn-Zn distances in Zn_3N_2 structure; and O-O, Zn-Zn in ZnO , after which this oscillations rapidly decrease to the noise level around the average density of the material.

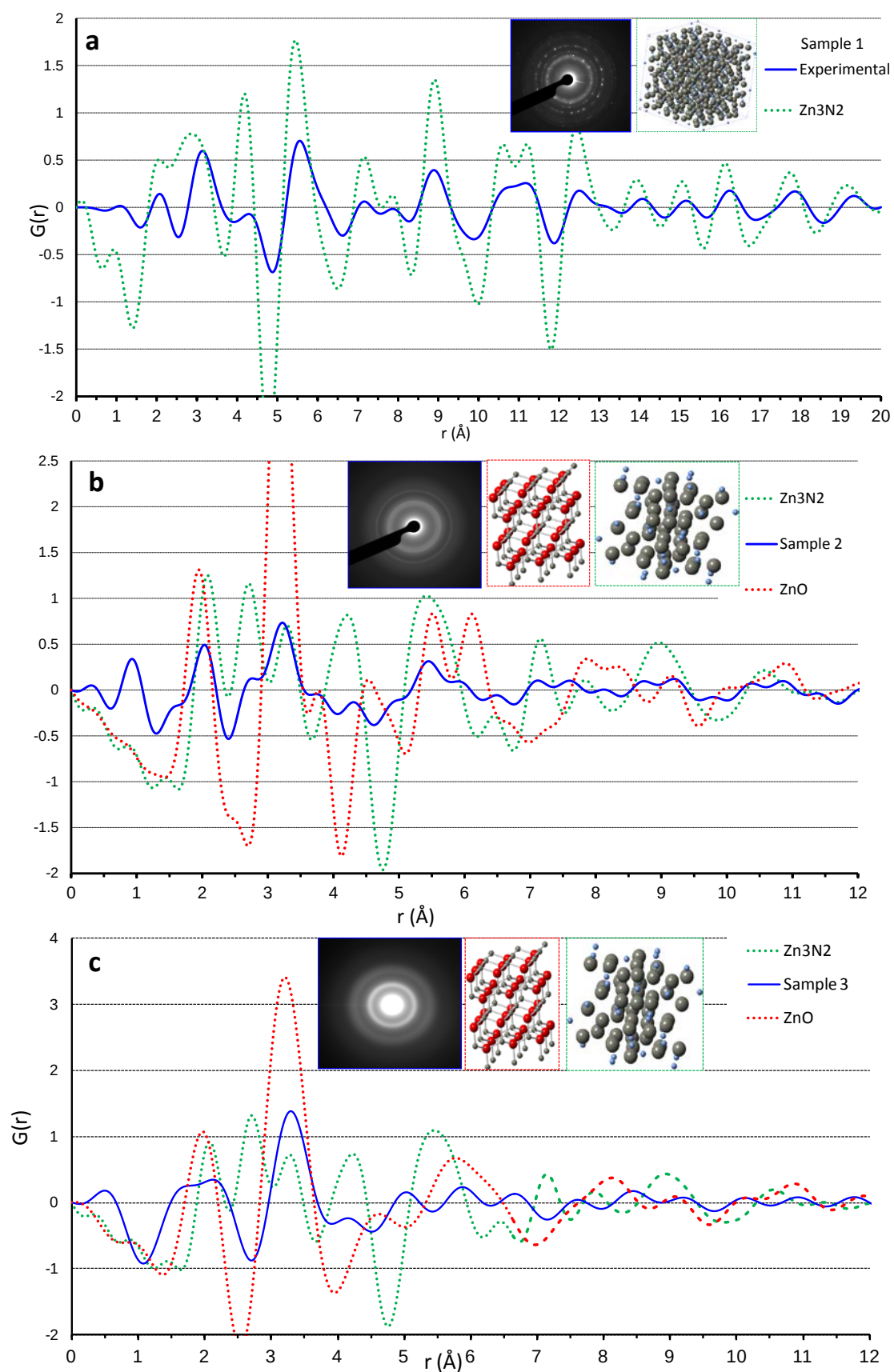


Figure 7.11 $G(r)$ calculated from diffraction data (a) obtained on sample 1 compared to model $2 \times 2 \times 2$ nm Zn_3N_2 supercell (b) sample 2 and (c) sample 3 compared to those calculated for a $\sim 1 \text{ nm}^3$ crystal of ZnO and one unit cell (9.7^3 Å^3) of Zn_3N_2 .

7.9 Optical Properties

As stated in the introduction, zinc nitride is believed to have a bulk band gap of around of 1.17eV[209] and therefore emits in the infrared region of the spectrum so that the largest particles appear black, as seen in the right hand vial in image (a) in Fig. 7.12 below. By controlling the size of the nanoparticles the emission wavelength may be tuned to the visible red/orange range, which is identifiable in the left hand vial in the photograph in the figure below and quantified by the PL data recorded at SLE in (b) and (c) which gave peak emission wavelengths of 660nm and 658nm (~ 1.88 eV) for the small uncapped and small capped particles respectively.

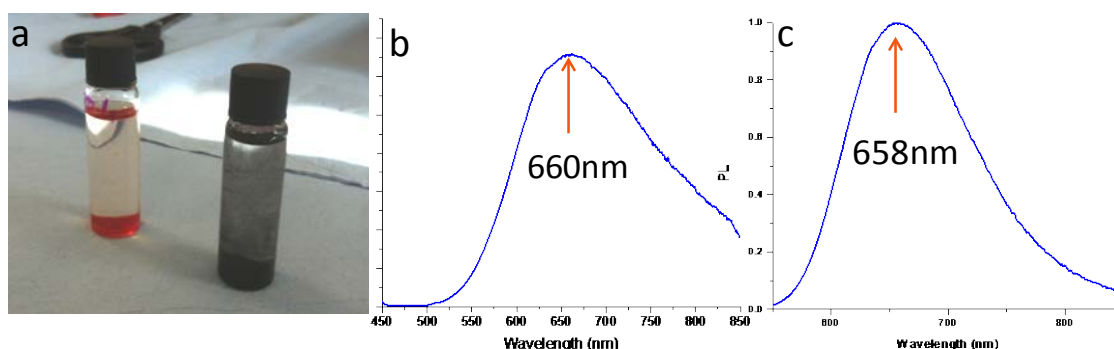


Figure 7.12 The optical properties of the Zn_3N_2 nanoparticles varied with their size as expected. (a) A photograph of the small uncapped and large uncapped particles in solution shows the difference in colour (the material has settled to the bottom of the vials). (b) and (c) Show the photoluminescence spectra of the small capped and small uncapped particles respectively.

7.10 Discussion

A diverse range of characterisation techniques have been utilised with the primary aim of confirming that Zn_3N_2 nanoparticles have been successfully synthesised. The following consideration of these combined results will show that this has been achieved but it will also analyse the secondary questions of: (1) what is the proportion of Zn_3N_2 present in the sample; (2) the difference between the samples in composition and crystallinity; (3) the nature of the rapid beam damage observed in the various samples; (4) the relation of these results to the optical properties.

7.10.1 Confirmation of the presence of Zn_3N_2

The peaks in the azimuthally averaged diffraction intensity of the sample 1 data, closely match the spacings of Zn_3N_2 and when considered along with the EDX spectra of Fig. 7.2 (a) which contains strong zinc and nitrogen signals in approximately the correct ratio, it can be stated with confidence that the circular objects observed in Fig. 7.1(a) are clusters of nanoparticles or extended polycrystalline structures containing Zn_3N_2 . The possibility of isolating individual particles via the addition of the capping agent suggests the structures are agglomerates of individual nanoparticles.

High resolution imaging, although challenging due to rapid change under the electron beam, revealed structures closely matching the spacings of the Zn_3N_2 anti-bixbyite both after exposure (see Fig.s 7.9(b)) and evidence at 80keV before any significant effect (Fig. 7.10(b, d)) strongly supporting the conclusions from the diffraction and EDX data. Finally, the RDF work, comparing the reduced density function calculated from experimental data to that from model crystallites of Zn_3N_2 in Fig. 7.11(a), shows a good match in the long range order and assists in confirming the successful synthesis of Zn_3N_2 nanoparticles.

This analysis primarily refers to the strongest evidence relating to data from sample 1 and leads to the second question of the differences between the samples.

7.10.2 Composition of samples 1 and 2: least squares fitting

The qualitative impression of the trend in Fig. 7.5 is of a decreasing proportion of Zn_3N_2 present through samples 1-3, with the increasing diffuseness of the patterns and broadness of the peaks likely relating to a decreasing crystallite size, to the extent of suggesting an amorphous structure in sample 3. The issue of composition will be tackled first followed by a discussion of a possible lack of crystallinity in the smaller sized particle samples.

The least squares fitting script in Matlab was developed in order to explore this question of composition more quantitatively and was applied to samples 1 and 2 – the sample 3 data believed to

be too diffuse, lacking the clear crystalline peaks to give any meaningful results. The results of this analysis, suggesting compositions of 31% and 18% in samples 1 and 2 before beam damage, agreed with the quantitative view of Fig 7.5 although it was somewhat surprising that this analysis gave such large components of ZnO and $\text{Zn}(\text{NH}_2)_2$ present in addition to the Zn_3N_2 .

Although it seems clear that this technique confirms a significantly reduced Zn_3N_2 fraction in sample 2 compared to sample 1, there remain a number of uncertainties in the interpretation of this analysis. One of the major difficulties was appropriate background subtraction with an empirical power law form used (as illustrated by the red line in the figure below) giving only a rough fit which likely left a remaining additional broad peak of intensity, not related to the diffraction peaks as roughly approximated by the shaded region in Fig. 7.13(a). This deviation from a power law fit may be attributed to plasmon and multiple scattering which is not accounted for by the fitting used. It may be possible that the fitting script accounts for this by the addition of the very broad zinc and ZnO components, particularly when it is noted that, while the sigma values for the nitride and amide components are roughly equal in each of the sample 1 and 2 fits, the zinc and oxide sigma values are much broader. The separated smaller sigma components, Zn_3N_2 and $\text{Zn}(\text{NH}_2)_2$ are given in Fig. 7.13(b) with the broader zinc and ZnO components in (c), illustrating how the former correspond to the main peaks observed in the diffraction data.

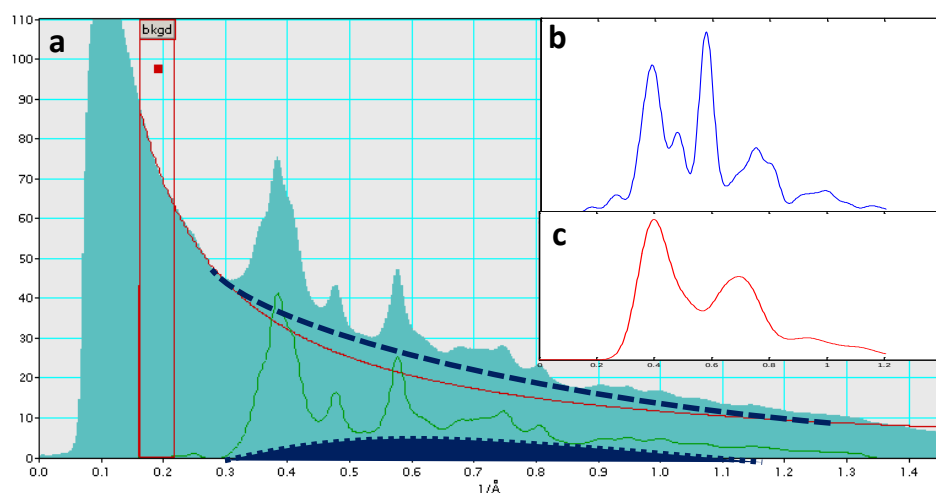


Figure 7.13 (a) An illustration of the empirical background fitting using a power law which leaves a residual band of intensity which may be accounted for by the addition of broad components in the best fit. (b) The smaller sigma nitride

and amide components of the fit and (c) the broader zinc and ZnO components – the latter perhaps amplified in the fitting to account for the inaccurate empirical background fitting.

Another issue, of particular relevance to sample 2 and discussed in more detail in the following subsection, is the possibility of the presence of amorphous material in the sample reducing the quality of the fit to the crystalline components used. This would likely lead to the addition of broad components, like that of Fig. 7.13(c), as a rough approximation to the scattering from amorphous regions of the sample.

Finally, another source of difficulty was the need to employ increased damping factors to bring the simulated diffraction intensity at higher angles down to that of the experimental intensity.

CrystalMaker allows atomic displacement parameters/Debye Waller factors to be entered when building the crystals before simulating diffraction data. Where possible values from the literature were used with: a room temperature Debye-Waller factor for zinc of $1.14\text{\AA}^2$ [312] used; temperature factor of $0.7\text{\AA}^2$ for ZnO at room temperature [311]; $1\text{--}3\text{\AA}^2$ for $\text{Zn}(\text{NH}_2)_2$; and $\sim 0.3\text{\AA}^2$, converted from the atomic displacement parameters of Zn_3N_2 [309]. Although the accuracy of these values is not certain, the fits actually required a much greater damping factor of around $B = 4\text{\AA}^2$ to give the best fit to the data which may be related to the thickness of the nanoparticle clusters.

These factors lead to a degree of uncertainty in interpreting the compositions output from the fitting program however, despite these problems, it seems reasonable to conclude that this analysis confirms a greater degree of zinc nitride present in sample 1 than sample 2 and also the presence of significant impurities in the form of ZnO and zinc amide. The extremely weak diffraction data from sample 3 appeared to not provide consistent results using this method; with the output varying significantly depending on the parameters used and is therefore considered separately below.

7.10.3 Composition and crystallinity of sample 3

There appear to be two major differences between sample 3 and the other two samples, namely the extreme broadness of the peaks and the fact that these broad peaks appear to more closely match

that of ZnO rather than Zn_3N_2 which is evidenced from a comparison with the expected spacings in Fig. 7.14 below. It is therefore important to consider whether there is sufficient evidence to confirm the likely presence of the nitride in this sample.

Considering first the closer match to ZnO, it might be proposed that the smaller size of these particles makes them more vulnerable to oxidation effects when exposed to air during transfer to the microscope.

In a study carried out on sample 2 uncapped particles, data was collected from the sample on a TEM grid prepared under nitrogen, taking the precautions to minimise air exposure as detailed in Section 7.2, and then compared to similar diffraction data after the grid had been removed from the microscope and reinserted after exposure to air for 5-10 minutes. A similar experiment was then also carried out with a prepared grid that had been exposed to air for a day. Although in the latter case the material had completely oxidised, in the case of the 10 minute exposure, no notable differences could be observed in the diffraction data. This lead to the conclusion that, the short exposure to air of a few seconds during the careful transfer procedure using the glove bag, was insignificant, particularly in comparison to the effect of change under the electron beam. However it could be argued that the further reduced size of the sample 3 particles renders them sensitive enough for this short exposure to be relevant.

Although there certainly appears to be a higher ZnO fraction in the sample 3 nanoparticles, the EELS data shown in figure 7.3 clearly shows a significant nitrogen peak present, with composition ratios consistent with the presence of the nitride in the sample. It may be that the extreme broadness of the diffraction peaks due to the limited crystallinity of the sample, shown below in figure 7.14, means the nitride component is more difficult to identify. Evidence of preferential growth of existing ZnO material and decomposition of the Zn_3N_2 was observed in sample 2 and it may be that this explains the diffraction peaks more closely matching ZnO after beam exposure.

Indeed, XRD data from similar small capped particles, given in Fig.7.15(a), shows peaks which match the spacings for the 400 and 440 reflections in Zn_3N_2 suggesting that the nitride is present in the material in solution before transfer to the microscope.

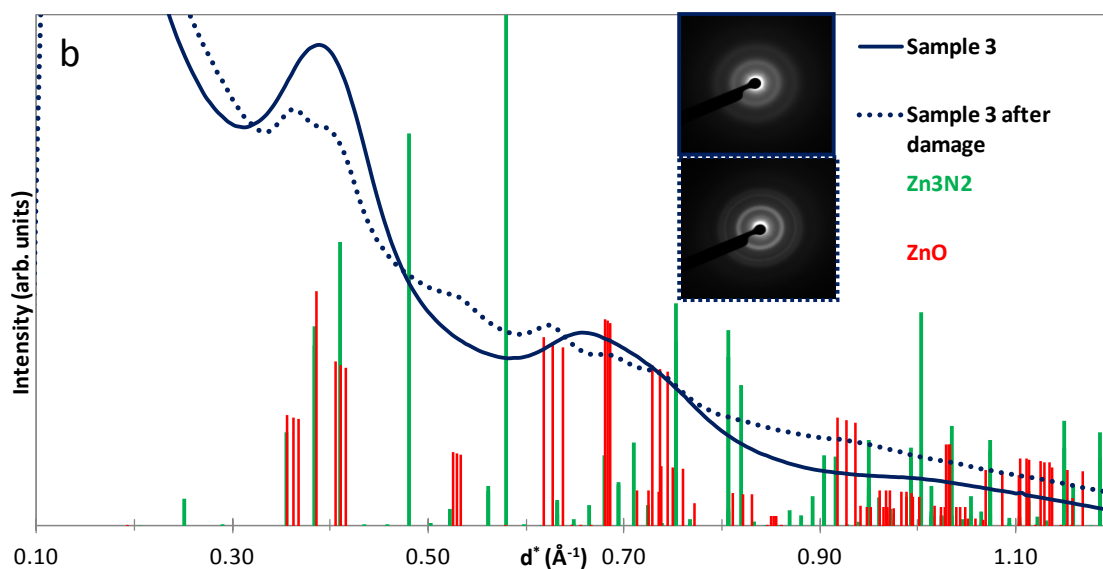


Figure 7.14 Electron diffraction data from sample 3, before and after extended beam exposure with broad peaks more closely matching those of ZnO .

Therefore considering the EELS, electron and X-ray diffraction together, the data is certainly consistent with a zinc nitride component present in the smallest nanoparticle sample.

Considering now the diffuse electron diffraction observed, one question of interest is whether this is accountable by Scherrer broadening from smaller sized crystalline particles or whether such a pattern is indicative of a greater lack of longer range order representative of an amorphous phase. Although the idea of crystalline order is really a continuum with the definition of the transition between amorphous and crystalline is not particularly clear, particularly at the nanoscale when surface relaxation results in a distortion of atomic positions - the complete lack of crystalline fringes observed in sample 3 particles in 80keV HRTEM, suggested that this sample was – at the point of observation in the microscope - certainly amorphous.

RDF analysis was therefore employed with the aim of exploring this potential lack of crystalline order in sample 3 and also to compare to that of the other two samples.

7.10.4 Range of crystalline order within samples

The lack of long range order is demonstrated by comparison of the experimental $G(r)$ of sample 3 in Fig. 7.11(c) with those of model Zn_3N_2 and ZnO films, only having grain dimensions of ~ 1 nm. The maxima (relating to inter atomic distances) expected for such crystals clearly are not present in the experimental data which only has 2 clear maxima in rough agreement with the models before oscillating around the average, likely being just noise. Although there is a trend in this RDF work in which the magnitude of the experimental peaks is much less than that of the models, it would be difficult to argue that this accounts for this discrepancy in sample 3 since these maxima are completely displaced from those of the models. This is particularly illustrated by a comparison with sample 1 in which the trend of the reduced intensity in the experimental data is observed but the maxima closely follow those of the model out to large distances suggesting that this sample is highly crystalline. Based on this microscopy characterisation work (the comparison to earlier XRD will be discussed below) these results together clearly point to an amorphous phase predominating in sample 3 and a highly crystalline phase predominating in sample 1.

There is evidence in the data to suggest that the sample 2 may consist of an intermediate stage between these two with the diffraction data of Fig. 7.5 indicating a significant broadening and reduction in intensity of certain peaks, suggesting a reduced crystalline component. There is of course some difficulty in separating this effect as distinct from a broadening of peaks associated with decreasing crystalline particle size but the RDF work of Fig. 7.11(b) shows a $G(r)$ with peaks matching those of Zn_3N_2 (with a possible ZnO component) over a short range but falling away after $\sim 7\text{\AA}$, less than the size of the Zn_3N_2 unit cell. The 80KeV data was more difficult to interpret with a range of particle types observed but, accepting the limited statistics, these observations could certainly be

consistent with the picture of a limited crystalline fraction as suggested by the broad area diffraction and RDF techniques.

7.10.5 Sample crystallinity with reference to XRD data

Having identified a possible trend of decreasing crystallinity with particle size in diffraction, RDF and HRTEM data, this may also be compared to the XRD data collected at SLE, see Fig. 7.15 below. The data for samples 1 and 2 is in very good agreement with the azimuthally averaged electron diffraction data of Fig. 7.5, with all of the main peaks present in sample 1 whereas 400, 440 and 222 are the only significant peaks in the much broader sample 2 data. However there is a discrepancy with the sample 3 data in which the two broad peaks of weak intensity are centred on the 400 and 440 Zn_3N_2 peaks rather than closer to the ZnO spacings as was observed in the diffraction data. As discussed above, this could suggest that, despite efforts to minimise air exposure to a few seconds, oxidation takes place in the sample during transfer to the microscope. As touched on above, one further possibility might be that since the XRD technique analyses a larger amount of material compared to the selected area diffraction approach the weak peaks in the XRD might derive from a small, more crystalline Zn_3N_2 component within an amorphous majority of the sample. The reduced sampling of the SAD and HRTEM approaches may then have only picked up the amorphous component which could correspond to the noisy broad intensity in the sample 3 XRD data, an idea illustrated in figure 7.15 below with the electron diffraction intensity aligned and overlaid on the XRD plot as a dotted line.

This idea is consistent with the output of the fitting procedure applied to samples 1 and 2 which gave a very broad ZnO component in addition to the narrower Zn_3N_2 component which matched the prominent peaks in the data – illustrated in Fig. 7.13(b) and (c) respectively - which adds further support to this explanation.

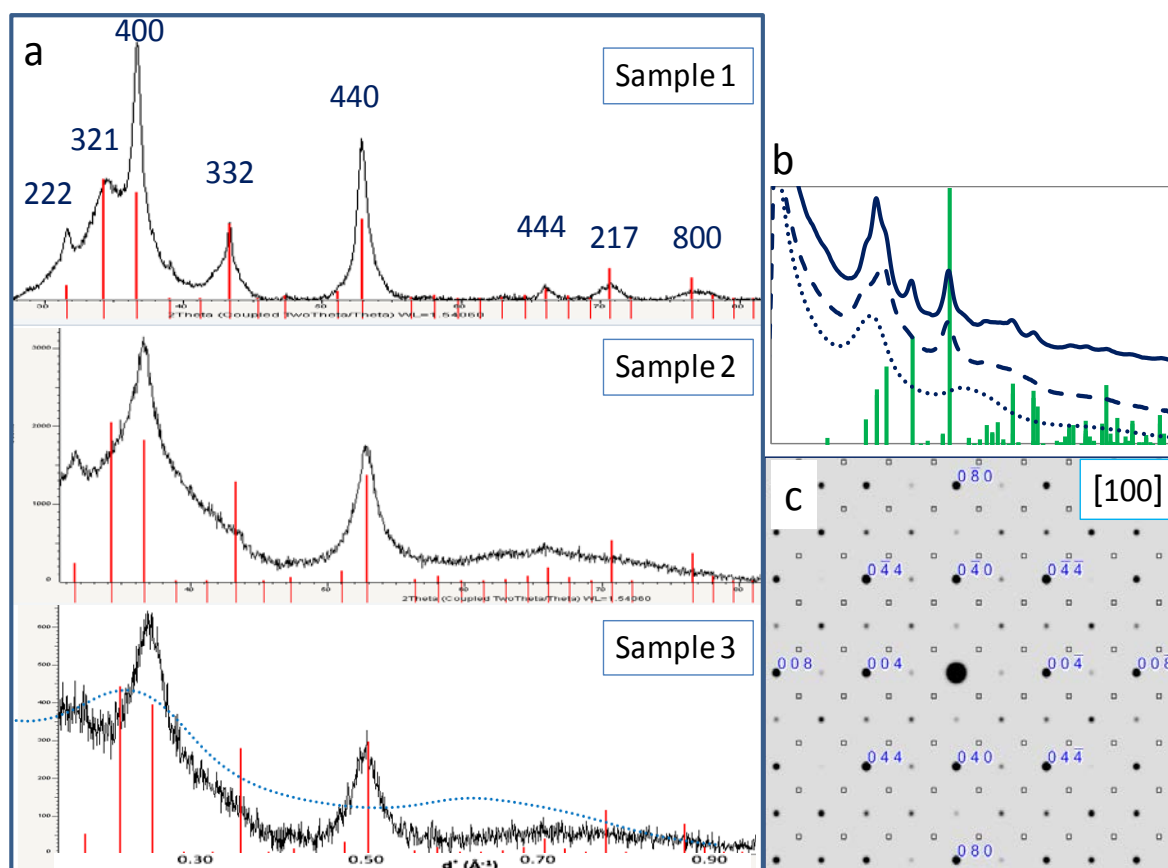


Figure 7.15 (a) XRD data collected at SLE from the three samples indicating a broadening and reduction in intensity of peaks. (b) A copy of the electron diffraction of Fig. 7.5 for comparison. (c) The [100] axis in Zn_3N_2

A further question is why certain peaks in both the XRD and electron diffraction data lose virtually all intensity while others remain prominent and how this fits in with a possible decreasing crystallinity with particle size as described above. One possibility could be preferential orientation of the particles since the most prominent peaks in each sample (the 400 and 440) are the major reflections present in the [100] zone axis as illustrated in the above figure. Such preferential orientation might be observed if growth of the particles were to occur initially predominantly in a [100] plane forming flat platelets initially giving just 400 and 440 peaks in the XRD data before continued growth results in extension in 3 dimensions and increased variation in orientation with the 222 and 332 peaks beginning to appear in the sample 2 data with all the major peaks present in the sample 1 data. It is also of note that the majority of HRTEM images indexed as Zn_3N_2 were along the [100] axis, although

an element of bias associated with the fact that [100] is an instantly recognisable cubic symmetry must be taken into account.

Such observations have been made previously in reports on the growth of Zn_3N_2 thin films that have commented on the presence of both crystalline and amorphous phases within the same sample and also the preferential orientation of the crystalline component in a [100] direction [314].

7.10.6 Change under the electron beam

The significant change in the material under illumination of the electron beam hampered the characterisation work but is an interesting process to consider in its own right. The exact form of the damage had some dependence on the sample examined but could be categorised by several common observations. The main effect is clearly that of crystal growth or ripening of existing nanoparticles under the electron beam which is illustrated clearly by the diffraction data in Figs. 7.8, 7.7 and 7.14 for samples 1, 2 and 3 respectively. These results are characterised by a change from the initially fairly broad diffuse diffraction patterns whereby the smooth rings break up into spottier but more defined rings indicating larger crystal grains with less diffuse background suggesting a reduction in amorphous material.

There are few reports of this process in the literature although similar observations of crystallisation via electron beam illumination have been made of germanium nanoclusters in an SiO_2 matrix[315] and amorphous GaAs[316]. As observed here, the rate of this process was dependent on the current density of the electron beam with atomic diffusion and defect rearrangement being cited as the mechanisms by which it progresses.

The quantitative approach of the fitting procedure applied to data from areas of sample 1 and 2 clusters before and after change under the beam revealed slightly differing results, see Fig. 7.6(b,d) for the change in sample 1 and (c,e) for that of sample 2. The reduced sigma values for both indicated a growth in particles as expected with the broad component of each (possibly related to

the amorphous area of the sample) mostly removed. The main difference was that whereas sample 1 contained a fairly similar ratio of $\text{Zn}_3\text{N}_2/\text{ZnO}$ before and after the change, the crystal growth in sample 2 was primarily ZnO with a reduction in Zn_3N_2 with only a small very broad component remaining, perhaps accounting for a remaining amorphous component. These results may reflect that the greater surface area of the sample 2 particles left them more vulnerable to oxidation during transfer to the microscope column, meaning a greater degree of ZnO present in the particles which then ripened into larger grains under the beam. Similarly the small peaks that appear after beam exposure in the diffraction data from sample 3 in Fig. 7.14 clearly match those of ZnO.

It is also interesting to note that the damage process in the sample 3 nanoparticles seemed to vary with the concentration of particles on the grid. In the 80keV work, in which the particles were more dispersed in order to facilitate high resolution imaging the effect was not to cause further crystallisation but rather the small particles seemed to lose mass and contrast and remain amorphous, with no discernible change in the FFT. Whereas in broad area diffraction work, in which there were many large clusters of particles on the grid, crystallisation was observed via the increasing strength of well defined diffraction rings as is clear from Fig 7.14, suggesting a threshold in the required amount of material for crystal growth under the beam to progress.

EDX data from before and after the change of sample 1 (Fig. 7.8) showed a much more prominent oxygen peak after change, which was also observed in the sample 2 data. Although fitting with the picture of ripening and grain growth observed in sample 2, this result is unexpected for sample 1 as diffraction data suggested the $\text{Zn}_3\text{N}_2/\text{ZnO}$ ratio remained fairly constant in the larger particles. This EDX signal may have been due to a particularly ZnO rich region since the HRTEM images of sample 1 in Fig. 7.9 which were recorded in the centre of a cluster after prolonged beam exposure showed large ZnO grains have developed, in addition to Zn_3N_2 .

It is also interesting to note that the fit in (d) and (e) is too broad to pick up the fine peaks at low scattering angles and it appears that a dependence of sigma on scattering angle may have provided

a better fit for the after-damage experimental data. This may be explained by non-uniform strain in the crystal grains after growth under the beam which would have the effect of introducing a linear dependence in sigma on scattering angle with the peaks getting broader at higher d^* .

The fact the rate of beam damage was reduced at lower kV suggests knock-on effects are responsible since the cross section increases with electron incident energy[317] and, since this is a surface process, it may explain why the smaller particle appear more vulnerable to change and in particular to oxidation from the surrounding air in the column. These results illustrate the care that needs to be taken in accounting for the effects of the high energy electron beam when analysing characterisation results.

7.10.7 Optical Properties

As expected the emission from the sample 1 particles is in the infrared range of the spectrum, consistent with the bulk bandgap of zinc nitride of around 1.1eV, which is expected since the observed clusters consisted of nanoparticles with an average size of 7-8nm. Both the uncapped and capped small sample 2 and 3 particle had a similar PL emission wavelength of 660 and 658nm respectively, indicating a shift in emission relating to the strong confinement regime. The rough average particle sizes of samples 2 and 3 of 4-5nm and 3-4nm respectively would give a greater difference in the emission spectra than that observed but there is a fair degree of error likely in these measurements since they were based on high resolution images of overlapping particle clusters in which it was difficult to accurately define the boundaries. In addition, the rapid onset of beam-induced ripening and crystal growth at the beam intensity required for HR imaging further hampered the measurement. The emission peaks are extremely broad which likely relates to a significant variation in particle size within both samples, with the capping applied to sample 3 accounting for the slightly narrower peak due to a greater degree of size control. There may also be a contribution to the emission from the observed amorphous regions of the sample since emission in this range has been observed in amorphous zinc oxynitride thin films [318][314].

7.11 Conclusions

A wide range of techniques, including selected area diffraction, EDX, HRTEM and radial distribution function analysis have been employed to confirm the successful synthesis of zinc nitride nanoparticles which show great promise for application as a phosphor material. A linear least squares fitting of simulated diffraction components from candidate materials to experimental data suggests compositions of roughly 30% and 20% Zn_3N_2 for large (7-8nm average) and small (4-5nm average) uncapped particle samples with significant impurities in the form of ZnO and zinc amide. Obtaining more accurate and reliable composition figures using this method was hampered due to difficulties with background subtraction and a potentially significant amorphous component in the material.

An apparent decrease in crystallinity with decreasing particle size, more significant than that expected due to increasing nanoscale surface in the smaller particles, was observed. Evidence for an increasing lack of long range order or an amorphous component in the smaller particles included: RDF $G(r)$ plots showing a lack of long range order not expected even for nanoparticles of the order of $\sim 1\text{nm}^3$; extremely broad, diffuse diffraction peaks; the results of the diffraction fitting script giving a very broad component and a crystalline Zn_3N_2 component indicative of crystalline and amorphous material present; HRTEM images of the smallest capped particles appearing exclusively amorphous and those of the small uncapped particles showing some amorphous material; and finally very broad PL emission.

A difficulty encountered in characterising the material in the electron microscope was the rapid onset of change in the material under the electron beam which was characterised by the growth of extended crystallites either by conversion of the amorphous material or ripening of the crystalline nanoparticles. This effect was found to have an increasing impact with acceleration voltage, suggesting knock-on effects were predominantly responsible for atomic diffusion and rearrangement in a more energy-minimising crystalline form. Diffraction, HRTEM and EDX data along

with the least squares fitting analysis suggested that oxidation occurred during this process with ZnO the primary component of the extended crystallite growth -apart from in the largest nanoparticles in which large Zn_3N_2 grains were observed with equal frequency likely due to their decreased surface area rendering them more resistant to the effect of oxidation during transfer to the microscope meaning there was less ZnO material present in the particles.

Photoluminescence data collected at Sharp Laboratories of Europe showed the smaller nanoparticles were in the strong quantum confinement regime with the emission blue shifted from bulk bandgap value of around 1.1eV to around 1.8eV illustrating the potential application as a phosphor across the visible range.

Chapter 8

Conclusions and Further Work

8.1 Introduction

Motivated by the pressures of dwindling fossil fuel reserves and the recognition of the impact of their use on the climate, high efficiency solid state lighting devices based on novel semiconductor nanomaterials are increasingly seen as a hugely promising area of research. To this end, a greater understanding of the relationship between the materials' optical properties and microstructure is required in order to refine the growth conditions and optimise the materials properties. This thesis documents electron microscope based characterisation work on three novel semiconductor nano/micro structures, namely GaN/InGaN core shell nanowires, n-GaN/InGaN/p-GaN core/multi-shell microrods and zinc nitride nanoparticles, all of which show promise as components in future optical devices.

The main conclusions of the experimental work are summarised below with particular emphasis on what can be learned with respect to future synthesis and development of these materials and some additional discussion of possible future experiments to extend the work documented here.

8.2 GaN/InGaN core/shell nanowires

8.2.1 Summary of conclusions

These structures have the potential of overcoming two issues in the performance of planar GaN/InGaN junctions; specifically, the high density of defects due to growth on mismatched substrates and the efficiency-reducing effects of QCSE due to growth in polar directions. The GaN nanowires comprising the core of the structures were grown via the VLS process in which nickel catalyst clusters on an a -plane sapphire substrate were heated to 920° in the presence of the vapour phase of the semiconductor. SEM of the growth substrate revealed an unexpected range of morphologies in the GaN nanostructures which grew upon the Ni islands in addition to the expected nanowires. The latter varied in diameter from 8nm to >200nm with typical lengths of 1-5µm but shared the morphological characteristics of being straight and uniform, often with the catalyst particle still present at the end of the wire. The vast majority of wires had the expected wurtzite crystal structure but there were some examples, <5%, of wires with the cubic zinc-blende structure which was determined by SAD. Using shadow imaging the growth directions of the wurtzite wires were found to be $\{1\bar{1}00\}$ m -axis and $\{11\bar{2}0\}$ a -axis in roughly equal proportion whereas the cubic wires had $\langle 220 \rangle$ orientations. Diffraction contrast and HRTEM showed the wurtzite wires to be completely defect free whereas the cubic wires had a high density of defects, most notably basal plane stacking faults running along the length of the wire separating cubic and hexagonal regions. The fraction of cubic wires observed may be due to GaN wires growing upon the Ni clusters rather than having an epitaxial relationship with the sapphire substrate. The pure GaN wires had a narrow

PL emission peak close to the strain free value for GaN, confirming the large surface area aids in accommodating any strain from the mismatch with the substrate or nickel catalyst clusters.

The InGaN shells deposited by MOCVD on the core GaN nanowires were found to be polycrystalline, which may be due to a layer of silicon identified at the core shell interface in cross section samples prepared with the dual beam FIB. STEM EDX of the core shell cross sections showed a variation in indium composition across the shell with a decrease away from the core suggesting strain plays a role in indium segregation as reported in the literature. Diffraction contrast and SAD work indicated a greater degree of well orientated InGaN growth on the c-plane core facets compared to the pyramidal planes which had small grains with a greater range of orientations and also revealed a large number of stacking faults within the InGaN grains. This was attributed to the documented difference in growth rates on the differing planes. The broad PL peak observed in the shelled structures was likely related to the observed variation in composition and defect related transitions, with the intensity reduced due to non-radiative recombination at the observed defects and grain boundaries.

In order to identify the core size in completely shelled wires a technique was developed in which the EDX signal from the Ni catalyst, still embedded with the wire, was used to infer the size of the core since it governs the initial wire diameter during VLS growth allowing for a high turnover study of the effect of core size on the shell morphology.

8.2.2 Future material development and further work

Clearly the first step needed in the ongoing development of these materials is to achieve single crystal shell growth which would give a much improved optical performance. The silicon contamination identified in the characterisation would need to be removed and the InGaN growth parameters adjusted to achieve this. A more controlled growth rate, keeping the InGaN layers thin would likely aid in producing coherent shell layers. In addition, dispersing the Ni droplets more finely could help in producing more uniform arrays of nanowires rather than the variety of structures

grown on top of the large Ni islands observed here. The next step would then be to prepare multi-shell heterostructures to realise the required p-n junction structure for application in a real device.

The high turnover identification of core size method could then be applied to study the relationship between core diameter and shell growth in order to compare to theoretical work on the critical geometries for core shell heterostructures. Another possible avenue of investigation is the impact of the catalyst particle on the materials properties. There was evidence in the STEM EDX work of nickel spreading within the shell region and this may lead to unintentional doping of the materials. This could be explored with HAADF z-contrast STEM to identify any nickel in cross sections prepared by the lift out method described in Chapter 3.

8.3 n-GaN/InGaN/p-GaN core/multi-shell microrods

8.3.1 Summary of conclusions

Core/shell microrods offer many of the same benefits as nanowires but without the drawbacks due to non-uniformity and sub-optimum growth conditions, however the initial growth of the core on sapphire leads to the question of the impact of misfit dislocations on the junction microstructure.

Growth was achieved via firstly masking and dry etching MOCVD-grown GaN films on sapphire to prepare top-down GaN micro-rods before depositing 50nm thick shells of n-GaN, InGaN and p-GaN. Two varieties of microrod with differing aspect ratios were investigated by preparing cross sections through the samples with a dual beam FIB and lifting out to analyse via TEM and STEM. Threading dislocations in the core region, due to the misfit with the original sapphire substrate were identified with diffraction contrast TEM and the Burgers vectors were determine to be mostly **a** and **a+c** as expected. Although occurrences of these core dislocations reaching the shell region were identified the vast majority remain confined to the core and are unlikely to have a detrimental effect on the

junction microstructure and therefore optical properties – a positive observation for the ongoing development of these materials within optical devices.

Despite attempts to heal the etch damage via deposition of an initial GaN shell, residual damage (likely in the form of altered stoichiometry and crystallinity) was identified as a region of differing contrast in (S)TEM images, particularly in the case of the smaller diameter sample. The major difference between the two samples however, was the presence of a high density of defects in the shell region of the smaller diameter sample. These defects likely contribute to a broader near band edge luminescence and emergence of a yellow band in the photoluminescence data of this sample.

The reason for the difference in defect density could not be determined with certainty, but differences in the PL of the samples suggested a greater degree of strain in the smaller diameter sample, possibly due to the differing curvature of the surface, which would explain the higher density of defects in the InGaN layer due to an increased lattice mismatch. In any case, the successful growth of largely coherent nonpolar GaN/InGaN junctions on the larger diameter rods is promising for their ongoing development as active materials in optoelectronic devices.

The unusual ‘flag’ defects found beginning in the InGaN region of the smaller rods were analysed in detail via $\mathbf{g \cdot b}$ diffraction contrast work, weak beam imaging and high resolution ADF STEM. The defects were found to be comprised of type I_1 basal plane stacking faults and both perfect and partial dislocation loops lying on pyramidal planes. Some of the basal plane stacking faults are likely to be formed due to etch damage on the core surface but the majority are formed via growth errors relating to the low temperatures required to grow InGaN films and the very low indium incorporation into m -plane material. The dislocation loops are believed to glide in from the free surface to relieve lattice mismatch strain and possibly stress relating to the stacking faults themselves, leading them to approach the stacking faults to a certain distance to neutralise the stress related to these BSFs. In the case of the partial dislocation loops, domains of differing stacking sequence may form which can have slight mistilts with respect to the surrounding material resulting

in the flag bounding regions of differing contrast in diffraction contrast TEM and ADF STEM images. These defects are likely to explain the broader near band edge peak and the yellow band in the photoluminescence seen in this sample, suggesting ongoing development should focus on the larger diameter rods.

8.3.2 Future material development and further work

Although the successful fabrication of large area, coherent non-polar junctions has been confirmed in the case of the larger rods, there are still a number of growth issues to focus on. In particular, the difficulty in achieving the intended indium composition may require investigation of the growth parameters needed in order to overcome the documented issues with indium incorporation on non-polar planes. Similarly, the doping was determined to not be active so further studies of the doping procedure in the deposited shells need to be carried out. In terms of developing the synthesis process, the next step would then be to fabricate multi-quantum well structures with more appropriate shell thicknesses to achieve the junction structures known to be successful in planar devices. It is possible that this alone may help with indium incorporation since phase separation in InGaN quantum wells is suppressed by the external strain from the mismatch with the GaN layers [41] [42]. Another development of the growth process would be to employ an N₂ plasma treatment or wet etch step to the etch-damaged surface of the rods after the initial etching of the GaN core rather than simply attempting to repair by further MOCVD growth. This may help avoid any detrimental effects of the dry etch damage on the over-grown shells.

In comparing the characterisation results of the core/shell microrods to those of the nanowires (these being rival candidates for the active material in LEDs) the conclusions of the work here would suggest that the development of the core/multi-shell microrods should be prioritised over the nanowires. The main reasons being: coherent non-polar junctions have been demonstrated in the core/shell microrods unlike the nanowires; the core dislocations relating to the initial c-axis growth of the rods (feared to be a detrimental factor) were shown to be contained away from the active

area; the growth direction means that the junctions on the rod sidewalls are all non-polar unlike the semi-polar junctions in the nanowires; the fabrication technique means that the rods are extremely uniform which would be beneficial in their application in devices; and finally, since a catalyst particle is not required in the microrod case, any detrimental effects of catalyst contamination such as unintentional doping are avoided.

There are several different techniques which could be used to explore the doping profiles in the shells including scanning capacitance microscopy [319] and off-axis electron holography [320]. Similarly scanning cathodoluminescence microscopy[321] would provide a powerful tool to link the observed microstructure to the local optical properties to explore the impact of defects and compositional inhomogeneity.

In terms of the characterisation of the defects, it would also be beneficial to attempt to prepare *m*-axis cross sections to study the structure in plan-view, as is customary in the characterisation of defects in thin films. This would require development of the FIB lift out technique in order to remove a slice from the very edge of a microrod deposited onto a substrate.

8.4 Zn₃N₂ nanoparticles

8.4.1 Summary of conclusions

Zinc nitride is a very promising material for application as a phosphor due to its appropriate bandgap energy whilst being non-toxic and comprised of abundant elements unlike conventional phosphor materials but it requires synthesis in nanoparticle form for this application to be realised. This was successfully achieved and demonstrated using a combination of SAD, HRTEM, EDX and radial distribution function analysis. A linear least squares fitting of simulated diffraction components from candidate materials to experimental data suggests compositions of roughly 30% and 20% Zn₃N₂ for

large (~7-8nm) and small (~4-5nm) uncapped particle samples with significant impurities in the form of ZnO and zinc amide.

Although the expected anti-bixbyite structure was confirmed in the largest sample, the smaller particles appeared to be less crystalline with the particles appearing to be increasingly amorphous with reduced size. Evidence for this included: RDF $G(r)$ plots showing a lack of long range order not expected even for nanoparticles of the order of $\sim 1\text{nm}^3$; extremely broad, diffuse diffraction peaks; the results of the diffraction fitting script giving a very broad component and a crystalline Zn_3N_2 component indicative of crystalline and amorphous material present; HRTEM images of the smallest capped particles appearing exclusively amorphous; and very broad PL emission.

A difficulty encountered in characterising the material in the electron microscope was the rapid onset of change in the material under the electron beam which was characterised by the growth of extended crystallites either by conversion of the amorphous material or ripening of the crystalline nanoparticles. The increase of this effect with increasing acceleration energy of the electrons suggested knock-on effects were predominantly responsible for atomic diffusion and rearrangement in a more energy-minimising crystalline form. Diffraction, HRTEM and EDX data along with the least squares fitting analysis suggested that oxidation occurred during this process with ZnO the primary component of the extended crystallite growth.

Photoluminescence data collected at Sharp Laboratories of Europe showed the smaller nanoparticles were in the strong quantum confinement regime with the emission blue shifted from bulk bandgap value of around 1.1eV to around 1.8eV illustrating the potential of application as a phosphor across the visible range.

8.4.2 Future material development and further work

Although the presence of Zn_3N_2 was successfully confirmed, the synthesis process must be optimised in order to increase the proportion of zinc nitride and remove the unwanted products such as zinc

amide and metallic zinc. Similarly further work needs to be carried out to improve the crystallinity of the smaller particles in which there is significant amorphous material present. This would likely involve a careful investigation of the relationship between size and structure by preparing a range of capped particles of different sizes which could be examined by low kV HRTEM or STEM to look at the crystal structure whilst avoiding the effects of beam damage.

The sensitivity to oxidation during exposure to air and moisture will clearly limit the potential of utilising this material as a phosphor and therefore a logical progression in this investigation would be to explore possible shelling materials in order to stabilise the particles. Techniques such as quantitative HAADF STEM may then be applied to study the shell coverage, composition and morphology in order to develop the desired core/shell structures.

A final possible extension to the work described in Chapter 7 involves a thorough study of the beam-damage process which leads to crystallisation and ripening under the electron beam. It would be of particular interest to investigate this process on isolated particles with low KV, high resolution imaging to observe the progression. Collecting data at a range of acceleration voltages to compare to theoretical models of the atomic rearrangement would be of particular interest and may lead to potential methods of crystallising the more amorphous particles to improve the optical properties for the intended application.

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