Growth and characterization of GaAs-based III-V-N material for p-i-n photodetectors using antimony as a surfactant

Cheah, Weng Kwong

2006

Cheah, W. K. (2006). Growth and characterization of GaAs-based III-V-N material for p-i-n photodetectors using antimony as a surfactant. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/46872>

<https://doi.org/10.32657/10356/46872>

Nanyang Technological University

Downloaded on 26 Apr 2023 18:12:18 SGT

~~4435722~~

4438539

**Growth and Characterization of GaAs-based
III-V-N Material for *p-i-n* Photodetectors
Using Antimony as a Surfactant**

Cheah Weng Kwong

School of Electrical & Electronic Engineering

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

2006

TK
7871.86
C514
2006

Acknowledgments

I sincerely thank my project and thesis supervisor Asst. Prof. Fan Weijun for his unswerving dedication to my research progress and countless hours spent discussing papers, correcting my journals, refining my research thoughts. I am grateful that he has given me this opportunity to develop myself in this field of research, while providing close guidance to my progress and yet able to give me leeway to explore the vast boundaries in my research areas. He has enlightened me on many aspects and it is due to him that I was able to grasp many physics concepts with ease and able to translate it to written papers. In this I salute him as a very committed, insightful and erudite supervisor.

I would like to offer my heartfelt gratitude to Prof. Yoon Soon Fatt who has supported my research in solid source molecular beam epitaxial (MBE) growth. I enjoyed his company on my trip to Boston for the Materials Research Society (MRS) Conference in the Fall of 2003, where we visited Prof. Clifton G. Fonstad, Jr. and his research team at the Massachusetts Institute of Technology (MIT), Department of Electrical Engineering and Computer Science.

I owe my MBE growth techniques to the combination of three growth masters, namely Dr. Wang Shan Zhong, Dr. Loke Wan Khai and Dr. Ng Tien Khee. I was able to extract the best techniques from the three growth masters and apply them to my own growths. Dr Wang who was involved in the initial development of the nitride growth process using SSMBE has taught me the intricate details to III-V-N growth. Dr Loke and Mr Ng has aided me greatly in MBE growth and further characterization techniques specifically, HRXRD and PL measurements.

I also thank my friends at the National University of Singapore (NUS) Surface Science Lab, Department of Physics, Dr Liu Rong and Andrew T. S. Wee for their support and time in assisting me with secondary-ion mass spectroscopy (SIMS) measurements.

I owe my enjoyable stay in Nanyang Technological University (NTU) to my colleagues and friends for their support, advice and encouragement throughout my research tenure. They are in no particular order: Dr Sun Zhong Zhe, Zhang Rong, Chew Kerlit, Satrio Wicaksono, Tan Kian Hua, Lew Kim Luong, Yew Kuok Chuin, Yuan Kai Hua and Huang Qing Feng.

I thank the dedicated Clean Room and Characterization Laboratory technical staff; Foo Tai Ho, Fauzi, Shamsul, and Chris Lim for their assistance in maintaining the MBE systems and characterization tools. I enjoy all the political discussions apart from the daily humdrum of work.

Last but not least, my sincere appreciation for my mother who has supported me all these years and made me what I am today.

I would like to thank NTU for the research fund scholarship and support for my PhD candidature, without which my studies will be impossible.

Summary

The work present in this thesis was initiated by the desire to design and fabricate a GaAs-based InGaAsN *p-i-n* photodetector operating at 1.3 μm , using solid source molecular beam epitaxy. III-V dilute nitrides such as the quaternary InGaAsN has attracted much attention due to its potential in optoelectronic device applications operating at the 1.3 and 1.55 μm wavelengths on the GaAs material system. These wavelengths are important for the next generation long-wavelength optical fiber communication systems. The conventional choices of active regions for lasers at these wavelengths are InGaAsP or InGaAs on InP substrates. However, these material systems exhibit poor temperature characteristics due to a shallow conduction band potential as compared to the III-V-N material system. InGaAsN is of technological interest because the incorporation of N into (In)GaAs causes a redshift with increasing N molar fraction, due to the large band gap bowing coefficient (in the order of ~ 20 eV) between the GaN and the GaAs binaries. Sb was proposed as a surfactant in III-V-N compound semiconductors in order to improve the quality of highly strained InGaAsN/GaAs quantum wells (QWs). 1.3 μm InGaAsN:Sb/GaAs multiple-quantum-well (MQW) laser diodes have been grown by SSMBE. The addition of Sb to InGaAsN not only serves as a surfactant, but also as an alloy constituent that red shifts the optical emission beyond 1.3 μm . The major accomplishments of this study are summarized as follows:

-
- (1) The effect of strain on GaAsN_x grown on GaAs is observed by monitoring the tilt angle, $\Delta\psi$, between the epilayers in two-dimensional [115] HRXRD rocking curves. The instance when the epilayer changes from highly strained to a relaxed state is observed in the form of peak profiles. The increase of growth rate is found to have an effect on maintaining the crystal quality and surface reconstruction. Interstitial N complex serves to lower the tensile strain due to its compressive nature, thereby increasing the critical thickness at very high N content. GaAsN/GaAs is able to exceed the critical thickness by nearly twice without any degradation in surface quality. We demonstrate that GaAsN_{0.048} can be coherently grown to 100 nm, exceeding the critical thickness by ~ 4.7 times after an optimization of the III-V-N growth by means of an increased growth rate.
- (2) Low temperature (10 K) PL measurements of GaAs_{1-x}N_x epitaxial layers grown on GaAs reveal an anomalous second peak in SSMBE. Rapid thermal annealing (RTA) of a specific GaAsN sample reveals a lower energy peak which redshifts and a higher energy peak which blueshifts under increasing annealing temperature. The band anticrossing model is used to identify the origins of the two peaks and we propose a model to explain the RTA observations by the concept of increased confinement in areas of higher N concentrations by trapped N localized states. This shows that more than one characterization techniques are required to confirm the N composition. A combination of PL and SIMS is used to understand the intricate relations between the photon emission and the epilayer microstructure.

-
- (3) The indium and nitrogen incorporation in InGaAsN/InGaAs/GaAsN grown on GaAs substrates is investigated by means of photoluminescence (PL) and secondary ion mass spectroscopy (SIMS) measurements. The simulations indicate that the epitaxial parameters in our growth of InGaAsN / InGaAs / GaAsN epilayers are consistent throughout the methods of analysis. By placing all the alloys on the same sample, the dependency of In and N in InGaAsN on GaAs has been investigated, giving us a better understanding of the relationships between the composition and PL characteristics.
- (4) The effects of doping Sb to dilute GaAsN_x ($x = 0.4$ %) are investigated. A transition region was found at $5 \times 10^{-9} < \text{Sb} < 10^{-8}$ Torr where below this, Sb behaves as an impurity and above it, Sb acts as a surfactant. The low temperature (4.5 K) PL peak intensities of prominent emissions were observed at 955 nm and 1017 nm in GaAsN:Sb samples. The 1017 nm peak is related to point defects from Sb doped III-V nitride under high arsenic overpressure. We have shown that for introducing dopant-like ($\times 10^{-9}$ Torr) flux of antimony into the bulk III-V-N epilayer has the effect of deteriorating the surface morphology and this is observed from atomic force microscopy (AFM) measurements.
- (5) Low temperature (4.5 K) photoluminescence measurements and two-dimensional [115] high resolution x-ray diffractometry rocking curves of antimony doped III-V-N on GaAs grown by solid source molecular beam epitaxy, shows a possible non-radiative recombination defect known as the Sb_{Ga} heteroantisite and another Sb-related defect peak at 1017 nm (~ 1.22 eV). The elimination of these defects can be a measure of the improvement in crystal quality of GaAsN:Sb. We find

that Sb behaves as an impurity and competes with N for As sites until the surfactant effect commences at 1.3×10^{-8} Torr. The Sb latency effect which results in a graded Sb composition at the interface was found by secondary ion mass spectroscopy measurements.

- (6) The surfactant effects of Sb enhances the carbon (C) dopant incorporation into substitutional sites in GaAsSb:C grown by SSMBE. A hole mobility greater than $50 \text{ cm}^2/\text{V.s}$ for doping levels over $9 \times 10^{19} \text{ cm}^{-3}$ was achieved using a solid CBr₄ source. 5.4×10^{-8} Torr of carbon flux giving a hole concentration of $\sim 7 \times 10^{19} \text{ cm}^{-3}$ in GaAs, reaches beyond $9 \times 10^{19} \text{ cm}^{-3}$ with the addition of $\sim 4 \times 10^{-8}$ Torr of Sb. With increasing Sb doping concentration, the rate of C incorporation into substitutional sites increases, the photoluminescence (PL) characteristics are improved and the net hole concentration increases due to the reduction of interstitial carbon. However when Sb doping is increased further, gallium vacancies and Sb_{Ga} antisites could create point defects, causing epitaxial degradation and defect scattering around the GaAs peak in 2D [115] HRXRD scans. As the C incorporation declines slightly due to Sb competition with excessive Sb flux, the acceptor concentration continues to increase, brought on by the formation of the native defects mentioned.
- (7) The coherent growth of bulk InGaAsN_{3.45%}Sb ($\sim 0.5 \text{ }\mu\text{m}$) with a lattice-mismatch of 2.6×10^{-3} can be achieved due to the surfactant properties of antimony, while bulk InGaAsN_{2%} at $0.5 \text{ }\mu\text{m}$ with 1.06×10^{-3} mismatch is fully relaxed. Besides maintaining coherency in the material, the presence of Sb prevents the formation of N-related interstitials. These effects ultimately improve the crystal quality and

prevent the diffusion of the material and intermixing of the $P-i-N$ structure interface profile. In and N out-diffusions are observed in the *in-situ* annealed sample without Sb, while the Sb-containing $P-i-N$ samples reveal abrupt profiles when subjected to rapid thermal annealing (RTA). The RTA resulted in full-width half-maximums (FWHM) of ~ 25 meV in low temperature PL measurements for InGaAsNSb samples. This is much smaller than that of InGaAsN under the same conditions.

- (8) GaAs-based double-heterojunction $p-i-n$ photodetectors using $\text{In}_z\text{Ga}_{1-z}\text{As}_{1-x-y}\text{N}_x\text{Sb}_y$ in the i -layer is fabricated for the first time using the solid source molecular beam epitaxy growth method. The surfactant effect generated by the presence of Sb in this material allows thick high quality dilute nitride material growth. A peak responsivity of ~ 0.29 A/W, corresponding to quantum efficiencies (QE) of 38 % is attained between $0.9 - 1.1 \mu\text{m}$ from the best $p-i-n$ device. The cutoff wavelength reaches $\sim 1.4 \mu\text{m}$ and the dark current is $\sim 0.43 \text{ mA/cm}^2$ at a reverse bias of 2 V. A Sb-free $p-i-n$ device consisting of InGaAsN/GaAs is also fabricated to compare the device performance with the InGaAsNSb/GaAs $p-i-n$ devices.

Table of Contents

Acknowledgments	i
Summary	iii
Table of Contents	viii
List of Figures	xi
List of Tables	xviii
 1. Introduction	 1
1.1 Background and Motivation	1
1.2 Motivations	4
1.3 Objectives	5
1.4 Major Contributions of the Thesis	7
1.5 Organization of the thesis	10
 2. MBE Growth and Characterization Tools	
2.1 Solid-State Molecular Beam Epitaxy (SSMBE)	11
2.1.1 Radio Frequency (rf) Nitrogen Plasma Source	14
2.1.2 Antimony (Sb) Source	15
2.2 Characterization Tools	17
2.2.1 Reflection of High Energy Electron Diffraction	17
2.2.2 <i>Ex-situ</i> Analysis	19
2.2.2.1 Photoluminescence (PL) Measurements	19
2.2.2.2 X-ray Diffractometry (XRD) Measurements.....	21
2.2.2.3 Atomic Force Microscopy (AFM) Measurements.....	23
2.2.2.4 Hall Measurements	24
2.2.2.5 Secondary-ion Mass Spectroscopy (SIMS) Measurements	25
 3. X-ray Reciprocal Space Mapping of Strain Relaxation in GaAs_{1-x}N_x on (001) GaAs by Molecular Beam Epitaxy	
3.1 Introduction	27
3.2 Experimental Details	28
3.3 Results and Discussion	29
3.3.1 High Resolution X-Ray Diffractometry (HRXRD)	29
3.3.2 Influence of N on Strain in Bulk and Surface Quality	37
3.3.3 Effect of rf Power on Interstitiality	39
3.4 Conclusions	41

4.	Interpretation of Anomalous Extra Peak in Photoluminescence Measurements of Bulk GaAs_{1-x}N_x Epitaxial Layer on GaAs	
4.1	Introduction	42
4.2	Experimental Details	44
4.3	Results and discussion	44
4.3.1	Photoluminescence peak spectra of annealed GaAsN	44
4.3.2	Identification of the photoluminescence peaks using the BAC model	50
4.4	Conclusions	56
5.	Investigation of N Incorporation in InGaAs and GaAs Epilayers on GaAs Using Solid Source Molecular Beam Epitaxy	
5.1	Introduction	57
5.2	Experimental Details	58
5.3	Photoluminescence and Secondary-Ion Mass Spectroscopy Measurements	60
5.4	Conclusions	70
6.	Surfactant and Impurity Properties of Antimony on GaAs and GaAs_{1-x}N_x on GaAs [100] by Solid Source Molecular Beam Epitaxy	
6.1	Introduction	71
6.2	Experimental Details	73
6.3	Results and Discussion	74
6.3.1	PL and SIMS Measurements	74
6.3.2	High Resolution X-Ray Diffractometry Measurements	84
6.4	Conclusions	89
7.	Co-doping Carbon tetrabromide (CBr₄) and Antimony (Sb) on GaAs (100) in Solid Source Molecular Beam Epitaxy	
7.1	Introduction	90
7.2	Experimental Details	91
7.3	Results and Discussion	93
7.3.1	Hall Measurements	93
7.3.2	Photoluminescence Measurements	98
7.3.3	High Resolution X-Ray Diffractometry Measurements	100
7.4	Conclusions	102

8.	Growth and Characterization of GaAs-based Double-heterojunction <i>P-i-N</i> Structures Using $\text{In}_z\text{Ga}_{1-z}\text{As}_{1-x-y}\text{N}_x\text{Sb}_y$ as the <i>i</i>-layer	
8.1	Introduction	103
8.2	Experimental Details	104
8.3	Results and discussion	106
8.3.1	High-resolution x-ray Diffraction and Secondary-ion Mass Spectroscopy Measurements	106
8.3.2	Photoluminescence (PL) Measurements and Rapid Thermal Annealing	114
8.4	Conclusions	118
9.	GaAs-based Heterojunction <i>p-i-n</i> Photodetectors Using Pentanary InGaAsNSb as the Intrinsic Layer	
9.1	Introduction	119
9.2	Experimental Details	120
9.3	Results and Discussion	123
9.3.1	<i>I-V</i> Measurements	123
9.3.2	Responsivity Measurements	125
9.4	Conclusions	127
10.	Conclusion and Recommendations	
10.1	Conclusion	128
10.2	Recommendations for Further research	132
Author's Publications		
	Journal Papers	134
	Conference Papers	136
References		137

List of Figures

	Page No.
Fig. 2-1 The typical layout of a molecular beam epitaxy growth chamber.	12
Fig. 2-2 The Sb and N cell orientation on a Riber 32 solid source molecular beam epitaxy growth chamber.	15
Fig. 2-3 Applied Epi Antimony (Sb) Cell. (extracted from Veeco Instruments at http://www.veeco.com/html/product_bymarket_proddetail.asp?productID=250&MarketID=3&Title=MBE)	16
Fig. 2-4 An illustration on the reflection high-energy electron diffraction setup in a growth chamber.	17
Fig. 2-5 The photoluminescence (PL) measurement setup.	21
Fig. 2-6 The work principle diagram for the Bragg Brentano θ - 2θ x-ray diffraction setup used for our measurements.	23
Fig. 2-7 A $3 \times 3 \mu\text{m}^2$ (AFM) scan on a sample.	24
Fig. 2-8 A schematic view of a Cameca IMS-6f. (extracted from Cameca, IMS-6f, User's Guide (1998))	26
Fig. 3-1 (Solid Line) – 2-dimensional (115) $\Delta\psi$ versus N (%) for 0.7 $\mu\text{m/hr}$, (Dotted Line) – Calculated $\Delta\psi$ for coherent GaAsN growth on GaAs, where deviation towards the Dashed Line means relaxation.	31
Fig. 3-2 The profile of GaAs (left)/GaAsN (right) peak for rf power (a) 200 W, (b) 220 W at growth rate of 0.7 $\mu\text{m/hr}$. (<i>continued</i>) The profile of GaAs (left)/GaAsN (right) peak for rf power (c) 240 W at growth rate of 0.7 $\mu\text{m/hr}$.	32-33

		Page No.
Fig. 3-3	The (004) XRD measurement of sample MN218.	33
Fig. 3-4	The profile of GaAs ((left)/GaAsN (right) peak for rf power at 285 W at growth rate of 1.0 $\mu\text{m/hr}$, where the horizontal axis is ω -2 θ ($^\circ$) and the vertical axis is $\Delta\psi$ ($^\circ$).	36
Fig. 3-5	300 $\times$ 300 nm ² AFM measurement of GaAsN on GaAs for nitrogen at a) 1.14 %, b) 2.21 %, c) 2.77 %, d) 3.62 % for a uniform thickness of 100nm.	38
Fig. 3-6	The PL intensity quenching due to the presence of N interstitials around 3% of nitrogen.	40
Fig. 4-1	Low temperature 10 K photoluminescence measurement of the as-grown and the annealed GaAsN _{1.3%} sample vs annealing temperature ($^\circ\text{C}$) in steps of 50 $^\circ\text{C}$.	45
Fig. 4-2	The SIMS measurement of the (a) as-grown and the (b) annealed GaAsN _{1.3%} sample at 750 $^\circ\text{C}$ with the nitrogen concentration (atm/cm^3) vs the sputtering depth (nm).	47
Fig. 4-3	A proposed model of the better confinement of localized N states at higher N concentrations. The solid line denotes the as-grown energy levels and the dotted line denotes the annealed energy levels.	49
Fig. 4-4.	The SIMS measurement of the as-grown GaAsN _{1.89%} and the annealed sample at 750 $^\circ\text{C}$ (10 min) with the nitrogen concentration (atm/cm^3) vs the sputtering depth (nm).	54

	Page No.
Fig. 4-5.	The low temperature 10 K photoluminescence measurement of the as-grown and the annealed GaAsN _{1.89%} sample vs annealing temperature (°C) in steps of 100 °C.
	55
Fig. 5-1	The growth structure of samples C54 and LM026, where the top is the growth direction.
	58
Fig. 5-2	(a) The 4.7 K PL measurement of C54. (b) The strained and unstrained energy bandgap emission peak (eV) vs N% of GaAsN on GaAs at 4.7 K, as derived from the band anticrossing model.
	61
Fig. 5-3	(a) The 4.7 K PL measurement of LM026. (b) The strained and unstrained energy bandgap emission peak (eV) vs In% of InGaAs on GaAs at 4.7 K.
	63
Fig. 5-4	The strained energy bandgap emission peak (eV) vs In % of InGaAsN on GaAs at 4.7 K for N content at 1 %, 2 % and 3 %.
	65
Fig. 5-5	(a) The SIMS measurement of LM026 with the concentration (atoms/cc) vs the sputtering depth (µm). (b) The SIMS measurement of LM026 with the secondary ion intensity (counts/sec) in log. scale vs the sputtering time (sec). Only Ga, In and N lines are shown.
	67
Fig. 5-6	The SIMS measurement of C54 with the secondary ion intensity (counts/sec) in log. scale vs the sputtering time (sec).
	68

	Page No.
Fig. 6-1 The PL peak intensity (cps) at 4.5 K versus wavelength (nm) for GaAsN:Sb (N1-N3) and the undoped GaAsN.	75
Fig. 6-2 The PL peak intensity (cps) at 4.5 K of GaAsN doped with antimony (N1, N4-5) in the region of the surfactant effect.	77
Fig. 6-3 The PL peak intensity (cps) at 4.5 K of GaAs doped with antimony. The Sb impurity related hump located at ~1000 nm.	79
Fig. 6-4 The Sb (%) from SIMS measurements, where solid dots denote the Sb (%) for GaAsN:Sb and solid squares for GaAs:Sb, compared against Sb flux (Torr). The hollow circles denote the N% from SIMS for GaAsN:Sb.	80
Fig. 6-5 The SIMS measurement of a typical GaAsN:Sb sample, N2. The latency effect and surface accumulation of Sb in the material is observed.	82
Fig. 6-6 The 2D (115) HRXRD mapping profile of GaAsN:Sb. (a) N3 (Sb - 3×10^{-9} Torr), (b) N2 (Sb - 4.8×10^{-9} Torr), (continued) (c) N1 (Sb - 9.5×10^{-9} Torr), (d) N4 (Sb - 13×10^{-9} Torr). The maximum intensity is 135786 cps.	84-85
Fig. 6-7 (a) The N(%) composition and surface roughness (nm) versus Sb flux (Torr). (continued) (b) The N(%) composition and GaAsN PL intensity (normalized to undoped GaAsN) versus Sb flux (Torr). The surfactant effects commences in the region of 1.3×10^{-8} Torr for a growth rate of $1 \mu\text{m/hr}$.	87-88

	Page No.
Fig. 7-1	(a) The variation of hole concentration with the Sb flux (Torr) under a fixed CBr ₄ flux of 2.2×10^{-8} Torr (circle), 4.4×10^{-8} Torr (square) and 5.4×10^{-8} Torr (triangle). (b) The variation of hole concentration and carbon concentration in the order of 10^{19} cm^{-3} with the Sb flux (Torr) under the fixed CBr ₄ flux of 4.4×10^{-8} Torr .
	93
Fig. 7-2	The SIMS concentrations of Sb (Square) and carbon (Circle) in atm/cc for a fixed CBr ₄ flux of 4.4×10^{-8} Torr versus Sb flux in the 10^{-8} Torr order.
	95
Fig. 7-3	The variation of the hole mobility ($\text{cm}^2 / \text{V.s}$) compared with the Sb flux (Torr) under a fixed CBr ₄ flux of 2.2×10^{-8} Torr (circle), 4.4×10^{-8} Torr (square) and 5.4×10^{-8} Torr (triangle).
	96
Fig. 7-4	The variation of the sheet resistance ($\Omega/\square$) compared with Sb flux (Torr) under a fixed CBr ₄ flux of 4.4×10^{-8} Torr. Saturation of the sheet resistance occurs $\sim 95 \Omega / \square$, for a hole concentration from 6 to $8 \times 10^{19} \text{ cm}^{-3}$.
	97
Fig. 7-5	The PL plot of intensity (arb. units) versus energy (eV) for GaAsSb:C (NA570, NA572 and NA573) from (a) 1.35 to 1.55 eV, (<i>continued</i>) from (b) 0.65 to 1.10 eV.
	98-99
Fig. 7-6	The 2D (115) HRXRD profile of NA570 (C – 4.4×10^{-8} Torr & Sb – 9.3×10^{-8} Torr).
	101
Fig. 7-7	The 2D (115) HRXRD profile of NA572 (C – 4.4×10^{-8} Torr & Sb – 5.5×10^{-8} Torr).
	101

		Page No.
Fig. 8-1	The two-dimensional [115] high resolution x-ray diffraction (HRXRD) measurement of (a) a relaxed sample D1, (<i>continued</i>) of (b) a coherent sample D3.	107
Fig. 8-2	The elemental composition (%) of indium (In), nitrogen (N) and antimony (Sb) with reference to the antimony flux (Torr). The lattice mismatch of InGaAsN(Sb) to GaAs is displayed in the order of 10^{-3} .	108
Fig. 8-3	(a) The secondary ion mass spectrometry (SIMS) measurements of D1 with Sb = 0×10^{-9} Torr, (b) D2 with Sb at 5×10^{-9} Torr, (c) D4 with Sb = 1×10^{-8} Torr. The vertical axis is the secondary ion intensity (count/s) and the horizontal axis is the sputtering depth (nm). The diagram on the inset of each figure is the annealed (761 °C/20 sec) SIMS measurement of the corresponding as-grown sample.	109-111
Fig. 8-4	(a) The low temperature (LT) 4.5K PL of the as-grown samples. (<i>continued</i>) (b) The low temperature (LT) 4.5K PL of the annealed <i>P-i-N</i> structures with optimized annealing conditions.	114-115
Fig. 8-5	The PL peak position in wavelength (nm) of bulk InGaAsNSb with different annealing conditions, plotted under temperature variation. The solid lines denote D2, dashed lines for D3 and dotted lines for D4. Solid squares denote the annealing condition at 714 °C for 20 sec, solid circles – 741 °C for 20 sec, solid triangles – 761 °C for 20 sec and solid diamonds – 793 °C for 10 sec.	117
Fig. 9-1	The mesa device structure layout of devices A (Sb=0), B (Sb= 5×10^{-9} Torr) and C (Sb= 10×10^{-9} Torr). The changes in the Sb concentration apply to the intrinsic (<i>i</i>) layer of the devices and other parameters remain the same.	120
Fig. 9-2	The elemental compositions (%) of the A, B, and C devices measured by SIMS versus the antimony flux (Torr). The tensile strain (ϵ) in the <i>i</i> -layer layer is depicted in the diagram.	121

	Page No.
Fig. 9-3 The dark current density (A/cm^2) of the three devices versus the bias voltage from -20 to 2 V.	124
Fig. 9-4 The room temperature responsivity (R) of the three devices as a function of wavelength in nanometers for zero bias and a reverse bias of 2 V.	126

List of Tables

	Page No.
Table 3-1. The nitrogen (%) with growth rate, rf power, critical thickness and C values.	36
Table 3-2. The time duration of RHEED observation for N > 3 % at 1.0 $\mu\text{m/hr}$.	40
Table 4-1. The data parameters of GaAs and GaN (zinc blende)	51
Table 5-1. The lattice constant (a_0), the elastic constant C_{11} and C_{12} and other parameters of GaAs, InAs, cubic GaN and cubic InN.	62
Table 5-2. The compositions for InGaAs, GaAsN and InGaAsN layers in LM026 and C54.	64
Table 6-1. The growth conditions, the SIMS and PL measurement results of GaAs(N):Sb samples. The asterisk shows that the automated valve position of the Sb cell is set to fully open at 300 mil, else the corresponding position value is cited beside the temperature. And the normalized PL intensity (to the undoped GaAsN transition peak) of the two observed peaks in the GaAsN:Sb samples (N1-N5) are depicted. N6-N9 are GaAs:Sb samples.	76
Table 6-2. The role of antimony at different flux levels.	78
Table 9-1. The room temperature quantum efficiency (QE) and responsivity (R) of the devices for zero bias and a reverse bias of 2 V at 940 nm and 1300 nm.	126

Chapter 1

Introduction

1.1 Background and Motivation

III-V dilute nitrides such as the quaternary InGaAsN have attracted much attention due to their potential in optoelectronic device applications operating at the 1.3 and 1.55 μm wavelengths on the GaAs material system. These wavelengths are important for optical fiber communication systems. The conventional choices of active regions for lasers at these wavelengths are InGaAsP or InGaAs on InP substrates. However, these material systems exhibit poor temperature characteristics due to a shallow conduction band potential as compared to the III-V-N material systems. InGaAsN is of technological interest because the incorporation of N into (In)GaAs causes a redshift with increasing N mole fraction, due to the large band gap bowing factor (in the order of ~ 20 eV) [1-3]. One of the most well-known models used to explain this redshift phenomenon is the band-anticrossing model, which is based on the repulsive behavior between the conduction band edge and the localized N resonant states [4]. Recently, there is considerable progress in the development of quantum well (QW) laser diodes, resonant-cavity enhanced (RCE) photodiodes and solar cells using the dilute nitride systems [5-8].

p-i-n structures are widely used in photodetectors. A thick high quality *i*-layer is necessary to achieve high responsivity. Lattice-matched (LM) semiconductors can be utilized to maximize the efficiency by minimizing non-radiative recombination caused by misfit dislocations. The precise tuning of the nitrogen and indium contents is a prerequisite for LM $\text{In}_x\text{GaAsN}_y$ grown on GaAs substrate by solid source molecular beam epitaxy (MBE) [2]. Bulk LM $\text{In}_x\text{GaAsN}_y$ can be theoretically grown on GaAs substrates when $x \approx 3y$. The challenge is to demonstrate thick (2-3 μm) $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ ($y > 0.02$) epilayers. To date, InGaAsN epilayers have been grown up to 3 μm on GaAs using high growth rate (GR), mainly by metal organic chemical vapor deposition (MOCVD) [9]. However, the thickness of LM $\text{In}_x\text{GaAsN}_y$ ($y > 2\%$) to GaAs in solid source MBE is seldom mentioned and to our knowledge, there are no reports of it exceeding 1.0 μm . This is because increasing the N and In composition to reduce the bandgap increases the tendency for alloy decomposition and phase separation. The formation of Ga-rich N-centered $\text{N-In}_p\text{Ga}_{4-p}$ ($0 \leq p \leq 4$) clusters dominated by In-N bonds, occurs when In is introduced to GaAsN. N-induced alloy fluctuations during InGaAsN growth, is believed to cause localization effects and spontaneous ordering. Moreover, the formation of N split interstitials and $\text{As}_{\text{Ga}}\text{-N}_{\text{As}}$ pairs is energetically favorable for high N concentration. Several methods have been found to improve the nitride layer quality. (i) Rapid thermal annealing (RTA) can be used to improve the epitaxial quality by eliminating nonradiative recombination centers. (ii) Single phase and two-dimension (2D) growth can be enhanced by imposing kinetic restrictions on the system, like decreasing the growth temperature and increasing the GR. (iii) In order to delay the occurrence of the 2D-3D growth mode transition, the mass transport at the surface can also be reduced by the use of surfactants.

Surfactants are typically elements which segregate to the growth front and alter the surface kinetic process, resulting in an increase in the critical thickness at which the growth mode maintains two-dimensional by inhibiting Stranski-Krastanov islanding. Sb was proposed as a surfactant in III-V-N compound semiconductors in order to improve the quality of highly strained InGaAsN/GaAs QWs and 1.3 μm InGaAsN:Sb/GaAs multiple-quantum-well (MQW) laser diodes have been grown by SSMBE [10]. Since then, InGaAsNSb/GaAsN QW structures are able to emit at 1.54 μm in room temperature [11] and single QW laser diodes using InGaAsNSb is able to operate at continuous-wave, emitting the 1.59 μm wavelength at room temperature [12]. 1.55 μm GaNAsSb *p-i-n* PDs using double QW active regions was also reported [13]. However, there are no reports of working devices with bulk InGaAsN(Sb) epitaxial layers for the 1.3 and 1.55 μm wavelengths.

1.2 Motivations

Photodiodes are important components and widely used in fiber optical communication systems. In order to achieve high responsivity, a thick (typically several to tens μm) intrinsic layer is sandwiched between the p -type and n -type layers. Such thick epilayers are required to be exactly lattice matched to the substrate to avoid strain relaxation and misfit dislocations. InGaAsP material can be lattice matched to the InP substrate to absorb at 1.3 μm and most optical communication diodes (1.3 μm) are based on the InP substrate. No GaAs-based 1.3 μm photodiode was reported because there was no epilayer material that is lattice-matched to the GaAs substrate and simultaneously absorbing at 1.3 μm until the novel GaInNAs material was reported in 1999. The material GaInNAs can be lattice-matched to GaAs when the In mole fraction is about 3 times that of the N mole fraction. The N composition can be designed to operate at the 1.3 μm wavelength. However, the material quality of GaInNAs is poor due to a large miscibility gap that limits its optoelectronic device application. Recently, Yang *et al.* [10] demonstrated that the use of Sb as a surfactant during GaInNAs MBE growth can greatly improve the epilayer quality. Therefore, the novel material GaInNAs:Sb provides us an opportunity to fabricate high quality GaAs-based bulk GaInNAs:Sb p - i - n photodiodes (PDs) operating at 1.3 μm [6,10]. Moreover, the cost of GaAs substrate is only one fifth of the InP substrate and we expect the costs of producing a GaAs-based p - i - n PD to be more economical. With this project, the research work in the area of MBE growth of Nanyang Technological University (NTU) will be strengthened and GaAs-based GaInNAs:Sb p - i - n PDs will be grown, fabricated, characterized and demonstrated.

1.3 Objectives

In this project, the InGaAsN/GaAs bandgap has to be designed for 1.3 μm and the corresponding compositions of In and N are to be found. The use of the solid source molecular beam epitaxy system (Riber 32P) and the use and ignition of N plasma from the rf N plasma source have to be mastered. The antimony (Sb) cracker will be installed and the Sb flux will be calibrated. The optimization of the GaInNAs:Sb epilayer growth conditions will be then carried out. This is done by first optimizing the growth temperature of the most elementary III-V-N/GaAs, which is GaAsN. The Sb cell characteristics are to be understood and the growth of rudimentary GaAs:Sb and GaAsSb will be conducted to find the optimized growth conditions. With that, we can set out to explore both InGaAsN and GaAsSbN on GaAs. It is also crucial to find out what growth temperature will be optimum for InGaAsNSb because both Sb and N will ultimately be used on the final material. We use carbon as a dopant in the *p*-type layer, hence the use of the CBr₄ source is also investigated. The surfactant Sb segregates to the surface and Sb may be present in the *p*-type layer to form GaAs:SbC or GaAsSb:C. We need to understand these material physics to control the actual growth processes. The characterization analysis conducted on the material will be subsequently used to optimize the device performance. The alloys to be investigated are GaAsN, InGaAs, InGaAsN, GaAs:Sb, GaAsN:Sb, GaAs:SbC and finally, InGaAsN:Sb.

Photoluminescence (PL), high resolution x-ray diffractometry (HRXRD) and secondary-ion mass spectroscopy (SIMS) measurements are techniques that allow us to

investigate aspects such as composition, bandgap, thickness, epitaxial quality and epitaxial profile. After growing the $p-i-n$ structure, we will fabricate the device using the standard equipment such as the mask aligner, evaporator etc. For the device performance tests, we will measure the photodiode's photocurrent responsivity spectrum, the dark current and the current-voltage curves. The use of *ex-situ* RTA will be carried out to improve the quality of the material.

1.4 Major Contributions of the Thesis

During this work, a great amount of time and effort were spent on the optimization of the nitride and antimonide growth. This involves the familiarization of the functions to the molecular beam epitaxy growth process and the characterization tools; and the special elemental sources such as the rf N plasma and Sb cracker. The optimized material is expected to be used for the development of the *p-i-n* PDs. This work also involves the device fabrication process and device performance analysis. With the optimized material and proper device control process, satisfactory performances have been readily achieved. This pioneering work for antimonide growth in our MBE group and the novel realization of the surfactant enhanced InGaAsN growth of GaAs-based *p-i-n* PDs absorbing at $\sim 1.3 \mu\text{m}$ will serve as an achievement for Nanyang Technological University (NTU). The significant contributions of this thesis are summarized as follows:

- 1) Strained GaAsN epilayers are grown by MBE and investigated by HRXRD. The increase of GR is found to maintain the crystal quality and surface construction. Interstitial N (N_i) which does not contribute to the lowering of the bandgap serves to offset the tensile strain being compressive in nature.

-
- 2) The conflicting reports on the blue and redshifting of the GaAsN PL peak in RTA measurements are fully and clearly investigated, by means of the band anticrossing model, PL and SIMS measurements. We find that when analyzing PL scans, we need to be mindful of the fact that not only the fundamental transitions are present, but also peaks arising from defects and other growth related effects. This is a very important issue when designing the photodetector absorption spectrum.
 - 3) The relationships between InGaAsN and its building blocks InGaAs and GaAsN are obtained by this research and the MBE growth techniques are fine tuned.
 - 4) With the introduction of the new antimony source, ultra dilute Sb in GaAs is investigated. With the introduction of Sb into GaAs(N), a possible non radiative recombination defect known as the Sb_{Ga} heteroantisite, reduces the PL intensities. The epitaxial quality observed from 2-dimensional HRXRD measurements is degraded correspondingly to the intensity of another defect peak situated at $\sim 1017\text{nm}$ in PL measurements. At this juncture, Sb competes with N for substitutional sites. Beyond 10^{-8} Torr of Sb, the surfactant effect commences when Sb segregates to the surface. The defect peak (1017 nm) and the non radiative defect are minimized. The PL intensity improves and the presence of surfactant Sb enhances N incorporation.
 - 5) Due to the fact that surfactant Sb segregates to the surface, the Sb which incorporates into the subsequent *p*-type layer may affect the device performance negatively. Hence, we set out to characterize GaAs:SbC and GaAsSb:C. Similar to GaAsN:Sb, surfactant Sb enhances the incorporation of C into substitutional sites and this increases the acceptor concentration. However, mobility is reduced in

regions of high dopant concentration and normally low in antimonide material. Hence, we formulate a growth progress to increase the substrate temperature to remove the segregation film of Sb from the *i*-layer surface before depositing the final *p*-type layer. This also provides an *in-situ* annealing effect which further improves the *i*-layer quality. This action improved the detector performance characteristics.

- 6) SIMS measurements of the *p-i-n* structures prove that Sb is able to maintain good epitaxial quality which prevents the *i*-layer from diffusing into the other regions under a raised temperature. Optimized *in-situ* annealing reveals true fundamental transition PL peak with full-width half-maximums (FWHMs) of only ~25 meV for the bulk *i*-layer, which is comparable to quantum well PL characteristics. Strain relaxation is also prevented with surfactant Sb.

- 8) GaAs-based double-heterojunction *p-i-n* mesa photodetectors using $\text{In}_z\text{Ga}_{1-z}\text{As}_{1-x-y}\text{N}_x\text{Sb}_y$ as the *i*-layer, is fabricated for the first time using the solid source MBE growth method. Quantum efficiencies (QE) up to 38 % are attained between 0.9 – 1.1 μm . A responsivity of 0.079 A/W, corresponding to a quantum efficiency of ~7.5 %, is detected from the best *p-i-n* device at the 1.31 μm detection wavelength. The cutoff wavelength for these devices is between 1.3 – 1.4 μm and the dark current spans between 70 – 853 nA at a reverse bias of 2 V.

1.5 Organization of the Thesis

Chapter 1 presents the entire background and motivation of the research work reported in this thesis. In chapter 2, we discuss the experimental techniques used in the accomplishment of the research work. In chapter 3, we look into the effects of strain on GaAsN, the most elemental III-V-N. We used 2D (115) HRXRD to monitor the strain and relaxation present in the epilayers and to identify the growth traits for good quality, thick bulk layers. The other main characterization tool, PL is used in conjunction with SIMS in chapter 4 to identify the fundamental transition and other growth phenomena such as compositional fluctuation/modulation and defects. Chapter 5 is dedicated to the understanding of InGaAsN and its relationship with GaAsN and InGaAs. Extensive characterization tools such as PL and SIMS measurements are used to identify the epitaxial composition and thicknesses for lattice matching and bandgap design. The effect of ultra dilute Sb on GaAs is investigated in chapter 6 to understand the surfactant formation process. Dilute Sb is introduced to form the surfactant process in GaAs and GaAsN at the optimized nitride growth temperature of 460 °C. In chapter 7, the incorporation of both C and Sb into GaAs is investigated to decide if Sb should be added to the *p*-type layer or eradicated. We move into the InGaAsNSb *p-i-n* structure growth in chapter 8, where SIMS, PL and RTA are conducted. In chapter 9, the fabrication of circular mesa *p-i-n* devices is reported. In the final chapter 10, we conclude the thesis and add various recommendations for future research.

Chapter 2

MBE Growth and Characterization Tools

2.1 Solid-State Molecular Beam Epitaxy (SSMBE)

Molecular beam epitaxy which uses the constituent elements as starting materials, is in principle, a rather elementary process. The surface phenomena is only involved in the crystal growth from the vapor phase and no foreign atoms are present at the gas solid interface and no by products are formed. The basic process of solid-source (SS) MBE of III-V semiconductors consists of the co-evaporation of the constituent elements (In, Ga, Sb, As, N) in the epitaxial layer and the dopants (Si for *n*-type and Be or C for *p*-type doping) onto a heated crystalline substrate, where they react chemically under ultra-high vacuum (UHV) conditions. The neutral molecular beams are generated by evaporating the elements in effusion cells. The Group III elements are always supplied as monomers by evaporation. The Group V elements are supplied as tetramers (As₄, Sb₄) or dimers (Sb₂) by dissociating the tetrameric molecules in a cracker of a two zone furnace. The GR is typically 0.5-1.0μm/hr, such that the dissociation and migration of the impinging species on the growing surface to the appropriate lattice sites, is ensured without causing crystalline defects. The composition of the layer and its doping level depend mainly on the relative arrival rates of the constituent elements which in turn depend on the evaporation rates of the respective sources. A typical layout of a MBE growth chamber is shown.

Fig. 2-1 The typical layout of a molecular beam epitaxy growth chamber.

The simple mechanical shutters in front of the evaporation sources are used to interrupt the beam fluxes in order to start and stop deposition and doping. Due to the slow GR of one monolayer per second (1 ml/sec), changes in composition and doping can be abrupt on an atomic scale. The MBE technique provides a 2D growth process which makes feasible the monolayer by monolayer deposition of a large variety of artificially layered solids. Crystalline materials in alternating layers of arbitrary composition with only a few atomic layers, can be fabricated in a reproducible manner. The stoichiometry of most III-V semiconductors during MBE growth is regulating as long as excess Group V molecules are introduced. The GR of the films is essentially determined by the arrival rates of the Group III elements. A good control of ternary III-III-V like InGaAs alloys can thus be achieved by supplying excess Group V species and adjusting the flux

densities of the impinging Group III beams, with the substrate temperature kept below the congruent evaporation limit of the less stable of the constituent binary III-V compound. The growth of III-V-V alloys like GaAsN by MBE is more complicated where even at moderate substrate temperatures, the relative amounts of the Group V elements incorporated into the growing layer are not simply the proportional to their relative arrival rates.

Advanced MBE systems consist of several basic UHV building blocks, like the growth chamber, the sample preparation chamber and the load lock chamber, which are separately pumped and interconnected via large-diameter channels and isolation valves. High quality layered semiconductor structures require a background vacuum in the low 10^{-11} Torr range to avoid the incorporation of background impurities into the growing layers. Therefore, extensive LN_2 cryoshrouds are used around the substrate to achieve a locally much lower background pressure of condensable species.

We use the Riber 32P for MBE crystal growth. This Riber 32P system is the most widely used throughout the world. It is a highly flexible epi reactor that can be adapted for the growth of classical III-V compounds, II-VI compounds and nitrides. The 8 cell ports are grouped together on the evaporation flange, which includes a cryogenic panel completely surrounding all the hot parts of the cells, ensuring maximum trapping of all residual species. This flange can be specifically adapted for the growth of nitrides with Group III elements. The pumping system which can include several types of pump, is adapted to each particular application. The introduction of samples is implemented by the use of: (1) loadlock chambers (R&D systems), or (2) modular transfer modules

(Modutrac™), enabling the addition of chambers for specific treatments (metallization, pre-treatment, analysis, outgassing, etc.).

2.1.1 Radio Frequency (rf) Nitrogen Plasma Source

A rf plasma source manufactured by EPI Inc., USA is used to provide active nitrogen (N) species. The mass flow controller (MFC) is mounted between the N supply line and the precision leak valve to control the N flow during growth. When the N source is not used, the leak valve isolates the N supply from the MBE growth chamber, thus maintaining an ultra high vacuum. The reactive species of N is regulated by a pyrolytic boron nitride (PBN) disc at the end of the plasma source and changing the number of holes (25, 50, 75) in the PBN disc alters the amount of N arriving on the substrate, which in turn affects the ignition of the N plasma. We make use of the high brightness plasma mode in our III-V dilute N growth. The precise N composition can be obtained by regulating the MFC and the rf power of the N source. Due to the lack of line of sight of the N cell in one of our MBE systems, the growth mode is dispersive in nature as shown in Fig. 2-2. The figure also shows that the Sb cell position having line of sight to the substrate position.

Fig. 2-2 The Sb and N cell orientation on a Riber 32 solid source molecular beam epitaxy growth chamber.

2.1.2 Antimony (Sb) Source

The EPI valved, cracked-antimony source is shown in Fig 2-3. The corrosive nature of antimony vapor has made the long-term use of any metallic crucible or valve unreliable and therefore unusable in MBE. As a result, the primary components of the present source are made entirely from PBN. The crucible consists of a 200 cm³ high-purity PBN bulk zone containing elemental antimony which narrows to a thin neck serving as the cracking zone, where the initial tetramer Sb₄ can be dissociated into dimers Sb₂ or monomers Sb₁. The cracking zone is terminated by a valve fixture that is also made from high purity PBN. In the investigation of GaAsSb as a basic building block for

InGaAsN:Sb growth, the normal operating range is 380°C to 510°C even though it can reach 600°C. The cracker is maintained at 900°C based on the literature provided, but it can reach 1200°C. To date, the optimized growth conditions for GaAsSb on GaAs are those that:

a) lead to a high growth temperature and
b) minimize the competition between Group V species, Sb, and As. It suggests the following should be carried out:

- An increase in the GR to a value near 1 ml/s to ensure that the Sb is independent of GR.
- A total Group V flux which maintains a high-quality growth surface.
- A low arsenic overpressure to ensure that Sb can be easily incorporated.
- A Sb–As ratio around 0.2.

Fig. 2-3 Applied Epi Antimony (Sb) Cell. (extracted from Veeco Instruments at http://www.veeco.com/html/product_bymarket_proddetail.asp?productID=250&MarketID=3&Title=MBE)

2.2 Characterization Tools

2.2.1 Reflection of High Energy Electron Diffraction

The most important method to monitor the *in-situ* surface crystallography and growth kinetics during MBE growth, is the reflection high-energy electron diffraction (RHEED). It is operated at 10-50 keV in the small glancing angle reflection mode. The diffraction pattern on the fluorescent screen, mostly taken in the [100] and [110] azimuths of the (001) oriented substrates, contains information from the topmost layers of the deposited material and thus can be related to the topography and the structure of the growing surface.

Fig. 2-4 An illustration on the reflection high-energy electron diffraction setup in a growth chamber.

A high energy beam (3-100 keV) is directed at the sample surface with a grazing angle. The electrons are diffracted by the crystal structure of the sample and then impinged on a phosphor screen mounted opposite. The resulting pattern is a series of streaks. The distance between the streaks is an indication of the surface lattice unit cell size. The grazing incidence angle ensures surface specificity despite the high energy of the incident electrons. If a surface is atomically flat, then sharp RHEED patterns are seen. If the surface has a rougher surface, the RHEED pattern will be more diffuse. The typical angle of incidence of RHEED is 1° , which gives a mean free path of $2.5 \text{ \AA}$ normal to the surface. The geometry of RHEED leaves the front of the sample open for instruments such as evaporators. This permits structural changes during deposition to be monitored and in certain cases, (principally for Frank-Van-der Merwe growth) oscillations in intensity of the specular reflected beam of monolayer periodicity can be seen. The grazing incidence makes RHEED highly sensitive to the surface morphology and any asperities, giving rise to a pattern of sharp spots corresponding to transmission electron diffraction. RHEED is routinely used in the calibration of substrate temperature, the determination of GR, monitoring of the oxide desorption of GaAs at 580°C .

2.2.2 *Ex-Situ* Analysis

2.2.2.1 Photoluminescence (PL) Measurements

Photoluminescence spectroscopy is a contact-less, nondestructive method of probing the electronic structure of materials. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called "photo-excitation." One way this excess energy can be dissipated by the sample is through the emission of light or luminescence. In the case of photo-excitation, this luminescence is called "photoluminescence." The intensity and spectral content of this photoluminescence is a direct measure of various important material properties. Specifically, photo-excitation causes electrons within the material to move into permissible excited states. When these electrons return to their equilibrium states, the excess energy is released and this may include the emission of light (a radiative process) or may not (a nonradiative process). The energy of the emitted light or photoluminescence is related to the difference in energy levels between the two electron states involved in the transition; that is, between the excited state and the equilibrium state. The quantity of the emitted light is related to the relative contribution of the radiative process.

PL is used for bandgap determination. The most common radiative transition in semiconductors is between states in the conduction and valence bands, with the energy difference being known as the bandgap. It is also used for impurity levels and defect detection. The radiative transitions in semiconductors involve localized defect levels. The photoluminescence energy associated with these levels can be used to identify specific defects and the amount of photoluminescence can be used to determine their

concentration. Recombination mechanisms can also be detected. As discussed above, the return to equilibrium, also known as "recombination," can involve both radiative and nonradiative processes. The amount of photoluminescence and its dependence on the level of photo-excitation and temperature are directly related to the dominant recombination process. The analysis in photoluminescence helps us to understand the underlying physics of the recombination mechanism. In general, nonradiative processes are associated with localized defect levels, whose presence is detrimental to material quality and subsequent device performance. Thus, material quality can be measured by quantifying the amount of radiative recombination. Good PL readings are depicted by large photo-excitation intensity with very narrow FWHM. The contrary is accepted as low crystalline quality growth.

A PL measurement system (Fig. 2-5) consists of an excitation source, a variable temperature cryostat, a sample holder assembly, a high resolution scanning spectrometer and a detection system. It is necessary to cool the sample to cryogenic temperatures to get the maximum amount of information from the radiative relaxation process. This is accomplished by mounting the sample with cryogenic thermally conductive grease on a gold-coated copper cold finger of a liquid helium cryostat equipped with optical windows. A Lambertian distribution of the luminescence from the sample is collected by a suitable lens. The laser beam is incident at an angle on the sample so that the reflected beam does not enter the collecting lens. A photomultiplier tube (PMT) is used to detect PL signal at 500-900 nm and a liquid nitrogen cooled Ge detector is used for longer wavelength (smaller bandgap) materials (800-1700 nm). The SPEX 750M system is used to carry out our PL measurement. LT PL measurements from 800-1700 nm are usually

performed at 10 K using the 5145 Å line of an Ar⁺ laser as the exciting source and a liquid nitrogen cooled Ge detector as the detection source with a standard lock-in technique.

Fig. 2-5 The photoluminescence (PL) measurement setup.

2.2.2.2 X-ray Diffractometry (XRD) Measurements

High-resolution XRD measurements are carried out to obtain the composition of the epilayer, to study the lattice properties of the grown layers and to gauge the strain relaxation in the layers. Rocking curves are obtained by performing (ω - 2θ) scan, where

ω is the angle between the incident beam and the sample surface and 2θ is the angle between the incident beam and the diffracted beam. We fit the ω - 2θ (004) symmetric reflection scan dynamic rocking curves to obtain data such as the epilayer thickness and the composition, thereby getting the GR of the epilayer. However, this is only possible for coherent growth. Pendellosung fringes and the sharp intense peaks in coherently strained layers will become a featureless broad hump that shifts towards the GaAs substrate peak position when relaxation occurs. The information which is obtained from diffraction patterns can determine the composition and uniformity of the epitaxial layers, their thicknesses, the built-in strain and strain relaxation, and the crystalline quality. The lattice spacing can be determined by Bragg's Law and is given by the following formula:

$$2d_{hkl} \sin \theta_B = n\lambda \quad (2.1)$$

where, d_{hkl} is the spacing of the lattice planes with Miller indices (hkl) , λ is the wavelength and θ_B the Bragg angle. When a monochromatic x-ray beam is projected onto a crystalline material at angle θ , diffraction occurs only when the distance traveled by the rays reflected from successive planes differs, by a complete number n of wavelengths. By varying the angle θ , the Bragg's Law conditions are satisfied by different d spacing in different materials. A pattern characteristic to the sample is produced by plotting the angular positions and intensities of the resultant diffraction peaks. We show a working principle diagram of our XRD setup in Fig. 2-6. The (004) HRXRD measurements were performed using a Phillips x-ray diffractometer with a conventional X-ray generator, with a copper target ($K\alpha_1=0.15406$ nm) as the radiation source.

Fig. 2-6 The work principle diagram for the Bragg Brentano θ - 2θ x-ray diffraction setup used for our measurements.

2.2.2.3 Atomic Force Microscopy (AFM) Measurements

Atomic Force Microscopy (AFM) measurements are performed using a Shimadzu Environment Controlled Scanning Probe Microscope (SPM-9500J2). The root mean square (RMS) values of the square average surface roughness in nanometers (nm) may be obtained from $3 \times 3 \mu\text{m}^2$ areas using a scan rate of 1 Hz. A result is shown in Fig. 2-7. This analysis method is for the observation of the surface morphology of the grown crystals.

Fig. 2-7 A $3 \times 3 \mu\text{m}^2$ (AFM) scan on a sample.

2.2.2.4 Hall Measurements

We can obtain the mobility and carrier concentration of samples from Hall measurements using the van der Pauw technique. This is especially important for the doping of semiconductor material with Be, C for *p*-type dopants and Si for *n*-type dopants. Layer growth should be greater than 400 nm because heating the indium (In) contacts will cause them infuse deep into the sample, rather than bond to the surface of the desired epilayer. Four small ohmic contacts are placed at the corners of the wafer. The contact quality and size are very important concerns in hall measurements.

2.2.2.5 Secondary-ion Mass Spectroscopy (SIMS) Measurements

All SIMS measurements are conducted using a Cameca IMS 6f magnetic sector ion microprobe to provide information on epitaxial profile and atomic concentration. The SIMS setup comprises three essential parts: the primary optics with ion mass filter, the secondary ion beam optics and the secondary ion detectors as seen in Fig. 2-8, which is extracted from Cameca's IMS-6f User's guide (1998). UHV is obtained from a combination of titanium sublimation with ion or turbo-molecular pumping. The system is equipped with a magnetic sector analyzer, which has superior maximum mass resolving power of at least 25000 m/Dm (10 % definition) providing excellent beam stability, as well as an ultra-fine minimum beam size (200 nm for Cs⁺). The key capabilities of this system include a low detection limit and a high resolving power in depth profiling. MCs⁺ secondary ions such as M = ¹²C, ¹⁴N, ¹⁶O, ²⁸Si, ⁶⁹Ga, ⁷⁵As, ¹¹⁵In and ¹²¹Sb are used in our measurements, as positive ions minimize the dependence on the matrix effect in III-V semiconductor compound matrix elements. The depth resolution of SIMS has typical values of 3–5 nm, caused by surface roughening and ion beam intermixing during sputtering. A primary accelerating voltage of 4.00 kV and 2.00 kV for secondary is used. The primary beam is rastered over a square region of 250 μm² and the secondary ions are collected using a physical aperture of 30 μm in diameter. These are the values used in SIMS measurements. If not, the correct dimensions will be mentioned in the chapters. The DEKTAK³ ST surface profiler is used to determine the depth profile of the crater to be analyzed.

Fig. 2-8 A schematic view of a Cameca IMS-6f. (extracted from Cameca, IMS-6f, User's Guide (1998))

Chapter 3

X-ray Reciprocal Space Mapping of Strain Relaxation in GaAs_{1-x}N_x on (001) GaAs by Molecular Beam Epitaxy

3.1 Introduction

To achieve the 1.3 μ m and 1.55 μ m operating wavelengths, nitrogen content greater than 2 % has to be incorporated into the epitaxial layer. However, when the N composition is increased, strain builds up rapidly, especially when thick bulk layers are desired. It is well known that kinetics like lowering the growth temperature can impede dislocation formation and increase the critical thickness [14]. In this chapter, we investigate the effects of GR on the relaxation in GaAsN alloys using high resolution $(\omega+\Delta\omega)/(\omega-2\theta)$ mapping methods [15-16] as the characterization technique to determine the tilt angle, $\Delta\psi$. This is also performed by Uesugi *et al.* [17] to understand the strain and relaxation mechanisms. The GaAs/GaAsN peak profile change is clearly documented when GaAsN epilayers grown on GaAs substrates, change from a slightly strained to a highly relaxed state. III-V nitrides are able to exceed the critical thickness by a few times, before strain is relieved by dramatic relaxation.

3.2 Experimental Details

An As/III flux ratio of ~ 25 of arsenic species As_4 , is used to perform oxide desorption at 590°C and for growing a $1000\text{ \AA}$ GaAs buffer at 580°C . After the GaAs buffer growth, the gallium (Ga) shutter is closed to block any incident flux before the substrate temperature was lowered to 460°C . Prior to striking the N plasma, an interruption of 3 min was allowed to stabilize substrate temperature at 460°C . Before the striking of plasma, the main and N shutters were closed to prevent affecting the integrity of the buffer surface due to high rf plasma impingement, where accelerated N ions introduce crystalline damages. Once the plasma is ignited and stabilized, we grow the $1000\text{ \AA}$ GaAsN epilayer. The Ga and N shutters are opened prior to the opening of the main shutter such that the Ga flux and N plasma can arrive on the substrate simultaneously. The same As/Ga flux ratio is used for the GaAs and GaAsN layers and gallium flux is unchanged during both GaAs and GaAsN growth in each sample. The final investigated structure is GaAsN (100 nm)/GaAs (100 nm). GaAsN samples grown at $0.7\text{ }\mu\text{m/hr}$ are characterized from a minimum rf power of 80 W, increasing the rf power to a point where the *in-situ* RHEED pattern begins to change from streaky towards a diffuse or slightly spotty observation. This is a method to decide the point where relaxation roughly takes place. From 80 W to 160 W, samples had streaky RHEED patterns, indicating good surface reconstruction. These are similar to the RHEED patterns published in our previous work [18]. The RHEED pattern for sample 217 (200 W) became short and diffused towards the end of the growth, indicating a non-2D surface. For sample 218 (240 W), the RHEED pattern became spotty, representing relaxation. Subsequently, another set of GaAsN samples was grown at $1\text{ }\mu\text{m/hr}$ to investigate the

effect of GR on strain relaxation, near the vicinity of relaxation for samples grown at 0.7 $\mu\text{m/hr}$.

XRD and AFM measurements were performed. The details to the SIMS measurements can be found at 2.2.2.5. A primary accelerating voltage of 2.52 kV and 2.00 kV for secondary was used. The primary beam was rastered over a square region of 300 μm^2 and the secondary ions were collected using a physical aperture of 60 μm in diameter.

3.3 Results and Discussion

3.3.1 High Resolution X-Ray Diffractometry (HRXRD)

The N composition of the capless GaAsN was determined by fitting dynamic rocking curves from (004) scans, using dynamic diffraction theory. This N composition was further verified by SIMS, which resulted in a maximum of $\pm 1.5\%$ fluctuation between the two characterization techniques for $N < 3\%$. We can obtain the perpendicular lattice constant of GaAsN ($a_{\perp}$) and the tilt angle, $\Delta\psi$, using the following equations [19].

$$a_{\perp} = a_{\parallel} + ((C_{11} + 2C_{12})/C_{11}) (a_0 - a_{\parallel}) \quad (3.1)$$

$$\Delta\psi = \tan^{-1} (\sqrt{2}/5) - \tan^{-1} (\sqrt{2} a_{\perp} / 5a_{\parallel}) \quad (3.2)$$

The C_{11} and C_{12} of GaAsN can be obtained by interpolating from cubic GaN (293/159 GPa respectively) and GaAs (118.79/53.76 GPa respectively) [20] using the N composition. The parallel lattice constant $a_{\parallel(\text{GaAsN})}$ is the same as that the lattice constant

of GaAs for coherently strained layers and a_0 is the lattice constant of cubic GaAsN. The contour space mapping of the samples were obtained by running $(\omega \pm \omega_0) / 2\theta$ scans for different offset angles ω_0 on a mechanically stable goniometer stage and recording the profiles. $\Delta\psi$ is measured as the separation in ω between the GaAs and GaAsN peak. By comparing the calculated and measured $\Delta\psi$, we acquire the magnitude of the GaAsN strain or relaxation. The relaxation ratio, R is the extent of relaxation.

$$R = (a_{//} - a_{\text{GaAs}}) / (a_0 - a_{\text{GaAs}}) \quad (3.3)$$

The tilt angle (Fig. 3-1) corresponds to the separation on the $\Delta\psi$ axis (Fig. 3-2) of the GaAsN peak from the GaAs peak in 2D (115) HRXRD [19]. When the measured tilt angle corresponds to the one on the dotted line in Fig. 3-1, the GaNAs layer is coherently grown on the GaAs substrate. The epilayer peak profile deviates from the coherent peak position to a smaller diffraction angle (Fig. 3-1) when relaxation occurs [17]. A fully relaxed sample will give $a_{\perp}(\text{epilayer}) = a_{//}(\text{epilayer})$, corresponding to the horizontal dashed line at $\Delta\psi = 0^\circ$.

Fig. 3-1 (Solid Line) – Two dimensional (115) $\Delta\psi$ versus N (%) for 0.7 μm/hr, (Dotted Line) – Calculated $\Delta\psi$ for coherent GaAsN growth on GaAs, where deviation towards the Dashed Line means relaxation.

In 0.7 μm/hr growth, the measured $\Delta\psi$ matches the calculated $\Delta\psi$ for rf power from 80 W to 160 W. Beyond that, it starts to fall away and in sample 218 (240 W), a dramatic deviation to $\Delta\psi = 0.06241^\circ$ was observed. N (%) from (004) scan gives a much lower composition of 2.65 %, due to relaxation of GaAsN peak. Fig. 3-2(c) depicts sample 218 as a highly relaxed epilayer, also circled in Fig. 3-1. This is further evidenced by a spotty RHEED pattern and the lack of Pendellosung fringes in the (004) XRD scan, seen in Fig. 3-3.

(a)

(b)

Fig. 3-2 The profile of GaAs (left)/GaAsN (right) peak for rf power (a) 200 W, (b) 220 W at growth rate of 0.7 $\mu\text{m/hr}$.

(c)
Fig. 3-2 (continued) The profile of GaAs (left)/GaAsN (right) peak for rf power (c) 240 W at growth rate of 0.7 $\mu\text{m/hr}$.

Fig. 3-3 The (004) XRD measurement of sample MN218.

(004) XRD scans closely resemble the superposition of all the 1-dimensional ω -2 θ (115) scans, viewed along the ω -2 θ plane. Any elongation in the diffracting vector direction corresponds to a strain gradient along that direction. As rf power increases, more active atomic N is incorporated into substitutional sites and more tensile strain is produced. Figure 3-2(a-c) depicts the $\Delta\omega$ versus ω -2 θ 2D (115) plots of the GaAs and GaAsN peak profile change from a distinct profile in a largely strained sample [Fig. 3-2(a)] to that of a nearly fully relaxed sample [Fig. 3-2(c)], with the transition phase occurring at Fig. 3-2(b). The peak profile of GaAs under low strain (low N %) is circular, pronounced and has a small spread. Sample 219 at 220 W [Fig. 3-2(b)], which is subjected to greater tensile strain loses the distinct GaAsN peak, while following closely to the coherent growth line (Fig. 3-1). The GaAs profile is more diffused and skewed in the direction where the GaAsN peak is, hinting the start of relaxation in both vector directions. Dramatic relaxation occurs for sample 218 grown at 240 W [Fig. 3-2(c)], with the GaAs returning to a circular profile after strain relief. From this observation, the GaAs profile changes when subjected to strain, indicating that both the GaAsN and GaAs interface are affected.

From the results, GaAsN can be grown to ~ 2.7 times of the critical thickness at a GR of 0.7 $\mu\text{m/hr}$. The Matthews and Blakeslee's mechanical equilibrium model which is described by the equation

$$h_c = \frac{b}{1 + \nu(x)4\pi f(x)} \left[\ln\left(\frac{h_c}{b}\right) + 1 \right]. \quad (3.4)$$

was used to calculate the critical thickness, h_c [21]. It depicts that for a thickness below h_c , the misfit strain is accommodated without the formation of misfit dislocations. x is the nitrogen (N) composition and the Poisson's ratio, $\nu(x)$ can be defined as

$$\nu = \frac{C_{12}}{C_{11} + C_{12}}. \quad (3.5)$$

The strain is denoted by $f(x)$. The Burger's vector, b can be described as

$$b = \frac{a_0}{\sqrt{2}}, \quad (3.6)$$

where a_0 is the lattice constant of GaAsN, interpolated from the lattice constants of GaAs and cubic GaN (4.5 Å). GaAsN was grown at 1 $\mu\text{m/hr}$ to observe the effect of GR on critical thickness. Samples 025 and 026 show some inconsistencies in the rf power and N % as compared to the rest of the samples because of a drift in chamber conditions after a chamber vent, despite using the same growth conditions. It is crucial to realize that GaAsN (160 W/N = 2.21 %) grown at 0.7 $\mu\text{m/hr}$ deviates from the coherent growth line, whereas GaAsN (250 W/N = 2.66 %) grown at 1.0 $\mu\text{m/hr}$ does not. We can infer that the increase of GR has an effect of maintaining the crystal quality and surface reconstruction. Sample J004 with N $\sim$ 4.8 % (1 $\mu\text{m/hr}$) was able to grow coherently for 100 nm on GaAs, as shown in Fig. 3-4, with a prominent GaAsN peak, compared to Fig. 3-2(b) and (c) of lower N %, grown at 0.7 $\mu\text{m/hr}$.

Table 3-1. The nitrogen (%) with growth rate, rf power, critical thickness and C values.

Sample	GaAs Growth Rate (μm/hr)	rf power (W)	N (%)	h_c (nm)	C = Thickness/ h_c	GaAsN Growth Rate (μm/hr)
214	0.7	80	0.56	186.36	0.408	0.5323
215	0.7	120	1.14	91.45	0.864	0.5533
216	0.7	160	2.21	47.08	1.763	0.5813
217	0.7	200	2.77	37.53	2.318	0.6093
219	0.7	220	3.1	33.51	2.686	0.6304
218	0.7	240	3.62	-	-	-
025	1.0	150	1.5	69.86	1.431	-
026	1.0	250	2.66	39.21	2.55	-
J002	1.0	250	3.4	30.61	-	-
J004	1.0	285	4.82	21.52	4.647	-

Fig. 3-4 The profile of GaAs ((left)/GaAsN (right) peak for rf power at 285 W at growth rate of 1.0 μm/hr, where the horizontal axis is $\omega-2\theta$ (°) and the vertical axis is $\Delta\psi$ (°).

3.3.2 Influence of N on Strain in Bulk and Surface Quality

N_2^+ and N_2^* reactive species readily incorporate to form clusters due to strong N-N bonds [18]. The high N bond strength associated with substitutional N causes threads to glide more slowly in the nitride. Hence more misfits must be nucleated and more threads must be generated in order to relieve the strain. This causes degradation in crystalline quality but lowering overall strain relaxation [22]. The need for thermal annealing is deemed as an essential step in acquiring device grade material quality when growing III-V-N, especially at N content greater than 1 %.

AFM measurements were performed for an area of $300 \times 300 \text{ nm}^2$ on samples 215 (N ~ 1.1 %) to 218 (N ~ 3.6 %) and the RMS values of the surface roughness (nm) were obtained. Fig. 3-5 shows the increase of surface roughness upon increasing the rf power periodically, whilst fixing the rest of the parameters. It is observed that surface morphology from 1.14 % to 2.21 % of N is nearly the same. Hence, the critical thickness of GaAsN on GaAs can be exceeded by ~1.8 times without any visual surface degradation. This is further verified by the coherent growth of sample 216 (N = 2.21 %) from 2D HRXRD (115). In Fig. 3-5(c), volcano-shaped defects with an average of 250 Å in diameter are observed. These volcano-shaped defects are produced when misfit dislocations propagate from the substrate to the surface to relieve the tensile strain buildup. These defects are different from the conventional oval defects caused by Ga droplets and are commonly accepted as micron-sized [23]. The 3-dimensional morphology in Fig. 3-5(d) is attributed to the increase in surface roughness due to pinned

dislocations caused by misfit dislocation strain fields, resulting in very high density pileups [24].

Fig. 3-5 300×300 nm² AFM measurement of GaAsN on GaAs for nitrogen at a) 1.14 %, b) 2.21 %, c) 2.77 %, d) 3.62 % for a uniform thickness of 100 nm.

3.3.3 Effect of rf Power on Interstitiality

Fan *et al.* [25] mentioned an underestimation of $N \sim 14.3\%$ in GaAsN_x for $x = 4.2$ % comparing the deviation between SIMS and HRXRD results. The discrepancy originates from the presence of N interstitials. As such, the increase of N towards 5 % brings about a sudden increase in interstitial N, confirmed by SIMS/HRXRD comparison as well as near exponential photoluminescence intensity quenching, (Fig. 3-6) which is believed to be caused by the presence of interstitials for $N > 3\%$. N atoms energetically prefer to move out from their substitutional site in the As sub-lattice to neighboring interstitial sites when N exceeds 2.9 % [26]. The formation of split interstitial N–As complexes induces a compressive strain, offsetting part of the tensile strain. Hence, when N % increases, it becomes less tensile strained than predicted by Vegard's Law, resulting in a greater critical thickness [25]. We derive a constant, C , which denotes the ratio of the thickness grown over the critical thickness (h_c) as a measure of the number of times critical thickness can be exceeded, shown in Table 3-1.

In the J000 series, we were able to show the properties of N interstitiality on critical thickness. This series has the same growth conditions with the 21X series and Table 3-2 shows the time duration where the RHEED display maintains from streaky to dovetail and spotty for a 6 min epilayer growth of GaAsN (100 nm). J002 and J003 follow the logical trend, whereby the increase of tensile strain brought on by higher rf power results in quicker conversion to a spotty result, since there is low concentrations of N_i . However, for J004 the RHEED maintained at dovetail for the whole growth duration. HRXRD shows coherent growth (Fig. 3-4) and for $N \sim 4.82\%$, it has exceeded the

critical thickness by ~ 4.6 times (Table 3-1). The increase of compressive split interstitial N–As, thus, offsets part of the tensile strain and the kinetic restrictions caused by a raised GR allows the critical thickness to be increased.

Fig. 3-6 The PL intensity quenching due to the presence of N interstitials around 3% of nitrogen.

Table 3-2. The time duration of RHEED observation for N > 3 % at 1.0 μ m/hr.

	rf (W)	Streaky	Dovetail	Spotty
J002	250	70s	30s	260s
J003	270	40s	20s	300s
J004	285	60s	300s	-

3.4 Conclusions

We have investigated the tilt angle, $\Delta\psi$ response to GaAsN on GaAs under increasing tensile strain, using two dimensional (115) HRXRD rocking curves. The GaAs and GaAsN_{4.8%} peak profile changes from a highly strained to partially relaxed, and a severely relaxed peak profile was observed, pointing to changes in both GaAs (substrate) and GaAsN (epilayer) interfaces when subjected to strain. GaAsN/GaAs is able to exceed the critical thickness by nearly twice without any degradation in surface quality. GaAsN_{4.8%} is grown to 100 nm without relaxation, exceeding the critical thickness by 4.6 times.

Chapter 4

Interpretation of Anomalous Extra Peak in Photoluminescence Measurements of Bulk GaAs_{1-x}N_x Epitaxial Layer on GaAs

4.1 Introduction

The introduction of N introduces a strong modification to the band structure of (In)GaAs. The band-anticrossing model, based on the repulsive behavior between the conduction band edge (CBE) and the localized N resonant states, is one of the models employed to describe this modification [4]. The large electronegativity of N atoms as compared to As significantly alters the III-As-N epilayer from that of an ideal random alloy. N atoms tend to incorporate into non-substitutional lattice sites and form defect complexes due to the small covalent radii of nitrogen. Besides that, dilute nitride growth also heralds a host of associated defects such as Ga vacancies, As_{Ga} antisites, which lead to the deterioration of the optical and electrical characteristics [27]. RTA can be used to improve the epitaxial quality by eliminating the impurity-related radiative and nonradiative recombination centres. The common observations from RTA include the blueshift of the PL peak position and the improvement of the PL efficiency by more than one order. The blueshift has been claimed to be caused by nitrogen outdiffusion at the

interfaces [28]. However, in recent research, it is unanimously agreed that the blueshift is caused by the homogenization of the bulk N composition, driven by strain relief during the RTA process [29-30]. In contradiction to the above mentioned work, Francoeur *et al.* reports that annealing causes a redshift for GaAsN_{0.019} [31]. To further complicate matters, two energy peaks in LT PL measurements have been reported in GaAsN_x ($0.5\% \leq x \leq 1.5\%$) grown by SSMBE [32-34]. The two emission peaks are claimed to be originated from spatial carrier localization and from regions of varying N composition, which blueshift with increasing annealing temperature. In this paper, our group also reports that 2 peaks are observed from the bulk GaAsN epitaxial layer from LT PL measurements. The most unique phenomenon is that the high energy peak (denoted by α) blueshifts and the lower energy peak in the PL spectra (denoted by γ) redshifts when subjected to increasing annealing temperature during RTA. Amid the confusion shrouding this issue, we attempt to interpret the origins of these peaks and the abnormality behind the red/blueshift using a model and substantiate it with SIMS measurements.

4.2 Experimental Details

A ~ 1000 Å GaAsN epilayer was grown at 490 °C on a 3000 Å GaAs buffer and subsequently capped with ~ 200 Å GaAs (580 °C) on semi insulating (100) orientated GaAs substrates. The rf power in high brightness mode is kept at about 100 W to allow an N composition of ~ 1.3 %. Rapid thermal annealing (RTA) is performed for 7×7 mm² samples diced from the GaAsN wafer. The samples were annealed each at a different temperature, in steps of 50 °C between 600 °C to 800 °C. The RTA is performed in nitrogen ambient for a fixed interval of 10 min. GaAs wafer proximity capping was used to prevent As desorption at elevated temperatures. LT PL measurements were performed at 10 K using the 5145 Å line of an Ar⁺ laser as the exciting source and a liquid nitrogen cooled Ge detector as the detection source with a standard lock-in technique. The details to the SIMS measurements can be found at 2.2.2.5.

4.3 Results and discussion

4.3.1 Photoluminescence peak spectra of annealed GaAsN

Figure 4-1 depicts the LT PL measurement of the as-grown and the annealed GaAsN_{1.3%} sample. The annealed samples are plotted in 50 °C intervals from 600 to 800 °C. We observe 2 peaks in the LT temperature PL spectra. Firstly, we introduce the lower energy peak in the PL spectra (denoted by γ) which exhibits an asymmetric line shape with a low-energy tail. The γ peak blueshifts by ~ 6 meV from the as-grown to 600 °C and

gradually redshifts by ~31 meV from 600 to 750 °C. The redshift observed is primarily caused by interstitial N entering substitutional sites at ~750 °C [31,35].

Fig. 4-1 Low temperature 10 K photoluminescence measurement of the as-grown and the annealed GaAsN_{1.3%} sample vs annealing temperature (°C) in steps of 50 °C.

Our observations for the γ peak fully support the trend that RTA at a LT of $\sim 650^\circ\text{C}$ can only remove the defects which originates from the dilute-N/GaAs interfaces, causing blueshift [36]. Defects originating from the bulk however, can only be eradicated by high temperature (HT) RTA, $\sim 750^\circ\text{C}$. The PL intensity improves with increasing annealing temperature and peaks at 750°C , giving the near-bandgap radiative recombination originating from excitons localized by GaAsN when most of the impurity-related recombination centers are eradicated. Beyond 750°C , a drastic blueshift results from the over-annealing and the N-As interdiffusion occurs at the interfaces at the elevated temperatures. At this juncture, the linewidth broadens and the PL intensity decreases rapidly due to the RTA induced defects. On the high energy side, the second weaker peak (denoted by α) is observed for annealing temperatures between $650 - 750^\circ$ at $\sim 1.267\text{ eV}$. The α peak is observed to slightly blueshift ($\sim 13\text{ meV}$) with increasing annealing temperature. In order to understand the two peaks, SIMS measurements are carried out. The SIMS profile of the (a) as-grown and (b) annealed sample at 750°C is shown in Fig. 4-2.

Fig. 4-2 The SIMS measurement of the (a) as-grown and the (b) annealed GaAsN_{1.3%} sample at 750 °C with the nitrogen concentration (atm/cm³) vs the sputtering depth (nm).

The interface are shown to be abrupt before and after annealing which supports the trend that the dominant peak shifting is bulk induced rather than interface induced interdiffusion. The substrate temperature of 490 °C (higher than the optimized temperature of dilute N at 460 °C) may increase the tendency of forming three-dimensional growth and create composition modulation which perturbs the local microstructure [29,32]. In Fig. 4-2(a), we find signatures of higher N concentration at ~98 and 123 nm from the surface, which are close to the position of the GaAsN/GaAs interface. One possible interpretation of the observation is the enhancement of the N incorporation due to the enrichment of the active N species between the transients. These include the N plasma ignition and the tuning of the coupling in the rf power input to the actual epitaxial deposition, which in our case is approximately 5 min. Even when the main shutter is closed, it is unlikely to be 100 % efficient in preventing nitridation, although it is minimized. After annealing at 750 °C [Fig. 4-2(b)], the inhomogeneous elemental N distribution has been reduced and the bulk N concentration is homogenized. From the discussions, a physical model of the observed PL is proposed in Fig. 4-3.

Fig. 4-3 A proposed model of the better confinement of localized N states at higher N concentrations. The solid line denotes the as-grown energy levels and the dotted line denotes the annealed energy levels.

The transition from the areas of higher N compositions in the as-grown sample is denoted by T_1 . The more homogeneous areas with lower N compositions give rise to a higher energy transition, denoted by T_2 . The localized state with higher N has a greater amount of interstitial N (N_i) as compared to that with lower N. Under an *ex-situ* thermal treatment of 10 min, the mobile interstitial N enters a As site to form substitutional N via a kick out mechanism [28]. Hence, the low energy transition (T_1) decreases into energy (T_1'),

leading to greater confinement which allows more carriers to recombine radiatively under laser excitation. This explains the higher PL intensity of the γ transition as compared to the α peak from the bulk. The decrease of N_i in the higher N areas with increasing annealing temperature leads to greater PL intensities at the γ peak transition till 750 °C. As for the T_2 transition which arises from the lower N regions, there is less N_i generated. The T_2' transition becomes higher than the T_2 transition from the profile homogenization and causes blueshift during the *ex-situ* annealing [29-30]. This is used to explain the observed photoluminescence trend in Figure 4-1, where the dominant low energy peak (γ) redshifts and the weaker high energy peak (α) blueshifts with the annealing temperature.

4.3.2 Identification of the photoluminescence peaks using the BAC model

The origins of the peaks can be confirmed by means of the fundamental energy transition peak derived from the band-anticrossing (BAC) model including the strain effect. The effective bandgap from tensile strained $\text{GaAs}_{1-x}\text{N}_x$ epilayers is formulated as:

$$E_{g(\text{strained})} = E_g(x) + 2a\left(1 - \frac{C_{12}}{C_{11}}\right)\varepsilon + b\left(1 + \frac{2C_{12}}{C_{11}}\right)\varepsilon \quad (4.1)$$

where $E_g(x)$ is the unstrained fundamental bandgap energy, the second component lowers the conduction band (CB) and the third component raises the valence band (VB) due to the tensile strain [37]. The strain, ε is denoted as $[a_0 - a(x)]/a_0$. The GaAsN parameters are assumed to be the interpolation of the GaAs and GaN parameters as tabulated in Table 4-1.

Table 4-1. The data parameters of GaAs and GaN (zinc blende) [37-38].

	GaAs	GaN
a_0 (Å)	5.6533	4.5
a (eV)	-8.33	-7.4
b (eV)	-1.7	-2
C_{11} (GPa)	118.79	293
C_{12} (GPa)	53.76	159

The unstrained fundamental bandgap can be derived from the BAC model [39],

$$E_k(x) = \frac{1}{2}[E_M(T) + E_N - \sqrt{(E_M(T) - E_N)^2 + 4V_{MN}^2}] \tag{4.2}$$

where $E_M(T)$ is the energy of the unperturbed conduction band edge of the semiconductor matrix and E_N is the energy of the N-related level relative to the top of the valance band. E_N is constant for small N values and the acceptable range of E_N is 1.65 – 1.71 eV [38]. The V_{MN} is the matrix element describing the interaction and the hybridization between the localized N states and the extended states. $V_{MN}^2 = C_{MN}^2 x$, where C_{MN} is assumed to be a temperature independent, constant value and x is the mole fraction of N, for randomly

distributed N atoms ($x < 5\%$). The range of C_{MN} is from 2.3 – 2.7 eV [38]. Shan and co-workers use $E_N = 1.65$ eV and $C_{MN} = 2.7$ eV in their dilute nitride work [40-41]. Klar *et al.* however lists E_N to be 1.71 eV and $C_{MN} = 2.5$ eV for $T < 20$ K [42]. We fitted E_N to be 1.67 eV and $C_{MN} = 2.6$ eV for our calculations for $T = 10$ K. It is found that Kudrawiec *et al.* states E_N to be 1.67 eV for their annealed GaAsN_{0.02} samples at 750 °C for 10 min and their $C_{MN} = 2.6$ eV for photon energies ~ 1.15 eV [43], which are in very good agreement with our results. The temperature dependence of the GaAs host matrix is determined by the well-known Varshni function,

$$E_M(T) = E_{g(GaAs)} - \frac{\alpha T^2}{\beta + T} \quad (4.3)$$

and using the GaAs parameters, $\alpha = 5.408 \times 10^{-4}$ eV/K, $\beta = 204$ K and $T = 10$ K, we find $E_M(T=10\text{ K})$ to be ~ 1.5118 eV using $E_{g(GaAs)}$ of 1.512 eV at 0 K [44]. We have the energy bandgap in terms of the N composition (x) which is comparable with the experimental data of the mentioned groups [41-42, 45]. The unstrained fundamental bandgap energy can then be used to calculate the strained energy bandgap in Eq. 4.1 with the data parameters in Table 4-1 to determine the origins of the PL peaks in Fig. 4-1. The as-grown SIMS data [Fig. 4-2(a)] reveal the lower N content of 1.3 % and the higher N concentration of $\sim 1.9\%$. This corresponds to the 1.251 eV and 1.176 eV PL peak positions respectively, which unsurprisingly show that the higher energy peak (α) is from the lower N of 1.3 % and that the lower energy peak (γ) comes from the higher N concentration of 1.9 %. The straight dashed and dotted lines in Fig. 4-1 serve as a guide to the eye, the position of the strained N composition. The curved lines show the

imaginary peak shift position in relation to annealing temperature. The SIMS measurements reveal the total concentration of N regardless of the site locality. In PL measurements, only the N situated at substitutional site contributes to redshift. At the optimized annealing temperature of 750 °C, most of the interstitial Ns enter substitutional sites, contributing to the maximum PL redshift. Hence, the redshift of the low energy γ peak does not exceed 1.176 eV (corresponding to the total N of 1.9 % measured by the SIMS).

The PL peak blue shifting with annealing temperature in GaAsN is widely reported [46]. We also find the normal PL peak blue-shifting in our uniformly (see Fig. 4-4) grown GaAsN_{1.89%} in Fig. 4-5. After annealing for 10 min at 750 °C, the N profile is further homogenized (Fig. 4-4). The 10 K PL measurement of the bulk GaAsN_{1.89%} sample (Fig. 4-5) shows a single PL peak blueshifting ~50 meV from 1116 meV (as-grown) to 1165.4 meV when the annealing temperature reaches 800 °C. This again is in good agreement with the BAC model and the SIMS measurements. The dominant mechanism present in the GaAsN_{1.89%} sample during annealing is the homogenization of the N profile which leads to the PL peak blueshifting [46].

Fig. 4-4. The SIMS measurement of the as-grown GaAsN_{1.89%} and the annealed sample at 750 °C (10 min) with the nitrogen concentration (atm/cm³) vs the sputtering depth (nm).

Fig. 4-5. The low temperature 10 K photoluminescence measurement of the as-grown and the annealed GaAsN_{1.89%} sample vs annealing temperature (°C) in steps of 100 °C.

4.4 Conclusions

In conclusion, the two peaks in the GaAsN LT PL measurements are explained using RTA, SIMS and the BAC model. The γ peak confines carriers more efficiently (T_1) in the as-grown sample. As more N_i become substitutional, the confinement increases (T_1) leading to a greater PL intensity from 600 – 750 °C. The as-grown sample does not show a α PL peak until ~650 °C due to the poor quality of as-grown dilute N and the trapping of carriers in T_1 . The α peak from the lower N regions blueshifts with increasing annealing temperature due to the homogenization of the N profile. However, as the confinement increases in T_1 , T_2 has less carriers and hence the PL intensity of the α peak decreases.

Chapter 5

Investigation of N Incorporation in InGaAs and GaAs Epilayers on GaAs Using Solid Source Molecular Beam Epitaxy

5.1 Introduction

P-i-N structures are typically used to extend the electrical field across the absorbing *i*-layer of solar cells. The use of LM semiconductors can prevent strain related defects from generating non-radiative pathways, thus maximizing the efficiency. The precise nitrogen and indium contents are the prerequisite for accurate lattice matching of $\text{In}_x\text{GaAsN}_y$ to GaAs in SSMBE growth [2]. It is a common practice to calibrate the In and N compositions of InGaAsN independently by analyzing the ternary GaAsN and InGaAs layers with the same composition. This can only be a good approximation for low In (%), due to the fact that the N content is inversely proportional to the Group III GR. Kurtz *et al.* recognized the challenge to demonstrate thick (2-3 μm) $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ ($y > 0.02$) epilayers [47]. To date, InGaAsN epilayers have been grown to 3 μm on GaAs using high GR, mainly by MOCVD [9,47]. It is difficult to use HRXRD to provide reliable x and y values for $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ layers to the LM condition without the reference GaAsN and InGaAs epilayers. Furthermore, the initial nitridation at the (In)GaAsN/GaAs interface

causes the first monolayer to be distorted, when N atoms readily exchange sites with As due to its high electronegativity, at the GaAs interface with the formation of GaN [48]. This surface-reconstruction induced subsurface strain sets the stage for strained growth and/or 3D growth. Hence, it is important to understand the interdependency of each element in the InGaAsN alloy and the effect of N and In on the energy bandgap. In this article, we investigate the In/N incorporation in InGaAsN by PL and SIMS measurements.

5.2 Experimental Details

Two samples consisting of InGaAsN/GaAsN/InGaAs spaced and capped by GaAs were grown by SSMBE using a Riber MBE 32. These structures are grown to show the change in N incorporation via changes in GR (Group III flux) contributed by both Ga and In. Fig. 5-1 shows the growth structure and the growth thickness of the samples.

	Thickness (nm)	
C54	Designed	Actual
GaAs	20.0	15.0
GaAsN	25.0	18.8
GaAs	20.0	15.0
InGaAs	20.0	15.0
GaAs	25.0	18.8
InGaAsN	45.0	33.8
GaAs	100.0	75.0

	Thickness (nm)	
LM026	Designed	Actual
GaAs	25.0	18.8
InGaAs	25.0	18.8
GaAs	25.0	18.8
GaAsN	50.0	37.5
GaAs	25.0	18.8
InGaAsN	100.0	75.0
GaAs	100.0	75.0

Fig. 5-1 The growth structure of samples C54 and LM026, where the top is the growth direction.

By combining InGaAsN/GaAsN/InGaAs on the same sample, the In and N composition discrepancies from sample to sample are minimized. The rf power was kept at 174W with the mass flow controller fixed at 0.1 sccm. Elemental gallium (7N), indium

and arsenic (6N) were used for growth on semi-insulating GaAs (001) orientated substrates. The V/III flux ratio of ~ 30 was used to perform oxide desorption at 590 °C and for growing a 1000 Å GaAs buffer at 580 °C. After the GaAs buffer growth, the gallium (Ga) shutter was closed to block the incident Ga flux before lowering the substrate temperature to 460 °C. An interruption of 3 min was allowed to stabilize the substrate temperature to 460 °C. Before the striking of plasma, the main and N shutters were closed to prevent affecting the integrity of the buffer surface due to the high rf plasma impingement. Once the plasma was ignited, the In, Ga and N shutters are opened prior to the opening of the main shutter, such that the Group III elements and the N plasma can arrive on the substrate simultaneously.

PL measurements were performed at 4.7 K using the 5145 Å line of an Ar^+ laser as the exciting source and a liquid nitrogen cooled Ge detector as the detection source with a standard lock-in technique. The details to the SIMS measurements can be found at 2.2.2.5. Epilayer thickness was obtained in sputtering time by approximation of the step function profile in the desired material. The time interval can be converted to thickness by obtaining the total sputtering depth found by the depth profiler and the total sputtering time. The small concentration of N in (In)GaAsN is assumed to have no significant influence on the sputtering rate and hence it is assumed to be same as that of (In)GaAs

5.3 Photoluminescence and Secondary-Ion Mass Spectroscopy Measurements

Figure 5-2(a) displays the 4.7 K PL measurement of C54, where the emission peaks of InGaAs, GaAsN and InGaAsN are observed. The origins of the peaks can be confirmed by means of the fundamental energy transition peak derived from the BAC model [4] and the strain effects on the band edge energies. Separate PL measurements of our previous tensile strained GaAsN_y samples [Fig. 5-2(b)] show the dependence of low temperature emission peak energy to the dilute N content. The tensile strained energy bandgap of GaAsN_y can be calculated using:

$$E_{g(strained)} = E_g(y) + 2a(1 - \frac{C_{12}}{C_{11}})\epsilon + b(1 + \frac{2C_{12}}{C_{11}})\epsilon \quad (5.1)$$

where $E_g(y)$ is the unstrained, fundamental bandgap energy, the second (hydrostatic) component lowers the bandgap and the third (shear) component raises the VB due to tensile strain [37]. The transition is from CB to light-hole (LH) for tensile strained epitaxial layers. The strain, ϵ is denoted as $[a_0 - a(y)]/a_0$, where a_0 and $a(y)$ are the lattice constants of GaAs and GaAsN_y respectively. The GaAsN parameters are assumed to be the interpolation of the GaAs and GaN parameters as tabulated in Table 5-1, extracted from Ref. 37 and 38.

Fig. 5-2 (a) The 4.7 K PL measurement of C54. (b) The strained and unstrained energy bandgap emission peak (eV) vs N % of GaAsN on GaAs at 4.7 K, as derived from the band anticrossing model.

Table 5-1. The lattice constant (a_0), the elastic constant C_{11} and C_{12} and other parameters of GaAs, InAs, cubic GaN and cubic InN.

Parameter	GaAs	InAs	GaN	InN
C_{11} (GPa)	118.79	83.29	293	187
C_{12} (GPa)	53.76	45.26	159	125
a_0 (Å)	5.6533	6.0584	4.5	4.98
a (eV)	-8.33	-6.08	-7.4	-3.35
b (eV)	-1.7	-1.8	-2	-1.2

The unstrained fundamental bandgap can be derived from the BAC model [4],

$$E_g(x) = \frac{1}{2} [E_M(T) + E_N - \sqrt{(E_M(T) - E_N)^2 + 4V_{MN}^2}] \quad (5.2)$$

where $E_M(T)$ is the energy of the unperturbed CB edge of the semiconductor matrix and E_N is the energy of the N-related level relative to the top of the valance band. The V_{MN} is the matrix element describing the interaction and the hybridization between the localized N states and the extended states. $V_{MN}^2 = C_{MN}^2 x$, where C_{MN} is assumed to be a temperature independent, constant value and x is the mole fraction of N, for randomly distributed N atoms ($x < 5\%$). The E_N is 1.67 eV and $C_{MN} = 2.6$ eV for our calculations. We observe that the PL trend of our GaAsN_x samples follow the theoretical strained nitride BAC model. However, it follows to the composition regime described in Taliercio *et al.* more strictly for N < 1 % [49]. With this information, the N composition in the GaAsN layers may be obtained if the GaAsN emission peak is present. The N composition of GaAsN in sample C54 is estimated and listed in Table 5-2.

Fig. 5-3 (a) The 4.7 K PL measurement of LM026. (b) The strained and unstrained energy bandgap emission peak (eV) vs In % of InGaAs on GaAs at 4.7 K.

Table 5-2. The compositions for InGaAs, GaAsN and InGaAsN layers in LM026 and C54.

LM026

Element	Layer	Composition from SIMS (%)	PL peak (nm)	in (eV)	Composition from PL (%)
In	InGaAs	12.40	917	1.3520	14.60
N	GaAsN	1.89	*1049	*1.1818	(unresolved)
In	InGaAsN	14.00	1089	1.1385	16.05
N	InGaAsN	2.16			2.04

C54

Element	Layer	Composition from SIMS (%)	PL peak (nm)	in (eV)	Composition from PL (%)
In	InGaAs	10.70	904	1.4202	12.90
N	GaAsN	1.890	1033	1.2002	1.735
In	InGaAsN	11.60	1085	1.1427	10.10
N	InGaAsN	2.40			2.30

* Estimated by BAC model using the N composition obtained from SIMS measurements

We can also obtain the In(%) composition for the InGaAs epilayer by using the PL measurement of C54 [Fig. 5-2(a)] and LM026 [Fig. 5-3(a)], since the unstrained low temperature energy bandgap equation is well established. Using

$$Eg_{In_{1-x}GaAs}(eV) = 0.475x^2 + 0.6337x + 0.4105 \tag{5.3}$$

for unstrained InGaAs at 2 K and Eq. (5.1), we can derive the compressive strained InGaAs energy bandgap, using the interpolated GaAs and InAs parameters shown in Table 5-1. The influence of the temperature difference between 2 K and 4.7 K is negligible. The transition in this instance is from CB to heavy-hole (HH) due to the compressive strain. The unstrained and strained InGaAs on GaAs bandgap emission energies at 4.7 K are plotted in Fig. 5-3(b) and the corresponding indium compositions of C54 and LM026 derived from the PL measurements are tabulated in Table 5-2.

The BAC model may be used to identify the composition of the InGaAsN peaks in the PL measurements. We slightly modify the E_N and C_{MN} parameters of Vurgaftman *et al.* [38] for In_xGaAsN to:

$$E_N(x) = 1.67(1-x) + 1.44x - 0.38x(1-x) \quad (5.4),$$

$$C_{MN}(x) = 2.6(1-x) + 2x - 3.5x(1-x) \quad (5.5)$$

The corresponding transition from CB to either HH or LH is taken, depending on whether the InGaAsN epilayer is compressive or tensile strained on GaAs. We plot the strained bandgap variation of In_xGaAsN_y for y values 1 %, 2 % and 3 % in Fig. 5-4 at 4.7 K.

Fig. 5-4 The strained energy bandgap emission peak (eV) vs In % of InGaAsN on GaAs at 4.7 K for N content at 1 %, 2 % and 3 %.

When we compare the low temperature PL measurements of C54 [Fig. 5-2(a)] with the epitaxial growth design parameters, we can infer that the leftmost peak is from the InGaAs layer, the middle peak is from the GaAsN layer and the rightmost peak is from the InGaAsN layer. However for sample LM026, the PL measurement [Fig. 5-3(a)] only shows two humps, which should come from the graded InGaAs and InGaAsN/GaAsN layers. We suggest that the GaAsN layer peak is enveloped by the broad InGaAsN hump. There is no definite way of determining the In and N composition, using solely the InGaAsN emission peak in PL measurements. It is a common practice to assume that the In composition in InGaAs and InGaAsN remains unchanged to derive a N composition for InGaAsN, using the BAC model and the PL measurements. Hence, unless all the epitaxial layers are well grown and all the peaks appear in PL measurements, inaccurate elemental composition values will result.

SIMS is a powerful tool to determine the In and N compositions in (In)GaAsN layers. Our sample LM026 is used as a standard for the InGaAsN/InGaAs/GaAsN material system. The standard SIMS sample [Fig. 5-5(a)], which is measured at Applied Microanalysis Labs becomes a lookup table with the SIMS measurement conducted in our laboratory [Fig. 5-5(b)]. The precise concentration (atom/cc) of nitrogen in (In)GaAsN and indium in InGaAs(N) for other samples, such as C54 (Fig. 5-6) can be derived if measured under the same sputtering conditions as LM026 [Figure 5-5(b)]. The concentration of N in GaAsN can be obtained by the following equation.

$$x_N = \frac{RSF}{2.21 \times 10^{22}} \times \frac{I_{NC_s}^+}{I_{GaC_s}^+} \quad (5.6)$$

Fig. 5-5 (a) The SIMS measurement of LM026 with the concentration (atoms/cc) vs the sputtering depth (μm). (b) The SIMS measurement of LM026 with the secondary ion intensity (counts/sec) in log. scale vs the sputtering time (sec). Only Ga, In and N lines are shown.

Fig. 5-6 The SIMS measurement of C54 with the secondary ion intensity (counts/sec) in log. scale vs the sputtering time (sec).

I_{NC^+} is the N secondary ion intensity (SII) in the measured sample and I_{GaC^+} is the Ga SII. The relative sensitivity factor (RSF) is used for the quantitative calibration of SIIs.

$$RSF = \frac{C_N}{\frac{I_N}{I_{ref}}} \quad (5.7)$$

I_N is the nitrogen SII and I_{ref} is the SII of the reference element, Ga for the GaAsN standard sample. C_N is the reference N concentration. Using this method, the N and In

composition of all the epitaxial layers in C54 can be acquired and are tabulated in Table 5-2. LM026 was found to have a N content of 1.89 % for GaAsN and 2.16 % for InGaAsN. Using the N SIMS results, the GaAsN PL peak position of LM026 should be at ~1049 nm. We also observe that the epilayer thicknesses are different from the designed values and we tabulate the actual thicknesses of the epilayers in Fig. 5-1, together with the nominal values. The actual GR is usually lower than that of the designed GR due to discrepancy in the calibration of the GR in the MBE growth chamber.

5.4 Conclusions

InGaAsN/GaAsN/InGaAs structures were successfully grown on GaAs substrates using MBE with a nitrogen rf plasma source. By placing all the alloys on the same sample, the dependency of In and N in InGaAsN on GaAs has been investigated by means of PL and SIMS measurements. We are able to prove that by using SIMS and PL measurements, we are able to correlate the bandgap emission peaks to the various epitaxial layers and determine the In and N compositions. We also confirm the compositions using HRXRD measurements, giving us a better understanding of the relationships between the composition and the PL characteristics.

Chapter 6

Surfactant and Impurity Properties of Antimony on GaAs and GaAs_{1-x}N_x on GaAs [100] by Solid Source Molecular Beam Epitaxy

6.1 Introduction

Surfactant mediated growth using Sb have gained interest recently in the III-V dilute nitride system besides the Si material system [50-52]. Surfactants are typically elements which segregate to the growth front and alter the surface kinetic process. This results in an increase in the critical thickness as the growth mode maintains two-dimensional by inhibiting Stranski-Krastanov islanding. The energetic and structural aspects of surfactant monolayers have been defined by means of a simple solid-on-solid model for Sb on Si and SiGe substrates [53]. Possibilities for device applications beyond 1.3 μm are opened for III-V-Ns since the presence of N results in a large bandgap bowing factor caused by a highly mismatched anion [2,19,54]. Sb was proposed as a surfactant in III-V-N compound semiconductors in order to improve the quality of highly strained InGaAsN/GaAs QWs [55]. 1.3 μm InGaAsN:Sb/GaAs multiple-quantum-well laser

diodes have been successfully grown by SSMBE [10]. The addition of Sb into InGaAsN not only serves as a surfactant, but also as an alloy constituent that redshifts the optical emission beyond 1.3 μm [56]. InGaAsNSb on GaAs QW lasers with emission at 1.5 μm , was demonstrated by the use of Sb flux in the order of 10^{-8} Torr [57]. The N incorporation rate can be strongly affected by a modification of the other Group V species [58]. It is reported that Sb has an influence on the N content in the pentanary InGaAsNSb as well as in the quaternary GaAsNSb, whereby the N and In content increases with increasing Sb flux [57, 59]. The effect of nitrogen on the electronic structure of GaAsN and GaAsSbN compounds has also been studied [60-61]. 100 Å GaAs_{0.825}Sb_{0.15}N_{0.025}/GaAs type-I QW structures [62] have been demonstrated to emit at 1.57 μm [63]. With such vast literature on the effects of Sb on III-V compounds, there are few reports on how Sb affects the crystalline quality of the material under low Sb doping concentrations. GaAsN:Sb grown by MBE was characterized to investigate the effects of low Sb doping in the order of 10^{-9} Torr. A transition region was found at $5 \times 10^{-9} < \text{Sb} < 10^{-8}$ Torr where below this, Sb behaves as an impurity and above it, Sb acts as a surfactant. LT (4.5 K) PL peak intensities of prominent emissions were observed at 955 and 1017 nm (1.22 eV) in GaAsN:Sb samples [64]. Due to the viability of III-V-N devices and to extend this research, this chapter uses 2D HRXRD, SIMS, PL and AFM measurements to clarify and provide some insight to the III-V-N material system with Sb mediation.

6.2 Experimental Details

A series of capless 100 nm GaAs:Sb and GaAsN:Sb samples were grown on GaAs buffers by SSMBE on a Riber MBE 32. A corrosive series valved cracker source from Applied Epi is used to provide the antimony flux. The Sb flux control is achieved by controlling an automated valve positioner, which is varied between 150 to 300 mils (fully open) and adjusting the Sb cell temperature between 400 to 450 °C. The sample information is tabulated in Table 6-1. The Sb cracker zone was set to 900 °C. A rf plasma source manufactured by EPI Inc. is used to provide the atomic nitrogen species. The rf plasma source was maintained at 500 W throughout all the nitride growths. Elemental gallium (7N) and arsenic (6N) were used for growth on semi-insulating GaAs (100) orientated substrates. The oxide desorption was performed at 590 °C to ensure a good surface reconstruction before growing a 100 nm GaAs buffer at 580 °C. The Ga flux was maintained at 4.5×10^{-7} Torr, giving a GaAs GR of ~ 1 $\mu\text{m/hr}$ and a V/III ratio of ~ 20 . The arsenic species present in our growth consists of As_4 . The GaAsN:Sb was grown at the optimal III-V-N substrate temperature (T_s) of 460 °C to investigate the properties of Sb in GaAsN:Sb. After the GaAs buffer growth, the Ga shutter was closed to block any incident flux before the substrate temperature was lowered to 460 °C. Before striking plasma for nitride growth, the main and N shutters were also closed to prevent affecting the integrity of the buffer surface due to high rf plasma impingement. Once the plasma was ignited and stabilized, the Ga and N shutters were opened prior to the opening of the main shutter such that the Ga flux and N plasma can arrive on the substrate simultaneously. For antimony doping ($\text{Sb} \leq 1\%$), the micro-valve was opened to the preset position for the desired flux when the main shutter was still in the closed position.

This prevents a Sb terminated surface prior to Group III (Ga) deposition. When the main shutter is opened, either GaAsN:Sb or GaAs:Sb is grown depending on whether the N plasma is ignited.

The N content (%) was fitted by dynamic rocking curves from [004] HRXRD scans. The (004) HRXRD measurement details are highlighted at 2.2.2.2. The details to the SIMS measurements can be found at 2.2.2.5. A primary accelerating voltage of 4.00 and 2.00 kV for secondary was used. The primary beam was rastered over a square region of $250\ \mu\text{m}^2$ and the secondary ions were collected using a physical aperture of $30\ \mu\text{m}$ in diameter [65]. The depth resolution in SIMS is determined by the ion mixing and the roughness induced by ion bombardment and mostly limited by initial surface roughness [66]. AFM measurements were performed using a Shimadzu Environment Controlled Scanning Probe Microscope (SPM-9500J2). The root mean square values of the square average surface roughness in nanometers (nm) were obtained from $1 \times 1\ \mu\text{m}^2$ areas using a scan rate of 1Hz. PL measurements were performed at 4.5 K and the PL measurement details are highlighted at 2.2.2.1.

6.3 Results and Discussion

6.3.1 PL and SIMS Measurements

GaAsN:Sb samples (N1 - N3) were grown with Sb flux in the 10^{-9} Torr range at $T_s = 460\ ^\circ\text{C}$. Subsequently, two more samples (N4 - N5) were grown in the 10^{-8} Torr range under the same growth conditions. Fig. 6-1 shows the 4.5 K PL measurements of the GaAsN:(Sb) samples (N1 - N3) and an undoped GaAsN sample of the same N composition. When Sb flux is first increased in the 10^{-9} Torr range, we observe that the

intensity of the GaAsN:Sb peak at 955 nm starts to lower to 30 % of undoped GaAsN. The defect peak at 1017 nm (1.22 eV) is attributed to antimony (Sb) doping [64]. Sb acts as an impurity at this low concentration. The other possible defect, Sb_{Ga} heteroantisite is known to play the role of a non-radiative recombination center. It is one of the contributors that decrease the PL intensity with increasing Sb doping as observed in Fig. 6-1 [67].

Fig. 6-1 The PL peak intensity (cps) at 4.5 K versus wavelength (nm) for GaAsN:Sb (N1-N3) and the undoped GaAsN.

Under this dopant-like conditions, there is no peak shift for GaAsN. The strain of GaAsN_x ($x \sim 0.4\%$) is too weak to cause the peak splitting (79 meV) between heavy and light holes and thus the 1017 nm peak cannot be due to the fundamental transition of

GaAsN. When the Sb flux is increased into the low 10^{-8} Torr range, the PL intensity improves beyond that of undoped GaAsN as seen in Table 6-1. We normalize all the sample PL intensities to that of the undoped GaAsN sample in Table 6-1.

Table 6-1. The growth conditions, the SIMS and PL measurement results of GaAs(N):Sb samples. The asterisk shows that the automated valve position of the Sb cell is set to fully open at 300 mil, else the corresponding position value is cited beside the temperature. And the normalized PL intensity (to the undoped GaAsN transition peak) of the two observed peaks in the GaAsN:Sb samples (N1-N5) are depicted. N6-N9 are GaAs:Sb samples.

Sample	Sb Cell Temp. (°C)	Sb Flux 10^{-9} (Torr)	SIMS N (%)	Normalized Peak Intensity (arb.units)	
				at 955 nm (1.3 eV)	at 1017 nm (1.22 eV)
GaAsN	-	0	1.06	1	-
N1	430*	9.5	0.95	0.2756	0.2804
N2	420*	4.8	0.9	0.456	0.41
N3	400*	3	0.97	0.494	-
N4	450 (150 mil)	13	1.25	1.006	-
N5	450 (185 mil)	15	1.25	1.168	-
N6	400*	3	-		
N7	420*	4.8			
N8	425*	7			
N9	450 (150 mil)	13			

* Denotes valve is fully open at 300mil

Fig. 6-2 depicts the sudden PL improvement with 0.95×10^{-8} to 1.5×10^{-8} Torr of Sb. There is adequate Sb on the surface to commence segregation for samples N4 and N5 and

the surfactant phenomenon is exhibited in these two samples. N5 depicts a ~16 % improvement in terms of PL intensity as compared to the undoped GaAsN sample.

Fig. 6-2 The PL peak intensity (cps) at 4.5 K of GaAsN doped with antimony (N1, N4-5) in the region of the surfactant effect.

We observe a low energy band tail in the PL measurements. One reason is due to a possible memory effect of Sb in the growth chamber. Another reason is that it is the inherent property of undoped GaAsN exhibiting a low energy tail due to localized excitons at low temperature. These PL measurements have also been investigated by other groups researching into dilute III-V nitride.

A surfactant must fulfill two criteria. It must be sufficiently mobile to avoid incorporation and it must surface segregate. From our characterization work, there exist

four regions of doping concentration in Sb, where different characteristics are exhibited.

(i) For $0 < \text{Sb} < 5 \times 10^{-9}$ Torr, antimony acts as an impurity, where a decrease in Sb content will improve the PL intensity and reduce surface roughness. This happens when there is not enough Sb to segregate to the surface to perform the surfactant role. As an impurity, Sb may kick out an existing atom or incorporate into a vacancy, causing defects. (ii) For $5 \times 10^{-9} < \text{Sb} < 10^{-8}$ Torr, the transition period, we see a decrease in the surface roughness, but the GaAsN PL peak intensity remains poor. In this period, the surface segregation effect commences and the Sb starts to act like a surfactant. (iii) $\text{Sb} > 10^{-8}$ Torr, we have verified in our samples that the PL intensity improves beyond that of undoped GaAsN and a better surface reconstruction than undoped GaAsN. This is the point where Sb is fully realizing its role as a surfactant, rather than an impurity. (iv) $\text{Sb} > 10^{-6}$ Torr, Sb fully incorporates into the semiconductor material to form an alloy [59]. The changes in the role of Sb in III-V-N, is highlighted in Table 6-2.

Table 6-2. The role of antimony at different flux levels.

	Role of Sb	$X = \Phi_{\text{Sb}}$ (Torr)	Citation
(i)	Impurity	$X < 5 \times 10^{-9}$	This work
(ii)	Impurity/Surfactant	$5 \times 10^{-9} < X < 10^{-8}$	This work
(iii)	Surfactant	$10^{-8} < X < 2 \times 10^{-7}$	This work, X. Yang <i>et al.</i> [55]
(iv)	Alloy	$\text{Sb} > 10^{-6}$	K. Vloz <i>et al.</i> [59]

Four GaAs:Sb (N6 – N9) samples (Fig. 6-3) were grown under the same growth conditions as the GaAsN:Sb samples to investigate the defect peak at 1017 nm (1.22 eV). The presence of sharp spikes in the PL spectrum is due to the low intensity of GaAs:Sb as compared to the GaAsN:Sb samples, which is greater than 1 order in magnitude.

Fig. 6-3 The PL peak intensity (cps) at 4.5 K of GaAs doped with antimony. The Sb impurity related hump located at ~1000 nm.

We attribute the origins of these sharp features in the low temperature PL spectrum to stray electrical signals in the detector circuit. The poor GaAs:Sb quality is mainly due to the low growth temperature. For ultra dilute Sb concentrations, N6 displays a prominent GaAs peak and a broad hump also appears at ~1000 nm (1.24 eV). The Sb flux for N6 is very close to the background pressure and as the Sb flux is increased in N7, the Sb-

related impurity peak and the heteroantisite being a non radiative recombination defect may again cause the disappearance of the GaAs peak when the Sb concentration is at impurity levels. The broad hump at ~ 1.24 eV increases in PL intensity with Sb flux at 4.8×10^{-9} Torr. The hump then decreases in PL intensity for Sb flux at 7×10^{-9} Torr (N8), when the surfactant effect starts. For Sb flux of 1.3×10^{-8} Torr (N9), a true GaAsSb alloy peak is observed at ~ 950 nm, when Sb is incorporated fully as an alloy constituent.

Fig. 6-4 The Sb (%) from SIMS measurements, where solid dots denote the Sb (%) for GaAsN:Sb and solid squares for GaAs:Sb, compared against Sb flux (Torr). The hollow circles denote the N % from SIMS for GaAsN:Sb.

Fig. 6-4 shows the content of Sb that is incorporated into GaAsN and GaAs for Sb flux values in the 10^{-9} Torr range as depicted in the previous figures. The ratio of Sb segregating on the surface to the Sb incorporated into the bulk material, is higher for GaAs than GaAsN, due to the scattering of the Sb atoms from the increased background pressure when the N plasma is ignited. The increase of the background pressure is ~ 2 orders in magnitude. Hence, the surface coverage of Sb in GaAs:Sb begins earlier and the surfactant effect exhibits itself earlier for GaAs:Sb samples than GaAsN:Sb samples. A greater amount of Sb is incorporated into the bulk GaAs:Sb when the surface Sb coverage is completed during the commencement of the surfactant effect. Hence, we observe that the gradient for the Sb incorporation for GaAs:Sb is much sharper than GaAsN:Sb. In the 10^{-9} Torr range, the N and Sb composition in the GaAsN:Sb samples are competing for As sites and the surfactant effect only commences in the 10^{-8} Torr range. Thus, there is an optimized dosage of Sb to invoke the surfactant effect for each material system, without affecting the crystalline quality and bandgap emission position.

Fig. 6-5 The SIMS measurement of a typical GaAsN:Sb sample, N2. The latency effect and surface accumulation of Sb in the material is observed.

We can understand how Sb is incorporated into the material from the SIMS measurement of a typical GaAsN:Sb sample (N2) in Fig. 6-5. The high rf power generates a high concentration of active N. The small atomic radius of N ensures a high bond strength to Ga and incorporates easily into the material, as compared to As₄ which easily desorbs from the surface. As the main shutter opens, all the flux arrives on the substrate simultaneously. The vertical dashed lines in the SIMS measurement serve as guides to the naked eye the position of interest in the depth profile. The nitrogen half maximum intensity at ~98 nm (point β) from the surface, is assumed to be the point where all the flux first reach the substrate, due to the high bond strength of N. We observe that Sb only starts to incorporate after 7 nm at point α , indicating a latency effect. A graded Sb composition at impurity levels is observed at the interface between the GaAs buffer and the antimonide epilayer (between α and β). If the sputtering depth is viewed with a linear vertical axis, the Sb incorporation is observed to increase gradually, rather than being abrupt. We also observe an accumulation of Sb at point γ towards the top surface, attributed to the segregation effect of the Sb film. We can still approximate the Sb segregation film to have ~4 times more Sb % than in the bulk material after ignoring the first few nanometers from the top surface due to the SIMS surface transient effects. The Sb surface segregation effect causes both the N and the Sb incorporation to be variable. The Sb composition calibrated on GaAsSb samples may not have the same composition of Sb in (In)GaAsNSb. This is the explanation to the ambiguity of the determination on the actual compositions of GaAsNSb layers as mention in Ref. 60.

6.3.2 High Resolution X-Ray Diffractometry Measurements

Fig. 6-6 The 2D (115) HRXRD mapping profile of GaAsN:Sb. (a) N3 (Sb - 3×10^{-9} Torr), (b) N2 (Sb - 4.8×10^{-9} Torr).

Fig. 6-6 (continued) (c) N1 ($Sb = 9.5 \times 10^{-9}$ Torr), (d) N4 ($Sb = 13 \times 10^{-9}$ Torr). The maximum intensity is 135786 cps.

The (115) HRXRD mapping profiles (Fig. 6-6) were performed on GaAsN:Sb samples with increasing Sb flux from 3×10^{-9} to 13×10^{-9} Torr, under a fixed N plasma rf power of 500 W. These were obtained by running $(\omega \pm \omega_0) / 2\theta$ scans for different offset angles ω_0 ($^\circ$) on a mechanically stable goniometer stage [15-16, 19]. We noticed that weak sub-peaks appear in samples N1 and N3. Very pronounced peaks in addition the GaAs and GaAsN:Sb peak are observed for N2. These extra peaks are not evident in sample N4 [Fig. 6-6(d)] when the Sb flux is at 1.3×10^{-8} Torr. It is observed that the magnitude of the Sb-related impurity PL peak (Fig. 6-1) situated at 1017 nm [64] corresponds in intensity with the prominence of the additional 2D HRXRD peaks in Fig. 6-6(a-c). However, the PL peak in N4 closely resembles the undoped GaAsN PL peak, comparing both Fig. 6-1 and Fig. 6-2. The 2D (115) HRXRD of N4 [Fig. 6-6(d)] does not show any of the prominent defect peaks mentioned earlier. Weaker defect-related peaks (not shown) are also observed in 2D HRXRD mapping of the GaAs:Sb samples. These peaks disappear more rapidly than those present in the GaAsN:Sb samples under increasing Sb flux, since it takes less Sb to exhibit the surfactant effects in GaAs:Sb. The principal problem associated with MBE-grown Sb based III-V semiconductors is the high level of extrinsic defects and Group III antisites (III_{Sb}), which have been postulated to be the dominant structural defect in these materials [68]. The additional distinct peaks indicate that the lattice parameter of the epitaxial layer is significantly different from that of GaAs and GaAsN due to the possibility of a higher concentration of defects [69]. In Fig. 6-7(a) we show a comprehensive diagram of the N composition and the surface roughness in relation to the Sb flux. And in Fig. 6-7(b), the N composition and the GaAsN peak PL intensity normalized to the undoped GaAs sample versus the Sb flux is

shown. The 10^{-9} Torr range of the Sb flux has not been analyzed by any other groups and it is widely acknowledged that the presence of Sb in the order of 10^{-8} Torr and greater, increases the N incorporation [58, 60]. Dimroth and coworkers observe that the N incorporation is reduced by Sb on GaAs grown by organometallic vapor phase epitaxy and the mechanism was explained by the simple Langmuir model, where nitrogen is dependent on surface coverage of Sb [50, 70].

Fig. 6-7 (a) The N(%) composition and surface roughness (nm) versus Sb flux (Torr).

Fig. 6-7 (continued) (b) The N (%) composition and GaAsN PL intensity (normalized to undoped GaAsN) versus Sb flux (Torr). The surfactant effects commences in the region of 1.3×10^{-8} Torr for a growth rate of $1 \mu\text{m/hr}$.

For a fixed rf power and GR for all samples, we observe that the N composition decreases as the Sb flux is initially added. This initial decrease is attributed to the Group V species competition by Sb when the Sb surface coverage at the growth front has not been completely formed. Beyond 1.3×10^{-8} Torr, sufficient Sb segregates to the growth

front and the surface energy is modified by surface kinetic processes such that there is enhanced N incorporation. Surface roughening decreases as the surfactant Sb enforces layer by layer growth by kinetically inhibiting island formation. The GaAsN peak intensity is observed to be inversely proportional to the surface roughness. At an optimized Sb doping level ($\sim 1.3 \times 10^{-8}$ Torr), we observe that the surface roughness and the PL intensity are improved beyond that of undoped GaAsN. Under excessive Sb doping, the surface degrades as extrinsic defects increases under tensile strain contributed by the elevated N incorporation.

6.4 Conclusions

In conclusion, the study of antimony doped GaAs and GaAsN shows that a transition exists at $5 \times 10^{-9} < \text{Sb} < 10^{-8}$ Torr where below this, Sb behaves as an impurity and above it, Sb acts as a surfactant. Under an As-rich environment in SSMBE, GaAsN:Sb growth introduces a Sb-related impurity peak located at 1017 nm (1.22 eV). The magnitude of the Sb-related defect PL peak is observed to be dependent on the intensity of the additional defect peaks in the 2D (115) HRXRD measurements. When ultra dilute Sb is first introduced and the Sb surface coverage at the growth front has not been completely formed, we observe a decrease in the N composition because of the Group V species competition by Sb. However, as the Sb incorporation increases beyond 1.3×10^{-8} Torr, the surfactant effect commences and the N incorporation increases. The PL peak emission intensity improves beyond the undoped samples at this juncture and enhanced N incorporation is observed.

Chapter 7

Co-doping Carbon tetrabromide (CBr₄)

and Antimony (Sb) on GaAs (100)

in Solid Source Molecular Beam Epitaxy

7.1 Introduction

Carbon tetrabromide (CBr₄) is the preferred *p*-type dopant precursor for GaAs growth by SSMBE. Doping GaAs with carbon results in hole mobilities surpassing that of beryllium (Be) and zinc (Zn) in GaAs [71-73]. Abrupt dopant profiles of dopant levels up to $\sim 10^{20} \text{ cm}^{-3}$ are essential to GaAs-based heterojunction bipolar transistors (HBTs) and laser applications. The C diffusion coefficient is at least an order of magnitude less than that of Be and Zn [73-75]. Techniques like MOCVD [71,76], metal-organic molecular beam epitaxy (MOMBE) [77] and SSMBE [78-80] are employed in GaAs:C epitaxial growth. However, with such excellent doping characteristics in GaAs, the use of

CB₄ in GaAsSb is rarely reported. Recently, the incorporation of carbon in GaAsSb as the base region in InP/ GaAs_{0.51}Sb_{0.49}/InP double heterojunction bipolar transistors (DHBTs) has been demonstrated [81-82]. In order to understand how GaAsSb:C can improve the device characteristics, this chapter investigates the effects of Sb on GaAs:C using a Riber 32P MBE system equipped with a CBr₄ source as described in Ref. 83. We perform a quantitative analysis of the epilayer and the elemental profile of the epilayers using SIMS and HRXRD. Hall measurements is used to analyze the electrical transport characteristics such as the hole concentration, mobility as well as the sheet resistivity.

7.2 Experimental Details

A series of 2000 Å capless GaAsSb:C samples was grown SSMBE. A corrosive series valved cracker from Applied Epi was used to provide the antimony flux. The flux was varied between 3.9×10^{-8} and 9.3×10^{-8} Torr using an automated valve positioner and the Sb cracker zone was set to 900 °C. Carbon doping was enabled by a high purity CBr₄ source. The CBr₄ flux was varied between 2.2×10^{-8} and 5.8×10^{-8} Torr by regulating an UHV precision leak valve, while keeping the temperature of the immersion bath fixed at 2 °C. Elemental gallium (7N) and As₄ (6N) were used for growth on semi-insulating GaAs (100) orientated substrates. The oxide desorption was performed at 590 °C to ensure a good surface reconstruction before growing a 1000 Å undoped GaAs buffer layer, followed by 2000 Å of GaAsSb:C at 580 °C. The GaAs GR was maintained at 1 μm/h ($\Phi_{\text{Ga}} = 4.5 \times 10^{-7}$ Torr). The As₄/Ga flux ratio was maintained at ~25 throughout all the growths. After the growth of the undoped GaAs buffer, the main shutter was

momentarily closed. Both the Sb micro-valve and CBr_4 leak valve were preset to the desired flux flow, before the main shutter is reopened to grow GaAsSb:C. Clear streaky (2×4) RHEED patterns better than undoped GaAs or GaAs:C were observed. The Van-der-Pauw Hall effect technique was used to measure the room temperature (300 K) hole concentration and the mobility. $1 \times 1 \text{ cm}^2$ samples were prepared with indium bonded contacts alloyed in nitrogen for 1 min at 380 °C. HRXRD was performed, using a Philips X'Pert material research diffractometer (MRD) with a conventional X-ray generator and a copper target ($K\alpha_1=0.15406 \text{ nm}$) as the radiation source. A rocking curve geometry using the (004) reflection was applied. 2D HRXRD scans were obtained by running $(\omega + \omega_o) / 2\theta$ scans for different offset angles ω_o and the intensity profiles were recorded [19]. The details to the SIMS measurements can be found at 2.2.2.5. The depth resolution of SIMS has typical values of 3–5 nm by surface roughening and ion beam intermixing during sputtering. PL measurements were performed at low temperature (4.5 K) using the 5145 Å line of an Ar^+ laser as the exciting source and a PMT detector as the detection source with a standard lock-in technique.

7.3 Results and Discussion

7.3.1 Hall Measurements

Fig. 7-1 (a) The variation of hole concentration with the Sb flux (Torr) under a fixed CBr_4 flux of $2.2 \times 10^{-8} \text{ Torr}$ (circle), $4.4 \times 10^{-8} \text{ Torr}$ (square) and $5.4 \times 10^{-8} \text{ Torr}$ (triangle). (b) The variation of hole concentration and carbon concentration in the order of 10^{19} cm^{-3} with the Sb flux (Torr) under the fixed CBr_4 flux of $4.4 \times 10^{-8} \text{ Torr}$.

The variation in hole concentration under three fixed CBr_4 fluxes as a function of varying Sb flux is shown in Fig. 7-1(a). Under the influence of Sb flux in the order of 10^{-8} Torr, the hole concentration is seen to increase for all values of the CBr_4 flux. 5.4×10^{-8} Torr of carbon flux which gives a hole concentration $\sim 7 \times 10^{19} \text{ cm}^{-3}$ in GaAs, reaches beyond $9 \times 10^{19} \text{ cm}^{-3}$ with the addition of $\sim 4 \times 10^{-8}$ Torr of Sb flux. Fig. 7-1(b) shows the variation of the hole concentration and the carbon concentration in the order of 10^{19} cm^{-3} with change in the Sb flux (Torr) under the fixed CBr_4 flux of 4.4×10^{-8} Torr. We find that the activation of carbon is not 100 % for CBr_4 flux at 4.4×10^{-8} Torr, considering the disparity between the hole carrier concentration and the carbon concentration in the absence of Sb. It is reported that 25 % of neutral carbon interstitials (C_i) exist for doping concentrations $> 5 \times 10^{19} \text{ cm}^{-3}$ using CCl_4 grown by both MOCVD and MOMBE [84]. Latest findings prove that CBr_4 doping efficiency is less than one when hole density (300 K) is plotted as a function of SIMS carbon concentration [85]. For our MBE growth, C_i are kept at a minimum by a high As overpressure of ~ 25 and a high substrate temperature of 580°C in GaAs:C [86]. It may be favorable for carbon to occupy an interstitial site to reduce lattice strain under high doping concentrations. The C-C interstitial couples (act as donors) form with the interstitial C and C_{As}^- acceptors to become the dominant compensation effect and this lowers the net hole concentration [87]. The rate of carbon incorporation into the substitutional sites may increase in the presence of compressive Sb which offsets the tensile strain. With the introduction of Sb flux $\sim 5 \times 10^{-8}$ Torr for a GR of $1 \mu\text{m/h}$, we observe a near 100 % activation of carbon. We also propose that the surface-mediation effects of antimony alters the growth mode of the film, whereby the C atom, in order to become an effective *p*-type dopant, must rapidly exchange sites with an Sb atom

and incorporate into the subsurface site, enhancing the C dopant substitutional incorporation into As sites (C_{As}) and decreasing the interstitial carbon formation [88]. Hence, the activation of C reaches 100 % due to the surfactant action of antimony on carbon. The surfactant effect of Sb on dopant incorporation has been reported in Ref. 89 & 90.

Fig. 7-2 The SIMS concentrations of Sb (Square) and carbon (Circle) in atm/cc for a fixed CBr_4 flux of 4.4×10^{-8} Torr versus Sb flux in the 10^{-8} Torr order.

SIMS measurements (see Fig. 7-2) show that under the fixed CBr_4 flux (4.4×10^{-8} Torr) the overall carbon concentration decreases with Sb flux, due to the competition for the same As sites. However, the acceptor concentration continues to increase, despite the carbon concentration decrease, and ultimately becomes greater than the carbon concentration at higher Sb flux. As Sb flux exceeds 5×10^{-8} Torr at this GR, Sb becomes an alloy constituent forming GaAsSb. The formation of $\text{V}_{\text{Ga}}\text{-Ga}_{\text{Sb}}$ defects which are native acceptors in GaAsSb, may have contributed to this increase in acceptor concentration and this will be discussed later.

Fig. 7-3 The variation of the hole mobility ($\text{cm}^2 / \text{V.s}$) compared with the Sb flux (Torr) under a fixed CBr_4 flux of 2.2×10^{-8} Torr (circle), 4.4×10^{-8} Torr (square) and 5.4×10^{-8} Torr (triangle).

Figure 7-3 shows that a majority carrier mobility greater than $50 \text{ cm}^2/\text{V.s}$ for a hole concentration exceeding $9 \times 10^{19} \text{ cm}^{-3}$ was achieved in carbon-doped GaAsSb. The mobility is diminished for hole concentration in the 10^{19} cm^{-3} doping range with the introduction of Sb. It is reported that this reduction is due to the large valence band offset of 1 eV between GaAs and GaSb [91]. Other scattering mechanisms include ionized impurity defects and phonons.

Fig. 7-4 The variation of the sheet resistance ($\Omega/\square$) compared with Sb flux (Torr) under a fixed CBr_4 flux of $4.4 \times 10^{-8} \text{ Torr}$. Saturation of the sheet resistance occurs $\sim 95 \Omega / \square$, for a hole concentration from 6 to $8 \times 10^{19} \text{ cm}^{-3}$.

Figure 7-4 depicts the sheet resistance of four GaAsSb:C samples with the CBr_4 flux fixed at $4.4 \times 10^{-8} \text{ Torr}$. Carbon doped GaAs samples with hole concentration lower

than $5 \times 10^{19} \text{ cm}^{-3}$ have sheet resistance values between 40 to 75 Ω/sq . When Sb flux increases beyond 5×10^{-8} Torr, the sheet resistance saturates at $\sim 95 \text{ } \Omega/\text{sq}$. This phenomenon could be due to the Sb coverage on the surface, whereby Sb monolayer coverage up to 4 nm is semiconducting and beyond 10 nm, the Sb film becomes semi-metallic [92]. Hence, we observed a rather constant sheet resistance when the surface is fully coated with antimony beyond 5×10^{-8} Torr of Sb flux.

7.3.2 Photoluminescence Measurements

Fig. 7-5 The PL plot of intensity (arb. units) versus energy (eV) for GaAsSb:C (NA570, NA572 and NA573) from (a) 1.35 to 1.55 eV.

Fig. 7-5 (continued) The PL plot of intensity (arb.units) versus energy (eV) for GaAsSb:C (NA570, NA572 and NA573) from (b) 0.65 to 1.10 eV.

The 4.5 K PL measurements collected from a dual grating spectrometer in the reflection direction for three samples of GaAsSb:C grown to 200 nm thick on a GaAs buffer. The heavily carbon doped GaAsSb exhibit the reduction of the band to acceptor transition of the GaAs substrate at ~ 1.495 eV (830 nm). The PL efficiency is severely reduced by the high hole concentration ($10^{19} - 10^{20} \text{ cm}^{-3}$) resulting from the reduction of excess carrier lifetime mainly due to Auger recombination. With a fixed carbon flux (4.4×10^{-8} Torr) giving a hole concentration of $\sim 5 \times 10^{19} \text{ cm}^{-3}$, we observe the main PL peak shift by ~ 20 meV when increasing Sb flux from 3.9×10^{-8} to 9.3×10^{-8} Torr. This shift [Fig. 7-5(a)] shows the increase in Sb incorporation into substitutional sites forming GaAsSb. The FWHM peak linewidth of NA570 and NA572 remained the same at ~ 45

meV and NA573 is 73 meV. The reduction in PL intensity in the main emission peak from NA572 to NA570 could be caused by an increased disorder due to the Ga_{Sb} antisite and gallium vacancy formation by the increase in Sb incorporation [67]. Figure 7-5(b) depicts an additional emission peak in the GaAsSb:C samples, of greater intensity than the main emission peak. The presence of this peak fixed at ~ 810 meV is also present in GaAsSb(N) growths around the same vicinity. The dip in intensity at ~ 895 meV is due to water absorption. The structural model of Sb terminated GaAs (001) (2×4) surface consists of ~ 0.5 ML of Sb dimer coverage and subsurface dimerization of Group III atoms (Ga) in the second bilayer, resulting in the formation of a thin layer of GaSb on the surface. With excess Sb flux and a fixed incorporation rate, the accumulation of Sb on the surface increases. The low temperature PL emission of GaSb is situated at 810 meV. However, the V_{Ga} PL emission at 5 K in GaAs is also situated at 810 meV. It is very likely that the epilayer has a high concentration of native acceptors thought to be isolated Ga vacancies and also those coupled with Ga_{Sb} antisites, leading to the increase in acceptor concentration with excess Sb flux. [93]

7.3.3 High Resolution X-Ray Diffractometry Measurements

HRXRD measurement is done on GaAsSb:C samples, where NA570 (C - 4.4×10^{-8} Torr, Sb - 9.3×10^{-8} Torr) is shown in Figure 7-6 and NA572 (C - 4.4×10^{-8} Torr, Sb - 5.5×10^{-8} Torr) in Figure 7-7.

Fig. 7-6 The 2D (115) HRXRD profile of NA570 (C – 4.4×10^{-8} Torr & Sb – 9.3×10^{-8} Torr).

Fig. 7-7 The 2D (115) HRXRD profile of NA572 (C – 4.4×10^{-8} Torr & Sb – 5.5×10^{-8} Torr).

Strain induced relaxation of the epitaxial layer contributes to the degradation of the epitaxial layer and hence, is widely linked to the lack of Pendellosung fringes in XRD measurements or distinct peaks in 2D HRXRD. However, for sample NA570 (GaAsSbC) which does not exhibit fringes, the composition of Sb (compressive) is $\sim 1.8\%$ and C (tensile) is at $\sim 0.3\%$, according to our SIMS measurement. With strain compensation and such low compositions, the epitaxial layer is not relaxed at a thickness of 200 nm from critical thickness calculations. The 2D (115) HRXRD (Fig. 7-6) of NA570 (greater Sb %) shows the presence of “noise” from a high concentration of $V_{\text{Ga}}\text{-Ga}_{\text{Sb}}$ point defect scattering around the GaAs peak, which is also evident in the low temperature measurements, having a PL peak at ~ 810 meV. Sample NA572 which shows less defects in the 2D HRXRD measurements, shows a lower PL peak at ~ 810 meV. Hence, we could attribute the lack of Pendellosung fringes to the presence of the above mentioned Ga-vacancy and Sb-related defects.

7.4 Conclusions

The hole concentration increases for all values of CBr_4 flux, under the influence of Sb flux in the order of 10^{-8} Torr. The presence of antimony modifies the carbon incorporation mechanism, ultimately enhancing the C dopant incorporation in substitutional sites, giving rise to the increase in the ratio of C_{As} to C_{I} , improving both the PL characteristics and the net hole concentration. However, when Sb doping is increased further, gallium vacancies and Ga_{Sb} antisites could create point defects, causing epi-layer degradation.

Chapter 8

Growth and Characterization of GaAs-based Double-heterojunction *P-i-N* Structures Using $\text{In}_z\text{Ga}_{1-z}\text{As}_{1-x-y}\text{N}_x\text{Sb}_y$ as the *i*-layer

8.1 Introduction

Sb can be incorporated into InGaAsN to form the pentanary InGaAsNSb, which is deemed as a plausible approach to lattice-match with GaAs (5.65325 Å) having an energy bandgap below 1 eV. Yang *et al.* demonstrated the use of the surfactants in InGaAsN:Sb/GaAs 1.2 μm single QW laser diodes (LDs) and 1.3 μm multi-quantum well MQW LDs [10, 55]. Subsequently, 1.53 μm room temperature (RT) PL was obtained from InGaAsNSb [94]. Recently, InGaAsNSb QW lasers with GaAsNSb barriers were fabricated [95] and the role of Sb was reported in highly strained MQW structures [59, 96]. This material system was restricted to QW laser applications and in this chapter, we report to the best of our knowledge, the first growth of *P-i-N* structures using bulk InGaAsNSb (~0.45 μm) for the intrinsic (*i*) region on n^+ GaAs substrates, obtaining RT PL emissions of ~1.3 μm.

8.2 Experimental Details

Three *P-i-N* structure samples consisting of GaAs:C (80 nm/*p* - $1 \times 10^{19} \text{ cm}^{-3}$) / $\text{In}_z\text{Ga}_{1-z}\text{As}_{1-x-y}\text{N}_x\text{Sb}_y$ (450 nm) / GaAs:Si (300 nm/*n* - $5 \times 10^{18} \text{ cm}^{-3}$), with different Sb content in the *i*-layer were grown, using a Riber MBE 32P system. One Sb-free *P-i-N* structure (D1) was grown with the same parameters to compare with the Sb-containing series. A corrosive series valved cracker from Applied Epi was used to provide the antimony flux. The Sb flux control was achieved using an automated valve positioner and the Sb cracker zone was set to 900 °C. A rf plasma assisted source manufactured by EPI Inc. was used to provide a controllable source of atomic N species. The rf plasma source was maintained at a rf power of 500 W and a mass flow of 0.1 sccm was used throughout all the *i*-layer growths. Elemental gallium (7N) and arsenic (6N) were used for the epilayer growth. The GR was kept $\sim 0.2 \text{ }\mu\text{m/hr}$ at 460 °C for the dilute N *i*-layer and $1.0 \text{ }\mu\text{m/hr}$ at 580 °C for both the *P* and *N*-type GaAs layers. Prior to the growth of the Sb-containing *i*-region, Sb flux ($\sim 1 \times 10^{-8} \text{ Torr}$) was introduced onto the GaAs:Si layer for 20 sec to allow a total Sb coverage of the growth front. The resultant Sb-terminated GaAs (001) surface observed from the RHEED pattern revealed a distinct and streakier 2×4 surface, as compared to As-rich clean GaAs surfaces because of the lower kink site density [97]. Unintentional *in-situ* annealing of the *i*-layer was performed for approximately 300 sec at 580 °C, while permitting the Ga (Group III) effusion cell temperature to stabilize after the GR increase from 0.2 to $1.0 \text{ }\mu\text{m/hr}$ and during the actual

P-layer epitaxial growth. At this juncture prior to the *P*-layer growth, the excess Sb was fully desorbed from the growth front, ensuring no Sb encroachment in the *P*-layer.

2D HRXRD contour mapping scans were obtained by running $(\omega + \omega_o) / 2\theta$ scans for different offset angles ω_o on a Phillips x-ray diffractometer with a conventional x-ray generator and a copper target ($K\alpha_1=0.15406$ nm). HRXRD only allows for the observation of coherency in growth and it is not suitable for the determination of the In, N and Sb content in InGaAsNSb without the reference epilayers such as InGaAs, GaAsN and GaAsSb. The interdependency of N and Sb also contributed to the inconsistency. SIMS was used to verify the elemental composition and profiles. The details to the SIMS measurements can be found at 2.2.2.5. RT PL measurements were performed using an ACCENT RPM2000 with 785 nm continuous wave (CW) LD operating at 35.1 mW. The detection was carried out from 1000 nm to 1800 nm using a InGaAs detector, with 150g/mm-125 grating and a slit width of 0.5 mm. LT PL measurements were performed at 4.5 K and the measurement details are highlighted at 2.2.2.1.

8.3 Results and Discussion

8.3.1 High-resolution x-ray Diffraction and Secondary-ion Mass Spectrometry Measurements

The RHEED pattern of the *i*-layer for D1 became diffused about 10 min into the growth and turned spotty by 50 min (~170 nm). This is caused by tensile strain, the onset of surface spinodal decomposition and morphological compositional instabilities at 460 °C since the GR is only ~0.2 ML/s [98-99]. The surface becomes rough and this is verified by atomic force microscopy. The 2D [115] HRXRD measurement of D1 [Fig. 8-1(a)] reveals a very poor crystal quality due to the relaxed *i*-layer and N-related defects. The (004) one-dimensional XRD measurement is used to confirm that no epilayer peaks are detected from sample D1. The coherency breakdown in strained epilayers is accepted to be dependent on lattice-mismatch and growth thickness. However, coherency is still maintained for all highly tensile strained bulk InGaAsNSb, such as InGaAsN_{3.45%}Sb (sample D4) grown to ~0.5 μm, having a mismatch of 2.6×10^{-3} . Figure 8-1(b) shows the coherent growth of the InGaAsNSb epilayer on GaAs for D3, with Sb flux $\sim 7 \times 10^{-9}$ Torr. The other two Sb-containing samples (D2 and D4) display similar epitaxial coherency as in Figure 8-1(b). Nitrogen deviates from the unity sticking coefficient and the Group III inverse proportionality dependence when III-V-N is grown at 0.1-0.3 ML/s [100-101]. At a relatively low growth temperature of 460 °C for MBE growth, the desorption of N is minimal due to the high electronegativity (EN) of N (3.04) compared to the rest of the elements.

Fig. 8-1 The two-dimensional [115] high resolution x-ray diffraction (HRXRD) measurement of (a) a relaxed sample D1.

Fig. 8-1 (continued) The two-dimensional [115] high resolution x-ray diffraction (HRXRD) measurement of (b) a coherent sample D3.

Fig. 8-2 The elemental composition (%) of indium (In), nitrogen (N) and antimony (Sb) with reference to the antimony flux (Torr). The lattice mismatch of InGaAsN(Sb) to GaAs is displayed in the order of 10^{-3} .

The size mismatch between Ga/In (136 pm/156 pm) and N (56 pm) tends to lower the substitutional energy, allowing N to incorporate into substitution sites as the growth progresses [102]. We observe that the presence of antimony further raises the solubility of N, causing the rate of N incorporation to be almost identical to that of Sb (Fig. 8-2) for a GR $\sim 0.2 \mu\text{m/hr}$. The 1.45 % increase in N with the addition of ~ 1.4 % of Sb can be only due to the surplus of active background N in the chamber and the reinstatement of the unity sticking coefficient in N. The In incorporation only increased slightly.

(a)

Fig. 8-3 (a) The secondary ion mass spectrometry (SIMS) measurements of D1 with $S_b = 0 \times 10^{-9}$ Torr. The vertical axis is the secondary ion intensity (count/s) and the horizontal axis is the sputtering depth (nm). The diagram on the inset of each figure is the annealed (761 °C/20 sec) SIMS measurement of the corresponding as-grown sample.

(b)

Fig. 8-3(b) The secondary ion mass spectrometry (SIMS) measurements of D2 with Sb at 5×10^{-9} Torr. The vertical axis is the secondary ion intensity (count/s) and horizontal axis is the sputtering depth (nm). The diagram on the inset of each figure is the annealed (761 °C/20 sec) SIMS measurement of the corresponding as-grown sample.

(c)

Fig. 8-3(c) The secondary ion mass spectrometry (SIMS) measurements of D4 with Sb at 1×10^{-8} Torr. The vertical axis is the secondary ion intensity (count/s) and the horizontal axis is the sputtering depth (nm). The diagram on the inset of each figure is the annealed (761 °C/ 20 sec) SIMS measurement of the corresponding as-grown sample.

Figure 8-3(a) shows the graded profiles of D1, typical of outdiffusion due to *in-situ* annealing. The interdiffusion depends on the concentration of the native point defects and their interaction with the other crystal atoms and with each other. Without Sb in D1, there are high concentrations of defects such as N-related interstitials (N_i) and Ga vacancies. Thus, the N-As interdiffusion which is assisted by these defects, increases during *in-situ* annealing at the interfaces. The more mobile N_i atoms occupy As lattice sites to become substitutional atoms via a kick-out mechanism. This annealing in turn improves the PL spectra in the later discussions. The In-Ga interdiffusion with Ga vacancies can be explained by a similar reason. Samples D2 and D4 [Fig. 8-3(b,c)] show extremely abrupt profiles due to the reduction of N-related interstitials and Ga vacancies. The defect-assisted interdiffusion mentioned, is heavily suppressed due to the surfactant action of antimony which improved the epitaxial quality. The SIMS measurements performed for *ex-situ* annealed samples are shown in the inset of Figure 8-3(a-c) for the same as-grown sample. The annealed D1 [Fig. 8-3(a)] has an indistinguishable FWHM difference from the as-grown sample, but it contains $\sim 5 \times$ more In and $\sim 1.5 \times$ more N at the surface comparing with the secondary ion intensity of the as-grown sample. We observe that the FWHM for D2 (Sb $\sim 5 \times 10^{-9}$ Torr) increased by ~ 20 nm after *ex-situ* annealing, with the *i*-layer losing the abrupt profile. D4 with the highest concentration of Sb (1×10^{-8} Torr) maintains its abrupt profile, with ~ 10 nm increase in the FWHM. This is also the resolution limits of the SIMS measurement since the effective primary energy used is large (5 keV). The inhomogeneity seen in the N profile in D4 is due to the use of different piece of the same sample.

When N is incorporated into a substitutional site, the high binding energy between Ga-N and In-N bonds suppresses interdiffusion in the material. The N-hopping process can be determined by the competition between chemical bonding and local strain. When D1 is subjected to a substrate temperature increase $> 460\text{ }^{\circ}\text{C}$ or annealing, there is a preference for the reconfiguration of the N bonds towards InN and GaAs to minimize strain in the bulk. D2 [Fig. 8-3(b)] and D4 [Fig. 8-3(c)] show extremely abrupt profiles, because N-hopping and interdiffusion are suppressed during *in-situ* annealing. The Sb dimer film coverage on the growth front which is bonded to the subsurface bi-layer of Group III (Ga/In) atoms, initiates a substitutional site exchange with the arriving N, minimizing the formation of mobile and loosely bounded interstitial N (N_i). Sb also prevents composition modulation in bulk LM InGaAsN on GaAs [98]. The modification of the surface diffusion kinetics and the surface energy by the surfactant Sb leads to layer-by-layer growth and streaky 2×4 RHEED patterns are observed during growth. Visual inspection reveals mirror-like surfaces and no cross-hatch patterns are observed under the microscope.

Besides maintaining 2D growth, antimony performs some additional tasks. The indium segregation to the growth front forms the large bond length InSb ($6.479\text{ \AA}$) of a low binding energy of 0.6 meV, which is easily broken to form InN (15.2 meV). GaSb ($6.09593\text{ \AA}$) at binding energy 2.0 meV also performs an anion exchange with N to form GaN (25.2 meV). Since indium readily segregates in GaAs and the bond breaking of InSb is easier than GaSb, the formation of InN bonds is favored and the reconfiguration of the N bonds when subjected to annealing is decreased. Sharp profiles for In and N are enabled despite the unintentional *in-situ* annealing and this is also proven in the latter

RTA portion. The high concentration of defects in D1 [Fig. 8-3(a)] also facilitate in the diffusion of the dopants, Si and C into the intrinsic layer. However, for Sb-containing samples D2 and D4 [Fig. 8-3(b,c)], this is suppressed due a lower concentration of interstitials and vacancies at the interface due to the preference for the formation of substitutional bonds during the surfactant phenomenon. We observe that the Si and C profiles of are distinctly abrupt as compared to D1.

8.3.2 Photoluminescence (PL) Measurements and Rapid Thermal Annealing

Fig. 8-4 (a) The low temperature (LT) 4.5 K PL of the as-grown samples.

Fig. 8-4 (continued) (b) The low temperature (LT) 4.5 K PL of the annealed *P-i-N* structures with optimized annealing conditions.

We observe in the LT PL that the as-grown dilute nitride material exhibits exponential intensity quenching with the increase of N from 2 % to 3.45 %. N interstitials act as non-recombination centers, quenching the PL intensity of D3 and D4 when the N content exceeds 3 % [Fig. 8-4(a)] [26]. The PL peaks of D1 and D2 are enveloped by the Ga vacancy and/or N-defect related transitions which form a hump from 1.3 – 1.6 μm [103]. *Ex-situ* annealing was performed under nitrogen (N_2) ambient with GaAs

proximity capping for durations of 20 sec at temperatures 714 °C, 741 °C and 761 °C and 10 sec at 793 °C. Optimized annealing conditions reveal the band-to-band transition peaks of the bulk InGaAsNSb [Fig. 8-4(b)], where the FWHM is ~25 meV for all bulk Sb-containing samples. The annealed bulk InGaAsN sample (D1) however, displays a very weak band-to-band transition peak ~1100 nm and the defect-related broad hump (~1.3 μm) which is present in the as-grown sample [Fig. 8-4(a)]. The annealed samples have larger PL intensities as compared to as-grown samples under the same PL measurement conditions, caused mainly by the reconfiguration of N_i to N_s . The samples D2-D4 with the various annealing conditions are presented in wavelength (nm) against temperature (K) in Figure 8-5. The blue-shifting of ~25 meV in the PL peak emission of bulk InGaAsNSb is seen as the annealing temperature is increased from 714 °C to 793 °C due to the fluctuation of N composition in the as-grown samples. The site switching from N_i to N_s may also contribute to some redshifting, which offsets the blue-shift slightly. When the annealing temperature is up to 793 °C, the temperature dependence of the energy gap (the wavelength in the Fig. 8-5) follows the Varshni relation. When the annealing temperature is less than 793 °C, this dependence deviates from the Varshni relation at low the PL temperature range (20-80 K in the Fig. 8-5) due to the N-related localized states in the samples.

Fig. 8-5 The PL peak position in wavelength (nm) of bulk InGaAsNSb with different annealing conditions, plotted under temperature variation. The solid lines denote D2, dashed lines for D3 and dotted lines for D4. Solid squares denote the annealing condition at 714 °C for 20 sec, solid circles – 741 °C for 20 sec, solid triangles – 761 °C for 20 sec and solid diamonds – 793 °C for 10 sec.

8.4 Conclusions

The coherency in the *i*-layers is maintained despite the high tensile strain for InGaAsNSb samples, while the InGaAsN *i*-region of the *P-i-N* device with half the amount of tensile strain is fully relaxed. Sb is found to increase the N incorporation dramatically at 0.2 $\mu\text{m/hr}$, while the In incorporation increase is negligible. Besides maintaining coherency in the material, the presence of Sb prevents the formation of N-related interstitials. These effects ultimately improve the crystal quality and prevent the diffusion of the material and intermixing of the *P-i-N* structure profile. Rapid thermal annealing is found to further improve the PL intensity and the redshift of the PL peak is observed with increasing Sb content.

Chapter 9

GaAs-based Heterojunction *p-i-n* Photodetectors Using Pentanary InGaAsNSb as the Intrinsic Layer

9.1 Introduction

Our group has also performed extensive research in the use of Sb as a surfactant and an alloy constituent in (In)GaAsN on GaAs. [104-105] In this chapter, we report to the best of our knowledge, the first mesa device fabrication of *p-i-n* PDs using bulk InGaAsNSb ($\sim 0.45\ \mu\text{m}$) for the *i*-region grown on n^+ GaAs substrates by MBE. With the increased N incorporation caused by surfactant Sb, the absorption edge is extended towards the longer wavelengths. The tensile strain generated by the increased N composition also lowers the bandgap described by the BAC model [41]. This ultimately leads to the achievement of both thick InGaAsN 2D growth and absorption edge at $1.31\ \mu\text{m}$.

9.2 Experiment Details

Two *p-i-n* PDs (B & C) consisting of GaAs:C (80 nm/ $p - 1 \times 10^{19} \text{ cm}^{-3}$) / $\text{In}_z\text{Ga}_{1-z}\text{As}_{1-x-y}\text{N}_x\text{Sb}_y$ (450 nm) / GaAs:Si (300 nm/ $n - 5 \times 10^{18} \text{ cm}^{-3}$), with different Sb content in the *i*-layer were grown using a Riber MBE 32P system (Fig. 9-1).

Fig. 9-1. The mesa device structure layout of devices A (Sb=0), B (Sb= 5×10^{-9} Torr) and C (Sb= 10×10^{-9} Torr). The changes in the Sb concentration apply to the intrinsic (*i*) layer of the devices and other parameters remain the same.

One Sb-free *p-i-n* PD (A) was grown with the same parameters to compare with the Sb-containing devices. The elemental composition measured by SIMS and strain in the *i*-layer are depicted in Fig. 9-2.

Fig. 9-2 The elemental compositions (%) of the A, B, and C devices measured by SIMS versus the antimony flux (Torr). The tensile strain (ϵ) in the *i*-layer layer is depicted in the diagram.

The details to the SIMS measurements can be found at 2.2.2.5. A standard SIMS sample, which is measured at Applied Microanalysis Labs, is used to calibrate the SIMS measurement conducted in our laboratory. The desired elemental concentration can be derived if measured under the same sputtering conditions as the standard sample. The strain (ϵ) in the active bulk InGaAsN(Sb) layer is derived by Eq. (9.1), where $a_{\text{InGaAsN(Sb)}}$ is the lattice constant of the bulk InGaAsN(Sb) and a_{GaAs} is the lattice constant of GaAs (5.65325 Å).

$$\varepsilon = \frac{a_{\text{InGaAsN(Sb)}} - a_{\text{GaAs}}}{a_{\text{GaAs}}} \quad (9.1)$$

$a_{\text{InGaAsN(Sb)}}$ is assumed to be the linear interpolation of its individual binary alloy constituents, using the elemental compositions from the SIMS measurements [106]. A negative ε will indicate that the lattice constant of InGaAsN(Sb) is smaller than that of GaAs and hence, tensile strained. We assume that the lattice constant deviation between GaAs:Si and GaAs is negligible, since the active bulk InGaAsN(Sb) is grown on GaAs:Si. A corrosive series valved cracker from Applied Epi is used to provide the antimony flux. Sb flux control is achieved using an automated valve positioner and the Sb cracker zone temperature was set to 900 °C. A rf plasma assisted N source manufactured by Applied Epi. is used to provide the atomic N. The rf plasma source is maintained at a rf power of 500 W and a mass flow of 0.1 sccm throughout all the *i*-layer growths. Elemental gallium (7N) and arsenic (6N) were used for the epilayer growth. The GR was kept at 1.0 $\mu\text{m/hr}$ at 580 °C for both the *p* and *n* layers. The GR is reduced to ~ 0.2 $\mu\text{m/hr}$ at 460 °C for the *i*-layer to enable a higher concentration of N due to the lack in line of sight for the N cell. Prior to the growth of the Sb-containing *i*-region, Sb flux ($\sim 1 \times 10^{-8}$ Torr) is introduced onto the GaAs:Si layer for 20 sec to allow total Sb coverage of the growth front. The resultant Sb-terminated GaAs (001) surface observed from the RHEED pattern reveals a distinct and streakier 2×4 surface as compared to As-rich clean GaAs surfaces because of a lower kink site density [97]. Unintentional *in-situ* annealing of the *i*-layer is performed for approximately 300 sec at 580 °C, while permitting the Ga (Group III) effusion cell temperature to stabilize after the GR increase from 0.2 to 1.0 $\mu\text{m/hr}$ and during the actual *p*-layer epitaxial growth. CBr₄ is used for the *p*-type doping

because the out-diffusion of GaAs:C is much lower than GaAs:Be. We use GaAs:C with a high active p -type carrier concentration to achieve a low series resistance and we design a thin p -layer of 80 nm to improve the frequency response of the device by a faster collection of carriers. Ohmic contacts are formed in a standard lift-off process. The p -type contact (Fig. 9-1) is made up of Ti/Au (500/2500 Å) and the n -type contact is Au/Ge/Ni/Au (280/70/88/840 Å). An array of 400 μm diameter circular mesa photodiodes was then fabricated by standard photolithography techniques to characterize the wafer. The active window area is approximately half the total area of the mesa PD. No passivation or anti-reflection coating is performed on the mesa windows.

9.3 Results and Discussion

9.3.1 I - V Measurements

Current-voltage (I - V) measurements were then carried out at 25 °C in ambient using a HP 4145B semiconductor parameter analyzer. The range of the bias voltage applied is -20.0 to 2.0 V and illumination was directed onto the mesa windows via a tungsten halogen lamp with monochromator grating. A high degree of uniformity was found across the devices and breakdown voltages in excess of -18 V were obtained for the Sb-containing devices. The devices depicted are all pseudomorphic. The dark current I - V characteristics are shown on Fig. 9-3.

Fig. 9-3 The dark current density (A/cm^2) of the three devices versus the bias voltage from -20 to 2 V.

The Sb-containing devices show lower turn-on voltages, attributed to the lower energy bandgap. At a reversed bias of -2 V, the dark current density for the Sb-free device (A) is $\sim 0.15 \text{ A}/\text{cm}^2$. With the addition of 5×10^{-9} Torr of Sb flux, the dark current density of device B falls to $0.43 \text{ mA}/\text{cm}^2$. Dilute nitride growth tends to form N clusters and 3D growth occurs easily when the N composition exceeds 1 %. This 3D growth is suppressed in the presence of surfactant Sb and the optical properties are improved. The high dark current density in device A also can be partly due to non-radiative centers (N-related defects), which reduce carrier lifetimes. The presence of Sb lowers the density of non-radiative centers which majority consists of N interstitials, by promoting N incorporation

into substitutional sites and the dark current density is decreased by ~ 350 times. However, a higher dark current $\sim 5 \text{ mA/cm}^2$ is observed at -2 V in device C when Sb is continually increased. This may be explained as below. The N composition increases with increasing Sb composition and the density of N-related and Sb-related defects increase significantly. This diminishes the surfactant's capacity. The higher strain in the *i*-layer may cause strain-induced N clustering with increasing Sb composition in device C.

9.3.2 Responsivity Measurements

The room temperature responsivity measurements were then carried out using a standard lock-in technique. The light was delivered to the devices by a lightwave fiber and the photoresponse was carried out on a probe station. It is observed that as the N composition increases, the absorption edge moves beyond $1.3 \text{ }\mu\text{m}$ in device C and increases to $\sim 1.41 \text{ }\mu\text{m}$, see Fig. 9-4. The peak responsivity (R_{peak}) of device A is $\sim 0.098 \text{ A/W}$ at 984 nm with a reversed bias of 2 V . Device A has no response at the $1.3 \text{ }\mu\text{m}$ wavelength due to the low composition of N. The responsivity (R) of device B is observed to be 0.097 A/W at $1.3 \text{ }\mu\text{m}$ and this corresponds to a QE of 9.21% . A R_{peak} of $\sim 0.29 \text{ A/W}$ is observed from device B with surfactant Sb at 1048 nm . This 3 time improvement in peak responsivity is negated in device C due to the similar reason as the dark current explanation. Table 9-1 shows the QE and R of the three devices at the wavelength of 940 and 1300 nm .

Fig. 9-4 The room temperature responsivity (R) of the three devices as a function of wavelength in nanometers for zero bias and a reverse bias of 2 V.

	940 nm		1300 nm	
	QE (%)	R (A/W)	QE (%)	R (A/W)
A (0 V)	1.45	0.01	-	-
A (-2 V)	13.11	0.099	-	-
B (0 V)	14.15	0.107	4.44	0.047
B (-2 V)	37.87	0.287	9.21	0.097
C (0 V)	8.1	0.061	3.22	0.034
C (-2 V)	12.52	0.095	4.622	0.049

Table 9-1. The room temperature quantum efficiency (QE) and responsivity (R) of the devices for zero bias and a reverse bias of 2 V at 940 nm and 1300 nm.

The QE at 940 nm of the device A is 13.11 %, compared to the QE at 940 nm of device B of 37.87 % for a reversed bias of 2 V. Even at zero bias, larger responsivity has been measured in Sb-containing device. Thus, the Sb-containing device may be used in the photovoltaic mode. The future work of device optimization, surface passivation/anti-reflection and *ex-situ* annealing may improve quantum efficiencies and device performance.

9.4 Conclusions

In conclusion, we have grown, fabricated and characterized InGaAsNSb/GaAs heterojunction *p-i-n* photodiodes on (001) n^+ type GaAs substrates. We have exhibited responsivity at $\sim 1.3 \mu\text{m}$ for the Sb-containing devices due to the enhanced incorporation of N. The Sb-containing device exhibited up to ~ 38 % QE at the peak photoresponse corresponding to a responsivity of $\sim 0.29 \text{ A/W}$. The cutoff wavelength is up to $\sim 1.4 \mu\text{m}$. This allows the implementation of high-performance photodiodes by the combination of device design and passivation during fabrication, based on the initial *p-i-n* device performances obtained.

Chapter 10

Conclusion and Recommendations

10.1 Conclusion

The results accumulated from this work demonstrates the feasibility of using antimony as a surfactant to aid in the growth of InGaAsN bulk intrinsic layers. This opens a new market for GaAs-based dilute nitride material operating at the 1.3 μm wavelength. Based on the material physics developed in this course of study, the proper growth optimization of the *p-i-n* structures lead to working devices. The most important part of the research is the refinement of surfactant Sb in dilute III-V nitrides, shown in the detailed characterization work. In conclusion:

- 1) We have investigated the response of the tilt angle, $\Delta\psi$ of GaAsN on GaAs under increasing tensile strain using two-dimensional (115) HRXRD rocking curves. GaAs and GaAsN peak profiles change from a highly strained, to partially relaxed and severely relaxed peak profile were observed, pointing to changes in both GaAs (substrate) and GaAsN (epilayer) interface when subjected to strain. Relaxation was impeded by a slower thread glide due to

more high energy substitutional N bonds introduced by a raised rf power to compensate the increase in GR. GaAsN/GaAs was able to exceed the critical thickness by nearly twice without any degradation to the surface quality. With an optimized III-V-N growth condition for high N%, GaAsN_{4.8%} was grown to 100 nm without relaxation, exceeding the critical thickness by 4.6 times.

- 2) Extra PL peaks other than the band-to-band transition have been observed in GaAsN on GaAs by various SSMBE groups. The band anticrossing model was used to identify the origins of peaks in our PL measurements and a model was proposed to explain them. RTA observations were also explained by the concept of increased confinement in areas of higher N concentrations by trapped N localized states. The γ peak is due to the accumulation of N content near the GaAs/GaAsN interface. Hence, this abnormal annealing behavior occurs in layers with non-uniform N concentration at the GaAsN/GaAs interface.
- 3) InGaAsN/GaAsN/InGaAs structures were successfully grown on GaAs substrates by SSMBE with a nitrogen rf plasma source. The dependency of In and N in InGaAsN on GaAs has been investigated by means of PL and SIMS measurements, by placing all the alloys on the same sample. We prove that by using SIMS and PL measurements, we are able to correlate the bandgap emission peaks to the various epitaxial layers and determine the In and N compositions.
- 4) We have used AFM, PL and HRXRD to characterize and compare the effects of low-level Sb doping ($Sb < 10^{-8}$ Torr) in dilute GaAsN under high arsenic

overpressure. A transition region was found at $5 \times 10^{-9} < \text{Sb} < 10^{-8}$ Torr where below this, Sb behaves as an impurity and above it, Sb acts as a surfactant. We have shown that incorporating dopant-like concentration of antimony into the bulk III-V-N epilayer has the effect of deteriorating the surface morphology and introducing an impurity PL peak for Sb flux in the order of 10^{-9} Torr. We then further explore the effects of Sb on the material for Sb flux in the 10^{-8} Torr region. Under a As-rich environment in SSMBE, GaAsN:Sb growth introduces a Sb-related impurity peak located at 1017 nm (1.22 eV). The magnitude of the Sb-related defect PL peak is observed to be relative to the intensity of the additional defect peaks in the 2D (115) HRXRD measurements. When ultra dilute Sb is first introduced and the Sb surface coverage at the growth front has not been completely formed, we observe a decrease in the N composition because of the Group V species competition by Sb. However, as the Sb incorporation increase beyond 1.3×10^{-8} Torr, the surfactant effect commences. The PL peak emission intensity improves beyond the undoped samples at this juncture and enhanced N incorporation is observed.

- 5) The hole carrier concentration increases for all values of CBr_4 flux, under the influence of Sb flux in the order of 10^{-8} Torr. The presence of antimony modifies the carbon incorporation mechanism, enhancing the C dopant incorporation in substitutional sites, thereby increasing the ratio of C_{As} to C_{I} . The PL characteristics is improved and the net hole concentration is increased. With further Sb incorporation, both Ga vacancies and antisites increase,

contributing to point defects. Diffuse scattering around the GaAs peak is observed to increase in 2D (115) HRXRD scans. As the C incorporation declines slightly due to Sb competition with excessive Sb flux, the acceptor concentration continues to increase, brought on by the formation of native defects as mentioned and main emission PL degrades as a consequence.

- 6) High quality, coherent bulk InGaAsN_{3.45%}Sb (~0.5 μm) can be achieved due to the surfactant properties of antimony despite a tensile strain of 2.6×10^{-3} . This cannot be realized in bulk InGaAsN_{2%} of ~0.5 μm . Besides maintaining coherency in the material, the presence of Sb prevents the formation of highly mobile interstitials and minimizes the N-reconfiguration of bonds. These effects ultimately improve the crystal quality and prevent the diffusion of the material and intermixing of the *p-i-n* heterostructure interface profile. A redshift in the PL peak is observed with increasing Sb content. RTA is found to further improve the PL intensity resulting in ~25 meV LT PL FWHMs.
- 7) We report the first mesa device growth/fabrication of *P-i-N* structures using bulk InGaAsNSb (~0.45 μm) for the intrinsic (*i*) region grown on n^+ GaAs substrates. The Sb-containing devices exhibited absorption at the 1.31 μm optical wavelength due to the enhanced incorporation of N. The unpassivated Sb-devices exhibited up to ~38 % QE at the peak photoresponse and a QE of ~7.5 % at 1.31 μm .

10.2 Recommendations for Future research

Due to the heavy usage of the molecular beam epitaxy chambers and the clean room facilities, the research has been constrained to the chapters documented in the thesis. Hence, according to me, there should be a number of research areas to be investigated.

The Optimization of the Device Structure

Our research group has found that the minority-carrier electron diffusion length of as-grown $\text{In}_{3\%}\text{GaAsN}_{1\%}$ to be ~ 140 nm and annealed $\text{InGaAsN}_{1\%}$ to be ~ 190 nm. This analysis was carried out by minority-carrier injection depth using a variable reverse-bias [107]. The quality of the bulk InGaAsN should be better than the as-grown material, with the aid of surfactants. However, the actual diffusion length is still unknown for this new material. One of the most crucial aspects of photodiode design is the thickness of the intrinsic layer. In our initial structure growths, we designed the i -layer to be ~ 0.5 μm for high responsivity. SIMS measurements detected the thickness to be closer to ~ 0.35 - 0.4 μm for N concentrations of ~ 2 - 3.5 %. However, the electric-field produced by the applied reverse bias is used to sweep out the carriers in the p - i - n devices, enabling the collection of carriers. Besides the i -layer thickness, the thickness of the p -type layer is also a consideration since the illumination passes through the GaAs:C layer and it has to be thin for maximum efficiency. Another method to consider is to etch a window down to the i -layer and subsequently apply surface passivation and anti-reflection coating to the air to i -layer interface. Hence, these processes can be optimized to improve the device performance.

Further optimization of the semiconductor material

We have done extensive work in the aspect of material physics. In the author's personal interests, there are still some areas that are not explored as they are somewhat beyond the scope of the research requirements. Di-carbon defects arise from annealing GaAs:C beyond 600 °C. This creates a limitation for *ex-situ* RTA on the *p-i-n* devices, where temperatures can reach 850 °C. Hence, we designed a recipe where the *i*-layer is annealed *in-situ* prior to the growth of the *p*-type layer. However, there may be other ways to circumvent this problem. We have not explored the usage of annealed GaAs:SbC. The surfactant effects of Sb may prevent or reduce the presence of di-carbon defects during annealing. With this, the *p-i-n* device can be subjected to RTA at temperatures greater than 600 °C to improve the material quality and also prevent the degradation of the *p*-type ohmic contact.

Author's Publications

Journal Papers:

1. W. K. Cheah, W. J. Fan, S. Wicaksono, S. F. Yoon, and K. H. Tan, "Low antimony-doped $\text{GaN}_x\text{As}_{1-x}$ on GaAs grown by solid-source molecular beam epitaxy", **J. Cryst. Growth**, vol. 254, no. 3, pp. 305-309, Jul. 2003.
2. W. K. Cheah, W. J. Fan, S. F. Yoon, S. Z. Wang, and W. K. Loke, "X-ray reciprocal space mapping of strain relaxation in $\text{GaAs}_{1-x}\text{N}_x$ on GaAs [100] by molecular beam epitaxy", **J. Appl. Phys.**, vol. 94, no. 6, pp. 3828-3833, Sep. 2003.
3. W. K. Cheah, W. J. Fan, S. F. Yoon, R. Liu, and A. T. S. Wee, "Co-doping carbon tetrabromide (CBr_4) and antimony (Sb) on GaAs [100] in solid source molecular beam epitaxy", **J. Cryst. Growth**, vol. 267, no. 1, pp. 364-371, Jun. 2004.
4. W.K. Cheah, W.J. Fan, S.F. Yoon, T.K. Ng, W.K. Loke, D.H. Zhang, T. Mei, R. Liu, and A.T.S. Wee, "Investigation of N incorporation in InGaAs and GaAs epilayers on GaAs using solid source molecular beam epitaxy," **J. Cryst. Growth**, vol. 275, no. 3, pp. 440-447, Mar. 2005.
5. W. K. Cheah, W. J. Fan, S. F. Yoon, K. H. Tan, R. Liu and A. T. S. Wee, "Surfactant and impurity properties of antimony on GaAs and $\text{GaAs}_{1-x}\text{N}_x$ on GaAs [100] by solid source molecular beam epitaxy", **Thin Solid Films**, vol. 488, no. 1, pp. 56-61, Sep. 2005.

6. W. K. Cheah, W. J. Fan, S. F. Yoon and W. K. Loke, "Interpretation of anomalous extra peak in photoluminescence measurements of bulk $\text{GaAs}_{1-x}\text{N}_x$ epitaxial layer on GaAs", (To be published in **J. Appl. Phys.**).
7. W. K. Cheah, W. J. Fan, K. H. Tan, S. F. Yoon, D. H. Zhang, T. Mei, R. Liu and A. T. S. Wee, "Characterizations of $\text{In}_z\text{Ga}_{1-z}\text{As}_{1-x-y}\text{N}_x\text{Sb}_y$ *P-i-N* structures grown on GaAs by Molecular Beam Epitaxy", **J. Mater. Sci. : Mater. in Electron.**, vol. 16, no. 5, pp. 301-307, May 2005.
8. W. K. Cheah, W. J. Fan, S. F. Yoon, D. H. Zhang, B. K. Ng, W. K. Loke, R. Liu and A. T. S. Wee, "GaAs-based heterojunction *p-i-n* photodetectors using pentanary InGaAsNSb as the intrinsic layer", **IEEE Photon. Technol. Lett.**, vol. 17, no. 9, pp. 1932-1934, Sep. 2005.
9. W. K. Cheah, W. J. Fan, S. F. Yoon, B. S. Ma, T. K. Ng, R. Liu and A. T. S. Wee, "The analysis and the optimization of the annealing mechanisms in (In)GaAsN on GaAs", (To be published in **Semicond. Sci Technol.**)
10. W. J. Fan, S. F. Yoon, W. K. Cheah, W. K. Loke, T. K. Ng, S. Z. Wang, R. Liu, and A. Wee, "Determination of nitrogen composition in $\text{GaN}_x\text{As}_{1-x}$ epilayer on GaAs", **J. Cryst. Growth**, vol. 268, no. 3, pp. 470-474, Aug. 2004.
11. S. Wicaksono, S. F. Yoon, K. H. Tan, and W. K. Cheah, "Concomitant incorporation of antimony and nitrogen in GaAsSbN lattice-matched to GaAs," **J. Cryst. Growth**, vol. 274, no. 3, pp. 470-474, Feb. 2005.

Conference Papers:

1. W. K. Cheah, W. J. Fan, S. F. Yoon, S. Wicaksono, R. Liu, and A. T. S. Wee, "Defects and surfactant action of antimony on GaAs and GaAs_{1-x}N_x on GaAs [100] by molecular beam epitaxy", 2003 MRS Fall Meeting, Boston (Material Research Society), Progress in compound Semiconductor Materials III – Electronic and Optoelectronic Applications, v799, 51-57 (2003).
2. W. K. Cheah, W. J. Fan, and S. F. Yoon, "Investigations of Strain Relaxation by x-ray Reciprocal Space Mapping of GaAs_{1-x}N_x on GaAs Solid Source Molecular Beam Epitaxy", International Conference on Materials for Advanced Technologies (ICMAT), Singapore, 7th Dec – 12th Dec 2003.
3. W. K. Cheah, W. J. Fan, S. F. Yoon, D. H. Zhang, B. K. Ng, W. K. Loke, R. Liu and A. T. S. Wee, "1.31 μ m GaAs-based heterojunction *p-i-n* photodetectors using InGaAsNSb as the intrinsic layer grown by molecular beam epitaxy", International Conference on Materials for Advanced Technologies (ICMAT), Singapore, 3rd Jul – 8th Jul 2005.

References

1. M. Kondow, K. Uomi, K. Hosomi, and T. Mozume, "Gas-Source Molecular Beam Epitaxy of $\text{GaN}_x\text{As}_{1-x}$ Using a N Radical as the N Source," *Jpn. J. Appl. Phys., Part 2*, vol. 33, no. 8A, pp. L1056-L1058, Aug. 1994.
2. M. Weyers, M. Sato, and H. Ando, "Red Shift of Photoluminescence and Absorption in Dilute GaAsN Alloy Layers," *Jpn. J. Appl. Phys., Part 2*, vol. 31, no. 7A, pp. L853-L855, Jul. 1992.
3. S. Sato, and S. Satoh, "Metalorganic chemical vapor deposition of GaInNAs lattice matched to GaAs for long-wavelength laser diodes," *J. Cryst. Growth*, vol. 192, no. 3, pp. 381-385, Sep. 1998.
4. W. Shan, W. Walukiewicz, 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," *Phys. Rev. Lett.*, vol. 82, no. 6, pp. 1221-1224, Feb. 1999.
5. J. M. Ulloa, A. Hierro, M. Montes, B. Damilano, M. Hugues, J. Barjon, J. -Y. Duboz, and J. Massies, "Impact of N on the lasing characteristics of GaInNAs/GaAs quantum well lasers from 1.29 to 1.52 μm ," *Appl. Phys. Lett.*, vol. 87, 251109, Dec. 2005.
6. J. B. Héroux, X. Yang, and W. I. Wang, "GaInNAs resonant-cavity-enhanced photodetector operating at 1.3 μm ," *Appl. Phys. Lett.*, vol. 75, no. 18, pp. 2716-2718, Nov. 1999.
7. C. W. Coldren, S. G. Spruytte, J. S. Harris, and M. C. Larson, "Group III nitride-arsenide long wavelength lasers grown by elemental source molecular beam epitaxy," *J. Vacuum Sci. Technol. B*, vol. 18, no. 3, pp. 1480-1483, May 2000.

8. A. J. Ptak, D. J. Friedman, S. Kurtz, and R. C. Reedy, "Low-acceptor-concentration GaInNAs grown by molecular-beam epitaxy for high-current p-i-n solar cell applications," *J. Appl. Phys.*, vol. 98, 094501, Nov. 2005.
9. R. A. Mair, J. Y. Lin, H. X. Jiang, E. D. Jones, A. A. Allerman, and S. R. Kurtz, "Time-resolved photoluminescence studies of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$," *Appl. Phys. Lett.*, vol. 76, no. 2, pp. 188-190, Jan. 2000.
10. X. Yang, J. B. Heroux, M. J. Jurkovic, and W. I. Wang, "High-temperature characteristics of 1.3 μm InGaAsN:Sb/GaAs multiple-quantum-well lasers grown by molecular-beam epitaxy," *Appl. Phys. Lett.*, vol. 76, no. 7, pp. 795-797, Feb. 2000.
11. H. D. Sun, S. Calvez, M. D. Dawson, J. A. Gupta, G. I. Sproule, X. Wu, and Z. R. Wasilewski, "Role of Sb in the growth and optical properties of 1.55 μm GaInN(Sb)As/GaNAs quantum-well structures by molecular-beam epitaxy," *Appl. Phys. Lett.*, vol. 87, no. 18, 181908, Oct. 2005.
12. Z. C. Niu, S. Y. Zhang, H. Q. Ni, D. H. Wu, H. Zhao, H. L. Peng, Y. Q. Xu, S. Y. Li, Z. H. He, Z. W. Ren, Q. Han, X. H. Yang, Y. Du, and R. H. Wu, "GaAs-based room-temperature continuous-wave 1.59 μm GaInNAsSb single-quantum-well laser diode grown by molecular-beam epitaxy," *Appl. Phys. Lett.*, vol. 87, no. 23, 231121, Dec. 2005.
13. H. Luo, J. A. Gupta, and H. C. Liu, "1.55 μm GaNAsSb photodetector on GaAs," *Appl. Phys. Lett.*, vol. 86, no. 21, 211121, May 2005.

14. S. M. Wang, T. G. Andersson, M. J. Ekenstedt, "Temperature-dependent transition from two-dimensional to three-dimensional growth in highly strained $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ ($0.36 \leq x \leq 1$) single quantum wells," *Appl. Phys. Lett.*, vol. 61, no. 26, pp. 3139-3141, Dec. 1992.
15. P.F. Fewster, "A high-resolution multiple-crystal multiple-reflection diffractometer," *J. Appl. Crystallogr.*, vol. 22, no. 1, pp. 64-69, Feb. 1989.
16. P.F. Fewster, "Simulation and interpretation of diffraction relaxed layer structures," *J. Appl. Crystallogr.*, vol. 25, no. 6, pp. 714-723, Dec. 1992.
17. K. Uesugi, and I. Suemune, "Metalorganic molecular beam epitaxy of GaNAs alloys on (0 0 1) GaAs," *J. Crystal Growth*, vol. 189-190, pp. 490-495, Jun. 1998.
18. S. Z. Wang, S. F. Yoon, T. K. Ng, W. K. Loke, and W. J. Fan, "Molecular beam epitaxial growth of $\text{GaAs}_{1-x}\text{N}_x$ with dispersive nitrogen source," *J. Cryst. Growth*, vol. 242, no. 1, pp. 87-94, Jul. 2002.
19. K. Uesugi, N. Morooka, and I. Suemune, "Reexamination of N composition dependence of coherently grown GaNAs band gap energy with high-resolution X-ray diffraction mapping measurements," *Appl. Phys. Lett.*, vol. 74, no. 9, pp. 1254-1256, Mar. 1999.
20. I. Vurgaftman, J. R. Meyer, and L. R. Ram-Mohan, "Band parameters for III-V compound semiconductors and their alloys," *J. Appl. Phys.*, vol. 89, no. 11, pp. 5815-5875, Jun. 2001.
21. J.W. Matthews, and A.E. Blakeslee, "Defects in epitaxial multilayers," *J. Cryst. Growth*, vol. 27, pp. 118-125, Dec. 1974.
22. M. Adamcyk, J. H. Schmid, T. Tiedje, A. Koveshnikov, A. Chahboun, V. Fink, and K. L. Kavanagh, "Comparison of strain relaxation in InGaAsN and InGaAs thin films," *Appl. Phys. Lett.*, vol. 80, no. 23, pp. 4357-4359, Jun. 2002.

23. M. Shinohara, and T. Ito, "Thermodynamic study on the origin of oval defects in GaAs grown by molecular-beam epitaxy," *J. Appl. Phys.*, vol. 65, no. 11, pp. 4260-4267, Jun. 1989.
24. A. Y. Kim, W. S. McCullough, and E. A. Fitzgerald, "Evolution of microstructure and dislocation dynamics in $\text{In}_x\text{Ga}_{1-x}\text{P}$ graded buffers grown on GaP by metalorganic vapor phase epitaxy: Engineering device-quality substrate materials," *J. Vacuum Sci. Technol. B*, vol. 17, no. 4, pp. 1485-1501, Jul. 1999.
25. W. J. Fan, S. F. Yoon, T. K. Ng, S. Z. Wang, and W. K. Loke, "Comparison of nitrogen compositions in the as-grown $\text{GaN}_x\text{As}_{1-x}$ on GaAs measured by high-resolution x-ray diffraction and secondary-ion mass spectroscopy," *Appl. Phys. Lett.*, vol. 80, no. 22, pp. 4136-4138, Jun. 2002.
26. S. G. Spruytte, C. W. Coldren, J. S. Harris, W. Wampler, P. Krispin, K. Ploog, and M. C. Larson, "Incorporation of nitrogen in nitride-arsenides: Origin of improved luminescence efficiency after anneal," *J. Appl. Phys.*, vol. 89, no. 8, pp. 4401-4406, Apr. 2001.
27. J. Toivonen, T. Hakkarainen, M. Sopanen, H. Lipsanen, J. Oila, and K. Saarinen, "Observation of defect complexes containing Ga vacancies in GaAsN," *Appl. Phys. Lett.*, vol. 82, no. 1, pp. 40-42, Jan. 2003.
28. S. G. Spruytte, C. W. Coldren, A. F. Marshall, and J. S. Harris, 2000 MRS Spring Meeting, San Francisco (Materials Research Society, Pittsburgh, 2000). K9-1.
29. A. Trampert, J.-M. Chauveau, K. H. Ploog, E. Tournié, and A. Guzmán, "Correlation between interface structure and light emission at 1.3–1.55 μm of (Ga,In)(N,As) diluted nitride heterostructures on GaAs substrates," *J. Vac. Sci. Technol. B*, vol. 22, no. 4, pp. 2195-2200, Jul. 2004.
30. E. Tournié, M. -A. Pinault, and A. Guzmán, "Mechanisms affecting the photoluminescence spectra of GaInNAs after post-growth annealing," *Appl. Phys. Lett.*, vol. 80, no. 22, pp. 4148-4150, Jun. 2002.

31. S. Francoeur, G. Sivaraman, Y. Qiu, S. Nikishin, and H. Temkin, "Luminescence of as-grown and thermally annealed GaAsN/GaAs," *Appl. Phys. Lett.*, vol. 72, no. 15, pp. 1857-1859, Apr. 1998.
32. A. R. Kovsh, J. S. Wang, L. Wei, R. S. Shiao, J. Y. Chi, B. V. Volovik, A. F. Tsatsul'nikov, and V. M. Ustinov, "Molecular beam epitaxy growth of GaAsN layers with high luminescence efficiency," *J. Vac. Sci. Technol. B*, vol. 20, no. 3, pp. 1158-1162, May 2002.
33. X. D. Luo, P. H. Tan, Z. Y. Xu, and W. K. Ge, "Selectively excited photoluminescence of GaAs_{1-x}N_x single quantum wells," *J. Appl. Phys.*, vol. 94, no. 8, pp. 4863-4865, Oct. 2003.
34. G. Mussler, Lutz Däweritz, K. H. Ploog, J. W. Tömm, and V. Talalaev, "Optimized annealing conditions identified by analysis of radiative recombination in dilute Ga(As,N)," *Appl. Phys. Lett.*, vol. 83, no. 7, pp. 1343-1345, Aug. 2003.
35. T. Ahlgren, E. Vainonen-Ahlgren, J. Likonon, W. Li, and M. Pessa, "Concentration of interstitial and substitutional nitrogen in GaN_xAs_{1-x}," *Appl. Phys. Lett.*, vol. 80, no. 13, pp. 2314-2316, Apr. 2002.
36. Pan, L. H. Li, W. Zhang, Y. W. Lin, R. H. Wu, and W. Ge, "Effect of rapid thermal annealing on GaInNAs/GaAs quantum wells grown by plasma-assisted molecular-beam epitaxy," *Appl. Phys. Lett.*, vol. 77, no. 9, pp. 1280-1282, Aug. 2000.
37. S. L. Chuang, *Physics of Optoelectronic Devices*, J. Wiley & Sons, New York, 1995, p. 441, and references there.
38. I. Vurgaftman, and J. R. Meyer, "Band parameters for nitrogen-containing semiconductors," *J. Appl. Phys.*, vol. 94, no. 6, pp. 3675-3696, Sep. 2003.
39. W. Shan, W. Walukiewicz, J. W. Ager III, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, "Effect of nitrogen on the band structure of GaInNAs alloys," *J. Appl. Phys.*, vol. 86, no. 4, pp. 2349-2351, Aug. 1999.

40. C. Skierbiszewski, P. Perlin, P. Wisniewski, T. Suski, J. F. Geisz, K. Hingerl, W. Jantsch, D. E. Mars, and W. Walukiewicz, "Band structure and optical properties of $\text{In}_y\text{Ga}_{1-y}\text{As}_{1-x}\text{N}_x$ alloys," *Phys. Rev. B*, vol. 65, no. 6, pp. 035207-035216, Dec. 2001.
41. W. Shan, K. M. Yu, W. Walukiewicz, J. W. Ager III, E. E. Haller, and M. C. Ridgway, "Reduction of band-gap energy in GaNAs and AlGaNaS synthesized by N^+ implantation," *Appl. Phys. Lett.*, vol. 75, no. 10, pp. 1410-1412, Sep. 1999.
42. J. P. Klar, H. Grüning, W. Heimbrod, J. Kock, F. Höhnsdorf, W. Stolz, P. M. A. Vicente, and J. Camassel, "From N isoelectronic impurities to N-induced bands in the $\text{GaN}_x\text{As}_{1-x}$ alloy," *Appl. Phys. Lett.*, vol. 76, no. 23, pp. 3439-3441, Jun. 2000.
43. R. Kudrawiec, G. Sek, J. Misiewicz, L. H. Li, and J. C. Harmand, "Experimental investigation of the C_{MN} matrix element in the band anticrossing model for GaAsN and GaInAsN layers," *Solid State Comm.*, vol. 129, no. 6, pp. 353-357, Feb. 2004.
44. P. Varshni, "Temperature dependence of the energy gap in semiconductors," *Physica (Utrecht)*, vol. 34, no. 1, pp. 149-154, 1967.
45. Chtourou, F. Bousbih, S. Ben Bouzid, F. F. Charfi, J. C. Harmand, G. Ungaro, and L. Largeau, "Effect of nitrogen and temperature on the electronic band structure of $\text{GaAs}_{1-x}\text{N}_x$ alloys," *Appl. Phys. Lett.*, vol. 80, no. 12, pp. 2075-2077, Mar. 2002.
46. L. Grenouillet, C. Bru-Chevallier, G. Guillot, P. Gilet, P. Ballet, P. Duvaut, G. Rolland, and A. Million, "Rapid thermal annealing in $\text{GaN}_x\text{As}_{1-x}/\text{GaAs}$ structures: Effect of nitrogen reorganization on optical properties," *J. Appl. Phys.*, vol. 91, no. 9, pp. 5902-5908, May 2002.
47. S. R. Kurtz, A. A. Allerman, E. D. Jones, J. M. Gee, J. J. Banas, and B. E. Hammons, "InGaAsN solar cells with 1.0 eV band gap, lattice matched to GaAs," *Appl. Phys. Lett.*, vol. 74, no. 5, pp. 729-731, Feb. 1999.

48. S. B. Zhang, and S. H. Wei, Nitrogen solubility and induced defect complexes in epitaxial GaAs:N," *Phys. Rev. Lett.*, vol. 86, no. 9, pp. 1789-1792, Feb. 2001.
49. T. Talicercio, R. Intartaglia, B. Gil, P. Lefebvre, T. Bretagnon, U. Tisch, E. Finkman, J. Salzman, M. -A Pinault, and E. Tournié," From GaAs:N to oversaturated GaAsN: Analysis of the band-gap reduction," *Phys. Rev. B*, vol. 69, no. 7, pp. 073303-073306, Feb. 2004.
50. Dimroth, A. Howard, J. K. Shurtleff, and G. B. Stringfellow, "Influence of Sb, Bi, Ti, and B on the incorporation of N in GaAs," *J. Appl. Phys.*, vol. 91, no. 6, pp. 3687-3692, Mar. 2002.
51. L. Zhang, H. F. Tang, J. Schieke, M. Mavrikakis, and T. F. Kuech, "The addition of Sb as a surfactant to GaN growth by metal organic vapor phase epitaxy," *J. Appl. Phys.*, vol. 92, no. 5, pp. 2304-2309, Sep. 2002.
52. K.-S. Kim, Y. Takakuwa, T. Abukawa, and S. Kono, "RHEED-AES observation of Sb surface segregation during Sb-mediated Si MBE on Si (0 0 1)," *J. Cryst. Growth*, vol. 186, no. 1, pp. 95-103, Mar. 1998.
53. E. Kaxiras, "Atomic structure of surfactant monolayers and its role in epitaxial growth," *Mater. Sci. Eng. B*, vol. 30, no. 2, pp. 175-186, Mar. 1995.
54. W. G. Bi, and C. W. Tu, "Bowing parameter of the band-gap energy of GaN_xAs_{1-x}," *Appl. Phys. Lett.*, vol. 70, no. 12, pp. 1608-1610, Mar. 1997.
55. X. Yang, M. J. Jurkovic, J. B. Heroux, and W. I. Wang, "Molecular beam epitaxial growth of InGaAsN:Sb/GaAs quantum wells for long-wavelength semiconductor lasers," *Appl. Phys. Lett.*, vol. 75, no. 2, pp. 178-180, Jul. 1999.
56. V. Gambin, W. Ha, M. Wistey, H. Yuen, S. R. Bank, S. M. Kim, J. S. Harris Jr., "GaInNAsSb for 1.3-1.6 μ m-long wavelength lasers grown by molecular beam epitaxy," *IEEE J. Sel. Top. Quantum Electron.*, vol. 8, no. 4, pp. 795-800, Aug. 2002.
57. S. Bank, W. Ha, V. Gambin, M. Wistey, H. Yuen, L. Goddard, S. Kim, and J. S. Harris, Jr., "1.5 μ m GaInNAs(Sb) lasers grown on GaAs by MBE," *J. Cryst. Growth*, vol. 251, no. 4, pp. 367-371, Apr. 2003.

58. J. C. Harmand, G. Ungaro, L. Largeau, and G. Le Roux, "Comparison of nitrogen incorporation in molecular-beam epitaxy of GaAsN, GaInAsN, and GaAsSbN," *Appl. Phys. Lett.*, vol. 77, no. 16, pp. 2482-2484, Oct. 2000.
59. K. Volz, V. Gambin, W. Ha, M. A. Wisetey, H. Yuen, S. Bank, J. S. Harris, "The role of Sb in the MBE growth of (GaIn)(NAsSb)," *J. Cryst. Growth*, vol. 251, no. 1-4, pp. 360-366, Apr. 2003.
60. J. -C. Harmand, A. Caliman, E. V. K. Rao, L. Largeau, J. Ramos, R. Teissier, L. Travers, G. Ungaro, B. Theys, and I. F. L. Dias, "GaNAsSb: How does it compare with other dilute III-V-nitride alloys?," *Semicond. Sci. Technol.*, vol. 17, no. 8, pp. 778-784, Aug. 2002.
61. F. Bousbih, S. Ben Bouzid, R. Chtourou, F. F Charfi, J. C. Harmand, and G. Ungaro, "Effect of nitrogen in the electronic structure of GaAsN and GaAsSb(N) compounds," *Mater. Sci. Eng. C*, vol. 21, no. 1, pp. 251-254, Sep. 2002.
62. S. A. Lourenço, I. F. L. Dias, L. C. Poças, J. L. Duarte, J. B. B. de Oliveira, and J. C. Harmand, "Effect of temperature on the optical properties of GaAsSbN/GaAs single quantum wells grown by molecular-beam epitaxy," *J. Appl. Phys.*, vol. 93, no. 8, pp. 4475-4479, Apr. 2003.
63. J. C. Harmand, G. Ungaro, J. Ramos, E. V. K. Rao, G. Saint-Girons, R. Teissier, G. Le Roux, L. Largeau, and G. Patriarche, "Investigations on GaAsSbN/GaAs quantum wells for 1.3-1.55 μm emission," *J. Cryst. Growth*, vol. 227, pp. 553-557, Jul. 2001.
64. W. K. Cheah, W. J. Fan, S. Wicaksono, S. F. Yoon, and K. H. Tan, "Low antimony-doped $\text{GaN}_x\text{As}_{1-x}$ on GaAs grown by solid-source molecular-beam epitaxy," *J. Cryst. Growth*, vol. 254, no. 3, pp. 305-309, Jul. 2003.

65. Y. Gao, "A new secondary ion mass spectrometry technique for III-V semiconductor compounds using the molecular ions CsM^+ ," J. Appl. Phys., vol. 64, no. 7, pp. 3760-3762, Oct. 1988.
66. P. K. Chu, Y. Gao, and J. W. Erickson, "Characterization of III nitride materials and devices by secondary ion mass spectrometry," J. Vacuum Sci. Technol. B, vol. 16, no. 1, pp. 197-203, Jan 1998.
67. R. Yakimova, P. Omling, B. H. Yang, L. Samuelson, J. -O Fornell, and L. Ledebo, "On the formation of the Sb_{Ga} heteroantisite in metalorganic vapour-phase epitaxial GaAs:Sb," Appl. Phys. Lett., vol. 59, no. 11, pp. 1323-1325, Sep. 1991.
68. P. D. Brewer, D. H. Chow, and R. H. Miles, "Atomic antimony for molecular beam epitaxy of high quality II-V semiconductor alloys," J. Vac. Sci. Technol. B, vol. 14, no. 3, pp. 2335-2338, May 1996.
69. R. P. Campion, K. W. Edmonds, L. X. Zhao, K. Y. Wang, C. T. Foxon, B. L. Gallagher, and C. R. Staddon, "High-quality GaMnAs films grown with arsenic dimers," J. Cryst. Growth, vol. 247, no. 1, pp. 42-48, Jan. 2003.
70. I. Langmuir, "The adsorption of gases on plane surfaces of glass, mica and platinum" J. Am. Chem. Soc., vol. 40, no. 9, pp. 1361-1403, Sep. 1918.
71. N. Watanabe, and H. Ito, "Saturation of hole concentration in carbon-doped GaAs grown by metalorganic chemical vapor deposition," J. Cryst. Growth, vol. 182, no. 1, pp. 30-36, Dec. 1997.
72. M. Konagai, T. Yamada, T. Akatsuka, K. Saito, E. Tokumitsu, and K. Takahashi, "Metallic p-type GaAs and GaAlAs grown by metalorganic molecular beam epitaxy," J. Cryst. Growth, vol. 98, no. 1, pp. 167-173, Nov. 1989.
73. C. R. Abernathy, S. J. Pearton, R. Caruso, F. Ren, and J. Kovalchik, "Ultrahigh doping of GaAs by carbon during metalorganic molecular beam epitaxy," Appl. Phys. Lett., vol. 55, no. 17, pp. 1750-1752, Oct. 1989.

74. B. T. Cunningham, L. J. Guido, J. E. Baker, J. S. Major, Jr., N. Holonyak, Jr., and G. E. Stillman, "Carbon diffusion in undoped n-type, and p-type GaAs," *Appl. Phys. Lett.*, vol. 55, no. 7, pp. 687-689, Aug. 1989.
75. D. L. Miller, M. Micovic, D. I. Lubyshev, W. Z. Cai, W. -Y. Hwang, and K. Zhang, "Iodine and carbon tetrabromide use in solid source molecular beam epitaxy," *J. Vac. Sci. Technol. B*, vol. 16, no. 3, pp. 1361-1366, May 1998.
76. S. L. Kim, M. S. Kim, S. K. Min, and C. Lee, "Experimental and theoretical photoluminescence study of heavily carbon doped GaAs grown by low-pressure metalorganic chemical vapor deposition," *J. Appl. Phys.*, vol. 74, no. 10, pp. 6128-6132, Nov. 1993.
77. D. M. Kozuch, M. Stavola, S. J. Pearton, C. R. Abernathy, and J. Lopata, "Hydrogen in carbon-doped GaAs grown by metalorganic molecular beam epitaxy," *Appl. Phys. Lett.*, vol. 57, no. 24, pp. 2561-2563, Dec. 1990.
78. W. E. Hoke, D. G. Weir, P. J. Lemonias, and H. T. Hendriks, "Carbon tetrabromide carbon doping of molecular beam epitaxial (GaAs) films," *Appl. Phys. Lett.*, vol. 64, no. 2, pp. 202-204, Jan. 1994.
79. D. W. Schulte, S. Subramanian, L. Ungier, H. M. Yoo, U. Venkateswaran, and J. R. Arthur, "Substrate orientation dependence of carbon doping of GaAs using CBr₄ source in molecular beam epitaxy," *J. Vacuum Sci. Technol. B*, vol. 16, no. 3, pp. 1356-1360, May 1998.
80. D. Lubyshev, M. Micovic, N. Gratteau, W. -Z. Cai, D.L. Miller, O. Ray, R.W. Streater, and A.J.S. Thorpe, "A comparative study of carbon incorporation in heavily doped GaAs and Al_{0.3}Ga_{0.7}As grown by solid-source molecular beam epitaxy using carbon tetrabromide," *J. Vacuum Sci. Technol. B*, vol. 17, no. 3, pp. 1180-1184, May 1999.
81. X. G. Xu, A. J. Hu, S. P. Watkins, N. Matine, M. W. Dvorak, and C.R. Bolognesi, "Metalorganic vapor phase epitaxy of high-quality GaAs_{0.5}Sb_{0.5} and its application to heterostructure bipolar transistors," *Appl. Phys. Lett.*, vol. 74, no. 7, pp. 976-978, Feb. 1999.

82. C. R. Bolognesi, N. Matine, M. W. Dvorak, X. G. Xu, J. Hu, and S. P. Watkins, "Non-blocking collector InP/GaAs_{0.51}Sb_{0.49}/InP double heterojunction bipolar transistors with a staggered lineup base-collector junction," *IEEE Electron. Dev. Lett.*, vol. 20, no. 4, pp. 155-157, Apr. 1999.
83. Q. F. Huang, S. F. Yoon, K. H. Tan, Z. Z. Sun, R. Zhang, J. Jiang, and L. H. Lee, "Carbon doping in GaAs using carbon tetrabromide in solid source molecular beam epitaxy," *J. Cryst. Growth*, vol. 252, no. 1, pp. 37-43, May 2003.
84. G. E. Hofler, and K. C. Hsieh, "Observation of interstitial carbon in heavily carbon-doped GaAs," *Appl. Phys. Lett.*, vol. 61, no. 3, pp. 327-329, Jul. 1992.
85. W. Z. Cai, D. I. Lubyshev, D. L. Miller, R. W. Streater and A. J. SpringThorpe, "Heavily carbon-doped In_{0.53}Ga_{0.47}As on InP (001) substrate grown by solid source molecular beam epitaxy," *J. Vacuum Sci. Technol. B*, vol. 17, no. 3, pp. 1190-1194, May 1999.
86. C. Giannini, C. Gerardi, L. Tapfer, A. Fishcer, and K. H. Ploog, "Carbon incorporation in GaAs and Al_xGa_{1-x}As layers grown by molecular-beam epitaxy," *J. Appl. Phys.*, vol. 74, no. 1, pp. 77-81, Jul. 1993.
87. W. Li, and M. Pessa, "Lattice contraction in carbon-doped GaAs epilayers," *Phys. Rev. B*, vol. 57, no. 23, pp. 14627-14629, Jun. 1998.
88. M. Copel, M. C. Reuter, E. Kaxiras, and R. M. Tromp, "Surfactants in epitaxial growth," *Phys. Rev. Lett.*, vol. 63, no. 6, pp. 632-635, Aug. 1989.
89. F. Dimroth, A. Howard, J. K. Shurtleff, and G. B. Stringfellow, "Influence of Sb, Bi, Ti, and B on the incorporation of N in GaAs," *J. Appl. Phys.*, vol. 91, no. 6, pp. 3687-3692, Mar. 2002.
90. J. K. Shurtleff, S. W. Jun, and G. B. Stringfellow, "Surfactant effects on doping of GaAs grown by organometallic vapor phase epitaxy," *Appl. Phys. Lett.*, vol. 78, no. 20, pp. 3038-3040, May. 2001.

91. S. P. Watkins, O. J. Pitts, C. Dale, X. G. Xu, M. W. Dvorak, N. Matine, and C. R. Bolognesi, "Heavily carbon-doped GaAsSb grown on InP for HBT applications," *J. Cryst. Growth*, vol. 221, no. 1, pp. 59-65, Dec. 2000.
92. C. J. Spindt, R. Rao, K. E. Miyano, I. Lindau, W. E. Spicer, and Y. -C. Pao, "Morphological study of Ag, In, Sb, and Bi overlayers on GaAs(100)," *J. Vac. Sci. Technol. B*, vol. 8, no. 4, pp. 974-979, Jul. 1990.
93. C. C. Ling, W. K. Mui, C. H. Ham, C. D. Beling, S. Fung, M. K. Lui, K. W. Cheah, K. F. Li, Y. W. Zhao, and M. Gong, "Gallium vacancy and the residual acceptor in undoped GaSb studied by positron lifetime spectroscopy and photoluminescence," *Appl. Phys. Lett.*, vol. 80, no. 21, pp. 3934-3936, May. 2002.
94. X. Yang, J. B. Heroux, L. F. Mei, and W. I. Wang, "InGaAsNSb/GaAs quantum wells for 1.55 μm lasers grown by molecular-beam epitaxy," *Appl. Phys. Lett.*, vol. 78, no. 26, pp. 4068-4070, Jun. 2001.
95. W. Ha, V. Gambin, S. Bank, M. Wistey, H. Yuen, S. Kim, and J. S. Harris, Jr., "Long-wavelength GaInNAs(Sb) lasers on GaAs," *IEEE J. Quantum Electron.*, vol. 38, no. 9, pp. 1260-1267, Sep. 2002.
96. L. H. Li, V. Sallet, G. Patriarche, L. Largeau, S. Bouchoule, L. Travers, and J. C. Harmand, "Investigations on GaInNAsSb quinary alloy for 1.5 μm laser emission on GaAs," *Appl. Phys. Lett.*, vol. 83, no. 7, pp. 1298-1300, Aug. 2003.
97. P. Moriarty, P. H. Beton, Y. -R. Ma, and M. Henini, "Adsorbed and substituted Sb dimers on GaAs(001)," *Phys. Rev. B*, vol. 53, no. 24, pp. R16148-R16151, Jun. 1996.
98. J. -M. Chauveau, A. Trampert, K. H. Ploog, M. -A. Pinault, and E. Tournié, "Interplay between the growth temperature, microstructure, and optical properties of GaInNAs quantum wells," *Appl. Phys. Lett.*, vol. 82, no. 20, pp. 3451-3453, May 2003.

99. M. -A. Pinault, and E. Tournié, "Influence of alloy stability on the photoluminescence properties of GaAsN/GaAs quantum wells grown by molecular beam epitaxy," *Appl. Phys. Lett.*, vol. 79, no. 21, pp. 3404-3406, Nov. 2001.
100. V. A. Odnoblyudov, A. Yu Egorov, A. R. Kovsh, A. E. Zhukov, N. A. Maleev, E. S. Semenova, and V. M. Ustinov, "Thermodynamic analysis of the MBE growth of GaInAsN," *Semicond. Sci. Technol.*, vol. 16, no. 10, pp. 831-835, Aug. 2001.
101. Z. Z. Sun, S. F. Yoon, K. C. Yew, W. K. Loke, W. J. Fan, S. Z. Wang, and T. K. Ng, "Incorporation of N into GaAsN under N overpressure and underpressure conditions," *J. Appl. Phys.*, vol. 94, no. 2, pp. 1069-1073, Jul. 2003.
102. S. B. Zhang, and A. Zunger, "Surface-reconstruction-enhanced solubility of N, P, As, and Sb in III-V semiconductors," *Appl. Phys. Lett.*, vol. 71, no. 5, pp. 677-679, Aug. 1997.
103. I. A. Buyanova, W. M. Chen, B. Monemar, H. P. Xin, and C. W. Tu, "Effect of growth temperature on photoluminescence of GaNAs/GaAs quantum well structures," *Appl. Phys. Lett.*, vol. 75, no. 24, pp. 3781-3783, Dec. 1999.
104. W. K. Cheah, W. J. Fan, S. F. Yoon, K. H. Tan, R. Liu, and A. T. S. Wee, "Surfactant and impurity properties of antimony on GaAs and GaAs_{1-x}N_x on GaAs [100] by solid source molecular beam epitaxy," *Thin Solid Films*, vol. 488, no. 1, pp. 56-61, Apr. 2005.
105. W. K. Cheah, W. J. Fan, K. H. Tan, S. F. Yoon, D. H. Zhang, T. Mei, R. Liu and A. T. S. Wee, "Characterizations of In_zGa_{1-z}As_{1-x-y}N_xSb_y P-i-N structures grown on GaAs by Molecular Beam Epitaxy", *J. Mater. Sci. : Mater. in Electron.*, vol. 16, no. 5, pp. 301-307, May 2005.

-
106. 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," *J. Cryst. Growth*, vol. 275, no. 3, pp. 440-447, Mar. 2005.
107. S. Y. Xie, S. F. Yoon, and S. Z. Wang, "Effects of thermal annealing on deep-level defects and minority-carrier electron diffusion length in Be-doped InGaAsN," *J. Appl. Phys.*, vol. 97, no. 7, pp. 073702-073707, Apr. 2005.