A study of dilute nitride compounds grown by molecular beam epitaxy for electronic application

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**A Study of Dilute Nitride Compounds
Grown by Molecular Beam Epitaxy
for Electronic Application**

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Summary

Dilute nitride InGaAsN has shown potential application in heterojunction bipolar transistors (HBTs) on GaAs substrates with low turn-on voltage. The application is based on two features of InGaAsN: firstly, InGaAsN can be lattice-matched to GaAs; secondly, the incorporation of small amounts of N into (In)GaAs reduces the band gap drastically. Hence, the growth and characterization of (In)GaAsN, especially *p*-type InGaAsN were investigated in this thesis, due to its potential usage in *n-p-n* HBT devices as the base layer.

Radio frequency (RF) plasma-assisted solid source molecular beam epitaxy (MBE) was used to grow (In)GaAsN on GaAs substrates. Beryllium (Be)-doping was used to achieve *p*-type InGaAsN. The hole concentration of $\sim 10^{19} \text{ cm}^{-3}$ and the hole mobility of $\sim 70 \text{ cm}^2/\text{V}\cdot\text{s}$ were achieved. These results are comparable to Be-doped GaAs, and make it possible to fabricate InGaAsN-based HBTs with low base resistance. Compared with undoped InGaAsN, increased tensile strain in Be-doped InGaAsN was observed and was attributed to the increase of N composition arising from Be incorporation. A possible mechanism is proposed: the high Be-N bond strength inhibits the loss of N from the growth surface.

Temperature-dependent PL properties of Be-doped InGaAsN were studied. The PL spectra were dominated by near-band-edge emission at high temperatures and localized excitonic (LE) emission plus a broad deep band at low temperatures. The deep PL band may originate from recombinations associated with N-related traps. The origins of the excitons are suggested to be related to the doping levels. At the light doping regime corresponding to non-degeneracy, the excitons could be bound to neutral acceptors accompanied by N clusters and have a larger localization energy. At the high doping regime corresponding to degeneracy, the excitons could be bound to N clusters solely and have a smaller localization energy.

Deep-level defects in Be-doped InGaAsN were investigated. Two hole traps (*HT1* and *HT4*) and two electron traps (*ET1* and *ET3*) were observed in the as-grown sample. The *HT1* and *ET3* traps could be N-related defects, and the *HT4* trap could

have a similar origin as the so-called EL2-type defect. Following postgrowth thermal annealing, the overall deep-level trap concentration decreases, with two hole traps (*HT2* and *HT3*) and one electron trap (*ET2*) observed. The *HT2* trap was created during annealing, and the *HT3* trap was found to have a similar origin as the *HT4* trap, i.e., the EL2-type. After thermal annealing, the leakage current of the InGaAsN/GaAs *p-n* junction diode decreases by 2~3 orders and the minority-carrier electron diffusion length in *p*-type InGaAsN increases by ~30%. These improvements indicate that thermal annealing may be implemented as a process step to improve the InGaAsN material quality.

An operational InGaP/In_{0.03}Ga_{0.97}As_{0.99}N_{0.01}/GaAs *n-p-n* DHBT was demonstrated. The narrower band gap of In_{0.03}Ga_{0.97}As_{0.99}N_{0.01} led to a 130 mV reduction in the turn-on voltage compared to the InGaP/GaAs SHBT.

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Introduction

1.1 Background and Motivation

1.1.1 Turn-on Voltage

Heterojunction bipolar transistors (HBTs) on GaAs substrates are widely used in high performance microwave and digital applications. Their characteristics are closely matched to the needs of linear and efficient power amplifiers operated with available batteries. However, there are several features that could be improved. One of these is the turn-on voltage, $V_{be,on}$, which is the base-emitter voltage required to generate a certain collector current density, J_C . The turn-on voltage is ~ 1.4 V for present GaAs-based HBTs. The power amplifier circuits are customarily operated using a battery as the voltage source. Lithium ion cells are widely used at present. The voltage provided by these cells is in the neighborhood of $3.4 \sim 3.6$ V, but can drop to 3.0 V near the end of the battery discharge cycle. Circuit considerations require that the turn-on voltage should be well below half of the minimum battery voltage, in order to implement temperature-compensated bias circuit in the amplifiers. The present value of the turn-on voltage for GaAs-based HBTs is marginal for these requirements. As a result, substantial benefits can be obtained by decreasing the turn-on voltage.

Under the condition of base transport limit, the output current is controlled mainly by the base transport rather than by the barriers at the base-emitter (BE) or base-collector (BC) junctions. Taking n - p - n HBT as an example, the turn-on voltage can be expressed as:

$$V_{be,on} = \frac{KT}{q} \ln \left(\frac{J_c \int_0^w p/n_i^2 dx}{qD_n} \right) \quad \text{Eq. 1-1}$$

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The above equation shows that $V_{be,on}$ is weakly dependent on the minority-carrier electron diffusion coefficient in the base, D_n , and the hole concentration in the base, p , as well as the width of the base, w [1]. The principal determinant of $V_{be,on}$ is the intrinsic carrier concentration in the base, n_i , and n_i is mainly controlled by the band gap of the base material. Therefore, the band gap of the base material determines the turn-on voltage of the HBT. In order to achieve lower turn-on voltage alternative base materials with smaller band gap should be used. Figure 1-1 illustrates the dependence of J_c on V_{be} for HBTs fabricated with a variety of material systems [2]. The turn-on voltage is smaller in Si bipolar junction transistor (BJT) than in GaAs HBT, and smaller yet in InP HBT with $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ base.

Figure 1-1 Dependence of J_c on V_{be} for HBTs fabricated with different material systems. Shaded region shows values obtainable with InGaAsN base. [2]

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The turn-on voltage for InP HBTs is inherently lower than GaAs HBTs. Used as the base material, $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ is lattice-matched to InP substrate and has a band gap of 0.75 eV [3]. $\text{GaAs}_{0.5}\text{Sb}_{0.5}$ ($E_g \sim 0.72$ eV) as the base material grown on InP substrate also provides a corresponding reduction in the turn-on voltage [4]. But due to substrate cost, concern over breakage, and possibly lack of 6-inch wafers, InP HBTs have not been adopted by commercial foundries.

InGaAs as the base material on GaAs substrate has had limited success in reducing turn-on voltage because the materials are not lattice-matched. The thickness and In composition of the InGaAs layer must be kept within the critical thickness so that the strain due to lattice mismatch can be absorbed elastically. If the InGaAs base layer is thicker than its critical thickness, misfit dislocations will occur and cause excessive recombination. $\text{In}_{0.08}\text{Ga}_{0.92}\text{As}$ -based HBTs on GaAs substrates have been successfully fabricated [5]. This composition of In translates into a turn-on voltage reduction of ~ 0.1 V, compared to GaAs-based HBTs. This small reduction is the practical limit for InGaAs-based HBTs with conventional base width.

To further reduce the turn-on voltage for HBTs on GaAs substrates, alternative base materials must be investigated. The use of InGaAsN material in the base can provide a technologically important decrease in the band gap, leading to J_c vs. V_{be} dependence in the shaded region of Figure 1-1.

1.1.2 An Overview of InGaAsN

Recently, InGaAsN has received wide attention. On the one hand, the incorporation of N into InGaAs reduces the net strain of the material grown on GaAs substrate. As shown in Figure 1-2, the incorporation of In into GaAs induces compressive strain while the incorporation of N induces tensile strain [6]. With roughly three times amount of In as that of N, InGaAsN can be lattice-matched to GaAs [7]. On the other hand, the incorporation of small amounts of N into (In)GaAs reduces the band gap drastically [8, 9]. The band gap of GaAsN can be approximated as the composition weighted linear average of the band gaps of GaAs and GaN plus a correction term [10]:

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$$E_g(GaAs_{1-x}N_x) = E_g(GaAs) \cdot (1-x) + E_g(GaN) \cdot x - bx(1-x) \tag{Eq. 1-2}$$

where b is the bowing coefficient. For conventional III-V alloys, b is typically a fraction of 1 eV. In contrast, the bowing coefficient in III-V-N is huge, i.e., of the order of 18 - 20 eV for the N composition lower than 5% [11].

Figure 1-2 Effect of N incorporation in (In)GaAs. [6]

These characteristics have motivated considerable research activities in this material and its device applications, such as low turn-on voltage HBTs [12], multijunction solar cells [13, 14], and long-wavelength semiconductor lasers [15, 16]. In order to provide a useful amount of turn-on voltage reduction for HBTs, the

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band gap of InGaAsN as the base layer should be in the range of 1.0 ~ 1.3 eV. Accordingly, the N composition in InGaAsN should be in the range of 0.5% ~ 2%.

1.1.3 An Overview of InGaAsN-based HBTs

The use of InGaAsN as the base of HBTs has been investigated recently [17-19]. A principal goal of these research activities is to demonstrate the reduction in the turn-on voltage without compromising the high microwave performance of the transistors. Some important parameters of two representative InGaAsN-based n - p - n and p - n - p HBTs are listed in Table 1-1 for comparison [20, 21]. $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$ was implemented as the base in both devices and it has a band gap of ~ 1.2 eV. Therefore, the turn-on voltage reduction is about 200 ~ 300 mV for both devices, compared to conventional GaAs-based HBTs.

As shown in Table 1-1, the p - n - p HBT has lower current gain cutoff frequency, f_T , and lower maximum frequency of oscillation, f_{max} . These make it unfit for applications in high-speed wireless communication. The low f_T of the p - n - p HBT is attributed to the short minority-carrier hole diffusion length in the n -type base. According to Kurtz *et al.*, the minority-carrier hole diffusion length is only 0.03 μm in MBE-grown InGaAsN, while the minority-carrier electron diffusion length is 0.5 μm [13].

To achieve high f_{max} , it is necessary to have high f_T and low base resistance. Conventional HBTs have a base sheet resistance $\rho_B = 300 \sim 600 \Omega/\text{sq}$. This value must not be increased significantly for the InGaAsN-based HBTs. The high ρ_B of the InGaAsN-based p - n - p HBT is attributed to the relatively low doping level of the n -type InGaAsN base, which is only $\sim 2 \times 10^{18} \text{ cm}^{-3}$ at present. In contrast, the doping level of p -type InGaAsN can reach as high as mid - 10^{19} cm^{-3} .

For the reasons mentioned above, this work is focused on InGaAsN-based n - p - n HBT only. As a matter of fact, most of the reported efforts in fabricating InGaAsN-based HBTs have focused on n - p - n .

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	InGaP / In _{0.03} Ga _{0.97} As _{0.99} N _{0.01} / GaAs <i>n-p-n</i> DHBT	AlGaAs / In _{0.03} Ga _{0.97} As _{0.99} N _{0.01} <i>p-n-p</i> SHBT
ΔE_C at BE junction	0.28 eV	0.5 eV
ΔE_V at BE junction	0.40 eV	0.15 eV
ΔE_C at BC junction	0.16 eV	0 eV
ΔE_V at BC junction	0.02 eV	0 eV
Base band gap E_g	1.24 eV	~1.2 eV
Base width w	70 nm	100 nm
Base sheet resistance ρ_B	900 $\Omega/\text{sq.}$	2300 $\Omega/\text{sq.}$
Peak DC Gain β	16	60
Ideality factor n_B	1.2	2.2
Ideality factor n_C	1.1	NA
$\Delta V_{be, on}$ ($I_C = 1 \mu\text{A}$)	250 mV	290 mV
Peak f_T	40 GHz	15 GHz
Peak f_{max}	72 GHz	10 GHz

Table 1-1 Comparison of InGaAsN-based *n-p-n* and *p-n-p* HBTs. [20, 21]

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Despite these, the *n-p-n* HBT has lower current gain compared with the *p-n-p* HBT. This is attributed to the band alignment of the structure: most of the band gap reduction of InGaAsN relative to GaAs occurs in the conduction band. This band alignment is relatively unfavorable for *n-p-n* HBTs because it produces a conduction band barrier for electrons at the junction, which is detrimental for transporting electrons. At the BE junction, the presence of the barrier dictates higher voltage to be applied to inject electrons into the base, and results in an increase in the turn-on voltage. At the BC junction, the barrier impedes the collection of electrons by the collector and causes electrons to stay in the base longer, leading to an increased base recombination current and reduced current gain. Thus, the heterostructure of the *n-p-n* HBT must be optimized in order to improve the current gain.

	InGaP /In _{0.01} Ga _{0.99} As _{0.997} N _{0.003} /GaAs DHBT	InGaP /In _{0.03} Ga _{0.97} As _{0.99} N _{0.01} /GaAs DHBT	GaAs /In _{0.11} Ga _{0.89} As _{0.98} N _{0.02} /GaAs DHBT
Base E_g	~ 1.3 eV	~ 1.24 eV	~ 0.98 eV
Base μ_p	85 cm ² /V·s	90 cm ² /V·s	50 cm ² /V·s
Base L_n	0.4 μm	< 0.5 μm	0.1 μm
Peak β	75	16	8.5
$\Delta V_{be, on}$ ($I_C=1\mu A$)	100 mV	250 mV	400 mV

Table 1-2 Comparison of InGaAsN-based *n-p-n* HBTs with different N compositions. [1, 20, 22]

So far several groups have demonstrated InGaAsN-based *n-p-n* HBTs with different N compositions [1, 20, 22]. Some of the performance parameters are listed in Table 1-2 for comparison. With increasing the N composition, the band gap of the InGaAsN base decreases and more turn-on voltage reduction is achieved. However, the majority-carrier hole mobility and the minority-carrier electron

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diffusion length in the base, as well as the peak current gain decrease with increasing the N composition. These indicate that the incorporation of N degrades the crystalline quality of the InGaAsN base. The more N incorporated the worse crystalline quality of InGaAsN. Therefore, a practical N composition of 1% was chosen in this work.

1.2 Objectives

The major objectives of this work are to grow lattice-matched $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$ on GaAs substrate using molecular beam epitaxy (MBE), to study the optical and electrical properties of Be-doped, *p*-type $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$, and to fabricate $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$ -based *n-p-n* HBTs.

In detail, the objectives of this work are outlined as follows:

- 1) To grow strained GaAsN on GaAs substrate with different N compositions using MBE.
- 2) To grow lattice-matched $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$ on GaAs substrate using MBE.
- 3) To incorporate Be in $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$ to achieve *p*-type material and investigate the effects of Be doping on N incorporation.
- 4) To investigate the temperature-dependent photoluminescence (PL) of Be-doped $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$.
- 5) To grow and fabricate $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$ /GaAs *p-n* junction diode.
- 6) To investigate deep-level defects and minority-carrier electron diffusion length in Be-doped $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$, as well as the effects of rapid thermal annealing on these properties.

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- 7) To grow and fabricate InGaP/In_{0.03}Ga_{0.97}As_{0.99}N_{0.01}/GaAs *n-p-n* HBT with reduced turn-on voltage.

1.3 Major Contributions of the Thesis

Dilute nitride (In)GaAsN with desired N composition was successfully grown using MBE and characterized using x-ray diffraction (XRD), PL, deep level transient spectroscopy (DLTS) and so on. InGaP/In_{0.03}Ga_{0.97}As_{0.99}N_{0.01}/GaAs *n-p-n* HBT was grown and fabricated and its DC performance was investigated. The most important contributions of the thesis are summarized as follows:

- 1) GaAs_{1-x}N_x alloys have been grown successfully on GaAs substrates using MBE. By tuning the RF power, controllable N composition can be achieved. The GaAsN epilayer is fully tensile strained up to the N composition of 2.8% with thickness of 100 nm.
- 2) In_{0.03}Ga_{0.97}As_{0.99}N_{0.01} lattice-matched to GaAs with a band gap of ~ 1.2 eV has been achieved.
- 3) *P*-type doping has been achieved in Be-doped InGaAsN, with the hole concentration of $\sim 10^{19}$ cm⁻³ and the corresponding hole mobility of ~ 70 cm²/V·s. These results are comparable to those of Be-doped GaAs, and make it possible to fabricate InGaAsN-based HBTs with low base resistance.
- 4) The influence of Be doping on N incorporation has been investigated. Increased tensile strain in Be-doped InGaAsN is observed and is attributed to the increase of N composition. The increase of N composition is caused by the Be incorporation.
- 5) Temperature-dependent PL properties of Be-doped InGaAsN have been studied. The PL spectra are dominated by near-band-edge emission at high temperatures and localized excitonic (LE) emission plus a broad deep band at low temperatures. The deep PL band may originate from recombination

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associated with N-related traps. The hole concentration dependence of the integrated intensity ratio of the LE emission peak to the deep PL band at 5 K can be separated into two doping regimes. The intensity ratio is linearly proportional to the hole concentration at the light doping regime corresponding to non-degeneracy. In this case the excitons are suggested to be bound to neutral acceptors accompanied by N clusters, and have a relatively larger localization energy. The intensity ratio saturates at the high doping regime corresponding to degeneracy, in which case the excitons are suggested to be bound to N clusters solely and have a relatively smaller localization energy. Thermal annealing improves the compositional and structural homogeneities and reduces the localization energy.

- 6) Deep-level defects in Be-doped InGaAsN have been investigated. Two hole traps (*HT1* and *HT4*) and two electron traps (*ET1* and *ET3*) are observed in the as-grown sample. The *HT1* and *ET3* traps could be N-related defects, and the *HT4* trap could have a similar origin as the so-called EL2-type defect. Following postgrowth thermal annealing, the overall deep-level defects concentration decreases, with two hole traps (*HT2* and *HT3*) and one electron trap (*ET2*) observed. The *HT2* trap is created during annealing, and the *HT3* trap is found to have a similar origin as the *HT4* trap, i.e., the EL2-type.
- 7) The minority-carrier electron diffusion length in Be-doped InGaAsN has been measured. A value of 0.14 μm is obtained in the as-grown layer. After postgrowth thermal annealing, the value increases by 30% and reaches ~ 0.19 μm .
- 8) InGaAsN/GaAs *p-n* junction diode has been grown and fabricated, and the leakage current of the diode has been investigated. The leakage current decreases by 2 ~ 3 orders after postgrowth thermal annealing.
- 9) InGaP/In_{0.03}Ga_{0.97}As_{0.99}N_{0.01}/GaAs *n-p-n* DHBT has been demonstrated. The use of InGaAs grading layer and δ -doping layer is believed to eliminate the conduction band barrier at the BC junction and result in a very low knee

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voltage (as low as that of SHBT). The narrower band gap of $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$ has led to a 130 mV reduction in turn-on voltage compared with the InGaP/GaAs SHBT.

1.4 Organization of the Thesis

Chapter 1 presents the background and motivation of the research work reported in this thesis. Chapter 2 presents experimental techniques that have been used in this work. Chapter 3 presents the epitaxial growth of strained GaAsN and the structural and optical characterization of GaAsN. The growth of $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$ lattice-matched to GaAs is described in Chapter 4. Chapter 5 presents *p*-type doping in $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$ and the effects of Be doping on N incorporation. PL properties of Be-doped $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$ are presented in Chapter 6. In Chapter 7, investigation of deep-level defects and minority-carrier electron diffusion length in Be-doped $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$ is presented. In Chapter 8, we demonstrated InGaP/ $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$ /GaAs *n-p-n* DHBT. Finally, conclusions and recommendations for future research are discussed in Chapter 9.

Chapter 2 Experimental Techniques

Chapter 2

Experimental Techniques

2.1 Solid Source Molecular Beam Epitaxy

A Riber32 solid source molecular beam epitaxy (MBE) system was used for sample preparation throughout this work. A general pictorial description of the system is shown in Figure 2-1. The growth chamber is maintained at ultrahigh vacuum through a complicated pumping system comprising of a dry diaphragm pump, a turbomolecular pump, an ion pump and a titanium sublimation pump. The group-III elements (Ga, In and Al) and dopant elements (Si and Be) are evaporated from conventional effusion cells. The group-V elements (As and P) are evaporated from valved cracker sources. The active nitrogen radicals are generated by a radio frequency (RF) plasma source. The chamber is also equipped with quadrupole mass spectrometer (QMS) and reflection high-energy electron diffraction (RHEED). QMS is used to check the level of the background impurities inside the chamber and RHEED is used to *in-situ* monitor the epitaxial growth. Routinely, RHEED is used to monitor the surface oxide desorption of substrates and to estimate the growth rate, as well as to monitor the changes of surface reconstruction. More fundamental concepts on the MBE growth technique of III-V compound semiconductors will not be given here. They can be found in a number of references [23-25].

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Figure 2-1 Schematic diagram of the MBE system.

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2.2 X-ray Diffraction

X-ray diffraction (XRD) is a powerful tool for nondestructive *ex-situ* investigation of epilayers. In this work, the rocking curve measurement on the (004) crystalline plane was used to determine the alloy compositions of GaAsN, InGaAs, InGaAsN and so on. The triple-axis diffraction measurement on the (115) crystalline plane was used to determine the mismatch and strain status of epilayers. The latter measurement is also called two-dimensional (2-D) mapping. A brief description of the principles is presented in this section. More information can be found elsewhere [26, 27].

In general, the lattice of an epilayer does not have the same cubic unit cell as that of the substrate. It will be distorted by the mismatch stress. If the epilayer is fully strained, i.e., the lattice constant parallel to the interface ($a_{\parallel}$) follows that of the substrate (a_s), then the lattice constant perpendicular to the interface ($a_{\perp}$) can be determined from the (004) rocking curve measurement in the case of epilayers grown on (001)-oriented substrates. The corresponding mismatch is given by:

$$\left(\frac{\Delta a}{a_s} \right)_{\perp} \equiv \frac{a_{\perp} - a_s}{a_s} = \frac{\sin \theta}{\sin(\theta + \Delta \theta)} - 1 \quad \text{Eq. 2-1}$$

where θ and $\theta + \Delta \theta$ are the Bragg angles of the (004) crystalline plane of the substrate and of the epilayer, respectively.

If the epilayer is not fully strained, i.e., partially or fully relaxed, then the (004) rocking curve will fail to give the value of $a_{\parallel}$. 2-D mapping should be used instead. During the 2-D mapping measurement, one of the Miller indices, e.g. l in the reciprocal lattice, is fixed, and the other two Miller indices, h and k , are varied by $\pm \Delta h$ and $\pm \Delta k$. The instrument is used in the following way: the detector (2θ) is scanned for a sequence of angular positions of the sample stage (ω), i.e., ω - 2θ scan. By measuring a number of ω - 2θ scans with different offsets to ω , a 2-D intensity contour map around the reciprocal lattice points (RELPS) of the substrate and the

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epilayer is obtained. The mismatch parallel or perpendicular to the interface is given by:

$$\left(\frac{\Delta a}{a_s} \right)_{\perp} \equiv \frac{a_{\perp} - a_s}{a_s} = -\Delta\theta \cot \theta + \Delta\phi \tan \phi \quad \text{Eq. 2-2}$$

$$\left(\frac{\Delta a}{a_s} \right)_{\parallel} \equiv \frac{a_{\parallel} - a_s}{a_s} = -\Delta\theta \cot \theta - \Delta\phi \cot \phi \quad \text{Eq. 2-3}$$

where ϕ is the angle between the (hkl) crystalline plane of the substrate and the sample surface, and $\Delta\phi$ is the angle between the (hkl) crystalline plane of the epilayer and that of the substrate.

Figure 2-2 shows an example of a GaAsN epilayer on GaAs substrate. The two peaks correspond to the RELPs (115 in this case) of GaAs and GaAsN, respectively. The angular separations between the two peaks in the horizontal and vertical direction are equal to $\Delta\theta$ and $\Delta\phi$, respectively, as indicated in the figure. Substituting $\Delta\theta$ and $\Delta\phi$ into Equation 2-2 and 2-3, the lattice mismatch can be calculated.

Figure 2-2 XRD (115) 2-D mapping of GaAsN.

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2.3 Deep Level Transient Spectroscopy

2.3.1 Introduction

The deep level transient spectroscopy (DLTS) technique is a sensitive tool to study the electrical properties of deep levels in semiconductors. It was first proposed by Lang in 1974 [28]. The method is based on measurements of capacitance transients of depletion layers during charge transfer in a Schottky or one-sided p - n junction diode. Using this method, the characteristics of deep-level traps can be obtained, such as the trap concentration, activation energy, carrier capture cross section and so on. The fundamental principle and data evaluation method are presented in this section. More detailed knowledge can be found in the overviews by Blood and Orton and by Schroeder [29, 30].

In this work DLTS measurements were carried out on InGaAsN/GaAs p - n junction diodes using a BIO-RAD DL8000 system to investigate the deep-level defects in InGaAsN alloys. The BIO-RAD DL8000 system is a PC-driven, software-based, digital system. Capacitance-time transients are digitized and discrete Fourier coefficients are formed *via* numerical transformations. These coefficients are used to calculate the amplitude and the time constant of the transients for discrete trap levels. The system supports measurements on a variety of device configurations such as Schottky or p - n junctions, metal-oxide-semiconductor (MOS) capacitors or three-terminal field effect transistors (FETs). A 100-mV and 1-MHz Boonton meter is used to measure the capacitance. Using compressed helium cryostat, the system supports temperature scan from 10 to 300 K, thus it is able to probe deep levels with activation energies between ~ 0.1 and ~ 1 eV.

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2.3.2 Experimental Principle

A one-sided p - n junction diode is used as a test vehicle to measure deep-level defects in the lower-doped layer. The diode is held at a fixed reverse-bias voltage, V_R . When a filling pulse voltage, V_P , is applied to the diode, the depletion width, X_d , is reduced, and free carriers flow into the depletion region and are captured by those empty deep-level defects. Following removal of the pulse, the depletion width relaxes back to its original value, and the trapped carriers are thermally emitted from the deep-level defects. This process is illustrated in Figure 2-3 for the case of electron capture and emission [31].

Figure 2-3 Schematic illustration of electron capture and emission from a deep level in the upper half of the band gap.

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The emission of trapped carriers gives rise to a capacitance transient and the transient is sampled at an interval of Δt . The period width $T_w = N\Delta t$ contains N intervals with $N+1$ real values $f_0, f_1 \dots f_N$ of the capacitance. The discrete Fourier coefficients c_n^D are formed *via* numerical Fourier transformations:

$$c_n^D = \frac{1}{N} \sum_{k=0}^{N-1} f_k \exp(-2\pi i n k / N), \quad n = 0, 1 \dots N-1. \quad \text{Eq. 2-4}$$

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

$$c_n^D = \frac{1}{2} (a_n - i b_n) \quad \text{Eq. 2-5}$$

As each coefficient contains information about the entire transient, few coefficients are sufficient for extraction of trap parameters. Generally b_1 is used as the DLTS signal. In the case of exponential transient, b_1 can be proven to be:

$$b_1 = \frac{4\pi\Delta C_0}{T_w^2 (1/\tau^2 + (2\pi/T_w)^2)} \exp(-t_0/\tau) \times (1 - \exp(-T_w/\tau)) \quad \text{Eq. 2-6}$$

where ΔC_0 is the amplitude of the capacitance transient, τ is the carrier emission time constant, and t_0 is the time between the end of the filling pulse and the start of the measurement of the capacitance transient.

A temperature scan is performed and the DLTS signal, b_1 , is measured and plotted vs. temperature. The DLTS signal shows a maximum at a temperature, $T_{\max}$, where the emission time constant of the observed deep level is equal to:

$$\tau(T_{\max}) = \frac{T_w}{\ln(1 + T_w/t_0)} \quad \text{Eq. 2-7}$$

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By varying T_W and t_0 and noting the temperature at which the DLTS peak occurs, a sequence of $(\tau(T_{max}), T_{max})$ pairs can be obtained from which information about the deep levels giving rise to the peaks can be determined.

2.3.3 Extraction of Trap Parameters

The carrier emission time constant is dependent on the carrier capture cross section and the energy separation of the energy level of the trap from the appropriate band edge. Taking electron emission as an example, the electron emission time constant can be expressed as:

$$\tau_n = \frac{1}{\sigma_n \langle v_n \rangle N_c} \exp\left(\frac{E_C - E_T}{K_B T}\right) \quad \text{Eq. 2-8}$$

where σ_n is the electron capture cross section, $\langle v_n \rangle$ is the electron root-mean-square thermal velocity and N_C is the effective density of states for the conduction band. And we have:

$$\langle v_n \rangle N_C = \left(\frac{3kT}{m_n^*}\right)^{1/2} 2 \left(\frac{2\pi m_n^* k_B T}{h^2}\right)^{3/2} = \gamma_n T^2 \quad \text{Eq. 2-9}$$

where the constant $\gamma_n = 3.11 \times 10^{21} (m_n^* / m_0) \text{ cm}^{-2} \text{ s}^{-1} \text{ K}^{-2}$. Substituting Eq. 2-9 into Eq. 2-8 results in:

$$\ln(\tau_n T^2) = \frac{E_C - E_T}{kT} - \ln(\gamma_n \sigma_n) = \frac{E_A}{k_B T} - \ln(\gamma_n \sigma_n) \quad \text{Eq. 2-10}$$

Assuming that σ_n is independent of temperature, the plot of $\ln(\tau_n T^2)$ versus $1/k_B T$ has a slope of $E_A = E_C - E_T$ and an intercept of $-\ln(\gamma_n \sigma_n)$. Therefore the trap activation energy and the electron capture cross section can be determined from a sequence of measured $(\tau_n(T_{max}), T_{max})$ pairs.

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The above analysis is based on the assumption that the quantity σ_n is independent of temperature; however, σ_n is actually temperature-dependent. Therefore, the apparent capture cross section derived from a straightforward analysis of Eq. 2-10 is not equal to the capture cross section in the temperature range of measurement, but is the value extrapolated to infinite temperature. The temperature dependence of σ_n is often accurately described by:

$$\sigma_n = \sigma_n^\infty \exp\left(-\frac{E_\sigma}{k_B T}\right) \quad \text{Eq. 2-11}$$

where σ_n^∞ is the carrier capture cross section extrapolated to infinite temperature, and E_σ is the cross-section activation energy. Substituting Eq. 2-11 into Eq. 2-10, one gets:

$$\ln(\tau_n T^2) = \frac{E_C - E_T + E_\sigma}{k_B T} - \ln(\gamma_n \sigma_n^\infty) \quad \text{Eq. 2-12}$$

Therefore the measured apparent activation energy, $E_A = E_C - E_T + E_\sigma$, is larger than the true activation energy, $E_C - E_T$, by an amount of E_σ .

The value of E_σ may be determined by measuring the amplitude of the capacitance transient, ΔC_0 , under a series of different filling pulse durations, t_p . The occupancy of the traps at the end of the filling pulse is dependent on the filling pulse duration, therefore, the amplitude of the capacitance transient is dependent on the filling pulse duration too, and it can be described by:

$$\Delta C_0 = \Delta C_0^\infty [1 - \exp(-\sigma_n \langle v_n \rangle n t_p)] \quad \text{Eq. 2-13}$$

where ΔC_0^∞ is the saturated amplitude of the capacitance transient at $t_p = \infty$, and n is the electron concentration. The plot of $\ln(1 - \Delta C_0 / \Delta C_0^\infty)$ vs. t_p has a slope proportional to σ_n . Therefore, by varying t_p a sequence of $(\Delta C_0, t_p)$ pairs can be obtained from which the value of σ_n at the temperature T_{max} can be determined.

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Substituting this value and the value of σ_n^∞ into Eq. 2-11, the cross-section activation energy, E_σ , can be determined. Then subtracting E_σ from the apparent activation energy, E_A , one can obtain the true activation energy, $E_C - E_T$.

Besides the activation energy and the carrier capture cross section, the trap concentration is another important characteristic parameter. It can be obtained by the method outlined below. To minimize quantization errors the measurement system selects an optimal value for t_0 , which satisfies:

$$\frac{T_W}{\ln(1 + T_W / t_0)} \approx 100\Delta t \quad \text{Eq. 2-14}$$

In our measurements $N = 512$ was used, therefore the above equation yields $t_0 \approx 0.006T_W$ and $\tau(T_{max}) \approx 0.2T_W$. Substituting these values into Eq. 2-6 results in $b_1 \approx 0.2\Delta C_0$. If the filling pulse duration is long enough so that all the traps are filled with carriers, then we can get:

$$\frac{\Delta C_0}{C_d} = \frac{N_T}{2N_D} \Rightarrow N_T \approx 10N_D \frac{b_1}{C_d} \quad \text{Eq. 2-15}$$

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

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2.4 Device Fabrication Process

2.4.1 Introduction

One of the main objectives of this work is to fabricate InGaP/In_{0.03}Ga_{0.97}As_{0.99}N_{0.01}/GaAs DHBT with reduced turn-on voltage. Therefore, the HBT fabrication process is outlined in this section, including wet etching, *n*- and *p*-type ohmic contacts, and the lift-off technique. The fabrication process relies mainly on the conventional photolithography and wet etching techniques. The process flow is based on the vertical mesa etched pyramid structure. Figure 2-4 shows the process flow diagram.

2.4.2 Wet Etching

In this work, wet etching process was used to form the mesa-type structure. A mixture of H₃PO₄ : H₂O₂ : H₂O (3 : 1 : 40) was used to etch GaAs or InGaAsN. The etch rate was observed to be ~ 150 nm/min. The InGaP layer was etched by using a mixture of HCl : H₂O (1 : 1) or HCl : HIO₃ (0.2 mol/l) : H₂O (1 : 1 : 40), which give an etch rate of 60 nm/min or 300 nm/min, respectively. The sequence of forming the emitter, base and collector mesas is described as below:

- 1) The HBT wafer is cleaned and coated with photoresist, then patterned using the emitter level mask to provide a wet etching mask.
- 2) After the highly doped GaAs cap is etched using H₃PO₄ : H₂O₂ : H₂O, the wafer is subject to HCl : H₂O or HCl : HIO₃ : H₂O to etch the InGaP emitter. The etching is stopped at the *p*⁺-InGaAsN base layer.
- 3) The base is then patterned and etched using H₃PO₄ : H₂O₂ : H₂O until the *n*⁺-GaAs subcollector layer is exposed.
- 4) Finally, the isolation mesa is patterned and etched using H₃PO₄ : H₂O₂ : H₂O. The mesa depth is confirmed using a DEKTAK profiler.

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Figure 2-4 Process flow diagram.

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2.4.3 Formation of Ohmic Contacts

After the mesa formation, ohmic contacts must be made to the emitter, base, and collector layers. The conventional lift-off technique was used in this work. Firstly, ohmic contact metal was deposited directly on top of the patterned material surface, then the unwanted metal was lifted-off by dissolving the underlying photoresist in acetone. An image reversal lithography process using the AZ 5214 photoresist was used to form an overhang structure of the photoresist. Such an overhang structure can prevent the continuity between the metal on the material surface and that on the photoresist, so that acetone can penetrate and dissolve the photoresist.

A AuGe-based metal system was used as the ohmic contacts on the *n*-type GaAs emitter and subcollector. The layer sequence is (from bottom to top) Ni/Ge/Au/Ni/Au (5/25/100/20/200 nm). After metal deposition, the sample was annealed in a rapid thermal process (RTP) furnace at 410 °C for 10 sec to make alloyed ohmic contacts. The specific contact resistance for these *n*-type contacts is $\sim 10^{-7} \Omega\text{cm}^2$. For the *p*-type InGaAsN base, a bi-layer metal system of 50-nm-thick Ti and 200-nm-thick Au was used. The Ti/Au metal system forms a non-alloyed ohmic contact. The specific contact resistance for this *p*-type contact is $\sim 10^{-5} \Omega\text{cm}^2$.

Chapter 3 Growth and Characterization of GaAsN

Chapter 3

Growth and Characterization of GaAsN

3.1 Introduction

In order to establish the optimal growth conditions for dilute nitrides with high crystalline quality, the growth and characterization of the ternary $\text{GaAs}_{1-x}\text{N}_x$ alloys are presented in this chapter. In particular, the structural and optical properties were investigated. The objective of this part of work is to achieve coherent GaAsN on GaAs substrate with the desired N composition of ~ 0.01 , which is to be used in Be-doped $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$ for the application of *n-p-n* heterojunction bipolar transistors (HBTs).

3.2 Experimental Details

3.2.1 Radio Frequency Plasma Nitrogen Source

In this work, the reactive nitrogen atoms and/or radicals were generated by a radio frequency (RF) plasma source manufactured by EPI Inc., USA. The ultra-pure N_2 gas (99.99999%) was supplied from a storage cylinder. A mass flow controller (MFC) enabled precise control of the N_2 flow rate during epitaxy and the maximum flow rate was 10 sccm. The nitrogen plasma can be ignited in two modes: high brightness mode and low brightness mode. The transition power from high brightness mode to low brightness mode is dependent on the nitrogen background pressure [32], as shown in Figure 3-1. Two modes of plasma and a no plasma region are indicated in the figure. High brightness mode of plasma was used throughout this work in order to generate sufficient nitrogen atoms and/or radicals for the growth of (In)GaAsN.

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Figure 3-1 Plot of transition power from high brightness to low brightness plasma mode vs. nitrogen background pressure. [32]

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3.2.2 Sample Preparation

The GaAsN samples were grown on (001)-oriented semi-insulated GaAs substrates using solid source molecular beam epitaxy (MBE). The beam equivalent pressures (BEPs) used for Ga and As were 3.3×10^{-7} and 1.1×10^{-6} Torr, respectively, so that the flux ratio of As/Ga was ~ 30 . The growth rate of GaAs was determined to be $\sim 0.7 \mu\text{m/hr}$ by time-resolved reflection high-energy electron diffraction (RHEED) measurements. The flow rate of N_2 gas was 0.05 sccm and the nitrogen background pressure in the growth chamber was $\sim 3.5 \times 10^{-6}$ Torr. The RF power was higher than the transition power to maintain the plasma in high brightness mode. Since only a small amount of N is to be incorporated into the nitride layer, we assume that the N incorporation does not affect the incorporation of group-III elements. Hence, the growth rate of GaAsN is expected to be the same as that of GaAs if the same Ga flux is used.

The growth sequence was initiated by desorbing the native oxide on the substrate surface at a temperature higher than 590 °C under arsenic overpressure, followed by depositing an undoped GaAs buffer layer of ~ 300 nm. Then, the substrate temperature was decreased to 460 °C and the RF plasma of nitrogen was ignited. During the process of ignition, the main shutter was kept closed to protect the substrate surface from the damage by energetic nitrogen ions. After the plasma was stabilized for ~ 3 min, a GaAsN epilayer of ~ 100 nm was grown. A series of RF powers were used for Samples M1 - M6 to achieve different N compositions, as listed in Table 3-1.

RHEED was used to monitor the surface reconstruction during the epitaxy. A clear surface reconstruction pattern of (2×4) was maintained during the entire growth process for Samples M1 - M5. However, for Sample M6 the pattern changed from streaky to spotty during the growth of GaAsN, indicating that strain relaxation occurred.

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Sample	RF Power (W)	$\Delta\phi(^{\circ})$	$\Delta\theta(^{\circ})$	$(\Delta a/a_s)_{ }$ (%)	$(\Delta a/a_s)_{\perp}$ (%)	[N %]
M1	80	0.02873	0.1052	0.005493	− 0.1969	0.5%
M2	120	0.07020	0.2476	0.005057	− 0.4626	1.2%
M3	140	0.1124	0.3900	0.02190	− 0.7270	1.9%
M4	160	0.1229	0.4507	0.01675	− 0.8353	2.2%
M5	200	0.1528	0.5573	0.01324	− 1.030	2.8%
M6	240	...	...	...	...	Relaxed

Table 3-1 RF power, lattice mismatch, and N composition of GaAsN samples.

3.2.3 X-ray Diffraction and Photoluminescence

Triple-axis x-ray diffraction (XRD) measurements on the (115) crystalline plane were performed to investigate the strain status of the GaAsN epilayers. The reciprocal space mapping (RSM) plots of the samples were obtained by running $(\omega+\omega_0)/2\theta$ scans for different offset angles, ω_0 , and plotting the recorded intensities in two-dimensional (2-D) reciprocal space frames. The lattice mismatch parallel or perpendicular to the interface was obtained from the RSM plots using the evaluation method introduced in Chapter 2. Then, for those fully strained samples, x-ray rocking curve measurements on the (004) crystalline plane were carried out and simulated to reveal the N composition in GaAsN.

The samples were characterized by low-temperature (5 K) photoluminescence (PL). Used as the excitation source, the 514.5-nm line of an Ar⁺ laser was mechanically chopped and focused onto the sample. The luminescence was spectrally dispersed

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by a monochromator and detected by a liquid-nitrogen cooled germanium (Ge) detector in association with a standard lock-in technique.

3.3 Results and Discussion

The RSM plots of Samples M1, M5, and M6 are shown in Figure 3-2. For Samples M1 and M5, two peaks are observed, corresponding to the (115) reciprocal lattice points (RELPs) of GaAs and GaAsN, respectively, as indicated in the figure. The two peaks are not aligned in the crystalline direction of (115), but in the growth direction of (001). This alignment indicates that the epilayer is fully strained (tensile strained). With increasing RF power, the strain increases and gives rise to larger spacing between the (115) RELPs of GaAsN and GaAs. This shows that more nitrogen is incorporated into GaAsN with increasing RF power. Samples M2, M3, and M4 are observed to show similar behavior and follow this trend. (The figures of these samples are not shown here).

For Sample M6, the (115) RELPs of GaAsN and GaAs become closer to each other and the intensity distribution is more disperse than the other samples. These indicate that strain relaxation occurred in Sample M6. Due to the high RF power used, a large amount of N was incorporated, so that the critical thickness of GaAsN was smaller than the epilayer thickness. As a result, misfit dislocations formed and degraded the crystalline quality. The fact that the (115) RELPs of GaAsN and GaAs are still roughly aligned in the direction of (001) indicates that the strain was not fully relaxed, but partially relaxed. These observations are in good agreement with the RHEED patterns during the epitaxy. A pattern of (2×4) was maintained during the entire growth process of Samples M1 - M5, whereas the pattern changed from streaky to spotty during the growth of Sample M6.

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Figure 3-2 RSM plots of Samples M1, M5, and M6. M1 and M5 are fully strained. M6 is partially relaxed. Sample details are listed in Table 3-1.

Chapter 3 Growth and Characterization of GaAsN

Since the GaAsN epilayers in Samples M1 - M5 are fully strained, XRD (004) rocking curve measurements and simulation can be used to determine the N composition. Taking Sample M5 as an example, the experimental and simulated curves are shown in Figure 3-3. Two main peaks and many small fringes are observed. The left main peak corresponds to the Bragg angle of the (004) crystalline plane of GaAs and the right one corresponds to that of GaAsN, as indicated in the figure. The simulation is based on the dynamical x-ray diffraction theory [33] and the simulated curve fits well the experimental curve. From the simulation the N composition in Sample M5 is obtained. Table 3-1 lists the values of the N compositions for all the samples. A maximum value of 2.8% is achieved without strain relaxation.

Figure 3-3 XRD (004) rocking curve and simulation of Sample M5. N composition is determined to be 2.8% from the simulation.

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Figure 3-4 Plot of N composition vs. RF power for Samples M1-M5. Solid line is the linear fitting result. N composition is linearly proportional to RF power.

The plot of N composition vs. RF power is shown in Figure 3-4. For fully strained samples (Samples M1 - M5), the N composition is linearly proportional to the RF power. It is reported that the N incorporation is dopant-like in dilute nitride [34]. The sticking coefficient of the nitrogen radicals generated by RF plasma is much higher than that of arsenic atoms. The N incorporation rate is defined as:

$$[N] = [GR] \times [N\%] \quad \text{Eq. 3-1}$$

where $[GR]$ is the growth rate of GaAsN and $[N\%]$ is the N composition in GaAsN. The N incorporation rate is mainly dominated by the N_2 flow rate, the RF power and the growth temperature. Under the conditions of a certain N_2 flow rate, RF

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power, and growth temperature, the N incorporation rate is almost constant and the N composition is reciprocally proportional to the growth rate. In our work, the growth rate was fixed and the N composition is proportional to the N incorporation rate. With increasing RF power, more nitrogen radicals were generated and incorporated, giving rise to higher composition of N.

Figure 3-5 XRD (115) 2-D mapping of Sample M5 in $(\omega-2\theta)-\Delta\omega$ coordinate, from which the mismatch parallel to the interface and that perpendicular to the interface are obtained. Data of mismatch are listed in Table 3-1.

As explained in Chapter 2, the mismatch parallel to the interface, $(\Delta a/a_s)_\parallel$, and the one perpendicular to the interface, $(\Delta a/a_s)_\perp$, can be obtained from the XRD (115) 2-D mapping measurements. Taking sample M5 as an example, Figure 3-5 shows the measurement result in the $(\omega-2\theta)-\Delta\omega$ coordinate. The horizontal spacing

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between the (115) RELPs of GaAsN and GaAs is $\Delta\theta = 0.5573^\circ$, and the vertical spacing is $\Delta\phi = 0.1528^\circ$. Substituting $\Delta\theta$ and $\Delta\phi$ into Eq. 2-2 and Eq. 2-3, $(\Delta a/a_s)_\parallel$ and $(\Delta a/a_s)_\perp$ were determined to be 0.01324% and -1.030%, respectively. The negative value of $(\Delta a/a_s)_\perp$ indicates that the epilayer is tensile strained. The mismatch of the other samples is listed in Table 3-1.

The mismatch of Samples M1 - M5 is plotted vs. N composition in Figure 3-6. The mismatch parallel to the interface is close to zero for all the samples, indicating that they are fully strained, as we have discussed previously. The mismatch perpendicular to the interface is linearly proportional to the N composition. Due to the smaller size of nitrogen atom than arsenic atom, GaAsN is tensile strained on GaAs substrate. Higher N composition leads to smaller lattice constant and larger tensile strain of GaAsN.

Figure 3-6 Plot of mismatch vs. N composition for Samples M1-M5. All these samples are fully strained. Detailed data are listed in Table 3-1.

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Figure 3-7 PL spectrum of Sample M2 at 5 K. The spectrum has an asymmetric lineshape with a sharp high-energy cutoff and an exponential low-energy tail.

PL measurements were performed at 5 K to investigate the band gap bowing effect of nitrogen when incorporated into GaAs. Figure 3-7 shows a typical PL spectrum of Sample M2. The PL emission has an asymmetric lineshape with a sharp high-energy cutoff and an exponential low-energy tail. This is usually explained in terms of localized excitonic (LE) emission due to potential fluctuations [35].

The PL properties of InGaAsN will be discussed in detail in Chapter 6. Now, we may estimate the localization energy of the excitons in GaAsN, based on the results of InGaAsN. The exciton localization energy is defined as:

$$E_{loc}(T) = E_g(T) - E_{PL}(T), \quad \text{Eq. 3-2}$$

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where $E_g(T)$ is the band gap energy and $E_{PL}(T)$ is the PL peak energy [36]. In our study of InGaAsN, the temperature-dependent PL peak showed an S-shaped behavior, and the excitons were suggested to be bound to neutral acceptors accompanied by N clusters. The corresponding localization energy was determined to be 34 meV at 5 K [37]. According to Mazzucato *et al.*, the S-shaped behavior in dilute nitrides is not related to indium [38]. Thus, we may assume that the localization energy in GaAsN is approximately equal to that in InGaAsN, i.e., 34 meV at 5 K.

Figure 3-8 Plot of band gap energy of Samples M1-M5 and GaAs at 5 K vs. N composition. Solid line is fitting result using second order polynomials, from which the band gap energy bowing coefficient of 20 eV is obtained.

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Based on the estimated value of the localization energy, the band gap energy of GaAsN at 5 K was calculated using Eq. 3-2 and is plotted vs. N composition in Figure 3-8. The band gap energy decreases with increasing N composition, which is consistent with the previous reports. The band gap energy of GaAs [39] is also plotted in the figure together with those experimental data of GaAsN. Using second order polynomials to fit these data points, the band gap energy of $\text{GaAs}_{1-x}\text{N}_x$ can be written as:

$$E_g(\text{GaAs}_{1-x}\text{N}_x) = E_g(\text{GaAs}) - 20x + 233x^2 \quad \text{Eq. 3-3}$$

Therefore, the bowing coefficient is determined to be 20 eV, which is consistent with the previous reports [11].

3.4 Conclusions

In summary, the ternary $\text{GaAs}_{1-x}\text{N}_x$ alloys were grown successfully using MBE. By tuning the RF power, different N compositions were achieved. The GaAsN epilayer was characterized to be fully tensile strained up to the N composition of 2.8% with thickness of 100 nm. An asymmetric lineshape of PL at 5 K was observed and was attributed to the LE emission. The localization energy of the excitons was estimated to be 34 meV at 5 K. The band gap energy was calculated accordingly, and was observed to decrease with increasing N composition. The band gap bowing coefficient was determined to be 20 eV, which agrees with the previous reports.

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Chapter 4

Growth and Characterization of

$\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$ Lattice-matched to GaAs

4.1 Introduction

When InGaAsN is used as the base in heterojunction bipolar transistor (HBT), its typical thickness is 50 ~ 100 nm. To prevent the formation of cross hatches and misfit dislocations, the alloy compositions in InGaAsN have to be tuned so that it is closely lattice-matched to GaAs. With roughly three times amount of In as that of N, InGaAsN can be lattice-matched to GaAs. Therefore, based on the established growth conditions for GaAsN, the growth and characterization of $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$ lattice-matched to GaAs are reported in this chapter. The determination of the alloy compositions in InGaAsN is also presented.

4.2 Experimental Procedure

Three InGaAsN samples, labeled as A1, A2, and A3, were grown on (001)-oriented semi-insulated GaAs substrates using radio frequency (RF) plasma-assisted solid source molecular beam epitaxy (MBE). The growth conditions were similar to those for the GaAsN samples presented in Chapter 3. The beam equivalent pressures (BEPs) for Ga and In were 3.3×10^{-7} and 1.7×10^{-8} Torr, respectively. This flux ratio of In/Ga was observed to result in an In composition of 0.03 in InGaAs. The RF power was 90, 100, and 110 W for the three samples, respectively, as listed in Table 4-1. The growth sequence was initiated by the deposition of a 300-nm-thick GaAs buffer layer at 580 °C. Then, the substrate temperature was decreased to 460 °C and the N plasma was ignited. After the plasma was stabilized, an 80-nm-thick InGaAsN layer was deposited, followed by a 20-nm-thick GaAs cap layer.

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Sample	RF Power	$\Delta\phi (^{\circ})$	$\Delta\theta (^{\circ})$	$(\Delta a/a_s)_{\parallel} (\%)$	$(\Delta a/a_s)_{\perp} (\%)$	[N%]
A1	90 W	~ 0	~ 0	~ 0	~ 0	1.1%
A2	100 W	0.02293	0.07121	0.01779	- 0.1350	1.5%
A3	110 W	0.04087	0.1555	0.01744	- 0.2897	1.9%

Table 4-1 RF power, lattice mismatch, and N composition of InGaAsN samples.

4.3 Results and Discussion

In this work, we assume that the In composition in InGaAsN is the same as that in InGaAs if they are grown under identical conditions except for N incorporation, i.e., the N incorporation will not affect the In composition. Therefore, if the In and Ga flux and the growth temperature for InGaAsN were the same as those for InGaAs, then the In composition would be the same in the two alloys. In order to obtain the proper In flux for the In composition of 0.03 in In_xGaAs , a series of In_xGaAs samples, labeled as A4, A5, and A6, were grown and characterized. The Ga flux was 3.3×10^{-7} Torr for all the three samples, and the In flux was 1.5×10^{-8} , 3.0×10^{-8} , and 4.7×10^{-8} Torr, respectively. The growth temperature was 460 °C, the same as that for InGaAsN samples. The In composition was determined by x-ray diffraction (XRD) rocking curve and was plotted vs. the flux ratio of In/Ga in Figure 4-1. In this small range of In composition, the In composition is approximately linearly proportional to the flux ratio of In/Ga. In order to achieve the In composition of 0.03, the flux ratio of In/Ga should be ~ 0.05 . Therefore the In flux for $\text{In}_{0.03}\text{Ga}_{0.97}\text{As(N)}$ was determined to be 1.7×10^{-8} Torr. This value of In flux was used during the growth of the InGaAsN samples.

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Figure 4-1 Plot of In composition vs. flux ratio of In/Ga for In_xGaAs Samples A4-A6.

XRD (115) two-dimensional (2-D) mapping measurements were performed on the InGaAsN samples to investigate the strain status of the InGaAsN epilayers. The reciprocal space mapping (RSM) plots are shown in Figure 4-2. For Sample A1, the (115) RELPs of InGaAsN and GaAs are overlapped with each other, indicating that the InGaAsN epilayer is closely lattice-matched to the GaAs substrate. For Samples A2 and A3, the (115) RELPs of InGaAsN and GaAs are separated along the (001) crystalline direction, indicating that the InGaAsN epilayer is tensile strained.

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Figure 4-2 RSM plots of Samples A1-A3. A1 is lattice-matched to GaAs. A2 and A3 are tensile strained.

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The mismatch parallel to the interface, $(\Delta a/a_s)_{\parallel}$, and the one perpendicular to the interface, $(\Delta a/a_s)_{\perp}$, were determined from the XRD (115) 2-D mapping measurements using the evaluation method introduced in Chapter 2. The data is listed in Table 4-1. The mismatch is plotted vs. N composition in Figure 4-3. The determination of N composition will be explained later. For Sample A1, the $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.989}\text{N}_{0.011}$ epilayer is lattice-matched to GaAs, therefore both $(\Delta a/a_s)_{\parallel}$ and $(\Delta a/a_s)_{\perp}$ are close to zero. For Samples A2 ($\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.985}\text{N}_{0.015}$) and A3 ($\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.981}\text{N}_{0.019}$), $(\Delta a/a_s)_{\parallel}$ is close to zero, while $(\Delta a/a_s)_{\perp}$ is linearly proportional to the N composition, indicating that both the samples are tensile strained. These observations are consistent with the analysis of RSM plots.

Figure 4-3 Plot of mismatch vs. N composition for Samples A1-A3. A1 is lattice-matched to GaAs. A2 and A3 are tensile strained. Sample details are listed in Table 4-1.

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Figure 4-4 XRD (004) rocking curves of Samples A1-A3.

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XRD (004) rocking curve measurements were performed on the InGaAsN samples and the results are shown in Figure 4-4. For Samples A2 and A3, two main peaks are observed, corresponding to the Bragg angles of the (004) crystalline planes of GaAs and InGaAsN, respectively. For Sample A1, the two Bragg peaks are overlapped and can hardly be distinguished, indicating lattice match of InGaAsN and GaAs. These observations are consistent with the 2-D mapping results discussed above. Besides the Bragg peaks, many small fringes are observed for all these samples, indicating that the InGaAsN epilayers have good interfacial and crystalline qualities. The N composition in InGaAsN was determined from simulation. When doing the simulation, we fixed the In composition at 0.03 and tuned the N composition and the thickness of the InGaAsN epilayer so that both the main peaks and the fringes fit the experimental curve well. Using this method, the N composition was determined to be 0.011, 0.015, and 0.019 for Samples A1, A2, and A3, respectively.

4.4 Conclusions

In conclusion, this chapter reported the growth and strain properties of InGaAsN. The growth conditions for $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$ lattice-matched to GaAs were obtained. The In composition in InGaAsN was fixed at 0.03, which was assumed to be the same as that in InGaAs grown under identical conditions. The N composition was varied and the strain properties of the corresponding InGaAsN were investigated. The In composition of 0.03 and N composition of 0.011 resulted in $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.989}\text{N}_{0.011}$ closely lattice-matched to GaAs.

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Chapter 5

Be-doping in InGaAsN and Influence of Be on N Incorporation

5.1 Introduction

In the context of *n-p-n* heterojunction bipolar transistor (HBT) devices, investigation of *p*-type doping in the InGaAsN base layer is of great importance. Beryllium (Be) was used as the *p*-type dopant throughout this work. Issues about the growth and characterization of Be-doped InGaAsN are reported in Chapter 5, 6, and 7. In particular, *p*-type doping and the influence of Be on N incorporation are reported in this chapter. *P*-type doping of $\sim 10^{19} \text{ cm}^{-3}$ was achieved in Be-doped InGaAsN and was compared with that in Be-doped GaAs. Furthermore, increased tensile strain was observed in Be-doped InGaAsN, compared to undoped InGaAsN. The origin of the increased tensile strain was analyzed and was found to be related to Be incorporation. The corresponding mechanism was suggested.

5.2 Experimental Procedure

The InGaAsN samples in this study were grown on (001)-oriented semi-insulated GaAs substrates using radio frequency (RF) plasma-assisted solid source molecular beam epitaxy (MBE). Be was used as the *p*-type dopant in the InGaAsN layers. The beam equivalent pressures (BEPs) of Ga and In were 3.7×10^{-7} and 1.6×10^{-8} Torr, respectively, which resulted in the In composition of 0.03 and Ga composition of 0.97. The growth rate of GaAs was observed to be 0.7 $\mu\text{m/hr}$. The flow rate of N_2 was 0.05 sccm and the RF power was 80 W. Under these conditions the nominal N composition was ~ 0.01 . An undoped GaAs buffer layer was first deposited at 590 °C. Following this, the substrate temperature was decreased to 460 °C and the N plasma was ignited for the growth of the N-containing layers (undoped InGaAsN or Be-doped InGaAsN). Sample B1 comprises a 200-nm-thick undoped InGaAsN layer and a 20-nm-thick GaAs cap layer. Sample B2 comprises a single layer of 200-nm-thick Be-doped InGaAsN

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with Be cell temperature of 710 °C. Samples B3, B4, and B5 comprise a 250-nm-thick undoped InGaAsN layer and a 300-nm-thick Be-doped InGaAsN layer. The Be cell temperature was 680, 710, and 740 °C, respectively. There was no growth interruption between the Be-doped and undoped layers. For comparison purpose, three Be-doped GaAs samples, labeled as C1, C2, and C3, were grown with the Be cell temperature of 630, 690, and 750 °C, respectively. The samples were characterized using Hall, x-ray diffraction (XRD) and secondary ion mass spectroscopy (SIMS) measurements. The SIMS measurement was performed using an ION-ToF SIMS system. The concentrations of In and N were measured by Cs^+ and Ar^+ ion bombardment, respectively, and analyzed by a Ga^+ gun.

5.3 Results and Discussion

Figure 5-1 shows the room temperature hole concentration and hole mobility in the Be-doped InGaAsN layers of Samples B3 - B5. The doping results of Be-doped GaAs Samples C1, C2, and C3 are also plotted for comparison. These Be-doped GaAs samples were grown under the same Ga flux as that for Be-doped InGaAsN. However, due to In incorporation, the actual growth rate of InGaAsN was slightly higher than that of GaAs. Hence the hole concentration in Be-doped InGaAsN is slightly lower than that in Be-doped GaAs, as shown in Figure 5-1 (a). On the other hand, as shown in Figure 5-1 (b), the hole mobility of Be-doped InGaAsN is reasonably good, although it is slightly inferior to that of Be-doped GaAs due to impurity scattering caused by In and N incorporation. Above all, good *p*-type doping was achieved in InGaAsN. The hole concentration can be up to $\sim 10^{19} \text{ cm}^{-3}$ and the corresponding hole mobility is $\sim 70 \text{ cm}^2/\text{V}\cdot\text{s}$. These results make it possible to fabricate InGaAsN-based HBT with low base resistance and good RF performance.

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Figure 5-1 Plots of room temperature hole concentration (a) and hole mobility (b) in Be-doped GaAs (Samples C1-C3, circles) and Be-doped InGaAsN (Samples B3-B5, squares) as function of Be cell temperature. Dotted lines are for eye guidance.

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Figure 5-2 shows the XRD (004) rocking curves of Sample B1 and Sample B2. For Sample B1, the undoped InGaAsN layer is closely lattice-matched to GaAs ($\Delta a/a_s < 2 \times 10^{-4}$). The N composition was determined to be 0.011 by simulation. For Sample B2, the hole concentration in the Be-doped InGaAsN layer is $4 \times 10^{18} \text{ cm}^{-3}$, and this Be-doped InGaAsN layer is lattice-mismatched to GaAs ($\Delta a/a_s = 3 \times 10^{-3}$).

Figure 5-2 XRD (004) rocking curves of Samples B1 and B2.

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Figure 5-3 XRD (115) 2-D mapping of Sample B2. The Be-doped InGaAsN epilayer is strained.

Figure 5-3 shows the XRD (115) two-dimensional (2-D) mapping of Sample B2 in reciprocal space. Two peaks are observed, corresponding to the (115) RELPs of GaAs and Be-doped InGaAsN, respectively, as indicated in the figure. The two peaks are aligned in the (001) growth direction, rather than the (115) crystalline direction, confirming that the InGaAsN layer is tensile strained.

Two factors may contribute to the increased tensile strain in the Be-doped InGaAsN sample. Firstly, because Be atoms usually substitute the Ga atom sites (Be_{Ga}), the smaller covalent radius of the Be atom (106 pm) compared to the Ga atom (126 pm) will result in tensile strain [40]. If this is the reason, then similar tensile strain should also be observed in Be-doped GaAs. However, the measurements carried out on the Be-doped GaAs Samples C1, C2, and C3 show negligibly small lattice mismatch values ($\Delta a/a_s < 2 \times 10^{-4}$).

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Figure 5-4 XRD (004) rocking curves of Be-doped GaAs samples C1-C3. No lattice mismatch is observed.

Figure 5-4 shows the XRD (004) rocking curves of the Be-doped GaAs Samples C1, C2, and C3. The measured room temperature hole concentration is 3.4×10^{17} , 2.7×10^{18} , and $2.7 \times 10^{19} \text{ cm}^{-3}$, respectively. The lattice mismatch is undetectable ($\Delta a/a_s < 2 \times 10^{-4}$), even up to the hole concentration of $2.7 \times 10^{19} \text{ cm}^{-3}$. This is due to the relatively small covalent radius difference of 20 pm between Be atom and Ga atom. For comparison, a larger covalent radius difference of 51 pm between N atom and As atom results in more obvious tensile strain in GaAsN ($\Delta a/a_s = 3 \times 10^{-4}$ when $[\text{N}] = 2.2 \times 10^{19} \text{ cm}^{-3}$) than that in Be-doped GaAs ($\Delta a/a_s < 2 \times 10^{-4}$ when $[\text{Be}] = 2.7 \times 10^{19} \text{ cm}^{-3}$). Therefore the mismatch caused by Be_{Ga} is rather insignificant, and the possibility of Be solely responsible for the increased tensile strain in Be-doped InGaAsN can be excluded.

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The second factor that could contribute to the increased tensile strain is the change of N or In composition in the Be-doped InGaAsN layer. Increase in N composition or decrease in In composition will contribute to tensile strain in the material. To examine the variation of N and In composition, SIMS measurements were carried out on Samples B1 and B2. The concentration profiles of N and In are shown in Figure 5-5. It is observed that the N concentration in Sample B2 is higher than that in Sample B1, while the In concentration is relatively unchanged. Thus, it is very likely that the increased tensile strain in the Be-doped InGaAsN layers was due to the increased N composition. XRD simulations show that the N composition in Sample B2 is 0.018, which is 0.007 more than that in Sample B1.

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Figure 5-5 SIMS profiles of N concentration (a) and In concentration (b) in Samples B1 (black line) and B2 (red line). The two samples have the same In composition, but different N composition.

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Figure 5-6 XRD (004) rocking curves of Samples B3-B5 with 2-in-1 structures.

Different N composition is observed between the upper Be-doped layer and the lower undoped layer.

In order to further verify whether the increase of N composition is related to the Be incorporation, or merely caused by the fluctuations of the growth conditions, 2-in-1 structures (Samples B3 - B5) were grown and characterized. For these samples, the fluctuations of the growth conditions were minimized by depositing the undoped InGaAsN layer and Be-doped InGaAsN layer continuously without interruption. Figure 5-6 shows the XRD (004) rocking curves of the 2-in-1

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structures. For all the three samples, two different N compositions were observed, corresponding to the undoped InGaAsN layer and Be-doped InGaAsN layer, respectively. The nominal N composition in the undoped InGaAsN layer was 0.011, but the actual N composition was 0.012, 0.011, and 0.009 for Samples B3 - B5, respectively. This is attributed to experimental fluctuations between the samples. Considering the above results and analysis, we can conclude that the N composition in the Be-doped InGaAsN layer was increased by 0.003 ~ 0.004, compared to the corresponding undoped InGaAsN layer. The increase of N composition must be related to the Be incorporation, since experimental fluctuations had been minimized between the undoped and Be-doped InGaAsN layers, and the Be incorporation was the only difference in the growth conditions between the layers. It is important to note that the increase of N composition in the 2-in-1 structures (0.003 ~ 0.004) is lower than that between Sample B2 and Sample B1 (0.007). This is because the latter value includes experimental fluctuations.

According to a report by Newman [41], the growth of GaN by MBE involves a meta-stable state, which is controlled by the competition between the forward reaction and the reverse reaction. The forward reaction depends on the arrival rate of active nitrogen species at the growth surface, which include excited neutral molecular nitrogen (N_2^*), ionized molecular nitrogen (N_2^+) and atomic nitrogen (N). All these species have sufficient energy for the forward reaction. Since solid GaN is thermodynamically unstable under the conditions of MBE growth, decomposition occurs during growth. A kinetic barrier to the decomposition process limits the reverse reaction rate. It is to be expected that the decomposition of Be-N has a higher kinetic barrier than that of Ga-N, based on the fact that the electronegativity difference between Be and N (1.47) is larger than that between Ga and N (1.23) [40]. Larger electronegativity difference means greater polarity and bond ionicity, and this generally results in a higher bond-dissociation energy. As a result, this barrier inhibits the loss of N from the growth surface, and increases the N composition in the material.

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5.4 Conclusions

In conclusion, this chapter reported the doping and strain properties of Be-doped InGaAsN. Reasonably good *p*-type doping was achieved in InGaAsN, which is comparable to that of Be-doped GaAs. The hole concentration of $\sim 10^{19} \text{ cm}^{-3}$ and the corresponding hole mobility of $\sim 70 \text{ cm}^2/\text{V}\cdot\text{s}$ make it possible to fabricate InGaAsN-based HBTs with low base resistance and good RF performance. Increased tensile strain in Be-doped InGaAsN was observed and was attributed to the increase of N composition. The increase of N composition was found to be caused by the Be incorporation. The high Be-N bond strength results in a high kinetic barrier to decomposition, and inhibits the loss of N from the growth surface during the epitaxy. This increases the N composition in the material.

Chapter 6

Photoluminescence Properties of Be-doped InGaAsN

6.1 Introduction

From the materials standpoint, the photoluminescence (PL) properties of (In)GaAsN quantum well (QW) have been studied extensively [42-44]. A characteristic S-shape behavior was reported for the temperature dependence of the QW emission, and was attributed to exciton localization. However, there are presently a few reports on the PL properties of bulk InGaAsN [45], especially *p*-type InGaAsN. Such an investigation is of particular interest due to its potential usage in *n-p-n* heterojunction bipolar transistor (HBT) devices as the base layer.

In this chapter, we have investigated the temperature-dependent PL characteristics of Be-doped, *p*-type bulk InGaAsN with different doping levels. Near-band-edge emission was observed at high temperatures and localized excitonic (LE) emission plus a broad deep band at low temperatures. The hole concentration dependence of the integrated intensity ratio of the LE emission to the deep PL band was analyzed. The mechanism of exciton localization was suggested.

6.2 Experimental Procedure

The InGaAsN samples in this study were grown on (001)-oriented semi-insulated GaAs substrates using radio frequency (RF) plasma-assisted solid source molecular beam epitaxy (MBE). Beryllium was used as the *p*-type dopant in the InGaAsN layers. The growth temperature for InGaAsN layers was 460 °C and the layer thickness was 300 nm. The nominal composition of $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.987}\text{N}_{0.013}$ results in a closely lattice-matched condition to the GaAs substrate ($\Delta a/a_s \sim 9 \times 10^{-4}$). InGaAsN Sample A was unintentionally doped with background hole concentration of $1.0 \times 10^{16} \text{ cm}^{-3}$, and Samples B, C, D, and E were Be-doped with room temperature hole concentration of 3.3×10^{17} , 1.4×10^{18} , 4.0×10^{18} , and $1.2 \times$

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10^{19} cm^{-3} , respectively. Thermal annealing was carried out in a rapid thermal processing (RTP) furnace at 750 °C for 1 min under N_2 ambient. The sample was capped with a 300-nm-thick SiO_2 layer to prevent the loss of arsenic at elevated temperatures. PL measurements were carried out between 5 and 290 K, as discussed in Section 3.2.3 of Chapter 3.

6.3 Results and Discussion

Figure 6-1 shows the temperature dependence of the PL spectra of as-grown Sample E. Two different peaks are observed at low temperatures and high temperatures, respectively. At low temperatures (5 ~ 80 K), the dominant PL peak has an asymmetric line shape. As the temperature increases from 5 to 80 K, the peak intensity becomes weaker and disappears at ~ 100 K, and the peak position experiences a redshift from 996 to 1021 nm. At high temperatures (100 ~ 290 K), another peak becomes dominant with a symmetric line shape whose position redshifts from 990 to 1043 nm as the temperature increases from 100 to 290 K. It has been reported that the low temperature PL peak arises from LE emission [35, 42], whereas the high temperature PL peak is due to the near-band-edge transition [46].

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Figure 6-1 Temperature dependence of PL spectra of as-grown Sample E. Two different peaks are observed at low temperatures and high temperatures.

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Figure 6-2 Temperature dependence of PL peak energy of as-grown Samples C and E. Solid lines are fitting with Varshni equation. Localization energy at 5 K is determined to be 34 and 24 meV for C and E, respectively.

The temperature dependence of the PL spectra of as-grown Sample C shows a similar behavior as as-grown Sample E. The PL peak energy of both samples as a function of temperature is shown in Figure 6-2. Above 100 K, both samples have similar PL peak position, which indicates that they have similar band gap values. The temperature-dependence of the band gap can be fitted by the empirical Varshni equation [47]:

$$E_g(T) = E_g(0) - \alpha T^2 / (\beta + T) \quad \text{Eq. 6-1}$$

where α and β are empirical parameters. By fitting the experimental results with Eq.

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6-1, the values of $E_g(0)$, α , and β for both samples were obtained. For Sample C (as-grown), $E_g(0) = 1.265$ eV, $\alpha = 0.53$ meV/K, and $\beta = 268$ K. For Sample E (as-grown), $E_g(0) = 1.267$ eV, $\alpha = 0.51$ meV/K, and $\beta = 233$ K.

Below 80 K, the emission mechanism changes from near-band-edge transition to LE emission; hence the PL peak position deviates from the fitted curve. We may define the exciton localization energy [36] as:

$$E_{loc}(T) = E_g(T) - E_{PL}(T) \quad \text{Eq. 6-2}$$

where $E_g(T)$ is the band gap defined by the Varshni model and $E_{PL}(T)$ is the PL peak energy. The localization energy at 5 K is 34 and 24 meV for as-grown Samples C and E, respectively. The difference in localization energy indicates that the LE emission has different physical origins in the two samples. We suggest that the LE emission originates from neutral acceptor-bound excitons in as-grown Sample C, whereas it originates from potential fluctuation in as-grown Sample E as discussed in the following.

Figure 6-3 shows the PL spectra at 5 K of as-grown Samples A to E. The spectra exhibited both the LE emission peak at ~ 1000 nm and a broad deep emission band at $1200 \sim 1700$ nm. The dip in the spectra at around 1400 nm is related to water vapor absorption. For Be-doped GaAs, which can be considered closely related to Be-doped InGaAsN for small amounts of In and N, the PL emission was attributed to band-acceptor transition and spectral redshift was observed with increasing doping levels [48]. On the contrary, in this study of Be-doped InGaAsN, the LE emission peak did not show spectral redshift as the doping level increases. Thus, it further confirms that the PL peak in Be-doped InGaAsN originates from LE emission, and not from band-acceptor transition.

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Figure 6-3 Low temperature (5 K) PL spectra of as-grown Samples A-E.

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As for the deep PL band, it may originate from recombinations associated with N-related traps. Because of the high electronegativity of the N atom, electrons are easily trapped by these defects to form negatively charged centers. By virtue of Coulombic interaction, these negatively charged centers attract holes and lead to recombination of trapped electrons and holes. Ptak *et al.* reported the presence of one N-related electron trap in InGaAsN, which remains at a constant energy separation of 0.9 eV from the valence band [49]. The energy level of this electron trap is in good agreement with the energy position of the deep PL band. In that report, the energy level of the trap is not a discrete level, but a continuum of defect states in the energy gap. This explains why the deep PL band has a full width at half maximum (FWHM) as large as ~ 200 meV in our InGaAsN samples.

The hole concentration dependence of the integrated intensity ratio of the LE emission to that of the deep PL band at 5 K is shown in Figure 6-4. As the hole concentration increases, this ratio increases in linear proportion to the hole concentration at the light doping regime ($1.0 \times 10^{16} \text{ cm}^{-3} < p < 2.1 \times 10^{18} \text{ cm}^{-3}$), and thereafter saturates at the high doping regime ($2.1 \times 10^{18} \text{ cm}^{-3} < p < 1.2 \times 10^{19} \text{ cm}^{-3}$). The hole concentration at which this ratio saturates ($2.1 \times 10^{18} \text{ cm}^{-3}$) is found to be consistent with the hole degeneracy level of $3.0 \times 10^{18} \text{ cm}^{-3}$ in Be-doped GaAs [48].

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Figure 6-4 Hole concentration dependence of the integrated intensity ratio of LE emission to deep PL band for as-grown Samples A-E. The dots are experimental data and the dashed line is for eye guidance.

When the doping level is below the saturation point ($p < 2.1 \times 10^{18} \text{ cm}^{-3}$) corresponding to non-degeneracy, the LE emission originates from neutral acceptor-bound excitons, as we have suggested for as-grown Sample C. Furthermore, the deep PL band is attributed to recombinations associated with N-related traps as discussed previously. Thus, the population of the photo-generated carriers (electrons and holes) in the samples satisfies the following continuity equations:

$$dn/dt = \alpha P_0 / E_0 - f N_T n / \tau_n - N_A g_e n (p_0 + p) + d_e n_e \quad \text{Eq. 6-3}$$

$$dp/dt = \alpha P_0 / E_0 - (1-f) N_T (p_0 + p) / \tau_p - N_A g_e n (p_0 + p) + d_e n_e \quad \text{Eq. 6-4}$$

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$$dn_e/dt = -c_e n_e + N_A g_e n(p_0 + p) - d_e n_e \quad \text{Eq. 6-5}$$

where n , p , and n_e are the population of photo-generated electrons, photo-generated holes and neutral acceptor-bound excitons, respectively. The acceptor-related hole concentration is denoted as p_0 . α is the absorption coefficient of InGaAsN, P_0 the excitation laser power, E_0 the photon energy of the excitation laser, and N_A the acceptor concentration. N_T is the trap concentration and f the fraction of empty traps. τ_n and τ_p are the lifetimes of electrons and holes associated with the trap-related recombination process, respectively. g_e , c_e , and d_e are the generation rate, recombination rate, and dissociation rate of excitons, respectively.

Under steady state conditions one can obtain from Eqs. 6-3 – 6-5:

$$f = \frac{(p_0 + p)/\tau_p}{n/\tau_n + (p_0 + p)/\tau_p} \quad \text{Eq. 6-6}$$

$$n_e = \frac{g_e}{c_e + d_e} N_A n(p_0 + p) \quad \text{Eq. 6-7}$$

At 5 K, most acceptors are “frozen”, which makes p_0 negligible compared to the carriers generated by laser excitation. So, we get $p_0 + p \approx p = n$.

The integrated intensity of the LE emission and the deep PL band can be expressed as:

$$I_1 = c_e n_e \approx c_e g_e N_A n^2 / (c_e + d_e) \quad \text{Eq. 6-8}$$

$$I_2 = (1-f) N_T (p_0 + p) / \tau_p \approx N_T n / (\tau_n + \tau_p) \quad \text{Eq. 6-9}$$

Hence, the integrated intensity ratio of the two emissions is expressed as:

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$$\frac{I_1}{I_2} \approx \frac{c_e g_e}{c_e + d_e} n(\tau_n + \tau_p) \frac{N_A}{N_T} \quad \text{Eq. 6-10}$$

This ratio is linearly proportional to N_A . It is also certainly linearly proportional to the room temperature hole concentration, which is in good agreement with our experimental results.

When the doping level exceeds the saturation point ($p > 2.1 \times 10^{18} \text{ cm}^{-3}$) corresponding to degeneracy, the Be acceptors are ionized and neutral acceptor-bound excitons could not exist. Therefore, the LE emission must originate from some other mechanism, for instance potential fluctuation induced by compositional and structural inhomogeneities in the N-containing layers [50]. Matsuda *et al.* suggested that the excitons are strongly localized in a potential minimum of locally N-rich regions (spontaneous N clusters) [43]. For such a case, the LE emission is independent of the doping level, thus the intensity ratio saturates at the high doping regime.

Since the compositional and structural inhomogeneities also exist in InGaAsN QWs and GaAsN epilayers [43, 51], it is naturally expected that they should also exist in all the InGaAsN layers in this study, and not solely in as-grown Sample E. In Be-doped InGaAsN, N clusters (NN_i) prefer the neighboring sites of substitutional Be (Be_{Ga}) due to the fact that the electronegativity difference between Be and N (1.47) is larger than that between Ga and N (1.23) [52]. Larger electronegativity difference means greater polarity and bond ionicity, and this generally results in higher bond dissociation energy. Moreover, the small size of the Be atom (106 pm) makes it easier to accommodate the N clusters. Thus, the $\text{NN}_i\text{-Be}_{\text{Ga}}$ complex formation is energetically and geometrically more favorable. In the case of non-degeneracy, the neutral acceptor-bound excitons are actually bound to the N clusters at the same time, i.e., bound to the $\text{NN}_i\text{-Be}_{\text{Ga}}$ complexes. This configuration results in an accumulative localization effect and relatively larger localization energy; for instance 34 meV at 5 K for as-grown Sample C. On the other hand, in the case of degeneracy, the Be acceptors interact with each other and become delocalized states. The N clusters are the only origin of exciton localization, leading to a relatively smaller localization energy; for instance 24

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meV at 5 K for as-grown Sample E. The neutral acceptors contribute to the localization energy difference between the two samples.

After thermal annealing, the samples show similar temperature-dependent behavior as the as-grown ones, except for different localization energies of the LE emissions. The PL peak energy of annealed Samples C and E as a function of temperature is shown in Figure 6-5. At temperatures higher than 80 K, the PL emission is due to near-band-edge transition. The PL peak energy, i.e. the band gap energy can be fitted by the Varshni equation Eq. 6-1. The fitting parameters are: $E_g(0) = 1.279$ eV, $\alpha = 0.44$ meV/K, and $\beta = 272$ K for annealed Sample C, and $E_g(0) = 1.282$ eV, $\alpha = 0.66$ meV/K, and $\beta = 519$ K for annealed Sample E. At temperatures lower than 80 K, the PL emission changes to LE emission; hence the PL peak position deviates from the fitted curve. According to Eq. 6-2, the localization energy at 5 K was determined to be 18 meV and 8 meV for annealed Samples C and E, respectively.

Figure 6-5 Temperature dependence of PL peak energy of annealed Samples C and E. Solid lines are fitting with Varshni equation. Localization energy at 5 K is determined to be 18 and 8 meV for C and E, respectively.

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The localization energy for the annealed samples decreased, compared to the corresponding as-grown samples. We suggest that thermal annealing improved the compositional and structural homogeneities of the materials, thus induced a significant reduction in the localization energy. The localization energy difference between the two annealed samples is 10 meV, the same as that between the as-grown samples, which indicates that the contributions to the localization effects from the neutral acceptors remained after thermal annealing. In addition, comparing Figures 6-2 and 6-5, a blueshift of the PL peak at both low and high temperatures is observed, which is attributed to atomic rearrangement during thermal annealing [44].

6.4 Conclusions

In conclusion, the temperature-dependent PL properties of Be-doped, *p*-type InGaAsN are presented in this chapter. The PL spectra were dominated by near-band-edge emission at high temperatures and LE emission plus a broad deep band at low temperatures. The deep PL band may originate from recombinations associated with N-related traps. The hole concentration dependence of the integrated intensity ratio of the LE emission peak to the deep PL band at 5 K can be separated into two doping regimes. The intensity ratio is linearly proportional to the hole concentration at the light doping regime corresponding to non-degeneracy. In this case, the excitons are suggested to be bound to neutral acceptors accompanied by N clusters, and have a relatively larger localization energy. The intensity ratio saturates at the high doping regime corresponding to degeneracy, in which case the excitons are suggested to be bound to N clusters solely and have a relatively smaller localization energy. Thermal annealing improves the compositional and structural homogeneities and reduces the exciton localization energy.

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Chapter 7

Deep-level Defects and Minority-carrier Electron Diffusion Length in Be-doped InGaAsN

7.1 Introduction

Dilute nitride materials such as InGaAsN, GaAsN, and more recently GaAsNSb have been demonstrated to have potential usage in long wavelength GaAs-based lasers, reduced turn-on voltage heterojunction bipolar transistors (HBTs), and high-efficiency multijunction solar cells. However, to date these devices have generally exhibited less than optimum performance due to relatively poor material quality, with a high concentration of deep-level defects [53, 54], and short minority-carrier diffusion length in InGaAsN [13, 55]. This may be due in part to the lower growth temperature generally used for dilute nitrides, compared to that for GaAs. Postgrowth thermal annealing has been shown to improve the properties of InGaAsN material and devices [13]. However, there are presently a few reports on the impact of thermal annealing on the performance of InGaAsN-based HBTs [56].

In this chapter, we have presented the deep-level defects and minority-carrier electron diffusion length in Be-doped, *p*-type InGaAsN and the properties of InGaAsN/GaAs *p-n* junction diode. The effects of postgrowth thermal annealing on these properties were also presented. The results show that the material quality and the diode performance can be improved significantly by postgrowth thermal annealing. This opens up the possibility of InGaAsN-based HBTs with enhanced performance.

7.2 Experimental Procedure

The $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$ sample used in this study was grown on (001)-oriented semi-insulated GaAs substrate using radio frequency (RF) plasma-assisted solid source molecular beam epitaxy (MBE). Figure 7-1 shows the sample structure. The

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epitaxial growth sequence was initiated by growing 600-nm-thick n^+ -GaAs ($n = 4 \times 10^{18} \text{ cm}^{-3}$), and followed by deposition of a 1- μm -thick p -InGaAsN ($p = 1 \times 10^{17} \text{ cm}^{-3}$) layer. A 100-nm-thick p^+ -InGaAsN ($p = 1 \times 10^{19} \text{ cm}^{-3}$) layer was further deposited for contact purpose. Si was used as the n -type dopant for the n^+ epitaxial layer, and Be was used as the p -type dopant for both the p and p^+ epitaxial layers. The InGaAsN layers were grown at 460 °C and x-ray rocking curve measurements indicated a lattice mismatch of 0.02% with the GaAs substrate. The band gap energy of the InGaAsN layer was determined to be 1.2 eV at room temperature by photoluminescence (PL) measurements. After growth, the sample was divided into two pieces for further analysis. One of the pieces was annealed in a rapid thermal process (RTP) furnace at 750 °C for 1 min under N_2 ambient, with a 200-nm-thick SiO_2 layer on top to prevent the loss of arsenic at elevated temperatures. Both samples were then deposited with Ti/Au on the p^+ -InGaAsN layer and Ni/Ge/Au/Ni/Au on the n^+ -GaAs layer to form ohmic contacts using standard fabrication procedures. The cross-sectional area of the p - n junction diodes defined by mesa etching is 0.79 mm^2 .

Figure 7-1 Structure of InGaAsN/GaAs p - n junction diode.

Trap activation energies, carrier capture cross sections, and trap densities were obtained from deep level transient spectroscopy (DLTS) measurements and the

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spectra were analyzed using standard techniques. For a p - n junction, the DLTS spectra mainly originate from deep-level defects in the lower-doped layer. Hence, information from the deep-level defects in the p -InGaAsN layer can be obtained from the DLTS measurements in this study.

7.3 Results and Discussion

7.3.1 Capacitance–voltage measurements

Capacitance–voltage measurements (C – V) were performed on the as-grown and annealed samples to determine the net acceptor concentration in the p -type InGaAsN layer, and the results are shown in Figure 7-2. As shown in the inset, the plot of $1/C^2$ vs. V is a straight line for both samples, indicating that the doping is uniform throughout the measured region of the p -type InGaAsN layer. The net acceptor concentration was determined to be $1.4 \times 10^{17} \text{ cm}^{-3}$ and $2.1 \times 10^{17} \text{ cm}^{-3}$ for the as-grown and annealed InGaAsN layers, respectively. There is an increase in the net acceptor concentration after thermal annealing. Kaplar *et al.* attributed it to depassivation of background carbon acceptors during thermal annealing, based on the carbon concentration of $\sim 3 \times 10^{17} \text{ cm}^{-3}$ in their InGaAsN grown by metal-organic chemical-vapor deposition (MOCVD) [57]. However, this is not the case in our study due to the ultrahigh vacuum environment and absence of carbon-containing sources in our MBE system.

Recently, a three-center complex, $\text{As}_{\text{Ga}}\text{--V}_{\text{As}}\text{--Ga}_{\text{As}}$, has been proposed for the microscopic origin of the EL2-type defect in GaAs [58]. Since the dominant $HT4$ trap in the as-grown InGaAsN is suggested to be an EL2-type defect, as discussed in Sec. 7.3.2, it is possible that the three-center complex could also be the microscopic origin of the $HT4$ trap. Before thermal annealing, the Coulombic interaction between Ga_{As}^- and As_{Ga}^+ pins the As atom at its Ga site. During thermal annealing, the Coulombic interaction is nullified leading to the breakage of the bond between As_{Ga} and Ga_{As} . The As atoms move towards the neighboring V_{As} , thus forming acceptorlike V_{Ga} , which is responsible for the increase in the net acceptor concentration.

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Figure 7-2 Plot of C - V characteristics of the as-grown and annealed samples. The inset shows $1/C^2$ vs. V plot from which the net acceptor concentration was determined.

7.3.2 Majority-carrier (hole) DLTS measurements

The results of DLTS measurements on both samples are shown in Figure 7-3. For clarity, the spectrum of the as-grown sample is shifted 0.1 pF upwards. For correct capacitance measurement, the reverse-bias leakage current must not greatly exceed 10 μA for a junction area of $\sim 1 \text{ mm}^2$ [59]. The as-grown sample has much higher reverse-bias leakage current than the annealed sample. Thus, different reverse-bias voltages (-0.6 and -2.0 V) were chosen for the two samples.

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Figure 7-3 Majority-carrier DLTS spectra of the as-grown and annealed samples. The spectra were obtained using period width of 20 ms and filling pulse voltage of -0.2 V with duration of 10 ms. Reverse-bias voltage was -0.6 V and -2.0 V for as-grown and annealed samples, respectively. The solid lines are experimental results, and the dotted lines are the fitting result using Gaussian functions. The inset shows the Arrhenius plot from which activation energies and hole capture cross sections for HT1, HT2, HT3, and HT4 were determined.

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In the case of $V_p < 0$ V, only majority carriers (holes) are significant in the p -type material, thus peaks from majority-carrier (hole) traps are observed in Figure 7-3. Two hole traps, labeled as *HT1* and *HT4*, are clearly discerned from the spectrum of the as-grown sample, and the Arrhenius plots of them are shown in the inset. The activation energies, ΔE_a , and the hole capture cross sections, σ_∞ , obtained from the Arrhenius analysis, as well as the traps concentration, N_T , are listed in Table 7-1. For calculations of the hole capture cross sections, the hole effective mass is assumed to be the same as that of GaAs, $m_h^* = 0.5m_0$, since the valence band structure of InGaAsN is thought to be similar to that of GaAs [60].

Trap	Apparent activation energy (eV)	Cross-section activation energy (eV)	Energy level (eV)	Concentration (cm ⁻³)	$T \rightarrow \infty$ capture cross section (cm ²)
<i>HT1</i>	0.18	0.06	$E_V + 0.12$	2×10^{14}	2×10^{-17}
<i>HT2</i>	0.39	0.21	$E_V + 0.18$	1×10^{14}	2×10^{-14}
<i>HT3</i>	0.41	0.17	$E_V + 0.24$	5×10^{14}	1×10^{-16}
<i>HT4</i>	0.59	0.33	$E_V + 0.26$	2×10^{15}	3×10^{-14}
<i>ET1</i>	0.09	...	...	5×10^{13}	2×10^{-18}
<i>ET2</i>	0.19	...	...	5×10^{13}	1×10^{-16}
<i>ET3</i>	0.41	...	...	6×10^{13}	6×10^{-13}

Table 7-1 Trap parameters determined from analysis of DLTS data.

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The *HT1* and *HT4* traps have activation energies of 0.18 and 0.59 eV (Table 7-1), respectively. Abulfotuh *et al.* reported a nitrogen-related shallow hole trap with an activation energy of 0.22 eV [61]. The *HT1* trap has an activation energy close to the reported value. Thus, similar nitrogen-related defects are postulated to be present in our study. Both Ptak *et al.* and Tanaka *et al.* have reported a similar trap as *HT4* in their studies of GaAs and InGaAsN [49, 62]. Their results suggest that the *HT4* trap is the so-called EL2-type defect widely observed in GaAs, and is not related to nitrogen incorporation. This is possible in our study because the *HT4* trap and the EL2-type defect have similar activation energy and similar thermal annihilation behavior [63], and the nonequilibrium growth conditions for InGaAsN make it possible to form arsenic antisites, arsenic vacancies, and arsenic atom clusters from which the EL2-type defects could originate [64]. In addition, we note that both peaks resulting from the *HT1* and *HT4* traps are broad. The ratio of the full width at half maximum (FWHM) to the peak temperature (FWHM/T_p) was found to be 0.22 for both traps. In contrast, this ratio is expected to be ~ 0.1 for a deep level due to an ideal point defect [65]. This indicates that the two traps are due to a distribution of deep levels, as opposed to well-defined discrete energy levels. This distribution of deep levels may result from a distribution of isolated point defects and/or point defect clusters in the InGaAsN layer.

After thermal annealing, a significant reduction in the deep-level trap concentration was observed. Because of the different reverse bias voltages used in the measurement of the as-grown and annealed samples, the peak heights in Figure 7-3 cannot be compared directly. Instead, one should compare the trap concentration as listed in Table 7-1. Two hole traps, labeled as *HT2* and *HT3*, were revealed when the spectrum of the annealed sample was fitted using Gaussian functions. The Arrhenius plots of the two traps are shown in the inset of Figure 7-3. An analysis similar to that described previously was performed and the results are listed in Table 7-1.

The peak temperature for the *HT3* and *HT4* traps is found to be close to each other, and one may expect them to originate from the same defect. However, their apparent activation energies obtained from the Arrhenius analysis are different

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(0.41 eV for *HT3* and 0.59 eV for *HT4*). The apparent activation energy is the sum of the true activation energy and the cross-section activation energy [66]. The cross-section activation energy, ΔE_σ , is correlated to the carrier capture cross section by:

$$\sigma(T) = \sigma_\infty \exp(-\Delta E_\sigma / k_B T) \quad \text{Eq. 7-1}$$

where k_B is the Boltzmann constant. Thus, in order to investigate the true activation energies of the hole traps, the hole capture cross sections were measured using variable pulse duration. The DLTS signal is the amplitude of the capacitance transient. For an ideal point defect, the capacitance transient has a characteristic exponential shape, and its amplitude, ΔC_0 , is related to the filling pulse duration t_p by:

$$\Delta C_0 = \Delta C_0^\infty [1 - \exp(-c_p t_p)] \quad \text{Eq. 7-2}$$

where ΔC_0^∞ is the saturated amplitude of the capacitance transient, and c_p is the hole capture rate. The plot of $\ln(1 - \Delta C_0 / \Delta C_0^\infty)$ vs. t_p is a straight line and the slope corresponds to the hole capture rate. The hole capture cross section is correlated to the hole capture rate by:

$$c_p = \sigma_p \langle v_{th} \rangle p \quad \text{Eq. 7-3}$$

where $\langle v_{th} \rangle$ is the hole thermal velocity and p is the hole concentration.

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Figure 7-4 DLTS signal as function of pulse duration for *HT4*. The inset shows plot of $\ln(1 - \Delta C_0 / \Delta C_0^\infty)$ vs. t_p and the capture rate is determined from the initial slope.

Figure 7-4 shows the measurement result of the *HT4* trap as an example. The DLTS signal increases monotonically with the filling pulse duration, and then saturates. As shown in the inset, the plot of $\ln(1 - \Delta C_0 / \Delta C_0^\infty)$ vs. t_p is not a straight line. This suggests that the deep-level defect does not behave as an ideal point defect with a distinct energy level. According to Balcioglu *et al.*, [67] one may still obtain the hole capture rate ($1.4 \times 10^5 \text{ s}^{-1}$) from the initial slope of the plot using Eq. 7-2. The hole capture cross section of the *HT4* trap obtained in this way is $6.3 \times 10^{-20} \text{ cm}^2$ using Eq. 7-3. Then, using Eq. 7-1, the cross-section activation energy of the *HT4* trap is determined to be 0.33 eV, indicating that its energy level is 0.26 eV above the valence band maximum (VBM). The cross-section activation energies

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and energy levels of the other hole traps are listed in Table 7-1. The energy levels of the *HT3* and *HT4* traps are close to each other, suggesting that they could be defects of similar origin, i.e., the EL2-type. After thermal annealing, the configuration of this defect was slightly changed. This leads to a decrease in the cross-section activation energy, while the energy level of the defect remains unchanged.

In addition to the deep-level traps described above, another shallow hole trap, *HT2*, is also observed in the annealed sample. One interesting observation is that while the overall trap concentration decreases after annealing, the *HT2* trap concentration increases. Tanaka *et al.* have also reported a defect created by annealing with an activation energy of 0.33 eV [62], which is close to that of the *HT2* trap (0.39 eV). They suggested that arsenic vacancy-type defects were created during annealing. Further studies are required to understand the microscopic origin of such annealing-induced defects.

7.3.3 Minority-carrier (electron) DLTS measurements

Since the performance of minority-carrier devices such as HBTs is likely to be sensitive to the presence of minority-carrier traps, DLTS measurements were performed to investigate the minority-carrier electron traps in the as-grown and annealed InGaAsN layers. In these measurements, the forward-biased filling pulse injects minority-carrier electrons into the *p*-type InGaAsN layer. Thus, both electron and hole traps can be observed.

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Figure 7-5 DLTS spectra of the as-grown and annealed samples under minority-carrier injection. The spectra were obtained using period width of 20 ms and filling pulse voltage of 0.5 V with duration of 10 ms. Reverse bias voltage was -0.6 V and -2.0 V for as-grown and annealed samples, respectively. The spectra intensity on the left of the dotted line is multiplied by 10. The inset shows the Arrhenius plot from which activation energies and electron capture cross sections for *ET1*, *ET2*, and *ET3* were determined.

Figure 7-5 shows the DLTS spectra of both samples under conditions of minority-carrier injection. Besides the positive peaks, which correspond to majority-carrier hole traps as described in Sec. 7.3.2, some negative peaks, which correspond to minority-carrier electron traps, are clearly seen. The Arrhenius plots of these electron traps are shown in the inset. Two electron traps, labeled as *ET1* and *ET3*, are observed in the as-grown sample, with activation energies of 0.09 and 0.41 eV,

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respectively. It has been reported that a nitrogen-related electron trap remains at a constant energy separation of 0.8 ~ 0.9 eV from VBM in InGaAsN and GaAsN [49, 68]. In our study, the band gap of the InGaAsN layer is ~ 1.2 eV. The energy-level separation between the *ET3* trap and VBM is ~ 0.8 eV, which is in agreement with the published report. This suggests that the *ET3* trap could be attributed to nitrogen-related defects in the material. Both the *ET1* and *ET3* traps were removed after thermal annealing. Meanwhile, a new electron trap, labeled as *ET2*, was created in the annealed sample, with an activation energy of 0.19 eV. Kaplar *et al.* have reported a continuous electron trap distribution between the conduction-band minimum (CBM) and 0.2 eV below CBM in Sn-doped InGaAsN [57]. Considering the shallow activation energies of the *ET1* and *ET2* traps, one may suggest that they have similar origins to those reported previously.

7.3.4 Minority-carrier (electron) diffusion length measurements

To investigate the effect of thermal annealing on minority-carrier electron diffusion length, measurements on minority-carrier injection depth were carried out using variable reverse bias. In these measurements, the fixed forward-biased filling pulse injects minority-carrier electrons into the *p*-type InGaAsN layer over a distance, X_i . The reverse-bias voltage is varied, and causes the quiescent depletion width, X_d , to vary accordingly. When $X_d - \lambda$ is smaller than X_i , the volume in which the minority-carrier traps are under observation is determined by $X_d - \lambda$, where λ is the transition distance. When $X_d - \lambda$ is larger than X_i , the volume in which the traps are under observation is determined by X_i because only the traps in this volume can be filled during the forward-biased filling pulse. The ratio of the capacitance transient amplitude, ΔC_0 , of a minority-carrier trap to the quiescent depletion capacitance, C_d , can be written as [29]:

$$\frac{\Delta C_0}{C_d} \propto \left(1 - \frac{\lambda}{X_d}\right)^2, \text{ in the case of } X_d - \lambda \leq X_i \quad \text{Eq. 7-4}$$

and

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$$\frac{\Delta C_0}{C_d} \propto \left(\frac{X_i}{X_d} \right)^2, \text{ in the case of } X_d - \lambda \geq X_i,$$

Eq. 7-5

Generally $\lambda \ll X_d$, hence $X_d - \lambda \approx X_d$. As the magnitude of the reverse bias increases, X_d extends from a depth shallower than X_i to deeper than X_i . When $X_d = X_i$, the value of $\Delta C_0/C_d$ reaches maximum. Thus, the value of X_i can be determined from the peak position of the plot of $\Delta C_0/C_d$ vs. X_d .

Figure 7-6 Plot of $\Delta C_0/C_d$ vs. X_d for ET3 in the as-grown sample and for ET2 in the annealed sample. The measurements were carried out using period width of 20 ms and filling pulse voltage of 0.5 V with duration of 10 ms. The injection depth is determined to be 0.14 and 0.19 μm for the as-grown and annealed sample, respectively.

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Measurements on the *ET3* trap for the as-grown sample and *ET2* trap for the annealed sample were carried out, and the results are shown in Figure 7-6. The peak exists at $X_d \approx 0.14 \mu\text{m}$ for the as-grown sample and at $X_d \approx 0.19 \mu\text{m}$ for the annealed sample. Thus, the injection depths under these measurement conditions were ~ 0.14 and $\sim 0.19 \mu\text{m}$, respectively. Separate experiments were carried out to optimize the measurement parameters so that the maximum possible injection depth was achieved. It is reasonable to assume that the minority-carrier electron diffusion length, L_n , is the most important factor that determines the value of X_i , i.e., $L_n \approx X_i$. Therefore, we have $L_n \approx 0.14 \mu\text{m}$ for the as-grown sample, which is in good agreement with the value of $0.1 \mu\text{m}$ reported by Welty *et al.* [69]. After thermal annealing, L_n was increased by $\sim 30\%$ to $\sim 0.19 \mu\text{m}$. This may be explained as a result of reduction in the deep-level defect concentration. However, the minority-carrier electron diffusion length in InGaAsN is smaller than that in GaAs, even after thermal annealing. Duggan *et al.* reported a value of $0.76 \mu\text{m}$ in Be-doped GaAs with a hole concentration of $4.5 \times 10^{18} \text{ cm}^{-3}$ [70]. We suggest that the shorter minority-carrier electron diffusion length in InGaAsN compared to GaAs could be due to a high concentration of recombination centers in InGaAsN induced by the nonequilibrium growth conditions, and possibly by bombardment effect of energetic nitrogen ions [71].

7.3.5 Current–voltage measurements

To investigate the effect of thermal annealing on the reverse-bias leakage current of the diode, current–voltage (I – V) measurements were performed on the as-grown and annealed samples. The results in Figure 7-7 show that the leakage current of the annealed sample is $2 \sim 3$ orders lower than that of the as-grown sample. Since the overall deep-level trap concentration decreases after thermal annealing, especially the hole trap *HT4*, we suggest that the *HT4* trap is an efficient generation-recombination center. Such a center can result in higher leakage current in reverse-biased diodes, and higher base current in forward-biased transistors with lower current gain. The thermal annihilation of generation-recombination centers suggests that thermal annealing could be implemented as a process step to improve the InGaAsN material quality if used as the base layer in HBTs.

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Figure 7-7 Plot of I – V characteristics of the as-grown and annealed samples. The reverse-bias leakage current of the annealed sample is much lower than that of the as-grown sample.

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7.4 Conclusions

In conclusion, this chapter has reported the deep-level defects and minority-carrier electron diffusion length in Be-doped, *p*-type InGaAsN. Two hole traps (*HT1* and *HT4*) and two electron traps (*ET1* and *ET3*) were observed in the as-grown sample. Our experiments have shown that the *HT1* and *ET3* traps could be nitrogen-related defects, and the *HT4* trap could have a similar origin as the so-called EL2-type defect. Following postgrowth thermal annealing, the overall deep-level defect concentration decreases, with two hole traps (*HT2* and *HT3*) and one electron trap (*ET2*) observed. The *HT2* trap was created during annealing, and the *HT3* trap was found to have a similar origin as the *HT4* trap, i.e., the EL2-type. The minority-carrier electron diffusion length increases by $\sim 30\%$ from $\sim 0.14\ \mu\text{m}$ in the as-grown layer to $\sim 0.19\ \mu\text{m}$ in the annealed layer and the leakage current of the *p-n* junction diode decreases by 2 $\sim$ 3 orders after thermal annealing. The increase of the net acceptor concentration after thermal annealing can be explained by an existing three-center-complex model. Our results indicate that thermal annealing may be implemented as a process to improve the InGaAsN material quality if used as the base layer in HBTs.

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Chapter 8

Demonstration of

InGaP/InGaAsN/GaAs *n-p-n* DHBT

8.1 Introduction

The growth and characterization of InGaAsN materials have been reported in previous chapters. In this chapter, we will demonstrate a heterojunction bipolar transistor (HBT) using InGaAsN as the base. In particular, the design, growth, fabrication, and characterization of InGaP/In_{0.03}Ga_{0.97}As_{0.99}N_{0.01}/GaAs *n-p-n* double HBT (DHBT) will be reported. The InGaAsN materials have improved quality after thermal annealing, showing an increase of luminescence efficiency, a decrease of deep-level defects, and an increase of minority-carrier diffusion length [45, 72]. Therefore, the effects of *ex-situ* thermal annealing on the performance of InGaAsN DHBT will also be reported.

8.2 Device Design

When N is incorporated into GaAs, both the conduction band, E_C , and the valence band, E_V , are lowered. When In is incorporated into GaAs, the E_C is lowered and the E_V is raised (refer to Figure 1-2). By incorporating N and In simultaneously, the E_C of the resulting InGaAsN would be drastically lowered because of the aggregate lowering effect from the incorporation of N and In. The energy level of E_V would depend on the amount of N incorporation. For In_{0.03}Ga_{0.97}As_{0.99}N_{0.01}, the effects on E_V from incorporation of N and In are compensated, and the E_V is relatively unchanged compared to the E_V of GaAs. According to Monier *et al.* [73], a conduction band offset ratio of $Q_C = 0.9$ is used to describe the distribution of the band gap difference between In_{0.03}Ga_{0.97}As_{0.99}N_{0.01} and GaAs. Therefore, the InGaP/InGaAsN/GaAs HBT structure has larger conduction band offset (ΔE_C) at both the base-emitter (BE) and the base-collector (BC) junctions. The effect of larger ΔE_C at the BC junction is detrimental for transporting electrons out of the

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base into the collector. It can cause electrons to stay in the base longer and result in increased level of the base recombination current. Without proper design, the larger ΔE_C at the BE junction also has adverse effects, by means of a large energy barrier for electrons before they can be injected into the base. It results in higher turn-on voltage and reduces the benefit of the smaller band gap of InGaAsN. Therefore, proper design of the BE and BC junctions is necessary in order to achieve a base-transport limited device.

Layer	Material	Thickness (nm)	Doping (cm ⁻³)
Cap	GaAs	200	$n = 7 \times 10^{18}$
Emitter	In _{0.48} Ga _{0.52} P	50	$n = 7 \times 10^{17}$
Spacer	GaAs	5	undoped
Base	In _{0.03} Ga _{0.97} As _{0.99} N _{0.01}	70	$p = 1 \times 10^{19}$
In _x Ga _{1-x} As grading ($x = 0.03 \rightarrow 0.20$)	In _x Ga _{1-x} As	5	$n = 5 \times 10^{16}$
	δ -doping	0	$n = 5 \times 10^{12} \text{ cm}^{-2}$
	In _x Ga _{1-x} As	25	$n = 5 \times 10^{16}$
Collector	GaAs	500	$n = 5 \times 10^{16}$
Subcollector	GaAs	500	$n = 7 \times 10^{18}$
SI-GaAs Substrate			

Table 8-1 Epilayer structure of the InGaP/InGaAsN/GaAs *n-p-n* DHBT.

As shown in Table 8-1, the basic structure of the InGaP/InGaAsN/GaAs *n-p-n* DHBT investigated in this work consists of a 500-nm-thick n^+ -GaAs subcollector layer, a 500-nm-thick n^- -GaAs collector layer, a 70-nm-thick p^+ -InGaAsN base layer, a 50-nm-thick n -InGaP emitter layer, and a 200-nm-thick n^+ -GaAs emitter contact layer. The base layer is made of p^+ -In_{0.03}Ga_{0.97}As_{0.99}N_{0.01} that is lattice-

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matched to GaAs, and its band gap is approximately 1.2 eV. A 5-nm-thick undoped GaAs spacer layer is inserted between the emitter and the base to allow Be out-diffusion which may occur during rapid thermal process (RTP). A strained InGaAs grading layer is inserted between the base and the collector to reduce the conduction band barrier at the BC junction. The In composition is gradually increased from 0.03 to 0.20 over a thickness of 30 nm so that the E_C is lowered from around the E_C of GaAs to around the E_C of $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$. The In composition of InGaAs needs to be 0.23 so that the ΔE_C between it and $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$ would become zero; however, to avoid strain relaxation, the In composition in this structure is limited to 0.20. The InGaAs grading layer still leaves a ΔE_C of about 0.03 eV at the BC junction, thus a δ -doping layer is inserted in the grading layer near the BC junction to further improve the transport characteristics of electrons across this interface. The resulting band alignment of the HBT structure is shown in Figure 8-1.

Figure 8-1 Band alignment of the InGaP/InGaAsN/GaAs DHBT.

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8.3 Experimental Procedure

The InGaP/InGaAsN/GaAs *n-p-n* DHBT epilayers were grown on (001)-oriented semi-insulated GaAs substrate using radio frequency (RF) plasma-assisted solid source molecular beam epitaxy (MBE). Si and Be were used as the *n*- and *p*-type dopants, respectively. The Ga cell temperature was fixed throughout the growth process, so that the growth rate for GaAs was fixed at 0.7 $\mu\text{m/hr}$. The In cell temperature was varied in order to achieve the corresponding In compositions in the InGaAs grading layer, the InGaAsN base layer, and the InGaP emitter layer. The growth of the *n*-type GaAs layers was carried out at 590 °C. The InGaAs grading layer and the InGaP emitter layer were grown at 490 °C. The InGaAsN base layer and the GaAs spacer layer were grown at 460 °C. The material compositions were calibrated using photoluminescence (PL) and x-ray diffraction (XRD). The doping levels were confirmed with Hall measurements. The surface morphology of the sample was uniform and smooth.

After the growth, the sample was divided into two pieces. One of the pieces was annealed in RTP furnace at 750 °C for 1 min under N₂ ambient, with a 300-nm-thick SiO₂ layer on top to prevent the loss of arsenic at elevated temperatures. Both samples were then fabricated into HBTs using a standard triple mesa process. Wet chemical etching was used to expose the base and the subcollector surfaces. The H₃PO₄ : H₂O₂ : H₂O (3 : 1 : 40) solution was used to etch GaAs and InGaAsN, and a diluted HCl or the HCl : HIO₃ (0.2 mol/l) : H₂O (1 : 1 : 40) solution was used to etch InGaP. Ni/Ge/Au/Ni/Au (5/25/100/20/200 nm) annealed at 410 °C for 10 sec was used for ohmic contacts on the *n*-type GaAs emitter cap and subcollector. Ti/Au (50/200 nm) formed nonalloyed ohmic contact on the *p*-type InGaAsN base. The size of the emitter of the final devices is 35 × 45 μm^2 . A conventional InGaP/GaAs single HBT (SHBT) with the base doping of $2 \times 10^{19} \text{ cm}^{-3}$ and a base width of 40 nm was processed for comparison purposes. The fabricated devices were tested using a Hewlett Packard 4156B semiconductor parameter analyzer.

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8.4 Results and Discussion

Figure 8-2 I_C – V_{CE} characteristics of the InGaP/InGaAsN/GaAs DHBT fabricated from the annealed sample.

The device fabricated from the as-grown sample was observed to behave as two diodes connected back-to-back, rather than a transistor. This shows that the minority-carrier electron diffusion length in the base is so short that almost all the electrons are recombined in the base and cannot be collected by the collector. After thermal annealing, the InGaAsN material quality was improved and the device fabricated from the annealed sample showed transistor characteristics.

Figure 8-2 shows the common-emitter I_C – V_{CE} characteristics of the device fabricated from the annealed sample. The offset voltage, V_{OFFSET} , is ~ 0.2 V and

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the knee voltage, V_{KNEE} , is less than 1 V. The V_{OFFSET} and V_{KNEE} of the InGaAsN DHBT are comparable with those of conventional InGaP/GaAs SHBTs ($V_{OFFSET}=0.15 \sim 0.2$ V, $V_{KNEE}=0.5 \sim 0.6$ V). The low value of V_{KNEE} suggests that the conduction band barrier at the BC junction is eliminated by inserting the InGaAs grading layer and the δ -doping layer. Hence, the current blocking effect does not occur. For V_{CE} lower than 6 V, the device shows a low positive output conductance. This positive output conductance is due to base width modulation. For V_{CE} larger than 6 V, the BC junction starts to breakdown.

Figure 8-3 shows the collector-emitter breakdown of the InGaAsN DHBT. A high value of the breakdown voltage, $BV_{CEO} = 16.3$ V, is achieved at $I_C = 10$ mA. The leakage current is 65 nA at $V_{CE} = 10$ V.

Figure 8-3 Collector-emitter breakdown of the InGaP/InGaAsN/GaAs DHBT fabricated from the annealed sample.

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Figure 8-4 Common-emitter Gummel plot of the InGaP/InGaAsN/GaAs DHBT fabricated from the annealed sample under $V_{BC} = 0$ V.

Figure 8-4 shows the common-emitter Gummel plot of the InGaP/InGaAsN/GaAs DHBT fabricated from the annealed sample. The base and collector ideality factors are $n_B = 1.1$ and $n_C = 1.3$, respectively. The base bulk recombination current dominates the base current and the base ideality factor is close to one. The collector current is too small and the generation-recombination current at the base-collector space charge layer cannot be neglected. Hence, the collector ideality factor is relatively larger. At high bias levels, large series resistance limits the base current and collector current. We attribute it to the high base sheet resistance, $\rho_B \sim 1.1$ k Ω /sq. As a comparison, the ρ_B of conventional InGaP/GaAs SHBTs is 300 ~ 400 Ω /sq.

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Figure 8-5 Incremental current gain vs. collector current for the DHBT fabricated from the annealed sample under $V_{CE} = 6$ V.

Figure 8-5 shows the incremental current gain vs. collector current for the DHBT fabricated from the annealed sample. The current gain is $\beta \sim 0.5$ at $I_C \sim 1$ mA. With I_C increasing to 10 mA, the current gain increases to ~ 1 , which can be ascribed to base width modulation. The low current gain indicates a high level of recombination in the base. As a result, the minority-carrier electron diffusion length in the base is very short. The expression for current gain is given by:

$$\beta = 2 \left(\frac{L_n}{w} \right)^2 \quad \text{Eq. 8-1}$$

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where w is the width of the base and L_n is the minority-carrier electron diffusion length in the base. Using the value of current gain $\beta \sim 0.5$, the minority-carrier electron diffusion length is estimated to be $L_n = 0.04 \mu\text{m}$. This value is around 1/5 of InGaAsN doped at $2 \times 10^{17} \text{ cm}^{-3}$. In the latter case it was $L_n = 0.19 \mu\text{m}$ [74]. The discrepancy arises from the high doping level of the base. The value of L_n for InGaAsN is significantly lower than that for GaAs with comparable doping. For instance, $L_n = 2.4 \mu\text{m}$ was reported for p^+ -GaAs doped to $\sim 10^{19} \text{ cm}^{-3}$ with Be dopant [75]. The low value of L_n for InGaAsN is presumably attributed to the reduced electron mobility and enhanced recombination. It is believed that there are alloy fluctuations in the InGaAsN material that cause localized potentials. A low-energy tail to the density of states of the conduction band is expected to form, and the states at the bottom of the conduction band tail are localized. In materials with band tails, the effective mobility is reduced from that of a perfect solid. In addition, a high concentration of deep-level defects in InGaAsN results in enhanced recombinations and a reduced minority-carrier lifetime [74]. As a consequence, the L_n for InGaAsN is significantly reduced.

The main advantage of employing the InGaAsN material is to narrow the band gap of the base for a lower turn-on voltage. To investigate this effect, the I - V characteristics of the BE junction are compared between the InGaP/InGaAsN/GaAs DHBT fabricated from the annealed sample and the InGaP/GaAs SHBT, as shown in Figure 8-6. A reduction in turn-on voltage, $\Delta V_{be,on} \sim 130 \text{ mV}$ is achieved. However, the turn-on voltage reduction is expected to be 0.2 V because the band gap of the $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$ base is $\sim 1.2 \text{ eV}$. The discrepancy is due possibly to two factors. Firstly, the GaAs spacer layer is not sufficient to eliminate thoroughly the conduction band barrier at the BE junction for the InGaAsN DHBT. The remaining barrier requires a higher voltage to be applied to inject electrons from the emitter to the base. Inserting a δ -doping layer in the emitter near the BE junction would further reduce the barrier. Whereas for the InGaP/GaAs SHBT, there is an undoped-GaAs setback layer inserted between the InGaP emitter and the GaAs base so that the barrier at the BE junction is eliminated. Secondly, the band gap of InGaAsN is increased after the RTA

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process, characterized by the blueshift of the PL peak position (refer to Figures 6-2 and 6-5).

Figure 8-6 I - V characteristics of BE junction under condition of open collector for the DHBT fabricated from the annealed sample (solid line) and the InGaP/GaAs SHBT (dotted line) used in this work.

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8.5 Conclusions

In conclusion, an operational InGaP/In_{0.03}Ga_{0.97}As_{0.99}N_{0.01}/GaAs *n-p-n* DHBT has been demonstrated in this chapter. DC measurements of the device were carried out. The use of InGaAs grading layer and δ -doping layer is believed to eliminate the conduction band barrier at the BC junction and result in a very low knee voltage (as low as that of SHBT). The narrower band gap of In_{0.03}Ga_{0.97}As_{0.99}N_{0.01} has led to a 130 mV reduction in turn-on voltage compared to the InGaP/GaAs SHBT, demonstrating the potential for application in low-power electronics. However, the turn-on voltage reduction is smaller than expected, due possibly to the remaining barrier at the BE junction and the increased band gap of In_{0.03}Ga_{0.97}As_{0.99}N_{0.01} after RTA. Furthermore, the device has a current gain of $\beta \sim 0.5$. The small current gain is due to the short minority-carrier electron diffusion length that is limited by the InGaAsN material quality. Further experimentation is needed to improve the device performance.

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Chapter 9

Conclusion and Recommendations for Future Research

9.1 Conclusion

This thesis reports the study of InGaAsN material and its application in heterojunction bipolar transistors (HBTs) with reduced turn-on voltage. The results are concluded in this chapter. The highlights include the growth and characterization of InGaAsN materials, as well as the design, growth, fabrication and characterization of InGaP/In_{0.03}Ga_{0.97}As_{0.99}N_{0.01}/GaAs *n-p-n* DHBT. The conclusions are summarized as follows:

- 1) The InGaAsN material and HBT device have been grown successfully using radio frequency (RF) plasma-assisted solid source molecular beam epitaxy (MBE). The In composition can be controlled by tuning the Ga and In cell temperature and the N composition can be controlled by tuning the RF power, so that In_{0.03}Ga_{0.97}As_{0.99}N_{0.01} lattice-matched to GaAs has been achieved with the band gap of ~ 1.2 eV.
- 2) Beryllium (Be) has been shown to be successful in achieving *p*-type InGaAsN. The hole concentration of $\sim 10^{19}$ cm⁻³ and the corresponding hole mobility of ~ 70 cm²/V·s has been achieved. These results are comparable to Be-doped GaAs, and make it possible to fabricate InGaAsN-based *n-p-n* HBT with low base resistance.
- 3) Compared with undoped InGaAsN, Be-doped InGaAsN has larger tensile strain due to increased N composition. The increase of N composition is caused by the incorporation of Be and a possible mechanism is: the high Be-N bond strength results in a high kinetic barrier to decomposition, and inhibits the loss of N from the growth surface during epitaxy, therefore increases the N composition in the material.

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- 4) Photoluminescence (PL) of Be-doped InGaAsN has been investigated between 5 and 290 K. The radiative recombination mechanisms are suggested. Near-band-edge emission dominates at temperatures higher than 100 K, whereas localized excitonic (LE) emission and a broad deep band dominate at temperatures lower than 100 K. The deep PL band is possibly associated with N-related traps. Such traps can trap electrons and form negatively charged centers, which further attract holes by virtue of Coulombic interaction and lead to recombination of trapped electrons and holes. The origin of localized excitons depends on the doping level. At the light doping regime corresponding to non-degeneracy ($p < 2.1 \times 10^{18} \text{ cm}^{-3}$), the excitons are bound to neutral acceptors accompanied by N clusters, i.e., bound to the $\text{NN}_i\text{-Be}_{\text{Ga}}$ complexes, and have a relatively larger localization energy. At the high doping regime corresponding to degeneracy ($p > 2.1 \times 10^{18} \text{ cm}^{-3}$), the excitons are bound to N clusters solely, i.e., NN_i , and have a relatively smaller localization energy. Accordingly, the integrated intensity ratio of the LE emission peak to the deep PL band at 5 K shows different behaviors at the two doping regimes: linearly proportional to the hole concentration at the light doping regime, and saturates at the high doping regime. Postgrowth thermal annealing improves the compositional and structural homogeneities and reduces the localization energy. These findings provide us with an insight into the localization phenomena in Be-doped InGaAsN, and suggest that thermal annealing can be used to reduce the localization effects.

- 5) Deep-level defects in Be-doped InGaAsN have been investigated. Two hole traps, labeled as *HT1* (0.18 eV) and *HT4* (0.59 eV), and two electron traps, labeled as *ET1* (0.09 eV) and *ET3* (0.41 eV), are revealed in the as-grown sample. The *HT1* and *ET3* traps could be N-related defects, and the *HT4* trap could have a similar origin as the so-called EL2-type defect. After postgrowth thermal annealing, the overall deep-level defect concentration decreases. Two hole traps labeled as *HT2* (0.39 eV) and *HT3* (0.41 eV), and one electron trap, labeled as *ET2* (0.19 eV), are revealed in the annealed sample. The *HT2* trap is newly created during annealing, and the

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HT3 trap has a similar origin as the *HT4* trap, i.e., the EL2-type. These results show that appropriate postgrowth thermal annealing could be implemented to improve the InGaAsN material quality by means of reducing the deep-level defects.

- 6) The net acceptor concentration in Be-doped InGaAsN increases after postgrowth thermal annealing. Depassivation of background carbon acceptors during thermal annealing is excluded as the origin. Instead, a proposed three-center complex, $\text{As}_{\text{Ga}}-\text{V}_{\text{As}}-\text{Ga}_{\text{As}}$, is responsible for this process. Before thermal annealing, the Coulombic interaction between Ga_{As}^- and As_{Ga}^+ pins the As atom at its Ga site. During thermal annealing, the Coulombic interaction is nullified leading to the breakage of the bond between As_{Ga} and Ga_{As} . The As atoms move towards the neighboring V_{As} , thus forming acceptorlike V_{Ga} , which is responsible for the increase in the net acceptor concentration.
- 7) The InGaAsN/GaAs *p-n* junction diode has been grown and fabricated. The leakage current of the diode decreases by 2 ~ 3 orders after postgrowth thermal annealing. The *HT4* trap is suggested to be an efficient generation-recombination center and may be responsible for the high leakage current in the as-grown diode.
- 8) Minority-carrier electron diffusion length in Be-doped InGaAsN has been investigated. After postgrowth thermal annealing the minority-carrier electron diffusion length increases by ~ 30%, from ~ 0.14 μm in the as-grown layer to ~ 0.19 μm in the annealed layer. The improvement may be explained as a result of reduction in deep-level defects.
- 9) An operational InGaP/ $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$ /GaAs *n-p-n* DHBT has been demonstrated. The narrower band gap of $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$ has led to a 130 mV reduction in turn-on voltage compared to the InGaP/GaAs SHBT. However, the turn-on voltage reduction is smaller than expected, due possibly to the remaining barrier at the BE junction and the increased band

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gap of $\text{In}_{0.03}\text{Ga}_{0.97}\text{As}_{0.99}\text{N}_{0.01}$ after RTA. The device has a current gain of $\beta \sim 0.5$. The small current gain is due to the small minority-carrier diffusion length that is limited by the InGaAsN material quality.

9.2 Recommendations for Future Research

The following section lists a number of research ideas that could further enhance the work that has been accomplished so far in this thesis:

- 1) Our present study has shown that the InGaAsN material quality limits the performance of the demonstrated InGaP/InGaAsN/GaAs DHBT. Therefore, it is necessary to optimize the growth parameters to improve the material quality, e.g. the growth temperature, the V/III ratio, and the way of plasma ignition. Covering As_4 on the growth surface during plasma ignition could be beneficial in protecting the surface from damage by energetic ions.
- 2) We have demonstrated an operational InGaP/InGaAsN/GaAs DHBT. The conduction band barrier at the BC junction is eliminated, but the one at the BE junction is still there. It reduces the benefit of the smaller band gap of InGaAsN. Therefore, proper design of the BE junctions is necessary. Inserting an undoped-InGaAsN setback layer between the emitter and the base, or inserting a δ -doping layer in the emitter near the BE junction can be attempted.
- 3) Our study has shown that RTP could be implemented to improve the InGaAsN material quality and device performance. So far we have tried a single annealing condition that is 750 °C for 1 min. This condition may not be optimal. Therefore, different annealing conditions need to be attempted to obtain the best results. In addition, it is also an interesting topic to study the effects of RTP on the InGaAsN material structure, the alloy compositions, and the HBT structure.

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