Development and characterization of gallium arsenide-based antimony-containing dilute nitride grown by molecular beam epitaxy

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Satrio Wicaksono

School of Electrical & Electronic Engineering

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

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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.

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Summary

The fast growing demand for internet bandwidth has spurred the need for low cost optoelectronic devices working at the optical communication window of 1.3–1.55 μm . The wavelength range is important due to the minimum laser attenuation windows in a silica optical fiber. However, the high cost of the incumbent InP-based optoelectronic devices has made optical network unfeasible compared to wireless/radio frequency networks, particularly for the “last mile” or fiber-to-premises applications. The emergence of dilute nitride compound semiconductors allows the growth of materials suitable for the 1.3 μm and 1.55 μm application on a cheaper and more robust GaAs substrate.

In particular, the antimony-containing dilute nitride material system, GaAsSbN, has not been widely studied compared to GaNAs, GaInNAs, and GaInNAsSb. In this thesis, the growth of GaAsSbN lattice-matched to GaAs was conducted using a solid-source molecular beam epitaxy (SS-MBE) system in conjunction with a radio frequency (r.f.) plasma N source and Sb valved-cracker source. Studies on GaAsSb/GaNAs/GaAsSbN/GaAs structure revealed two important properties of GaAsSbN growth. Firstly, in the growth rate range of 0.1-1 $\mu\text{m/hr}$, the N incorporation in GaAsSbN is inversely proportional to the growth rate. This is due to the presence of Sb that enhances N incorporation, allowing more than 2.5% of N to be incorporated in GaAsSbN grown at 0.2 $\mu\text{m/hr}$ and reducing the energy bandgap of GaAsSbN to 0.95 eV range. Secondly, lattice matching to GaAs can be preserved

regardless of the growth rate by maintaining the Sb flux at approximately 2×10^{-8} Torr while keeping the As₄/Ga ratio and the r.f. plasma source parameters the same.

In order to improve the quality of the as-grown GaAsSbN layer, the effect of growth temperature was studied using a GaAs/GaAsSbN/GaAs *p-i-n* photodiode (PD) structure. The growth temperature of the GaAsSbN i-layer was varied from 420–480°C. The *p-i-n* PD samples exhibit reasonably low dark current of ~0.3–0.5 mA/cm² at 2V reverse bias, photoresponse at 1.3μm with up to ~33 mA/W responsivity, and RC-limited bandwidth of up to 920MHz. Comparison with some existing GaInNAs *p-i-n* samples suggests the presence of Sb suppresses the N clustering and increases the N concentration. This leads to improvement in the dark current and responsivity at 1.3 μm exhibited by the GaAsSbN *p-i-n* PD compared to the reference GaInNAs *p-i-n* samples. Furthermore, DLTS study reveals two types of defect states in the GaAsSbN i-layer: (i) HT₁: a shallow N-related trap ($E_a \sim 0.10\text{--}0.12$ eV) and (ii) HT₂: midgap trap with $E_a \sim 0.42\text{--}0.43$ eV. Reduction in growth temperature from 480 °C to 420 °C reduces the HT₂ trap concentration from 4×10^{15} cm⁻³ to 1×10^{15} cm⁻³, while it increases the HT₁ trap concentration from 1×10^{14} cm⁻³ to 7×10^{14} cm⁻³. The ~4 dBm improvement in photoresponse under 1.3 μm laser excitation, and ~8 times reduction in dark current at 8 V reverse bias were attributed to the reduction in the overall trap concentration and mainly the As_{Ga} midgap trap concentration in the sample grown at 420 °C.

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maxima (FWHM) and their respective peak temperature.

Introduction

Long wavelength optoelectronics operating at 1.3–1.55 μm wavelength have become increasingly important due to the increase of bandwidth demand for local area networks (LAN) and metro area networks (MAN). However, suitable material systems for the respective wavelengths on a low-cost GaAs platform are still lacking. Dilute nitride materials have the potential to overcome this problem due to their unique properties. GaAsSbN can be grown closely lattice-matched to GaAs, while achieving the 0.95 eV bandgap required for the optical communication wavelength of 1.3 μm . This thesis will present the characterization of the GaAsSbN material system grown closely lattice-matched to the GaAs substrate. The growth experiments were conducted using a solid-source molecular beam epitaxy (SS-MBE) system in conjunction with Sb valve cracker cell and radio frequency (r.f.) plasma N source. This chapter will highlight the background and motivation behind the long wavelength optoelectronic application of dilute nitride materials, particularly GaAsSbN. The research objectives of the thesis will be discussed, followed by the major contribution of the thesis. This chapter will be concluded with a brief description of the organization of this thesis.

1.1 Background and Motivation

The growth of the internet and its increasing role in everyday lives has led to the rapid expansion of the local area network (LAN) and metro area network (MAN). To keep up with the bandwidth demand, the data transmission rate of the optical network has increased from the initial 100 Mbps to 1–10 Gbps. This bandwidth push increases the demand for low-cost optoelectronic devices operating at 1.3 μm and 1.55 μm , particularly for optical networks in fiber-to-premises or “last mile” application. This choice of operating wavelengths was determined by the low attenuation windows in the single mode silica optical fiber as shown in Figure 1-1 (After Miya *et al.* [1]). The three minimal attenuation windows used in optical communications are the 0.85 μm , 1.3 μm , and 1.55 μm wavelengths.

Fig. 1-1 The theoretical and experimental attenuation of light that travels in a silica fiber are plotted against the light’s wavelength [1].

As seen from Fig. 1-1, the intrinsic loss in the optical fiber is dominated by Rayleigh scattering. Rayleigh scattering is caused by the small imperfections within the fiber that is relatively smaller than the wavelength of the light traveling in the optical fiber. These imperfections can be caused by refractive index or compositional fluctuations that occur during the cooling of the fiber. Figure 1-1 shows the lowest attenuation in the fiber is achieved by using 1.55 μm wavelength. However, it is vital to point out that the 1.3 μm wavelength is also important due to its zero-dispersion property. Currently, devices grown on InP substrate are the mainstay of 1.3 μm and 1.55 μm optoelectronic devices due to the availability of lattice-matched material systems within this wavelength range.

Figure 1-2 shows transmission distance vs. the bit rate/bandwidth of various laser wavelengths traveling in single mode (SMF) or multimode (MMF) optical fibers [2]. Based on Fig. 1-2, the transmission range of 850 nm GaAs-based laser with 100 Mbps bit rate is $\sim 7\text{-}8$ km. However, its transmission range decreases to a paltry ~ 50 m when the bit rate is increased to 10 Gbps due to attenuation and dispersion within the optical fiber. This distance is clearly unacceptable compared to standard wireless network and demonstrates the preference for emitters and detectors operating at the 1.3 μm and 1.55 μm minimum fiber attenuation window. On the other hand, the implementation of optical communication network, especially for in the “last mile” applications, becomes costly compared to the wireless option due to the high cost of InP-based detectors and emitters [3]. Compared to InP substrate, GaAs substrate is less expensive and more robust, which led to the availability of larger diameter GaAs wafers and higher yield. The Al(Ga)As/GaAs distributed Bragg reflectors is also

superior to the GaInAsP/InP system due to the higher refractive index difference and better thermal conductivity. Thus, GaAs substrate clearly stands out from both the economical and technical point of view. However, suitable material systems lattice-matched to GaAs substrate that can operate at 1.3 μm and/or 1.55 μm are still lacking. This material system problem is clearly a research gap that has to be resolved in order to realize the GaAs-based optoelectronic devices for long wavelength optical communication.

Fig. 1-2 Transmission distance of different laser wavelengths in various types of optical fiber vs. the data bit rate/bandwidth [2].

A. Brief Overview of Dilute Nitride Materials

III-V compound semiconductors are important materials for electronic and photonics applications. Some of these III-V compound semiconductors are direct bandgap materials, which is clearly an advantage for optoelectronic applications over the indirect bandgap Si. Furthermore, the room temperature low-field electron

mobilities in GaAs ($\sim 8500 \text{ cm}^2/\text{V.s}$) and InP ($\sim 4000 \text{ cm}^2/\text{V.s}$) are higher than in Si ($1450 \text{ cm}^2/\text{V.s}$). These properties have given III–V compound semiconductors a niche application opportunity in high speed and optoelectronic devices despite their tremendous economical disadvantage over Si.

The use of N-containing III–V compound semiconductor has well been reported as early as the 1970's in N-doped GaAsP light emitting diodes (LED) [4]. However, the actual potential of dilute nitride III–V compound semiconductor (III–V–N) was not realized until the year 1992, when a metal-organic vapor phase epitaxy (MOVPE) of GaAs:N was performed by cracking high-purity NH_3 gas using a experimental radio frequency (r.f.) plasma N source [5]. The incorporation of N in GaAs resulted in bandgap reduction despite the fact that the bandgap energy of GaN is $\sim 2\text{eV}$ larger than GaAs. Furthermore, the bandgap reduction shows larger bowing than any other preexisting III–V ternary materials. In addition to the unique bandgap reduction, the lattice constant of GaNAs decreases with increasing N concentration.

The unique properties of dilute nitride-arsenide have prompted some researchers in Hitachi to propose the GaInNAs quaternary material as a potential material for GaAs-based optical communication devices [6]. The incorporation of N reduces the lattice constant of GaAs and induces tensile strain that compensates the compressively strained GaInAs. It was reported that the In/N atomic ratio must be kept at ~ 3.0 to maintain the lattice-matched condition of GaInNAs to GaAs [7]. In addition, the incorporation of N also causes further reduction of the bandgap of GaInNAs that allows the material to reach the optical communication wavelengths of

1.3 μm and 1.55 μm , as shown in Figure 1-3. Beside the aforementioned advantages from using GaAs material system, GaInNAs has better electron confinement due to its 350 meV conduction band offset compared to the 100 meV of the GaInAsP/InP material system [6]. This is particularly important for laser devices, where better electron confinement between the active and the barrier layer leads to better characteristic temperature (T_0). The prediction leads to numerous attempts to utilize this material in a vertical cavity surface emitting laser (VCSEL) structures by different epitaxial methods [2,8,9]. Furthermore, the availability of a narrow bandgap material system that can be lattice-matched to GaAs opens the window of opportunity for other device applications. For instance, the efficiency of a Ge/GaInP/GaAs multiple-junction solar cell can be improved using 1 eV bandgap GaInNAs layer closely lattice matched to GaAs to enhance the absorption of the near infrared region [10,11]. Closely lattice-matched GaInNAs layer was also applied as the intrinsic layer in GaAs-based *p-i-n* photodiode (PD) for 1.3 μm optical communication wavelength [12,13]. In addition, the use of strained GaInNAs layer with narrower bandgap for base material in GaAs-based heterojunction bipolar transistors (HBT) has been reported with lowered turn-on voltage and improved the current gain [14-16].

Fig.1-3 Bandgap energy of some III-V compound semiconductor materials plotted against their cubic lattice constants. The solid and dashed vertical lines marks compound semiconductors lattice matched to GaAs and InP, respectively. The horizontal red line covers the optical communication wavelength of 1.3–1.55 μm .

B. Antimony-Containing Dilute Nitride Materials

One of the problems realized in the GaInNAs material system is the poor quality of the material, mostly due to its miscibility gap [17-21]. The use of antimony (Sb) as a surfactant on molecular beam epitaxy (MBE)-grown GaInNAs was proposed to improve the interface of the GaInNAs/GaAs and the overall quality of the GaInNAs layer [22-32]. The term surfactant was used in Ge on Si heteroepitaxy to describe a surface-active group V species that alters the surface energy and making it

more suitable for the layer-by-layer or two-dimensional (2D) epitaxial growth to occur [33,34]. Massies and Grandjean [35] defines the behavior of surface-active species that occupies the substitutional site and reduces the surface diffusion length during growth as the “reactive-surfactant” behavior [35,36]. The reduction of the surface diffusion length in GaInNAs:Sb and GaInNAsSb leads to suppression of N-clustering and relaxation due to islanding. As a result, layer-by-layer (two-dimensional) growth is promoted, leading to improvement in the crystalline and interfacial quality of the epitaxial layer. Because the process involves the occupation of the substitutional sites by the surfactant, the reactive surfactant behavior can be observed in both Sb-doped and Sb-containing GaInNAs. Subsequently, the five-element III-V material of GaInNAsSb was proposed as another GaAs-based material for 1.3 and 1.55 μm application [28,29,31].

Another GaAs-based compound semiconductor suitable for long wavelength application is GaAsSbN. The material was proposed in 1999 by Ungaro *et al.* [37]. GaAsSbN can also be grown lattice-matched to GaAs, incorporating N to compensate the compressively strained GaAsSb. In addition, by having all three group V elements bond with Ga instead of two, the effect of N clustering which arises from preferential bonding of In-N atoms can be reduced. Furthermore, Harmand *et al.* compared the of bandgap reduction between GaInAs/GaAs and GaAsSb/GaAs quantum wells as a function of In/Sb concentration and found larger bandgap reduction in GaAsSb/GaAs compared to GaInAs for the same indium or antimony atomic concentrations [38]. In addition, comparison between GaNAs, GaInNAs, and GaAsSbN shows that the presence of Sb promotes the incorporation of N, which further reduces the bandgap of GaAsSbN [39]. These findings suggest that GaAsSbN has great potential to reach the

narrow bandgap region for optical communication. However, the great research interest in GaAs-based devices appears to be more focused on GaInNAs and GaInNAsSb material systems. This is particularly true for laser applications due to the weaker conduction band offsets of GaAsSbN/GaAs compared to GaInNAs/GaAs. On the other hand, since the conduction band offset issue is only critical for the electron confinement in laser applications, the potential application of GaAsSbN for GaAs-based devices remains as a research gap that needs to be exploited.

C. Lattice-Matched GaAsSbN for Long Wavelength GaAs-Based Photodetector Application

As shown in Fig. 1-3, $\text{Ga}_{0.47}\text{In}_{0.53}\text{As}$ can be grown lattice-matched to InP with bandgap of ~ 0.73 eV. This layer can be used as the intrinsic layer (i-layer) of a *p-i-n* photodiode (PD) structure for optical communication application with operating wavelength in the 1.3 and 1.55 μm region [40]. However, application of the same GaInAs layer on GaAs substrate is not so straightforward. The lattice-mismatch between the $\text{Ga}_{0.47}\text{In}_{0.53}\text{As}$ layer and GaAs is approximately 3.5%. The larger the lattice mismatch, the critical thickness of the epilayer reduces tremendously. When an epilayer is grown beyond its critical thickness, the epilayer relaxes the strain caused by the lattice mismatch by forming misfit dislocations. The misfit dislocations can act as non-radiative recombination centers, which is detrimental to the device performance.

Two approaches were introduced to circumvent the lattice mismatch problem, the metamorphic growth approach, and the pseudomorphic (strained layer) growth

approach. The metamorphic growth technique involves growing a $\text{Ga}_x\text{In}_{1-x}\text{P}$ graded buffer layer from the GaAs substrate to InP-terminated layer on top of which the GaInAs layer will be grown. The purpose of the graded GaInP layer is to confine the formation of misfit dislocation away from the absorption layer. However, in some cases part of the strain is still relieved by accumulation of misfit dislocation formation particularly in the [110] direction. This will result in surface oscillations that protrude up to the absorption layer, which is detrimental to the device performance [41].

The pseudomorphic technique substitutes the thick GaInAs absorption layer with series of GaAs/GaInAs/GaAs quantum wells that act as the absorption layer. The In concentration was reduced from 53% to 28% to obtain bandgap of 0.95 eV and to reduce the lattice mismatch to GaAs. Some promising results have been reported in GaAsSb/GaAs avalanche photodiode (APD) with RCE structure [42,43]. However, the pseudomorphic approach may be viable only for the 1.3 μm wavelength and still has to overcome the lattice-mismatch problem to reach 1.55 μm . This may be solved by using dilute nitride quantum wells such as GaInNAs or GaAsSbN [24,44]. However, this structure suffers from low responsivity that must be solved by using a resonant cavity-enhanced (RCE) structure. One of the major drawbacks of the RCE structure is that it is more complicated to grow and fabricate compared to the standard *p-i-n* PD structure. Hence, in terms of growth and fabrication, the lattice-matched solution still offers the better platform for GaAs-based photodetector for optical communication purposes. In addition, the *p-i-n* PD structure will be an excellent test structure to study the material properties of GaAsSbN, which is still relatively unknown, compared to its dilute nitride predecessors.

Theoretically, lattice matching of GaAsSbN to GaAs can be achieved by tuning the Sb and N atomic concentration. The lattice constant of GaAsSbN can be estimated by Vegard's Law. Vegard's law approximates the lattice constant of ternary or quaternary materials using a linear interpolation of the lattice constants of its constituent binary systems. For GaAsSbN, the lattice constant ($a(\text{GaAs}_{(1-x-y)}\text{Sb}_y\text{N}_x)$) can be calculated using,

$$a(\text{GaAs}_{(1-x-y)}\text{Sb}_y\text{N}_x) = (a_{\text{GaN}} \times x) + (a_{\text{GaSb}} \times y) + (a_{\text{GaAs}} \times (1 - x - y)) \quad 1-1$$

where, a_{GaN} , a_{GaSb} , and a_{GaAs} are the lattice constants of cubic GaN, GaSb and GaAs, respectively, while x and y , are the N and Sb atomic concentrations, respectively. The cubic lattice constants of the constituent binaries [45] are listed as follows

$$a_{\text{GaN}} = 4.5 \text{ \AA}$$

$$a_{\text{GaSb}} = 6.0959 \text{ \AA}$$

$$a_{\text{GaAs}} = 5.65325 \text{ \AA}$$

By solving equation 1-1 with $a(\text{GaAs}_{(1-x-y)}\text{Sb}_y\text{N}_x) = a_{\text{GaAs}}$, the Sb/N atomic ratio for lattice-matched GaAsSbN was obtained at 2.60. From this point forward, the term "lattice-matched" will be used exclusively for a lattice-matched condition to GaAs, unless stated otherwise. Consequently, the lattice constant of GaAsSbN can be kept matched to GaAs while the bandgap can be narrowed by adding more Sb and N to achieve the desired bandgap, as shown in Fig.1-3. The vertical line drawn downward from the GaAs data point represents the theoretically lattice-matched quaternary materials, GaInNAs and GaAsSbN (solid line), while the one drawn from the InP data point represents its ternary materials lattice-matched to InP, GaInAs and GaAsSb (dashed line).

1.2 Objectives and Major Contributions of the Thesis

Growth of GaAsSbN on GaAs substrates was performed on a solid-source molecular beam epitaxy (SS-MBE) system in conjunction with an Sb valved cracker source and an r.f. plasma N source. The experiment began with a study on GaAsSb, which is one of the two constituent ternary alloys of GaAsSbN. Although the growth of GaAsSb is a very mature process, its optimum growth condition is far from the typical dilute nitride growth condition. The incorporation of Sb in GaAsSb grown under dilute nitride growth condition was studied by low temperature photoluminescence (PL) and x-ray diffraction (XRD). The results of this GaAsSb study was found to show preferential incorporation of Sb over As. The Sb sticking coefficient under these growth conditions was found to be 6.7 times the As sticking coefficient. Good quality GaAsSb can still be obtained using the dilute nitride growth condition. However, the critical thickness of the GaAsSb layer reduces with the increase of Sb concentration, preventing the growth of thick GaAsSb layer with high Sb concentration. Epilayer relaxation and the formation of misfit dislocation have been observed in GaAsSb samples grown beyond the critical thickness as predicted by Matthews-Blakeslee model.

In order to reduce the bandgap further and to achieve the lattice-matched condition, N was incorporated to the GaAsSb material in order. Investigation on the concomitant incorporation of N and Sb was conducted using multilayer structures of GaAsSb, GaNAs, and GaAsSbN layers grown on the same GaAs substrate. Two structures were chosen for this purpose, GaNAs/GaAsSbN/GaAs and GaAsSb/GaNAs/GaAsSbN/GaAs. Further reduction of the bandgap energy to ~ 0.95

eV region was attempted by increasing the N and Sb atomic concentrations, while preserving the lattice-matched condition of Sb/N ~ 2.60 . In particular, the effect of growth rate on the incorporation of N and Sb in GaAsSbN was also investigated. The multilayer structures were characterized by combination of low temperature photoluminescence (PL), x-ray diffraction (XRD), and secondary ion mass spectroscopy (SIMS), which reveals two important properties of GaAsSbN growth. Firstly, in the growth rate range from 0.1 to 1 $\mu\text{m/hr}$, the N incorporation in GaAsSbN is found to be inversely proportional to the growth rate. Secondly, the lattice-matched condition can be preserved regardless of the growth rate by maintaining the Sb flux at approximately 2×10^{-8} Torr while keeping the As_4/Ga ratio and the r.f. plasma source parameters the same. This is observed on lattice-matched GaAsSbN/GaAs grown under 1, 0.5, and 0.2 $\mu\text{m/hr}$. From the multilayer structure experiments, the following has been observed in the growth of GaAsSbN. Firstly, GaAsSbN samples exhibits improved PL intensity compared to the PL intensity exhibited by the reference GaNAs sample with similar N content. This suggests the presence of reactive surfactant properties of Sb in the growth of GaAsSbN similar to what has been reported in Sb-containing GaInNAs. Secondly, the presence of Sb enhances N incorporation, allowing more than 2.5% of N to be incorporated in GaAsSbN grown at 0.2 $\mu\text{m/hr}$. This helps to reduce the bandgap of GaAsSbN to 0.95 eV.

The second objective of this thesis was to study the effect of rapid thermal annealing (RTA) on the material quality of GaAsSbN. Dilute nitride materials are known to have poor as-grown quality, particularly the ones grown using the r.f. plasma N source. In this part of the thesis, RTA experiments were conducted using RTA temperature range of 450–900 $^{\circ}\text{C}$ under N_2 ambient for 5 minutes. Two series of

samples underwent the *ex-situ* rapid thermal annealing (RTA) process. The first series is a GaAsSbN quantum well (QW) sample with estimated Sb and N concentrations of 12% and 0.7%, respectively. The other series is a GaAsSbN bulk layer lattice-matched to GaAs with Sb and N concentrations of 2.2% and 0.5%, respectively. The optimum annealing temperature and the mechanism behind the annealing-induced redshift–blueshift was investigated using PL and XRD.

Significant improvement in PL intensity was observed in the annealed samples, suggesting annihilation of impurities and defects in the GaAsSbN layer. The optimum annealing temperature for both the bulk and QW samples was 700 °C. Low temperature PL shows RTA-induced bandgap reduction followed by bandgap increase, particularly in the annealed QW samples. The redshift is probably due to the interstitial to substitutional “kick-out” mechanism of N atoms similar to what was observed in annealing of GaNAs layers [46]. Although the annealed GaAsSbN QW has lower N content, its RTA-induced bandgap reduction occurs at lower annealing temperature (~500 °C) compared to the GaNAs reference (650–725 °C). This may be attributed to the interdiffusion of As–Sb atoms that readily occurs during the annealing of GaAsSbN. The interdiffusion process supplies vacant group V substitutional sites for highly mobile N atoms to occupy. The As–Sb interdiffusion also contributed to the bandgap increase that occurs at RTA temperature over 500 °C.

The RTA-induced bandgap increase in dilute materials can be attributed to a number of factors. Group V short range ordering (SRO), N profile homogenization in the growth direction, and N out-diffusion can all contribute to the bandgap increase. Room temperature PL and XRD studies on the annealed bulk samples revealed that the

N out-diffusion dominates over the other factors when the RTA temperature exceeds 750 °C and above. Thus by keeping the RTA temperature at the optimum temperature of 700 °C, the blue shift should still be suppressed. This is observed in the low temperature PL spectra of the annealed bulk GaAsSbN with N content 0.5%, where the RTA-induced bandgap increase is only ~20 meV for RTA temperature of 700 °C. However, when the lattice-matched GaAs_{0.904}Sb_{0.07}N_{0.026} was annealed under the optimum condition, its low temperature PL spectra showed ~105 meV of bandgap increase. Although the annealed GaAs_{0.904}Sb_{0.07}N_{0.026} layer also exhibits 15 times improvement of the low temperature PL intensity, the large blue shift made the GaAs_{0.904}Sb_{0.07}N_{0.026} layer unsuitable for the 1.3 μm photodiode application. The limitation comes from the r.f. plasma N source that is not in line-of-sight in this work. The lack of XRD rocking curve peak shift has led to the conclusion that the N out-diffusion from the GaAsSbN layer is still minimal. Therefore, the blueshift is attributed to the group V SRO, which is more severe in GaAsSbN with high N content.

The third objective of this thesis was to demonstrate the use of 0.95 eV bandgap GaAsSbN as the intrinsic layer (i-layer) in a GaAs/GaAsSbN/GaAs *p-i-n* photodiode (PD) structure. The effect of the growth temperature of the i-layer was studied by PL and XRD. In addition, responsivity spectra and dynamic photoresponse measurements were conducted to study the effect of growth temperature of the GaAsSbN i-layer on the photodiode performance. This demonstrates the potential of GaAsSbN material for 1.3μm wavelength optical communication application. The growth temperature of the GaAsSbN i-layer was varied from 420 to 480°C. Close lattice matching of the GaAsSbN layer to GaAs has been achieved in all samples. The

p-i-n PD samples exhibit reasonably low dark currents of $\sim 0.3\text{--}0.5\text{mA/cm}^2$ at 2V reverse bias and photoresponse up to $1.3\mu\text{m}$. Comparison with reference GaInNAs *p-i-n* samples suggests the presence of Sb suppresses the N clustering and increases the N concentration. This leads to improvement in the dark current and responsivity at $1.3\mu\text{m}$ exhibited by the GaAsSbN *p-i-n* PD compared to reference GaInNAs *p-i-n* samples. However, the responsivity of the as-grown *p-i-n* samples is lower than the commercially available InP-based photodiodes. Asymmetrical XRD reciprocal space maps (RSM) show reduction of diffused scattering with reduction of growth temperature to 420°C , which suggests suppression of the point defect formation.

Furthermore, deep level transient spectroscopy (DLTS) measurements were conducted on the GaAs/GaAsSbN/GaAs *p-i-n* PD samples to obtain information on the defect states within the GaAsSbN i-layer. The measurement was performed on the *p-i-n* PD, where the growth temperature of the GaAsSbN i-layer was varied at 420°C and 480°C . DLTS reveals two types of defect states in the GaAsSbN i-layer: (i) HT_1 : a shallow N-related trap ($E_a \sim 0.10\text{--}0.12\text{ eV}$) and (ii) HT_2 : midgap trap with $E_a \sim 0.42\text{--}0.43\text{ eV}$. Reduction in growth temperature from 480°C to 420°C reduces the HT_2 trap concentration from $4 \times 10^{15}\text{ cm}^{-3}$ to $1 \times 10^{15}\text{ cm}^{-3}$, while it increases the HT_1 trap concentration from $1 \times 10^{14}\text{ cm}^{-3}$ to $7 \times 10^{14}\text{ cm}^{-3}$. Reduction in the HT_2 trap concentration following growth temperature reduction was attributed to the reduction of As_{Ga} point defect-related midgap defects, as also suggested by comparison of the XRD RSM. Evidence of possible change from the As_{Ga} -related midgap state to a shallow level defect due to the formation of $\text{As}_{\text{Ga}}\text{--N}_{\text{As}}$ pairs was suggested by the increase of the shallow HT_1 trap concentration in the sample grown at 420°C . A $\sim 4\text{ dBm}$ improvement in photoresponse under $1.3\mu\text{m}$ laser excitation, and ~ 8 times

reduction in dark current at 8 V reverse bias were attributed to the reduction in the overall trap concentration and mainly the As_{Ga} midgap trap concentration in the sample grown at 420 °C. The DLTS results correlate well with the improvement in the photodiode performance and the asymmetrical XRD RSM of the [115] plane. Thus, the formation of point defects that is detrimental to the *p-i-n* PD performance can be suppressed by reducing the growth temperature of the GaAsSbN i-layer to 420 °C. Dynamic photoresponse measurement was performed under 1.3 μm laser pulse excitation, where the *p-i-n* PD sample with GaAsSbN i-layer grown at 420 °C exhibits RC time constant-limited bandwidth up to 920 MHz. This demonstrates the potential of lattice-matched GaAsSbN layer for the intrinsic layer on a GaAs-based *p-i-n* PD applicable for optical communication wavelength at 1.3 μm .

1.3 Organization of Thesis

The first chapter is the introduction of this thesis, where the background and motivation for the research work performed in this thesis were presented. The research objective, major contributions and the organization of this thesis were presented in this chapter as well. Chapter II consists of the theoretical work on *p-i-n* PD, literature review on the bandgap calculation of GaAsSbN, and the models used to predict the critical thickness of heteroepitaxial layer. The growth setup and the characterization techniques used in this work are presented in Chapter III. Chapter IV presents the characterization results of GaAsSb layers grown using the dilute nitride growth conditions. The chapter also presents the growth of GaAsSbN using multilayer structures, which provides information on the incorporation of N in GaAsSbN as a function of growth rate. The chapter was concluded by demonstration of lattice

matched GaAsSbN with bandgap energy within the 0.95 eV region. Following this, the study on rapid thermal annealing (RTA) is described in Chapter V. The growth and characterization of GaAs/GaAsSbN/GaAs *p-i-n* PD samples with the GaAsSbN i-layer grown at different substrate temperature is presented in Chapter VI. Chapter VII presents the DLTS results that reveal the types of defects in the GaAsSbN i-layer grown at 480 °C and 420 °C. Finally, the conclusions of the research work and some recommendations for future research are presented in Chapter VIII.

CHAPTER II Theoretical Work and Literature Review

This chapter consists of three parts; the first part contains a brief discussion on the basic physics of a *p-i-n* photodiode (PD). The nature of light absorption in direct and indirect bandgap materials will be reviewed, followed by theoretical calculation of the bandwidth and quantum efficiency of a top illuminated GaAs *p-i-n* PD. The second part of this chapter consists of a review of the approaches used to predict the bandgap of dilute nitride materials. The bandgap of lattice-matched GaAsSbN was calculated using a phenomenological equation and the band anti-crossing model calculation. The calculation results were used to predict the N and Sb atomic concentrations required for lattice-matched GaAsSbN with bandgap energy in the ~ 0.95 eV region. The third part presents a literature review on the epitaxial critical thickness. This includes a brief review on Matthews-Blakeslee and People-Bean critical thickness models. The models were used to complement the GaAsSb epilayer XRD study, which will be presented in Chapter IV of this thesis.

2.1 Intrinsic Optical Absorption in Semiconductor Materials

Photon absorption or absorption is a process in which the incident photon with energy higher than the semiconductor's bandgap excites electrons in the semiconductor to a higher energy state. The term fundamental absorption is used for absorption that excites the valence band electrons to occupy the empty states in the conduction band. Absorption process can also occur extrinsically through intraband transition or impurity/defect-level-to-band transitions. However, these absorption processes involves a more complicated structure such as a multiple quantum well

structure and not suitable for the objective of this thesis. Therefore, the discussion of absorption in this section will be limited to the fundamental absorption. The fundamental absorption mechanism in a semiconductor is characterized by its absorption coefficient (α) which determines light attenuation as it transverses in a distance of x within the semiconductor. The light attenuation can be correlated with α and x using,

$$I_x = I_0 e^{-\alpha x} \quad 2-1$$

where I_x is the attenuated light intensity in the semiconductor material, I_0 is the initial light intensity, x is the length of semiconductor material that the light transverses. The absorption coefficient (α) is a function of the photon energy and it is determined by the bandgap type of the semiconductor material.

Figure 2-1 illustrates the typical absorption coefficient of (a) direct bandgap and (b) indirect bandgap material as a function of the photon frequency [47]. It is clearly shown that the conduction band minima (CBM) and valence band maxima (VBM) of direct bandgap materials (i.e. GaAs, InP) have the same wave vector (k) value. Thus, absorption in a direct bandgap material occurs with minimal phonon absorption/emission and the absorption coefficient (α) has a square root dependence on the photon energy,

$$\alpha \sim (h\nu - E_g)^{\frac{1}{2}} \quad 2-2$$

where, ν is the frequency of the photon, E_g is the bandgap energy of the semiconductor material. As shown in Fig. 2-1(b), the CBM and VBM of indirect band gap materials (i.e. Ge, Si) are located at different k values. Therefore, the photon absorption process must involve phonon emission/absorption. Consequently, the

absorption process is a two-step process and the absorption coefficient is proportional to the square of the excess photon energy after photon absorption and phonon emission/absorption, which can be written as equation 2-3,

Fig.2-1 E vs. k plots for (a) direct bandgap and (b) indirect bandgap semiconductor are shown with their corresponding absorption spectra below the respective E - k diagram. (After Pankove [47])

$$\alpha \sim \frac{(h\nu \pm E_p - E_g)^2}{(e^{E_p/kT} - 1)} \tag{2-3}$$

where, E_p is the phonon energy, the plus and minus sign denote phonon emission and absorption, respectively. The two-step absorption process of the indirect bandgap material that involves the phonon absorption/emission will be a disadvantage

compared to the single step process of a direct bandgap material, particularly for high frequency applications. Figure 2-2 shows the absorption coefficients of some direct and indirect bandgap semiconductor as a function of the photon wavelength, where the difference of the bandgap type can be observed from the abruptness of the absorption coefficient cutoff [48].

Fig. 2-2 Absorption coefficients of indirect and direct bandgap semiconductors are plotted as a function of the photon wavelength and light penetration depth.
(Taken from Senior [48])

2.2 Device Physics of the p-i-n Photodiode

Based on the relevant absorption mechanism, semiconductor photodetectors can be divided into two types, the intrinsic and extrinsic photodetectors. An intrinsic photodetector uses band-to-band transition, which requires the photon energy to be equal to or larger than the bandgap energy of the absorbing layer. In an intrinsic photodetector, the long wavelength cutoff λ_c is determined by the bandgap of the intrinsic material (E_g) using,

$$\lambda_c = \frac{hc}{E_g} \tag{2-4}$$

where, c is the velocity of light in vacuum and h is the Planck constant. Figure 2-3 shows typical quantum efficiency/responsivity spectra of some *p-i-n* PDs with different intrinsic materials. The figure also shows the long wavelength cutoff of the

Fig.2-3 Quantum efficiency of different photodetector materials plotted against the photon wavelength. (from Senior [48])

responsivity spectra, λ_c , which determines the working spectra of the photodetector. On the other hand, an extrinsic photodetector detects photon energy by means other than the band-to-band transition. This can be accomplished by using intra-band transitions such as the Si/Ge multiple quantum well (MQW) structures [49,50] or impurity/defect-level-to-band transition such as LT-GaAs [51]. However, these extrinsic photodetectors involve a more complicated designs such as resonant cavity enhanced photodetectors or phototransistors due to its low responsivity [49-51]. In addition, the purpose of this thesis is to study the intrinsic properties of the dilute nitride material GaAsSbN for optical communication applications.

In this thesis, we focused on the intrinsic photodetector using the *p-i-n* PD structure shown in Figure 2-4, which was chosen for the following reasons. First, *p-i-n* PD is one of the most common structures used in the commercial optical communication photodetectors. The structure was chosen due to its simplicity in terms of growth and fabrication processes. Second, the *p-i-n* PD structure provides a suitable test structure that enables further study of the material properties of GaAsSbN. Detailed information on the *p-i-n* PD and its design considerations presented in this chapter can also be found in a number of references [48,52,53].

The underlying physics of the *p-i-n* PD can be described as follows: when photons with sufficient energy were absorbed, electron-hole pairs (EHP) will be generated within the i-layer. The photo-generated carriers will travel across the i-layer due to the drift mechanism for EHP generated within the reverse bias electric field or diffusion mechanisms for the EHP generated at the p^+ and n^- layers. Subsequently, these photo-generated carriers will be collected at the ohmic contacts and injected into

Fig.2-4 The typical band diagrams of a GaAs/ GaAsSbN/ GaAs heterojunction *p-i-n* PD are shown under **(a)** equilibrium condition and **(b)** under reverse biased condition. E_c , E_f , and E_v denote the conduction band, Fermi level, and valence band, respectively.

an external circuit. The theoretical band diagram for GaAs/ GaAsSbN/ GaAs *p-i-n* PD in equilibrium and under reverse bias condition are shown in Figure 2-4. For top-illuminated GaAs/ GaAsSbN/ GaAs heterojunction *p-i-n* PD, the top GaAs layer is transparent to the 1.3 μm wavelength. Consequently, the diffusion current contribution caused by photo-generation of carriers in the GaAs layers is considered negligible. Therefore, most of the photon absorption occurs within the undoped GaAsSbN i-layer.

As a measure of how effective the conversion from photon energy to electrical energy, the term quantum efficiency was introduced. The quantum efficiency (η) of a photodetector is defined as the fraction of incident photons that was turned into electrical carriers [52]. If r_e is the carrier generation rate (electron/second) and r_p is the photon arrival rate, then the quantum efficiency can be written as,

$$\eta = \frac{r_e}{r_p} \quad 2-5$$

However, this expression of η does not contain the information of photon energy and wavelength. The responsivity (R) is more often used as a measure of how sensitive the photodetector is to photon excitation. The photodetector responsivity (R) is defined as the ratio between the photocurrent (I_p) with the incident photon power (P_o),

$$R = \frac{I_p}{P_o} \quad 2-6$$

Assuming monochromatic incident radiation, the incident photon rate, r_p , can be obtained from the incident photon power (P_o) as,

$$r_p = \frac{P_o}{h\nu} \quad 2-7$$

Thus, the photocurrent can be expressed in terms of quantum efficiency and the incident photon rate as,

$$I_p = \eta r_p \cdot q = \eta \frac{P_o q}{h\nu} \quad 2-8$$

where q is the electron charge, h is the Planck's constant, and ν is the photon frequency. Therefore, the quantum efficiency of a photodetector is directly proportional to its responsivity, as shown in this expression below,

$$R = \frac{I_p}{P_o} = \eta \frac{q}{h\nu} \quad 2-9$$

Since the absorption of 1.3 μm light that occurs at the top GaAs layer is assumed negligible, the portion of the incident photon energy absorbed along the i-layer is greatly influenced by the absorption coefficient of the i-layer (α), the i-layer thickness (w), and the Fresnel reflection coefficient at the semiconductor-air interface (r). Thus, the photocurrent can be expressed in the following manner,

$$I_p = \frac{qP_o}{h\nu} (1-r)(1-e^{-\alpha w}) \quad 2-10$$

Using equation 2-8 and 2-10, the relation between the quantum efficiency and the absorption coefficient of the i-layer (α),

$$\eta = (1-r)(1-e^{-\alpha w}) \quad 2-11$$

The other important characteristic of the p - i - n PD is the bandwidth, which depends on the transit time and the diode capacitance of the device. The transit time depends on the carrier velocities and electric field across the depletion region. Assuming the electric field is such that the i-layer is completely depleted, transit time-limited bandwidth of a p - i - n PD structure can be approximated from the i-layer thickness (w) and the carrier saturation velocity (v_{sat}) using,

$$f_{tr} = 0.45 \frac{v_{sat}}{w} \quad 2-12$$

On the other hand, the capacitance-limited bandwidth can be related to the device area (A) and i-layer thickness (w) by,

$$f_{RC} = \frac{1}{2\pi R \left(\epsilon_r \epsilon_0 \frac{A}{w} \right)} \quad 2-13,$$

where, R is the total resistance of the device, ϵ_r is the dielectric constant of the intrinsic material and ϵ_0 is the permittivity in vacuum. The total response time of a p-i-n PD can be approached by the mean square root of the sum of its transit time component, the diffusion component, and the RC time constant [54]. Since the diffusion component is neglected for reasons that has been mentioned above, the total frequency response can be calculated using Eq. 2-14,

$$\frac{1}{f_{3dB}} \approx \sqrt{\left(\frac{1}{f_{tr}} \right)^2 + \left(\frac{1}{f_{RC}} \right)^2} \quad 2-14$$

where, f_{tr} and f_{RC} were obtained from equations 2-13 and 2-14, respectively, using $v_{sat} = 6 \times 10^4 \text{ m.s}^{-1}$, which is room temperature hole saturation drift velocity for GaAs, $R = 50 \text{ } \Omega$, and $\epsilon_r = 12.4$.

Figure 2-5 shows the calculated bandwidth (f_{3dB}) of a GaAs homojunction *p-i-n* PD with different mesa diameters based on Equation 2-14. The dashed line is the calculated transit time-limited bandwidth (f_{tr}). Comparison between equation 2-11 and 2-14 shows a trade-off between the quantum efficiency and bandwidth, the former increases with i-layer thickness while the latter decreases with i-layer thickness. This trade-off is the characteristic of the top illuminated *p-i-n* PD structure. The low quantum efficiency can be improved using a resonant-cavity-enhanced (RCE) structure, where the i-layer was sandwiched by two reflectors. The quantum efficiency vs. bandwidth trade-off can be avoided by using edge-illuminated waveguide structure. In this structure, the light path is perpendicular with the current

Fig. 2-5 The calculated bandwidth (f_{3dB}) of GaAs homojunction $p-i-n$ PD with mesa diameters of 40, 80, and 200 μm are plotted against its intrinsic layer thickness. The dashed line is the calculated transit-time limited bandwidth.

paths, which allows the bandwidth and quantum efficiency to be optimized independently. Although these alternative structures are potentially better in terms of quantum efficiency or bandwidth optimization [53], the details of such study are beyond the scope of this thesis.

2.3 Prediction of Bandgap Energy of GaAsSbN

Due to great urgency in the study of dilute nitride materials for laser diode applications, bandgap energy calculation of dilute nitride materials may have been overlooked in the early studies of dilute nitride materials. It was assumed, like any other III-V ternary and quaternary materials systems, the bandgap energy of dilute nitride materials could be extrapolated using the bandgap energy of the constituent

binary materials and a parameter known as the bowing coefficient. For GaNAs, that equation can be written as follows,

$$E_g(\text{GaN}_x\text{As}_{1-x}) = xE_g(\text{GaN}) + (1-x)E_g(\text{GaAs}) - x(1-x)b \quad 2-15$$

where, x is the N atomic concentration, $E_g(\text{GaN})$ and $E_g(\text{GaAs})$ are the binaries bandgap energy, and b is the bowing factor. In 1993, Sakai *et al.* [55] used $b = 11$ eV to fit the data points of GaNAs samples from Ref. [5]. However, this prediction turns out to be inaccurate as the calculation overestimates the decrease of the bandgap energy of GaNAs for N concentration over 2%. In 1997, Bi and Tu conducted transmission measurement of GaNAs samples with N content up to 15% and observed a composition-dependent bowing factor [56]. However, the accuracy of these empirical models relies on the availability of the experimental data points, which is a drawback due to the difficulty in obtaining GaNAs of good quality with high N atomic concentration.

Similar problem also existed in the bandgap prediction of the dilute nitride quarternary materials. A phenomenological empirical model to calculate the bandgap energy of GaInNAs lattice-matched to GaAs was proposed by Chow *et al.* [7]. In this model, the bandgap reduction due to the addition of N to GaInAs was approached by the difference of lattice mismatch between GaInNAs and GaInAs for a given indium concentration and multiplied by a fitting constant, C . The phenomenological equation modified for GaAsSbN can be described as follows,

$$E_g(\text{GaN}_x\text{As}_{(1-x-y)}\text{Sb}_y) = E_g(\text{GaAs}_{(1-y)}\text{Sb}_y) - C \times \Delta e(x, y) \quad 2-16$$

where, $E_g(\text{GaAsSbN})$ and $E_g(\text{GaAsSb})$ are the bandgap energy for GaAsSbN and GaAsSb, respectively. The $\Delta e(x, y)$ is the mismatch difference between GaAsSbN and

GaAsSb, which can be obtained from the lattice constants of the ternary and quaternary materials from the following relation:

$$\Delta e(x, y) = \left[\left(\frac{a_{GaAs} - a_{GaN_xAs_{(1-x-y)}Sb_y}}{a_{GaN_xAs_{(1-x-y)}Sb_y}} \right) - \left(\frac{a_{GaAs} - a_{GaAs_{(1-y)}Sb_y}}{a_{GaAs_{(1-y)}Sb_y}} \right) \right] \quad 2-17$$

where, x and y are the atomic concentrations of N and Sb, respectively. However, this approximation of the GaAsSbN bandgap energy does not take into account the composition-dependant bowing coefficient properties of dilute nitride.

In 1999, Shan and Walukiewicz proposed the band anticrossing (BAC) theory to explain the anomalous bandgap reduction of dilute nitride materials [57]. Due to the large electronegativity of N atoms (3.0 eV), addition of a small atomic concentration of N to GaAs will induce a highly localized N level (E^N) located above the GaAs conduction band minima. As shown in Figure 2-6, E^N appears to intersect with the GaAs conduction band. This is not possible according to the Pauli's Exclusion principle, thus the two bands will "anti-cross" and form two energy levels (E_+ and E_-) because of this interaction. The presence of E^N will split the GaAs conduction band into two levels E_+ and E_- , where E_- becomes the new conduction band minima. With increasing N atomic concentration, the repulsion between the E_+ and E_- levels increases. Thus, the separation between them increases and reduces the effective bandgap energy further. The band anticrossing model concentrates more on the effect of nitrogen incorporation on the conduction band, which explains the lack of influence of the nitrogen atoms on the valence band. The two hybrid levels, E_+ and E_- can be calculated by,

$$E_{\pm} = \frac{1}{2} \left(E^N + E^C \pm \sqrt{(E^C - E^N)^2 + 4V_{MN}^2 x} \right) \quad 2-18$$

Fig.2-6 Band diagram illustration of the nitrogen state (E^N) shows it splits the GaAs conduction band (E^C), which “anti-cross” with each other and form two energy levels E_- and E_+ . (After Vurgaftmann *et al.* [58])

where, E^C and E^N are the unperturbed conduction band minima of the non-nitride binary/ternary material and the N isoelectronic impurity level with respect to the valence band, respectively [58]. V_{MN} is the matrix element describing the interaction potential between E^C and E^N and x is the nitrogen concentration. Literatures [58-60] on GaAsSbN have reported varying V_{MN} values ranging between 2.7 to 3.44. E^C can be calculated from the bandgap equation of GaAsSb, while the position of E^N with reference to the valence band maxima is determined by the Sb composition (y), and the recommended relation [58] for E^N in GaAsSbN is,

$$E^N = 1.65(1-y) + 1.44y - 0.38x(1-y) \quad 2-19$$

Figure 2-7 displays the calculation results using the BAC model and the phenomenological equation for lattice-matched GaAsSbN plotted against the atomic concentration of N. The bandgap energy of GaAsSb required for the calculation can be obtained from the work of Teissier *et al.* [61], which is best fitted for GaAsSb/GaAs with Sb concentration $y < 30\%$,

$$E^C = E_g(GaAs_{(1-y)}Sb_y) = 1.43 - 2.24y + 1.97y^2 \tag{2-20}$$

Experimental data points from various literatures [62-64] on closely lattice-matched GaAsSbN/GaAs with different N content were included for curve fitting. By using the least-squared error method, we obtained fitting constants of $C = 69.7 \text{ eV}$ and $V_{MN} =$

Fig.2-7 Calculated bandgap of lattice-matched GaAsSbN using the BAC model (solid line) and phenomenological equation (dashed line). More than 2% of N is required to achieve bandgap energy of 0.95 eV.

3.18 eV. As seen from the figure, the difference between the phenomenological approach and the BAC model lies in the bowing of the bandgap energy of GaAsSbN as a function of the N concentration. The phenomenological approach shows a single bowing coefficient behavior, while the BAC model shows a reduced bowing coefficient with increasing N concentration. This explains the crossover point at $x \sim 2.5\%$, where the bandgap reduction predicted by the BAC model is smaller than what is predicted by the phenomenological approach.

Despite the simplicity of the BAC model, the extent of dilute nitride material physics that can be explained with this model is still a matter of debate. For example, the observation of strong bowing in the valence-band shear deformation potential in GaNAs [65] contradicts the proponents of the BAC model, who believe in a weak N-induced valence band perturbation. Furthermore, pseudopotential calculations results suggests that the interaction between the E^N nitrogen level with the Γ , L , and X bands played a significant part in the reduction of the bandgap [66,67]. The proponents of this “band-mixing” theory suggest that the bandgap redshift will be strongly dependent of the atomic arrangement of the N atoms. A more complete picture of the effect of N was offered by Kent and Zunger [68,69], who suggest that the bandgap reduction must take into account not only the band anti-crossing and the band mixing, but also the interaction with N clusters states. Such detailed discussions require theoretical calculation involving first-principles calculation that is beyond the scope of this thesis.

2.4 Epitaxial Growth and the Epilayer Critical Thickness

The root of the word “epitaxy” originated from two Greek words, “*epi*” which means placed or resting upon, and “*taxis*”, which means arrangement. Thus, the word “epitaxy” can be used to describe deposition or “growth” of crystalline layer on top a crystalline substrate. As illustrated in Figure 2-8, epitaxial layer growth on a substrate with identical lattice parameter with the layer is called homoepitaxy (i.e. GaAs/GaAs), while the term heteroepitaxy was used to describe epilayer growth on a substrate with different lattice parameter (i.e. GaInAs/GaAs, GaAsSb/GaAs). In heteroepitaxy, the mismatch in lattice parameter will be accommodated by straining the epitaxial layer (pseudomorphic epilayer) or by formation of defect dislocations (relaxed epilayer). Transition from pseudomorphic growth to dislocation-accommodated growth takes place after the epilayer exceeds the critical thickness, h_c .

Matthews and Blakeslee proposed a model to calculate the critical thickness of a single epitaxial layer using a force balance approach [70]. They defined h_c as the epitaxial layer thickness where accommodation of the lattice mismatch by straining the epitaxial layer becomes larger than the force of the line tension due to a misfit dislocation. Critical thickness of a single epitaxial layer according to Matthews and Blakeslee (MB) can be described as follows,

$$h_c = \frac{b(1 - \nu \cos^2 \theta)}{2\pi f(1 + \nu)\cos \phi} \ln\left(\frac{h_c}{b} + 1\right) \quad 2-21$$

where f is the lattice mismatch, ν is the Poisson ratio, θ is the angle between the dislocation line and the Burgess vector (b) = 4 Å for GaAs substrate, and ϕ is the angle between the slip direction and the direction in the epilayer plane that is perpendicular

to the line of intersection between the slip plane and the interface. The values for ϕ and θ for $\langle 001 \rangle$ growth [71] are $\theta = \phi = 45^\circ$.

Fig.2-8 Illustration of homoepitaxy and heteroepitaxy layers, as well as the lattice relaxation when a heteroepitaxy layer was growth beyond its critical thickness, h_c .

Another model which is widely used to predict the critical thickness of a pseudomorphic epitaxial layer was proposed by People and Bean [72]. Their definition of h_c is the thickness where the areal energy density of misfit dislocation exceeds the areal energy density of the strained epitaxial layer. The critical thickness according to People and Bean (PB) can be correlated with the Poisson ratio (ν) and the lattice mismatch (f) in the following manner,

$$h_c \cong \left(\frac{1-\nu}{1+\nu} \right) \left(\frac{1}{16\pi\sqrt{2}} \right) \left[\frac{b^2}{a(x,y)} \right] \left[\left(\frac{1}{f^2} \right) \ln \left(\frac{h_c}{b} \right) \right] \quad 2-22$$

where, $a(x,y)$ is the lattice constant of the epitaxial layer, and b is the burgers vector = $4\text{\AA}$ for GaAs. The difference between equations 2-22 and 2-23 can be seen clearly in the correlation between the critical thickness and the lattice mismatch (f). The MB model has $h_c \propto f^{-1}$, while in the PB-model $h_c \propto f^{-2}$. Figure 2-9 shows the calculated critical thickness using the two models, where the critical thickness calculated by the PB model appears to be two orders higher than what is obtained from the MB model. This is expected because the MB model assumes that after the critical thickness is exceeded, the formation of misfit dislocation is energetically preferred to relieve the strain in the epilayer, while the PB model assumes all the strain in the epilayer will be replaced by misfit dislocation once the critical thickness is exceeded [73].

Because these models were developed for SiGe/Si heteroepitaxy, their application on III-V material systems has yielded varying results. Several literatures suggested that their results is in agreement with the MB-model [74,75], while others suggest that the critical thickness has f^{-4} dependence [76] or $f^{-3/2}$ dependence [77]. It was also suggested that the temperature stress has a profound effect on the critical thickness of SiGe/Si and GaInAs/GaAs systems [78]. Results on dilute nitride materials also vary, some reported critical thickness exceeding the predicted value from the MB-model [31,79,80], while other reported critical thickness lower than the predicted value of MB-model [81]. These varying results obviously indicate that growth parameters have a major influence on the critical thickness. Surprisingly,

some of the works in the strained GaAsSbN/GaAs quantum wells(QW) by Harmand *et al.* [38,39,82] and Luo *et al.* [44], did not report the critical thickness model that they used. The critical thickness models presented in this section was used as a guide to complement the GaAsSb epilayer XRD study in Chapter IV.

Fig.2-9 Calculated critical thickness obtained by the MB-model (Eq.2-21) and PB-model (Eq.2-22) plotted against the lattice mismatch (f) between the fully strained film and the substrate.

CHAPTER III Growth and Characterization Techniques

This chapter consists of two parts; the first part is a brief overview on the solid source molecular beam epitaxy (SS-MBE) growth technique. This includes literature studies on the usage of r.f. N-plasma source and Sb valved cracker cell used in this thesis. The second part consists of two of the main characterization techniques used in this thesis, which are x-ray diffraction (XRD) and deep level transient spectroscopy (DLTS).

3.1 Solid source Molecular Beam Epitaxy (SS-MBE)

Solid source molecular beam epitaxy (SS-MBE) is a technique of epitaxial growth where the constituent elements are evaporated, and travel towards the crystalline substrate in a beam-like manner. This property of MBE is what separates it from any other vacuum evaporation methods due to its precise control of the atomic beams, which allow growth of high purity crystalline layers. This is due to the design of the MBE systems that allows the growth to take place in an ultra high vacuum (UHV) condition. In the vacuum evaporation theory, the term “mean free path” is used to define the average distance between collision of gas molecules or atoms. Assuming ideal gas conditions, the mean free path (L) can be derived using kinetic theory of gases to arrive at the following relation [83]:

$$L = \frac{RT}{\sqrt{2}\pi d^2 N_A P} \quad 3-1$$

where, R is the universal gas constant, T is the ambient temperature, d is the molecule diameter, N_A is the Avogadro's number, and P is the chamber pressure. It can be seen from this expression, that the mean free path is inversely proportional to the chamber pressure. For arsenic molecules with covalent bond radius of $\sim 120 \times 10^{-12}$ m, the mean free path (L) can be expressed as a function of the chamber pressure,

$$L \sim \frac{3 \times 10^{-6}}{P} \quad 3-2$$

where, P is the chamber pressure in Torr. MBE systems are equipped with complex pumping systems comprises of ion pumps, turbo pump, and Ti-sublimation pump to maintain this ultra high vacuum (UHV) condition. In addition, liquid N_2 cryopanel are strategically placed around the chamber to preserve the UHV condition during growth, where the typical pressure is $\sim 10^{-7}$ – 10^{-8} Torr. Based on Eq. 3-2, the λ value of a typical MBE chamber is in the order of tens of meters. This means no molecular collision will occur within the chamber walls as long as the chamber's wall to source distance does not exceed this λ value. The UHV environment of the MBE chamber ensures the evaporated molecules from the cells will travel in a beam-like manner.

Figure 3-1 shows the schematic of the SS-MBE growth chamber used in this work, with some of the major components such as:

- Standard Knudsen effusion cells for the group III elements (Ga, Al, In) and n-type dopant (Si). The materials are contained in high purity pyrolytic boron nitride (PBN) crucibles, which can withstand high temperature due to its high

dissociation temperature ($>1400\text{ }^{\circ}\text{C}$). Individual mechanical shutters are placed in front of the cells to achieve precise control of the beam fluxes.

- Valved-cracker cells were used for group V elements (As and Sb) due to their higher vapor pressure than the group III elements. The use of valved cell allows precise control and delivery of the group V flux while preventing quick depletion of the source materials.

Fig.3-1 Schematic of a typical SS-MBE system equipped with r.f. plasma N source, As and Sb valved-cracker cells. The system is equipped with *in-situ* characterization tools such as reflection high-energy electron diffraction (RHEED) and quadrupole mass spectrometer (QMS).

- Radio frequency N plasma source: High purity N_2 gas is cracked using the r.f. plasma, the resulting N atoms was used to form the dilute nitride (III-V-N) compound semiconductor epilayers.
- For p-type doping, a carbon tetrabromide (CBr_4) source was used (not shown in the diagram). Carbon is a very effective p-type dopant in GaAs with minimum out-diffusion compared to beryllium. The use of this carbon source setup has been extensively studied and reported in numerous publications [62,84,85].

In addition to the III-V and doping sources, the UHV environment allows in-situ characterization with reflection high-energy electron diffraction (RHEED) to monitor the surface reconstruction during growth and quadruple mass spectrometer (QMS) to monitor the atomic and molecular species inside the chamber. Moreover, the chamber is equipped with a complex assembly of substrate holder/manipulator that allows substrate heating, substrate rotation, and molecular beam flux measurement. The basic theory and fundamentals of MBE will not be discussed in detail in this thesis as it can be found in a number of references [86,87].

A. Radio Frequency (r.f.) Plasma Nitrogen Source

Nitrogen molecules have triple covalent bonds, which make thermal dissociation of N_2 to form atomic N extremely difficult. However, N_2 gas is a favorable N source for MBE systems as it is easily pumped out from an ultra high vacuum system and it does not possess additional elements that can behave as unwanted impurities. The r.f. plasma N source has been demonstrated as an

alternative method to crack the N_2 gas to grow III-V-N materials. In this work, an r.f. plasma N source (Applied EPI, Inc.) was used to crack high purity N_2 gas to “active N” flux. This active N flux can be in the form of N atoms, ions, or molecules (all of which can be in the excited state). The active N is regulated by pyrolytic boron-nitride disc at the end of the plasma source. A choice of PBN discs with 25, 50, 75, and 100 holes of 0.2mm diameter provide sufficient active N species while minimizing the damage caused by the ionic species. A mass flow controller (MFC) with a maximum flow of 10 standard cubic centimeters (SCCM) was mounted between the N_2 supply line and a precision leak valve. The precision leak valve completely isolates the N_2 line the UHV growth chamber during idle condition and the MFC offers precise control of the N_2 gas flow during epitaxial growth.

Different methods have been reported to improve the performance of this type of N source, with the dispersive N source method being one of the most prominent. One can simply put the shutter to block the direct active N species [88]. Another dispersive method is to use a valved r.f. plasma source. This is done by putting a moveable molybdenum plate in front of the orifice [38]. Regardless of the technique, a clear improvement of the GaNAs quality has been reported by using this dispersive method. The origin of this improvement may have been due to reduction of direct plasma damage during plasma ignition or blocking the non-dispersive active N species that is kinetically more energetic during the growth. Other modifications of the N source such as optical characterization of the plasma light to identify the active N species, installing the ion deflection plates to deflect ionic N species, or isolating the N source in a separate UHV chamber during plasma ignition have been proven useful to improve the performance of this r.f. plasma N source [89]. Nevertheless, such

modifications of N source are beyond the scope of this work. The author recommends the excellent PhD thesis by Adamcyk [89] for detailed information regarding this subject.

The position of r.f. plasma N source used in this work is not in-line-of-sight with the substrate. Although the position is beneficial in reducing the plasma damage caused by direct impingement of the energetic N species, the N incorporation obtained from this setup is somewhat compromised. The N incorporation in GaNAs using this r.f. plasma N source setup has been thoroughly characterized by Sun *et al.* [90]. The growth of the GaNAs layers done by Sun *et al.* and the growth of dilute nitride layers presented in this thesis were performed on an identical MBE chamber with similar growth parameters (i.e. growth temperature and As₄/Ga flux ratio). Therefore, direct comparison between the dilute nitride growths can be justified. Figure 3-2 shows the N concentration as function of (a) r.f. plasma power and (b) N₂ flux for GaNAs samples grown at 1 μm/hr and substrate temperature of 480 °C, as reported by Sun *et al.* [90]. The amount of the reactive atomic N species from the plasma source can be increased by increasing of the plasma power (Fig. 3-2a) and the N₂ flux (Fig. 3-2b). Furthermore, Sun *et al.* has observed the incorporation of N in GaNAs as a function of the growth rate and proposed a kinetic model of N incorporation, as illustrated by Figure 3-3. The dotted line assumes unity N sticking ratio, and the solid line is calculated from the kinetic model for N incorporation in GaNAs proposed by Sun *et al.* [90]. The reduction of growth rate leads to the increase of N concentration of up to 2.5%. The bandgap energy calculation in Chapter II suggested that to reduce the bandgap of lattice-matched GaAsSbN to 0.95 eV more than 2% of N is required. Therefore, the effect of growth rate on the N incorporation in GaAsSbN must be studied further.

Fig.3-2 N concentration obtained from GaNAs layer grown under different (a) r.f. power, and (b) different N_2 flux (After Sun *et al.* [90]).

Fig.3-3 Nitrogen concentration of the GaNAs plotted as a function of growth rate as reported by Sun *et al.* [90]. The dotted line is the predicted N concentration using the unity sticking assumption and the solid line is predicted using the kinetic model.

B. Valved Antimony Cracker Source

Valved cracker cells have been used for group V elements, as opposed to standard effusion cells, due to the higher vapor pressure of group V elements. The valve allows complete isolation of the cell from the growth chamber, allowing the operating temperature of the cell to be maintained without rapid depletion of the charge material. In addition, thermal dissociation of the group V tetramers (i.e. As₄ or Sb₄) to its dimers (As₂ or Sb₂) is necessary because the group V dimers' sticking coefficient is directly proportional to the Ga flux, whereas the maximum sticking ratio of the group V tetramers is only 0.5 [87]. The reason for the lower sticking ratio is

that when a group V tetramer arrives on the substrate, it has to be thermally dissociated into dimers in order to bond with the group III atoms on the substrate. However, only half of the thermally dissociated dimers will bond with the group III atoms. The other half of the dimers recombine into tetramer and evaporate from the substrate. The reaction for this surface thermal dissociation process for GaAs is as follows [87],

Similar reactions also occur in epitaxy growths involving antimony species. Thus, by having a group V cracker cell, the thermal dissociation of the group V tetramers will take place in the cracker instead of the substrate. The Sb cracker cell used in this work is divided into two regions, the bulk crucible region, where the charge material is evaporated, and the cracker region where the Sb_4 vapor can be further thermally dissociated into dimers (Sb_2) and/or monomers (Sb_1). The corrosive nature of antimony vapor has rendered the use of metallic crucible and valve components unreliable and unsuitable for UHV application. For that reason, components made out of high purity PBN are used in this valved antimony cracker cell.

Figure 3-4a shows the schematics of Sb PBN-crucible that consists of a 200cm^3 high-purity PBN bulk crucible region containing elemental antimony, which narrows to a thin neck that serves as the cracking region. The cracking region is terminated by a valve that is also made from high-purity PBN. Precise control of the flux is made

possible with the automatic valve positioner that shows reproducible flux at specific valve position for a given cell and cracker temperature and rapid stabilization of flux after valve opening and closing [91]. The temperature of the cracking region determines the cracking efficiency of Sb_4 , as shown by Fig.3-4b, Sb_4 will be completely dissociated thermally at cracker temperature $> 800\text{ }^\circ\text{C}$, where cracker temperature of $900\text{ }^\circ\text{C}$ gives the best GaAsSb PL intensity [92].

3.2 High Resolution X-ray Diffraction (HR-XRD)

Structural characterization by x-ray diffraction has a distinct advantage of being a non-destructive characterization. The x-ray diffraction from crystal planes is governed by the Bragg Law:

$$\lambda = d_{hkl} \sin 2\theta \quad 3-3$$

where λ is the x-ray wavelength, θ is the diffraction angle, and d is the spacing between (hkl) planes, which for cubic crystal was determined by:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad 3-4$$

where, a is the lattice constant of the cubic crystal, and the h , k , and l are the Miller indices number corresponds to the (hkl) plane. The XRD measurements carried out on this thesis are performed on a high-resolution x-ray diffractometer with a triple-axis stage. The x-ray source is generated by using the $\text{K}\alpha_1$ of Cu with photon energy of 8.05keV corresponding to x-ray wavelength of $1.54056\text{\AA}$. The atomic concentration of the ternary materials are obtained by fitting the (004) rocking curves with the simulated curve generated by the X'Pert Epitaxy simulator based on the dynamical diffraction theory work of Halliwell *et al.* [93].

Fig.3-4 (a) Schematics of the Sb valved cracker cell entirely made out of pyrolytic boron nitride (From Hall *et al.* [91]). (b) Sb monomers, dimers, and tetramers fraction plotted as a function of cracking zone temperature. For cracker temperatures exceeds 800°C, the tetramers are completely cracked into monomers and dimers. (From Brewer *et al.* [92])

In the (004) diffraction for epitaxial layers grown on (001) oriented substrates, the spacing of (004) planes is given by $a_{\perp}/4$ where $a_{\perp}$ is the lattice parameter in the epitaxial layer growth direction. Normally in this direction, the tilt is negligible and the mismatch of the epitaxial layer is given by,

$$\left(\frac{\Delta a}{a}\right)_{\perp} = \frac{a_{\perp} - a_s}{a_s} = \frac{\sin \theta_B}{\sin(\theta_B + \Delta\theta)} - 1 \quad 3-5$$

where a_s is the lattice constant of the substrate, θ_B is the Bragg angle corresponding to the substrate and $\Delta\theta$ is the measured separation-angle between the Bragg peaks of the substrate and the epilayer. For $\Delta\theta \ll 2/(\tan \theta_B + 2)$, the mismatch of the epitaxial layer can be rewritten as follows,

$$\left(\frac{\Delta a}{a}\right)_{\perp} = \frac{a_{\perp} - a_s}{a_s} = -\frac{\Delta\theta}{\tan \theta_B} \quad 3-6$$

Equation 3-6 shows if there is no relaxation on the epilayer, the perpendicular lattice mismatch is proportional to $\Delta\theta$, the angular separation between the (004) Bragg peaks of the substrate and the epilayer. This is illustrated clearly in Figure 3-5, where (004) XRD rocking curve of fully strained GaAsSb epilayer grown on (001) GaAs substrate with similar epilayer thickness (~ 1000 Å) and different Sb concentrations.

The information from a symmetrical scan such as the (004) rocking curve, however, will be inaccurate when epilayer relaxation occurs. This is due to broadening and XRD peak-shift caused by the relaxation-induced lattice parameters distortion. Therefore, to obtain the lattice parameters perpendicular and parallel to the substrate, an asymmetrical XRD mapping of the (115) or (224) crystal is required. The XRD mapping can be constructed by repeatedly scanning the ω - 2θ scans with different ω offsets angle ($\Delta\omega$). A 2-D intensity contour map around the reciprocal lattice points of the substrate and the epilayer can be obtained. The separation of the ω - 2θ and $\Delta\omega$ between the substrate peak and the epilayer peak can be used to calculate the perpendicular and parallel lattice parameter mismatch using the following equation [94,95],

Fig.3-5 (004) XRD rocking curves of 1000 Å GaAsSb epilayers with different Sb concentration grown on (004) GaAs substrate. The Sb concentrations are obtained from curve fitting.

$$\Delta\psi = \tan^{-1}(\sqrt{2}/5) - \tan^{-1}(\sqrt{2}a_{\perp}/5a_{\parallel}) \quad 3-7$$

$$a_{\perp} = a_{\parallel} + ((C_{11} + 2C_{12})/C_{11})(a_0 - a_{\parallel}) \quad 3-8$$

where, $a_{\parallel}$ is the lattice parameter parallel to the substrate, C_{11} and C_{12} are the elastic constants of the epilayer, a_0 is the lattice constant of the epilayer, and $\Delta\psi$ are the $\Delta\omega$ axis separation between the substrate and epilayer peaks. Figure 3-6a shows the asymmetrical XRD ($\omega-2\theta$) vs. $\Delta\omega$ 2D contour plot or map around the (115) diffraction peaks from a GaAsSb epilayer grown on GaAs (001) substrate. Subsequently, one can plot the asymmetrical XRD map in a reciprocal space axes, where the horizontal ($q_{[\bar{1}0]}$) and vertical ($q_{[001]}$) axes are in reciprocal lattice units

$(10^4 \times \text{\AA}^{-1})$. This can be seen in Figure 3-6b, where $q_{[1\bar{1}0]}$ represents the $[1\bar{1}0]$ plane perpendicular to the substrate, and $q_{[001]}$ represents the $[001]$ plane parallel to the substrate. The position of the epilayer diffraction peak relative to the substrate peak on the asymmetrical XRD map can be used to determine the degree of relaxation of the epilayer. The epilayer peak and GaAs peak shown in Fig. 3-6b are located directly on one vertical line in the RSM, indicating similar in-plane lattice parameter ($a_{\parallel}$) between the epilayer and the GaAs substrate. This suggests that the epilayer is pseudomorphically grown on the GaAs substrate.

Fig.3-6 Asymmetrical (115) XRD mapping result of ~1000 Å-thick GaAsSb layer grown on GaAs plotted in (a) ω - 2θ vs. $\Delta\omega$ axes and (b) perpendicular vs. parallel reciprocal lattice direction.

3.3 Defects in Dilute Nitride Material

The study of defect states in GaAsSbN are still lacking compared to the studies on GaNAs and GaInNAs. Recent x-ray absorption fine-structure (XAFS) experiment on the Sb K-edge x-ray absorption of GaAsSbN/GaAs samples has shown evidence of Sb-Sb short range order clustering [96]. However, further reports on the defects related to other constituent elements have not been reported. Furthermore, first-principles calculation simulation results on the formation energy of the native defects in GaAsSbN and the effect of those defects on the band structure are currently not available for reference. Thus, it has to be assumed that some of the native defects present in GaAs, GaAsSb, GaNAs, and GaInNAs can be found in GaAsSbN given the similar growth conditions and group V elements. For instance, As_{Ga} (As atom found in the Ga site) is a form of antisite defects that is commonly found in GaAs and low temperature grown (LT)-GaAs [97-101]. Another point defect, Sb_{Ga} , has been reported in GaAsSb growth [102-104]. In addition, first-principles calculations have predicted the formation of N-N split interstitials, N-As split interstitials, or nearest neighbor pairs such as $\text{As}_{\text{Ga}}\text{-N}_{\text{As}}$ and $\text{V}_{\text{Ga}}\text{-N}_{\text{As}}$ to be the native defects in GaNAs [105-107]. One of the results [107] suggests shallow acceptor level related to Ga vacancies (V_{Ga}) at 0.03–0.18eV above the valence band maximum (VBM) of GaNAs.

Experimental results have corroborated the presence of these defects in dilute nitride materials. N-As and N-N split interstitials in GaNAs have been detected indirectly by combination of secondary ions mass spectroscopy (SIMS) and high resolution x-ray diffraction (HR-XRD) of GaNAs. These defects are responsible for the deviation of Vegard's Law in GaNAs with N concentration >2.5% [108,109].

Positron-annihilation measurement and nuclear reaction analysis (NRA) on Rutherford backscattering spectroscopy (RBS) experiments have shown traces of N interstitials and gallium vacancies in GaNAs and GaInNAs [108,110,111]. Optically-detected magnetic resonance (ODMR) measurement has also found evidence of As_{Ga} in GaNAs [112-117].

The presence of the As_{Ga} and V_{Ga} in dilute nitride material are expected due to the similarities of its growth conditions with the low temperature (LT)-GaAs [100]. The GaAsSbN i-layer was also grown at low temperature ($<500^{\circ}C$) under As-rich condition to prevent Ga-N phase separation and promote two-dimensional (2D) layer-by-layer growth [20]. In fact, LT-GaAs grown at $400^{\circ}C$ have been reported with high concentration of the EL2 midgap defects ($\sim 10^{19} \text{ cm}^{-3}$) [98]. The presence of this midgap defect are expected in GaInNAs and GaAsSbN, as similar EL2 defects have been observed in GaNAs [118].

Recently, DLTS was also used to study the presence of defects in closely lattice-matched GaInNAs absorption layer with the bandgap of 1eV for multi-junction solar cells [11,119-123], base material in n-p-n GaAs-based heterojunction bipolar transistor (HBT) [124], and i-layer in GaAs-based photodiode [125]. The presence of a midgap trap along with some N-related shallow traps have been found to exhibit non-localized defect behavior that indicate continuous distribution of states or discrete but closely-spaced energy levels [126-128]. Although several authors suggest that the midgap defect state may have resembled the EL2 defect [123,124], theoretical or experimental studies on GaAsSbN are still lacking.

A. Deep Level Transient Spectroscopy

Deep level transient spectroscopy (DLTS) is an effective characterization method to study the electrical properties of deep levels in a semiconductor layer. The method is proposed by Lang [129] based on the depletion region transient capacitance measurement during impurity charge transfer in a one-one sided p-n junction or a Schottky diode. Figure 3-7 shows a one sided p-n junction under a quiescent reverse bias voltage. A majority carrier pulse was introduced by reduction of the reverse bias voltage for the duration of t_p . The application of the filling pulse reduces the depletion width and fills the previously empty deep levels with carriers. After the carrier injection pulse, the trapped carriers will be thermally emitted, changing the capacitance in the process. A more detailed explanation on the carrier capture and emission involving a deep level and the extraction of trap parameters from the DLTS measurement can be found in the PhD thesis of Kaplar [122].

Fig.3-7 After the introduction of the filling pulse, carrier capture, and the subsequent emission by a defect level which lead to a capacitance transient (After Lang [129]).

B. DLTS Fundamentals

In general, the thermal emission rate of the carriers (e) can be expressed as the emission time constant,

$$\frac{1}{e} = \tau_n = \frac{1}{\sigma_n \langle v_{th} \rangle N_c} \exp\left(\frac{E_T - E_C}{kT}\right) \quad 3-9$$

where, e is the electron emission rate, τ_n is the electron emission time constant, k is the Boltzmann constant, $(E_T - E_C)$ is the activation energy of the trap with reference to the conduction band, σ_n is electron capture cross-section, $\langle v_{th} \rangle$ is electron thermal velocity and N_C is the effective density of states of conduction band. The product of v_{th} and N_c can be rewritten in the following manner,

$$\langle v_{th} \rangle N_C = \left(\frac{3kT}{m_e^*}\right)^{1/2} 2 \left(\frac{2\pi m_e^* kT}{h^2}\right)^{3/2} = \gamma_e T^2 \quad 3-10$$

where, $\gamma_e = 3.256 m_e^* \times 10^{21} \text{ cm}^{-2} \text{ s}^{-1} \text{ K}^{-2}$, and m_e^* is the electron effective mass ratio.

By conducting the measurement in a cryostat, one can vary the temperature of this carrier emission at a constant rate window, as shown in Figure 3-8a, to obtain the time constant of the capacitance transient at the temperature where the DLTS peak occurs. This time constant (τ_{max}) is given by,

$$\tau_{max} = \frac{t_1 - t_2}{\ln(t_1/t_2)} \quad 3-11$$

Fig.3-8 After Lang [129], (a) DLTS peak can be obtained from the capacitance difference between two sampling points. (b) DLTS spectra of two hole traps in GaAs taken at different rate windows.

where, $t_1 - t_2$ is the rate window of the transient measurement. Thus, by changing the rate window, the temperature where $\tau_{\max}$ occurs will shift, just as

demonstrated in Figure 3-8b. The $(\tau_{\max}, T(\tau_{\max}))$ data points can be correlated with the trap parameters by substituting Eq. 3-9 to 3-8, thus obtaining the Arrhenius plot,

$$\ln(\tau T^2) = \frac{E_a}{kT} - \ln(\sigma_{\infty} \gamma_n) \quad 3-12$$

where, τ is the electron emission time constant, T is the absolute temperature, E_a is the activation energy of the trap, σ_{∞} is the carrier capture cross-section, k is the Boltzmann constant, $\gamma_n = 3.256 m_n^* \times 10^{21} \text{ cm}^{-2} \text{ s}^{-1} \text{ K}^{-2}$, and m_n^* is the electron effective mass ratio.

The activation energy of the trap can be obtained from the gradient of and the capture cross-section can be obtained from the intercept with the y-axis of the plot of $\ln(\tau T^2)$ vs. $1/T$. In addition, the activation energy obtained from the Arrhenius analysis is often referred to as the apparent activation energy, which is the sum of the true activation energy and the cross-section activation energy [127]. This cross-section activation energy ΔE_{σ} can be correlated to the carrier capture cross section by:

$$\sigma(T) = \sigma_{\infty} \exp(-E_{\sigma}/kT) \quad 3-13$$

where k is the Boltzmann constant and T is the temperature where the DLTS signal maxima occurs. Substituting Eq. 3-13 to Eq. 3-12, one will obtain,

$$\ln(\tau_n T^2) = \frac{E_C - E_T + E_{\sigma}}{kT} - \ln(\gamma_n \sigma_n^{\infty}) \quad 3-14$$

Thus, the carrier capture cross section $\sigma(T)$ is needed to obtain the true activation energy and E_{σ} of the trap. Assuming the trap is an ideal point defect, the change of capacitance as a function of the filling pulse duration (t_p) in an isothermal measurement has a distinct exponential shape,

$$\Delta C_0 = \Delta C_0^\infty \left[1 - \exp(-\sigma_n \langle v_{th} \rangle n t_p) \right] \quad 3-15$$

where, ΔC_0^∞ is the saturated amplitude of the capacitance transient at $t_p = \infty$ and n is the electron concentration. The plot of $\ln(1 - \Delta C_0 / \Delta C_0^\infty)$ vs. t_p has a slope proportional to the capture cross-section, which can be obtained by measuring the change of capacitance with different t_p at the temperature of $\tau_{\max}$. One can obtain the true activation energy of the trap using the carrier capture cross-section σ_n and cross-section energy E_σ on equations 3-13 and 3-14, respectively.

C. Experimental Setup

To investigate the deep level defect states in the GaAsSbN intrinsic layer, DLTS measurements was carried out on GaAs/GaAsSbN/GaAs *p-i-n* structure using a BIO-RAD DL8000 system. The BIO-RAD DL8000 system is a PC-driven, software-based, digital system. It applies a technique in which capacitance-time transients are digitized and discrete Fourier coefficients are formed via numerical transformation. This method is often referred as the deep level transient Fourier spectroscopy (DLTFS) method, which is based on the work of Weiss and Kassing [130]. The capacitance measurements were carried out using a 1 MHz Boonton bridge capacitance meter. The transient measurements were conducted by sampling N discrete equidistant capacitance data with Δt as the sampling interval, within the period width (T_w). The relaxation of the depletion width gives rise to a capacitance transient and the transient is sampled in N discrete equidistant times $k\Delta t$, $k = 0, 1 \dots N-1$. Δt is the sampling interval. The period width $T_w = N\Delta t$ contains N intervals with $N+1$ real

values $f_0, f_1 \dots f_N$ of the capacitance. The discrete Fourier coefficients c_n^D are formed by numerical Fourier transformation:

$$c_n^D = \frac{1}{N} \sum_{k=0}^{N-1} f_k \exp(-2\pi i n k / N), \quad n = 0, 1 \dots N-1. \quad 3-16$$

Since f_k is real, the cosine coefficient (a_n) and the sine coefficients (b_n) are real, too, and represent real and imaginary parts of c_n^D :

$$c_n^D = \frac{1}{2} (a_n - i b_n) \quad 3-17$$

From capacitance transients measured at different temperatures from 40K to 340K, Fourier transform can be carried out on the recorded capacitance transients $C(t)$ using [131]:

$$C(t) = \frac{a_0}{2} + \sum_{n=1}^{N-1} a_n (2\pi n t / T_W) + \sum_{n=1}^{N-1} b_n (2\pi n t / T_W) \quad 3-18$$

where, $k = 0, 1, 2 \dots N-1$, a_0 is the transient offset, t is the time and $N = T_W / \Delta t$ is the amount of sampling on the transient ($N = 512$ in this work). The coefficients, a_n and b_n , are the n^{th} order cosine and sine coefficients, respectively, from which the time constant of the carrier emission, can be calculated as follows:

$$\tau = \frac{1}{n\omega} \frac{b_n}{a_n} \quad 3-19$$

where, τ is the carrier emission time constant, a_n, b_n , are the cosine and sine coefficient of the n^{th} order, and $\omega = 2\pi / T_W$. The Arrhenius plot can be obtained from the plot of τ vs. T^{-1} . In this work, b_1 was chosen as the DLTS signal, where it is proportional to the capacitance change amplitude,

$$\Delta C = \frac{T_W}{2} b_1 \frac{\exp(t_0/\tau)}{[1 - \exp(-T_W/\tau)]} \frac{1/\tau^2 + \omega^2}{\omega} \quad 3-20$$

where, t_0 is the start of transient measurement. Since the trap concentration is proportional to the capacitance change that occurs at $\tau_{\max}$, the trap concentration (N_T) can be obtained from,

$$\frac{\Delta C_0}{C_d} = \frac{N_T}{2N_D} \quad 3-21$$

where, ΔC_0 is the capacitance transient change, C_d is the quiescent depletion capacitance, and N_D is the donor concentration. To minimize the quantization errors of the measurement the system selects an optimum value of t_0 , which satisfies,

$$\tau_{\max} = \frac{T_W}{\ln(1 + T_W/t_0)} \approx 100\Delta t \quad 3-22$$

For $N = 512$ used in this work, the above equation yields $t_0 \approx 0.006T_W$ and $\tau_{\max} \approx 0.2T_W$. Substituting these values into Eq. 3-20, we get $\Delta C_0 \approx 5b_1$. Thus, using Eq.3-21,

$$N_T \approx 10N_D \frac{b_1}{C_d} \quad 3-23$$

where, N_D is the donor concentration and C_d is the quiescent depletion capacitance. This equation gives an approximate expression for the trap concentration in terms of the measurable parameters N_D , b_1 , and C_d .

CHAPTER IV Growth of Lattice-matched GaAsSbN with Bandgap Energy of 0.95 eV

The growth of GaAsSb/GaAs and GaAsSbN/GaAs epilayers was presented in this chapter. In the first part, GaAsSb/GaAs was studied using high-resolution x-ray diffraction (XRD) and low temperature photoluminescence (PL). Subsequently, N was incorporated to GaAsSb in order to reduce the lattice mismatch. However, it is difficult to determine the Sb and N concentrations just from the (004) XRD rocking curve of a GaAsSbN single layer. Therefore, in the second part, two-layer structure of GaAsSbN and GaNAs, and three-layer structure of GaAsSbN, GaNAs, and GaAsSb were grown on the same GaAs substrate. The purpose of these structures is to estimate the Sb and N content in the GaAsSbN from the atomic concentration(s) of the ternary layers. A more precise measurement of the Sb and N atomic concentrations will require different characterization method such as secondary ion mass spectroscopy (SIMS) or x-ray photoelectron spectroscopy (XPS). In this work, SIMS measurements were used to complement the results of the multilayer structures. Consequently, the multilayer study reveals the effect of growth rate on the Sb and N incorporation. This allows the growth of lattice-matched GaAsSbN with bandgap energy in the 0.95 eV region, which is demonstrated in the third part of this chapter. The lattice-match condition allows the GaAsSbN epilayer to be coherently grown up to ~2000 Å thick. The conditions are potentially applicable on a GaAs-based *p-i-n* PD for 1.3 μm optical communication wavelength.

4.1 Growth of GaAsSb Epilayers on GaAs Substrate Using Antimony Valved Cracker Cell

A. Preferential Antimony Incorporation Observed on GaAsSb Epilayers Grown under Low Temperature and High Arsenic Overpressure

Numerous authors have reported the growth of GaAsSb epilayers by SS-MBE over a wide range of substrate temperature from 480 °C to 530 °C [42,132,133]. These growths used relatively lower As overpressure values compared to the dilute nitride growth condition. Preferential incorporation of Sb over As in MBE-grown arsenide-antimonide alloys has been well documented [42,132-135]. The difference in sublimation energy ($Sb_4 > As_4$) and atomization energy ($Sb < As$) increases the surface lifetime of Sb atoms on the growth surface and their chances to bond with Ga atoms [132,136]. This preferential incorporation can be described as the sticking coefficient ratio between Sb and As ($S_{Sb/As}$), which can be related to the Sb and As flux ratio in the following manner [132],

$$\frac{y}{1-y} = \left(S_{Sb/As} \right) \left(\frac{\Phi_{Sb}}{\Phi_{As}} \right) \quad 4-1$$

where, y is the Sb/As atomic content ratio in the GaAsSb epilayer, $S_{Sb/As}$ is the sticking coefficient ratio, while Φ_{Sb} and Φ_{As} are the Sb and As flux, respectively. Sticking coefficient here is defined as the ratio between the group V atoms that bonds to Ga, thus “sticking” to the substrate and the group V atoms that arrives on the substrate.

Dilute nitride materials are grown at lower growth temperature and under higher As overpressures, compared to the aforementioned GaAsSb growth conditions,

to prevent Ga-N phase separation and preserve a layer-by-layer growth [20]. Therefore, to study the Sb incorporation under the dilute nitride growth conditions, series of samples of $\sim 1000\text{\AA}$ -thick GaAsSb epilayer were grown on (001) GaAs substrates. The Ga flux is calibrated to deliver $1\text{ }\mu\text{m/hr}$ growth rate, while the As_4/Ga overpressure was kept at ~ 20 . The Sb cracker temperature was kept at $900\text{ }^\circ\text{C}$ to ensure total thermal dissociation of the Sb tetramers into Sb dimers and monomers. Before the growth of the GaAsSb epilayer, $\sim 1000\text{ }\text{\AA}$ thick GaAs buffer layer was grown at $580\text{ }^\circ\text{C}$ to improve the starting surface crystalline quality. Subsequently, a growth interruption step was introduced for ~ 10 minutes to lower the substrate temperature to $460\text{ }^\circ\text{C}$ for the growth of the GaAsSb epilayer.

Figure 4-1a shows the linear relation between Sb content of the GaAsSb/GaAs epilayers and the Sb flux. The Sb concentrations of each epilayers were obtained from curve fitting of the (004) XRD rocking curves of the GaAsSb/GaAs samples shown in Figure 4-1b. All the samples exhibit Pendellosung fringes indicating good interfacial and crystalline quality, except for the GaAsSb/GaAs sample with 9.7%. The lack of fringes and the broadening of the GaAsSb epilayer peak in this sample suggest possible epilayer relaxation. However, further study of the layer relaxation conducted by the asymmetrical XRD mapping technique shows that the layer is still fully strained. The detailed results of this experiment will be presented in the next section.

Fig.4-1 (a) Sb concentrations vs. Sb flux obtained from GaAsSb layer grown at 1 $\mu m/hr$ under As_4/Ga flux ratio of ~ 20 and substrate temperature of 460 °C. (b) The (004) XRD rocking curve from which the Sb concentration was obtained, the offset in the intensity was given for clarity.

Figure 4-2 shows the plot of atomic ratio vs. the flux ratio between Sb and As. Using Equation 4-1, the sticking ratio between Sb and As in this work is found to be 6.7, indicating preferential Sb incorporation over As. Our finding agrees with the work of Wu *et al.* [135], where Sb incorporation is higher in the low Sb flux region. Lowering the growth temperature to 420 °C increases the Sb incorporation, which was also reported in other MBE-grown GaAsSb [42,132]. However, our sticking ratio appears to be ~50-100% higher depending on the growth temperature. This is attributed to the use of Sb valved cracker cell, which supplies Sb dimers and monomers instead of Sb₄ supplied by the standard effusion cell. The use of the valved-cracker cell will simplify the Sb incorporation from a two-step process that involves surface cracking of the Sb₄ to form Sb₂ before it is incorporated into the epilayer. Using similar reaction shown in Section 3.1-B,

It can be seen that by cracking the Sb₄ into Sb₂ before the tetramer arrives on the substrate, eliminates the desorption process that occurs on half the arriving group V atoms. This increases the theoretical Sb sticking coefficient up to 100%, which is close to what is observed in this work.

Fig.4-2 The plot of Sb/As atomic concentration ratio vs. the Sb/As flux ratio was obtained from GaAsSb/GaAs samples grown at 460 °C (solid circles) and 420 °C (solid squares). The open circle is a comparison from the work of Wu *et al.* [135] using uncracked Sb cell.

B. Structural and Optical Characterization of the GaAsSb/GaAs Epilayers

Asymmetrical XRD of the (115) plane mapping study was performed on the GaAsSb/GaAs samples to obtain clearer information on the relaxation of the epilayer. Optical characterization was carried out using a low temperature (4K) photoluminescence (PL) measurement. Figures 4-3a–c show the $\Delta\omega$ vs. ω -2 θ contour maps from asymmetrical XRD scans of the (115) planes of GaAsSb/GaAs Samples A, B, and C, with Sb content of 6.2%, 9.7%, and 13.6%, respectively. The intercept of the black solid lines indicates the GaAs reciprocal lattice point and the intercept of the red dashed lines indicates GaAsSb reciprocal lattice point, respectively. Using equations 3-7 and 3-8, the $\Delta\psi$ offset between the GaAs peak and a fully strained GaAsSb epilayer can be calculated. On a fully strained epilayer, the parallel lattice parameter ($a_{//}$) is equal to the substrate lattice parameter. The fully relaxed lattice parameter of the GaAsSb epilayer, a_0 , can be calculated using the Vegard's law,

$$a_0 = a_{GaSb}y + a_{GaAs}(1 - y) \quad 4-2$$

where, y is the Sb concentration, a_{GaAs} and a_{GaSb} are the lattice constant of GaAs and GaSb, respectively.

Fig.4-3 The ω - 2θ vs. $\Delta\omega$ plot of asymmetrical (115) scans from ~ 1000 Å-thick GaAsSb/GaAs epilayers with (a) 6.2% Sb, (b) 9.7% Sb, and (c) 13.6% Sb. The intercept of the solid lines and the dashed lines indicate the GaAs and the GaAsSb peaks, respectively. The measured $\Delta\psi$ determines the degree of relaxation in the epilayer.

Figure 4-4 shows the calculated $\Delta\psi$ of a fully strained GaAsSb plotted against the Sb atomic concentration (dashed line). The measured $\Delta\psi$ data points from the GaAsSb epilayers from the previous section are shown as the solid triangles. The figure shows that the GaAsSb/GaAs epilayers are coherently grown up to the Sb concentration of 9.6%. It also shows that sample C is partially relaxed. Using the experimental parallel lattice parameter ($a_{||}$), the degree of relaxation, R , can be calculated from the following relation,

$$R = (a_{||} - a_{GaAs}) / (a_0 - a_{GaAs}) \quad 4-3$$

where, the degree of relaxation in sample C was found to be ~37%.

Critical thickness calculated by Matthews-Blakeslee (MB) model (Eq.2-22) and People-Bean (PB) model (Eq.2-23) are shown in Figure 4-5. The difference between the two models, described earlier in Section 2.4, is due to the different definition of the critical thickness in the two models. In the MB-model, misfit dislocation will start to form once the critical thickness is exceeded. On the other hand, PB-model considers that all the strain in the epilayer will be replaced by formation of misfit dislocation. According to the MB model, the formation of misfit dislocation occurs after the Sb concentration exceeds 6%. This is in agreement with the experimental results, as shown by the increase of diffused scattering around the GaAsSb peak on the contour map of Sample B compared to Sample A in Fig.4-3. This suggests the onset of misfit dislocations formation in Sample B that leads to relaxation observed in Sample C.

Fig.4-4 The calculated $\Delta\psi$ of fully strained GaAsSb layers plotted against their Sb atomic concentration (dashed line). The solid triangles are measured $\Delta\psi$ data points from the GaAsSb epilayers from the previous section.

The effect of the relaxation can be observed in the low temperature PL of the GaAsSb epilayers. The low temperature PL peak data shown in Figure 4-6 was fitted using Eq 2-21 modified by the Varshni equation,

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{(\beta + T)} \tag{4-4}$$

where, $E_g(T)$ is the bandgap energy at absolute temperature T , the α and β values for GaAsSb are 4.2×10^{-4} eV/K and 189 K, respectively [137]. The normalized PL spectra of Samples A, B, and C are shown in the inset of Fig. 4-6. There is a weak higher energy peak exhibited by sample A and lower energy peak/shoulder exhibited by Samples A, B, and C. The origin of these weaker peaks is still unclear. The high-

Fig.4-5 Critical thickness as calculated by the PB (dashed line) and MB (solid line) models. The open circles are the 1000 Å-thick GaAsSb/GaAs samples.

energy peak in Sample A could be a radiative transition related to Sb out-diffusion into the GaAs layer. Comparison between the broad lower energy shoulder/peaks to their respective GaAsSb peak shows that it is weaker in Sample A and it is more prominent in Sample B and C. These low-energy peaks maybe originated from regions with higher Sb concentration than the bulk GaAsSb layer due to the Sb-surface segregation layer. This is supported by the increase of the distance between the broad low energy shoulder and their respective main peak. As the Sb flux increases from Sample A to Sample C, the concentration of the Sb segregating on the surface increases. This high concentration antimony layer may have diffused back into the low concentration region, resulting in a redshift of the lower energy peak. These structural and optical characterizations of the GaAsSb epilayers clearly illustrate the limitation of the

material for GaAs-based optical communication *p-i-n* photodiode. While Sb concentration ~30% is required for 1.3μm wavelength, the layer thickness will be limited by the critical thickness. Therefore, the addition of N is necessary to reduce the lattice mismatch and the bandgap energy further.

Fig.4-6 Low temperature PL peaks fitted by the combination of empirical equations Eq.2-20 and 4-4. The inset shows PL spectra of Samples A, B, and C. Formation of misfit dislocation is the cause of the PL broadening with increasing Sb concentration.

4.2 Study of Concomitant Incorporation of Nitrogen and Antimony to the GaNAs/GaAsSbN/GaAs Two-layer Structure under Varied Antimony Flux

A. Nitrogen-induced Lattice Mismatch Reduction Observed on the GaNAs/GaAsSbN/GaAs Two-layer Structure

In GaInNAs, the In and N atoms occupy different sites in the zinc-blende lattice. This allows minimal interaction between In and N during the growth of GaInNAs. Therefore, the atomic concentrations of In and N in GaInNAs can be calibrated easily by growing separate layers of GaInAs and GaNAs with the same growth parameters [138,139]. This is very convenient for the growth of GaInNAs layer because the standard method of curve fitting of XRD rocking curve cannot determine the atomic concentrations in the dilute nitride quaternary materials due to their strain compensating effect. On the other hand, the incorporation of N and Sb in GaAsSbN is not that straightforward because both are group V atoms and aggravated by the enhanced incorporation of N in the presence of Sb [39]. This causes atomic concentration differences between ternary layers, where the Sb and N atoms are incorporated separately, and the quaternary layer, where the Sb and N atoms are concomitantly incorporated, even when the growth parameters of these layers are identical. Consequently, there is an uncertainty of the N concentration in the characterization of a single layer GaAsSbN if it was grown without a reference GaNAs layer grown on the same sample.

In this experiment, a two-layer structure of GaNAs/GaAsSbN was grown on (001) GaAs substrate to obtain an estimated Sb and N content in the GaAsSbN epilayer. Using the same Sb flux values from Section 4.1., samples with ~ 1000 Å-thick GaAsSbN epilayer were grown after the GaAs buffer layer. All the growth parameters are kept the same as the GaAsSb epilayer growth described in Section 4.1. The difference of Sb concentration between the GaAsSb reference samples and the corresponding GaAsSbN layer grown with the same Sb flux is negligible; which is the standard assumption for GaAsSbN calibration [39]. This assumption is necessary due to the increase of N incorporation in the presence of Sb. On top of the GaAsSbN layer, ~ 1000 Å thick GaNAs layer was grown. The high-purity N_2 gas flow was kept at 0.12 standard cubic centimeters (SCCM), with r.f. power of 500 W for both the GaAsSbN and GaNAs layers. It must be highlighted once more that the purpose of this two-layer structure is to have a more accurate estimate of the N concentration in the GaAsSbN layer by having a reference GaNAs layer.

The (004) rocking curve of the two-layer structure (solid lines) and the (004) rocking curve of the GaAsSb epilayers grown with the same Sb flux (dashed lines) are shown in Figure 4-7. A closely lattice-matched condition to GaAs was obtained on GaAsSbN grown at Sb flux of $\sim 2 \times 10^{-8}$ Torr. In addition, the (004) XRD rocking curve of GaAsSbN epilayer grown with Sb flux of 1.5×10^{-7} Torr exhibits better Pendellosung fringes compared to its GaAsSb/GaAs reference (Sample B in the previous section). This is clearly due to the reduction of lattice mismatch in the epilayer attributed to the addition of N.

Fig.4-7 Rocking curves obtained from (004) XRD of the GaNAs/GaAsSbN/GaAs two-layer structures with different Sb flux. Comparison between the GaAsSbN layers (solid lines) and the GaAsSb layers (dashed lines) shows reduction of the lattice mismatch due to incorporation of N.

B. Reactive Surfactant Behavior Observed on GaNAs/GaAsSbN/GaAs

Two-layer Structure

Figure 4-8 shows the low temperature PL peak energies of GaAsSb layer and the GaNAs/GaAsSbN two-layer structure plotted against the respective Sb concentration. The Sb concentration was based on the GaAsSb layer calibration shown in section 4.1. It was assumed that the variation of Sb contents between the GaAsSbN layer and the GaAsSb layer grown with the same Sb flux are negligible. The experimental data points are fitted with the similar equations 3-20 and 4-4, with additional offset of ~ 180 meV to fit the two-layer structure peaks. This 180 meV offset was based on our calculation using the BAC-model (Equation 2-18) for $\sim 0.5\%$ N. Comparison between the PL peaks exhibited by the GaAsSb layer and the two-layer samples yielded similar redshift (~ 160 meV vs. ~ 150 meV) for samples grown with Sb flux of 1.5×10^{-7} Torr.

The PL spectra of the two-layer structure are shown in Figure 4-9. Two effects can be observed from the figure. First, the PL peaks of Sb-containing samples are stronger than the GaNAs/GaAs reference sample. The intensity improves with increasing Sb concentration, except for the sample grown with the highest Sb flux. This is probably due to the formation of misfit dislocations due to excess compressive strain of the GaAsSbN layer. This improvement of PL spectra in the Sb containing dilute nitride samples highlighted the reactive surfactant property of Sb. As explained in Chapter I, the term “reactive surfactant” was proposed by Massies *et al.* [35] to define the surface segregating atoms (i.e. Sb) that occupies the substitutional site and

Fig.4-8 Low temperature PL spectra obtained from the GaAsSbN/GaNAs two-layer structure shows similar trend with GaAsSb epilayer with Sb atomic concentration increase.

reduces the surface diffusion length during growth. This phenomenon has been reported in GaInNAs:Sb [22,23,25,26], GaInNAsSb alloys [29,32,140-144], and GaAsSbN [84].

Second, the PL spectra of the two-layer structure suggest that the bandgap energy redshift also occurs in the top GaNAs layers. As shown in Fig. 4-9, PL spectrum of the GaNAs layer has a high-energy cutoff at ~1.38 eV. However, the rest of the two-layer spectra exhibit smaller high-energy cutoff with increase of Sb flux. This is peculiar, because the top GaNAs layers were grown with the same r.f. plasma N source conditions. Furthermore, the two-layer sample grown with the largest Sb

Fig.4-9 Low temperature PL obtained from the two-layer structure shows increasing redshift with the increase of Sb flux. The solid lines are from the two-layer structure. The dashed line is from a reference GaNAs single layer grown with the same growth parameters as the GaNAs layer in the two-layer structure.

flux exhibits high-energy cutoff at ~1.21eV (blue curve). This is equivalent to 170 meV redshift from the reference GaNAs sample (open squares). The redshift of the high-energy cutoff is close to the 160meV redshift from the reference GaAs peak exhibited by GaAsSb epilayer grown with the same Sb flux (Fig. 4-8). This clearly suggests a reduction in the bandgap of the top GaNAs layers of the two-layer structure.

To understand the reason behind this bandgap reduction, the growth sequence of the two-layer structure must be explained. Upon completion of the GaAsSbN layer

growth, a growth interruption was introduced by closing the main shutter. This allows enough time to close the Sb cell valve, while all the other growth parameters are maintained. Shortly after, the growth was resumed with GaNAs layer growth. By closing the Sb valve, a rapid decrease of Sb flux is expected without any memory effect [91]. However, during the growth of the GaAsSbN layer, an Sb floating-layer can be formed by surface-segregating Sb atoms [30,32,35]. The presence of this floating-layer can alter the N incorporation rate or have Sb diffused into the GaNAs layer, all of which can contribute to the redshift in the GaNAs peak. This is supported by Figure 4-10, where the intensity (relative to the GaAs peak) of the GaNAs XRD peaks reduces and full width at half-maxima (FWHM) increases with increase of Sb flux. This is despite the fact that Sb valve and Sb shutter are closed during the GaNAs layer growth. This peak broadening is likely due to inhomogeneous compositional distribution along the growth direction of the GaNAs layer caused by Sb atoms diffusing from the residual Sb floating-layer. Further evidence of this floating layer was indicated from SIMS measurements conducted on the three-layer structure, which will be presented in the next section.

Fig.4-10 The relative intensity (solid circles) and full width at half maxima (FWHM, open circles) of the GaNAs layer peak from the two-layer structure normalized to its respective GaAs peak. The GaNAs peaks broaden and decrease in intensity with increasing Sb flux, even though the Sb valve and shutter are closed during the GaNAs growth. This suggests that the GaNAs layer is altered by the residual Sb-floating layer from the GaAsSbN layer.

4.3 The Study on the Effect of Growth Rate on Concomitant Incorporation of Nitrogen and Antimony in GaAsSbN Layer

A. Growth of GaAsSb/GaNAs/GaAsSbN/GaAs Three-layer Structure and Quantification of the Nitrogen and Antimony Content

It has been mentioned that quantification of the Sb and N concentration in GaAsSbN alloy is not as straightforward as its constituent ternary alloys, due to the strain-compensating effect of adding Sb and N together. Furthermore, interaction between the three group V elements (N, As, Sb) is known to alter the N incorporation rate. In the absence of Sb, the incorporation rate of N in dilute nitride materials is known to be inversely proportional to the growth rate [145,146]. In that condition, the N sticking coefficient, S_N , is said to be equal to or close to unity. However, others have reported different circumstances where $S_N < 1$. In growth rate $< 0.4 \mu\text{m/hr}$, MBE-grown GaNAs has shown $S_N < 1$ [90]. The evidence that $S_N < 1$ was also observed in Sb-containing dilute nitride materials where the an Sb-enhanced N incorporation rate was reported [32,39,134,139,147,148]. The mechanism of this Sb-enhanced N incorporation is still unclear, despite the overwhelming evidence of its existence.

In order to study the Sb and N interdependence further, a three-layer structure of GaAsSb/GaNAs/GaAsSbN was grown on a (001) GaAs substrate. The growth rate, V/III ratio, Ga, As, and Sb flux values and the RF nitrogen source conditions across the three layers were kept identical. The As_4/Ga flux ratio was kept at ~ 20 . The N r.f. plasma source was operated with N_2 gas flow at 0.12 SCCM and r.f. power of 500W.

Using growth rate of 0.5 $\mu\text{m/hr}$ and growth temperature of 460 $^{\circ}\text{C}$, three-layer structure samples D, E, and F were grown using three different Sb fluxes of 1.5×10^{-8} , 2×10^{-8} and 2.5×10^{-8} Torr, respectively. Following the growth of a GaAs buffer layer, a GaAsSbN layer was grown up to 5000 $\text{\AA}$ thick or until the RHEED pattern deteriorated, which ever occurred first. Using the same growth parameters as the GaAsSbN layer, 1000 $\text{\AA}$ -thick GaNAs and GaAsSb layers were grown, except in the GaNAs layer of sample D where the RHEED pattern deteriorated just before the layer reached the thickness of 500 $\text{\AA}$. The RHEED traces show streaky (2×4) patterns during the growth of all layers, indicating coherent growth with minimum relaxation.

Combination of SIMS measurement and XRD rocking curve fitting was used to compare the composition of Sb and N in the ternary materials and the quarternary material. Figure 4-11 shows the SIMS results of the three-layer structure samples D, E, and F. The As, N, and Sb atomic concentrations are plotted against the sputtering depth from the substrate surface. Thus, the epilayers from left to right are GaAsSb, GaNAs, and GaAsSbN, respectively. The N and Sb concentration were used as a guide to fit the (004) XRD rocking curve displayed in Figure 4-12. The SIMS depth profile also shows a grading of antimony in the GaNAs layer, particularly in sample E. This Sb-grading appears more severe due to the logarithmic scale of the Y-axis. However, it can be seen that the antimony grading Sb only extends from $\sim 1\%$ from the GaAsSbN/GaNAs interface to $\sim 0.01\%$ for a thickness of $\sim 500\text{\AA}$. This amount of “grading” can be considered negligible especially compared to the tensile strain caused by N atoms. Furthermore Due to the complexity of fitting the three-layer structure, it has to be assumed that the samples have abrupt interfaces between layers and uniform concentrations within the layers. These assumptions have little effect on the

Fig.4-11 SIMS results of three-layer structure Samples D, E, and F.

discrepancy between the SIMS and the XRD because the SIMS results came with $\pm 5\%$ margin of error. The fitting results, mismatch values, and the thickness of the

GaAsSbN layer of Samples D, E, and F, are summarized in Table IV-1. The Sb and N concentrations shown in Table IV-1 were obtained from XRD fitting.

The SIMS results provide more evidence of the Sb floating layer that was observed in the previous section. Firstly, all three samples exhibit an increase in Sb count at the surface, which suggests accumulation of Sb in the form of Sb floating layer during the growth of the GaAsSb layer. This agrees well with the SIMS study on Sb-doped GaNAs layers reported by Cheah *et al.* [149]. This surface accumulation of Sb atoms also occurs during the growth of the GaAsSbN layer, as indicated by residual Sb that is unintentionally incorporated into the GaNAs layer. Since the GaAsSbN/GaNAs interface in this structure is the same with the interface in the two-layer structure, the diffusion of Sb atoms from the GaAsSbN layer into the GaNAs layer suggests the formation of Sb floating layer during the growth of GaAsSb and GaAsSbN.

Figure 4-12 shows the (004) XRD rocking curves of the three-layer structure samples with their respective simulated curves. All three samples exhibit closely lattice-matched GaAsSbN layers. Assuming the Sb content of the GaAsSb layer and the GaAsSbN layer are the same, the N concentrations in the GaNAs and GaAsSbN layers were obtained using curve fitting. The N and Sb content, the Sb/N ratio, the measured and calculated mismatch values are listed in Table IV-1. It can be seen that the Sb/N ratio of the lattice matched GaAsSbN in sample E is 2.56, which is comparable with the calculated value of 2.60. This lattice-matched condition was achieved in the sample grown under Sb flux of 2×10^{-8} Torr.

Table IV-1 The N and Sb contents of the individual layers on the three-layer structure samples were obtained from XRD curve fitting. The measured and calculated mismatch between the GaAsSbN and the GaAs layers are also listed with the GaAsSbN layer thickness.

Sample	Sb%	N%		Sb/N ratio	Measured mismatch (ppm)	Calculated mismatch (ppm)	GaAsSbN thickness (Å)
		GaNAs layer	GaAsSbN layer				
D	1.8	0.9	0.9	2.00	-818	-828	3000
E	2.3	0.9	0.9	2.56	0	67	5000
F	2.9	0.9	1.0	2.90	400	444	3000

B. The Effect of Growth Rate on the Incorporation of Antimony and Nitrogen in GaAsSbN

It is necessary to point out that the closely lattice-matched GaAsSbN/GaAs grown at 1 μm/hr growth rate in the previous section was also obtained using Sb flux of $\sim 2 \times 10^{-8}$ Torr. This is crucial for obtaining the lattice-matched GaAsSbN with 0.95 eV bandgap. It also suggests that the lattice-matched GaAsSbN can be grown at different growth rates with minimal adjustment of the Sb flux. This is likely due to the constant As-overpressure between samples with different growth rate. Consequently, the As flux had to be reduced for lower growth rates, which leads to the increase of Sb/As flux ratio in an inversely proportional manner to the growth rate. Since the Sb/As flux ratio is proportional to the Sb concentration, the Sb content in GaAsSb and GaAsSbN will be inversely proportional to the growth rate as well (Figure 4-13).

Fig.4-12 (004) XRD rocking curves were obtained from the three-layer structure. The GaNAs peak of sample D is weaker because it was grown up to 500 Å instead of 1000 Å as planned. The N and Sb content of all three layers (shown on Table IV-I) were obtained from curve fitting between the measured curve and the simulated curves shown directly below their respective experimental curves.

Fig.4-13 The Sb concentrations were obtained from GaAsSb or GaAsSbN layers grown at different growth rate under constant temperature 460 °C, As₄/Ga ratio of 20, and Sb flux of 2×10⁻⁸ Torr. The increase of Sb concentration is inversely proportional to the growth rate.

As previously mentioned in Chapter III, Section 3.1.A., the effect of growth rate on N content of GaNAs layer using this particular growth setup has been thoroughly studied. However, the addition of Sb has altered the N incorporation rate as predicted. Figure 4-14 shows the experimental (open triangle) and theoretical (dotted and dashed lines) N concentration of GaNAs layers grown at different growth rates from Sun *et al.* [90]. The N concentration of GaNAs (solid squares) and GaAsSbN (solid circles) layers obtained from samples grown in this work are also

included, with the solid line serves as a guide for the eyes. The error bar is $\pm 5\%$ from the margin of error of the SIMS measurement.

Figure 4-14 shows that the N content of our GaNAs layers closely follows the kinetic model (dashed line) from reference [90]. However, in the low growth rate region $<0.4 \mu\text{m/hr}$, the N incorporation in GaAsSbN deviates from the kinetic model and moves towards the N concentration predicted by the doping incorporation model [5,90,150]. This is obviously due to the Sb-enhanced N-incorporation reported in other MBE-grown dilute nitride materials [24,32,39,134,139,147,148]. This enhanced incorporation of N will be beneficial in achieving the bandgap energy of 0.95 eV.

Fig.4-14 The N concentration obtained from the GaNAs or GaAsSbN layers grown with and without the influence of Sb marked with solid squares and solid circles, respectively. The open triangles are the GaNAs experimental data points and the calculated N concentrations (the dashed and dotted lines) are taken from the GaNAs work of Sun *et al.* [90].

4.4 The Growth of Lattice-matched GaAsSbN with 0.95 eV Bandgap Using 0.2 $\mu\text{m/hr}$ Growth Rate

Two important characteristics of the GaAsSbN growth have been established in the previous section. Firstly, the Sb flux required for closely lattice matched growth of GaAsSbN/GaAs on a given substrate temperature, N r.f. plasma condition and As/Ga overpressure was found relatively constant regardless of the GaAsSbN growth rate. Approximately 2×10^{-8} Torr of Sb flux is required to grow lattice-matched GaAsSbN under substrate temperature of 460 °C with As₄/Ga overpressure ~ 20 , N₂ gas flow of 0.12 SCCM, and r.f. power of 500 W. Secondly, the N incorporation was enhanced by the presence of Sb, allowing more than $\sim 2.5\%$ of N to be incorporated in to GaAsSbN at 0.2 $\mu\text{m/hr}$.

Three samples of ~ 2000 Å-thick GaAsSbN/GaAs were grown at 0.2 $\mu\text{m/hr}$ growth rate. Samples X, Y, and Z were grown with Sb flux of 2.0, 2.1, and 2.3×10^{-8} Torr, respectively. During flux calibration, the background pressure was kept below $\sim 1 \times 10^{-10}$ Torr and the flux measured during ~ 15 minutes of flux calibration relatively stable. The flux resolution was chosen after considering the 6.7 Sb/As sticking ratio observed in Section 4.1. In addition, the repeatability of the flux is not an issue as long as the cell and cracker temperatures are kept the same. A much smaller flux range ($3 - 7 \times 10^{-9}$ Torr) was used in the study of Sb surfactant in GaNAs and GaInNAs [30,84,149]. The other growth parameters such as substrate temperature, As/Ga flux ratio, Sb cracker temperature, N₂ gas flow and r.f. power were kept identical with the values mentioned in the previous paragraph. Figure 4-15a shows the (004) XRD rocking curve of the GaAsSbN samples, where closely lattice-matched

conditions (mismatch value <0.3%) have been achieved in all of the three samples. The samples exhibit low temperature PL spectra with peak energy around 0.95 eV (Figure 4-15b). At the low energy region, the PL spectra exhibit defect-related broad shoulder similar to what is commonly observed in GaNAs [5,151,152].

Table IV-2 shows the N and Sb contents of the GaAsSbN layers grown with different Sb fluxes together with the layers' mismatch, low temperature PL position, intensity, and FWHM. The increase of Sb concentration from samples X to Z can be observed from the SIMS results and the shift of the GaAsSbN XRD peak indicating an increase in the lattice parameter of the GaAsSbN layer. This is expected with the increase of Sb flux. Furthermore, the N content of the GaAsSbN layer exceeds 1.8%, which is the value of the reference GaNAs sample grown without the influence of Sb (Fig.4-14). However, the difference of N concentration between the samples appears to be within the SIMS error margin. As seen from Table IV-2, the increase of Sb flux improves the PL peak intensity and FWHM. Furthermore, the defect-related peak intensity relative to its respective PL peak was also suppressed with increasing Sb concentration. This improvement is less likely due to the strain effect, because the lattice mismatch in sample X and Z is similar. The effect of Sb flux on the PL spectra may be explained by the change of the growth condition from N overpressure to N underpressure, which improves crystalline quality of GaNAs [90]. Another plausible explanation for the PL peak improvement is due to the reactive surfactant effect of Sb, which occurs at Sb flux between $1 \times 10^{-8} - 2 \times 10^{-7}$ Torr [22,24-27,84,149].

Fig.4-15 (a) (004) XRD rocking curves taken from the single layer GaAsSbN shows closely lattice-matched condition in all three samples. (b) Low temperature PL spectra exhibited by the single layer GaAsSbN grown at different Sb flux. The samples exhibit defect-related low energy shoulders, which decrease with increasing Sb flux.

Table IV-2 The Sb flux used in the growth of single layer GaAsSbN samples X, Y, and Z are shown with the respective XRD mismatch and low temperature PL results. The N and Sb content were obtained from SIMS measurement. The defect-related PL peak intensities are normalized to the respective GaAsSbN PL peak.

Sample	Sb flux (10 ⁻⁸ Torr)	N%	Sb%	XRD mismatch (ppm)	PL peak position (eV)	PL peak intensity (arb.u.)	PL FWHM (meV)	Defect peak relative intensity
X	2.0	2.6 ± 0.2	6.0 ± 0.3	-2800	0.942	66	78	1.0
Y	2.1	2.3 ± 0.2	7.0 ± 0.4	700	0.970	413	76	0.4
Z	2.3	2.4 ± 0.2	9.0 ± 0.5	2600	0.944	400	59	0.2

4.5 Summary

Calibration of Sb valved-cracker cell was performed by growing series of GaAsSb/GaAs samples under dilute nitride growth conditions of low growth temperature (460 °C) and high As/Ga ratio (~20). An Sb-As sticking ratio of ~6.7 suggests preferential Sb incorporation. Good quality GaAsSb can still be obtained using the dilute nitride growth condition. However, the critical thickness of the GaAsSb layer reduces with the increase of the Sb concentration, preventing the growth of thick GaAsSb layer with high Sb concentration. Reciprocal space mapping of asymmetrical XRD of (115) plane shows crystalline quality degradation for samples grown beyond their critical thickness, which was predicted by the MB-model.

To reduce the lattice mismatch, N must be added during the growth of GaAsSb layer. Calculation using Vegard's law shows that GaAsSbN will be lattice-matched to GaAs when the Sb/N ratio is 2.60. The growth of GaAsSbN was studied by using two-layer and three-layer structures, where GaNAs/GaAsSbN and GaAsSb/GaNAs/GaAsSbN layers are grown on the same GaAs substrate. The structures were studied by combination of low temperature PL, XRD, and SIMS, which reveals two important properties of GaAsSbN growth. First, in the growth rate range of 0.1-1 $\mu\text{m/hr}$, the N incorporation in GaAsSbN is inversely proportional to the growth rate. Second, the lattice-matched condition can be preserved regardless of the growth rate by maintaining the Sb flux at approximately 2×10^{-8} Torr while keeping the As₄/Ga ratio and the r.f. plasma source parameters the same. These properties are observed on GaAsSbN grown under 1, 0.5, and 0.2 $\mu\text{m/hr}$. GaAsSbN samples exhibits improved PL intensity compared to the PL intensity exhibited by the reference GaNAs sample with similar N content. This suggests the presence of reactive surfactant properties of Sb in the growth of GaAsSbN. In addition, the presence of Sb enhances N incorporation, allowing more than 2.5% of N to be incorporated in GaAsSbN grown at 0.2 $\mu\text{m/hr}$. This helps to reduce the bandgap of GaAsSbN to reach 0.95 eV.

CHAPTER V Effect of Rapid Thermal Annealing on the Optical and Structural Properties of GaAsSbN

Rapid thermal annealing (RTA) has played an important role in improving the crystalline quality of dilute nitride materials grown with plasma-assisted MBE. There are numerous papers that report the degradation of dilute nitride crystalline quality with increasing N concentration [5,38,110,153]. The quality degradation is attributed to the increase of N-related point defects, which are most likely in the form of N-As or N-N split interstitials [109,111]. The low temperature PL of GaAsSbN samples grown with different N concentrations shown in Figure 5-1 also exhibit this behavior. Like other dilute nitride materials, RTA improves the crystalline quality of GaAsSbN by point defect annihilation and atomic rearrangement within the group V sub-lattice [38,62,82,96,154]. This chapter presents the study on the effect of *ex-situ* RTA on GaAsSbN, which includes determining the optimum annealing temperature and understanding the mechanism behind the RTA-induced bandgap shift in GaAsSbN.

Fig.5-1 Low temperature PL of GaAsSbN/GaAs epilayers with different N concentration shows reduction in intensity with increasing N content that accompanies the peak redshift.

5.1. Rapid Thermal Annealing Experiments on GaAs/GaAsSbN/GaAs Strained Quantum Well and Lattice-Matched GaAsSbN with ~0.5% Nitrogen Content

A. Experimental Details and Photoluminescence Characteristics of the Annealed GaAsSbN/GaAs Quantum Wells

A GaAs/GaAsSbN/GaAs quantum well (QW) sample was grown with substrate temperature of 460 °C, 1µm/hr growth rate, and As₄/Ga flux ratio of ~ 20. The growth of a 6 nm thick GaAsSbN well layer was carried out using an Sb flux of 1×10^{-7} Torr, supplied using the valved-cracker source with the cracker temperature kept at 900 °C. The incorporation of N was performed using the N r.f. plasma source with the N₂ gas flow at 0.10 SCCM and r.f. power of 500 W. The GaAs barrier layers were grown at 580 °C at the same growth rate and As₄ overpressure as the GaAsSbN well layer. The increase of substrate temperature prior to the growth of the GaAs cap layer also ensures that the Sb floating-layer will be evaporated from the surface of the GaAsSbN layer. The Sb-floating layer and the use of a growth interruption to remove it were also reported during the growth of Sb-doped GaNAs [149] and GaInNAsSb [30,32]. From the PL peak energy and previous calibration samples, the N and Sb concentrations are estimated to be 0.7% and 13%, respectively. The sample was annealed under N₂ ambient for 5 minutes at RTA temperatures ranging from 450 °C to 900 °C.

Low temperature PL spectra of the as-grown and annealed sample are shown in Figure 5-2. The PL spectra show improvement of the PL intensity and FWHM at

RTA temperatures of 600 to 750 °C. This optimum temperature range agrees with most literatures on the *ex-situ* annealing of GaAsSbN [38,82,96,134,155-157], although others [154] have used higher temperature (850 °C) with shorter annealing time (10 seconds). The improvement of PL spectra is attributed to the annihilation of point defects and impurities within the GaAsSbN layer. The annealing temperature range obtained from this work also agrees with annealing results on GaNAs [46,110,158] and GaInNAs [159-162], which suggests a common origin of the point defects within these dilute nitride materials. Reduction of point defects such as N-interstitials or As_{Ga} antisites has greatly improved the crystalline quality of dilute nitride materials [11,110,114,120,124,158,160,163,164].

Figure 5-3a shows the low temperature PL spectra of the as grown sample along with samples annealed at 650 °C, 700 °C, and 750 °C. Figure 5-3b shows the room temperature PL spectra exhibited by the annealed samples, with the PL intensity normalized to the sample with the strongest PL intensity. At the optimum annealing temperature of 700 °C, the low temperature PL peak intensity increases tremendously accompanied with energy blueshift of ~36 meV. The low energy defect-related peak that exists on the low temperature PL spectra of the as-grown sample is also reduced in the annealed samples. As seen in Fig. 5-3b, the best room temperature PL is also exhibited by the sample annealed at 700 °C. However, the peak energy blueshift from the room temperature signal cannot be determined due to the poor quality of the as-grown sample. The increase of peak energy blueshift as a function of temperature is expected as the quantum well interface becomes less abrupt with higher annealing temperature [59]. The PL peak energy shift will be discussed further in Section 5.2.

Fig.5-2 Low temperature PL intensity (solid circles) and FWHM (open squares) of the GaAsSbN/GaAs QW are plotted against the RTA temperature. Optimum annealing temperature occurs at 700 °C.

Fig.5-3 (a) Low temperature PL spectra exhibited by GaAsSbN/GaAs quantum wells annealed at different temperatures for 5 minutes. (b) Room temperature PL spectra of the same set of GaAsSbN/GaAs quantum well samples.

B. Experimental Details and Photoluminescence Characteristics of the Annealed Lattice-matched GaAsSbN Bulk Layer

RTA experiments were performed on 1000 Å-thick GaAsSbN grown closely lattice-matched to GaAs. This sample will be referred to as the bulk sample throughout the chapter. The GaAsSbN layer was grown at a substrate temperature of 460 °C, 1 μm/hr growth rate, and As₄/Ga flux ratio 20. An Sb flux of 2×10^{-8} Torr was supplied using the valved-cracker source with the cracker temperature kept at 900 °C. The incorporation of N was performed using the N r.f. plasma source with the N₂ gas flow at 0.10 SCCM and r.f. power of 500 W. The GaAs cap and buffer layers were grown at 580 °C with the same growth rate and As₄ overpressure as the GaAsSbN well layer. The Sb flux of $\sim 2 \times 10^{-8}$ Torr was used to achieve the closely lattice-matched condition to GaAs. Figure 5-4 shows the closely lattice-matched condition of the simulated and measured (004) XRD rocking curves of the sample. From curve fitting and PL peak position, the N and Sb atomic concentration are estimated to be 0.5% and 2.2%, respectively. The samples went through an RTA experiment performed under N₂ ambient at different temperature for 5 mins to study the annealing-induced PL peak blueshift.

Figure 5-5 shows the double-peak structure of the temperature-dependent low temperature PL spectra performed on GaAsSbN sample annealed at 600 °C. The details of the experiments can be found in the published work of Wang *et al.* [165]. The two peaks arise from the recombination of carriers at the alloy band-edge states (Peak A) and the lower energy emission from the localized band-tail states and N-related states caused by the N clusters and interstitial N pairs (Peak B). This is

Fig.5-4 The (004) XRD rocking curve exhibited by the ~1000 Å thick GaAsSbN layer (solid line). The atomic concentrations of 2.2% Sb and 0.5% N were obtained from the curve fitting (dashed line)

consistent with other annealing studies on GaAsSbN [62,82,155], as well as other dilute nitride materials [165]. With increase in temperature, the carriers trapped by the localized states can be thermally activated into the alloy band edge. Therefore, the thermal depopulation of the carriers in the localized N-related states leads to a rapid redshift of the PL peak of the lower energy peak (marked peak A in Fig.5-7). Due to this S-shape behavior in the temperature-dependent PL spectrum, room temperature PL will be a more appropriate measure of the GaAsSbN bandgap.

Fig.5-5 PL studies performed by Wang *et al.* [165] on the GaAsSbN bulk sample annealed at 600 °C for 5 minutes.(a) Temperature dependent PL measurement shows a double peak structure arises from the localized band tail or N-cluster states (A) and the band-to-band recombination (B). (b) The GaAsSbN PL exhibits S-shape temperature dependent peak shift characteristics.

Figure 5-6 shows the low temperature (a) and room temperature (b) PL of the annealed bulk samples. At 4K, the annealed samples exhibit double-peak structure similar to what is observed in Fig.5-5a. The shoulder and the long exponential tail is attributed to the localized states (Peak A), while the higher energy peak (Peak B) is related to the band-edge recombination. On the other hand, the room temperature PL spectra only show a single peak related to GaAsSbN. This is due to the rapid decrease

of Peak A as the temperature increases as explained in the previous paragraph. The GaAsSbN bulk sample annealed at 700 °C exhibits the highest intensity at room temperature, similar to the QW results in the previous section. Further comparison between the two samples will be discussed in the following section.

Fig.5-6 PL spectra exhibited by of the as-grown and annealed GaAsSbN bulk sample: (a) Low temperature PL spectra exhibit double-peak structure. (b) Room temperature PL spectra reach optimum point at RTA temperature of 700 °C for *ex-situ* RTA duration of 5 minutes under N₂ ambient.

C. Comparison of Room Temperature Photoluminescence Results of Annealed GaAsSbN Bulk and Quantum Well Samples

Figure 5-7 shows the plots of peak energy and normalized intensity of the GaAsSbN-related and GaAs-related peaks for the bulk samples (a) and QW samples (b) against their respective annealing temperature. It is clearly shown that the optimum RTA temperature of both the QW and bulk samples is 700 °C. It was also observed that when the annealing temperature exceeds 700 °C, the intensity of the GaAs peak begins to increase and peaked at 850 °C. This is maybe due to the annihilation of As_{Ga} point defects when the annealing temperature is ~ 800 °C [105]. In addition, the increase of the GaAs peak occurs as the GaAsSbN peak decreases, which suggests homogenization of the group V atoms along the growth direction that leads to the degradation of the GaAsSbN/GaAs interface. A bandgap blueshift was also observed in the room temperature PL of the bulk and QW samples. The bulk sample exhibits smaller blueshift (~ 10 meV) compared to the QW sample (~ 100 meV) at the optimum RTA condition. The mechanism of this RTA-induced bandgap energy shift in GaAsSbN will be studied further in the next section.

Fig.5-7 Room temperature PL peak energy and normalized intensity of the annealed bulk samples **(a)** and the quantum well samples **(b)**. The intensity is normalized to the strongest PL peak of the series. The solid symbols and the open symbols denote the GaAsSbN-related and the GaAs-related peaks, respectively.

5.2 Mechanism of the Annealing-induced Bandgap Shift on GaAsSbN

Figure 5-8 shows the low temperature PL peak energy of the bulk and QW samples plotted against the RTA temperature. The bandgap redshift that occurs at RTA temperature of 450–550 °C can be attributed to the interstitial-to-substitutional interdiffusion process [166] of N atoms. Loke *et al.* [46] observed similar RTA-induced bandgap redshift-blueshift in *ex-situ* annealed GaNAs layers, which was attributed to N-interstitials that move into the substitutional sub-lattice by “kicking-out” the substitutional As. The mechanism can be caused by the impurity-like nature of the N atoms in dilute nitride materials [167], which allows hopping of N atoms from substitutional sites to interstitial ones and vice a versa. This diffusion process must follow the simple equilibrium reaction, where for every N atom leaving its substitutional site (S), an interstitial N (I) and N vacancy (V) will be generated, ($S \leftrightarrow V+I$). The “kick-out” mechanism hypothesis was supported by nuclear-reaction-analysis (NRA) experiments that shows reduction of interstitial N atoms in annealed GaNAs [111]. First-principles calculations by Arola *et al.* [106] also show that such “kick-out” mechanism of N atoms will cause bandgap reduction in GaNAs. The lack of bandgap redshift exhibited by the room temperature PL spectra (Fig.5-7) also suggests that it is related to the localized states due to N clusters or interstitial N pairs.

The redshift in our GaAsSbN experiments reach the largest value at annealing temperature of ~500 °C, lower than the 650 °C and 725 °C reported by Loke *et al.* [46]. In GaNAs, the redshift occurs at lower temperature when the N concentration is

increased, because there will be more N-interstitials that can dislodge or “kick out” the substitutional As atoms. However, our N concentration ($\sim 0.5\%–0.7\%$) is much lower than what is reported in GaNAs work by Loke *et al.* (2.2% and 1.3%). We attributed this discrepancy to the As–Sb interdiffusion process that occurs simultaneously with the rapid movement of N atoms during annealing of GaAsSbN. This interdiffusion process will be explained further in the discussion regarding the bandgap blueshift in the following paragraphs. Due to the presence of Sb in the material system, the As–Sb interdiffusion allows interstitial N to occupy the substitutional sites without having to rely on the “kick-out” mechanism. Consequently, this will reduce the amount of energy required to induce the bandgap redshift in GaAsSbN.

The difference between the PL blueshift from the bulk sample and the QW samples is expected because the PL peak position of QW samples are more prone to the annihilation of N-related defects within the well layer and the annealing-induced interfacial changes compared to the thick lattice-matched samples. However, transmission electron microscopy (TEM) studies on annealed GaAsSbN layers have ruled out N out-diffusion from GaAsSbN QWs [38,82,168]. Therefore, the effect of N out-diffusion in dilute nitride materials is secondary to the interdiffusion of the other group V atoms, especially at annealing temperature below 750 °C [159]. One can assume that only As-Sb interdiffusion is responsible for the blueshift in the annealed GaAsSbN/GaAs QWs. Based on that assumption, Dang *et al.* reported As–Sb interdiffusion coefficient of $\sim 10^{-17} – 10^{-16}$ cm/s and activation energy of 1.0 ± 0.4 eV from the annealed QW samples in this work [59], which is in close agreement with the reported values from GaAsSb/GaAs QWs [169,170].

Fig.5-8 Low temperature PL peak positions of the bulk GaAsSbN samples (solid line) and the QW samples (dashed line) are plotted against their RTA temperature.

Theoretically, GaAsSbN should have a minimal bandgap blueshift compared to GaInNAs due to its single group III characteristic. Contrary to this hypothesis, several authors have reported varying degree of annealing-induced blueshift, which are listed in Table V-1. The exact nature of this RTA-induced PL blueshift, however, is more complicated to explain. This is due to the four phenomena that occur simultaneously during annealing of dilute nitride materials. The annihilation of non-radiative recombination centers [38], homogenization of N atom distribution along the growth direction [171], atomic short range ordering (SRO) [38,82,160,172,173], and N out-diffusion can all contribute to the PL blueshift. Cheah *et al.* performed annealing

studies on GaNAs and GaInNAs QWs and pointed out that these phenomena are highly dependent of the duration and temperature of the RTA [159].

Table V-1 GaAsSbN annealing conditions and PL blueshift from various references are sorted by the increasing bandgap blueshift.

References	Layer type	N%	Sb%	T (°C)	duration	4K PL Blueshift
Bian <i>et al.</i> [62]	Bulk:1μm	2%	6%	700	60s	9meV
This work [174]	Bulk:0.1μm	0.5%	2.2%	700	5mins	20meV
This work [174]	QW	0.7%	12%	700	5mins	40meV
Yuen <i>et al.</i> [134]	QW	3%	10%	720 - 820	60s	50meV
Peake <i>et al.</i> [154]	QW	1%	30%	825	10s	55meV
Harmand <i>et al.</i> [38]	QW	1%	26%	680	10mins	115meV

Further structural characterization is required to determine which phenomenon is more dominant at a specific RTA temperature. Unfortunately, the QW samples' sizes are too small and too thin to be studied by SIMS and XRD measurement. Therefore, (004) XRD measurement was conducted on the annealed GaAsSbN bulk samples to provide further insight on the bandgap blueshift. The resulting (004) XRD rocking curves are shown in Figure 5-9. At annealing temperatures from 500–650 °C, the GaAsSbN peak shows minimal shift, which suggests the region where the short range ordering and interdiffusion between the interstitial and substitutional N atoms dominates. However, the Pandelosung fringes that are still obvious at 500 °C, started

Fig.5-9 Rocking curves obtained from the (004) XRD of the annealed GaAsSbN bulk samples. The (004) rocking curve of samples annealed at 750 °C and 850 °C exhibit evidence of N out-diffusion.

to fade at 650 °C followed by broadening of the layer peak. The peak broadening suggests interfacial degradation between the GaAs and the GaAsSbN layer due to the As-Sb interdiffusion. The GaAsSbN layer peak also shifts slightly towards a compressively strained condition at annealing temperature ≥ 600 °C. This suggests that a slight N out-diffusion has occurred, and it is apparent that the out-diffusion becomes more severe when the annealing temperature exceeds 750 °C. This coincides with the increase of GaAs-related PL peak intensity shown in Fig.5-7, which suggests that the GaAsSbN PL peak diminishes due to the severe N out-diffusion and the interfacial degradation. At annealing temperature of 850 °C, the XRD rocking curve is completely broadened indicating the loss of distinct interface between the GaAs and

GaAsSbN layers due to the out-diffusion process. Therefore, to minimize the effect of interfacial degradation and N out-diffusion, the RTA temperature should not exceed 750 °C for RTA conditions defined in this experiment.

5.3 Rapid Thermal Annealing Experiment on Lattice-matched

GaAs_{0.904}Sb_{0.07}N_{0.026}

Using the optimized annealing condition from the previous sections, the effect of RTA was studied on the lattice-matched GaAsSbN with 0.95eV bandgap energy. Approximately 0.5μm thick GaAsSbN layer was grown at a substrate temperature of 460 °C, 0.2μm/hr growth rate, and As₄/Ga flux ratio of ~ 20. Sb flux of $\sim 2.1 \times 10^{-8}$ was used, where the Sb cracker temperature was kept at 900 °C. The N source was kept identical to the growth condition in the previous sections. The GaAs buffer and 100nm cap layer were grown at 580 °C. The Sb and N concentrations are ~2.6% and 7%, respectively. The sample was annealed for 5 minutes under N₂ ambient with annealing temperature of 700 °C.

The low temperature PL of the as-grown (dotted line) and annealed sample (solid line) shows ~14 times improvement in the intensity, as shown in Figure 5-10a. This is clearly due to the annihilation of point defects and impurity from the GaAs_{0.904}Sb_{0.07}N_{0.026} layer. A very large blueshift of ~105meV accompanies the intensity improvement, which contradicts with our previous findings on the annealed bulk samples. Despite the large blueshift, the (004) XRD rocking curves shown on Figure 5-10(b) indicated minimal change between the annealed and as-grown sample.

This means the N out-diffusion is minimal in the annealed $\text{GaAs}_{0.904}\text{Sb}_{0.07}\text{N}_{0.026}$ layer. Therefore, we conclude that the atomic short-range ordering and N profile homogenization within the $\text{GaAs}_{0.904}\text{Sb}_{0.07}\text{N}_{0.026}$ is the more dominant cause for this blueshift. The reduction of point defects due to annealing can be seen on the reciprocal space maps (RSMs) of (115) XRD of the as-grown and annealed samples, shown in Figure 5-11. The reduction of the diffused scattering in the RSM of the annealed sample compared to the as-grown sample suggests the annihilation of point defects [158], which contributed greatly to the improvement of the PL intensity.

Fig.5-10 (a) Low temperature PL exhibited by the as grown (dotted line) and the annealed (solid line) ~5000 Å-thick GaAs_{0.904}Sb_{0.07}N_{0.026} single layer. (b) (004) XRD rocking curve exhibited by the same set of samples.

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Fig.5-11 Asymmetrical reciprocal space maps of [115] crystal plane XRD from the (a) as-grown and (b) annealed $\text{GaAs}_{0.904}\text{Sb}_{0.07}\text{N}_{0.026}$ sample. Significant reduction of the diffused scattering suggests annihilation of point defects in the GaAsSbN layer due to RTA.

5.4 Summary

Rapid thermal annealing (RTA) improves the quality of dilute nitride materials, particularly the one grown using r.f. plasma N source. In this thesis, the effect of RTA on GaAsSbN was studied using PL and XRD. Two series of samples underwent *ex-situ* rapid thermal annealing (RTA) process under N₂ ambient for the duration of 5 minutes, with the RTA temperature range from 450-900 °C. The first series is a GaAsSbN quantum well (QW) sample with estimated Sb and N concentrations of 12% and 0.7%, respectively. The other series is a GaAsSbN bulk layer lattice-matched to GaAs with Sb and N concentrations of 2.2% and 0.5%, respectively. Significant improvement in PL intensity was observed in the annealed samples, suggesting annihilation of impurities and defects in the GaAsSbN layer. The optimum annealing temperatures for both the bulk and QW samples were obtained at 700 °C. Low temperature PL shows RTA-induced bandgap redshift followed by blueshift, particularly in the annealed QW samples. The redshift is probably due to the interstitial to substitutional “kick-out” mechanism of N atoms similar to what was observed in annealed GaNAs samples. Although the annealed GaAsSbN QW has lower N content, its RTA-induced bandgap redshift occurs at lower annealing temperature (~500 °C) compared to the GaNAs reference (650–725 °C). This may be attributed to the interdiffusion of As–Sb atoms that readily occurs during the annealing of GaAsSbN. The interdiffusion process supplies vacant group V substitutional sites for highly mobile N atoms to occupy. The As–Sb interdiffusion also contributed to the bandgap blueshift that occurs at RTA temperature over 500 °C.

The RTA-induced bandgap blueshift in dilute materials can be attributed to a number of factors. Group V short range ordering (SRO), N profile homogenization in the growth direction, and N out-diffusion can all contribute to the bandgap blueshift. Room temperature PL and XRD studies on the annealed bulk samples revealed that the N out-diffusion dominates over the other factors when the RTA temperature exceeds 750 °C. Thus by keeping the RTA temperature at the optimum temperature of 700 °C, blueshift should still be suppressed. This is observed in the low temperature PL spectra of the annealed bulk GaAsSbN with N content 0.5%, where the RTA-induced bandgap blueshift is only ~20 meV for RTA temperature of 700 °C. However, when the lattice-matched $\text{GaAs}_{0.904}\text{Sb}_{0.07}\text{N}_{0.026}$ was annealed under the optimum condition, its low temperature PL spectra showed ~105 meV of bandgap blueshift. Although the annealed $\text{GaAs}_{0.904}\text{Sb}_{0.07}\text{N}_{0.026}$ layer also exhibits 15 times improvement of the low temperature PL intensity, the large blueshift made the $\text{GaAs}_{0.904}\text{Sb}_{0.07}\text{N}_{0.026}$ layer unsuitable for the 1.3 μm photodiode application. The limitation comes from the r.f. plasma N source that is not in line-of-sight in this work. The lack of XRD rocking curve peak shift has led to the conclusion that there is still minimal N out-diffusion from the $\text{GaAs}_{0.904}\text{Sb}_{0.07}\text{N}_{0.026}$ layer. Therefore, the blueshift is more likely due to the group-V short-range ordering, which is more severe in $\text{GaAs}_{0.904}\text{Sb}_{0.07}\text{N}_{0.026}$ with higher N content. It will be interesting to study the effect *in-situ* (vacuum) annealing in the ultra-high vacuum enclosure of the MBE chamber under arsenic overpressure, particularly for suppressing the desorption of Sb and N from the active layer[175], which was concluded as one of the critical cause of the PL peak energy blueshift.

CHAPTER VI Effect of Growth Temperature on Lattice-Matched GaAsSbN i-layer for GaAs-based 1.3 μm *p-i-n* Photodiode

In Chapter IV, the growth conditions for closely lattice-matched GaAsSbN/GaAs with varying growth rate have been presented. The SS-MBE growth of closely lattice-matched GaAsSbN/GaAs with bandgap energy ~ 0.95 eV has been demonstrated using the 0.2 $\mu\text{m/hr}$ growth rate. In Chapter V, *ex-situ* annealing at the optimum temperature of 700 $^{\circ}\text{C}$ was shown to improve the optical quality of the 0.95 eV GaAsSbN layer. However, the accompanying blueshift of ~ 105 meV has led to the need for other alternatives in improving the GaAsSbN material quality for 1.3 μm *p-i-n* photodiode application.

In this chapter, we applied the 0.95 eV closely lattice-matched GaAsSbN layer as the intrinsic (i-) layer on a GaAs-based *p-i-n* photodiode (PD) structure. The quality of GaAsSbN layer can be reflected in the device performance as well as the standard material characterization results. The growth temperature of the GaAsSbN layer in the *p-i-n* PD will be varied from 420–480 $^{\circ}\text{C}$. PL and XRD measurements on the samples were complemented by the device characterization such as dark current, responsivity, and dynamic photoresponse measurement.

6.1 Experimental Details

Three *p-i-n* PD samples were prepared on (001) n^+ GaAs substrates with $\sim 4500\text{\AA}$ GaAsSbN i-layers grown at 420 °C, 460 °C, and 480 °C (labeled Samples A, Sample B, and Sample C, respectively). The GaAsSbN layers were grown at $\sim 0.2\mu\text{m/hr}$; under constant As flux overpressure of $\sim 1.8 \times 10^{-6}$ Torr equivalent to $\sim 20 \times$ the Ga flux. The growth rate was chosen to deliver higher N concentration to compensate for the off line-of-sight N source position, and was calibrated to deliver $\sim 2.5\%$ N concentration based on our calibration work in Chapter IV. During the growth of the GaAsSbN layer, the Sb flux was controlled by changing the needle valve opening while maintaining the reservoir and cracker temperature at 560 °C and 900 °C, respectively. The Sb flux was tuned to be $\sim 2.1 \times 10^{-8}$ Torr to preserve the lattice-matched condition. The r.f. plasma source is maintained at an r.f. power of 500 W and the N_2 gas flow at 0.10 SCCM for the GaAsSbN i-layer growth.

In-situ monitoring using reflection high energy electron diffraction (RHEED) pattern showed streaky 2×4 diffraction pattern indicating coherent layer growth with minimum relaxation has been achieved. Prior to the growth of the i-layer, a $3000\text{\AA}$ -thick GaAs:Si layer was grown at 580 °C, with $1\mu\text{m/hr}$ growth rate, and As_4/Ga flux ratio of 20. A growth interruption of $\sim 15\text{mins}$ was introduced to lower the substrate temperature to the desired i-layer growth temperature and to start the r.f. plasma N source. Subsequently after the i-layer growth, $\sim 500\text{\AA}$ thick GaAs:C layer was grown under the identical growth rate, V/III ratio, and substrate temperature used during the growth of the GaAs:Si layer. Another growth interruption of $\sim 15\text{mins}$ was introduced between the p-type layer and i-layer growth to ramp up the substrate temperature back

to 580 °C and the Ga cell to 1 $\mu\text{m/hr}$ growth rate. This interruption step is also useful to evaporate the residual Sb floating-layer [30]. The Si and CBr_4 sources were calibrated to deliver doping concentration of $5 \times 10^{18} \text{ cm}^{-3}$ and $1 \times 10^{19} \text{ cm}^{-3}$, respectively. For comparison purposes, similar GaAs-based *p-i-n* PD samples were grown using ~5000 Å-thick of closely lattice-matched $\text{Ga}_{0.96}\text{In}_{0.04}\text{As}_{0.98}\text{N}_{0.02}$ and $\text{Ga}_{0.90}\text{In}_{0.10}\text{As}_{0.967}\text{N}_{0.033}$ as the i- layer. The details of these *p-i-n* PD structure have been published elsewhere [12,32].

6.2 Device Fabrication and Characterization

Standard fabrication procedure was carried out on the back-polished *p-i-n* samples. Ohmic contacts were made by depositing Ti/Au and Ge/Ni/Au alloys on the n- and p-sides of the sample, respectively. Mesa structures of ~200 μm diameter were formed using standard lithography and lift-off process to reduce the surface leakage current. Responsivity measurement was carried out using a setup comprising a 100W quartz tungsten halogen lamp and a monochromator (Oriel 77200 $\frac{1}{4}$ m) in conjunction with a lock-in amplifier (Stanford Research SR830). The setup was calibrated using a combination of a Ge photodiode and an optical power meter. Dynamic photoresponse measurement was carried out on the *p-i-n* PDs by exciting the devices with a distributed feedback (DFB) 1.3 μm laser coupled to a single mode optical fiber with calibrated power of 5 mW (as shown in Figure 6-1). Sample with smaller mesa diameter of 80 μm was fabricated to improve the high frequency response as discussed in Section 6.3D (Figure 6-1(Right)). The laser was modulated using an r.f. sweep generator from 10 MHz to 26.5 GHz. The frequency response from the photodiode was measured by a spectrum analyzer.

Fig.6-1 (Left) A microscope image obtained from the photodiode with 200 μm mesa diameter on the dynamic response measurement setup. (Right) Surface electron microscope image obtained from the photodiode with 80 μm mesa diameter that was used to solve the RC-limited bandwidth (Section 6.3D).

6.3 Results and Discussions

A. Structural and Optical Characterization of the Closely Lattice-matched GaAsSbN Intrinsic-layer Grown at Different Substrate Temperature

Three *p-i-n* PD samples (A, B, and C) with GaAsSbN closely lattice-matched to GaAs have been grown using SS-MBE, where the details of the samples are listed in Table VI-1. In Chapter III, it was shown that the incorporation of Sb increases with the reduction of substrate temperature. This has been reported in other GaAsSb [42,132] and in GaAsSbN growths as well [134,139]. On the other hand, N

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incorporation is relatively unaffected by the change in growth temperature [90,134,176]. For these reasons, different Sb flux of 1.7×10^{-8} Torr was used during the growth of Sample A.

By so doing, coherent growth of GaAsSbN i-layers have been achieved with lattice mismatch <0.4%, as shown in Figure 6-2. The figure shows the (004) rocking curve of Samples A,B, and C, where the GaAsSbN diffraction peak appears close to the GaAs peak in all three curves. Samples A, B, and C also exhibit clear Pendellosung fringes indicating good interfacial quality. SIMS profile obtained using Cs⁺ as the primary ion source also shows minimum N and Sb diffusion and segregation as shown in Figure 6-3. Comparison between the SIMS Sb counts shown in Fig. 6-2 and Fig. 4-11 indicated that the growth interruption prior to the growth of the p⁺ GaAs on the p-i-n samples layer helps to reduce the Sb floating layer and ensures good interface between GaAs and GaAsSbN layer. This confirms the results reported by Cheah *et al*[149]. that was mentioned in Sections 4.3 and 5.1. The SIMS results indicated all samples have Sb concentration of ~6% and N concentration of ~2.5%–2.8%, with variations due to the SIMS error margin of ± 5% (Table VI-1).

Table VI-1 Growth conditions, lattice-mismatch and PL data. All samples exhibit lattice-mismatch values below 4000ppm.

Sample	GaAsSbN	Sb Flux	SIMS data		Sb/N	(004) XRD	Low temperature PL		
	growth	(torr)	N %	Sb %	ratio	mismatch	PL	PL	PL
	temperature					(ppm)	peak	intensity	FWHM
	(°C)						position	(a.u.)	(meV)
							(eV)		
A	420	1.7×10^{-8}	2.8 ± 0.2	5.8 ± 0.3	2.07	-3060	0.94	307	41
B	460	2.1×10^{-8}	2.6 ± 0.2	6.6 ± 0.3	2.54	-1154	0.93	213	42
C	480	2.1×10^{-8}	2.5 ± 0.2	6.1 ± 0.3	2.44	-1936	0.96	307	47

Fig.6-2 (004) XRD rocking curves exhibited by of the $p\text{-}i\text{-}n$ PD samples with i-layer grown at different substrate temperature.

Figure 6-4 shows the low temperature PL spectra of the three $p\text{-}i\text{-}n$ PD samples at the 1.3 μm wavelength region, with the PL intensity, peak position, and FWHM (full width at half-maximum) listed in Table VI-1. Typically, the PL intensity of dilute nitride materials tends to decrease with narrower bandgap energy due to the increase of N-related defects. However, Sample A and Sample C exhibited similar intensity with Sample A having narrower bandgap. Sample B exhibits lower PL intensity with redshift of $\sim 16\text{meV}$ from Sample A, while Sample C shows PL intensity recovery accompanied by blueshift of $\sim 32\text{ meV}$ from Sample B. This suggests that the 420 $^{\circ}\text{C}$ maybe the preferred growth temperature for this material.

Fig.6-3 Typical SIMS profile of the *p-i-n* PD samples, the profile shown here was obtained from Sample A. Other samples exhibit similar profile.

Table VI-1 shows that the Sb concentration obtained from SIMS measurement is relatively constant between Samples A, B, and C. The N concentrations obtained from SIMS measurement are also constant as the variations between them are still within the SIMS error margin. However, SIMS measures the total N content of the GaAsSbN layer, which includes the substitutional and interstitial N atoms. This is important as one of the characteristics of dilute nitride material is the increase of interstitial N concentration when the substitutional N exceeds 2.5% [109,111]. Unlike the substitutional N atoms, the presence of interstitial N atoms has minimal effect on the bandgap and the lattice parameter of the dilute nitride materials. Hence, the energy position of the PL peak variations exhibited by the *p-i-n* samples can be attributed to the variations of substitutional N atoms within the i-layer. More information, such as

Fig.6-4 Low temperature (4K) PL spectra exhibited by the *p-i-n* samples with i-layer grown at different temperatures.

the ratio of interstitial and substitutional N in the i-layer, is required to establish a clearer relation between the PL peak energy positions with the growth parameters.

B. Asymmetrical X-ray Diffraction Reciprocal Space Map Study

XRD reciprocal space maps (RSMs) in [115] crystal orientation of the *p-i-n* samples are shown in Figure 6-5. The horizontal ($q_{[1\bar{1}0]}$) and vertical ($q_{[001]}$) axes are in reciprocal lattice units ($10^4 \times \text{\AA}^{-1}$), where $q_{[1\bar{1}0]}$ represents the $[1\bar{1}0]$ plane perpendicular to the substrate, and $q_{[001]}$, represents the [001] plane parallel to the substrate. All reciprocal space maps show the GaAsSbN peak (dashed line) and GaAs peak (solid line) are located directly on one vertical line, indicating that the in-plane lattice parameter of the GaAsSbN layer and GaAs substrate are relatively similar. This confirms that coherent growth of the GaAsSbN layer on GaAs was achieved.

However, there are small features near the GaAs (115) peak (dashed arrows), which suggest local concentration fluctuations of N or Sb. The space maps exhibit diffusively scattered x-ray signal around the GaAsSbN/GaAs reciprocal lattice points. The diffusive scattering is very distinct in Samples B and C and greatly reduced in Sample A. The diffusive scattering may arise from point defects-related charge fluctuations, which could be from As_{Ga} point defect native to GaAs, N-related defects such as N-N or N-As pairs, or Sb-related such as Sb_{Ga} antisite. The nature of these point defects will be studied further by DLTS measurement and presented Chapter VII.

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Fig.6-5 Reciprocal space maps of PIN-PD sample with different i-layer growth temperature. Dashed arrows indicate signs of local concentration fluctuations. The horizontal ($q_{[1\bar{1}0]}$) and vertical ($q_{[001]}$) axes are in reciprocal lattice units ($10^4 \times \text{\AA}^{-1}$).

C. Dark Current and Responsivity Measurement of GaAs/GaAsSbN/GaAs *p-i-n* Photodiode

Current-voltage (I-V) measurement, shown in Figure 6-6, indicates that Samples A, B, and C have dark current density of $\sim 0.3\text{--}0.5\text{ mA/cm}^2$ at -2 V bias. This value is lower than 28 mA/cm^2 at the operating voltage of 90% breakdown reported in GaAsSb/GaAs RCE *p-i-n* PD, although their value is considerably smaller ($\sim 0.03\text{ mA/cm}^2$) at -2 V bias [42,43]. The dark current density obtained in our samples is also comparable to 0.45 mA/cm^2 at -2 V obtained in GaAs/GaInNAs(Sb)/GaAs *p-i-n* PD [32]. As the reverse bias increases, it was observed that Sample A exhibits the slowest increase in the leakage current (0.32 mA/cm^2 at -5 V bias). In contrast, the dark current in sample D, with the GaAsSbN i-layer grown at $520\text{ }^\circ\text{C}$ reaches 5.7 A/cm^2 at -5 V bias. In addition, the GaInNAs *p-i-n* sample (Sample E, solid squares) shows higher dark current compared to Sample D. The higher dark current suggests a transition to a three-dimensional (3D) growth mode during the intrinsic layer growth of Samples D and E. The N clustering is widely known to take place when the nitrogen concentration exceeds 1% allowing the transition from layer-by-layer (2D) growth to 3D growth mode to occur readily. The presence of Sb appears to have suppressed this N clustering, even when the nitrogen concentration in the GaAsSbN ($\sim 2.7\%$) is relatively higher than in the GaInNAs intrinsic layer ($\sim 2.0\%$). This reactive surfactant behavior limits N clustering by reducing the surface diffusion length [35], resulting in the suppression of N clustering and the preservation of the 2D growth mode.

Fig.6-6 I-V curve of $p\text{-}i\text{-}n$ samples under reverse bias were taken under no light excitation. Another sample with GaAsSbN i-layer grown at 520°C (Sample D) and a GaInNAs $p\text{-}i\text{-}n$ PD (Sample E: data from ref. [32]) were added for comparison purposes.

Room temperature responsivity measurement results of the GaAsSbN $p\text{-}i\text{-}n$ photodiodes under reverse bias of -2 V are shown in Figure 6-7. For comparison purposes, $p\text{-}i\text{-}n$ samples with lattice-matched GaInNAs are included. The N concentrations the GaInNAs i-layer in Samples E and F are 2.0% (Ref. [32]) and 3.3% (Ref. [12]), respectively. The poor responsivity of Sample D is expected, because it was grown under high substrate temperature that allows N clustering and 3D growth to occur readily. At the photoresponse peak ($\sim 0.95\ \mu\text{m}$), sample E has the highest response followed by Samples A, C, B, F, and D. However, at $1.3\ \mu\text{m}$, the highest response was exhibited by Sample A, followed by Samples C, B, F, and D.

Fig.6-7 Room temperature photoresponse of the *p-i-n* PD samples reverse biased at 2 V. At 0.950 μm , sample A exhibits the strongest response followed by Samples C and B. Photoresponse from GaInNAs *p-i-n* PD samples (solid symbols, from references [12] and [32]) measured under the same conditions are included for comparison. At 1.3 μm , Samples A–C exhibit higher responsivity compared to Samples D–F.

Sample E does not have a response at 1.3 μm , because its cutoff wavelength is only at 1.25 μm . On the other hand, Sample F was grown in a different MBE chamber with N-source setup that is capable of delivering 3.3% N into the GaInNAs layer [12].

Comparison between the GaAsSbN and GaInNAs *p-i-n* sample E shows the peak photocurrent response (at ~ 950 nm wavelength) of the GaInNAs *p-i-n* sample is still higher than the GaAsSbN *p-i-n* PD sample. There are two reasons for such reduction in the responsivity. Firstly, the nitrogen incorporation in the GaAsSbN is promoted by the presence of Sb. This leads to the higher cutoff wavelengths of the GaAsSbN *p-i-n* samples compared to GaInNAs *p-i-n* sample E, although sample E is grown under the condition in the same chamber as the GaAsSbN *p-i-n* samples [32,177]. Thus, despite the fact that the growth rate, the r.f. plasma source condition, and As₄/Ga ratio during the GaAsSbN and GaInNAs i-layer growth are all identical, the nitrogen content in GaAsSbN i-layers are higher than the GaInNAs i-layer. However, the enhanced N incorporation also increases the N-related defects that contribute to the reduction in the responsivity in the GaAsSbN *p-i-n*.

Secondly, the Sb concentration incorporated in lattice-matched GaAsSbN/GaAs is significantly higher ($\sim 6\%$) as compared to the amount Sb used for surfactant purposes. Consequently, there are three group V atoms competing for the group V substitutional lattice point, which might lead to formation of group V point defects such as group V antisites and split interstitials, as described in Chapter III. The presence of these defects was studied using DLTS and the results will be discussed in Chapter VII. Therefore, the combination of enhanced N incorporation and group V-related point defects contributes to the reduction of the responsivity in the GaAsSbN/GaAs *p-i-n* PD. However, it is important to note that at $1.3\mu\text{m}$, the GaAsSbN *p-i-n* PD A–C exhibit the higher responsivity compared to samples D–F.

CHAPTER VI Effect of Growth Temperature on Lattice-Matched GaAsSbN i-layer for GaAs based 1.3 μ m *p-i-n* Photodiode

Comparison of the breakdown voltage of the dark current and the photocurrent responsivity between samples A–C, as shown in Table VI-2, correlates very well with the low temperature PL spectra and XRD RSMs results in the previous sections. Sample A exhibits the best DC photodiode performance, followed by samples C and B. However, room temperature photocurrent measurement indicates that the responsivity and quantum efficiency calculated by Eq. 2-8 is still low. Currently, we attribute this to the group V point defects and split interstitial and possibly local concentration fluctuations of N and Sb as indicated on the RSMs. These defects can act as non-radiative recombination centers with detrimental effect on the responsivity of the *p-i-n* PD.

Table VI-2 Relation between GaAsSbN i-layer growth temperature and I-V characteristic, photocurrent response and PL of the respective *p-i-n* PD samples.

Sample	Intrinsic layer	Dark current	Response @1300nm		Wavelength		
	growth	density	Responsivity	Quantum	RT	4K PL peak	4K PL
	temperature	@ -5V	(mA/W)	efficiency	photocurrent	position	intensity
	(°C)	(mA.cm ⁻²)			cutoff (nm)	(nm)	
A	420	0.32	33.0	3.2%	1380	1314	307
B	460	1.45	26.4	2.5%	1385	1336	213
C	480	2.20	27.8	2.7%	1365	1290	307
D	520	5748	5.2	0.5%	1355	n.a.	n.a.

**D. Dynamic Photoresponse Measurement of GaAs/GaAsSbN/GaAs
p-i-n Photodiode using a Modulated 1.3 μm Wavelength Laser**

Figure 6-8 shows the dynamic photoresponse measurement results from sample A under different reverse bias voltage. The responsivity increases with the reverse bias, which is expected out of a *p-i-n* PD. The increase of responsivity with reverse bias is due to the stronger reverse bias electric field that separates the photo-generated electron-hole pairs (EHP). The stronger electric field allows more photo-generated EHP to be created within the same time duration, thus increasing the photoresponse. The measured bandwidth (f_{3dBm}) increases from 200MHz to 260MHz when the reverse bias was increased from 0.5 V to 1 V, and it remains at 260 MHz even when the reverse bias is increased to 4 V. This suggests that the GaAsSbN i-layer has been fully depleted at 1 V reverse bias.

The increase of the photoresponse occurs at the expense of the increase of dark current. Thus, the photoresponse measurements on the other photodiode samples are limited by the dark current. Comparison of dynamic photoresponse from the GaAs/GaAsSbN/GaAs *p-i-n* sample was performed under -1V reverse bias and 1.3 μm laser excitation. The results are shown in Figure 6-9. Sample A exhibits the highest photoresponse (-38 dBm at the low frequency plateau-region) followed by Sample B (-39 dBm), Sample C (-42 dBm) and Sample D (-52 dBm). The magnitude dynamic photoresponse is significantly lower than the DC responsivity, which suggests some power loss. This can be due to the improper alignment of the optical fiber that can

Fig.6-8 Dynamic photoresponse of GaAs/GaAsSbN/GaAs $p\text{-i-n}$ PD sample A measured under different reverse bias.

contribute significantly to the coupling loss, along with other reasons that is currently under investigation.

The bandwidth of the photodiodes still shows similar trend with the DC characteristics and PL spectra. The photodiodes exhibit f_{3dBm} of 260 MHz for sample A and 200 MHz for Samples B and C, respectively. These results are still below the required bandwidth for long haul optical communication purposes. However, it is important to mention that the measured bandwidth is RC time-constant limited. At -1V bias, the capacitance of Samples A and C obtained from C-V measurements are $\sim 16\text{pF}$ and $\sim 9\text{pF}$, respectively. The capacitance (C), resistance (R), and the measured bandwidth (f_{3dBm}) can be correlated using Equation 2-14, which can be rewritten as,

Fig.6-9 Dynamic photoresponse obtained from GaAsSbN *p-i-n* PD samples of 200 μm mesa diameter under 1 V reverse bias. The excitation source is a 1.3μm laser.

$$f_{3dBm} = \frac{1}{2\pi RC} \tag{6-1}$$

On a 50 Ω measurement-circuit, these C values will result in bandwidth of 360MHz and 200MHz for samples A and C, respectively. The calculated f_{3dBm} values are consistent with the experimental values, where sample B has higher f_{3dBm} than sample A. Subsequently, the RC time constant limit can be lowered by reducing the mesa diameter of the device. Figure 6-10 shows the normalized photoresponse of sample A with different mesa diameter of 400 μm, 200 μm, and 80 μm, under laser excitation wavelengths 1.3μm and reverse bias of -1V. The plot of 3dB cut-off frequency vs. mesa diameter is shown in the inset. It was observed that by reducing the mesa

diameter by half, the f_{3dBm} value improved by a factor of ~ 4 . Thus, the f_{3dBm} is inversely proportional to the area of the mesa structure, and this further confirms the RC time-constant limited nature of the photodiode dynamic response. Figure 6-10 shows the bandwidth for GaAs *p-i-n* photodiode with different mesa diameter as a function of the i-layer thickness calculated by Eq.2-14. The permittivity and the hole saturation velocity of GaAsSbN were approached using the GaAs values. The solid squares are the measured bandwidth shown in Fig. 6-9. The difference between the experimental and calculated values may have originated from a higher permittivity or slower hole saturation velocity than GaAs, both of which may have occurred in a material with poorer crystalline quality. However, It can be seen from the bandwidth prediction that GHz-region bandwidth is still achievable by reducing the mesa diameter or by growing a thicker i-layer to reach the transit time-limited operating region. A thicker i-layer is achievable because the closely lattice-matched condition on GaAs has been established. However, the present dilute nitride growth setup involves the use of 0.2 $\mu\text{m/hr}$ growth rate to incorporate the required N concentration. The use of the low growth rate leads to longer growth time that allows more impurities to be incorporated into the i-layer resulting in a defective intrinsic layer. Solution to this low growth rate problem involves repositioning the nitrogen plasma source to a line-of-sight position to the substrate, which is beyond the discussion of this thesis. A study on the effect of these defects on the photodiode performance will be presented in the next chapter.

Fig.6-10 Normalized dynamic photoresponse of GaAsSbN p - i - n PD with different mesa diameters were obtained under 1.3 μm laser excitation.

Fig.6-11 Calculated bandwidth of a GaAs-based p - i - n photodiode shown together with the bandwidth measurement results from Fig.6-9.

6.4 Summary

In order to find other ways to improve the quality of the GaAsSbN layer, the effect of growth temperature were studied using a GaAs/GaAsSbN/GaAs *p-i-n* photodiode (PD) structure. The growth temperature of the GaAsSbN i-layer was varied from 420–480°C. Closely lattice-matched condition of the GaAsSbN layer to GaAs has been achieved in all samples. The *p-i-n* PD samples exhibit reasonably low dark current of $\sim 0.3\text{--}0.5\text{mA/cm}^2$ at 2V reverse bias and photoresponse of up to 1.3 μm , which suggests the potential for optical communication application. Comparison with some existing GaInNAs *p-i-n* samples suggests the presence of Sb suppresses the N clustering and increases the N concentration. This leads to improvement in the dark current and responsivity of the GaAsSbN *p-i-n* PD compared to the reference GaInNAs *p-i-n* samples. However, the responsivity of the as-grown *p-i-n* samples are still low compared to the commercially available InP-based photodiodes. This may be attributed to point defects such as group V-related antisites, N-related split interstitials, and other dilute nitride-related complexes. Asymmetrical XRD reciprocal space maps (RSM) shows reduction of diffused scattering with reduction of growth temperature to 420 °C, which suggests suppression of the point defect formation. Furthermore, dynamic photoresponse measured on the best *p-i-n* sample shows an RC time constant-limited bandwidth of up to 920 MHz. This demonstrates the potential high frequency application of GaAs/GaAsSbN/GaAs *p-i-n* photodiodes. Further improvement of the bandwidth can be done by increasing the intrinsic layer thickness or making the device diameter smaller.

CHAPTER VII Effect of Growth Temperature on Defect States of GaAsSbN i-layer in GaAs/GaAsSbN/GaAs *p-i-n* Photodiode for 1.3 μm Application

In the previous chapter, we have demonstrated *p-i-n* photodiodes with responsivity of up to 1.3 μm wavelength. The effect of the growth temperature on the device performance has been linked to the reduction of the point defects within the GaAsSbN i-layer. In this chapter, we described deep level transient spectroscopy measurements made on the *p-i-n* photodiode samples to study the defect states within the GaAsSbN intrinsic layer.

7.1 Introduction

Compared to other dilute nitride materials, studies on the defect states in GaAsSbN are still lacking. Due to the competition between the group-V elements, the formation of point defects in the form of group V antisites or split interstitials is expected. One of those defects is As_{Ga} antisites, which are native to GaAs [97-100] and have been reported in other dilute nitride materials such as GaNAs and GaInNAs [114-117]. There are also other types of group V point defects such as Sb_{Ga} antisites native to GaAsSb [102-104], N-As and N-N split interstitials native to GaNAs [107,109,111], and other complexes related to dilute nitride materials such as $\text{V}_{\text{Ga}}\text{-N}_{\text{As}}$ or $\text{As}_{\text{Ga}}\text{-N}_{\text{As}}$ complexes [107,178]. Therefore, DLTS measurements were performed on GaAs/GaAsSbN/GaAs *p-i-n* structures with the GaAsSbN i-layer grown at 420 °C and 480 °C. The samples are identical with Samples A and C from the previous

chapter, and will be referred as such in this chapter. A correlation was made between the DLTS result and the respective *p-i-n* photodiode performance from the previous chapter.

7.2 Experimental Procedure

The DLTS measurement was performed on two samples of GaAs/GaAsSbN/GaAs photodiodes, with i-layer grown under different growth temperatures of the i-layer. The growth temperature of the p-type and n-type GaAs layer was kept constant at 580 °C, while the i-layer growth temperature was kept at 420 °C for Sample A and 480 °C for Sample C. The details of the growth, fabrication, and characterization of the photodiodes can be found in the Chapter VII.

For deep-level study purposes, capacitance-voltage (C-V) and DLTS measurements were carried out on samples A and C using a digital DLTFs system equipped with a 1 MHz bridge capacitance meter. The theoretical details of the DLTFs measurement can be found in Section 3.3 of Chapter III. Deep level transient Fourier spectroscopy (DLTFs) was conducted by sampling N values from each capacitance transients measured at different temperatures from 40K to 340K. The DLTS spectra of the majority carriers were obtained from the photodiodes using sampling number $N = 512$, filling pulse of -0.01 V , filling pulse duration of 40ms and period width of 2ms. Since Sample C exhibits higher dark current than Sample A, a lower reverse bias voltage was chosen for sample C (-2 V for Sample C and -4 V for Sample A). Discrete Fourier coefficients can be obtained from the capacitance transient measurements, from which the carrier emission rate can be determined by

using Equation 3-14. Thus, carrier emission rate at different temperature can be obtained from the capacitance transients at different temperatures. Subsequently, E_a and σ_∞ can be obtained from the standard Arrhenius equation (Eq. 3-10) for hole emission:

$$\ln(\tau T^2) = \frac{E_a}{kT} - \ln(\sigma_\infty \gamma_p) \quad 7-1$$

where τ is the hole emission time constant, T is the absolute temperature, σ_∞ is the carrier capture cross-section, k is the Boltzmann constant, $\gamma_p = 3.256 m_p^* \times 10^{21} \text{ cm}^{-2} \text{ s}^{-1} \text{ K}^{-2}$, and m_p^* is the hole effective mass ratio. For GaAsSbN in this work, $m_p^* = 0.50$ was used for the DLTS calculations, based on the calculations by Park [60] for GaAsSbN with N and Sb atomic concentrations close to our GaAsSbN i-layer.

7.3 Results and Discussions

A. Capacitance-Voltage Measurement

Room temperature capacitance-voltage (C-V) measurements on the photodiode samples were used to determine the net acceptor concentration of the i-layer (Figure 7-1). As shown in the inset, the plot of $1/C^2$ vs. V formed a straight line for both photodiodes. This suggests uniform background doping concentration profile of the i-layer for both photodiodes. The p-type doping concentration was found to be $2.7 \times 10^{17} \text{ cm}^{-3}$ and $1.1 \times 10^{17} \text{ cm}^{-3}$ for i-layers grown at 420 $^\circ\text{C}$ (Sample A) and 480 $^\circ\text{C}$ (Sample C), respectively.

Fig.7-1 Room temperature C-V plot of photodiodes with i- layer grown at 480°C and 420°C. **Inset:** Plot of $1/C^2$ vs. V from which the background doping concentration was determined.

B. DLTS Spectra of GaAs/GaAsSbN/GaAs Photodiodes

The DLTS spectra of the majority carrier (Figure 7-2) were obtained from the photodiodes using sampling number $N = 512$, filling pulse of -0.01 V, filling pulse duration of 40 ms and period width of 2 ms. The samples were measured under reverse bias voltage of -4 V and -2 V for Samples A and C, respectively. As seen in Table VII-1, all four DLTS peaks exhibit broadening as indicated by the $FWHM/T_p$, which is the ratio between the full width half maximum (FWHM) of the DLTS signal and its respective peak temperature (T_p). The $FWHM/T_p$ values are all larger than the

Fig.7-2 DLTS spectra of the *p-i-n* PD samples were obtained using filling pulse of -0.01 V, pulse duration of 40 ms, and period width of 2 ms. The reverse bias for Samples A and C are 4 V and 2 V, respectively. Activation energy and hole capture cross sections were determined from the Arrhenius plots shown in the inset.

DLTS peak value from an ideal point defect, where the expected FWHM/T_p is ~ 0.1 [126]. The broadening of the DLTS spectra suggests that the defect states may have a continuous distribution of states or discrete but closely spaced energy levels, due to a distribution of isolated point defects or point defect clusters. However, it is important to note that this broadening does not change the peak temperature of the DLTS peak for a given rate window [127], which allows the trap activation energy to be obtained from Equation 3-12

Each sample exhibits two hole traps (HT_1 and HT_2), with their respective Arrhenius plots shown in the inset of Fig. 7-2. Subscripts 1 and 2 indicate the first (low temperature) and the second (high temperature) defect peaks, while subscripts A and C indicate the sample from which the defect peak was originated. The spectra of HT_1 were multiplied by 10 and HT_{2A} was multiplied by 2 for clarity. By lowering the growth temperature from 480 °C to 420 °C, the HT_1 DLTS signal maxima increases by ~ 2 times and the HT_2 DLTS signal maxima decreases by ~ 17 times. The hole traps HT_{1C} and HT_{1A} have activation energies of 0.12 eV and 0.10 eV, respectively (Table VII-1). These values are within the range for N-related shallow hole-traps in GaNAs (0.03–0.18 eV above the valence band maximum or VBM) and GaInNAs (0.10–0.21 eV above the VBM) [107,120]. Thus, the HT_1 defect states are most likely to be related to the N-N and N-As defects. On the other hand, HT_{2C} and HT_{2A} trap levels have activation energies of 0.42eV and 0.43eV, respectively. The HT_2 hole traps are located close to midgap; approximately 0.46–0.47 of the i-layer bandgap energy (E_g), which is relatively close to the $0.43E_g$ reported for EL2 defect in GaAs [101]. LT-GaAs grown under similar growth temperature (400⁰C) also reported high concentrations of EL2 ($\sim 10^{19} \text{ cm}^{-3}$) and $\text{EL2}^+ (< 5 \times 10^{17} \text{ cm}^{-3})$ [98]. The formation of As_{Ga} defects in GaNAs grown at low temperature under As-rich conditions has also been predicted [105].

We observed similar As_{Ga} -related midgap defects with activation energy $\sim 0.43E_g$ in GaAs/GaInNAs/GaAs and GaAs/GaInNAs:Sb/GaAs photodiodes [125]. The midgap defects act as non-radiative recombination centers, which effectively degrade the GaInNAs/GaAs photodiode responsivity. The reduction of the midgap

trap greatly improves the responsivity of the GaInNAs:Sb/GaAs photodiode. Although Sb_{Ga} defects found on GaAs:Sb/GaAs was known to form a midgap defect state [102-104], the activation energy of the midgap defect states found in this work ($0.46\text{--}0.47E_g$) is much closer to the value of the As_{Ga} defects ($0.43E_g$) than the Sb_{Ga} defects ($0.40E_g$). Thus, it is plausible that the HT_2 defect states found in this work may have also originated from the As_{Ga} defects.

In order to examine the true activation energy of these hole traps, the hole capture cross sections were measured by varying the filling pulse time (t_p) at the temperature where the DLTS signal maxima occurred. In the case of an ideal point defect, the capacitance transient will have an exponential shape and the plot of $\ln(1 - \Delta C_0 / \Delta C_0^\infty)$ vs. t_p will form a straight line with c_p as its slope. The relation between the transient amplitude ΔC_0 and t_p can be described as:

$$\Delta C_0 = \Delta C_0^\infty [1 - \exp(-c_p t_p)] \quad 7-2$$

where ΔC_0^∞ is the saturated amplitude of the capacitance transient, and c_p is the hole capture rate. However, this behavior was not observed in the plot of $\ln(1 - \Delta C_0 / \Delta C_0^\infty)$ vs. t_p of the hole traps in Figure 7-3. The DLTS signal of $\text{HT}_{1\text{C}}$ increases monotonically following increase in the filling pulse and the subsequent $\ln(1 - \Delta C_0 / \Delta C_0^\infty)$ vs. t_p plot shown on the inset does not exhibit a straight line as anticipated. The behavior was observed in all of the other hole traps as well. The $\ln(1 - \Delta C_0 / \Delta C_0^\infty)$ vs. t_p plot suggests that the hole traps behavior are more like an extended defect than an ideal point defect with a distinct energy level. In the case of an extended defect state, the hole capture rate will be a function of the logarithmic of

Fig.7-3 DLTS signal from HT_{1C} are plotted against the filling pulse (t_p). The plot $\ln(1 - \Delta C_0 / \Delta C_0^\infty)$ as function of t_p is shown in the inset, where the capture rate was determined from the initial slope.

the filling pulse [128] and this behavior has also been reported in various DLTS studies on GaInNAs [121,124,125]. Nevertheless, Balcioglu *et al.* [121] suggested that one can still obtain the hole capture rate from the initial slope of the plot as shown in the inset of Fig.7, using the correlation with the hole capture cross section:

$$c_p = \sigma_p \langle v_{th} \rangle p \tag{7-3}$$

where v_{th} is the thermal velocity and p is the hole concentration. Thus, using Eq. (7), the cross section activation energy of HT_{1C} was determined to be 0.07eV, suggesting that its energy level is 0.05eV above the VBM. The cross section activation energies and the trap energy levels of HT_{1A}, HT_{1C}, HT_{2A}, and HT_{2C} are listed in Table VII-1.

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i-layer in GaAs/GaAsSbN/GaAs p-i-n Photodiode for 1.3 μm Application

Table VII-1 Trap parameters determined from DLTS analysis. $FWHM/T_p$ is the ratio of the DLTS peaks' full width at half maxima (FWHM) and their respective peak temperature.

Hole Trap	Sample	FWHM/ T_p	Activation energy, E_a (eV), (ratio with E_g)	Cross section activation energy, E_σ (eV)	Energy level, (eV)	Trap Concentration (cm^{-3})	Apparent carrier capture Cross section, σ_a (cm^2)
HT _{1C}	C:480°C	0.56	0.12 (0.13 E_g)	0.07	$E_v + 0.05$	1×10^{14}	2.9×10^{-17}
HT _{1A}	A:420°C	0.59	0.10 (0.11 E_g)	0.05	$E_v + 0.05$	7×10^{14}	2.4×10^{-17}
HT _{2C}	C:480°C	0.17	0.42 (0.46 E_g)	0.24	$E_v + 0.17$	4×10^{15}	6.6×10^{-17}
HT _{2A}	A:420°C	0.32	0.43 (0.47 E_g)	0.26	$E_v + 0.18$	1×10^{15}	8.2×10^{-17}

C. The Effect of Growth Temperature Reduction on the Defect States of GaAsSbN Intrinsic layer

Reduction in the i-layer growth temperature from 480 °C to 420 °C has two implications for the deep level spectra: (i) the concentration of shallow N-related traps (HT₁) increases (from $1 \times 10^{14} \text{ cm}^{-3}$ to $7 \times 10^{14} \text{ cm}^{-3}$) and (ii) the concentration of midgap traps (HT₂) decreases (from $4 \times 10^{15} \text{ cm}^{-3}$ to $1 \times 10^{15} \text{ cm}^{-3}$). At first glance, this trend defies the general principle that the trap concentrations of HT₂ increases and HT₁ reduces as the growth conditions become more arsenic-rich (i.e. increased V/III ratio, reduced growth temperature). However, similar to As_{Ga} defects, the formation energy of As_{Ga}–N_{As} defects also decreases following reduction in the growth temperature. This is significant, because the formation of As_{Ga}–N_{As} pairs will push the As_{Ga} midgap state nearer to the VBM [105]. This explains the decrease in the midgap trap concentration in Sample A and the increase in shallow N-related trap

concentration as the growth temperature is lowered and the growth condition moves towards the As-rich condition. This increase in the shallow N-related traps contributed to the increase of the intrinsic doping concentration from $2.7 \times 10^{17} \text{ cm}^{-3}$ in Sample C to $1.1 \times 10^{17} \text{ cm}^{-3}$ in Sample A.

The decrease in the midgap trap level in Sample A also explains the improvement in the photoresponse observed in Figure 7-4, since the midgap states act as non-radiative recombination centers in GaAs and GaInNAs as well. The overall reduction in trap concentration in Sample B also correlates with the reduction in the diffused scattering of the XRD RSMs as shown in Fig.6-4. The $\sim 4\text{dB}$ improvement in photoresponse under 1.3 μm laser excitation, and ~ 8 times reduction in dark current at -8V reverse bias can be correlated to the reduction in the overall trap concentration and mainly the As_{Ga} midgap trap concentration in Sample A.

7.4 Summary

To study the effect of growth temperature on the defect states in the GaAsSbN i-layer, deep level transient spectroscopy (DLTS) measurement was performed on GaAs/GaAsSbN/GaAs *p-i-n* photodiodes grown at 420 °C and 480 °C. DLTS reveals two types of defect states in the GaAsSbN i-layer: (i) HT_1 : a shallow N-related trap ($E_a \sim 0.10\text{--}0.12 \text{ eV}$) and (ii) HT_2 : midgap trap with $E_a \sim 0.42\text{--}0.43 \text{ eV}$. Reduction in growth temperature from 480 °C to 420 °C reduces the HT_2 trap concentration from $4 \times 10^{15} \text{ cm}^{-3}$ to $1 \times 10^{15} \text{ cm}^{-3}$, while increases the HT_1 trap concentration from $1 \times 10^{14} \text{ cm}^{-3}$ to $7 \times 10^{14} \text{ cm}^{-3}$. Reduction in the HT_2 trap concentration following growth temperature reduction was attributed to the reduction of As_{Ga} point defect-related

Fig.7-4 The *p-i-n* PD characteristics exhibited by Samples A and C with mesa diameter 200 μm , where (a) dynamic photoresponse obtained from the *p-i-n* PD mesa and (b) the dark current density as a function of the reverse bias voltage.

midgap defects, as also suggested by comparison of the XRD RSM. Evidence of possible change from the As_{Ga} -related midgap state to a shallow level defect due to the formation of $\text{As}_{\text{Ga}}\text{-N}_{\text{As}}$ pairs was suggested by the increase of the shallow HT_1 trap concentration in the sample grown at 420 $^{\circ}\text{C}$. The ~ 4 dBm improvement in photoresponse under 1.3 μm laser excitation, and ~ 8 times reduction in dark current at 8 V reverse bias were attributed to the reduction in the overall trap concentration and mainly the As_{Ga} midgap trap concentration in the sample grown at 420 $^{\circ}\text{C}$. The DLTS results correlate well with the improvement in the photodiode performance and the asymmetrical XRD RSM of the [115] plane presented in Chapter VI.

CHAPTER VIII Conclusions and Recommendations

8.1 Conclusions

A. Solid-state Molecular Beam Epitaxy Growth of GaAsSbN Closely Lattice-matched to GaAs

Preferential incorporation of Sb over As was observed in GaAsSb layers grown at low temperature (460 °C) under high As₄/Ga flux ratio (~20). The Sb sticking coefficient under these growth conditions was found to be ~6.7 times the As sticking coefficient. Good quality GaAsSb can still be obtained using the dilute nitride growth condition. However, the critical thickness of the GaAsSb layer reduces with the increase of Sb concentration, preventing the growth of thick GaAsSb layer with high Sb concentration. Epilayer relaxation and formation of misfit dislocation have been observed in GaAsSb samples grown beyond the critical thickness predicted by Matthews-Blakeslee model.

To reduce the lattice mismatch, N must be added during the growth of GaAsSb layer. Calculation using Vegard's law shows that GaAsSbN will be lattice-matched to GaAs when Sb/N ratio is 2.6. The growth of GaAsSbN was studied by using a two-layer and three-layer structures, where GaNAs/GaAsSbN and GaAsSb/GaNAs/GaAsSbN layers are grown on the same GaAs substrate. The structures were studied by combination of low temperature photoluminescence (PL), x-ray diffraction (XRD), and secondary ion mass spectroscopy (SIMS), which reveals two important properties of GaAsSbN growth. Firstly, in the growth rate ranging from

0.1 to 1 $\mu\text{m/hr}$, the N incorporation in GaAsSbN is inversely proportional to the growth rate. Secondly, the lattice-matched condition can be preserved regardless of the growth rate by maintaining the Sb flux at approximately 2×10^{-8} Torr while keeping the As₄/Ga ratio and the r.f. plasma source parameters the same. This is observed on lattice-matched GaAsSbN/GaAs grown under 1, 0.5, and 0.2 $\mu\text{m/hr}$. GaAsSbN samples exhibits improved PL intensity compared to the PL intensity exhibited by the reference GaNAs sample with similar N content. This suggests the presence of reactive surfactant properties of Sb in the growth of GaAsSbN similar to what has been reported in Sb-containing GaInNAs. In addition, the presence of Sb enhances N incorporation, allowing more than 2.5% of N to be incorporated in GaAsSbN grown at 0.2 $\mu\text{m/hr}$. This enables us to reduce the bandgap of GaAsSbN to as low as 0.95 eV while maintaining the closely lattice-matched condition to GaAs. This approach allows the first time demonstration of GaAs-based photodiode using ~500nm thick GaAsSbN i-layer with photoresponse of up to 1.3 μm .

B. Rapid Thermal Annealing of GaAsSbN/GaAs

Rapid thermal annealing (RTA) improves the quality of dilute nitride materials, particularly those grown using r.f. plasma N source. In this thesis, the effect of RTA on GaAsSbN was studied using PL and XRD. Two series of samples underwent *ex-situ* rapid thermal annealing (RTA) process under N₂ ambient for the duration of 5 minutes, with the RTA temperature range from 450-900 °C. The first series is a GaAsSbN quantum well (QW) sample with estimated Sb and N concentrations of 12% and 0.7%, respectively. The other series is a GaAsSbN bulk layer lattice-matched to GaAs with Sb and N concentrations of 2.2% and 0.5%, respectively. Significant

improvement in PL intensity was observed in the annealed samples, suggesting annihilation of impurities and defects in the GaAsSbN layer. The optimum annealing temperatures for both the bulk and QW samples were obtained at 700 °C. Low temperature PL shows RTA-induced bandgap redshift followed by blueshift, particularly in the annealed QW samples. The redshift is probably due to the interstitial to substitutional “kick-out” mechanism of N atoms similar to what was observed in annealed GaNAs samples. Although the annealed GaAsSbN QW has lower N content, its RTA-induced bandgap redshift occurs at lower annealing temperature (~500 °C) compared to the GaNAs reference (650–725 °C). This is due to the interdiffusion of As-Sb atoms that readily occurs during the annealing of GaAsSbN. The As-Sb interdiffusion also contributed to the bandgap blueshift that occurs at RTA temperature over 500 °C.

The RTA-induced bandgap blueshift in dilute materials can be attributed to a number of factors. Group V short range ordering (SRO), N profile homogenization in the growth direction, and N out-diffusion can all contribute to the bandgap blueshift. Room temperature PL and XRD studies on the annealed bulk samples revealed that the N out-diffusion dominates over the other factors when the RTA temperature exceeds 750 °C and above. Thus by keeping the RTA temperature at the optimum temperature of 700 °C, blueshift should still be suppressed. This is observed in the low temperature PL spectra of the annealed bulk GaAsSbN with N content 0.5%, where the RTA-induced bandgap blueshift is only ~20 meV for RTA temperature of 700 °C. However, when the lattice-matched $\text{GaAs}_{0.904}\text{Sb}_{0.07}\text{N}_{0.026}$ was annealed under the optimum condition, its low temperature PL spectra showed ~105 meV of bandgap blueshift. Although the annealed $\text{GaAs}_{0.904}\text{Sb}_{0.07}\text{N}_{0.026}$ layer also exhibits 15 times

improvement of the low temperature PL intensity, the large blueshift made the $\text{GaAs}_{0.904}\text{Sb}_{0.07}\text{N}_{0.026}$ layer unsuitable for the $1.3\mu\text{m}$ photodiode application. The limitation comes from the r.f. plasma N source that is not in line-of-sight in this work. The lack of XRD rocking curve peak shift has led to the conclusion that there is still minimal N out-diffusion from the GaAsSbN layer. Therefore, the blueshift is more likely caused by the group V short-range ordering, which is more severe in GaAsSbN with high N content. Despite this blueshift, the optimum annealing range that was discovered in this work is consistent with dilute nitride literatures and will be useful in other applications of this material such as a 1eV absorption layer in solar cells or base material for heterojunction bipolar transistors.

C. Characterization of As-grown GaAs/GaAsSbN/GaAs *p-i-n* Photodiode

In order to find other means to improve the quality of the GaAsSbN layer, the effect of growth temperature was studied using a GaAs/GaAsSbN/GaAs *p-i-n* photodiode (PD) structure. The growth temperature of the GaAsSbN i-layer was varied from 420–480°C. Closely lattice-matching condition of the GaAsSbN layer to GaAs has been achieved in all samples. The *p-i-n* PD samples exhibited reasonably low dark current of $\sim 0.3\text{--}0.5\text{mA/cm}^2$ at 2V reverse bias and photoresponse of up to $1.3\mu\text{m}$, which suggests the potential for optical communication application. Comparison with some existing GaInNAs *p-i-n* samples suggests the presence of Sb suppresses the N clustering and increases the N concentration. This leads to improvement in the dark current and responsivity of the GaAsSbN *p-i-n* PD compared to the reference GaInNAs *p-i-n* samples. However, the responsivity of the as-grown

p-i-n samples are still low compared to the commercially available InP-based photodiodes. This may be attributed to point defects such as group V-related antisites, N-related split interstitials, and other dilute nitride-related complexes. Asymmetrical XRD reciprocal space maps (RSM) shows reduction of diffused scattering with reduction of growth temperature to 420 °C, which suggests suppression of the point defect formation. This results correlates well with the improvement in the photodiode performance. Furthermore, the dynamic photoresponse measured on the best *p-i-n* sample shows an RC time constant-limited bandwidth of up to 920 MHz. This is a first-time demonstration of the communication wavelength high-speed response of a GaAs-based photodiode using thick GaAsSbN i-layer, which demonstrates the potential of GaAsSbN for high frequency application. Further improvement of the bandwidth can be done by increasing the intrinsic layer thickness or making the device diameter smaller.

D. The Effect of Growth Temperature on the Defect States of GaAsSbN Intrinsic Layer

DLTS measurement on GaAs/GaAsSbN/GaAs *p-i-n* photodiodes reveals two types of defect states in the GaAsSbN i-layer: (i) HT₁: a shallow N-related trap ($E_a \sim 0.10\text{--}0.12$ eV) and (ii) HT₂: midgap trap with $E_a \sim 0.42\text{--}0.43$ eV. Reduction in growth temperature from 480 °C to 420 °C reduces the HT₂ trap concentration from $4 \times 10^{15} \text{ cm}^{-3}$ to $1 \times 10^{15} \text{ cm}^{-3}$, while increases the HT₁ trap concentration from $1 \times 10^{14} \text{ cm}^{-3}$ to $7 \times 10^{14} \text{ cm}^{-3}$. Reduction in the HT₂ trap concentration following growth temperature reduction was attributed to the reduction of As_{Ga} point defect-related midgap defects, as also suggested by comparison of the XRD reciprocal space maps.

The reduction of growth temperature may have also caused possible change from the As_{Ga} -related midgap state to a shallow level defect related to the formation of $(\text{As}_{\text{Ga}}-\text{N}_{\text{As}})$ pairs. The ~ 4 dBm improvement in photoresponse under $1.3\ \mu\text{m}$ laser excitation, and ~ 8 times reduction in dark current at -8V reverse bias were attributed to the reduction in the overall trap concentration and mainly the As_{Ga} midgap trap concentration in the sample grown at $420\ ^\circ\text{C}$. These results provide more clues to the material properties of the GaAsSbN, as the study on this material is still lacking compared to its predecessor, GaInNAs.

8.2 Recommendations for Future Research

This thesis has demonstrated the potential of GaAsSbN for intrinsic layer in a low cost GaAs-based *p-i-n* photodiode. GaAsSbN can be grown closely lattice-matched to GaAs, while having much smaller bandgap energy than GaAs. This leads to the possibility of using GaAsSbN for other GaAs-based devices such as the absorption layer with the bandgap of $1\ \text{eV}$ for multi-junction solar cells or the base material in n-p-n GaAs-based heterojunction bipolar transistor (HBT). Another objective of this research is to demonstrate a GaAs- based *p-i-n* photodiode working at $1.3\ \mu\text{m}$ optical communication wavelength. Therefore, high frequency performance in the GHz region must be achieved. The experimental and calculation results in this thesis shows that higher bandwidth can be achieved by making the mesa diameter of the device smaller, with the GHz region achieved at mesa diameter $\sim 10\text{--}40\ \mu\text{m}$. Furthermore, our device dynamic performance is still RC time constant-limited bandwidth. This problem can be addressed by lowering the parasitic capacitance of the device using smaller mesa diameter or thicker i-layer.

Despite the promising results, the responsivity of the GaAs/GaAsSbN/GaAs *p-i-n* photodiodes is still low compared to the commercially available InP-based photodiodes. This is due to the defective nature of dilute nitride material, which in this case was intensified by the use of a low growth rate. Although higher N concentration can be achieved by growing at 0.2 $\mu\text{m/hr}$, the longer growth period leads to longer exposure to the r.f. plasma N source, thus increasing the density of the N-related defect. Therefore, it is recommended to shift the r.f. plasma N source to an inline-of-sight position. By moving the r.f. plasma N source to a more favorable position, the growth of GaAsSbN can be performed at a higher growth rate and higher N incorporation rate is expected. Further improvement of the r.f. plasma N source mentioned by Adamcyk [89] such as ion deflection plate and separating the N source with the growth chamber during plasma ignition is also recommended to reduce the direct energetic ion bombardment on the substrate. All these modifications to the r.f. plasma N source setup are required to improve the quality of the as-grown GaAsSbN layer.

Another important finding reported in this thesis is the optimum RTA temperature of GaAsSbN of 700 $^{\circ}\text{C}$. However, the ensuing blueshift that occurs on the GaAsSbN layer with $\sim 2.6\%$ N still requires further studies. Series of RTA experiment with shorter duration than 5 minutes may be enough suppressed the blueshift and allows the use of higher annealing temperature without detrimental effect on the material. The change of the r.f. plasma N source position may also open up the possibility of increasing the N content to compensate for the blueshift. In addition, *in-situ*

annealing experiments maybe beneficial for future research due to the UHV environment of the MBE chamber.

Despite the promising results from the DLTS, the information revealed by DLTS can only offer a broad picture of the defect states in GaAsSbN. A more precise study involving first-principles simulation within the density functional theory is required to confirm stability of the aforementioned defects and their position in reference to the bandgap of GaAsSbN. Experiment techniques such as optically-detected EPR [98,102,103] and x-ray absorption spectroscopy [96,179,180] are essential tools to study the atomic and electronic structure of the defects. These theoretical and experimental experiments on GaAsSbN are still lacking. In addition, the use of DLTS to study the effect of annealing on the defect states within the GaAsSbN layer will be another interesting experiment recommended for future research.

Author's Publications

The results obtained in this thesis have been published in refereed journals and conferences. Some of them are listed here in chronological order:

- [1] W.K. Cheah, W.J. Fan, **S. Wicaksono**, S.F. Yoon, K.H. Tan, "Low antimony-doped GaN_xAs_{1-x} on GaAs grown by solid-source molecular-beam epitaxy", Journal of Crystal Growth 254 (2003) 305
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- [3] **S. Wicaksono**, S.F. Yoon, W.J. Fan, W.K. Loke, "The effect of rapid thermal annealing on GaAsSbN quantum-well and GaAsSbN bulk lattice-matched to GaAs", 2005 International Conference on Indium Phosphate and Related Materials (2005) 421.
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- [11] **S. Wicaksono**, S.F. Yoon, W.K. Loke, K.H. Tan, K.L. Lew, M. Zegaoui, J.P. Vilcot, D. Decoster, J. Chazelas, "Effect of growth temperature on defect states of GaAsSbN intrinsic layer in GaAs/GaAsSbN/GaAs photodiode for $1.3\ \mu\text{m}$ application", Journal of Applied Physics 102 (2007) 044505

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