Molecular beam epitaxial growth of GaNAs and GaInNAs and their characterization

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Molecular Beam Epitaxial Growth of GaNAs and GaInNAs and Their Characterization

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School of Electrical and Electronic Engineering

A thesis submitted to the Nanyang Technological University in
fulfilment 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.

24 April 2005

Date

Ng Tien Khee

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Summary

This thesis presents the systematic growth and characterization studies of the GaInNAs/GaAs Quantum Well (QW) and related GaNAs bulk material by Molecular Beam Epitaxy (MBE) technique. The motivation of this work lies in the significant advantage in growing optoelectronic devices on GaAs substrate compared to InP substrate. The availability of N plasma source and MBE ensure the incorporation of sufficient N in the GaInNAs material. They also make low temperature growth possible, which is essential for reducing phase separation in the material. As-grown and annealed GaInNAs/GaAs QWs were characterized by Photoluminescence (PL), Time-Resolved Photoluminescence (TR-PL), and X-Ray Diffraction (XRD) to examine their optical and structural quality. The integrity of the GaAs cap layer grown on the QW samples and annealed by Rapid Thermal Annealing (RTA) equipment was confirmed by Atomic Force Microscopy (AFM).

The growth conditions for as-grown GaNAs and GaInNAs/GaAs QWs are established in Chapter 2 and Chapter 3, respectively, using the newly installed N-plasma source. The initial hurdle in this study was due to non-optimised N plasma source configuration, which resulted in excessive generation of N flux, and non-optimised growth conditions. Hence, the investigation on methods to incorporate N in the simplest small bandgap III-V nitride material (GaNAs) was carried out and reported. It was found that maintaining a low chamber background pressure between 2.8×10^{-6} Torr and 3.5×10^{-6} Torr was a prerequisite to achieve better N-composition control by varying the RF power or growth rate, with open/close N shutter configuration.

A number of GaInNAs/GaAs QW samples were grown and their PL properties, such as PL peak emission wavelength, PL intensity and Full-Width at Half-Maximum (FWHM) were studied. As-grown GaInNAs/GaAs QW with emission wavelength as long as 1580nm was measured at 4K. This QW has a relatively small Full-Width at Half-Maximum (FWHM) of $\sim 100\text{nm}$. Another as-grown GaInNAs/GaAs QW that emitted at 1500nm had downshifted to 1238nm after RTA. However, the peak emission wavelength would extend to $\sim 1320\text{nm}$ at room temperature, following the *Varshni* relationship with fitting parameters established in this study. This peak emission wavelength of near $1.3\mu\text{m}$ is desirable for the development of long wavelength optical transmission devices.

Surface nitridation of substrate growth front was observed during N plasma ignition using Reflection High-Energy Electron Diffraction (RHEED). To reduce nitridation on the GaAs substrate, it was essential to close the main-shutter and N-shutter of the MBE chamber during plasma ignition. During the growth optimization process, it was found that surface nitridation at the well-barrier interface and the well layer can be further reduced by growing the GaInNAs/GaAs QW with high In composition of $>30\%$ and high $V_{\text{As}}/III_{\text{Ga}}$ of 30. Consequently, 3D growth mode was suppressed in the GaInNAs well layer, and the beneficial effect of strain-relief by incorporating N in GaInAs prevailed. The optical quality of as-grown GaInNAs/GaAs QW was improved By Rapid Thermal Annealing (RTA) at 840°C for 10min albeit with downshifted PL peak wavelength.

The contributing factors for the PL peak wavelength downshift of GaInNAs/GaAs QWs after RTA at 840°C for 10mins are presented in Chapter 4. The improvement is suggested to be due to the annihilation of N-ion-induced damage through defect-assisted N-As interdiffusion and the enhancement of Ga and In atoms interdiffusion at the GaAs/GaInNAs/GaAs interfaces at high temperature. The downshift of the PL peak wavelengths of the GaInNAs/GaAs and GaInAs/GaAs QWs are found to be dependent on the In composition. While high In composition in the GaInNAs/GaAs QW could extend the PL emission wavelength, and make the QW less affected by N-related defect, its high compressive strain could contribute to a larger PL peak downshift after annealing.

The effect of material defects in **as-grown** GaInNAs/GaAs QW on the change of PL peak energy vs. temperature is investigated in Chapter 5. The as-grown GaInNAs/GaAs QW has In $\sim$ 30% and N $\sim$ 2.5%, and well width of $\sim$ 6nm. Localized states are suggested to dominate the low temperature region ($<80\text{K}$) of the as-grown QW, which exhibits larger temperature dependent energy redshift. On the other hand, smaller temperature dependent downshift is observed in the high temperature region ($\sim 80\text{K} - 150\text{K}$). This is the characteristic of the e_0-hh_0 transition, which is similar to the temperature dependent downshift of annealed GaInAs/GaAs QW. The experiment shows that annealing is an essential process to improve the temperature stability of GaInNAs/GaAs QW.

Many reports in existing literature demonstrated that RTA improves the PL characteristics of GaInNAs/GaAs QWs, by showing increased PL intensities and reduced PL FWHM. However when the QWs were used for laser applications, the

resulting threshold current density values after RTA were still high. In Chapter 6, a phenomenological fitting scheme is used to investigate the quenching mechanisms of **annealed** GaInNAs/GaAs QW with In = 30% and N = 1.5%, and -7nm well width. The QW showed main localization center with an activation energy of $E_B = 9\text{meV}$ even after annealing. An *EL6* defect level at the GaAs barrier with activation energy of $E_A = 38\text{meV}$ is also suggested to contribute to carrier loss. The localized transitions were due to In-N interaction, and compositional or well-width fluctuations, while the *EL6* was most likely resulted from low growth temperature of 460°C and low $V_{\text{As}}/\text{III}_{\text{Ga}}$ of 15. This experiment suggests the localized transitions and *EL6* defect level are potential reasons for poor threshold current density observed in the GaInNAs/GaAs QW-laser.

In Chapter 7, the localized transitions in **annealed** GaInNAs/GaAs QW with 16% In and 1.5% N are further characterised by Time-Resolved Photoluminescence (TR-PL) measurements. The localized transition shows emission-energy-dependent PL decay time characteristic for the low-energy regime (below 1.045eV) and a nearly constant decay time of about 0.14ns at the high-energy regime, which corresponds to the $e_0\text{-}hh_0$ transition lifetime. The main localization center could form carrier traps that reduce the $e_0\text{-}hh_0$ PL transition efficiency, and hence could potentially affect laser performance.

CHAPTER 1

Introduction

1.1 Motivation

The first compound semiconductor was reported by *Welker et al.* [1] in 1952. This report suggested that compound semiconductor materials made up of group-III and group-V elements in the periodic table exhibit semiconducting characteristics. Since then, III-V compound semiconductors and their applications have been extensively investigated, especially in the field of photonic and high frequency electronic devices. Compared to Silicon (Si), III-V compound semiconductors have their niche in high frequency microwave device operation due to their superior transport properties over Si, such as higher electron mobility and drift velocity. They are therefore widely used in military applications, modern communication systems and high frequency measuring equipment. Compared to Si, which has an indirect bandgap, most III-V compound semiconductors are efficient photonic materials because of their direct bandgap. This property makes them suitable candidates for making optical devices such as laser, waveguides and optical modulators.

In addition, by combining more than two elements from group-III and group-V columns in the periodic table, ternary or quaternary compound semiconductors can be formed. This opens an opportunity to change the strain condition of compound semiconductor materials with reference to the substrate used, while achieving the desired bandgap in electronic and optical devices. Hence III-V compound

semiconductor materials can be grown to have compressive strain, tensile strain or lattice-matched conditions. In particular, the compressive-strained condition of a material is suitable for semiconductor laser or laser diode, due to its improved device characteristics compared to the lattice-matched laser diode. In this project, compressive-strained Quantum-Well (QW) is studied experimentally by increasing the indium (In) composition in the well region.

One of the key applications of III-V compound semiconductor material is in high-speed data link and optical networks. To achieve this, the optoelectronic industry has currently chosen the wavelengths around $1.3\mu\text{m}$ or $1.55\mu\text{m}$, and has utilised Erbium-doped optical fiber amplifiers. The GaInPAs/InP material system, which can emit at the above wavelengths, is currently the mainstream technology in long wavelength transmission. This thesis studies an emerging technology that is based on GaAs substrate, which could provide several niche advantages over the mainstream technology.

From an economic viewpoint, GaInNAs-based lasers use GaAs substrate, which is cheaper and more robust compared to the expensive and fragile InP substrate used in the GaInPAs-based lasers. Hence, lasers grown on GaAs substrates could potentially increase production yield. Also, in realising long-wavelength GaInNAs-based Vertical-Cavity Surface-Emitting Lasers (VCSELs) [2] on the cheaper GaAs substrate, the readily available GaInAs-based VCSEL structure and GaAs-substrate-based fabrication technologies could be used for the production of GaInNAs-based VCSEL with minimum modification. This further motivates the scientific and technological research on GaInNAs materials and GaInNAs-based lasers [3-6].

One of the figures of merit for a laser is the characteristic temperature (T_o). A large T_o value indicates a weak temperature sensitivity of threshold current density (J_{th}), as J_{th} is empirically proportional to $e^{(T/T_o)}$, where T is temperature [7]. Lasing radiation in a laser would therefore occur at above a pre-designed J_{th} value over a large temperature range. For the GaInPAs/InP based lasers [8], the reported T_o value is relatively poor, with a typical value of ~60K [9]. By using AlGaInAs/InP material systems, a slight improvement was achieved at $T_o = 80K$ [10]. Compared to a 0.98 μm GaInAs/GaAs-based laser diode with T_o of ~150K or above, the temperature performance of the phosphide-based laser is considered poor. Hence, a thermal-electric cooler is needed to dissipate heat generated by the phosphide-based lasers so that they can function properly at elevated temperatures (> room temperatures). The external cooling components can incur additional cost for each and every laser diode employed. Therefore, the investigation of alternate material structure that emits at 1.3 μm or 1.55 μm , and with high T_o values, is desirable. The T_o value comparable or exceeding that of the GaInAs/GaAs-based laser diode would probably be a benchmark to aim for.

GaInNAs/GaAs material system was therefore explored and proposed by Kondow *et al.* [11]. They have demonstrated a Single-Quantum-Well (SQW) laser with a high T_o of 127K although the wavelength achieved was only 1.2 μm . Subsequently, several research groups have obtained 1.3 μm laser diode which were based on the GaInNAs/GaAs material system grown by various techniques, such as Molecular Beam Epitaxy (MBE) [12], and Metal-Organic Chemical Vapour Deposition (MOCVD) [13]. A high T_o of 215 K was reported by Kitatani *et al.* for a 1.3 μm

GaInNAs/GaAs SQW laser under pulsed operation from 20°C to 80°C, though the threshold current density increased from 2.86kA/cm² to 3.82kA/cm², respectively [12]. This is the highest T_o reported for a 1.3 μm edge-emitting GaInNAs/GaAs SQW laser suitable for optical-fiber communication systems. Compare to GaInPAs-based QW grown on InP that has a conduction band offset of 100meV, GaInNAs-based QW grown on GaAs has a higher conduction band offset of 350meV [14]. This give rise to a better electron confinement and a higher T_o in the latter.

Despite its improved T_o characteristics, as well as the availability of technology and process transfer for the GaInNAs-based devices, there are several challenges in improving the GaInNAs/GaAs material structure quality, before the full potential of the GaInNAs-based lasers can be unleashed. The above threshold current density values are still large, mainly due to the material quality of the GaInNAs layer. It is known that as-grown GaInNAs material is relatively defective, which is caused by the large difference in the atomic sizes of Ga, In and As atoms compared to N atom, and bombardment of energetic nitrogen species during growth. The material quality of GaInNAs inevitably degraded. Annealing [15-20] is therefore required to annihilate the defects generated, and to achieve better Photoluminescence (PL) properties. However, the threshold current density of GaInNAs/GaAs lasers can still be high even after annealing [15]. Hence, before GaInNAs can be utilised in laser diode applications, the intrinsic properties of the material system has to be characterized, and key issues related to material degradation need to be identified and clarified.

First and foremost, it is essential to obtain suitable growth conditions of the nitride compound semiconductor using a newly installed N plasma source. The characteristics of the plasma source have to be examined to understand the methods that can be used to tune the N composition in the GaNAs bulk material. Once this is established, the growth conditions for the GaInNAs/GaAs QW that emits at $>1.3\mu\text{m}$ PL peak emission wavelength need to be investigated.

Annealing increases the PL intensity and reduces the PL FWHM of GaInNAs/GaAs QW. However, this is accompanied by a reduction of the PL peak emission wavelength. The improvement in the PL characteristics of the GaInNAs/GaAs QW is due to the annihilation of material defects; while the underlying mechanisms that promote this would need further investigation as it is still under debate. This has significant implication to the QW-laser design and processing, as the peak emission wavelength of as-grown GaInNAs/GaAs QW would need to emit at a much longer wavelength than $1.3\mu\text{m}$ to make provision for the annealing induced peak wavelength downshift. It is believed that defects and strain, which are related to N and In composition, in the GaInNAs promote annealing induced downshift. The underlying reason for this needs further clarification.

It is also important to understand the mechanisms that contribute to the degradation of optical characteristics in as-grown and annealed GaInNAs/GaAs QWs, as such studies are lacking. Photoluminescence (PL) characterization is therefore a useful and non-destructive method to gauge the optical quality of the GaInNAs/GaAs QWs before and after annealing. At present, the band structure study of GaInNAs/GaAs and related materials is attracting the attention of a number of researchers [21-27].

Some of the work has been devoted to the prediction of the required In and N compositions in achieving long wavelength emission of $>1.3\ \mu\text{m}$ [21,22]. GaInNAs materials have many other unique properties; such as the profound effects N have on the band structure of the GaInNAs materials. It was found that N may give rise to a resonant state below the extended state in bulk GaNAs and bulk GaInNAs materials [28,29,30,31], which could give rise to anomalous behaviours, such as localization behaviour in both as-grown GaNAs and GaInNAs bulk materials. However, studies of N-induced Photoluminescence (PL) behaviour in GaInNAs/GaAs QW structure grown by Solid Source Molecular Beam Epitaxy (SSMBE) are lacking in the literature. This study would clarify the anomalous behaviours seen in the PL characteristics in such material system, and would provide insight that could address the large threshold current density problem in the GaInNAs/GaAs lasers.

1.2 Objectives

As explained in Section 1.1, there were two major challenges which are related to the growth and annealing process, and in using the GaInNAs material for laser applications. These inter-related issues are translated into the following objectives:

(a) Growth:

- Investigate the growth conditions and properties of compressively strained GaInNAs and related GaNAs bulk material.
- Obtain compressively strained GaInNAs Quantum-Well (QW) emitting at $> 1.3\mu\text{m}$ wavelength with the eventual goal of using the material for $1.3\mu\text{m}$ laser applications.

-
- Understand the mechanisms for annealing induced downshift in the GaInNAs/GaAs QW.

(b) PL efficiency study and annealing:

- Understand the temperature dependent characteristics of as-grown GaInNAs QW with GaAs barrier.
- Study the quenching mechanisms in annealed GaInNAs/GaAs QW by PL.
- Investigate the effect of localization on the PL properties of annealed GaInNAs/GaAs QW, such as PL efficiency and lifetime.

1.3 Major contributions

The present work was initiated by the need to understand the growth conditions and material characteristics of compressive-strained GaInNAs/GaAs Quantum-Wells (QWs) and related materials. High quality GaInNAs/GaAs material structure is difficult to grow for three main reasons. Firstly, the atomic size difference between nitrogen and other constituent elements in the III-V-nitrides, such as gallium, indium, and arsenic, is large, and therefore the crystal lattice is easily distorted. Secondly, a large lattice mismatch of $>1.5\%$ between GaInNAs and GaAs [14] exists for the QW to emit at a long wavelength ($\sim 1.3\mu\text{m}$). Thirdly, the interaction between In and N results in clustering in the GaInNAs material, and therefore increases the level of difficulty of growing GaInNAs/GaAs QWs.

However, with the fundamental study of GaNAs bulk material, growth characteristics for the GaInNAs material can be deduced. Extensive investigations of GaInNAs/GaAs QW, and the related GaNAs bulk material growth were conducted using a solid source molecular beam epitaxy (SSMBE) in conjunction with a newly installed RF nitrogen source. The dopant-like growth characteristic of N incorporation in nitride materials was confirmed in the SSMBE system used in this study. It was found that increasing group-III flux reduces the incorporation of N composition in GaNAs and GaInNAs material possibly due to the reduction of the N flux density. Although increasing In and N compositions will extend the wavelength of the GaInNAs/GaAs QW or GaNAs bulk material, increasing N composition degrades material quality. Hence it was suggested that reducing the N flux density, by either increasing the In, Ga or As flux could improve the optical quality of GaInNAs/GaAs QW-structure, while achieving $\sim 1.3\mu\text{m}$ PL emission.

In the process of establishing optimum growth conditions for GaInNAs/GaAs QW, methods to reduce surface nitridation during the growth of GaInNAs/GaAs have been identified. As-grown GaInNAs/GaAs QW with 4K PL peak emission wavelength of $\sim 1600\text{nm}$ has been grown. Another GaInNAs/GaAs QW that was annealed at 840°C for 10min could possibly emit at $1.3\mu\text{m}$, according to the *Varshni* relationship. This has potential application in $1.3\mu\text{m}$ optoelectronic applications.

Although annealing could improve the PL intensities of both growth methods, the setback of increasing the In composition, instead of the N composition is the larger annealing-induced wavelength downshift. The reasons for the annealing-induced wavelength downshift or energy blueshift is still a subject under debate [32]. Understanding the underlying reasons that result in the larger downshift would be essential to improving the quality of the material system. For this purpose, a comparison of two GaInNAs/GaAs QWs with high and low indium compositions of 22% and 30%, respectively, were studied. The annealing-induced PL peak wavelength downshift in the GaInNAs/GaAs QWs were found to be dependent on the In composition as deduced from PL and XRD measurements, as well as RHEED observation. The dominant mechanisms contributing to the downshift of the PL peak wavelength of the GaInNAs/GaAs QW with high In composition are residual-strain-induced GaAs/GaInNAs/GaAs interfaces interdiffusion and defect-assisted diffusion. However, for GaInNAs/GaAs QW with low In composition, the nitrogen-ion-damage-assisted N-As interdiffusion effect at the GaAs/GaInNAs/GaAs interfaces dominates the observed wavelength downshift.

Addition of small atomic size N into the host matrix with Ga, In and As, which have much larger atomic sizes, may contribute to various anomalous behaviour. The PL quenching investigation was lacking despite its great importance in understanding the underlying optical characteristics of as-grown and annealed GaInNAs/GaAs QW, while the anomalous behaviour needs further clarification. This thesis has also contributed significantly to the investigation of PL mechanisms of as-grown GaInNAs/GaAs QW by temperature dependent PL measurements. An anomalous two-segmented trend in the PL peak energy *vs.* temperature curve was observed for an as-grown QW with a ~6nm GaInNAs well layer having In and N compositions of ~30% and ~2.5%, respectively, and with GaAs barrier layer grown at 0.8 μ m/hr. It shows higher temperature-dependent characteristics at low temperature range of ~5K – ~80K, and lower temperature-dependent characteristics at temperatures above ~80K. This two-segmented PL peak energy *vs.* temperature characteristic provides insight into the unconventional trends in the GaInNAs/GaAs material system, and suggests that this effect could be important in the theoretical prediction of GaInNAs/GaAs QW characteristics.

As for the annealed QW, this thesis identified possible quenching mechanisms for a thermal-annealed ~7nm GaInNAs/GaAs quantum well (QW) with In = 30% and N = 1.5%, with GaAs growth rate fixed at 1 μ m/hr. This was studied by fitting the PL efficiency *vs.* $1/kT$ data from 4K to 150K with a double activation energy model. One of the PL loss centers with low activation energy, $E_B = 9\text{meV}$, is thought to originate from a localized state that traps carriers at temperatures below ~100K. Another center with larger activation energy $E_A = 38\text{meV}$ has a more significant PL

quenching effect at temperatures above $\sim 120\text{K}$. This center is possibly contributed by the *EL6* defect level in the GaAs barrier layer, as a result of low V/III ratio of 15, and low growth temperature of 450°C .

In order to further understand the carrier dynamics of the localization effects in GaInNAs/GaAs QW, variable temperature Photoluminescence (PL), and Time-Resolved PL (TR-PL) measurements of a thermal-annealed 6nm GaInNAs/GaAs QW with In = 30% and N = 1.5% is carried out. This sample was grown with higher V/III ratios of ~ 20 in order to minimize possible effect of barrier-related defect. It was found that the effect of carrier localization, which remained after thermal annealing, is possibly due to a center characterized by a transition with activation energy of 13.7meV below the e_0 state, as obtained by fitting the PL efficiency vs. $1/kT$ data with a single-activation-energy (SAE) model. TR-PL measurements at 17K showed larger lifetime and emission-energy-dependent PL decay time characteristic for the low-energy regime (below 1.045eV) that corresponds to the main localization center's lifetime. As for the high-energy regime (above 1.045eV), a nearly constant decay time of about 0.14ns was obtained, which corresponds to the $e_0\text{-}hh_0$ transition's lifetime. The TR-PL study suggests that the main localization center, which is close to the e_0 state and having longer lifetime, could form carrier traps that reduce the $e_0\text{-}hh_0$ PL transition efficiency, and therefore could possibly affect lasing characteristics in GaInNAs-based laser.

1.4 Organization of the Thesis

The motivation and objectives of this project are explained in Chapter 1. The theoretical background related to the growth technique of solid source molecular beam epitaxy in conjunction with a nitrogen plasma source is reviewed in Chapter 2. In addition, an overview of the compressively strained GaInNAs/GaAs Quantum-Well (QW) is briefly described in Chapter 2. The process development of GaInNAs/GaAs QWs is presented in Chapter 3. The high temperature annealing of GaInNAs/GaAs QWs, and group-III diffusion in GaInNAs/GaAs QW are studied in Chapter 4.

In Chapter 5 and Chapter 6, the temperature dependent PL peak energy characteristics for as-grown and annealed GaInNAs/GaAs QWs are studied. Further study on the localization effect in GaInNAs/GaAs QW is reported in Chapter 7. Finally, concluding remarks and future plan are presented in Chapter 8.

CHAPTER 2

Experimental Background and Details

This Chapter presents an overview of Solid Source Molecular Beam Epitaxy (SSMBE) system and its key features, such as the characteristics of RF nitrogen (N) plasma source and the use of Reflection High-Energy Electron Diffraction (RHEED) for *in-situ* growth monitoring process.

2.1 Solid Source Molecular Beam Epitaxy (SSMBE)

Molecular Beam Epitaxy (MBE) is an advanced technique for depositing solid films and is a valuable tool in the development of layer structures for sophisticated electronic and optoelectronic devices. MBE has become a versatile technique for fabricating structured semiconductor layers used for making devices such as lasers, High Electron Mobility Transistors (HEMTs), Heterojunction Bipolar Transistors (HBTs), and microwave devices.

Although vacuum evaporation was used as early as in the 1950s for preparing semiconductors, molecular beam epitaxial growth conditions were not realised until 1980s with the advancement of vacuum technology, especially in the design and control of the evaporation sources and substrate cleaning procedures. Solid Source Molecular Beam Epitaxy (SSMBE) is essentially an Ultra High Vacuum (UHV) evaporation technique where solid source materials such as gallium (Ga), indium (In) and arsenic (As) are evaporated onto a heated GaAs single crystal substrate

inside a vacuum chamber with background pressure less than 10^{-10} Torr at stand-by condition.

In the case of solid sources, the vapours from the heated sources form molecular beams, and travel through the vacuum ambient before arranging themselves to form crystalline lattice based on the heated substrate's lattice. During this process, the background pressure may reach 10^{-6} Torr or low 10^{-5} Torr depending on the amount of the evaporated sources used. Such a low pressure results in molecular beams with long mean free path, and thus almost eliminate molecular collisions. The MBE growth process is therefore determined entirely by heterogeneous reactions on the substrate surface [33].

The main components of the MBE growth chamber (see Fig.2-1) are:

- ❑ Molecular beam sources or cells with their individual shutters. These cells are made from non-reactive refractory materials (mostly made of Pyrolytic Boron Nitride, PBN), which can withstand high temperatures.
- ❑ RF nitrogen (N) plasma source. In this thesis, the symbol N is used to represent either the nitrogen gas or the nitrogen species generated by the nitrogen plasma source, such as radicals and ions.
- ❑ A RHEED system, which is used to monitor the surface reconstruction, growth rate, and growth mode.
- ❑ A valved arsenic cracker cell. This evaporation technique for solid arsenic overcomes the conventional problems associated with the handling of hydrides and metalorganics employed in growth processes involving the use of gas sources. The use of a valve in the cracker cell enables precise delivery and control of the arsenic flux required for the growth process without rapid depletion of the source materials.
- ❑ Excellent temperature control with an accuracy of $\sim 1^\circ\text{C}$.
- ❑ Externally controlled mechanical shutters in front of each effusion cell facilitates rapid changing of the beam species so that the composition and/or doping of the growing film can be abruptly altered.

In addition, since MBE growth follows a kinetic growth mode, it can be conducted at a relatively low growth temperature of $< 500^\circ\text{C}$ compared to Metal-Organic Chemical Vapour Deposition (MOCVD) method. Phase separation that tends to occur in GaNAs and GaInNAs materials for growth temperature $> 500^\circ\text{C}$ can therefore be greatly reduced [34]. Also, the hydrogen-free growth environment in

SSMBE helps to eliminate hydrogen-related defects that are found in GaInNAs materials grown in MOCVD systems [35].

Fig.2-1 Schematic of Solid Source Molecular Beam Epitaxy (SSMBE) system.

As for the N species from the RF plasma source, the GaNAs and GaInNAs materials can also be grown when the shutter in front of the N plasma source is closed. This mode of growth is termed dispersive mode nitride growth because N radicals can travel in a dispersive manner (instead of a directed manner) to the heated substrate in the growth chamber.

2.2 Characteristics of Radio Frequency (RF) N plasma source and various aspects of N incorporation in GaNAs

The characteristics of the N plasma cell was studied using the simplest GaNAs ternary material, instead of the quaternary GaInNAs material, as the N composition in the ternary material can be more accurately determined by XRD. The knowledge derived from the ternary GaNAs material growth can later be applied to the quaternary GaInNAs material growth. In addition, GaNAs barrier could be used in the future to replace the GaAs barrier material for GaInNAs well, which could potentially improve the PL characteristics of the GaInNAs/GaAs QW. Hence it is equally important to master the growth process of the GaNAs material. Fig.2-2 shows that there are four ways of controlling the N compositions in the GaNAs materials, namely open/close N shutter, changing the background pressure of the growth chamber by changing the N gas flow rate, changing the RF power and changing the growth rate.

As the N flux generated from the RF plasma source is dispersive in nature, N can be incorporated on a heated substrate even when the N shutter is closed. In Fig.2-2, the N compositions at open shutter (—□—) and closed shutter (—●—) configurations are higher and lower, respectively, under a fixed background pressure of 3.5×10^{-6} Torr and a fixed growth rate of $1 \mu\text{m/hr}$. The ratio of N composition between the open shutter and closed shutter configurations are $\sim 5x$ and $\sim 4x$ at RF power of 150W and 450W, respectively. Hence open/close N shutter is an effective method of controlling the N composition.

It was also found that a high background pressure was less controllable in varying the N compositions in the GaNAs materials. This is evident in Fig.2.2, where even under closed shutter configuration that gives lower N compositions, a small RF power of $\sim 70\text{W}$ would result in a high N compositions of $\sim 1\%$ and $\sim 2\%$, respectively, in the GaNAs materials, with growth rate fixed at $1\mu\text{m/hr}$ and with background pressures of $6.8 \times 10^{-6}\text{Torr}$ ($\blacktriangle$) or $1.0 \times 10^{-5}\text{Torr}$ ($\blacklozenge$). As the background pressures are high, N compositions $< 1\%$ in the GaNAs materials are not achievable under such high background pressure conditions.

Fig.2-2 N composition in GaNAs vs. RF power at different background pressure or growth rate.

There is another problem associated with plasma ignition with high background pressure. The interruption time will be longer as more time is required to pump away the admitted N gas after plasma ignition. Instead of a long 3min interruption time, a lower background pressure of between 2.8×10^{-6} Torr and 3.5×10^{-6} Torr will only require a short 1min interruption time after plasma ignition to pump away most of the N gases. Hence the N gas flow admitted to the RF plasma source is fixed at 0.1sccm and this contributed to the chamber background pressure of between 2.8×10^{-6} Torr and 3.5×10^{-6} Torr, depending on the incoming ultra-high-purity N gas pressure. This background pressure is considered optimum for nitride material growth.

The optimum flow rate of 0.1sccm also ensures the ease of N plasma ignition and high-brightness mode of N-plasma operation. Fig.2-3 shows the minimum RF power required for high-brightness mode of operation vs. background pressure. The RF source is operated at high-brightness mode, in contrast to low-brightness mode, to promote efficient generation of N radicals. This was observed during a GaNAs bulk layer growth, with less than 0.5% nitrogen is incorporated under low-brightness mode of operation, and with open shutter configuration, even though a high RF power of 300W was applied to the N gas. Therefore the low-brightness mode of operation is not effective for the generation of N species. For comparison, by operating the chamber in high brightness mode and open shutter configuration (see in Fig.2-2), and by varying the RF power from 150W – 350W while fixing the flow rate (0.1sccm) and maintaining the chamber background pressure (3.5×10^{-6} Torr), the N composition in GaNAs materials increases from 1.5% – 3.5%.

Fig.2-3 Minimum RF power required for high-brightness mode of operation vs. background pressure.

In Fig.2-2, by decreasing the growth rate of the GaNAs from $1\mu\text{m/hr}$ ($\text{---}\square\text{---}$) to $0.8\mu\text{m/hr}$ ($\text{---}\circ\text{---}$), the N incorporation increases significantly above 150W. Other growth conditions in both sets of samples were the same, except for a small difference in the background pressure values of 3.5×10^{-6} Torr and 2.8×10^{-6} Torr, respectively. In this case the rate of change of N composition per unit change of RF power for GaNAs grown at $1\mu\text{m/hr}$ and $0.8\mu\text{m/hr}$ are smaller and larger, respectively, and thus the former provides a better tuning capability than the latter. In GaInNAs/GaAs QW laser growth, the growth rate of GaInNAs may need to be reduce to $\sim 0.8\mu\text{m/hr}$ in order to cater for the high Al composition in the AlGaAs cladding layer. Hence obtaining the change in N composition in nitride materials with different growth rate is useful for future QW laser structure growth.

As growth rate is determined by the group-III flux, an empirical relationship between the N composition and the growth rate of the bulk nitride (GaNAs or GaInNAs) materials can be established. This is particularly important in GaInNAs material as In flux would contribute to overall increase in growth rate, and hence reduction in N compositions. In Fig.2-4, the hollow circles represent the N compositions measured on GaAs/GaNAs/GaAs heterostructures using (004) XRD rocking curve. The growth rate for each hollow circle is changed by changing the Ga flux. The data can be fitted by the following empirical equation (Eq.2-1):-

$$1/N = -0.15 + 0.33e^{(R/0.85)} \quad (2-1)$$

where N is the nitrogen composition in % and R is growth rate in $\mu\text{m/hr}$

Fig.2-4 Plot of inverse N composition vs. growth rate of GaNAs bulk material.

Fig.2-5 Plot of In/Ga flux ratio vs. In composition in GaInAs.

The growth rate of GaNAs follows that of GaAs, which depends on the group-III flux and can be determined from RHEED by detecting the intensity oscillation of the specular reflection from the semiconductor surface. The change with N composition with growth rate relationship can be used to determine the N composition in the GaInNAs material. The growth rate of GaInNAs can be obtained by using Eq.2-2 and Eq.2-3. In Eq.2-2, x_{In} and x_{Ga} are the In and Ga fractional compositions, respectively, and R_{InAs} and R_{GaAs} are the growth rates for InAs and GaAs, respectively. For GaInNAs, the In composition can be determined by a pre-calibrated curve shown in Fig.2-5, which relates the ratio of In flux and Ga flux to the In composition. The total growth rate, R , has the same definition as that of Eq.2-1. Hence, by using Eq.2-1 and the pre-calibrated N composition curves obtained in Fig.2-2, the reduction of N composition with the increment of growth rate due to In incorporation can be determined.

$$R_{InAs} = R_{GaAs} \frac{x_{In}}{1 - x_{In}} \quad (2-2)$$

$$R = R_{GaAs} + R_{InAs} \quad (2-3)$$

In short, maintaining a low background pressure of between 2.8×10^{-6} Torr and 3.5×10^{-6} Torr was found to be a prerequisite in achieving better controllability of the N compositions in GaNAs. A fairly good control of N compositions can then be achieved by varying the RF power or growth rate using open/close N shutter configuration.

2.3 Details of growth, post-growth treatment and characterization equipment

Typical growth and annealing steps will be described in this section. The specific experimental methods will be described at the beginning of each chapter.

The samples grown and investigated in this project are either Double-Quantum-Wells (DQWs) having this structure: GaAs cap / GaInAs well / GaAs barrier / GaInNAs well / GaAs buffer; or Single-Quantum-Wells (SQWs) having this structure: GaAs cap / GaInNAs well / GaAs buffer. Taking the SQW as an example, the growth and annealing details will be described in the following.

The structure was grown on a (001) semi-insulating GaAs substrate using a SSMBE system in conjunction with a N plasma source. Prior to growth, the GaAs substrate was out-gassed at 500°C for 15min in a transfer chamber in order to remove the adsorbed particles on the substrate and substrate holder. The sample was then transferred into an Ultra-High-Vacuum (UHV) growth chamber. The substrate holder temperature was ramped at a rate of ~20°C/min from ~20°C to a temperature when the Reflection High-Energy Electron Diffraction (RHEED) pattern showed (2x4) surface reconstruction. In order to protect the GaAs surface from excessive As loss, As overpressure was introduced on the GaAs surface above substrate temperature of 250°C. The emergence of the (2 x 4) surface reconstruction indicated the GaAs surface oxide desorption temperature, which occurred at ~590°C was achieved. This was used as a means to calibrate the substrate temperature as

measured by a thermocouple, which was located at the back of the substrate holder. After that, the substrate holder temperature was increased by another 20°C and maintained for 10min to complete the oxide desorption process. The temperature was then decreased back to 590°C to grow the first layer of 300nm GaAs buffer material at a growth rate of 1 μ m/hr.

After the GaAs buffer growth, the substrate temperature was allowed to ramped down at a rate of ~20°C/min from 590°C to 460°C. A normal transition of surface reconstruction patterns from (2 x 4) to (2 x 2) during the temperature ramp was observed. When the substrate temperature reached 460°C, the main shutter of the growth chamber was closed for 3min for N plasma ignition, RF matching and regulation of N gas flow. If the main shutter was opened during this process, the surface reconstruction could change from (2 x 4) to (1 x 3) or (3 x 3), suggesting possible nitridation of GaAs surface [36]. On the other hand, closing the main shutter would protect the GaAs surface against the N radicals that slipped through the N shutter blockage. In addition, the chamber background pressure was maintained at 1 $\times 10^{-7}$ Torr to sustain sufficient arsenic (As) overpressure on the GaAs substrate, and hence these precautionary steps ensured a clear (2 x 4) surface reconstruction throughout the plasma ignition process.

For thermal annealing of GaInNAs/GaAs QW, a Rapid Thermal Annealing (RTA) equipment was used. The equipment was calibrated by comparing the pyrometer temperature range between 350-950°C with a standard thermocouple. The deviation of the temperature measured by the pyrometer was then adjusted automatically to that of the thermocouple by a built-in software. A long preheating time of 10mins at 380°C could provide a uniform starting temperature across a sample. A long annealing duration of 10min was used to ensure uniform heating during the annealing step in the RTA chamber. Fig.2-6 shows the surface morphologies of as-grown and annealed GaAs cap layers. They have comparable surface roughness of ~4nm as measured by Atomic Force Microscopy (AFM). This shows that the annealed process was properly conducted, and the integrity of the GaAs surfaces was preserved.

After growth and annealing, the GaInNAs/GaAs QW structure was typically characterized by photoluminescence (PL) to obtain its peak emission wavelength or energy, PL intensity, and its Full-Width at Half-Maximum (FWHM). The samples were mounted on a cryostat's cold finger in a PL system, and cooled down to a low temperature of ~5K. The PL measurements were carried out under constant 514.5nm Ar-ion laser excitation power, and the QW signal was collected using a liquid-N₂ cooled Ge detector. The PL signals were measured as a function of temperature up to 150K by heating up a resistive strip that was attached to the cold finger. An automatic PID controller regulated the measurement temperature at the desired set point. X-ray diffraction was also used to study the structural properties of the QW structures.

Fig.2-6 Atomic Force Microscopy (AFM) images for as-grown and annealed GaAs surface after RTA at 840°C for 10mins.

Time-Resolved Photoluminescence (TR-PL) measurements were also carried out to obtain insights for the carrier dynamics of annealed QW. For such measurements, the QW sample was mounted in a closed-cycle He-cryostat, and excited using a mode-locked Ti:Sapphire laser with pulse width of 100fs and repetition rate of 82MHz. The TR-PL signals were detected using a streak camera in conjunction with a monochromator.

CHAPTER 3

Growth Considerations for GaInNAs/GaAs Quantum Wells

This Chapter summarises key experiences in the growth development of GaInNAs/GaAs QW using the newly installed N plasma source. In addition to obtaining optimum growth conditions for GaInNAs/GaAs QWs, the characterization of the N degradation effect in the well or at the well-barrier interfaces is essential as this provides the insight to grow a good starting GaInNAs/GaAs material structure for subsequent annealing process. As-grown or annealed GaAs/GaInAs/GaAs/GaInNAs/GaAs Double-Quantum-Wells (DQWs) or GaAs/GaInNAs/GaAs Single-Quantum-Wells (SQWs) were used for this purpose. Reflection High-Energy Electron Diffraction (RHEED), Photoluminescence (PL) and X-Ray Diffraction (XRD) characterization techniques were used to study the material quality, PL peak emission wavelength, and PL Full-Width at Half-Maximum (FWHM) of the as-grown or annealed GaInNAs/GaAs QWs.

3.1 Achieving long PL emission wavelength in as-grown GaInNAs/GaAs QW.

Fig.3-1 4K PL spectrum from two GaAs/GaInAs/GaAs/GaInNAs/GaAs DQWs with different N and In compositions.

Fig.3-1 shows the 4K PL spectrum of two DQWs with In compositions of 24% (→) and 27%(--), respectively. Each of them has a 8nm top GaInAs well and a bottom GaInNAs well, with GaAs barrier between them. The samples were grown at growth

temperature of 460°C with V_{As}/III_{Ga} of -15, and GaAs growth rate of 1 $\mu\text{m/hr}$. To grow the GaInNAs well layers, the same RF power of 480W and closed N-shutter growth conditions were used. The closed N-shutter growth configuration, as discussed in Chapter 2, has beneficial effect in reducing ion-induced damage caused by the RF plasma. The estimated N compositions in the GaInNAs well layers for the solid line (—) and dashed-line (--) were 0.2% and 0.16%, respectively. The reduction of N compositions with increasing In composition was due to the dopant-like incorporation behaviour, as described in Chapter 2.

Fig.3-1 shows that both GaInAs/GaAs QWs with 24% and 27% In compositions have small FWHM of ~20nm compared to ~30nm for both GaInNAs/GaAs QWs. This indicates that N incorporation degraded the GaInNAs quality. Fig.3-2 shows the PL spectrum of both GaInNAs/GaAs QWs with their peaks aligned along the wavelength axis. Although they have comparable FWHM of ~30nm, it is evident that the GaInNAs/GaAs QW with higher N composition (—) showed a more gradual long-wavelength or low-energy tail compared to the GaInNAs/GaAs QW with lower N composition (--). The low energy tail in the high N composition GaInNAs/GaAs QW (→) indicates that the material quality was compromised, as a result of ion-induced damage [34], N localization effects [38], and effect of compositional fluctuation along the well layer [52]. The significance of the results in Fig.3-2 is that increasing N composition may increase the PL emission wavelength but at the same time may reduce the material quality of GaInNAs/GaAs QW. A further study of the localization effect has been carried out using Time-Resolved Photoluminescence (TR-PL), and will be presented in Chapter 8.

Fig.3-2 A comparison of the 4K PL spectrum of GaInNAs/GaAs QWs with low (--) and high (→) N compositions, respectively.

On the other hand, although the closed N-shutter growth configuration may help to block the destructive ions from the N plasma, the N radical flux was very much reduced, and hence the resulting PL emission wavelengths of the GaInNAs/GaAs QWs were short (~1100nm and 1165nm, respectively), as shown in Fig.3-1. An open N-shutter configuration was therefore more suitable for GaInNAs/GaAs QW growth since this configuration supplied higher N flux that increased N composition in nitride materials (see Chapter 2). This is beneficial in increasing the PL peak emission wavelength above 1.3μm. This was evident in Fig.3-3 that shows another two GaInNAs/GaAs QWs grown with In compositions of 27%, and with open N-shutter configuration. The samples were grown at a growth temperature of 460°C,

V/III of -15 , and GaAs growth rate of $1\mu\text{m/hr}$, similar to the growth conditions in the closed N-shutter configuration in Fig.3-2. The two 4K PL peaks at 1464nm and 1500nm in Fig.3-3 were obtained by setting the RF power at 250W and 350W , respectively. The GaInNAs/GaAs QWs were good candidates for long wavelength optical communication systems. However, the large PL FWHM of 113nm and 122nm for the QWs grown at 250W and 350W , respectively, needs to be reduced significantly for lasers applications, by means of *in-situ* or *ex-situ* annealing process. The annealing studies will be presented in Chapter 4, Chapter 6, and Chapter 7 of this thesis. In the following sections, issues related to the growth process improvement for the GaInNAs/GaAs QWs will be discussed.

Fig.3-3 4K PL Intensity vs. wavelength of GaInNAs/GaAs QWs grown at RF power of 250W and 350W, respectively. Other growth conditions were fixed at In = 27%, growth temperature = 460°C, $V_{As}/III_{Ga} = 15$, GaAs growth rate = 1 μ m/hr, and with open N-shutter configuration.

3.2 Effect of N on the GaInNAs/GaAs interface and wavelength downshift after annealing.

A GaInNAs/GaAs QW grown with the N plasma source fixed at RF power = 350W with long emission wavelength near 1500nm has been achieved at 4K as shown in Fig.3-3. However the peak emission wavelength has downshifted significantly from 1500nm to 1238nm (see Fig.3-4) after RTA process of 840°C for 10mins, partly due to In or N out-diffusion [37]. Its FWHM reduces from 122nm to 30nm, which was larger than a typical FWHM of ~15nm for an as-grown GaInAs/GaAs QW having the same In composition. According to the Varshni relationship that is established in Chapter 5 for annealed GaInNAs/GaAs QW, with $\alpha = 0.74\text{meV/K}$ and $\beta = 813\text{K}$, and with E_o at their respectively ~10K PL emission energy (see Chapter 5), room temperature PL peak emission wavelength would be at ~1.32 μm . Hence, these growth and annealing conditions are suitable for 1.3 μm QW laser development.

$$E(T) = E_o - \frac{\alpha T^2}{(\beta + T)} \quad (3-1)$$

Fig.3-4 4K PL spectra of annealed GaInNAs/GaAs QW. This annealed QW would emit at $\sim 1320\text{nm}$ at room temperature based on the *Varshni* equation for annealed GaInNAs/GaAs QW in Chapter 5. Before Rapid Thermal Annealing (RTA), the corresponding as-grown QW emits at 1500nm .

In order to obtain better growth conditions for as-grown GaInNAs/GaAs QWs emitting at $>1.3\mu\text{m}$, further understanding on the factors that govern the annealing induced PL downshift are required. For this purpose, three DQWs having GaAs/GaInAs/GaAs/GaInNAs/GaAs structure were grown. The GaInAs/GaAs and GaInNAs/GaAs QWs in each DQWs have the same thickness of $\sim 8\text{nm}$, and the same In composition. The samples were grown with As flux over Ga flux ratio ($V_{\text{As}}/III_{\text{Ga}}$) of ~ 15 . Fig.3-5 shows the PL wavelength downshift after annealing of GaInNAs/GaAs QWs at 840°C for 10mins. The In compositions of the three as-

grown GaInNAs/GaAs QWs are between 23%-25% as labeled in the figure. It was found that the amount of wavelength downshift increased from 124nm to ~200nm as N composition increased from ~ 0.5% to ~ 0.8%.

Fig.3-5 4K Wavelength downshift vs. N composition of three GaInNAs/GaAs QWs after annealing. The wavelength downshift for this particular set of QWs increases with N composition regardless of In compositions (23% or 25%).

The wavelength downshift was due to a number of reasons, such as change of well or barrier compositions, and defect-induced In or N out-diffusion at the well-barrier interface [31]. However, as wavelength downshift appeared to increase with N composition regardless of In composition (Fig.3-5), the likely reason for such behaviour was the introduction of N at both GaInNAs/GaAs interfaces, in addition to the GaInNAs well layer itself. This is evident in Fig.3-6(a) where the annealed GaInAs/GaAs QW for DQW #3 has negligible wavelength downshift, indicating

insignificant change to the well or barrier composition, while the annealed GaInNAs/GaAs QW with a high N composition of $\sim 0.8\%$ showed a large wavelength downshift of $\sim 200\text{nm}$, and accompanied by a reduction of FWHM from 66nm to 24nm . Hence, the FWHM reduction suggested annihilation of defects caused by N incorporation.

Fig.3-6 (a) 4K PL spectrum, and (b) XRD rocking curves, of as-grown and annealed DQW #3.

Defects related to N incorporation affected the GaInNAs/GaAs QW in a number of ways. It is known that a N plasma contains many ions and high-energy electrons [38]. These plasma species could escape into the growth chamber and travel with a long mean free path and damage the growth front of a GaAs substrate upon

collision. The mean free path (L) can be calculated using $L = 3.11 \times 10^{-24} (T/pd^2)$ [39], where T is temperature, p the pressure of N , and d the diameter of the N species ($d = 1.5 \text{ \AA}$ for N atom). With $p = 4 \times 10^{-4} \text{ Pa}$ as measured using a flux gauge, and assuming $T = 300 \text{ K}$, L is approximately 104 m , which is much longer than the distance between the orifice of the plasma chamber and the substrate surface.

This is evident during a 3min growth interruptions used for RF plasma ignition: the RHEED reconstruction on the substrate surface changes from streaky (2×4) to streaky (3×3) when the RF N plasma was ignited. This showed that N species changes the growth front to form N -enriched interfacial layer before the GaInNAs layer growth. Similar (3×3) surface reconstruction was observed by Jung *et al.* while intentionally nitriding the GaAs surface under As-stabilised condition [40]. This happened because As atom on the GaAs barrier layer can be readily displaced by N radical flux [41]. With low impinging As_4 flux, the effect of N -enriched interfacial layer may have been further promoted.

As the N -enriched interfacial layer contains many interstitial N -As complexes [42, 43, 44], the interface so formed becomes a source of N -related defects. These N -complex species and defects could then assist N out-diffusion from the GaInNAs well layer to the GaAs barrier layers through a kick-out mechanism [43, 45]. Fig.3-6(b) shows the XRD (400) reflection of as-grown and annealed DQW #3. The broad hump of the rocking curve for the annealed sample is slightly left-shifted along the negative-angle region, indicating an increase in compressive strain after annealing. This suggests a reduction in N composition in the GaInNAs well layer. Dynamical simulations on both the annealed and as-grown samples (see Fig.3-6(b)) gives an

estimated a reduction in N composition of the GaInNAs/GaAs QW from ~0.8% to ~0.4%, while the In composition of GaInNAs/GaAs QW is only reduced by about 0.2%, and thus resulting in the hump shown (Fig.3-6(b)).

3.3 Effect of N on the GaInNAs well layer during growth

In addition to the GaInNAs/GaAs interface, N could also degrade the GaInNAs well layer itself through promoting 3D or island growth. For GaInNAs/GaAs QW #3 (Section 3.2), although the calculated compressive strain for the GaInNAs well layer (strain = -0.015) was smaller than the corresponding GaInAs well layer's compressive strain (strain = -0.0165), the surface reconstruction of the GaInNAs and GaInAs well layers showed disjointed-streak (2×1), and continuous-streak (2×1) surface reconstructions, respectively. The disjointed-streak (2×1) surface reconstruction suggests an early sign of transformation from 2D growth mode to 3D growth mode in the GaInNAs well layer. This may be promoted by the interaction of In and N under the low V_{As}/III_{Ga} of 15. This interaction, in worst-case scenarios, has been reported to promote lateral compositional clustering [41, 46], and QD formation [41, 47] in the GaInNAs well layer. The RHEED observations were not expected, because with the strain compensation effect of N, the GaInNAs well layer should have shown better 2D growth characteristics than the higher strain GaInAs well layer.

In addition, attempts to increase the In composition above 27% were unsuccessful at $V_{As}/III_{Ga} = 15$, as the surface reconstruction for 8nm GaInNAs well layer turned progressively spotty, which indicated a 3D growth mode, when RF power was

increased from 150W to 350W. The PL characteristics are shown in Fig.3-7(a). The PL emission wavelength of these QWs (—●—) varied from ~1330nm to 1500nm as the RF power was increased from 150W to 350W. The QWs showed a progressively spotty trend in the surface reconstruction, which was promoted by the interaction of In and N as discussed above.

To further protect the GaAs growth front during plasma ignition, both the main shutter that blocked the group-III and group-V sources, and the shutter for the N-source were closed during plasma ignition. A high V_{As}/III_{Ga} of ~30 was also used during growth to protect the well-barrier interfaces. These measures eliminated the (3x3) surface reconstruction on the substrate surface, which was due to interface nitridation during plasma ignition, and reduced 3D growth in the GaInNAs well layer. The high V_{As}/III_{Ga} of ~30 also ensured sufficient As_4 overpressure that protected the GaAs growth front when the main shutter was closed for plasma ignition.

With the above modification to the growth process, In composition was successfully increased to >30% without spotty surface reconstruction. Fig.3-7(a) shows that by fixing In = 34% (—□—), and by varying the RF power from 200W to 400W, the ~4K PL peak emission wavelength increased from 1350nm to 1580nm, which was much longer than the required 1300nm. More importantly, the GaInNAs/GaAs QWs grown at In = 34% (see Fig.3-7(b)) has lower FWHM of between 50nm to 100nm (—□—) as the RF power was varied from 200W to 400W; while the GaInNAs/GaAs QWs grown at In = 27% (see Fig.3-7(b)) has higher FWHM of between 100nm to 120nm (—●—) as the RF power was varied from 150W to

350W. As the In composition was increased, both high As₄ flux and lower N incorporation contributed to lower FWHM values, which were between 50nm to 100nm. This suggested that a high As₄ flux (V_{As}/III_{Ga} of ~30 instead of 15), and high In composition of >30% with less N incorporation were essential factors for the successful growth of good quality GaInNAs material. Hence, a trade-off between achieving long emission wavelength and reducing material clustering is required in GaInNAs material growth. On one hand, higher RF power increased the incorporation of N in the GaInNAs well layer, and hence increased the PL peak emission wavelength; on the other hand, the material quality of the GaInNAs well layer will be degraded as a result of atomic clustering.

Fig.3-7 Plot of (a) PL wavelength vs. RF power, and (b) PL FWHM vs. RF power for two sets of GaInNAs/GaAs QWs measured at 4K. The QWs with high In composition of 34% and high V_{As}/III_{Ga} of 30 showed relatively smaller FWHM.

3.4 Summary

This Chapter focused on examining the beneficial and detrimental effects of N during the growth of GaInNAs/GaAs QW, and the effect of peak wavelength downshift in the GaInNAs/GaAs QW during the subsequent annealing process. The FWHM of as-grown QW were large due to clustering or localization effects, and therefore annealing was required to improve its optical quality. Annealed GaInNAs/GaAs QW with long emission wavelength of 1238nm at 4K, with a small FWHM of 30nm, was obtained even under non-optimised growth conditions. As Varshni equation predicted that the QW would emit at 1.32 μ m at room temperature, the growth and annealing process for this QW is potentially suitable for long wavelength QW-laser applications.

The growth steps in which N could degrade the quality of GaInNAs/GaAs QW structure were also identified in this Chapter. Modifications to the growth procedures that reduced the degradation effect of N incorporation, and favoured the strain compensation effect of N incorporation were established. The presented experimental results suggested a trade-off between achieving long peak emission wavelength of >1.3 μ m, and increasing N incorporation in the GaInNAs layer. Key factors to achieving this trade-off were using high V_{As}/III_{Ga} of ~ 30 , using high In composition of >30% during growth, and closing the main shutter and N shutter during the N plasma ignition period. This effectively suppressed the interface nitridation of the well-barrier interface, which was one of the sources of defects in the GaInNAs/GaAs QW. In addition, nitridation on the interface could also promote

In and N out-diffusion during annealing. Therefore, this improvement step is highly desirable.

CHAPTER 4

Effect of In Composition on the Photoluminescence Downshift of GaInNAs/GaAs Quantum Wells Annealed at High Temperature

4.1 Introduction

Previous developments in GaInNAs-based QW showed room temperature operation of 1.3 μm emission wavelength edge-emitting lasers [48,49,50] and room temperature pulsed operation of 1.18 μm emission wavelength Vertical-Cavity Surface-Emitting Lasers (VCSELs) [2,48]. The GaInNAs alloy has great potential for realizing long-wavelength VCSELs by using GaAs substrate because of the readily available GaInAs/GaAs VCSEL structures. However, threshold current of these devices is generally high because of the poor optical quality of the GaInNAs active layer [48]. As discussed in Chapter 1, it is known that as-grown GaInNAs materials are relatively defective as a result of the large difference in atomic sizes of Ga, In, and As atoms compared to the N atom, and bombardment of energetic N ions during growth. Post-growth thermal treatment [51,52] is therefore required to anneal the defects to obtain better Photoluminescence (PL) properties, which are essential for laser applications.

Although there are reports on post-growth annealing of GaInNAs grown using Metal Organic Chemical Vapour Deposition (MOCVD) [53] and Chemical Beam Epitaxy

(CBE) [54,55,56], few reports exist on high temperature ($> 800^{\circ}\text{C}$) treatment of this material grown by a Radio Frequency (RF) N plasma source in conjunction with a Solid-Source Molecular Beam Epitaxy (SSMBE). High-temperature treatment of the GaInNAs material is essential to improve its quality. Pan *et al.* [57] reported that annealing at a different temperature range results in the removal of defects of different nature in GaInNAs materials with the same In composition and grown by a DC-activated N plasma source. Only high-temperature annealing ($> 800^{\circ}\text{C}$) could remove both defects originating from the GaAs/GaInNAs/GaAs interfaces (caused by N-ion-induced damage) and the GaInNAs layer (caused by insufficient surface migration of In and Ga atoms during growth). On the other hand, low temperature annealing (650°C) could only remove defects caused by N-ion-induced damage originating from the GaAs/GaInNAs/GaAs interfaces. The end result is a smaller wavelength shift ($< 10\text{nm}$) after low temperature (650°C) annealing (LTA) and a greater wavelength shift ($\sim 30\text{nm}$) after high temperature ($> 800^{\circ}\text{C}$) annealing (HTA).

In order to further clarify the mechanisms of large PL wavelength downshift in GaInNAs after high temperature annealing, the PL properties of GaInNAs/GaAs QWs with two different In compositions after a 10mins high temperature (840°C) post-growth thermal annealing cycle was investigated. The mechanisms that influence the large PL wavelength downshift of GaInNAs/GaAs QW after high temperature annealing, which were found to be dependent on the In composition, are described.

4.2 Experimental methods

Table 4-1: Growth details of Sample A and Sample B.

Details	Sample A	Sample B
GaAs Cap Thickness (nm)	80	80
GaInAs Thickness (nm)	6	6
GaAs Barrier Thickness (nm)	100	100
GaInNAs Thickness (nm)	6	6
GaAs Buffer Thickness (nm)	300	300
Growth Temperature (°C)	480	480
In Beam Equivalent Pressure (Torr)	2.1×10^{-7}	2.8×10^{-7}

The sample structure consists of a GaInNAs/GaAs Quantum-Well (QW) grown above a GaAs buffer layer followed by a GaInAs/GaAs QW. A GaAs cap layer was grown at the top. The nominal thickness values of the GaInNAs and GaInAs well layers were 6nm. Details of the sample structures are tabulated in Table 4-1. The corresponding PL characteristics are shown in Table 4-2.

The samples were subjected to post-growth thermal annealing in a system heated by an array of upper and lower lamps under N flow. The annealing temperature was fixed at 840°C for 10min. The sample was capped with a GaAs wafer during annealing to prevent arsenic loss at elevated temperatures, as discussed in Chapter 2. The PL measurements were carried out at 4K, and the PL intensities of all samples were normalized to the same incident power (250mW) to enable direct comparison between the results.

Table 4-2: Effects of thermal annealing on (a) PL peak wavelength, (b) FWHM, and (c) PL peak wavelength blueshift of GaInNAs/GaAs and GaInAs/GaAs QWs.

(a) PL peak wavelength (nm)

Sample	Before Annealing		After Annealing	
	GaInNAs QW	GaInAs QW	GaInNAs QW	GaInAs QW
A	1093	950.5	1021	941
B	1101.5	1021	1014.5	962

(b) FWHM (meV)

Sample	Before Annealing		After Annealing	
	GaInNAs QW	GaInAs QW	GaInNAs QW	GaInAs QW
A	63.1	7.8	16.3	7.2
B	23.2	14.5	14	8.4

(c) PL peak wavelength blueshift (nm)

Sample	GaInNAs QW	GaInAs QW
A	$\Delta\lambda_{A,\text{GaInNAs}} = 70$	$\Delta\lambda_{A,\text{GaInAs}} = 10$
B	$\Delta\lambda_{B,\text{GaInNAs}} = 87$	$\Delta\lambda_{B,\text{GaInAs}} = 60$

4.3 Characterization of annealed GaInNAs/GaAs QWs

In Fig.4-1(a) and Fig.4-1(b), the solid line and dotted line indicate the PL spectrum (at 4 K) of Sample A and Sample B before annealing (as-grown) and after annealing at 840°C for 10mins, respectively. The GaInAs/GaAs QW in Sample A has lower In composition ($y = 22\%$) compared to that in Sample B ($y = 30\%$). Therefore, the as-grown GaInAs/GaAs QW in Sample A emits PL at shorter wavelength (950.5nm) compared to that in Sample B (1021nm). Due to the higher growth rate in Sample B, caused by the greater In flux during growth, the amount of N incorporated in Sample B's GaInNAs layer was reduced. Hence this results in a smaller difference between the PL peak wavelength positions of the as-grown GaInAs/GaAs and GaInNAs/GaAs QWs in Sample B ($\Delta\lambda_{B,as-grown} = 80\text{nm}$) compared to that in Sample A ($\Delta\lambda_{A,as-grown} = 143\text{nm}$). The N content, in Sample A and Sample B was estimated to be $\sim 1.2\%$ and $\sim 0.6\%$, respectively.

In Fig.4-1(a), the as-grown GaInAs/GaAs QW exhibits a high intensity (3500a.u.) at 950.5nm with a full-width at half maximum (FWHM) of 7.8meV. However, the as-grown GaInNAs/GaAs QW exhibited a relatively poor PL emission (at $\sim 1093\text{nm}$), indicating the presence of defective material. Thermal annealing at 840°C for 10mins resulted in a significant increase in PL emission intensity (at $\sim 1021\text{nm}$) from the GaInNAs/GaAs QW by 30 times (to 6700a.u.), and reduction in FWHM from 63.1meV to 16.3meV. This improvement was comparable to results reported in existing literature [58,59].

This indicated that the high-temperature post-growth thermal annealing has a dramatic effect on improving the optical quality of the GaInNAs/GaAs QW. The high temperature thermal annealing also has a beneficial effect on the optical quality of the GaInAs/GaAs QW, which was evident from the slight reduction in the FWHM from 7.8meV (before annealing) to 7.2meV (after annealing). The results of FWHM change in Samples A and B arising from the thermal annealing are summarized in Table 4-2(b).

Fig.4-1 Comparison of PL (4K) intensity vs. wavelength before and after annealing for: (a) Sample A, (b) Sample B.

Pan *et al.* [57] have previously reported the improvement in the GaInAs/GaAs and GaInNAs/GaAs QW optical quality arising from thermal annealing. They studied the mechanisms for GaInNAs quality improvement by applying high temperature and low temperature annealing to 3 samples of the same In composition, but prepared under different applied magnetic fields to the plasma. The magnetic field, which was applied perpendicular to the path of the N ion plasma flux, served to deflect the ion flux. The deflection effect was stronger at higher magnetic field, and therefore fewer defects due to N-ion-induced damage were created. Such samples showed a less significant change in PL properties after LTA, due to the presence of fewer defects. In addition, the wavelength shift after LTA was attributed by Pan *et al.* to Ga and In diffusion at the GaAs/GaInNAs/GaAs interfaces, rather than N-As diffusion.

Pan *et al.*'s study also showed that HTA results in removal of defects caused by insufficient surface migration of Ga and In at low growth temperature and removal of N-ion-induced defects. The wavelength downshift after HTA was attributed to N-As, and Ga and In diffusion. As the GaInNAs peak PL intensities increased rapidly in the beginning of HTA and reached a maximum in 5sec, it is also suggested that N-As diffusion was dominant at the beginning of the HTA process when N-ion-induced defects were plentiful, and Ga and In diffusion were dominant after most of the defects were removed [57,60].

The results from our annealing study on two GaAs/GaInAs/GaAs/GaInNAs/GaAs samples with different In compositions were consistent with the above. The defects

resulted from N-ion-induced damage and insufficient surface migration of Ga and In atoms during low temperature growth were removed, as evident from the increase in PL intensity of the GaInAs emission peak as shown in Fig.4-1(a). Therefore, the annealing temperature of 840°C used in our study should have the effect of eliminating defects resulted from N-ion-induced damage, as well as defects resulting from insufficient Ga and In surface migration during low temperature growth, as reported by Pan *et al.* [57]. The GaInNAs/GaAs QW in Sample A clearly shows a significantly higher PL intensity (Fig.4-1(a)) and smaller FWHM (Table 4-2(b)) as a result of the annealing process.

To understand the mechanism of PL peak wavelength shift after thermal annealing, we first examined the GaInAs/GaAs QW. The effect of GaAs/GaInNAs/GaAs interfaces diffusion of the host atoms (Ga and In) is shown in Fig.4-1(a), where the PL position of the GaInAs/GaAs QW emission peak (Sample A) has shifted downwards from 950.5nm to 941nm after annealing (a change in wavelength of $\Delta\lambda_{A,GaInAs} = 10\text{nm}$). The relatively defective as-grown GaInNAs material exhibited a larger wavelength shift of $\Delta\lambda_{A,GaInAs} = 70\text{nm}$ (from 1093nm to 1021nm) after annealing, due to In and Ga interdiffusion as well as N-ion-damage-defect-assisted diffusion at the GaAs/GaInNAs/GaAs interfaces. As for Sample B (Fig.4-1(b)), the PL peak position of the GaInAs/GaAs QW emission has shifted from 1021nm to a lower wavelength of 962nm after annealing, and that of GaInNAs has shifted from 1101.5nm to 1014.5nm. The change in peak wavelength of the GaInAs/GaAs QW in Sample B ($\Delta\lambda_{B,GaInAs} = 60\text{nm}$) was significantly larger than that in Sample A ($\Delta\lambda_{A,GaInAs} = 10\text{nm}$). The results of the PL wavelength shift in Samples A and B arising from the annealing are tabulated in Table 4-2(c).

As the annealing conditions for both Sample A and Sample B were the same, and both samples were grown under nominally identical conditions with the exception of the In flux, the mechanism which contributed to the observed large PL peak shift could not be caused by the difference in annealing temperature (as studied by Pan *et al.*), but rather it was caused by the difference in In composition. We suggest that the higher In composition in Sample B has contributed to the greater $\Delta\lambda_{\text{B,GaInNAs}}$ after annealing, due to the residual-strain induced interdiffusion [61,62] and defect-induced interdiffusion as a result of In incorporation. As the In composition in Sample B was higher, more severe residual-strain-induced interdiffusion of Ga and In atoms at the GaAs/GaInAs/GaAs interfaces may occur.

However, such effects are lower in Sample A due to its lower In composition. Also, the argument of defect-assisted interdiffusion in the GaInAs/GaAs QW during annealing was supported by the lower crystal quality of the as-grown GaInAs/GaAs QW in Sample B as observed in the PL FWHM (see Table 4-2(b)). The as-grown GaInAs/GaAs QW PL FWHM of 14.5meV in Sample B was larger than that of the as-grown GaInAs/GaAs QW in Sample A (7.8meV). This correlated well with the Reflection High-Energy Electron Diffraction (RHEED) observation during growth. The time required for Sample B (with higher In composition) to transform from a streaky (2 x 4) surface reconstruction to disjointed streaks (2 x 1) surface reconstruction during the initial stage of GaInAs well layer growth was significantly shorter than that of Sample A. The RHEED observation showed that three-dimensional (3D) growth as a result of surface strain occurred earlier in Sample B

than in Sample A. It was possible that the 3D growth resulted in a higher number of defects in Sample B than in Sample A.

Following the above argument of residual-strain-induced interface interdiffusion and defect-assisted diffusion in GaInAs/GaAs QW, it was expected that the GaInNAs/GaAs QW in Sample B would show a larger PL wavelength shift compared to Sample A. This is shown in Table 4-2(c), where the wavelength shift of the GaInNAs/GaAs QW in Sample B before and after annealing ($\Delta\lambda_{B, \text{GaInNAs}} = 87\text{nm}$) was larger than that in Sample A ($\Delta\lambda_{A, \text{GaInNAs}} = 70\text{nm}$). Because the GaInNAs/GaAs QW in Sample B has lower N content compared to Sample A, the defect density related to energetic N ion bombardment should be lower than that in Sample A. This is evident in Fig.4-1, where the intensity and FWHM of the as-grown GaInNAs/GaAs QW in Sample B are higher and lower, respectively, than those in Sample A.

Therefore, the effect of N-ion-damage-defect-assisted N-As diffusion and PL wavelength downshift contributed by this effect in Sample B's GaInNAs/GaAs QW should be lower than that in Sample A. However, because $\Delta\lambda_{B, \text{GaInNAs}}$ (87nm) was larger than $\Delta\lambda_{A, \text{GaInNAs}}$ (70nm), the residual-strain induced GaAs/GaInNAs/GaAs interfaces interdiffusion and defect-induced diffusion were considered to be the dominant effects that contributed to the large PL peak shift of the GaInNAs/GaAs QW in Sample B. Therefore, this indicated that N-ion-damage-defect-assisted N-As diffusion was more dominant in GaInNAs/GaAs QW with low In content, while residual-strain induced interdiffusion and defect-induced diffusion were more dominant in GaInNAs/GaAs QW with high In composition.

The X-ray diffraction (XRD) scans in the (004) plane were used to investigate the structural change in Sample A and Sample B before and after thermal annealing. In Fig.4-2(a) and Fig.4-2(b), the broad humps along the negative-angle region of the XRD spectrum increased in intensity and shifted towards the substrate peak after annealing. The shifting of the broad humps was more obvious in the spectrum of Sample B (Fig.4-2(b)) compared to that of Sample A (Fig.4-2(a)), indicating greater change in the In composition in Sample B. The calculated strain [63] in the GaInNAs well layers for Sample A and Sample B were -0.013 and -0.020 , respectively. The negative sign indicates the GaInNAs layers are compressively strained. The results showed that the GaInNAs layer strain in Sample B was greater than that in Sample A. This further supports the above argument of residual-strain-induced PL peak downshift.

In addition, very clear and high peak-to-peak intensities of the *Pendellosung* fringes on the humps were observed in the spectrum of the as-grown and annealed Sample A (Fig.4-2(a)), indicating the presence of an abrupt layer interfaces and good crystalline quality before and after annealing. The lower peak-to-peak intensities of the *Pendellosung* fringes in Fig.4-2(b) indicated that the layer interfaces were less well defined in Sample B, and this could possibly be a source of defects at the interfaces. This was consistent with the PL FWHM observations discussed earlier and further supports the defect-assisted interdiffusion effect that partly contributed to the large PL peak downshift of the GaInAs/GaAs and GaInNAs/GaAs QWs.

Fig.4-2 Comparison of XRD scans in the (004) plane before (as-grown) and after annealing for: (a) Sample A, (b) Sample B.

4.4 Summary

This Chapter reports the effect of high temperature post-growth thermal annealing on GaInAs/GaAs and GaInNAs/GaAs QWs grown by a RF N plasma source in SSMBE. It was found that annealing at 840°C for 10min can significantly improve the GaInNAs/GaAs QW quality. This improvement is due to the annealing of N-ion-induced damage through defect-assisted N-As interdiffusion and the enhancement of Ga and In atoms interdiffusion at the GaAs/GaInNAs/GaAs interfaces at high temperature. The downshift of the PL peak of the GaInNAs/GaAs and GaInAs/GaAs emission was found to be dependent on the In composition. The dominant mechanisms contributing to the blueshift of the PL peak wavelength of the GaInNAs/GaAs QW with high In composition were residual-strain-induced interdiffusion at the GaAs/GaInNAs/GaAs interfaces, and defect-assisted diffusion. However, for GaInNAs/GaAs QW with low In composition, the N-ion-damage-assisted N-As interdiffusion effect at the GaAs/GaInNAs/GaAs interfaces dominated. The results were supported by evidence from PL and XRD measurements, as well as RHEED observations.

CHAPTER 5

Temperature Dependent Photoluminescence Peak Shift of As-grown and Annealed GaInNAs/GaAs Quantum Wells

This Chapter investigates the Photoluminescence (PL) peak shift of as-grown GaInNAs/GaAs QW with temperature to provide insight for the PL mechanisms of as-grown QW. For comparison, the peak shifts of annealed GaInNAs/GaAs QWs were presented.

5.1 Experimental details

The ~6nm GaInNAs well was grown by open-N shutter configuration, and the Ga and In fluxes were maintained at $\sim 5 \times 10^{-7}$ Torr and $\sim 3 \times 10^{-7}$ Torr, respectively, which gives an In composition of ~30% as described in Chapter 2. The estimated N composition is about 2.5%. A 20nm GaAs cap layer was then grown on top of the GaInNAs well layer.

5.2 Temperature dependent photoluminescence characterization of as-grown GaInNAs/GaAs QW

In Fig.5-1, the PL intensity reduces by 40 times and the Full-Width at Half-Maximum (FWHM) increased from 71meV to 84meV when the measurement temperature were increased from ~5K to 150K. The large FWHM values were due to the defective nature of the as-grown GaInNAs materials as a result of high N incorporation of ~2.5%. Also, the PL peak energy redshifted from 0.984eV

(1.26 μm) to 0.95eV (1.305 μm) when the measurement temperature was increased from ~5K to 150K. The PL spectrum at ~5K has asymmetrical line-shape (see Fig.5-1(a)) with exponential low-energy tail, which is a characteristic of localized excitonic recombination [64,65,66]. This low-energy tail represents the density of states of the localized exciton due to potential fluctuation in the confinement potential energy of the as-grown GaInNAs/GaAs QW heterostructure [65]. However, the PL spectrum at 150K became more symmetrical. This suggested a reduced contribution from the localized excitonic recombination at a higher temperature of 150K.

Fig.5-1 PL intensity vs. energy spectrum of as-grown GaInNAs/GaAs QW at: (a) ~5K, and (b) 150K, respectively.

To further identify the cause of the change in the PL line shapes, a study of the PL peak energy vs. temperature was conducted. The natural logarithmic PL efficiency, $\ln(\eta)$, of the GaInNAs/GaAs QW, with η defined as in Eq.5-1, is plotted against $1/kT$ as shown in Fig.5-2. I_0 is defined as the PL integrated intensity at ~5K while $I(T)$ is defined as the integrated intensity at the respective PL measurement temperature: The data was then fitted with a phenomenological expression [64,65] as in Eq.5-2. E_A represents the activation energy for a loss center, while A is the fitting constant, k is the Boltzmann constant, and T the absolute temperature.

$$\eta = \frac{I(T)}{I_o} \quad (5-1)$$

$$\frac{1}{\eta} = 1 + Ae^{-E_A/kT} \quad (5-2)$$

As seen in Fig.5-2, the experimental data can be well fitted by Eq.5-2, and hence this equation was sufficient to describe the major PL mechanisms of the QW within the ~5K to 150K temperature range. This suggested that there was only one loss center that contributed to the reduced PL efficiency of the e_0-hh_0 state within the temperature range under study. The fitting gave $A \approx 300$ and $E_A = 34\text{meV}$, suggesting that the main localized transition energy could be located at ~34meV below the desired e_0-hh_0 state under the current PL experimental conditions. In addition, the PL FWHM clearly showed two trends (inset in Fig.5-2), namely an increasing FWHM from 71meV to ~82meV (Linear region) below ~80K, and an almost flat region with FWHM ~82meV-84meV (Saturation region) above ~80K. This suggests that each of the two competing mechanisms dominated at the two temperature regimes, respectively.

Fig.5-2 Plot of PL efficiency vs. $1/kT$ curve of as-grown GaInNAs/GaAs QW. The inset shows the change in PL FWHM vs. temperature of the as-grown QW.

The localized transitions could be contributed by several factors, such as composition fluctuation of the GaInNAs alloy, or QW-barrier interface roughness, N localization, or a combination of the above [64,65,66,67]. For the first two factors, the composition fluctuation was observed in Transmission Electron Microscopy (TEM) as undulation pattern across the GaInNAs alloy layer [52]. It was also reported that in the GaInNAs alloy, there could be high local In or N composition as a result of clustering during growth, that results in the above localized transitions [20].

The localized transitions could contribute to anomalous behaviour in the PL peak energy vs. temperature characteristic, which has been observed to have two different temperature dependences at $< 80\text{K}$ and $> \sim 80\text{K}$, and will be presented later. Before examining this anomalous behaviour in as-grown QW, annealed QWs will be presented first as they would better represent the peak energy vs. temperature characteristics of homogeneous GaInNAs/GaAs QW.

These characteristics are shown in Fig.5-3, which show the characteristics for two GaInNAs/GaAs QWs (in QW #4 and QW #5) and one reference GaInAs/GaAs QW that were all annealed at 840°C for 10mins. The *Varshni* equation (Eq.5-3), which is an empirical formula to describe the PL peak energy variation with temperature, was used to analyse the results in Fig.5-3, with E denoting the PL peak energy, T the absolute temperature, and α and β the fitting parameters. The fitted *Varshni* curves will later be useful in the analysis of the as-grown GaInNAs/GaAs QW.

$$E(T) = E_o - \frac{\alpha T^2}{(\beta + T)} \quad (5-3)$$

Fig.5-3 PL peak energy vs. temperature plot of annealed GaInAs/GaAs QW, annealed GaInNAs/GaAs QW #4 and annealed GaInNAs/GaAs QW #5.

There were two major observations in Fig.5-3. Firstly, although the annealed GaInNAs QW #4 and annealed GaInNAs QW#5 have different nominal growth conditions, they can be well fitted using $\alpha = 0.74\text{meV/K}$ and $\beta = 813\text{K}$, and with E_0 at their respective $\sim 10\text{K}$ PL peak energy. This is denoted as *Fit-GaInNAs* in Fig.5-3. The annealed GaInNAs QW #4 has well width of $\sim 6\text{nm}$ with In and N compositions of 30% and 0.1%, respectively; while the annealed GaInNAs QW#5 has well width of $\sim 8\text{nm}$ with In and N compositions of 25% and 0.5%, respectively. This showed that the annealed GaInNAs QWs grown by our system has similar temperature-dependent PL peak energy change. This agrees well with the *Varshni* equation fitting for bulk nitride materials reported in [67], where the same *Varshni* fitting parameters of $\alpha = 0.61\text{meV/K}$ and $\beta = 560\text{K}$ can be used for several bulk GaNAs materials under investigation.

Secondly, the annealed GaInAs QW, which has well width of 6nm with In composition of 30% exhibited relatively larger temperature-dependent PL peak energy shift as compared to that of annealed GaInNAs QW. For comparison, it is found that the amount of PL peak energy redshift between $\sim 5\text{K}$ to 150K (denoted as $\Delta 150\text{K}$ in Fig.5-3) for annealed GaInAs QW is relatively larger (25meV) compared to that of the annealed GaInNAs QW#4 and annealed GaInNAs QW#5 of between 20meV - 22meV . As for the 4K to 270K range (denoted as $\Delta 270\text{K}$), it was again evident that the PL peak energy redshift values (denoted as $\Delta 270\text{K}$ in Fig.5-3) for the annealed GaInAs QW was much larger (71meV) compared to that of the annealed GaInNAs QW #4 and annealed GaInNAs QW #5 of between 62meV - 64meV . The *Varshni* equation for the annealed GaInAs QW was obtained using the

fitting parameters of $\alpha = 0.74\text{meV/K}$ and $\beta = 500\text{K}$, and denoted as *Fit-GaInAs* in Fig.5-3. Hence, a single temperature-dependent PL peak energy fitting curve was required to fit each of the PL data obtained from annealed QWs. These observations will be used in the following paragraph to understand and analyse the anomalous temperature-dependent PL-redshift feature in as-grown GaInNAs QW.

In Fig.5-4, it seemed that the data in the low-temperature ($\sim 5\text{K}$ to $\sim 80\text{K}$) and high-temperature ($\sim 80\text{K}$ to 150K) ranges have to be fitted with two separate sets of fitting values. The two *Varshni* curves are labelled as *Fit_low* and *Fit_high*, denoting the *Varshni* relationships obtained from two sets of fitting parameters for the low- and high-temperature curves, respectively. The fitting parameters for *Fit_low* are $\alpha = 0.79\text{meV/K}$ and $\beta = 214.5\text{K}$, respectively, which represent a large temperature-dependent PL peak energy redshift. The $\Delta_{150\text{K}}$ value obtained from the extrapolation of *Fit_low* to 150K was 35meV . This was much larger than the values obtained for other curves in Fig.5-3. In addition, the experimental data at the high-temperature range, namely *Fit_high*, were found to be best fitted using the α and β values for *Fit_GaZnAs*, instead of those for *Fit_GaInNAs*, possibly due to the N localization effect that reduces substitutional N incorporation in GaInAs, leading to the GaInAs-like *Varshni* relationship.

Fig.5-4 PL peak energy vs. temperature plot of as-grown GaInNAs/GaAs QW.

The temperature (~80K) at which the PL peak energy vs. temperature changed from *Fit_low* to *Fit_high* correlated well with the temperature at which the PL FWHM changed from linear trend to almost constant trend in the inset of Fig.5-2. This further explains the change in the GaInNAs/GaAs QW line shape from asymmetrical in Fig.5-1(a) to more symmetrical in Fig.5-1(b).

Such transition from one temperature-dependent curve to another as temperature increased suggested the existence of two competing PL mechanisms, each of which dominated at different temperature regions. Therefore, the localized transitions dominated the PL transition at low temperature; while at high temperature the localized transitions were slowly suppressed and replaced by the e_0 state transition. This suggested that the localized transitions are located below the e_0 state. As

temperature increased, the electrons from the localized state would be depopulated due to excitation of its electrons to the e_0 state, a process called band-filling effect. Hence, the e_0 - hh_0 transition was expected to dominate the PL transition at increasing temperature, and would therefore shift the temperature-dependent PL peak energy from *Fit_low* trend to *Fit_high* trend, which was equivalent to the migration of the PL mechanism from the localized-exciton dominated transition to the e_0 - hh_0 dominated transition.

5.3 Summary

The Varshni equation fitting parameters for as-grown and annealed GaInNAs/GaAs QW were established in this Chapter. Only a **single** temperature-dependent PL peak energy fitting curve was required to fit each of the PL data obtained from **annealed** QWs. On the other hand, an anomalous **two-segmented** temperature-dependent PL peak energy curve was observed in **as-grown** GaInNAs/GaAs QW. By using two-segmented *Varshni* equation fitting for the as-grown GaInNAs/GaAs QW, localized transitions were found to dominate the low-temperature ($\sim 5\text{K}$ - 80K) PL transition and results in larger PL peak energy redshift; while the e_0 - hh_0 state dominates the high-temperature (above $\sim 80\text{K}$) PL transition. Analysis of the PL efficiency vs. temperature curve for the as-grown QW shows that the localized transitions have a characteristic activation energy of $\sim 34\text{meV}$ below the fundamental transition of e_0 state, as fitted using a phenomenological expression. In addition, the temperature ($\sim 80\text{K}$) at which the PL FWHM changes from linear trend to almost constant trend correlates well with the temperature at which the PL peak energy vs. temperature changes from *Fit_low* to *Fit_high*. This further supports the argument of the existence of two competing PL transitions in the as-grown GaInNAs/GaAs QW under study, which are dominant at different temperature region.

CHAPTER 6

Photoluminescence Quenching Mechanisms in Annealed GaInNAs/GaAs Quantum Well

In this chapter, the Photoluminescence (PL) quenching characteristics of a thermal-annealed ~7nm GaInNAs/GaAs Quantum Well (QW) with In = 30% and N = 1.5% were studied from 4K to 150K. The study aimed to identify the mechanisms that could quench the PL emission in the GaInNAs/GaAs QW.

6.1 Introduction

Due to the large size difference between the N atom and other constituent atoms in the GaInNAs material, and the use of energetic N radicals from a plasma source, the PL efficiency is generally poor, as discussed in Chapter 1. It was equally well known that thermal annealing was one way of enhancing the PL intensity of the QW. However, thermal annealing of the GaInNAs material does not necessarily guarantee strong photoluminescence intensity at room temperature, which is one of the essential requirements of GaInNAs/GaAs QW lasers grown on GaAs substrate. Hence, a detailed understanding of the PL quenching mechanisms in thermal-annealed GaInNAs QWs, which is lacking in existing literature, is essential for providing insight for explaining the mechanisms that contribute to change in PL efficiency of the GaInNAs/GaAs QW.

6.2 Experimental procedures

The Double-Quantum-Well (DQW) in this Chapter was grown at a low growth temperature of 450°C. The DQWs used in this study has GaInNAs/GaAs QW and a reference GaInAs/GaAs QW nominal thickness of ~7nm. This study will mainly focus on the GaInNAs/GaAs QW, while the reference GaInAs/GaAs QW was used mainly for *in-situ* monitoring purpose during growth. During growth, the In and Ga BEP were maintained at 2.8×10^{-7} Torr and 4.6×10^{-7} Torr, respectively, to obtain In composition of ~30%. The RF power applied to the N plasma source was fixed at 350W using open-shutter configuration in which the N shutter was fully open during the growth of the nitride layer. The ratio of As flux to Ga flux of 15 was measured using an ion-gauge.

After growth, the sample was annealed at 840°C for 10mins by Rapid Thermal Annealing (RTA) process to improve the GaInNAs crystalline quality. This annealing condition was found to enhance PL intensity from the study in Chapter 4.

6.3 Temperature dependent photoluminescence characteristics of annealed GaInNAs/GaAs QW

Fig.6-1(a) shows PL spectrum of the annealed GaInNAs/GaAs QW. As expected, the thermal anneal results in significant improvement of the as-grown GaInNAs/GaAs QW's optical quality (see Fig.6-1(b)). The PL (4K) intensity increased by almost 6x after anneal, and the Full-Width at Half-Maximum (FWHM) decreases from 66meV to 26.4meV. The PL peak energies of the GaInNAs/GaAs QW before and after anneal are 0.825eV and 1eV, respectively. The blueshift in the

PL peak energy could be the result of either N-As or In-Ga outdiffusion as discussed in Chapter 4. The as-grown and annealed GaInNAs/GaAs QW PL spectrum can be fitted phenomenologically by two Gaussian functions as represented by Curve L and Curve D in Fig.6-1(a) [64]. This fitting agrees well the TR-PL experiment for another annealed QW to be presented at the end of Chapter 7, that shows two distinguishable PL peaks at low laser excitation power. During the auto-fitting process, the peak energy and FWHM of the two Gaussian functions were allowed to vary. Similarly, the as-grown GaInNAs/GaAs QW PL spectrum can be decomposed in the same manner. It will be shown in this Chapter that Curve D was attributed to the e_0-hh_0 transition, which is the desired transition; while Curve L was attributed to the impurity related transition called the main localization-like state. By comparing the decomposed PL spectrum of Fig.6-1(a) and Fig.6-1(b), it was found that the relative peak intensity of Curve D to Curve L increases from ~0.8 to 2 after annealing, suggesting the improvement in the PL efficiency of the GaInNAs/GaAs QW was related to the suppression of localized states and enhancement of the e_0-hh_0 state. The following paragraphs will describe the analysis of temperature dependent PL properties including this localized state.

Fig.6-1 4K PL characteristics of (a) thermal-annealed GaInNAs/GaAs QW, and (b) as-grown GaInNAs/GaAs QW. Both are fitted with two Gaussian functions.

In order to ascertain the origin of Curve L and Curve D in Fig.6-1, which could provide the physical insight for the PL quenching in the annealed GaInNAs/GaAs QW, the change of PL characteristics with temperature was investigated. Only five of the PL spectra are shown in Fig.6-2 for the purpose of clarity. As temperature increased from 4.5K to 80K, the PL intensity reduces by 20 times. Also, the PL peak energy of the GaInNAs/GaAs QW shifted slightly by 7meV as temperature increased from 4.5K to 150K (see inset in Fig.6-2) due to temperature dependent energy shrinkage (Varshni relationship). As compared to the larger PL peak energy change of 23meV for the reference GaInAs/GaAs QW within the 4.5K to 150K temperature range (not shown here), the GaInNAs/GaAs QW showed better thermal stability. The PL efficiency, η , with respect to measurement temperature was then calculated from the above experiment. η (see Eq.6-1) is defined as the ratio between the PL intensity at temperature T, $I(T)$, and PL intensity at 4K, I_o . At 4K, the thermal energy contribution to carrier excitation, and non-radiative recombination is assumed to be minimal. Hence,

$$\eta = \frac{I(T)}{I_o} \quad (6-1)$$

Also, it will be shown later that the η vs. T data was well fitted by a Dual-Activation-Energy (DAE) model, instead of a Single-Activation-Energy (SAE) model. Exponential relationships between PL efficiency and temperature were used, and the overall PL efficiency was formulated as [68]:

$$\frac{1}{\eta} = \frac{I_o}{I(T)} = 1 + Ae^{-E_A/kT} + Be^{-E_B/kT} \quad (6-2)$$

where, A and B are constants, k is Boltzmann's constant, and T the absolute temperature. By plotting $\ln(\eta)$ vs. $1/kT$, the unknown parameters in Eq.(6-2) can be obtained.

Fig.6-2 Change of PL intensity in the annealed GaInNAs/GaAs QW with temperature. The inset shows the change in the PL peak energy of the annealed GaInNAs/GaAs QW with temperature.

As evident in Fig.6-3, an SAE model (dotted line) fitted relatively poorly the experimental data over the temperature range from 4K to 150K. Setting $B=0$ and $E_B=0$ in Eq.(6-2) satisfied the SAE model, yielding activation energy of E_A . On the other hand, a DAE model (solid line) as described by Eq.(6-2) fitted the

experimental data very well. This result suggested the existence of intermediate energy levels (in addition to e_0) that facilitate carrier loss by thermal and optical excitation. These intermediate energy levels can be quantified by fitting the experimental data in Fig.6-3 with the DAE model, yielding $E_A \sim 38\text{meV}$ and $E_B \sim 9\text{meV}$.

Fig.6-3 Plot of PL efficiency vs. inverse of temperature. The SAE model (dotted line) and DAE model (solid line) were used to fit the experimental data.

The value of E_B ($\sim 9\text{meV}$) was close to the energy separation between Curve D and Curve L of 11meV in Fig.6-1(a). In order to investigate the origin of E_B , the original temperature dependent PL spectra were fitted with two Gaussian functions as in Fig.6-1. The same notation of Curve D and Curve L were used in Fig.6-4(a) to indicate the trend of the PL intensity of the high-energy and low-energy Gaussian functions. Hence E_B was related to the activation of carriers from the low energy

impurity state to a higher energy e_0 state as describe in the above. It was believed that the impurity state was related to localization effect as a result of N incorporation [66]. This was evident in the change in peak PL intensity with temperature as shown in Fig.6-4(a) where the e_0 state (Curve D) tends to increase linearly with increasing laser excitation power while the localized state (Curve L) tends to saturate with the same treatment above $\sim 100\text{mW}$. In the low excitation power region of below $\sim 100\text{mW}$ in Fig.6-4(a), although the peak intensities of Curve L and Curve D may look close to each other, their intensity difference were actually large. For example the relative intensities of Curve D to Curve L was about 3.4 times and 4 times at excitation power of $\sim 12\text{mW}$ and 20mW , respectively. Obvious intensity saturation of Curve L only occurred above $\sim 200\text{mW}$. The above observation was consistent with the experimental observation of *Luo et al.* in nitride materials [66] and hence, confirmed the assignment of E_B as main-localized-state-related activation energy. The results can be further explained based on the band filling effect. At low temperature, carriers tend to stay at low energy state, and therefore the carriers are trapped by the localized states (low-energy Gaussian function). This is evident in Fig.6-4(b) where the integrated intensity of the localized state (low energy Gaussian function) was higher than that of the e_0 state (high energy Gaussian function) at low temperature. Following an increase in temperature, the carriers in the localized states acquire more energy to populate the e_0 state, leading to higher integrated PL intensity for the high-energy Gaussian function. Hence, the integrated PL intensity of the localized states, which has limited carrier density, quenched faster as temperature was increased.

Fig.6-4 Plot of (a) 4K PL peak intensity vs. laser excitation power, and (b) integrated PL intensity vs. temperature.

A separate study on the localized states in GaInNAs/GaAs QW by Time-Resolved Photoluminescence (TR-PL) measurements presented in Chapter 8 further confirmed the findings of this Chapter. In the investigation, stronger emission-energy-dependent carrier lifetime has been observed in GaInNAs/GaAs QW, as compared to the reference GaInAs/GaAs QW. As for this Chapter, the experiments

only concentrate on using PL studies to address two types of transitions that could affect the desired e_0 - hh_0 transition, namely the main localized state presented in the above, and a GaAs-barrier-defect-related transition in the following. The assignment of this defect will be presented first, followed by the explanation for the creation of such carrier loss center at increasing PL measurement temperature.

Fig.6-5 Energy band diagram of the PL quenching model for GaInNAs/GaAs QW.

As measurement temperature increased beyond $\sim 120\text{K}$, the center with activation energy $E_A = 38\text{meV}$ further quenched the PL intensity of the QW. This center was attributed to the presence of defect in the GaAs barrier, and it was determined based on QW calculation [63]. The defect occurs naturally during material growth as will be discussed in the following.

From room temperature GaInNAs/GaAs QW calculations, the confined energy states of $e_0 = 44\text{meV}$ and $hh_1 = 15\text{meV}$, with respect to the conduction band and

valence band, respectively, are obtained. Together with the calculated conduction band offset and valence band offset of 414meV and 177meV, respectively, the Defect State, as labelled in Fig.6-5, was found to be located at 0.34eV from the conduction band. This value is close to the 0.35eV defect state of EL6, which was reported to be a Ga vacancy–As vacancy ($V_{\text{Ga}}-V_{\text{As}}$) complex [69]. This defect in GaAs could dissociate at high temperature and then reform after thermal annealing and hence, was likely to occur in the GaInNAs/GaAs QW used in this study due to the choice of growth conditions.

Although carriers were mostly trapped in the QW layer, and one would logically deduce that PL transition would only occur in the well layer, and not in the thin GaAs barrier layer (80nm in this study) in ideal situation. However, Vening *et al.* has deduced in his study that barrier layer defects created during growth can contribute to the thermal quenching of their GaInAs/AlGaAs QW's PL efficiency [70], through the detrapping process of carriers into the barrier layer. Hence their finding supports the argument in this Chapter that the above GaAs-barrier defects could contribute to the PL efficiency reduction in the GaInNAs/GaAs QW. In this study, the creation of the $V_{\text{Ga}}-V_{\text{As}}$ defect in the GaAs barrier during growth could be promoted primarily by a low V/III ratio of 15, and secondarily by a low growth temperature of 450°C. All the above results were consolidated into a PL quenching model as depicted in Fig.6-5.

6.4 Summary

In conclusion, this Chapter reported a study of the PL quenching mechanisms in GaInNAs/GaAs QW. The physical mechanism of carrier localization in the annealed GaInNAs QW was analysed from the change in PL spectra with temperature and laser excitation power. By fitting, phenomenologically, the individual PL spectrum with two Gaussian functions, the signature of the main localized and e_0 states can be identified. The existence of two PL quenching states (E_A and E_B) results in significant PL intensity reduction following increase in temperature. The activation energy E_B is confirmed to be a localized state, and an EL6 defect level was identified, both of which could degrade PL efficiency in GaInNAs/GaAs QW. The results indicated that, for future development, improving the barrier material quality and reducing the localized transitions in the GaInNAs QW could potentially lead to enhanced PL efficiency in such a material system.

CHAPTER 7

Study of Localization Effect in Annealed GaInNAs/GaAs Quantum Well by Photoluminescence Spectroscopy

In this chapter, variable temperature Photoluminescence (PL) measurement of a thermally annealed 6nm GaInNAs/GaAs Quantum Well (QW) was carried out to further examine the localization effect in GaInNAs/GaAs QW. The existence of the localization effect in annealed GaInNAs/GaAs QW was further examined by Time-Resolved Photoluminescence (TR-PL) experiments.

7.1 Introduction

Although GaInNAs-based laser structures grown on GaAs substrates provide competitive advantages in terms of lower cost and higher substrate robustness compared to similar devices grown on InP substrates, fundamental studies on the GaInNAs/GaAs QW photoluminescence (PL) mechanisms are somewhat lacking. One of the key issues concerns the fast PL quenching of the thermally annealed GaInNAs QW at room temperature, even though its 4K PL efficiency increases after thermal annealing. Such characteristic is undesirable for current 1.3 μm and 1.55 μm laser technology that require devices to operate at room temperature. Hence, an insight for the carrier dynamics of the GaInNAs/GaAs QW has become an important study area, that can be elucidated by PL and TR-PL measurements.

7.2 Experimental details

In this Chapter, a Double-Quantum-Well (DQW) with the following structures were grown: GaAs cap / GaInAs well / GaAs barrier / GaInNAs well / GaAs buffer. The GaAs barrier thickness of 80nm was chosen to minimize the interaction between the two QWs' wave functions. Both QWs were of the same nominal thickness of ~6nm, and they were grown at 460°C, and with V_{As}/III_{Ga} ratio of ~30. The top GaInAs QW served as a reference to estimate the In composition of the GaInNAs QW by PL measurements. The In and N compositions were 16% and 1.5%, respectively. The sample was subjected to post-growth thermal annealing at 840°C for 10mins.

7.3 Study of localization effects in GaInNAs/GaAs QW by Photoluminescence (PL) spectroscopy and Time-Resolved Photoluminescence (TR-PL) spectroscopy

Fig.7-1(a) shows an enhancement of PL intensity of the GaInNAs/GaAs QW by almost 6x after thermal anneal, while its Full-Width at Half-Maximum (FWHM) decreases significantly from ~45meV to ~21meV. Furthermore, the PL line-shape of the GaInNAs QW becomes more symmetrical after annealing. It was proposed that the PL spectrum be fitted with two Gaussian functions; (a) a low-energy Gaussian function, which characterizes the main localized state and (b) a high-energy Gaussian function, which characterizes the e_0 - hh_0 transition of the annealed GaInNAs QW. This fitting agrees well with the TR-PL experiment to be presented at the end of this Chapter, which shows two distinguishable PL peaks.

This approach provides a quantitative means to compare the characteristics of the localized and e_0 states in the annealed GaInNAs/GaAs QW. The fitting by two Gaussian functions of the annealed and as-grown PL spectra revealed a reduction in the PL peak energy between the localized and e_0 state from 26meV (Fig.7-1(b)) to 11meV (Fig.7-1(c)), suggesting a reduction in the localization effect arising from N or In composition fluctuation in the QW [16]. This reduction in energy separation between the two fitted Gaussian functions in the annealed and as-grown PL spectra could be due to partial dissociation of N or In localization sites after annealing.

Fig.7-1 4K PL characteristics of: (a) as-grown and thermal-annealed GaInNAs/GaAs QW, (b) as-grown GaInNAs/GaAs QW fitted with two Gaussian functions, and (c) thermal-annealed GaInNAs/GaAs QW fitted with two Gaussian functions.

To ascertain the contribution of the localized state that would reduce the $e_0\text{-}hh_0$ transition efficiency of the annealed GaInNAs/GaAs QW, the natural logarithmic function of the PL efficiency, η , is plotted in Fig.7-2 as function of inverse temperature. A single-activation-energy (SAE) model as defined by Eq.(7-1) was found to fit the experimental data well. The factor C is a constant and E_C denotes the activation energy of a center that degrades the $e_0\text{-}hh_0$ PL emission, while k is the Boltzmann constant and T the absolute temperature.

$$\frac{1}{\eta} = 1 + Ce^{-E_C/kT} \quad (7-1)$$

The fitting of the $\ln(\eta)$ vs. $1/kT$ curve of the annealed GaInNAs/GaAs QW in Fig.7-2 was achieved using E_C of $\sim 13.7\text{meV}$ and C of ~ 450 . This could mean that at temperature below $\sim 60\text{K}$, there existed an intermediate energy level that facilitated carrier loss from the $e_0\text{-}hh_0$ state. It was noted that the E_C value of $\sim 13.7\text{meV}$ was close to the peak energy difference between the main localized state and e_0 state of 11meV obtained in Fig.7-1(c). Hence E_C was attributed to the carrier localization effect that remains in the GaInNAs/GaAs QW after thermal annealing. For comparison, the PL efficiency of the annealed GaInAs//GaAs QW is shown in Fig.7-2. It did not quench as fast compared to the annealed GaInNAs/GaAs QW within the above temperature range, suggesting that incorporation of N in GaInAs promotes such localization behaviour.

Fig.7-2 Plot of $\ln(\eta)$ vs. $1/kT$ of annealed GaInAs/GaAs QW (solid dots), and annealed GaInNAs/GaAs QW (hollow dots). The annealed GaInNAs/GaAs QW data, which is the main focus of this Chapter, is fitted using the single-activation-energy (SAE) model indicated as solid line.

The localized exciton effect in the annealed GaInNAs/GaAs QW was further observed in the plot of PL peak energy of the high- and low-energy Gaussian functions vs. temperature as shown in Fig.7-3. The dotted lines denote the declining trends of both functions' peak energies following an increase in temperature. The PL peak energy difference between $\sim 5\text{K}$ and 45K is 7meV and 23meV for the high- and low-energy functions, respectively. The larger redshift in energy of the low-energy state compared to the high-energy state provided further evidence for the existence of localized states [66].

Fig.7-3 Plot of the PL peak energy vs. temperature of the annealed GaInAs/GaAs QW (hollow squares), and the high- (solid dots) and low-energy (hollow dots) Gaussian functions for the annealed GaInNAs/GaAs QW. The dotted lines show the declining trend of the high- and low-energy Gaussian functions' peak energies with temperature.

The S-shaped temperature dependence of PL peak energy was commonly observed in as-grown nitride materials, and was attributed to the strong effect of localization. *Luo et al.* [66] reported such an effect from 10K to 60K, and attributed it to carrier trapping by localized states, and hence, domination of the PL spectrum by such an effect. As temperature was increased, the carriers in the localized state possessed more energy to populate the e_0 state. Because the peak energy of the localized state (low energy state) red-shifted at a faster rate compared to the e_0 state following an

increase in temperature, this band filling effect resulted in competition between the localized and e_0 excitons, and hence, the anomalous behaviour observed by *Luo et al.*. In this study, the anomalous behaviour was not observed, due to the effect of thermal annealing in possibly reducing alloy compositional fluctuation [18] and hence, reducing but not totally eliminating the carrier localization effect in the annealed GaInNAs/GaAs QW.

In the event of the existence of neighbouring short lifetime e_0 and long lifetime main localized states (as will be verified later in this study), competition for carriers between these states at low temperature could lead to the decrease in peak energy by about 23meV. As temperature was increased, carriers occupying the localized states nearer to the e_0 state gain sufficient energy to occupy the e_0 state, leading to the larger (23meV) peak energy downshift of the main localized state. In addition, in earlier investigations with lower nitrogen composition of $< \sim 1\%$, the GaInNAs/GaAs QW peak energy hardly downshifted within the same temperature range of $\sim 50\text{K}$ (not shown in this Chapter). In this study, the high nitrogen composition of 1.4% in the well region could have contributed to a stronger temperature-dependent GaInNAs/GaAs QW peak energy downshift, and therefore the small (7meV) downshift of the e_0 state. On the other hand, the annealed GaInAs/GaAs QW (Fig.7-3) did not show such behaviour as evident in its predominantly single Gaussian function PL spectra with its peak energy remained at 1.337eV over the same temperature range of study in Fig.7-3.

Fig.7-4(a) shows the TR-PL spectrum of the annealed GaInNAs/GaAs QW sample measured at 17K. The TR-PL spectrum was taken from an average of 10 original

TR-PL spectra around the PL peak position to reduce possible random error of individual spectrum. The localized peak was clearly distinguishable from the e_0 peak. Likewise, two Gaussian functions denoted by the dotted spectra, were used to fit the original spectrum. It was noted that the energy separation between the peaks of the two fitted Gaussian functions was 11meV. This value was identical to the energy separation between the localized and e_0 state as shown in Fig.7-1(c). In addition, the data in Fig.7-1 to Fig.7-3 were collected using the same PL system, while the data in Fig.7-4 were collected using a TR-PL system. The difference in the peak intensities of the main localized state and e_0 state in Fig.7-1(c) and Fig.7-4(a) was most likely due to the difference in laser excitation power used in both systems, and not due to the measurement temperature. This was because higher laser excitation power could excite the electrons in the localized state to occupy the e_0 state, thereby reducing the PL peak emission of the localized state in Fig.7-1(c), and *vice versa*. This was evident in Fig.7-4(a) where the low- and high-energy Gaussian functions have comparable peak intensity at low laser excitation. Their saturation behaviour and linear dependence behaviour, respectively, at increasing laser excitation intensity as obtained from PL experiments (inset of Fig.7-4(a)) further showed the above difference in their peak intensities. Hence, the above energy separation of 11meV confirmed the reproducibility of the results using two separate measurement systems, and the validity of using the two-Gaussian-function approach to fit the PL spectra in this study. As for the annealed GaInAs QW, only a normal linear dependence behaviour was present (inset of Fig.7-4(b)) as no strong localization was observed in its PL spectra.

In addition, it was noted that as the laser excitation intensity on the sample surface was reduced from 540mW to 12.1mW, in a separate experiment, the peak PL energy decreased from 1.067eV to ~1.060eV in a non-linear manner especially at low excitation power regime, indicating the influence of PL excitation intensity on the PL peak energy. It was expected that the PL peak energy could reduce further if the excitation was lowered. However, this was not done for the PL measurements due to the limitation of the equipment set-up. This observation was an indication of the existence of impurity states, such as the localized state studied in this Chapter, whose intensity increases with decreasing excitation intensity, as observed by *Luo et al.*. The low intensity localized-state Gaussian-function (Fig.7-1(c)) was itself an indication of high excitation intensity has been used for the PL measurement. On the other hand, the high intensity localized-state Gaussian-function in the TR-PL measurement (Fig.7-4(a)) indicated low excitation intensity has been used instead. This was consistent with the studies by *Luo et al.*.

Also, the decay time or carrier lifetime of the annealed GaInNAs/GaAs QW and annealed GaInAs/GaAs QW are plotted in Fig.7-4(a) and Fig.7-4(b), respectively, as solid dots. It was found that the decay time characteristic obtained from the time constant, τ , of the QW transition was predominantly single-exponential in nature;

$$I = I_o e^{-t/\tau} \quad (2)$$

where, I and I_o are the measured PL intensity, and initial peak PL intensity, respectively, while t is the time of flight. Each solid dot in the figure represents the decay time deduced from fitting the average intensity of 20 consecutive TR-PL spectra over a ~2.4meV energy range. The carrier localization effect in the annealed GaInNAs/GaAs QW was further confirmed by the dependence of the decay time on

PL emission energy [16] below $\sim 1.045\text{eV}$. The decay time decreased as energy increased due to distribution of localized excitons with the main exciton localization energy at 11meV below the e_0 state. The decay time then decreased to $\sim 0.14\text{ns}$, which was that of the e_0 state. At lower energy of 1.037eV , the higher decay time of $\sim 1.15\text{ns}$ was attributed to the radiative recombination process of the lower energy localized carriers. As for the annealed GaInAs/GaAs QW which did not exhibit localization effect, its lifetime remained at an average value of $\sim 0.2\text{ns}$ over the energy range of its PL spectrum as shown in Fig.7-4(b).

Due to the longer decay time of the main localized state in the annealed GaInNAs/GaAs QW, which was located at lower energy, the laser excitation was unable to efficiently excite most of the electrons to fill the higher energy e_0 state. The e_0 state's radiative decay time only dominates at increasing energy further from the main localized state. The localized state distribution would therefore form carrier loss centers for the e_0 state at low temperature. Instead of having electrons from the e_0 state recombining directly with the hh_1 state, they could be trapped by the localized states that were characterized by the main localized state energy at 11meV below the e_0 state, thereby reducing the desired e_0 - hh_0 recombination efficiency.

Fig.7-4 Plot of exciton decay time vs. photon energy and TR-PL intensity vs. photon energy for (a) annealed GaInNAs/GaAs QW, and (b) annealed GaInAs/GaAs QW. The TR-PL spectrum for the annealed GaInNAs/GaAs QW is fitted with two Gaussian functions indicated as dotted curves, while that of the annealed GaInAs/GaAs QW is by itself a single-Gaussian function. The insets show the change in the respective PL peak intensity with laser excitation power.

7.4 Summary

In conclusion, this Chapter reported an investigation of the carrier dynamics of an annealed GaInNAs/GaAs QW by PL and TR-PL. Measurements confirmed the existence of a main localized state at $\sim 11\text{meV}$ below the e_0 state. The presence of the main localized state was further examined by fitting a single-activation-energy model to the $\ln(\eta)$ vs. inverse temperature data. The results showed a faster rate of energy redshift for the main localized state. TR-PL measurements further confirmed the existence of the main localized state and e_0 state in the annealed GaInNAs QW, from observation of strong energy-dependent decay time characteristic that was not observed in the annealed reference GaInAs/GaAs QW. The results indicated the localized states behave as carrier loss sites for the desired $e_0\text{-}hh_0$ transition, and thus contributing to reduction in the $e_0\text{-}hh_0$ PL efficiency at low temperature.

CHAPTER 8

Concluding Remarks and Recommendations

In this thesis, systematic studies of the GaInNAs/GaAs Quantum Well (QW) growth and characterization are presented. The QWs were grown on GaAs substrate by Solid Source Molecular Beam Epitaxy (SSMBE) in conjunction with an RF N-plasma source. The as-grown and annealed GaInNAs/GaAs QWs were characterized by Photoluminescence (PL), Time-Resolved Photoluminescence (TR-PL), X-Ray Diffraction (XRD) to assess their optical and structural quality. The integrity of the GaAs cap layer grown on the QW samples and annealed by Rapid Thermal Annealing equipment was confirmed by Atomic Force Microscopy (AFM). This Chapter summarizes the results presented in this thesis and provides some suggestions for future research.

Hence, the goal of this project is, firstly, to establish growth conditions for the GaNAs and GaInNAs/GaAs QWs using a newly installed N-plasma source. The capability of the N-plasma source has been evaluated using mainly the GaNAs material and presented in Chapter 2. The process development for GaInNAs/GaAs QW and the problems associated with surface nitridation during growth have been studied in Chapter 3. Closing the main-shutter and N-shutter during plasma ignition has been effective in reducing nitridation on the GaAs substrate as observed by Reflection High-Energy Electron Diffraction (RHEED).

Chapter 3 showed that as-grown GaInNAs/GaAs QW with a long emission wavelength of $\sim 1580\text{nm}$ at 4K and with a relatively small spectral spread of $\sim 100\text{nm}$ was achievable. This small spread was achieved by growing QWs with high In composition of 30% and high $V_{\text{As}}/\text{III}_{\text{Ga}}$ of 30, which has the effect of reducing the N incorporation in the GaInNAs well layer, and further reducing surface nitridation at both the well-barrier interface and the well layer. Consequently, the 3D growth mode has been suppressed in the GaInNAs well layer, and the beneficial effect of strain relief by incorporating N in GaInAs prevails. The optical quality of as-grown GaInNAs/GaAs QW has been improved by Rapid Thermal Annealing (RTA) at 840°C for 10 mins albeit with a downshifted PL peak wavelength. One of the as-grown GaInNAs/GaAs QW that emits 4K PL at 1500nm has downshifted to 1238nm after RTA. However, the peak emission wavelength would extend to $\sim 1320\text{nm}$ at room temperature following *Varshni* relationship with fitting parameters established in this thesis. This peak emission wavelength of near $1.3\text{ }\mu\text{m}$ is desirable for future long wavelength optical transmission devices development.

In Chapter 4, the contributing factors for the PL peak wavelength downshift after RTA at 850°C for 10mins have been presented. The improvement was suggested to be due to the annihilation of N-ion-induced damage through defect-assisted N-As interdiffusion and the enhancement of Ga and In atoms interdiffusion at the GaAs/GaInNAs/GaAs interfaces at high temperature. The downshift of the PL peak wavelength of the GaInNAs/GaAs and GaInAs/GaAs emission was found to be dependent on the In composition. While high In composition GaInNAs/GaAs QW is the preferred way in extending the PL emission wavelength, as this is less affected

by N-related defect, the resulting high compressive strain could contribute to larger PL peak downshift after annealing.

In Chapter 5, the change of PL peak energy vs. temperature of as-grown GaInNAs/GaAs QW with In ~ 30% and N ~ 0.9%, and well width of ~6nm has been investigated. A two-segmented PL peak energy vs. temperature fitting scheme was applied to the QW. The low-temperature region (<80K) was associated with localized transitions, as it exhibited larger temperature dependent energy redshift. On the other hand, the high-temperature region (~80K -150K) showed smaller temperature dependent downshift, which is characteristic of the e_0-hh_0 transition, similar to that of annealed GaInAs/GaAs QW. As for annealed GaInNAs/GaAs QW, a much smaller temperature dependence energy redshift has been demonstrated. This shows that the PL transitions in as-grown GaInNAs/GaAs QW are dominated by localized transitions. On the other hand annealed GaInNAs/GaAs QW showed less influence from the localized transitions as a single PL peak energy vs. temperature fitting scheme was found to be sufficient. In addition, the annealed GaInNAs/GaAs QW has much better temperature stability than annealed GaInAs/GaAs QW.

The quenching mechanisms of annealed GaInNAs/GaAs QW with In = 30% and N = 1.5%, and well width of ~7nm have also been studied in Chapter 6 by phenomenological fitting of PL efficiency vs. temperature data. It was found that the annealed GaInNAs/GaAs QW shows main localization center with activation energy of $E_B = 9\text{meV}$ even after annealing, The EL6 defect level at the GaAs barrier with activation energy of $E_A = 38\text{meV}$ further contributes to carrier loss. The localized transitions are due to In-N interaction, and compositional or well-width fluctuations,

while the *EL6* is most likely due to the low growth temperature of 460°C and low V_{As}/III_{Ga} of 15 used for growing the QW.

Chapter 7 further confirmed and characterized the localized transitions in another annealed GaInNAs/GaAs QW, with as-grown In and N compositions of 16% and 1.5%, respectively, by Time-Resolved Photoluminescence (TR-PL) measurement. The localized transition showed emission-energy-dependent PL decay time characteristic for the low-energy regime (below 1.045eV) and nearly constant decay time of about 0.14ns at the high-energy regime, which corresponds to the e_0-hh_0 transition lifetime. The main localization center could form carrier traps that reduce the e_0-hh_0 PL transition efficiency, and hence affect future laser performance. As the localized transitions in the GaInNAs are contributed to by the introduction of N, increasing the In composition instead of the N composition in GaInNAs well layer is recommended for work effort to extend the PL peak emission wavelength beyond 1.3μm.

In addition, the following are recommended for future research:-

1. Strain relief barrier for the GaInNAs well layer

The large amount of strain build-up between the GaInNAs well and the GaAs barrier results in both degradation in material quality as well as large PL peak wavelength downshift after annealing. In recent years, the strain relief method has been utilised to counter the material degradation problem. GaNAs barrier was used to reduce the strain of the overall QW-barrier strain with respect to the GaAs substrate. In addition a strain-mediating layer was inserted in between the well and barrier to relieve the well-barrier interface strain [71, 72].

2. GaInNAsSb well layer

The incorporation of Antimony (Sb) in GaInNAs has, in recent years, showed promising results in incorporating more N composition without 3D growth, and in extending the PL peak wavelength to near 1.6 μm . Hence this could solve a key challenge in the growth of GaInNAs/GaAs QW.[73]

3. Time-resolved photoluminescence measurements

Due to time-constraint and other unforeseen circumstances, further characterization of as-grown and annealed GaInNAs/GaAs QWs by TR-PL or other complementing techniques was not pursued. The change in carrier lifetime in GaInNAs/GaAs QW with annealing temperature and time are important areas of studies. This could further justify the goodness of annealing process.

4. Study of intrinsic carrier concentration and mobility

It is reported that the intrinsic p-type carrier concentration of lattice matched GaInNAs material is $\sim 10^{17} \text{cm}^{-3}$. However, the carrier type converts to n-type $\sim 10^{17} \text{cm}^{-3}$ after annealing [74]. Whether the above carrier type conversion would occur in strained GaInNAs needs further investigation. The intrinsic carrier concentration and the corresponding mobility values of strained GaInNAs could be obtained in this investigation using Hall effect measurements.

AUTHOR'S PUBLICATIONS

A. Journal Papers

1. T.K. Ng, S.F. Yoon, S.Z. Wang, W.K. Loke, W.J. Fan, "Photoluminescence Characteristics of *GaInNAs Quantum Wells* Annealed at High Temperature", *Journal of Vacuum Science & Technology B*, **20**(3) 964 (2002).
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 6. **Tien Khee Ng, Soon Fatt Yoon, Wan Khai Loke, and Satrio Wicaksono**,
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B. Conference Papers

1. T.K. Ng, S.F. Yoon, S.Z. Wang, W.K. Loke, and W.J. Fan, "Study of High Nitrogen Compositions *GaN*s and *GaInN*s Material Quality by X-ray *Diffraction* and Photoluminescence", Materials Research Society Fall Meeting, Oct/Nov 2001, Boston USA.
2. T.K. Ng, S.F. Yoon, S.Z. Wang, W.K. Loke, W.J. Fan, K.C. Yew, and Z.Z. Sun, "Photoluminescence Behaviour of *GaInN*s Quantum Wells annealed at High Temperature", 14th Indium Phosphide and Related Materials Conference, May 12-16, 2002, Stockholm, Sweden.
3. Ng Tien Khee, Yoon Soon Fatt, and Fan Weijun, "Analysis of Photoluminescence *Efficiency* in Annealed *GaInN*s Quantum Well Grown by Solid Source Molecular Beam *Epitaxy*", Materials Research Society Fall Meeting, Dec 2003, Boston USA.
4. Ng Tien Khee, Yoon Soon Fatt, and Fan Weijun, "Laser Power and Temperature Dependent *Photoluminescence* (PL) Characteristics of Annealed *GaInN*s/*GaAs* Quantum Well", Materials Research Society Fall Meeting, Dec 2003, Boston USA.

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