# The Growth and Characterisation of the Dilute Nitride InGaAsN

Submitted by

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## **List of Abbreviations**

$2\theta$	Angle of rotation of the detector relative to the straight through
	beam in HRXRD
θ	Bragg angle in HRXRD
λ	X-ray wavelength
Ø	Angle of rotation around the <i>z</i> -axis in HRXRD
Ψ	Angle of rotation around the <i>x</i> -axis in HRXRD
ω	Angle of rotation of the sample relative to the straight through
	beam (around the y-axis) in HRXRD
a.u.	Arbitrary units
AES	Auger electron spectroscopy
AFM	Atomic force microscopy
BTJ	Buried tunnel junction
BN	Boron nitride
CBE	Chemical beam epitaxy
DBR	Distributed Bragg reflector
DI	De-ionised
DC	Direct current
DMHy	Dimethylhydrazine
DQW	Double quantum well
ECR	Electron cyclotron resonance
EEL	Edge emitting laser
ELO	Epitaxial lift-off
FWMH	Full width at half maximum
GS-MBE	Gas-source molecular beam epitaxy
HBT	Heterojunction bipolar transistor
HRXRD	High resolution x-ray diffraction

IRM	Ion removal magnet
LAN	Local area network
LED	Light emitting diode
MAN	Metro area network
MBE	Molecular beam epitaxy
ML	Monolayer
MOCVD	Metal-organic chemical vapour deposition
MOMBE	Metal-organic molecular beam epitaxy
MOVPE	Metal-organic vapour phase epitaxy
MQW	Multi quantum well
MSM	Metal-semiconductor-metal
PBN	Pyrolytic boron nitride
PID	Proportional-integral-derivative
PL	Photoluminescence
QMS	Quadrupole mass spectrometer
QW	Quantum well
RF	Radio frequency
RHEED	Reflection high energy electron diffraction
RWG	Ridge wave-guide
SCSL	Strain compensating superlattice
SIMS	Secondary ion mass spectrometry
SLD	Superluminescent diode
SQW	Single quantum well
SS-MBE	Solid-source molecular beam epitaxy
TEM	Transmission electron microscopy
TQW	Triple quantum well
UHV	Ultra-high vacuum
VCSEL	Vertical cavity surface-emitting laser
VCSOA	Vertical cavity semiconductor optical amplifier
VDW	Van der Waals
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

#### Abstract

The aim of this work was to investigate issues related to the determination of the nitrogen mole fractions in epitaxial layers of the dilute nitride GaAsN. Research of these issues is essential to laboratories working with these materials since comparisons cannot be made if nitrogen mole fractions are not standardised. Similar issues plagued work on the material AlGaAs for several decades, before resolution of the issues was finally possible. Furthermore, the motivations also come from the needs for more efficient devices. Samples were grown on GaAs (001) substrates using molecular beam epitaxy (MBE) with an electron cyclotron resonance (ECR) nitrogen plasma source. A new approach to calibrate the nitrogen mole fraction y in  $GaAs_{1-\nu}N_{\nu}$  epitaxial layers has been developed. The method employs strain cancellation in GaAsN by the incorporation of indium. The concept was to take a tensile layer of GaAsN, with a perpendicular lattice constant which could be measured accurately by high resolution x-ray diffraction (HRXRD) and consequently to determine the mole fraction x of indium which must replace gallium to exactly cancel the tensile strain in the GaAsN layer. The data yielded a relationship between the strain cancelling indium mole fraction x required and the perpendicular lattice parameter of the GaAsN layer. The analysis also suggested that Poisson's ratio of GaAsN at low nitrogen mole fractions is 0.31.

There are several other issues that must be considered when dealing with composition determination in any materials system, such as whether Vegard's law holds true, what is Poisson's ratio for the material and what are the critical layer thicknesses since these should not be exceeded. All of these issues were investigated

in this work. Within experimental error the lattice constant of GaAsN shows a linear relationship with the nitrogen mole fraction for y < 0.012 when grown at 460°C, suggesting no deviation from Vegard's law over this limited range of nitrogen compositions. Measurements were also made of the GaAsN Poisson ratio as a function of nitrogen mole fraction, using HRXRD and secondary ion mass spectrometry. These measurements yielded a value of 0.31, in agreement with the value suggested by the work on strain cancellation by the incorporation of indium in GaAsN. Transmission electron microscopy (TEM) measurements were also performed in order to confirm that all grown GaAsN layers in this work were not affected by misfit dislocation formation or any other strain-relieving defect. The experiments showed that interfacial coherence is maintained across most of the interfacial area up to layer thicknesses which are a factor of between five and six times thicker than that predicted by theory.

## **Statement of Authorship**

Except where reference is made in the text of the thesis, this thesis contains no material published elsewhere or extracted in whole or in part from a thesis submitted for the award of any other degree or diploma.

No other person's work has been used without due acknowledgement in the main text of the thesis.

The thesis has not been submitted for the award of any degree or diploma in any other tertiary institution.

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### **1** Introduction

Group III/V compound semiconductors such as GaAs and InP are popular materials for the fabrication of devices for photonic and optoelectronic applications. While the growth of InGaAsP on InP substrates allows the band gap of the material to be changed to cover optical network requirements while maintaining the lattice matching condition, GaAs is preferred for the production of devices for these applications as it is associated with a mature radio frequency (RF) circuit technology and is a more robust and cost-effective substrate material. The growth of the compound semiconductors GaAsN and InGaAsN on GaAs substrates became popular after Weyers et al. [1, 2] found a decrease in the band gap energy following the addition of small amounts of nitrogen to GaAs. These materials are commonly referred to as the dilute nitrides since they contain less than about 5% nitrogen mole fractions. Since 1996 when Kondow et al. [3] first experimented with InGaAsN grown on GaAs substrates as a candidate for near infra-red devices (1300 to 1550 nm), there has been considerable interest in this material (e.g. [4-13]). InGaAsN can be grown lattice-matched to a GaAs substrate when the ratio of the atomic mole fractions of indium to nitrogen is approximately three, however this composition does not achieve the band gap reduction required to realise a material capable of operating in the 1300 to 1550 nm band. There are limits to the levels of atomic nitrogen incorporation that can be achieved because at higher levels rather than growing a homogeneous material the nitrogen phase separates to form regions of GaN within a GaAs matrix. Therefore nitrogen levels must be limited to a maximum of about 5%, however to create a material capable of operating at 1300 to 1550 nm the indium levels must be considerably higher than a factor of three of the nitrogen

levels and levels of 20% to 40% are commonly employed (e.g. [14-18]). The progress that has been made in developing this material has made it one of the most widely studied for the purpose of developing devices operating in the 1300 to 1550 nm wavelength ranges as well as for specialised applications such as photovoltaic solar cells.

While there have been many reports of the electronic and optical properties of GaAsN and InGaAsN alloys, there have been few studies of methods for determining the nitrogen mole fractions in these materials (e.g. [19-21]). There are also contradictory findings about the linearity of the GaAsN lattice constant as a function of nitrogen mole fraction [22-27] and there has been no experimental determination to date of the value of GaAsN's Poisson ratio.

This thesis reports on a study of the dilute nitride GaAsN grown by molecular beam epitaxy (MBE) on GaAs substrates using an ECR nitrogen plasma source covering nitrogen mole fractions up to about 0.012. The main objective of this study was to investigate the determination of the nitrogen mole fraction in GaAsN layers using HRXRD, the technique which is most commonly used for this purpose. In using HRXRD there are a number of assumptions which are commonly made, most of which have not been tested experimentally. These assumptions are (i) that the GaAsN/GaAs interface is coherent, (ii) that the GaN binary end-point lattice parameter is known, (iii) that the GaAsN natural lattice constant obeys Vegard's law, that is, it is linear with nitrogen mole fraction, (iv) that the elastic constants of GaAsN are known, together with their dependence on composition and (v) that the growth of GaAsN only involves nitrogen atoms replacing arsenic atoms within the arsenic sub-lattice. Most, but not all, of these assumptions have been investigated in this work and a number of important conclusions can be drawn which largely validate the conventional use of HRXRD to infer the nitrogen mole fraction in GaAsN layers. Additionally, this work has lead to the development of a new approach to calibrate nitrogen mole fractions in GaAsN by determining the indium

mole fraction x in an  $In_xGa_{1-x}As_{1-y}N_y$  epitaxial layer which exactly cancels the strain present in a  $GaAs_{1-y}N_y$  layer with the same nitrogen content.

Chapter 2 reviews the dilute nitride literature starting with a history of the development of this material and a description of its applications. This is followed by a discussion of some of the technical issues associated with growing this material, such as managing lattice mismatch and setting the nitrogen source operating conditions. The influence of arsenic, which competes with nitrogen to incorporate during the growth of (In)GaAsN, will also be discussed. Chapter 3 explains the equipment and experimental procedures, including MBE growth, structural characterisation by HRXRD and chemical analysis by secondary ion mass spectrometry (SIMS). This chapter also covers some of the basic theory elements of relevance to this work, such as a description of the GaAs lattice structure, the interpretation of HRXRD results, linear elasticity theory, Vegard's law, lattice tilts and line defects. Chapter 4 includes preliminary observations regarding interfacial coherence in GaAsN layers using TEM. It also reports SIMS measurements to investigate the effects of the incorporation of molecular nitrogen on the GaAs lattice constant. Chapter 5 introduces a novel approach to use strain cancellation by the addition of indium to GaAsN for the purpose of calibrating nitrogen mole fractions. Chapter 6 reports details of an experiment to determine GaAsN's Poisson ratio. An epitaxial layer lift-off technique was used for this experiment, with structural properties measured using symmetric and asymmetric HRXRD reflections. Chapter 7 reports on experiments to verify the linearity of the lattice constant of GaAsN epitaxial layers with nitrogen mole fraction. A combination of HRXRD and SIMS measurements were used to characterise samples in order to validate the linearity of the GaAsN lattice constant for nitrogen mole fractions less than about 0.012. The last chapter makes some concluding remarks and recommendations for future work.

### 2 Dilute Nitride (In)GaAsN Literature Review

Dilute nitride compound semiconductors such as InGaAsN have attracted the attention of researchers due to their potential for application in optoelectronic devices operating in the 1300 to 1550 nm wavelength band. This chapter reviews these materials, especially InGaAsN and GaAsN grown on GaAs substrates by MBE.

#### 2.1 Development of the Dilute Nitride (In)GaAsN

The rapid growth of optical transmission technologies in local area networks (LAN) and metropolitan area networks (MAN) has put demands on developing emitters that are suitable for high speed transmission. Many semiconductor materials suitable for the fabrication of optoelectronic devices are grown on InP substrates because InGaAsP can be grown lattice matched across a range of band gaps spanning the requirements for 1300 to 1550 nm applications. However, it would be preferable to grow materials on GaAs (001) substrates since it is compatible with a mature RF circuit technology and is less expensive when compared to InP. Moreover, AlGaAs/GaAs or AlAs/GaAs distributed Bragg reflectors (DBR) can be used as mirrors for GaAs-based vertical cavity surface-emitting lasers (VCSEL) which can be easily packaged and coupled to optical fibres. The compatibility of VCSELs grown on GaAs with DBR mirrors is one of the major strengths for the development of GaAs-based long wavelength lasers emitting at the communication wavelengths between 1300 and 1550 nm. However, the use of InGaAs quantum wells as the active layers in VCSELs restricts emission wavelengths to less than approximately 1200 nm.

Generally, most devices have relied on the InGaAsP/InP material system for the development of sources for long distance optical communications [28]. This is because InGaAsP/InP is the only versatile lattice matching material system capable of allowing the development of long wavelength lasers emitting in the range between 1300 and 1550 nm. However, the production costs for InGaAsP/InP devices are expensive and therefore not suitable for use in LAN and MAN networks due to the high volume of emitters and receivers required for these networks. Furthermore, devices fabricated within the InGaAsP/InP material system exhibit relatively low power capacity and poor heat conductivity. This is because the low characteristic temperature ( $T_0$ ) associated with the threshold current density due to a small conduction band offset between InGaAsP and InP gives poor carrier confinement, resulting in poor thermal stability. Therefore, devices fabricated from this material must be cooled during operation.

It would be preferable if the emitters used in optical fibre communication systems consisted of a VCSEL that can be easily matched with a fibre optic cable. However, the InGaAsP/InP system is not suited to VCSEL structures due to the small difference in the refractive index between InGaAsP and InP. Otherwise a relatively large number of periods is needed in order to achieve the high mirror reflectivity required for the DBR structures in a VCSEL. From these considerations, it appears that the solution is to find alternative materials that are suitable for long wavelength GaAs-based VCSELs which will consequently lead to a cost-effective solution for LAN and MAN networks.

The InGaAsN/GaAs system that was first investigated by Kondow et al. [3] is currently the most promising material for the fabrication of optoelectronic devices operating at the longer wavelengths required for transmission through an optical fibre. InGaAsN is a compound semiconductor which can be grown on GaAs substrates and might overcome many of the problems associated with the InGaAsP/InP system. Nitrogen is a small atom with a high electro-negativity which has a large effect on the GaAs band gap. As a general rule for group III/V materials, substituting an element with one with a smaller atomic radius should reduce the lattice constant and increase the band gap however it has been determined that replacing a small fraction of the arsenic atoms in GaAs by nitrogen strongly reduces the band gap [1] and the lattice constant [3]. This is associated with a larger conduction band offset in InGaAsN/GaAs compared to the commonly used InGaAsP/InP material system. Hence InGaAsN/GaAs gives stronger carrier confinement resulting in an improved thermal stability with a higher  $T_0$ . Therefore, it is expected that devices fabricated from this material could be produced at a reduced manufacturing cost and operated without additional cooling.

Devices fabricated from InGaAsN/GaAs could produce high output powers at 1300 nm, for example as reported by Kovsh et al. [29] who demonstrated a 200 mW single mode InGaAsN/GaAs ridge waveguide laser. In the following year, Qu et al. [30] fabricated a 962 mW ridge waveguide InGaAsN triple quantum well (TQW) laser grown using metal-organic chemical vapour deposition (MOCVD). The  $T_0$  of the InGaAsN/GaAs laser diode was found to be rapidly reducing with increasing emission wavelength from 1000 to 1500 nm [31]. By using GaAs as the substrate, InGaAsN/GaAs can be used as the active region in a 1300 nm VCSEL structure and this has been demonstrated by several researchers as discussed in the following section. These advantages suggest that InGaAsN is a suitable material to replace InGaAsP in optoelectronic applications for the LAN and MAN networks. The following sections discuss the history of the development of the dilute nitride InGaAsN and some of its applications.

#### 2.1.1 History of (In)GaAsN

The studies of nitride containing semiconductors began in the mid 1960s when Thomas et al. [32, 33] reported that nitrogen molecules had been found to create a bound state in the forbidden band gap of GaP. Research on the alloy GaP continued but the nitrogen state in GaAs was only observed in 1990 (e.g. [34, 35]). A year later Baillargeon and Cheng [36] found a photoluminescence (PL) peak centred at 584.6 nm when approximately  $2 \times 10^{20}$  cm<sup>-3</sup> of nitrogen atoms were added to create GaPN. The layer was grown by gas-source molecular beam epitaxy (GS-MBE) using ammonia as the nitrogen precursor. The improvement in growth of the dilute nitrides is explained in the following paragraphs.

The successful growth of the dilute nitride GaAsN on a GaAs substrate was first reported in 1992. Weyers et al. [1, 2] were the first to report on the properties of GaAsN when they observed the unusual reduction in the band gap of GaAsN when nitrogen was incorporated in the layer. The growth technique used in this experiment was low pressure MOCVD with ammonia cracked in a microwave plasma cell as the nitrogen source. The nitrogen composition was limited to about 1.5% and optical emission from the GaAsN layers showed a strong PL red-shift relative to GaAs. These researchers identified that the band gap decreased almost linearly with increasing nitrogen concentration. From a report by Sakai et al. [37], an alloy containing sufficient nitrogen was expected to have negative band gap energy due to the high electro-negativity of nitrogen atoms, for a range of nitrogen compositions from about 10% to 87%. However, the large lattice constant difference of about 20% between GaAs and GaN causes the growth of GaAsN and InGaAsN alloys with high nitrogen mole fractions challenging. GaN and GaAs exhibit lattice constants of 4.5 Å [38] and 5.65325 Å respectively [38, 39].

In 1994, Kondow et al. [40] reported the GS-MBE growth of GaAsN on GaAs using a nitrogen radical as the nitrogen source. They proposed the growth of GaAsN/GaAs with the potential for the material to be fabricated on silicon wafers. Nitrogen contents of up to 1.5% were achieved and the bowing parameter associated with the band gap energy relationship with composition was estimated at 18 eV. The method employed by Kondow was the same as that used by Weyer et al. [1], namely a microwave plasma cell using high purity nitrogen gas as a precursor to produce atomic nitrogen. Sato [41] also found that using plasma-cracked nitrogen gas for the growth of GaAsN by MOCVD allowed more nitrogen atoms to be incorporated in the layer when compared with using plasma-cracked ammonia. The red-shift of the PL signal with increasing nitrogen content was first observed by Weyer et al. [1] and confirmed by Kondow et al. [40] and Sato [41].

In the following years, research focussed on the physics behind the strong band gap bowing associated with GaAsN (e.g.[42-45]) and little experimental work was conducted (e.g.[46]). However, in 1996 Kondow et al. [3] proposed the quaternary alloy InGaAsN for development of a laser based on growth on a GaAs substrate, emitting at communications wavelengths with a high characteristic temperature  $T_0$ . Based on their calculations, the combination of InGaAsN with a wide gap material would allow a large band gap discontinuity of over 350 meV to be achieved in the conduction band with a  $T_0$  of about 180 K. These researchers also demonstrated the growth of In<sub>0.3</sub>Ga<sub>0.7</sub>As<sub>0.99</sub>N<sub>0.01</sub>/GaAs using GS-MBE, with the PL spectrum measured at room temperature peaking at 1232 nm. This was followed by the announcement of the first continuous wave operation of an InGaAsN/GaAs quantum well laser with an emission wavelength of 1113 nm [47]. In the same year, Kondow et al. [48] successfully fabricated an InGaAsN/GaAs laser diode with a lasing wavelength of about 1200 nm under pulsed conditions at room temperature, with a  $T_0$  of about 127 K, the highest value reported at that time. The same research group also demonstrated an InGaAsN laser diode operating under continuous-wave conditions at room temperature [49]. This confirmed InGaAsN as a new material for laser diodes operating in the 1300 to 1550 nm emission range with predicted excellent high-temperature performance due to the large conduction band offsets which could be achieved.

Following this pioneering work, Sato et al. [50] demonstrated the first InGaAsN/GaAs edge emitting laser (EEL) operating at 1300 nm and soon after the first continuous wave operation was demonstrated at this wavelength with a nitrogen content of about 1% [51]. In the same year, Xin and Tu [52] successfully grew an InGaAsN/GaAs multi quantum well (MQW) on a GaAs substrate using GS-MBE with nitrogen compositions increased from 0.9% to 3%. They observed the red-shift

in the PL wavelength with increasing nitrogen content in their InGaAsN layers. The room temperature PL peak was at 1300 nm for a nitrogen mole fraction of 0.02.

There have been several studies on the current and temperature characteristics of InGaAsN materials grown on GaAs with the intention to emit light at 1300 nm [53-55] with larger threshold current densities of more than 1000 A/cm<sup>2</sup> being measured. In 2000, Riechert et al. [56, 57] and Sato [58] reported lower threshold current densities of 500 to 920 A/cm<sup>2</sup> and in the following year Kawaguchi et al. [59] reported an InGaAsN laser emitting at 1280 nm with a threshold current density of 450 A/cm<sup>2</sup>. In 2005, Wang et al. [60] demonstrated a record low threshold current density of about 300 A/cm<sup>2</sup> for a cavity length of 1200  $\mu$ m with 1300 nm emission wavelength. A number of dilute nitride InGaAsN/GaAs VCSELs have also been successfully fabricated, the first in 1997 operating at 1300 nm with 1220 nm optical pumping [61], followed by an electrically-pumped version a year later, emitting at a wavelength of about 1180 nm [62]. Subsequently, VCSELs operating at 1300 nm were demonstrated using optical [63-65] and electrical pumping [66-72]. Riechert et al. [73] published a review of the progress that had been made in the development of 1300 nm InGaAsN VCSELs.

Although the development of a 1300 nm technology looked promising, no research group had yet been able to achieve lasing at 1550 nm. This changed in early 2000 when Sopanen et al. [74] reported the GS-MBE growth of InGaAsN quantum dots with 4% nitrogen mole fraction and observed optical emission at up to 1500 nm. For the first time the fabrication of 1550 nm InGaAsN quantum dot lasers on GaAs substrate looked possible. In July 2000, Fischer et al. [15] successfully grew InGaAsN/GaAs double quantum well (DQW) laser diodes operating at 1520 nm. They used solid source molecular beam epitaxy (SS-MBE) with a radio frequency (RF) nitrogen plasma source to supply nitrogen atoms. The nitrogen content was about 5% and their results showed the potential of InGaAsN/GaAs as the active layer in EELs and VCSELs operating at 1550 nm. In the following year, they were able to fabricate ridge wave-guide (RWG) laser diodes operating under pulsed conditions up

to temperatures of 80°C with an emission wavelength of 1540 nm [75]. A year later, the same research group reported a significant improvement in the laser design with emission at 1500 nm at a low threshold current of 120 mA [76]. Research on the dilute nitride InGaAsN by this group has continued (e.g. [4, 77-79]).

In 2004, Wang et al. [80] reported the growth of single InGaAsN quantum wells (SQW) with high nitrogen content grown on GaAs substrates for 1550 nm applications. The technique used was SS-MBE with an RF nitrogen plasma source to supply atomic nitrogen at levels from 2.2% to 5.3% with the indium mole fraction kept constant at 34%. They grew InGaAsN quantum wells (QW) about 65 Å thick in order to avoid the formation of misfit dislocations. The longest wavelength they achieved was about 1590 nm at a 5.3% nitrogen composition. These results again demonstrated the potential for the fabrication of 1550 nm InGaAsN QW lasers on GaAs substrates. A year later, another research group was also able to achieve a wavelength beyond 1500 nm with nitrogen concentrations of about 4% and 40% indium [81]. They also employed MBE using an RF nitrogen plasma source for the growth and their QW thickness was about 75 Å. In the following year, Liu et al. [82] reported the effect of growth temperature on the optical and structural properties of InGaAsN/GaAs MQWs emitting at 1600 nm. They found that the growth temperature was critical in order to obtain high quality 1550 nm InGaAsN MQWs. There are other publications reporting InGaAsN compounds that could emit in the 1300 to 1550 nm wavelength range using MBE combined with an RF nitrogen plasma source [83-89]. There are also several publications that review the progress in the development of long wavelength lasers fabricated from III/V dilute nitride materials, especially the InGaAsN/GaAs system [28, 90-93]. Until now, research on dilute nitride InGaAsN/GaAs lasers capable of emission wavelengths beyond 1300 nm is still in progress and recent publications on the applications of these devices are discussed in section 2.1.2.2.

#### 2.1.2 Applications of GaAsN and InGaAsN

In modern telecommunication applications most of the important semiconductors developed for the fabrication of high speed devices are from the group III/V family of alloys such as InP and the dilute nitrides, that are able to be used in the wavelength band between 1300 and 1550 nm. The main device applications for these materials are in the field of optoelectronics such as for photodetectors, light emitting diodes (LEDs) and laser diodes. In this section, the applications of materials such as GaAsN and InGaAsN are discussed.

#### 2.1.2.1 GaAsN

GaAsN/GaAs avalanche photodiodes fabricated following MBE growth and operating at 940 nm [94] and 1064 nm [95] were fabricated in 2000. The external quantum efficiency was 59% at 1064 nm and a radio control limit below 2 GHz was achieved. In 2001, Gotthold et al. [96] reported the successful fabrication of GaAsN avalanche photodiodes exhibiting low dark currents of less than 1  $\mu$ A. The device contained 1.75% nitrogen and achieved a quantum efficiency of 27% at 1064 nm.

GaAsN/GaAs heterostructures could also be used as the active region in metalsemiconductor-metal (MSM) photodetectors as demonstrated by Sciana et al. [97] in 2008. The device structures were grown on GaAs (100) using atmospheric pressure metal-organic vapour phase epitaxy (MOVPE) and the nitrogen concentrations in the GaAsN layers varied from 0.5% to 1.74%.

Sarmiento et al. [98] demonstrated the first 1530 nm electrically-pumped VCSEL operating in pulsed and continuous wave modes at room temperature when they employed an InGaAsNSb/GaAsN MQW structure as the active region in a laser. The structures were grown on *n*-type GaAs substrates using SS-MBE, the nitrogen content in the GaAsN layers was 3.3% and the device emitted beyond 1500 nm.

The use of GaAsN layers in InGaAsN/GaAsN laser diodes resulted in significant improvements in device performance. It was shown by Gollub et al. [76] and Fischer

et al. [78] that fabrication of InGaAsN double quantum wells separated by a GaAsN barrier layer exhibited emission at 1490 nm. The threshold current was reduced by a factor of about three when compared with conventional InGaAsN/GaAs laser diodes. Liu et al. [99] used (In)GaAsN in barrier and spacer layers in MBE grown InGaAsN/GaAs MQWs to achieve improved optical performance at 1550 nm. The results showed a significant improvement in the PL spectra when the nitrogen concentrations in the GaAsN barrier and spacer layers increased from 0.7% to 1%. There have also been some other publications on InGaAsN/GaAsN heterostructures being utilised in the fabrication of laser diodes [89, 100-102].

In 2005, Schumann et al. [103] reported the use of GaAsN as a capping layer grown on InAs quantum dots resulting in a strong red-shift in the emission wavelength to beyond 1300 nm. This was due to the lower conduction band energy of the GaAsN layer with respect to GaAs which caused a decrease in the electron energy confinement. Mamutin et al. published results on strain-compensated InAs/InGaAsN/GaAsN [104] and InAs/GaAsN/InGaAsN [105] heterostructures, showing improvements in PL emission at 1500 and 1760 nm respectively. The heterostructures were grown on GaAs (001) substrates using the MBE technique and there are other publications on similar heterostructures by this group [106-108]. From the above citations, improvements in the optical properties of devices were achieved when GaAsN was used instead of other materials although the use of InAs/In<sub>0.25</sub>Ga<sub>0.75</sub>As/GaAs<sub>0.99</sub>N<sub>0.01</sub> heterostructure grown on GaAs (001) only achieved PL emission at wavelengths up to 1230 nm [109]. Okada et al. [110] successfully fabricated p-i-n quantum dot solar cells using ten-period InAs/GaAsN strain compensated structures grown on GaAs (001) substrates using MBE combined with an RF nitrogen plasma source. The thicknesses of the GaAsN layers were reduced from 40 to 15 nm and the nitrogen content was increased from 0.5% to 1.5%, to balance the strain condition in the layers, which reduced the open-circuit voltage of the devices.
#### 2.1.2.2 InGaAsN

Since Kondow's [3, 111] first investigation of InGaAsN grown by MBE, research on this novel alloy faces many challenges in the quest to achieve emission between 1300 and 1550 nm. However, in recent years significant progress has been made in the development of semiconductor devices capable of emitting in this range, especially on lasers. A Review of the progress made in the development of InGaAsN lasers has been given in section 2.1.1 and a review of InGaAsN/GaAs applications in solar photovoltaic applications has been published by Geisz and Friedman [112]. Some of the recent publications on InGaAsN lasers are discussed in the following paragraphs.

In 2006, Liu et al. [113] reported on InGaAsN TQW RWG lasers fabricated from material grown using the MOCVD technique, with a threshold current density of 130 A/cm<sup>2</sup> and emission at 1300 nm. In the following year, Kasai et al. [114] reported the fabrication of InGaAsN/GaAs TQWEELs and obtained a threshold current of 4.3 mA and an emission wavelength of 1290 nm. The growth of their InGaAsN/GaAs QW structures employed the MBE technique and used an RF plasma as the nitrogen source. In 2008, Zhao et al. [115] fabricated In<sub>0.38</sub>Ga<sub>0.62</sub>As<sub>0.993</sub>N<sub>0.007</sub>/GaAs<sub>0.989</sub>N<sub>0.011</sub>/GaAs TQW lasers with the material grown using MBE. The threshold current density of the lasers was about 400  $\mbox{A/cm}^2$  and they emitted at 1290 nm. Wang et al. [6, 116] demonstrated InGaAsN MQW EELs emitting at 1300 nm fabricated from material grown using the MBE technique and capable of direct modulation at up to 10 Gbit/s at temperatures up to 100°C without any cooling. In<sub>0.38</sub>Ga<sub>0.62</sub>As<sub>0.955</sub>N<sub>0.045</sub> QW distributed feedback laser diodes emitting at 1500 nm were first demonstrated by Bisping et al. [117] in 2008. The material was grown on n-type GaAs (100) substrates using SS-MBE combined with an RF nitrogen plasma source. The laser was operated in continuous-wave and was electrically-pumped with a threshold current of 44 mA. The results showed that InGaAsN QWs have potential in applications at communication wavelengths.

InAs/InGaAsN quantum dots emitting at 1550 nm at room temperature were fabricated for the first time by Odnoblyudov et al. [118]. The structures were grown

on GaAs (001) substrates with nitrogen concentrations up to 2% using SS-MBE. InAs/InGaAsN/GaAs heterostructures were used as strain compensating superlattices (SCSL). Mamutin et al. [119] employed similar structures in their work and observed PL emission at wavelengths up to 1800 nm, which was the longest wavelength achieved for InGaAsN/GaAs heterostructures at that time. Their work used MBE growth combined with an RF nitrogen plasma source.

InGaAsN can be used in VCSEL structures with a buried tunnel junction (BTJ). The acronym for this new device is InGaAsN BTJ-VCSEL and it has been demonstrated by Onishi et al. [120]. The maximum output power of the laser was about 4.2 mW and it operated at 10 Gbit/s and 1300 nm.

Most of the device applications of InGaAsN materials are in EELs and VCSELs as discussed above and in section 2.1.1. However, currently more attention has been given to VCSELs due to some advantages they have over EELs. For EEL structures, photons are emitted horizontally from the edge of the semiconductor wafer and guided using mirrors whereas photons are emitted vertically from the wafer surface in the case of a VCSEL. Another disadvantage of EELs is that the testing process can only be performed at the end of the production process, not at intermediate stages. In contrast VCSELs can be tested at several stages throughout the fabrication process to check for material quality and processing issues. VCSELs can also be fabricated side by side on a wafer to produce thousands simultaneously on a 76.2 mm diameter GaAs wafer. This has a big impact on manufacturing efficiency and cost. Due to these advantages, VCSELs have replaced EELs in applications for short-range fibre optic communications. There are some publications on the simulation of VCSELs to allow design and analysis to be performed (e.g. [121-123]).

There are many other device applications of InGaAsN/GaAs that have been demonstrated in the past few years, such as laser discs [124], vertical cavity semiconductor optical amplifiers (VCSOA) [125-127], photodetectors [128-131], superluminescent diodes (SLD) [7], solar cells [132-134], modulators [135] and

heterojunction bipolar transistors (HBT) [136]. Table 2.1 shows a summary of the applications of GaAsN and InGaAsN as discussed in sections 2.1.2.1 and 2.1.2.2.

Device type	Structure	Wavelength (nm)
Avalanche photodiodes	GaAsN/GaAs	940 to 1064
MSM photodetectors	GaAsN/GaAs	1300
VCSEL	InGaAsNSb/GaAsN	1530
Laser diodes	InGaAsN/GaAsN	1490
Lasers	InAs/InGaAsN/GaAsN	1500
Lasers	InAs/GaAsN/InGaAsN	1760
TQW RWG lasers	InGaAsN/GaAs	1300
TQW lasers	InGaAsN/GaAsN/GaAs	1290
MQW EELs	InGaAsN/GaAs	1300
Laser diodes	InGaAsN/GaAs	1500
Lasers	InAs/InGaAsN	1550
Lasers	InAs/InGaAsN/GaAs	1800
BTJ-VCSEL	InGaAsN/GaAs	1300

Tabel 2.1: A summary of GaAsN and InGaAsN device applications.

# 2.2 Technical Issues Associated with Growing Dilute Nitride Compounds

There are several technical issues that need to be considered when growing high quality III/V dilute nitride compound semiconductors such as GaAsN and InGaAsN. The most important technical issues are the lattice mismatch between the dilute nitride compound and its growth substrate, the effect of immiscibility and the efficiency of the nitrogen source in producing atomic nitrogen. Kondow et al. [137] considered that addressing these issues was responsible for their success in the growth of GaAsN using GS-MBE combined with an RF plasma source, achieving nitrogen concentrations of up to about 10%. The following sections discuss these three technical issues associated with growing GaAsN and InGaAsN epitaxial layers.

# 2.2.1 Lattice Mismatch

The lattice mismatch between an epitaxial layer and its growth substrate is the most important issue to be addressed in growing high quality GaAsN and InGaAsN epitaxial layers. GaN and InN can both crystallise in zinc-blende, cubic or wurtzite structures, however in this work the binary compounds GaN and InN of zinc-blende structure are relevant because all substrates used in the experiment were GaAs. The lattice constant values for GaN and InN (zinc-blende crystal structures) used in this work are shown in Table 3.2 in section 3.3.1.4. For the InGaAsN quaternary alloy, the binary compounds GaN and InN have smaller lattice constants than GaAs while InAs has a larger lattice constant. However, the lattice constant difference between GaAs and GaN is the largest of all the binary compounds in InGaAsN. The lattice constant and band gap energy of an InGaAsN alloy can be controlled by adjusting the ratios of indium to gallium and nitrogen to arsenic. Increasing the indium to gallium ratio causes a reduction in the band gap and an increase in the lattice constant, while increasing the nitrogen to arsenic ratio also causes a band gap reduction, but with a decrease in the lattice constant. Therefore, InGaAsN gives some modest flexibility of control over both band gap and lattice constant. The InGaAsN alloy can be lattice-matched to GaAs by setting the indium to nitrogen mole fraction ratio to about 3:1. The problem associated with the lattice mismatch between InGaAsN epitaxial layers and the GaAs growth substrate can be solved in this way, but it does not result in a material capable of light emission in the 1300 to 1550 nm band. For this purpose higher levels of indium must be used, resulting in compressively strained layers with a finite layer critical thickness before the onset of misfit dislocation formation.

There are several methods that could be employed to deal with the lattice-mismatch problem in MBE growth, as have been described by Arthur [138]. The common method is to grow an epitaxial layer with a thickness less than the critical layer thickness. As long as the layer thickness is below the critical value, a planar and coherent epitaxial layer can be grown on a mismatched substrate. The practice of growing a graded buffer layer can also be applied to grow this class of compounds. By varying the composition from the substrate to the epitaxial layer, the lattice constant of the layer can be altered, although misfit dislocations are inevitably formed. Another approach is to introduce a strained super-lattice buffer containing

alternating layer strains either in tension or compression as a strategy to filter dislocations generated at the strained layer-substrate interface. The advantage of this method is that it can to a certain extent limit the penetration of dislocations into the device layers of interest. A chart of bandgap versus lattice constant for the various binary alloys that discussed in this section is shown below. The red horizontal line indicates the line of wavelength for the 1550 nm.



Figure 2.1: A chart of band gap versus lattice constant for GaAsN.

# 2.2.2 Immiscibility

Immiscibility is a significant problem since it limits the levels of nitrogen that can be introduced into epitaxial layers. Some of the factors contributing to this problem are the differences in the bond lengths and lattice constants of GaN and GaAs binary compounds. For the ternary alloy GaAsN, the large lattice constant difference of 20% between GaAs and GaN makes the equilibrium solubility of nitrogen in GaAs about 2% when grown at 527°C [42]. Zhang and Wei [139] calculated the maximum

solubility of nitrogen to be about 4% when grown at a substrate temperature of 650°C. The large miscibility gap in GaAsN compounds therefore makes binary compounds phase-separate when the nitrogen content becomes appreciable [140]. This makes the crystal quality of dilute nitride compounds deteriorate with increasing nitrogen concentration due to phase separation. Generally in GaAsN compounds, nitrogen atoms incorporate substitutionally on arsenic lattice sites causing tensile strain in the layer. However, due to the low solubility of nitrogen in GaAs a proportion of the nitrogen atoms incorporate non-substitutionally, which degrades the electronic and optical properties of the layers.

Thomas et al. [141] reported a study of nitrogen incorporation in InGaAsN and GaAsN near the solubility limit using chemical beam epitaxy (CBE) as the growth method. They found that thick InGaAsN and GaAsN layers containing nitrogen below the solubility limit showed good crystalline quality. To overcome the immiscibility issue, highly non-equilibrium growth techniques such as MBE or MOVPE have been used to grow epitaxial layers with high crystalline quality. As explained before however, the layer thickness must be less than its critical value in order to avoid the formation of misfit dislocations. Epitaxial layers grown thinner than the critical thickness have coherent interfaces, whereas thicker layers have enough strain energy to force the formation of structural defects which results in incoherent interfaces.

# 2.2.3 Nitrogen Sources

Using a highly efficient nitrogen source to generate reactive nitrogen species is essential for the growth of the dilute nitrides InGaAsN and GaAsN on GaAs (001) substrates. The use of ammonia and dimethylhydrazine (DMHy) compounds as nitrogen sources is not compatible with an ultra-high vacuum (UHV) environment. Currently, nitrogen plasma sources are widely used for the growth of the III/V dilute nitrides, producing beams of neutral and charged atoms and molecules. The beams from the nitrogen plasmas contain a variety of nitrogen species (i.e. N, N<sub>2</sub>, N<sup>+</sup>, N<sup>+</sup><sub>2</sub>, N<sup>-</sup>and N<sup>-</sup><sub>2</sub>) however only atomic nitrogen is required for the growth of the nitride compounds. The presence of nitrogen ions in the growth chamber can affect the quality of GaAsN and InGaAsN layers by striking and damaging the epitaxial layer surface. The damaged surface could contribute a higher number of non-radiative recombination centres which will result in a decreased PL peak intensity [142-146] and associated surface roughness [146, 147].

Several methods can be used to eliminate nitrogen ions from the growth process, such as using ion removal magnets (IRMs) [143] or ion traps [142, 144, 145]. Their function is to prevent ions from hitting the substrate during the growth process by capturing or deflecting all charged species. There are also several kinds of nitrogen plasma sources such as RF plasma, direct current (DC) plasma and ECR plasma sources. While RF plasma sources are the most commonly used today for the production of atomic nitrogen, in this work an ECR nitrogen plasma source was used as a source of atomic nitrogen from high purity  $N_2$  gas. The advantages of an ECR nitrogen plasma source when compared with other sources are described in the next section.

There are still remaining difficulties in obtaining high quality 1550 nm InGaAsN materials and devices due to the miscibility problem and consequent phase separation. It is therefore important to understand the technical issues associated with growing GaAsN and InGaAsN epitaxial layers for technological purposes. The optimisation of the growth conditions and the choice of growth methods are thus critical in order to achieve satisfactory quality epitaxial layers of GaAsN and InGaAsN. The following section describes the growth conditions required to obtain good quality dilute nitride compounds.

# 2.3 MBE Growth of the Dilute Nitrides

The MBE growth conditions are important factors in determining the success or otherwise of dilute nitride growth. The effect of the growth conditions on the rate of incorporation of nitrogen and the resulting properties of GaAsN and InGaAsN epitaxial layers are discussed below.

# 2.3.1 Nitrogen Incorporation

In MBE growth, there are several ways to raise the incorporation rate of nitrogen atoms during growth, such as increasing the power of the nitrogen plasma source [60, 142, 148-151], increasing the molecular nitrogen flux to the source [52, 142, 149, 150], reducing the group III growth rate [19, 143, 149, 151-158] or reducing the growth temperature [82, 148, 149, 151, 152, 154, 155, 159, 160]. Increasing the power and/or molecular nitrogen flux results in an increase in the nitrogen concentration [148-151] but can also significantly reduce the PL intensity due to a decreased efficiency of radiative recombination [52, 60, 142]. The option of reducing the growth rate is preferred because this can still result in strong room temperature PL as demonstrated by Wang et al. [157] and Zhao et al. [19]. They reduced the growth rate from 1 to 0.125  $\mu$ m/h for the growth of an 18 nm thick strained GaAsN/GaAs QW, producing emission at a wavelength of about 1440 nm. They showed that the incorporated concentration of substitutional nitrogen varies linearly with the inverse of the GaAsN growth rate up to about a nitrogen concentration of 5.9% and for a growth rate of more than 0.2  $\mu$ m/h. Wang et al. [151] showed that the nitrogen content in GaAsN reduced from 2.82% to 2.03% as the growth rate was increased from 0.5 to 1  $\mu$ m/h. Pan et al. [152, 154] reported that the nitrogen concentration in InGaAsN layers dropped from about 0.85% to 0.4% when the growth rate was increased from about 0.9 to 2  $\mu$ m/h. There are also other reports showing the nitrogen concentration in InGaAsN reduces with increasing growth rate [143, 156].

Reducing the growth temperature can also have an effect on nitrogen incorporation rates and on the optical properties of the resulting material. Pavelescu et al. [160] reported on the effect of the growth temperature on the nitrogen incorporation rate for InGaAsN/GaAs epitaxial layers grown using SS-MBE. Using x-ray diffraction to measure nitrogen content, they found that the nitrogen concentration in InGaAsN layers decreased when the growth temperature increased from 410°C to 470°C and the relationship appeared to be linear over this temperature range. Nishikawa et al. [159] also found the nitrogen concentration in GaAsN reduced with increasing

growth temperature, having investigated the temperature range from  $530^{\circ}$ C to  $600^{\circ}$ C, which supports the previous report on GaAsN growth at temperatures from 550°C to 620°C [148]. Wang et al. [151] reported the nitrogen content in GaAsN dropped from 2.65% to 0.85% as the growth temperature was increased from  $460^{\circ}$ C to  $580^{\circ}$ C. Some groups have found that the nitrogen concentration in GaAsN and InGaAsN layers was independent of growth temperature from 420°C to 500°C but dropped at temperatures above 500°C [149, 152, 154, 155]. Liu et al. [82] observed strong room temperature PL at 1580 nm when InGaAsN/GaAs MQWs were grown at 375°C, but the intensity decreased when samples were grown at 350°C and 400°C. Their x-ray diffraction (XRD) results showed that the satellite peaks from InGaAsN MWQs grown at 375°C had better intensity and narrower peak full width at half maximum (FWHM's) than samples grown at 350°C and 400°C, indicating improved crystalline quality. According to Jaschke et al. [81] the optimum growth temperature to grow InGaAsN and obtain the maximum PL intensity at 1480 nm was about 350°C (quite low compared to the other cited publications) in layers with a 4% nitrogen concentration. The effect of the growth temperature on the rate of nitrogen incorporation also depends on the type of nitrogen plasma source that is used during growth and this matter is discussed in the next paragraph.

The nitrogen concentration in GaAsN begins to reduce rapidly at growth temperatures above about 500°C when using an RF nitrogen plasma source [148, 149, 159, 161, 162] and the same result was obtained by Pan et al. [152, 154] in InGaAsN QWs although they were using a DC plasma as their nitrogen source. However, according to Mars et al. [14] and Usher et al. [145, 163], there is a weak dependency of the nitrogen concentration in GaAsN on the substrate growth temperature between 400°C and 600°C when using MBE growth and an ECR nitrogen plasma source. Thus the growth temperature and the type of nitrogen plasma source used are critical to obtaining high quality dilute nitride layers. The benefit in using an ECR plasma source instead of an RF plasma source is that the dilute nitride layers can be grown at 600°C without significant loss of nitrogen, as described in references [14, 145, 163]. Since the optimum growth temperature for MBE grown

GaAs is about 600°C, it is expected that a similar growth temperature will be optimum for the growth of dilute nitride layers. In contrast, there is a decrease in the nitrogen concentration in GaAsN and InGaAsN layers when grown at substrate temperatures higher than 500°C when using an RF plasma or DC plasma source. Consequently, GaAsN and InGaAsN layers must be grown at substrate temperatures of about 480°C when using RF plasma and DC plasma source with a concomitant reduction in the epitaxial layer quality when compared with growth at 600°C using an ECR plasma source.

Since an ECR nitrogen plasma source was used in this work, reducing the growth rate and increasing the plasma power were more effective than other methods to control the rate of incorporation of atomic nitrogen in the epitaxial layers. By changing the group III growth rate, while keeping the plasma power and nitrogen flux constant, the nitrogen concentration in layers could be changed since the nitrogen concentration is then inversely proportional to the GaAs growth rate. The plasma power could also be increased, or the molecular nitrogen flow rate increased, to achieve higher nitrogen incorporation rates. The growth temperature used to grow GaAs and dilute nitride epitaxial layers were 600°C and 540°C respectively for the work reported here. However, some GaAsN layers were grown at the lower substrate temperature of 460°C for reasons that will be explained in chapter 6.

For the growth of InGaAsN quaternary alloys, it is important to be aware of the relationship between the rates of indium and nitrogen incorporation in a layer. Harmand et al. [164] reported that nitrogen incorporation was not affected by the presence of indium in an InGaAsN layer, based on SIMS and XRD data. For the SIMS measurements, the sample structure consisted of a GaAsN reference layer from which the nitrogen content in the layer would be determined, together with layers containing increasing amounts of indium. They showed that the nitrogen incorporation rate was almost independent of the indium composition. These researchers XRD from GaAs/GaAsN/InGaAsN compared spectra and GaAs/GaAsN/InGaAs structures, and their investigation showed that the

compositions of indium and nitrogen were similar in all layers. This is in agreement with the work of Kondow and Kitatani [156], who also showed that nitrogen incorporation was almost unchanged at different indium mole fractions. Litvinov et al. [165] found that the indium content in InGaAs and InGaAsN samples were identical based on XRD scans, showing that the indium concentration was not affected by the presence of nitrogen in InGaAsN layers.

However, Wang et al. [151], Rubini et al. [166], Liu et al. [167] and Zhou et al. [168] suggested that there is a dependency between the rates of nitrogen and indium incorporation in InGaAsN layers. Wang et al. [151] demonstrated that rates of nitrogen incorporation in InGaAsN epitaxial layers decreased with increasing indium concentration. They grew two InGaAsN samples with different indium compositions of about 25% and 36% and the nitrogen composition in the samples were found to be 0.85% and 0.45% respectively. The results were verified by measuring the nitrogen composition in GaAsN layers grown under the same growth conditions as the two samples containing InGaAsN layers, and the nitrogen composition was found to be about 1%. They suggested that the main reason for this could be due to the increase in the growth rate with increasing indium flux during the growth of InGaAsN layers. Rubini et al. [166] discovered that the indium incorporation rate reduces monotonically with increasing nitrogen concentration in InGaAsN compared with the rate of indium incorporation in InGaAs. They suggested that this was due to the stronger bond energy of GaN (i.e. 2.24 eV [169]) compared to InN (i.e. 1.93 eV [169]) which makes the tendency for nitrogen to attach to gallium higher than to attach to indium. Liu et al. [167] demonstrated that the incorporation of nitrogen in InGaAs also appears to increase the indium segregation coefficient from 0.75 to 0.81. All of the research discussed above used SS-MBE as their growth method with the exception of Zhou et al. [168] who used metal-organic molecular beam epitaxy (MOMBE) and observed an increase in nitrogen concentration with increasing indium mole fraction in InGaAsN layers. They compared their results with previous publications and found that the growth method was the main factor determining the relationship between rates of indium and nitrogen incorporation in the alloy

InGaAsN. Table 2.2 shows a summary of the nitrogen incorporation reviews for InGaAsN layers discussed above.

Table 2.2. The summary of introgen meorporation review for mourisivitayers.				
Authors	Growth Method	Experiment result		
Harmand et al. [164]	SSMBE	N incorporation not		
		affected by In		
Kondow and Kitatani [156]	SSMBE	N incorporation not		
		affected by In		
Wang et al. [151]	SSMBE	N incorporation		
		affected by In		
Rubini et al. [166]	SSMBE	N incorporation		
		affected by In		
Liu et al. [167]	SSMBE	N incorporation		
		affected by In		
Zhou et al. [168]	MOMBE	N incorporation		
		affected by In		

Tabel 2.2: The summary of nitrogen incorporation review for InGaAsN layers.

#### 2.3.2 Influence of Arsenic on the Growth of GaAsN

There have been contradictory reports in the literature regarding the effect of arsine pressure on the growth of GaAsN layers. The arsenic pressure has an influence on the rate of nitrogen incorporation in III/V dilute nitride epitaxial layers at lower growth rates but not at growth rates above 0.4 monolayer (ML)/s. Sun et al. [149] observed that the nitrogen concentration was significantly influenced by changes in arsenic flux for GaAsN layers grown at lower growth rates but that this effect has little influence on nitrogen concentrations at higher growth rates. They used MBE in combination with an RF plasma source to grow the GaAsN samples. Other researchers have also found that the nitrogen concentration in GaAsN and InGaAsN layers was not affected by changes in arsenic pressure at fixed nitrogen fluxes and growth rates above 0.4 ML/s [152-154]. This suggests that the nitrogen atom has close to unit sticking coefficient at higher growth rates. It also shows that the arsenic pressure does not have to be accurately controlled to achieve reproducible nitrogen concentrations in GaAsN and InGaAsN layers grown at growth rates above 0.4

ML/s. In this respect, the GaAsN/GaAs and InGaAsN/GaAs systems seem to have a distinct advantage over other material systems.

The arsenic pressure can also influence some of the other properties of dilute nitride layers, such as the structural quality and surface morphology. Fujimoto et al. [148] reported an improved surface morphology of GaAsN when grown at lower arsenic fluxes towards a gallium-rich regime as monitored by observing a reflection high energy electron diffraction (RHEED) pattern. They observed a spotty RHEED pattern, indicative of three dimensional growth, at high arsenic pressures when the surface is in an arsenic-rich condition and the sample surface morphology was milky under these conditions. This observation has been confirmed by Nishikawa et al. [159], that the optimum arsenic pressure for the growth of dilute nitride materials was just above the minimum arsenic pressure required to maintain stoichiometric growth. Their results showed that the intensity ratio of the GaAsN layer to the GaAs substrate peak in XRD spectra displayed a maximum under these minimum arsenic conditions and the surface roughness as determined by atomic force microscopy (AFM) remained low. They also showed that increasing the arsenic pressure resulted in an increased surface roughness and a decrease in the layer to substrate peak intensity ratio. The effect of arsenic pressure on the optical properties of dilute nitride layers is discussed in the next paragraph.

The influence of the arsenic pressure on PL intensity is of interest and Li et al. [143] found that the PL peak intensity was decreased in InGaAsN QW layers emitting at 1250 nm when GaAs buffer layers were grown under a higher arsenic pressure. It seems that the nitrogen concentration in InGaAsN layers is affected by changing the arsenic pressure during growth of GaAs buffer layers. Therefore, the quality of the buffer layers plays an important role in determining the quality of subsequent InGaAsN layers. Egorov et al. [155] reported the sticking coefficient in GaAsN layers decreased with increasing arsenic to nitrogen flux ratio at constant nitrogen flux. Pavelescu et al. [170] investigated the influence of arsenic pressure on PL intensities and structural properties of InGaAsN/GaAs QWs grown under different

V/III arsenic pressure ratios with all other growth parameters kept constant. They found that the strongest emission was obtained at a V/III beam equivalent pressure ratio of 10 in layers designed to emit at 1300 nm. The emission wavelength remains unchanged for ratios between 8 and 12 which means, in this range, the V/III flux ratio does not affect the alloy composition or the sticking coefficient. But nitrogen incorporation into the layer is increased if the ratio is less than 8 and decreased if the ratio is more than 12. However, Jaschke et al. [81] reported that employing low V/III flux ratios for the growth of InGaAsN resulted in increases in PL intensity and wavelength for V/III flux ratios between 1 and 1.2 before dropping rapidly for V/III flux ratios of more than 1.2. Their nitrogen concentrations and emission wavelengths were about 4% and 1530 nm respectively.

On the other hand, Kondow and Kitatani [156] recorded PL spectra from InGaAsN/GaAs layers grown using different arsine flow rates and V/III flux ratios. For arsine, the optimum flow rate was 10 sccm which is equivalent to a V/III flux ratio of about 6 as suggested by the PL peak intensities from InGaAsN. The growth rate and substrate temperature used were 1  $\mu$ m/h and 460°C respectively. When using metal arsenic, the PL intensity from InGaAsN layers was found to increase for V/III flux ratios between 1.1 and 7.0. For these experiments a higher growth rate of 3  $\mu$ m/h was used. Based on these results, InGaAsN crystal quality can be improved using a combination of higher V/III flux ratios and higher growth rates. These results appear contradictory to some of the work cited earlier, where PL intensities decreased as the arsenic pressure was increased.

# **3** Equipment and Experimental Procedures

The equipment and experimental methods used to grow group III/V dilute nitride compound semiconductor epitaxial layers may vary from one research group to another. This chapter explains in detail the equipment and experimental procedures employed to grow and study the samples discussed in this thesis.

# 3.1 Semiconductor Growth

A variety of growth techniques are used to grow compound semiconductor epitaxial layers, for example MOCVD, MOVPE, MOMBE, GS-MBE and SS-MBE. All of these techniques have been developed with the expectation of producing high quality materials and material structures which can be used to produce high performance devices. However, MBE is one of the most popular techniques to study the growth of group III/V dilute nitride compound semiconductors because it is compatible with a range of vacuum based analytical tools such as RHEED, auger electron spectroscopy (AES) or x-ray photoelectron spectroscopy (XPS), which can be used in-situ to monitor the physical and chemical properties of a layer. The MBE technique involves the evaporation of atoms and molecules originating from individually shuttered elemental or molecular evaporation sources, onto a heated semiconductor substrate surface. Some other advantages MBE has over other techniques are the possibility of slower growth rates and the ability to create sharp interfaces by the rapid operation of mechanical shutters situated in front of the effusion cells. Accurate regulation of the source temperatures allows precise control of beam fluxes and therefore layer thicknesses, layer compositions and doping levels during the growth of complex multilayered structures. The operation time of the mechanical shutters is

significantly less than the time taken to grow a monolayer, which is typically one second. MBE takes place in a UHV chamber with background pressures typically in the range of  $10^{-9}$  to  $10^{-10}$  Torr which minimises the probability of the molecular beams suffering gas phase collisions and reduces the probability of incorporation of impurity atoms.

The technique employed to grow the samples discussed in this thesis was SS-MBE in which solid arsenic was used as the  $As_4$  source. The use of solid arsenic during InGaAsN epitaxial growth yields improved crystal quality compared to epitaxial layers grown using arsine gas in GS-MBE [171]. In SS-MBE, the source atoms or molecules are heated in separate effusion cells until they evaporate or sublime. The cells are held at temperatures such that their vapour pressures are sufficiently high to generate the required atomic or molecular beam fluxes. The beams of atoms or molecules from these effusion cells are incident on a semiconductor substrate which is at a temperature lower than that of the cells (with the exception of arsenic) which makes them condense onto the substrate to produce a crystalline epitaxial layer. Normally, MBE systems are configured for a specific material system and for this work also the system was configured for the growth of group III/V compound semiconductors on GaAs substrates. The materials grown for the study discussed in this thesis were InGaAsN, GaAsN, InGaAs, GaAs and AlAs.

# 3.1.1 MBE Growth System

The MBE system used for the growth of all samples discussed in this thesis was a highly modified Varian MBE-360 system as shown in Figure 3.1. This photo shows the growth chamber on the left, the intermediate chamber in the centre foreground and the entrance load-lock and associated ion pump in the right background. The system thus consisted of three chambers separated by two gate valves and each of the chambers was pumped independently, by ion pumps for the growth and intermediate chambers and by a turbo-molecular pump for the load-lock.



Figure 3.1: The III/V SS-MBE system at La Trobe University.

After samples were loaded into the load-lock and satisfactory vacuum conditions achieved, they were transferred from chamber to chamber at lower and lower vacuum conditions using transfer rods. A further description of each chamber and its role is given below:

a) The load-lock chamber was pumped by a 230 l/s turbo-molecular pump which was backed by a diaphragm pump to achieve a pressure between 10<sup>-6</sup> and 10<sup>-7</sup> Torr. This chamber was used to move samples into and out of the MBE system without compromising the main chamber's vacuum. During sample exchange the load-lock chamber was flushed with dry nitrogen gas, the blow-off from a bulk liquid nitrogen vessel, to minimise water contamination of the chamber. All samples loaded into the chamber were soldered to molybdenum (Mo) blocks with indium. Up to four Mo blocks could be mounted onto a stainless steel carousel for introduction into the load-lock chamber. The carousel was installed onto a transfer rod in this chamber and was pumped for at least two hours before being transferred into the intermediate chamber.

- b) The intermediate chamber was pumped by a 180 l/s ion pump to achieve a chamber base pressure of about 10<sup>-9</sup> Torr. The chamber functioned as a buffer between the load-lock and growth chambers and samples were kept overnight in this chamber before being transferred to the growth chamber.
- c) The growth chamber was pumped by a 400 l/s ion pump to achieve a residual gas pressure between  $10^{-9}$  and  $10^{-10}$  Torr. The ion pump could be isolated from the growth chamber in the event that it had to be let up to air by an isolating gate valve.

Connected to the growth chamber via an all-metal bakeable valve was a roughing manifold to which were connected two sorption pumps which could be used to evacuate the entire system from atmospheric pressure to between  $10^{-4}$  and  $10^{-6}$  Torr should the chamber need to be opened for repairs or to recharge sources. Following evacuation of the chamber by the sorption pumps, the bakeable valve was closed using a torque wrench and leak tested by admitting nitrogen gas to the roughing manifold and monitoring the N<sub>2</sub> peak on a quadrupole mass spectrometer (QMS), to ensure it had sealed completely.

In addition to the vacuum chambers, Figure 3.1 also shows the manipulator which is used to rotate the sample between the loading and growth positions and these movements were controlled manually. In this MBE system the sample was oriented vertically in the growth chamber and there were three view ports with which to view the interior during sample exchange and growth.

## 3.1.1.1 MBE Growth Chamber

The growth chamber is the most important part of an MBE system and there were several components located within the La Trobe system which were used to control and monitor epitaxial growth. The MBE growth chamber used in this work was equipped with an analytical RHEED system, a QMS and an ion gauge as shown in Figure 3.2. The RHEED system was used to monitor the sample surface prior to and during epitaxial growth and consisted of a 10 keV RHEED gun and a phosphor screen. The 10 keV RHEED gun emitted electrons that were incident on a GaAs substrate at an angle of about 2.4° and the diffraction pattern generated was observed on the phosphor screen.



Figure 3.2: Schematic top view of the RHEED, QMS and substrate assemblies in the growth chamber. The inset shows a side view of the ion gauge and substrate assembly.

The QMS was in close proximity to the sample position and was used to monitor the background gas composition before and during epitaxial growth and to monitor the species emerging from the beam sources. The main components of the QMS were an RF generator, a probe (containing ioniser, quadrupole mass filtering section, a Faraday cup or electron multiplier) and a control console.

The ion gauge used in the MBE growth chamber was positioned at  $90^{\circ}$  to the Mo block and was used to measure the background pressure or the source beam equivalent pressures by manually rotating it to face the furnaces.

Figure 3.3 shows a schematic view of the sample, Mo block, sample heater assembly and thermocouple. The Mo block was heated by four tungsten filaments connected in series and the block's temperature was measured by a thermocouple positioned behind, but not in contact with, the Mo block. The thermocouple was not attached directly to the sample because the sample must be able to be rotated continuously. This means that there was a significant difference between the true sample temperature and the temperature measured by the thermocouple. The temperature was calibrated against changes in the RHEED surface reconstruction pattern for each sample, as is explained in section 3.2.2.

In addition to the main ion pump, the MBE growth chamber also contained a liquid nitrogen shroud which helped maintain satisfactory vacuum conditions, mainly by pumping water vapour very efficiently. The liquid nitrogen from this vessel was recycled into a doughnut surrounding the sources which helped to trap gases in the growth chamber in the vicinity of the growth surface, thus reducing the levels of unintentional impurity doping in epitaxial layers.



Figure 3.3: Schematic view of the sample heater, thermocouple for temperature measurement, Mo block with bayonet pins and acceptance slots for these pins.

# 3.1.1.2 MBE Sources

The beam sources used in the MBE system were group III elemental sources of gallium, indium and aluminium and group V sources of arsenic and nitrogen and Figure 3.4 shows the configuration of the beam sources in the growth chamber. Nitrogen and hydrogen were the only gas sources in the MBE system, however only the nitrogen source was used in this work. The purity of the nitrogen gas was better than 99.9999% and the details of the nitrogen source's operation are given in section 3.1.1.2.1. The silicon and beryllium sources could be used as n and p-type dopants, however they were not required in this study. The solid source cells were made from refractory materials and the elements in these effusion cells were evaporated from pyrolytic boron nitride (PBN) crucibles. The crucibles were fabricated from PBN because this material has a low rate of gas evolution, is chemically stable up to

1500°C and does not contribute to the molecular beams. The source materials were all high-purity (above 99.9999%) materials.



Figure 3.4: Schematic rear view of the MBE source flange.

Each of the solid source effusion cells employs a thermocouple to measure its temperature, which was controlled using a computer interfaced PID (proportional-integral-derivative) controller, providing a flux stability of about  $\pm 1\%$ . The stability of the effusion cell temperatures is crucial because fluxes are strongly dependent on temperature. All cells were equipped with individual mechanical beam shutters that were pneumatically driven from outside the growth chamber. Operation of the shutters allowed rapid changing of the beam species in order to abruptly alter the composition of a growing epitaxial layer at the surface.

The effusion cells were arranged such that their fluxes were focussed onto the centre of the substrate surface. By choosing appropriate effusion cell and substrate temperatures, epitaxial layers of the desired chemical composition could be grown. The effusion cells were thermally separated by a solid aluminium wheel which was cooled to prevent thermal cross talk between cells. The coolant circulating in the aluminium wheel was supplied from a water chiller situated outside the MBE lab. For extra cooling purposes, the external throats of the effusion cells were wrapped with copper coils through which coolant flowed from the same water chiller.

All sources and beam shutters could be operated manually or by computer control. By using computer control, the substrate and effusion cell temperatures and temperature ramp rates, as well as complex shutter operations could easily be programmed. The control software allowed the growth of complex multilayer structures under full computer control.

#### 3.1.1.2.1 Nitrogen Plasma Source

High-purity nitrogen gas flowed from a cylinder into the plasma source. Atomic nitrogen was generated by an ECR microwave nitrogen plasma source (Tectra<sup>TM</sup>) with the microwaves coming from a magnetron operating at 2.45 GHz. The ECR plasma was created by the resonant absorption of microwave energy by electrons following which they are stripped from their host nitrogen molecules which become unstable and dissociate. A schematic view of the nitrogen plasma source is shown in Figure 3.5.

The microwave generator could deliver power up to a maximum of 50 W and was monitored and controlled by a PID control circuit. The minimum current which had to be supplied to the magnetron to ignite the plasma was about 10 mA and the maximum current could not exceed 25 mA. The currents used in this work were in the range from 12 to 18 mA. With reference to Figure 3.5, microwave energy from the magnetron is transferred to the boron nitride (BN) plasma chamber via a resonant coupler and an antenna. The flow of nitrogen gas to the BN plasma chamber was regulated by a precision variable leak valve which was opened and closed by a stepper motor connected through a 50:1 gearbox, which could be controlled electronically or manually. The nitrogen gas pressure in the growth chamber was monitored via the mass 28 peak from a QMS or via the ion pump current which was a measure of the high background  $N_2$  pressure and proved to correlate well with the atomic nitrogen flux (see chapter 5 section 5.2).



Figure 3.5: Schematic view of the nitrogen plasma source (redrawn from Reference [172]).

The plasma was confined to a BN chamber which was connected to the MBE growth chamber via a BN aperture containing 100 holes, each with a diameter of 0.2 mm. The pressure in the plasma chamber was considerably higher than in the MBE growth chamber, to allow the plasma to strike. The BN aperture provided flow resistance and thus allowed for a significant pressure difference between the plasma chamber and the growth chamber. The nitrogen plasma produces many nitrogen species, for example positive and negative nitrogen ions, excited nitrogen molecules and atoms. Therefore, an ion trap (a pair of parallel metal plates) was situated at the BN aperture exit to extract ions from the plasma and eliminate them from the growth process. The potential on the plates could be increased from 0 to 5 kV, however in this work the ion trap voltage was set to 50 V for reasons as reported by Usher et al. [145, 163]. Increasing the trap voltage resulted in evidence of defect formation and structural damage, probably caused by ions from the trap plates. The nitrogen plasma

source was also equipped with a water cooling system in order to avoid damaging the magnetron.

# 3.2 MBE Growth Procedures

The growth procedures, which included substrate preparation, setting source and substrate temperatures, and the growth process itself are important elements in the MBE process because they influence the quality of the epitaxial layers grown. The following sections describe the growth procedures followed in this work.

# 3.2.1 Substrate Preparation

Substrate preparation is an essential step for successful MBE growth because any contamination of a substrate can severely interrupt the growth process. Any contamination of the substrate can also create defects in an epitaxial layer, such as stacking faults and dislocations [173] and in extreme cases may completely destroy the possibility of epitaxial growth. The substrates used in this work were all GaAs (001). For a material study of this nature only small samples are required, of the order of 10 mm x 10 mm. Therefore, wafers were scribed with a diamond tip along [110] and  $[1\bar{1}0]$  directions and cleaved to create such pieces. All substrates were degreased and etched using semiconductor grade chemicals as explained in the next paragraph.

The substrates were degreased for three to five minutes in Teflon beakers containing 10 ml of trichloroethylene and placed in an ultra-sonic bath to enhance the process of removing any organic materials from the surface. The beaker was drained of trichloroethylene and rinsed twice in 10 ml of acetone to completely dissolve the trichloroethylene. It was immersed in 10 ml of acetone and again placed in an ultra-sonic bath for three to five minutes before being rinsed twice in 10 ml of methanol. The beaker was then drained of methanol and the substrate rinsed in de-ionised (DI) water at least three times to dissolve any residual methanol and then immersed in 10 ml of concentrated sulphuric acid ( $H_2SO_4$ ) (96%), a highly hygroscopic liquid, to

dissolve any remaining water. The substrate could be left in the  $H_2SO_4$  for many hours before the commencement of the next step.

The next step was chemical etching of the substrates, with a freshly prepared mixture of  $6H_2SO_4$ : $1H_2O_2$ : $1H_2O$ . For etchant preparation, hydrogen peroxide ( $H_2O_2$ ) (30%) and water were premixed in the proportions of 1:1 and the mixture stored at 4°C, together with  $H_2SO_4$ , to ensure that both mixtures were cool before being used. The  $H_2O_2$ : $H_2O$  mixture was then added to  $H_2SO_4$  in the ratio of 1:3 and stirred using a clean Teflon rod to ensure they mix completely. This mixing of the etchant initiates an exothermic reaction and the temperature of the etchant increases to give a greater etching rate. It is to reduce the temperature of the etch and therefore the etch rate that the  $H_2O_2$ : $H_2O$  and  $H_2SO_4$  reactants were refrigerated before mixing. The  $H_2SO_4$  was drained from the substrate and the etchant added while the beaker was shaken gently by hand to ensure the accumulation of etch products did not interfere with the etching process. The etching process was continued for 90 seconds and the etch rate was approximately 7.7  $\mu$ m/minute, enough to remove non-organic contaminants from the substrate surface.

The etchant was drained from the substrate before being flooded with DI water to stop the etching process. The substrate was then rinsed three times in DI water and immediately mounted on a Mo block. The block was heated to about 160°C on a hot plate and the centre evenly wetted with high-purity indium before the substrate was placed onto the indium layer and moved gently using tweezers to ensure it wet the substrate back evenly. During this time the block was kept only just above the indium melting temperature (about 157°C) to limit oxidation of the indium. Any excess indium on the block was removed using a scalpel blade after the substrate had been soldered to the block. In preparation for growth, the substrate temperature was increased well above the indium melting temperature but the substrate remained attached to the Mo block due to surface tension. The indium provided good thermal conduction between the block and the GaAs substrate, thus ensuring a uniform temperature across the substrate.

Several substrates were prepared at a time and up to four blocks with mounted samples were placed on a carousel before being introduced into the load-lock chamber. After pumping for at least two hours, the carousel was transferred from the load-lock into the intermediate chamber using a transfer rod. When the pressure in the intermediate chamber had returned to about  $10^{-9}$  Torr, the substrates were loaded one at a time into the growth chamber. The procedures followed during growth are described in the following sections.

## 3.2.2 Growth Process

The solid source furnaces in the growth chamber were degassed for several hours by setting the gallium, indium, aluminium and arsenic furnace temperatures a little above their operating values, while the furnaces not required for the growth remained idle at 100°C and this helped reduce the residual gas background in the growth chamber. Following the cleaning process described in the previous section, oxides of gallium and arsenic remain on the substrate surface and these were removed thermally before growth, the final cleaning step for the substrates.

The arsenic shutter remained open throughout the oxide removal process to maintain the stoichiometry of the GaAs surface once the oxides had been removed, the arsenic background being monitored using a QMS or an ion gauge. The ion gauge could be used to measure the arsenic beam equivalent pressure by rotating it to occupy the same position as the substrate during growth. Oxide removal was monitored in-situ using the RHEED system, with the diffraction pattern showing a diffuse halo indicating a polycrystalline or amorphous layer on the substrate surface prior to oxide removal. After some time the RHEED pattern changed to a pattern characteristic of a GaAs single crystal with clear Kikuchi bands. The surface oxides were removed between indicated temperatures of 540°C and 640°C, the temperature varying from block to block. It was important to ensure all oxides had been completely removed from the substrate's surface as any remaining oxides would affect the quality of the grown layer or even destroy the growth process completely. Therefore, after the surface oxides had been removed, the substrate temperature was reduced by  $10^{\circ}$ C and held at this temperature for at least 10 to 15 minutes. Subsequently, a GaAs buffer layer was grown first at this substrate temperature, known from experience to be approximately 600°C, to smooth the surface. The RHEED pattern generally changed from spotty to streaky after a few minutes of GaAs growth and a clear 4x2 RHEED diffraction pattern was then obtained.

Following the establishment of a smooth surface the substrate temperature was reduced slowly in order to observe the RHEED pattern transition between the 2x4 and c(4x4) surface reconstructions, known to occur at a true surface temperature of 530°C [172]. Because the thermocouple and substrate surface temperatures will be equal at room temperature, the relationship between the temperature  $T_{ind}$  indicated by the thermocouple and the real temperature  $T_{real}$  of the sample surface is approximately given by:

$$T_{ind} \approx \left(\frac{T_{t,m}}{T_{t,r}}\right) T_{real}$$
 (3.1)

where  $T_{t,m}$  is the measured or indicated transition temperature and  $T_{t,r}$  is the real transition temperature . The real transition temperature assumed in this work was taken to be 530°C [172] at the arsenic background pressure being used of about 10<sup>-5</sup> Torr. This calibration process allowed determination of the indicated temperature at which the real substrate temperature was 600°C for GaAs growth, 540°C for the growth of layers containing indium and 460°C or 540°C for the growth of layers containing indium and 460°C or 540°C for the growth of layers.

After obtaining the transition temperature, the substrate temperature was increased to 600°C and a GaAs buffer layer of thickness about 100 to 200 nm was grown at a rate of approximately 1 ML/s. 600°C is the optimal substrate temperature for the MBE growth of GaAs [145] under arsenic-rich conditions. Following initiation of GaAs buffer layer growth, the growth rate could be checked by monitoring RHEED intensity oscillations.

For two-dimensional layer by layer growth, the arsenic flux in the growth chamber should be close to the minimum necessary for stoichiometric growth. Under these conditions the RHEED oscillations were persistent, however any further reduction of the arsenic flux could result in a metal rich surface and catastrophic failure of the growth. This is caused by the formation of gallium droplets on the surface, a situation from which it is difficult to recover. In this study, the arsenic furnace temperature ranged from 300°C to 400°C depending on the level of the remaining arsenic charge.

After GaAs buffer layer growth, the substrate temperature was changed to that desired and the required structure could be grown, generally with none or minimal growth interruptions. Following the growth process, the samples were removed from the MBE system and the samples removed from the Mo blocks by slowly heating them on a hot plate to just above the indium melting point. Since the indium soldering process was not 100% reproducible and the Mo blocks were coated to varying degrees with amorphous source phases, their thermal properties changed with time. That is why the transition temperatures were usually different and needed to be determined before each growth.

In this study, all samples were grown for the purposes of structural or chemical characterisation and no dopants were added to achieve any specific electronic or optical properties. The substrate temperature used to grow the GaAsN epitaxial layers reported on in this work was 540°C since at higher temperatures there is some loss of atomic nitrogen, which at a growth temperature of 600°C is about 6% [145, 163]. The same substrate temperatures were also used for growing InGaAs and InGaAsN epitaxial layers where evaporative loss of indium is also negligible. However, for some particular purposes, GaAsN layers were grown at 460°C as described in chapters 4 and 7. AlAs layers were grown at the same temperature as the GaAs layers.

#### 3.2.3 Source Temperatures and Flux Rates

Solid source beam fluxes are determined by the source temperature and so it was necessary to determine the relationship between the source temperatures and their flux rates so that the temperatures required could be determined for a specific structure before growth. The relationship between the source temperature T (absolute temperature) and the corresponding atomic arrival rate  $\gamma$  at the growth surface can be described by an Arrhenius relationship [174]:

$$\gamma = A \exp\left(-\frac{E}{kT}\right) \tag{3.2}$$

where E is the activation energy for evaporation or sublimation, k is the Boltzmann constant and A is a constant. Equation 3.2 can be rewritten as:

$$\ln \gamma = A' - \left(\frac{E'}{T}\right) \tag{3.3}$$

where E' is the same activation energy E but expressed in temperature units (i.e. E' = E/k) and A' is the constant ln A. Rearranging Equation 3.3 we have:

$$T = \left(\frac{E'}{A' - \ln\gamma}\right). \tag{3.4}$$

Equation 3.4 was used to determine the source temperature required to obtain a particular flux rate for the purpose of growing a particular structure. However, the constants A' and E' in Equation 3.4 had to be determined first. This was done by growing a series of samples at various source temperatures to vary the flux rates. For example, by growing a series of samples consisting of a ten-period In<sub>x</sub>Ga<sub>1-x</sub>As/GaAs MQW grown at various indium and gallium source temperatures, the indium and gallium flux rates could be determined from x-ray analysis [175] and this method will be explained in chapter 5 section 5.3.3.2. Since the source temperature *T* and

flux rate  $\gamma$  are known, plotting ln  $\gamma$  versus 1/*T* allows determination of *A'* and *E'*. This was done for the indium, gallium and aluminium sources and examples of values for *A'* and *E'* for these sources are shown in Table 3.1. The values of *A'* and *E'* needed to be updated from time to time, based on x-ray analysis of the latest samples grown. The literature values for *E'* for each of these materials (shown as  $E_L$ ) are calculated from their latent heats of vaporisation [176] per atom or molecule and expressed in temperature units as shown in the table.

Table 3.1: The values of the constants A' and E' for indium, gallium and aluminium furnaces, including literature values for  $E'(E_L')$ .

Parameters	Indium	Gallium	Aluminium
A'	22.38	19.44	24.09
E'	27111	26752	36825
$E_L'$	27917	33693	37303

The relationships between incorporation rates and composition for the quaternary compound  $In_xGa_{1-x}As_{1-y}N_y$  grown in this work are shown in Equations 3.5 and 3.6:

$$x = \frac{I_{In}}{I_{In} + I_{Ga}} \tag{3.5}$$

$$y = \frac{I_N}{I_N + I_{As}} \tag{3.6}$$

where x and y are the atomic mole fractions of indium and nitrogen respectively and  $I_{In}$ ,  $I_{Ga}$ ,  $I_N$  and  $I_{As}$  are the indium, gallium, nitrogen and arsenic incorporation rates. In this work, the nitrogen flux rate was kept constant and the gallium flux rate was changed to achieve changes in the nitrogen mole fraction. All species except arsenic have unity sticking coefficients at the growth temperatures used, and the arsenic incorporation rate is given by:

$$I_{As} = I_{Ga} - I_N \tag{3.7}$$

and by substituting Equation 3.7 into Equation 3.6, the relationship between the nitrogen atomic mole fraction y and the gallium and nitrogen incorporation rates becomes:

$$y = \frac{I_N}{I_{Ga}}.$$
(3.8)

If the sticking coefficients of nitrogen and gallium are unity, as has been confirmed by experiment [145, 205], incorporation rates can be replaced by nitrogen and gallium flux rates,  $\gamma_N$  and  $\gamma_{Ga}$  respectively, to yield:

$$y = \frac{\gamma_N}{\gamma_{Ga}} \tag{3.9}$$

where  $\gamma_N$  and  $\gamma_{Ga}$  are the flux rates of nitrogen and gallium. This shows that at constant atomic nitrogen flux the nitrogen mole fraction is expected to be inversely proportional to the gallium flux, and so the atomic mole fraction *y* of nitrogen can be changed by changing the gallium flux. Equation 3.9 also shows that the atomic mole fraction of nitrogen is independent of the arsenic flux, assuming the sticking coefficient of nitrogen is unity.

# 3.3 Semiconductor Structural Analysis

There are several techniques that can be applied to the analysis of semiconductor structures. One of the most common techniques is x-ray diffraction and this section explains the concepts involved in semiconductor structural analysis, as they apply to this study.

## 3.3.1 Basic Concepts

## 3.3.1.1 GaAs Lattice Structure

GaAs is a binary alloy having each arsenic atom tetrahedrally bonded to four gallium atoms and vice-versa. The GaAs crystal has a zinc-blende structure and the arrangement of the atoms and the bonding between them within the GaAs unit cell are shown in Figure 3.6. The anions (As) are occupying one face-centred cubic (fcc) sub-lattice, while the cations (Ga) sit on another fcc sub-lattice as shown in the figure. Only one parameter *a* is required to describe the unit cell dimension as shown in the figure and for the binary alloys related to this work (i.e. InAs, GaN, InN and AlAs) the zinc-blende forms are relevant. Since the GaAsN and InGaAsN layers were grown on GaAs substrates with a zinc-blende structure, they too would adopt the zinc-blende crystal structure. There was no growth of GaN and InN in this thesis. The lattice constant values for GaAs, InAs, GaN and InN used in this work are shown in Table 3.2 in section 3.3.1.4.



Figure 3.6: The GaAs unit cell structure.

# 3.3.1.2 Bragg's Law and Lattice Plane Spacings

Bragg [177] proposed a theory to explain the diffraction of x-ray beams from a crystal, the so called Bragg's law:

$$2d\sin\theta = \lambda \tag{3.10}$$

where *d* is the lattice plane spacing,  $\theta$  is the angle between the incident beam and the lattice planes and  $\lambda$  is the x-ray wavelength.

Miller indices are used to define the orientation of planes within a crystal lattice [178] and the lattice spacing *d* is the perpendicular distance between adjacent parallel planes. For a zinc-blende crystal with lattice constant *a*, the distance  $d_{hkl}$  between planes with Miller indices *h*, *k*, and *l* is given by:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}.$$
(3.11)

As an example, for a symmetric (004) reflection from an (001) crystal surface Equation 3.11 becomes:

$$d_{004} = \frac{a_{001}}{\sqrt{0^2 + 0^2 + 4^2}} = \frac{a_{001}}{4}.$$
(3.12)

## 3.3.1.3 Linear Elasticity Theory

For a natural or relaxed zinc-blende unit cell, the perpendicular lattice parameter  $a^{\perp}$  is the same as the parallel lattice parameter  $a^{\parallel}$ . However, if the parallel lattice parameter of an epitaxial layer is expanded or compressed to maintain interfacial coherence with its growth substrate then the perpendicular lattice parameter will also change. This effect is illustrated in Figure 3.7 where the perpendicular lattice parameter of an epitaxial layer is expanded when grown on a substrate with a smaller lattice constant than the natural lattice constant  $a_{Epi}$  of the layer and this phenomenon is called the Poisson effect [178].



Figure 3.7: Schematic illustration of the distortion of an epitaxial layer due to coherent epitaxial growth on a substrate with a smaller lattice constant.

In the case of a compressive  $In_xGa_{1-x}As$  layer grown coherently on a GaAs substrate, the natural unit cell lattice parameter of the epitaxial layer will be compressed parallel to the substrate interface to match the parallel lattice constant of the substrate  $(a_{Sub} = a^{\parallel})$  and as a result the epitaxial layer is expanded in the perpendicular direction. On the other hand, a tensile GaAs<sub>1-y</sub>N<sub>y</sub> layer expands to match the GaAs substrate and the perpendicular lattice constant  $a^{\perp}$  of the layer is reduced. Both situations are described as tetragonal distortion and quantifying this process requires some knowledge of the elastic properties of the layer and elasticity theory. In all cases considered in this work the epitaxial layer is much thinner than the substrate and therefore the substrate is assumed to remain unstrained and all distortions are taken up by the epitaxial layer. However, the presence of a strained epitaxial layer on one side of a substrate wafer will introduce bending of the substrate and in certain circumstances this effect needs to be recognised.

Tetragonal distortion can be explained quantitatively by an extension of Hooke's law to three dimensions. The governing matrix equation is [179]:

$$\begin{cases} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{xy} \\ \sigma_{xz} \\ \sigma_{yz} \end{cases} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{bmatrix} \begin{pmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ \varepsilon_{xy} \\ \varepsilon_{xz} \\ \varepsilon_{yz} \end{pmatrix}$$
(3.13)

where  $\sigma_{mn}$  are the stresses,  $C_{mn}$  the elastic constants and  $\varepsilon_{mn}$  the strains in the material and *m* and *n* [179] represent *x*, *y* or *z* in the case of stresses and strains and 1 to 6 in the case of the elastic constants. For a cubic structure its cube axes are symmetric to 90° rotations, so that the elements of the matrix  $C_{mn}$  take values of:

$$C_{mm} = C_{11}$$

$$C_{mn} = C_{12}$$

$$m \le 3,$$

$$C_{mm} = C_{44}$$

$$C_{mn} = 0$$

$$m \ge 4,$$

$$C_{mn} = 0$$

$$n \ge 4$$

$$C_{mn} = 0$$

$$n \ge 4$$

$$C_{mn} = 0$$

$$n \le 3.$$

and

Hence, there are only three independent elastic constants ( $C_{11}$ ,  $C_{12}$  and  $C_{44}$ ) and so Equation 3.13 simplifies to [179]:

$$\begin{cases} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{xy} \\ \sigma_{xz} \\ \sigma_{yz} \end{cases} = \begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{bmatrix} \begin{bmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ \varepsilon_{xy} \\ \varepsilon_{xz} \\ \varepsilon_{yz} \end{bmatrix} .$$
(3.14)
For growth on a cubic (001) oriented substrate, the stress in the growth direction ( $\sigma_{zz}$ ) is zero because no force acts in this direction due to the surface stress boundary condition:

$$\sigma_{nn} n_n = 0 \tag{3.15}$$

where  $\sigma_{mn}$  is the stress acting in the *m* direction on a surface with normal in the *n* direction. For the case of tetragonal distortion where there are no shear stresses:

$$\sigma_{xy} = \sigma_{xz} = \sigma_{yz} = 0 \tag{3.16}$$

and Equation 3.14 reduces to:

$$\sigma_{xx} = C_{11}\varepsilon_{xx} + C_{12}\varepsilon_{yy} + C_{12}\varepsilon_{zz}, \qquad (3.17)$$

$$\sigma_{yy} = C_{12}\varepsilon_{xx} + C_{11}\varepsilon_{yy} + C_{12}\varepsilon_{zz} \tag{3.18}$$

and

$$\sigma_{zz} = C_{12}\varepsilon_{xx} + C_{12}\varepsilon_{yy} + C_{11}\varepsilon_{zz} = 0.$$
(3.19)

For coherent growth on a cubic substrate, the strains imposed on the layer in the direction parallel to the interface are equal and therefore Equations 3.17 and 3.18 imply  $\sigma_{xx} = \sigma_{yy}$ . By convention the strains  $\varepsilon_{xx}$  and  $\varepsilon_{yy}$  in the layer in the *x* and *y* directions are designated  $\varepsilon^{\parallel}$  and the perpendicular strain  $\varepsilon_{zz}$  is designated  $\varepsilon^{\perp}$ . Equations 3.17, 3.18 and 3.19 can then be written as:

$$\sigma_{xx} = C_{11}\varepsilon^{\parallel} + C_{12}\varepsilon^{\parallel} + C_{12}\varepsilon^{\perp}, \qquad (3.20)$$

$$\sigma_{yy} = C_{12}\varepsilon^{\parallel} + C_{11}\varepsilon^{\parallel} + C_{12}\varepsilon^{\perp}$$
(3.21)

and

$$0 = C_{12}\varepsilon^{\parallel} + C_{12}\varepsilon^{\parallel} + C_{11}\varepsilon^{\perp}.$$
(3.22)

$$\varepsilon^{\perp} = -\left(\frac{2C_{12}}{C_{11}}\right)\varepsilon^{\parallel} \tag{3.23}$$

where the strains in the parallel and perpendicular directions are defined as:

$$\varepsilon^{\parallel} = \frac{a^{\parallel} - a_{Epi}}{a_{Epi}} \tag{3.24}$$

and

$$\varepsilon^{\perp} = \frac{a^{\perp} - a_{Epi}}{a_{Epi}}.$$
(3.25)

By substituting Equations 3.24 and 3.25 into Equation 3.23 and solving for  $a_{Epi}$  we obtain:

$$a_{Epi} = \left(\frac{2C_{12}}{2C_{12} + C_{11}}\right) a^{\parallel} + \left(\frac{C_{11}}{2C_{12} + C_{11}}\right) a^{\perp}.$$
(3.26)

For the case of tetragonal distortion of a cubic unit cell Poisson's ratio v is defined as:

$$v = \frac{C_{12}}{C_{12} + C_{11}}.$$
(3.27)

Following some algebraic manipulation Equation 3.26 can be expressed in terms of Poisson's ratio to yield:

$$a_{Epi} = \left(\frac{2\nu}{1+\nu}\right)a^{\parallel} + \left(\frac{1-\nu}{1+\nu}\right)a^{\perp}.$$
(3.28)

In the case of a coherently strained epitaxial layer,  $a^{\parallel} = a_{sub}$  and  $a^{\perp}$  can be measured directly from an (004) x-ray diffraction scan. The natural lattice constant can then be calculated if the values of the elastic constants (or Poisson's ratio) are known. The

chemical composition of a layer can then also be determined from the calculated natural lattice constant if the relationship between composition and lattice constant is known and this matter is discussed in the following section.

#### 3.3.1.4 Vegard's Law

Vegard's law assumes a linear relationship between lattice constant and alloy composition. For ternary alloys, Vegard's law is expressed in the form:

$$a_{A_x B_{1-x} C} = x a_{AC} + (1 - x) a_{BC}$$
(3.29)

where  $a_{A_xB_{1-x}C}$  is the natural lattice constant of a ternary alloy containing two group III elements (e.g. InGaAs), of which a fraction *x* is of the binary material *AC* (e.g. InAs) and a fraction (1 - *x*) is of the binary material *BC* (e.g. GaAs). Similarly:

$$a_{AB_yC_{1-y}} = ya_{AB} + (1 - y)a_{AC}$$
(3.30)

where  $a_{AB_yC_{1,y}}$  is the natural lattice constant of a ternary alloy containing two group V elements (e.g. GaAsN), of which a fraction *y* is of the binary material *AB* (e.g. GaN) and a fraction (1 - *y*) is of the binary material *AC* (e.g. GaAs).

For a quaternary alloy, Vegard's law suggests:

$$a_{A_x B_{1-x} C_{1-y} D_y} = xy a_{AD} + y(1-x) a_{BD} + x(1-y) a_{AC} + (1-x)(1-y) a_{BC}$$
(3.31)

where  $a_{A_xB_{1-x}C_{1-y}D_y}$  is the natural lattice constant of a quaternary alloy containing two group III (*A* and *B*) and two group V (*C* and *D*) elements (e.g. InGaAsN). It therefore contains a fraction *xy* of the binary *AD* (e.g. InN), a fraction *y*(1 - *x*) of the binary *BD* (e.g. GaN), a fraction *x*(1 - *y*) of the binary *AC* (e.g. InAs) and a fraction (1 - *x*)(1 - *y*) of the binary *BC* (e.g. GaAs). For many group III/V compound semiconductor alloys, there is evidence that Vegard's law does not hold however it is reasonable to assume its truth if more detailed data is not available.

If a non-linear relationship between composition and lattice parameter is indicated, a bowing parameter can be used to accommodate deviation from a linear relationship. Hence, for a non-linear composition to lattice constant relationship, Equation 3.29 can be modified to give:

$$a_{A_x B_{1-x} C} = x a_{AC} + (1 - x) a_{BC} + b_0 x (1 - x)$$
(3.32)

where  $b_0$  is a bowing parameter associated with the ternary compound  $A_x B_{1-x} C$ . Similarly for a quaternary, Equation 3.31 can be modified to include non-linearity according to:

$$a_{A_xB_{1-x}C_{1-y}D_y} = xya_{AD} + y(1-x)a_{BD} + x(1-y)a_{AC} + (1-x)(1-y)a_{BC}$$
$$-[b_1x + b_2(1-x)]y(1-y) - [b_3y + b_4(1-y)]x(1-x)$$
(3.33)

where the bowing parameters associated with the quaternary compound include the bowing parameter  $b_1$  for alloy *ACD*,  $b_2$  for alloy *BCD*,  $b_3$  for alloy *ABD* and  $b_4$  for alloy *ABC*.

The lattice and elastic constants of GaAs [38, 39], InAs [38], GaN [38] and InN [38] used in calculations and analysis in this thesis are shown in Table 3.2. The values of Poisson's ratio v shown in the table are calculated from the elastic constants  $C_{11}$  and  $C_{12}$ . However, the value of the GaAs Poisson's ratio used in this thesis is  $0.322 \pm 0.005$  as determined by Usher et al. [180]. The reason for using this value was because it was obtained from the same laboratory as the experiments reported in this thesis were performed.

Parameters	GaAs[38, 39]	InAs[38]	GaN[38]	InN[38]
<i>a</i> (Å)	5.65325	6.0583	4.5	4.98
$C_{11} (10^{11} \text{N/m}^2)$	1.174	0.833	2.93	1.87
$C_{12} (10^{11} \text{N/m}^2)$	0.526	0.453	1.59	1.25
Vcalculated	0.309	0.352	0.352	0.401

Table 3.2: Lattice and elastic parameter values.

# 3.3.1.5 Lattice Tilt

Tilting of an epitaxial layer can occur when there is a lattice mismatch between the layer and its growth substrate. It can be caused by the presence of misfit dislocations in the layer or by the substrate being cut and polished slightly off the intended surface plane. If crystal planes in a layer are tilted relative to the corresponding planes in the substrate then this will result in a shift of the layer's x-ray diffraction peak relative to the substrate (refer to section 3.3.2 for details on the XRD technique). The effect of epitaxial layer tilt is illustrated in Figure 3.8 where  $\beta$  is the tilt angle and  $\Delta \omega_1$  and  $\Delta \omega_2$  are the peak separations measured by x-ray rocking curves with interchanged incident and diffracted beam directions.



Figure 3.8: Illustration of epitaxial layer tilt by an angle  $\beta$  relative to the substrate and its effect on measured peak separations.

It can be seen from Figure 3.8 that  $\Delta \omega_1 \neq \Delta \omega_2$  and in fact:

$$\Delta \omega_1 = \theta_{Sub} - \theta_{Epi} - \beta \tag{3.34}$$

and

$$\Delta \omega_2 = \theta_{Sub} - \theta_{Epi} + \beta \tag{3.35}$$

where  $\theta_{Sub}$  and  $\theta_{Epi}$  are the Bragg angles associated with the substrate and the layer *d*-spacings respectively. It can be seen from Equations 3.34 and 3.35 that:

$$\theta_{Sub} - \theta_{Epi} = \frac{\Delta \omega_1 + \Delta \omega_2}{2}$$
(3.36)

and so the effect of tilt can be eliminated by collecting two spectra for which the incident and diffracted beam directions are reversed (shown by red and blue arrows in Figure 3.8). Another method to measure and therefore take account of the effects of tilt is to average the HRXRD peak separation data from a set of four rocking curves recorded by rotating the sample about the surface normal by 90° between each spectrum (i.e. azimuthal angles of 0°, 90°, 180° and 270°). The mean of the peak separations  $\Delta\omega_0$ ,  $\Delta\omega_{90}$ ,  $\Delta\omega_{180}$  and  $\Delta\omega_{270}$  is then related to the difference in Bragg angles between substrate and layer according to:

$$\theta_{Sub} - \theta_{Epi} = \frac{\Delta\omega_0 + \Delta\omega_{90} + \Delta\omega_{180} + \Delta\omega_{270}}{4}.$$
(3.37)

The peak separation data collected at azimuthal angles of  $0^{\circ}$ ,  $90^{\circ}$ ,  $180^{\circ}$  and  $270^{\circ}$  can also be fitted by a sine function as will be explained in chapter 5 section 5.3.3.1. This method has been employed by other research groups (e.g. [181-183]) and has been important to this work since it allowed a spectrum to be collected at an azimuthal angle at which the tilt had no effect. This was important sometimes because the HRXRD simulation software available did not allow layer tilts to be included in the simulation.

#### 3.3.1.6 Line Defects

The existence of dislocations, a structural line defect, in any epitaxial layer in a sample can strongly degrade device performance, even leading to device failure, particularly in the case of devices requiring heavy current injection by altering the optoelectronic properties of the material. Misfit dislocations can form in the interface between an epitaxial layer and its growth substrate if its layer thickness exceeds a critical value. The development of an incoherent interface due to misfit dislocation formation will lead to strain relaxation in the layer, which of itself might not be a problem. However, catastrophic strain relaxation is always accompanied by the creation of a high density of threading dislocations and these can extend through all layers causing a significant deterioration in device performance. In 1974, Matthews and Blakeslee [184] developed a model of critical thickness for the formation of misfit dislocations in single and double heterostructures. In 1990, Fox and Jesser [185] reported misfit dislocation morphologies which evolve during the growth of pand *n*-type GaAsP layers on GaAs (001) substrates. They suggested that the Peierls barrier, a frictional force opposing dislocation motion, should be considered in critical thickness calculations.

Based on the model of critical thickness developed by Matthews and Blakeslee, the expression for the critical thickness  $h_c$  of a single layer is given by:

$$h_c = \frac{b(1 - v\cos^2\varphi)}{8\pi f(1 + v)|\cos\lambda|} \left[ \ln\left(\frac{h_c}{b}\right) + 1 \right]$$
(3.38)

where *f* is the lattice mismatch between the epitaxial layer and the substrate, *b* is the magnitude of the Burgers vector and *v* is Poisson's ratio for the epitaxial layer.  $\varphi$  is the angle between the Burgers vector and the intersection of the slip plane and the interface plane and  $\lambda$  is the angle between the Burgers vector and the perpendicular to the intersection of the slip plane and the interface plane which lies in the interfacial plane.

The Burgers vector is the closure vector required to complete a Burgers circuit which steps via atomic positions around a dislocation in a crystal lattice and the direction of the vector depends on the nature of the dislocation.

The lattice mismatch f is given by:

$$f = \frac{a_{Epi} - a_{Sub}}{a_{Epi}} \tag{3.39}$$

where  $a_{Epi}$  and  $a_{Sub}$  represent the lattice constants of the epitaxial layer and the substrate respectively. The magnitude of the Burgers vector *b* is:

$$b = \frac{a_{Epi}}{\sqrt{2}} \tag{3.40}$$

for the 60° type dislocations which are common in the class of III/V compound semiconductors of concern here. Since the substrates used for all experiments reported in this work were GaAs (001), the interface plane is also an (001) plane. In this work, the value of the critical thickness  $h_c$  for all epitaxial layers was calculated based on the assumptions:

- a) That the shear modulus of the GaAs substrate and the epitaxial layer are approximately the same.
- b) Poisson's ratio v of all layers in this work was taken to be  $0.322 \pm 0.005$  [180].
- c) The Peierls barrier was neglected.
- d) For the (001) interface plane, the values of  $\varphi$  and  $\lambda$  are both 60°.

These assumptions are reasonable because while the critical thickness calculation is itself approximate the TEM observations reported in Chapter 4 confirmed that the theoretical critical layer thicknesses for misfit dislocation formation was significantly smaller than was measured, so better accuracy is unjustified.

Equation 3.38 then becomes:

$$h_{c} = \frac{b(4 - v)}{16\pi f(1 + v)} \left[ \ln\left(\frac{h_{c}}{b}\right) + 1 \right].$$
(3.41)

Since the value of Poisson's ratio v is approximately 0.3, with little error it can be ignored in the numerator and Equation 3.41 simplifies to:

$$h_c = \frac{b}{4\pi f(1+\nu)} \left[ \ln\left(\frac{h_c}{b}\right) + 1 \right]. \tag{3.42}$$

All values of critical thickness  $h_c$  calculated in this work used Equation 3.42. The TEM observations to check critical layer thicknesses for misfit dislocation and other strain-relieving defects formation in GaAsN layers will be discussed in chapter 4 section 4.2.

## 3.3.2 The HRXRD Technique

The equipment used to record rocking curves from samples prepared in the course of this work was a multiple crystal x-ray diffraction system. This system could be used to perform many types of experiments including to collect standard rocking curves and reciprocal space maps [186]. The HRXRD equipment used in this work was a PANalytical X'pert PRO materials research diffractometer (MRD) system and is shown in Figure 3.9. Figure 3.10 shows more detailed views of some parts of the equipment which will be discussed further below.



Figure 3.9: The PANalytical X'pert PRO MRD system at La Trobe University.



Figure 3.10: Detailed views of the essential elements of the PANalytical X'pert PRO MRD system used to perform the measurements reported in this work.

The main elements of the system comprise a copper x-ray source, parabolic multilayer mirror, automatic beam attenuator, monochromator, crossed slits, sample stage and detector. The copper x-ray source ( $Cu_{Ka1}$ ,  $\lambda = 1.54060$  Å) was operated in line focus mode and a 1/4° fixed divergence slit was inserted at the entrance to the parabolic multilayer mirror. The mirror increased the useable intensity by a factor of about ten by converting a divergent x-ray beam from the source into a quasi-parallel beam. The quasi parallel beam passed through an automatic beam attenuator which was mounted on the front of the mirror and was used to automatically attenuate the incident beam should it be required, as for example when measuring the position of the full undiffracted beam.

The monochromator was a Bartels style using asymmetric four-bounce Ge (220) reflections. Only one wavelength satisfies the Bragg angle at all crystals and the diffracted beam from the last crystal reflection exits the monochromator via crossed slits. The horizontal and vertical slits are used to control the x-ray beam size on the sample and were adjusted according to the sample dimensions and the angle of incidence of the beam on the sample. For most measurements, the incident beam on the sample irradiated an area of approximately 1 mm x 1 mm, in which case the height of the vertical slit was set to 1 mm since the vertical height of the beam on the sample would only change slightly as the Psi angle ( $\psi$ ) was optimised to maximise the diffracted intensity. Figure 3.11 shows the beam length on the sample for a particular reflection.



Figure 3.11: View from above of the beam length of the incident beam on the sample.

With reference to Figure 3.11, the horizontal width  $w_H$  required for the slit can be calculated from the required horizontal length *L* of the incident beam on the sample and the angle of incidence  $\omega$  of the incident beam, so that:

$$w_H = L \sin \omega \tag{3.43}$$

where the angle  $\omega$  depends on the reflection used.

The sample stage allowed translation in the *x*, *y*, and *z* directions as well as rotation of the  $\omega$ ,  $\psi$  and  $\emptyset$  axes as shown in Figure 3.10. Each of these axes has an associated reproducibility as given in Table 3.3 and the minimum step size for the  $\omega$  and  $2\theta$  axes were 0.0001° or 0.36 arcseconds.

Axis	Reproducibility	
x	± 0.1 mm	
У	± 0.1 mm	
Z.	$\pm$ 1.0 $\mu$ m	
Ø	$\leq 0.01^{\circ}$	
Ψ	$\leq 0.01^{\circ}$	
ω	$\leq 0.001^{\circ}$	
$2\theta$	$\leq$ 0.001°	

Table 3.3: Reproducibility of the translation and rotation axes of the PANalytical X'pert PRO MRD system.

The detector arm held two proportional counter detectors as shown in Figure 3.10, with detector 1 having an analysing crystal mounted in front of it. The open detector 2 was used for standard rocking curve measurements while detector 1, with a three-bounce analysing crystal (Ge 220 reflection) in front of it could be used to record reciprocal space maps, although such measurements were not required in this work.

There are two types of theory describing the scattering of x-rays from crystals, the kinematical and dynamical theories. The dynamical theory is more suitable for the analysis of semiconductor structures, while the kinematical theory is used mainly for weakly scattering materials. The generalised dynamical diffraction theory proposed by Takagi [187, 188] and Taupin [189] is the most commonly used in commercial simulation software and the simulated x-ray diffraction spectra shown in this thesis were obtained by using the X'pert Epitaxy and Smoothfit 4.0a PANalytical software which is based on this approach. Experimental HRXRD curves were compared with dynamical simulations to determine angular peak separations between the GaAs substrate and epitaxial layer peaks. Several parameters in the simulation software such as wafer curvature, layer thickness and composition and background noise could be changed in order to obtain agreement between simulated and experimental spectra. The simulation software was also used to test sample designs before performing growths, to minimise peak interferences.

#### 3.3.2.1 The Rocking Curve Technique

The rocking curve method is one of the most popular x-ray diffraction techniques for the structural characterisation of semiconductor epitaxial layers. In this method the sample is rotated, or rocked, about the Bragg angle to change the incident angle of the x-ray beam, so that diffraction peaks from both epitaxial layers and the substrate can be recorded. The *d*-spacing of reflecting planes in the epitaxial layers can be calculated from the peak separations between the layer peaks and the substrate reference. Rocking curves were collected using an open detector, scanning over the desired  $\omega$  range, for a chosen counting time and  $\omega$  step resolution. Since HRXRD is a non-destructive measurement tool, sample preparation was not required. The *x*, *y* and *z* positions were adjusted with the aid of a tool to ensure the x-ray beam was incident on the sample surface at the desired position. The HRXRD analysis techniques applied to MQW structures and the issues associated with the collection and analysis of asymmetric reflections were described in detail in chapter 5 and 6 respectively.

# 3.4 Secondary Ion Mass Spectrometry (SIMS)

SIMS is a technique that is capable of detecting elements, molecules and clusters in a surface layer with sensitivity between the parts per million (ppm) and parts per billion (ppb) ranges. The following sections describe in detail the depth profiling SIMS undertaken as a part of this study.

## 3.4.1 Introduction to SIMS

Typically, a SIMS instrument consists of a primary ion gun, primary ion column, high vacuum sample chamber, ion lenses, mass analyser and detector. The surface of the sample is bombarded by high energy ions exiting the primary ion column with energies in the kilo electron volt (keV) range. This leads to the emission of secondary ions, atoms, molecules, clusters and electrons from the sample surface and near surface layers. The primary ions could be gaseous elements (e.g. argon or oxygen) or metal sources (e.g. cesium). The secondary ions (positive or negative) are collected by an ion lens and filtered according to their atomic mass to charge ratios and then detected by a Faraday cup or electron multiplier. The SIMS measurements made in this work used depth profiling and details about this technique are explained in the following paragraph.

In depth profiling, sputtering erodes the sample surface until all layers of interest have been penetrated. This process allows the variation in composition of a sample as a function of sputtering time to be measured and thus a chemical depth profile can be obtained. During the depth profiling process the elements contained in the sample are sputtered in a variety of ionic and neutral forms (e.g.  $M, M^+, M$ ), where M is the element to be quantified. "Matrix effects", that is the effect of the main material on the ion yield of all other elements studied, is one of the main problems in SIMS data interpretation. Emission of molecular Cs $M^+$  secondary ions, when using Cs<sup>+</sup> ions as the primary beam, results in significantly decreased matrix effects in SIMS measurements [190, 191]. According to Gao [190], by collecting Cs $M^+$  rather than either  $M^+$  or M ions, the concentration of the element M can be determined with an absolute accuracy of better than 2%. Therefore,  $CsM^+$  secondary ions were collected for all the SIMS measurements reported in this thesis. These species were <sup>133</sup>Cs<sup>14</sup>N<sup>+</sup>, <sup>133</sup>Cs<sup>16</sup>O<sup>+</sup>, <sup>133</sup>Cs<sup>69</sup>Ga<sup>+</sup>, <sup>133</sup>Cs<sup>75</sup>As<sup>+</sup> and <sup>133</sup>Cs<sup>115</sup>In<sup>+</sup>. From the collected secondary ions, <sup>133</sup>Cs<sup>14</sup>N<sup>+</sup> was the element of interest in GaAs<sub>1-y</sub>N<sub>y</sub> layers grown on GaAs substrates. The intensity of the <sup>133</sup>Cs<sup>14</sup>N<sup>+</sup> yield was much lower when compared to <sup>133</sup>Cs<sup>69</sup>Ga<sup>+</sup> and <sup>133</sup>Cs<sup>75</sup>As<sup>+</sup>, due to the low nitrogen mole fractions in GaAsN.

Since the nitrogen mole fraction was low compared with arsenic, it was a good approximation to assume that the concentrations of gallium and arsenic both remained close to 50%. Therefore, either arsenic or gallium could be used as the matrix element against which relative nitrogen yields could be measured. In order to decide which matrix element to use, some analysis was done and is reported in chapter 7 section 7.4.1.

## 3.4.2 The SIMS instrument at the University of Western Sydney

The SIMS measurements reported on in this thesis were performed on a Cameca IMS 5fE7 SIMS, as shown in Figure 3.12, located at the Hawkesbury Campus of the University of Western Sydney (UWS). The figure shows the main components of the SIMS instrument in side view, namely the <sup>133</sup>Cs<sup>+</sup> ion source, primary ion column, sample load-lock, reflector, Faraday cup and electron multiplier. Access to the instrument was supported by the Australian Institute of Nuclear Science and Engineering (AINSE). The measurements were performed according to the experimental parameters required by the author, who was present during all measurements. The instrument had both cesium and oxygen primary ion sources, which could be used for depth profiling or imaging. All SIMS measurements reported in this thesis were performed using  ${}^{133}Cs^+$  as the primary ions with a spot size of diameter 75  $\mu$ m. The <sup>133</sup>Cs<sup>+</sup> primary ions were accelerated to 10 keV and then retarded to an energy of 5 keV at the sample surface. The primary ion currents were typically between 11.5 and 13 nA and varied depending on the nature of the analysed sample and the type of information being sought. The primary beam raster covered an area of 250  $\mu$ m x 250  $\mu$ m and secondary ions were collected from a 100  $\mu$ m x 100

 $\mu$ m area at the centre of the rastered area. The mass spectrometer was operated at a mass resolution of  $m/\Delta m = 500$ , where *m* is the secondary ion mass. All secondary ions were collected and analysed using a Faraday cup or electron multiplier depending on their intensities. Depth profiling was continued until the growth substrate had been penetrated and for each sample this depth was measured using a KLA Tencor Alpha-StepIQ profilometer to assist in the reconstruction of the chemical composition versus depth profile.



Figure 3.12: The Cameca IMS 5fE7 SIMS instrument at the University of Western Sydney.

To avoid the inevitable oxygen contamination yield at the sample surface, all samples were capped with approximately 50 to 60 nm of GaAs. Thin layers of InGaAs containing low levels of indium mole fraction were used to mark the boundaries between the thick layers of interest.

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Ensuring interfacial coherence between group III/V dilute nitride compound semiconductor epitaxial layers and their growth substrate is of particular significance because the interpretation of most HRXRD results is predicated on this assumption. Therefore, TEM observations to check critical layer thicknesses for misfit dislocation and other strain-relieving defects' formation are reported in this chapter. In addition, details of SIMS measurements to check the effect of incorporated molecular nitrogen on the GaAs lattice constant are given.

# 4.1 Introduction

Most of the samples containing GaAsN or InGaAsN layers reported on in this thesis were grown below their critical layer thicknesses for misfit dislocation formation, however in this chapter we report on layers grown with thicknesses up to approximately six times larger than their critical thickness. While the misfit dislocation density was very low in most of these layers (six times larger than their critical thickness), another type of strain-relieving defect has been identified from TEM observations as will be discussed in the following section. The significance of this observation is discussed in the context of its effect on the HRXRD results reported on subsequently in this thesis.

# 4.2 Checking Interfacial Coherence in GaAsN Structures

There were two factors to be considered when designing the many sample structures grown for this study of the dilute nitride GaAsN. Firstly, the thicknesses of GaAsN epitaxial layers were limited to below their Matthews and Blakeslee [184] (M&B) mechanical equilibrium model of critical layer thickness to avoid the formation of misfit dislocations in the layers as was explained in chapter 3 section 3.3.1.6. Secondly and opposing this requirement, is the preference for thicker GaAsN layers to simplify the process of determining the structural properties of layers using HRXRD. Thin GaAsN layers yield peaks in HRXRD spectra that are broad and of low intensity. These broad layer peaks can overlap each other as well as the GaAs substrate peak, which can make determining the angular position of peaks difficult. While the first of these requirements cannot be compromised, there is evidence in the literature (e.g. [23-27, 148, 192-197]) that the critical thickness for misfit dislocation or other strain-relieving defects' formation may be considerably larger in GaAsN than is suggested by the M&B model. For these reasons it was decided to grow thicker layers (up to approximately six times the M&B critical thickness) of GaAsN and investigate the limits to coherent growth.

Calculated values of M&B single layer  $GaAs_{1-y}N_y$  critical thicknesses for  $0.003 \le y \le 0.013$  are plotted in Figure 4.1 as a function of nitrogen mole fraction and percentage lattice mismatch. The governing equation for this plot is Equation 3.42 in section 3.3.1.6 and the values of Poisson's ratio and lattice constants used in the calculation are shown in Table 3.2 in chapter 3 section 3.3.1.4.

The TEM observations reported here were undertaken to test the validity of the M&B model as it applies to the tensile GaAsN/GaAs material system.



Figure 4.1: Theoretical critical layer thickness versus nominal nitrogen mole fraction and lattice mismatch from Matthews and Blakeslee's mechanical equilibrium model for  $GaAs_{1-y}N_y$  grown on GaAs substrates.

## 4.2.1 Sample Structure and Growth

A set of five samples with nominal nitrogen mole fractions 0.009 were grown for TEM analysis in order to check for the formation of misfit dislocations or other strain-relieving defects in GaAsN layers and Table 4.1 shows the specifications of all the samples. The TEM technique is well suited to the task of detecting signs of interfacial incoherence because it has the resolution to easily identify misfit dislocations and other strain-relieving defects.

The GaAsN layer thicknesses varied from 80 to 500 nm and based on the M&B theory, the theoretical critical thickness for misfit dislocation formation in GaAsN layers with a nominal nitrogen mole fraction of 0.009 is 76 nm. With reference to the

Figure 4.1 plot, for nitrogen mole fraction between 0.008 and 0.01 the approximate variation in the critical thickness is from 88 to 62 nm.

		, , , , , , , , , , , , , , , , , , , ,		
Sample	Design value	Thickness	Thickness	Theoretical
designator	for nitrogen	of GaAsN	of GaAs	M&B
	mole	layer	buffer and	critical
	fraction y	(nm)	cap layers	thickness
			(nm)	(nm)
S1060312	0.009	80	70, 50	76
S2060312		150	30, 20	
S3060312		300	20, 10	
S1070312		400	20, 10	
S1080312		500	20, 10	

Table 4.1: Sample specifications (sample number # followed by growth date in the format S#ddmmyy) showing the design values for the nitrogen mole fraction *y*, the GaAsN layer, GaAs buffer and cap layer thicknesses.

The sample structures all contained AlAs, GaAs and GaAsN layers as shown in Figure 4.2. The thickness of the AlAs layer was 50 nm, while the thicknesses of the GaAs buffer and cap layers varied from sample to sample between 10 and 70 nm. A lift-off process was employed in these experiments in order to separate the GaAs/GaAsN/GaAs layers from their GaAs growth substrates and this was the purpose of the AlAs release layer. This yielded large area samples for TEM analysis and details of the lift-off process will be explained in chapter 6 section 6.2.2. The total epitaxial layer thickness following lift-off was about 200 nm which is suitable for TEM observations. The AlAs layers were grown at a temperature of 600°C and at a growth rate of approximately 0.3 ML/s while the GaAsN epitaxial layers were grown at 460°C to avoid the effects of nitrogen blocking of arsenic sites [198] which can cause the surface to become metal rich during the long growth times required for each GaAsN layer. The optimum growth temperature for a GaAs layer is 600°C, however in these experiments the GaAs buffer and cap layers were grown at 460°C because the short layer growth times required did not allow time for temperature ramping and it was preferred that there were no growth interruptions.



Figure 4.2: The structure of all samples with layer thicknesses other than that of AlAs omitted. The substrate temperatures employed for the growth of each layer are also shown.

In these experiments, the rate of delivery of nitrogen to the plasma source and subsequently to the growth chamber was kept constant at 79 mV (reading on a multimeter connected to the ion pump controller 0-100 mV pressure record output as will be explained in chapter 5 section 5.2). The nitrogen plasma current was also controlled at 18 mA for all growths. All samples were taken to the Materials Technology Centre, part of the National Science and Technology Development Agency, Thailand, for TEM analysis following x-ray analysis of all samples<sup>\*</sup>.

# 4.2.2 Results and Discussion

This section presents the spectra from HRXRD measurements, the images obtained from TEM observations and an interpretation of the results.

# 4.2.2.1 HRXRD Analysis

Examples of five HRXRD rocking curves obtained from all samples are shown in Figure 4.3. The tensile GaAsN epitaxial layer peaks (labelled *Y*) are on the high angle side of the GaAs substrate peaks and the layer peak intensities become higher and their full width at half maximum narrower as their thicknesses increase from sample S1060312 to S3060312. The GaAsN peak from sample S1070312 has broadened and shifted slightly closer to the substrate peak while for sample S1080312 the GaAsN layer peak is very broad and clearly closer to the GaAs

<sup>\*</sup> The TEM specimen preparation and observations were made by a team lead by Dr Chanchana Thanachayanont and supported by Dr Bralee Chayasombat and Visittapong Yordsri.

substrate and of lower intensity even though it was the thickest (500 nm) of all the layers grown.



Figure 4.3: Examples of HRXRD (004) rocking curves obtained from samples (a) S1060312, (b) S2060312, (c) S3060312, (d) S1070312 and (e) S1080312. The symbols *Y* identify the positions of the GaAsN layer peaks and the diffraction profiles are shifted vertically for clarity.

Pendellösung fringes spaced about 90 arcseconds apart which are observed clearly in the spectra from samples S1060312 and S2060312, are less pronounced for sample S3060312 and have disappeared completely from samples S1070312 and S1080312. The existence of strong fringes in the first two samples suggests coherent interfaces between all layers and they are therefore likely to be free of strain-relieving interfacial defects. The weakening of the fringes in sample S3060312 suggests there might be some loss of interfacial coherence although it is unlikely this would be accompanied by measurable strain relaxation. The shift of the GaAsN peak towards the substrate in the spectrum from sample S1080312 suggests that significant layer relaxation had taken place in this sample. A loss of interfacial coherence as a result of misfit dislocation formation or the introduction of any other strain-relieving defects would also account for the absence of Pendellösung fringes. However, the shift of the GaAsN peak towards the substrate in the spectrum from sample S1070312 could also be due to a change in the nitrogen mole fraction in the GaAsN layer from that which was intended since the TEM results shown in the following section suggest a low density of defects in sample S1070312.

Measurement of the angular peak separations between the GaAsN layers and the GaAs substrate  $\Delta \omega_{GaAsN-GaAs}$  allowed the perpendicular lattice parameter  $a_{GaAsN}^{\perp}$  of the GaAsN layers to be determined by the same method as will be outlined in chapter 5 section 5.2.1. This allowed the relationship between  $a_{GaAsN}^{\perp}$  and the layer thicknesses to be plotted for all samples as shown in Figure 4.4. The GaAsN perpendicular lattice constant was calculated with an error of ±0.00013 Å, while the error in their thicknesses was ±1 nm. It can be seen that the perpendicular lattice parameter was, within experimental error, constant for the three thinnest layers but had increased for the two thicker layers, making it clear that there has been some relief of tensile strain in sample S1080312 containing the thickest GaAsN layer.



Figure 4.4: Plot of the GaAsN perpendicular lattice constant  $a_{GaAsN}^{\perp}$  versus layer thickness for samples with nominal nitrogen mole fractions 0.009.

# 4.2.2.2 TEM Analysis

Examples of [001] zone axis dark field TEM images from samples S2060312 and S1070312 are shown in Figure 4.5. The GaAsN layer thicknesses in these samples were 150 nm and 400 nm respectively. The TEM images reveal that while there are few misfit dislocations in either sample there are some triangular defects which are similar to those observed by Walter and Gerthsen [199]. They grew CdMgSe layers (layer thicknesses of 78 nm, 1  $\mu$ m and 1.2  $\mu$ m) on InAs (001) substrates by MBE. They identified these defects as stacking faults and found higher stacking fault densities in thicker layers. Reason et al. [193] and Suemune et al. [200] also found stacking fault defects within 500 nm and 1000 nm GaAsN layers grown on (001) GaAs substrates by MBE for nitrogen compositions of 3.0% and 4.3% respectively. Ok et al. [201] observed stacking faults laying on (111) planes as well as threading

dislocations in  $GaAs_{0.957}N_{0.043}$  layers grown on (001) GaAs substrate by MOMBE. Wang et al. [157] found stacking faults in 18 nm GaAsN layers having higher nitrogen mole fractions of about 6%.

Fujimoto et al. [148] investigated critical thicknesses in  $GaAs_{0.978}N_{0.022}$  layers grown on GaAs substrates and found very few misfit dislocations generated below 300 nm but significant numbers were observed at a thickness of 400 nm. From their results, they concluded the critical thickness for misfit dislocation formation in GaAs<sub>0.978</sub>N<sub>0.022</sub> layers grown on GaAs was approximately 300 nm. Li et al. [196] observed an array of 60° dislocations in 500 nm GaAs<sub>0.97</sub>N<sub>0.03</sub> layers grown on (100) GaAs substrates.

With reference to Figure 4.5 some interesting observations can be made regarding the size of the triangular stacking faults in both images because while their density does not appear to be increasing with layer thickness the size of the defects is clearly increasing. The reason for this appears to be that the stacking faults extend from the bottom of the GaAsN layer to the top surface of the structure and as the GaAsN layer thicknesses increase the size of the defects increases as can be explained in the following paragraph.



Figure 4.5: TEM planar zone [001] dark field micrographs from samples (a) S2060312 and (b) S1070312 with the GaAsN layer thicknesses  $h_{GaAsN}$  shown.

Figure 4.6 shows a triangular feature QRS laying on the (111) plane, with a height a and length projected onto the (001) plane of OP and the relationship between a and OP can be established as follows.



Figure 4.6: Illustration of a stacking fault QRS that lies in a (111) plane.

Referring to Figure 4.6, if *S* lays in the top interface of the layer and the *xy* plane is the bottom interface of the layer then the layer thickness is *a*. The projected length of the stacking fault onto the *xy* plane is *OP*.

However,

$$OP^2 + PQ^2 = a^2 \tag{4.1}$$

and:

$$PQ = OP \tag{4.2}$$

because OPQ is a 45° isosceles triangle. Therefore:

$$2OP^2 = a^2 \tag{4.3}$$

and

$$OP = \frac{a}{\sqrt{2}}.\tag{4.4}$$

Therefore if *a* is the height of a stacking fault, then the lateral extent of such a defect laying on a (111) plane should be  $a/\sqrt{2}$ .

Based on the calculation above, the *OP* values for samples S2060312 and S1070312 (from Figure 4.5) should have been 120 nm and 290 nm respectively, where a was taken to be the sum of the GaAsN and GaAs cap layer thicknesses. The observed *OP* value for sample S2060312 is 137 nm, while the measured value for sample S1070312 is about 286 nm, both of which are close to the calculated values.

Another very important observation to be made is that there are large areas of the surface that are not affected by this type of defect. The situation in heterostructures such as InGaAs/GaAs is that strain-relieving misfit dislocations flood the surface, leaving no areas unaffected by the strain-relieving process (e.g. [202]). When making HRXRD measurements in cases like that it is extremely important to avoid the onset of misfit dislocation formation since the pervasive subsequent relaxation of strain will compromise structural analyses that assume interfacial coherence. The observations made here on GaAsN layers show that there is no uniform relaxation of strain over the sample surface, rather the defects are generated at locations which are generally isolated from each other. For example, sample S2060312 shows that the distance between each defect area on the GaAsN surface was about 800 nm apart. The effect this will have on HRXRD measurements is that areas of the surface where the (004) lattice parameter has changed significantly due to the defect will not contribute or distort Bragg peaks arising from defect free areas of the surface. These areas are effectively eliminated from the measurements, allowing layers thicker than the M&B critical thickness to be grown and thus facilitate ease of HRXRD measurements on areas of the surface that remain coherent.



Figure 4.7: TEM planar zone [001] dark field micrographs from sample S1080312 and the GaAsN layer thickness  $h_{GaAsN}$  is 500 nm.

Figure 4.7 shows [001] zone axis dark field TEM images from sample S1080312 which contained a GaAsN layer of thickness 500 nm. The TEM images reveal that as well as the stacking faults which were present in thinner GaAsN layers, there is a high density of misfit dislocations in the sample also. The misfit dislocations cover all areas of the sample surface which is consistent with the observation from the HRXRD spectrum shown in Figure 4.3 that shows a very broad GaAsN layer peak suggesting that the GaAsN layer in this sample was relaxed and tilted. The limit to growth of GaAsN with nitrogen mole fraction 0.009, so that the assumption of interfacial coherence is true, appears to be a layer of thickness between 400 nm and 500 nm. Defects appearing in thinner layers eliminate areas of the surface from x-ray measurements but do not destroy interfacial coherence over most of the surface.

# 4.3 Uptake of $N_2$ during GaAs Growth and its Effect on the Lattice Parameter

The purpose of this work was to investigate whether nitrogen molecules are being incorporated in GaAs layers and if so what is the effect of incorporation on the GaAs lattice constant. Ideally, only nitrogen atoms are substitutionally incorporated on

arsenic lattice sites during the growth of GaAsN layers and this clearly affects its lattice constant as can be quantified by HRXRD. However, there is a possibility for nitrogen molecules to be incorporated or trapped in GaAs or GaAsN layers due to the high nitrogen background pressure in the growth chamber during normal operation of the nitrogen plasma source (approximately 10<sup>-5</sup> Torr). Therefore, several samples were prepared during which the nitrogen background pressures were varied during the growth of GaAs layers without igniting the nitrogen plasma source. Only the top GaAsN layer was grown with the nitrogen plasma source operating to provide an internal standard for SIMS measurements. The concentrations of nitrogen molecules in each layer were expected to be different when the nitrogen background pressure was varied from layer to layer. The nitrogen mole fraction in the top layer of GaAsN was estimated from HRXRD measurements and SIMS was used to measure the nitrogen content in all layers. After completing the SIMS measurements, sample S1131211 was etched to remove the GaAsN layer and subsequent HRXRD measurements were made to determine if the incorporation of N<sub>2</sub> had a measurable effect on the GaAs lattice parameter as will be explained later. The following sections outline the sample structures and their growth and also present the results of SIMS and HRXRD measurements and a discussion of those results.

# 4.3.1 Sample Structure and Growth

Six samples were grown at different substrate temperatures and gallium growth rates as shown in Table 4.2. Three sets of samples were grown at substrate temperatures of 600°C, 540°C and 460°C and each set consisted of two samples grown at growth rates of 1 and 0.59 ML/s in order to achieve nominal nitrogen mole fractions in the GaAsN layer of 0.006 and 0.01. All samples were grown with a nitrogen background pressure which was monitored and controlled between 0 and 79 mV using a multimeter connected to the ion pump controller 0-100 mV pressure record output as will be described in chapter 5 section 5.2.

				-
Set	Sample	Substrate growth	Gallium	Thickness
	designator	temperature	growth rate	of GaAsN
		(°C)	(ML/s)	layer (nm)
1	S1071211	600	1.00	300
	S2131211	600	0.59	50
2	S1021211	540	1.00	300
	S1131211	540	0.59	50
3	S3060112	460	1.00	300
	S1070112	460	0.59	300

Table 4.2: Experimental parameters for all samples.

The GaAsN layer on the top of the structure was grown with a nitrogen plasma current of 18 mA while all the other layers were grown without igniting the plasma source. The reason for growing the GaAsN layer on top of the structure was to avoid the presence of nitrogen atoms during the growth of the GaAs layers. Details of the sample structure are explained in the following paragraph.

The thicknesses of the GaAsN layers in samples S2131211 and S1131211 were only 50 nm in order to avoid surface milkiness as will be explained in chapter 7 section 7.3.1, while the other samples were grown with GaAsN layers thicknesses of 300 nm. Figure 4.8 shows the structure of sample S1131211 grown with all five GaAs layers having thicknesses of 300 nm. The GaAsN and GaAs layers were separated by InGaAs marker layers with indium mole fractions of about 0.07. The nitrogen background pressures were varied from layer to layer (i.e. 0, 13.2, 26.3, 52.7 and 79 mV) and the nitrogen shutter was open during the growth of these layers in order to have the same conditions as for the growth of the top most GaAsN layer. A 60 nm GaAs cap layer was grown to protect the sample and to prevent environmental nitrogen from interfering with nitrogen measurements deeper into the structure during SIMS. Figure 4.8 also shows layers that were removed during the etching process, labelled as Etch 1 and Etch 2. The growth process was interrupted for a few minutes after the completion of each of the GaAs layers when all shutters were closed to allow the nitrogen background pressure to be changed. Growth was resumed when the nitrogen background pressure was stable at each new setting. The RHEED diffraction pattern was also monitored during this time to ensure a good

quality GaAs surface prior to the growth of the next layer. All layers within a sample were grown at the same substrate temperature as shown in Table 4.2.



Figure 4.8: Schematic of the structure of sample S1131211 within which the nitrogen background pressures were progressively increased during the growth of the individual layers. The top GaAsN layer was the only one grown with the nitrogen plasma operating.

# 4.3.2 Results and Discussion

The results of the SIMS and HRXRD measurements are discussed in this section. Since the HRXRD measurements were performed before and after the SIMS measurements the SIMS analysis is presented first.

# 4.3.2.1 SIMS Analysis

The SIMS experiments reported here used a  ${}^{133}Cs^+$  primary ion current between 11.5 and 13 nA with a 1800  $\mu$ m field aperture. The clusters recorded were  ${}^{133}Cs^{14}N^+$ ,  ${}^{133}Cs^{16}O^+$ ,  ${}^{133}Cs^{69}Ga^+$ ,  ${}^{133}Cs^{75}As^+$  and  ${}^{133}Cs^{115}In^+$  with counting times of 10 seconds for  ${}^{133}Cs^{14}N^+$  and 1.04 seconds for all other clusters. Since nitrogen was the element of interest, the  ${}^{133}Cs^{14}N^+$  cluster was measured for longer times in order to improve the counting statistics.

Figure 4.9 shows the SIMS yields for nitrogen (red curve) and indium (green curve) depth profiles for sample S1071211 where the centres of mass of the <sup>133</sup>Cs<sup>115</sup>In<sup>+</sup> peaks are shown by the vertical dashed lines. The <sup>133</sup>Cs<sup>14</sup>N<sup>+</sup> yields used in calculations for this work were taken from their average values as marked by the solid blue horizontal bars in the figure. The width of the bars indicates the start and end times used to determine the average of the <sup>133</sup>Cs<sup>14</sup>N<sup>+</sup> yield for individual layers. There is a spike in the <sup>133</sup>Cs<sup>14</sup>N<sup>+</sup> yield initially due to environmental contamination. Similar depth profiles, but with different yields, were observed for the other samples.



Figure 4.9: SIMS depth profile obtained from sample S1071211. The lower red curve shows the  ${}^{133}Cs{}^{14}N^+$  yield with the solid blue horizontal bars indicating the average values in the layers. The upper green curve shows the  ${}^{133}Cs{}^{115}In^+$  yield with the centres of mass of the individual peaks indicated by the vertical dashed lines.

Figure 4.10 shows a linear plot of the  ${}^{133}Cs^{14}N^+$  yields from sample S1071211 to focus attention on the low nitrogen levels in GaAs layers grown without igniting the plasma source. It can be seen that the  ${}^{133}Cs^{14}N^+$  yield rises as the nitrogen background pressures were increased, although the yields were always low. As can be seen from both Figures 4.9 and 4.10 the levels of molecular nitrogen incorporated or trapped in GaAs epitaxial layers were of the order of about  $\frac{1}{200}$ th of the  ${}^{133}Cs^{14}N^+$  yield in the top most GaAsN layer which was grown with the nitrogen plasma operating.



Figure 4.10: Linear plot of the SIMS depth profile from sample S1071211.

As for the SIMS analysis described in chapter 7, the nitrogen yields were normalised to arsenic in a manner that will be explained in section 7.4.1. Then using the estimated nitrogen mole fraction in the top most GaAsN layer as an internal standard, the nitrogen mole fractions  $y_{Nor}$  in all other layers were estimated. The value of  $y_{Nor}$  was determined from Equation 7.11 in section 7.4.2. The constant factor k was calculated from the ratio of  ${}^{133}Cs{}^{14}N^+$  to  ${}^{133}Cs{}^{75}As^+$  yields when compared with the estimated nitrogen mole fractions y obtained from HRXRD analysis of the top most GaAsN layer in each sample as shown in Table 4.4. The constant factor k was calculated from the top most GaAsN layer and was used as a reference to determine the normalised nitrogen mole fractions  $y_{Nor}$  in the other layers. Table 4.3 shows a summary of the SIMS data for all layers grown without ignited the plasma source. It shows the intensity ratio of  ${}^{133}Cs{}^{14}N^+$  to  ${}^{133}Cs{}^{75}As^+$  and  $y_{Nor}$ , calculated from the estimated nitrogen mole fraction in the top most GaAsN layer, for all samples studied.

Sample	GaAs (N <sub>2</sub> )	Intensity ratio of	<i>YNor</i>
	layer	$^{133}\text{Cs}^{14}\text{N}^+$ to $^{133}\text{Cs}^{75}\text{As}^+$	$(\pm 0.01 \times 10^{-5})$
	the	(x10 <sup>-5</sup> )	(Estimate only)
S1071211	5 <sup>th</sup> layer	$0.43 \pm 0.08$	2.30
	4 <sup>th</sup> layer	$0.23 \pm 0.05$	1.25
	3 <sup>rd</sup> layer	$0.19 \pm 0.05$	1.03
	$2^{nd}$ layer	$0.17 \pm 0.05$	0.90
	1 <sup>st</sup> layer	$0.14 \pm 0.04$	0.78
S2131211	5 <sup>th</sup> layer	$0.28 \pm 0.15$	2.33
	4 <sup>th</sup> layer	$0.14 \pm 0.10$	1.16
	3 <sup>rd</sup> layer	$0.10 \pm 0.08$	0.84
	2 <sup>nd</sup> layer	$0.09 \pm 0.08$	0.76
	1 <sup>st</sup> layer	$0.09 \pm 0.07$	0.74
S1021211	5 <sup>th</sup> layer	0.27±0.07	1.28
	4 <sup>th</sup> layer	$0.15 \pm 0.05$	0.73
	3 <sup>rd</sup> layer	0.12±0.05	0.59
	2 <sup>nd</sup> layer	$0.11 \pm 0.04$	0.52
	1 <sup>st</sup> layer	$0.11 \pm 0.04$	0.51
S1131211	5 <sup>th</sup> layer	0.36±0.13	2.39
	4 <sup>th</sup> layer	$0.12 \pm 0.07$	0.77
	3 <sup>rd</sup> layer	$0.11 \pm 0.07$	0.70
	2 <sup>nd</sup> layer	$0.09 \pm 0.07$	0.63
	1 <sup>st</sup> layer	$0.06 \pm 0.05$	0.40
S3060112	5 <sup>th</sup> layer	0.27±0.09	1.17
	4 <sup>th</sup> layer	$0.09 \pm 0.05$	0.37
	3 <sup>rd</sup> layer	$0.07 \pm 0.06$	0.32
	2 <sup>nd</sup> layer	$0.07 \pm 0.05$	0.31
	1 <sup>st</sup> layer	$0.05 \pm 0.04$	0.20
S1070112	1 <sup>st</sup> layer	1.33±0.17	6.37
	2 <sup>nd</sup> layer	$0.35 \pm 0.08$	1.67
	3 <sup>rd</sup> layer	$0.15 \pm 0.06$	0.74
	4 <sup>th</sup> layer	$0.11 \pm 0.05$	0.53
	5 <sup>th</sup> layer	$0.11 \pm 0.05$	0.52

Table 4.3: Summary of SIMS measurements obtained from all samples for layers grown without igniting the plasma source.

Figure 4.11 shows a plot of normalised nitrogen mole fractions from Table 4.3 obtained from six samples as a function of nitrogen background pressures between 0 and 79 mV. It can be seen that the normalised nitrogen mole fractions rise with increasing nitrogen background pressures. The errors associated with normalised
nitrogen mole fractions and nitrogen background pressures are small, about  $\pm 0.00001\%$  and  $\pm 1$  mV as shown in the plot.



Figure 4.11: Plot of normalised nitrogen mole fractions y in the layers (without igniting the plasma source) against the nitrogen background pressure in the growth chamber.

#### 4.3.2.2 HRXRD Analysis

All samples grown for this work were characterised by HRXRD prior to the SIMS measurements. This was to ensure that all samples grown for the SIMS measurements were of good structural quality with clear GaAsN layer peaks. In addition, the nominal nitrogen mole fraction *y* in the top most GaAsN layer could be determined from the GaAsN-GaAs peak separation, providing an internal nitrogen reference in each sample. The nominal nitrogen mole fractions could be calculated using the same method as will be explained in chapter 5 section 5.3.5 and the values obtained for all samples grown in these experiments are shown in Table 4.4.

Set	Sample	Substrate	Gallium	Thickness	у
		growth	growth rate	growth rate of GaAsN	
		temperature	(ML/s)	layer	$(\pm 0.0001)$
		(°C)		(nm)	
1	S1071211	600	1.00	300	0.0063
	S2131211	600	0.59	50	0.0116
2	S1021211	540	1.00	300	0.0065
	S1131211	540	0.59	50	0.0120
3	S3060112	460	1.00	300	0.0055
	S1070112	460	0.59	300	0.0100

Table 4.4: Summary of HRXRD measurements of estimated nitrogen mole fractions *y* obtained from the top most GaAsN layer in each sample.

The data in Figure 4.11 shows that the levels of  $N_2$  molecules incorporated in each layer was very low, however it was important to determine if these levels of  $N_2$  had a measureable effect on the GaAs lattice constant. Following removal of the GaAsN layer which was the only layer grown with the nitrogen plasma operating, the structure which remains is an InGaAs/GaAs ( $N_2$ ) MQW which has a characteristic XRD fringe pattern arising from the periodicity in the structure. The position of the zeroth fringe peak is determined by the average perpendicular lattice parameter of the structure, the average of the (constant) InGaAs perpendicular lattice parameter and the GaAs ( $N_2$ ) perpendicular lattice parameter. If the GaAs ( $N_2$ ) perpendicular lattice parameter were different when the  $N_2$  levels were higher (as in the top most GaAs ( $N_2$ ) layer) then removal of this layer should result in a shift in the position of the zeroth peak. The following experiment was designed to determine whether there was such a shift or not.

Sample S1131211 was selected for this experiment and the GaAs cap, InGaAs and GaAsN layers were removed by etching. Before proceeding, small pieces of black wax were used to cover three of the corners on the sample, so that AFM measurements could be performed to measure the depths of a series of etch steps to ensure that layers were removed as required. Details about the use of the black wax as a mask and epilayer support will be explained in chapter 6 section 6.2.2. The sample was then etched in a cooled polishing etchant consisting of

 $H_2SO_4(96\%)$ : $H_2O_2(30\%)$ : $H_2O$  mixed in the volume proportions 8:1:1 for 7 seconds initially with subsequent etch steps if required. Details of the etching process will be explained in chapter 5 section 5.3.4. Figure 4.12 shows the remaining structure of sample S1131211 following etching, where *B* in the figure shows partial removal of the second InGaAs layer from the top during the etching process.

	}
300 nm GaAs; $V = 79$ mV; I = 0 mA	
5 nm InGaAs	
300 nm GaAs; $V = 2/3 \ge (79) = 52.7 \text{ mV};$ I = 0  mA	
5 nm InGaAs	
300 nm GaAs; $V = 1/3 \ge (79) = 26.3 \text{ mV};$ I = 0  mA	
5 nm InGaAs	
300 nm GaAs; $V = 1/6 \ge (79) = 13.2 \text{ mV};$ I = 0  mA	
5 nm InGaAs	
300 nm GaAs; $V = 0$ mV; I = 0 mA	
5 nm InGaAs	
500µm GaAs substrate + buffer	

Figure 4.12: Schematic of the sample structure after the GaAs cap, top most InGaAs and GaAsN layers had been removed, with a little of the second InGaAs layer also being removed (labelled *B*).

After completing the etching steps, the sample was scanned again to obtain a HRXRD spectrum that included only the GaAs substrate, the remaining InGaAs marker layers and the GaAs ( $N_2$ ) (grown without igniting the plasma source) layer peaks. The next step was to etch another 300 nm layer of GaAs ( $N_2$ ) as was done before and the resulting structure is shown in Figure 4.13. The sample was then scanned again to obtain another set of (004) HRXRD rocking curves. Figure 4.14 shows an example of HRXRD spectra before any etch, after the first etch and after the second etch.



Figure 4.13: Schematic of the sample structure after the second etch, with a little of the third InGaAs layer also being removed (labelled *B*).

From Figure 4.14 (b) and (c), it can be seen that there is no GaAsN layer peak on the high angle side of the GaAs substrate after the first and second etches, while Figure 4.14 (a) shows a broad peak originating from the 50 nm GaAsN layer before any etching. All the fringes in the spectra arise from the repetitive growth of InGaAs/GaAs ( $N_2$ ) layers.



Figure 4.14: Examples of HRXRD rocking curves obtained from sample S1131211 (a) before any etching showing a single peak from the 50 nm GaAsN epitaxial layer as well as MQW fringes, (b) after the first etch and (c) after the second etch.

Figure 4.15 shows a linear plot of the spectra obtained from sample S1131211 before any etch (green) and after the first etch (blue) and it can be seen that the position of the zeroth order peak for both spectra are the same.



Figure 4.15: HRXRD rocking curves from sample S1131211, before any etch (green) and after the first etch (blue) plotted on a linear scale. The black dashed line indicates the position of the substrate peak and the blue dashed line is the position of the zeroth order peak for both spectra.

The results of HRXRD spectra obtained after the first etch (blue) and after the second etch (red) are shown in Figure 4.16 on a linear plot. As can be seen, the positions of the zeroth order peaks in the two spectra are virtually identical (the difference is about 2 arcseconds).



Figure 4.16: HRXRD rocking curves from sample S1131211, first etch (blue) and second etch (red) plotted on a linear scale. The black dashed line indicates the position of the substrate peak, while the blue and red dashed lines are the positions of the zeroth order peaks after the first and second etch respectively.

Since both Figures 4.15 and 4.16 show no significant difference in their zeroth order peak positions it can be concluded that the uptake of nitrogen in GaAs layer did not significantly change its perpendicular lattice constant.

# 4.4 Summary

To summarise, HRXRD and TEM measurements were performed to check the interfacial coherence between GaAsN layers and their GaAs growth substrates for different GaAsN layer thicknesses. From the results presented in this chapter, it is obvious that the M&B critical thickness theory is not applicable to tensile GaAsN layers containing low levels of nitrogen mole fraction. However, stacking fault defects have been observed but they do not compromise the assumption of interfacial coherence made when interpreting HRXRD data because for the GaAsN layer compositions and thicknesses grown for the studies reported in all other chapters a high percentage of the interfaces would be coherent.

SIMS measurements were used to detect molecular nitrogen in GaAs layers grown under varying nitrogen background pressures without igniting the nitrogen plasma source during their growth. These measurements clearly show that the level of molecular nitrogen incorporated in GaAsN during the MBE growth of GaAsN is low even at high nitrogen background pressures. Therefore, the low concentrations of nitrogen molecules incorporated or trapped in GaAsN layers are negligible compared to the large concentrations of nitrogen atoms in layers. It was also confirmed that the uptake of small amounts of nitrogen in GaAs layers did not have any appreciable effect on its lattice constant.

# **5** Strain Cancellation by Indium Incorporation for the Calibration of Nitrogen Mole Fractions in GaAsN

There have been many reports of the electronic and optical properties of GaAsN and InGaAsN alloys, candidates for device applications at wavelengths 1300 to 1550 nm (e.g. [9, 115, 134, 203, 204]). However, there are only a few studies of methods for determining the nitrogen mole fractions in these materials (e.g. [19-21]). This is of considerable importance, because results from different laboratories cannot be correlated if different methods potentially producing contradictory results are employed for the determination of nitrogen mole fractions. This is particularly the case when HRXRD is used in conjunction with simulation software since the assumptions made in the simulation software regarding material and elastic properties are often inaccessible to the user. This chapter discusses strain cancellation in  $GaAs_{1-v}N_v$  epitaxial layers by the addition of indium as a method for calibrating nitrogen mole fractions. The advantage of this approach is that  $In_xGa_{1-x}As$ layers grown on GaAs substrates have been studied extensively and we have excellent knowledge of indium mole fractions x in such layers and so can establish the lattice-matching indium equivalence with nitrogen mole fractions y with confidence, a step forward of significant value. It should be made very clear that at no time do we intend to assert the nitrogen mole fraction in any of our samples and any mention of such fractions implicitly means "nominal" fractions only. Such fractions are commonly asserted in the literature, however they are usually made in the context of making untested assumptions, such as that Vegard's law holds, that lattice and elastic constants are known precisely and that the host GaAs lattice has

been changed in only one significant way, that a fraction of arsenic sites have been substituted by nitrogen atoms.

## 5.1 Introduction

Except for the uninteresting case of homoepitaxial growth, epitaxial growth always results in interfacial strain between the layer and the growth substrate. The main objective of the work reported in this chapter was to determine the indium mole fraction x in an  $In_xGa_{1-x}As_{1-y}N_y$  epitaxial layer which would exactly cancel the strain present in a  $GaAs_{1-y}N_y$  layer with the same nitrogen mole fraction y. In this study all layers were grown on a GaAs substrate. The idea is to take a tensile layer of  $GaAs_1$ .  $_{y}N_{y}$  with nitrogen mole fraction y, and determine the indium mole fraction x which must replace gallium to exactly cancel the tensile strain in the layer. The indium mole fraction x has an equivalent but opposite effect on layer strain to the nitrogen mole fraction y. We do not assert the nitrogen mole fraction y, rather we measure the as-grown perpendicular lattice constant of the  $GaAs_{1-\nu}N_{\nu}$  layer, something that most laboratories studying this material system would do routinely. Since the measurement of indium mole fractions is more straight forward, this provides an alternative avenue for laboratories to specify their nitrogen mole fractions. For any nitrogen mole fraction y, the strain cancelling mole fraction x is found by plotting  $In_xGa_{1-x}As_{1-y}N_y$ -GaAs peak separations against varying indium mole fraction x, which crosses through zero arcseconds when there is exact lattice-matching of the layer to the substrate.

This is an alternative to asserting nitrogen mole fractions in  $GaAs_{1-y}N_y$  layers on the basis of x-ray measurements, when the values and linearity of lattice and elastic constants with nitrogen composition has not yet been established. For example, the GaAsN Poisson's ratio and its dependence on nitrogen composition is untested. Since there is no information available in the literature about the Poisson's ratio of cubic GaAsN, most researchers calculate it from the elastic constants of the endpoint binary compounds GaAs and GaN, assuming linearity with composition [38]. All uncertainties regarding these matters will be demonstrated later.

# 5.2 Nitrogen Calibration Procedure

As explained in chapter 3 section 3.1.1.2.1, the ECR nitrogen plasma source used a leak valve on the gas inlet line to regulate the nitrogen flow from a high-purity nitrogen cylinder into the source. However, the flow was not measured directly, instead, the background nitrogen pressure in the growth chamber was monitored using either a QMS nitrogen ion current measurement or measuring the growth chamber ion pump controller 0-100 mV pressure recording output. The nitrogen flow rate into the plasma source was assumed to be proportional to the background nitrogen partial pressure in the growth chamber. The atomic nitrogen output of the plasma source depended on two experimental variables, the nitrogen flow rate into the source and the plasma current and increasing either increased the atomic nitrogen flux rate. By changing the gallium growth rate at a constant nitrogen flow rate and nitrogen plasma current, the nitrogen composition could also be changed. While it would have been preferable to minimise the number of growth variables by selecting one value of plasma current, this would not have allowed access to the full range of nominal nitrogen mole fractions of interest in this study ( $0 < y \le 0.012$ ). For example, a nitrogen plasma current of 18 mA only allows for a minimum nitrogen mole fraction of about 0.0059 while a nitrogen plasma current of 12 mA allows minimum and maximum nitrogen mole fractions between 0.003 and 0.008 for a growth rate of 1 ML/s. An alternative approach to obtaining lower nitrogen mole fractions was to increase the layer growth rate, however using a higher growth rate creates another set of difficulties in MBE growth. Therefore, two values of plasma current (12 and 18 mA) were used in this work to allow growth of GaAsN with the range of nominal nitrogen mole fractions of interest.

In the early stages of experiments, the QMS was used to monitor the nitrogen partial pressure in the growth chamber. However, it proved convenient to use the growth chamber ion pump controller pressure recording output due to its relative stability and ease of control of the total pressure in the chamber. This output, which is approximately proportional to the log of the growth chamber pressure, is dominated by background  $N_2$  during nitride growth, being at least three or four orders of

magnitude higher than the partial pressure of the next most common gaseous species and arsenic does not contribute to the ion pump current. In the absence of nitrogen, even if the arsenic pressure is  $10^{-6}$  Torr the ion pump current will be indicating a pressure of  $10^{-9}$  to  $10^{-10}$  Torr. Therefore, this method was employed for all growths following completion of the first two sample sets. To check the relationship between the growth chamber ion pump controller pressure recording output and front panel ion pump pressure meter, pure nitrogen gas was admitted through the plasma source, although the source was not energised at the time. Prior to starting these measurements the growth chamber pressure was less than  $10^{-9}$  Torr, so it was dominated by nitrogen throughout the measurements. Figure 5.1 shows the relationship between the pressure reading obtained from a multimeter connected to the pressure record output from the ion pump controller with the log of the pressure reading obtained from the controller front panel ion pump pressure meter. Both sets of data were collected simultaneously, covering pressures between  $10^{-9}$  and  $10^{-5}$  Torr.

The relationship between the multimeter mV reading V and the growth chamber ion pump pressure reading P observed on the ion pump controller front panel meter that was used to generate the plot in Figure 5.1 was governed by the equation:

$$V = A \log_{10} P + B \tag{5.1}$$

where P is the pressure reading on the front panel meter of the ion pump controller, while A and B are constants to be determined. The plot of Figure 5.1 was used as a guide to set the nitrogen flow rate such that the pressure record output reading corresponded to the required nitrogen pressure. The correspondence between these pressures and the nominal nitrogen mole fraction obtained is discussed in the next paragraph.



Figure 5.1: Plot of the 0-100 mV reading V from a multimeter connected to the pressure record output of the growth chamber ion pump controller against the log of the pressure P read from the front panel meter of the ion pump controller with a line of best fit following Equation 5.1.

A higher nitrogen plasma power was used to grow samples with higher nominal nitrogen mole fractions to limit the pressure the growth chamber ion pump was exposed to. Separate growths were performed in order to determine the relationship between the pressure reading taken from the front panel meter of the ion pump controller and the nominal nitrogen mole fraction *y* obtained for nitrogen plasma currents of 12 and 18 mA. Nominal values of nitrogen mole fraction were obtained from samples consisting of a single GaAsN epitaxial layer followed by a GaAs cap layer, grown on GaAs (001) substrates. The thicknesses of the GaAsN epitaxial layers in each sample were designed to be less than the critical thickness for misfit dislocation formation. Figure 5.2 shows a plot of these relationships for two sets of samples. Samples S2300511, S1300511 and S1270511 were grown at a growth rate

of 0.8 ML/s with a nitrogen plasma current of 12 mA. The pressure in the growth chamber was monitored and controlled at ion pump controller pressure record settings of 68, 74 and 80 mV for samples S2300511, S1300511 and S1270511 respectively. A second set of samples, S3250511, S1250511 and S2250511, were grown at a growth rate of 1 ML/s using a nitrogen plasma current of 18 mA and the growth chamber pressures were set and controlled at 67, 73 and 79 mV for these samples respectively. A linear relationship between ion pump pressure and nominal nitrogen mole fraction is suggested by the lines of best fit associated with both sets of data. These relationships were used to determine the value of V (in Equation 5.1) needed for the growth of a GaAsN layer containing a particular nitrogen mole fraction, for plasma currents of 12 and 18 mA.



Figure 5.2: Plot of the ion pump pressure reading *P* against nitrogen mole fraction *y* showing lines of best fit for nitrogen plasma currents of 12 and 18 mA.

The estimated nitrogen mole fractions for samples S2300511, S1300511 and S1270511 were 0.0029, 0.0038 and 0.0048, while for samples S3250511, S1250511 and S2250511 they were 0.0065, 0.0070 and 0.0081 respectively. These mole fractions were estimates only because they were calculated from the GaAsN to GaAs peak separations obtained from HRXRD measurements and analysed using commercial XRD simulation software, for which the internal processing steps were largely unknown. The method employed to determine the GaAsN to GaAs peak separations will be explained in detail in section 5.3.5. In order to achieve different nitrogen mole fractions under constant plasma source conditions (chamber pressure and plasma current), the layer growth rates could be changed as is explained in chapter 3 section 3.2.3.

#### 5.2.1 Nitrogen Reproducibility

It was important to check the nitrogen mole fraction reproducibility from one growth to another, and for this purpose, a set of four nominally identical samples were grown on the same day under the same conditions. In these experiments, the rate of delivery of nitrogen to the plasma source and subsequently to the growth chamber, as measured by the pressure record output from the ion pump controller, was kept constant at 79 mV. The nitrogen plasma current was set to 18 mA with a gallium growth rate of 0.5 ML/s for all samples. It was assumed that a constant growth chamber pressure indicated similar if not identical nitrogen flow rates to the plasma source and consequently identical atomic nitrogen fluxes to the growth surface. The sample structures all consisted of  $GaAs_{1-y}N_y$  and GaAs epitaxial layers as shown in Figure 5.3. The  $GaAs_{1-y}N_y$  layers were grown at a substrate temperature of 540°C and the GaAs layers were grown at 600°C as a protective cap to the nitride layer. The 50 nm thickness of the GaAsN layer was lower than its critical thickness so that interfacial coherence could be assumed, the nitrogen composition was designed to be about 1% and there were no growth interruptions.



Figure 5.3: Schematic of a structure consisting of a single GaAsN quantum well for the purpose of nitrogen mole fraction reproducibility experiments.

Examples of four HRXRD rocking curves obtained from these samples are shown in Figure 5.4. The tensile GaAsN epitaxial layer peaks are on the high angle side of the GaAs substrate peaks and are broad due to the limited thickness of the GaAsN layers.



Figure 5.4: Examples of HRXRD (004) rocking curves obtained from four GaAsN/GaAs samples as indicated. The diffraction profiles are shifted vertically for clarity.

The angular positions of the GaAsN peaks relative to the substrate appear similar for samples S2211210 and S3211210, however sample S1211210 is slightly closer to the substrate peak while sample S4211210 is further away. Measurement of the angular

peak separations between the GaAsN layers and the GaAs substrates,  $\Delta \omega_{GaAsN-GaAs}$ , allowed the perpendicular lattice constants of the GaAsN layers,  $a_{GaAsN}^{\perp}$ , to be determined. Since the GaAsN layer peaks are broad, the GaAsN-GaAs peak separations had to be determined with the aid of the X'Pert Epitaxy and Smoothfit 4.0 software and the process followed will now be described in some detail.

Simulation software was used to fit curves to the experimental data as shown in Figure 5.5. The process followed by the simulation software is not transparent, for example the assumptions made regarding elasticity theory and the validity or otherwise of Vegard's law are not known. Nevertheless the simulation employs the dynamical theory of x-ray diffraction and accounts well for peak broadening and shifting to higher angles as a result of the GaAsN layer being relatively thin. The software used for the analysis in this work also did not give any information about the perpendicular lattice constant of the layers after the simulation had been completed and the spectra well-matched. Therefore, following successful simulation software in order to magnify and narrow the peak and allow its separation from the substrate to be determined accurately. This process is illustrated in Figure 5.6 which shows an example of one of the four spectra collected from sample S2211210 at Phi angles of  $0^{\circ}$ ,  $90^{\circ}$ ,  $180^{\circ}$  and  $270^{\circ}$ .



Figure 5.5: Experimental (blue) and simulated (red) HRXRD rocking curves for sample S2211210.



Figure 5.6: Experimental (blue) and simulated (red) HRXRD rocking curves for sample S2211210. The GaAsN layer thickness was increased to 300 nm in the simulation to allow the peak separation for a thicker layer of the same composition to be easily determined.

Table 5.1 shows the results obtained following measurement of the GaAsN-GaAs peak separations  $\Delta \omega_{GaAsN-GaAs}$ , from which the GaAsN perpendicular lattice constants  $a_{GaAsN}^{\perp}$  and nominal nitrogen mole fractions *y* were found for all samples. The values of *y* in the table are only estimated values since some untested assumptions have been made in their calculation, as will be explained in section 5.4.1. The measurements shown in the table were obtained from the mean of the scanned data at Phi angles of 0°, 90°, 180° and 270°. The results revealed that the peak separations and therefore the nominal nitrogen mole fractions spanned a range of about ±13% from the mean. With the experimental facilities available for this work, it was difficult to achieve more consistent nitrogen mole fractions, sometimes it could be less or more than this, however strategies for compensating for the effects of this variation are outlined in section 5.4.1.

Sample	$\Delta \omega_{GaAsN-GaAs}$ (arcsec) (±3 arcsec)	$a_{GqAsN}^{\perp}$ (Å) (±0.00013 Å)	y (Estimate) (±0.0001)
S1211210	475	5.63330	0.0089
S2211210	535	5.63080	0.0100
S3211210	545	5.63039	0.0102
S4211210	612	5.62757	0.0114
Mean	542	5.63052	0.0101

Table 5.1: The structural parameters obtained from all samples, testing nitrogen mole fraction reproducibility.

These experiments proved that it could be difficult to achieve constant nominal nitrogen mole fractions from sample to sample or from one set of samples to another. Therefore, some samples needed to be excluded from a set because of unacceptable variation in the nominal nitrogen mole fraction.

## 5.3 Experiments

Experiments to determine the indium mole fraction x in an  $In_xGa_{1-x}As_{1-y}N_y$  layer which exactly cancels the strain in a  $GaAs_{1-y}N_y$  with the same nitrogen content are described in this section.

Figure 5.7 shows a flowchart describing the experimental procedures followed in this work. The details of the MBE sample growth process have already been presented in chapter 3 section 3.2. The structures were similar for all samples, consisting of individual InGaAsN and GaAsN layers followed by a ten-period InGaAs/GaAs MQW for accurate indium and gallium flux calibration, a part of the structure that was analysed by methods that will be explained in section 5.3.3.2. Following MBE growth, all samples were scanned using HRXRD to obtain (004) rocking curves which were analysed first in order to determine the properties of the InGaAs/GaAs MQW layers. Samples were then chemically etched to remove the top most InGaAs/GaAs MQW layers and this process is explained in detail in section 5.3.4. The purpose of removing these layers was to eliminate interferences between MQW

peaks and the GaAsN and InGaAsN single layer peaks, thus making analysis of the GaAsN and InGaAsN layers straight forward and unambiguous. The (004) rocking curve measurements were repeated for all samples after the InGaAs/GaAs MQW layers were removed and all spectra were simulated using X'Pert Epitaxy and Smoothfit 4.0. The experimental curves were fitted to simulations only for the purpose of determining the angular peak separations between the GaAs substrate peak and the GaAsN and InGaAsN single layer peaks, not to determine the compositions of the layers.



Figure 5.7: Flowchart describing the experimental procedure followed for all sets of samples.

#### 5.3.1 Sample Structure

All structures were grown on 500  $\mu$ m GaAs (001) substrates and the generic structure and layer growth temperatures are shown in Figure 5.8. The ten-period

 $In_xGa_{1-x}As/GaAs$  MQW was designed to allow accurate calibration of the indium and gallium fluxes and thus allow determination of the indium mole fraction x in the  $In_xGa_{1-x}As_{1-y}N_y$  single layer, assumed to be the same as in the  $In_xGa_{1-x}As$  layers in the MQW. The InGaAs and GaAs layers in the MQW structure were designed to be between 10 and 20 nm and between 20 and 30 nm thick respectively, yielding fringes in HRXRD spectra that could be readily analysed. There were buffer layers of thickness 160 nm between the InGaAsN and GaAsN layers and between the GaAsN and MQW layers, for the purpose of allowing substrate temperature changes in preparation for the growth of subsequent layers, thus avoiding the need for growth interruptions. This allowed the InGaAsN, GaAsN and InGaAs/GaAs MQW layers to be grown at the design temperature of 540°C where evaporative loss of indium and nitrogen is negligible [145, 163], while growth of the GaAs buffer layers was at 600°C, which is ideal for GaAs, ensured that the starting growth surface was smooth as indicated by the two-dimensional streaks evident in the RHEED pattern. These ideal GaAs growth conditions were compromised slightly because at the beginning of the buffer layer growth the temperature was ramped from 540°C towards 600°C and on completion of the layer ramped back to 540°C. The 160 nm buffer layer between the GaAsN layer and the InGaAs/GaAs MQW also provided a margin of safety when the MQW layers were removed by etching, making it unlikely that the GaAsN would be etched inadvertently.



Figure 5.8: The structure of all samples with layer thicknesses other than those of the GaAs buffers omitted. The substrate temperatures employed for the growth of each layer are also shown.

The thicknesses of the InGaAsN and GaAsN layers were designed to be lower than their critical thicknesses, as determined from the force-balance model of Matthews and Blakeslee [184] (M&B), which has been described in section 3.3.1.6. This was important to avoid misfit dislocation formation in the layer interfaces which would result in a loss of interfacial coherence, since the structural analysis of all layers was based on the assumption of interfacial coherence. In all samples it was intended that the InGaAsN layers would be closely, but not exactly, lattice-matched to the substrate and so they had low interfacial misfits and correspondingly large critical layer thicknesses, allowing them to be grown with thicknesses between 200 and 400 nm. They were therefore as thick as possible for ease of x-ray analysis but not too thick as to result in the loss of interfacial coherence. Since the nitrogen content was generally low, the chosen GaAsN layer thicknesses of between 50 and 100 nm were expected to be considerably below the M&B critical layer thickness and literature reports [27, 148, 193, 195-197, 206] and the author's observations as reported in chapter 4 section 4.2 suggest that these thicknesses were conservatively low.

A number of assumptions underpin the design of these sample structures. Firstly, that the nitrogen concentration in the InGaAsN epitaxial layer of each sample was independent of the indium concentration and that any changes in the indium flux from sample to sample had no effect on the nitrogen composition in the InGaAsN layers. Since the indium flux rates used in this experiment were typically between 0.6% and 4.3% of the gallium flux rate, this assumption would appear reasonable. It was assumed that there would be no significant effect if the nitrogen incorporation is not independent since the percentage of nitrogen used was less than 1.5%. Secondly, since the MBE growth chamber pressure (which was dominated by nitrogen) and the plasma power used were constant throughout the growth of any individual sample, the nitrogen concentrations in the InGaAsN and GaAsN epitaxial layers were assumed to be the same. Thirdly, the indium concentration in the InGaAsN layer was assumed to be the same as that in the InGaAs layers in the MQW.

The temperatures required for the indium and gallium furnaces were calculated based on flux rates that had been obtained from the analysis of the most recent samples containing InGaAs/GaAs MQW's as discussed previously in section 3.2.3. The intended sample structures were simulated using X'Pert Epitaxy and Smoothfit 4.0 prior to growth, to ensure all layer peaks were at convenient angular positions and that interferences between single layer and MQW peaks were absent or uncommon.

#### 5.3.2 Sample Design

Five sets of samples were grown, intended to give the same nominal nitrogen mole fraction y in each sample within a set. Each sample included an  $In_xGa_{1-x}As_{1-y}N_y$  and a  $GaAs_{1-\nu}N_{\nu}$  layer with both layers assumed to have the same nominal nitrogen mole fraction y. The nominal nitrogen mole fractions were increased from one sample set to another between about 0.003 and 0.012. The five sets of samples have been designated as 1, 2, 2b, 3 and 4 and the intended nitrogen mole fractions and plasma conditions used are shown in Table 5.2. Each set of four samples included two containing compressively strained InGaAsN layers and two with InGaAsN layers in tension, except for set 2 that only had one sample with a tensile strained InGaAsN layer. The purpose of set 2b was to repeat the growths of set 2 since the analysis of this set showed inconsistencies in the measured perpendicular lattice constants and therefore the nominal nitrogen mole fractions y. The set 2b results exhibited more consistent GaAsN layer perpendicular lattice constants and so more confidence could be put in this set than in the original set 2. Sets 3 and 4 consisted of three samples with only one of the InGaAsN layers in each set in compression and tension respectively, with the other two samples having the opposite strain state.

Sets 1 and 2 as described in Table 5.2 were grown at a nitrogen plasma current of 12 mA with the growth chamber pressure stabilised by manual adjustment of the nitrogen leak valve to achieve a QMS multiplier current of  $4.5 \times 10^{-9}$  Amps when tuned to the N<sub>2</sub> peak. Higher nitrogen mole fraction growths (for sets 2b, 3 and 4) were performed at a nitrogen plasma current of 18 mA with the pressure in the growth chamber being measured and controlled using the ion pump controller

pressure record output setting of 79 mV for all samples. Different nominal nitrogen mole fractions were obtained by varying the layer growth rate, as explained in section 5.2.

Set	Sample	InGaAsN	Nitrogen	Nitrogen chamber	Design
	designator	layer	plasma	pressure	value for
		strain	current	(QMS N <sub>2</sub> ion current	nitrogen
			(mA)	or ion pump 0-100 mV	mole
				pressure record output)	fraction y
1	S2071009	Tensile	12	$4.5 \times 10^{-9}$ Amps	0.003
	S1011209	Compresive			
	S2011209	Compresive			
	S4011209	Tensile			
2	S1280110	Compresive	12	$4.5 \times 10^{-9}$ Amps	0.006
	S2280110	Tensile			
	S1290110	Compresive			
	S2290110	Compresive			
2b	S1070311	Compresive	18	79 mV	0.007
	S2070311	Tensile			
	S1090311	Compresive			
	S2090311	Tensile			
3	S1100211	Compresive	18	79 mV	0.010
	S2100211	Tensile			
	S2230211	Tensile			
4	S2310111	Tensile	18	79 mV	0.012
	S1020211	Compresive			
	S1230211	Compresive			

Table 5.2:	Sets	of	samples	with	their	designations	and	the	intended	nitrogen	mole
	fract	ion	s y.								

### 5.3.3 MQW HRXRD Measurements

This section explains the process by which the properties of the MQW could be determined, the indium and gallium flux rates calculated and therefore the indium mole fraction x in the MQW and the  $In_xGa_{1-x}As_{1-y}N_y$  layer found. HRXRD (004) rocking curves were collected from all as-grown samples so that their structural properties could be obtained. All spectra were analysed in order to determine the properties of the  $In_xGa_{1-x}As/GaAs$  MQW from its satellite peak positions and this

process is described in detail in section 5.3.3.2. Spectra were collected at Phi angles of  $0^{\circ}$ ,  $90^{\circ}$ ,  $180^{\circ}$  and  $270^{\circ}$  for each sample to identify and account for any layer tilts. Any simple tilt effects could be observed from this data, with the satellite or layer to GaAs substrate peak separations following a sine function with an amplitude equal to the tilt angle. Details of the analysis of the lattice tilts are given in section 5.3.3.1.

The Phi angles at which the sine function equals its average give a condition for which the tilt has no effect on the spectrum and a fifth HRXRD spectrum was collected at this angle. This was necessary because the commercial dynamical simulation software did not allow the inclusion of layer tilts in simulations. From this spectrum the layer properties and consequently the indium and gallium flux rates could be calculated from the InGaAs/GaAs MQW properties and this procedure was repeated for all samples. The value of the indium mole fraction obtained from the fifth HRXRD spectrum was then used to fit simulations to experimental rocking curve spectra showing the GaAsN and InGaAsN single layer peaks, with spectra being collected at Phi angles of 0°, 90°, 180° and 270° following chemical removal of the InGaAs/GaAs MQW layers. The same procedure as before was repeated in order to identify and account for any tilts in the GaAsN and InGaAsN layers.

#### 5.3.3.1 Lattice Tilt Analysis

The peak separations obtained from the (004) x-ray rocking curve spectra collected at Phi angles of  $0^{\circ}$ ,  $90^{\circ}$ ,  $180^{\circ}$ ,  $270^{\circ}$  arising from any MQW or single layer peak were fitted by a sine wave function using Matlab for the purpose of layer tilt analysis. The function used in the program was:

$$\Delta\omega(\mathbf{\emptyset}) = \Delta\omega_{ave} + A\sin(\mathbf{\emptyset} + B) \tag{5.2}$$

where  $\Delta\omega(\emptyset)$  is the measured peak separation at Phi angle  $\emptyset$ ,  $\Delta\omega_{ave}$  is the mean peak separation associated with the function, *A* is the amplitude and *B* is the phase shift associated with the sine function. A detailed explanation of this method can be found in Reference [207]. The parameters  $\Delta\omega_{ave}$ , *A* and *B* were optimised using a least-

squares  $\chi^2$  criterion. The peak separations between the GaAs substrate peak and the zeroth satellite peak labelled *SL*0 in Figure 5.9 from the InGaAs/GaAs MQW were determined from (004) x-ray rocking curves obtained at Phi angles of 0°, 90°, 180° and 270° for each sample. Figure 5.9 shows all HRXRD rocking curves for sample S2230211, collected at these Phi angles. All MQW satellite peaks are labelled according to their positions. From an initial inspection of the spectra, the peak separations between the GaAs substrate and *SL*0 peaks appear to be similar for all Phi angles, however there is a small but significant variation due to layer tilt. In fact the measured peak separations of 194, 193, 195 and 201 arcseconds at Phi angles of 0°, 90°, 180° and 270° respectively suggest a small tilt amplitude of about 4 arcseconds. The process of determining this tilt amplitude will now be described.



Figure 5.9: HRXRD (004) rocking curves obtained from sample S2230211 at Phi angles of  $0^{\circ}$ ,  $90^{\circ}$ ,  $180^{\circ}$  and  $270^{\circ}$ . The diffraction profiles are shifted vertically for clarity.

An example of a sine function plot of this data is shown in Figure 5.10 for sample S2230211, where the x-axis plots the Phi angle in degrees and the y-axis represents the peak separation between the GaAs substrate peak and the SLO peak, in arcseconds. Five data points have been plotted with the fifth data point at a Phi angle of  $360^{\circ}$  having the same value as at a Phi angle of  $0^{\circ}$ , to complete the sine wave function for one period.  $\Delta \omega_{ave}$  is shown by the solid horizontal line in the plot, at about 195 arcseconds, and it can be seen that the values of Phi angles at which the tilt had no component in the plane of diffraction are  $168^{\circ}$  and  $348^{\circ}$  (labelled *a* and *b* in Figure 5.10). Since all data points are well fitted by the sine function, it is clear that the peak separation variation is due to a simple layer tilt in the sample, with an amplitude of about 4 arcseconds. HRXRD scans at Phi angles of 168° or 348° were subsequently collected since at this angle the effect of lattice tilt is eliminated and this spectrum could be compared directly with a dynamical simulation to confirm the MOW layer properties determined from the analysis, as will be described in section 5.3.3.2. These procedures were repeated for all as-grown samples before the InGaAs/GaAs MQW's were removed by etching to simplify the interpretation of spectra collected when only the GaAsN and InGaAsN single layers were present.



Figure 5.10: Sine wave function fitting peak separations  $\Delta \omega(\emptyset)$  between GaAs substrate and zeroth MQW peak as a function of Phi angle for sample S2230211. The solid horizontal line shows the mean  $\Delta \omega_{ave}$  of the sine function at about 195 arcseconds.

After removal of the InGaAs/GaAs MQW layers, the InGaAsN-GaAs and GaAsN-GaAs peak separations could be obtained from spectra collected at four azimuthal angles which were again fitted to a sine function to allow layer tilts to be identified and taken into account. Figure 5.11 shows examples of sine wave function plots for (a) GaAsN-GaAs and (b) InGaAsN-GaAs peak separations obtained from sample S2310111. From the figure, the mean  $\Delta \omega_{ave}$  of the sine functions associated with the GaAsN-GaAs and InGaAsN-GaAs peak separations are about 638 and 40 arcseconds respectively, allowing lattice parameters to be calculated from these figures.



Figure 5.11: Sine wave functions fitting peak separations  $\Delta \omega(\emptyset)$  plotted as a function of Phi angle for sample S2310111 which contained a tensile strained InGaAsN layer and a tensile GaAsN layer. (a) GaAsN-GaAs peak separations and (b) InGaAsN-GaAs peak separations.

#### 5.3.3.2 MQW Analysis for Indium and Gallium Flux Rate Calibration

Prior to growing each set of samples, a ten-period  $In_xGa_{1-x}As/GaAs$  MQW structure as shown in Figure 5.12. These samples were grown for the purpose of calibrating the indium and gallium flux rates. Each MQW period of thickness *P* consisted of an InGaAs and a GaAs epitaxial layer. Following analysis the layer thicknesses and indium mole fraction x could be determined and this allowed flux rates to be determined accurately. A requirement for this analysis of a MQW structure is that the layer thicknesses must be less than their critical thicknesses, otherwise the interfaces will not be coherent. The details of these calculations follow the approach of Usher and Zhou [175].



Figure 5.12: Schematic of a typical InGaAs/GaAs MQW structure for indium and gallium flux rate calibration.

Figure 5.13 shows a typical (004) HRXRD rocking curve obtained from a ten-period InGaAs/GaAs MQW grown on a GaAs substrate. It is one of four spectra collected at Phi angles of 0°, 90°, 180° and 270° from sample S1290311. The growth times for the InGaAs and GaAs layers in each period were 60 and 120 seconds respectively. This spectrum clearly shows the GaAs substrate peak, satellite peaks as far out as order  $\pm 3$  as labelled in the figure and the zeroth order satellite peak which is labelled as *SL*0. The separations between the satellite peaks depends on the thickness of one period of the InGaAs/GaAs MQW with thicker InGaAs/GaAs MQW layers resulting in smaller satellite peak separations. The angular position of the zeroth peak is determined by the mean perpendicular lattice constant through the entire MQW

structure. Identifying the zeroth order peak which is not necessarily the most intense satellite peak, was done by calculating the expected average perpendicular lattice constant and its corresponding Bragg angle. This usually lined up with one of the experimental peaks very well and was later confirmed by simulation.



Figure 5.13: HRXRD (004) rocking curve of a ten-period InGaAs/GaAs MQW (sample S1290311).

The x-ray spectrum obtained from an (004) reflection contains a zeroth peak, which will be located at a Bragg angle  $\theta_{SL0}$  such that:

$$2d_{ave}\sin\theta_{SL0} = \lambda \tag{5.3}$$

where  $\lambda$  is the wavelength of the radiation used and  $d_{ave}$  is the lattice plane spacing averaged over the thicknesses of the layers in the structure. For the (004) reflection,

$$d_{ave} = \frac{a_{SL0}^{\perp}}{4} \tag{5.4}$$

where  $a_{SL0}^{\perp}$  is the mean perpendicular lattice constant of the entire MQW structure. The mean perpendicular lattice constant  $a_{SL0}^{\perp}$  of the MQW structure is given by:

$$a_{SL0}^{\perp} = \frac{a_{GaAs}^{\perp}h_{GaAs} + a_{InGaAs}^{\perp}h_{InGaAs}}{h_{GaAs} + h_{InGaAs}}$$
(5.5)

where  $a_{GaAs}^{\perp}$  and  $a_{InGaAs}^{\perp}$  are the perpendicular lattice constants of GaAs and InGaAs respectively while  $h_{GaAs}$  and  $h_{InGaAs}$  are the respective thicknesses of the GaAs and InGaAs layers.

From Equations 5.3 and 5.4, the angular position of the zeroth peak  $\theta_{SL0}$  could be calculated from:

$$\theta_{SL0} = \sin^{-1} \frac{\lambda}{2\left(\frac{a_{SL0}^{\perp}}{4}\right)}.$$
(5.6)

From Equations 3.10 and 3.12 in chapter 3 section 3.3.1.2, the angular position of the (004) GaAs substrate peak  $\theta_{GaAs}$  could be found from:

$$\theta_{GaAs} = \sin^{-1} \frac{\lambda}{2\left(\frac{a_{GaAs}}{4}\right)}.$$
(5.7)

Since  $a_{GaAs}$  is 5.65325 Å [38, 39] and  $\lambda$  is 1.5406 Å, the angular position of the GaAs substrate peak  $\theta_{GaAs}$  is equal to 33°97" and the peak separation between the GaAs substrate and the zeroth satellite peak  $\Delta \omega_{GaAs-SL0}$  as labelled in Figure 5.13 is given by:

$$\Delta\omega_{GaAs-SL0} = \theta_{GaAs} - \theta_{SL0}.$$
(5.8)

The peak separation was measured accurately using X'Pert Epitaxy and Smoothfit 4.0 however it should be emphasised that the MQW layer properties were not extracted from the simulation results, rather they were obtained entirely by identifying the angular positions of all MQW satellite peaks relative to the substrate peak and performing an analysis of that data.

The period P of the InGaAs/GaAs MQW was determined from the highest and lowest angle satellite peak positions that were measureable, and is given by:

$$P = \frac{(i-j)\lambda}{2\left|\sin\theta_i - \sin\theta_j\right|}$$
(5.9)

where *i* and *j* are the order of any two satellite peaks, and  $\theta_i$  and  $\theta_j$  are the diffraction angles associated with those peaks.

A self-consistent value for the perpendicular lattice constant of the InGaAs epitaxial layer  $a_{InGaAs}^{\perp}$  and the indium mole fraction *x* could then be calculated from Equations 5.10, 5.11 and 5.12 below:

$$\frac{a_{InGaAs}^{\perp}}{a_{GaAs}} = \left(\frac{t_{GaAs}}{t_{InGaAs}}\right) \left(\frac{a_{GaAs} - a_{SL0}^{\perp}}{a_{SL0}^{\perp} - a_{InGaAs}^{\perp}}\right) (1 - x)$$
(5.10)

$$a_{InGaAs}^{\perp} = x(a_{InAs} - a_{GaAs}) \left(\frac{1 + v_{InGaAs}}{1 - v_{InGaAs}}\right) + a_{GaAs}$$
(5.11)

and

$$v_{InGaAs} = x(v_{InAs}) + (1 - x)v_{GaAs}$$
(5.12)

where  $t_{GaAs}$  and  $t_{InGaAs}$  are the growth times for the respective layers,  $a_{GaAs}$  and  $a_{InAs}$  are the GaAs and InAs lattice constants and  $v_{GaAs}$ ,  $v_{InAs}$  and  $v_{InGaAs}$  are Poisson's ratios of GaAs, InAs and InGaAs respectively.

From the information extracted above, the thicknesses  $h_{GaAs}$  and  $h_{InGaAs}$  of the GaAs and InGaAs epitaxial layers could also be calculated from:

$$h_{GaAs} = P\left(\frac{a_{SL0}^{\perp} - a_{InGaAs}^{\perp}}{a_{GaAs} - a_{InGaAs}^{\perp}}\right)$$
(5.13)

and

$$h_{InGaAs} = P\left(\frac{a_{GaAs} - a_{SL0}^{\perp}}{a_{GaAs} - a_{InGaAs}^{\perp}}\right)$$
(5.14)

where the value of P could be determined from Equation 5.9 and is also equivalent to:

$$P = h_{GaAs} + h_{InGaAs}.$$
 (5.15)

The GaAs layer growth rate  $l_{GaAs}$  in atomic layers per second could then be calculated from:

$$l_{GaAs} = \left(\frac{h_{GaAs}}{t_{GaAs}}\right) \left(\frac{2}{a_{GaAs}}\right)$$
(5.16)

and the gallium flux rate  $\gamma_{Ga}$  was then given by:

$$\gamma_{Ga} = (N_0)(l_{GaAs}) \tag{5.17}$$

where  $N_0$  is the substrate surface site density for group III or V atoms which could be calculated from:

$$N_0 = 2\left(\frac{1}{a_{GaAs}}\right)^2.$$
(5.18)

The factor of 2 arises because in the (001) unit cell surface there are two group III or group V atoms and since  $a_{GaAs}$  is equal to 5.65325 Å then  $N_0 = 6.258 \times 10^{14}$  atoms/cm<sup>2</sup>. By substituting the gallium flux rate  $\gamma_{Ga}$  and the indium mole fraction *x*, the indium flux rate  $\gamma_{In}$  could be determined by:

$$\gamma_{In} = \frac{x(\gamma_{Ga})}{1 - x}.$$
(5.19)

Figure 5.14 shows examples of three (004) rocking curves obtained from samples in sets 2b, 3 and 4, for nominal nitrogen mole fractions of about 0.007, 0.010 and 0.012 respectively, showing all MQW and layer peaks. All spectra were obtained from selected HRXRD scans at Phi angles of 0°, 90°, 180° and 270°. Sample S1070311 had a nominal nitrogen mole fraction of about 0.007 while samples S1100211 and S2310111 contained nominal nitrogen mole fractions of about 0.010 and 0.012 respectively. The spectra show clear zeroth and higher order satellite peaks from the InGaAs/GaAs MQW layers as labelled in the figure. All InGaAsN layer peaks are denoted by an X in the figure. Both samples S1070311 and S1100211 contained compressively strained InGaAsN layers, while sample S2310111 contained a tensile strained layer. The compressive InGaAsN layer peaks are on the low angle side and the tensile layer peak is on the high angle side of the GaAs substrate peak. The tensile InGaAsN layer peak for sample S2310111 is close to the GaAs substrate peak and the compressive InGaAsN layer peaks are between the GaAs substrate and the zeroth order MQW peak for samples S1070311 and S1100211. The GaAsN layer peaks for all samples are on the high angle side of the GaAs substrate peak and these layer peaks are overlapping with the GaAs buffer layer and positive order satellite peaks. Furthermore, these layer peaks are broad and low in intensity due to the fact that they originate from thin layers (between 50 and 100 nm) and so they are not particularly clear in these spectra. However, following removal of the MQW from each sample the positions of the GaAsN peaks became clearer.



Figure 5.14: Examples of HRXRD (004) rocking curves obtained from samples in sets 2b, 3 and 4. The symbols *X* identify the positions of the InGaAsN layer peaks and the diffraction profiles are shifted vertically for clarity.

## 5.3.4 MQW Etching Process

After completing the MQW analysis to obtain the indium and gallium flux rates, the next step was to remove the MQW structure from each sample by etching. The samples etched in polishing etchant consisting of were а  $H_2SO_4(96\%):H_2O_2(30\%):H_2O$  mixed in the volume proportions of 8:1:1. The preparation of the  $H_2O_2(30\%)$ :  $H_2O$  has been explained in chapter 3 section 3.2.1 and this mixture was then added to H<sub>2</sub>SO<sub>4</sub> in the ratio of 1:4 and stirred thoroughly before being stored in a bottle and refrigerated. The etchant was refrigerated for at least six hours to ensure its temperature had stabilised at about 4°C before the
etching process was started. A cool etchant was preferred as better control could be exercised when using a slower etch than with a fast hot etchant.

Before performing any etching, the etch rate was calibrated from step height measurements using an AFM. Several small pieces of GaAs were used to calibrate the etch rate by etching them for different times. Prior to etching, small pieces of white wax were placed on the centre of each piece of GaAs and then heated on a hot plate until the wax melted at about 80°C and spread to form a circular mask. The wax was then left to cool before proceeding to etching. Each of the GaAs substrates was etched for different times before being rinsed thoroughly in DI water. Another reason for using a cool etch was to avoid the possibility of melting the wax at this step. The GaAs was left submerged in DI water before being dried using filtered dry nitrogen gas. The white wax was then removed from the GaAs surfaces by rinsing in trichloroethylene after which the pieces were rinsed in acetone, methanol and DI water before being dried again using filtered dry nitrogen gas. After removal of the white wax, the etched and unetched areas of the GaAs surfaces could easily be seen by eye. AFM measurements were performed on each of the pieces to determine the etch step heights. Figure 5.15 shows the step height data plotted against etching time, indicating an etch rate of approximately 12 nm/s for the volume ratio of 8:1:1 used. The errors were  $\pm 1$  second and  $\pm 5$  nm for the etch time and step height measurements respectively. The readings from the AFM had a variation of about 3.3% when measured at different step positions on the sample. This etchant was then used to remove the MQW's from all samples, as explained in the next paragraph.



Figure 5.15: Plot of the step height as measured by AFM against etch time for etch rate calibration. The line of best fit is for two GaAs etch tests with a point at the origin assumed.

Each 10 mm x 10 mm sample was scribed with a diamond tip and cleaved into four equal pieces to give backup should the MQW etch process have any problems. Before cleaving, a small dot was marked on each piece in order to ensure that each sample could be x-ray scanned again in the same orientation as before cleaving and removal of the MQW. One of the pieces was then etched with the etching time calculated according to the known thickness of the InGaAs/GaAs MQW. It was important to ensure that the entire InGaAs/GaAs MQW had been removed during the etching process, with the GaAs buffer layer on top of the GaAsN epitaxial layer protecting the GaAsN layer from a deeper etch than intended. Following removal of the InGaAs/GaAs MQW, each sample was scanned again to obtain a HRXRD spectrum that included only the GaAs substrate and the individual InGaAsN and GaAsN layer peaks, and these results are presented in the following section. Figure 5.16 shows a schematic of the sample structures after the InGaAs/GaAs MQW had

been removed and the B in the figure shows partial removal of the GaAs buffer during the etching process.



Figure 5.16: Schematic of the sample structure after the InGaAs/GaAs MQW had been removed, showing that a little of the GaAs buffer had also been removed (labelled *B*).

## 5.3.5 HRXRD Rocking Curves after MQW Removal

The layer perpendicular lattice constants in the growth direction were determined from the differences in the Bragg angles between peaks originating from the GaAs substrate and from the individual InGaAsN and GaAsN layers. Examples of HRXRD spectra obtained after removal of the InGaAs/GaAs MQW are shown in Figure 5.17 (the same set of samples as displayed in Figure 5.14). The Pendellösung fringes appearing in all of the spectra indicate smooth and coherent interfaces and the GaAsN peaks (on the high angle side of the GaAs substrate peaks) are broad and indistinct except for the high nominal nitrogen mole fraction ( $y \approx 0.01$ ) samples S1100211 and S2310111. The GaAsN peaks are broad because they originate from a thin layer and it is therefore difficult to identify the position of these peaks, particularly in the case of sample \$1070311. In addition, for this sample, its nominal nitrogen mole fraction was relatively low, about 0.007, so that it tends to be obscured somewhat by the wide Lorentzian tails associated with the GaAs substrate peak. However, this problem could be solved by using simulation software and this will be explained later. The InGaAsN peaks (labelled with an X) can be seen clearly since they originate from thicker layers, and while the InGaAsN layer peak from sample

S2310111 was very close to the GaAs substrate, its angular position could be determined unambiguously following simulation.



Figure 5.17: Examples of HRXRD (004) rocking curves from samples in sets 2b, 3 and 4 after removal of the InGaAs/GaAs MQW. The symbols *X* identify the positions of the InGaAsN layer peaks and the diffraction profiles are shifted vertically for clarity.

The peak separations between InGaAsN and GaAsN layer peaks and the GaAs substrate peak for all x-ray rocking curves were accurately measured using X'Pert Epitaxy and Smoothfit 4.0 software by fitting a simulation to the experimental curves. An example of experimental and simulated curves from sample S1100211 is shown in Figure 5.18. The compressively strained InGaAsN layer peak is on the low angle side of the GaAs substrate while the GaAsN peak is on the high angle side of the substrate peak. Some of the fringes in the simulation are not seen in the

experimental curve, suggesting some interfacial roughness even though the thicknesses of each layer were significantly less than their theoretical critical thicknesses. Measurement of the peak separation between the InGaAsN layer (labelled X in the figure), and GaAs substrate could be found directly from the simulated spectrum. There is a high angle "shoulder" (labelled with an S) to the experimental GaAs substrate peak due to interferences between the GaAs substrate, GaAs buffer and GaAsN layer peaks.



Figure 5.18: Experimental (blue) and simulated (red) HRXRD rocking curves from sample S1100211.

The GaAsN layer is relatively thin and consequently its diffraction peak has low intensity and is very broad, making it difficult to identify its peak separation relative to the GaAs substrate. The simulation software used in this work did not give any information on the perpendicular lattice constants of any of the layers after the simulation had been completed. Therefore, following simulation, the thickness of the GaAsN layer in the simulated structure was increased to give a higher intensity and narrower width GaAsN peak allowing ready measurement of its separation from the GaAs substrate peak as shown in Figure 5.19. Simulation based on dynamical x-ray diffraction theory was also very useful in helping to determine the InGaAsN-GaAs peak separations when the InGaAsN layer peak was very close to the substrate and not clearly resolved. For example, the InGaAsN-GaAs layer peak separation for sample \$2310111 (see Figure 5.17) could be found following simulation by increasing the InGaAsN layer thickness until its angular position relative to the

substrate was clear. It was then possible to calculate the perpendicular lattice constant of the InGaAsN layer by the same method as was used for the GaAsN layer.



Figure 5.19: Experimental (blue) and simulated (red) HRXRD rocking curves for sample S1100211. The GaAsN layer thickness was increased to 200 nm in the simulation to allow the peak separation of a thicker layer of the same composition to be determined.

The same value of indium mole fraction x as found from the analysis of the MQW's was used in the  $In_xGa_{1-x}As_{1-y}N_y$  layer to achieve a self-consistent fit between simulated and experimental rocking curves for all spectra collected at Phi angles of  $0^{\circ}$ ,  $90^{\circ}$ ,  $180^{\circ}$  and  $270^{\circ}$ . This value of indium mole fraction was obtained from the analysis of the fifth HRXRD spectrum collected from each sample, for which lattice tilt effects had been eliminated. Since the same indium mole fraction x was used in the simulation of all spectra collected from any one sample, the nitrogen mole fraction y was the only variable to be changed in the simulation in order to fit the simulated InGaAsN and GaAsN peaks to the experimental spectrum. The values of nitrogen mole fraction used for the InGaAsN layer peak was the same as that used for simulation of the GaAsN layer peak. The thicknesses of the InGaAsN, GaAsN and GaAs buffer layers used in the simulation were calculated according to the layer growth times and knowledge of the predominant indium and gallium fluxes obtained from analysis of the MQW's. A wafer bending parameter (wafer radius of curvature) was adjusted to obtain the best agreement between the simulated and experimental curves.

The estimated nitrogen mole fraction *y* in a GaAs<sub>1-y</sub>N<sub>y</sub> epitaxial layer was calculated from measurement of the peak separation between the GaAsN epitaxial layer and the GaAs substrate  $\Delta \omega_{GaAsN-GaAs}$ . The angular position of the GaAsN epitaxial layer peak  $\theta_{GaAsN}$  could be determined from:

$$\theta_{GaAsN} = \theta_{GaAs} + \Delta \omega_{GaAsN-GaAs} \tag{5.20}$$

and the perpendicular lattice constant of the GaAsN epitaxial layer  $a_{GaAsN}^{\perp}$  could be calculated from Equations 3.10 and 3.12 in chapter 3 section 3.3.1.2 to yield:

$$a_{GaAsN}^{\perp} = \frac{4\lambda}{2(\sin\theta_{GaAsN})}.$$
 (5.21)

For tetragonal distortion linear elasticity theory allows the natural lattice constant  $a_{GaAsN}$  of the GaAsN layer to be calculated from:

$$a_{GaAsN} = \left(\frac{2\nu}{1+\nu}\right) a_{GaAsN}^{||} + \left(\frac{1-\nu}{1+\nu}\right) a_{GaAsN}^{\perp}$$
(5.22)

where  $a_{GaAsN}^{||} = a_{GaAs}$  and *v* is Poisson's ratio for the layer, while  $a_{GaAsN}^{\perp}$  is calculated from Equation 5.21. Therefore, the nitrogen mole fraction *y* could be found from Equation 5.23 when  $a_{GaAsN}$  was known since:

$$a_{GaN_yAs_{I-y}} = ya_{GaN} + (1 - y)a_{GaAs}.$$
 (5.23)

The values of the lattice constants for GaN and GaAs were taken from Table 3.2 in chapter 3 section 3.3.1.4.

# 5.4 Results and Discussion

The results presented here include the raw experimental data and a plot of  $In_xGa_{1-x}As_{1-y}N_y$ -GaAs peak separations against indium mole fraction *x* at particular nitrogen mole fractions *y*. Also presented are the methods used for data analysis and a plot of the relationship between GaAs<sub>1-y</sub>N<sub>y</sub>-GaAs peak separations and the equivalent indium mole fraction required to exactly cancel the strain in such a layer.

#### 5.4.1 Data Analysis

The results obtained from all samples in each set are summarised in Table 5.3. The values of the indium mole fraction *x* shown in the table were found from an analysis of the In<sub>*x*</sub>Ga<sub>1-*x*</sub>As/GaAs MQWs by the method explained in section 5.3.3.2 and in Reference [175]. Negative signs in the InGaAsN-GaAs peak separations indicate that the layers were on the low angle side of the GaAs substrate and therefore compressively strained. For tensile InGaAsN layers, when the peaks were on the high angle side of the GaAs substrate, the peak separations are positive. The estimated or nominal values of nitrogen mole fractions *y* for each sample in the table were calculated from the GaAsN-GaAs peak separations as explained in section 5.3.5. These values are only nominal since various untested assumptions have been made in their calculation. The error associated with determination of the peak separations from all HRXRD spectra were  $\pm 3$  arcseconds as shown in the table. This is the main contribution to the errors of  $\pm 0.001$  and  $\pm 0.0001$  in the indium and nominal nitrogen mole fractions respectively.

The raw data displayed in Table 5.3 is subject to experimental error, however additionally the calculation of x and y were subjected to certain assumptions and it is important to make these assumptions clear here. Firstly, the lattice and elastic constant values for GaAs [39], InAs [38], GaN [38] and InN [38] required for the analysis and shown in Table 3.2 in chapter 3 section 3.3.1.4 are the best values we have, but are not necessarily correct, particularly those for the nitrides. Secondly, the parallel lattice constants  $a^{\parallel}$  of all layers were assumed to be identical to the GaAs

substrate, in fact the TEM analysis in chapter 4 confirms that our x-ray results are unaffected by interfacial misfit dislocations or any other strain-relieving defects and the prominent thickness (Pendellösung) fringing in HRXRD spectra supports the assertion that it is unlikely that any interfaces were incoherent in any of these samples. In further support of this conclusion, the presence of a significant density of interfacial misfit dislocations, such that measurable strain relief has occurred, is generally accompanied by dramatic peak broadening, an asymmetry in the peak shape and layer tilting of the order of tens of arcseconds. We observe small layer tilts but there were no tilts of this order and none of the other symptoms of layer strain relaxation were evident.

Set	Sample	$\Delta\omega_{InGaAsN-GaAs}$	$\Delta\omega_{GaAsN-GaAs}$	x	У
		(arcsec)	(arcsec)	(±0.001)	(Estimate)
		(±3 arcsec)	(±3 arcsec)		(±0.0001)
1	S2071009	+35	185	0.008	0.0035
	S1011209	-111	205	0.017	0.0038
	S2011209	-94	184	0.015	0.0034
	S4011209	+52	168	0.006	0.0031
2	S1280110	-172	229	0.022	0.0043
	S2280110	+96	414	0.017	0.0077
	S1290110	-116	279	0.022	0.0052
	S2290110	-47	323	0.020	0.0060
2b	S1070311	-138	383	0.029	0.0072
	S2070311	+86	376	0.015	0.0070
	S1090311	-49	394	0.025	0.0074
	S2090311	+156	388	0.013	0.0073
3	S1100211	-152	526	0.037	0.0098
	S2100211	+95	527	0.024	0.0098
	S2230211	+106	492	0.021	0.0092
4	S2310111	+40	638	0.032	0.0119
	S1020211	-183	609	0.043	0.0114
	S1230211	-65	638	0.039	0.0119

Table 5.3: Results from the analysis of rocking curves obtained from all samples.

Thirdly, Poisson's ratio v for all layers was assumed to be equal to that of the GaAs substrate, namely  $0.322 \pm 0.005$  [180]. This should be reasonable because the nominal nitrogen mole fractions are low, of the order of 0.3% to 1.2% and the indium mole fractions are also low, of the order of three times the nitrogen mole fractions. Therefore, all layers are close to the composition of GaAs and this assumption would seem reasonable in the absence of better data on the dilute nitride Poisson's ratios. Fourthly, it has been assumed that isotropic linear elasticity theory holds for all epitaxial layers and that the relationships between lattice constants, lattice strain and Poisson's ratio v can be expressed according to Equations 3.27 and 3.28 in chapter 3 section 3.3.1.3. Lastly, it was assumed the materials were homogeneous and that Vegard's law holds, that there was a linear relationship between composition and natural (unstrained) lattice constant for all ternary or quaternary layers as discussed in section 3.3.1.4.

All of these assumptions were made based on the best information available from the literature, however some of these assumptions were tested and are reported on in other chapters. For example, experiments on Poisson's ratio and lattice constants of GaAsN for y < 0.012 will be discussed in chapters 6 and 7 respectively. Chapter 6 reports the results of experiment which were undertaken to measure Poisson's ratio in the dilute nitride GaAs<sub>1-y</sub>N<sub>y</sub> for y = 0.0065, not in the expectation of achieving high precision, but to check that our assumption that it is close to that of GaAs is reasonable. This is because it is well known that the addition of low levels of "impurities" to a host material can have dramatic effects on its elastic properties, for example carbon in iron or silicon in aluminium. In addition, interfacial coherence in GaAs/GaAsN heterostructures at nominal nitrogen mole fraction of 0.009 was confirmed using TEM as was explained in chapter 4 section 4.2.

Within each set of samples the nominal nitrogen mole fraction y in both the GaAs<sub>1-</sub> <sub>y</sub>N<sub>y</sub> and In<sub>x</sub>Ga<sub>1-x</sub>As<sub>1-y</sub>N<sub>y</sub> layers were intended to be constant. However, as can be seen from Table 5.3 this was more true in the case of some sets than for others. The variation of nominal nitrogen mole fractions for set 2 was about 33% from its mean while the other sets of samples had smaller variations in nominal nitrogen mole fractions, being 10.6%, 2.5%, 4.4% and 3.1% for sets 1, 2b, 3 and 4 respectively. The reproducibility of the nominal nitrogen mole fractions was tested in samples grown for this purpose and it varied by about  $\pm 13\%$  from the mean, as discussed in section 5.2.1.

Figure 5.20 shows a plot of the InGaAsN-GaAs peak separation data against the indium mole fractions in the InGaAsN layers from Table 5.3. Each of the sets of experimental data in Table 5.3 is plotted using different symbols. The diagonal lines in the plot are theoretical lines of constant nitrogen mole fraction y, showing y = 0and higher values between 0.003 and 0.0125 in increments of 0.0005. The functional form of these lines is developed in the following paragraphs. The fact that the results for each set did not lay on or close to one of the lines of constant nitrogen mole fraction means that their nitrogen mole fractions were not the same for each set. Therefore, in order to avoid a large variation in nominal nitrogen mole fractions, the data from set 2 was not included in any further analysis. In addition, sample S1011209 was also excluded from further analysis of the set 1 data so that the variation of nominal nitrogen mole fractions in set 1 was reduced from 10.6% to 6% from its mean. The horizontal dashed line in the plot represents zero peak separation between a peak from an InGaAsN layer and from the GaAs substrate. From this plot, it can be observed that some points are above the zero peak separation line and others are beneath it, corresponding to tensile and compressively strained InGaAsN layers respectively.



Figure 5.20: Plot of InGaAsN-GaAs peak separations against indium mole fraction x at various values of y for all data sets in Table 5.3. The solid lines represent constant nitrogen mole fractions y, based on the assumptions that Poisson's ratio and lattice constants are known and that Vegard's law holds.

A theoretical relationship between InGaAsN-GaAs peak separations and indium mole fraction x at particular nitrogen mole fractions y as shown by the solid lines in Figure 5.20 was developed as follows.

Assuming Vegard's law, the natural lattice constant of an InGaAsN layer  $a_{InGaAsN}$  is given by:

$$a_{In_xGa_{1-x}N_yAs_{1-y}} = xya_{InN} + y(1-x)a_{GaN} + x(1-y)a_{InAs} + (1-x)(1-y)a_{GaAs}$$
(5.24)

where x and y are the indium and nitrogen mole fractions respectively. The relationship between the natural or relaxed InGaAsN lattice constant  $a_{InGaAsN}$  and the

parallel  $(a_{InGaAsN}^{||})$  and perpendicular  $(a_{InGaAsN}^{\perp})$  lattice parameters, when a layer is tetragonally strained, is given by:

$$a_{InGaAsN} = \left(\frac{2\nu}{1+\nu}\right) a_{InGaAsN}^{||} + \left(\frac{1-\nu}{1+\nu}\right) a_{InGaAsN}^{\perp}$$
(5.25)

where *v* is Poisson's ratio for the layer. By rearranging Equation 5.25, the perpendicular lattice parameter  $a_{InGaAsN}^{\perp}$  can be shown to be:

$$a_{InGaAsN}^{\perp} = \left[a_{InGaAsN} - \left(\frac{2va_{InGaAsN}^{||}}{1+v}\right)\right] \left[\frac{(1+v)}{(1-v)}\right]$$
(5.26)

where  $a_{InGaAsN}^{||} = a_{GaAs}$ . For an (004) reflection from a tetragonally strained InGaAsN layer, the peak separation between such an InGaAsN layer and the GaAs substrate  $\Delta \omega_{InGaAsN-GaAs}$  is then given by:

$$\Delta \omega_{InGaAsN-GaAs} = \sin^{-1} \left( \frac{2\lambda}{a_{InGaAsN}^{\perp}} \right) - \sin^{-1} \left( \frac{2\lambda}{a_{GaAs}} \right).$$
(5.27)

By substituting for  $a_{InGaAsN}$  from Equation 5.24 into Equation 5.26 and then for  $a_{InGaAsN}^{\perp}$  from Equation 5.26 into Equation 5.27 the relationship between peak separation  $\Delta \omega_{InGaAsN-GaAs}$  and indium mole fraction *x* is established, with *y* treated as an adjustable parameter. The variation in nominal nitrogen mole fractions within each set meant that some data manipulation would be required to allow determination of an indium equivalent of a GaAsN nominal nitrogen mole fraction as measured by the GaAsN-GaAs peak separation. Therefore, three different approaches have been taken to analyse the data collected in this study and these approaches are explained in the following sections. It will be seen that each approach brings us to the same conclusions, with only small variations in the details of those conclusions.

## 5.4.1.1 The First Method

In this method, a line of best fit was plotted through experimental data points within a set as shown in Figure 5.21. It can be seen that the lines of best fit are approximately parallel to the theoretical lines of constant nitrogen mole fraction y, indicating the similarity in nitrogen mole fractions within each set. The point where each line crosses the horizontal zero peak separation line indicates the zero strain case for the  $In_xGa_{1-x}As_{1-y}N_y$  layer, thus giving the indium mole fraction x required to exactly cancel the strain in a  $GaAs_{1-y}N_y$  layer with a particular perpendicular lattice constant. The GaAsN-GaAs peak separation was taken to be the average of the data values within each set. The indium mole fractions thus determined at zero InGaAsN-GaAs peak separation, together with the mean GaAsN-GaAs peak separations are displayed in Table 5.4. The errors associated with each set reflect the variation of nitrogen content, as shown in the table.



Figure 5.21: Plot of InGaAsN-GaAs peak separations against indium mole fraction x for various values of y. The solid lines are lines of constant nitrogen mole fraction y, based on the assumptions that Poisson's ratio and lattice constants are known and linear with composition. The dashed lines are lines of best fit to the experimental data for each set and the vertical dashed lines indicate the indium mole fractions at zero InGaAsN-GaAs peak separations.

Set	Mean value of $\Delta \omega_{GaAsN-GaAs}$ (arcsec)	$x \text{ at } \Delta \omega_{InGaAsN-GaAs} = 0$ (±0.001)
1	179±11	0.010
2b	385±9	0.021
3	515±23	0.028
4	628±19	0.034

Table 5.4: Results showing the strain cancelling indium mole fraction at zero InGaAsN-GaAs peak separation and the corresponding GaAsN-GaAs mean peak separation for a GaAsN layer with the same nitrogen content.

Development of a theoretical relationship between GaAsN-GaAs peak separations and strain cancelling indium mole fraction x, to account for the data of Table 5.4, will be done in the next paragraph. This development assumes a common nitrogen mole fraction y in the In<sub>x</sub>Ga<sub>1-x</sub>As<sub>1-y</sub>N<sub>y</sub> and GaAs<sub>1-y</sub>N<sub>y</sub> layers and finds the indium mole fraction x at which the InGaAsN layer is exactly lattice-matched with a GaAs substrate.

Assuming Vegard's law holds, the natural lattice constant of a GaAsN layer  $a_{GaAsN}$  is given by Equation 5.23 in section 5.3.5, namely:

$$a_{GaN_yAs_{I-y}} = ya_{GaN} + (1 - y)a_{GaAs}$$
  
=  $y(a_{GaN} - a_{GaAs}) + a_{GaAs}.$  (5.28)

The relationship between the natural GaAsN lattice parameter  $a_{GaAsN}$  and the parallel  $(a_{GaAsN}^{||})$  and perpendicular  $(a_{GaAsN}^{\perp})$  lattice parameters when tetragonally strained, is given by:

$$a_{GaAsN} = \left(\frac{2\nu}{1+\nu}\right) a_{GaAsN}^{||} + \left(\frac{1-\nu}{1+\nu}\right) a_{GaAsN}^{\perp}$$
(5.29)

and by rearranging Equation 5.29, the GaAsN perpendicular lattice constant  $a_{GaAsN}^{\perp}$  is given by:

$$a_{GaAsN}^{\perp} = \left[a_{GaAsN} - \left(\frac{2va_{GaAsN}^{\parallel}}{1+v}\right)\right] \left[\frac{(1+v)}{(1-v)}\right]$$
(5.30)

and the peak separation between a GaAsN layer and the GaAs substrate  $\Delta \omega_{GaAsN-GaAs}$  for an (004) reflection is then given by:

$$\Delta \omega_{GaAsN-GaAs} = \sin^{-1} \left( \frac{2\lambda}{\left[ \left\{ y(a_{GaN} - a_{GaAs}) + a_{GaAs} \right\} - \left( \frac{2\nu a_{GaAsN}^{||}}{1 + \nu} \right) \right] \left[ \frac{(1 + \nu)}{(1 - \nu)} \right]} \right)$$
$$- \sin^{-1} \left( \frac{2\lambda}{a_{GaAs}} \right)$$
(5.31)

where  $a_{GaAsN}^{||} = a_{GaAs}$ .

For the nitrogen mole fraction *y* involved in the peak separation Equation 5.31, we need to find the indium mole fraction *x* which will exactly cancel the strain in the  $GaAs_{1-y}N_y$  layer. When an InGaAsN layer is exactly lattice-matched to its GaAs growth substrate, the natural lattice constants of InGaAsN and GaAs are equal. Equating the natural lattice constant of InGaAsN from Equation 5.24 with the GaAs lattice constant yields:

$$xya_{InN} + y(1 - x)a_{GaN} + x(1 - y)a_{InAs} + (1 - x)(1 - y)a_{GaAs} = a_{GaAs}.$$
 (5.32)

By manipulation of Equation 5.32, a relationship between x and y can be established for the case when the InGaAsN layer is perfectly lattice-matched to the growth substrate, so we have:

$$x(a_{InAs} - a_{GaAs}) + y(a_{GaN} - a_{GaAs}) - xy(a_{InAs} - a_{GaAs} + a_{GaN} - a_{InN}) = 0.$$
(5.33)

By making the substitutions  $\alpha = a_{InAs} - a_{GaAs}$ ,  $\beta = a_{GaN} - a_{GaAs}$  and  $\gamma = a_{GaN} - a_{InN}$ , Equation 5.33 becomes:

$$x\alpha + y\beta - xy(\alpha + \gamma) = 0. \tag{5.34}$$

Rearranging Equation 5.34, the relationship between *x* and *y* is given by:

$$x = \frac{y}{y\delta + \varepsilon}$$
(5.35)

where  $\delta = \frac{\alpha + \gamma}{\beta}$  and  $\varepsilon = \frac{-\alpha}{\beta}$ .

The connection between the peak separation Equation 5.31 and the indium mole fraction *x* which cancels the strain in the  $GaAs_{1-y}N_y$  layer, as shown in Equation 5.35, is the nitrogen mole fraction *y*. By varying the nitrogen mole fraction *y* as a parameter, GaAsN-GaAs peak separations can be related to stress cancelling indium mole fractions *x*.

Since evaluation of Equation 5.31 depends on the values of the binary end-point lattice constants (GaAs, GaN, InN and InAs) and Poisson's ratio v, any change in these values will modify this equation and thus the theoretical relationship between GaAsN-GaAs peak separations and strain cancelling indium mole fraction x. This is also true of Equation 5.35 which involves the binary end-point lattice constants. Therefore, it is necessary to test whether our data can be accounted for by varying the GaAsN Poisson's ratio or whether changing the relatively ill-defined nitride lattice constants could also account for our observations.

From the data in Table 5.4, a plot of GaAsN-GaAs peak separations against indium mole fraction x has been made in Figure 5.22. This figure plots measured GaAsN-GaAs peak separations against indium mole fractions x for which the tensile strain in the GaAs<sub>1-v</sub>N<sub>v</sub> layer with the same nitrogen content as in an In<sub>x</sub>Ga<sub>1-x</sub>As<sub>1-v</sub>N<sub>v</sub> layer would be exactly cancelled. Each data point in the plot comes from the analysis of a set of samples as labelled in the figure. The theoretical lines are plotted using Equations 5.31 and 5.35 for values of Poisson's ratio between 0.3 and 0.33 whilst assuming Vegard's law holds. Values of all the lattice parameters used in the plot were taken from Table 3.2 in section 3.3.1.4. From the figure, the importance of Poisson's ratio in determining the relationship between GaAsN-GaAs peak separations and strain cancelling indium mole fractions is clear. The curves are almost linear over the range of the data and suggest a value of Poisson's ratio for GaAsN with low nominal nitrogen mole fractions of about 0.31. Interestingly, this value of 0.31 for Poisson's ratio agrees exactly with the independent measurement of Poisson's ratio which is presented in chapter 6. Certainly there is no justification for considering any non-linearity in Poisson's ratio over this range of nitrogen mole fractions.



Figure 5.22: Plot of GaAsN-GaAs peak separations versus strain cancelling indium mole fraction *x*. The solid symbols are the experimental results and the lines assume Vegard's law and are calculated for different values of Poisson's ratio *v*.

As mentioned earlier, the trend in the data shown in Figure 5.22 might also be accounted for by varying the binary end-point lattice constants (GaAs, InAs, GaN, InN) or by relaxing Vegard's law to allow for some non-linearity in the GaAsN and InGaAsN lattice constants with composition. The lattice constants of GaAs and InAs are well defined, however the nitrides GaN and InN are not commonly available in bulk form and therefore their lattice constants are associated with large errors [38]. Figures 5.23 and 5.24 show the effects of changing the values of the end-point binary lattice parameters for GaN and InN respectively and the value of Poisson's ratio used for both plots is 0.31.

Figure 5.23 shows the same data points as are shown in Figure 5.22 and the theoretical lines are plotted for values of the GaN lattice constant between 4.0 and 5.05 Å whilst assuming Vegard's law holds. The values of GaN lattice constant of 4.0, 4.5 and 5.05 Å used in the plot span a much wider range then the normally accepted values which are between 4.34 and 4.59 Å (e.g. [208-211]). There are two points to be made about this plot. Firstly, that the GaN lattice parameter has to be changed considerably to give a clearly different theoretical curve over the very limited range of nitrogen mole fractions studied here. Secondly, that the experimental data points are best fitted to a theoretical line corresponding to a GaN lattice constant of about 4.5 Å, which is similar to the value of GaN lattice constant appearing in the literature and used in this thesis.



Figure 5.23: Plot of GaAsN-GaAs peak separations versus strain cancelling indium mole fraction *x*. The solid symbols are the experimental results while the theoretical lines assume Vegard's law and are calculated for different values of the GaN lattice constant.

Similarly, in Figure 5.24 theoretical lines are plotted for different values of the InN lattice constant between 3.95 and 6.0 Å whilst assuming Vegard's law holds. The values of InN lattice constant used in this plot also span a much wider range than the values found in the literature (normally between 4.92 and 5.03 Å [212]), but they were chosen so that their impact could be seen clearly in the plot. A best fit would be achieved with an InN lattice parameter of 4.98 Å, which is again similar to the value of InN lattice constant appearing in the literature and used in this thesis.



Figure 5.24: Plot of GaAsN-GaAs peak separations versus strain cancelling indium mole fraction *x*. The solid symbols are the experimental results and the theoretical lines assume Vegard's law and are calculated for different values of the InN lattice constant.

Based on the plots in Figures 5.23 and 5.24, it is clear that the choice of lattice constants for GaN or InN used in this thesis does not have a significant impact on the theoretical lines for  $0 \le x \le 0.04$  for the value of Poisson's ratio of 0.31. Therefore these plots were not repeated for the other methods of analysis below.

### 5.4.1.2 The Second Method

In this method, only samples with InGaAsN-GaAs peak separations close to the zero line were considered in the analysis as indicated in Figure 5.25. The samples that were included were S2071009, S1090311 and S2310111 from sets 1, 2b and 4 respectively. These samples were selected because the InGaAsN layers were already very close to lattice-matched with the GaAs substrate. From each of the data points a line was projected parallel to the theoretical constant nitrogen mole fraction lines until it crossed the zero peak separation line which represents the zero strain or lattice-matched case for the InGaAsN layer. Extrapolating data points along lines parallel to the theoretical constant nitrogen mole fraction lines should introduce negligible error as the extrapolations were made over a very small range. The values that result for the indium mole fractions *x* required to exactly cancel the strain in a GaAs<sub>1-y</sub>N<sub>y</sub> layer with a particular GaAsN-GaAs peak separation are shown in Table 5.5.



Figure 5.25: Plot of InGaAsN-GaAs peak separations against indium mole fraction *x* for three samples from sets 1, 2b and 4. The solid lines are lines of constant nitrogen mole fraction *y*, assuming Poisson's ratio is known and linear with composition and that Vegard's law holds. The diagonal dashed lines are projected from the selected experimental points parallel to the lines of constant nitrogen mole fractions at zero InGaAsN-GaAs peak separations.

The GaAsN-GaAs peak separations  $\Delta \omega_{GaAsN-GaAs}$  shown in Table 5.5 are from Table 5.3 and the strain cancelling *x* values are found from the intersection of the projected lines in Figure 5.25 and the horizontal line plotted at InGaAsN-GaAs peak separation zero. From these data a plot of GaAsN-GaAs peak separations against indium mole fractions *x* could be plotted as shown in Figure 5.26. As for the first method, the theoretical lines are plotted using Equations 5.31 and 5.35 for values of Poisson's ratio between 0.3 and 0.33 whilst assuming Vegard's law holds. Values of all the lattice parameters used to plot the theoretical lines were taken from Table 3.2 in

section 3.3.1.4. From this plot, a line of best fit was again found for a Poisson's ratio of about 0.31. Since variations in GaN and InN lattice parameters cannot account for the observed data, the tests done as part of the first method have not been repeated here.

Table 5.5: Results from the second method of analysis, showing GaAsN-GaAs peak separations and their corresponding strain cancelling indium mole fractions at zero InGaAsN-GaAs peak separation.

Set	Sample	$\Delta \omega_{GaAsN-GaAs}$ (arcsec) (±3 arcsec)	x at $\Delta \omega_{InGaAsN-GaAs} = 0$ (±0.001)
1	S2071009	185	0.010
2b	S1090311	394	0.022
4	S2310111	638	0.034



Figure 5.26: Plot of GaAsN-GaAs peak separations versus strain cancelling indium mole fraction *x*. The symbols are the experimental results and the lines assume Vegard's law and are calculated for different values of Poisson's ratio *v*.

### 5.4.1.3 The Third Method

A scaling method was employed in this analysis which was similar to the second method but was applied to a larger data set than the three used in the second method. Samples were scaled within a set to bring them onto a common nitrogen mole fraction line, and the InGaAsN-GaAs peak separations were also scaled in a consistent manner. This method of scaling assumed that lattice and elastic constants are known and linear with composition and that Vegard's law holds. The shifts in nominal nitrogen mole fractions were small enough that any failure of these assumptions should not introduce a significant error. The method adjusted all data points within a set to give them the same nitrogen mole fraction, following which a line of best fit could be plotted and the point where this line crossed the zero peak separation line indicated the zero strain case for the InGaAsN layer.

The scaling process resulted in adjustments being made to the InGaAsN-GaAs peak separations for each sample within a set. This adjustment was small since there was only a few percent ( $\leq 6\%$ ) variation in the nominal nitrogen mole fractions within each set. The scaling process started by calculating the natural lattice constant of an InGaAsN layer using the value of nominal nitrogen mole fraction y from a chosen reference sample (one of the samples in a set) while maintaining the value of the indium mole fraction x. Then, from its natural lattice constant, the perpendicular lattice constant was determined from linear elasticity theory and a new value of the InGaAsN-GaAs peak separation could be calculated. In order to eliminate bias in this process, all samples within a set were chosen in turn to be the reference sample in the scaling process. For example in set 1, samples S2011209 and S4011209 were scaled to sample S2071009 to allow all data points to lie on one nitrogen mole fraction line, then a line of best fit was plotted through these data points to give one value of x at zero In<sub>x</sub>Ga<sub>1-x</sub>As<sub>1-y</sub>N<sub>y</sub>-GaAs peak separation. Then, samples S2071009 and S4011209 were scaled to sample S2011209, with the same method being followed to determine x at zero InGaAsN-GaAs peak separation as before. Lastly, samples S2071009 and S2011209 were scaled to sample S4011209. This process resulted in three values of xat zero InGaAsN-GaAs peak separation from all samples in set 1, from which a mean

was calculated. A similar process was applied to all samples in sets 2b, 3 and 4 as shown in Figure 5.27. The new scaled data from each sample is not displayed in the plot to avoid confusion, only the lines of best fit resulting from each scaling process are shown as the dashed lines in the plot.



Figure 5.27: Plot of InGaAsN-GaAs peak separations against indium mole fraction x for various values of y. The solid lines are lines of constant nitrogen mole fraction y, based on the assumptions that Poisson's ratio and lattice constants are known and linear with composition and that Vegard's law holds. The dashed lines are lines of best fit to the scaled data from each set of data.

Table 5.6 shows the results obtained from this method. Similar to the first method, the values of GaAsN-GaAs peak separation shown were the means from each sample within a set. The values of x at zero InGaAsN-GaAs peak separation were also the mean of the values obtained from scaling to each sample within a set.

Set	Mean value of	Mean value of <i>x</i> at
	$\Delta \omega_{GaAsN-GaAs}$	$\Delta \omega_{InGaAsN-GaAs} = 0$
	(arcsec)	$(\pm 0.001)$
1	179±11	0.010
2b	385±9	0.021
3	515±23	0.028
4	628±19	0.033

Table 5.6: Results from the third method of analysis, showing the mean value of the strain cancelling indium mole fractions at zero InGaAsN-GaAs peak separation and the corresponding GaAsN-GaAs mean peak separations for each set.

In common with the other two methods, a plot of GaAsN-GaAs peak separations against indium mole fractions x is shown in Figure 5.28. All the theoretical lines are plotted using Equations 5.31 and 5.35 for values of Poisson's ratio between 0.3 and 0.33 whilst assuming Vegard's law holds and values of all the lattice parameters used to plot the theoretical lines were taken from Table 3.2 in section 3.3.1.4. Each data point in the plot comes from the analysis of a set of samples as labelled in the figure. For this method, a line of best fit from all four data points was found between the theoretical lines for Poisson's ratio of 0.31 and 0.322.



Figure 5.28: Plot of GaAsN-GaAs peak separations versus strain cancelling indium mole fraction *x*. The solid symbols are the experimental results and the lines assume Vegard's law and are calculated for different values of Poisson's ratio *v*.

# 5.5 Summary

In conclusion, a method to determine the indium mole fraction required to exactly cancel the tensile strain in a GaAsN layer, as a method of calibrating the nitrogen mole fraction, has been presented in this chapter. This situation occurs when the HRXRD peak separation between an InGaAsN layer and its GaAs growth substrate is zero, meaning the epitaxial layer is lattice-matched to the GaAs substrate. The strategy of this method was to grow several sets of samples consisting of InGaAsN, GaAsN, GaAs and InGaAs/GaAs MQW layers with constant nominal nitrogen mole fraction from sample to sample within a set. The InGaAs/GaAs MQW was used as a standard to calibrate the indium and gallium flux rates during growth, which also

gave an accurate value of the indium mole fraction x in the  $In_xGa_{1-x}As_{1-y}N_y$  layer. By assuming the nominal nitrogen mole fractions y were constant through all layers in a sample, the nitrogen mole fraction was specified by measuring the peak separation between the GaAs<sub>1-v</sub> $N_v$  layer and the GaAs substrate, from which the perpendicular lattice constant of the GaAsN layer could be determined. This measurement was done using HRXRD and simulation software, with only the nitrogen mole fraction y needing to be adjusted to obtain a fit between experimental and simulated curves from structures containing InGaAsN, GaAsN and GaAs layers, while the value of indium mole fraction was obtained from the MQW analysis. The experimental  $In_xGa_{1-x}As_{1-y}N_y$ -GaAs peak separation data could then be plotted against indium mole fraction x. When the peak separation between the InGaAsN layer and GaAs substrate is zero, the strain in the GaAsN layer is exactly cancelled and the indium mole fraction at which this occurs is found. A plot of GaAsN-GaAs peak separations versus strain cancelling indium mole fractions x could be made which gives information on the relationship between the GaAsN-GaAs peak separation and the strain cancelling indium mole fraction x. Any laboratory can use this relationship to establish the strain cancelling indium mole fraction equivalent of the nitrogen mole fraction in their layers, as measured by the perpendicular lattice parameter of the layer.

Based on the results reported in this chapter, Poisson's ratio of GaAsN is key to accounting for the relationship between indium and nitrogen mole fractions at which the strain has been exactly cancelled in an InGaAsN quaternary alloy. Any uncertainties in GaN and InN lattice constants cannot explain our data since the values required to bring agreement between theory and experiment are similar to the currently accepted literature values. The next step in this study was to independently confirm the value of Poisson's ratio for GaAsN and this will be discussed in the following chapter.

From the dilute nitride GaAsN literature most researchers have assumed that the lattice constant of the alloy is linear between the lattice constants of GaAs and cubic GaN (Vegard's law) [213]. Since the validity of Vegard's law as it applies to the ternary GaAsN is also untested in this material system, this matter is considered in chapter 7.

# 6 Poisson's Ratio of GaAsN

It was found in the previous chapter that the value of Poisson's ratio plays an important role in defining the relationship between GaAsN-GaAs peak separations and the indium mole fraction x that exactly cancels the tensile strain in a GaAsN layer. A method for determining Poisson's ratio of a GaAs<sub>1-y</sub>N<sub>y</sub> epitaxial layer at nominal nitrogen mole fraction y of about 0.0065 will be presented in this chapter.

# 6.1 Introduction

Poisson's ratio is an important parameter in any structural analysis of strained epitaxial layers, including the dilute nitride compound semiconductors GaAsN and InGaAsN. The use of the GaAs Poisson's ratio for these dilute nitrides looks reasonable due to the low percentages of nitrogen and indium in the layers, however it is important to check the value of Poisson's ratio to confirm this assumption. To the best of the authors' knowledge, there have been no experimental studies of Poisson's ratio  $v_{GaAsN}$  of the dilute nitride GaAs<sub>1-y</sub>N<sub>y</sub>. Most researchers have estimated the value of Poisson's ratio of GaAsN from data relating to the binary endpoint compounds GaAs and GaN by assuming it varies linearly with composition. For example, the value of Poisson's ratio was calculated by Wu et al. [214] for a GaAs<sub>0.962</sub>N<sub>0.038</sub> layer and found to be 0.314, estimated from the data for GaAs and GaN by assuming a linear relationship between the two binary end-point compounds. In their calculation, the values of Poisson's ratio used for GaAs and GaN were 0.312 [215] and 0.366 [216].

For many binary compounds (e.g. GaAs), Poisson's ratio has been determined directly from their elastic constants (Equation 3.27 in chapter 3 section 3.3.1.3) which were usually obtained from acoustic measurements [217]. However, in the context of semiconductor structural measurements by HRXRD, it is almost always the case that information about the properties of an unstrained layer is deduced from measurements on a tetragonally strained layer. It is therefore an appropriate approach to determine Poisson's ratio by making structural measurements on a layer in two strain states. The first strain state was the as-grown state, in which the interface between the GaAsN layer and its GaAs growth substrate was coherent. A second strain state was achieved by using the epitaxial lift-off (ELO) technique to separate a GaAsN epitaxial layer from its GaAs substrate, which allowed the strain in the GaAsN epitaxial layer to change from fully strained to partially relaxed. The ELO technique has been successfully used previously to determine Poisson's ratios of GaAs [180] and AlAs [218] within the same research group. Symmetric and asymmetric HRXRD reflections were used to measure the GaAsN epitaxial layer unit cell parameters after separation, from which  $v_{GaAsN}$  could be calculated.

# 6.2 Sample Structure and Growth

The MBE growth process followed to prepare a sample has been discussed previously in chapter 3 section 3.2. In this work, one sample (S1260611) was grown containing a GaAs<sub>1-y</sub>N<sub>y</sub> epitaxial layer with a nominal nitrogen mole fraction of 0.0065. The sample was grown at a nitrogen plasma current of 18 mA and the nitrogen pressure in the growth chamber was 79 mV as monitored and controlled using a multimeter connected to the ion pump controller 0-100 mV pressure record output as explained in chapter 5 section 5.2. The sample was grown on a 500  $\mu$ m GaAs (001) substrate and its structure is shown in Figure 6.1. The 50 nm AlAs epitaxial layer could be preferentially etched to separate the epitaxial layers above from their GaAs growth substrate. Thin layers of GaAs were grown on either side of the GaAsN layer, the buffer layer to ensure a smooth starting growth surface prior to growing the GaAsN layer and the cap layer to protect the epitaxial structure from oxidation and to make the structure mechanically balanced following lift-off. The 5

nm GaAs layers were thin so that they do not excessively inhibit the process of strain relaxation of the GaAsN layer following lift-off. As the tensile GaAsN layer relaxes, it compresses the GaAs layers as mechanical equilibrium is established following lift-off. The thickness of the GaAsN epitaxial layer was 100 nm, which was thinner than its critical thickness to avoid the formation of misfit dislocations as determined from the force-balance model of Matthews and Blakeslee [184].



Figure 6.1: The structure of sample S1260611 showing substrate temperatures employed for the growth of each layer and all layer thicknesses.

The sample was designed to have the maximum possible GaAsN layer thickness so that its layer peak could be easily observed in a HRXRD spectrum, but not so thick that the layer critical thickness was exceeded. The AlAs layer was grown at a temperature of 600°C and at a growth rate of approximately 0.3 ML/s while the GaAsN epitaxial layer was grown at 540°C where evaporative loss of nitrogen is negligible [145, 163]. The GaAs layers were also grown at 540°C because of the short layer growth time of 15 seconds and so there were no growth interruptions.

#### 6.2.1 HRXRD Measurements

(004) HRXRD rocking curves were collected before the lift-off process. The sample was scanned at Phi angles of  $0^{\circ}$ ,  $90^{\circ}$ ,  $180^{\circ}$  and  $270^{\circ}$  to detect any tilt in the GaAsN layer as was explained in chapter 5 section 5.3.3.1. An example of an (004) HRXRD rocking curve from the as-grown sample S1260611 is shown in Figure 6.2 where the dashed line indicates the position of the GaAs substrate peak. The spectrum shows

the tensile GaAsN layer peak on the high angle side and well resolved from the GaAs substrate peak.



Figure 6.2: Example of an (004) HRXRD rocking curve from as-grown sample S1260611.

In Figure 6.3 the experimental HRXRD curves were compared with simulated spectra obtained using X'Pert Epitaxy and Smoothfit 4.0 software, to determine the angular separations between the GaAsN and GaAs substrate peaks. The fringes in the simulation are also present in the experimental curve, suggesting coherence at all interfaces. After achieving a good fit, the thickness of the GaAsN layer employed in the simulation was increased to give a clear GaAsN peak (this approach was explained in chapter 5 section 5.2.1), allowing ready measurement of its separation from the GaAs substrate peak. This was necessary because the software did not reveal the lattice parameters employed in the simulation.



Figure 6.3: Experimental (blue) and simulated (red) (004) HRXRD rocking curve from sample S1260611.

### 6.2.2 The ELO Technique

The ELO technique was invented by Konagai et al. [219] in 1978 to facilitate the transfer of GaAs solar cells onto aluminium plates and in 1987 Yablonovitch et al. [220] proposed the use of Apiezon-W black wax in an ELO process. Since this technique is central to the results obtained and reported in this chapter, it is explained in detail in this section. The ELO process began by covering the centre of the sample surface with black wax as shown in Figure 6.4. The sample was then placed on a glass microscope slide and heated on a hot plate until the black wax melted to form a circular shape of about 5 mm diameter. The hot plate temperature was set at the black wax melting temperature of about 80°C and controlled to allow the wax to flow and obtain a regular shaped circular film. The sample was then annealed at 100°C for 30 minutes to reduce residual stresses in the wax, but leave enough stress so that during chemical release the wax edges curled upwards to facilitate the release of etch products and replacement by fresh etch, before being cooled to room temperature [220]. Another purpose of the black wax was to provide mechanical support to the sample structure underneath it during the etching process.


Figure 6.4: Black wax applied to the centre of the sample.

The sample was then etched in a cooled polishing etchant consisting of  $H_2SO_4(96\%)$ : $H_2O_2(30\%)$ : $H_2O$  mixed in the volume proportions 8:1:1 for 10 minutes and details about the etching process are explained in chapter 5 section 5.3.4. With an etch rate of about 12 nm/s, this process removed about 7200 nm of the surrounding area of the sample surface that was not covered by the black wax, resulting in the situation shown in Figure 6.5. This ensured that the perimeter of the AlAs release layer would be exposed during the lift-off process. The sample was then rinsed three times in DI water and blown dry using filtered dry nitrogen gas.



Figure 6.5: H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O etching of the area not covered by black wax to expose the AlAs perimeter.

Before lift-off, small black wax tags were used to attach the supporting black wax to two corners of the substrate as shown in Figure 6.6. The tags were melted onto the substrate using a soldering iron set to a temperature which was just enough to melt the tags. The purpose of the tags was to maintain the epitaxial layer orientation relative to the growth substrate, necessary to collect HRXRD spectra from asymmetric planes following the lift-off process.



Figure 6.6: Top view of the sample after the black wax tags had been attached.

The sample was then immersed in 10% HF acid and kept refrigerated for between one and three days to ensure the AlAs layer had been totally removed. The etching was performed at 4°C because lower temperatures enhance the differential between the rate of etching of AlAs and GaAs. Figure 6.7 shows an intermediate step in the lift-off process and following release the sample was rinsed in DI water and partially dried, but keeping some of the DI water trapped between the epitaxial structure and the substrate. This water plays a role during the Van der Waals (VDW) bonding process as is explained in the following paragraph.



Figure 6.7: The HF etches the AlAs layer preferentially in order to release the GaAsN epitaxial structure from its growth substrate.

After lift-off, a 0.5 kg weight was applied giving a pressure of about  $1.5 \times 10^5$  N/m<sup>2</sup> for about 24 hours, as shown in Figure 6.8.



Figure 6.8: A 0.5 kg weight was placed on top of the sample to facilitate VDW bonding.

Following VDW bonding, the black wax on the surface was removed using trichloroethylene resulting in the structure shown in Figure 6.9, before proceeding to HRXRD scans of the structure in its second strain state.



Figure 6.9: The sample structure after removing the black wax, showing the GaAs/GaAsN/GaAs film sitting on the GaAs substrate.

# 6.2.3 HRXRD Measurements after ELO and Rebonding

Following ELO and rebonding the HRXRD measurements were repeated. For pseudomorphic structures, a single (004) rocking curve measurement is often sufficient for the purpose of determining the composition and thickness of a ternary epitaxial layer, because the in-plane lattice constant of the layer is equal to that of the substrate and the layer distortion is purely tetragonal. However, for a partially relaxed layer, x-ray rocking curve measurements must determine both the parallel and perpendicular lattice constants. For this reason, rocking curves were also collected for asymmetric (224) reflections.

An example of an (004) HRXRD spectrum from sample S1260611 obtained after ELO and rebonding is shown in Figure 6.10. The GaAsN layer peak is located on the high angle side of the substrate peak as labelled in the figure. There are no Pendellösung fringes in the spectrum as a result of the loss of coherence at the interface between the GaAsN layer and its GaAs growth substrate.



Figure 6.10: Example of an (004) HRXRD rocking curve from sample S1260611 after ELO and rebonding.

Figure 6.11 shows the same spectrum plotted on a linear intensity scale and it can be seen that the GaAsN layer peak is barely resolved from the strong substrate peak and certain measures were required to determine their peak separation.



Figure 6.11: Linear plot of an (004) HRXRD rocking curve from sample S1260611 after ELO and rebonding.

#### 6.2.3.1 Asymmetric Reflections

Asymmetric reflections needed to be collected to enable a complete description of the GaAsN epitaxial layer unit cell to be made following ELO and rebonding. While there are a number of inclined planes (*hkl*) which could be used, such as (335), (115) or (224), in this work the incident x-ray beam was diffracted from (224) planes. Figure 6.12 shows the relationships between the Bragg angle  $\theta_{224}$ , the angle of incidence  $\omega_{224}$  and the offset angle  $\tau_{224}$  between the surface and the GaAs substrate (224) planes for asymmetric reflections collected at large  $\omega_{224}^L$  and small  $\omega_{224}^S$  angles. Eight asymmetric reflections are required from the (224), ( $\overline{224}$ ), ( $\overline{224}$ ) and ( $2\overline{24}$ ) planes, one for each of the two possible x-ray beam directions.



Figure 6.12: Asymmetric (224) reflection geometry for (a) the large incidence angle  $\omega_{224}^L$  and (b) the small incidence angle  $\omega_{224}^S$  cases.

A theory to account for x-ray measurements on an arbitrarily oriented and distorted epitaxial layer unit cell [221] is described in this section. Following epitaxial lift-off a layer will inevitably be arbitrarily distorted and misoriented with respect to the GaAs substrate unit cell. This means that corresponding unit cell defining planes in a layer can be tilted with respect to the substrate by angles  $\gamma$  at phases  $\delta$  as shown in Figure 6.13. Figure 6.13 (a) shows a GaAs substrate unit cell with the defining (001) planes intersecting the *x*, *y*, and *z* axes at (*a*,0,0), (0,*b*,0) and (0,0,*c*) while (b) shows the corresponding epitaxial layer planes which are tilted and intersect the *x*', *y*' and *z*' axes at (*a*',0,0), (0,*b*',0) and (0,0,*c*'). From the figure, it can be seen that the maximum tilt  $\gamma_3$  of the (001) unit cell layer plane relative to the corresponding plane in the substrate occurs at a phase angle of  $\pi/2 - \delta_3$ . The maximum tilts of  $\gamma_1$  and  $\gamma_2$  also occur at phase angles  $\pi/2 - \delta_1$  and  $\pi/2 - \delta_2$  for the (100) and (010) planes respectively. The epitaxial layer unit cell structure is therefore defined by nine parameters, *a*', *b*', *c*',  $\delta_1$ ,  $\gamma_1$ ,  $\delta_2$ ,  $\gamma_2$ ,  $\delta_3$  and  $\gamma_3$ .



Figure 6.13: (a) GaAs substrate and (b) epitaxial layer unit cells. (Adapted from References [221] and [207]).

All nine unit cell parameters can be determined following collection of at least nine spectra. In this work there were eight (224) reflections and four (004) reflections, sufficient to allow a full determination of the epitaxial layer unit cell parameters following lift-off.

The offset angle  $\tau_{224}$  between the (001) reference and (*hkl*) substrate planes is given by:

$$\tau_{hkl} = \tan^{-1}\left(\frac{\sqrt{h^2 + k^2}}{l}\right) \tag{6.1}$$

while the angle  $\tau'_{hkl}$  between the (001) substrate reference and epilayer (*hkl*) planes is given by:

$$\tau'_{hkl} = \tan^{-1} \left[ I_3 \sqrt{\left(\frac{1}{I_1}\right)^2 + \left(\frac{1}{I_2}\right)^2} \right]$$
(6.2)

where  $I_1$ ,  $I_2$  and  $I_3$  are the points where the corresponding (*hkl*) plane in the epitaxial layer intersects the coordinate axes x', y' and z' respectively, as shown in Figure 6.13 (b). A relationship between the three coordinates ( $x_1$ ,  $y_1$ ,  $z_1$ ), ( $x_2$ ,  $y_2$ ,  $z_2$ ) and ( $x_3$ ,  $y_3$ ,  $z_3$ ) of the primitive axes OX, OY and OZ of the epitaxial unit cell can be related to the unit cell parameters in matrix form by:

$$KX = L \tag{6.3}$$

where

$$\mathbf{K} = \begin{pmatrix} 1 & k_1 & k_2 \\ k_3 & 1 & k_4 \\ k_5 & k_6 & 1 \end{pmatrix}, \tag{6.4}$$

$$\mathbf{X} = \begin{pmatrix} x_1 & x_2 & x_3 \\ y_1 & y_2 & y_3 \\ z_1 & z_2 & z_3 \end{pmatrix},$$
(6.5)

and

$$\mathbf{L} = \begin{pmatrix} a' & 0 & 0\\ 0 & b' & 0\\ 0 & 0 & c' \end{pmatrix}.$$
 (6.6)

The off-diagonal elements of K are related to the (001) like layer tilt and phase angle parameters (see Reference [221]).

The (*hkl*) plane in the epitaxial layer passes through the points  $(1/h)(x_1, y_1, z_1)$ ,  $(1/k)(x_2, y_2, z_2)$  and  $(1/l)(x_3, y_3, z_3)$  and each of these points will satisfy:

$$\frac{x}{I_1} + \frac{y}{I_2} + \frac{z}{I_3} = 1 \tag{6.7}$$

and so for each of these points we have the equations:

$$\frac{x_1}{I_1} + \frac{y_1}{I_2} + \frac{z_1}{I_3} = h,$$
(6.8)

$$\frac{x_2}{I_1} + \frac{y_2}{I_2} + \frac{z_2}{I_3} = k,$$
(6.9)

and

$$\frac{x_3}{I_1} + \frac{y_3}{I_2} + \frac{z_3}{I_3} = l \tag{6.10}$$

which can be expressed in matrix form as:

$$IX = M \tag{6.11}$$

where

$$\mathbf{I} = \frac{1}{I_1} + \frac{1}{I_2} + \frac{1}{I_3} \tag{6.12}$$

and

$$\mathbf{M} = (hkl). \tag{6.13}$$

From Equation 6.11:

$$I = MX^{-1}$$
 (6.14)

and by substituting for X from Equation 6.3, an expression for I is given as:

$$I = ML^{-1}K.$$
 (6.15)

Since L is a matrix with all off-diagonal elements zero its inverse is simply given by:

$$\mathbf{L}^{-1} = \begin{pmatrix} \frac{1}{a'} & 0 & 0\\ 0 & \frac{1}{b'} & 0\\ 0 & 0 & \frac{1}{c'} \end{pmatrix}.$$
 (6.16)

The nine parameters associated with the epilayer unit cell, *a'*, *b'*, *c'*,  $\gamma_1$ ,  $\gamma_2$ ,  $\gamma_3$ ,  $\delta_1$ ,  $\delta_2$ and  $\delta_3$  allow the peak separations between substrate and epilayer diffracting planes (*hkl*) to be calculated. These calculated values were compared with measured values and the nine parameters adjusted according to a recursive least-squares  $\chi^2$  criterion to obtain the best agreement between theory and experiment. Table 6.1 shows the various (224) diffracting planes involved in collecting large  $\omega_{224}^L$  and small  $\omega_{224}^S$ angle data and the Phi angles associated with each of them.

Phi angle	(224) large reflection	(224) small reflection		
	$\omega_{224}^L$	$\omega_{224}^S$		
0°	224	224		
90°	$\overline{2}24$	$2\overline{2}4$		
180°	224	224		
270°	$2\overline{2}4$	$\overline{2}24$		

Table 6.1: The various (224) diffracting planes and their associated Phi angles.

Figure 6.14 shows an example of a  $\omega_{224}^L$  reflection collected from sample S1260611 following ELO and rebonding and as for the (004) spectrum no Pendellösung fringes are observed. There is also a clear broadening of the GaAsN peak and a reduction of the maximum GaAsN layer peak intensity, as might be expected following the ELO process.



Figure 6.14: An example of a (224) large angle HRXRD rocking curve from sample S1260611 following ELO and rebonding.

The spectra in Figures 6.15 and 6.16 also show (224) reflections at large  $\omega_{224}^L$  and small  $\omega_{224}^S$  angles respectively from sample S1260611 following ELO and rebonding, plotted on a linear intensity scale.



Figure 6.15: An example of a (224) large angle HRXRD rocking curve obtained from sample S1260611 after ELO and rebonding.



Figure 6.16: An example of a (224) small angle HRXRD rocking curve obtained from sample S1260611 after ELO and rebonding.

Because the GaAsN layer peaks were not always well resolved from the GaAs substrate peak, a GaAs substrate spectrum was subtracted from the experimental curve with the difference being fitted to a Gaussian function to allow the peak separation between the GaAsN layer and the GaAs substrate to be determined. An example of this process is shown in Figure 6.17. A scaled (224) small angle  $\omega_{224}^S$  GaAs substrate (red) reflection is superimposed on the experimental (224) small angle  $\omega_{224}^S$  curve (blue) to yield the difference between these two curves. The result of such subtraction yields a curve (light blue in the plot) and a Gaussian function has been fitted to this curve as shown by the black dashed curve. The light blue curve is only plotted in the range between 50 and 1400 arcseconds since small differences between the original spectrum and the GaAs substrate curve being subtracted leads to

unreliable results in the near vicinity of the GaAs peak. This method allows determination of the GaAsN-GaAs peak separations and the process was repeated for all Phi angles.



Figure 6.17: HRXRD (224) rocking curve (blue) from sample S1260611 after ELO and rebonding and the (224) GaAs substrate curve (red). The light blue curve is the difference between the blue and red curves which is fitted by a Gaussian function as shown by the black dashed curve.

Figure 6.18 shows the result of summing the substrate curve used for subtraction and the Gaussian fitted to the difference between the blue and red curves and this is shown as a green dashed curve. The Gaussian properties were adjusted to give as close an agreement as possible between the original data curve and the matching green dashed curve being used to extract the peak separation.



Figure 6.18: HRXRD (224) rocking curve (blue) from sample S1260611 after ELO and rebonding and the (224) GaAs substrate curve (red) used for subtraction. The black dashed curve is a Gaussian function while the green dashed curve sums the substrate and Gaussian curves.

# 6.3 Results and Discussion

This section reports the experimental results, shows how the unit cell parameters were determined and explains the calculation of Poisson's ratio.

### 6.3.1 Unit Cell Measurements

The GaAsN epitaxial layer unit cell parameters were extracted using a Matlab program developed by Saengkae [207]. This allowed determination of the unit cell parameters (*a'*, *b'*, *c'*,  $\gamma_1$ ,  $\gamma_2$ ,  $\gamma_3$ ,  $\delta_1$ ,  $\delta_2$  and  $\delta_3$  as explained in section 6.2.3.1) by minimising the differences between calculated and experimentally measured GaAsN-

GaAs peak separations according to a least-squares  $\chi^2$  criterion. Using data from GaAsN-GaAs (004) and (224) peak separations collected at Phi angles of 0°, 90°, 180° and 270° a full epilayer unit cell determination was possible and this was done after the ELO and rebonding process.

Table 6.2 presents the data for the (004) and (224) angular separations between the GaAsN layer and GaAs substrate peaks  $\Delta \omega_{GaAsN-GaAs}$  for sample S1260611 at Phi angles of 0°, 90°, 180° and 270°. The table also shows calculated (004) and (224) angular separations obtained after running the Matlab program after the ELO and rebonding process. The data shows good agreements between the experimental and calculated separations for the (004) and (224) large angle reflections with errors less than or equal to two arcseconds and less than or equal to seven arcseconds for the (224) small angle reflections.

Table 6.2: Measured and calculated separations between the GaAsN layer and GaAs substrate peaks after ELO and rebonding. Only measured peak separations are shown for the (004) reflections before lift-off.

Phi angle	$\Delta\omega_{GaAsN-GaAs}$			$\Delta\omega_{GaAsN-GaAs}$ for (224) large		$\Delta\omega_{GaAsN-GaAs}$ for (224) small	
ungro	(arcsec)		reflection $\omega_{224}^L$		reflection $\omega_{224}^S$		
	(±3 arcsec)		(arcsec)		(arcsec)		
				(±3 arcsec)		(±3 arcsec)	
	Before	After l	ift-off	After	lift-off	After	lift-off
	lift-off	Expt	Calc	Expt	Calc	Expt	Calc
0°	346	244	243	207	209	350	357
90°	353	234	236	190	191	358	360
180°	353	236	235	215	216	345	351
270°	342	240	242	181	182	355	361

### 6.3.2 Poisson's Ratio of GaAsN

For a tetragonally distorted GaAsN layer, its Poisson's ratio  $v_{GaAsN}$  is defined by:

$$\varepsilon^{\perp} = \left(\frac{-2\nu_{GaAsN}}{1 - \nu_{GaAsN}}\right)\varepsilon^{\parallel} \tag{6.17}$$

where  $\varepsilon^{\perp}$  and  $\varepsilon^{||}$  are the perpendicular and parallel strains respectively. Defining:

$$\delta = \frac{-2v_{GaAsN}}{1 - v_{GaAsN}} \tag{6.18}$$

Equation 6.17 becomes:

$$\varepsilon^{\perp} = \delta \varepsilon^{\parallel}. \tag{6.19}$$

A theoretical relationship between the perpendicular and parallel lattice parameters of a GaAsN layer in two strain states can then be developed as follows.

By substituting for  $\varepsilon^{\perp} = \frac{a_{GaAsN}^{\perp} - a_{GaAsN}}{a_{GaAsN}}$  and  $\varepsilon^{\parallel} = \frac{a_{GaAsN}^{\parallel} - a_{GaAsN}}{a_{GaAsN}}$  into Equation 6.19, we

have:

$$\frac{a_{GaAsN}^{\perp} - a_{GaAsN}}{a_{GaAsN}} = \delta \left( \frac{a_{GaAsN}^{\parallel} - a_{GaAsN}}{a_{GaAsN}} \right)$$

or

$$a_{GaAsN}^{\perp} - a_{GaAsN} = \delta \left( a_{GaAsN}^{||} - a_{GaAsN} \right).$$
(6.20)

Applying Equation 6.20 to two different strain states yields the expressions:

$$a_1^{\perp} - a_y = \delta \left( a_1^{\parallel} - a_y \right) \tag{6.21}$$

and

$$a_{2}^{\perp} - a_{y} = \delta \left( a_{2}^{||} - a_{y} \right)$$
 (6.22)

where the subscripts 1 and 2 denote two different strain states and  $a_y$  is the natural lattice constant of the GaAsN layer. By subtracting Equation 6.22 from Equation 6.21, we have:

$$a_1^{\perp} - a_2^{\perp} = \delta \left( a_1^{||} - a_2^{||} \right)$$
(6.23)

and so:

$$\delta = \frac{a_1^{\perp} - a_2^{\perp}}{a_1^{\parallel} - a_2^{\parallel}}.$$
(6.24)

By substituting Equation 6.18 into Equation 6.24 we obtain:

$$\frac{-2v_{GaAsN}}{1 - v_{GaAsN}} = \frac{a_1^{\perp} - a_2^{\perp}}{a_1^{\parallel} - a_2^{\parallel}}$$
(6.25)

and this equation can be manipulated to obtain an expression for Poisson's ratio of GaAsN  $v_{GaAsN}$ , which is given by:

$$v_{GaAsN} = \frac{1}{1 - 2\left(\frac{a_1^{\parallel} - a_2^{\parallel}}{a_1^{\perp} - a_2^{\perp}}\right)}.$$
(6.26)

### 6.3.2.1 Theoretical Analysis of GaAsN SQW Strain Relaxation

The expected final strain state of a GaAsN layer sandwiched between two GaAs layers can be calculated from elasticity theory by minimising its strain energy with respect to its in-plane or parallel lattice constant following ELO release from its GaAs growth substrate.



Figure 6.19: A GaAs/GaAsN/GaAs structure that has been rebonded to a GaAs substrate after the ELO process.

The strain energy *E* associated with a layer of thickness *h* under biaxial strain  $\varepsilon^{\parallel}$  is given by:

$$E = k \left(\varepsilon^{\parallel}\right)^2 h \tag{6.27}$$

where

$$k = 2G\left(\frac{1+\nu}{1-\nu}\right) \tag{6.28}$$

and

$$\varepsilon^{\parallel} = \frac{a^{\parallel} - a}{a} \tag{6.29}$$

where  $a^{\parallel}$  and a are the parallel and relaxed or natural lattice parameters of the layer and G and v are the shear modulus and Poisson's ratio of the material. While the tensile GaAsN layer shown in Figure 6.19 relaxes by contracting its in-plane lattice parameter, coherence at the two GaAs/GaAsN interfaces results in the GaAs layers being put into compression. Assuming that following ELO the substrate exerts no stresses on the layers above, the total energy  $E_T$  of the system is given by:

$$E_T = E_v + 2E_o \tag{6.30}$$

where the subscript y refers to the GaAsN epitaxial layer and o to the two cladding GaAs layers. By substituting parameters,  $E_T$  can be expressed as:

$$E_T = 2G_y \left(\frac{1+v_y}{1-v_y}\right) \left(\frac{a^{||} - a_y}{a_y}\right)^2 h_y + 4G_o \left(\frac{1+v_o}{1-v_o}\right) \left(\frac{a^{||} - a_o}{a_o}\right)^2 h_o$$
(6.31)

where  $a_o$  is the relaxed or natural lattice constant of the GaAs and  $a_y$  is the relaxed lattice constant of the GaAsN layer. Following lift-off, the parallel lattice constant of the structure will change from that of GaAs to a value  $a^{\parallel}$ , such that the total energy  $E_T$  is a minimum. Differentiating the total energy with respect to this parallel lattice constant and setting it to zero yields:

$$\frac{dE_T}{da^{||}} = 2G_y \left(\frac{1+v_y}{1-v_y}\right) \left(\frac{2a^{||}-2a_y}{a_y^2}\right) h_y + 4G_o \left(\frac{1+v_o}{1-v_o}\right) \left(\frac{2a^{||}-2a_o}{a_o^2}\right) h_o = 0.$$
(6.32)

This equation can be solved to find the parallel lattice constant at the minimum strain state of the structure following partial relaxation of the GaAsN layer strain. The final parallel lattice constant is then given by:

$$a^{\parallel} = \frac{a_y a_o \left(\alpha a_o + \beta a_y\right)}{\alpha a_o^2 + \beta a_y^2} \tag{6.33}$$

where

$$\alpha = 4G_y h_y \left(\frac{1+v_y}{1-v_y}\right) \tag{6.34}$$

and

$$\beta = 8G_o h_o \left(\frac{1+v_y}{1-v_y}\right). \tag{6.35}$$

A relationship between the percentage relaxation of the GaAsN layer and its final parallel lattice constant can be derived as follows.

The percentage relaxation of a GaAsN layer can be expressed as [183, 222]:

% Relaxation = 
$$\left(\frac{\varepsilon_i - \varepsilon_f}{\varepsilon_i}\right) \ge 100$$
  
=  $\left(1 - \frac{\varepsilon_f}{\varepsilon_i}\right) \ge 100$  (6.36)

where  $\varepsilon_i$  and  $\varepsilon_f$  are the in-plane strain in the initial and final states respectively. For coherent growth on a GaAs substrate these strains are given by:

$$\varepsilon_i = \frac{a_o - a_y}{a_y} \tag{6.37}$$

and

$$\varepsilon_f = \frac{a^{||} - a_y}{a_y}.$$
(6.38)

Then Equation 6.36 becomes:

% Relaxation = 
$$\left[\frac{a_o - a^{\parallel}}{a_o - a_y}\right]$$
 x 100. (6.39)

By substituting Equation 6.33 into Equation 6.39 we obtain:

% Relaxation = 
$$\left[\frac{a_o \cdot \left(\frac{a_y a_o \left(\alpha a_o + \beta a_y\right)}{\alpha a_o^2 + \beta a_y^2}\right)}{a_o \cdot a_y}\right] \times 100$$
(6.40)

and following algebraic manipulation this equation can be expressed in the form:

% Relaxation = 
$$\left[\frac{\alpha a_o^2}{\left(\alpha a_o^2 + \beta a_y^2\right)}\right] \ge 100.$$
 (6.41)

The analysis above allows the measured percentage relaxation of the structure following ELO and rebonding to be compared with our theoretical expectation. This is done in the analysis of results in the next section. This equation was only the theoretical analysis of GaAsN single layer strain relaxation. The parameter G and h were not varied in the experiment.

### 6.3.2.2 Analysis of Results

By referring to Equation 6.20, it can be seen that the perpendicular lattice parameter  $a_{GaAsN}^{\perp}$  is a linear function of the parallel lattice parameter  $a_{GaAsN}^{\parallel}$  with slope  $\delta$  and yaxis intercept  $a_{GaAsN}(1 - \delta)$  and this relationship has been plotted in Figure 6.20 for sample S1260611. This line intersects the parallel lattice parameter line at the natural lattice parameter of the layer, yielding a figure of 5.64542  $\pm$  0.00013 Å. There are three strain states shown in the figure, as-grown, after ELO and rebonding and fully relaxed. The fully relaxed data point was a theoretical point at the intersection of the parallel and perpendicular lattice constant lines in Figure 6.20. The solid square and circle symbols are experimental data points for the parallel and perpendicular lattice constants (as shown in Table 6.3) respectively, obtained from HRXRD measurements before and after the ELO and rebonding process. From this plot, the percentage of GaAsN layer strain relaxation could be calculated and was found to be 69%. This value was lower than the 91% expected from the earlier theoretical analysis, however there are factors at play that account for this. For example, following ELO the sample was rebonded back onto the GaAs substrate with the wax still on top of the partially relaxed epitaxial structure, quite likely inhibiting the process of GaAsN strain relaxation and following rebonding no further relaxation was possible even after the wax had been removed. X-ray measurements confirmed this since the epilayer strain state before and after removal of the supporting wax was unchanged.



Figure 6.20: Plot of perpendicular and parallel lattice parameters against parallel lattice parameter for sample S1260611. The solid squares and circles represent measurements of the parallel and perpendicular lattice constants respectively and the solid triangle is the predicted natural lattice constant of the GaAsN layer.

Equation 6.24 allows  $\delta$  (and therefore Poisson's ratio) to be found by considering pairs of different strain states. Taking the as-grown and after ELO and rebonding as one pair, and the as-grown and fully relaxed (the predicted zero strain state) as another pair, two data points could be plotted as shown in Figure 6.21. The differences in the perpendicular lattice constants for the two pairs of strain states are plotted vertically and the differences in the parallel lattice constants for the two pairs of strain states are plotted horizontally. The star symbol in the plot arises from considering the as-grown and after ELO and rebonding pair of strain states, while the diamond symbol arises by considering the as-grown and fully relaxed pair of strain states.



Figure 6.21: Plot of the differences between perpendicular and parallel lattice constants for sample S1260611. The solid symbols show the data points and the straight line of best fit represents Equation 6.24.

The straight line plot through the data points is from Equation 6.24 and it passes through the origin as shown in Figure 6.21, representing the case when a pair of strain states are in fact the same. The slope  $\delta$  of the straight line in Figure 6.21 is equal to  $-0.92 \pm 0.05$  and Poisson's ratio v is calculated by comparing this slope with Equation 6.18, yielding a value of  $0.31 \pm 0.02$  as shown in Table 6.3. The estimate of the nominal nitrogen mole fraction y was based on the GaAsN-GaAs peak separations measured from (004) HRXRD spectra collected from the as-grown sample. Knowing the nitrogen mole fraction is not critical, the main point of these measurements was to test the assertion that Poisson's ratio of the dilute nitrides is close to that of GaAs. The lattice parameters of the GaAsN layer both before and after the ELO and rebonding process are shown in Table 6.3 where the errors in the lattice parameter determinations are  $\pm 0.00013$  Å. Before lift-off, the parallel lattice constant of the GaAsN layer is assumed to be the same as the GaAs lattice constant (5.65325 Å [28, 29]) and after lift-off, the parallel lattice parameter of the GaAsN layer was found from the average of the in-plane unit cell parameters (*a*' and *b*' as explained in sections 6.2.3.1 and 6.3.1). The lattice parameters after the ELO and rebonding process were found from the analysis of the x-ray data presented in section 6.2.3 which lead to a determination of the GaAsN epitaxial layer unit cell [217].

 Table 6.3: Measured parallel and perpendicular lattice constants and calculated Poisson's ratio.

Sample	$a^{  }_{GaAsN} \ ({ m \AA})$		$a_{GaAsN}^{\perp}$ (Å)		$v_{GaAsN}$ (±0.02)	y (Estimate)
	(±0.00	013 Å)	(±0.00013 Å)			$(\pm 0.0001)$
	Before	After	Before	After		
	lift-off	lift-off	lift-off	lift-off		
S1260611	5.65325	5.64782	5.63825	5.64322	0.31	0.0065

Figure 6.22 plots the calculated Poisson's ratio v at the estimated nitrogen mole fraction y against a limited nitrogen mole fraction range  $0 \le y \le 0.012$ . The plot shows horizontal dashed lines representing literature values for the GaAs and GaN Poisson's ratios of 0.322 [180] and 0.352 [38] respectively. The result shows that the value of the GaAsN Poisson's ratio for a nominal nitrogen mole fraction of approximately 0.0065  $\pm$  0.0001 is, within experimental error, the same as that of GaAs.



Figure 6.22: Plot of Poisson's ratio v versus nitrogen mole fraction y for sample S1260611. The horizontal dashed lines indicate the literature values of the GaAs and GaN Poisson's ratios.

Figure 6.23 shows the GaAsN Poisson's ratio data of Figure 6.22 plotted over the full range of nitrogen mole fractions  $0 \le y \le 1$ . To the author's knowledge, there have been no experimental studies of the zinc-blende GaN Poisson's ratio reported in the literature, although Moram et al. [223] reported on the wurtzite GaN structure. However, there have been many studies of the elastic constants ( $C_{11}$  and  $C_{12}$ ) of zinc-blende GaN based on first principle calculations (e.g. [224] and [225]). For example, Bouhemadou et al. [224] found the GaN Poisson's ratio was 0.3517 when calculated from the elastic constants. Most values of the zinc-blende GaN Poisson's ratio that have been calculated from the elastic constants are in the range between 0.303 [226] and 0.377 [227], with many values in between (e.g. [39, 194, 208, 228, 229]). All of these calculated values for GaN were not included in the Figure 6.23 plot in order to avoid making the plot too confusing. However, the wide range of values cannot be

discriminated by this experiment because the low nominal nitrogen mole fraction of 0.0065 in our nitride layer made its composition very close to that of the GaAs endpoint binary. Any linear interpolation between the GaAs Poisson's ratio and either of the extreme values for GaN would not produce significantly different answers. In addition, the main purpose of this experiment was to investigate the GaAsN Poisson's ratio at low nominal nitrogen mole fraction to see whether it is different to the GaAs Poisson's ratio or not. It is significant that in the last chapter, the indium strain cancelling experiments suggested that the value of Poisson's ratio that best described the data relating to  $0.003 \le y \le 0.012$  was a value of 0.31 also. It may well be that the difference between this value and Poisson's ratio of GaAs, which has been previously measured and found to be  $0.322 \pm 0.005$  [180], is significant.



Figure 6.23: The variation of GaAs<sub>1-y</sub>N<sub>y</sub> Poisson's ratio  $v_{GaAsN}$  with nitrogen mole fraction y for  $0 \le y \le 1$ .

# 6.4 Summary

The GaAs<sub>1-y</sub>N<sub>y</sub> Poisson's ratio at a nominal nitrogen mole fraction of 0.0065 has been calculated following structural measurements using HRXRD. The ELO technique employed in this work allowed Poisson's ratio to be determined by measuring the structural properties of a GaAsN epitaxial layer in two strain states. This allowed the natural lattice constant to be determined and therefore Poisson's ratio to be found. Within experimental error Poisson's ratio was found to be the same as that for GaAs, as was expected given that the layer studied was stoichiometrically very similar to GaAs. However, taken together with the results of the analysis of strain cancellation in chapter 5, the difference between the two independent and identical values obtained for Poisson's ratio of GaAsN and that of Poisson's ratio of GaAs may be significant.

To the author's knowledge, there are no reports of experimental determinations of the zinc-blende GaAsN Poisson's ratio at low nitrogen mole fractions. The method used in this experiment could be employed by other research groups in order to determine GaAsNs Poisson ratio at any nitrogen mole fraction of interest, within the experimental error implicit in the approach used.

# 7 Linearity of the Lattice Constant of GaAsN with Nitrogen Mole Fraction

There are examples in the literature of studies of GaAsN epitaxial layers grown on GaAs substrates by MBE which assume linearity of the natural lattice constant with nitrogen mole fraction (e.g. [159, 164, 214]). In this chapter this assumption is tested by measuring the perpendicular lattice constants of tensile GaAs<sub>1-y</sub>N<sub>y</sub> layers (y < 0.012) grown by MBE. Relative nitrogen mole fractions in these layers were measured by SIMS and the analysis of the results seeks to check if there is any evidence of non-linearity in the lattice constant-composition relationship. While we are not measuring the linearity of the natural lattice constant itself, any deviation from linearity will lead to non-linearity in the perpendicular lattice parameter which we are measuring in the as-grown layers, as will be shown in section 7.4.2.

# 7.1 Introduction

The measurements reported in this chapter combine SIMS and HRXRD to correlate chemical composition with lattice parameter measurements on GaAsN epitaxial layers. Vegard's law asserts the linearity of the natural lattice constant with nitrogen mole fraction and the intention here is to test Vegard's law by using SIMS to provide a measure of the relative nitrogen mole fractions in a series of GaAsN epitaxial layers and to use HRXRD to measure the perpendicular lattice constants of the same layers. It is known that Vegard's law does not hold for some compounds which have been subjected to extensive study, such as InGaAs (e.g. [230]) and AlGaAs (e.g. [231]) and so it would be no surprise if it did not hold for GaAsN. Any deviation from Vegard's law could, for example, be due to the incorporation of non-

substitutional nitrogen atoms or interstitial nitrogen complexes (e.g. [22-26]). Hence, it is important to test the validity of Vegard's law for GaAsN as a part of the work reported in this thesis.

There are related questions which impact on methods of determining nitrogen mole fractions in GaAsN, regarding the lattice parameter of GaN and the elastic constants of the dilute nitride GaAsN. Experimental lattice constant measurements on cubic GaN grown and measured using different techniques have been made by several research groups (e.g. [232-237]) and the values found are in the range from 4.49 to 4.53 Å. The three digit precision quoted illustrates the relatively high uncertainties associated with these measurements when compared with most III/V or II/VI compound semiconductors which have lattice constant measurements typically quoted to five or six significant figures. There are also many values for the elastic constants of GaN reported in the literature, either from theoretical calculations or experimental measurements (e.g. [193, 224, 226, 228]). Despite these uncertainties, as a starting point the values of the GaN elastic constants used in this work are documented in Table 3.2 in chapter 3 section 3.3.1.4.

Chapter 6 has already described measurements to determine whether Poisson's ratio, an elastic parameter particularly suited to describing the effects of tetragonal strain on unit cell lattice parameters, is significantly different to that of GaAs, the end-point binary component to which the dilute nitride GaAsN is most closely related. That work concluded that the measured difference was within experimental error, although chapters 5 and 6 have independently yielded the same value of 0.31 for Poisson's ratio of GaAsN at low nitrogen mole fractions and the difference between their value and that of the GaAs value of 0.322 may be significant.

# 7.2 Sample Growth

The TEM results presented in chapter 4 section 4.2 suggest that there was no measurable loss of interfacial coherence apparent from HRXRD measurements made on samples with GaAsN layer thicknesses up to 300 nm when the nominal nitrogen

mole fraction was approximately 0.009. Similar observations have been made by several other research groups [23-27, 148, 192-195]. This allowed the growth of relatively thick layers in experiments performed to check the linearity of the perpendicular GaAsN lattice parameter with nitrogen composition.

Four samples were grown, one with three layers and the others with two layers of GaAsN with different nitrogen compositions in the layers in each sample. HRXRD spectra were simulated for all planned structures using X'Pert Epitaxy and Smoothfit 4.0 prior to growth, to ensure that clear GaAsN layer peaks would be observed in HRXRD spectra collected following growth of the samples. Table 7.1 shows the GaAsN layer growth parameters for each sample, such as nitrogen plasma current, nitrogen pressure in the growth chamber, design or intended nitrogen mole fraction and layer thicknesses.

Sample	Nitrogen	Nitrogen chamber	Design values for	GaAsN
designator	plasma	pressure (mV)	nitrogen mole	layer
	current	(ion pump 0-100	fraction y in each	thicknesses
	(mA)	mV pressure	layer	(nm)
		record output)		
S1050112	18	79	0.007, 0.005, 0.009	300
S3050112	18	79	0.0045, 0.01	300, 200
S2070112	12	69	0.0019, 0.0047	350, 300
S1060112	12	58	0.0013, 0.0034	350, 300

Table 7.1: Experimental parameters for the growth of all GaAsN samples.

Samples S1050112 and S3050112 were grown at a plasma current of 18 mA, suited to achieving high nominal nitrogen mole fractions while samples S2070112 and S1060112 were grown at a lower plasma current of 12 mA to achieve lower nominal nitrogen mole fractions. The GaAsN layers thicknesses were between 200 and 350 nm depending on the nominal nitrogen mole fractions in each layer, designed to avoid the formation of misfit dislocations or other strain-relieving defects. The nitrogen background pressure in the growth chamber was monitored and controlled at 79 mV (reading on a multimeter connected to the ion pump controller 0-100 mV

pressure record output as explained in chapter 5 section 5.2) for samples S1050112 and S3050112. For growth of the lower nitrogen mole fraction samples, the ion pump controller pressure record output was set to 69 and 58 mV for samples S2070112 and S1060112 respectively. Further details on the sample structures are given in the following section.

### 7.2.1 Sample Structures

All structures were grown on 500  $\mu$ m thick GaAs (001) substrates with the designs tailored to meet the requirements of SIMS analysis. All samples were prepared as described in chapter 3 section 3.2 with the growth rate, nitrogen background pressure and nitrogen plasma current varied from sample to sample in order to obtain the required nominal nitrogen mole fractions in each GaAsN layer. The growth temperature for all samples was 460°C to avoid the effects of nitrogen blocking of arsenic sites [198]. Figure 7.1 shows the structure of sample S1050112 containing three layers of GaAsN each 300 nm thick. The nominal nitrogen mole fractions in each layer were designed to be 0.007, 0.005 and 0.009 and these were to be achieved by maintaining a constant nitrogen flux and varying the gallium flux rate. Five InGaAs layers of thickness 5 nm were used as markers to clearly identify the positions of the GaAsN-GaAs interfaces when performing SIMS depth profiling and the indium mole fraction required for this purpose was only about 0.02. The two 50 nm GaAs buffer layers were designed to smooth the growth surface prior to commencing the next GaAsN layer and to minimise the effects of knock-on during the SIMS measurements. The 50 nm GaAs cap layer was included so there was enough time for the SIMS measurement to differentiate nitrogen yield measured from atmospheric contamination of the surface from nitrogen sputtered from the topmost GaAsN layer. The growth process was interrupted for a few minutes following the growth of each GaAs buffer and resumed when the gallium furnace was stable at the temperature required to grow the next GaAsN layer.



Figure 7.1: The structure of sample S1050112 showing the layer compositions and thicknesses and the substrate temperatures employed for the growth of each layer.

Figure 7.2 shows the structure of samples containing two layers of GaAsN of different nitrogen mole fractions and the logic behind the sample design is the same as for the structure shown in Figure 7.1.



Figure 7.2: The structure of samples containing two GaAsN layers, showing the substrate temperatures employed for the growth of each layer and all layer thicknesses except for the GaAsN layers.

# 7.3 HRXRD and SIMS Measurements

All samples grown in these experiments were characterised by HRXRD and SIMS and this section presents the results of those measurements.

# 7.3.1 HRXRD Measurements

All as-grown samples were characterised by HRXRD by collecting (004) rocking curves at Phi angles of 0°, 90°, 180° and 270° prior to the SIMS measurements. The separations between each GaAsN layer peak relative to the GaAs substrate peak could be measured accurately in each sample since all GaAsN layers were relatively thick and their peaks were sufficiently intense and narrow to allow their angular positions to be easily determined. Figure 7.3 shows examples of experimental (004) rocking curves obtained from the four GaAsN samples grown for this experiment,

with nominal nitrogen mole fractions between 0.0013 and 0.0103. All GaAsN epitaxial layer peaks are labelled *Y* with three peaks observed from sample S1050112 and two peaks from each of the other three samples. All GaAsN layer peaks are well resolved in each spectrum, and all four samples have clear Pendellösung fringes suggesting that the GaAsN/GaAs interfaces were coherent.



Figure 7.3: Examples of HRXRD (004) rocking curves collected from the as-grown samples (a) S1050112, (b) S3050112, (c) S2070112 and (d) S1060112. The symbols *Y* show the GaAsN layer peaks and the diffraction profiles are shifted vertically for clarity.

The error associated with determining the GaAsN layer perpendicular lattice parameters depends on how accurately the GaAsN peak positions can be determined relative to the GaAs substrate peak. Figure 7.4 shows a linear plot of one of the
HRXRD rocking curves collected from sample S1050112 and since all GaAsN layer peaks are clearly observed in the spectrum, there was no difficulty in identifying their separations from the GaAs substrate peak using X'pert Epitaxy and Smoothfit 4.0 software. The perpendicular lattice parameters of each of the GaAsN layers could then be calculated from the peak separations using the same method as was explained in chapter 5 section 5.2.1.



Figure 7.4: A linear plot of one of the HRXRD rocking curves obtained from asgrown sample S1050112 showing clear GaAsN layer peaks labelled *Y*.

#### 7.3.2 SIMS Measurements

Following the HRXRD measurements the samples were chemically analysed by SIMS depth profiling using <sup>133</sup>Cs<sup>+</sup> primary ions accelerated to 10 keV and then retarded to an energy of 5 keV at the sample surface. The clusters recorded were <sup>133</sup>Cs<sup>14</sup>N<sup>+</sup>, <sup>133</sup>Cs<sup>16</sup>O<sup>+</sup>, <sup>133</sup>Cs<sup>69</sup>Ga<sup>+</sup>, <sup>133</sup>Cs<sup>75</sup>As<sup>+</sup> and <sup>133</sup>Cs<sup>115</sup>In<sup>+</sup> and the counting time used for <sup>133</sup>Cs<sup>14</sup>N<sup>+</sup> was 10 seconds while the other clusters were counted for 1.04 seconds, reflecting the relative yields of the species or their importance to subsequent analysis. The aperture limiting the field of view of the mass spectrometer was 1800  $\mu$ m in diameter while the analysed area was 150  $\mu$ m in diameter. The SIMS sputtering rate was about 0.27 nm/s and all samples in this work were analysed under identical experimental conditions. Details of the SIMS instrument have been presented in chapter 3 section 3.4.2.

Figure 7.5 shows the nitrogen (red curve) and indium (green curve) yields resulting from depth profiling sample S1050112. The average <sup>133</sup>Cs<sup>14</sup>N<sup>+</sup> yields in the layers are shown by the solid blue horizontal bars with the bar lengths showing the time period over which the average was calculated. The <sup>133</sup>Cs<sup>14</sup>N<sup>+</sup> yield clearly shows three different yield levels representing the three different nitrogen compositions in each of the GaAsN layers. The centres of the <sup>133</sup>Cs<sup>115</sup>In<sup>+</sup> yield peaks are shown by the vertical dashed lines located at the rising and falling edges of the <sup>133</sup>Cs<sup>14</sup>N<sup>+</sup> yield curves as expected from the structure design. Similar depth profiles, but with only two <sup>133</sup>Cs<sup>14</sup>N<sup>+</sup> yield peaks, were observed for the other samples. Figure 7.6 shows a linear plot of the <sup>133</sup>Cs<sup>14</sup>N<sup>+</sup> yields measured in sample S1050112 to better illustrate the range of nitrogen mole fractions achieved in this sample.



Figure 7.5: SIMS depth profile obtained from sample S1050112. The red curve shows the  ${}^{133}Cs^{14}N^+$  yield and the solid blue horizontal bars indicate the average values of this yield in the layers. The green curve shows the  ${}^{133}Cs^{115}In^+$  yield with the centres of mass of the individual peaks indicated by the vertical dashed lines.



Figure 7.6: A linear plot of  ${}^{133}Cs^{14}N^+$  yields measured in sample S1050112 with averages of 142, 86 and 117 in each layer.

### 7.4 Results and Discussion

This section presents the analysis of the HRXRD and SIMS data to show the relationship between GaAsN perpendicular lattice parameters and normalised nitrogen mole fractions. Linear and non-linear theoretical relationships between the GaAsN perpendicular lattice parameter and nitrogen mole fraction will also be developed in this section.

#### 7.4.1 SIMS Analysis

Figure 7.7 shows  ${}^{133}Cs^{69}Ga^+$  and  ${}^{133}Cs^{75}As^+$  yields plotted against the intensity ratio of  ${}^{133}Cs^{75}As^+$  to  ${}^{133}Cs^{69}Ga^+$  for all GaAsN layers in each sample (as labelled in the figure). The average of the  ${}^{133}Cs^{75}As^+$  to  ${}^{133}Cs^{69}Ga^+$  yield ratios for GaAsN layers within each sample vary between 0.204 and 0.237. The statistical counting errors

associated with the horizontal and vertical axes change with signal intensities  $(^{133}Cs^{69}Ga^+ \text{ and } ^{133}Cs^{75}As^+ \text{ yields})$  as shown in the plot. However, the statistical counting error associated with the vertical axis cannot be observed in this plot. For example, the statistical counting errors for  $^{133}Cs^{69}Ga^+$  and  $^{133}Cs^{75}As^+$  yields from sample S1050112 are 0.2% and 0.3% respectively. This means that this is not the cause of the variations in the  $^{133}Cs^{69}Ga^+$  and  $^{133}Cs^{75}As^+$  yields observed.



Figure 7.7: Plot of  ${}^{133}Cs^{69}Ga^+$  and  ${}^{133}Cs^{75}As^+$  yields versus the  ${}^{133}Cs^{75}As^+$  to  ${}^{133}Cs^{69}Ga^+$  yield ratio obtained from all samples.

There are two data points for each of samples S1060112, S2070112 and S3050112 while sample S1050112 shows three data points with two of them so close as to appear almost as one. From this figure, it is clear that the  ${}^{133}Cs^{75}As^+$  to  ${}^{133}Cs^{69}Ga^+$  ratio is not constant within samples, nor from sample to sample. As shown in Table 7.2, the variations in  ${}^{133}Cs^{75}As^+$  to  ${}^{133}Cs^{69}Ga^+$  yield ratios within each sample were

between 0.5% and 1.1% of their mean. The table also shows that the  ${}^{133}Cs^{75}As^+$  yield variations within samples S1050112, S2070112 and S3050112 were less than that of  ${}^{133}Cs^{69}Ga^+$ . A possible reason for this could be due to inconsistency of the  ${}^{133}Cs^+$  yield from sample to sample (its variation was between 3.1% and 22.3%) even though all samples were analysed on the same day. However, referencing  ${}^{133}Cs^{75}As^+$  and  ${}^{133}Cs^{69}Ga^+$  to the  ${}^{133}Cs^+$  yield did not result in better consistency in their ratios between or within samples. Therefore,  ${}^{133}Cs^{75}As^+$  was selected as the matrix reference against which other yields were scaled for all the SIMS analyses presented in this chapter. This results in significantly decreased matrix effects in SIMS measurements when using CsAs<sup>+</sup> rather than  ${}^{133}Cs^{69}Ga^+$ .

Table 7.2: The variations in  ${}^{133}Cs^{75}As^+$ ,  ${}^{133}Cs^{69}Ga^+$  and  ${}^{133}Cs^{75}As^+/{}^{133}Cs^{69}Ga^+$  yields from their mean, for each sample.

Sample	$^{133}Cs^{75}As^{+}$	$^{133}Cs^{69}Ga^{+}$	<sup>133</sup> Cs <sup>75</sup> As <sup>+</sup> / <sup>133</sup> Cs <sup>69</sup> Ga <sup>+</sup>
	% variation	% variation	% variation
	within sample	within sample	within sample
	(%)	(%)	(%)
S1050112	0.8	1.4	0.6
S1060112	1.6	0.9	0.7
S2070112	6.0	7.1	1.1
S3050112	2.9	3.4	0.5

Table 7.3 displays the data obtained from the HRXRD and SIMS measurements made on all samples grown for these experiments. The error associated with the nominal nitrogen mole fractions  $y_{XRD(nom)}$  determined from the HRXRD data is ±0.0001, while the statistical counting errors associated with determination of the intensity ratios of <sup>133</sup>Cs<sup>14</sup>N<sup>+</sup> to <sup>133</sup>Cs<sup>75</sup>As<sup>+</sup> are shown in the table for each layer. The GaAsN perpendicular lattice constant was calculated with an error of ±0.00013 Å.

Sample	GaAsN layer	Intensity ratio of ${}^{133}Cs^{14}N^{+}$ to ${}^{133}Cs^{75}As^{+}$	<i>YXRD(nom)</i> (Estimate)	$a_{GaAsN}^{\perp}$ (Å)
		$(x10^{-3})$	(±0.0001)	(±0.00013 Å)
S1050112	$1^{st}$	1.7±0.1	0.0091	5.63276
	$2^{nd}$	1.0±0.1	0.0051	5.64184
	$3^{rd}$	$1.4\pm0.1$	0.0071	5.63726
S1060112	$1^{st}$	0.9±0.1	0.0034	5.64551
	$2^{nd}$	0.3±0.1	0.0013	5.65031
S2070112	$1^{st}$	$1.0\pm0.2$	0.0047	5.64275
	$2^{nd}$	0.5±0.1	0.0019	5.64909
S3050112	$1^{st}$	2.4±0.3	0.0103	5.63008
	$2^{nd}$	$1.1\pm0.2$	0.0045	5.64309

Table 7.3: Summary of data from HRXRD and SIMS measurements made on all samples.

# 7.4.2 Relationships between GaAsN Perpendicular Lattice Constant and Nitrogen Mole Fraction for Vegard's Law True and Not True

A non-linear relationship between the GaAs<sub>1-y</sub>N<sub>y</sub> natural lattice constant  $a_{GaAsN}$  and nitrogen mole fraction y can be expressed as:

$$a_{GaN_{v}As_{1-v}} = ya_{GaN} + (1 - y)a_{GaAs} + by(1 - y)$$
(7.1)

where  $a_{GaAs}$  and  $a_{GaN}$  are the natural lattice constants of GaAs and GaN, y is the nitrogen mole fraction and b is a bowing parameter. Rearranging Equation 7.1 it becomes:

$$a_{GaN_yAs_{1-y}} = -by^2 + y(b + \Delta a) + a_{GaAs}$$

$$(7.2)$$

where  $\Delta a = a_{GaN} - a_{GaAs}$ . Assuming linear elasticity theory, the natural lattice constant  $a_{GaAsN}$  of the GaAsN layer can be related to its parallel and perpendicular lattice parameters  $a^{\parallel}$  and  $a^{\perp}$  in a tetragonally strained state according to:

$$a_{GaN_yAs_{1-y}} = a_{GaAsN}^{||} \left(\frac{2v_{GaAsN}}{1 + v_{GaAsN}}\right) + a_{GaAsN}^{\perp} \left(\frac{1 - v_{GaAsN}}{1 + v_{GaAsN}}\right)$$
(7.3)

where  $v_{GaAsN}$  and  $a_{GaAsN}^{\perp}$  are Poisson's ratio and the perpendicular lattice parameter of GaAsN and  $a_{GaAsN}^{\parallel}$  is the GaAsN parallel lattice parameter. For coherent growth the parallel lattice parameter of the GaAsN layer adopts that of the GaAs substrate and so  $a_{GaAsN}^{\parallel} = a_{GaAs}$ . If Poisson's ratio of GaAsN  $v_{GaAsN}$  is assumed to be linear with composition then:

$$v_{GaAsN} = yv_{GaN} + (1 - y)v_{GaAs} \tag{7.4}$$

where  $v_{GaN}$  and  $v_{GaAs}$  are the Poisson's ratios of GaN and GaAs. Equation 7.4 can be rewritten as:

$$v_{GaAsN} = y\Delta v + v_{GaAs} \tag{7.5}$$

where  $\Delta v = v_{GaN} - v_{GaAs}$ . By equating Equations 7.2 and 7.3 and employing some algebraic manipulation we have:

$$-by^{2}(1 + v_{GaAsN}) + y(b + \Delta a)(1 + v_{GaAsN}) = (1 - v_{GaAsN})(a_{GaAsN}^{\perp} - a_{GaAs})$$
(7.6)

and by substituting Equation 7.5 into Equation 7.6 we obtain:

$$b\Delta vy^{3} + b[(1 + v_{GaAs}) - (b + \Delta a)\Delta v]y^{2} - [(b + \Delta a)(1 + v_{GaAs}) + \Delta v(a_{GaAsN}^{\perp} - a_{GaAs})]y + (1 - v_{GaAs})(a_{GaAsN}^{\perp} - a_{GaAs}) = 0.$$
(7.7)

Rearranging Equation 7.7 to express  $a_{GaAsN}^{\perp}$  in terms of all other lattice and elastic parameters we obtain:

$$a_{GaAsN}^{\perp} = \left[\frac{-by^3 - y^2 \left[\frac{b(1 + v_{GaAs})}{\Delta v} - (b + \Delta a)\right] + y \left[\frac{(b + \Delta a)(1 + v_{GaAs})}{\Delta v}\right]}{\left[-y + \left(\frac{1 - v_{GaAs}}{\Delta v}\right)\right]} + a_{GaAs}.$$
 (7.8)

If Vegard's law holds then b = 0 and Equation 7.8 reduces to:

$$a_{GaAsN}^{\perp} = \frac{-(\Delta a)\Delta v y^2 - (\Delta a)(1 + v_{GaAs})y}{y\Delta v - (1 - v_{GaAs})} + a_{GaAs}$$
(7.9)

which is also non-linear in *y* because Poisson's ratio is composition dependent. If Poisson's ratio can be considered to be constant and equal to the GaAs value over the low and limited range of nitrogen mole fractions in the layers we have been investigating, then Equation 7.9 reduces further to:

$$a_{GaAsN}^{\perp} = \frac{\Delta a (1 + v_{GaAs}) y}{(1 - v_{GaAs})} + a_{GaAs}$$
(7.10)

which is linear in the nitrogen mole fraction *y*.

Equation 7.8 was used to test for any non-linearity in the relationship between the natural lattice constants and normalised nitrogen mole fractions measured in all of the samples. Parameters such as  $a_{GaAs}$ ,  $a_{GaN}$ ,  $v_{GaAs}$  and  $v_{GaN}$  were fixed at 5.65325 Å [38, 39], 4.5 Å [38], 0.322 [180] and 0.352 [38] and the bowing parameter used for the test was 0.1 which is likely to be an over estimate since for example the bowing parameter associated with the AlGaAs system is of the order of 2 x 10<sup>-3</sup>. Equation 7.9 was used to test for linearity in the relationship between the natural lattice constant and normalised nitrogen mole fractions measured in the samples. Neither relationship yields a straight line in a plot of perpendicular lattice parameter versus nitrogen mole fraction because Poisson's ratio is taken to be composition dependent for both.

The tests of the two relationships between GaAsN perpendicular lattice constants and normalised nitrogen mole fractions for the two models of a linear or a non-linear lattice constant/composition relationship are plotted separately. The values of GaAsN perpendicular lattice constant were taken directly from Table 7.3 while the values on the horizontal axis were scaled values of the intensity ratio of  ${}^{133}Cs{}^{14}N^{+}$  to

<sup>133</sup>Cs<sup>75</sup>As<sup>+</sup>. The horizontal axis data points were scaled by a factor  $k_i$  which was different for each sample *i*, in order to best align the data on a common theoretical line. The raw intensity ratios of <sup>133</sup>Cs<sup>14</sup>N<sup>+</sup> to <sup>133</sup>Cs<sup>75</sup>As<sup>+</sup> were scaled by  $k_i$  according to:

$$y_{Nor} = \frac{\text{Intensity ratio of } ^{133}\text{Cs}^{14}\text{N}^{+} \text{ to } ^{133}\text{Cs}^{75}\text{As}^{+}}{k_{i}}$$
(7.11)

where  $y_{Nor}$  was the normalised nitrogen mole fraction for each layer within a sample *i*. This scaling process was optimised using a least-squares  $\chi^2$  criterion in order to minimise the error between the experimental and theoretical data points by adjusting the value of  $k_i$ . The value of  $k_i$  for each sample was different for the two models we are considering.

Figure 7.8 shows GaAsN perpendicular lattice constants plotted against normalised nitrogen mole fraction  $y_{Nor}$  for sample S1050112, for both Vegard's law true and not true. At  $y_{Nor} = 0$ , the perpendicular lattice constants are equal to 5.65325 Å (the GaAs lattice constant) as indicated by a solid circle in each plot. These relationships were established for all samples and then the data from all samples were plotted together, one plot for the true case and one for the not true case.



Figure 7.8: Plots of GaAsN perpendicular lattice constants  $a_{GaAsN}^{\perp}$  against normalised nitrogen mole fraction  $y_{Nor}$  for sample S1050112 (a) Vegard's law true and (b) Vegard's law not true.

Figure 7.9 shows a plot of GaAsN perpendicular lattice constants against normalised nitrogen mole fractions  $y_{Nor}$  for all experimental data points from all samples following scaling, and includes a plot of the relationship for when Vegard's law is true given by Equation 7.9.



Figure 7.9: Plot of GaAsN perpendicular lattice constants  $a_{GaAsN}^{\perp}$  against normalised nitrogen mole fractions  $y_{Nor}$ . The solid line is the relationship given by Equation 7.9.

Figure 7.10 similarly shows GaAsN perpendicular lattice constants plotted against normalised nitrogen mole fractions  $y_{Nor}$  for all experimental data points from all samples, separately scaled to the Vegard's law not true relationship of Equation 7.8 with a bowing parameter b = 0.1.



Figure 7.10: Plot of GaAsN perpendicular lattice constants  $a_{GaAsN}^{\perp}$  against normalised nitrogen mole fractions  $y_{Nor}$ . The dashed line is the curve from Equation 7.8 with a bowing parameter b = 0.1.

It is apparent from the plots in Figures 7.9 and 7.10 that it is not possible to discriminate between the two models for the lattice constant/composition relationship based on the data available, since over the limited range of normalised nitrogen mole fractions it was possible to grow for this work, both relationships appear to be approximately linear. This point is better appreciated from Figure 7.11, which shows GaAsN perpendicular lattice constants plotted against normalised nitrogen mole fractions for  $0 \le y_{Nor} \le 1$ . Despite the bowing parameter introducing additional non-linearity into the relationship, it is indiscernible from the Vegard's law true relationship over the limited range of nitrogen mole fractions accessible in this and other studies of the dilute nitride GaAsN. Increasing the bowing parameter *b* even further beyond what already seems a realistic limit would not change this situation.



Figure 7.11: The variation of GaAsN perpendicular lattice constant  $a_{GaAsN}^{\perp}$  with normalised nitrogen mole fraction  $y_{Nor}$  ( $0 \le y_{Nor} \le 1$ ) between GaAs and GaN. The dashed line is the Vegard's law not true curve from Equation 7.8 while the solid line is the Vegard's law curve from Equation 7.9.

### 7.5 Summary

HRXRD and SIMS measurements were used to check the form of the relationship between perpendicular lattice constants and normalised nitrogen mole fractions  $y_{Nor}$ in a series of GaAs<sub>1-y</sub>N<sub>y</sub> samples with  $y_{Nor} < 0.012$ . The results indicate that there is no observable deviation from Vegard's law for GaAs<sub>1-y</sub>N<sub>y</sub> epitaxial layers with y from 0 to 0.01 and in the absence of more detailed data it is reasonable to assume the validity of Vegard's law.

## **8** Conclusions and Future Work

This chapter summarises the four major outcomes of the experiments that have been performed in the course of this study and makes some recommendations for work that could be continued in the future to advance our understanding of issues relevant to the growth and determination of nitrogen mole fractions in the dilute nitride GaAsN.

### 8.1 Conclusions

The overall goal of the research reported here was to determine nitrogen mole fractions in the ternary compound GaAsN using high resolution x-ray diffraction. The application of HRXRD to the determination of composition in compound semiconductors is wide-spread, however it is not always appreciated that there are a number of important assumptions which are commonly made when analysing HRXRD results, all or some of which have been tested to a lesser or greater degree for a broad range of material systems. For example, the ternary semiconductor  $Al_xGa_{1-x}As$  grown on GaAs substrates has been studied extensively enough that we are able to say that (i) for all but the highest aluminium mole fractions x, layers with thicknesses of the order of 1  $\mu$ m are coherent with their growth substrate, (ii) the  $Al_xGa_{1-x}As$  end-point binary GaAs and AlAs lattice parameters are known to sufficient accuracy and the ternary compound natural lattice constant does not obey Vegard's law although the bowing parameter is known and (iii) the elastic constants and Poisson's ratio are known with reasonable accuracy. In the case of the ternary III/V compound semiconductor GaAsN, which is a relative newcomer to the set of studied III/V compounds, none of these conclusions could be drawn prior to the performance of the work reported herein. This work addresses most of these shortcomings.

Because of the considerable uncertainty surrounding the questions of (i) interfacial coherence, (ii) end-point binary lattice parameters and the validity of Vegard's law and (iii) the values of elastic constants and Poisson's ratio for GaAsN, a range of experiments have been designed and performed. These experiments have not only tested some of these questions but have also investigated several other important issues which arise as a consequence of the nature of the nitrogen plasma source, which floods the growth chamber with molecular nitrogen. In a separate set of detailed experiments the bilayer strain present in GaAsN layers has been cancelled by the addition of indium. Following analysis of all of the results obtained from these sets of experiments we are able to draw the following conclusions:

A. The Matthews and Blakeslee formulation of the critical strained-layer thickness before misfit dislocation formation does not hold for GaAsN grown on a GaAs substrate. While stacking fault defects form at small layer thicknesses, their size and density means that they cover only part of the surface with most of the surface remaining coherent up to thicknesses about a factor of four times higher than the M&B critical layer thickness theory predicts. While there is a very low concentration of misfit dislocations present in these layers, the catastrophic loss of interfacial coherence occurs at a strained-layer thickness prediction. The loss of interfacial coherence observed by TEM is confirmed by HRXRD measurements of the relaxation of strain in the thickest GaAsN layers studied. Therefore x-ray measurements of layers considerably thicker than were expected to be coherent can be interpreted as originating from coherent material, with areas which are not coherent due to the presence of stacking faults or low levels of misfit dislocations not participating in the diffraction process.

B. The validity of Vegard's law for the GaAsN lattice parameter has been tested and the results obtained do not suggest there is any need to allow for deviation from a linear relationship between the GaAsN perpendicular lattice constants and the normalised nitrogen mole fractions. These results agree with other GaAsN research reported in the literature for low nitrogen mole fractions of less than 0.012.

C. Poisson's ratio has been determined by measuring the unit cell dimensions in a GaAsN layer in two strain states. The results of these measurements and the subsequent analysis suggest that within experimental error the GaAsN Poisson's ratio of 0.31 is the same as that of GaAs at the low nitrogen mole fractions involved in this study (estimated to be up to a little over 1%). However, in an independent study performed in the course of this work and reported in chapter 5, the same figure of 0.31 was obtained, suggesting that the difference between this value and the GaAs figure may be significant.

D. The presence of high background nitrogen pressures results in the incorporation of low levels of molecular nitrogen during the growth of GaAs layers, however the levels are a factor of about one two-hundredth of the levels of atomic nitrogen found in GaAsN layers grown with the plasma source ignited. Measurements have confirmed that the presence of these low levels does not impact significantly on the GaAs lattice constant.

An outstanding issue for x-ray characterisation of GaAsN layers is the appropriate value of the end-point binary lattice constants of cubic GaN and InN. Unlike most other semiconductor materials, for which six figure values are available, the GaN and InN lattice constants are quoted to only three figures. More will be said of this in future work.

Notwithstanding the shortcomings in our knowledge of the GaN and InN lattice constants, we can conclude following the observations that have been made above that x-ray analysis of nitrogen mole fractions in GaAsN layers as reported in the

literature are in most cases reasonably accurate. This study has eliminated some of the more serious uncertainties regarding those x-ray analyses and thus provides validation of the HRXRD approach to compositional determination of nitrogen mole fractions in GaAsN. This work would recommend that the value of Poisson's ratio that should be employed for dilute  $GaAs_{1-y}N_y$  with y < 0.012 is 0.31, rather than the GaAs value of 0.322. In addition to this work another significant study was undertaken as described below.

E. A new approach to calibrating nitrogen mole fractions in tensile GaAsN layers by the addition of indium has been developed. In this work the indium equivalent x in an unstrained In<sub>x</sub>Ga<sub>1-x</sub>As<sub>1-y</sub>N<sub>y</sub> layer grown with the same nitrogen mole fraction y as in a GaAs<sub>1-y</sub>N<sub>y</sub> layer has been determined for a range of nitrogen mole fractions. This approach does not assert the nitrogen mole fractions in layers, rather it establishes the indium equivalent, which is a convenient measure since the InGaAs/GaAs system has been extensively studied and laboratories will generally be more confident of their knowledge of indium mole fractions than they are of their nitrogen mole fractions. This provides a method whereby nitrogen content, as manifested in the tensile strain it causes in a GaAsN layer, is calibrated according to the mole fraction of indium required to exactly cancel that strain. Apart from the scientific imperative to document mole fractions accurately, there are many situations where a knowledge of mole fractions is essential, particularly if laboratories wish to replicate the results of others. This is the main value in this approach.

#### 8.2 Future Work

The experiments on critical layer thickness determinations using TEM revealed some very interesting differences between the tensile GaAsN/GaAs and compressive InGaAs/GaAs material systems. The observation of stacking faults needs to be followed up to determine whether they are being nucleated heterogeneously and if so at what type of defect. If the stacking faults can be reduced or eliminated then defect free GaAsN layers grown to thicknesses four times that of the M&B critical layer thickness should be achievable. This would have significant benefits in reducing the

band-widening effect of quantum confinement as well as having benefits for solar photovoltaic applications with thicker absorbing layers. Further detailed studies of the process of misfit dislocation formation in thicker layers, that leads to a loss of coherence across the entire surface should be made. There are many questions to answer in this regard, such as what are the Burgers vectors of these dislocations, do they glide or climb, how do they interact when their densities increase and what is the change in the density of threading dislocations reaching the surface as this dense network develops?

It is also recommended that experimental improvements be made to reduce the variation in the rate of flow of pure nitrogen to the plasma source as this was a significant source of experimental error and any improvement in control would benefit the accuracy of some of the results obtained in the course of this study.

Another outstanding question is what are the correct values of the cubic GaN and InN lattice constants which should be applied when interpolating between the InGaAsN or GaAsN end-point binaries to establish nitrogen mole fractions? This is a vexing question because bulk samples are not readily available for x-ray analysis and in any case may not always be identical. This is certainly the case for more established substrate materials such as GaAs, which can be measured in any modern HRXRD system to determine their lattice parameters, which invariably vary from substrate to substrate. It is also not possible to grow epitaxial GaAsN layers beyond nitrogen mole fractions of about 5% because of phase separation problems, so strain cancellation with indium at higher mole fractions is not possible. However, the question is important enough that it should be raised and addressed if possible.

In addition to the future work that has been mentioned above, more work could be done to consolidate the findings of Chapters 6 and 7. Further experiments could be performed to resolve the issue of whether Poisson's ratio is 0.31 or 0.322. The Vegard's law experiment in Chapter 7 were made more difficult by the expectation that critical layer thicknesses were in agreement with the analysis of Matthews and

Blakeslee. Those experiments could be repeated with greater layer thicknesses to better test the form of the relationship between perpendicular lattice constants and normalised nitrogen mole fractions  $y_{Nor}$  for  $y_{Nor} < 0.012$ .

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# **List of Publications**

- 1) H. Hashim and B. F. Usher, "Strain cancellation by indium incorporation for the calibration of nitrogen fractions in GaAsN", in *Semiconductor Electronics* (*ICSE*), 2010 IEEE International Conference on, pp. 8-11, June, 2010.
- H. Hashim and B. F. Usher, "The Incorporation of In in GaAsN as a Means of N Fraction Calibration", in *International Conference on Applied Mathematics*, *Mechanics and Physics* Singapore: World Academy of Science, Engineering and Technology, p. 217, September, 2011.
- 3) B. F. Usher, S. Saengkae, H. Hashim, A. Rahman, A. Loygaew and M. Goodarzi, "Semiconductor Materials Research at La Trobe University", in *Science and Technology Community Development 2011 & International Symposium on Material Science Engineering and Energy Technology*, July, 2011.