Study of nitrogen incorporation into (In, Ga) as grown by metal organic chemical vapor deposition

Sentosa, Deny

2009

Sentosa, D. (2009). Study of nitrogen incorporation into (In, Ga) as grown by metal organic chemical vapor deposition. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/46988>

<https://doi.org/10.32657/10356/46988>

Nanyang Technological University

Downloaded on 26 Apr 2023 18:35:25 SGT

Study of Nitrogen Incorporation into (In, Ga) As Grown by Metal Organic Chemical Vapor Deposition

DENY SENTOSA

**SCHOOL OF ELECTRICAL AND ELECTRONICS
ENGINEERING**

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

2009

Acknowledgments

I sincerely thank my supervisor, Dr. Tang Xiaohong, for his guidance and advices during my PhD period. I am also grateful to my co-supervisor, Prof. Chua Soo Jin, Institute for Materials Research and Engineering (IMRE), for the fruitful discussions on results and many suggestions for the experiments.

I want to thank my family and friends for their continuous supports and encouragement. Special thanks for Dr. Hendrix Tanoto for his endless help in experiments and discussions, Dr. Yin Zongyou, and Ms. Zhao Jinghua for their input in experimental results; Ms. Chow Shue Yin and Ms. Doreen Lai Mei Ying (IMRE) for their sincere help in TEM and SIMS measurements together with their invaluable knowledge in the experiments; Dr. Soh Chew Beng and Andrew for their friendship and helps in many ways; Dr. Tripathy and Ms. Sue Ann (IMRE) for their help in Raman measurement.

I also want to convey my heartfelt gratitude to A*Star for the scholarship and NTU for the facilities, without which this research would not have been possible.

Table of Contents

Acknowledgments..... ii

Table of Contents..... iii

Summaryvii

List of Figures xi

List of Tables xvi

Chapter 1 1

Introduction..... 1

1.1 Motivation..... 1

1.2 Objective..... 7

1.3 Major Contributions of the Thesis..... 8

1.4 Organization of the Thesis..... 10

Chapter 2 12

Background Information 12

2.1 Introduction 12

2.2 III-V-N Semiconductor Alloys 12

2.3 Metalorganic Chemical Vapor Deposition (MOCVD)..... 15

2.4 Material Characterizations 20

2.4.1 X-Ray Diffraction (XRD)..... 21

2.4.2 Raman Spectroscopy 25

2.4.3 Transmission Electron Microscopy (TEM)..... 28

2.4.4 Photoluminescence (PL)..... 29

2.4.5 Secondary Ion Mass Spectroscopy (SIMS)..... 32

2.5	<i>Summary</i>	34
-----	----------------------	----

Chapter 3 36

Growth and Nitrogen Incorporation of (In)GaAsN 36

3.1	<i>Introduction</i>	36
3.2	<i>MOCVD Growth of GaAsN and InGaAsN</i>	37
3.2.1	Growth temperature and reactor pressure optimization	38
3.2.2	Effect of growth temperature, reactor pressure, and TMGa flow rate on the growth rate of GaAsN and InGaAsN	41
3.3	<i>Effect of MOCVD growth conditions to the nitrogen incorporation</i> ·	48
3.3.1	Growth temperature and reactor pressure on N incorporation.....	48
3.3.2	DMHy to (DMHy + TBAs) and carrier gas on N incorporation	50
3.3.3	Effect of group V to group III molar ratio on N incorporation.....	52
3.4	<i>Effect of N content on surface roughness and growth rate</i>	54
3.5	<i>Summary</i>	57

Chapter 4 59

Nitrogen Interstitials in GaAsN 59

4.1	<i>Introduction</i>	59
4.2	<i>Nitrogen-Nitrogen (N-N) pairs interstitials</i>	61
4.3	<i>Nitrogen interstitials calculation</i>	70
4.4	<i>Summary</i>	78

Chapter 5 79

Optical properties of GaAsN and InGaAsN 79

5.1	<i>Introduction</i>	80
5.2	<i>The effect of nitrogen content in (In)GaAsN alloy</i>	81

5.2.1	GaAsN and InGaAsN band-to-band energy with nitrogen	82
5.2.2	Raman measurement of GaAsN and InGaAsN alloys.....	89
5.3	<i>Thermal Annealing of GaAsN materials</i>	94
5.3.1	Annealing effect on GaAsN materials.....	95
5.3.2	Effect of SiO ₂ cap on GaAsN annealed epilayer.....	100
5.4	<i>Summary</i>	104
Chapter 6		106
Study of InAsN Alloy		106
6.1	<i>Introduction</i>	106
6.2	<i>Theoretical calculation of band structure of InAsN</i>	107
6.2.1	Tight-binding calculation	107
6.2.2	Pseudopotential theory	109
6.2.3	Density functional theory	112
6.2.4	InAsN band structure calculated by DFT	114
6.3	<i>MOCVD growth of InAsN</i>	120
6.3.1	Effect of DMHy/V molar ratio on N incorporation in InAsN epilayer 121	
6.3.1	Effect of carrier gas	125
6.3.2	InAsN single quantum wells and their optical properties.....	128
6.4	<i>Summary</i>	134
Chapter 7		136
Conclusion and Recommendations.....		136
7.1	<i>Conclusion</i>	136
7.2	<i>Recommendations</i>	139
Author's Publications		142

Publications in refereed journals 142

Conference/symposium presentations 142

Bibliography..... 144

Appendix 155

Summary

A small amount of nitrogen incorporated into III-V semiconductor alloys leads to a band gap energy reduction of these dilute nitride alloys. The band gap energies of III-V-N materials are much reduced from the band gap energies of their III-V alloys. This property makes dilute nitride semiconductor alloys interesting materials to be studied. GaAs is an important III-V material for light emitting devices (~ 870 nm emission wavelength), such as laser diodes, solar cells, integrated circuits, and other applications. The introduction of nitrogen into GaAs can stretch its emitting wavelength to 1300 nm for fiber optics communication. InAs is another III-V material which is important for infrared detectors in the wavelength range of 1000 nm to 3000 nm. Dilute nitride InAs is able to extend its emission wavelength to longer mid-infrared (MIR) wavelength region. The mid-infrared devices are very useful for atmospheric pollution monitoring, leak detection, laser surgery and other MIR applications. Nonetheless, nitrogen incorporation into these III-V semiconductor alloys during epitaxy growth is not easy. This thesis presents studies on nitrogen incorporation in GaAs, InAs, as well as InGaAs semiconductor alloys grown by metalorganic chemical vapor deposition (MOCVD). The effect of growth conditions to nitrogen incorporation as well as the effect of nitrogen to various properties in (In,Ga)As alloys are explored.

GaAsN alloys grown by MOCVD have been studied extensively with respect to their nitrogen incorporation under different MOCVD growth conditions. It has been found that reactor pressure, V/III molar ratio, and carrier gas play important roles in increasing the nitrogen incorporation of GaAsN alloys in MOCVD growth. Nitrogen carrier gas can increase nitrogen incorporation by

three times compared to that of GaAsN grown with hydrogen carrier gas under the same growth conditions. Nitrogen incorporation in GaAsN epilayers increases linearly with the ratio of asymmetrical dimethylhydrazine (DMHy) to tertiarybutylarsine (TBAs) flow rates. GaAsN with nitrogen content up to 5% has been successfully grown. Optimized growth temperature and reactor pressure for GaAsN growth have been obtained for good quality epilayer growth.

Introduction of nitrogen in GaAsN alloys degrades their optical emission intensities. Thermal annealing is known to improve the luminescence property of GaAsN materials. At optimal annealing conditions the highest photoluminescence (PL) intensity is obtained. The optimum annealing condition is found to vary with nitrogen content in GaAsN alloys. The optimum annealing temperature is found to decrease with higher N composition of the GaAsN alloys. For example, optimum annealing temperature of a GaAsN sample with 1.3% N is 625°C as compared to 725°C for a sample with 0.7%N. Capping GaAsN epilayer with an oxide layer before annealing also affects its optical performance. The optical performance of oxide-capped GaAsN alloys after annealing is better than uncapped ones.

The miscibility of nitrogen in GaAsN not only causes non-radiative defects to be generated which degrade its optical intensity of the band-to-band transition, but also introduce an additional peak in its PL spectrum. The additional peak under study was found to be due to nitrogen interstitials. So far no PL spectra have been reported on N-N interstitials. These interstitials cause a distinct PL peak with an energy 0.2 eV below the band-to-band transition peak. The N-N interstitials are found in GaAsN epilayers grown under nitrogen carrier gas and they are not observed in the samples grown under hydrogen carrier gas. The reason for this is attributed to the reaction species available on the growing surface.

An empirical equation to calculate the percentage amount of the nitrogen interstitials in the GaAsN epilayers has been derived. It is found that the calculated interstitials concentration is within 10% of the experimental values. The empirical equation encompasses five parameters used in GaAsN growth conditions: the type of carrier gas used, growth temperature, reactor pressure, and group V to group III molar ratio as well as nitrogen to total group V molar ratio during the MOCVD growth. The model provides a good prediction of growth conditions to minimize N-N interstitial incorporation for high quality growth of GaAsN epilayers grown with nitrogen carrier gas.

To further increase the wavelength emission available with GaAsN, InAsN alloy was studied. The energy band gap of InAsN reported in the literature was calculated by tight binding and pseudopotential methods. The former overestimated while the latter underestimated the InN band gap energy that influences the overall results of the calculated band gap energy of InAsN alloys. To improve the computational results, we theoretically calculated the band gap energy using density functional theory. The fit is found to be reasonable with available experimental results. The minimum band gap energy predicted for $\text{InAs}_{1-x}\text{N}_x$ is found to be 0.075 eV when its N composition $x = 0.45$. Through curve fitting, the more accurate band gap energy bowing parameter of unstrained $\text{InAs}_{1-x}\text{N}_x$ alloys is revised to be 2.072 eV, which is lower than the value obtained by using the tight binding (4.22 eV) and higher than that of pseudopotential (1.6 eV) methods.

MOCVD growth of InAsN has also been studied with different carrier gases: hydrogen and nitrogen carrier gases. It is found that InAsN grown with hydrogen carrier gas has phase separated into InAs with a very low concentration of nitrogen and InAsN alloys. However, it is not found in InAsN grown with

nitrogen carrier gas. InAsN alloys incorporate up to 7.3% mole fraction of nitrogen at a DMHy to TBAs flow ratio of 19. To study the nitrogen incorporation effect on InAsN optical properties, InAsN/InGaAs single quantum well (SQW) structures have been grown by MOCVD with nitrogen carrier gas. An InAs/InGaAs SQW with the same thickness and grown under similar conditions is used for comparison. PL measurements show that the InAsN/InGaAs SQWs emission peak red shifts as compared to that of InAs/InGaAs SQW. InAsN SQWs with increasing DMHy to TBAs flow ratio have larger red shift, an indication that more nitrogen is incorporated in the InAsN well layer. InAsN SQW with higher nitrogen content require higher annealing temperature to improve their optical performance. The nitrogen content of the InAsN well layer with DMHy to TBAs flow ratio of 7.3 is at least 1.1%.

List of Figures

Figure 1.1 Ball and stick drawings of possibilities of nitrogen preferential bonding configurations	5
Figure 2.1 Band gap energy versus lattice constant for different compound semiconductors [56]. Dotted lines, dashed lines, and shaded region are the band gaps of InAsN, GaAsN, and InGaAsN, respectively.	13
Figure 2.2 MOCVD simplified schematic layout and the reactions inside the reactor chamber during growth.	16
Figure 2.3 Dependency of growth rate on growth temperature in the MOCVD process. .	19
Figure 2.4 X-ray passes through parallel planes with distance, d , and the diffracted angle θ	21
Figure 2.5 Schematic diagram of Phillips MRD high resolution X-ray diffractometer.	22
Figure 2.6 X-Ray diffraction (004) measurement of a GaAsN epilayer on a GaAs substrate; the inset shows the structure of the sample.	23
Figure 2.7 Diagram of a mismatched layer experiencing stress due to $a_L > a_S$	24
Figure 2.8 (a) Schematic diagram of micro Raman measurement of GaAsN for $z(x, x) z$ geometry and (b) Raman spectra of GaAsN epilayer.	27
Figure 2.9 Superlattice representation in real and reciprocal space.	28
Figure 2.10 Systematic diagram of PL's principle.	30
Figure 2.11 A simplified schematic diagram of PL set-up.	32
Figure 2.12 Schematic diagram of secondary mass ion spectroscopy set up.	33
Figure 2.13 An example to determine the epilayer thickness by SIMS.	34
Figure 3.1 X-ray diffraction peaks of the GaAsN epilayers with fringes and without fringes to show the epilayer quality. Only S4 has fringes in its X-ray rocking curve indicative of a high-quality result.	39
Figure 3.2 (a) 4K PL intensity of S1 to S5 with their respective growth temperature or reactor pressure; (b) PL spectra of S1 to S5.	40
Figure 3.3 GaAsN epilayer thickness against growth temperature and reactor pressure. The inset shows the depth, x , of the crater formed by SIMS sputtering. Inset2: TEM micrographs of GaAsN epilayers grown at the reactor pressure of 20 and 100 mbar.	42
Figure 3.4 XRD profiles of the InGaAsN epilayer grown with different Ga/III molar ratio while other growth conditions are kept constant.	44
Figure 3.5 Growth rate (reflected in epilayer thickness) of InGaAsN epilayer on InP substrate to the Ga/III molar ratio.	45

Figure 3.6 SIMS profile of the phosphorous diffusion into the InGaAsN epilayer for Ga/III molar ratio of 0.18 (solid lines) and Ga/III molar ratio of 0.26 (dashed lines).....	46
Figure 3.7 TEM image of dislocations taken from the cross section of InGaAsN epilayer grown on InP with Ga/III molar ratio of 0.12.	46
Figure 3.8 Periodical lattice of a high indium content InGaAsN epilayer with occurrence of phosphorus diffusion (dotted line).....	47
Figure 3.9 Nitrogen composition of S1 to S5 to respective growth temperature or reactor pressure.	49
Figure 3.10 (a) Nitrogen composition (%) in GaAsN epilayers versus DMHy/(DMHy+TBAs) molar ratio for different reactor pressure and carrier gas; our samples are shown in squares; (b) Our data replotted %N in GaAsN epilayers grown with nitrogen carrier gas versus DMHy/TBAs molar ratio for reactor pressures 20 and 100 mbar.....	51
Figure 3.11 Study of (a) V/III molar ratio to nitrogen content in GaAsN epilayers and (b) Nitrogen incorporation efficiency to V/III ratio and DMHy/TBAs ratio.....	53
Figure 3.12 AFM micrographs of GaAsN with 0.6% N with area of investigation of 3 x 3 μm^2	55
Figure 3.13 Plot of AFM root-mean-square roughness to nitrogen content of GaAsN alloys.....	56
Figure 3.14 GaAsN epilayer thickness against nitrogen composition.....	57
Figure 4.1 Ball and stick drawings of atomic structure of (a) N-As and (b) N-N interstitial	61
Figure 4.2 A simple diagram of the energy level of N-N interstitial and N-As interstitial in GaAsN band gap.....	62
Figure 4.3 (a) 20K-PL spectra of as-grown sample GaAsN with 0.7%, 0.8% and 0.95% N; (b) GaAsN with 0.95% N annealed at 675 °C.	63
Figure 4.4 Cross sectional TEM image of 0.7% N sample. The circled area at the interface between GaAs buffer and GaNAs epilayer does not show any nitrogen-rich cluster (inset).....	64
Figure 4.5 Nitrogen composition measured from XRD (x_{XRD}) Vs nitrogen composition measured from SIMS (x_{SIMS}) of samples with different growth conditions. The dotted line is when $x_{\text{XRD}} = x_{\text{SIMS}}$	68

Figure 4.6 20K-PL spectra of sample GaAsN with 0.7 %N at annealing temperatures of 625, 675, 725, and 775 °C. Inset: Gaussian approximation of sample annealed at 725 °C	69
Figure 4.7 Percentage nitrogen interstitial versus growth temperature (a) and reactor pressure (b).	72
Figure 4.8 Experimental and calculated %N interstitial against V/III molar ratio. Errors are within 10% as shown by error bars.....	77
Figure 5.1 4K-PL spectra of as-grown samples with different nitrogen composition. Inset: P1 peaks shift with nitrogen composition.....	83
Figure 5.2 Plot of P1 and P2 peak energy (E1 and E2, respectively) versus nitrogen composition of GaAsN epilayer.	84
Figure 5.3 Activation energy (meV) of P1 versus nitrogen content (%) in GaAsN epilayer.	86
Figure 5.4 20-K PL of InGaAsN with different Ga/III molar ratio, i.e. different In content in InGaAsN. Inset: InGaAsN with different nitrogen composition.....	88
Figure 5.5 Raman spectra of GaAsN epilayers with different nitrogen compositions; inset: N-local mode in GaAsN.	90
Figure 5.6 Raman shift of GaAs-like (a) LO phonon (b) TO phonon against nitrogen content estimated by XRD.....	91
Figure 5.7 Raman spectra of $\text{In}_y\text{Ga}_{1-y}\text{As}_{1-x}\text{N}_x$ epilayers with $y = 0.13$, $x = 0.0086$ and $y = 0.68$, $x = 0.0182$	93
Figure 5.8 20K-PL spectra of 625, 675, 725, and 775 °C annealed GaAsN sample with 0.7% N. As-grown GaAsN is included as comparison with annealed samples.	95
Figure 5.9 20K-PL peak positions (in nm) and intensity (a.u.) of GaAsN sample with 0.7% N after annealing at 625, 675, 725, and 775 °C. The squares refer to P1, while the circles refer to P2. Solids are for peak positions (left axis) and hollows are for peak intensities (right axis). The lines are drawn to guide the eye.....	96
Figure 5.10 Optimum annealing temperatures measured for different N compositions of GaAsN. The optimization refers to annealing temperatures that yield the highest peak P1 integrated intensity.	98
Figure 5.11 Activation energy E_a versus annealing temperature of $\text{GaAs}_{0.993}\text{N}_{0.007}$	99
Figure 5.12 20K-PL spectra of a GaAsN sample with 1.3% N (a) without and (b) with a SiO_2 cap layer at annealing temperatures of 625, 675, 725, and 775 °C.	101

Figure 5.13 20K-PL peak positions (in nm) and intensity (a.u.) of GaAsN sample with 1.3% N after annealing at 625, 675, 725, and 775 °C without (a) and with (b) SiO ₂ cap. The squares refer to P1, while the circles refer to P2. Solids are for peak positions (left axis) and hollows are for peak intensities (right axis). The lines are drawn to guide the eye.....	103
Figure 6.1 Band gap energy dependence on composition x for $\text{InN}_x\text{As}_{1-x}$ alloy by tight-binding calculation [51] compared with experimental result by Naoi [45] (square) and Emawly [47] (triangle).	108
Figure 6.2 Band gap energy dependence on nitrogen content, x , for $\text{InAs}_{1-x}\text{N}_x$ by PM [53]; hollow and filled triangles represents experimental band gaps for 6%N and 18%N, which are 0.12eV [45] and 0.19 eV [47], respectively.	111
Figure 6.3 Zinc blende atomic structure of $\text{InN}_x\text{As}_{1-x}$ alloy with N composition $x=0.25$ for the simulation	116
Figure 6.4 The calculated energy band diagram of (a) InAs and (b) InN.....	117
Figure 6.5 The calculated energy band gap of InAsN as a function of its N composition (dash-dot line). The experimental results of this work are presented in cross (x). The solid circles are calculated values and hollow square, triangle, and circles are experimental results [45, 47, 103]. InAsN energy band gaps calculated by tight binding [51] and pseudopotential [53] methods are included for references in solid squares (full line) and triangles (dash line), respectively.	119
Figure 6.6 (a) XRD of InAsN epilayers grown under hydrogen carrier gas with different DMHy to total group V molar ratio; (b) Difference (in arc second) of X1' and InAs diffraction peaks Vs DMHy/V molar ratio.....	122
Figure 6.7 DMHy to total group V molar ratio versus nitrogen composition estimated by XRD of InAsN epilayers grown with hydrogen carrier gas.....	124
Figure 6.8 Elements count in InAsN R5 epilayer by SIMS.....	125
Figure 6.9 XRD of R5 and R7 grown with hydrogen and nitrogen as the carrier gas, respectively. DMHy to total group V molar ratio is 0.9.	126
Figure 6.10 Raman spectra of R5 and R7 grown with hydrogen and nitrogen carrier gas, respectively.	127
Figure 6.11 InAs and InAsN single QW structure grown on InP substrate with InGaAs barrier.....	128
Figure 6.12 Low temperature (30K) PL of as-grown samples of W1, W2, and W3.....	129

Figure 6.13 As-grown W1, W2, and W3 PL peak position dependence of excitation PL
power. 130

Figure 6.14 Low temperature (30K) PL of as-grown and annealed samples of W1, W2,
and W3..... 132

Figure 6.15 PL peak position of S80, S81, S82 against as-grown and annealed samples.
..... 134

List of Tables

Table 3.1 GaAsN epilayers grown with varied growth temperatures and reactor pressures.38

Table 3.2 InGaAsN samples with various Ga/III molar ratios.43

Table 4.1 Percentage of nitrogen interstitials versus different V/III and N/V molar ratios with T = 550 °C.....73

Table 4.2 Percentage of nitrogen interstitials versus different carrier gas used during the growth for samples with similar nitrogen composition.....76

Table 5.1 InGaAsN samples growth conditions and their nitrogen and indium concentration in the epilayers.....87

Table 6.1 Simulated band-gap energies of InAs_{1-x}N_x alloys compared with the experimental results.....118

Table 6.2 InAsN epilayers grown with different DMHy to group V molar ratio and carrier gas.121

Chapter 1

Introduction

1.1 Motivation

One of III-V semiconductor alloys is GaAs that has the direct band gap (E_g) of 1.42 eV at room temperature. It can generate photons upon carrier relaxations and thus, it is an important III-V semiconductor alloy for light emitting devices (~ 870 nm LEDs). Semiconductor lasers for fiber optics communications are mostly made of GaAs or InP alloys. Currently, most commercially available light emitting devices with 1300-nm or 1550-nm wavelength emission are InP based. However, GaAs has advantages over InP in terms of its economical value and material purity.

It is known that a small amount of nitrogen incorporated into the GaAs semiconductor alloy causes a large bowing effect in its energy band gap leading to band gap energy reduction [1-11]. The band gap of GaAs is reduced by ~ 100 meV with every percent of N incorporated (up to 4% N) into it [12]. The introduction of nitrogen into GaAs can stretch the emitting wavelength to 1300 nm [13] – an optical wavelength for fiber optic communications. However, nitrogen incorporation into GaAs during epitaxial growth is not easy. The nitrogen incorporation into GaP is five times more efficient than into GaAs [14]. The highest incorporated nitrogen in GaAs is 8.68% attained by metal-organic molecular beam epitaxy (MOMBE) [15], 5% by molecular beam epitaxy (MBE) [16], and 6% by metal-organic chemical vapor deposition (MOCVD) [12]. It is

crucial to alloy more nitrogen with GaAs, while maintaining a good epilayer quality.

Nitrogen incorporation into GaAs is determined by conditions during MOCVD growth. The first growth parameter is growth temperature (T_g) that influences the nitrogen or arsenic rate of desorption from the surface during growth, thus affecting nitrogen content in the GaAsN layer. The precursors used during growth determine T_g . Ammonia and arsine, which are used as nitrogen and arsenic sources, respectively, in MOCVD growth of III-V-N semiconductors, have high decomposition temperature ($> 530\text{ }^{\circ}\text{C}$) [9, 11] leading to high growth temperature. Dimethylhydrazine (DMHy) is employed together with tertiarybutylarsine (TBAs) as nitrogen and arsenic precursors, respectively [7, 17] to replace those hydrides, due to their low decomposition temperatures. By using these precursors, T_g can be as low as $450\text{ }^{\circ}\text{C}$ for MOCVD. Another growth parameter is the reactor pressure. Depending on the pressure, a kinetically limited regime or selective epitaxy growth will occur. Furthermore, carbon contamination and the growth rate of the epilayer depend on reactor pressure [18]. Effects of reactor pressure on epitaxial lateral overgrowth have also been studied [19]. Despite all these studies, the effect of reactor pressure on nitrogen incorporation into GaAs has not been properly studied. Carrier gas as one of the growth parameters also affects nitrogen composition [7-8]. However, no study of nitrogen incorporation into GaAs with full nitrogen carrier gas instead of mixed nitrogen and hydrogen carrier gases [8] has been carried out. There is a potential of increasing nitrogen content [N] of GaAsN by using pure nitrogen carrier gas.

Although nitrogen incorporation is advantageous for energy band gap reduction in dilute III-V nitride semiconductor alloys, its effect on the optical properties of III-V-N semiconductor alloys cannot be ignored. The addition of nitrogen tends to degrade the optical quality of the III-V-N alloys. The degradation in the alloy's optical properties is due to non-radiative (NR) centers originating from defects which are introduced by the incorporation of nitrogen into the alloy during epitaxial growth. When the nitrogen concentration increases, luminescence of the alloys decrease. One way to improve the optical properties of the alloys is to anneal the samples. Rapid thermal annealing (RTA) can eliminate some of NR centers from the epitaxially grown materials [20-24] and improve the PL intensity of a band gap transition. However, the effect of annealing differs for different groups. One group reported a red shift [25] while another group reported a blue shift [26] of emission peaks after annealing. The reason behind these contradictions needs to be clarified.

Another way to improve emission intensity of III-V-N alloys is by capping of the sample before thermal annealing. Si_3N_4 [27-28] or SiO_2 [27] capping will hinder out-diffusion of As or N during thermal annealing. The effect of the capping on the improvement in III-V-N alloy's PL emission intensity is worth investigating.

Besides NR defects, nitrogen incorporated into III-V alloys introduces additional energy levels in the band gap resulting in emission wavelengths longer than those originating from the band-to-band transition of the alloy. For example in the GaAsN alloy, nitrogen bound states assigned as NN pairs (NN_i), cause additional lower energy peaks in the PL spectra [29-33]. A nitrogen atom in the

vicinity of another nitrogen atom will interact with each other to create an energy level within the energy band gap of GaAsN. The energy level of these N-bound states depends on the distance between nitrogen atoms. The nearest interacting N-N pair is called NN_1 and its energy level is the furthest from the conduction band minimum (CBM) [32]. Another cause of the additional emission peaks is defects in the GaAsN alloy. These defects include a gallium vacancy (V_{Ga}) [34] or an arsenic vacancy (V_{As}) [35] depending on the group V to group III molar ratio during growth. An arsenide antisite (As_{Ga}) [35], substitutional oxygen on the arsenide site (O_{As}) [35], or nitrogen clustering at the GaAs and GaAsN interface [10, 31] can be the causes of additional peaks due to growth conditions. Yet another cause for the additional peak in GaAsN can be isoelectronic traps [36]. The properties of these traps are similar to those of GaP, one of the dilute nitride III-V host alloys [36]. Another possible cause of defects related emissions from the GaAsN alloy is an interstitial defect [20, 37-39]. The N-As interstitial defect has been studied for MBE grown GaAsN [38]. The defect results in long tail emission from the energy band gap transition of a GaAsN epilayer with the energy level which is 0.1 eV below CBM. On the other hand, the N-N interstitial defect in GaAsN was theoretically predicted to reside at a larger energy below the CBM and was experimentally verified by the deep-level transient Fourier spectroscopy (DLTFS) [39]. It is interesting to note that a theoretical prediction shows that the defect can happen in the alloy only under certain growth conditions; i.e., an N-N interstitial may happen in a GaAsN epilayer grown by MOCVD with nitrogen carrier gas [39]. With so many causes of additional lower

energy peaks, one need to know the origin of these peaks so that PL intensity of the energy band gap (E_g) of GaAsN can be improved.

Due to the limitation in nitrogen solubility in GaAsN and thus, the emission wavelength will be restricted to less than 1500 nm, InGaAsN quaternary alloys emerge to stretch the emission wavelength further (>1500 nm). These alloys can be lattice matched to InP and also to GaAs. The wavelength of InGaAsN can be tuned to 1.3 or 1.55 μm for optical communication applications. A few percent nitrogen is sufficient to achieve the desired wavelength. Infrared emission of more than 2 μm can be achieved by increasing the indium content of InGaAsN alloys. However, the nitrogen content decreases with the indium content [40]. It is desirable to achieve a longer emission wavelength with high indium and nitrogen incorporation in InGaAsN alloys.

Figure 1.1 Ball and stick drawings of possibilities of nitrogen preferential bonding configurations

Nitrogen in InGaAsN has several preferential bonding possibilities with group III atoms: nitrogen fully bonds with either Ga or In, or it partially bonds with Ga and In as shown in Fig. 1.1. The nitrogen bonding configuration depends on the indium (or gallium) content and growth conditions of InGaAsN. In most cases, nitrogen prefers to bond with In, due to the lower bonding energy (1.93 eV) as compared to the bonding with Ga (2.24 eV) [41]. However, in the case of reducing local strain, nitrogen will prefer bonding to Ga [41-43]. Raman spectroscopy is utilized to study nitrogen preferential bonding. The optical longitudinal (LO) phonon modes of the Raman spectra of InGaAsN differ for In-N and Ga-N. InN has a LO phonon signal located at 558 cm^{-1} [44], while the GaN LO phonon signal lies at 741 cm^{-1} [42]. A study on preferential bonding will facilitate the determination of nitrogen and indium contents in InGaAsN.

InAs is another III-V material for infrared devices in the wavelength range from 1000 nm to 3000 nm. Dilute nitride InAs is able to extend the wavelength to mid-infrared (MIR) region [45-46]. Mid-infrared devices are useful for atmospheric pollution monitoring, leak detection, and laser surgery. However, nitrogen incorporation into InAs is more difficult than into GaAs. Only a few studies have succeeded to produce InAsN. As high as 18% nitrogen in MOCVD grown InAsN multi-quantum wells (MWQ) has been achieved [47] with PL emission at $6.5\text{ }\mu\text{m}$ and broad full width at half maximum (FWHM) of $3.5\text{ }\mu\text{m}$ at 39 K [48]. Growth of lattice-matched InAsN with 38%N on a GaAs substrate had been achieved by molecular beam epitaxy [6], although no PL has been reported. MOCVD growth of high nitrogen content in InAsN had a two-phase separation in the film: InAsN and InAs phases. The carrier gas used in this growth was

hydrogen. It is important to eliminate this phase separation to achieve high-quality InAsN layers. One possible way to prevent the phase separation is to change hydrogen carrier gas to nitrogen carrier gas because hydrogen carrier gas is more reactive than nitrogen carrier gas [49]. The quality of InAsN grown by MOCVD with nitrogen carrier gas has yet to be explored.

Theoretical studies have emerged to predict the behavior of InAsN alloys with different nitrogen compositions. The band gap energy of $\text{InAs}_{1-x}\text{N}_x$ has been studied by using the tight-binding and pseudopotential calculations [50-53], but the band-gap bowing parameter, c , appears to be largely different for each calculation. Yang *et al.* estimated a bowing parameter of 4.22 eV by using a tight binding calculation [51]. In the calculation, E_g of wurtzite InN of 1.8 eV was used instead of recently found E_g of InN of 0.78 eV [54-55]. Nakajima *et al.* estimated c to be approximately 1.6 eV from the pseudopotential method [53]. Although E_g of $\text{InAs}_{1-x}\text{N}_x$ obtained in their calculation & shows a decreasing value with increasing nitrogen composition in $\text{InAs}_{1-x}\text{N}_x$, their calculation of E_g of InN was found to be below 0 eV, which is not the value measured by experiments. Another computational method is needed to obtain more accurate E_g for InAsN.

1.2 Objectives

The objectives of my work are to study the nitrogen incorporation in (In, Ga), grown by metal organic chemical vapor deposition (MOCVD). They consist of several sections: (i) optimization of growth conditions to obtain a good (In, Ga)AsN epilayer quality with nitrogen content as high as possible, (ii) determination of the types of defects in as-grown GaAsN alloys, (iii) study of the

effects of MOCVD growth conditions, such as growth temperature, reactor pressure, group V to group III molar ratio and the type of carrier gas, on nitrogen as well as the defect incorporation into as-grown (In,Ga)AsN, (iv) improvement of optical quality of (In,Ga)AsN, (v) theoretical study of the band gap energy of InAsN with different nitrogen compositions to obtain a more accurate c , and (vi) incorporation of nitrogen into InAs.

1.3 Major Contributions of the Thesis

It has been found that nitrogen incorporation into GaAs-based alloys can be increased by using nitrogen rather than hydrogen as a carrier gas, reducing the reactor pressure down to 20 mbar, and keeping the group V to group III molar ratio at 15-20. The nitrogen incorporation can be increased by more than seven times when using these growth conditions.

The additional broad peak at $\sim 1.1 \mu\text{m}$ in the PL spectra of GaAsN has been identified as emission from nitrogen-nitrogen interstitials. It has a distinct PL peak with an energy of 0.2 eV below the band-to-band transition peak. This is the first observed PL emission from nitrogen-nitrogen interstitials.

An empirical equation to calculate the relative amount of nitrogen interstitials in the GaAsN epilayers has been derived. It is found that the calculated interstitials concentration is within 10% of the experimental values. The empirical equation encompasses five parameters used in GaAsN growth: the type of carrier gas used, growth temperature, reactor pressure, and the group V to group III molar ratio as well as the nitrogen to total group V molar ratio during MOCVD growth. The model provides a good prediction for growth conditions to

minimize the N-N interstitial incorporation for high-quality growth of a GaAsN epilayer grown with nitrogen carrier gas.

Strain in GaAsN with different nitrogen contents has been studied by Raman measurements. The study can be used to determine the nitrogen content in GaAsN, based on the measured GaAs-like LO or TO phonon shifts. For the InGaAsN epilayer, the Raman measurement reveals a preferable nitrogen bonding configuration for different indium compositions. InGaAsN with low indium and nitrogen contents, [In] and [N] prefers the In_3GaN configuration, while the InGa_3N configuration is found in InGaAsN with high [In] and [N].

Thermal annealing improves the optical properties of GaAsN. After RTA, PL intensity of the band-to-band transition peak of GaAsN improved the wavelength and was red-shifted relative to those of the as-grown samples. The PL red-shift after annealing is attributed to a change from nitrogen interstitials to substitutional nitrogen in GaAsN. The optimum annealing temperature is found to decrease with higher N composition. Capping the GaAsN epilayer with an oxide layer before annealing results in better optical performance than that of an uncapped case.

The calculated band gap energy of $\text{InAs}_{1-x}\text{N}_x$ with various mole fractions of N, x , have been found to be in reasonable agreement with experimental results. The theoretical band gap bowing parameter of $\text{InAs}_{1-x}\text{N}_x$ has been revised to 2.072 eV. This value is quite accurate; the energy band gaps of InN reported in the literature calculated by tight binding and pseudopotential methods were overestimated and underestimated, respectively, leading to an inaccurate values of the InAsN band gap bowing parameter.

MOCVD growths of InAsN have also been studied under different growth conditions. It has been found that the carrier gas plays an important role in MOCVD growth of InAsN. InAs and InAsN phase separation in InAsN has been avoided by growing an InAsN epilayer with the nitrogen carrier gas. Luminescence from an InAsN/InGaAs single quantum well (SQW) with nitrogen incorporation of 1.1% in the InAsN QWlayer has been achieved.

1.4 Organization of the Thesis

This thesis consists of seven chapters. Motivation, objectives, and major contributions of the thesis are presented in chapter 1. Chapter 2 provides an overview of III-V-N semiconductor alloys, MOCVD growth, and characterization techniques employed in this study, which include structural characterization by X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM), optical characterization by photoluminescence (PL), layer profile by secondary ion mass spectroscopy (SIMS), and surface profile by atomic force microscopy (AFM). Chapter 3 presents MOCVD growth of GaAsN. The nitrogen incorporation efficiency is studied with respect to the growth temperature, reactor pressure, nitrogen-to-group V molar flow rate, and group V-to-group III molar flow rate. Nitrogen-nitrogen interstitial defects in MOCVD grown GaAsN are studied in chapter 4. The number of nitrogen interstitials in GaAsN depends on MOCVD growth conditions. The optical property of GaAsN is reported in Chapter 5. Improvements in optical properties by thermal annealing are studied in this chapter. Chapter 6 focuses on the InAsN material both theoretically and experimentally. A new band gap bowing of InAsN has been determined from the

theoretical study. The MOCVD growth of InAsN with different carrier gases is studied. Chapter 7 summarizes the thesis with recommendations for future work.

Chapter 2

Background Information

2.1 Introduction

In this chapter, the background of III-V-N semiconductor alloys is presented. MOCVD growth is described. The characterization techniques employed are documented.

2.2 III-V-N Semiconductor Alloys

As described briefly in the previous chapter, a small amount of nitrogen incorporated into III-V semiconductors introduces a bowing effect on their energy band gap [1-11]. Fig. 2.1 shows the bowing effect of GaAsN and InAsN. The band gap of GaAsN can be lower than that of GaAs, due to its nitrogen-induced bowing effect. Fig. 2.1 also shows that GaAsN with 4% nitrogen has a band gap energy of 0.95 eV (~ 1300 nm emission wavelength). The band gap energy of $\text{GaAs}_{0.96}\text{N}_{0.04}$ is remarkably lower than that of GaAs (1.42 eV). However, nitrogen incorporation into GaAs is limited due to the nitrogen solubility in GaAsN. Furthermore, increasing nitrogen content in GaAsN will not cause its band gap energy to keep decreasing as shown in Fig. 2.1. Thus, the emission wavelength of this material is restricted to be shorter than 1500 nm. InGaAsN quaternary alloys emerge to stretch the emission wavelength further (>1500 nm). This alloy can be lattice-matched to InP and to GaAs (the shaded region of Fig. 2.1). The wavelength of InGaAsN can be tuned to 1.3 or 1.55 μm for optical

communication applications. A few percent of nitrogen is sufficient to achieve 1.55 μm . Infrared emission beyond 2 μm is achievable by increasing [In] or [N] in InGaAsN.

Figure 2.1 Band gap energy versus lattice constant for different compound semiconductors [56]. Dotted lines, dashed lines, and shaded region are the band gaps of InAsN, GaAsN, and InGaAsN, respectively.

Emission at $\lambda > 3 \mu\text{m}$ is in the mid-infrared region. Lasers operating at this wavelength have very important applications in areas such as atmospheric pollution monitoring, leak detection, drug detection, aid for the medical diagnosis of disease, and laser surgery [57]. One way to realize mid-infrared (MIR) lasers is to employ the principle of resonant tunneling and optical transitions between quantized conduction band states, or even valence band states (intraband transition) [57] in a low-dimensional structure such as quantum wells or

superlattices. Intersubband transitions take place between two electronic states in the conduction (valence) band [57]. This is the principle of a quantum cascade (QC) laser. An example of heterostructures of the QC lasers is an AlInAs/GaInAs superlattice [58]. Because the superlattice must be controlled precisely during layer growth, the fabrication is very difficult so that mass production of the devices may be quite limited.

Another approach to develop MIR lasers is to use III-V heterostructures that possess larger differences in band gap energies or band discontinuities allowing the formation of deep confining QW's (interband transition) [59]. One advantage of the III-V's is their compactness and size when compared to quantum cascade lasers. Examples of semiconductor MIR lasers are Sb-based active regions made of GaInAsSb/AlGaAsSb or GaInAsSb/GaSb quantum wells and InAs/GaInSb structures [59]. However, these MIR lasers suffer from a cryogenic effect; i.e., they require low chip temperatures to operate because of their small conduction band offsets (ΔE_c).

For a large band discontinuity, the active region must consist of semiconductors with small and large band gaps. InSb with the 0.12 eV energy band gap (as shown in Fig. 2.1) meets a criteria of the small band gap material. However, there is no suitable large band gap semiconductor alloy and no substrate with lattice constants close to that of InSb. InAsN ternaries, however, have small band gap energies (as shown in Fig. 2.1) and can be lattice-matched to GaAs or InP. The conduction band offset of InAsN with GaAs ($\Delta E_c \sim 1$ eV) and with InP ($\Delta E_c \sim 0.95$ eV) is larger than that of the GaInAsSb/AlGaAsSb structure (~ 0.3

eV) [60] or the InAs/GaInSb structure (~ 0.56 eV) [61]. Thus, InAsN is a promising material for MIR emitters and photo detectors.

2.3 Metalorganic Chemical Vapor Deposition (MOCVD)

Epitaxial growth techniques have been studied extensively for producing state-of-the-art materials, structures and devices. Molecular beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD) have emerged as the commonly used growth methods for high precision control of film thickness and abrupt interfaces. MOCVD can offer large scale, high growth rate, and high-quality wafers with good uniformity and reproducibility.

MOCVD comprises metalorganic (MO) sources used for chemical vapor deposition (CVD). MO refers to the precursor molecules and CVD is the process whereby the precursors react in the chamber and deposit a layer on the substrate surface. A simplified schematic design together with the reactions taking place inside the reactor during MOCVD growth is depicted in Fig. 2.2. Preceding the MOCVD growth, a substrate is placed on the susceptor. The gas used to carry the MO sources to the reactor chamber can be nitrogen, hydrogen, or mixture of these gases. Hydrogen carrier gas is purified by a Pd-cell to achieve parts per billion (ppb) impurity level. The growth reactor pressure is set in the range from 20 mbar to 1000 mbar (1 atmospheric pressure). The susceptor is heated by IR lamps to the growth temperature (T_g) which is set in the range of $450\text{ }^{\circ}\text{C} \leq T_g \leq 800\text{ }^{\circ}\text{C}$. Usually, the group V precursor is flowed into the reactor chamber when the susceptor temperature reaches $300\text{ }^{\circ}\text{C}$ to prevent out-diffusion of group V elements from the substrate. When the temperature in the reactor chamber has

reached a desired growth temperature, the MO sources are delivered to the chamber by the carrier gas to start layer growth. The IR lamps are turned off after layer growth and the susceptor undergoes cooling. The supplies of group III atom fluxes are stopped after layer growth, while the supplies of group V atom fluxes are continued until the susceptor temperature is cooled down to 300 °C. Then the reactor pressure is increased to atmospheric pressure. The substrate with the deposited layers can be taken out when it reaches room temperature and the reactor pressure reaches atmospheric value.

Figure 2.2 MOCVD simplified schematic layout and the reactions inside the reactor chamber during growth.

In the MOCVD system, the MO sources are placed in cooling baths with set temperatures. The cooling bath temperature is termed as a bubbler temperature and is set at a stable range between the melting and the boiling points. If a higher flow rate is required, its bubbler temperature is set at a higher temperature to maintain a higher vapor pressure. Likewise, for a lower flow rate the bubbler temperature is set at a lower temperature to reduce the precursor vapor pressure. The data on vapor pressure of several precursors are presented in Appendix A. The precursors used in our experiments are discussed in the section below.

Group III precursors

Trimethyl compounds (TMGa and TMIIn) are used as group III gallium and indium sources. The atomic structures of both compounds are $\text{Ga}(\text{CH}_3)_3$ and $\text{In}(\text{CH}_3)_3$. The boiling point of TMGa (TMIIn) is 55.8 °C (88 °C) [18]. The bubbler temperatures for TMGa and TMIIn are set at 3.6 °C and 17 °C, respectively. The Ga-CH₃ (or In-CH₃) bond is fairly weak, and thus the decomposition of the molecules can occur at low temperature (~ 480 °C for TMIIn and ~ 500 °C for TMGa).

Group V precursors

Tertiarybutyl compounds (TBAs and TBP) are used as group V arsenic and phosphorous sources to replace the hydrides such as arsine (AsH_3) and phosphine (PH_3). The boiling point of TBAs (TBP) is 65 °C (54 °C) [18]. TBAs ($\text{AsH}_2\text{C}(\text{CH}_3)_3$) and TBP ($\text{PH}_2\text{C}(\text{CH}_3)_3$) have bubbler temperatures kept at 10 °C. Arsine and phosphine not only have high decomposition temperature of more than 600 °C [62] and 850 °C [63], respectively, but also require safety monitoring and waste treatment due to high toxicity and high cost of storage. Due to the weak

bond between As (or P) with butyl components, the decomposition temperature of these TB- compounds is at a much lower temperature ($< 500\text{ }^{\circ}\text{C}$) than those of hydrides. For these reasons, TBAs and TBP are preferred over arsine and phosphine.

Asymmetrical dimethyldiazine (DMHy) replaces ammonia as the nitrogen source because of its low decomposition temperature. Ammonia normally requires high decomposition temperature ($> 530\text{ }^{\circ}\text{C}$) [9, 11] due to N-H bond being fairly strong (4.05 eV). With the use of hydrazine, the growth temperature can be decreased to around $500\text{ }^{\circ}\text{C}$. The bubbler temperature for DMHy $((\text{NH})_2(\text{CH}_3)_2)$ is kept at $15\text{ }^{\circ}\text{C}$.

An example of MOCVD growth is GaAs epilayer growth. In GaAs epilayer growth, TMGa and TBAs decompose at the growth temperature as follows.

AsH and AsH₃ from reaction (2.4) and (2.5) will decompose at the growth temperature to form As. Adsorption of Ga and As occurs followed by the diffusion of these atoms on the substrate surface to kink sites. GaAs layer is thus formed on the substrate surface. The excess of Ga or As atoms desorbed from the surface are carried away to the exhaust scrubber.

There are three regimes of the MOCVD growth process when growth temperature increases: kinetically limited growth, mass transport limited growth, and thermodynamics regimes, as shown in Fig 2.3. The thermodynamics regime occurs at high T_g , while the kinetically limited regime occurs at low T_g . In the thermodynamics regime, the growth rate decreases with increasing temperature. However, in the kinetically limited growth regime, the growth rate increases with T_g . In this regime, the reaction rate on the surface of the substrate limits the growth rate. On the other hand, in the mass transport limited regime, the growth rate is relatively independent of T_g ; i.e., the growth rate is proportional to the flow of incoming atoms irrespective of T_g . This last regime is the desired growth process in our MOCVD growth. To further limit the dependency of the growth rate on the incoming atom fluxes, the total group V to group III molar ratio is set larger than one ($\gg 1$) so that the growth rate is independent of group V species and only depends on group III incoming atoms.

Figure 2.3 Dependency of growth rate on growth temperature in the MOCVD process.

During our MOCVD process, growth temperature, reactor pressure, and group V to group III molar ratio need be considered properly. Growth temperature is important to obtain a good quality epilayer. Too high T_g may introduce more impurities, whereas too low T_g introduces defects in the epilayer. The reactor pressure ranges from 20 mbar to 100 mbar, depending on our growth process. Below 20 mbar reactor pressure is not possible due to the limitation of the system and above 100 mbar reactor pressure is not desirable due to a higher growth rate which degrades the epilayer quality. Besides limiting the growth rate to the group III incoming species, high V/III ratio ($\gg 1$) also reduces vacancies in the epilayer since the group V species are more volatile than group III species and thus easily undergo desorption from the surface of the substrate. It is found that GaAs growth with a high V/III ratio yields good surface morphology as compared to a low V/III ratio. In our case, a V/III ratio > 20 gives good surface morphology for III-V-N alloys.

2.4 Material Characterizations

Crystalline quality and structures, material compositions, and optical properties of this work are characterized by high-resolution X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM), photoluminescence (PL), and secondary ion mass spectroscopy (SIMS).

Principles and applications of the characterization techniques, such as XRD, Raman, TEM, PL, and SIMS will be introduced in this section. XRD, Raman, and PL are non-destructive methods to determine the alloy's lattice constant, phonon spectral information, spontaneous emission of the optically

excited semiconductor, respectively. The results are useful to infer the composition, layer thickness, lattice strain, structural disorder, bonding configuration, and energy transition of the semiconductor alloy. TEM and SIMS are destructive methods to study the thickness, crystalline quality, and material composition of the semiconductor alloy.

2.4.1 X-Ray Diffraction (XRD)

XRD is a non-destructive and useful technique to estimate lattice mismatch between two or more layers, composition of the materials, thickness of the layer, and lattice stress or strain. An XRD spectrum originates from the diffraction patterns of X-rays passing through a crystal. The principle behind this technique is Bragg's law, as shown in Fig. 2.4:

$$n\lambda = 2d \sin \theta, \quad (2.6)$$

where λ is the x-ray wavelength, normally Cu K α with $\lambda = 1.542 \text{ \AA}$; n is an integer multiple of λ ; d is the distance between two parallel planes; θ is the Bragg angle and also the angle of X-ray diffraction peaks.

Figure 2.4 X-ray passes through parallel planes with distance, d , and the diffracted angle θ .

In Bragg's law, the conditions of diffraction are met when the angle of incidence and the angle of diffraction are the same, causing the scattered X-rays to emerge in phase from the crystal.

Figure 2.5 Schematic diagram of Phillips MRD high resolution X-ray diffractometer.

The diagram of XRD is shown in Fig. 2.5. A $\text{Cu K}\alpha$ X-ray beam is passed through a 4-crystal monochromator to limit the angular and spectral divergence of the X-ray beam resulting in a monochromatic beam. The beam then strikes on the sample and the diffraction condition obeys Bragg's law. The diffracted beam is detected, and the computer processes the data. The output, called a rocking curve, is displayed in the computer screen. An example of the rocking curve of a GaAsN layer on a GaAs substrate is shown in Fig. 2.6. Interpretation of the rocking curve depends on the studied parameters, such as mismatch and thickness of the overlayer. Mismatch or composition of the layer is determined by the splitting distance between the layer and substrate peak. The layer thickness can be determined from the fringe period in an X-ray rocking curve.

Figure 2.6 X-Ray diffraction (004) measurement of a GaAsN epilayer on a GaAs substrate; the inset shows the structure of the sample.

For layers grown with different lattice constants, there would exist mismatch, dislocations, or relaxation. The diagram of mismatch is shown in Fig. 2.7. The lattice of Fig. 2.7 undergoes compressive strain after its deposition onto the substrate layer. This mismatch will cause an additional X-ray diffraction peak to be detected (Fig. 2.6).

To calculate amount of the mismatch between the epilayer and the substrate, equation (2.6) is differentiated with respect to θ .

$$\frac{d\lambda}{d\theta} = 2d \cos \theta \cdot \delta\theta + 2 \sin \theta \cdot \delta d \quad (2.7)$$

Since $\frac{d\lambda}{d\theta} = 0$ for a conditioned and monochromated X-ray beam, in (004)

reflection, equation (2.7) can be modified to

$$\frac{\delta d}{d} = -\cot \theta \cdot \delta \theta = \frac{\delta a}{a} = m^* \quad (2.8)$$

where $\delta \theta$ is the angle difference between the X-ray diffraction peaks of the layers,

$\frac{\delta a}{a}$ is the lattice mismatch between the epilayer and the substrate, and m^* is the

value of the experimental mismatch. The true mismatch is expressed as

$$m = \frac{a_L - a_S}{a_S} \quad (2.9)$$

The relationship between m and m^* is

$$m = m^* \frac{1 - \nu}{1 + \nu} \approx \frac{m^*}{2} \quad (2.10)$$

where ν is the Poisson's ratio and is approximately $\frac{1}{3}$ for GaAs or InP substrate

[64].

Figure 2.7 Diagram of a mismatched layer experiencing stress due to $a_L > a_S$.

Epilayer thickness, t , can be obtained by substituting d with t and θ with ϖ in equation (2.6). For example, using fringes n_1 and n_2 of Fig. 2.6, t can be calculated as follows.

$$t = \frac{(n_1 - n_2)\lambda}{2(\sin \varpi_1 - \sin \varpi_2)} \approx \frac{(n_1 - n_2)\lambda}{2\Delta\varpi \cos \varpi} \text{ where } \varpi = (\varpi_1 + \varpi_2)/2 \quad (2.11)$$

where n_1 and n_2 are the fringes positions, ϖ_1 and ϖ_2 are the θ scan in degrees of fringes 1 and 2.

Thus, Fig. 2.6 contains a few data that can be analyzed to get information about:

1. Lattice mismatch from the diffraction peak separation, $\delta\theta$, in degrees by using equation (2.8)
2. Epilayer lattice constant, a_L , when the substrate lattice constant, a_S , is known by using equation (2.9) and (2.10)
3. Composition (given by a mole fraction x) by utilizing Vegard's Law if the epilayer lattice constant is known on assumption that the lattice constant linearly depends on x .

$$a_L = a_{\text{GaAs}_{1-x}\text{N}_x} = (1-x)a_{\text{GaAs}} + x.a_{\text{GaN}} \quad (2.12)$$

where a_{GaAs} is the GaAs lattice constant (5.65 Å) and a_{GaN} is the GaN lattice constant (4.51 Å).

4. Thickness of the epilayer by the fringe separation calculation by using equation (2.11).

2.4.2 Raman Spectroscopy

Raman spectroscopy utilizes light interaction with the optical modes of atomic vibrations in the lattice. It is another nondestructive technique to study

vibrational, rotational, and other low-frequency modes in a material. It offers insight into the lattice properties of crystalline materials, such as lattice strain from the phonon frequency shift, structural disorder from the broadening of phonon frequency, and bonding configuration from the phonon frequency. In the ternary compounds, the phonon frequency is also a measure of the atomic components, and the intensity of that frequency is an indication of the atomic composition.

In Raman measurements, visible light from a monochromatic laser is incident onto the sample. The light is then scattered by atoms of the sample. If the light interacts with the sample to produce vibrational modes, the amount of scattered light is reduced corresponding to the energy of the vibrational transition. This is known as Raman scattering with phonon emission and absorption as the main elements. To indicate the direction of the incident and scattering light, a commonly used notation is employed. For example, to indicate the direction of the incident and scattering light in z direction and the incident and scattering polarization in x direction, the $z(x,x)\bar{z}$ notation is employed for the scattering geometry.

The schematic diagram of a micro Raman measurement in $z(x,x)\bar{z}$ geometry for GaAsN is shown in Fig. 2.8 (a), and its Raman spectra is shown in Fig. 2.8 (b). Raman signals have modes which are allowed or not allowed in the certain scattering geometry. For example, the GaAs-TO local mode is actually forbidden in Raman measurement of pure GaAs in the $z(x,x)\bar{z}$ direction but

allowed in the $z(x, y) \bar{z}$ direction. However in the GaAsN epilayer, the GaAs-TO mode appears because of nitrogen-induced disorder in the alloy.

Figure 2.8 (a) Schematic diagram of micro Raman measurement of GaAsN for $z(x, x) \bar{z}$ geometry and (b) Raman spectra of GaAsN epilayer.

The excitation source in this Raman study is the 514.5 nm line of a SPECTRA PHYSICS Ar^+ laser with the output power of 100 – 200 mW. The laser beam is focused onto the sample and the scattered light is collected normal to the sample surface and analyzed by the monochromator. The signal is picked up by using a high-light-throughput visible JY-T64000 triple spectrograph system equipped with LN_2 cooled CCD.

In the strain study of GaAsN on GaAs, strain can be inferred from the GaAs-LO mode shift from Raman spectra of a GaAsN epilayer on a GaAs substrate. The shift can be converted to the percentage of nitrogen incorporated into the GaAsN layer. The vibrational modes as well as their intensities in (In, Ga) AsN materials are useful for the bonding configuration as well as the alloys' composition. Later chapters provide further discussion in this field.

2.4.3 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) is a diffraction method used to study the thickness and the crystalline quality of III-V-N materials in this work. Electrons are diffracted through a prepared thin layer and then imaged in reciprocal space or converted into a real image. TEM resolution is in the scale of angstroms due to the short wavelength of electron.

TEM images are formed in two steps. The first step is the scattering of incident electron beam on a specimen forming the diffraction pattern of the scattered wave in the reciprocal space. The Fourier transform of the diffraction pattern constructs the image in the real space. The information obtained from an electron diffraction pattern includes unit-cell parameters, order-disorder recognition, and crystal symmetry. For example, the real space and the reciprocal space of a superlattice are shown in Fig. 2.9. The symmetry is preserved where the real space, a , becomes the reciprocal space, a^* , in a shorter distance. Distinct spots mean a good crystalline material, while a ring or a circle in the reciprocal space would mean that the alloy is polycrystalline. The brightest part in the reciprocal space is the center of the circle.

Figure 2.9 Superlattice representation in real and reciprocal space.

Two types of imaging for the diffraction pattern are bright field (BF) and dark field (DF) imaging. The bright field imaging excludes scattered electrons and makes use of transmitted ones to form the diffraction pattern. Thus, the regions of the specimen that are thicker or denser appear darker in BF image because these regions will scatter electrons more strongly. DF images are formed by using scattered electrons from the specimen. So the thicker regions will appear brighter due to strong electron scattering.

Sample preparation for TEM measurements is a tedious process and needs patience. The first step of the sample preparation involves sticking two pieces of the same materials together by using epoxy. The glued sample is then clamped and cured at 100 °C for 30-45 minutes. The temperature is low enough so that annealing of the sample is avoided. The edge of the sample is then polished manually to approximately 50 μm -thick by using 800, 1000, and 2400 grit SiC. Next, the sample is polished mechanically by using a dimpler down to 10-20 μm -in thickness. Finally, the sample is ion milled by using a Gatan Ar^+ ion miller until a tear is formed in the cross section of the epoxy. The operating voltage of the ion miller in our experiments is 5 V and 3.5 V at an incidence angle of 8° and 4°, respectively. The TEM is then performed using a Phillips CM300 field emission gun. The images in both dark and bright fields are obtained under two typical beam conditions in the $\langle 002 \rangle$ or $\langle 110 \rangle$ crystal axis.

2.4.4 Photoluminescence (PL)

Photoluminescence (PL) spectroscopy is a non-destructive technique used to determine spontaneous emission of the optically excited semiconductor. It is

used to determine the energy band gap of the III-V material and to decide upon the composition. In ternary materials, the composition can be determined from the energy peak of the PL spectra. For quaternary alloys, PL spectra and X-ray rocking curves are utilized to estimate their compositions. The excitation source in the PL measurement has a photon energy ($h\nu$) greater than the band gap energy (E_g) of the semiconductor. Electrons absorb the photon energy, $h\nu$, and are excited above the band gap energy of the semiconductor. After a certain time, the electrons relax to the conduction band minimum (CBM), while emitting phonons or transferring the excess energy to neighboring atoms. When an electron and a hole recombine, a photon with energy of about E_g is emitted. The principle of PL is shown in Fig. 2.10.

Figure 2.10 Systematic diagram of PL's principle.

Fig. 2.10 shows an ideal case where the carriers involved are electrons and holes only. For doped semiconductors, trap electrons (donors) and trap holes (acceptors) dominate the energy transition process. The energy levels of these

traps are in the energy band gap. Another energy transition involves impurities or defects with their energy levels within E_g or sometimes above the CBM. For example, in the ultra dilute nitrogen regime for III-V-N materials, the isolated nitrogen level is 180 meV above the CBM [30, 65-67]. The PL method can be used to study the origin of the energy transition of the alloy.

The PL measurement is usually performed at low temperature (4 K to 77 K) because the PL spectra will be narrow in full width at half maximum (FWHM) and high in the PL intensity. Low-temperature PL spectra exhibit more detailed peaks and, thus, contain more information about the energy transitions. Excitonic transitions are only observed at low-temperature PL since excitons and their complexes are not stable at high temperature, due to their small localization energy. At higher temperatures, some peaks are not present due to enhanced phonon scattering and non-radiative recombinations.

The PL peak wavelength depends on the PL measurement temperature of the alloy. Lower temperature will cause the peak wavelength a blue shift as the bulk band gap energy, $E_g(T)$, increases at low temperature (Varshni equation):

$$E_g(T) = E(0) - \frac{\alpha T^2}{(\beta + T)} \quad (2.13)$$

$E_g(T)$ is the band gap energy at temperature T , $E(0)$ is the band gap energy at 0 K, T is the temperature in Kelvin, and α and β are empirical constants [68].

A simplified schematic diagram of the PL set-up in this research is presented in Fig. 2.11. The samples are mounted inside a He-cryostat. The cryostat is then cooled down to 20-30 K for low-temperature PL measurement. A laser beam from an Ar^+ ion laser emitting at a wavelength of 488 nm or 514.5 nm

and with a maximum beam power of 120 mW is mechanically chopped before it is incident on the sample. The chopper modulates the laser signal and provides a reference frequency signal for phase sensitive detection with a lock-in amplifier. The luminescence signal from the sample is passed through the monochromator to be dispersed by an optical grating and detected by an electrically cooled InGaAs (800 – 1700 nm) or PbS (800 – 3000 nm) or a liquid nitrogen-cooled Ge (700 – 1400 nm) photo-detector. The lock-in amplifier amplifies the detected signal which is processed by a computer. The results are then displayed on the computer screen. The PL at 4 K is also carried out to freeze out the traps and study the intrinsic property of the bulk semiconductor. A liquid nitrogen-cooled Ge (700 – 1400 nm) detector was utilized in this system.

Figure 2.11 A simplified schematic diagram of PL set-up.

2.4.5 Secondary Ion Mass Spectroscopy (SIMS)

SIMS is used for characterization of atomic or molecular components of semiconductor alloys. It is a destructive technique used to estimate the composition of the sample by sputtering a selected surface area. Ionized secondary particles from the sample are analyzed by using a mass spectrometer. A

schematic diagram of SIMS is presented in Fig. 2.12. A beam of 1 to 20 keV primary ions sputters the sample's surface area. Since our samples are GaAsN, InGaAsN, and InAsN alloys, the primary ion beam used is 3 keV Cs^+ rather than a Ga^+ because of higher sensitivity to nitrogen element. The ionized secondary particles sputtered off of the sample are collected by the extractor and selectively channeled according to their masses to the detector. The detector detects the presence of the particles and the results are then displayed on a computer screen as an element spectrum.

Figure 2.12 Schematic diagram of secondary mass ion spectroscopy set up.

Thickness of the epilayer can also be determined by SIMS. In the case of our GaAsN epilayer on GaAs, the sputtering process is terminated when the nitrogen signal drops abruptly. The sample is then taken out and measured by a surface profiler to determine the depth of the crater thus formed. The epilayer thickness deduced from a depth measurement is confirmed with measurement obtained by TEM observation. This sputtering technique is a simple and effective

method to approximately determine the epilayer thickness. A sample of this measurement is shown in Fig. 2.13.

Figure 2.13 An example to determine the epilayer thickness by SIMS.

2.5 Summary

In this chapter, the importance of III-V-N semiconductor alloys is discussed. The band gap energies of III-V-N materials are much reduced from the band gap energies of the same binary III-V alloys. Nitrogen incorporation into InAs can extend its emission wavelength to the mid-infrared (MIR) region, which is very useful for atmospheric pollution monitoring, leak detection, laser surgery, and other MIR applications. One of the epitaxial growth techniques for III-V-N semiconductor alloys is metalorganic chemical vapor deposition (MOCVD).

After the growth, III-V-N alloys are subjected to several characterization techniques, such as high resolution X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM), photoluminescence (PL), and secondary ion mass spectroscopy (SIMS), to study their material compositions, optical and electrical properties, as well as the quality and structures. XRD is used to estimate lattice mismatch between two or more layers, composition of the material,

thickness of the layer, and layer's stress or strain. Raman spectroscopy offers insight on the lattice properties of crystalline materials, such as lattice strain from the phonon frequency shift, structural disorder from the broadening of phonon frequency, and bonding configuration from the phonon frequency. TEM is a diffraction method used to study the thickness and crystalline quality of the grown III-V-N materials in this work. PL is employed to determine spontaneous emission of the optically excited semiconductor. The band gap energy of the III-V materials and also the material composition can be found by this method. Atomic or molecular components of the semiconductor alloys are characterized by SIMS.

Chapter 3

Growth and Nitrogen Incorporation of (In)GaAsN

3.1 Introduction

Nitrogen incorporation into III-V alloys reduces their energy band gaps, due to a nitrogen bowing effect. [1-11]. Band gap energies of the III-V-N's are much reduced from the band gap energies of their III-V alloys. However, the nitrogen content inside the epilayers is limited to less than 10% for $\text{GaAs}_{1-x}\text{N}_x$ grown by MOCVD as well as by molecular beam epitaxy (MBE) [12, 15-16]. Alloying more than 3% nitrogen with InGaAs with more than 20% indium is also difficult. The challenge is to increase the nitrogen content of the epitaxial (In)GaAsN alloys.

This chapter describes the growth of GaAsN and InGaAsN by MOCVD. The main goal is to grow (In)GaAsN and study nitrogen incorporation into it during MOCVD and focus on the relationship between the MOCVD growth conditions and the nitrogen contents of the alloys. Effects of nitrogen incorporation on the roughness of the surface of the growing layer and the growth rate are investigated too.

The nitrogen incorporation is studied by X-ray Diffraction (XRD) in the [004] direction. The GaAsN epilayer is tensile-strained when grown on the GaAs substrate, but the InGaAsN epilayer is compressively strained on InP or GaAs substrates in this study. Both photoluminescence (PL) and XRD measurements are employed to determine the nitrogen and indium concentrations in InGaAsN.

3.2 MOCVD Growth of GaAsN and InGaAsN

Growth of GaAsN starts with the optimization of MOCVD growth conditions. It is carried out to obtain a good GaAsN epilayer quality with the nitrogen content as high as possible. Two main growth parameters in this procedure are growth temperature and reactor pressure. Then the effect of these parameters to the growth rate of GaAsN and InGaAsN is investigated so that the accurate growth rate of (In,Ga)AsN can be determined for low-dimensional layer growth.

The GaAsN and InGaAsN epilayers were deposited onto GaAs (001) and InP (001) substrates, respectively. Indium, gallium, arsenic, and nitrogen precursors are trimethylindium (TMIn), trimethylgallium (TMGa), tertiarybutylarsine (TBAs), and asymmetrical dimethylhydrazine (DMHy), respectively. For optimization of the growth temperature and reactor pressure, the GaAsN samples are grown with different growth temperatures and reactor pressures while the other parameters are kept fixed by setting the TMGa flow at around 20 $\mu\text{mol/min}$, the group V to group III molar ratio at around 20, and DMHy to a (DMHy + TBAs) molar ratio at around 0.5. Purified nitrogen gas is used as a carrier gas. GaAsN (InGaAsN) epilayers are grown on the GaAs (InP) buffer for 40 minutes. Before the buffer layer growth, annealing takes place on the GaAs (InP) substrate for 10 minutes at 680 °C. The TBAs source flows into the reactor chamber when the substrate temperature reaches 300 °C to protect the substrate surface. The growth temperature and reactor pressure are then adjusted to the designated values for the optimization of the epilayer quality.

3.2.1 Growth temperature and reactor pressure optimization

Table 3.1 shows some details of growth temperature and reactor pressure of five samples. The other growth parameters have been mentioned in the earlier section. Three growth temperatures and three reactor pressures are set for the GaAsN growth.

Table 3.1 GaAsN epilayers grown with varied growth temperatures and reactor pressures.

Sample	Growth temperature (°C)	Reactor pressure (mbar)
S1	520	100
S2	550	100
S3	580	100
S4	550	20
S5	550	60

All the surfaces of as-grown GaAsN epilayers are mirror-like. XRD and PL measurements are employed to determine the epilayer quality. In the XRD measurement, abrupt interfaces between the epilayer and the buffer layer of GaAsN / GaAs can be deduced from the appearance of fringes in their X-ray rocking curves. Figure 3.1 shows the X-ray diffraction peaks of the sample S1 to sample S5. S4 has an abrupt interface and good crystalline quality as deduced from its fringes as compared to those of S1, S2, S3, and S5. Another indication of a good epilayer quality can be seen in the PL spectra of GaAsN.

Figure 3.1 X-ray diffraction peaks of the GaAsN epilayers with fringes and without fringes to show the epilayer quality. Only S4 has fringes in its X-ray rocking curve indicative of a high-quality result.

Optical properties of S1 to S5 are characterized by low-temperature PL. The measurement is made at low temperature to minimize the effects of scattering and lattice vibrations which can cause a reduction in PL intensity of GaAsN. Fig. 3.2 (a) shows PL intensity of S1 to S5 as a function of growth temperature or reactor pressure. PL intensity decreases with increasing temperature; above 100 K the intensity is very weak. There is also another peak at a longer wavelength, due to crystalline defects which will be elaborated in the next chapter.

In the samples grown at varied temperatures, while other growth conditions are kept constant (S1 to S3), PL intensity of sample S2 prepared at 550 °C is the highest. Low growth temperature (S1) causes less decomposition of the precursors, resulting in incomplete distribution of the group III or group V

atoms in the epilayer formation [69]. This incomplete distribution leads to the creation of vacancy defects in the epilayer. Likewise, high growth temperature (S3) causes the epilayer quality to degrade, due to an increase in group V atoms desorption from the surface [18].

Figure 3.2 (a) 4K PL intensity of S1 to S5 with their respective growth temperature or reactor pressure; (b) PL spectra of S1 to S5.

At growth temperature 550 °C, for the group grown with varied reactor pressures (S2, S4, and S5), sample S4 deposited at the lowest pressure of 20 mbar exhibits the highest PL intensity. This is because a high reactor pressure (>20 mbar) introduces more defects into the epilayer [18] due to site competition, which will lead to nitrogen interstitials. Furthermore, S4 has the highest nitrogen content (0.6% as seen in the X-ray diffraction peak shift, Fig. 3.1) when compared to that of S2 and S5 (0.47 – 0.48%). S1 and S3 have $x = 0.42\%$ and $x = 0.45\%$.

S2 exhibits the highest PL intensity among the samples prepared at the elevated reactor pressure of 100 mbar, but does not reach the same level as that of

S4 prepared at 20 mbar. We conclude, therefore, about the closely optimal growth temperature and reactor pressure are 550 °C and 20 mbar, which yield the highest nitrogen content and the highest PL intensity.

3.2.2 Effect of growth temperature, reactor pressure, and TMGa flow rate on the growth rate of GaAsN and InGaAsN

The growth rate of the epilayer is deduced from the thickness and growth time of an epilayer. Layer thickness is measured by SIMS and verified by cross-sectional TEM. The determination of layer thickness by SIMS has been explained in chapter 2, section 2.4.5. The growth time for all GaAsN samples is fixed to be 40 minutes. The growth rate is found to differ for the GaAsN epilayers when grown at various growth temperatures and reactor pressures with a fixed 20 $\mu\text{mol/min}$ TMGa flow rate. In such a case, the growth process is not group III mass transport limited and thus the growth rate is not fully determined by the group III flow rate. Fig. 3.3 plots the GaAsN layer thickness of S1 to S5 against growth temperature and reactor pressure. The inset shows the depth, x , of the crater formed in the epilayer.

Figure 3.3 GaAsN epilayer thickness against growth temperature and reactor pressure. The inset shows the depth, x , of the crater formed by SIMS sputtering. Inset2: TEM micrographs of GaAsN epilayers grown at the reactor pressure of 20 and 100 mbar.

The growth rate increases with the reactor pressure and growth temperature while other growth conditions, such as TMGa flow, V/III molar ratio, and DMHy/V molar ratio, are kept constant. High growth temperature causes a high decomposition rate of the precursors leading to the higher growth rate. As previously explained in chapter 2, when the reactor pressure affects the growth rate, the process is not diffusion limited anymore. Higher reactor pressure causes more MO molecules to impinge on the surface, resulting in a higher formation rate of the III-V-N's [18], and giving rise to a higher growth rate. It is found that the reactor pressure of 100 mbar yields a growth rate that is almost two and half times faster than that obtained at the reactor pressure of 20 mbar.

The next set of experiments is designed to study the effect of InGaAsN growth rate as a function of TMGa/(TMGa+TMIn) flow rate. The Ga/III molar ratio was reduced from 0.35 to 0.12. The TMIn flow rate is fixed at 20 $\mu\text{mol/min}$. T_g and P are set at 630 $^{\circ}\text{C}$ and 100 mbar, respectively. To keep nitrogen composition in the solid constant, the ratio of DMHy/(DMHy + TBAs) is therefore kept at 0.6. The group V to group III (V/III) molar ratio determines the quality of the film. Referring to the previous growth results, the best epilayer quality is obtained for a group V/III ratio range of 15-22. We therefore set this ratio at 21. The InGaAsN samples grown for this study are presented in Table 3.2.

Table 3.2 InGaAsN samples with various Ga/III molar ratios.

Sample no.	T_g : 630 $^{\circ}\text{C}$, P : 100 mbar, V/III ratio: 21			
	TMIn: 20 $\mu\text{mol/min}$		DMHy/(DMHy+TBAs): 0.6	
	TMGa ($\mu\text{mol/min}$)	Ga/III ratio	DMHy ($\mu\text{mol/min}$)	TBAs ($\mu\text{mol/min}$)
IS1	10.87	0.352	387.6	258.3
IS2	8.154	0.290	348.8	232.5
IS3	7.067	0.261	338.6	227.2
IS4	5.436	0.214	303.2	219.1
IS5	4.349	0.179	298.1	200.6
IS6	2.718	0.120	290.8	196.0

Decreasing the Ga/III molar ratio while keeping TMIn flow constant results in a higher indium composition in InGaAsN. This will yield higher compressive strain and degradation in epilayer quality. Only IS1 experiences tensile strain. Fig. 3.4 shows XRD rocking curve of InGaAsN with increasing In content.

Figure 3.4 XRD profiles of the InGaAsN epilayer grown with different Ga/III molar ratio while other growth conditions are kept constant.

The two furthest InGaAsN XRD profiles in Fig. 3.4 are from samples IS5 and IS6 grown with the Ga/III molar ratio less than 0.2. Increasing the In content means increasing the lattice constant of InGaAsN; i.e., increasing lattice mismatch between InGaAsN and InP. Large lattice mismatch causes lattice relaxation, misfit dislocations, and compositional fluctuations which lead to degradation in epilayer quality, as revealed by the broadening of the InGaAsN XRD profiles.

The growth rate of InGaAsN on InP *versus* Ga/III molar ratio is displayed in Fig. 3.5.

Figure 3.5 Growth rate (reflected in epilayer thickness) of InGaAsN epilayer on InP substrate to the Ga/III molar ratio.

The growth rate decreases when the Ga/III molar ratio decreases from 0.35 to 0.22. Reducing the Ga/III molar ratio further causes an increase in growth rate. This may be due to phosphorous (P) diffusion from the InP buffer layer into the InGaAsN epilayer. This behavior is observed from SIMS measurments for the samples having the Ga/III molar ratio less than 0.2 (Fig. 3.6). For sample, for IS3 with the Ga/III molar ratio of 0.261, no phosphorous is detected in InGaAsN.

The driving force for phosphorus diffusion is due to increasing strain in the samples with the Ga/III molar ratio <0.2. As more In atoms are incorporated into the lattice, mismatch between InGaAsN and InP increases. By having a low Ga content, high compressive strain is generated in the epilayer, which in turn creates deformation dislocations, and P diffuses into the epilayer *via* these dislocations.

Figure 3.6 SIMS profile of the phosphorous diffusion into the InGaAsN epilayer for Ga/III molar ratio of 0.18 (solid lines) and Ga/III molar ratio of 0.26 (dashed lines).

Fig. 3.7 shows a TEM image of dislocations taken from the cross section of an InGaAsN epilayer with the Ga/III molar ratio of 0.18 grown on InP. The epilayer has many dislocations, due to high compressive strain.

Figure 3.7 TEM image of dislocations taken from the cross section of InGaAsN epilayer grown on InP with Ga/III molar ratio of 0.12.

The simplified lattice structure of high-indium InGaAsN with an occurrence of P diffusion is presented in Fig. 3.8. Because of P diffusion, In and Ga not only can bond with As and N, but also with P. This results in a higher growth rate of InGaAsN(P).

Figure 3.8 Periodical lattice of a high indium content InGaAsN epilayer with occurrence of phosphorus diffusion (dotted line).

The above results show that for a good InGaAsN epilayer, P diffusion should be prevented. Since P diffusion occurs when strain in the epilayer is high, one way to solve this is to incorporate more nitrogen into the epilayer or to reduce indium content in the epilayer. Both directions are advantageous. Increasing nitrogen content into the epilayer can push the emission wavelength towards long region which is advantageous for infrared applications. Decreasing indium content in the epilayer can result in 1.3 μm or 1.55 μm emission which is useful for telecommunication applications. In this set of samples, good quality of epilayer can be obtained with Ga/III ratio of 0.26 and DMHy/(DMHy+TBAs) ratio of 0.6.

3.3 Effect of MOCVD growth conditions to the nitrogen incorporation

In this section, we investigate the relationship of MOCVD growth conditions, i.e., growth temperature, reactor pressure, V/III molar ratio, DMHy/(DMHy+TBAs) molar ratio, and the carrier gas used in the MOCVD growth on the nitrogen content of the alloys. The aim is to increase nitrogen incorporation into GaAsN and at the same time, to achieve a GaAsN epilayer of good quality.

For this study, one growth parameter is varied while other parameters are kept fixed. The N content in GaAsN is determined by XRD measurements. The N content can also be deduced from PL measurements. For the InGaAsN alloys, XRD and PL together are employed to determine the N and In mole fractions.

3.3.1 Growth temperature and reactor pressure on N incorporation

Samples for this study are presented in Table 3.1. The TMGa flow and V/III molar ratio are set at around 20 $\mu\text{mol/min}$ and 20, respectively. The DMHy/(DMHy+TBAs) molar ratio is 0.5. Fig. 3.9 shows the effect of growth temperature or reactor pressure on nitrogen composition.

Figure 3.9 Nitrogen composition of S1 to S5 to respective growth temperature or reactor pressure.

For the group of samples grown at the same growth temperature of 550 °C, the sample grown at the reactor pressure of 20 mbar (S4) has the highest nitrogen content. Each nitrogen and arsenic has the same kinetic energy. Due to the difference in atomic masses of nitrogen and arsenic [70], nitrogen has a higher velocity than arsenic and thus, nitrogen can reach the growing surface faster. The reactor pressure affects the amount of nitrogen and arsenic supplied in the reactor [18]. A low reactor pressure causes the number of nitrogen and arsenic to decrease. This results in an increasing mean free path for nitrogen and arsenic atoms. Since nitrogen has a higher velocity, it can be incorporated faster than arsenic, resulting in higher nitrogen incorporation at reactor pressure of 20 mbar. The increase of the nitrogen content is almost 30% in S4 as compared to that of S2 and S5.

For the group grown at the same reactor pressure of 100 mbar, the sample grown at 550 °C (S2) gives the highest nitrogen content. However, this group of samples has less variation in N content as compared to the 550 °C growth temperature group. The 100-mbar reactor pressure causes a decrease in mean free path, due to a higher number of nitrogen and arsenic atoms. Although the kinetic energy increases with growth temperature, incorporation of nitrogen into GaAsN does not vary significantly, due to large scattering occurred in the reactor. Less N content at low growth temperature is due to less decomposition of the nitrogen precursor (DMHy) yielding less N incorporation. At high growth temperature, carbon incorporation decreases the incorporation of nitrogen [71-72] and, thus, leads to less nitrogen content in the grown GaAsN alloys.

It can be concluded that growth temperature at 550 °C and reactor pressure at 20 mbar are the suitable growth parameters for GaAsN giving rise to good epilayer quality of GaAsN and the highest N incorporation.

3.3.2 DMHy to (DMHy + TBAs) and carrier gas on N incorporation

As explained in chapter 2, carrier gas has a significant role in increasing the nitrogen content. Miyamoto *et al.* [7] have grown GaAsN under hydrogen carrier gas, while Auvray *et al.* [49] have carried out the growth under mixed nitrogen and hydrogen carrier gas of 4 to 1. The growth temperatures of both studies are 570 °C and 530 °C, respectively. Fig. 3.10 plots the nitrogen composition of GaAsN epilayers *versus* DMHy to total group V molar ratio (DMHy/(DMHy + TBAs) molar ratio) for different carrier gases and reactor pressures from our MOCVD growths and the data taken from Refs. 7 and 49.

Growth temperature is 550 °C and TMGa flow is around 20 $\mu\text{mol/min}$. Our samples are plotted in squares, while Miyamoto's and Auvray's are in circles and triangles, respectively.

The relationship between the N incorporation and DMHy/TBAs is a positive linear relationship as shown in Fig. 3.10 (b); i.e., higher DMHy/TBAs implies a higher N content in GaAsN because a higher DMHy/TBAs molar ratio means more nitrogen atoms arriving at the sample surface to react with Ga.

Figure 3.10 (a) Nitrogen composition (%) in GaAsN epilayers versus DMHy/(DMHy+TBAs) molar ratio for different reactor pressure and carrier gas; our samples are shown in squares; (b) Our data replotted %N in GaAsN epilayers grown with nitrogen carrier gas versus DMHy/TBAs molar ratio for reactor pressures 20 and 100 mbar.

The effect of the carrier gas on nitrogen incorporation into GaAsN is clearly seen in Fig. 3.10 (a). Miyamoto's samples grown with hydrogen carrier gas and Auvray's samples grown with mixed hydrogen – nitrogen carrier gas

show a similar trend with regard to nitrogen incorporation *versus* DMHy/(DMHy+TBAs) molar ratio. But the nitrogen incorporation is 20% less in Miyamoto's, due to the usage of pure hydrogen carrier gas [7]. Nitrogen is an inert gas, so it does not react with the active nitrogen atom from DMHy. On the other hand, hydrogen can possibly cause a reaction with active nitrogen to form ammonia or related components [49]. The effect of the carrier gas on nitrogen incorporation is more significant than the effect of the reactor pressure. Therefore, the higher nitrogen content in Auvray's samples compared to that of Miyamoto's is, in principle, due to the effect of carrier gas used. Our GaAsN epilayer grown with hydrogen carrier gas has almost three times less nitrogen relative to the epilayer prepared with nitrogen carrier gas, other conditions being the same.

Figure 3.10 (a) also shows that by increasing the DMHy/(DMHy+TBAs) molar ratio, the reactor pressure strongly affects nitrogen incorporation. The nitrogen incorporation is 30% higher when the GaAsN epilayer is grown at 20 mbar as compared to that grown at 100 mbar with all the other growth conditions kept the same. In conclusion, from our study, the highest nitrogen incorporation is achieved when the samples are grown with pure nitrogen carrier gas at a reactor pressure of 20 mbar.

3.3.3 *Effect of group V to group III molar ratio on N incorporation*

The effect of total group V (DMHy + TBAs) to group III (TMGa) (V/III) molar ratio during MOCVD growth on nitrogen incorporation in GaAsN is also studied. The V/III ratio is varied by changing the DMHy and TBAs molar flow, while keeping the DMHy/(DMHy+TBAs) molar ratio constant, other growth

conditions being the same. The amount of vapor phase nitrogen (DMHy) that can be incorporated as solid nitrogen (nitrogen content) in GaAsN is termed as a nitrogen incorporation efficiency. The incorporation efficiency (η) of nitrogen is

$$\eta = \frac{x_N / x_{As}}{DMHy / TBAs} \quad (3.1)$$

where x_N and x_{As} are the nitrogen and arsenic contents in GaAsN, respectively.

Nitrogen content in GaAsN increases as the V/III molar ratio decreases, see Fig. 3.11 (a). This is due to less scattering during growth with the lower V/III molar ratio. A lower V/III molar ratio means a smaller number of nitrogen and arsenic atoms, increasing the mean free path. Nitrogen can be incorporated faster into the growing surface because its velocity is higher than that of arsenic. Furthermore, due to its volatility, arsenic atoms desorb away from the surface faster than nitrogen atoms, resulting in more As vacancies which are filled in by nitrogen atoms [18, 70, 73].

Figure 3.11 Study of (a) V/III molar ratio to nitrogen content in GaAsN epilayers and (b) Nitrogen incorporation efficiency to V/III ratio and DMHy/TBAs ratio.

Increasing the DMHy/TBAs ratio increases the nitrogen content [N] in GaAsN. Fig. 3.11 (b) shows the nitrogen incorporation efficiency to the V/III ratio for different DMHy/TBAs ratios. η has a linear relationship with the V/III ratio meaning that a lower V/III ratio leads to a higher nitrogen incorporation efficiency. However, more supply of nitrogen in the vapor phase (DMHy), i.e., higher DMHy/TBAs, leads to lower, η . This is because additional nitrogen introduces higher lattice mismatch between GaAsN and GaAs. Each percent of nitrogen incorporated into GaAsN causes 0.2% lattice strain [74]. This amount is large enough to hinder incorporation of nitrogen. The more nitrogen atoms are incorporated into GaAsN, the smaller becomes the lattice constant of the epilayer causing higher mismatch with GaAs. For strained GaAsN on the GaAs layer, more energy is required to overcome the strain energy. Thus, this strain energy impedes the incoming nitrogen atoms to be incorporated into the epilayer leading to less nitrogen in the solid phase [69].

3.4 Effect of N content on surface roughness and growth rate

Surface quality of the material is important when one needs to design a multilayer structure to prevent accumulated defects or dislocations. Since nitrogen degrades the optical quality of the material, it is expected that nitrogen incorporation will affect the material's surface roughness. The growth rate of an alloy is normally assumed to be constant for a certain flow rate of group III precursors because growth occurs within the diffusion limited regime. However, the growth rate is influenced by the nitrogen content.

Surface roughness of GaAsN deposited with different nitrogen contents is investigated by atomic force microscopy (AFM). Useful parameters measured by AFM are the maximum roughness and the root mean square (RMS) of the surface across the measured area. The maximum roughness is measured from the maximum height of the “hills” to the minimum depth of the “valleys”. RMS is an average of “hills” and “valleys” across the intended surface area.

Root mean square (RMS) roughness of GaAsN increases with increasing nitrogen composition. Fig. 3.12 shows AFM micrographs of GaAsN with 0.6% N with an area of investigation of $3 \times 3 \mu\text{m}^2$. The RMS roughness is determined to be less than 0.3 nm, an indication of smooth surface, for the GaAsN samples grown at reactor pressure of 20 mbar. The nitrogen content of these samples is less than 1.1%. This knowledge can be useful when heterostructure devices are to be grown with GaAsN as an active layer, where good interfacial structures are required for good device performance features.

Figure 3.12 AFM micrographs of GaAsN with 0.6% N with area of investigation of $3 \times 3 \mu\text{m}^2$.

Fig 3.13 shows the trend of RMS roughness of the grown GaAsN epilayers with their nitrogen contents. Roughness of the epilayer increases with

[N], as lattice mismatch between GaAsN to GaAs increases. RMS roughness of our GaAsN with 1% N is less than 0.3 nm. Surface morphology of MOCVD-grown GaAsN alloys has been reported [9, 11]. Their surface roughness for a similar nitrogen content was reported to be more than 0.6 nm. The differences are in the the type of carrier gas and nitrogen precursor used during the growth. Nonetheless, the type of precursor used for generating nitrogen has been shown to exhibit less significant impact on surface roughness [75]. Thus, it is obvious that the nitrogen carrier gas plays a leading role in improving the material's surface quality because it is not reactive with the epilayer surface during MOCVD growth.

Figure 3.13 Plot of AFM root-mean-square roughness to nitrogen content of GaAsN alloys.

GaAsN epilayers grown with different nitrogen contents have different growth rates. Growth conditions are kept fixed at certain values, except for the DMHy/TBAs molar ratio. Fig. 3.14 plots GaAsN epilayer thickness against nitrogen composition. The growth time (t_g) was fixed at 40 minutes for every growth.

The growth rate decreases with increasing [N]. However, for samples (sample A and B) grown at 100 mbar with nitrogen composition > 2%, the growth rate is saturated. The same growth rate trend applies to the samples grown at 20 mbar. At 20 mbar, the growth rate saturates for nitrogen > 1%. The trend can be explained as follows. For low-nitrogen-GaAsN, lattice strain remains small at the beginning of growth for GaAsN on GaAs. The incoming nitrogen can occupy group V sites faster. When the nitrogen content is high, strain becomes large [42]. The incoming nitrogen is more difficult to be incorporated into GaAs. The time required to form an atomic layer of high N content of GaAsN is longer than that required for low-N-content-GaAsN, leading to a slower GaAsN growth rate.

Figure 3.14 GaAsN epilayer thickness against nitrogen composition.

3.5 Summary

Nitrogen incorporation in GaAsN and InGaAsN epilayers has been studied under different MOCVD growth conditions. GaAsN samples have been

characterized by XRD at (004) rocking curves to determine x in $\text{GaAs}_{1-x}\text{N}_x$. In the case of InGaAsN , XRD and PL are employed to determine the $[\text{N}]$ and $[\text{In}]$ of the quaternary alloy.

The optimized growth temperature and reactor pressure for GaAsN have been concluded by studying the PL intensity of samples S1 to S5. 550 °C and 20 mbar are closely optimized growth temperature and reactor pressure for GaAsN . The growth rate of GaAsN increases with growth temperature and reactor pressure.

Nitrogen incorporation increases with reactor pressure of 20 mbar, growth temperature of 550 °C, low V/III molar ratio, and using nitrogen as carrier gas. The use of nitrogen carrier gas triples nitrogen incorporation into GaAsN compared to the case of hydrogen carrier gas. The reactor pressure of 20 mbar doubles nitrogen incorporation when compared to the reactor pressure of 100 mbar. The V/III molar ratio chosen to be 15 – 20 also increase nitrogen incorporation into GaAsN . However, the efficiency of nitrogen incorporation decreases with increasing DMHy flow, due to larger strain incorporated for higher nitrogen content in the GaAsN epilayer.

Surface morphology and growth rate with increasing N content in GaAsN have been studied. The GaAsN epilayers with higher $[\text{N}]$ have rougher surfaces but still within a permissible value ($< 0.3\text{nm}$) for $[\text{N}] < 1.1\%$. The use of nitrogen carrier gas reduces surface RMS roughness. The growth rate decreases with higher $[\text{N}]$.

Chapter 4

Nitrogen Interstitials in GaAsN

4.1 Introduction

Although the energy band gap of III-V-N semiconductors can be reduced by alloying nitrogen with the III-IV's [76-81], nitrogen tends to degrade the optical quality of the sample. Degradation in optical properties is mainly due to non-radiative (NR) centers generated by incorporation of nitrogen into the alloy. These NR centers have been studied in details and are attributed to different defects generated during growth. This degradation in optical properties is sometimes followed by an appearance of additional emission peaks [10, 29-35, 37-38, 82-84], other than band-to-band transitions.

Efforts have been made to explain the nature of the additional peaks. Nitrogen bound states, assigned as NN pairs (NN_i), are one of the causes of the additional low energy peaks in PL [29-33]. A nitrogen atom in the vicinity of another nitrogen will interact with each other to create an additional energy level within the energy band gap. This energy level depends on the distance between the nitrogen atoms. The nearest nitrogen pair is assigned as NN_1 , where $i = 1$. In PL, these NN_i pairs create sharp peaks with closely separated energy lines and are less than 0.15 eV below the conduction band minimum (CBM) of GaAsN. Other defects in GaAsN cause additional peaks. These include a gallium vacancy (V_{Ga}) [34] or an arsenide vacancy (V_{As}) [35] that depend on the group V to group III molar flow rate ratio during growth. Arsenide antisite (As_{Ga}) [35], substitutional

oxygen on arsenide site [35], or nitrogen clustering at the GaAs and GaAsN interface [10, 31] are other causes for additional peaks. These are also interstitial defects: N-As or N-N interstitials [20, 37-39, 83, 85-86]. The N-As interstitials have been studied in MBE grown GaAsN [38]. They result in long-tail emission at 0.1 eV below CBM. This result is supported by a nuclear reaction analysis [86] which reveals that while the concentration of nitrogen interstitials remains nearly constant, the amount of substitutional nitrogen increases linearly across the studied regime. The N-N interstitial defects have also been studied theoretically [37, 39, 82, 84] and experimentally [20, 39]. The theory shows that the N-N interstitials are only generated in GaAsN under certain growth conditions [37], when GaAsN is grown by MOCVD with nitrogen as a carrier gas [86]. This interstitial was predicted to reside at a larger energy below CBM and was experimentally verified by the deep level transient Fourier spectroscopy (DLTFS) [39]. However, no PL spectra have been reported on N-N interstitials.

A further study regarding how the growth temperature, reactor pressure, or other parameters affect the number of nitrogen interstitials in GaAsN is required to reduce these defects.

In this chapter, N-N interstitials of MOCVD grown GaAsN are studied. The PL study reveals that the interstitials' energy level exists as a deep level in the GaAsN energy band gap. The interstitial PL signal is more obvious in GaAsN grown by nitrogen carrier gas than that grown by hydrogen carrier gas. The secondary ion mass spectroscopy (SIMS) and X-ray diffraction (XRD) measurements have provided a ground to predict which growth conditions cause more nitrogen interstitials. Some details are presented here.

4.2 Nitrogen-Nitrogen (N-N) pairs interstitials

In a tetrahedral structure of III-V semiconductor alloys, there are group III and group V sites. Gallium occupies group III site and arsenic or nitrogen randomly occupies the group V site. A nitrogen interstitial occurs when nitrogen attached itself to the occupied group V site as shown in Fig. 4.1.

Figure 4.1 Ball and stick drawings of atomic structure of (a) N-As and (b) N-N interstitial

When the group V site has been occupied by arsenic, the nitrogen attachment process is called a N-As interstitial. In the N-N interstitial, nitrogen attached itself to another nitrogen atom on the group V site. The N-N interstitial in GaAsN is at a deeper energy level than the N-As interstitial [37] as shown in Fig. 4.2. The nature of this interstitials is in the form of N-N, occupying group V sites with the energy level below CBM. This N-N interstitial is of interest, due to a contradiction in theoretical studies of its energy position in the GaAsN band gap. One group [37] assigned the N-N interstitial level as 0.66 eV below CBM, while

another group [82] estimated it to reside 0.03 eV below CBM. There is no experimental report of the effect of the nitrogen content of GaAsN on the N-N interstitial energy levels. Furthermore, no PL study of the N-N interstitial has been published as far as we are aware.

Figure 4.2 A simple diagram of the energy level of N-N interstitial and N-As interstitial in GaAsN band gap.

MOCVD growth of the GaAsN epilayers has been described in section 3.2. For this study, growth temperature of GaAsN is set at 550 °C. The DMHy/(DMHy + TBAs) ratio is varied from 0.5 to 0.87 for different N compositions. [N] of GaAsN is found to be in the range 0.3% to 3% by X-Ray diffraction (XRD) measurements at (0 0 4) Bragg reflection. The Raman spectroscopy shows that GaAsN is strained [74].

The PL spectra of 0.7%, 0.8%, and 0.95% [N] samples are presented in Fig. 4.3 (a). The samples are used as representatives of GaAsN exhibiting a two-peak behavior. The band-to-band transition peak (assigned as P1) is at a high photon energy. The additional peak (P2) is broad and large in its integrated intensity. All the GaAsN samples grown under pure nitrogen carrier gas, which give PL emission, have nitrogen content less than 3% and they always show the two peaks P1 and P2 at 20 K. No PL emission is observed for GaAsN with [N] > 3%.

Figure 4.3 (a) 20K-PL spectra of as-grown sample GaAsN with 0.7%, 0.8% and 0.95% N; (b) GaAsN with 0.95% N annealed at 675 °C.

To investigate the effect of annealing on P1 and P2, thermal annealing is conducted on the sample with 0.95% [N] at temperatures varying from 625 °C to 775 °C for 60 seconds under nitrogen ambient. The GaAsN sample is covered with GaAs wafers to prevent out-diffusion of As during annealing. The P1 intensity increases upon annealing, due to the removal of non-radiative recombination centers (Fig. 4.3 (b)). PL intensity of P2 upon annealing at 675 °C decreases tremendously. P2 is assigned as a defect-related peak because of this

behavior. The band-to-band transition has a long tail observed after annealing at 675 °C. A detailed explanation will be presented shortly.

The energy difference between P1 and P2 for the three studied samples is within 0.20 – 0.23 eV. P2 originates from defects but due to its deep energy emission only two origins are possible. Emission may originate from nitrogen clusters at the interface between the GaAs buffer and GaAsN epilayer. Nitrogen clustering at the interface is known to have PL emission at energy lower than that of the band gap (0.15-0.25 eV below CBM), due to the higher nitrogen content in the thin clustering layer [10, 31]. Fig. 4.4 shows a TEM cross sectional image of a sample with 0.7 % N. The cross section of this sample is to check evidence for clustering or the presence of defects in the epilayers. The circled area at the interface between the GaAs buffer and GaAsN epilayer is enlarged and presented in the inset of Fig. 4.4. No nitrogen-rich clustering is observed at the GaAs/GaAsN interface.

Figure 4.4 Cross sectional TEM image of 0.7% N sample. The circled area at the interface between GaAs buffer and GaAs epilayer does not show any nitrogen-rich cluster (inset).

Another possible cause of this emission is the presence of an N interstitial in GaAsN since a theoretical prediction shows that this defect could occur in GaAsN [37, 39, 82, 84]. An observed trap with the energy of 0.25 eV below conduction band ($E_c - 0.25$ eV) has been measured by DLTS and is assigned to an N-N interstitial [39]. The N-As interstitials are located at about 0.1 eV below CBM [83]. P2 of our GaAsN sample occurs at 0.20 – 0.23 eV lower than P1. Hence, P2 could have arisen from recombination at the N-N interstitials.

The formation of N-N interstitials is thought to be supported by several MOCVD growth factors: the use of DMHy as nitrogen precursor and nitrogen gas as a carrier gas. DMHy contains two nitrogen atoms, two molecules of methyl (CH_3) and two hydrogen atoms (see chapter 2). Upon heating, DMHy will decompose into two radicals: NH_2 and $\text{N}(\text{CH}_3)_2$. Since the N-C bond in $\text{N}(\text{CH}_3)_2$ does not cleave easily [87], only NH_2 can contribute to nitrogen incorporation. Each of these radicals undergoes multiple collisions with the surrounding inert nitrogen carrier gas causing N-C and N-H bonds to break. Reaction (4.1) probably happens to form the N-N dimer.

*H and *CH_3 are radical products that may react with other radicals. During growth the probability that an N-N dimer arriving at the lattice site to form an interstitial is high. Some of the NH_2 molecules survive and arrive at the lattice site to form substitutional N. It is different in the case of hydrogen carrier gas because

hydrogen is more reactive than N. Both of the radicals have a high probability to react with hydrogen due to high hydrogen concentration [88]. Ammonia and amine, products of reaction (4.2) and (4.3), are stable at 550 °C [89]. Only NH_2 has a greater possibility to react with the surface to occupy the lattice site as substitutional nitrogen.

Furthermore, due to the miscibility of N, As, and Ga, the energy formation of N-N is lower than single substitutional N. Despite that, the N-N interstitial is not observed in MBE-grown GaAsN. This may be due to the nitrogen source used in MBE where nitrogen molecules are pre-cracked in the cell to form nitrogen monomers. Because the N-N interstitial consists of two nitrogen atoms, a SIMS measurement will indicate a higher [N] than that deduced from XRD measurement.

SIMS measurements are made to determine the amount of nitrogen in the GaAsN epilayers. A Cs^+ beam is used for sample surface sputtering. The effective primary ion energy is 3 keV. The rastered region is 150 μm and the secondary ions are collected from the sputtered area of 100 μm . A standard sample is used to calibrate the nitrogen composition.

Fig. 4.4 shows the nitrogen content of GaAsN measured by XRD, x_{XRD} , versus that determined by using SIMS, x_{SIMS} . The nitrogen count is first calibrated using a standard sample which has known nitrogen composition and nitrogen count measured by XRD and SIMS, respectively. x_{SIMS} is determined from the relative sensitivity factor (RSF) obtained from the calibrated sample and from the ratio between nitrogen and gallium counts of the samples [90].

$$\text{RSF} = X \times \frac{C_{\text{Ga}}}{C_{\text{N}}} \quad (4.4)$$

$$x_{SIMS} = RSF \times \frac{c_N}{c_{Ga}} \quad (4.5)$$

where X is the nitrogen content of the standard sample, C_{Ga} and C_N are gallium and nitrogen counts from the standard sample, respectively, and c_{Ga} and c_N are gallium and nitrogen counts from the measured sample, respectively. x_{XRD} is determined by Vegard's law from GaAsN lattice constant for a strained layer.

Fig. 4.5 shows the nitrogen contents estimated by using SIMS, x_{SIMS} , and XRD, x_{XRD} . The dotted line for $x_{XRD} = x_{SIMS}$ is drawn. The nitrogen contents estimated by using SIMS are larger than those estimated by using XRD. Samples with higher nitrogen content cause larger difference in $(x_{SIMS} - x_{XRD})$. This difference means that excess nitrogen atoms detected by SIMS do not only come from N_{As} but also from nitrogen bonded in other way beside N_{As} , such as $(N-N)_{As}$. The N-N interstitial is another form of nitrogen bonding which causes excess nitrogen atoms to be measured by SIMS. Coupled with the fact that P2 emission comes from a deep level below CBM, and further evidence by DLTS [39], the P2 PL peak is likely to originate from emission of the N-N interstitial.

Figure 4.5 Nitrogen composition measured from XRD (x_{XRD}) Vs nitrogen composition measured from SIMS (x_{SIMS}) of samples with different growth conditions. The dotted line is when $x_{XRD} = x_{SIMS}$.

The form of interstitials may change when subjected to non-equilibrium conditions, such as thermal annealing [85]. Step-by-step increase in temperature during thermal annealing can reveal a change from N-N interstitials to N-As interstitials. At high-temperature annealing, the N interstitial is changed to an N substitutional. Annealing also improves band-to-band transitions, due to the removal of non-radiative centers.

Figure 4.6 20K-PL spectra of sample GaAsN with 0.7 %N at annealing temperatures of 625, 675, 725, and 775 °C. Inset: Gaussian approximation of sample annealed at 725 °C

Fig. 4.6 shows the PL spectra of the as-grown and annealed GaAsN samples with 0.7% N. With the annealing temperature being increased, the intensity of P1 emission increases while that of the P2 emission decreases. After annealed at 625 °C, two peaks – P1 and P2 – are clearly seen. The focus here is on the P2 energy shift after annealing (P1 energy shift will be discussed in the next chapter). There is a lower energy tail emission at annealing temperature, T_{ann} , 675 °C. Using Gaussian approximation, P1 and its lower energy tail, assigned as P2' (clearly shown in the inset), can be distinguished. The energy difference between P2 emission peak and P2' emission peak is 140 meV. P2' emission peak corresponds to the transition of the N-As interstitial which resides at the energy level ~ 0.1 eV below the CBM. Thermal annealing causes some N-N interstitial

bonds to break and form N_{As} or N-As interstitial. P2' represents an N-As interstitial which resides at a smaller energy level (~ 0.1 eV) below CBM. Because growth temperature is 550 °C, annealing below 600 °C does not yield significant changes in PL peak behavior of GaAsN. Annealing at $T_{ann} \geq 675$ °C causes the amount of nitrogen interstitials to decrease and results in decrease in the P2' PL intensity.

4.3 Nitrogen interstitials calculation

The relationship between nitrogen interstitials and growth conditions is analyzed to obtain a minimum number of nitrogen interstitials. The amount of nitrogen interstitials depends on growth conditions. The amount of interstitials (N_i) in the vicinity of total nitrogen in GaAsN can be generalized as follows.

$$N_i = G_T + R_P + V_{III} + N_V + C \quad (4.6)$$

N_i is the percentage of nitrogen interstitials, G_T is a nitrogen interstitial influenced by growth temperature, R_P is the reactor pressure, V_{III} is the group V to group III molar ratio, N_V is nitrogen to the total group V molar ratio, while C is a constant. Although G_T , R_P , V_{III} , N_V , and C seem a lone standing for each growth condition, they are actually influenced by one another. To avoid dealing with a complicated relationship, each component is first treated as an isolated case to study the trend of N_i with one varied growth condition at a time.

The amount of nitrogen interstitials in GaAsN is the difference between %N deduced by SIMS (x_{SIMS}) and XRD (x_{XRD}) measurements. Thus, the %N interstitial is defined as.

$$\%N \text{ interstitial} = \frac{x_{SIMS} - x_{XRD}}{x_{XRD}} \times 100 \quad (4.7)$$

Fig. 4.7 shows the percentage of nitrogen interstitials *versus* growth temperature and reactor pressure. Nitrogen interstitials increase linearly with growth temperature, as the other growth parameters are kept unchanged, as shown in Fig. 4.7 (a). The range of growth temperature (T_g) in this study is from 520 °C to 580 °C. Further lowering or increasing T_g will cause the epilayer quality of GaAsN alloys to degrade. Nitrogen interstitials affected by growth temperature (G_T) is

$$G_T = aT_g + b \quad (4.8)$$

The variable $a = 0.51085$, b is a constant which will be combined to form C , and T_g is the growth temperature. a is positive because N_i increases with T_g .

As T_g increases, the decomposition rates of nitrogen and arsenic precursors increase because both precursors start to decompose at 450 °C. In other words, there will be more arsenic and nitrogen in the surroundings. However, a gallium decomposition rate is rather constant at this growth temperature variation [18]. With increasing growth temperature, the kinetic energies of N and As atoms also increase, causing N to move faster than As, due to their different atomic masses. The N atom will collide with other N atom and form N-N before attaching itself to the group V sites.

(a)

(b)

Figure 4.7 Percentage nitrogen interstitial versus growth temperature (a) and reactor pressure (b).

Fig. 4.7 (b) shows that the reactor pressure affects nitrogen interstitials at least in a second-order polynomial term while other growth conditions are fixed. The range of reactor pressure in the study is from 20 to 100 mbar. As explained in chapter 3, the reactor pressure determines the amount of N and As radicals in the reactor. Higher reactor pressure causes higher amount of radicals. The N atom

will have more collisions, such as with another N atom to form N-N, in the reactor chamber before attaching itself to the group V sites. Thus, there are more N-N interstitials incorporated into GaAsN when the reactor pressure is higher. From Fig. 4.7 (b), the reactor pressure is presumed to affect the amount of nitrogen interstitials quadratically. The nitrogen interstitials influenced by the change in reactor pressure (R_p) is

$$R_p = hP^2 + kP + l \tag{4.9}$$

By fitting the curve from Fig. 4.7 (b), we attain $h = 0.00266$ and $k = 0.05869$, where P is the reactor pressure. The constant l is part of C of equation (4.6).

The effect of T_g and P on nitrogen interstitials is a straightforward relationship depicted from the graph. However, the amount of nitrogen interstitials *versus* V/III molar ratio and N/V molar ratio is more complex because the V/III and N/V molar ratios affect each other subtly. Table 4.1 presents the percentage of nitrogen interstitials (N_i) in the GaAsN samples *versus* varied V/III molar ratio as well as N/V molar ratio.

Table 4.1 Percentage of nitrogen interstitials versus different V/III and N/V molar ratios with $T = 550\text{ }^{\circ}\text{C}$.

Sample	V/III	N/V	P (mbar)	N_i (%)
S6	15.2	0.625	20	8.04
S7	23.8	0.625	20	6.76
S8	35.6	0.625	20	52.96
S9	44.6	0.8	100	57.08
S10	44.6	0.867	100	55.97
S11	22.3	0.867	100	7.50

From S6 to S8, the only varied parameter is the V/III molar ratio. It can be concluded from the minimum amount of nitrogen interstitials in sample S7, that the relationship of N_i and V/III molar ratio is quadratic. N_i is also sensitive to the V/III molar ratio, as shown in samples S10 and S11. The relationship between N_i and the N/V molar ratio is roughly linear. Thus the total effects of the V/III and N/V molar ratios on nitrogen interstitials are summarized as follows.

$$V_{III} + N_V = pv^2 + qv + yn + z + E \quad (4.10)$$

Here, v is the V/III molar ratio, n is the N/V molar ratio, z is a constant (part of C), and E is an equation combining v and n . To find the values of p , q , and y , initial values of p , q , and y are first defined. The second order dependency of N_i to V/III, p , is first set to 0.5 based on samples S6 and S7. The value of q is first set to -10 to reduce the strong effect of V/III on N_i (see S7 and S8). Based on S9 and S10, the dependency of N_i to N/V is almost 1 and thus, y is initially set to be 1. The preliminary calculated result, based on these initial parameters (p , q , and y) and the experimental one, has a discrepancy of $> 10\%$. Then based on the Levenberg-Marquardt chi-square minimization of the non-linear squares fitter (NLSF), the next parameters are set to minimize the discrepancy. After several iterations, the final values are $p = 0.19714$, $q = -7.82033$, and $y = -16.27$ for equation (4.10). The calculated interstitial, based on these values, is the best fit with the experimental result, N_i . The parameters will again be adjusted after the formation of E . The implication of p and q is that the V/III molar ratio has stronger influence on the amount of nitrogen interstitials when this ratio is larger than 20. This is obvious from samples S9 and S10.

As mentioned earlier, N_i is more sensitive to the change in V/III molar ratio than to the change in N/V molar ratio. Equation E needs to encompass the sensitivity factor for these two growth conditions.

$$E = i \left(\frac{dv^j}{n^s} \right) \quad (4.11)$$

The values of j and s are first set at 1 and 2, respectively. s is set to 2 because the decrease in nitrogen interstitials is less significant when $n \geq 0.6$. After first setting $i = 1$ and $d = 5$, the calculated results from equation (4.10) are compared to the experimental results. The obtained error is re-evaluated by chi-square minimization, and d, i, j, p, q, s , and y are adjusted for smaller errors. The newly obtained d, i, j, p, q, s , and y are then fitted into the equation. The steps are iterated until the error is less than 10%. It was found that the initial values of $j_1 = 1$ and $s_1 = 2$ have been adjusted to higher order to $j_2 = 2$ and $s_2 = 8$ to minimize the error. This means that high n will not decrease the amount of nitrogen interstitials in the vicinity of high v , *i.e.* As-rich [85]. The amount of nitrogen interstitials will still increase considerably as shown in samples S6 and S10. Thus equation (4.10) is modified to be

$$V_{III} + N_V = 0.122v^2 - 6v - 120n + 0.0039 \left(\frac{(v-15)^2}{n^8} \right) \quad (4.12)$$

Finally, the carrier gas also affects the incorporation of N_i . Nitrogen as the carrier gas is known to increase the nitrogen incorporation efficiency [49]. Hydrogen as the carrier gas is more likely to react with free radical nitrogen in the chamber to form NH_x , thus decreasing nitrogen incorporation. On the other hand, this characteristic of hydrogen carrier gas also reduces the amount of nitrogen

interstitials. The final equation for N_i consists of each component of growth conditions.

$$N_i = (0.51805T_g - 0.05869P + 0.00266P^2 - 6v + 0.122v^2 - 120n + 0.0039(\frac{(v-15)^2}{n^8}) - 137)G \quad (4.13)$$

N_i is the percentage of additional nitrogen (nitrogen interstitial) with respect to [N] of the strained GaAsN epilayer measured by XRD; v is the group V to group III molar ratio; n is the nitrogen to total group V molar ratio; and G is the variable for the carrier gas. The value of G depends on the carrier gas used during MOCVD.

Table 4.2 Percentage of nitrogen interstitials versus different carrier gas used during the growth for samples with similar nitrogen composition.

Sample	carrier gas	N_i (%)
S12	nitrogen	62.33
S13	full hydrogen	10.3
S14	mixed nitrogen and hydrogen	16.9

The value of G for full nitrogen carrier gas is our reference and is set to be unity. Table 4.2 shows a comparison nitrogen interstitials for samples grown with different carrier gas. All three samples had similar nitrogen content. For pure hydrogen carrier gas, N_i can be reduced by six times (as shown in S12 and S13) and therefore G for pure hydrogen gas is set to be 0.164. G for nitrogen mixed with hydrogen carrier gas with ratio 1 : 1 is set as 0.273 (sample S12 and S14) because hydrogen is more reactive than nitrogen [49] and comparing the experimental N_i of pure nitrogen and pure hydrogen.

Equation (4.13) has been applied to every GaAsN as-grown samples with errors less than 10%. Fig. 4.8 shows the experimental and calculated %N interstitial (N_i) versus V/III molar ratio.

Figure 4.8 Experimental and calculated %N interstitial against V/III molar ratio. Errors are within 10% as shown by error bars.

The error bars are for errors within 10%. Each calculated N_i is obtained by substituting the growth conditions for each sample in the equation (4.13). The calculated N_i is then plotted against varied V/III molar ratio. The experimental N_i of GaAsN is obtained by calculating the $(x_{SIMS} - x_{XRD})/x_{XRD}$. To plot the experimental and calculated N_i versus other growth conditions, the similar method is utilized. The errors between the experimental and calculated interstitials are within a 10% range.

Equation (4.13) can be used to reduce the amount of nitrogen interstitials in as-grown GaAsN by adjusting growth conditions accordingly. For example, to

grow a good GaAsN epilayer, the V/III molar ratio should be >10 , $T \approx 550$ °C, and $P \approx 20$ mbar. In this case, equation (4.13) becomes:

$$N_i = (283.86 - 6v + 0.122v^2 - 120n + 0.0039(\frac{(v-15)^{1.8}}{n^8}) - 137)G \quad (4.14)$$

To minimize N_i , v should be as close to 15 as possible, n should be as high as possible, and hydrogen should be used as the carrier gas. Samples S6, S7, and S11 grown with nitrogen carrier gas have N_i of 8.04%, 6.76%, and 7.5%. When these samples are grown with hydrogen as the carrier gas, their N_i are predicted to be less than 1.5%. Thus, it is possible to grow the GaAsN alloy with low N_i . MOCVD growth conditions can be set to minimize N_i by utilizing equation (4.13).

4.4 Summary

Optical emission of GaAsN epilayers reveals two distinct PL peaks. The first peak P1 at higher energy is attributable to the band-to-band transitions. The other emission peak P2 at a lower energy has higher integrated intensity and broader FWHM than those of band-to-band emission. P2 identified as N-N interstitials in GaAsN. This N-N interstitial defect is deduced from its energy position with respect to CBM in GaAsN epilayers and from the increase in N content measured by SIMS as compared to XRD. Annealing shows a step-by-step change in this interstitial defect.

An empirical equation to calculate the number of nitrogen interstitials with respect to the MOCVD growth conditions of GaAsN has been derived. From the equation, the amount of nitrogen interstitials has higher dependency on the reactor pressure, V/III molar ratio, and N/V molar ratio. It is found that reducing the reactor pressure and the V/III molar ratio together with increasing the N/V molar

ratio decrease the incorporation of N interstitials significantly. The model can be utilized to minimize N-N interstitial incorporation in GaAsN by adjusting certain growth parameters.

Chapter 5

Optical properties of GaAsN and InGaAsN

5.1 Introduction

Though the addition of nitrogen is advantageous for energy band gap reduction of the alloy, nitrogen is also known to degrade the optical properties of III-V-N materials. The band gap of GaAs reduces by ~ 100 meV with every percent of N incorporated in it [77-81]. Thus, emission from the $\text{GaAs}_{1-x}\text{N}_x$ ternary alloy covers the spectral range from near infrared ~ 1300 nm for $x=0.045$ [13] to ultraviolet ~ 350 nm for GaN. Adding indium in GaAsN lowers the energy band gap. The InGaAsN quaternary alloy can be lattice-matched to InP, and the emission wavelength of the alloy can be tuned to 1.3 or 1.55 μm for optical communications.

Degradation in optical properties of GaAsN or InGaAsN is due to the appearance of non-radiative (NR) centers that originate from defects introduced by incorporation of nitrogen into the alloys. When the nitrogen concentration increases, luminescence of the alloys becomes worse. One way to improve the optical properties is to anneal the samples. Rapid thermal annealing (RTA) can eliminate the NR centers [20-24] and improve PL intensity of the radiative band gap transitions. However, the effect of annealing differs from one work to another. One group reported a red shift [25] while the other group reported a blue shift [26] in emission after annealing. The reason behind these contradictions needs to be clarified.

Another way to improve light emission from the III-V-N alloys is to cap the sample prior to annealing. Si_3N_4 [27-28] or SiO_2 [27] capping will assist out-

diffusion of defects during thermal annealing. The effect of capping on PL emission of the III-V-N alloy is studied in this chapter.

Lattice strain in GaAsN on GaAs is investigated by Raman measurements. The GaAs-like LO phonon shift of GaAsN Raman spectra determines whether the grown epilayer is strained or relaxed. When there is larger strain in the epilayer, i.e., larger lattice mismatch, the GaAs-like LO phonon shift will be larger.

In the InGaAsN alloys, Raman measurements are utilized to study nitrogen preferential bonding. The incorporated nitrogen has preferential bonding either to Ga or In. In most cases, nitrogen prefers to bond with In, due to its lower bonding energy (1.93 eV) [41] as compared to Ga (2.24 eV) [41]. However, in the case of reducing local strain, nitrogen will prefer to bond with Ga [41]. InN has a LO phonon located at 558 cm^{-1} [44], while the GaN LO phonon signal lies at 470 cm^{-1} [41].

This chapter will focus on the energy band gaps of GaAsN and high indium content InGaAsN alloys *versus* their nitrogen composition, strain in the GaAsN epilayer, nitrogen preferential bonding in InGaAsN, the effect of thermal annealing, and the effect of capping used during annealing on the GaAsN optical properties.

5.2 The effect of nitrogen content in (In)GaAsN alloy

Nitrogen in (In)GaAsN causes a reduction in band gap energy. Studies of the band gap energy are usually carried out by PL measurements. If the amount of nitrogen incorporated into the alloy increases, the PL peak energy red shifts. Besides the band gap energy, information of the activation energy (E_a) can be

obtained by temperature-dependent PL studies. The activation energy is related to the impurity binding energy or the carrier/exciton localization energy [91-92] as well as compositional fluctuations [93]. In this study, E_a will be used to determine qualitatively the impurity as well as the compositional fluctuations in GaAsN alloys.

Due to the small atomic size of nitrogen, the lattice constant of (In)GaAsN decreases when [N] increases. Hence, the GaAsN epilayer on GaAs experiences strain. If strain is too large, GaAsN may relax back to its original lattice constant. This relaxation causes deformation in the epilayer and degrades quality. When GaAsN is not lattice strained; i.e., relaxed, there will be broken or missing lattices in GaAsN. A Raman measurement is a simple method to study strain in the epilayer. A strain study is important to determine the maximum nitrogen content in GaAsN allowed to maintain its strained structure. In addition to the strain study, the Raman measurement enables investigations of elemental bonding in InGaAsN. This measurement can determine the preferential bonding of nitrogen. It is useful for composition estimation, especially in quaternary alloys [41, 94-95], based on Raman intensity and local optical modes TO and LO.

5.2.1 GaAsN and InGaAsN band-to-band energy with nitrogen

Fig. 5.1 shows 4K-PL spectra of as-grown GaAsN samples with different nitrogen compositions. PL measurements are done at 4 K to minimize the effect of scattering and lattice vibrations which would reduce PL intensity. Two peaks in PL from the as-grown GaAsN samples are observed. P1 is related to the band gap transitions in the GaAsN epilayer and can be fitted with a GaAsN band-gap anti-

crossing (BAC) model [96]. P2 is due to interstitial defects, as discussed in the previous chapter. As [N] increases, P1 shifts to longer wavelengths, due to the band gap bowing introduced by nitrogen.

Figure 5.1 4K-PL spectra of as-grown samples with different nitrogen composition. Inset: P1 peaks shift with nitrogen composition.

Fig. 5.2 shows the relationship between P1 and P2 *versus* [N]. P2 also red-shifts, as nitrogen composition increases, which implies that P2 is related to nitrogen incorporation. The low-temperature band gap energy of P1 can be expressed as:

$$E_g(\text{GaAs}_{1-x}\text{N}_x) = a + bx + cx^2 \text{ (eV)} \quad (5.1)$$

After fitting equation (5.1) to the experimental data of P1 in Fig. 5.2, the calculated values are $a = 1.459$, $b = -0.193$ and $c = 0.0257$. The GaAs band gap measured at low temperature is the variable a , and bowing parameter is the

variable c , both are expressed in eV. The derived c is 26 meV, and is smaller than the reported values of 5-20 eV [76] and 6-25 eV [77]. For P2, the calculated a_2 , b_2 , and c_2 are 1.247, - 0.1416, and 0.00905, respectively. The bowing parameter of 9.05 meV shows a dependency of the P2 energy level on [N].

Figure 5.2 Plot of P1 and P2 peak energy (E_1 and E_2 , respectively) versus nitrogen composition of GaAsN epilayer.

The activation energy (E_a) of GaAsN with different [N] is studied by temperature-dependent PL. Since E_a is an impurity binding energy or a carrier/exciton localization energy [91], it is expected that E_a increases with [N]. Equation (5.2) shows the relationship between E_a and PL temperature [91].

$$I(T) = \frac{I_0}{1 + Ce^{-E_a/(k_B T)}} \quad (5.2)$$

$$E_a \sim T \ln(I(T)) \quad (5.3)$$

$I(T)$ is integrated PL intensity at respective temperature (in Kelvin), T , I_0 is integrated PL intensity at 0 K (but 4 K can be used because the difference in temperature can still be tolerated), and C is a constant.

The as-grown GaAsN with 3% N does not exhibit any PL. Therefore, its E_a is obtained from temperature-dependent PL of the 625 °C-annealed sample. Since the annealing temperature is quite low, fluctuations in the composition and relaxation of the GaAsN lattice are minimized. Therefore, this annealed GaAsN sample can be used as a representative for GaAsN with 3% nitrogen content.

A large amount of nitrogen causes higher E_a , as non-radiative (NR) or trap centers as well as compositional fluctuations increase in numbers (Fig. 5.3). These NR or trap centers hinder carriers' radiative recombination. GaAsN epilayer with high [N] has a higher activation energy as the carriers are trapped and not able to recombine. In a later section, thermal annealing helps to decrease NR or trap centers and compositional fluctuations in the epilayer.

The activation energy *versus* [N] of GaAsN alloys reaches saturation when [N] > 3%. There is no information available about the activation energy for GaAsN with > 5% because of absence of PL emission. In our GaAsN, N-N interstitials are the dominant factors to trap the carriers. However, the number of these interstitials could not increase indefinitely because for GaAsN with good epitaxial quality, the growth conditions are pre-determined. Thus, according to equation (4.13), the amount of nitrogen interstitials will be reduced for a high N/V ratio, i.e., a high N content in GaAsN.

Figure 5.3 Activation energy (meV) of PL versus nitrogen content (%) in GaAsN epilayer.

Next, to investigate the PL peak shift with nitrogen and indium compositions, a series of InGaAsN samples are grown by MOCVD. We also want to achieve an indium content as high as possible while nitrogen is incorporated into InGaAsN in order to increase the emission wavelength. All the samples were grown on InP substrates at 630 °C and at the reactor pressure of 100 mbar. The V/III molar ratio and growth time are fixed at 21 and 40 minutes, respectively. From XRD and PL measurements, In and N contents are determined based on Gokhale’s band gap cutoff wavelength of InGaAsN [97].

The InGaAsN samples with their growth conditions and compositions are presented in Table 5.1.

Table 5.1 InGaAsN samples growth conditions and their nitrogen and indium concentration in the epilayers.

Sample	N/V molar ratio		Ga/III molar ratio	% N	% In
IS1	0.6		0.352	0.22	52.7
IS2	0.6		0.29	0.18	58.35
IS3	0.6		0.261	0.35	60.55
IS8	0.9		0.352	0.7	56.5
Sample	T _g (°C)	N/V	Ga/III	% N	% In
IS9	630	0.75	0.29	0.37	58.87
IS10	550	0.667	0.248	1.82	67.7

PL from InGaAsN is presented in Fig. 5.4. It is deteriorated by increasing indium. PL from the as-grown InGaAsN alloys is observed until [In] reaches 61%, beyond which no PL emission is observed due to a large number of defects in the high-lattice-mismatched InGaAsN epilayer. InGaAsN with 61% In and 0.35% N (IS3) emits at a wavelength of 1.76 μm . To obtain InGaAsN alloys emitting at longer wavelength and also to reduce InGaAsN lattice mismatched with InP substrate, decreasing [In] and increasing [N] in InGaAsN should be considered [97]. Nitrogen causes a larger band gap bowing than indium. However, with the same DMHy/TBAs ratio, the nitrogen content in InGaAsN is less than that in GaAsN. With the same N/V molar ratio, the highest [N] achieved by us in InGaAsN is 0.7%, more than five times lower than that in GaAsN ($> 3\%$ N). There are several causes for this low [N] in InGaAsN. Firstly, the decrease in nitrogen incorporation is due to an increase in In content [98-99]. Additionally, the lower nitrogen content is probably caused by 630 $^{\circ}\text{C}$ growth temperature used

for preparing InGaAsN. Growth at 630 °C decreased the nitrogen adsorption rate in InGaAsN. Moreover, since the In-N bond (1.93 eV) is weaker than the Ga-N bond (2.24 eV), the nitrogen atom can break from the In-N bond and desorb away from its lattice space. The previously nitrogen-occupied space is then replaced by arsenic.

Figure 5.4 20-K PL of InGaAsN with different Ga/III molar ratio, i.e. different In content in InGaAsN. Inset: InGaAsN with different nitrogen composition.

Fig. 5.4 shows PL spectra of InGaAsN with different indium contents. The inset shows PL of InGaAsN with different nitrogen content. A single peak is observed in the PL spectra, i.e., P1. In GaAsN, P2 is caused by N-N interstitials due to the reaction between radicals NH_2 and $\text{N}(\text{CH}_3)_2$ with nitrogen carrier gas. This reaction happens when there are free NH_2 molecules, which are incompletely captured by the surface. In InGaAsN, NH_2 now can react with either In or Ga and therefore decrease the probability of formation of nitrogen interstitials. Therefore,

increasing [N] in InGaAsN does not cause optical degradation as much as it does in GaAsN, due to less N-N interstitials in the InGaAsN alloys (compare insets of Fig. 5.4 to Fig. 5.1).

The effect of growth temperature on nitrogen incorporation into InGaAsN is studied briefly. Samples IS9 and IS10 from Table 5.1 are two InGaAsN grown with different growth temperatures. IS9 has a higher DMHy/(DMHy+TBAs) molar ratio. However, IS10 has [N] and [In] of 1.82% and 67.7%, respectively, while IS9 has [N] and [In] of 0.37% and 58.87%. The cause of higher nitrogen and indium contents of sample IS10 is primarily due to lower T_g in its epilayer growth. High T_g causes the In-N bond to break because of its weak bond strength and instability, but at low T_g , the In-N bond can survive. Nitrogen can now bond with In and Ga, resulting in a higher nitrogen content in the InGaAsN epilayer. Hence, IS10 has a higher N content because of its low T_g .

5.2.2 Raman measurement of GaAsN and InGaAsN alloys

For GaAsN on GaAs, a Raman measurement can determine whether the epilayer is strained or relaxed, based on GaAs-like LO phonon shifts. The shifts in GaAs-LO and GaAs-TO phonons can be used to determine [N] of GaAsN.

A Raman study of GaAsN reveals that the overlayers are strained; i.e., pseudomorphical. Fig. 5.5 shows Raman spectra of GaAsN epilayers with different nitrogen contents. The GaAs-LO phonon shift depends on the degree of strain of GaAsN.

Figure 5.5 Raman spectra of GaAsN epilayers with different nitrogen compositions; inset: N-local mode in GaAsN.

With increasing nitrogen, lattice strain encountered by GaAsN causes GaAs-LO phonons to red-shift and intensity to decrease. On the other hand, the GaAs-TO phonon forbidden for a perfectly ordered crystal increases in intensity with higher N, due to substitutional disorder introduced by nitrogen. The N-local mode at 471 cm^{-1} is shown in the inset of Fig. 5.5. When nitrogen content is larger than 4.5%, the LO phonon of GaAsN returns to the original GaAs-LO phonon (291.2 cm^{-1}). This is due to the fact that a critical layer thickness of GaAsN has been exceeded and it results in the relaxation of GaAsN epilayer.

The GaAs-like LO phonon shift at low $[N] < 1\%$ will be used as a reference to derive an equation involving the LO phonon shift and nitrogen content in GaAsN. The data on LO shift of low nitrogen content GaAsN epilayers is used because these layers are normally fully strained on GaAs; i.e., no

relaxation happens in the GaAsN epilayer. When $[N] > 1\%$, there is a possibility that relaxation occur in the epilayer. Equation (5.4) shows the relationship between the GaAs-like LO phonon shift and the percentage of $[N]$ (calculated “ x ” in the equation) in GaAsN.

$$\text{GaAs-like LO (cm}^{-1}\text{)} = 291.2 - 0.65x \quad (5.4)$$

Equation (5.4) is for strained GaAsN on the GaAs substrate. The line based on equation (5.4) is drawn in Fig. 5.6 (a). It is extended until $x = 4.5\%$. The GaAs-like LO phonon shifts of GaAsN with $x > 2\%$ are placed in Fig. 5.6 (a). It is shown that our GaAsN with $x > 2\%$ are fully strained up to $x = 4.5\%$ (forming pseudomorphic layer) because the GaAs-LO phonon shifts follow equation (5.4).

Figure 5.6 Raman shift of GaAs-like (a) LO phonon (b) TO phonon against nitrogen content estimated by XRD.

Nitrogen content in GaAsN affects the GaAs-like TO phonon shift as shown in Fig. 5.6 (b), due to N-induced disorder. The shift is observed up to 2% nitrogen content. This shift is advantageous for estimating low nitrogen content ($<1.5\%$), compared to the LO phonon shift. The observed shift in GaAs-like LO

phonon is very small for $N < 1.5\%$ while the observed shift in GaAs-like TO is more obvious for $N < 1.5\%$. If $N > 1.5\%$, GaAs-like LO phonon shift is suitable for study of strain and $[N]$ in GaAsN alloys. Since Raman measurement characterizes the phonon of GaAsN, the amount of relaxation in the epilayer does not matter as long as the layer is partially or fully strained. The amount of strain can be determined qualitatively from the intensity of GaAs-like phonon. Therefore, by using equation (5.4) together with nitrogen content of GaAsN alloys deduced from XRD measurement, one can determine whether the epilayer grown is a strained or relaxed layer.

In quaternary InGaAsN alloys, Raman measurements are utilized to study nitrogen preferential bonding. The GaN-like LO_2 phonon lies at the frequency of 470 cm^{-1} and is accompanied by low and high frequency sides at 458 cm^{-1} and 488 cm^{-1} [42]. The InN LO lies at 558 cm^{-1} [44]. Fig. 5.7 shows Raman spectra for two InGaAsN samples with different $[N]$ and $[In]$.

At low $[In]$, there are an obvious InN-LO peak and a less resolved GaN- LO_2 peak. When the indium content increases, InN-LO peak intensity decreases followed by an increase in GaN- LO_2 peak intensity and the appearance of GaN- LO_2 low- and high-frequency sides. These form a broad GaN- LO_2 peak. These behaviors are explained as follows. At low $[N]$, there are many arsenic atoms. Most of them will bond with Ga because the Ga-As bonding energy (1.63 eV) is stronger than that of In-As (1.55 eV) [100]. N is then left to bond with In. However, the In-N bond is unstable, so that an In_3GaN configuration is more favorable, due to its reduced local strain [41]. Therefore, In-N configuration is dominant at low $[In]$ and $[N]$ in InGaAsN.

Figure 5.7 Raman spectra of $\text{In}_y\text{Ga}_{1-y}\text{As}_{1-x}\text{N}_x$ epilayers with $y = 0.13$, $x = 0.0086$ and $y = 0.68$, $x = 0.0182$.

When the nitrogen and indium flow rates are high during growth of InGaAsN, most of the In-N bonds (1.93 eV) formed at the beginning of the growth are unstable, due to the increasing strain in the epilayer. More indium means a larger lattice constant which causes higher strain in InGaAsN on an InP substrate. Therefore, N prefers to bond with Ga in InGaAsN with high [In] because of strain reduction and Ga-N bond (2.24 eV) stability [41]. At high [In] and [N] of InGaAsN, InGa_3N configuration is preferred over Ga_4N because of its low local strain [100]. Whether there is any relationship between the bonding configuration (such as InGa_3N or In_3GaN) and the band gap of InGaAsN is a subject of a future study.

5.3 Thermal Annealing of GaAsN materials

Nitrogen incorporation into GaAsN or InGaAsN is known to cause degradation in optical properties. Annealing the samples improves the optical properties by removing NR centers from the semiconductors [20]. However, the effect of RTA on the emission peak shift of annealed samples varies. Besides removal of NR centers, annealing can cause diffusion of group III and/or V elements inside the material and yield a red shift [25] or a blue shift [26] in PL emission peaks. Thermal annealing can also affect a change in nitrogen composition. The two emission peaks, P1 and P2, of GaAsN are affected differently by thermal annealing.

Capping the sample before thermal annealing can further improve the optical properties of annealed specimens. Capping the sample with Si_3N_4 [27-28] or SiO_2 [27] will assist out-diffusion of defects during thermal annealing. It is important to look into this aspect to further improve PL emission intensity.

GaAsN samples with different nitrogen compositions are used for investigation of thermal annealing. Each as-grown sample is cut into several pieces. The pieces are covered with 300 nm thick SiO_2 layers before annealing. These samples are then annealed at 625 - 775 °C in steps of 50 °C for 60 s under nitrogen ambient. Each sample is covered with a GaAs substrate to prevent As-out diffusion during annealing. After annealing, the SiO_2 cap layer is removed by wet-etching using hydrogen fluoride (HF). The annealed samples are measured by XRD.

5.3.1 Annealing effect on GaAsN materials

Fig. 5.8 shows the 20K-PL spectra of GaAsN samples with $[N] \approx 0.7\%$ before and after RTA treatment at 625, 675, 725, and 775 °C. The two peaks in the PL spectrum of as-grown GaAsN appear (P1 and P2 at $\lambda = 928$ nm and $\lambda = 1068$ nm, respectively).

Figure 5.8 20K-PL spectra of 625, 675, 725, and 775 °C annealed GaAsN sample with 0.7% N. As-grown GaAsN is included as comparison with annealed samples.

RTA reduces P2 intensity drastically. With an increase of annealing temperature P1 intensity becomes stronger, since non-radiative recombination centers in the GaAsN epilayer are annealed out. However, at RTA > 725 °C, the P1 peak intensity decreases. This decrease occurs because of surface decomposition through out-diffusion of As and N, diffusion of defects from the epilayer [11], and RTA-induced defects [15]. Therefore, during annealing, there

are two mechanisms oppose to each other: *improvement* in P1 peak intensity due to removal of NR centers, and *degradation* in P1 peak intensity due to introduction of RTA-induced defects and surface degradation that traps photons. These two mechanisms compensate each other during thermal annealing.

The P2 peak intensity of annealed samples decreases when T_{ann} increases. The decrease in P2 peak intensity is due to a change in nitrogen location from an interstitial site to a substitutional site, as described in the previous chapter.

Figure 5.9 20K-PL peak positions (in nm) and intensity (a.u.) of GaAsN sample with 0.7% N after annealing at 625, 675, 725, and 775 °C. The squares refer to P1, while the circles refer to P2. Solids are for peak positions (left axis) and hollows are for peak intensities (right axis). The lines are drawn to guide the eye.

A summary of the 20K-PL peak positions (in nm) and intensities of GaAsN with 0.7% N after being annealed at 625, 675, 725, and 775 °C is given in Fig. 5.9. All annealed samples undergo a red-shift with regards to the as-grown

GaAs_{0.993}N_{0.007} sample. The red-shift of P1 of the samples annealed at 675 °C is up to 14 nm. This red-shift for GaAsN had been observed by Loke *et al.* [25] and is attributed to hopping of N atoms from interstitial sites to substitutional sites. Chapter 4 has explained the change of nitrogen-nitrogen interstitial to substitutional nitrogen during annealing. Upon annealing, an increase in [N] of GaAsN is observed, accounting for a reduction in GaAsN band gap and corresponding red-shift. The red-shift is predicted by a theoretical simulation [82]. However, at high T_{ann} , nitrogen atoms out-diffuse from GaAsN, reducing red-shift.

Intensity of P1 increases monotonically until $T_{ann} = 725$ °C. The intensity is the highest when $T_{ann} = 725$ °C (shown in Fig. 5.9). This is taken to be optimum T_{ann} for GaAs_{0.993}N_{0.007}; the peak intensity obtained at $T_{ann} = 725$ °C is 10 times bigger than that obtained for the as-grown sample.

Four samples with different [N] are annealed to study the dependency of optimal T_{ann} on [N] of GaAsN, see Fig. 5.10. The optimum T_{ann} for GaAsN with $N > 1.3\%$ is 625 °C.

The optimum annealing temperature decreases when the nitrogen content increases (Fig. 5.10). This result can be explained as follows. During annealing, a removal of NR centers and introduction of RTA-induced defects compensate each other. If the removal of NR centers dominates, PL peak will increase. As already noted, the density of defects in GaAsN increases with [N]. At low T_{ann} , NR centers are largely removed and RTA-induced defects are created [26]. However, due to a high concentration of defects in GaAsN with high [N], not all NR centers can be removed meanwhile RTA-induced defects increase the number of defects in the epilayer. When T_{ann} increases, the number of the annealed-out NR centers is

less than the number of the RTA-induced defects in the epilayer. As a result, P1 peak intensity of GaAsN with high [N] only increases at low T_{ann} , and thus this GaAsN sample has the low optimum annealing temperature. These results agree with those of GaAsN epilayers grown by MBE [26].

Figure 5.10 Optimum annealing temperatures measured for different N compositions of GaAsN. The optimization refers to annealing temperatures that yield the highest peak P1 integrated intensity.

The activation energy of P1 and P2 of annealed GaAsN with 0.7% N is also investigated to study the relationship between band-to-band transition E_a of the annealed sample and the optimum annealing temperature. The relationship of E_a of N-N interstitials and defects in the annealed sample is also studied. Fig. 5.11 shows a plot of the activation energy against annealing temperature of $\text{GaAs}_{0.993}\text{N}_{0.007}$.

Figure 5.11 Activation energy E_a versus annealing temperature of $\text{GaAs}_{0.993}\text{N}_{0.007}$.

The activation energy E_a of the band-to-band transitions of P1 and N-N interstitials (P2) are obtained from equation (5.2). E_a of the band-to-band transitions does not vary much with T_{ann} because there are not many NR centers in the GaAsN sample with 0.7% N content. Thus, the carrier localization energy has a weak dependency on annealing temperature. The activation energy of P1 decreases with an increase of T_{ann} until $T_{ann} = 725$ °C. It then increases slightly. The increase means that annealing-induced defects have dominated the carrier recombination process. 725 °C annealing temperature yields a minimum E_a , indicating a closely optimum annealing temperature for this sample (see Fig. 5.10).

E_a of N-N interstitial of $\text{GaAs}_{0.993}\text{N}_{0.007}$ is 113 meV. This activation energy decreases with an increase of T_{ann} . Thermal annealing causes N-N interstitials to

be changed to N-As interstitials and N substitutionals. The decrease in N-N interstitials is shown in the decreasing E_a of N-N interstitials of the annealed sample. Higher annealing temperature removes more N-N interstitials and causes a further reduction in E_a of N-N interstitial.

5.3.2 Effect of SiO_2 cap on GaAsN annealed epilayer

Capping the sample with oxide before thermal annealing can improve the peak intensity of band-to-band (P1) transition energy [27]. The increase in P1 peak intensity is larger for an oxide capped sample than that of the sample without an oxide cap [27]. To study the effect of the SiO_2 cap during annealing on GaAsN PL peak intensity, a $\text{GaAs}_{0.987}\text{N}_{0.013}$ epilayer is used. At this nitrogen content, the defect density is high so that the effect of annealing with and without the SiO_2 cap layer can be observed clearly.

Before annealing, P1 is very weak. PL of the sample annealed without the SiO_2 cap layer shows improved intensity of P1 and decreased intensity of P2 (Fig. 5.12 (a)). Capping the GaAsN epilayer with SiO_2 during RTA shows further increase in P1, while P2 decreases. A substantial increase of P1 can be observed in Fig. 5.12 (b), where P1 for the as-grown $\text{GaAs}_{0.987}\text{N}_{0.013}$ sample is hardly discernable; P1 is suppressed due to a large number of non-radiative recombination centers.

(a)

(b)

Figure 5.12 20K-PL spectra of a GaAsN sample with 1.3% N (a) without and (b) with a SiO₂ cap layer at annealing temperatures of 625, 675, 725, and 775 °C.

P2 of the annealed samples with a SiO₂ cap undergoes large reduction (by a factor of 100, Fig. 5.12(b)) compared to that of the as-grown GaAs_{0.987}N_{0.013} sample, while the annealed sample without SiO₂ only has intensity reduction of a factor of 10 (Fig. 5.12 (a)). Annealing the samples with SiO₂ is more effective because the SiO₂ cap assists diffusion of defects. There were vacancies created at the interface of SiO₂/GaAsN interface during annealing process. These vacancies caused defects to out-diffuse towards the top surface [27]. This mechanism improves PL intensity of P1 and further decreases intensity of P2.

Fig. 5.13 summarizes the 20K-PL peak positions (in nm) and intensity (a.u.) of the GaAsN sample with 1.3% N after annealing at 625, 675, 725, and 775 °C without (a) and with (b) the SiO₂ cap. The P1 peak positions for the annealed samples with and without SiO₂ experience the red-shifts of 54 nm and 14 nm, respectively. The SiO₂ cap could promote faster diffusion of N atoms from interstitial sites to substitutional sites *via* vacancy diffusion to the oxide layer [27], resulting in a higher N content in GaAsN. Therefore, with the same annealing temperature, a larger red-shift is observed for GaAsN with SiO₂ capping than that without the capping.

Figure 5.13 20K-PL peak positions (in nm) and intensity (a.u.) of GaAsN sample with 1.3% N after annealing at 625, 675, 725, and 775 °C without (a) and with (b) SiO₂ cap. The squares refer to P1, while the circles refer to P2. Solids are for peak positions (left axis) and hollows are for peak intensities (right axis). The lines are drawn to guide the eye.

The P2 peak of the sample with 1.3% N content annealed at high temperature (775 °C) with and without SiO₂ experiences a blue-shift. The trend is similar for the sample with 0.7% N content (Fig. 5.9). This is due to a change of N-N interstitials to N-As interstitials and N substitutionals upon annealing. The P1 blue-shift at 625 °C and 675 °C is caused by a removal of growth-induced point defects by RTA [26]. Lower concentration of these defects causes saturation of defect-related states and occupation of higher lying states. Higher annealing temperature can completely remove these defects.

The P1 peak intensity decreases when T_{ann} increases because surface degradation and RTA-induced defects often accompany RTA. This results in a decrease in P1 intensity. P2 peak intensity of the sample annealed with the SiO₂ cap has a larger intensity reduction than that of the sample annealed without SiO₂.

Therefore, the GaAsN samples annealed with SiO₂ cap layers increase radiative band-to-band transitions and the peak shift more than the samples that are annealed without the SiO₂ caps.

5.4 Summary

Optical properties of the GaAsN and InGaAsN alloys with different nitrogen concentrations have been studied. For $N < 3\%$, the band bowing parameter for the band-to-band transition energy is 26 meV. The interstitial peak energy has the band bowing parameter of 9 meV, indicating a dependency of nitrogen content.

Raman measurements have also been carried out to study lattice strain of the GaAsN epilayers with different nitrogen contents. An equation to determine

the nitrogen content in GaAsN has been derived based on GaAs-like LO phonon shifts. The GaAs-like TO phonon shift can be utilized to determine nitrogen composition of GaAsN when $[N] < 1.5\%$. When $[N] < 5\%$, GaAsN is strained. For the InGaAsN epilayer, Raman measurements are applied to study a preferable bonding configuration of nitrogen with different indium compositions. InGaAsN with low $[In]$ and $[N]$ prefers In_3GaN configuration, while InGaAsN with high $[In]$ and $[N]$ prefers $InGa_3N$ configuration.

Thermal annealing is known to improve PL of GaAsN. Under closely optimal annealing conditions the highest PL intensity is obtained. The optimum annealing temperature is found to decrease with higher N composition. For example, optimum T_{ann} for $GaAs_{0.987}N_{0.013}$ is $625^\circ C$, while for $GaAs_{0.993}N_{0.007}$ it is $725^\circ C$. Capping GaAsN with an oxide layer before annealing affects optical performance. The optical performance for an oxide capped GaAsN alloy after annealing is better than for the uncapped one.

Temperature-dependent PL can be used to derive the activation energy E_a of the band-to-band transition peak (P1) and the interstitial peak (P2). The activation energy of P1 increases with $[N]$ of GaAsN, indicating a high number of traps or carrier/exciton localization energy and compositional fluctuations. P1 activation energy *versus* annealing temperature may be employed to study the optimum annealing temperature for the sample.

Chapter 6

Study of InAsN Alloy

6.1 Introduction

Nitrogen incorporated into InAs leads to the band gap energy reduction of InAsN alloys. $\text{InN}_x\text{As}_{1-x}$ [45-48, 101-105] has a low band gap energy for mid-infrared (MIR) applications, such as atmospheric pollution monitoring devices, leak detectors, lasers for surgery and other MIR devices. Nonetheless, nitrogen incorporation into InAs during epitaxial growth is not easy. Experimental as well as theoretical studies have emerged to investigate the InAsN alloys.

The band gap energy, E_g , of $\text{InN}_x\text{As}_{1-x}$ has been studied by using tight-binding and pseudopotential calculations [50-53]. The calculated band gap bowing parameter, c , of InAsN is different for each calculation. Yang *et al.* estimated a bowing parameter of 4.22 eV; they employed the tight binding calculation [51]. In the calculation, the 1.8 eV band gap energy of wurtzite InN was used instead of the recently found InN band gap energy of 0.78 eV [54-55]. Nakajima *et al.* estimated a bowing parameter of 1.6 eV from a pseudopotential method [53]. The calculated InN band gap energy is below 0 eV which is not the value measured by experiments. Therefore, a proper estimation for the band gap bowing parameter, based on numerical simulations of $\text{InN}_x\text{As}_{1-x}$ band gap energies, is necessary for a future experimental reference. Our study utilizes the density functional theory (DFT) to estimate the band gap energies of InAsN alloys.

InAsN epilayers grown are mostly with $[N] < 6\%$ although as high as 18% nitrogen in MOCVD-grown multi-quantum wells (MWQ) InAsN has been achieved [47-48] with an emission wavelength of 6.5 μm and a broad FWHM of 3.5 μm . Growth of InAsN alloys lattice-matched to GaAs and with 38%N has been achieved by molecular beam epitaxy [106] although no PL was reported.

In this chapter, a theoretical study of the band gaps of InAsN alloys with different nitrogen contents is presented. MOCVD growth of InAsN is also studied with different carrier gases.

6.2 Theoretical calculation of band structure of InAsN

Intense efforts have been done to predict the band structure of III-(N-V) alloys theoretically where part of the group V elements of the III-V semiconductor is replaced by nitrogen. Tight-binding calculation, pseudopotential method, and density functional theory are often used to calculate the electronic band structure of the alloys.

6.2.1 Tight-binding calculation

The tight-binding (TB) method plays a key role in understanding the trends of the binding energy of deep impurities in tetrahedrally bonded semiconductors. Because TB uses a basis of localized atomic orbitals, it can provide significant insight into the influence of localized perturbations on the electronic structure, and can also be used to derive the modified k-p model needed to describe the band-edge dispersion. It utilizes Hamiltonian to describe the

electronic structure. This method had been used to predict the band structure of $\text{InAs}_{1-x}\text{N}_x$ [50-53].

Fig. 6.1 shows the calculated band gap energy of InAsN of different nitrogen contents by using the TB method [51]. The band bowing parameter, c , in this TB calculation is 4.22 eV. The component, c , is obtained from the quadratic equation of the energy band gap of InAsN as follows, where x is the nitrogen content in InAsN .

$$E_{g(\text{InAs}_{1-x}\text{N}_x)} = a + bx + cx(x-1) \quad (6.1)$$

Figure 6.1 Band gap energy dependence on composition x for $\text{InN}_x\text{As}_{1-x}$ alloy by tight-binding calculation [51] compared with experimental result by Naoi [45] (square) and Emawy [47] (triangle).

There are some discrepancies of the theoretical results when compared to experimental results. For $[\text{N}]$ of 0.06, E_g of InAsN is estimated to be 0.17 eV,

whereas, according to the experimental value by Naoi *et al.* E_g is 0.12 eV [45]. The band gap energy for 18% of nitrogen content from the Fig. 6.1 is around 0 eV, but it is reported that E_g with that composition to be 0.19 eV [48]. There is a significant difference between the experimental and the theoretical values. Theoretically, E_g of InAsN is minimal around 20-25%N. Experimentally – unfortunately, there are no paper mentioning about E_g of InAsN for nitrogen contents above 18%. This is due to high defects introduced in InAsN epilayer as [N] increases. 0.12 eV is the lowest band gap energy of InAsN with 6%N [45]. Furthermore, it is recently known that the E_g of InN is 0.78 eV [54-55], instead of 1.8 eV [107-108] used the the TB calculations in Fig. 6.1.

TB calculations suffer from small basis sets used, and thus TB is unable to produce details of the electronic structure. Furthermore, TB is an empirical method that lacks transferability. The tight binding parameters are only fitted to bulk InAs and InN. In the InAsN system, local atomic environment around N can be different from the bulk and, thus, the TB parameters based on bulk InAs and InN may not be applicable [109]. Nevertheless, the TB method serves as a base for the next theoretical study.

6.2.2 Pseudopotential theory

The tight-binding method suffers from small basis sets; and thus it is unable to reproduce details of the electronic structure. The empirical pseudopotential method (EPM) is able to study very large – hence potentially very dilute or impurity-like – systems and is able to evaluate the electronic

consequences of, for example, specified small clusters or characteristic arrangements of nitrogen atoms, on the overall properties of an nitrogen alloy.

The pseudopotential theory utilizes an effective potential, or pseudopotential, to replace the complicated effects of the motion of the core (i.e. non-valence) electrons of an atom and its nucleus [1]. The initial Schrödinger equation (eq. (6.2)) contains a Coulombic potential term for core electrons. With this theory, the Schrödinger equation now contains a modified effective potential term (eq. (6.3)).

$$\left\{ -\frac{1}{2}\nabla^2 + \sum_{\alpha,n} v_{\alpha}(\vec{R}_{\alpha,n}) \right\} \psi_i = \varepsilon_i \psi_i \quad (6.2)$$

is expanded in a plane-wave basis

$$\psi_j(r) = \sum_G^{G_{\max}} A_G^j e^{iGr} \quad (6.3)$$

where v_{α} is one electron potential and $\vec{R}_{\alpha,n}$ is the occupied wavefunction.

In EPM the forces between atoms are calculated using a simple ‘balls and springs’ Hamiltonian which includes both bond-stretching (α) and bond-bending (β) terms. EPM uses electronic eigenfunctions of the Hamiltonian. The eigenfunctions and eigenvalues of this Hamiltonian are determined by using the folded spectrum method [1]. This numerical technique produces single-particle eigensolutions in a given energy window without having to obtain (and orthogonalize to) lower energy eigensolutions. As a result, the overall method scales linearly in computational time with the number N of atoms in the supercell, while conventional band structure methods – that require self-consistency of the crystal potential and knowledge of all occupied levels – exhibit time scaling of N^3 .

Troullier, *et al.* [110] provides the detail on solving a pseudopotential based on plane wave calculations to obtain the band structure.

The band gap versus nitrogen composition calculated by using the pseudopotential method is plotted in Fig. 6.2. The calculated band gaps from the pseudopotential and TM methods are different. The pseudopotentially calculated band gap energies of $\text{InAs}_{1-x}\text{N}_x$ are 0.003 eV and 0.004 eV for $x = 0.5$ and 0.75, respectively, whereas, the TB-calculated band gap for $x = 0.5$ is almost the same as E_g obtained by pseudopotential method but different for $x = 0.75$ ($E_g \approx 0.7$ eV).

Figure 6.2 Band gap energy dependence on nitrogen content, x , for $\text{InAs}_{1-x}\text{N}_x$ by PM [53]; hollow and filled triangles represents experimental band gaps for 6%N and 18%N, which are 0.12 eV [45] and 0.19 eV [47], respectively.

Another discrepancy lies in pseudopotentially calculated InAs and InN band gap energies as compared to the E_g 's of experimental values. The calculated E_g 's of InAs and InN are 1 and -0.2 eV, respectively, which are totally different

from the experimental E_g 's of InAs (0.36 eV) and InN (0.78 eV). Furthermore, the experimental E_g 's of InNAs for 6%N is 0.12 eV and 18%N is 0.19 eV, respectively. These results do not fit the curve produced by using PM.

The EPM band bowing parameter, c , for the direct band gap of InNAs is 1.6 eV, which is much smaller than 4.22 eV calculated from the tight-binding method [51]. The lack of a plane wave basis set combined with underestimation of LDA causes negative band gap energies (as in Fig. 6.2); i.e., the band structure becomes semi-metallic. This underestimation may be enhanced, due to the localized nature of the valence charge density in these materials including nitrogen. Inaccuracy of the band structure of InAsN by using the pseudopotential method calls for another band calculation method that would offer higher accuracy. The density functional theory (DFT) is deemed suitable to rectify the discrepancy presented by tight-binding and pseudopotential method with experimental results.

6.2.3 Density functional theory

The density functional theory (DFT) developed by Hohenberg and Kohn (1964, later generalized by Levy, 1979) states that all the ground-state properties are functional of the electron density n [111]. The equations are based on n Schrödinger-like equations for n non-interacting electrons moving in an effective potential as shown in equation (6.4).

$$\left(-\frac{\hbar^2 \nabla^2}{2m} + V_{ext} + V_{eff} \right) \psi_i = \epsilon_i \psi_i \quad (6.4)$$

Equation (6.4) is a one-electron Schrödinger-like equation. ψ_i is n^{th} one-electron wavefunctions, V_{ext} is the external potential of the nuclei, and V_{eff} is the effective potential.

DFT is based on two simple principles:

- the total energy of a system of electrons and nuclei is a unique functional of the electron density
- the variational minimum of the energy is exactly equivalent to the true ground-state energy

The ground-state energy is defined as

$$E_0 = \langle \psi_0 | V_{ext} | \psi_0 \rangle \quad (6.5)$$

where the contribution of the external potential, V_{ext} , can be written explicitly in terms of the density.

$$V_i = \int V_{ext}(\vec{r}) n(\vec{r}) d^3r \quad (6.6)$$

In DFT, there is no need to solve the many-body wave-function because the energy is written in terms of electron density as given in equation (6.7).

$$E = E[\rho(\vec{r})] = \int d\vec{r} V_{ext}(\vec{r}) \rho(\vec{r}) + \vec{F}[\rho(\vec{r})] \quad (6.7)$$

When the second principle of DFT is applied to the energy functional, the density is written as wavefunctions of non-interacting electrons as shown below.

$$\rho(\vec{r}) = \sum_{i=1}^n \psi_i^*(\vec{r}) \psi_i(\vec{r}) \quad (6.8)$$

Then $\vec{F}$ is written as

$$\vec{F}[\rho(\vec{r})] = E_K[\rho(\vec{r})] + E_H[\rho(\vec{r})] + E_{xc}[\rho(\vec{r})] \quad (6.9)$$

where E_H is the Hartree-Coulomb term, which does not include exchange correlation effects; E_K is the electron kinetic energy of a system of non-interacting electrons; E_{xc} is the exchange-correlation functional.

Although the functions have been defined in terms of electron density, the complexity of interactions between electrons still exists. It is a tough task to find a functional E_{xc} that contains the required information. Hence, approximation is required to solve the functional energy. Kohn and Sham introduced the local-density approximation (LDA), which states that E_{xc} can be assumed to be a uniform electron gas of density $\rho = \rho(\vec{r})$, for each infinitesimal element of density $\rho(\vec{r})d(\vec{r})$. Then,

$$E_{xc} = \int d\vec{r} \rho(\vec{r}) + \varepsilon_{xc}(\rho(\vec{r})) \quad (6.10)$$

where ε_{xc} is the exchange-correlation energy per electron in a uniform gas of density ρ .

Although the charge density is non-uniform around atoms, this approximation is capable of yielding accurate properties for many systems [112]. Using the CASTEP simulation program, the energy band structures and the density of electronic states of $\text{InAs}_{1-x}\text{N}_x$ have been calculated by solving equation (6.7). The electron exchange-correlation energy is assumed to be uniform (equation (6.10)).

6.2.4 InAsN band structure calculated by DFT

In the lattice structure of a semiconductor crystal, each cell (or supercell) is assumed as a box and treated as a periodic system for the semiconductor

crystal. Thus each electronic wave function in the lattice can be represented as a product of a cell-periodic part and a wave-like part, as stated by Bloch's theorem. Results will vary with the system size (single or supercell), number of k -points, error tolerances in electronic energy, etc. A large number of k -points ensures smoothness of the band structure, but the calculation will take longer time to finish. One should realize that a change in energy band structure is negligible for k -points that are close together. Thus, the number of k -points chosen for the calculation should be carefully exercised. In our calculation, a 12- k -points arrangement is sufficient to represent the main nodes to form the electronic band gap structure.

For energy band gap calculation, the cell structure for InAsN is tetrahedral zinc blende with P-43m symmetry [113]. InAs, InN and GaAs have this structure [112-113]. Atomic composition is set by replacing atoms with the same group (group III or V) of the substituted atom. The atomic positions of the lattice are fixed in space and spin-orbit interaction effects are not taken into account in the calculation.

Fig. 6.3 shows a unit lattice structure (zinc blende) of $\text{InAs}_{1-x}\text{N}_x$ which has 8 atoms: 4 atoms belong to the group III element (indium) and another 4 atoms belong to the group V elements (arsenic and nitrogen). Using one lattice cell structure for the calculation, it is possible to calculate the $\text{InAs}_{1-x}\text{N}_x$ alloy with N compositions $x = 0, 0.25, 0.5, 0.75$, and 1 by replacing 0, 1, 2, 3, and 4 arsenic atoms in the lattice with nitrogen atoms, respectively. To calculate $\text{InAs}_{1-x}\text{N}_x$ with other N compositions, more lattice cells are needed.

Figure 6.3 Zinc blende atomic structure of $\text{InN}_x\text{As}_{1-x}$ alloy with N composition $x=0.25$ for the simulation

In this numerical simulation, energy band gaps of $\text{InAs}_{1-x}\text{N}_x$ with $x = 0, 0.0625, 0.0833, 0.1875, 0.25, 0.5, 0.75$, and 1 have been calculated. Compared to the results reported by Kuo, *et al.* [114], the band gap energies of $\text{InAs}_{1-x}\text{N}_x$ obtained by us are not underestimated. Therefore, there is no necessity to correct the direct band structure obtained from the simulation.

The calculated energy band diagrams of zinc blende InAs and InN are presented in Fig. 6.4. Fig. 6.4 (b) shows the simulated energy band diagram of InN which is not available from any reference for this study. InN is previously shown to have wurtzite structure [107-108] with its energy band gap of 1.8 eV. However, recent experimental studies had shown that InN exists in zinc blende structure [54-55]. Our calculated direct energy band gap (Γ point) of zinc blende InN is 0.75 eV which matches a recent experimental result of 0.78 eV [54-55]. The energy band diagram of InAs calculated by us is almost the same as received by Alves and Madelung [115-116]. The direct energy band gaps of InAs at Γ and X

points, $E(\Gamma_{6c})_{sim}$ and $E(X_{6c})_{sim}$, are 0.45 and 2.5 eV, respectively. These values are close to those obtained by Madelung [116], 0.37 and 2.28 eV for $E(\Gamma_{6c})$ and $E(X_{6c})$, respectively.

Figure 6.4 The calculated energy band diagram of (a) InAs and (b) InN.

Table 6.1 summarizes the calculated band gap energies of $InAs_{1-x}N_x$ alloys with different N composition and compares our calculated band gap energy of

$\text{InAs}_{1-x}\text{N}_x$ with available published experimental results. The calculated band gap energies of InAs and InN are very close to the recent experimental results [54-55].

Table 6.1 Simulated band-gap energies of $\text{InAs}_{1-x}\text{N}_x$ alloys compared with the experimental results.

No.	Alloy	Band-gap energy (eV)	Experimental band- gap energy (eV)
1.	InAs	0.45	0.4
2.	$\text{InAs}_{0.9375}\text{N}_{0.0625}$	0.4	~ 0.12 [45]
3.	$\text{InAs}_{0.9167}\text{N}_{0.0833}$	0.38	-
4.	$\text{InAs}_{0.8125}\text{N}_{0.1875}$	0.26	~ 0.19 [48]
5.	$\text{InAs}_{0.75}\text{N}_{0.25}$	0.09	-
6.	$\text{InAs}_{0.5}\text{N}_{0.5}$	0.12	-
7.	$\text{InAs}_{0.25}\text{N}_{0.75}$	0.175	-
8.	InN	0.75	0.78 [54-55]

Fig. 6.5 plots the calculated E_g of $\text{InAs}_{1-x}\text{N}_x$ versus its N composition, x , from our study as well as tight binding and pseudopotential studies. A large bowing effect of E_g has been received by alloying N with InAs in the range from $x = 0$ to $x = 0.9$. Our calculation shows that the minimum band gap energy of $\text{InAs}_{1-x}\text{N}_x$ is obtained when x is 0.45 instead of $x = 0.25$ as predicted by the tight binding method [51]. Some experimental results of $\text{InAs}_{1-x}\text{N}_x$ band gap energies, with $x < 0.2$ so far available, are also included in the plot. The experimental band gap energies of $\text{InAs}_{1-x}\text{N}_x$ with low N composition ($< 0.3\%$) [99] confirm a similar trend as our numerical calculations. The experimental band gap of InAsN with

18% nitrogen [48] has a similar energy band gap as our calculated band gap of InAsN with the same composition.

Figure 6.5 The calculated energy band gap of InAsN as a function of its N composition (dash-dot line). The experimental results of this work are presented in cross (x). The solid circles are calculated values and hollow square, triangle, and circles are experimental results [45, 47, 103]. InAsN energy band gaps calculated by tight binding [51] and pseudopotential [53] methods are included for references in solid squares (full line) and triangles (dash line), respectively.

To determine the band gap bowing coefficient of $\text{InAs}_{1-x}\text{N}_x$ alloy, the calculated band gap energy of $\text{InAs}_{1-x}\text{N}_x$ alloy *versus* x has been fitted using equation (6.1). The calculated results are well fitted with the formula with the constant a equaling to 0.45 (eV), which corresponds to the E_g of InAs; b equals to 0.25, while $a+b=0.7$ eV with $x = 1$ in equation (6.1) is E_g of InN. Thus, the band gap bowing parameter c of $\text{InAs}_{1-x}\text{N}_x$ in this work equals 2.072 (eV).

This value of c is different from that obtained from calculations by using the tight binding and pseudopotential methods [51, 53]. From the tight binding theory, the bowing parameter of 4.22 eV is estimated for $\text{InAs}_{1-x}\text{N}_x$ with E_g of InN 1.8 eV [44, 107-108] which disagrees with the recently measured E_g of 0.78 eV [54-55]. This larger E_g used in an empirical tight binding calculation caused the larger energy band gap bowing coefficient of $\text{InAs}_{1-x}\text{N}_x$. Using the pseudopotential method, the bowing coefficient of $\text{InAs}_{1-x}\text{N}_x$ was obtained to be 1.6 eV [53]. However in this calculation, E_g dependence on the N content has the largest underestimation for the band gap energy (~ -0.2 eV), which may cause large discrepancies in the band bowing coefficient. The 2.072 eV band bowing parameter of $\text{InAs}_{1-x}\text{N}_x$, which we have obtained, is reasonable when the 0.38 eV difference in band gap energies between InAs and InN is considered.

6.3 MOCVD growth of InAsN

Epitaxial growth of InAsN is challenging, due to difficulties with nitrogen incorporation into InAs. Phase separation of InAsN and InAs is observed for InAsN grown at high N content ($>6\%$) [46]. It is important to eliminate this phase separation to achieve high quality in epitaxy of InAsN. The MOCVD growth of InAsN utilized hydrogen gas as a carrier gas and has been reported [45, 47-48, 103-104]. It is interesting to study the effect of hydrogen and nitrogen carrier gases on the quality and the nitrogen incorporation into the InAsN epilayer.

In this section, InAsN epilayers grown by MOCVD on InP substrates will be studied. The effect of two types of carrier gases, nitrogen and hydrogen, on nitrogen incorporation and epilayer quality is investigated. Due to the low

decomposition temperature of TMIn and weak In-N bond [41], 500 °C is set as the growth temperature of InAsN epilayers. The reactor pressure is 20 mbar. The TMIn flow is set at 28 $\mu\text{mol}/\text{min}$, and the (DMHy+TBAs)/TMIn molar ratio ranges from 20 to 24. The InP buffer layer is grown first. Table 6.2 lists our InAsN epilayers grown by MOCVD with different DMHy/(DMHy+TBAs) molar ratios and carrier gases used. The Nitrogen composition is deduced from the epilayer X-ray diffraction peak.

Table 6.2 InAsN epilayers grown with different DMHy to group V molar ratio and carrier gas.

Sample	Carrier gas	DMHy /V molar ratio
R1	Hydrogen	0.5
R2	Hydrogen	0.8
R3	Hydrogen	0.85
R4	Hydrogen	0.88
R5	Hydrogen	0.9
R6	Hydrogen	0.95
R7	Nitrogen	0.9

6.3.1 Effect of DMHy/V molar ratio on N incorporation in InAsN epilayer

To study the nitrogen incorporation in InAsN, samples with different DMHy/(DMHy+TBAs) molar ratios are grown with hydrogen as a carrier gas. XRD rocking curves of InAsN grown with hydrogen carrier gas (R1 to R6) have one or two additional peaks beside the InP substrate peak assigned as X1' and Y1, as shown in Fig. 6.6 (a).

(a)

(b)

Figure 6.6 (a) XRD of InAsN epilayers grown under hydrogen carrier gas with different DMHy to total group V molar ratio; (b) Difference (in arc second) of X1' and InAs diffraction peaks Vs DMHy/V molar ratio.

The definition of X1' and Y1 is as follows, according to us. Assuming X1' is the InAsN peak and fulfills Vegard's law, the nitrogen content in InAsN should

be 8.5%. However, if Vegard's law is not observed, due to the large lattice mismatch between InP and InAs(N), as mentioned in Ref. 105, X1' is the InAs peak.

Shih *et al.* have grown InAsN epilayers on InP substrates by plasma-assisted gas-source MBE [105]. Their reference sample was InAs on InP with a 1.18° difference in diffraction peaks [105]. Since X1' and the InP diffraction peaks are separated by about 1.18° , X1' seems to be an InAs peak, especially for X1' with the DMHy/V ratio < 0.88 . However, X1' and InAs diffraction peaks shift with respect to the DMHy/V ratio, Fig. 6.6 (b). Up until the DMHy/V ratio = 0.85, the arc second difference between X1' and reference InAs peak is the same. X1' then moves to a further distance from the reference InAs peak until DMHy/V ratio = 0.9. It then moves nearer to the InP peak.

The above behavior can be explained in terms of nitrogen incorporation. Nitrogen incorporation is almost nil when the DMHy/V ratio < 0.88 , due to the high miscibility gap between nitrogen and indium [117]. Y1 at this DMHy/V ratio does not appear. Then at the DMHy/V ratio = 0.88, nitrogen starts to be incorporated into the InAsN epilayer. However, high miscibility between nitrogen and indium causes phase separation. X1' and Y1 appear for the DMHy/V ratio > 0.85 . In this region, nitrogen and arsenide may occupy the same lattice site, (N-As)_{As}, causing a slight increase in the lattice due to a longer bond length [37]. Due to hydrogen as the carrier gas, (N-N)_{As} is less probable to form because of the reasons stated in previous chapter. The number of (N-As)_{As} increases as the DMHy/V ratio increases to 0.9 whereby X1' keeps moving away from the InP peak. Y1, on the other hand, shifts closer to the InP XRD peak, as the DMHy/V

ratio increases. Phase separation becomes significant when the DMHy/V ratio = 0.945, causing the angular regions of Y1 and X1' to overlap. X1' is closer to the InP XRD peak because the X1' region now contains In-N surrounded by In-As or In-(N-As)_{As}. Therefore, Y1 is the InAsN ternary layer and X1' is InAsN with high arsenic content and an ultra-dilute nitrogen region.

Nitrogen is incorporated into InAs although phase separation occurs. The estimated nitrogen composition in InAsN layer *versus* DMHy/(DMHy+TBAs) molar ratio is plotted in Fig. 6.7. It is assumed that the InAsN is relaxed ($m = m^*$, see chapter 2). The assumption may hold true due to degradation in the epilayer quality due to phase separation or lattice relaxation [46, 101]. The highest nitrogen incorporation into InAsN is for sample R6 with 7.3%N at the DMHy/(DMHy+TBAs) flow ratio of 19.

Figure 6.7 DMHy to total group V molar ratio versus nitrogen composition estimated by XRD of InAsN epilayers grown with hydrogen carrier gas.

Fig. 6.7 implies that incorporation of nitrogen into InAsN needs a high DMHy/V molar ratio. In GaAsN, no “N/V molar ratio threshold” is observed. This is due to larger miscibility between nitrogen and indium atoms in InAsN epilayer compared to that of nitrogen and gallium atoms in GaAsN. Though growth of InAsN has been confirmed by XRD and SIMS (Fig. 6.8), the epilayer quality is not good. Nitrogen compositional fluctuation is shown in the nitrogen count in Fig. 6.8. The fluctuation of [In] is small ($\sim 0.1\%$ to 0.2%) as compared to [N] fluctuation.

Figure 6.8 Elements count in InAsN R5 epilayer by SIMS.

6.3.1 Effect of carrier gas

Carrier gas may have an important role in improving InAsN epilayer quality. X-ray diffraction peaks of InAsN grown with nitrogen and hydrogen as carrier gases are shown in Fig. 6.9. Both samples were prepared under the same growth conditions. InAsN grown with nitrogen carrier gas does not have phase

separation as oppose to that grown with hydrogen carrier gas at the DMHy/(DMHy+TBAs) molar ratio of 0.9. XRD rocking curves show that InAsN grown with nitrogen carrier gas (R7) also has good structural quality despite 4.13% lattice mismatch between the epilayer and the InP substrate. Furthermore, the sample has a specular surface, another indicator of a good-quality crystalline structure.

Figure 6.9 XRD of R5 and R7 grown with hydrogen and nitrogen as the carrier gas, respectively. DMHy to total group V molar ratio is 0.9.

There are two X-ray diffraction peaks for sample R7: an InP substrate peak and another peak labelled as X1. X1 of R7 is similar to X1' of R1 to R6. The difference between X1 and reference InAs [107] is 1.18° , indicating that X1 originates from an InAs layer. Although X1 is determined to be the InAs peak, nitrogen should be incorporated into the epilayer. To confirm nitrogen

incorporation, Raman measurements are carried out for R5 and R7. This method is able to determine same nitrogen bonding in the epilayer, confirming that nitrogen have incorporated into the layer.

R5 and R7 are made under the same growth conditions, except for the carrier gas (Table 6.2). Fig. 6.10 shows Raman spectra of R5 and R7. An InN-like phonon (443 cm^{-1} [118]) of R5 is weaker than in R7. Additionally, there is a shift in the InAs-like peak of R5. This shift is assigned to anitrogen-influenced InAs-like phonon shift [119]. Y1 (from Fig. 6.7 (a)) is likely responsible for this shift. The preferred bonding configuration of InAsN of R5 is InAs_3N . Because the InN-like phonon peak is obvious for R7, In_4N or InN_4 bonding configuration is preferred. Therefore, R7 has nitrogen incorporated into its InAsN epilayer.

Figure 6.10 Raman spectra of R5 and R7 grown with hydrogen and nitrogen carrier gas, respectively.

6.3.2 InAsN single quantum wells and their optical properties

A single quantum well (SQW) is designed, grown, and studied. An InAsN/InGaAs SQW structure is shown in Fig. 6.11. The growth temperature for growth of the quantum well (QW) and the quantum barrier (QB) is set at 500 °C. The TMGa/III ratio was 0.364 for the InP lattice-matched InGaAs barrier. The growth conditions for the InAs(N) follow those of sample R7. An InAs SQW is grown as a reference (W1). Two InAsN SQWs are grown with different DMHy/V molar ratios of 0.88 and 0.9 (W2 and W3) with DMHy flow rate of 500 μmol/min and 600 μmol/min, respectively.

InGaAs ~ 40 nm
InAs(N) ~ 2.5 nm
InGaAs ~ 32 nm
InP buffer
InP substrate

Figure 6.11 InAs and InAsN single QW structure grown on InP substrate with InGaAs barrier.

Low-temperature (30 K) PL spectra of three as-grown samples W1, W2, and W3 are shown in Fig. 6.12. W2 exhibits a red-shift relative to W1, the InAs SQW. The red-shift increases with increasing DMHy to (DMHy+TBAs) molar ratio, indicating higher nitrogen incorporation into the QW with a higher DMHy/V ratio (%N of W3 > %N of W2). The growth rate of InAs and InAsN can be assumed to be constant, since the QW layer is thinner than 3 nm. The red-shift shows the trait of nitrogen incorporation into the W2 and W3 SQW.

Strong emission from the three samples is observed. The PL from the as-grown sample InAsN SQW (W2) deteriorates almost twice as much as PL of the as-grown InAs SQW (W1). This is due to the nitrogen content in W2, which is known to degrade PL intensity. Similarly, sample W3 with the highest N content in SQW has the lowest PL intensity.

Figure 6.12 Low temperature (30K) PL of as-grown samples of W1, W2, and W3.

Excitation PL power is plotted against PL peak position for as-grown W1, W2, and W3 samples in Fig. 6.13. There is less dependency of the W1 PL peak position on excitation power in the high power regime (>25 mW). The overall PL peak shift in W1 is roughly constant, indicating that InAs QW only has one quantum confined energy level. Because of weaker PL from W2 and W3, excitation power ≤ 20 mW does not yield useful PL. W2 and W3 have depend on excitation power. This dependency may be due to compositional fluctuations in

the QW layer [104]. Compositional fluctuation results in quantum state broadening. With increasing excitation power, the increased generated carriers overflow to higher energy states, and hence a further blue-shift will take place at high excitation power. W3 peak position changes more significantly than W1 and W2 with different excitation power. This shows that sample W3 has more compositional fluctuation caused by its nitrogen incorporation. Thus, W3 has more nitrogen incorporated into the QW layer.

Figure 6.13 As-grown W1, W2, and W3 PL peak position dependence of excitation PL power.

From the difference in peak energy of W2 to W1 and W3 to W1, [N] in QW layer of W2 and W3 is estimated. Band gap bowing of InAsN obtained from the previous section is also utilized to estimate nitrogen compositions of W2 and W3. Fluctuation of ± 0.2 nm in QW layer thickness, due to nitrogen incorporation, is

obtained in our estimation. The nitrogen content in QW of W2 is about 0.55 – 0.6 % and in QW of W3 about 1.1 – 1.21%.

Annealing can improve the PL intensity of the samples. The effect of annealing temperature on W1, W2, and W3 is studied. The samples are annealed at 600 °C for 1, 2, and 3 minutes and 700 °C for 30 seconds and 1 minute under nitrogen ambient gas. Spruytte *et al.* [120] stated that annealing temperature (T_{ann}) at shorter time has a similar effect as lower T_{ann} at longer annealing time (t_{ann}). In our case, $(T_{ann}, t_{ann})_1$ and $(T_{ann}, t_{ann})_2$ are chosen so that their influence on the PL of the samples should not be the same, i.e., the next T_{ann}, t_{ann} will have more effect on the samples than the previous T_{ann}, t_{ann} . All annealed samples are covered with an InGaAs sample to prevent As-out diffusion and In diffusion.

Fig. 6.14 shows the from annealed SQW of W1, W2, and W3. PL intensity of W1 and W2 is the highest at T_{ann} and t_{ann} of 600 °C and 3 minutes, while W3 has the highest intensity at T_{ann} and t_{ann} of 700 °C and 30 seconds. This indicates that W3 has a larger amount of defects in its QW than does W2. Since nitrogen incorporation generates defects in the alloy, W3 has a higher nitrogen content than W2. Thermal annealing removes nitrogen-induced defects, causes In-Ga diffusion, thus increases the PL intensity. At the same time, RTA-induced defects are generated (chapter 5) causing a decrease in PL intensity at $T_{ann} \geq 700$ °C and $t_{ann} > 30$ seconds. The broadening in W3 after annealing at 700 °C for 30 seconds is because higher QW intermixing [121-123] induced by higher [N].

Figure 6.14 Low temperature (30K) PL of as-grown and annealed samples of W1, W2, and W3.

Fig. 6.15 shows a plot of PL energy against annealing conditions. The PL peaks of annealed samples shift towards shorter wavelengths, indicating In-Ga and As-N (W2 and W3) diffusion [124]. Annealed samples of W2 and W3 show a similar PL peak shift trend as shows W1. Effects of annealing can be observed from the peak shifts when T_{ann} increases. The trend of the graph can be expressed by equation

$$Peak_{PL} \sim \frac{F_{ann}}{Ann_{T,t}} \quad (6.11)$$

$Peak_{PL}$ is PL peak position in nm; F_{ann} is the influence of annealing on the sample (annealing factor); and $Ann_{T,t}$ is the variable comprises of annealing temperature and annealing time. The effect of annealing at low temperature and long period of time could be the same as that of annealing at high temperature and short period of time. In our experiment, $Ann_{T,t}$ of 700°C and 30 seconds on InAsN samples will have higher impact on their PL intensity than $Ann_{T,t}$ of 600°C and 3 minutes.

By fitting the curve, the annealing factors, F_{ann} , for W1, W2, and W3 are 0.38, 0.5, and 0.7, respectively. Due to its low PL intensity (Fig. 6.13), NR centers in the W3 active QW layer are more than those in the W2 QW layer. Thus, thermal annealing is more effective for sample with the highest F_{ann} ; i.e., sample W3.

Figure 6.15 PL peak position of S80, S81, S82 against as-grown and annealed samples.

6.4 Summary

To further increase the emission wavelength in the mid-infrared region, InAsN is studied. E_g of InAsN reported in the literature is calculated by tight binding and pseudopotential methods. The former overestimates while the latter underestimates the InN band gap energy, which influences the overall results of the calculated band gap energy of InAsN. To improve the computational results, we compute E_g using density functional theory (DFT). In DFT, the many-body wave-function is replaced with electron density. Therefore, there is no need to solve equations involving many variables. Instead, it will be simpler to solve the energy in terms of the electron density. From DFT calculations, agreement is found reasonable with the available experimental results. The minimum band gap energy predicted for $\text{InAs}_{1-x}\text{N}_x$ with $x = 0.45$ is 0.075 eV. Through curve fitting, a

more accurate band gap energy bowing parameter c of unstrained $\text{InAs}_{1-x}\text{N}_x$ alloys is revised to be 2.072 eV, which is lower than c obtained from the tight binding method (4.22 eV) and higher than c of the pseudopotential (1.6 eV) method.

MOCVD growths of InAsN have also been studied with different carrier gases: hydrogen and nitrogen carrier gases. It is found that InAsN grown with hydrogen carrier gas has phase separated into InAs with a very low concentration of nitrogen and InAsN alloys. Such a phase separation is not found for InAsN when prepared with nitrogen as a carrier gas. InAsN incorporates up to 7.3% mole fraction of nitrogen at a DMHy-to-TBAs flow ratio of 19. To study nitrogen incorporation effect on InAsN optical properties, InAsN/InGaAs single quantum well (SQW) structures are grown with nitrogen as a carrier gas. InAs/InGaAs SQW with the same thickness under similar growth conditions is used for comparison. PL measurements show that the InAsN SQW emission peak red-shifts with respect to InAs/InGaAs SQW. InAsN SQW with a higher DMHy-to-TBAs flow ratio has a larger red-shift, an indication that more nitrogen is incorporated into the InAsN QW. The InAsN SQW with a higher nitrogen content requires higher T_{ann} to improve its optical performance. The nitrogen content of the InAsN QW with a DMHy-to-TBAs flow ratio of 7.3 is at least 1.1%.

Chapter 7

Conclusion and Recommendations

7.1 Conclusion

This thesis presents studies on nitrogen incorporation into GaAs, InAs, and InGaAs semiconductor alloys which are grown by metalorganic chemical vapor deposition. Effects of growth conditions on nitrogen incorporation as well as effects of nitrogen on various physical properties of (In,Ga)As are explored.

GaAsN has been studied extensively with respect to its nitrogen incorporation under different MOCVD growth conditions. It has been found that the reactor pressure, V/III molar ratio, and carrier gas play important roles in increasing the nitrogen content of GaAsN. Nitrogen carrier gas can increase nitrogen incorporation by a factor of three compared to hydrogen carrier gas under the same growth conditions. Nitrogen incorporation into GaAsN increases linearly with the ratio of asymmetrical dimethylhydrazine (DMHy) to tertiarybutylarsine (TBAs) flow rates. GaAsN with nitrogen content up to 5% has been successfully grown. The optimized growth temperature and reactor pressure for GaAsN growth have been determined for good-quality epilayers.

Nitrogen in GaAsN degrades optical properties of the alloy. Thermal annealing is known to improve PL from GaAsN materials. At optimal annealing conditions the highest intensity is obtained. The optimum annealing condition is found to depend on nitrogen content. Optimal T_{ann} decreases, as the amount of N in GaAsN increases. For example, optimum T_{ann} at 1.3% N is 625°C as compared

to 725°C for the sample with 0.7%N. Capping the GaAsN epilayer with an oxide layer (SiO₂) before annealing affects the optical performance. The optical performance of oxide-capped GaAsN alloy after annealing is better than the uncapped ones.

The miscibility gap of nitrogen in GaAsN not only generates non-radiative defects, which degrades band-to-band transitions, but also introduces an additional peak in PL. The additional peak under study is found to be due to nitrogen interstitials. There exist no PL spectra reported on N-N interstitials, but we find that these interstitials cause a distinct PL peak with an energy of 0.2 eV below the band-to-band transition peak. The N-N interstitials are found in GaAsN epilayers grown under nitrogen carrier gas, but they are not observed in the samples grown under hydrogen carrier gas. The reason for this is attributed to reaction species available on the growing surface.

An empirical equation to calculate the percentage of nitrogen interstitials in the GaAsN epilayers has been derived. It is found that the concentration of interstitials is within 10% of the experimental values. The empirical equation encompasses five parameters used in GaAsN growth conditions: the type of carrier gas used, growth temperature, reactor pressure, and group V-to-group III molar ratio as well as nitrogen-to-total group V molar ratio during MOCVD growth. The model provides a good prediction of growth conditions to minimize N-N interstitial incorporation for high-quality growth of GaAsN using nitrogen carrier gas.

To further increase the emission wavelength available with GaAsN, the InAsN alloy is studied. The energy band gap of InAsN reported in the literature

was calculated by tight binding or pseudopotential methods. The former overestimates, while the latter underestimates the InN band gap energy that influences the overall results of the calculated band gap energy of InAsN. To improve the computational results, we calculate E_g using the density functional theory. The agreement is found to be reasonable with the available experimental results. The minimum E_g predicted for $\text{InAs}_{1-x}\text{N}_x$ is 0.075 eV when $x = 0.45$. Through curve fitting, a more accurate band gap energy bowing parameter of unstrained $\text{InAs}_{1-x}\text{N}_x$ alloys is revised to be 2.072 eV, which is lower than the value obtained by using the tight binding (4.22 eV) but higher than that of pseudopotential (1.6 eV) method.

MOCVD of InAsN have also been studied using different carrier gases: hydrogen and nitrogen carrier gases. It has been found that InAsN grown with the hydrogen carrier gas has phase-separated into InAs (with a very low concentration of nitrogen) and InAsN. The phase separation has not been found when the nitrogen carrier gas is employed. InAsN incorporates up to 7.3% mole fraction of nitrogen at the DMHy to TBAs flow ratio of 19. To study the nitrogen incorporation effect on InAsN optical properties, InAsN/InGaAs single quantum well (SQW) structures have been grown with nitrogen carrier gas. An InAs/InGaAs SQW with the same thickness and grown under similar conditions is used for comparison. PL measurements show that the InAsN SQWs emission peak red-shifts relative to the InAs/InGaAs SQW. InAsN SQWs with a higher DMHy to TBAs flow ratio have larger red shifts, which implies that more nitrogen was incorporated in InAsN QW. InAsN SQW with higher nitrogen content requires higher annealing temperature to improve its optical performance.

[N] in the InAsN QW layer prepared with a DMHy-to-TBAs flow ratio of 7.3 is at least 1.1%.

7.2 Recommendations

InGaAsN is an interesting material for infrared applications. However, there is a difficulty in determining the indium (or gallium) and nitrogen contents. Normally, XRD and PL studies are combined to deduce the indium and nitrogen contents of the alloy. However, it is challenging to obtain emission from InGaAsN with high indium and/or nitrogen contents, i.e., no PL appears. Raman spectra can be utilized to determine bonding configuration of the alloys. The relationship between nitrogen and indium bonding configurations to the nitrogen and indium contents of the alloy is worth investigating. Furthermore, the relationship between nitrogen or indium preferential bonding configuration in the InGaAsN alloys and the energy band gap E_g of the alloys are interesting to be studied.

InAsN is predicted to have emission wavelengths at far infrared regions. However, any study of InAsN is deterred by difficulties in incorporating nitrogen into the InAsN epilayer. Luminescence properties are obtained from quantization of the band gap energy, i.e., InAsN QW's or quantum dots. To continue from this thesis, growth conditions for the InAsN epilayer on the InP substrate should be optimized. The relationship of nitrogen incorporation in the InAsN epilayer *versus* growth temperature, reactor pressure, V/III molar ratio, and the type of carrier gas used during growth should be investigated in details. Substrate orientation, such as (111) instead of (100), is another factor to be considered to increase nitrogen incorporation. The optimization of growth conditions aims to achieve good

epilayers with fewer defects or dislocations. Antimony is known to reduce dislocations [125] and improve the epilayer quality [126]. TEM and XRD have been employed to determine that the grown epilayer is good in structural quality.

After optimization of the growth conditions, emission from InAsN with different nitrogen contents is the next goal. The band gap obtained from a PL study will be compared with a theoretical study in chapter 6 section 6.2.4 (Fig. 6.6). If the experimental band bowing parameter of InAsN is similar to the calculated one, the bowing parameter of 2.072 eV is established for InAsN. If there is a discrepancy between the experimental and calculated bowing parameters, then the calculation parameter, such as the cell numbers, k -points, and atomic structure of InAsN, will be adjusted.

Thermal annealing studies of light emission from InAsN will be carried out for samples exhibiting with weak emission or no emission at all. Because thermal annealing can promote In-Ga or N-As interdiffusion causing a blue-shift in PL [124], a study to prevent or reduce the interdiffusion should be carried out. Capping the samples with Si_3N_4 is reported to prevent such interdiffusion [28]. A study on the type of capping for the sample before thermal annealing to prevent interdiffusion is interesting. Further study on the effectiveness of thermal annealing over epilayer degradation should be carried out.

Next, InAsN single quantum well, multiple quantum wells, or quantum dots can be studied to obtain high emission intensity. However, the structures will cause the emission peak to blue-shift as compared to emission of the epilayer. Choice of the barrier layer should be carefully chosen to obtain the emission

wavelength as long as possible and the emission intensity as high as possible.

Thermal annealing of the sample should also be considered to achieve the goal.

Author's Publications

Publications in refereed journals

1. Deny Sentosa, Tang Xiaohong, Yin Zongyou, Chua Soo Jin, "Thermal annealing effect on GaNAs epilayers with different nitrogen compositions grown by MOVCD", *Journal of Crystal Growth* **307**, 229- 234 (2007).
2. Deny Sentosa, Tang Xiaohong, Chua Soo Jin, "InN_xAs_{1-x} band gap energy and band bowing coefficient calculation", *The European Physical Journal Applied Physics* **40**, 247-251 (2007).
3. Deny Sentosa, Tang Xiaohong, Chua Soo Jin, Yin Zongyou, "Below Bandgap Emission with Intensity Higher than Band-to-Band Transition in GaAsN", *Physica Status Solidi (c)* **5**, 464–466 (2008).
4. Deny Sentosa, Tang Xiaohong, Chua Soo Jin, "Luminescence from the deep level N-N interstitials in GaAsN grown by metal organic chemical vapor deposition", *submitted to Crystal Engineering Communications*.
5. Deny Sentosa, Tang Xiaohong, Chua Soo Jin, "Investigation of N-N Interstitials in GaAsN Grown by Metal Organic Chemical Vapor Deposition", *submitted to materials science in semiconductor processing*.

Conference/symposium presentations

1. Deny Sentosa, Tang Xiaohong, Yin Zongyou, Zhao Jinghua, "Photoluminescence of GaNAs epilayers on GaAs grown by MOCVD", *International Conference on Materials for Advanced Technologies (ICMAT)*, Singapore 2005.
2. Deny Sentosa, Tang Xiaohong, Yin Zongyou, Chua Soo Jin, "Thermal annealing effect on GaNAs epilayers with different nitrogen compositions

grown by MOVCD”, *International Conference on Materials for Advanced Technologies (ICMAT)*, Singapore 2005.

3. Deny Sentosa, Tang Xiaohong, Chua Soo Jin, Yin Zongyou, “Below Bandgap Emission with Intensity Higher than Band-to-Band Transition in GaAsN”, *European Materials Research Society (EMRS) Spring*, Strasbourg 2007.
4. Deny Sentosa, Tang Xiaohong, Chua Soo Jin, Yin Zongyou, “Nitrogen Interstitial Defects in GaNAs Films Grown by MOCVD”, *International Conference on Materials for Advanced Technologies (ICMAT)*, Singapore 2007.

Bibliography

- [1] P. R. C. Kent, L. Bellaiche, Alex Zunger, "Pseudopotential theory of dilute III-V nitrides", *Semiconductor Science and Technology* **17**, 851-859 (2002).
- [2] I. A. Buyanova, G. Pozina, P. N. Hai, W. M. Chen, H. P. Xin, C. W. Tu, "Evidence for type I band alignment in GaNAs/GaAs quantum structures by optical spectroscopies", *Physica E* **13**, 1074-1077 (2002).
- [3] J. R. Lee, Y. Y. Chen, C. R. Lu, Wei-I Lee, S. C. Lee, "Electrooptical properties of GaNAs/GaAs multiple quantum well structures", *Material Science and Engineering B* **100**, 248-251 (2003).
- [4] A. Lindsay, E. P. O'Reilly, "Influence of nitrogen resonant states on the electronic structure of $\text{GaN}_x\text{As}_{1-x}$ ", *Solid State Communications* **118**, 313-317 (2001).
- [5] P. N. Hai, W. M. Chen, I. A. Buyanova, B. Monemar, H. P. Xin, C. W. Tu, "Properties of GaAsN/GaAs quantum wells studied by optical detection of cyclotron resonance", *Material Science and Engineering B* **82**, 218-220 (2001).
- [6] A. Lindsay, S. Tomić, E. P. O'Reilly, "Derivation of a 10-band $\mathbf{k}\cdot\mathbf{p}$ model for dilute nitride semiconductors", *Solid-State Electronics* **47**, 443-446 (2003).
- [7] T. Miyamoto, S. Sato, Zhong Pan, D. Schlenker, F. Koyama, K. Iga, "GaNAs/GaInAs short-period superlattice quantum well structures grown by MOCVD using TBAs and DMHy", *Journal of Crystal Growth* **195**, 421-426 (1998).
- [8] F. Saidi, F. Hassen, M. Maaref, L. Auvray, H. Dumont, Y. Monteil, "Excitons localization effects in GaAsN/GaAs epilayers grown by MOCVD", *Materials Science and Engineering C* **21**, 245-249 (2002).
- [9] Hyunseok Na, Hyun Jin Kim, Euijoon Yoon, C. Sone, Y. Park, "Arsenic incorporation and growth mode of GaNAs grown by low-pressure metal-organic chemical vapor deposition", *Journal of Crystal Growth* **248**, 437-440 (2003).
- [10] M. Takahashi, A. Moto, So Tanaka, T. Tanabe, S. Takagishi, K. Karatani, M. Nakayama, K. Matsuda, T. Saiki, "Observation of compositional fluctuations in GaNAs alloys grown by metalorganic vapor-phase epitaxy", *Journal of Crystal Growth* **221**, 461-466 (2000).
- [11] A. Kimura, H. F. Tang, T. F. Kuech, "Growth of GaNAs alloys on the N-rich side with high As content by metalorganic vapor phase epitaxy", *Journal of Crystal Growth* **265**, 71-77 (2004).

- [12] S. Sanorpim, F. Nakajima, R. Katayama, K. Onabe, "MOVPE growth window for high-Nitrogen GaAsN alloy films for long wavelength emission", in *International Conference on Materials for Advanced Technologies (ICMAT)*, Singapore, 2007.
- [13] A. Nishikawa, R. Katayama, K. Onabe, Y. Shiraki, "MBE growth and photoreflectance study of GaAsN alloy films grown on GaAs (0 0 1)", *Journal of Crystal Growth* **251**, 427-431(2003).
- [14] H. Carrere, X. Mariel, B. Messant, M. Boutillier, O. Gauthier-Lafaye, S. Bonnefont, F. Lozes-Dupuy, B. Dagens, F. Alexandre, "Optical gain in 1.55 μm tensile strained InGaAsN/InP lasers", in *European Materials Research Society (EMRS) Spring*, Strasbourg, France, 2007.
- [15] K. Uesugi, Ikuo Suemune, "Metalorganic molecular beam epitaxy of GaNAs alloys on (0 0 1)GaAs", *Journal of Crystal Growth* **189/190**, 490-495 (1998).
- [16] Z. Pan, Y. T. Wang, L. H. Li, W. Zhang, Y. W. Lin, Z. Q. Zhou, R. H. Wu, "X-ray double-crystal characterization of the strain relaxation in GaAs/Ga_{N_x}As_{1-x}/GaAs(0 0 1) sandwiched structures", *Journal of Crystal Growth* **217**, 26-32 (2000).
- [17] A. Ougazzaden, Y. Le. Bellego, E. V. K. Rao, M. Juhel, L. Leprince, G. Patriarche, "Metal organic vapor phase epitaxy growth of GaAsN on GaAs using dimethylhydrazine and tertiarybutylarsine", *Applied Physics Letter* **70**, 2861-2863 (1997).
- [18] G. B. Stringfellow, *Organometallic Vapor-Phase Epitaxy: Theory and Practice*, Academic Press, Inc., 1989.
- [19] H. Miyake, A. Motogaito K. Hiramatsu, "Effects of reactor pressure on epitaxial lateral overgrowth of GaN via low-pressure metalorganic vapor phase epitaxy", *Japanese Journal of Applied Physics* **38**, L1000-L1002 (1999).
- [20] M. Ramsteiner, D. S. Jiang, J. S. Harris, K. H. Ploog, "Nonradiative recombination centers in Ga(As,N) and their annealing behavior studied by Raman spectroscopy", *Applied Physics Letter* **84**, 1859-1861 (2004).
- [21] S. Francoeur, G. Sivaraman, Y. Qiu, S. Nikishin, H. Temkin, "Luminescence of as-grown and thermally annealed GaAsN/GaAs", *Applied Physics Letter* **72**, 1857-1859 (1998).
- [22] J. F. Chen, J. S. Wang, M. M. Huang, N. C. Chen, "Annealing dynamics of nitrogen-implanted GaAs films investigated by current-voltage and deep-level transient spectroscopy", *Applied Physics Letter* **76**, 2283-2285 (2000).

- [23] P. Klangtakai, S. Sanorpim, K. Yoodee, W. Ono, F. Nakajima, R. Katayama, K. Onabe, "Post-growth thermal annealing of high N-content GaAsN by MOVPE and its effect on strain relaxation", *Journal of Crystal Growth* **298**, 140-144 (2007).
- [24] L.F. Bian, D.S. Jiang, S.L. Lu, "Optical investigation on the annealing effect and its mechanism of GaInAs/GaNAs quantum wells", *Journal of Crystal Growth* **253**, 155-160 (2003).
- [25] W. K. Loke, S. F. Yoon, S. Z. Wang, T. K. Ng, W. J. Fan, "Rapid thermal annealing of GaN_xAs_{1-x} grown by radio-frequency plasma assisted molecular beam epitaxy and its effect on photoluminescence", *Journal of Applied Physics* **91**, 4900-4903 (2002).
- [26] G. Mussler, J. M. Chauveau, A. Trampert, M. Ramsteiner, L. Däweritz, K. H. Ploog, "Nitrogen-dependent optimum annealing temperature of Ga(As,N)", *Journal of Crystal Growth* **267**, 60-66 (2004).
- [27] H. F. Liu, C. S. Peng, J. Likonen, T. Jouhti, S. Karirinne, J. Konttinen, M. Pessa, "Influence of nitride and oxide cap layers upon the annealing of 1.3 μm GaInNAs/GaAs quantum wells", *Journal of Applied Physics* **95**, 4102-4104 (2004).
- [28] S. Gwo and S. Y. Huang, T. R. Yang, "Enhancement of the direct optical transition in nanocrystallized GaAsN alloys", *Physical Review B* **64**, 113312 (2001).
- [29] B. A. Weinstein, S. R. Stambach, T. M. Ritter, J. O. Maclean, D. J. Wallis, "Pressure studies of conduction-band N-pair-state mixing in dilute GaAs_{1-x}N_x alloys", *Physica E* **20**, 317-320 (2004).
- [30] X. Liu, M.E. Pistol, L. Samuelson, S. Schwetlick, W. Seifert, "Nitrogen pair luminescence in GaAs", *Applied Physics Letter* **56**, 1451-1453 (1990).
- [31] P. R. C. Kent, A. Zunger, "Theory of electronic structure evolution in GaAsN and GaPN alloys", *Physical Review B* **64**, 115208 (2001).
- [32] Y. Zhang, A. Mascarenhas, J. F. Geisz, "Discrete and continuous spectrum of nitrogen-induced bound states in heavily doped GaAs_{1-x}N_x", *Physical Review B* **63**, 085205 (2001).
- [33] Y. Zhang, A. Mascarenhas, "Isoelectronic impurity states in GaAs:N", *Physical Review B* **61**, 15562-15564 (2000).
- [34] J. Toivonen, J. Oila, K. Saarinen, T. Hakkarainen, M. Sopanen, H. Lipsanen, "Vacancy-type defects in GaAsN grown by metalorganic vapor phase

- epitaxy”, in *Indium Phosphide and Related Materials (IPRM) Conference 14th*, 245-248 (2002).
- [35] A. Y. Polyakov, N. B. Smirnov, A. V. Govorkov, A. E. Botchkarev, N. N. Nelson, M. M. E. Fahmi, J. A. Griffin, A. Khan, S. Noor Mohammad, D. K. Johnstone, V. T. Bublik, K. D. Chsherbachev, M. I. Voronova, V. S. Kasatochkin, ”Optical properties and defects in GaAsN and InGaAsN films and quantum well structures”, *Solid State Electronics* **46**, 2147-2153 (2002).
- [36] H. Yaguchi, G. Biwa, S. Miyoshi, D. Aoki, K. Arimoto, K. Onabe, R. Ito, Y. Shiraki, ”Temperature dependence of photoluminescence of GaP_{1-x}N_x alloys”, *J. Cryst. Growth* **189/190**, 496-499 (1998).
- [37] S. B. Zhang, S. H. Wei, ”Nitrogen solubility and N-induced defect complexes in epitaxial GaAs :N”, *Physica B* **308-310**, 839-842 (2001).
- [38] W. J. Fan, S. F. Yoon, T. K. Ng, S. Z. Wang, W. K. Loke, R. Liu, A. Wee, ”Comparison of nitrogen compositions in the as-grown GaN_xAs_{1-x} on GaAs measured by high-resolution x-ray diffraction and secondary-ion mass spectroscopy”, *Applied Physics Letter* **80**, 4136-4138 (2002).
- [39] P. Krispin, S. G. Spruytte, J. S. Harris, K. H. Ploog, ”Deep-level defects in MBE-grown Ga(As,N) layers”, *Physica B* **308-310**, 870-873 (2001).
- [40] S. Thomas, S. White, P. R. Chalker, T. J. Bullough, T. B. Joyce, ”Nitrogen incorporation in GaInNAs and GaAsN near the solubility limit”, *Journal of Materials Science: Materials in Electronics* **13**, 525-529 (2002).
- [41] J. Wagner, T. Geppert, K. Kohler, P. Ganser, M. Maier, ”Bonding of nitrogen in dilute GaInAsN and AlGaAsN studied by Raman spectroscopy”, *Solid-State Electronics* **47**, 461-465 (2003).
- [42] J. Wagner, T. Geppert, K. Kohler, P. Ganser, N. Herres, ”N-induced vibrational modes in GaAsN and GaInAsN studied by resonant Raman scattering”, *Journal of Applied Physics* **90**, 5027-5031 (2001).
- [43] P.J. Klar, H. Grüning, J. Koch, S. Schafer, K. Volz, W. Stolz, W. Heimbrodt, A. M. Kamal Saadi, A. Lindsay, E. P. O'Reilly, ”(Ga, In)(N, As)-fine structure of the band gap due to nearest-neighbor configurations of the isovalent nitrogen”, *Physical Review B* **64**, 121203 (2001).
- [44] Y. Saito, H. Harima, E. Kurimoto, T. Yamaguchi, N. Teraguchi, A. Suzuki, T. Araki, Y. Nanishi, ”Growth Temperature Dependence of Indium Nitride Crystalline Quality Grown by RF-MBE”, *Physica Status Solidi B* **234**, 796-800 (2002).

- [45] H. Naoi, Y. Naoi, S. Sakai, "MOCVD growth of InAsN for infrared applications", *Solid State Electronics* **41**, 319-321 (1997).
- [46] H. Naoi, D. M. Shaw, Y. Naoi, G. J. Collins, S. Sakai, "Growth of InNAs by low-pressure metalorganic chemical vapor deposition employing microwave-cracked nitrogen and in situ generated arsine radicals", *Journal of Crystal Growth* **222**, 511-517 (2001).
- [47] A. A. El-Emawy, H. J. Cao, E. Zhmayev, J. H. Lee, D. Zubia, M. Osinski, "MOCVD Growth of $\text{InN}_x\text{As}_{1-x}$ on GaAs Using Dimethylhydrazine", *Physica Status Solidi (b)* **228**, 263-267 (2001).
- [48] M. Osinski, "InNAs – a new optoelectronic material for mid-infrared applications", *Opto-Electronics Review* **11**, 321-326 (2003).
- [49] L. Auvray, H. Dumont, J. Dazord, Y. Monteil, J. Bouix, C. Bru-Chevallier, L. Grenouillet, "MOVPE growth of GaAsN: surface study by AFM and optical properties", *Materials Science in Semiconductor Processing* **3**, 505-509 (2000).
- [50] Nacir Tit, M. W. C. Dharma-wardana, "Electronic structure of $\text{InN}_x\text{As}_{1-x}$ alloys from tight-binding calculations", *Applied Physics Letter* **76**, 3576-3578 (2000).
- [51] T. Yang, S. Nakajima, S. Sakai, "Tight-binding calculation of electronic structures of InNAs alloys", *Japanese Journal of Applied Physics* **36**, L 320-L 322 (1997).
- [52] E. P. O'Reilly, A. Lindsay, S. Tomić, M. Kamal-Saadi, "Tight-binding and k-p models for the electronic structure of Ga(In)NAs and related alloys", *Semiconductor Science and Technology* **17**, 870-879 (2002).
- [53] S. Nakajima, D. Ikeda, S. Sakai, "Electronic structures of GaNP and InNAs ordered alloys calculated by the pseudopotential method", *Institute of Pure and Applied Physics Conference Series* **1**, 441-443 (2000).
- [54] J. Wu, W. Walukiewicz, K.M. Yu, J.W. Ager III, S.X. Li, E.E. Haller, Hai Lu, William J. Schaff, "Universal band gap bowing in group-III nitride alloys", *Solid State Communications* **127**, 411-414 (2003).
- [55] I. Vurgaftman, J. R. Meyer, "Band parameters for nitrogen-containing semiconductors", *Journal of Applied Physics* **94**, 3675-3696 (2003).
- [56] K. Iga, S. Kinoshita, *Process Technology for Semiconductor Lasers*, Springer Series in Materials Science, 1995.
- [57] C. Sirtori, J. Nagle, "Quantum cascade lasers: the quantum technology for semiconductor lasers in the mid-far-infrared", *Comptes Rendus Physique* **4**, 639-648 (2003).

- [58] F. Capasso, A. Tredicucci, C. Gmachl, D. L. Sivco, A. L. Hutchinson, A. Y. Cho, G. Scamarcio, "High-performance superlattice quantum cascade lasers", *IEEE Journal of Selected Topics in Quantum Electronics* **5**, 792-807 (1999).
- [59] A. Joullié, P. Christol, "GaSb-based mid-infrared 2-5 μm laser diodes", *Comptes Rendus Physique* **4**, 621-637 (2003).
- [60] G. Xiuying, Y. Bauhua, M. Yindi, G. Fensheng, Yu Ying, H. Wenjian, L. Xuefeng, Xi Jinying, W. Zuango, L. Lanying, "Liquid phase epitaxy growth and properties of GaInAsSb/ AlGaAsSb/ GaSb heterostructures", *Japanese Journal of Applied Physics* **30**, 1343-1347 (1991).
- [61] Seung-Hwan Kim, S. S. Li, "Theoretical investigation of InAs/ GaInSb type-II superlattice infrared detectors for long wavelength and very long wavelength infrared applications", *Physica E* **16**, 199-208 (2003).
- [62] S. P. DenBaars, B. Y. Ma, P. D. Dapkus, A. D. Danner, H. C. Lee, "Homogeneous and heterogeneous thermal decomposition rates of trimethylgallium and arsine and their relevance to the growth of GaAs by MOCVD", *Journal of Crystal Growth* **77**, 188-193 (1986).
- [63] C. A. Larsen, G. B. Stringfellow, "Decomposition kinetics of OMVPE precursors", *Journal of Crystal Growth* **75**, 247-254 (1986).
- [64] Sadao Adachi, *Physical properties of III-V semiconductor compounds: InP, InAs, GaAs, GaP, InGaAs, and InGaAsP*, Wiley-VCH, 1992.
- [65] D. J. Wolford, J. A. Bradley, K. Fry, and J. Thompson, "Nitrogen isoelectronics traps in GaAs", in *Proceedings of the 17th International Conference of the Physics of Semiconductors*, San Francisco, CA, USA, Springer-Verlag, New York, 627-630 (1985).
- [66] J. D. Perkins, A. Mascarenhas, Yong Zhang, J. F. Geisz, D. J. Friedman, J. M. Olson, S. R. Kurtz, "Nitrogen-Activated Transitions, Level Repulsion, and Band Gap Reduction in $\text{GaAs}_{1-x}\text{N}_x$ with $x < 0.03$ ", *Physical Review Letter* **82**, 3312-3315 (1999).
- [67] X. Liu, M.-E. Pistol, L. Samuelson, "Excitons bound to nitrogen pairs in GaAs", *Physical Review B* **42**, 7504-7512 (1990).
- [68] M. M. E. Fahmi, Arif Khan, J. A. Griffin, G. L. Harris, L. H. Robins, A. G. Birdwell, Y. S. Kang, D. J. Smith, T. Steiner, S. N. Mohammad, "Nitrogen-activated bowing of dilute $\text{In}_y\text{Ga}_{1-y}\text{As}_{1-x}\text{N}_x$ based on photorefectance studies", *Journal of Applied Physics* **94**, 7576-7580 (2003).

- [69] M. J. Jou, G. B. Stringfellow, "Organometallic vapor phase epitaxial growth studies of $\text{GaP}_{1-x}\text{Sb}_x$ and $\text{InP}_{1-x}\text{Sb}_x$ ", *Journal Crystal Growth* **98**, 679-689 (1989).
- [70] G. B. Stringfellow, "Thermodynamics aspects of organometallic vapor phase epitaxy", *Journal of Crystal Growth* **62**, 225-229 (1983).
- [71] C. Jin, Y. Qiu, S.A. Nikishin, H. Temkin, "Nitrogen incorporation kinetics in metalorganic molecular beam epitaxy of GaAsN", *Applied Physics Letter* **74**, 3516-3518 (1999).
- [72] Z. Pan, L.H. Li, W. Zhang, Y.W. Lin, R.H. Wu, "Kinetic modeling of N incorporation in GaInNAs growth by plasma-assisted molecular-beam epitaxy", *Applied Physics Letter* **77**, 214-216 (2000).
- [73] G. B. Stringfellow, M. J. Cherng, "OMVPE growth of $\text{GaAs}_{1-x}\text{Sb}_x$: solid composition", *Journal of Crystal Growth* **64**, 413-415 (1983).
- [74] D. Sentosa, Tang Xiaohong, S. J. Chua, and Zongyou Yin, "Below bandgap emission with intensity higher than band-to-band transition in GaAsN", *Physica Status Solidi (c)* **5**, 464-466 (2008).
- [75] Sarah Kurtz, R. Reedy, B. Keyes, Greg D. Barber, J.F. Geisz, D.J. Friedman, W.E. McMahon, J.M. Olson, "Evaluation of NF_3 versus dimethylhydrazine as N sources for GaAsN", *Journal of Crystal Growth* **234**, 323-326 (2002).
- [76] W. G. Bi, C. W. Tu, "Bowing parameter of the band-gap energy of $\text{GaN}_x\text{As}_{1-x}$ ", *Applied Physics Letter* **70**, 1608-1610 (1997).
- [77] L. Bellaiche, S. H. Wei, Alex Zunger, "Band gaps of GaPN and GaAsN alloys", *Applied Physics Letter* **70**, 3558-3560 (1997).
- [78] X. Salzmänn, R. Tempkin, "III-V-N compounds for infrared applications", *Materials Science and Engineering B* **50**, 148-152 (1997).
- [79] H. Grüning, L. Chen, T. Hartmann, P.J. Klar, W. Heimbrod, F. Hohnsdorf, J. Koch, W. Stolz, "Optical spectroscopies studies of N-related bands in $\text{Ga}(\text{N},\text{As})$ ", *Physica Status Solidi (b)* **215**, 39-45 (1999).
- [80] P.J. Klar, H. Grüning, W. Heimbrod, J. Koch, W. Stolz, P.M.A. Vicente, A.M. Kamal Saadi, A. Lindsay, E.P. O'Reilly, "Pressure and Temperature Dependent Studies of $\text{GaN}_x\text{As}_{1-x}$ /GaAs Quantum Well Structures", *Phys. Status Solidi (b)* **223**, 163-169 (2001).
- [81] B. Gil, "Elementary description of the optical properties of GaAsN alloys with small nitrogen content", *Solid State Communications* **114**, 623-626 (2000).
- [82] E. Arola, J. Ojanen, H. P. Komsa, T. T. Rantala, "Atomic and electronic structures of N interstitials in GaAs", *Physical Review B* **72**, 045222 (2005).

- [83] S. Z. Wang, S. F. Yoon, W. K. Loke, C. Y. Liu, S. Yuan, "Origin of photoluminescence of GaAsN/GaN(0 0 1) layers grown by plasma-assisted solid source molecular beam epitaxy", *Journal of Crystal Growth* **255**, 258-265 (2003).
- [84] P. Carrier, S. H. Wei, S. B. Zhang, and S. Kurtz, "Evolution of structural properties and formation of N-N split interstitials in GaAs_{1-x}N_x alloys", *Physical Review B* **71**, 165212 (2005).
- [85] T. Ahlgren, E. Vainonen-Ahlgren, J. Likonen, W. Li, and M. Pessa, "Concentration of interstitial and substitutional nitrogen in GaN_xAs_{1-x}", *Applied Physics Letter* **80**, 2314-2316 (2002).
- [86] W. K. Cheah, W. J. Fan, S. F. Yoon, T. K. Ng, W. K. Loke, D. H. Zhang, T. Mei, R. Liu, A. T. S. Wee, "Investigation of N incorporation in InGaAs and GaAs epilayers on GaAs using solid source molecular beam epitaxy", *Journal of Crystal Growth* **275**, 440-447 (2005).
- [87] Y. M. Sun, D.W. Sloan, M. McEllistrem, A.L. Schwaner, J.M. White, "Surface chemistry of 1,1-dimethylhydrazine on GaAs(100)", *Journal of Vacuum Science and Technology A* **13**, 1455-1460 (1995).
- [88] A.J. Ptak, Sarah Kurtz, C. Curtis, R. Reedy, J.M. Olson, "Incorporation effects in MOCVD-grown (In)GaAsN using different nitrogen precursors", *Journal of Crystal Growth* **243**, 231-237 (2002).
- [89] D.J. Friedman, A.G. Norman, J.F. Geisz, S.R. Kurtz, "Comparison of hydrazine, dimethylhydrazine, and t-butylamine nitrogen sources for MOVPE growth of GaInNAs for solar cells", *Journal of Crystal Growth* **208**, 11-17 (2000).
- [90] Y. Gao, "A new secondary ion mass spectrometry technique for III-V semiconductor compounds using the molecular ions CsM⁺", *Journal of Applied Physics* **64**, 3760-3762 (1988).
- [91] C. B. Soh, S. J. Chua, W. Liu, M. Y. Lai, S. Tripathy, "Anomalous optical transitions in AlInGaN/GaN heterostructures grown by metalorganic chemical vapor deposition", *Solid State Communications* **136**, 421-426 (2005).
- [92] R. J. Potter, N. Balkan, "Optical properties of GaNAs and GaInAsN quantum wells", *Journal of Physics: Condensed Matter* **16**, S3387-S3412 (2004).
- [93] I. A. Buyanova, W. M. Chen, G. Pozina, P. N. Hai, B. Monemar, H. P. Xin, C. W. Tu, "Optical properties of GaNAs/GaAs structures", *Materials Science and Engineering B* **82**, 143-147 (2001).
- [94] A. Hashimoto, T. Kitano, A.K. Nguyen, A. Masuda, A. Yamamoto, S. Tanaka, M. Takahashi, A. Moto, T. Tanabe, S. Takagishi, "Raman characterization of lattice-

- matched GaInAsN layers grown on GaAs (0 0 1) substrates”, *Solar Energy Materials & Solar Cells* **75**, 313-317 (2003).
- [95] A. Hashimoto, T. Furuhashi, T. Kitano, A.K. Nguyen, A. Masuda, A. Yamamoto, “RF-MBE growth and Raman scattering characterization of lattice-matched GaInNAs on GaAs(0 0 1) substrates”, *Journal of Crystal Growth* **227–228**, 532-535 (2001).
- [96] W. Shan, W. Walukiewicz, and J. W. Ager III, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, “Band Anticrossing in GaInNAs Alloys”, *Physical Review Letters* **82**, 1221-1224 (1999).
- [97] M. R. Gokhale, J. Wei, HS Wang, S. R. Forrest, “Growth and characterization of small band gap (~ 0.6 eV) InGaAsN layers on InP”, *Applied Physics Letter* **74**, 1287-1289 (1999).
- [98] D.J. Friedman, J.F. Geisz, S.R. Kurtz, J.M. Olson, R. Reedy, “Nonlinear dependence of N incorporation on In content in GaInNAs”, *Journal of Crystal Growth* **195**, 438-443 (1998).
- [99] T. Miyamoto, T. Kageyama, S. Makino, D. Schlenker, F. Koyama, K. Iga, “CBE and MOCVD growth of GaInNAs”, *Journal of Crystal Growth* **209**, 339-344 (2000).
- [100] K. Kim, A. Zunger, “Spatial Correlations in GaInAsN Alloys and their Effects on Band-Gap Enhancement and Electron Localization”, *Physical Review Letter* **86**, 2609-2612 (2001).
- [101] M. Hao, S. Sakai, T. Sugahara, T. S. Cheng, C. T. Foxon, “Transmission electron microscopy investigation of InNAs on GaAs grown by molecular beam epitaxy”, *Journal of Crystal Growth* **189/190**, 481-484 (1998).
- [102] W. K. Hung, K. S. Cho, M. Y. Chern, Y. F. Chen, D. K. Shih, H. H. Lin, C. C. Lu, T. R. Yang, “Nitrogen-induced enhancement of the electron effective mass in $\text{InN}_x\text{As}_{1-x}$ ”, *Applied Physics Letter* **80** (5), 796-798 (2002).
- [103] D. K. Shih, H. H. Lin, L. W. Sung, T. Y. Chu, T. R. Yang, “Band Gap Reduction in InAsN Alloys”, *Japanese Journal of Applied Physics* **42**, 375-383 (2003).
- [104] S. Kuboya, Q.T. Thieu, W. Ono, F. Nakajima, R. Katayama, K. Onabe, “MOVPE and characterization of InAsN/GaAs multiple quantum wells”, *Journal of Crystal Growth* **298**, 544-547 (2007).
- [105] D. K. Shih, H. H. Lin, L. W. Sung, T. Y. Chu, “Bulk InAsN Films Grown by Plasma-Assisted Gas Source Molecular Beam Epitaxy”, in *Proceeding of 13th Indium Phosphide and Related Materials*, Nara, Japan, 2001.

- [106] S. Sakai, T. S. Cheng, T. C. Foxon, T. Sugahara, Y. Naoi, H. Naoi, "Growth of InNAs on GaAs (1 0 0) substrates by molecular-beam epitaxy", *Journal of Crystal Growth* **189/ 190**, 471-475 (1998).
- [107] M. E. Levinshtein, S. L. Rumyantsev, M. Shur, ed., *Handbook series on semiconductor parameters* Vol. 1 and 2, New Jersey: World Scientific, 1996.
- [108] Harrison WA, *Electronic structure and properties of solids*, New York: Dover; 1989.
- [109] H. Benaissa, A. Zaoui, M. Ferhat, "First principles calculations for dilute InAs_{1-x}N_x alloys", *Journal of Applied Physics* **102**, 113712 (2007).
- [110] N. Troullier, J. L. Martins, "Efficient pseudopotentials for plane-wave calculations", *Physical Review B* **43**, 1993-2006 (1991).
- [111] Helmut Eschrig, *The fundamentals of density functional theory*, Stuttgart, 1996.
- [112] I. N. Remediakis, E. Kaxiras, "Band-structure calculations for semiconductors within generalized-density-functional theory", *Physical Review B* **59**, 5536-5543 (1999).
- [113] G. Burns, A. M. Glazer, *Space Groups for Solid State Scientists*, 2nd ed., Academic Press, 1990.
- [114] Y. K. Kuo, W. W. Lin, "Band-Gap Bowing Parameter of the Al_xGa_{1-x}N Derived from Theoretical Simulation", *Japanese Journal of Applied Physics* **41**, 73-74 (2002).
- [115] J. L. A. Alves, J. Hebenstreit, M. Scheffler, "Calculated atomic structure and electronic properties GaP, InP, GaAs, and InAs (110) surfaces", *Physical Review B* **44**, 6188-6198 (1991).
- [116] Otfried Madelung, *Semiconductor: Data Handbook*, Springer, 2003.
- [117] I. Ho, G.B. Stringfellow, "Solubility of nitrogen in binary III-V systems", *Journal of Crystal Growth* **178**, 1-7 (1997).
- [118] H. Ch. Alt, A. Yu. Egorov, H. Riechert, J. D. Meyer, B. Wiedemann, "Incorporation of nitrogen in GaAsN and InGaAsN alloys investigated by FTIR and NRA", *Physica B* **308-310**, 877-880 (2001).
- [119] J. Wagner, K. Köhler, P. Ganser, M. Maier, "Bonding of nitrogen in dilute InAsN and high In-content GaInAsN", *Applied Physics Letter* **87**, 051913 (2005).
- [120] S. G. Spruytte, C. W. Coldren, A. F. Marshall, M. C. Larson, J. S. Harris, "Incorporation of nitrogen in group III-nitrides-arsenides grown by molecular beam epitaxy (MBE)", in *197th Meeting of the Electrochemical Society*, STOPACS, Toronto, Canada, 2000.

- [121] A. S. Helmy, J. S. Aitchison, J. H. Marsh, "The kinetics of intermixing of GaAs/AlGaAs quantum confined heterostructures", *Applied Physics Letter* **71**, 2998-3000 (1997).
- [122] O. P. Kowalski, C. J. Hamilton, S. D. McDougall, J. H. Marsh, A. C. Bryce, R. M. De La Rue, B. Vogeles, C. R. Stanley, C. C. Button, J. S. Roberts, "A universal damage induced technique for quantum well intermixing", *Applied Physics Letter* **72**, 581-583 (1998).
- [123] G. Li, S. J. Chua, S. J. Xu, X. C. Wang, A. S. Helmy, M. L. Ke, J. H. Marsh, "Silica capping for $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}/\text{GaAs}$ and $\text{In}_{0.2}\text{Ga}_{0.8}\text{As}/\text{GaAs}$ quantum well intermixing", *Applied Physics Letter* **73**, 3393-3395 (1998).
- [124] M. Albrecht, V. Grillo, T. Remmele, H. P. Strunk, A. Yu. Egorov, Gh. Dumitras, H. Riechert, A. Kaschner, R. Heitz, A. Hoffmann, "Effect of annealing on the In and N distribution in InGaAsN quantum wells", *Applied Physics Letter* **81**, 2719-2721 (2002).
- [125] J.L. Liu, S. Tong, Y.H. Luo, J. Wan, K.L. Wang, "High-quality Ge films on Si substrates using Sb surfactant-mediated graded SiGe buffers", *Applied Physics Letter* **79**, 3431-3433 (2001).
- [126] X. Yang, J.B. Heroux, M.J. Jurkovic, W.I. Wang, "High-temperature characteristics of 1.3 μm InGaAsN:Sb/GaAs multiple-quantum-well lasers grown by molecular-beam epitaxy", *Applied Physics Letter* **76**, 795-797 (2000).

Appendix

Vapor pressure and weight of metalorganic precursor calculations

$$\log(P_{part}) = B - \frac{A}{T}$$
 (A.1)

$$weight = \frac{flow}{22400} \times mass \times \frac{P_{part}}{P_{curr} - P_{part}}$$
 (A.2)

Precursor	Melting point, °C [103]	Boiling point, °C [103]	Vapor pressure		Mass
			A	B, K	
TBP	4	54	1539	7585.7	90
TBAs	-1	65	1562.3	7.5	148.2
DMHy	-57	63-64	1812.3	8.272	60.1
TMGa	-15.8	55.8	1703	8.07	114.83
TMIn	88	135.8	3014	10.52	159.93