The molecular beam epitaxy growth of InSbN compound and its characterization

Lim, Kim Peng

2012

Lim, K. P. (2012). The molecular beam epitaxy growth of InSbN compound and its characterization. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/50466>

<https://doi.org/10.32657/10356/50466>

**THE MOLECULAR BEAM EPITAXY GROWTH OF
INSBN COMPOUND AND ITS
CHARACTERIZATION**

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**SCHOOL OF ELECTRICAL AND ELECTRONIC
ENGINEERING**

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

2012

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

Date

Lim Kim Peng

Dedicated

To

My supportive mother

Acknowledgements

First of all, I would like to express my gratitude and utmost appreciation to my Ph.D. supervisor Professor Yoon Soon Fatt for giving me the golden opportunity to be a part of his prestigious research team to pursue a doctoral study in the field of compound semiconductors. I thank him for his kind understanding and consideration and the financial support given to my research. Under his guidance, I am now more analytical and logical in thinking.

I would also like to sincerely thank the elite senior team members: Dr. Loke Wan Khai, Dr. Tan Kian Hua, Dr. Satrio Wicaksono and Dr. Ng Tien Khee, Dr. Johan Fredrik Falth for their noble teaching and sharing of the knowledge on molecular beam epitaxy (MBE) growth and the aspects of dilute nitride semiconductors physics. Without their assistance and technical support, I would not have been able to progress smoothly in the research.

Besides the above senior colleagues, I am especially grateful to Dr Pham Huynh Tram for her companionship and perpetual assistance in my research project. Dr Pham has been very patient with me throughout the frequent research discussions and her help in fabricating the InSbN devices is greatly cherished. Her presence and opinions are valuable and she has contributed tremendously to the achievements in my project.

Special thanks should also be reserved for the other key research team members: Dr. Lew Kim Luong, Dr. Andrew Ngo Chun Yong, Dr. Hendrix Tanoto, Chen Kah Pin and Liang Yu Yan for sharing their experiences on MBE growth, device fabrication, transmission electron microscopy analysis and manuscript preparation. In addition, I would like to extend my gratefulness to Dr. Liu Chongyang, Dr. Tong Cunzhu, Dr. Lee Shun Ying, Cao Qi, Liliana Tjahjana, Zhao Hanxue, Lee Daosheng, Xu Dawei, Xu Zhe, Wang Yang, Wang Rui, Yeo Chiew Yong and Yu Ying for their friendship and emotional support. With such strong camaraderie in our group, my research journey in the laboratory is never monotonous.

My sincere acknowledgement is also extended to Dr. Tripathy Sudhiranjan and Dr. Yakovlev Nikolai from the Institute of Materials Research Engineering and Dr. Markwitz Andreas from National Isotope Centre, GNS Science, for their scientific contribution to this project.

Finally, I would like to say a big thank you to all the personnel at the characterization and cleanroom laboratories, such as Muhd Fauzi Bin Abdullah, Mohamad Shamsul Bin Mohamad and Seet Lye Ping for their timely technical assistance and support.

Table of contents

Acknowledgements.....	i
Table of contents	iii
Abstract.....	v
List of captions	viii
Author's publication lists	xvii
Chapter 1 Introduction.....	1
1.1 Background.....	1
1.2 Motivation and objective.....	6
1.2.1 N incorporation in InSbN	6
1.2.2 InSb on a GaAs substrate.....	11
1.2.3 Post-growth annealing treatment	13
1.2.4 <i>In situ</i> annealing process.....	14
1.3 Major contributions of the thesis.....	14
1.4 Organization of the thesis.....	17
Chapter 2 Principles of band gap, growth and characterization.....	20
2.1 Band gap of InSbN.....	20
2.2 Growth Technology – Solid source molecular beam epitaxy	24
2.2.1 Substrate temperature	32
2.2.2 RF Nitrogen Plasma.....	34
2.2.3 Experimental growth details	36
2.3 Post-growth characterization techniques.....	39
2.3.1 Structural characterizations.....	39
2.3.2 Electrical characterizations	54
2.3.3 Optical characterizations.....	56
2.4 Device principles.....	62
2.4.1 Photoconductive detector.....	62
2.4.2 Photocurrent setup	64
Chapter 3 N-induced defects in InSbN/InSb	67
3.1 Effects of a high substrate temperature and a high plasma power range ..	67
3.1.1 Introduction.....	67
3.1.2 Homoepitaxy growth of InSbN on InSb substrate	68
3.1.3 Characteristics from Raman scattering	69
3.1.4 Characteristics from X-ray diffraction.....	77
3.1.5 Mechanisms for defect formation	80
3.1.6 Summary.....	82
3.2 Effect of a low substrate temperature and a low plasma power range.....	83
3.2.1 Introduction.....	83

3.2.2	Sample preparation of InSbN.....	83
3.2.3	Incorporation of N from X-ray diffraction.....	84
3.2.4	Secondary ion mass spectroscopy and nuclear reaction analysis.....	87
3.2.5	Summary.....	94
Chapter 4	Properties of as-grown InSbN on GaAs substrate	95
4.1	Introduction.....	95
4.2	Heteroepitaxial growth of InSbN/GaAs.....	96
4.3	Effect of two-step InSb buffer layers	98
4.4	Results from transmission electron microscopy	100
4.5	Carrier concentration and mobility measurements	101
4.6	Fourier transform infrared studies.....	104
4.7	Band filling effects.....	105
4.8	Summary.....	108
Chapter 5	Effect of thermal annealing in InSbN/GaAs.....	109
5.1	Introduction.....	109
5.2	Preparation for annealing process	110
5.3	Annealing effects from X-ray diffraction	110
5.4	Hall effect measurements.....	113
5.5	Results from Raman scattering	115
5.6	Optical results from Fourier Transform Infrared	117
5.7	Summary.....	119
Chapter 6	InSbN photodetectors by <i>in situ</i> annealing	120
6.1	InSbN photoconductors.....	120
6.1.1	Introduction.....	120
6.1.2	Sample preparation of photoconductors	121
6.1.3	N content from XRD.....	122
6.1.4	Electrical properties of InSb _{1-x} N _x	123
6.1.5	Images from transmission electron microscopy.....	125
6.1.6	Spectral response of InSb _{1-x} N _x photoconductors	127
6.1.7	Band anticrossing model at 77 K.....	130
6.1.8	Summary.....	131
6.2	InSbN photodiodes.....	132
6.2.1	Introduction.....	132
6.2.2	Device design and fabrication.....	133
6.2.3	Current-voltage characterization.....	134
6.2.4	Capacitance-voltage measurements	138
6.2.5	Micrographs from transmission electron microscopy.....	140
6.2.6	Summary.....	141
Chapter 7	Conclusions and Recommendations	142
7.1	Conclusions.....	142
7.2	Recommendations for future research	146
References.....		148

Abstract

In this thesis, indium antimonide nitride ($\text{InSb}_{1-x}\text{N}_x$) alloys were grown using a solid-source molecular beam epitaxy (MBE) system in conjunction with a radio frequency (RF) plasma N source. This work provides an enhanced understanding of this potentially significant alloy by investigating the structural, electrical and optical properties of the $\text{InSb}_{1-x}\text{N}_x$ alloys using different core characterization techniques.

InSbN has a high percentage of interstitial N due to the large difference in size between the Sb and N atoms. In this thesis, InSbN was first characterized using Raman scattering and x-ray diffraction (XRD) techniques. The effects of a higher range of growth temperature (330 °C to 420 °C) and a RF plasma power range (200 W to 500 W) on the possible N-induced defects were studied. From the Raman scattering spectra, Sb antisite defects from the $A_{1g}\text{Sb}$ elemental mode were observed to be dominant at a high growth temperature and at a low plasma power level. On the other hand, a high growth temperature and a high plasma power also induced the formation of interstitial Sb-N defects. A reduction of Sb related defects was observed at the lowest substrate temperature (330 °C) and at the lowest plasma power (200 W). Based on the experimental results, a possible mechanism of the defect formation is suggested.

Since most of the N was incorporated as interstitial N–Sb in the high-temperature regime (380 °C to 420 °C) and as substitutional N_{Sb} in the low-temperature regime

(~330 °C), the next design of experiments was carried out in a lower temperature range. The effects of a low growth temperature (270 °C to 330 °C) and a low nitrogen plasma power (150 W to 180 W) on the N incorporation were studied. From the XRD, secondary ion mass spectroscopy, and the nuclear reaction analysis ($^{14}\text{N}(\text{d},\text{p}_5)^{15}\text{N}$), it was determined that the highest ratio of N_{Sb} over the undesired interstitial N, is yielded at the lower temperature limit of 270 °C. Like N_{Sb} , a large amount of interstitial N-N will also contribute to lattice contraction. Increasing the plasma power (180 W) increased the interstitial N in the [110] direction.

Due to the closeness in the band gap between InSbN and the underlying high conductivity InSb substrate, the optical and electrical measurements of the InSbN epilayer were difficult to conduct. To ease this problem, an InSbN epilayer was grown on a semi-insulating (SI) GaAs substrate in order to explore its suitability for practical device integration. The effects of a two-step thin InSb buffer layer grown at 330 °C and 380 °C and the properties of the InSbN grown at substrate temperatures (270 °C to 380 °C) are studied. Subsequently, the crystalline quality of the InSbN material was significantly improved by the underlying two-step buffer layer due to defect suppression.

A known problem in as-grown InSbN/GaAs alloys lies in their high intrinsic background electron concentration (n_e) of $\sim 10^{18} \text{ cm}^{-3}$ which is caused by the interstitial defects. Thus, in this project, *ex situ* annealing effects on the properties of as-grown InSbN films were carried out. By applying thermal annealing at 430 °C, the

n_e was reduced by two orders to $\sim 10^{16} \text{ cm}^{-3}$ which is near the intrinsic concentration of the material. Moreover, the electron mobility was improved by a factor of 7. The reduction of the carrier concentration reduced the Burstein-Moss shift and shrunk the band gap of InSbN to $\sim 0.15 \text{ eV}$. Corresponding signatures for the reduced defects were also apparent in the Raman spectra.

Even though the *ex situ* annealing process reduced the n_e , this process also degraded the alloy sample's surface significantly due to the creation of Sb vacancy defects. Moreover, the effect of *in situ* annealing on the $\text{InSb}_{1-x}\text{N}_x$ based devices and their physical properties are not well understood. Therefore, the effect of *in situ* annealing (350°C , 380°C , and 430°C) on the electrical and optical properties of $\text{InSb}_{1-x}\text{N}_x$ was studied. The N_{Sb} incorporation was found to be the highest at the lowest annealing temperature of 350°C and an absorption wavelength of up to $10 \mu\text{m}$ infrared range was also demonstrated. $\text{InSb}_{1-x}\text{N}_x$ photoconductors at 77 K were also realized. The measured wavelengths were also in good agreement with the band gaps of the alloys calculated using a two-level band anticrossing model.

The grown InSbN structures, however, showed a low photoresponsivity compared to InSb devices (likely due to the presence of defects). Therefore, the operating characteristics of the InSbN p-n diode were studied to provide further evidence on the crystal defects. Compared to the N free InSb layer, planar growth defects were observed in the InSbN layer. These defects contributed to a high reverse dark current and to series resistances.

List of figure captions

- Figure 1.1** Transmission of atmosphere for a 6000 foot horizontal path at sea level. Adopted from [3]..... 2
- Figure 1.2** Band-gap vs. lattice constant for the family of III-V semiconductors, showing the behaviour of the dilute arsenide and antimonide nitrides. Adopted from [12]..... 5
- Figure 1.3** The dispersion of the conduction subbands (E_+ and E_-) and light and heavy hole valence bands (V_{lh} and V_{hh}) calculated for InSbN with $x=0.003$ (solid black curve, lower E_+ band and upper E_- band) and 0.007 (dashed curve, upper E_+ band and lower E_- band). The conduction band profile for InSb, E_C , is plotted for comparison (short dashed curve) along with the nitrogen level, E_N , at 740 meV (short dashed curve). Adopted from [24]..... 8
- Figure 1.4** Diagram of the research methodology of this thesis..... 19
- Figure 2.1** Illustration of the effects of anti-crossing on the conduction band structure between the N state, E_N (dash-dotted line), and the extended state of the conduction band E_{InSb} (dashed line) in the vicinity of the Γ -point minimum. Adopted from [35]. The

	anti-crossing results in the formation of the subbands E_+ and E_- .	
	The effect on the valence band is neglected.....	21
Figure 2.2	The band gap calculation for the $\text{InSb}_{1-x}\text{N}_x$ alloy versus nitrogen composition at 300 K and 77 K. The shaded area is the useful band gap ranges of operating in the LWIR region from 8 to 14 μm ..	23
Figure 2.3	Epitaxy – An ordered crystal growth.....	24
Figure 2.4	The Riber 32P MBE system used in this work.	27
Figure 2.5	A schematic view of a typical SSMBE system equipped with In, Sb, and RF plasma N sources.....	28
Figure 2.6	RHEED patterns of (a) (100) GaAs after oxide desorption and (b) Initial InSb deposition on lattice mismatched GaAs substrate..	31
Figure 2.7	A schematic illustration of the surface processes that occur during MBE film growth.....	33
Figure 2.8	A schematic diagram of the RF plasma control system used in this thesis project.....	35
Figure 2.9	RHEED patterns of (a) LT InSb buffer layer deposition and (b) Initial InSbN layer deposition on GaAs substrate.....	38
Figure 2.10	Diagram of Bragg's Law for diffraction.....	41

Figure 2.11 The schematic of $2\theta/\omega$ geometry in HRXRD measurement.... 42

Figure 2.12 Schematic illustration of the biaxial compressive ($a_{f\perp} > a_s$) and tensile strain ($a_{f\perp} < a_s$). The $a_{f\parallel}$ lattice constant remained unchanged and the $a_{f\perp}$ lattice constant was either increased (compressive in plane strain) or decreased (tensile in plane strain). 43

Figure 2.13 Principles of SIMS..... 45

Figure 2.14 The measurement of N in an InSb matrix. The plot of the ion counts as a function of time..... 47

Figure 2.15 A schematic diagram showing the scattering of particles in NRA with x being the incoming projectile, y the scattered particle, X the target, and Y the nucleus that recoiled..... 49

Figure 2.16 The diagram of an electron-sample interaction for TEM..... 52

Figure 2.17 The schematic for measuring the Hall effect..... 55

Figure 2.18 A schematic of the Raman scattering spectrum showing the Rayleigh line, Stokes scattering, and anti-Stokes scattering [48]. Wavenumber scales with the Rayleigh line defining the zero exhibited by Raman spectrometers are also shown..... 57

Figure 2.19	An example of an FTIR spectrum [50].....	60
Figure 2.20	Typical absorption profile in the semiconductor.....	62
Figure 2.21	The geometry of a photoconductor slab illustrated with light...	63
Figure 2.22	The spectral power distribution of the incident light source.....	65
Figure 2.23	The block diagram of the photocurrent measurement system used in this project.....	66
Figure 3.1	Structure of the nitride sample on the InSb substrate.....	69
Figure 3.2	The room temperature Raman spectra of the InSb reference sample.....	70
Figure 3.3	The room temperature Raman spectra of the four InSbN alloy samples with varying substrate temperatures (330 °C to 420 °C) and RF plasma power ranges (200 W to 500 W).....	71
Figure 3.4	The Raman spectra comparing the TO and LO phonon modes of the samples grown at a fixed 200 W with the different substrate temperatures of 330 to 420 °C. A redshift of the LO phonon line was observed along with a blueshift of the TO phonon line as the substrate temperature was reduced from 420 to 330 °C.....	74
Figure 3.5	Comparison of the TO/LO phonon intensity ratio.....	76

Figure 3.6	A graph of the XRD diffraction for the samples grown at different substrate temperatures (330 °C to 420 °C) and at different RF plasma power ranges (200 W to 500 W).....	77
Figure 3.7	The comparison of the integrated intensity of $A_{1g}Sb$, and the lattice mismatch of the four nitride samples.....	79
Figure 3.8	XRD $2\theta/\omega$ scans in the (004) reflection.....	84
Figure 3.9	The asymmetric (115) space mappings of the two samples grown at 270 °C with the different plasma power ranges of (a) 150 W and (b) 180 W.....	85
Figure 3.10	The SIMS profile of the samples grown at 270 °C with different plasma power ranges of 150 W and 180 W.....	88
Figure 3.11	The comparison of the ratio of the N content by XRD over the N content measured by SIMS and NRA	89
Figure 3.12	The comparison of the NRA products as a function of energy between the InSbN sample grown at 270 °C/180 W and the reference InSb substrate sample.....	91
Figure 3.13	The NRA yields for a random direction and aligned to [100] from the InSbN epilayer grown at 270 °C/180 W.....	92

Figure 4.1	The XRD diffraction of the InSbN/LT InSb samples grown at the different substrate temperatures of 270 to 380 °C and of the reference InSb sample.....	98
Figure 4.2	The XRD spectrum of the InSbN/HT InSb/LT InSb/GaAs samples grown at 270 °C and 300 °C.....	99
Figure 4.3	The TEM images of (a) InSbN/LTInSb/GaAs and (b) InSbN/HTInSb/LTInSb/GaAs heterostructures.....	100
Figure 4.4	RT transmission spectrum of the InSb reference and InSbN samples grown at different temperatures.....	104
Figure 4.5	The effects of carrier concentration (10^{16} – 10^{18} cm ⁻³) on the absorption energy edge of InSbN with 1%N _{Sb}	107
Figure 5.1	The XRD scans of the as-grown InSbN sample and of the samples annealed at different annealing temperatures.....	111
Figure 5.2	The SIMS profile of the as-grown InSbN and the sample annealed at 400 °C.....	112
Figure 5.3	The electron concentration and the mobility of the sample as a function of the annealing temperature.....	114
Figure 5.4	The Raman spectra of the as-grown InSbN and the sample annealed at 430 °C.....	115

Figure 5.5	The plot of the photon energy of the as-grown InSbN and InSbN samples annealed at 430 °C.....	117
Figure 6.1	Optical photograph plan view of the degraded InSbN sample after <i>ex situ</i> annealing at 430 °C.....	120
Figure 6.2	The plot of $2\theta/\omega$ scans obtained from the (004) reflection of the InSb _{1-x} N _x samples <i>in situ</i> annealed at 350 °C, 380 °C, and 430 °C.....	122
Figure 6.3	A TEM image of as-grown InSbN material in [001] plan view.....	125
Figure 6.4	The TEM images of (a) InSbN annealed at 350 °C and (b) InSbN annealed at 430 °C.....	126
Figure 6.5	An optical photograph plan view of the contact patterns. The inset shows the connection of the contact patterns by Au wires.....	127
Figure 6.6	The spectral response for the reference InSb sample and the InSb _{1-x} N _x samples annealed at 350 °C, 380 °C, and 430 °C at 1 V bias.....	128
Figure 6.7	The PDR of the fabricated InSb _{1-x} N _x photoconductors annealed at 350 °C and 430 °C.....	129

- Figure 6.8** The calculated band gap edge level in the $\text{InSb}_{1-x}\text{N}_x$ samples at 77 K as a function of N composition. 130
- Figure 6.9** A plot of normalized responsivity versus wavelength at 20 K under -0.5 V bias. The inset at the bottom shows the epilayer structures for InSbN and the reference InSb photodiodes..... 133
- Figure 6.10** The current-voltage characteristics of the InSbN and InSb p-n device at 20 K. The black solid line and the red dashed line show the results of fitting with a transcendental equation..... 135
- Figure 6.11** The dependence of series resistance on a forward current for the InSbN and InSb devices..... 137
- Figure 6.12** The capacitance-voltage characteristics of the InSbN and InSb devices at 20 K and 50 K..... 138
- Figure 6.13** The TEM micrographs for the (a) InSb p-n structure and (b) InSbN p-n structure. (I) and (II) are the high-resolution TEM analysis corresponding to the specified regions in (a) and (b), respectively. The open squares show the planar defects and the open circles indicate the dislocations..... 140

List of table captions

Table 3.1	The comparison of the N composition in the samples at different growth conditions.....	87
Table 4.1	The different layer structures under growth conditions for various measurement methods.....	97
Table 4.2	RT and 77 K Hall measurements of the reference InSb sample and the InSbN samples grown at different temperatures from 270 °C to 380 °C.....	101
Table 6.1	Summary of the Hall effect measurements of the three bulk InSb _{1-x} N _x samples on GaAs substrate.....	124

Author's Publication Lists

1. **K. P. Lim**, S. F. Yoon, H. T. Pham, and S. Tripathy, "Defect characterization of $\text{InSb}_{1-x}\text{N}_x$ grown using radio frequency nitrogen plasma-assisted molecular beam epitaxy," *Journal of Physics D: Applied Physics* vol. 41, pp. 165301 (2008).
2. **K. P. Lim**, S. F. Yoon, and H. T. Pham, "Properties of InSbN grown on GaAs by radio frequency nitrogen plasma-assisted molecular beam epitaxy," *Journal of Physics D: Applied Physics* vol. 42, pp. 135419 (2009).
3. **K. P. Lim**, H. T. Pham, S. F. Yoon, A. Markwitz, and N. Yakovlev, "Growth temperature and plasma power effects on nitrogen incorporation in InSbN grown by molecular beam epitaxy," *Physica Status Solidi RRL* 3, No. 7-8, pp. 263-265 (2009).
4. **K. P. Lim**, H. T. Pham, S. F. Yoon, C. Y. Ngo and S. Tripathy, "Effect of thermal annealing on properties of InSbN grown by molecular beam epitaxy," *Applied Physics Letters* vol. 96, pp.161903 (2010).

5. **K. P. Lim**, H. T. Pham, S. F. Yoon, K. H. Tan and C. Y. Ngo, “InSb_{1-x}N_x/InSb/GaAs alloys by thermal annealing for mid infrared photodetection,” *Applied Physics Letters* vol. 97, pp. 221112 (2010)
6. **K. P. Lim**, H. T. Pham, S. F. Yoon and K. H. Tan, ”Effect of N incorporation on the characteristics of InSbN p-n diodes,” *Thin Solid Films* vol. 520, pp. 2269-2271 (2012)

Chapter 1 Introduction

1.1 Background

Infrared (IR) detectors operating from 3 to 14 μm wavelength regions are usually used for thermal imaging and for the detection of environmental gases such as SO_2 , NH_3 and CO_2 . IR radiation was first discovered by Sir William Herschel in 1800 [1]. Since then, IR detection technologies have been further developed for a variety of imaging applications for fields such as the military, medicine, and earth resources. The seemingly impossible task of detecting an object in the dark or hidden in a scene is now possible because all objects which are at temperatures higher than 0 °C emit some IR radiation which covers wavelengths from 1 to 20 μm [2]. This detected IR radiation can be translated into imagery which shows the energy differences among the objects at different temperatures.

As most IR applications require transmission through the air, the radiation from an object is attenuated by the process of absorption [3]. As shown in Fig. 1.1, the radiation is absorbed by specific bands of water or by carbon dioxide in the atmosphere. As a result, this restricts the IR emission spectrum to two particular atmospheric windows. The first atmospheric window is at 3 to 5 μm which is known as medium wavelength IR (MWIR). The second atmospheric window is at 8 to 14 μm which is known as long wavelength IR (LWIR). IR detectors at these wavelengths are of great importance, especially those developed for the 8 to 14 μm band. This window band is highly preferred for space-borne operations such as

global atmospheric temperature profiles and for high performance thermal imaging because of its higher sensitivity to ambient temperature objects and its better transmission through smoke and mist [4].

Figure 1.1 Transmission of atmosphere for a 6000 foot horizontal path at sea level.

Adopted from [3].

In the early 1940s, many new materials were developed for IR sensing. These new materials included lead selenide (PbSe), lead telluride (PbTe), and indium antimonide (InSb) [5]. InSb is a group III-V compound semiconductor which provides sensitivity in the 3-5 μm atmospheric window. By the end of the 1950s, many different narrow gap semiconductor alloys in the chemical table group III-V, IV-VI, and II-VI material systems were also introduced. The band gaps of these

alloys and, hence, their spectral response can be controlled for any desired optoelectronics (OE) applications.

At present, most of the photodetectors on the market are made from $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ (Mercury cadmium telluride, MCT), a group II-VI material, due to its tuneable band gap properties, high electron mobility and easily available doping techniques [6]. Hence, this alloy represents the most widely used material for IR detectors. However, MCT is known to suffer from surface and interface instability which can lead to large variations in stoichiometry and transport properties [7]. In addition, MCT also encounters non-uniformity problems over a large sample area during growth due to the high Hg vapour pressure [8]. Therefore, a new complementary detector technology with superior bond strength and material stability is needed.

As introduced earlier, InSb is a direct energy gap semiconductor with a smallest band gap of 0.17 eV at room temperature (RT). When cooled with liquid nitrogen to 77 K, the band gap of InSb is increased to 0.23 eV, enabling it to cover the entire MWIR region [9]. No other group III-V binary semiconductor exhibits a smaller energy gap than InSb. Interest in InSb not only comes from its small energy gap but also from the fact that a high quality crystal form of it can be prepared. Today, up to 3-inch InSb wafers are commercially available. However, an operating wavelength of $\sim 6\text{ }\mu\text{m}$ is a sensitivity limit for the InSb material system which therefore makes it unsuitable to detect the longer 8 to 14 μm atmospheric band.

However, in 1996, Kondow *et al.* [10] laid the groundwork for a breakthrough in band gap engineering when they introduced quaternary gallium indium arsenide nitride (GaInNAs). Researchers began to realize that the incorporation of a small fraction of nitrogen (N) to the various binary III-V semiconductors can reduce their band gaps significantly.

This band gap bowing effect has given rise to novel materials such as gallium arsenide nitride (GaNAs) and indium arsenide nitride (InAsN). These important classes of ‘dilute nitrides’ provide many interesting properties which have generated new technological applications such as lasers and light emitting devices in the 1.3 to 1.55 μm range [11]. Based on the above phenomena, alloying N with InSb could extend the absorption wavelength of InSb to the 8–14 μm window band. Figure 1.2 shows the potential band gap bowing effect for the various dilute nitrides.

Figure 1.2 Band-gap vs. lattice constant for the family of III-V semiconductors, showing the behaviour of the dilute arsenide and antimonide nitrides. Adopted from [12].

1.2 Motivation and objective

1.2.1 N incorporation in InSbN

Besides the incorporation of the smaller N atoms, larger elements like the Group V elements arsenic (As) and bismuth (Bi) and a group III element thallium (Tl) have been added to InSb to try to cover the LWIR region.

Investigations have shown that $\text{InAs}_{1-x}\text{Sb}_x$ alloys can cover the 8 to 12 μm range, indeed, when operating at a near ambient temperature [13]. However, the large amount of As incorporation ($\sim 60\%$) required leads to a poor material quality which is not suitable for high performance detectors [14]. Adding Tl or Bi to the InSb lattice has also shown a potential for extending the wavelength to more than 8 μm [15, 16]. However, the large miscibility gap limits the Tl incorporation in the $\text{In}_{1-x}\text{Tl}_x\text{Sb}$ alloy to high compositions of $x = 15\%$, which is experimentally difficult to achieve [17]. Likewise, due to the large solubility limit of Bi, efforts to grow high quality $\text{InSb}_{1-x}\text{Bi}_x$ epitaxial layers have been unsuccessful [18, 19].

$\text{InSb}_{1-x}\text{N}_x$ alloys can offer several potential advantages over the above alternative material systems. Compared to the InAsSb material, InSbN alloys do not have an InAs component. Therefore, possible surface passivation, which could reduce the recombination velocity, can be performed easily [20].

In addition, according to the theoretical band anti-crossing (BAC) model [21], the N incorporation required in $\text{InSb}_{1-x}\text{N}_x$ to reduce the band gap from 0.17 to 0.1 eV is

about $x = 1\%$ which is a much lower requirement compared to both the InTlSb and InSbBi alloys. From the preliminary studies, using a secondary ion mass spectroscopy (SIMS) analysis (an alloy with a nominal composition of $\text{InSb}_{0.965}\text{N}_{0.035}$) has shown an absorption edge of $11\text{ }\mu\text{m}$ at 290 K through time-resolved optical measurements [22].

In addition, the incorporation of N into $\text{InSb}_{1-x}\text{N}_x$ could enhance the electron effective masses due to the flattening of the conduction band at large wavevectors [23] (as shown in Fig. 1.3). The small curvature at the Fermi level implies a large effective mass according to the curvature of the dispersion relation:

$$\frac{1}{m_{-}^{*}(k)} = \frac{1}{\hbar^2 k} \left| \frac{\partial E_{-}(k)}{\partial k} \right| \quad (1.1)$$

A larger effective mass could then suppress the energy loss from Auger recombination. In addition to an increase in the electron effective mass, diode junction breakdown through tunnelling may also be suppressed, which is particularly important for LWIR detection [21].

Figure 1.3 The dispersion of the conduction subbands (E_+ and E_-) and light and heavy hole valence bands (V_{lh} and V_{hh}) calculated for InSbN with $x=$ 0.003 (solid black curve, lower E_+ band and upper E_- band) and 0.007 (dashed curve, upper E_+ band and lower E_- band). The conduction band profile for InSb, E_c , is plotted for comparison (short dashed curve) along with the nitrogen level, E_N , at 740 meV (short dashed curve). Adopted from [24].

Despite the encouraging findings observed for the InSbN band gap, several unresolved issues related to the growth of InSbN alloys remain. First, it is challenging to control the content of N (covalent radius, $r_N = 0.75 \text{ \AA}$) atoms that sit on the Sb (covalent radius, $r_{Sb} = 1.40 \text{ \AA}$) lattice sites (N_{Sb}) [25]. As a result, the formation of defect complexes in this material is prevalent. These unwanted defects, which alter the stoichiometry of the crystalline alloy, could affect the operating characteristics of this semiconductor device significantly. Second, electron cyclotron resonance assisted molecular beam epitaxy (ECR-MBE) was used during the initial research work on this material system. The ECR plasma N source could enable efficient cracking of N_2 , generating N flux for incorporation into the InSb material [26]. However, this ECR plasma is known to produce a high density of ions or impurities which will be detrimental to the quality of the material.

Reports from the experimental measurements on light emitting diodes (LEDs) comprising a superlattice of the $\text{InSb}_{0.945}\text{N}_{0.055}/\text{InSb}$ structure have demonstrated an emission wavelength of $10.5 \text{ \mu m}$ at 77 K . However, a comparison with the BAC reduction theory suggests that only 10% of the nitrogen is active (i.e. N substituting Sb) whereas the rest of the nitrogen is likely to locate at interstitial sites which cause dilation of the lattice.

In order to improve the amount of N_{Sb} incorporation, Veal *et al.* [27] intentionally introduced another element, hydrogen, to the ECR source to enable the N plasma to be sustained at lower pressures. Veal *et al.* found that adding hydrogen increased the

nitrogen incorporation by two times. However, the mixed nitrogen and hydrogen in the plasma not only bonded with both In and Sb atoms, they produced undesirable N-H complexes. This experiment resulted in a lower total percent of N incorporation and, thus, a reduced anion substitution.

In addition, information on how to determine the exact amount of N_{Sb} is still lacking. To date, the N content reported was determined by high resolution X-ray diffraction (HRXRD), SIMS, or X-ray photoelectron spectroscopy (XPS). Used independently, these instruments could not measure the amount of N_{Sb} accurately [27-29].

The ion damage to the InSbN material during growth can be reduced by using a radio frequency (RF) plasma-assisted N source. This RF N source is reported to generate lower ion counts, leading to more neutral atomic N species compared to the ECR plasma. A recent report [30] on the InSbN growth using RF plasma-assisted MBE has shown to increase the substitutional N to ~2%. In addition, theoretical studies for the $InSb_{1-x}N_x$ alloy highlight the possibility of achieving a negative band gap (the material becomes metallic) when the x fraction exceeds 0.022 or 2.2% [31]. This implies a limited window range to control the percent of N incorporation. Therefore, further investigation on the growth parameters to vary the amount of N_{Sb} is needed.

Thus, in this thesis, $InSb_{1-x}N_x$ alloys were grown using a solid-source MBE system in conjunction with an RF plasma N source. Growth parameters are studied to improve the material quality after the N incorporation. Since the substrate temperature is a

key parameter in MBE growth, variations of both the substrate temperature and the RF plasma power were used to investigate the control of the fractional substitutional N and, at the same time, reduce the interstitial N. A combination of characterization measurements were employed to evaluate the results.

1.2.2 InSb on a GaAs substrate

A monolithic structure where all of the detection functions are formed in a similar material such as InSbN on InSb substrate could be an ideal architecture. Such homoepitaxy growth is preferred to yield high quality epilayers because the lattice mismatch between the interfaces is kept to a minimum. However, not much information can be gathered from a monolithic structure other than its epilayer crystal quality. In addition, the measurement of the electrical properties of InSbN alloys on the InSb substrate is not ideal due to the large parallel conductivity from the InSb which could degrade the signal of the InSbN layer significantly. Therefore, in order to investigate the electrical properties of InSbN alloys and explore their suitability for the integration of existing ubiquitous semiconductors, heteroepitaxy growth or the growth of InSbN film on a different substrate is necessary.

To characterize the optical properties or the small band gap of InSbN material, the known applied measurement techniques are the Fourier transform (FT) photo-modulation spectroscopy [32] and the traditional Fourier transform infrared (FTIR) transmission spectroscopy. However, FT photo-modulation spectroscopy is not easily available and this technique produces mechanical and intensity instability.

In order to conduct an FTIR measurement, a thick InSbN epitaxial layer of at least ~ 2 μm must be grown on a non-absorbing or transparent substrate. If an InSb substrate is used, the FTIR beam source will probe deeply into the similar substrate material, degrading the sensitivity probing of the surface InSbN epitaxy layer.

To overcome the above constraints, the integration of InSbN on semi-insulating (SI) GaAs substrates is studied in this thesis project. GaAs substrates are widely available and are commonly used due to their electrical isolation, low cost, and strong mechanical strength. Since the heteroepitaxy growth of InSb on GaAs has been widely published in the literature [26-28], the information revealed in this study will help to speed up the ability to grow and fabricate InSbN/GaAs detectors.

Even though the growth of InSb on a GaAs substrate is complicated by the lattice mismatch of 14.6% at 300 K, the growth still facilitates accurate electrical measurements of InSb and, hence, provides a practical route for device integration [33]. In this thesis, buffer structures comprising of InSb material were studied to yield the subsequent growth of high quality InSbN epitaxial layers on the GaAs substrate. The physical properties of the InSbN epilayers were then studied using essential and readily available characterization tools such as XRD, the Hall effect, and transmission electron microscopy (TEM).

1.2.3 Post-growth annealing treatment

Band filling effects were expected to come into play in the InSbN material system as the narrow gap InSb host matrix is known to shift towards degenerate n-type doping levels. From the RT FTIR and the Hall effect measurements [29], it was shown that the as-grown InSbN alloys indicate considerable Burstein-Moss (BM) band filling behaviour where the high background electron concentration (n_e) is $\sim 10^{18} \text{ cm}^{-3}$. This effect results in a shift of the absorption edge to higher energies as compared to InSb. This shift is undesirable since the aim of introducing N into the alloy is to reduce the energy gap.

Since the blueshift of the absorption edge in the measured spectra made the direct measurement of the band gap reduction difficult, attempts were made to subtract the BM shifts to infer a net redshift in the band gap for InSbN. However, this method would not work for working devices since high n_e is detrimental to device performance (the background concentration of 10^{16} cm^{-3} is preferred for device applications). Such cause of the high n_e is likely due to N related defect complexes.

Initial experiments using annealing for InSbN have been observed to partially remove hydrogen from N-H complexes [27]. Even though there is only a slight reduction in n_e from 2.1 to $1.8 \times 10^{18} \text{ cm}^{-3}$ after an 8 hour long anneal at 300°C , this technique still warrants further investigation. Postgrowth annealing is a well-known process in other dilute nitrides such as GaAsN since it helps to remove N defects. This removal results in an improvement in the optical and electrical properties of

GaAsN. Hence, in this thesis, the effect of *ex situ* thermal annealing at different temperatures on the carrier concentration of InSbN alloys and on the mobility of these alloys is studied.

1.2.4 *In situ* annealing process

The *ex situ* annealing process mentioned in the previous section produces a severely deteriorated surface quality which could affect the device performance. An alternative and promising method to improve the crystalline quality of the alloy involves applying *in situ* thermal annealing with Sb overpressure in the growth chamber. This technique involves directing a beam of Sb flux on the alloy's surface during annealing and it could suppress the Sb desorption from the surface and prevent surface degradation. As a result, better quality photodetectors could be fabricated and their performance could be evaluated.

In this thesis, we studied the $\text{InSb}_{1-x}\text{N}_x$ alloys prepared by an *in situ* annealing process in Sb ambience. Information on the N incorporation, electrical properties, and optical properties was investigated.

1.3 Major contributions of the thesis

The InSbN materials studied in this thesis were grown on InSb and GaAs substrates using a solid-source MBE system in conjunction with an antimony valved cracker source and an RF plasma nitrogen source. The effects of MBE growth parameters

such as substrate temperature and N plasma power on the level of N_{Sb} incorporation were studied.

Based on the Raman scattering results and the XRD results, the growth of InSbN on an InSb substrate at higher substrate temperatures and plasma power regimes reduced the N_{Sb} content and increased the interstitial Sb-N defects. A decrease in the substrate temperature and the plasma power improved the N_{Sb} content and also reduced other Sb related defects such as Sb antisites.

Further investigations at a lower substrate temperature and plasma power regime showed an improved N_{Sb} incorporation up to $\sim 1.35\%$. For the first time, the N compositions in the InSbN alloys were investigated by a combination of structural characterization techniques using XRD, SIMS, and nuclear reaction analysis (NRA). Like N_{Sb} , an interstitial defect such as N-N was shown to result in lattice contraction.

To measure the electrical and optical properties of the InSbN alloys, InSbN films were grown on the lattice-mismatched SI GaAs substrate. From the XRD and TEM investigations, the use of two-step InSb buffer layers was shown to improve the crystalline quality of the InSbN alloys. InSbN alloys grown at a lower substrate temperature, however, exhibited an increase in n_e from $\sim 10^{16}$ to $\sim 10^{18} \text{ cm}^{-3}$. This indicated that the lower substrate temperature which improved the N incorporation also increased the donor N defects. The existence of the high n_e caused a blueshift in the measured absorption edge energy up to 0.26 eV. By taking into account the BM

effect in a model, the blueshift was subtracted during analysis. As a result, the true band gap energy of the InSbN (0.1 eV) was deduced.

A heat treatment process or postgrowth thermal annealing at different temperatures was studied to remove the effect of the high n_e . The reduction of n_e from $\sim 10^{18}$ to intrinsic level of $\sim 10^{16} \text{ cm}^{-3}$ and the corresponding redshift in the absorption edge from ~ 6 to $8 \text{ }\mu\text{m}$ were demonstrated. Such findings will assist those who are developing InSbN photodetectors. The *in situ* annealing process which improves the surface quality of the InSbN alloys was also studied. We observed a near intrinsic level of electron concentration in all of the samples and an increase in N incorporation at a reduced annealing temperature. In addition, we also showed InSb_{1-x}N_x photoconductors operating at $10 \text{ }\mu\text{m}$. These results demonstrated the potential of the InSb_{1-x}N_x alloy for LWIR optoelectronics.

InSbN p-n diodes were also fabricated to study the crystalline quantity of the InSbN films. Besides showing long wavelength absorption, we observed significant planar growth defects in the InSbN layer that could affect the electrical characteristics of the diodes.

1.4 Organization of the thesis

This thesis is organized into six main chapters. Chapter 1 highlights the introduction of the thesis in which the background, motivation, and objectives of the project are presented. In addition, a short description of the contributions and organization is presented.

Chapter 2 presents the theoretical calculation of the InSbN band gap and covers the key features of the operations of the solid source MBE and the various characterization techniques. With a basic understanding of the growth conditions and the characterization tools, the reader will comprehend the data results from the measurements.

Chapter 3 covers the homoepitaxy growth of InSbN films. Based on the different growth conditions, information on the structural properties of the InSbN alloys is investigated using key techniques such as XRD, Raman scattering, SIMS, and NRA.

Chapter 4 reports the heteroepitaxy growth of InSbN on SI GaAs substrates at different growth parameters. The effect of N incorporation on the electrical and optical properties of the InSbN is studied by measurement tools such as Hall and FTIR.

Chapter 5 presents the effects of different postgrowth annealing temperatures on the properties of the InSbN alloys. Chapter 6 covers the photoconductivity results of the $\text{InSb}_{1-x}\text{N}_x$ photodetectors after the *in situ* annealing process. In addition, the electrical properties of the photodetectors are also investigated in this chapter.

Finally, Chapter 7 summarizes the results of the research in this thesis and recommends some directions for future research on this material system.

A diagram of the research methodology of this thesis appears in Fig 1.4.

Figure 1.4 Diagram of the research methodology of this thesis.

Chapter 2 Principles of band gap, growth and characterization

2.1 Band gap of InSbN

As mentioned in Chapter 1, the substitution of a few percent of N on the group V lattice sites in $\text{InSb}_{1-x}\text{N}_x$ is predicted to result in a band-gap bowing effect [21, 26]. The BAC model introduced by Shan *et al.* [34] is used to determine the band structure of InSbN in this thesis.

In this model, the introduction of N into an InSb lattice could result in the formation of a localized resonant N band which is located close to the conduction band edge. The interaction of this N level with the extended conduction band edge states of the host InSb matrix gives rise to two nonparabolic subbands: E_+ and E_- . The dispersion of these subbands can be calculated using the equations:

$$E_+(T) = \frac{1}{2}[(E_{\text{InSb}_k}(k) + E_N) + \sqrt{(E_{\text{InSb}_k}(k) - E_N)^2 + 4V^2x}] \quad (2.1)$$

$$E_-(T) = \frac{1}{2}[(E_{\text{InSb}_k}(k) + E_N) - \sqrt{(E_{\text{InSb}_k}(k) - E_N)^2 + 4V^2x}] \quad (2.2)$$

where $E_{\text{InSb}_k}(0)$ is the band gap of the host InSb at wavevector $k = 0$, E_N is the energy associated with the N states, and V describes the interaction between $E_{\text{InSb}_k}(0)$ and E_N . As shown in Fig. 2.1, the subband edge E_- retains the characteristic of the extended InSb-like conduction band whereas the E_+ edge exhibits a more localized characteristic due to the E_N states.

Figure 2.1 Illustration of the effects of anti-crossing on the conduction band structure between the N state, E_N (dash-dotted line), and the extended state of the conduction band E_{InSb} (dashed line) in the vicinity of the Γ -point minimum. Adopted from [35]. The anti-crossing results in the formation of the subbands E_+ and E_- . The effect on the valence band is neglected.

According to a tight binding model [22], the $E_{InSb-k}(0) = 0.177$ eV, the E_N nitrogen is level energy with respect to the valence band maximum = 0.647 eV, and V the interaction potential = 2.2 eV. The band gap of InSbN is equal to E_- at $k = 0$.

The effective E_N level could move down when the atomic N concentration is increased which leads to a lowering of the E_- subband. This increase in N content, x on the energy of the N resonant level, is given by:

$$E_N = E_{NO} - \alpha_N x \quad (2.3)$$

where E_{NO} is the initial N level and $\alpha_N x$ describes the decrease in E_N . E_N is taken to be independent of temperature.

To account for the temperature dependence of the band gap energy of $InSb_{1-x}N_x$, the temperature dependence of the conduction band E_{InSb} follows the Varshni relation:

$$E_{InSb}(T) = E_0 - \alpha T^2 / (\beta + T) \quad (2.4)$$

where $E_0 = 0.24$ eV is the band gap at 0 K while $\alpha = 2.7 \times 10^{-4}$ eV/K and $\beta = 106$ K are the Varshni coefficients [36].

Using Eq. (2.3) and (2.4), the band gap as a function of the N content x is plotted in Fig. 2.2. As shown in Fig. 2.2, the band-gap of the alloy is predicted to decrease to 90 meV at 1% N, which is a change of almost 50%.

Figure 2.2 The band gap calculation for the $\text{InSb}_{1-x}\text{N}_x$ alloy versus nitrogen composition at 300 K and 77 K. The shaded area is the useful band gap ranges of operating in the LWIR region from 8 to 14 μm .

2.2 Growth technology – solid source molecular beam epitaxy

Compound semiconductor alloys are more likely to be produced for commercial devices when they are grown to a high degree of crystallinity (i.e. with minimal defects). As illustrated in Fig. 2.3 below, the epitaxial growth (i.e. the crystalline growth of InSbN epilayers on a crystalline substrate described in this thesis) was performed using a solid source molecular beam epitaxy (SSMBE) system.

Figure 2.3 Epitaxy – An ordered crystal growth.

The SSMBE technology is an atomic layer-by-layer growth technique based on the reaction of the molecular or atomic beams of various pure elemental sources with a heated crystalline substrate in an ultrahigh vacuum (UHV) region. This MBE method is essentially a line-of-sight technique from the source to the substrate and

the beams or fluxes of the constituents can be varied either by changing the evaporation conditions or by physically interrupting the beam using rapid action mechanical shutters.

An important aspect of the MBE is the slow deposition rate (~1000 nm/hr) which allows the random adatoms (the source atoms or molecules which have impinged on the substrate surface) to land on the substrate surface, condense, and build up systematically to form crystalline layers. As a result, extremely high quality solid films with well controlled doping, composition, and thickness can be produced [37]. The key features associated with the MBE process include the vacuum requirements, the MBE components (such as the sources, shutters, substrate heating, and manipulation), and MBE analytical facilities.

Vacuum provides a unique environment in which materials are prepared and characterized and, thus, it plays an important role in a wide range of technologies. The MBE system needs to operate in an UHV environment ($<1 \times 10^{-9}$ Torr) in order to serve two main purposes. From the kinetic theory of gases, the mean free path of a particle is the average distance that the particle travels between collisions with other moving particles. The mean free path can be expressed by:

$$\lambda_{mfp} = \frac{k_B T}{\sqrt{2} \pi p d^2} \quad (2.5)$$

where k_B is the Boltzmann constant, T is the ambient temperature, p is the pressure and d is the molecular diameter of the particle.

Under the UHV environment, the mean free path of the molecules from the elemental sources is of the order of tens of meters. This path is much longer than the distance between the source and the substrate. Thus, the evaporated molecules do not interact with each other or with the chamber residual gases until they arrive at the substrate, travelling in a beam-like directional manner. Hence, the name “molecular beam epitaxy” was adopted for this technology.

Second, the residual gases or contaminants which exist in the background of the growth chamber could cause adverse effects on the growth process by colliding with the depositing source species or by hitting the growing surfaces. Thus, they may incorporate in the layers. This number of residual gas atoms (which can limit the purity of the layers) can be expressed as:

$$N_i = p \sqrt{\frac{1}{2 \pi k_B m_i T}} \quad (2.6)$$

where m_i is the atomic or molecular mass. Therefore, from Eq. (2.6), the requirement of an UHV environment (low pressure) could limit the incorporation of residual gas atoms, ensuring high purity and a clean surface.

To attain the UHV environment, a combination pumping system is installed in MBE chambers. This pumping system includes turbomolecular pumps, ion pumps and titanium sublimation pumps. During growth, the chamber walls are also cooled by liquid N₂ shroud which further improves the vacuum quality by reducing the evaporation of residual atoms from the large surface area.

Figure 2.4 shows the picture of the actual SSMBE system used in the growth of the samples reported in this thesis and Fig. 2.5 shows the schematic of a typical SSMBE growth chamber with the main components used to grow InSbN material.

Figure 2.4 The Riber 32P MBE system used in this work.

Figure 2.5 A schematic view of a typical SSMBE system equipped with In, Sb, and RF plasma N sources.

Summary of the major MBE components:

- ◆ Knudsen-type geometry sources. These are effusion cells which are used to evaporate the constituent elements of the semiconductor (such as Ga, In and Al) in order to generate flux. The elements are contained in high purity pyrolytic boron nitride (PBN) crucibles, which can withstand high temperatures due to their high dissociation temperature (>1400 °C). Thermocouples, which are in close contact with the crucibles, register the source material temperatures and control the power to the heater via a feedback loop and, thus, control the temperature of the sources. These cells

are kept at standby temperatures when they are not in operation. These standby temperatures are 600 °C for the Ga cell, 450 °C for the In cell, and 750 °C for the Al cell.

- ◆ Valved cracker cells. These cells were used to generate group V elements such as As and Sb which usually exist as As₄ and Sb₄ respectively. To prevent such tetrameric molecules from complicating the incorporation process, valved crackers which consist of two zones are used. The first zone is a low temperature reservoir zone used to evaporate the molecules and the second zone is a high temperature cracking zone used to crack the molecules, yielding As and Sb atoms. In addition, due to the volatile nature of As and Sb, the use of a valved cell which utilizes a needle valve allows for the precise control and delivery of the group V fluxes while preventing the rapid depletion of these materials.

- ◆ RF nitrogen plasma source. High purity N₂ gas is cracked to generate atomic N atoms in order to improve the N incorporation efficiency in our samples.

- ◆ Carbon tetrabromide (CBr₄) source. CBr₄ was used as the p-type dopant. The use of C dopant minimizes the outward diffusion problem as compared to other p-type dopants, such as beryllium and zinc.

- ◆ Shutters. The mechanical shutters either provide a rapid stop or they initiate the beam fluxes from the sources. As a result, the growth composition and the doping of the growing layer can be abruptly altered.
- ◆ Substrate holder. This holder (made of molybdenum which has a low vapour pressure) provides a mechanical means of holding and transporting the semiconductor substrate in and out of the MBE chamber.
- ◆ Quadruple mass spectrometer (QMS). The QMS helps to check and monitor the levels of atomic and molecular species inside the growth chamber.
- ◆ Reflection high energy electron diffraction (RHEED). This in-growth or *in situ* surface characterization technique provides the crystal grower with immediate feedback and with improved control of the growth process. RHEED is an essential system which is used to monitor the surface reconstruction, growth rate, and mode.

In RHEED measurements, high energy electron beams (~ 5 KeV to 40 KeV) are reflected from the substrate surface at a very shallow angle ($\sim 1^\circ$ to 5°) as shown in Fig. 2.5.

These reflected electrons are diffracted by the outmost atomic layers at the surface and are then imaged on the RHEED screen which is coated with phosphor. This shallow angle of incidence makes the electron beam very sensitive to the long range order for the construction of the substrate surface and the grown epilayers. As shown in Fig 2.6 (a) and (b), the diffraction of these electrons from a smooth surface or a rough surface could result in the formation of a series of streaks or spots on the phosphor screen, respectively.

Figure 2.6 RHEED patterns of (a) (100) GaAs after oxide desorption and (b) Initial InSb deposition on lattice mismatched GaAs substrate.

Thus, useful information on the surface crystallography, which is dependent on the growth conditions, can be deduced from the RHEED patterns.

2.2.1 Substrate temperature

The first key parameter that is studied for the growth of InSbN is the substrate temperature. The mounting of the substrate was by indium free clamping onto the holder which provided a more uniform heating of the substrate from the substrate heater. The substrate temperature can be measured by a thermocouple located at the back of the substrate holder or by an optical pyrometer located within the view of the substrate. In this thesis, the substrate temperature was mainly determined from the thermocouple reading with the assistance of RHEED pattern. For example, the temperature's reproducibility for InSb was confirmed by observing the transition from a diffuse background to clear diffraction pattern of pseudo (1x3) reconstruction [38]. The observed thermocouple reading was then used as the deoxidation temperature of the InSb substrate. Assuming a near linear temperature relation between the thermocouple reading and the InSb substrate, the growth temperature of the subsequent layer (InSbN) was then determined. The substrate temperature for the growth of InSbN on GaAs was also calibrated from the construction of the RHEED pattern during the oxide desorption of GaAs substrates.

By choosing the appropriate source (In, Sb or N) and the substrate temperature, epitaxial films of the desired chemical composition were obtained. Selected temperatures for the substrate growth and the source of the constituent beams have a direct effect on the growth process. Usually the substrates undergo an outgassing process in a UHV preparation chamber prior to growth to remove the residual water

molecules. After this process, an oxide desorption step is further carried out to remove the amorphous thin oxide layers.

A series of surface processes could take place on the heated substrate. The following processes (depicted in Fig. 2.7) are the most significant ones:

- ◆ Adsorption. After the source atoms or molecules have impinged on the substrate surface, they are known as adatoms.
- ◆ Surface migration and dissociation. The movement of the adatoms or the diffusion and the breaking up of adsorbed molecules on the substrate surface.
- ◆ Incorporation and nucleation. The inclusion and the clustering of the source atoms into the crystal lattice of the substrate or the grown epilayer.

Figure 2.7 A schematic illustration of the surface processes that occur during MBE film growth.

- ◆ Thermal desorption. The adatoms acquire sufficient energy to overcome the attractive forces and to leave or evaporate from the crystal lattice.

The growth mechanism is based on kinetic processes. The sides of any nucleated island could serve as new step edges for the incorporation of newly arriving elements, leading to two-dimensional growth.

In this thesis, the growth rate of the InSbN is independent of the range of substrate temperature. However, the growth rate depends on the ratio of group V element flux to group III element flux. Thus, the choice of the group V to group III flux ratio is crucial. Group V atoms are known to be volatile when excess group V atoms on the substrate re-evaporate easily at a higher temperature except for the group V atoms that have reacted with the group III atoms on the substrate surface. To ensure stoichiometry, the growth is usually terminated under excess group V pressure (referred to as the “Sb stabilized condition” in this thesis).

2.2.2 RF Nitrogen Plasma

The next growth parameter is the RF plasma power. The growth of the InSbN material in our experiments used a high purified N₂ gas source with 7N (99.99999%) purity. This N₂ gas, which is very stable and non-reactive, was first filtered through a MicroTorr PS11 gas purifier to minimize the presence of oxygen and other impurities which might have compromised the quality of the InSbN layer.

Subsequently, in order to create reactive N atoms for growth, these inert N₂ molecules were cracked by passing through an RF plasma cell operating at 13.56 MHz. The flow of N₂ gas to the plasma source was controlled and regulated by a mass flow controller.

In this thesis, the gas flow rate of the N₂ gas was between 0.15 to 0.26 standard cubic centimetres per minute (SCCM) and the RF plasma power range studied was between 150 to 500 W. Figure 2.8 contains a schematic diagram of the RF plasma control system.

Figure 2.8 A schematic diagram of the RF plasma control system used in this thesis project.

The background vacuum pressure in the chamber during the growth of InSbN was $\sim 8 \times 10^{-6}$ Torr. The impedance of the plasma source was tuned to achieve a zero reflected power of the plasma in order to achieve a stable operating point with minimal ion production. The plasma intensity was optically monitored by an optical detector. Increasing the RF power led to an increase in the plasma intensity and, hence, an increase in the generation of atomic N species. Such an increase in the RF plasma may also have generated more N ions.

2.2.3 Experimental growth details

The growth of high quality $\text{InSb}_{1-x}\text{N}_x$ on InSb (001) substrates was investigated at temperature regimes from 270 °C to 420 °C with plasma power ranges of 150 W to 500 W. These two important growth parameters will be examined in Chapter 3.

The epi-ready substrates were mounted onto quarter size In-free Mo blocks without prior chemical etching. These substrates were first thermally outgassed at 250 °C for 30 minutes in a UHV environment. Next, a process of oxide desorption at 420 °C from the substrate surface was carried out under Sb flux at the vacuum condition of $\sim 4 \times 10^{-7}$ Torr.

The surface morphology of the substrate was constantly monitored by RHEED. After achieving a streaky diffraction pattern (which indicated good surface crystallinity) [38, 39], the growth of the 0.3 μm thick InSb buffer layer was carried out to improve the surface morphology further.

The temperature for the buffer growth was set at 420 °C since the surface was reported to be extremely smooth under atomic force microscopy (AFM) observation [38]. The V/III ratio = 2 was chosen for the growth of the InSb buffer to provide a Sb stabilized condition where its surface reconstruction, pseudo (3x1), was expected to be structurally more stable compared to a In stabilized condition.

The growth rate used was ~0.6 to 1 $\mu\text{m/h}$ which was verified by a surface profile measurement of the thickness of the grown layers. As the N flux generated from the RF plasma source is rather dispersive in nature, the selected range of the N flow rate helped to maintain a stable plasma at a sufficiently low background pressure of about $\sim 10^{-6}$ Torr [30].

The effect of the growth temperature (270 °C to 380 °C) on the structural, electrical, and optical properties of $\text{InSb}_{1-x}\text{N}_x$ on GaAs (001) substrates was also studied. These GaAs substrates were put through similar outgassing and oxide desorption processes as described for the InSb substrates. The temperature's reproducibility for GaAs was confirmed by observing the formation of (2x4) reconstruction on the RHEED pattern. The observed thermocouple reading was then used as the deoxidation temperature for the GaAs substrate.

In this investigation, an InSb buffer was first grown onto a GaAs substrate so that the generation of misfit dislocations is confined at the InSb-GaAs interface. A two-step

growth process was utilized to obtain high quality InSb thin films on the GaAs substrate as reported [40-42].

The recipe for the two-step growth process consists of an initial low temperature (LT) InSb buffer layer grown at 330 °C followed by a higher temperature (HT) InSb intermediate layer grown at 400 °C. The selected thickness of the LT buffer layer of about 30 nm may have reduced the dislocation density and improved the crystalline quality of the subsequent HT InSb layer [43]. The InSbN layer at different substrate temperatures and RF plasma power ranges was then grown on top of the InSb buffer to complete the growth. Figure 2.9 (a) showed the RHEED pattern during LT InSb deposition on a GaAs substrate whereas Figure 2.9 (b) shows the RHEED pattern during the InSbN growth.

Figure 2.9 RHEED patterns of (a) LT InSb buffer layer deposition and (b) Initial InSbN layer deposition on GaAs substrate.

2.3 Post-growth characterization techniques

Different levels of doping and other material parameters could influence the properties of $\text{InSb}_{1-x}\text{N}_x$ alloys. We need to know, for example, how much N is incorporated in the material and the possible issues that affect the N incorporation efficiency.

Therefore, the characterization tools are of paramount importance since they provide information on the physical properties of the InSbN alloys. The core experimental techniques used in this thesis were HRXRD, SIMS, NRA, TEM, the Hall effect, Raman spectroscopy, FTIR, and photoconductivity.

2.3.1 Structural characterizations

High Resolution X-Ray Diffraction (HRXRD)

HRXRD has developed into a powerful tool for the nondestructive *ex situ* investigation of the crystal structure of the grown epitaxial layers. Since the wavelength of an X-ray source is comparable to the interplanar spacing of atoms, HRXRD is ideally suited for probing the structural arrangement of atoms and molecules in the material. Basically, HRXRD involves the study of scattering of incident x-rays by crystal atoms (atomic planes) which produce a diffraction pattern.

In this project, the most important information which was obtained from the diffraction pattern was the content of N_{Sb} in the crystalline InSbN layers.

X-rays are diffracted from the atomic planes when the Bragg's Law is met:

$$\lambda = 2d \sin \theta \quad (2.7)$$

where λ is the wavelength of the incident X-ray (1.5406 Å), θ is the diffraction angle, and d is the spacing between the adjacent atomic (hkl) planes. It is worth noting that because of the lack of calibration of the XRD equipment, angle shifts in the reference substrate peak (InSb and GaAs) will be detected.

The d spacing for cubic crystals can be further expressed as:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (2.8)$$

where a is the lattice constant of the crystal and h, k , and l are the Miller indices corresponding to the (hkl) plane.

In this work, the InSbN material has a zinc blende structure. Therefore (004) reflection plane is used to allow the detection of the lattice constant variations perpendicular to the sample surface. For the measurements of both perpendicular and parallel lattice constants which contribute to the lattice spacing, the asymmetric plane (115) is then used. Furthermore the diffraction intensities from the (004) and (115) planes are intense.

Figure 2.10 diagrams the Bragg's Law for diffraction [44].

Figure 2.10 Diagram of Bragg's Law for diffraction.

Several methods are commonly used for scanning the intensity of the Bragg reflection. In this thesis, the $2\theta/\omega$ scan was utilized as shown in Fig. 2.11. The $2\theta/\omega$ scan involves a moving or rocking sample stage (ω) and a detector (2θ) around the Bragg angle.

Figure 2.11 The schematic of $2\theta/\omega$ geometry in HRXRD measurement.

When the InSbN film with an unconstrained lattice constant of a_f was deposited on the substrate which had a different lattice constant of a_s , the film initially grew with the lattice constant equal to the substrate. At this fully strain situation, the in-plane lattice constant $a_{f\parallel}$ was identical to that of a_s and a tetragonal distortion of the InSbN film occurred. Such distortion or mismatch was accommodated by the different strains in the layer of growth direction, $a_{f\perp}$ as shown in Fig. 2.12.

Figure 2.12 Schematic illustration of the biaxial compressive ($a_{f\perp} > a_s$) and tensile strain ($a_{f\perp} < a_s$). The $a_{f\parallel}$ lattice constant remained unchanged and the $a_{f\perp}$ lattice constant was either increased (compressive in plane strain) or decreased (tensile in plane strain).

Therefore, when the smaller N atoms substituted the larger Sb atoms, tensile strain was observed.

From the value of $a_{f\perp}$ obtained from the diffraction pattern, a_f is then determined by:

$$a_{f\perp} = a_{f\parallel} + (a_f - a_{f\parallel})(C_{11} + 2C_{12}) / C_{11} \quad (2.9)$$

where $C_{11} = 6.67 \times 10^{11}$, $C_{12} = 3.65 \times 10^{11}$ dyn/cm² are the elastic stiffness of the crystals [45]. The form $(C_{11} + 2C_{12}) / C_{11} = C$ will be used in the calculations in Chapter 3.

The N composition x was then determined by a_f using Vegard's law:

$$a_f = xa_{InN} + (1 - x)a_{InSb} \quad (2.10)$$

where a_{InN} and a_{InSb} were the lattice constants of InN and InSb, respectively.

Secondary Ion Mass Spectroscopy (SIMS)

SIMS is a technique used to study the composition of solid thin films by sputtering and ionizing the atoms and molecules from the surface of a sample with a focused primary ion beam and by analyzing the ejected secondary ions (as shown in Fig. 2.13). These resulting secondary ions are then accelerated into a mass spectrometer which separates the ions according to their mass-to-charge ratios. Because each element has its own mass, an analysis of the mass spectrum allows scientists to determine what elements are present in the sample.

Figure 2.13 Principles of SIMS.

The detection limits in SIMS for most trace elements are between 10^{12} and 10^{16} atoms/cm³, which makes it the most sensitive surface analysis technique. As SIMS can only measure the ions created in the sputtering process and not the neutral atoms or clusters, the detection limit of an element is likely to be affected by how efficiently it ionizes. The ionization efficiency of an element is referred to as its ion yield. In fact, the ion yield of a particular element A is simply the ratio of the number of A ions to the total number of A atoms sputtered from the mixing zone.

Thus, in order to increase the yield of the negative N ions, the sample surface of the InSbN alloys was bombarded by cesium (Cs^+) in this thesis. The enhanced negative N ion yields produced with Cs^+ sputtering can be explained by work functions that are reduced by the implantation of Cs^+ into the sample surface. As a result, more secondary electrons are excited over the surface potential barrier and the increased availability of electrons increases negative ion formation. In this thesis, a dual beam technique was utilized where a Cs^+ current beam was used for sputtering whereas a Ga^+ current beam was used for mass analysis.

The measurement of the N concentration depth profile of a sample is done by first monitoring the secondary ion count rate of the N as a function of time. The conversion of signal intensity (count/s) to concentration (atoms/cm^3) requires a standard reference sample with a composition and matrices similar to the sample of interest (MBE grown InSbN samples). This requirement is necessary to reduce the matrix effects where the secondary ion yield (for example, N) could vary by several orders of magnitude from one matrix to another.

In this thesis, the standard sample was made by the ion implantation of N with a controlled dose. Therefore, the accuracy of the SIMS analysis was dependent on the standard sample that was used for quantification. The standard samples made from ion implantation usually exhibit an error margin of 30%.

Figure 2.14 shows the raw data for the measurement of N in an InSb matrix. The sample was prepared by ion implantation of N into an InSb wafer.

Figure 2.14 The measurement of N in an InSb matrix. The plot of the ion counts as a function of time.

As Fig. 2.14 illustrates, the exceedingly high N ion counts in the first 100 seconds in an InSb matrix are due to the oxide layer on the sample surface which affects the ion yield. Therefore, the first several data points from the first 100 seconds are usually disregarded. To convert the time axis into depth, a profilometer is used to measure the sputter crater depth.

The vertical axis of ion counts is converted into concentration by a Relative sensitivity factor (RSF). The RSF can be calculated by:

$$RSF = \frac{Dose}{Craterdepth} \times \frac{I_M}{I_i} \quad (2.11)$$

where the Dose (atoms/cm²) is the implant dose provided by the manufacturer, I_M is the ion intensity of the reference element, which is Sb, and I_i is the average ion intensity of the N implant.

Using the RSF value from a standard sample, the N concentration in the InSbN samples was then obtained by:

$$C_N = RSF \times \frac{I_N}{I_M} \quad (2.12)$$

where I_N is the intensity of N in the InSbN samples.

Nuclear Reaction Analysis (NRA)

NRA is a well established technique used to study low-Z elements such as C, N, and O in thin films. NRA uses energetic, low mass ions such as protons and deuterons (incident projectile) to induce nuclear reactions of these light elements. The product particles emitted by these nuclear reactions are then detected. In this thesis, deuterium beams were used to quantify the N concentration.

According to Einstein [46], the energy of a particle at rest can be calculated using the equation: $E = Mc^2$, where M is the mass of the particle in atomic mass units (amu) and c is the speed of light. The basic principle of the nuclear reaction in NRA, $X + x \rightarrow Y + y + Q$ is presented in a scattering geometry as shown in Fig. 2.15 where X is the target nucleus, x the incident projectile, y the emitted particles or photons, and Y is the residual nucleus (which is generally a heavy particle carrying a very low energy which remains in the target material and cannot be detected).

Figure 2.15 A schematic diagram showing the scattering of particles in NRA with x being the incoming projectile, y the scattered particle, X the target, and Y the nucleus that recoiled.

Q is the amount of energy released in the reaction. In addition, Q is the difference between the total energy at rest before the reaction takes place and after the reaction has occurred and can be given by:

$$Q = (M_1 + M_2) c^2 - (M_3 + M_4) c^2 \quad (2.13)$$

This energy of the reaction products is a function of the energy of the incoming ions. From the intensity of the radiation, one is able to determine the concentration of the particular atomic element, producing a spectrum of particle yield versus energy.

Broad-beam NRA can be highly sensitive, with typical detection limits of 10^{19} atoms/cm³ depending on the reaction involved. Because this method relies on nuclear reactions, it is insensitive to the matrix effects encountered by SIMS. Hence, NRA is easily made quantitative without reference to standard samples and can act as a complementary tool to SIMS.

Some common reactions used for the detection analysis are (d, a), (d, p), and (p, a). NRA signals with the above reaction product particle detections are very useful for N analysis. The notation used for nuclear reactions assumes that (x, yz) denotes the incident beam particle “x” and the reaction products “y” and “z”, where “p” is a proton, “d” is a deuteron (²H), and “a” is an alpha particle (⁴He). “p” denotes an inelastically scattered proton (it leaves the target nucleus in an excited state).

The concise form of a nuclear reaction usually expressed by nuclear physicists is:

$$\mathbf{X(x,y)Y} \quad (2.14)$$

Therefore, in this aspect, the reaction $^{14}\text{N(d,p)}^{15}\text{N}$ represents that a deuteron reacts with a ^{14}N atom, forms a ^{15}N atom, and emits a proton.

This nuclear reaction to profile N can also be written in the following form:

where Q_{R} is the energy released in the reaction.

Transmission Electron Microscopy (TEM)

TEM is an analytical tool that allows a detailed micro structural examination of the material crystal through high resolution and high magnification imaging. Magnifications of up to 500,000x and detail resolution below 100 nm can be achieved routinely. This remarkable magnification range is facilitated by the small wavelength of the incident electrons and is the key to the unique capabilities associated with TEM analysis. Thus, quantitative and qualitative elemental analysis can be provided from features smaller than 1 nm, imaging the exact atomic arrangement of a single crystal.

Unlike an optical microscope, TEM is a diffraction method where a beam of electrons is transmitted through an ultra thin sample ($<1\ \mu\text{m}$ thick) and interacts with the sample as it passes through (see Fig. 2.16).

Figure 2.16 The diagram of an electron-sample interaction for TEM.

As illustrated in Fig. 2.16, the electrons interact with the material in two ways: (a) by inelastic scattering and (b) by elastic scattering. For TEM, inelastic scattering which leads to absorption is usually avoided since it contains no local information. The electron beam will be only elastically scattered (i.e. diffracted) since the lattice and the defects presented in the sample material will modulate the amplitude and phase

of the primary beam and the diffracted beams, resulting in the TEM image collected at the camera.

Basically, TEM offers two methods of sample observation: (a) the diffraction mode and (b) the image mode. In this thesis, the bright-field image mode was used. In bright-field microscopy, a small objective aperture is used to block all diffracted beams and to allow only the transmitted (undiffracted) electron beam to pass. The function of the objective aperture is to select the electrons which will contribute to the image, and, thereby, could affect the appearance of the image. The image mode produced is a contrast image of the illuminated sample area with details related to the sample microstructure brought about by mass contrast due to spatial separations between distinct atomic constituents.

TEM has no inherent ability to distinguish atomic species. Nevertheless, the electron scattering is very sensitive to the target element. Heavy atoms having large positively charged nuclei will scatter electrons more effectively and to higher angles of deflection than light atoms will. The magnitude of the elastic electron-nucleus interaction scales with the charge of the nucleus and, therefore, with atomic number Z . As the higher scattered intensity is removed by the objective aperture, regions of high- Z material will appear darker than low- Z matrix material in the TEM image.

The most important aspect of using the TEM technique is preparing high quality thin material foils from the sample for observation. Instead of polishing the bulk material down into thin slabs which could compromise its material quality, a focused ion beam (FIB) technique is used to prepare the foils. FIB cuts through the material and causes little damage to adjacent structures by using a fine focused beam of ions that operate at high beam currents to mill out the embedded tiny structures from the sample for cross-section TEM viewing.

2.3.2 Electrical characterizations

The Hall Effect

The Hall effect is the consequence of the forces exerted on moving charges across an electrical conductor by electric and magnetic fields. A magnetic field applied to the conductor that is perpendicular to the current flow produces an electric field that is perpendicular to the magnetic field and to the current.

The key feature of Hall measurements is to distinguish whether an extrinsic semiconductor (InSbN) is n-type (addition of excess electrons) or p-type (addition of excess holes) and to determine the majority carrier concentration and the majority carrier mobility.

Figure 2.17 illustrates the Hall effect. A current I_x flows in the (x) direction with the magnetic field (B_z) in the (z) direction. The electrons and the holes in the semiconductor experience a force known as the Lorentz force in the (−y) direction as

indicated in the diagram. In a p-type (n-type) semiconductor, a build-up of excess holes (electrons) will occur on the $y = 0$ surface of the semiconductor.

The net charge which induces an electric field in the (y) direction is called the Hall field (E_H) and the corresponding voltage is known as the Hall voltage (V_H). This polarity of the Hall voltage is then used to determine whether the semiconductor is n-type where the V_H is negative or a p-type where the V_H is positive [47]. The magnetic field used in all the experiments was fixed at ~ 0.32 T. The conductivity was measured using a Van der Pauw technique with the sample size of $\sim 5 \times 5 \text{ mm}^2$. An injection current of ~ 20 mA is used.

Figure 2.17 The schematic for measuring the Hall effect.

Assuming an n-type semiconductor, the majority carrier electron concentration (n_e) is determined from I_x , B_z , and V_H :

$$n_e = -\frac{I_x B_z}{qdV_H} = -\frac{1}{qR_H} \quad (2.16)$$

where q is the magnitude of the electronic charge, d is the sample thickness, and R_H is the Hall coefficient. The Hall mobility in this semiconductor μ_H is defined by:

$$\mu_H = R_H q \mu_e n_e \quad (2.17)$$

where μ_e is the electron conductivity mobility.

2.3.3 Optical characterizations

Raman Spectroscopy

Raman spectroscopy is a useful tool to characterize the details of defects and the disorder of the arrangement of bonds in grown epitaxial material. Raman spectroscopy is based on the inelastic scattering process that corresponds to the interaction between the incident light photons and the optical modes of the lattice vibration in the sample.

When the scattered photons are reradiated at the same energy or frequency as that of the incident light, a strong central line component known as the Rayleigh scattering is formed (see Fig. 2.18). The measured unit in wavenumber (measured in cm^{-1}) is

proportional to the frequency and to the photon energy but it is reciprocal of the wavelength.

Figure 2.18 A schematic of the Raman scattering spectrum showing the Rayleigh line, Stokes scattering, and anti-Stokes scattering [48]. Wavenumber scales with the Rayleigh line defining the zero exhibited by Raman spectrometers are also shown.

If the energy of the scattered photon (E_s) is lower (i.e. some energy is transferred to the sample), exciting the vibration modes (E_{exc}), then Raman lines known as “Stokes scattering” will appear in the spectrum at frequencies less than that of the incident beam. If the scattered photon has a higher energy due to existing vibrations in the sample (which is excited by a thermal process), higher side bands known as “anti-stokes” scattering will appear at higher wavenumbers. These scattering events can be written as:

$$E_i \pm E_{exc} = E_s \quad (2.18)$$

The separation of these two side bands from the Rayleigh line is a direct measure of the vibrational frequencies of the sample. In fact, these two side bands are mirror images on opposite sides of the Rayleigh line. The stokes-shifted scattering light is usually measured, however, because of its much stronger intensity.

The Raman spectrum of crystals is usually composed of a pattern of relatively sharp lines. The spectrum has a high density of information and can be used as a fingerprint for the identification of unknown materials by comparing it against a reference database. Raman intensity usually decreases as the fourth power of the incident wavelength of the light source, therefore the choice of the light source could affect the Raman intensity.

For crystals with lattice defects or for other systems with structural disorders, the spectra could exhibit a pronounced line broadening in comparison with ordered structures. According to the symmetry selection rules (Raman-active phonon modes) [49], a longitudinal optical (LO) phonon was observed in the materials with a zincblende structure for (100) orientation in this thesis.

However, any appearance of the forbidden transverse optical (TO) phonon scattering could indicate symmetry changes in the lattice structure. In addition, the positive and negative shift of the Raman peaks can also provide an indication of the residual strains. These concerns are discussed in detail in Chapter 3.

Fourier transform infrared transmission spectroscopy (FTIR)

FTIR is a technique which can be used to study the infrared spectrum of absorption or the transmission characteristics of a material through the vibrations of chemical bonds. However, unlike Raman spectroscopy which studies the scattering effect, IR radiation is passed directly through the material in the FTIR setup and the final spectrum represents a molecular fingerprint of the material.

This technique uses a well-known mathematical technique (Fourier Transformation) to decode the measured signal and then presents the code in the desired spectral information. Hence, the name “Fourier Transform Infrared spectroscopy” was given to this technique. Figure 2.19 shows an example of the FTIR spectrum.

Figure 2.19 An example of an FTIR spectrum [50].

As shown in Fig. 2.19, the infrared spectra are plotted with a high wavenumber on the left and a low wavenumber on the right. This means that the spectrum is read from the left to right (from high energy to low energy). If the Y-axis is in absorbance, the upward pointing peaks represent wavenumbers at which the sample absorbed IR radiation. If the Y axis is plotted in transmittance, the peaks will point down (representing less transmitted IR radiation).

In this thesis, the optical band gap of the InSbN material at 300 K was inferred from its optical spectrum plotted against the wavelength or energy. For photon energies greater than the band gap, the material was opaque. If the photon energy was less than the band gap, then the material was transparent (no absorption).

To compute the transmission spectrum, the intensity of the light incident upon the sample can be defined as I_0 and I to be the intensity of the beam after the interaction with the sample. The transmission coefficient (T) is then defined as:

$$T = \frac{I}{I_0} = e^{-\alpha x_t} \quad (2.19)$$

where x_t is the thickness of the sample in cm and α is the absorption coefficient (typically in cm^{-1}). It is noted that the transmittance data is normalized in the transparent region. This allows us to neglect the Fresnel reflections at the semiconductor-substrate and substrate-air interfaces and the optical scattering loss. By plotting α^2 versus energy and extrapolating the linear part of the measurement to zero, the value of the band gap is obtained.

Light traversing a semiconductor is likely to decrease in intensity along the propagation direction due to the absorption process. Figure 2.20 shows the typical absorption profile in the material with a thickness of x_t .

Figure 2.20 Typical absorption profile in the semiconductor.

A larger α implies a faster decrease in light intensity and, hence, more photon absorption.

2.4 Device principles

2.4.1 Photoconductive detector

Another alternative method used to determine the band gap of the semiconductor is a photodetector device. Photodetectors absorb the optical light energy and convert it to electrical energy in the form of a photocurrent.

A photoconductor is the simplest form of a photodetector. A photoconductor consists of a bulk semiconductor material of a specific resistance attached to two metal electrodes. These metallic contacts are ohmic. Upon the illumination of incident light onto the semiconductor surface, the generated excess electrons and holes either

increase the conductivity or reduce the resistance of the sample (see Fig. 2.21). These carriers are then detected in terms of the photocurrent I_{ph} flowing out from the sample.

Figure 2.21 The geometry of a photoconductor slab illustrated with light.

The conductivity σ of the semiconductor is given by:

$$\sigma = q\mu_e n_e + q\mu_h p_h \quad (2.20)$$

where μ_h is the hole conductivity mobility and p_h is the hole concentration.

The change in the conductivity, known as photoconductivity is:

$$\Delta \sigma = q\mu_e \Delta n_e + q\mu_h \Delta p_h \quad (2.21)$$

since the electrons and the holes are generated in pairs. The photocurrent is then given by:

$$I_{ph} = \Delta \sigma E w d \quad (2.22)$$

where E is the electric field across the semiconductor, w is the width, and d is the depth of the semiconductor. Thus, the band-to-band absorption process can be detected by this photocurrent absorption spectroscopy that creates free carriers in the valence or conduction band. The lowest energy of this band-to-band transition (which is the band gap) is also known as the fundamental absorption edge.

2.4.2 Photocurrent setup

The photoconductor measurements were performed using a ceramic infrared light source. Figure 2.22 shows the spectral power distribution, P_o of the infrared source. High-pass filters of 3, 5 and 8 μm were used to prevent higher order light components from contributing to the absorption by the InSbN samples.

Figure 2.22 The spectral power distribution of the incident light source.

Subsequently, a photodetector is characterized by its photoresponsivity value,

R (A/W):

$$R = \frac{I_{ph}}{P_0} = \frac{\eta q \lambda}{hc} \quad (2.23)$$

where η is the quantum efficiency of the photodetector, λ is the radiation wavelength, h is the Planck's constant, and c is the speed of light.

Prior to passing through the high-pass filters, the light beam is passed through a chopper which generates an alternating current-like (AC) incident beam at a selected frequency. This AC incident beam is then passed through the monochromator (Triax 320) which mechanically transmits a selectable narrow band wavelength of light.

Figure 2.23 shows the simplified block diagram of the photocurrent setup used in this project. The high-pass filters were placed at the exit of the monochromator. The output photocurrent from the samples is then passed through the current amplifier with a certain gain. At a designated frequency, this signal is then extracted by the lock-in amplifier which amplifies the chosen signal of the reference frequency. The output signal from the lock-in amplifier is then forwarded to the computer for analysis in the form of a direct current.

Figure 2.23 The block diagram of the photocurrent measurement system used in this project.

Chapter 3 N-induced defects in InSbN/InSb

3.1 Effects of a high substrate temperature and a high plasma power range

3.1.1 Introduction

The growth of InSbN is challenging due to the difficulty of incorporating N into the material. In the recent InSbN growth using RF nitrogen plasma-assisted MBE, higher ranges of substrate temperatures (330 °C to 420 °C) and RF plasma power ranges (200 W to 500 W) were reported to produce a negligible improvement in the total amount of N incorporation [30]. This may suggest that InSbN would have a higher percentage of interstitials. Although these N induced defects will cause difficulties in determining the N_{Sb} composition and the corresponding band gap reduction, the details of N induced defects in the InSbN material system are still not fully reported in the literature. Since the physical property of InSbN is sensitive to the variation of the N content [21], further study on any significant structural disorder caused by N is necessary.

In this section, Raman spectroscopy and HRXRD were used to study the compositional disorder and strain in the InSbN samples grown at the higher ends of substrate temperatures (330 °C to 420 °C) and plasma power ranges (200 W to 500 W). The optical phonon modes observed in the Raman spectrum provide information

on lattice dynamics while the HRXRD data revealed the overall effect of N incorporation on the lattice strain.

3.1.2 Homoepitaxy growth of InSbN on InSb substrate

The samples discussed in this section were grown on n-type epitaxy-ready InSb (100) substrates. A 0.3 μm InSb buffer layer was grown at the substrate temperature of 420 $^{\circ}\text{C}$ prior to the growth of the InSbN epitaxy layer as shown in Fig. 3.1 below. Further information on the growth procedures on the InSb substrates is discussed on section 2.23. The thickness of the InSbN layer was verified by a surface profile measurement. The average growth rate for all the samples was about 0.6 $\mu\text{m/hr}$. The V:III flux ratio was kept approximately at 2:1.

Two InSbN samples were grown at the same substrate temperature of 420 $^{\circ}\text{C}$. One of these samples was grown with an RF power of 200 W while the second was grown at an RF power of 500 W. In addition, another two InSbN samples were grown at two different substrate temperatures (380 $^{\circ}\text{C}$ and 330 $^{\circ}\text{C}$) and at a fixed RF power of 200 W. The nitride layer thickness in the first three samples was $\sim 0.6 \mu\text{m}$ while the fourth sample (the one grown at 330 $^{\circ}\text{C}$) had a thickness of 40 nm. This was due to its partially relaxed condition which is observed by RHEED [30]. Finally, an additional fifth sample, which consisted of the homoepitaxial InSb layer grown on InSb substrate at 420 $^{\circ}\text{C}$, was used as a reference.

Figure 3.1 Structure of the nitride sample on the InSb substrate.

3.1.3 Characteristics from Raman scattering

The micron-Raman measurement was carried out at room temperature using the 514.5 nm line of an Argon (Ar) ion laser. The scattered light or backscattering was dispersed along the [001] direction through a JY-T64000 triple monochromator system attached to a liquid nitrogen cooled charge-coupled device (CCD) detector.

The Raman spectra were acquired in the backscattered (z(x,x)-z) configuration (the Porto notation). The four symbols in this notation represent the following measurements: (a) the first symbol is the direction of the input laser beam, (b) the second symbol is the polarization direction of the laser, (c) the third symbol is the polarization direction of the scattered beam; and (d) the last symbol is the direction of the scattered beam. This configuration permits scattering only by longitudinal optical (LO) phonons in (001) oriented InSb. The laser excitation power was held

below 2mW to avoid the thermal redshift of optical phonons. For crystalline InSb, the penetration depth ($\sim 1/\alpha$) is about 18 nm which allowed us to profile the nitride layers with negligible interference from the buffer layer and the substrate [51].

Figure 3.2 shows the Raman scattering spectra of the InSb reference sample. The well-defined first order LO phonon peak (190 cm^{-1}) with the second order 2LO peak (380 cm^{-1}) and the very weak TO phonon scattering in the InSb reference sample indicate the high crystalline quality of the InSb epitaxy layer.

Figure 3.2 The room temperature Raman spectra of the InSb reference sample.

Figure 3.3 shows the Raman scattering of the four InSbN samples. As N was introduced, the LO peak intensity in the InSbN samples reduced with respect to the corresponding TO peak. This indicated the presence of a structural disorder in the InSbN material. In addition, the appearance of the forbidden TO peaks at 180 cm^{-1} indicated a relaxation of the symmetry selection rules. This relaxation can be attributed to changes in the local lattice structure due to the incorporation of N.

Figure 3.3 The room temperature Raman spectra of the four InSbN alloy samples with varying substrate temperatures (330 °C to 420 °C) and RF plasma power ranges (200 W to 500 W).

The vibrational phonon properties of the InSbN samples grown at 420 °C, 380 °C, and 330 °C under the same RF power (200 W) were first compared. An intense peak at 145 cm⁻¹ was observed in the spectra for the samples grown at 420 °C and 380 °C, which was not seen in the InSb reference sample. This energy peak was attributed to the A_{1g} phonon mode of Sb which suggests a possible deformation along the crystal axis [52, 53].

This elemental A_{1g}Sb mode could be due to the effects of random Sb clustering (segregation) or to Sb antisite (Sb-Sb) defects. Since the A_{1g}Sb peak exhibited a symmetrical lineshape and a relatively high intensity compared to the InSb phonon peak, this suggests that the Sb phase has a good crystallinity. Hence, Sb antisite defects are more likely to be the reason for the appearance of the A_{1g}Sb mode. Another broad-band range between 240 to 285 cm⁻¹ was also observed and was attributed to second order scattering by the Sb optical phonon modes [54]. As the substrate temperature was reduced to 330 °C, the intensity of the A_{1g}Sb peak dropped significantly. Furthermore, the A_{1g}Sb peak for the sample grown at 330 °C was blue-shifted by 5 cm⁻¹. This positive frequency shift of the A_{1g}Sb mode of Sb reveals a compression strain [55] as compared to other samples.

The Raman spectra of the samples grown at 420 °C with different RF power ranges of 200 W and 500 W were then compared in order to study the effect of RF plasma power (see Fig. 3.3). Increasing the RF plasma power was observed to exhibit an effect similar to the effect produced by reducing the substrate temperature. The integrated intensity of the $A_{1g}Sb$ elemental peak for the sample grown at the higher RF power of 500 W was lower compared to the sample grown at the lower RF plasma power of 200 W.

Exhibiting a similar spectrum to the sample grown at 330 °C, the $A_{1g}Sb$ peak of the sample grown at 420 °C with a RF power of 500 W was blueshifted and the second order Sb phonon mode was not observed. We concluded that the Sb antisite defects were reduced at a high plasma power and a high substrate temperature (500 W and 420 °C) or at a low plasma power and a low substrate temperature (200 W and 330 °C).

Figure 3.4 The Raman spectra comparing the TO and LO phonon modes of the samples grown at a fixed 200 W with the different substrate temperatures of 330 to 420 °C. A redshift of the LO phonon line was observed along with a blueshift of the TO phonon line as the substrate temperature was reduced from 420 to 330 °C.

As shown in Fig. 3.4, the spectral region of the TO and LO InSb phonon modes for the InSbN samples grown at 420 °C, 380 °C, and 330 °C with the same RF power of 200 W were enlarged to study the effects of the in-plane strain from the N incorporation. The Raman shifts were investigated by curve fitting using multi-Lorentzian peak deconvolution. It was observed that modification of the phonon lineshape was due to an N induced lattice disorder.

The degree of lattice disorder was evaluated based on the relative intensity of the TO phonon mode with respect to the relative intensity of the LO phonon mode (i.e. $I_{\text{TO}}/I_{\text{LO}}$), and the frequency shift of the TO and LO lines. First, it was observed that the $I_{\text{TO}}/I_{\text{LO}}$ intensity increased as the substrate temperature was reduced from 420 °C to 330 °C. This increase indicated that the crystalline quality degraded at a lower substrate temperature.

Second, there was a redshift of 1 cm^{-1} in the LO line and a blueshift of 1 cm^{-1} in the TO line of the sample grown at 330 °C compared to the samples grown at 420 °C and 380 °C. This redshift or tensile strain of the LO line frequency was a result of a shortening of correlation length (L), which corresponds to the presence of an increased disorder by the higher amount of N incorporation [56]. According to the spatial correlation model, the first order Raman intensity $I(\omega)$ can be expressed as:

$$I(\omega) = \int_0^L \exp\left(\frac{-q_0^2 L^2}{4}\right) \frac{d^3 q}{[\omega - \omega(q_0)]^2 + (\Gamma_0/2)^2} \quad (3.1)$$

where q_0 is in the unit of $2\pi/a$, a is the lattice constant, d is the distance between the two different atoms, and Γ_0 ($\sim 3 \text{ cm}^{-1}$) is the line width (full width at half maximum) of LO peak. Based on the one-dimensional linear chain model, the dispersion $\omega(q_0)$ is expressed as:

$$\omega^2(q_0) = A_1 + \{A_1^2 - B_1[1 - \cos(\pi q_0)]\}^{\frac{1}{2}} \quad (3.2)$$

where $A_1 = \beta(m + M)/(mM)$, $B_1 = (4\beta^2)/(mM)$, $\beta = dC_{11}$, and M and m are the masses of the two different atoms.

The frequency change of the TO line was likely caused by lattice contraction [57]. In close relation to the I_{TO}/I_{LO} intensity, the frequency shift of the LO and TO lines of the sample grown at 330 °C indicated a higher degree of lattice distortion compared to the other samples, which is due to a higher N incorporation at the lower substrate temperature of 330 °C.

Figure 3.5 clearly illustrates that the I_{TO}/I_{LO} ratio decreased with an increasing growth temperature and plasma power.

Figure 3.5 Comparison of the TO/LO phonon intensity ratio.

3.1.4 Characteristics from X-ray diffraction

HRXRD (004) diffraction was used to further investigate the effect of different growth conditions on the lattice strain as shown in Fig. 3.6. The strain properties of the InSbN layers were evaluated from a $2\theta/\omega$ reflection obtained from (004) atomic plane diffraction. Compressive strain was observed for the samples that were grown at substrate temperatures and at RF plasma power ranges of 380 °C/200 W, 420 °C/200 W, and 420 °C/500 W while tensile strain was only observed in the sample grown at 330 °C/200 W. The broad peak observed at 57.3° is part of the Pendellosung fringes which indicates a high epitaxial film quality.

Figure 3.6 A graph of the XRD diffraction for the samples grown at different substrate temperatures (330 °C to 420 °C) and at different RF plasma power ranges (200 W to 500 W).

This compressive strain indicated that the sample grown at a lower substrate temperature of 330 °C had the highest N_{Sb} . Thus, Eq. (2.9) can be rewritten in the form of relaxed lattice mismatch:

$$\frac{\Delta a}{a} = \frac{a_f - a_s}{a_s} = \left(\frac{C-1}{C}\right)\left(\frac{a_{f\parallel} - a_s}{a_s}\right) + \frac{1}{C}\left(\frac{a_{f\perp} - a_s}{a_s}\right) \quad (3.3)$$

From (3.3), most of the N substitute Sb, $a_{f\perp} < a_s$ and the lattice mismatch was negative as in the sample grown at 330 °C. However, to cause $a_{f\perp} > a_s$ or a positive mismatch (> 800 ppm), it was necessary to consider the effects of interstitials. Based on a lattice mismatch model [30], we propose that interstitial Sb-N defects dominate at high substrate temperatures and plasma power ranges.

We note that only the elemental Sb mode was present in the Raman spectrum. Therefore, we should first consider the possible effect of the Sb-Sb bond on the lattice strain measured by XRD. As discussed earlier, the $A_{1g}\text{Sb}$ elemental peak observed in our samples was due to the Sb antisite defects. Since the atomic size of Sb and In atoms are comparable, the replacement of In by Sb atom, i.e Sb-Sb, would have negligible effect on the lattice strain. Therefore, these interstitial Sb-N defects could have contributed to the lattice compressive strain in the samples grown at 420 °C/200 W, 420 °C/500 W, and 380 °C/200 W while the tensile strain in the sample grown at 330 °C/200 W was mainly due to N_{Sb} . The In-N and Sb-N modes are not easily detected due to their lack of resonance with existing Raman excitation lines.

The use of a 325 nm UV line [58] to improve the scattering intensity also did not reveal any associated In-N vibrational modes in our samples, which may be due to the highly disordered nature of the materials. In fact, Haworth *et al.* [53] reported the existence of elemental Sb and Sb-N modes in the process of InSb nitridation. Therefore, the compressive strain observed in the XRD measurements for the samples grown at 420 °C with RF powers of 200 W and 500 W and for the sample grown at 380 °C/200 W must be due to the existence of another defect, the interstitial Sb-N.

Figure 3.7 includes the comparison of the integrated A_{1g} Sb intensity obtained from the Raman measurements with the lattice mismatch of the InSbN/InSb measured by XRD.

Figure 3.7 The comparison of the integrated intensity of A_{1g} Sb, and the lattice mismatch of the four nitride samples.

As the substrate temperature and the RF plasma power was increased in the samples grown at 380 °C/200 W, 420 °C/200 W and 420 °C/500 W, the lattice mismatch extracted from the XRD increased in positive value due to an increase in the interstitial Sb-N defects. Higher contents of Sb-N defects reduced the tensile strain in InSbN caused by N_{Sb} .

On the other hand, when the substrate temperature was increased and the RF plasma power was reduced for the two samples grown at 420 °C (which had a RF power of 500 W and 200 W, respectively), the intensity of $A_{1g}Sb$ increased. This intensity increase indicates an increase in Sb antisite defects. However, Sb antisite defects were not found in our InSb reference sample, which was grown under the same substrate temperature and fluxes as the four nitride samples.

3.1.5 Mechanisms for defect formation

To explain the co-existence of Sb antisites with Sb-N defects and their dependence on the substrate temperature and the RF plasma power, a competitive process of anion exchange between Sb and N is proposed. Reactions (3.4) and (3.5) for the MBE growth of $InSb_{1-x}N_x$ are described below. During the growth, In atoms will bond with either Sb or N atoms. In this section, x is the proportion of the In bond with N or Sb.

To produce Sb-Sb and Sb-N products, other concurrent mechanisms similar to the nitridation process (N ion implantation) are suggested:

where y is the proportion of Sb exchanging with N. This anion exchange reaction (3.6) is favoured as the substrate temperature is increased under a fixed plasma power where the bonding between In and Sb becomes more volatile. Dependent on the available Sb-In fluxes, the amount of generated reactive Sb atoms could then lead to the competitive formation of Sb-Sb and Sb-N through the reactions described in (3.7) or (3.8):

where z is the proportion of Sb bonding with N. The reactions described in (3.7) and (3.8) resulted in a high intensity of the $A_{1g}Sb$ peak and in compressive strain for the samples grown at the high substrate temperatures of 420 °C and 380 °C and at a fixed plasma power of 200 W. An increase in the plasma power from 200W to 500W at 420 °C yielded more Sb-N bonds due to the presence of excess N (as shown in the reaction expressed in (3.8)). As a result, this reaction pathway reduces the amount of reactive Sb that is available to form Sb-Sb bonds in the reaction described in (3.7). This explains why the sample grown at 420 °C/500 W had a significantly lower

$A_{1g}\text{Sb}$ intensity and a larger compressive strain compared to the sample grown at 420 °C/200 W.

3.1.6 Summary

In summary, we studied the first-order Raman scattering results and correlated these results with the HRXRD results for InSbN grown by MBE at different substrate temperatures (330 °C to 420 °C) and at different RF plasma power ranges (200 W to 500 W).

Both Sb antisite and Sb-N defects were present in the InSbN samples and were found to be dependent on the growth conditions. Reactive Sb, a product from the nitridation process, could contribute to the formation of Sb related defects. At a low plasma power of 200 W, Sb antisite and Sb-N defects increased as the substrate temperature increased from 330 to 420 °C due to the excessive reactive Sb generated at the higher temperature.

On the other hand, at a high substrate temperature of 420 °C, increasing the RF plasma power to 500 W yielded more N to form Sb-N defects and reduced the reactive Sb available to form Sb-Sb. These observations indicate that a low substrate temperature and a RF power of 330 °C/200 W reduce both Sb antisite and Sb-N defects.

3.2 Effect of a low substrate temperature and a low plasma power range

3.2.1 Introduction

In the previous section, the substrate or growth temperature from ~ 330 to 420°C showed that most of the N is incorporated as interstitial N-Sb at the high temperature of 380 to 420°C and as N_{Sb} at the low temperature regime ($\sim 330^\circ\text{C}$). However, a recent report from Jefferson et al. [29], which studied the growth temperature from 330 to 340°C , indicated the presence of only N_{Sb} at the low temperature of 330°C . also In addition, Bi and Tu [59] reported that reduced growth temperatures improve the N incorporation in GaAsN. Hence, the sensitivity of the N incorporation in InSbN at the lower temperature needs to be verified.

In this section, the study of N incorporation in InSbN grown at the nominal low substrate temperatures of 270 to 330°C and at the RF plasma power ranges of 150 to 180 W is carried out. As the XRD or SIMS analysis alone could not independently determine an accurate amount of N_{Sb} , a combination of the characterization tools of XRD, SIMS and NRA were used to investigate the concentration of N_{Sb} and the possible interstitials in InSbN.

3.2.2 The sample preparation of InSbN

All our samples were grown on n-type epitaxial-ready InSb (001) substrates. The average growth rate for all the samples was $0.6\text{ }\mu\text{m/h}$ and the V: III flux ratio used was approximately $2:1$. A $\sim 150\text{ nm}$ thick InSbN layer was grown on a $0.3\text{ }\mu\text{m}$ thick

InSb buffer layer. The nitrogen flow rate was kept at 0.26 SCCM with a low background pressure of pressure of 5×10^{-6} to 2×10^{-5} Torr. The growth temperature was varied from 270 to 330 °C and the plasma power from 150 to 180 W. All the samples exhibited a streaky RHEED pattern during growth.

3.2.3 Incorporation of N from X-ray diffraction

XRD $2\theta/\omega$ scans in the symmetrical (004) Bragg reflection (as shown in Fig. 3.8) determined the strain of the InSbN epilayer in the growth direction $(\Delta a/a)_{\perp}$ which is perpendicular to the substrate surface. All the samples grown were under tensile strain and this strain increased significantly as the growth temperature was reduced. In addition, the Pendellosung fringes clearly observed in the $2\theta/\omega$ scans indicated a high epitaxial film quality.

Figure 3.8 XRD $2\theta/\omega$ scans in the (004) reflection.

Figure 3.9 shows the results of the two samples grown at 270 °C/150 W and at 270 °C/180 W using asymmetric (115) XRD space mapping (two-dimensional reciprocal). This measurement, which determines the strain in the parallel direction ($\Delta a/a$), was performed in line-focus mode with a Ge (220) analyzer in front of the detector.

Figure 3.9 The asymmetric (115) space mappings of the two samples grown at 270 °C with the different plasma power ranges of (a) 150 W and (b) 180 W.

As shown in Fig. 3.9, Q_x and Q_y in the axes are the coordinates in the reciprocal lattice units which can derive the $a_{f\perp}$ and $a_{f\parallel}$ through the following expressions [60]:

$$Q_x = \frac{\sqrt{h^2 + k^2}}{a_{f\parallel}} \quad (3.9)$$

$$Q_y = \frac{l}{a_{f\perp}} \quad (3.10)$$

Fig. 3.9 shows that the substrate peak and the InSbN layer peak lie approximately on a straight line with the same Q_x . This straight line indicates that the InSbN layers grown at the different plasma power ranges of 150 W and 180 W were strained with negligible lattice relaxation (i.e. $a_{f\parallel} \approx a_s$). Assuming that all of the N atoms in the samples incorporated on Sb sites, the N_{Sb} content ($[N_{\text{Sb}}]$) can be calculated from the lattice mismatch using Vegard's law in (2.10).

3.2.4 Secondary ion mass spectroscopy and nuclear reaction analysis

As shown in Table 3.1, the highest $[N_{sb}]$ was observed at the lowest growth temperature and the lowest plasma power range. On the other hand, as the plasma power was increased from 150 to 180 W, a lower $[N_{sb}]$ was indicated. Next, the total N content ($[\Sigma N]$) in the InSbN measured by SIMS and NRA is also shown in Table 3.1 below. At the fixed growth temperature of 270 °C, the SIMS data indicated that the total N concentration as the plasma power increased.

Table 3.1 The comparison of the N composition in the samples at different growth conditions.

Growth conditions	XRD relaxed mismatch (ppm)	N composition by XRD	Total N by SIMS (cm ⁻³)	Total N by NRA (cm ⁻³)
270°C/180W	768	~0.35%	~4.5 X 10 ²⁰	~4.7 X 10 ²⁰
270°C/150W	3197	~1.35%	~3.1 X 10 ²⁰	~4.7 X 10 ²⁰
300°C/150W	1450	~0.61%	~3.1 X 10 ²⁰	~4.3 X 10 ²⁰
380°C/150W	165	~0.08%	~2.8 X 10 ²⁰	~3.1 X 10 ²⁰

Figure 3.10 The SIMS profile of the samples grown at 270 °C with different plasma power ranges of 150 W and 180 W.

The N concentration profile of the samples grown at 270 °C with plasma power of 150 W and 180 W from the SIMS is shown in Fig. 3.10.

For the broad-beam NRA measurement, the deuteron beam energy of 0.920 MeV by quadrupole focusing of the beam from a 3 MV Van de Graff accelerator was used. The NRA signals related to the N nuclear reaction were calibrated with an N standard (350 nm Si₃N₄ layer on (100) Si) produced by chemical vapour deposition. The disparity between the SIMS and the NRA data observed in Table 3.1 was likely due to the difference in the standard materials used.

As shown in Fig. 3.11, the ratio of the N_{Sb} content measured by XRD to the total N content by SIMS or NRA, $[N_{Sb}]/[\sum N]$, was always smaller than 1, indicating the presence of non-substitutional or interstitial N. It was noted that XRD determined the lattice spacing and not directly the N content of the InSbN alloys since the XRD calculations require assumptions on the lattice parameters and the elastic constants with N composition. The use of Vegard's law was assumed to be justified.

This ratio reduced significantly as the growth temperature was increased from 270 to 330 °C or as the plasma power was increased from 150 to 180 W.

Figure 3.11 The comparison of the ratio of the N content by XRD over the N content measured by SIMS and NRA.

To examine the effect of the growth conditions on the ratio of interstitial N and N_{Sb} concentrations, the law of mass action [61] was applied to the interchange reaction between N_{Sb} and the interstitial site (N_{int}), $N_{Sb} \leftrightarrow N_{int}$:

$$\frac{[N_{int}]}{[N_{Sb}]} \propto e^{-\Delta E / kT} \quad (3.11)$$

where k is the Boltzmann constant, T is the growth temperature, and ΔE is the change in the free energy of the reaction. From Eq. (3.11), $[N_{int}]/[N_{Sb}]$ will decrease if the growth temperature of the samples is reduced. This decrease is in agreement with the above experimental results (330 °C to 270 °C).

We also noted that a high ratio of $[N_{int}]/[N_{Sb}]$, which induces lattice dilation, occurred in the InSbN grown at the high substrate temperatures (380 °C to 420 °C) in section 3.1. However, the increase in plasma power to 180 W at 270 °C reduced $[N_{Sb}]$. This result suggests a reduction in ΔE that increased the concentration of interstitials. Another likely possibility is that the higher plasma generated at the selected flow rate produced a higher concentration of energetic N ions [62]. To study the possible interstitial N, NRA channelling in (001) direction on the sample grown at 270 °C/180 W was performed.

Figure 3.12 The comparison of the NRA products as a function of energy between the InSbN sample grown at 270 °C/180 W and the reference InSb substrate sample.

Figure 3.12 shows the NRA spectrum of the InSb substrate as a reference and the InSbN sample grown at 270 °C/180 W. A series of nuclear reaction products are visible in the spectrum where the higher energies in the vertical x-axis scale correspond to a smaller depth below the surface. As observed, the reference InSb sample was free of N reaction products. From the spectrum of the InSbN sample, the preferred choice of the reaction product to be used for the N analysis is $^{14}\text{N}(\text{d},\text{p}_5)^{15}\text{N}$ which has the highest yield.

Figure 3.13 The NRA yields for a random direction and aligned to [100] from the InSbN epilayer grown at 270 °C/180 W.

Figure 3.13 illustrates the nuclear reaction yield obtained for a random direction and aligned to [100] (surface normal) from the InSbN sample grown at 270 °C/180 W. Negligible differences in the NRA yield of random and [100] channelling directions suggested that close to 100% of N in the InSbN sample ($\sim 4.7 \times 10^{20} \text{ cm}^{-3}$) sat at interstitial sites.

Next, we considered the effect of interstitial N-related defects such as N-Sb and N-N on the lattice strain as follows:

$$\frac{\Delta a}{a} = \left(\frac{C_{11} - 2C_{12}}{C_{11}} \right) \frac{1}{d_0 [N_0]} \left([N_{Sb}] (d_{N_{Sb}} - d_0) + [N_{int}] (d_{N_{int}} - d_0) \right), \quad (3.12)$$

where $d_{N_{Sb}} = r_{In} + r_N$ ($d_{N_{Sb}} = 2.19 \text{ \AA}$) and where r_{In} and r_N are the radii of the In and N atoms, respectively. $d_0 = r_{In} + r_{Sb}$ ($d_0 = 2.82 \text{ \AA}$) where r_{Sb} is the radius of the Sb atoms and $d_{N_{int}}$ is the nearest distance from the interstitial to the In atom. $[N_{Sb}] + [N_{int}] = [\Sigma N]$ where $[\Sigma N]$ is measured by SIMS and NRA. $[N_0]$ is the concentration of the matrix atoms.

Since only a large amount of interstitial isolated N ($>10^{21} \text{ cm}^{-3}$) can affect the lattice strain [63], its presence can be neglected. The distance $d_{N_{int}}$ for interstitial N-N and N-Sb splitting in the [100], [110], [111] directions was obtained as $d_{N_{int}} = 2.53, 2.76, 2.94, 2.96, 3.30, \text{ and } 3.52 \text{ \AA}$, respectively [30]. Since tensile strain was observed from the XRD measurements, only split interstitial N-N in the [100] and [110] directions, which have $d_{N_{int}} < d_0$, were considered. As the split interstitial N-N in the [100] direction could have been shadowed in the channelling direction used [64], the interstitial defects detected by NRA channelling were most likely split interstitial N-N in the [110] direction.

In addition, according to Eq. (3.12) and $[\Sigma N]$, the ratio of $[N_{int}]/[N_{sb}]$ was found to be more than two orders of magnitude, which suggested a negligible amount of N_{sb} . Since $d_{N_{int}} > d_{N_{sb}}$, the sample with the plasma power of 180 W could have caused a reduced lattice contraction compared to the lower power of 150 W which had a higher N_{sb} . These results indicated that the split interstitial N-N defects could have introduced an overestimation of the N_{sb} from the XRD analysis and that increasing the plasma power increases the content of interstitial N-N.

3.2.5 Summary

In summary, a combination of HRXRD, SIMS, and NRA was used to study the N incorporation in InSbN materials grown at a very low temperature (270 °C to 330 °C) and at a RF plasma power of 150 W and 180 W.

Reducing the growth temperature produced a higher ratio of N_{sb} content over the undesired interstitial N. As observed from the XRD, the amount of N_{sb} increased as the growth temperature was lowered to 270 °C. However, increasing the plasma power could have possibly resulted in an increase in interstitial N, which was most likely [110] N-N, and increasing the plasma power also reduced the N_{sb} . In addition, a large amount of interstitial N-N could have induced lattice contraction, which leads to an overestimation of N_{sb} .

Chapter 4 Properties of as-grown InSbN on GaAs substrate

4.1 Introduction

InSbN-based photodetectors on highly conductive InSb substrates are likely to complicate optical measurements due to the effects of their low signal-to-noise ratio. In addition, these InSbN photodetectors are likely to complicate electrical measurements due to the effects of their parallel conduction. Therefore, InSbN film must be grown on wide band-gap semi-insulating (SI) substrates such as GaAs in order to explore their suitability for the practical integration of devices.

Since not much information is available on the heteroepitaxial growth of InSbN using RF MBE, further studies are needed to investigate this system. There are two challenging issues in the growth of InSbN on a GaAs substrate. First, threading dislocation defects arising from the lattice mismatch between the InSbN epilayer and the GaAs substrate may affect the optical and electrical properties of the InSbN epilayer. Thus, optimized growth conditions for InSbN on a GaAs substrate are needed.

Second, regardless of the lattice mismatch between the InSb and the GaAs materials, point defects due to N incorporation [65, 66] can introduce high background carrier concentration. This high density of carrier concentration could cause the optical absorption spectra of the InSbN to shift undesirably to a shorter wavelength range.

Hence, the dependence of the physical properties of heteroepitaxial InSbN/GaAs from the growth conditions is studied in this chapter. Prior to the growth of InSbN, a two-step thin InSb buffer growth process was applied. This strategy of including thin InSb buffer layers was essential to restrict the high density of dislocation at the interface and to improve the subsequent growth of the top InSbN epilayer.

XRD, TEM, the Hall effect, and FTIR measurements were used to study the structural, electrical, and optical properties of the InSbN epilayer.

4.2 Heteroepitaxial growth of InSbN/GaAs

The InSbN samples were grown on a (001) GaAs substrate. The average growth rate was 0.6 $\mu\text{m/h}$ and the Sb/In flux ratio was kept at 1.7. Further information on the growth procedures on GaAs substrates is discussed on section 2.23 on page 37. The nitrogen flow rate was kept at 0.26 SCCM and the RF plasma power was fixed at 150 W.

A 30 nm InSb buffer layer was first grown at a low temperature (LT) of 330 °C to allow the In atoms and the Sb atoms to migrate slowly on the GaAs substrate surface in order to form a good nucleation layer. This thin LT InSb buffer layer was essential to restrict the buildup of dislocations at the InSbN/GaAs interface. Next, a 300 nm InSbN layer was grown directly on the LT InSb buffer layer. The nominal substrate temperatures for the InSbN layers were kept at 270 °C, 300 °C, and 380 °C in the three separate samples.

These thin InSbN samples were used for XRD measurement as shown in Table 4.1. A 300 nm InSb layer grown at 380 °C on LT InSb/GaAs was then created for reference. On the other hand, three samples of a 2 µm thick InSbN epilayers grown at 270 °C, 300 °C, and 380 °C were also grown for the Hall effect and FTIR measurements. However, prior to the growth of these thicker InSbN layers, additional 300 nm InSb buffer layers grown at high temperatures (HT) of 380 °C on top of each LT InSb buffer layer were required. These additional layers acted as virtual substrates for the subsequent nitride epilayer. Finally, another sample of a 2 µm thick InSb epilayer was grown at 380 °C on the 300 nm thin InSb epilayer on the LT InSb/GaAs substrate for reference.

Table 4.1 The different layer structures under growth conditions for various measurement methods.

Growth conditions	Layer structure on GaAs substrate	Experimental Methods
270°C	300nm InSbN/LT InSb	XRD
300°C	300nm InSbN/LT InSb	XRD
380°C	300nm InSbN/LT InSb	XRD
270°C	2µm InSbN/HT InSb/LT InSb	Hall and FTIR
300°C	2µm InSbN/HT InSb/LT InSb	Hall and FTIR
380°C	2µm InSbN/HT InSb/LT InSb	Hall and FTIR

4.3 Effect of the two-step InSb buffer layers

Figure 4.1 shows the XRD (004) diffraction of the 300 nm-thick InSbN epilayers grown on the 30-nm LT InSb buffers. The shifting of the InSbN peaks compared to the InSb reference in the XRD spectra indicated the effects of N incorporation. The sample grown at 380 °C exhibited a compressive strain of ~165 ppm, which was likely due to interstitial defects such as N-Sb (as studied in Chapter 3). On the other hand, the sample grown at 270 °C exhibited a tensile strain of ~430 ppm due to a possible increase in N_{Sb} .

Figure 4.1 The XRD diffraction of the InSbN/LT InSb samples grown at the different substrate temperatures of 270 to 380 °C and of the reference InSb sample.

Furthermore, the XRD full-width at half-maximum (FWHM) was observed to increase as the substrate temperature decreased. This indicated that the increase in the incorporation of N_{Sb} at a lower substrate temperature could deteriorate the crystalline quality of the layer. We noted that InSbN grown at 270 °C had a FWHM of ~510 arcsec.

However, the crystallinity of the InSbN epilayer was observed to improve significantly with the insertion of an intermediate 300-nm HT InSb buffer layer grown at 380 °C between the 30-nm LT InSb buffer layer and the InSbN epilayer. Figure 4.2 shows the XRD spectrum of the InSbN samples grown at 270 °C and 300 °C with the two-step 300 nm HT InSb/LT InSb buffer layer.

Figure 4.2 The XRD spectrum of the InSbN/HT InSb/LT InSb/GaAs samples grown at 270 °C and 300 °C.

Figure 4.2 shows that the XRD peaks of the InSb buffer layer and the InSbN epilayer grown at 270 °C are clearly resolved which gives an estimation of $\sim 1\%$ N_{Sb} . The InSbN sample grown at the higher temperature of 300 °C had a lower N_{Sb} content of $\sim 0.25\%$. In addition, the InSbN peak at 270 °C had a smaller FWHM of ~ 300 arcsec. The total N content for all of the samples according to the SIMS measurement was $\sim 3 \times 10^{20} \text{ cm}^{-3}$ which corresponded to a 2% N incorporation and indicated the presence of non-substitutional nitrogen or defects.

4.4 Results from transmission electron microscopy

The structural effects of the two-step growth process were further studied using the cross-sectional bright-field image by TEM shown in Fig. 4.3.

Figure 4.3 The TEM images of (a) InSbN/LTInSb/GaAs and (b) InSbN/HTInSb/LTInSb/GaAs heterostructures.

In Fig. 4.3 (a), the serial stripes observed from the InSbN epilayer grown only on the LT InSb buffer indicated misfit dislocations generated from the ~14% lattice mismatch between the substrate and epilayer. These defects were not as pronounced in the InSbN layer grown with the addition of the HT InSb buffer as shown in Fig. 4.3 (b). Furthermore, the sharp interface observed between the InSbN epilayer and HT InSb buffer layer indicated that the HT intermediate layer acted as a virtual substrate for the above nitride layer.

4.5 Carrier concentration and mobility measurements

The electrical properties of the 2 μm InSbN epilayer and the reference 2 μm InSb epilayer grown on the two-step InSb buffer layer were characterized by the Hall effect measurement at room temperature (RT) and at 77 K as shown in Table 4.2.

Table 4.2 RT and 77 K Hall measurements of the reference InSb sample and the InSbN samples grown at different temperatures from 270 °C to 380 °C.

Growth Conditions	RT Hall mobility (cm ² /V.s)	77 K Hall mobility (cm ² /V.s)	RT Hall concentration (cm ⁻³)	77K Hall concentration (cm ⁻³)
270°C InSbN	399	962	$\sim 1.8 \times 10^{18}$	$\sim 9.0 \times 10^{18}$
300°C InSbN	1140	1130	$\sim 7.8 \times 10^{17}$	$\sim 4.9 \times 10^{18}$
380°C InSbN	2140	1880	$\sim 9.0 \times 10^{16}$	$\sim 1.1 \times 10^{17}$
380°C InSb	57900	800	$\sim 2.2 \times 10^{16}$	$\sim 1.6 \times 10^{16}$

At RT, the InSb/GaAs reference sample yielded high electron mobility and near intrinsic electron concentration. These results were consistent with the values reported for other high quality 2- μm -thick InSb/GaAs films grown by MBE [41, 42]. As the substrate temperature decreased from 380 to 270 $^{\circ}\text{C}$, the electron mobilities of the InSbN samples were observed to reduce from ~ 2000 to $400 \text{ cm}^2/\text{V.s}$ whereas the electron concentration of the samples increased from $\sim 9.0 \times 10^{16}$ to $1.8 \times 10^{18} \text{ cm}^{-3}$. Defect complexes introduced after the N incorporation at a lower substrate temperature may contribute to the additional source of free carriers in the InSbN layer [67].

The electron mobility of the InSbN and InSb epilayers on the GaAs substrate could have been influenced by the effects of various scattering mechanisms as expressed by Matthiessen's rule:

$$\frac{1}{\mu^j} = \frac{1}{\mu_a^j} + \frac{1}{\mu_l^j} + \frac{1}{\mu_i^j} + \frac{1}{\mu_d^j} \quad (4.1)$$

where μ^j is the total mobility and j denotes the InSb or InSbN layers. $\mu_a^j, \mu_l^j, \mu_i^j, \mu_d^j$ is mobility limited by alloy scattering, lattice scattering, ionized impurities, and dislocation defects due to heteroepitaxy, respectively. μ_a^j is dependent on the N composition [68]. μ_l^j is dominant at RT, while μ_i^j and μ_d^j are dominant at 77 K [69]. It is worth noting that lattice scattering will not dominate at RT if defect scattering is very high.

At RT, the electron mobility in the InSbN epilayer ($\sim 2000 \text{ cm}^2/\text{V.s}$) was significantly lower than the electron mobility of the InSb epilayer ($\sim 5.8 \times 10^4 \text{ cm}^2/\text{V.s}$) and it decreased with the substrate temperature. The decrease in mobility was attributed to an increase in alloy scattering with increasing N_{Sb} incorporation which was significant especially for the sample grown at 270°C . Therefore a very low RT electron mobility was observed. In addition, the increase in the electron effective mass as the N_{Sb} concentration increased may have also limited the carrier mobility in the InSbN epilayer. It was noted that the electron mobility of the InSb epilayer was ~ 19400 , ~ 49500 and $\sim 54600 \text{ cm}^2/\text{V.s}$ with InSb thickness at 300 nm , $1 \mu\text{m}$ and $1.4 \mu\text{m}$, respectively.

While the RT mobility was limited by lattice and by alloy scattering, it could have been constrained by ionized impurity and dislocation defects at 77 K . At 77 K , the mobility of the reference $2 \mu\text{m}$ thick InSb/GaAs dropped significantly to $800 \text{ cm}^2/\text{V.s}$ with an electron concentration of $\sim 2 \times 10^{16} \text{ cm}^{-3}$ [70]. In addition, it was also noted that the 77 K mobility reduced to $\sim 600 \text{ cm}^2/\text{V.s}$ with a 300 nm thick InSb epilayer. Such observation indicated the strong effects of threading dislocations at the InSb/GaAs interface. The low 77 K electron mobility in all the nitrides samples indicate that ionized impurity scattering dominated the InSbN epilayers. Therefore, we concluded that μ_a^{InSbN} and μ_i^{InSbN} dominated over μ_d^{InSbN} because μ^{InSbN} reduced following an increase in N_{Sb} and in carrier concentration. In addition since $1/\mu^{\text{InSbN}} < 1/\mu^{\text{InSb}}$ and $1/\mu_i^{\text{InSbN}} > 1/\mu_i^{\text{InSb}}$, from (4.1) we obtained $1/\mu_d^{\text{InSbN}} < 1/\mu_d^{\text{InSb}}$. This

agrees well with the TEM observation in Fig. 4.3, where strong defect clusters or dislocations were visible only in the InSb buffer layer.

4.6 Fourier transform infrared studies

Figure 4.4 compares the FTIR transmission spectrum of the 2 μm thick InSbN and InSb reference samples grown on the two-step HT InSb/LT InSb buffer layer.

Figure 4.4 RT transmission spectrum of the InSb reference and InSbN samples grown at different temperatures.

The InSbN sample grown at 380 °C had a cut-off wavelength at ~8 μm which was equivalent to the absorption edge energy of ~0.16 eV. As the substrate temperature reduced to 270 °C, the cut-off wavelength was blue-shifted to ~4.8 μm (0.26 eV) despite having a higher content of N_{Sb}. This blueshift in energy (which was higher than the reference InSb) was due to the BM effect resulting from the high electron concentration (~10¹⁸ cm⁻³) existing in the LT as-grown InSbN samples [29].

4.7 Band filling effects

The band gap energy E_- of the InSbN sample grown at the low temperatures of 270 °C and 300 °C can be calculated by taking into account each of the three effects and can be expressed as:

$$E_- = E_{abs} - E_{BM} + E_{BGN} \quad (4.2)$$

where E_{abc} is the absorption edge energy as measured from FTIR, E_{BM} is the energy shift due to the BM effect, and E_{BGN} is the band gap narrowing energy where a high background concentration could decrease the band gap energy. Ideally, $E_- = E_{abc}$ without taking the high background concentration into consideration.

E_{BM} can be expressed as:

$$E_{BM} = E_F - E_C + E_V \quad (4.3)$$

where E_F is the Fermi energy in the conduction band, E_C is the conduction band edge energy, and E_V is the valence band.

By basing the InSbN material as a degenerately doped n-type material where $E_F - E_C \gg KT$, the BM shift in the limit of extreme degeneracy is defined as [61]

$$E_F - E_C = \left[(3/4) \sqrt{\pi} n_e / N_c \right]^{2/3} KT \quad (4.4)$$

where N_C is the effective density of the states at the conduction band edge. K is the Boltzmann constant. E_V is then expressed as:

$$E_V = \frac{\hbar^2 k_F^2}{2m_h^*} \quad (4.5)$$

where $\hbar$ is the reduced Planck's constant, m_h^* is the effective mass of parabolic heavy-hole valence band based on InSb, and k_F is the Fermi wave number which is dependent on carrier concentration (n_e) as $k_F = (3\pi^2 n_e)^{1/3}$.

E_{BGN} is represented by:

$$E_{BGN} = - \frac{q^3 \sqrt{m_h^* (3n_e)^{1/3}}}{4\pi^{5/3} \epsilon^{3/2} \hbar} \quad (4.6)$$

where ϵ is the dielectric of the material.

Fig. 4.5 shows the plot of E_{abc} for the InSbN grown at 270 °C and 300 °C versus the effects of different n_e (10^{16} to 10^{18} cm⁻³).

Figure 4.5 The effects of carrier concentration (10^{16} – 10^{18} cm^{-3}) on the absorption energy edge of InSbN with 1% N_{Sb} .

As shown in Fig. 4.5, E_{BM} dominated when n_e was higher than $9 \times 10^{16} \text{ cm}^{-3}$ which was the case for the InSbN samples grown at 270 °C and 300 °C. When n_e was less than or equal to $9 \times 10^{16} \text{ cm}^{-3}$, E_{abs} was close to E_- . Therefore, from Eq. (4.2), the E_- of the samples grown at 380 °C, 300 °C, and 270 °C should be ~0.16 eV, 0.15 eV, and 0.1 eV. According to the BAC model, these values correspond to ~0.2%, 0.25%, and 1% N_{Sb} , respectively. These values are in reasonable agreement with the percent of N deduced from the tensile strain measured by XRD.

4.8 Summary

In summary, the growth of InSbN epilayers at temperatures ranging from 270 °C to 380 °C on GaAs substrate was studied.

The effect of the two-step 300 nm HT InSb/30 nm LT InSb buffer layer process was observed to improve the crystalline quality of the InSbN epilayers due to the defect suppression. The electrical and optical properties of the InSbN samples are dependent on the growth temperature. The results showed the increased content of N_{Sb} at a lower temperature which was consistent with the results in Chapter 3. However, the Hall measurements showed a high electron concentration ($\sim 10^{18} \text{ cm}^{-3}$), which caused a blueshift in the absorption edge energy (resulting in a shorter wavelength).

The effect of a high carrier concentration that masks the real absorption edge of the InSbN samples was further supported by taking into account the BM effect and the band gap narrowing effect. The calculation results were consistent with the absorption band edge measured for the N composition from the XRD measurement. However, in order to realize InSbN devices, the higher electron concentration must be reduced.

Chapter 5 Effect of thermal annealing in InSbN/GaAs

5.1 Introduction

The earlier chapters have shown that there is an increase in N incorporation in InSbN at a low substrate temperature. Nevertheless, the persistent challenge of this growth condition lies in its high n_e (10^{17} to 10^{18} cm⁻³) which is detrimental for device performance.

The most likely causes of high n_e can be attributed to N⁺ interstitials since the RF plasma source could create charged species [62]. Recent theoretical and experimental studies have also shown that these interstitial defects are abundant in MBE dilute nitrides because of their low formation energy [71]. As such, these donor defects result in the BM effect which causes an undesirable blueshift in the E_{abc} .

Post-growth annealing has been reported to improve the optical and electrical properties of GaAsN alloys significantly by reducing the interstitial defects [72]. While the annealing experiment (300 °C for 8 hrs) has been carried out for InSbN [27], the results are not promising since n_e only reduces slightly from 2.1 to 1.8×10^{18} cm⁻³. In this chapter, we study the effect of thermal annealing at temperatures from 310 to 460 °C on the properties of InSbN alloys using HRXRD, the Hall effect, Raman spectroscopy, and FTIR.

5.2 Preparation for annealing process

The InSbN material was grown on GaAs (100) semi-insulating substrate. The average growth rate was 1 $\mu\text{m/hr}$ and the Sb/In flux ratio was kept at ~ 2 . A two-step InSb buffer layer was grown prior to the InSbN epilayer growth. The details of this process were recorded in Chapter 4.

Subsequently, the InSbN films were grown at a fixed lowest temperature of 270 $^{\circ}\text{C}$ with a RF plasma power of 150 W. The samples with a film thickness of 100 nm were characterized by HRXRD and Raman whereas the samples with a film thickness of 2 μm were prepared for the Hall effect and absorption analysis. Using SIMS analysis, the total N content $[\Sigma N]$ was $\sim 1\%$. Smaller wafer pieces were cut from the as-grown samples for *ex situ* thermal annealing. This post growth annealing process was carried out at an outside independent chamber under flowing N_2 ambient at 310 to 460 $^{\circ}\text{C}$ for 1 min. The samples that were annealed at temperatures of 400 $^{\circ}\text{C}$ and above were carried out in the MBE growth chamber under Sb flux. In addition, a reference as-grown InSb sample was created for comparison.

5.3 Annealing effects from X-ray diffraction

The effect of annealing on the lattice strain was investigated using HRXRD. Figure 5.1 compares the $2\theta/\omega$ scans obtained from the (004) reflection of the as-grown InSbN sample and from the samples that are annealed at different temperatures. Through the lattice mismatch dynamical simulation, the initial N incorporation from

the as-grown InSbN sample was 0.6%. This value was lower than $[\Sigma N]$ determined by SIMS and indicated the presence of N interstitials. After annealing from 310 °C, the InSbN diffraction peak started to shift towards the main InSb peak. As the annealing temperature increased to 460 °C, the intensity of this nitride peak receded until it was no longer detectable.

Figure 5.1 The XRD scans of the as-grown InSbN sample and of the samples annealed at different annealing temperatures.

From the studies in Chapter 3, the source of the tensile strain observed before annealing in Fig. 5.1 could be contributed by other point defects such as N-N interstitials rather than solely by the N_{Sb} . As the range of the annealing temperature was much lower than the dissociation temperature (>550 °C) of strong N-In bonds [73], the annealing process most likely removed the N-N interstitials. At this point, we did not rule out the possible reduction of N_{Sb} as a result of the annealing process.

From the lattice mismatch model [30], the possible defects that could have contributed to the tensile strain were [100]-split interstitial N-N and [110]-split interstitial N-N. In addition, there was a change in the total N content after annealing according to the SIMS measurement as shown in Fig. 5.2. This indicates the possibility of N out-diffusion from our bulk structures.

Figure 5.2 The SIMS profile of the as-grown InSbN and the sample annealed at 400 °C.

However we noted that the N content in GaAsN after annealing was reported to diffuse inside the GaAsN material and to improve the concentration of substitutional N [74, 75], therefore N should not out-diffuse from our samples. In addition, the sample used in this SIMS analysis was annealed in the growth chamber at $\sim 400^\circ\text{C}$ under Sb flux. This meant that the InSbN sample (a separated new wafer) was not from the same as-grown wafer because the *ex situ* annealing process at higher temperature under N flux degraded the sample's surface which resulted in difficulties analyzing the SIMS results.

The shift in the InSbN peak or the change in the relaxed lattice mismatch could indicate the possibility of the decomposition of split interstitial N-N to single interstitial N atom. Since N is small, it will not have contributed to the strain as it could do on substitutional sites. As further observed in Fig. 5.1, the temperature for the likely annihilation of these N-N interstitials was observed to be $\sim 430^\circ\text{C}$ at which the relaxed lattice mismatch between the InSbN and InSb peaks is reduced significantly. Studying beyond this annealing temperature is not feasible since it approaches the melting point of the InSb ($\sim 500^\circ\text{C}$).

5.4 The Hall effect measurements

The effect of split interstitial N-N was further investigated through a comparison of the electrical properties of as-grown and annealed films. The RT n_e and the mobility for the as-grown and annealed InSbN films are shown in Fig. 5.3.

Figure 5.3 The electron concentration and the mobility of the sample as a function of the annealing temperature.

The decrease in n_e and the increase in mobility with the annealing temperature shown in Fig. 5.3 correspond closely with the decrease in the lattice mismatch in Fig. 5.1. A significant reduction of n_e from $\sim 10^{18}$ to InSb intrinsic level of $1.9 \times 10^{16} \text{ cm}^{-3}$ was observed at the activation temperature of 430 °C. The correlation between the HRXRD and the Hall effect measurement supports the fact that N-N interstitial could be the main cause of the high carrier concentration.

Since N (N bonded to In) has been reported as an isoelectronic acceptor (electron traps) [76], it however does not activate its acceptor-type nature (thus resulting in high n_e) in the as-grown InSbN crystal. This could indicate that the sample grown at a relatively low temperature was far from thermodynamic equilibrium. The N atoms

could have been randomly distributed as complex interstitials since low temperature MBE growth is known to promote random epitaxy. Therefore, the high temperature annealing at 430 °C could have dissociated the N-N split interstitial atoms into single interstitials. In addition, the inverse relation between the electron mobility and n_e indicated that the electron mobility is likely limited by the ionized defect scattering. Therefore, the increase in the electron mobility was due to the removal of N-N defects.

5.5 Results from the Raman scattering measurements

Raman measurements were carried out to study the effect of annealing temperature of 430 °C on the crystallinity of the lattice material.

Figure 5.4 The Raman spectra of the as-grown InSbN and the sample annealed at 430 °C.

A strongly forbidden TO phonon peak from the grown InSbN sample was observed (see Fig. 5.4). This indicated a high degree of lattice distortion due to the N incorporation. The detection of the elemental $A_{1g}Sb$ mode at 145 cm^{-1} in the spectrum was attributed to Sb antisite defects due to the excess Sb atoms.

The investigation on the as-grown InSb revealed that n_e only increased slightly to $3 \times 10^{16}\text{ cm}^{-3}$. This indicated that excess Sb may have contributed to an increase in n_e by introducing shallow levels [77]. However, no significant change in the n_e for the as-grown InSb was observed after the annealing.

The appearance of a weaker mode at 450 cm^{-1} was assigned as a $A_1(\text{TO})$ InN phonon-like mode [78]. This plasmon-LO phonon coupling mode was induced by the presence of excess electrons in the conduction band. After annealing at 430°C , the $A_1(\text{TO})$ InN peaks and the $A_{1g}Sb$ peaks were significantly suppressed which indicated the reduction of electrons in the conduction band. In addition, the annealing-induced reduction of these Raman signatures and $I_{\text{TO}}/I_{\text{LO}}$ proves the effect of the decomposition of N-N interstitials. Furthermore, the appearance of the second order mode of the LO peak (2LO) suggests that the material exhibited a significant improvement in crystalline quality after annealing.

5.6 The optical results from Fourier Transform Infrared

Figure 5.5 shows the RT photon energy dependence of the as-grown InSbN sample and the InSbN sample annealed at 430 °C evaluated from the transmission spectrum measurements. Due to the high n_e , the absorption edge energy of the as-grown InSbN blueshifted to 0.2 eV or $\sim 6 \mu\text{m}$ with respect to the reference InSb sample (0.17 eV). However, upon thermal annealing to 430 °C, the absorption edge energy redshifted to 0.15 eV ($\sim 8 \mu\text{m}$). This result was expected since annealing decomposes the interstitial N [79]. Therefore, the band gap was observed to be reduced. The small peak for the InSb sample at 0.15 eV was due to the Fabry-Perot oscillations produced during the FTIR transmission measurements.

Figure 5.5 The plot of the photon energy of the as-grown InSbN and InSbN samples annealed at 430 °C.

Thus, the band filling theoretical method presented in Chapter 4 is not needed and we can obtain the band gap directly from the absorption spectroscopy.

From the BAC model, this band gap energy corresponds to an N_{Sb} content of $\sim 0.3\%$. This indicates that thermal annealing reduced the N_{Sb} content. The remaining N content of $\sim 0.7\%$ probably could have existed as single interstitial N and N pairs. Although the results from XRD strongly suggest a predominance of the N-N interstitials before annealing, we do not rule out the existence of N pairs in insignificant quantities as N pairs could be found in MBE dilute nitrides. These N pairs are inert with no polarity.

According to Lindsay *et al.* [80], these N-N pairs as well as large clusters (N_3 , N_4) have little influence in the InSbN energy gap. Even though these different N atom clusters introduce different defect levels, they all lie above the InSbN conduction band edge. Hence, the origins of high n_e are still the N-N interstitials and Sb antisites. Under the as-grown condition, Sb antisites could form levels close to the conduction band. Upon annealing to 430°C , the dominant N-N interstitials are decomposed to single interstitial N, hence reducing the n_e .

5.7 Summary

The effect of thermal annealing temperatures ranging from 310 to 460 °C on the properties of InSbN films was studied.

By increasing the annealing temperature from 310 to 460 °C, there was a reduction in the tensile strain from the shift in the N peak. Such an annealing-induced shift in the N peak from the XRD was due to the annihilation of donor-type defects in N-N interstitials. Reduction of N_{Sb} content from thermal annealing was also observed. Results from the Hall measurements demonstrated the reduction of n_e from 10^{18} to the intrinsic level of 10^{16} cm^{-3} upon annealing at 430 °C. In addition, Raman results suggested the decomposition of N-N interstitials to single interstitial N through the reduction of the $A_1(\text{TO})$ InN phonon-like mode. After thermal annealing, the RT absorption edge of the InSbN alloy redshifted from ~6 to ~8 μm , indicating a smaller band gap.

Chapter 6 InSbN photodetectors by *in situ* annealing

6.1 InSbN photoconductors

6.1.1 Introduction

To date, it has been a challenge to demonstrate LWIR $\text{InSb}_{1-x}\text{N}_x$ devices such as photodetectors due to their high background n_e . Even though the *ex situ* annealing process reduced n_e to a device compatible level, the surface quality of the InSbN alloy deteriorated. Such degradation of the $\text{InSb}_{1-x}\text{N}_x$ surface at a high annealing temperature could be due to the propagation of Sb vacancy point defects created by excessive desorption as shown in Fig. 6.1.

Figure 6.1 Optical photograph plan view of the degraded InSbN sample after *ex situ* annealing at 430 °C.

In order to implement LWIR photodetectors utilizing the annealing process, we solely applied thermal annealing for the samples inside the main growth chamber under the Sb environment [81]. Directing a beam of Sb flux during annealing could possibly suppress the Sb desorption from the surface, thus preventing surface degradation. In this section, we investigate the optical properties of $\text{InSb}_{1-x}\text{N}_x$ alloys at three different *in situ* annealing temperatures (350 °C to 430 °C). Information on the N incorporation and on the electrical and optical properties of the InSbN is also presented.

6.1.2 The sample preparation of photoconductors

Three $\text{InSb}_{1-x}\text{N}_x$ samples were grown on (100)-oriented semi-insulating GaAs substrates. Two-step InSb layers were used again as buffers for the subsequent $\text{InSb}_{1-x}\text{N}_x$ epilayer. The growth rate was 1 $\mu\text{m/hr}$ and the Sb/In beam equivalent pressure ratio was kept at ~ 2 .

After the growth of the InSb buffer, 2 μm thick $\text{InSb}_{1-x}\text{N}_x$ layers were grown at a low temperature of 270 °C with a RF plasma power of 220 W. Subsequently, these three samples were ramped up at a rate of 8 °C/min to annealing temperatures of 350 °C, 380 °C, and 430 °C. The *in situ* annealing process was carried out in the same MBE growth chamber under Sb overpressure and lasted for 20 minutes. It is noted that the RHEED streaks were weak as the background vacuum pressure is $\sim 9 \times 10^{-6}$ Torr after the InSbN layer growth. Using SIMS analysis, the total N content in these three samples was $\sim 1.2\%$. In addition, a reference as-grown InSb sample was also

prepared. No surface degradation was observed (all of the samples exhibited mirror-like surfaces).

6.1.3 N content from XRD

The N incorporation in the $\text{InSb}_{1-x}\text{N}_x$ samples was first investigated using the HRXRD measurement. Figure 6.2 shows the (004) $2\theta/\omega$ scans of the *in situ* annealed samples.

Figure 6.2 The plot of $2\theta/\omega$ scans obtained from the (004) reflection of the $\text{InSb}_{1-x}\text{N}_x$ samples *in situ* annealed at 350 °C, 380 °C, and 430 °C.

A multi-Gaussian deconvolution was performed (dashed lines) for the samples annealed at 350 °C and 380 °C in order to extract the $\text{InSb}_{1-x}\text{N}_x$ distinguished peaks. We noted that the tensile strain in these $\text{InSb}_{1-x}\text{N}_x$ samples reduced with the increase in annealing temperature. This reduction in the tensile strain indicated a possible loss of N_{Sb} as the annealing temperature increased. This trend is similar to the *ex situ* annealing results presented in the previous chapter.

Using the lattice mismatch dynamical simulation, the N_{Sb} content was ~1%, 0.6%, and 0.3% in the samples annealed at 350 °C, 380 °C, and 430 °C, respectively. Compared to the total N content measured by SIMS (1.2%), ~92% of the N atoms for the sample annealed at 350 °C were located at the Sb lattice sites. Recent studies [82, 83] show that thermal annealing could induce a change in In-N bonding and that a higher annealing temperature reduces the In-N bond lengths. The alternation of the In-N bonding states with a higher annealing temperature could explain the reduction of the active N_{Sb} content. Such a change in absorption wavelength will be further demonstrated below.

6.1.4 Electrical properties of $\text{InSb}_{1-x}\text{N}_x$

The study of the different annealing temperatures on the electrical properties was further investigated using the Hall measurements at 300 K (as shown in Table 6.1).

Table 6.1 Summary of the Hall effect measurements of the three bulk $\text{InSb}_{1-x}\text{N}_x$ samples on GaAs substrate.

Annealing temperature ($^{\circ}\text{C}$)	Electron concentration (cm^{-3})	Mobility (cm^2/Vs)	N_{Sb} incorporation (%)
350	4.2×10^{16}	4690	1
380	4.0×10^{16}	4970	0.6
430	1.7×10^{16}	7080	0.3

The Hall coefficients of the three samples were negative, indicating apparent n-type conductivity. In addition, the electron concentrations of all of the samples were close to the InSb intrinsic level of $1.9 \times 10^{16} \text{ cm}^{-3}$. This showed that the *in situ* annealing process had reduced the donor N defects.

However, the existence of other donor defects such as Sb antisites were not ruled out, especially in the InSbN sample annealed at 350°C since it exhibited the highest electron concentration of $4.2 \times 10^{16} \text{ cm}^{-3}$ with an electron mobility of $\sim 4600 \text{ cm}^2/\text{Vs}$. The presence of Sb antisites was not surprising given that N is incorporated into InSb through the N-Sb exchange that could lead to excess Sb atoms.

6.1.5 Images from transmission electron microscopy

Comparing the material quality of the InSbN layer was worthwhile. Figure 6.3 shows a TEM image of the as-grown InSbN layer prior to any annealing process.

Figure 6.3 A TEM image of as-grown InSbN material in [001] plan view.

The black spot which is circled was one of the many randomly observed clusters with a density of $\sim 1.6 \times 10^{16} \text{ cm}^{-2}$ in the InSbN layer. These clusters were also seen in the InSb buffer layer. In fact, similar clusters were observed in N-free InSb films. Hence, these clusters in the InSbN matrix may be contributed from Sb.

The effects of different annealing temperatures on the InSbN crystalline film is shown in Fig. 6.4.

Figure 6.4 The TEM images of (a) InSbN annealed at 350 °C and (b) InSbN annealed at 430 °C.

In Fig. 6.4(a), mosaic-like structures with dislocations (marked in rectangle shapes) were observed in the InSbN film annealed at 350 °C. The higher annealing temperature of 430 °C, however, induced a reformation change in the material where the dislocations were replaced by clusters dispersed all over the InSbN layer (see Fig. 6.4(b)). This appearance could be associated with an N segregation in the Sb clusters since the N_{Sb} incorporation was significantly reduced at 430 °C.

6.1.6 Spectral response of $\text{InSb}_{1-x}\text{N}_x$ photoconductors

The InSbN samples annealed at 350 °C, 380 °C, and 430 °C were fabricated into photoconductors using interdigitated patterns which were then covered with Ti/Au (30/250 nm) to form ohmic contact as shown in Fig. 6.5. The interdigitated pattern had fingers measuring 5 μm wide and 500 μm long with a 100 μm spacing in between. Furthermore, the spectrum and the power of the infrared light source were calibrated using a pyroelectric detector.

Figure 6.5 An optical photograph plan view of the contact patterns. The inset shows the connection of the contact patterns by Au wires.

Figure 6.6 shows the normalized photoresponsivity at 77 K of the InSb reference sample and the $\text{InSb}_{1-x}\text{N}_x$ samples annealed at 350 °C, 380 °C, and 430 °C where the spectral shape of the photoconductive response was independent of bias. The

as-grown $\text{InSb}_{1-x}\text{N}_x$ sample was not used as a reference since we could not fabricate a photoconductor from it due to its high electron concentration.

Figure 6.6 The spectral response for the reference InSb sample and the $\text{InSb}_{1-x}\text{N}_x$ samples annealed at 350 °C, 380 °C, and 430 °C at 1 V bias.

The photoresponsivity of all the $\text{InSb}_{1-x}\text{N}_x$ samples show extended cutoff wavelengths compared to the photoresponsivity of the reference InSb. In particular, the sample annealed at 350 °C clearly exhibited the longest photoresponse (up to 10 μm). From the relationship between the optical wavelength and the associated photon energy, the optical band gap of the material was deduced to be <120 meV. As shown in the spectrum for the annealed samples at 380 °C and 430 °C, the cutoff wavelengths were ~6.8 μm and ~6.3 μm, respectively. This showed that a higher

annealing temperature reduces the N_{Sb} content which is consistent with the conclusions drawn earlier.

Figure 6.7 compares the photo-to-dark current (PDR) ratio of the samples annealed at 350 °C and 430 °C. The PDR of both samples was found to be higher than 50 and it increased with the applied voltage. These results are consistent with basic photoconductivity theory and also demonstrate that the quality of the samples annealed at 350 °C and 430 °C was not affected by their significant difference in N_{Sb} content.

Figure 6.7 The PDR of the fabricated $\text{InSb}_{1-x}\text{N}_x$ photoconductors annealed at 350 °C and 430 °C.

6.1.7 Band anticrossing model at 77 K

The experimental results from the HRXRD and the 77 K photoconductivity measurements of the three samples were considered against the BAC model with the Varshni relation as in Eq. (2.4) in Chapter 2. Figure 6.8 shows that the calculation of the $\text{InSb}_{1-x}\text{N}_x$ band gap edge resulted from the band anticrossing effect between the N states and the InSb conduction band as a function of N composition at 77 K.

Figure 6.8 The calculated band gap edge level in the $\text{InSb}_{1-x}\text{N}_x$ samples at 77 K as a function of N composition.

At the temperature of 77 K, an N_{Sb} content of ~1.4% was needed to achieve a band gap of 0.1 eV (i.e. 12 μm). The opened circle, triangle, and inverted triangle were the band gap energy from the photoconductive measurements with their respective N incorporation from the HRXRD.

As observed, a reasonably good agreement between the theory and the experiment was obtained. From the BAC model, the measured band gaps of the annealed samples at 350 °C, 380 °C, and 430 °C from the photoconductive experiment could correspond to the N_{Sb} content of ~1.1%, ~0.45%, and ~0.3%, respectively. The slight discrepancy of the N_{Sb} values estimated can be contributed to: (a) the existence of other interstitial defects which induced a smaller tensile strain in the $InSb_{1-x}N_x$ layer compared to the N_{Sb} lattice, (b) experimental errors in accuracy for photoconductivity measurements, and (c) the theoretical uncertainties of the model.

6.1.8 Summary

In conclusion, we studied the effect of post-growth *in situ* annealing (350 °C, 380 °C, and 430 °C) on the electrical and optical properties of $InSb_{1-x}N_x$.

We realized $InSb_{1-x}N_x/GaAs$ photodetectors operating near 10 μm by applying *in situ* thermal annealing. Besides achieving a low background electron concentration of $\sim 10^{16} cm^{-3}$, the amount of N incorporation in Sb lattice sites was found to depend strongly on the annealing temperature and the active N_{Sb} content was the highest at the lowest annealing temperature.

6.2 InSbN photodiodes

6.2.1 Introduction

In the previous section, we demonstrated InSbN photoconductive detectors with an operating wavelength up to $\sim 10\ \mu\text{m}$. The annealing process is necessary to reduce the background electron concentration of the absorption InSbN layer from 10^{18} to $10^{16}\ \text{cm}^{-3}$, which is useful for the InSbN devices' performance. Even though the N substituting Sb caused a reduction in the material band gap, there have been no reports on the operating characteristics of the InSbN devices.

These InSbN devices, which are grown by MBE, are likely to demonstrate a lower photoresponsivity compared to InSb devices. It is probable that the incorporation of N could deteriorate the quality of the alloy. Since the electrical characteristic of a device is useful to gauge the quality of the alloy, a study of the InSbN photodetector is necessary.

Thus, this section compares the characteristics of the InSbN against a reference InSb p^+-n junction. Despite a significant extension of the absorption wavelength, poor electrical characteristics of the InSbN p^+-n was observed with the presence of N-related crystal defects from the TEM images.

6.2.2 Device design and fabrication

The p^+-n structures on GaAs (100) semi-insulating substrate are as shown in Fig. 6.9. The Sb/In flux ratio was still kept at ~ 2 to ensure a Sb stabilized surface condition. Details of the InSbN and InSb growth and the annealing process were reported in the previous section. The photoabsorption layer of the InSbN photodiode comprised a 2 μm thick InSbN layer of $\sim 1\%$ N_{Sb} with a not intentionally doped (n.i.d) electron concentration of $\sim 4 \times 10^{16} \text{ cm}^{-3}$. The absorbed wavelength is $\sim 9 \mu\text{m}$ wavelength as shown in Fig. 6.9.

Figure 6.9 A plot of normalized responsivity versus wavelength at 20 K under -0.5 V bias. The inset at the bottom shows the epilayer structures for InSbN and the reference InSb photodiodes.

In comparison, the 2 μm thick InSb absorption layer of the reference InSb photodiode had a n.i.d electron concentration of $\sim 1 \times 10^{16} \text{ cm}^{-3}$. The p^+ layer of both devices was a 50 nm thick C-doped InSbN with a doping concentration of $\sim 1 \times 10^{19} \text{ cm}^{-3}$. The use of C as the p-type dopant was known to minimize the outward diffusion and enable the formation of an abrupt p-n junction [84]. There was no significant difference between the characteristics of the devices which used C-doped InSbN and C-doped InSb as the p^+ layer. This implied that the main diode performance was determined by the n-type absorption layer. These devices were fabricated using a standard lithography process and mesa etching was performed using a solution of $\text{H}_3\text{PO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (1:1:10). The diameter of the device illumination window was 50 μm . The ohmic p^+ and n contacts were formed by 250 nm thick Ti/Au.

6.2.3 Current-voltage characterization

Figure 6.10 shows the measured current-voltage (I - V) curves of the InSbN and InSb p-n diodes at 20 K. The InSb diode exhibited asymmetric I - V characteristics with small dark reverse current densities of 1.6 mA/cm^2 and 12.7 A/cm^2 , respectively, at 0 and -1.5 V and with a turn on voltage of $\sim 0.23 \text{ V}$ which is in close agreement with the InSb band gap.

However, the InSbN diode displayed symmetric I - V under positive and negative bias, with higher reverse current densities of 33 mA/cm^2 and 39 A/cm^2 at bias voltages of 0 and -1.5 V , respectively.

Figure 6.10 The current-voltage characteristics of the InSbN and InSb p-n device at 20 K. The black solid line and the red dashed line show the results of fitting with a transcendental equation.

The I - V data was fitted using an equivalent circuit of a diode [85] with a series resistance R_s and a parallel leakage resistance R_l given by:

$$I = I_s \left(e^{\frac{q}{nKT}(V - R_s I)} - 1 \right) + \frac{1}{R_l} (V - R_s I) \quad (6.1)$$

where I_s is the reverse saturation current considered to be constant and n is the ideality factor.

The parallel leakage resistance from the modeling in the InSbN device was $\sim 270 \, \Omega$ which is one order lower compared to the parallel leakage resistance of the InSb diode. This is likely due to the presence of N related defects [86] which introduce defect states within the band gap and enhance the trap-assisted tunnelling between the conduction band and the valence band [84].

Figure 6.11 shows the comparison of the series resistance between the InSbN and the reference InSb devices. The slight non-linearity of the series resistances for both devices at low currents indicated the characteristics of a diode. However, the InSbN device displayed a higher series resistance which contributed to the increase in turn on voltage. The high series resistance of the InSbN diode is likely due to its low electron mobility caused by the N related defects.

Figure 6.11 The dependence of series resistance on a forward current for the InSbN and InSb devices.

6.2.4 Capacitance-voltage measurements

The effect of the N related defects were further studied by the capacitance-voltage (C - V) measurements of the InSbN and InSb diodes at a high frequency of 1 MHz. The capacitance at this high frequency measurement usually approaches the geometric capacitance [87]. Figure 6.12 shows the C - V characteristics at 20 K and 50 K. Despite checking carefully that parasitic elements did not influence the data, a negative capacitance was observed for the InSbN diode and it decreased with an increasing negative bias.

Figure 6.12 The capacitance-voltage characteristics of the InSbN and InSb devices at 20 K and 50 K.

The InSbN device also exhibited a decreasing negative capacitance under positive bias similar to that exhibited under negative bias (symmetrical C - V curve) which is expected as a result of the I - V behaviour.

According to the transient current analysis [87], this negative phenomenon observed in a variety of semiconductor devices is attributed to the existence of a large reactive conduction current over the displacement current that relates to the charging effect of the geometric capacitance. The shunted conduction current is likely associated with the high leakage current from the trap-assisted tunnelling at the InSbN p^+ - n junction.

The increase in the negative capacitance from 20 K to 50 K is due to the expected increase in the conduction current with temperature. The InSb device also displayed a negative capacitance except at a smaller reverse bias and its negative capacitance decreased steeply as the bias was increased towards positive values. This suggests that the presence of shallow levels caused by the excess Sb atoms in the InSb epitaxy may also contribute to the conduction current at a small bias.

6.2.5 Micrographs from transmission electron microscopy

The physical existence of the defects introduced by the N incorporation was further evidenced by TEM. The bright-field TEM micrographs of the InSbN and InSb devices in the (001) orientation are shown in Fig. 6.13.

Figure 6.13 The TEM micrographs for the (a) InSb p-n structure and (b) InSbN p-n structure. (I) and (II) are the high-resolution TEM analysis corresponding to the specified regions in (a) and (b), respectively. The open squares show the planar defects and the open circles indicate the dislocations.

Significant planar defects were observed in the InSbN film as compared to the N free InSb film. The generation of these dislocations may have been contributed by the partial relaxation of the InSbN layer. In addition, high magnification TEM images at the p-n junction interface show that the InSb n-layer (region I) has a good crystallinity. In contrast, the InSbN n-layer in region II exhibits very high dislocation densities which are repeated on the top p^+ epilayer. It is unclear why these dislocation patterns due to N incorporation are oriented at [011] and [0-11] directions. However, the presence of these structural defects after the N incorporation in the InSbN film is likely to degrade the electrical characteristic of the device significantly [88].

6.2.6 Summary

In conclusion, we have shown that the N incorporation leads to an increased absorption wavelength in the InSbN p-n photodetector. However, structural planar defects in the InSbN film could affect the electrical characteristics of the InSbN photodiode (such as the display of symmetric I - V and negative capacitance behaviour).

Chapter 7 Conclusions and recommendations

7.1 Conclusions

In this thesis, $\text{InSb}_{1-x}\text{N}_x$ alloys were grown using an advanced crystal growth technology: solid-source molecular beam epitaxy in conjunction with a RF plasma N source. The molecular beam epitaxy was chosen for its slow deposition rate which enables the adatoms of In, Sb, and N to build up systematically to form crystalline layers. A RF plasma source was preferred because of its low generation of ion species which could introduce damage into the InSbN material.

The growth of InSbN is challenging due to the difficulty in incorporating the N atoms in the Sb sites. Therefore, InSbN has a high percentage of interstitial defects. We began the project by growing the InSbN material based on the reported growth conditions by varying the growth temperature (330 °C to 420 °C) and the RF plasma power ranges (200 W to 500 W). Using characterization techniques such as visible wavelength Raman scattering and x-ray diffraction, the effect of the growth temperature and the plasma power on the N defects was studied. Both Sb antisite and Sb-N defects were observed in the InSbN samples and were found to be dependent on the growth temperature and on the plasma power. In addition, reactive Sb, a product from the nitridation process, contributed to the formation of Sb related defects. At the low plasma power of 200 W, Sb antisite and Sb-N defects increased as the substrate temperature increased from 330 to 420 °C due to excessive reactive

Sb generated at the high temperature. At the highest substrate temperature of 420 °C, an increase in the RF plasma power to 500 W yielded more N to form Sb-N defects and reduced the reactive Sb available to form Sb-Sb. These results in the first section of Chapter 3 indicated that a low substrate temperature and a RF power of 330 °C/200 W reduced both Sb antisite and Sb-N defects.

The next set of experiments was carried out at 330 °C and lower temperature ranges. These experiments were also necessary because another author [29] reported the presence of N_{Sb} at only 330 °C. Therefore, we needed to verify the sensitivity of the N incorporation in the InSbN at these low temperature regimes. A combination of characterization techniques comprising XRD, SIMS, and NRA was used to investigate the concentration of N_{Sb} and the possible interstitials in the InSbN grown at low temperatures (270 °C to 330 °C) and at RF plasma power ranges from 150 to 180 W. A high epitaxial film quality was observed and the lower growth temperature was also found to increase the ratio of N_{Sb} content over the interstitial N. However, increasing the plasma power to 180 W at the lowest growth temperature resulted in an increase in interstitial N-N and reduced the N_{Sb} content. In addition, from the lattice strain modeling, large amounts of interstitial N-N contributed to the lattice contraction like N_{Sb} . These results were shown in the second section of Chapter 3.

Next, the study of the heteroepitaxial growth of InSbN on a GaAs substrate was needed to explore its suitability for practical device integration. The effects of two-step thin InSb buffer layers grown at 330 °C and 380 °C and the properties of the

InSbN grown at substrate temperatures (270 °C to 380 °C) were studied. The crystalline quality of the InSbN was significantly improved by the two-step buffer layer due to defect suppression at the InSb/GaAs interface. The shifting in the absorption edge of the InSbN from ~5 to 8 μm following an increase in the substrate temperature was co-related to the reduction in free carrier concentration from $\sim 10^{18}$ to 10^{16} cm^{-3} and to the increase in the concentration of N substituting Sb from ~0.2 to 1%. These results suggest the potential for further investigation on the pseudo-monolithic integration of InSbN detectors on GaAs platform.

From the XRD results, the N incorporation in InSbN/GaAs could increase at a low substrate temperature. Nevertheless, the high electron concentration (10^{17} to 10^{18} cm^{-3}) at this growth condition is detrimental for device performance. This band filling effect caused by the presence of N donor defects could result in an undesirable blueshift in the absorption edge energy. Therefore, we studied the annealing effects on the properties of as-grown InSbN films. The annihilation of donor defects in the form of N-N interstitials is suggested by the shifting of N induced tensile strain from the XRD results and by an associated decrease in the free electron concentration from $\sim 1 \times 10^{18}$ to a device level of $\sim 2 \times 10^{16} \text{ cm}^{-3}$. These findings support the analysis that N interstitials thermally dissociate into single N and that higher annealing temperatures increase the reduction in the electron concentration. Corresponding signatures for the reduced Sb antisites and the N-N interstitial defects were also apparent in the Raman spectra.

Nonetheless, although the *ex situ* annealing process reduced the electron concentration down to 10^{16} cm^{-3} , the surface quality of the InSbN alloy deteriorated. This deterioration could limit the device performance. Therefore, the alternative *in situ* annealing process at different temperatures was studied and the annealed InSbN alloys were fabricated into devices. The XRD results indicated that the amount of N incorporation in Sb lattice sites is dependent on the annealing temperature. However, a low annealing temperature increases the N incorporation and extends the absorption to the long wavelength infrared range. InSb_{1-x}N_x/GaAs photoconductors with ~1% N operating near 10 μm at 77 K were also realized. The measured wavelengths were in good agreement with the band gaps of the alloys calculated using a two-level band anticrossing model with the Varshni relation.

In addition to the demonstration of InSb_{1-x}N_x photodetection in the long wavelength infrared range with the photoconductor structure on GaAs substrate, the operating characteristics of the InSbN p⁺-n devices were also studied. The results correlated the poor electrical characteristics of the InSbN p⁺-n with the presence of N related crystal defects through TEM images. The N incorporation led to structural planar defects in the InSbN film which affected the electrical characteristics of the InSbN photodiode. As a result, symmetric *I-V* behaviour and negative capacitance are observed.

7.2 Recommendations for future research

The MBE grown InSbN/InSb films indicated a higher amount of Sb antisite and Sb-N defects at a high growth temperature and a high plasma power as described in Chapter 3. These defects could have been generated by the large amount of reactive Sb and N. Even though a lower growth temperature ($<330\text{ }^{\circ}\text{C}$) and a lower plasma power ($\sim 200\text{ W}$) has been shown to reduce these defects, there is room for further improvement in the crystalline quality of the InSbN layer. In future work, we suggest that researchers study the V/III ratio and the growth rate to optimize the growth conditions further.

We also showed that an increased RF plasma power at the lowest growth temperature yields a lower N incorporation despite an increase in the total N content from SIMS. The XRD measurement of the strained InSbN/InSb films showed a reduction of $\sim 1\%$ N_{Sb} with an increase in the RF power of 30 W . We suspect that the increase in plasma power introduces more N ions which contribute to the overall reduction of the N_{Sb} incorporation. To overcome this problem, it is necessary to investigate a method to lower the N ions at the higher RF power (such as reducing the N flow rate) and to lower the N related defects.

For the heteroepitaxial growth of InSbN/GaAs, a two-step buffer layer is useful to improve the crystalline quality of the InSbN films in Chapter 4. The misfit dislocation defects from the lattice mismatch between the buffer layer and the GaAs substrate could still affect the properties of the InSbN layer as reflected in the low

mobility values at 77 K. To improve the mobility, the structure of the buffer layer such as the layer thickness has to be optimized so that it reduces the effect of the misfit dislocations. In addition, there is a significant reduction of the electron concentration since the growth temperature for the InSbN increases which leads to a redshift in absorption energy. Further analysis on the high range of growth temperature would be useful to understand the effects on the electron concentration (which is an important factor in device performance).

In this thesis, InSbN films were grown at a low growth temperature and a thermal annealing process was utilized which was capable of reducing the electron concentration significantly to 10^{16} cm^{-3} for photodetector applications. The XRD measurement result of the annealed InSbN layer showed a significant reduction of N_{Sb} with an increase in the annealing temperature due to an alternation of the In-N bonding states. In order to improve the N_{Sb} and thus extend the absorption wavelength, further investigation on the thermal annealing process is required.

Improving the crystalline quality of the annealed InSbN layer in order to reduce the N related defects (which lead to a high series resistance and a dark current) is also necessary. Intuitively, the N defects will be lowered at a reduced N content. Due to the lack of equipment such as a positron annihilation spectroscopy, the N related defects could not be easily studied and identified. It would be interesting to investigate the N defect characteristics so that the optimized growth conditions can be carried out.

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