Semiconductor quantum well photodetector for fibre optical communication application

Li, Dao Sheng

2009

Li, D. S. (2009). Semiconductor quantum well photodetector for fibre optical communication application. Master's thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/47037>

<https://doi.org/10.32657/10356/47037>

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SEMICONDUCTOR QUANTUM WELL PHOTODETECTOR FOR FIBER OPTICAL COMMUNICATION APPLICATION

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School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of requirement for the degree of
Master of Engineering

2009

Acknowledgment

I would like to express my sincere gratitude to my supervisor Assoc. Prof. Fan Weijun for giving me the opportunity to work on this project and for his guidance, patience, and encouragement. The knowledge I have learnt from him is not only about the project itself, but also about how to be a scientific researcher. I would like to thank NTU's financial support throughout the course of my study. I would also like to thank Assoc. Prof. Zhang Daohua for his help in experimental facilities.

My sincere gratitude and appreciation also goes to Dr. Ma Baoshan who has taught me characterization skills, and Mr. Dang Yuxing who has enlightened me in the theoretical aspects of the electronic band structure calculation. Throughout my candidature of more than two years, I am also grateful to the countless help and advice from Mr. Liu Wei and Dr. Ng Tien Khee.

Special thanks go to my friends in Clean Room: Dr. Ding Ying, Dr. Lew Kim Luong, Dr. Li Hong, Dr. Liu Chongyang, Dr. Loke Wan Khai, Dr. Tong Cunzhu, Dr. Xu Qiang, Cao Qi, Chen Jian, Chen Kah Pin, Liu Zhihong, Lu Fen, Pham Huynh Tram, Wang Rui, Wang Yang and Yu Ying for their help in lab work, discussions and friendship. I am also grateful to technicians in clean room and other staffs in NTU who has helped me in one way or another.

Last, but not least, I would like to thank my parents and my wife for their love and support throughout my studies.

Abstract

The theoretical and experimental investigations on n-type GaAs based and GaAsN based double barrier quantum wells infrared photodetectors (DB QWIPs) were systematically discussed in this thesis. Firstly, the introduction of this project, the fundamental of double barrier quantum well (DBQW), and simulation models including the 8-band and 10-band $k \cdot p$ methods, and the methodology of major characterization tools and fabrication procedure were presented or reviewed. The energy band structures of GaAs/AlAs/AlGaAs QWs with different well widths, and GaAsN/AlAs/AlGaAs QWs with different nitrogen contents were calculated and analyzed using 8-band and 10-band $k \cdot p$ models, respectively. The results showed good agreement with the experimental results. Finally, the characterization results of XRD, TEM and EDX, PL, PLE, FTIR, and photocurrent analysis on GaAs/AlAs/AlGaAs QWs and GaAsN/AlAs/AlGaAs QWs were discussed in detail. Particularly, with increasing well widths or increasing nitrogen content in well region, PL and PLE properties and darkcurrent levels of different samples were compared and analyzed. With nitrogen incorporation, an S-shaped shift of PL peak with increasing temperature was observed and its origin was discussed. For the first time, evident PLE spectra of GaAs/AlAs/AlGaAs QW structures were presented and the transitions related to PLE absorption edges were discussed. Through investigations, GaAs(N) based QWIPs exhibited some novel and promising properties, which deserve further investigation in future research.

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Chapter 1 Introduction

1.1 Motivation

In the photonics industry, III-V compound semiconductors are the most important materials for light-emitting devices and for optical detectors. Their direct bandgaps permit very efficient photon coupling. Meanwhile, the direct bandgap energies of the various III-V materials cover the entire spectral from ultra-violet to near-infrared, making them ideal for fiber optical applications which typically operate in the 1310 nm, or 1550 nm optical fiber transparency windows.

Conventional photodetectors such as Mercury Cadmium Telluride (MCT) detectors employ interband optical absorption that involves photoexciting carriers across the bandgap, i.e. promoting an electron from valence-bands to conduction-bands. However, the material bandgap must be controlled to be very small to realize IR detection. Such small bandgap materials are well known to be more difficult to grow, process, and fabricate into devices than the larger bandgap semiconductors. These difficulties thus motivate the study of novel “artificial” materials or novel device structures in order not only to easily grow and fabricate detectors or cut down the cost but also to open another way to some special applications. For example, some conventional photodetectors for 1.31 μm and 1.55 μm applications, such as the InGaAs metal-semiconductor-metal (MSM) photodetectors or the InGaAs avalanche ones, although well developed or with simple device structures, are built on expensive InP substrate. The large lattice mismatch between InGaAs and GaAs prohibits the implementation of InGaAs material onto relative cheaper GaAs substrate. Therefore, for the objectives in our project, we designed and developed GaAsN based double barrier quantum well infrared photodetectors (QWIPs) to realize 1.31 μm or 1.55 μm applications, which uses intersubband transition (ISBT) in the QWs with large bandgap ($E_g > 1\text{eV}$) semiconductors. Compared to conventional photodetectors utilizing interband absorption, the significance of investigation on quantum well

infrared photodetectors (QWIPs) utilizing intersubband transition (ISBT) comes from not only another way to realize these applications but also the fact that these QWIPs are intrinsically high-speed devices with their short time lifetime, which are well suited for high frequency applications [1-3].

In order to create the discrete states within the conduction or valence bands, quantum wells are used. Quantum well infrared photodetectors (QWIPs) operate by photoexcitation of electrons between the ground and the first excited state of multi-quantum wells (MQWs), for example, GaAs/AlGaAs, which are artificially fabricated by placing thin layers of two different, large-bandgap semiconductor materials alternately. The bandgap discontinuity of two materials creates quantized subbands in the potential wells. The structure parameters are designed so that the photo-excited carriers can escape from potential wells and be collected as photocurrent.

The quantum well infrared photodetector (QWIP) technology have been highly developed very quickly over the past 20 years. West and Eglash *et al.* [4] first observed the strong optical intersubband transition in GaAs/AlGaAs multi-quantum well (MQW). Levine *et al.* [5] demonstrated the first GaAs QWIP, and various intersubband transition schemes and material systems have been developed and widely investigated. For example, QWIPs based on bound-to-bound (BTB), bound-to-quasi-bound (BTQB), bound-to-miniband (BTM), and bound-to-continuum (BTC) transitions have been developed. Current developments in the area of QWIPs mainly include QWIPs with very short detection wavelength [6], multi-color and multi-band QWIPs [7, 8], T-Hz (i.e. very long detection wavelength) range QWIPs [9], quantum dots infrared photodetectors with very high working temperature [10, 11], large aluminum-free QWIP plane arrays [12], high absorption (>90%) QWIPs [13], n-type QWIPs structures for detecting normal incident light [14], etc.

Many efforts have been devoted to realize the devices operating in the optical fiber communication window of 1.3 or 1.55 μm . Since the material systems based on GaAs

enjoy the mature material growth and device fabrication technology, they are surely the available options for QWIPs in the communication applications. In order to realize and optimize the performance, except for the option of the double barrier scheme, there is an important approach: variations of GaAs material systems (e.g. introduction of Indium or Nitrogen to GaAs) can be utilized to enhance the intersubband transition energy and confinement of carriers in the QWs. As a good candidate, a novel compound semiconductor alloy, InGaAsN, in recent years has received considerable attention. It has been found that the introduction of small amounts of nitrogen in these materials greatly reduces the bandgap. Only 2% nitrogen reduces the bandgap by more than 30% [15]. This reduction (of about 0.1 eV per % of N for N composition < 3%) occurs because of the band anticrossing (BAC) interaction between the conduction band edge and a higher-lying nitrogen resonant band [16] and dramatically changes the electronic structure [17], thus offering a new route to band structure engineering. Luna *et al.* reported near-infrared detection for a double-barrier QWIP based on a 30Å GaAsN quantum well in 2003 [6, 18]. The as-grown sample exhibits a detection wavelength of 1.64 μm at 25 K and the detection peak experiences a red shift to 1.67 μm following rapid thermal annealing at 850°C for 30s.

Short wavelength intersubband absorption easily obtained in InGaAsN-based quantum-well structures, comes from large conduction band discontinuity induced by the small bandgap of InGaAsN. For instance, the conduction band discontinuity of $\text{In}_{0.17}\text{Ga}_{0.83}\text{As}_{0.99}\text{N}_{0.01}/\text{In}_{0.49}\text{Ga}_{0.51}\text{P}$ quantum well is about 550 meV. Furthermore, If AlAs is selected as the barrier material and well width is at 2-3 nm, the energy difference between ground states E_1 and the first excited states E_2 is almost 800 meV corresponding to 1.55 μm . As a result, QWIPs for fiber optical applications can be realized by employing this system. With the consideration of the fact that the performance of n-type QWIPs is superior to p-type QWIPs for our applications [19], Our project focuses on n-type GaAs/AlAs/AlGaAs and (In)GaAsN/AlAs/AlGaAs QWIPs.

In this thesis, all QWIPs discussed, except that specially indicated, refer to the n-type ones.

1.2 Objectives

The objectives of this project are as following:

- To grow GaAs(N)/AlAs/AlGaAs double barrier quantum wells (DBQWs) and develop QWIPs with 1.3 μm or 1.55 μm absorption.
- To systematically study the energy structures and photoluminescence (PL) or photoluminescence excitation (PLE) properties of GaAs(N) based DBQW structures by theoretical and experimental work.
- To demonstrate double barrier QWIPs based on (In)GaAs(N) material systems with effective photocurrent generation induced by incident infrared light, and investigate the dark current and response of QWIPs under various experiment conditions.

1.3 Significance

Only very few reports have been published on intersubband transition and QWIPs with GaAsN materials in the area of the fiber optical communication applications. As an effort to realize GaAsN based quantum well infrared photodectors for fiber optical communication, the study in this project will serve to investigate the energy levels, photon-absorption properties of these material systems and the role of nitrogen incorporation within the double barrier scheme. The success of this project will pave a novel way to realize and improve fiber optical communication applications with GaAsN or GaAs based material systems. Since GaAsN alloys exhibit some unique properties compared to conventional semiconductor materials, we also anticipate the

QWIPs based on GaAsN may show some features different from conventional QWIP devices.

1.4 Major contributions to the project

Since joined NTU in 2006, I have fabricated and characterized several GaAs/AlGaAs, GaAs/AlAs/AlGaAs and GaAsN/AlAs/AlGaAs quantum well infrared photodetector (QWIP) samples. I investigated their structural properties with high resolution X-Ray diffraction (HRXRD), absorption properties with Fourier Transform Infrared Spectroscopy (FTIR), tested and analyzed the Photoluminescence (PL) and Photoluminescence Excitation (PLE) results of these samples. In addition, I have measured and analyzed the dark current properties of fabricated QWIP devices as well.

I also have utilized 8-band $k \cdot p$ method and 10-band $k \cdot p$ method integrating BAC theory, to simulate the energy subbands, wave functions and absorption coefficients of GaAs based and GaAsN-based DBQW structures, respectively. These theoretical results agree well with experiment results.

As a participant, our group observed the photodetection at $1.24 \mu\text{m}$ with InGaAsN/AlAs/AlGaAs QWIP, which is the shortest wavelength intersubband transition ever reported in GaAs based QWIPs. The observation is in good agreement with the theoretical results using 10-band $k \cdot p$ method.

1.5 Thesis overview

In this thesis, in chapter 1, the motivation of this project and the main objectives are described. In chapter 2, the theoretical review on QWIPs is conducted. In chapter 3, the methodology utilized in this project, major characterization tools and fabrication procedure are briefly reviewed. In chapter 4, results of simulation, characterization and fabrication for two main types of QWIPs (GaAs/AlAs/AlGaAs with different well

widths and GaAsN/AlAs/AlGaAs with different nitrogen concentrations) are reported in detail, followed by summaries. The last chapter gives conclusion of the whole thesis and future work.

Chapter 2 Literature Review

All Quantum Well Infrared Photodetectors (QWIPs) are based on “band engineering” of layered structure of different materials with wide bandgap. These structures are designed so that the energy separation between the two states in subbands matches the energy of the infrared photons to be detected. Fundamental of QWIPs and intersubband transition theory are reviewed in this chapter.

2.1 Fundamental

A typical semiconductor quantum well is comprised of a thin layer of a relative narrow bandgap semiconductor sandwiched by two layers of a relative wide bandgap semiconductor. The interfaces are called semiconductor heterojunctions. There are confined quantum states (also called subbands shown in Figure 2-1) within the conduction band well or the valence band well if the center layer is thin enough. Transitions between subbands are called intersubband transitions (ISBT).

Figure 2-1 An illustration of a typical semiconductor quantum well (square QW) and confined states.

From quantum mechanics, we know that the position and number of confined states can be varied by changing the well width and the well depth. This provides the basic

concepts of semiconductor band engineering: Modulation of the energy separation between confined states by changing the quantum-well well width or the alloy composition of the barrier material. Since molecular beam epitaxy (MBE) can deposit material with atomic level precision, energy level positions and their separation can be finely tuned almost continuously. However, semiconductor heterojunctions and quantum wells can be formed only between certain semiconductors whose lattice constants match well, such as GaAs and AlAs. Introduction of proper content of indium or nitrogen will add strains to quantum wells (QW). Therefore, it is important to delicately choose material elements in QW design.

Figure 2-2 Schematic conduction band diagram of a bound to quasibound (BTQB) QW using GaAs QWs and AlAs/AlGaAs barriers.

As shown in Figure 2-2, the double barrier QW (DBQW), was proposed by Schneider *et al.* [20] which simultaneously enhances the detectivity and the confinement of carriers in QWs. It consists of a well layer surrounded by two high inner barriers followed by two lower outer barriers. The traditional bound-to-bound transition in square QWIPs (as shown in Figure 2-1) thus can be transferred to a bound-to-quasibound transition (BTQB) where ground state E_1 is lower than both inner and outer barriers and the first excited states E_2 are lower than inner barriers but higher than outer ones. In the later scheme with large band discontinuity of GaAs(N)/AlAs, the

transition energies can be tuned more readily to reach the IR region, and photoexcited carriers can coherently tunnel through the thin high (indirect) inner barrier to be collected as photocurrent. Providing this barrier is thin, the transit time for carriers is rapid compared to the Γ -X scattering time [21], hence few carriers are lost in this way [22].

By using the more complex double-barrier structure, we can enhance the photoexcited coherently tunneling out of the quantum well, while simultaneously impeding the incoherent sequential tunneling out the doped ground state. The double barrier QWIP can be operated at much lower bias, while still maintaining the same high response as a result of the efficient coherent tunneling out of the photoexcited states. Therefore, because of this lower bias, the dark current in DBQW is now two orders of magnitude lower than that achieved in simple square tunneling barriers, thus this coherent double-barrier QWIP has an order-of-magnitude larger detectivity. In addition, compared to square QWs, multispectra can be achieved with DBQW in that there may be not only one kind of transition from E_1 to E_2 in DBQW.

However, intersubband transition potential in the conduction band of QWs is maybe restricted to long wavelengths due to the small conduction band offsets (e.g. < 0.5 eV for GaAs/AlGaAs). There are numerous efforts to increase the intersubband transition (ISBT) energy to the optical communication regime (the NIR range). One of major approaches is variation of materials which maybe bring bandgap reduction or strains from mismatched lattices. For example, in InGaAs/AlAs QWs with high indium contents (whose conduction band offset is adjustable by the content of indium), the lattice mismatch between InGaAs and AlAs limits the indium content and number of QWs that can be grown. This can be solved with an InGaAs buffer layer with linearly graded indium composition prior to the growth of multiple QWs. Using the same method, Smet *et al.* were able to achieve an ISBT at 0.8 eV ($1.55 \mu\text{m}$) [23] in a 3 monolayer (ML) sample. Several other materials systems have been used for achieving NIR ISBTs: Gopal *et al.* achieved $1.35 \mu\text{m}$ in InGaAs/AlAsSb single

quantum well [24]; ISBTs at 1.3 μm and 1.55 μm in a coupled InGaAs-AlAsSb DQW were reported by Yoshida *et al.*[25], Guzman *et al* reported 1.67 μm in GaAsN/AlAs/AlGaAs DBQWs [18], and recently Ma *et al.* observed 1.24 μm in InGaAsN/AlAs/AlGaAs DBQWs [26].

2.2 Simulation models

We utilized 8-band $k \cdot p$ method to investigate the subband structure of GaAs based quantum wells. When nitrogen is introduced into GaAs based QWs, the strong interaction between the N resonant states and the conduction band edge means that the conventional 8-band $k \cdot p$ method cannot be well applied to (In)GaAsN related QW structures. Therefore 10-band $k \cdot p$ method integrating the BAC theory was developed and utilized to analyze subband structures of dilute nitride alloy quantum wells. The 8-band $k \cdot p$ method, BAC theory and 10-band $k \cdot p$ method are introduced in this section.

2.2.1 Eight-band $k \cdot p$ method

The $k \cdot p$ and envelop function method is an effective method for the semiconductor band structure calculation. From the Effective Mass Theory for degenerate bands, the Schrödinger Equation with a perturbation $U(r)$ as a quantum-well potential is

$$[H + U(r)]\Psi(r) = E\Psi(r) \quad (2.1)$$

where quantum-well potential $U(r)$ is

for the conduction band

$$U(z) = \begin{cases} \Delta E_c & |z| \geq L_w/2 \\ 0 & |z| < L_w/2 \end{cases} \quad (2.2)$$

and for the valance band

$$U(z) = \begin{cases} -\Delta E_v & |z| \geq L_w/2 \\ 0 & |z| < L_w/2 \end{cases} \quad (2.3)$$

z denotes the QW growth direction and L_w is the well width. ΔE_c and ΔE_v are the band-edge discontinuities of conduction band and valence band, respectively.

In the eight-band scheme, the total wave function in each layer can be written as

$$\psi(r) = \sum_{j=1}^8 F_j(r) u_j(r) = \sum_{j=1}^8 \exp(ik_{\parallel} \cdot \rho) \phi_j(z) u_j(r), \quad j = 1, 2, \dots, 8 \quad (2.4)$$

where $k_{\parallel} = (k_x, k_y)$ is a two dimensional in-plane wave vector which is a good quantum number, $\rho = (x, y)$ is a two dimensional in-plane space vector, and $r = (\rho, z)$. ϕ_j is slowly varying envelope function, and u_j is the periodic part of the Bloch basis functions at the zone center which are chosen to be eigenfunctions of the total angular momentum operators J and J_z . These basic functions $u_j = |J, J_z\rangle$ are linear combinations of the band-edge Bloch functions $|S\rangle, |X\rangle, |Y\rangle, |Z\rangle$, which have the same symmetry properties as the atomic s, x, y and z functions. The explicit expressions are given as follows:

$$u_1 = u_{c\uparrow} = |S\uparrow\rangle \quad (2.5a)$$

$$u_2 = u_{c\downarrow} = |S\downarrow\rangle \quad (2.5b)$$

$$u_3 = |3/2, +3/2\rangle = u_{hh\uparrow} = -\frac{i}{\sqrt{2}} |(X + iY)\uparrow\rangle \quad (2.5c)$$

$$u_4 = |3/2, +1/2\rangle = u_{th\uparrow} = -\frac{i}{\sqrt{6}} |(X + iY)\downarrow - 2Z\uparrow\rangle \quad (2.5d)$$

$$u_5 = |3/2, -1/2\rangle = u_{th\downarrow} = \frac{i}{\sqrt{6}} [(X - iY)\uparrow + 2Z\downarrow] \quad (2.5e)$$

$$u_6 = |3/2, -3/2\rangle = u_{hh\downarrow} = \frac{i}{\sqrt{2}} |(X - iY)\downarrow\rangle \quad (2.5f)$$

$$u_7 = |1/2, +1/2\rangle = u_{so\uparrow} = \frac{i}{\sqrt{3}} [(X + iY)\downarrow + Z\uparrow] \quad (2.5g)$$

$$u_8 = |1/2, -1/2\rangle = u_{so\downarrow} = \frac{i}{\sqrt{3}} [(X - iY)\uparrow - Z\downarrow] \quad (2.5h)$$

The 8×8 $k \cdot p$ Hamiltonian H including the electron, heavy hole, light hole and spin-orbit splitting bands is used. It is given by Ref [27, 28].

$$H_k = \begin{bmatrix} C & 0 & \frac{-1}{\sqrt{2}}P^+ & \sqrt{\frac{2}{3}}P^z & \frac{1}{\sqrt{6}}P^- & 0 & \frac{1}{\sqrt{3}}P^z & \frac{1}{\sqrt{3}}P^- \\ 0 & C & 0 & \frac{-1}{\sqrt{6}}P^+ & \sqrt{\frac{2}{3}}P^z & \frac{1}{\sqrt{2}}P^- & \frac{1}{\sqrt{3}}P^+ & \frac{-1}{\sqrt{3}}P^z \\ c.c & 0 & H & \alpha & \beta & 0 & \frac{1}{\sqrt{2}}\alpha & \frac{1}{\sqrt{2}}\beta \\ c.c & c.c & c.c & L & 0 & \beta & -\sqrt{2}D & -\sqrt{\frac{3}{2}}\alpha \\ c.c & c.c & c.c & 0 & L & -\alpha & -\sqrt{\frac{3}{2}}\alpha^* & \sqrt{2}D \\ 0 & c.c & 0 & c.c & c.c & H & -\sqrt{2}\beta^* & \frac{1}{\sqrt{2}}\alpha^* \\ c.c & c.c & c.c & c.c & c.c & c.c & S & 0 \\ c.c & c.c & c.c & c.c & c.c & c.c & 0 & S \end{bmatrix} \quad (2.6)$$

where $c.c.$ denotes the complex conjugate of the corresponding symmetrical item along the diagonal line.

Where

$$C = E_g + \frac{\hbar^2}{2m_0} (k_x^2 + k_y^2 + k_z^2) \tilde{\gamma}_c \quad (2.7a)$$

$$H = \frac{\hbar^2}{2m_0} \left[- (k_x^2 + k_y^2) (\tilde{\gamma}_1 + \tilde{\gamma}_2) - k_z^2 (\tilde{\gamma}_1 - 2\tilde{\gamma}_2) \right] \quad (2.7b)$$

$$L = \frac{\hbar^2}{2m_0} \left[- (k_x^2 + k_y^2) (\tilde{\gamma}_1 - \tilde{\gamma}_2) - k_z^2 (\tilde{\gamma}_1 + 2\tilde{\gamma}_2) \right] \quad (2.7c)$$

$$S = \frac{\hbar^2}{2m_0} \left[- (k_x^2 + k_y^2 + k_z^2) \tilde{\gamma}_1 \right] - \Delta_0 \quad (2.7d)$$

$$(2.7e)$$

$$P_{\pm} = P(k_x \pm ik_y) \quad (2.7f)$$

$$P_z = Pk_z$$

$$\alpha = \frac{\hbar^2}{2m_0} 2\sqrt{3} [k_z (k_x - ik_y) \tilde{\gamma}_3] \quad (2.7g)$$

$$(2.7h)$$

$$\beta = \frac{\hbar^2}{2m_0} \sqrt{3} [(k_x^2 - k_y^2) \tilde{\gamma}_2 - 2ik_x k_y \tilde{\gamma}_3] \quad (2.7i)$$

$$D = \frac{\hbar^2}{2m_0} \left[2k_z^2 - (k_x^2 + k_y^2) \right] \tilde{\gamma}_2 \quad (2.7i)$$

$$\tilde{\gamma}_c = \frac{1}{m_e^*} - \frac{E_p}{3} \left(\frac{2}{E_g} + \frac{1}{E_g + \Delta_0} \right) \quad (2.7j)$$

$$\tilde{\gamma}_1 = \gamma_1 - \frac{E_p}{3E_g} \quad (2.7k)$$

$$\tilde{\gamma}_2 = \gamma_2 - \frac{E_p}{6E_g} \quad (2.7l)$$

$$\tilde{\gamma}_3 = \gamma_3 - \frac{E_p}{6E_g} \quad (2.7m)$$

And the p-matrix element P satisfies Ref. [29, 30].

$$E_p = \frac{2m_0}{\hbar^2} P^2 \quad (2.7n)$$

k_x , k_y and k_z are the wavevectors. E_g is the unstrained bandgap of the bulk material. Δ_{so} is the spin-orbit split off energy. The valence band parameters ($\tilde{\gamma}_1, \tilde{\gamma}_2, \tilde{\gamma}_3$) in the above equations are modified Luttinger parameters.

2.2.2 Ten-band $k \cdot p$ method

As we know, the incorporation of small amounts of nitrogen in these well materials greatly reduces the bandgap. The BAC (band anticrossing) model [31] successfully describes the macroscopic behavior of the material. According to BAC theory, the introduction of N into InGaAs or GaAs leads to a strong interaction between the conduction band-edge states of the matrix (E_M) and a narrow resonant band formed by localized N states (E_N). The overall effect is the formation of two conduction subbands, one of them with much higher band-edge energy than the matrix conduction band (E_+), and the other with much lower band-edge energy (E_-) which defines the new bandgap. That would be the origin of the strong bandgap reduction.

By adding two more spin-degenerated states (nitrogen-induced level)

$$\begin{bmatrix} N & 0 & V_{NC}\sqrt{y} & 0 \\ 0 & N & 0 & V_{NC}\sqrt{y} \\ V_{NC}\sqrt{y} & 0 & C & 0 \\ 0 & V_{NC}\sqrt{y} & 0 & C \end{bmatrix} \quad (2.8)$$

to the eight-band Hamiltonian(as shown in Eq. (2.6)), the ten-band $k \cdot p$ Hamiltonian is formed and given by the following matrix [28].

$$\begin{bmatrix} N & 0 & V_{NC}\sqrt{y} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ c.c & N & 0 & V_{NC}\sqrt{y} & 0 & 0 & 0 & 0 & 0 & 0 \\ c.c & c.c & C & 0 & \frac{-1}{\sqrt{2}}P^+ & \sqrt{\frac{2}{3}}P^z & \frac{1}{\sqrt{6}}P^- & 0 & \frac{1}{\sqrt{3}}P^z & \frac{1}{\sqrt{3}}P^- \\ c.c & c.c & c.c & C & 0 & \frac{-1}{\sqrt{6}}P^+ & \sqrt{\frac{2}{3}}P^z & \frac{1}{\sqrt{2}}P^- & \frac{1}{\sqrt{3}}P^+ & \frac{-1}{\sqrt{3}}P^z \\ c.c & c.c & c.c & c.c & H & \alpha & \beta & 0 & \frac{1}{\sqrt{2}}\alpha & \frac{1}{\sqrt{2}}\beta \\ c.c & c.c & c.c & c.c & c.c & L & 0 & \beta & -\sqrt{2}D & -\sqrt{\frac{3}{2}}\alpha \\ c.c & c.c & c.c & c.c & c.c & c.c & L & -\alpha & -\sqrt{\frac{3}{2}}\alpha^* & \sqrt{2}D \\ c.c & c.c & c.c & c.c & c.c & c.c & c.c & H & -\sqrt{2}\beta^* & \frac{1}{\sqrt{2}}\alpha^* \\ c.c & c.c & c.c & c.c & c.c & c.c & c.c & c.c & S & 0 \\ c.c & c.c & c.c & c.c & c.c & c.c & c.c & c.c & c.c & S \end{bmatrix} \quad (2.9)$$

where $c.c.$ denotes the complex conjugate of the corresponding symmetrical items along the diagonal line. The nitrogen-related elements N is defined as $N = E_N$; V_{NC} is the matrix element linking the N state and the host material conduction band edge which is determined by the respective layer material, and y is the N composition. The detailed calculations of E_N and V_{NC} will be discussed later. All the other ten-band Hamiltonian matrix elements are defined as ones in Eq. (2.6).

We choose the ten basis functions as follows:

$$u_1 = u_{N\uparrow} = |S_N\uparrow\rangle \quad (2.10a)$$

$$u_2 = u_{N\downarrow} = |S_N\downarrow\rangle \quad (2.10b)$$

$$u_3 = u_{c\uparrow} = |S\uparrow\rangle \quad (2.10c)$$

$$u_4 = u_{c\downarrow} = |S\downarrow\rangle \quad (2.10d)$$

$$u_5 = |3/2, +3/2\rangle = u_{hh\uparrow} = -\frac{i}{\sqrt{2}}|(X + iY)\uparrow\rangle \quad (2.10e)$$

$$u_6 = |3/2, +1/2\rangle = u_{lh\uparrow} = -\frac{i}{\sqrt{6}}|(X + iY)\downarrow - 2Z\uparrow\rangle \quad (2.10f)$$

$$u_7 = |3/2, -1/2\rangle = u_{lh\downarrow} = \frac{i}{\sqrt{6}}|[(X - iY)\uparrow + 2Z\downarrow]\rangle \quad (2.10g)$$

$$u_8 = |3/2, -3/2\rangle = u_{hh\downarrow} = \frac{i}{\sqrt{2}}|(X - iY)\downarrow\rangle \quad (2.10h)$$

$$u_9 = |1/2, +1/2\rangle = u_{so\uparrow} = \frac{i}{\sqrt{3}}|[(X + iY)\downarrow + Z\uparrow]\rangle \quad (2.10i)$$

$$u_{10} = |1/2, -1/2\rangle = u_{so\downarrow} = \frac{i}{\sqrt{3}}|[(X - iY)\uparrow - Z\downarrow]\rangle \quad (2.10j)$$

The Hamiltonian describing strain, H_s , can be derived by simply substituting $\varepsilon_{\alpha\beta}$ into k_α, k_β with $\alpha, \beta = x; y; z$; The strain Hamiltonian H_s and the diagonal matrix $V(z)$ follow the same denitions for the eight-band $k \cdot p$ model.

2.3 Design method

The design of an optimized QWIP involves choosing the following parameters: well width L_w , barrier height V_b , barrier width L_b , well doping density resulting in a two dimensional (2D) carrier density N_d , and number of wells N .

According to various material systems and structure schemes, we have developed different simulation programs, cataloged by 8-band models for the GaAs based square QW and DBQW, 10-band model for the (In)GaAsN based DBQW. With the above and other parameters as input variances, we can utilize these models to calculate and analyze subband profiles in different structures. According to the equation $\hbar\omega = \hbar c / \lambda = 1239.8 / \lambda$, where $\hbar\omega$ is in eV when λ is in μm , the result of $E_2 - E_1$ (energy separation of the first excited state and the ground one) corresponds to specific response wavelength. In this scheme, we can also tune the appropriate parameter composition to the predicted wavelength usually by changing composition and well widths.

For the GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ or GaAs/ $\text{AlAs}/\text{Al}_x\text{Ga}_{1-x}\text{As}$ QWs, The conduction band edge is not shifted by strain in that $\text{Al}_x\text{Ga}_{1-x}\text{As}$ lattice roughly matches GaAs lattice. For the

bandgap energy and electron effective mass of $\text{Al}_x\text{Ga}_{1-x}\text{As}$, they are decided by

$$E_g(\text{Al}_x\text{Ga}_{1-x}\text{As}) = 1.59 + 1.447x - 0.15x^2 \text{ (eV)} \quad \text{at 0 K, for } x < 0.4 \quad (2.11a)$$

$$m_e(\text{Al}_x\text{Ga}_{1-x}\text{As}) = 0.067 + 0.083x \quad (2.11b)$$

Except for bandgap energy and electron effective mass, other parameters (e.g. lattice) of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ are obtained by linear interpolation between the parameters of AlAs and GaAs.

$$P(\text{Al}_x\text{Ga}_{1-x}\text{As}) = xP(\text{AlAs}) + (1-x)P(\text{GaAs}) \quad (2.12)$$

For the $(\text{In})\text{GaAsN}/\text{AlAs}/\text{Al}_x\text{Ga}_{1-x}\text{As}$ QWs, the bandgap energy of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{Ny}$ is calculated by the BAC model in the following form [16, 32]

$$E_g(\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{Ny}) = \left[E_g(\text{In}_x\text{Ga}_{1-x}\text{As}) + E_N - \sqrt{[E_g(\text{In}_x\text{Ga}_{1-x}\text{As}) - E_N]^2 + 4V_{NC}^2(1-y)} \right] / 2 \quad (2.13)$$

Where

$$E_g(\text{In}_x\text{Ga}_{1-x}\text{As}) = (1-x)(E_g(\text{GaAs}, T)) + x(E_g(\text{InAs}, T)) - 0.477(1-x) \quad (2.14)$$

And the effective mass of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{Ny}$ as predicted by the BAC model is given by

$$m_e^*(\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{Ny}) = \frac{2m_e^*(\text{In}_x\text{Ga}_{1-x}\text{As})}{\left[1 - \frac{E_g(\text{In}_x\text{Ga}_{1-x}\text{As}) - E_N}{\sqrt{[E_g(\text{In}_x\text{Ga}_{1-x}\text{As}) - E_N]^2 + 4V_{NC}^2y}} \right]} \quad (2.15)$$

where the effective mass of $\text{In}_x\text{Ga}_{1-x}\text{As}$ is given by

$$m_e^*(\text{In}_x\text{Ga}_{1-x}\text{As}) = (1-x)m_e^*(\text{GaAs}) + xm_e^*(\text{InAs}) - 0.0091x(1-x) \quad (2.16)$$

Note that the bowing factors and 0.0091 in $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{Ny}$ equations of bandgap energy and the effective mass, respectively, are recommended by Ref. [29]. In above equations, the E_N and V_{NC} can be expressed as Ref. [33]

$$E_N = 1.65(1-x) + 1.44x - 0.38x(1-x) \quad (2.17a)$$

$$V_{NC} = 2.7(1-x) + 2.0x - 3.5x(1-x) \quad (2.17b)$$

Except for the bandgap energy and electron effective mass, most parameters for $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{Ny}$ materials are obtained using a linear interpolation between the parameters of the relevant binary semiconductors.

$$P(\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{Ny}) = xyP(\text{InN}) + (1-x)(1-y)P(\text{GaAs}) + (1-x)yP(\text{GaN}) + x(1-y)P(\text{InAs}) \quad (2.18)$$

The material parameters used in calculation for binary semiconductors come from Ref. [29]

Chapter 3 Experimental Methods

3.1 Molecular beam epitaxy (MBE)

Molecular beam epitaxy (MBE) was developed in the early 1970s as a means of growing high-quality epitaxial layers of semiconductors, allowing precise control of layer thickness, doping and chemical composition. Since then, it has evolved into a popular technique for growing III-V compound semiconductors and several other materials.

In essence, MBE is a precisely controlled vacuum evaporation technique, in which the semiconductors in the form of molecular beams are deposited onto the substrate to form thin epitaxial layers. The molecular beams are typically produced by the evaporation or sublimation of the heated solid or liquid sources contained in effusion cells. The molecular beams travel in the ultra-high vacuum and impinge on a heated substrate to form epitaxial thin film. The n-type and p-type dopants, such as Si and Be, are also heated in the effusion cells and incorporated into the layers during the growth. The layer composition and the doping level are principally controlled by the molecular beam fluxes, and hence the temperatures of the cells. Each effusion cell has a movable shutter so that atomically abrupt changes in doping and composition can be achieved. Layers are grown at the rate of approximately $1\text{ }\mu\text{m/hr}$ or about one monolayer per second.

A Riber MBE 32P system equipped with a nitrogen (N) RF plasma source was used for sample preparation. Using this solid source MBE system for growth of phosphorus-containing materials overcomes the conventional problems associated with the handling of hydrides and metal-organics employed in the growth processes involving gas sources.

The reflection high-energy electron diffraction (RHEED) is one of the most useful tools for *in situ* monitoring of the growth. It can be used to calibrate growth rates, observe removal of oxides from the surface, calibrate the substrate temperature,

monitor arrangement of the surface atoms, determine the proper arsenic overpressure, give feedback on surface morphology, and provide information about growth kinetics. As shown in Figure 3-1, the RHEED gun emits high-energy electrons of which strike the sample surface at a shallow angle, making it a sensitive probe of the semiconductor surface. Electrons reflect from the surface and strike a phosphor screen forming a pattern consisting of a reflection and a diffraction pattern from which characterize the surface crystallography.

Figure 3-1 Schematic diagram of the MBE growth chamber.

3.2 X-ray diffraction (XRD)

Figure 3-2 Schematic diagram for Bragg's Law.

High-resolution XRD measurements are carried out to obtain the composition of the epilayers, to study the lattice properties of the grown layers and to gauge the strain relaxation in the layers. A crystal lattice is a regular three-dimensional distribution (cubic, rhombic, etc.) of atoms in space. These are arranged so that they form a series of parallel planes separated from one another by a distance, which varies according to the nature of the material. For any crystal, planes exist in a number of different orientations- each with its own specific d spacing. As shown in Figure 3-2, any measurement of lattice spacing is in principle determined by Bragg's Law is given by the following formula:

$$2d_{hkl} \sin \theta_B = n\lambda$$

where d_{hkl} is the spacing of lattice planes with Miller indices (hkl) and θ_B is the corresponding Bragg angle. This equation follows from kinematic diffraction theory and neglects the fact that the refractive index of matter for X-ray is less than 1 and so the incident beam is refracted to an internal angle slightly smaller than the external one.

When a monochromatic X-ray beam with wavelength λ is projected onto a crystalline material at an angle θ , diffraction occurs only when the distance traveled by the rays reflected from successive planes differs by a complete number n of wavelengths. By varying the angle θ , the Bragg's Law conditions are satisfied by different d spacing in different materials. Plotting the angular positions and intensities of the resultant diffracted peaks of radiation will produce a pattern from which is characteristic of the sample.

Artificially structured multilayer has become an important class of new materials that offer unique electronic, optical, magnetic and mechanical properties. Along growth direction, usually two layers of different chemical composition are alternatively deposited. The one-dimensional periodicity with period D is the origin of a one-dimensional periodic potential, which is superimposed on the three-dimensional crystal potential, the period of which is determined by the lattice constants of the materials. For all properties listed above the structural perfection of a multilayer system is decisive.

3.3 Photoluminescence (PL)

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

PL measurement is used for bandgap determination. The most common radioactive transition in semiconductors is between states in the conduction and valence bands, with the energy difference being known as the bandgap. It is also used for impurity levels and defect detection. The radioactive transitions in semiconductors involve localized defect levels. The photoluminescence energy associated with these levels can be used to identify specific defects and the amount of photoluminescence can be used to determine their concentration. Recombination mechanisms can also be detected. As discussed above, the return to equilibrium, also known as "recombination," can involve both radioactive and nonradioactive processes. The amount of photoluminescence and its dependence on the level of photo-excitation and temperature are directly related to the dominant recombination process. The analysis in photoluminescence helps us to understand the underlying physics of the

recombination mechanism. In general, nonradiative processes are associated with localized defect levels, whose presence is detrimental to material quality and subsequent device performance. Thus, material quality can be measured by quantifying the amount of radiative recombination. Good photoluminescence (PL) readings are depicted by large photo-excitation intensity with very narrow FWHM. The contrary is accepted as low crystalline quality growth.

Figure 3-3 Schematic diagram of the photoluminescence (PL) setup.

A schematic photoluminescence (PL) system as shown in Figure 3-3 consists of an excitation source, a variable temperature cryostat, a sample holder assembly, a high resolution scanning spectrometer and a detection system. It is necessary to cool the sample to cryogenic temperatures to get the maximum amount of information from the radiative relaxation process. A Lambertian distribution of the luminescence from the sample is collected by a suitable lens. The laser beam is incident at an angle on the sample so that the reflected beam does not enter the collecting lens. Low temperature PL measurements from 500-900 nm wavelengths are usually performed at 5 K, using the 5145 Å line of an Ar^+ laser as the exciting source and PMT detector as the detection source, therefore, the chopper and lock-in amplifier were off for our short wavelength applications.

3.4 Photoluminescence Excitation (PLE)

Photoluminescence excitation (PLE) is a slight modification of the basic PL technique. The luminescence spectrum is held fixed at some peak and the incident excitation spectrum is scanned. The resulting spectrum of PL intensity versus wavelength is then related to the absorption coefficient of the semiconductor. PLE aids in identification of PL peaks, since strong absorption occurs for only band-to-band transition.

Figure 3-4 Schematic diagram of the photoluminescence excitation (PLE) setup.

Photoluminescence Excitation spectroscopy (PLE) was used to characterize the high-order transitions in the quantum well structures. A schematic PLE measurement system as shown in Figure 3-4 consists of several excitation sources, an excitation monochromator, a variable temperature cryostat, a sample holder assembly, an emission monochromator and PMT/InGaAs detection system. Because the PLE measurement is based on PL measurement for detection wavelength, our system can complete both PL and PLE measurements. In a standard PLE measurement procedure, normal PL analysis is initially conducted with line excitation of fixed wavelength

(usually 532 nm in our cases) and detection in a specific scanning range. PL theory can refer to the section 3.3. With the PL measurement, PL intensity versus wavelength can be automatically plotted to show several possible interested peaks. With these peak positions as detection wavelengths, respectively, PLE measurements can be conducted with line excitation of a specific scanning range and detection at detection wavelength. During PLE measurement, higher-order nonradiative subbands are populated while the light is scanned, and thermalize to the lower energy transition, where they recombine and emit light of energy equal to the PL transition energy. Thus, maxima in the resulting spectra correspond to these higher energy levels. PLE spectra provide a more direct view of the “unrelaxed” excitonic absorption features.

For PLE measurements in our cases, the tunable light source was provided by a 250 W tungsten-halogen lamp dispersed by a TRIAX 320 monochromator. The luminescence was analyzed by another TRIAX 320 monochromator and detected by a PMT detector.

3.5 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 3-5 Schematic diagram of the FTIR setup.

Fourier Transform Infrared Spectroscopy (FTIR) is an effective analytical instrument

by producing an infrared absorption spectrum. In Figure 3-5, a Fourier transform spectrometer consists of two mirrors located at a right angle to each other and oriented perpendicularly, with a beam splitter placed at the vertex of the right angle and oriented at a 45° angle relative to the two mirrors. Radiation incident on the beam splitter from one of the two "ports" is then divided into two parts, each of which propagates down one of the two arms and is reflected off one of the mirrors. After reflection from a fixed and a movable mirror, respectively, the two partial waves are combined by the same beam splitter and focused on the detector over there they interfere and yield the total intensity. When the position of movable mirror is continuously varied along the axis of the corresponding arm, for different positions of the movable mirror, the two partial waves get different phase shifts. Therefore, on the detector the radiation field is superimposed with a time-delayed copy of itself. Hence what is basically measured when the detector signal is recorded while the mirror moves is the autocorrelation function of the radiation field (which is called the interferogram in FTIR spectroscopy). The Fourier transform of this autocorrelation function is the desired power spectrum in the frequency domain.

Figure 3-6 Schematic diagram of (a) the FTIR sample holder and (b) the waveguide geometry.

For our QW structure samples, we use a sample holder shown in Figure 3-6. With such waveguide geometry, the incident radiation undergoes several total internal reflections in the samples, leading to an increased coupling strength.

3.6 Photocurrent measurement

Figure 3-7 The schematic diagram of the photocurrent measurement.

The photocurrent spectra were obtained usually at 20 K or various temperatures above 20 K. In Figure 3-7 we show the diagram of the photocurrent spectra measurement system. The infrared light is coming from an Oriel 6575 infrared light source and collected by lens. It was chopped before passing through a TRIAX 320 monochromator. The outgoing light dispersed by the monochromator is reflected by two parallel mirrors before it finally incidents on the sample surface through cryostat's optical window. When a photocurrent measurement undergoes, a low noise current pre-amplifier is applied to provide the bias voltage for the device and pre-amplify the current signal. At the same time, it converts the current signal to voltage signal. A lock-in amplifier is used to measure the voltage signal.

When a darkcurrent measurement undergoes, with the cryostat optical window is sealed with Al foil, a Keithley 236 measure unit is applied to supply and gradually increase the bias voltage on the device in the preset ranges, and at the same time, collect the current signal from device.

3.7 Fabrication procedure

Figure 3-8 QWIP device processing flow chart.

Figure 3-9 Picture of the QWIP device. Round ones: mesa islands and upper contact metal, boundary: bottom contact metal, cross: the align symbol.

To transfer samples with QW structures to QWIP devices pending for photocurrent measurement, we have developed a procedure of the QWIP device fabrication described in Figure 3-8. Initially, the QWIP materials are etched into mesas with

standard photolithography and wet etching processes specific for GaAs based material systems. The round mesas in $300\ \mu\text{m}$ diameter are etched out till n-type contact layer below QW layers available for electrode contact. Then electrode pairs are formed as shown in Figure 3-9 after the Ni-Ge-Au-Ni-Au alloy is deposited on unetched top surface on mesas and etched contact layer and annealed to form Ohm contact. The devices on the sample are assembled and connected after the wafer edge was polished to realize 45° optical coupling as shown in Figure 3-10 to enhance the photon absorption in QWIPs.

Figure 3-10 The schematic diagram of the QWIP device measurement.

Chapter 4 Results and Discussion of

GaAs/AlAs/AlGaAs QWIP Samples

4.1 Introduction

Figure 4-1 Diagram of the GaAs/AlAs/AlGaAs DBQW structures.

Since observation of the intersubband transition in quantum wells, there has been a great deal of interest in applying them for infrared detectors [19]. Our project mainly focuses on two types of QWIPs for our investigation. One is n-type GaAs/AlAs/AlGaAs QWIP samples which we define as sample D2, D4 and D6 according to their well widths, described and discussed in this chapter, and the other is n-type GaAsN/AlAs/AlGaAs QWIP samples described and discussed in the next chapter. As shown in Figure 4-1, The GaAs/AlAs/AlGaAs QWIP sample D2, D4 and D6 were grown by molecular beam epitaxy (MBE) on (100) semi-insulating GaAs substrate with the same QW parameters except well widths and growth conditions. They were designed to consist of 15 periods of QWs sandwiched by 0.8 μm top and 1 μm bottom Si-doped ($2 \times 10^{18} \text{ cm}^{-3}$) GaAs contact layers. Each period consists of a 30 nm $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ outer barrier layer, 2 nm AlAs inner barrier layer and a Si-doped

($1 \times 10^{18} \text{ cm}^{-3}$) GaAs Well layer with 2 nm, 4 nm and 6 nm well widths for sample D2, D4 and D6, respectively. In this chapter, results of simulation, characterization and fabrication for these QWIPs are reported in details, followed by analysis concerning their PL /PLE results and nitrogen behaviors.

4.2 Simulated results with 8-band $k \cdot p$ method

Figure 4-2 Energy positions in the GaAs/AlAs/Al_{0.3}Ga_{0.7}As QWs at 10 K with 2nm inner barrier, 35 nm outer barrier and different well widths.

The eight-band $k \cdot p$ model is utilized to simulate 10 K's subband profiles of QW structures with different well widths to find the subband dependency on well widths and decide the QW structures desired. In our calculations, energy reference is taken as the top of GaAsN valence band, and conduction band offset (CBO) ratio as 0.67, temperature as 10 K.

Figure 4-2 shows the calculated resonance energies as a function of well widths, in which two horizontal lines indicate the indirect AlAs barrier and AlGaAs barrier and the circles on the curve $E_2 - E_1$ correspond to a transition in $1.73 \mu\text{m}$ (718 meV), $3.02 \mu\text{m}$ (410 meV) and $5.08 \mu\text{m}$ (244 meV), for the well widths of 2 nm, 4 nm and 6 nm, respectively. From this figure, we can see that the interband transition (IBT) energy

E_1 - HH_1 and intersubband transition (ISBT) energy E_2-E_1 will both decrease with the increasing well widths from 2 nm to 6 nm. We can also see that when the well width is less than 3 nm, E_1 is higher than AlGaAs outer barrier, which means that the QW confinement for electrons on ground states is not good.

Figure 4-3 Schematic conduction band potential diagram of one period of the GaAs/AlAs/Al_{0.24}Ga_{0.76}As DBQW with 2 nm well width, 2 nm inner barrier and 35 nm outer barrier at 10 K, where the dot curves from bottom to top stand for excited states in outer barrier and can be defined as $B_1, B_2, B_3, \dots$ etc, respectively.

With the parameters verified by XRD, TEM or EDX analysis methods applied to simulate energy structures, Figure 4-3, Figure 4-4 and Figure 4-5 show schematic conduction band potential diagram of sample D2, D4 and D6, respectively. These three figures show the movement dependency of excited states on well widths where solid curves stand for states in quantum wells and dotted curves ones in outer barriers.

Figure 4-4 Schematic conduction band potential diagram of one period of the GaAs/AlAs/Al_{0.3}Ga_{0.7}As DBQW with 4 nm well width 2 nm inner barrier and 35 nm outer barrier at 10 K, where the dot curves from bottom to top stand for excited states in outer barrier and can be defined as $B_1, B_2, B_3, \dots$ etc, respectively.

Figure 4-5 Schematic conduction band potential diagram of one period of the GaAs/AlAs/Al_{0.3}Ga_{0.7}As DBQW with 6 nm well width, 2 nm inner barrier and 33 nm outer barrier at 10 K, where the dot curves from bottom to top stand for excited states in outer barrier and can be defined as $B_1, B_2, B_3, \dots$ etc, respectively.

In Figure 4-3 for sample D2, the ground state E_1 (the lower solid curve) in QW region is higher than AlGaAs conduction band minimum (CBM) and the first excited state E_2

(the upper solid curve) in QW region is higher than AlAs inner barrier, which will degrade QWIP performance. In Figure 4-4 for sample D4, the ground state E_1 (the lowest solid curve) in QW region is lower than AlGaAs CBM, and the first excited state E_2 and the second excited state E_3 (two upper solid curves) are confined only by AlAs inner barrier. Similarly to Sample D4, in Figure 4-5 for sample D6, we can see that the ground state E_1 (the lowest solid curve) in QW region is lower than AlGaAs CBM, and the first excited state E_2 , the second excited state E_3 and the third excited state E_4 (three upper solid curves) are confined only by AlAs inner barrier. With comparison among three figures, the numbers of excited states in QW regions and the confinement of QW are shown to decrease with deduced well widths.

4.3 TEM and EDX Results

Figure 4-6 TEM image of the sample D2.

Figure 4-7 TEM image of the sample D4.

Figure 4-8 TEM image of the sample D6.

TEM (Transmission Electron Microscope) is designed for inspecting the topographies of specimens at extremely high magnifications. Usually, TEM sample slice needs to be mechanically polished (followed by Argon Ion Milling) to a thickness less than 0.2 μm (depends on sample properties). With assistance of focused ion beam (FIB), TEM is even more powerful to do precision cross-sectioning imaging, and three TEM samples were prepared by FIB. Figure 4-6, Figure 4-7, Figure 4-8 show TEM images of sample D2, sample D4 and sample D6, respectively. These bright-field TEM images were obtained from Philips CM200 system at 200 kV and the crystal direction were shown in images. In these three images, two white layers nearby can be clearly observed, which can be identified as AlAs layers. These white AlAs layers are parallel to the (100) surface and their widths range from 1.8 nm to 2.2 nm in these three figures. Between AlAs layers, the dark regions can be identified as GaAs QW regions and their widths are 1.8 nm, 3.9 nm and 6 nm for sample D2, sample D4 and sample D6, respectively. These dimensional parameters of quantum wells from TEM analysis can add support to or further verify the indirect results from XRD simulations or EDX analysis. The dark regions outside two nearby AlAs layers are identified as AlGaAs outer barriers and their widths shown in the images range from 33 nm to 35 nm. In three images, clear interfaces between the AlAs layers and GaAs QW regions mean good crystal quality. QW layer thickness ranges were summarized in Table 4-1.

Well widths (nm)	GaAs QW		AlAs		AlGaAs
	Min	Max	Min	Max	
2	1.7 nm	2.1 nm	1.8 nm	2.2 nm	35 nm
4	3.9 nm	4.2 nm	1.9 nm	2.1 nm	35 nm
6	5.94 nm	6.2 nm	1.9 nm	2.1 nm	33 nm

Table 4-1 QW layer thickness ranges for Sample D2, D4 and D6.

Energy Dispersive X-ray (EDX) is a technique used for identifying the elemental composition of the specimen. During EDX Analysis, the specimen atom electrons are bombarded with an electron beam inside the scanning electron microscope, emitting

an X-ray. Because the atom of every element releases X-rays with unique amounts of energy, the identity of the atom from which the X-ray was emitted can be established by measuring the amounts of energy present in the X-rays. The EDX spectrum is just a plot of how frequently an X-ray is received for each energy level. Each of these peaks is unique to an atom, and therefore corresponds to a single element. The higher a peak in a spectrum, the more concentrated the element is in the specimen. Although difficult to accurately determine the composition of the ternary compound, EDX analysis can add support to composition estimates from indirect XRD simulation. With the aid of EDX spectrum as shown in Figure 4-9, we can obtain Table 4-2 from EDX software for sample D2's element fraction. Specially for Al fraction, we roughly achieve Al fraction: Al content (%) = $11.6 / (11.6 + 37.3) = 0.24$, so we can conclude that sample D2's outer barrier is of $\text{Al}_{0.24}\text{Ga}_{0.76}\text{As}$ which agrees well with XRD simulation.

Figure 4-9 EDX spectrum of the sample D2.

Elem	Weight%	Atom%
AlK	04.60	11.60
GaK	38.60	37.30
AsK	56.80	51.10

Table 4-2 Element contents for Sample D2.

4.4 X-Ray Diffraction results

Figure 4-10 HRXRD pattern of sample D2 and the matched simulated pattern of GaAs/AlAs/Al_{0.24}Ga_{0.76}As QW with 2 nm well width, 2nm inner barrier and 35 nm outer barrier.

Figure 4-11 HRXRD pattern of sample D4 and the matched simulated pattern of GaAs/AlA/Al_{0.3}Ga_{0.7}As QW with 4 nm width, 2nm inner barrier and 35 nm outer barrier.

Figure 4-12 HRXRD pattern of sample D6 and the matched simulated pattern of GaAs/AlAs/ $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ QW with 6 nm well width, 2nm inner barrier and 33 nm outer barrier.

High-resolution X-ray diffraction XRD analysis was performed on the Philips HRXRD system and showed the evidence for the structure parameters. Figure 4-10, Figure 4-11 and Figure 4-12 show the (004) GaAs Bragg reflection rocking curves of sample D2, D4 and D6, respectively. In these three figures, the upper curves show the measured results while lower curves show the simulated results with the best fitting structure parameters. The simulated QW structure for sample D2 is of GaAs /AlAs / $\text{Al}_{0.24}\text{Ga}_{0.76}\text{As}$ with 2 nm well width, 2nm inner barrier and 35 nm outer barrier, the one for sample D4 is of GaAs /AlAs / $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ with 4 nm well width, 2nm inner barrier and 35 nm outer barrier and the one for sample D6 is of GaAs /AlAs / $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ with 6 nm well width, 2nm inner barrier and 33 nm outer barrier. Although HRXRD will not yield a unique solution for the width of the well and the barrier but rather a set of possible solutions, however, the best values obtained from XRD simulation are the only ones which can be verified or supported by from TEM or EDX analysis. These above parameters from XRD simulation come close to the ones from TEM or EDX analysis in the above sections. Compared among these three figures, it can be found that with increasing well widths from sample D2 to sample D6,

there are more clear-cut periodical features in the rocking curves which suggest the better interface in the grown superlattice structures, at the same time, the reduced angular spacing between the satellite peaks even can be observed.

4.5 PL and PLE Results

Figure 4-13 Sample D2's PL spectrum with 532 nm line excitation at 10 K.

Figure 4-14 Sample D4's PL spectrum with 532 nm line excitation at 10 K.

Sample D2, D4 and D6 were analyzed by PL function of PLE system, with 532 nm

line excitation and at 10 K. Their results are shown in Figure 4-13, Figure 4-15 and Figure 4-16, respectively. For all three samples investigated, quantum well regions are all doped with silicon ($1 \times 10^{18} \text{ cm}^{-3}$) which will weaken the signals related to QWs.

Figure 4-15 Sample D6's PL spectrum with 532 nm line excitation at 10 K.

Figure 4-13 shows sample D2's PL curve with PL function of PLE system, and with 532 line excitation and at 10 K. With the aids of simulation results with verified sample QW parameters, we can assign the 1490 meV peak to bulk material GaAs and the 1840 meV peak to AlGaAs outer barrier (1863 meV in theory). For the PL peak from GaAs quantum well, we simulated it around 1975 meV, however, we failed to detect such a peak around there. Figure 4-14 and Figure 4-15 show the PL spectra of sample D4 and D6, respectively. With comparison with simulated results, for sample D4, we can assign the 1725 meV peak to GaAs quantum well (1732 meV in theory); For sample D6, we can assign the 1639 meV peak to GaAs quantum well (1632 meV in theory). With increased well width, QW PL peak of sample D4 is red shifted from 1725 meV to 1639 meV, which agrees with the tendency of the E_2-E_1 curve shown in Figure 4-2. Compared to sample D4 and sample D6 which both were also doped in QW regions, sample D2 fails to show the evident PL peak from QW region. One of the possible reasons is the doped silicon in QW region weakens the PL intensity, and

another one is the fact that the ground state E_1 higher than outer barrier will facilitate excited electrons' tunneling out of QW regions to AlGaAs barrier regions with lower energy, therefore further weaken the already weak PL signal.

With further PLE measurements and the aids of simulation results with verified sample QW parameters, we can further confirm sources of the PL peaks. Figure 4-16, Figure 4-17 and Figure 4-18 show PLE spectra for sample D2, D4 and D6, respectively. For sample D2, according to PLE principal described in the section 3.4, due to the too weak PL intensity from QWs, the PLE peak related to quantum wells is too weak to be detected with our PLE system, Figure 4-16, in facts, shows PLE information of AlGaAs barrier-well with the fixed detection energy 1840 meV. In Figure 4-16, we can assign the 1940 meV maximum to the AlGaAs's transition E_2-HH_2 (1902 meV in theory); For sample D4 in Figure 4-17, with the fixed detection energy 1725 meV, we can assign the 1801 meV maximum to the GaAs well's

Figure 4-16 Sample D2's PLE spectrum at 10 K.

Figure 4-17 Sample D4's PLE spectrum at 10 K.

Figure 4-18 Sample D6's PLE spectrum at 10 K.

transition E_1-HH_1 (1732 meV in theory) and the 1926 meV maximum to the AlGaAs barrier's transition E_1-HH_1 (1938 meV in theory) and transition E_1-LH_1 (1947 meV in theory); For sample D6 in Figure 4-18, with the fixed detection energy 1639 meV, we can assign the 1675 meV maximum and the 1694 meV maximum to the GaAs well's transition E_1-HH_1 (1632 meV in theory) and transition E_1-LH_1 (1650 meV in theory), respectively. For the 1970 meV maximum, we can conclude that it belongs to the

AlGaAs well's transition E_1-HH_1 (1940 meV in theory), the one E_1-LH_1 (1946 meV in theory) and GaAs barrier's transition E_2-HH_2 (1946 meV in theory). For sample D4 and D6, respectively, we obtained the Stokes shifts (energy difference between detection energy and the nearest absorption peak E_1-HH_1) of 76 meV and 36 meV. Compared to the latter one with less value, the front one means poorer crystal quality [34-36], or more defects which can be verified by comparison of these two samples' XRD, TEM, PL and darkcurrent results.

4.6 FTIR results

Figure 4-19 The FTIR plot of sample D6 with D2's for comparison.

FTIR characterization was conducted with quartz beam splitter to probe absorption performance of sample D2, D4 and D6. Figure 4-19 shows FTIR spectrum of sample D6 together with sample D2's curve for comparison, where we can easily identify the absorption valley on D6 curve around 239 meV which is near to our calculated value 243 meV. As the targeted absorption positions are near the FTIR equipment's scanning limitation, especially for sample D2 and D4, the absorption signals are too weak to be detected in our measurements.

4.7 Photocurrent results

Figure 4-20 The plot of sample D2's darkcurrent versus bias voltage with increasing temperature.

Figure 4-21 The plot of sample D4's darkcurrent versus bias voltage with increasing temperature.

With the related procedures described in chapter 3, sample D2, D4 and D6 were fabricated into QWIP devices. With the assembled devices under measurement described in section 3.6, we have only obtained darkcurrent spectra from three samples as of now, and further photocurrent measurements are in process. Figure 4-

20, Figure 4-21 and Figure 4-22 show plots of dark current versus bias voltage of the n-type QWIP devices from sample D2, D4 and D6, respectively under different temperature conditions. It can be seen that, for all three samples, the dark current I_d all increases with increasing bias voltage and temperature.

Figure 4-22 The plot of sample D6's darkcurrent versus bias voltage with increasing temperature.

However, we have not achieved the photo response from sample D2, D4 and D6 as of now, this may be due to the following possible reasons:

- A. For sample D2, due to AlGaAs's barrier lower than GaAs QW's ground states E_1 , excited electrons in QW regions, before recombination, are easy to tunnel to outer barriers regions where electrons will recombine with holes, thus, this process also depletes the photoexcited carriers.
- B. For sample D4, relatively high darkcurrent veils the response signal which is more difficult to be extracted out.
- C. For sample D6, some imperfectness in sample growth or fabrication for the specific devices under test may affects photocurrent performance.

Although the above possible reasons, further characterization are planned in the future.

4.8 Summary for GaAs/AlAs/AlGaAs QW structures with different well widths

For GaAs/AlAs/AlGaAs QW structures with different well widths, the eight-band $k \cdot p$ model was applied to simulate and plot the subband level and ISBT energy dependence on the well widths. We have characterized and compared GaAs/AlAs/AlGaAs quantum well (QW) structures with well widths of 2 nm, 4 nm and 6 nm, respectively, to analyze subband energy dependency on well widths in DBQW structures. With the QW parameters verified by HRXRD, TEM or EDX, we utilized the eight-band $k \cdot p$ model to plot schematic conduction band potential diagram on these three QW structures. With analysis of simulated results and photoluminescence ones, we can find good agreements among calculated results, PL peak positions and PLE maxima. Through PLE characterization analysis, we can further confirm the identification of both PL peaks and PLE maxima for sample D4 and D6, with exception of sample D2's PLE maximum from QW's intersubband transitions due to its weak PL peak. The reason comes from sample D2's weak PL peak due to ground states higher than AlGaAs barrier, and the fact that the large magnitude of PL peak as detection wavelength is very important for the obvious PLE maxima.. In addition, sample D6's FTIR spectrum clearly shows an absorption signal on the curve near 239 meV, which agrees well with simulated results.

Chapter 5 Results and Discussion of

GaAsN/AlAs/AlGaAs QWIP Samples

5.1 Introduction

Figure 5-1 Diagram of the GaAsN/AlAs/AlGaAs DBQW structures.

Another focus of our project and our investigation is n-type GaAsN/AlAs/AlGaAs QWIP samples, which we define as sample N1 and N2 according to their nitrogen contents. The GaAsN /AlAs/AlGaAs based QWIP samples N1, N2 had the similar quantum well structures to the GaAs/AlAs/AlGaAs ones’, and were grown by molecular beam epitaxy (MBE) on (100) semi-insulating GaAs substrate, with the same QW parameters except for the nitrogen contents (1% nitrogen content for N1, 1.8% for N2, respectively). As shown in Figure 5-1, both samples consist of 15 periods of QWs sandwiched by 0.7 µm top and 1 µm bottom Si-doped ($2 \times 10^{18} \text{cm}^{-3}$) GaAs contact layers. Each period is designed to consist of a 20 nm $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ outer barrier layer, 2 nm AlAs inner barrier layer and a 3 nm Si-doped ($1 \times 10^{18} \text{cm}^{-3}$) GaAsN Well layer. Both samples N1 and N2 were annealed. The samples were comprehensively investigated with different characterization tools to evaluate and

compare the properties of these two QW structures. In particular, nitrogen related behaviors in QW structures are investigated with the aid of characterization and simulation results.

5.2 Simulated Results with 10-band $k \cdot p$ method

Ten-band $k \cdot p$ model was utilized to simulate energy levels in GaAsN/AlAs/AlGaAs QWs with different nitrogen contents and well widths. Compared to the eight-band one, the introduction of N into InGaAs or GaAs leads to a strong interaction between the conduction band-edge states and one band such as E_1 or E_2 splitting into two such as E_{1-} and E_{1+} , or E_{2-} and E_{2+} , respectively. With the calculated results, we plot and analyze the subband dependence on the N concentration from 1.0% to 2.0% and the subband dependence on the well widths from 2.5 nm to 4 nm. Out of simulated results with verified QW parameters, the conduction band potential diagrams of one period of the DBQWs and dispersions of the conduction subbands in the well are plotted. In our calculations, energy reference is taken as the top of GaAsN valence band, and conduction band offset (CBO) ratio as 0.59, temperature as 5 K.

Figure 5-2 and Figure 5-3 show the dependence of the subbands (E_{1-} , E_{2-} , E_{1+} , E_{2+}) and the energy separation E_{21} ($=E_{2+}-E_{1-}$) on the well width from 2.5 nm to 4 nm, for 1% N concentration and 1.8% N concentration, respectively. Figure 5-4 shows the dependence of the subbands such as E_{1-} , E_{2-} , E_{1+} , and E_{2+} and the energy separation E_{21} ($=E_{2+}-E_{1-}$) on the increasing N concentration from 1% to 2%, for 3 nm well width. In these three figures, the solid lines are the subbands being localized in the well region (E_{1-} , E_{2+} from bottom to top). The dotted lines are the subbands being localized in the AlGaAs barriers (B_1 , B_2 , B_3 and B_4 , from bottom to top). There is monotonic decrease or increase in intersubband transition (ISBT) energy with increase of well widths from 2.5 nm to 3.0 nm or the nitrogen contents from 1% to 2%, respectively.

Figure 5-2 Dependence of subbands and ISBT energy E_{21} (separation between E_{2+} and E_{1-}) on well widths in $\text{GaAsN}_{0.01}/\text{AlAs}/\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ with 2nm inner barrier and 20 nm outer barrier, solid curves (except the lowest one) stand for excited states in QW and dash dot curves for ones in outer barrier.

Figure 5-3 Dependence of subbands and ISBT energy E_{21} (separation between E_{2+} and E_{1-}) on well widths in $\text{GaAsN}_{0.018}/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ with 2nm inner barrier and 20 nm outer barrier, solid curves (except the lowest one) stand for excited states in QW and dash dot curves for ones in outer barrier.

Figure 5-4 Dependence of subbands and ISBT energy E_{21} (separation between E_{2+} and E_{1-}) on the N concentration in $\text{GaAsN}/\text{AlAs}/\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ with 3nm well width, 2nm inner barrier and 20 nm outer barrier, solid curves (except the lowest one) stand for excited states in QW and dash dot curves for ones in outer barrier.

Figure 5-5 Schematic conduction band potential diagram of one period of the $\text{GaAsN}_{0.01}/\text{AlAs}/\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ DBQW with 2.9 nm well width, 2 nm inner barrier and 20.2 nm outer barrier, where the dot curves from bottom to top stand for excited states in outer barrier and can be defined as $B_1, B_2, B_3, \dots$, respectively.

Figure 5-6 Dispersions of the conduction subbands of one period of the GaAsN0.01/AlAs/Al0.25Ga0.75As DBQW with 2.9 nm well width, 2 nm inner barrier and 20.2 nm outer barrier.

Figure 5-7 Schematic conduction band potential diagram of one period of the GaAsN0.178/AlAs/Al0.3Ga0.7As DBQW with 2.85 nm well width, 2 nm inner barrier and 19.1 nm outer barrier, where the dot curves from bottom to top stand for excited states in outer barrier and can be defined as B1, B2, B3, ..., respectively.

Figure 5-8 Dispersions of the conduction subbands of one period of the GaAsN_{0.178}/AlAs/Al_{0.3}Ga_{0.7}As DBQW with 2.85 nm well width, 2 nm inner barrier and 19.1 nm outer barrier.

With simulated parameters by XRD analysis, we can utilize the ten-band $k \cdot p$ method to calculate energy levels for comparison with photoluminescence (PL) results. For sample N1, the intersubband transition energy was calculated as 807.2 meV (1.54 μm) and the interband transition (PL peak) energy as 1533.9 meV (808 nm); For sample N2, the intersubband transition energy was calculated as 921.6 meV (1.34 μm) and PL peak energy as 1462.8 meV (848 nm).

Figure 5-5 and Figure 5-7 show the schematic conduction band potential diagrams and dispersions of the conduction subbands of the GaAsN_{0.01}/AlAs /Al_{0.25}Ga_{0.75}As DBQW with 2.9 nm well width, 2 nm inner barrier and 20.2 nm outer barrier and GaAsN_{0.178} /AlAs /Al_{0.3}Ga_{0.7}As DBQW with 2.85 nm well width, 2 nm inner barrier and 19.1 nm outer barrier, respectively. The sub-band energy levels being confined in the well region are denoted by curved solid lines and those being confined in the outer barrier region are denoted by curved dotted lines. For both QW structures, the ground states are E_{1-} and the first excited states E_{2+} . With such double barrier schemes, carriers on E_{1-} confined by both inner and outer barriers mean low darkcurrent levels,

while carriers on E_{2+} confined only by the thin inner barrier mean more photoexcited electrons tunneling. Figure 5-6 and 5-8 show dispersions of the conduction subbands in GaAsN_{0.01}/AlAs /Al_{0.25}Ga_{0.75}As DBQW with 2.9 nm well width, 2 nm inner barrier and 20.2 nm outer barrier and GaAsN_{0.178} /AlAs /Al_{0.3}Ga_{0.7}As DBQW with 2.85 nm well width, 2 nm inner barrier and 19.1 nm outer barrier, respectively. At $k=0$, the highest and the lowest subbands are identified as S-like and the other two states as S_N-like, and the latter two are more flatten ones which come from nitrogen.

5.3 X-ray Diffraction results

Figure 5-9 HRXRD pattern of the sample N1 and the matched simulated one for GaAsN_{0.01}/AlAs /Al_{0.25}Ga_{0.75}As DBQW with 2.9 nm well width, 2 nm inner barrier and 20.2 nm outer barrier.

High-Resolution X-ray diffraction (HRXRD) analysis was performed on the Philips HRXRD system and showed the evidence for the structure parameters by fitting QW parameters to achieve the best ones. Figure 5-9 and Figure 5-10, for sample N1 and N2, respectively, show the Bragg reflection rocking curves and simulation results with best fitting parameters shown in legends. For sample N1, GaAsN well width is

verified as 2.9 nm, the N content as 1%, the AlGaAs barrier width as 20.2 nm, and the Al composition as 25%; For sample N2, GaAsN well width was verified as 2.85 nm, the N content as 1.78%, the AlGaAs barrier width as 19.1 nm, and the Al composition as 30%. For both sample N1 and N2, because the lattice constant of GaAsN is smaller than that of GaAs, it gives rise to the tensile strain in QWs, therefore, strong satellite features were observed at the right side of the GaAs (004) substrate peaks, as shown in Figure 4-30 and Figure 4-31. We can also conclude that the structural quality of sample N2 deteriorates with more nitrogen incorporation from the fact that the satellite peaks' magnitudes of sample N2 is a bit weaker than the ones of sample N1.

Figure 5-10 HRXRD pattern of the sample N2 and the matched simulated pattern for GaAsN_{0.178}/AlAs/Al_{0.3}Ga_{0.7}As DBQW with 2.85 nm well width, 2 nm inner barrier and 19.1 nm outer barrier.

5.4 Photoluminescence results

For the PL measurements, both samples N1 and N2 were etched till QW layers for better luminescence, and the 514.5 nm Ar⁺ laser was used as excitation. The luminescence signals were filtered by a 690 nm high pass filter, then dispersed by a Spex 0.75m monochromator and finally detected by a PMT photodetector.

Photoluminescence characterization on sample N1 and N2 was done in the same experimental conditions, and results of sample N1 and N2 were shown in Figure 5-11 and Figure 5-12, respectively.

Figure 5-11 Sample N 1's PL spectrum with the 514.5 nm Ar+ laser excitation at 5 K.

Figure 5-12 Sample N 2's PL spectrum with the 514.5 nm Ar+ laser excitation at 5 K.

For sample N1, the 1490 meV peak can be assigned to GaAs bulk material (large magnitude comes from more substrate exposed to laser incidence), the 1554 meV

peak to GaAsN QW (1533.9 meV in theory) and the 1874 meV peak to AlGaAs barrier(1872.8 meV in theory); For sample N2, the 1426 meV peak can be assigned to GaAsN QW (1462.8 meV in theory), the 1490 meV peak to GaAs bulk material, and the 1857 meV peak to AlGaAs barrier(1864.5 meV in theory). There are overall good agreements between experimental and calculated ones by ten-band $k \cdot p$ method, however, sample N2's energy difference between experiment and simulated results is larger than that of sample N1's. We think it is due to poor growth performance when more nitrogen atoms are incorporated. With comparison between Figure 5-11 and Figure 5-12, for IBT in wells, the 128 meV (1554 meV-1426 meV) energy reduction (71.1 meV in theory) can be observed and considered as a direct result of nitrogen content increase; For IBT in outer barrier-wells, the energy reduction of 17 meV (8.8 meV in theory) from 1874 meV (1872.8 meV in theory) to 1857 meV (1864.5 meV in theory) can be observed, and the reason is that with more nitrogen incorporation, energy levels are reduced more in outer AlGaAs barrier-well.

Figure 5-13 Sample N1's PL magnitude dependence of energy.

Figure 5-14 Peak energy dependence of temperature.

When we plot peak energies with increasing temperature as shown in Figure 5-13, an S-shaped shift as shown in Figure 5-14 can be observed on sample N1. In Figure 5-13 and 5-14, a red shift appeared with temperature increased from 5 K to 50 K, and from 90 K to 250 K, however, an abnormal blue shift appeared during the total red shift tendency with measurement temperature increased from 50 K to 90 K. This kind of S-shaped shift with increasing temperature was also shown in the Ref. [37-39] and considered as related to nitrogen localizations. As we know, the red shift is normally explained as a bandgap reduction with increasing temperature by the conventional Varshni's law, and the PL emission from 5 K to 50 K in Figure 5-13 and Figure 5-14 comes from localized states located a few tens of meV below E_{1HH_1} and closely following the E_{1HH_1} dependence with temperature; For the blue shift from 50 K to 90 K in these two figures, we can understand it as that, with increased temperature, some carriers have sufficient thermal energy to reach E_{1HH_1} , so radiative recombinations come from both E_{1HH_1} and the localized states [37-42].

5.5 Photocurrent results

Figure 5-15 The plot of sample N1's darkcurrent versus bias voltage

Figure 5-16 The plot of sample N2's darkcurrent versus bias voltage.

With the procedures described in the chapter 3, samples N1 and N2 were fabricated into QWIP devices. With the assembled devices under measurement, we obtained the sample's dark current. Figure 5-15 and Figure 5-16 show plots of the dark current

versus bias voltage for devices from sample N1 and N2, respectively. When the bias voltage increases to around 2V, I_d of sample N1 reaches 10^{-9} A order of magnitude and I_d of sample N2 reaches 10^{-7} A order of magnitude. Although nitrogen is incorporated in QW regions, it can be seen that the dark current levels are overall very slow due to good QW confinement of electrons on ground states. Furthermore, we can also see that the dark current level of N2 QWIP device is overall higher than that of N1 due to higher nitrogen concentration of N2.

As of now, we have not achieved the evident photo response from sample N1 and N2, this obstacle may be due to the nitrogen related defects that affect the intersubband transition.

5.6 Summary for GaAsN/AlAs/AlGaAs QW structures with different N contents

The ten-band $k \cdot p$ model was applied to simulate and plot subband levels and ISBT energy dependence on the N concentration and well widths. We characterized and compared GaAsN/AlAs/AlGaAs quantum well (QW) structures with nitrogen contents of 1% and 1.8%, respectively, to analyze the nitrogen related behaviors in QW structures. With the parameters verified by HRXRD, we utilized the ten-band $k \cdot p$ model to plot schematic conduction band potential diagram and dispersions of the GaAsN conduction subbands for both QW structures. With analysis of simulated and photoluminescence results for different nitrogen contents, we can find good agreements between calculated results and PL peak positions. Through comparison of PL peaks between samples of 1% and 1.8% N contents, 128 meV IBT energy reduction in wells and 17 meV in outer barriers for nitrogen increase were observed. PL peak energy shows an S-shaped shift with increasing temperature, and is considered as related to nitrogen localizations. In addition, although nitrogen incorporated in QW regions worsens crystal quality and will increase dark current levels, QWIPs of GaAsN/AlAs/AlGaAs DBQW can overall obtain low dark current

levels due to good QW confinement of electrons on ground states. Finally, it can also be found that crystal quality deteriorate with more nitrogen incorporation, which is verified by XRD characterization and higher dark current level from devices of more N content.

Chapter 6 Conclusions and Recommendations for Future Work

6.1 Conclusions

Two kinds of DBQW, GaAs/AlAs/AlGaAs and GaAsN/AlAs/AlGaAs, were experimentally and numerically investigated. For GaAs/AlAs/AlGaAs, the eight-band $k \cdot p$ model was applied to simulate and plot the subband level and ISBT energy dependence on the well widths. We characterized and compared GaAs/AlAs/AlGaAs quantum well (QW) structures with well widths of 2 nm, 4 nm and 6 nm, respectively, to analyze subband energy dependence on well widths in DBQW structures. With the QW parameters verified by HRXRD, TEM or EDX, we utilized the eight-band $k \cdot p$ model to plot schematic conduction band potential diagram on these three QW structures. With analysis of simulation and photoluminescence results, we can find good agreements among calculated results, PL peak positions and PLE maxima. Through PLE characterization, we can further confirm the identification of both PL peaks and PLE maxima for sample D4 and D6, with exception of sample D2's PLE maximum from QW's intersubband transition due to its weak PL peak. The reason comes from sample D2's weak PL peak due to ground states higher than AlGaAs barrier, and the fact that the large magnitude of PL peak as detection wavelength is very important for the clear PLE maxima. In addition, sample D6's FTIR spectrum evidently shows an absorption signal on the curve, which agrees well with simulated results.

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structures. With the parameters verified by HRXRD, we utilized the ten-band $k \cdot p$ model to plot schematic conduction band potential diagram and dispersions of the GaAsN conduction subbands for both QW structures. With analysis of simulation and photoluminescence results for different nitrogen contents, we can find good agreements between calculated results and PL peak positions. Through comparison of PL peaks between samples of 1% and 1.8% N contents, 128 meV IBT energy reduction in wells and 17 meV in outer barriers for nitrogen increase were observed. In addition, PL peak energy shows an S-shaped shift with increasing temperature, and is considered as related to nitrogen localizations. Finally, it can also be found that crystal quality deteriorates with more nitrogen incorporation, which is verified by XRD characterization and higher dark current level from devices of more N content.

6.2 Recommendations for future work

As stated in the previous section, the desirable photo response (photocurrents) of the GaAs(N)/AlAs/AlGaAs double barrier quantum structures were not obtained in this project till now. This is caused by many factors such as poor QW confinement, the poor material quality, defects related to nitrogen, unperfected procedures and skills of fabrication and photocurrent characterization, etc. Therefore, fabrication and photocurrent characterization of GaAs based and GaAsN based double barrier QWIPs need to further be optimized for good photocurrent performance. Further FTIR characterization and photocurrent measurement of existing samples and new samples are recommended.

To further understand change of energy band structures and nitrogen behaviors in GaAs(N)/AlAs/AlGaAs DBQW, further PLE analysis (including the ones under increasing temperature) on GaAsN/AlAs/AlGaAs DBQW and on original and annealed GaAs/AlAs/AlGaAs DBQW samples with different conditions are recommended. Origins and temperature behaviors of the Stokes Shift can be further probed and investigated.

Besides the above experimental efforts on GaAs(N) based DBQW structures, investigations on applications of ten-band $k \cdot p$ model in DBQW samples of high nitrogen contents with higher precise are recommended.

Publication list

1. **D. S. Li**, W. J. Fan, Y. X. Dang, B. S. Ma, D. H. Zhang and S. F. Yoon, "Investigation of Intersubband Transition in GaAs/AlGaAs Quantum Well Infrared Photodetectors", *Advanced Material Research*. 31, 105 (2008)
2. **D. S. Li**, W. J. Fan, "Optical characterization of GaAsN/AlAs/AlGaAs Quantum Wells", *Proc WCEEENG 2009*, Cairo, Egypt (accept in 2008)
3. **D. S. Li**, W. J. Fan, B. S. Ma, Y. X. Dang and D. H. Zhang, "Investigation of energy band structures and opto-electrical properties in GaAs/AlAs/AlGaAs Quantum Well structures" (submitted)

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