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Intersubband Transitions and Anneal-induced Interdiffusion Effects in III-V-N Quantum Wells

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A Thesis Submitted To The Nanyang Technological University
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Abbreviations

BAC	Band-Anticrossing
BEP	Beam Equivalent Pressure
CBO	Conduction Band Offset
CQW	Coupled Quantum Well
DBQW	Double-Barrier Quantum Well
FWHM	Full Width at Half Maximum
HBT	Heterojunction Bipolar Transistor
IBT	Interband Transition
IR	Infrared
ISA	Intersubband Absorption
ISBT	Intersubband Transition
LCAO	Linear Combination of Atomic Orbitals
MME	Momentum Matrix Element
N	Nitrogen
PL	Photoluminescence
QCL	Quantum-Cascade Laser
QW	Quantum Well
QWIP	Quantum Well Infrared Photodetector
RHEED	Reflection High-Energy Electron Diffraction
RTA	Rapid Thermal Annealing

SQW	Single Quantum Well
SS-MBE	Solid-Source Molecular Beam Epitaxy
VCSEL	Vertical-Cavity Surface-Emitting Laser

Symbols

a_0	Lattice Constant
bw	Width of the Barrier
c	The Speed of Light
$c.c.$	The Complex Conjugate of the Corresponding Symmetrical Item
	Along the Diagonal Line
D	Diffusion Coefficient
E_a	Activation Energy
E_c	Conduction Band Energy
ΔE_c	Strained Conduction Band Offset
E_F	Quasi-Fermi Level
E_g	Energy Gap
E_N	Nitrogen-Related Energy Level
E_v	Valence Band Energy
ΔE_v	Strained Valence Band Offset
ϵ_0	Free-Space Dielectric Constant

h_c	Critical Thickness
k	Wave Vector
L	Periodicity of the Quantum Well
L_d	Diffusion Length
m_0	Free Electron Mass
m_e^*	Effective Mass of Electron
n_r	Refractive Index
ω	Photon Frequency
$\mathbf{p}$	Momentum Operator
Φ	Envelop Function
Ψ	Total Wavefunction
Q_c	Strained Conduction Band Offset Ratio
Q_v	Strained Valence Band Offset Ratio
$\mathbf{r}$	Position Vector
σ	Poisson's Ratio
Δ_{SO}	Spin-Orbit Splitting Energy
ww	Width of the Well
z	Coordinate in the Growth Direction

Table of contents

Acknowledgements	i
List of Figures	ix
List of Tables	xv
Summary	xvii
1 Introduction	1
1.1 Background and motivation	1
1.2 Objectives	4
1.3 Major contributions	6
1.4 Organization of the thesis	7
2 Theoretical models and calculations on the related parameters	8

2.1	Formalism and solution by the $k \cdot p$ method	8
2.1.1	The eight-band $k \cdot p$ method	10
2.1.2	The ten-band $k \cdot p$ method	18
2.2	Calculation of band structure related parameters	22
2.2.1	Linear interpolation method	22
2.2.2	Calculation of E_g and m_e^* within the eight-band and the ten-band $k \cdot p$ regime	23
2.2.3	Strained band offset ratios Q_C and Q_V	28
2.2.4	Critical thickness	32
2.2.5	Calculation of strain related parameters for different QW structures	34
2.2.6	Effects of interdiffusion	36
2.2.7	Effects of the electric field	40
2.3	Mathematical formulation of the optical absorption in QW systems . .	41
3	Study of 3-5 and 8-12 μm intersubband transitions in InGaAsN/GaAs quantum wells	44
3.1	Introduction	44
3.2	Experimental details	46
3.3	Results and discussion	47

3.4	Summary	55
4	Study of intersubband transitions in InGaAsN/AlAs/AlGaAs double-barrier quantum wells for absorptions at 1.31 and 1.55 μm	56
4.1	Introduction	56
4.2	Results and discussion	58
4.2.1	Calculation with the eight-band $k \cdot p$ model	58
4.2.2	Calculation with the ten-band $k \cdot p$ model	68
4.2.3	Comparison of the results by the eight-band model with the ten-band model	86
4.3	Summary	87
5	Study of inter-well intersubband transitions in InGaAsN/AlAs coupled quantum wells for emissions at 3-5 μm	88
5.1	Introduction	88
5.2	Results and discussion	90
5.3	Summary	106
6	Study of anneal-induced interdiffusion effects in InGaAsN/GaAs and GaAsSbN/GaAs quantum wells	107
6.1	Introduction	107

6.2	Results and discussion	110
6.2.1	Effects of interdiffusion in InGaAsN/GaAs quantum well structure emitting at $1.3\ \mu\text{m}$	110
6.2.2	Effects of interdiffusion in GaAsSbN/GaAs quantum well structure	116
6.3	Summary	124
7	Conclusion and recommendations	126
7.1	Conclusion	126
7.2	Recommendations for future research	129
	Author's Publications	130
	Bibliography	133

List of Figures

2.1	One period of a single quantum well structure along the growth direction.	12
2.2	One period of a double-barrier quantum well structure along the growth direction.	13
2.3	One period of a coupled quantum well structure along the growth direction.	13
2.4	Dependence of Q_C for $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ QWs on the indium composition.	30
2.5	Dependence of Q_V for $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}$ heterostructures on the antimonide composition.	31
2.6	Potential profiles for a strained SQW or a CQW structure.	34
2.7	Potential profiles for a strained DBQW structure.	37
3.1	(a) Interband transitions, and (b) intersubband transitions.	45
3.2	Dependence of subband energy and transition energy in the conduction band of the $\text{InGaAsN}/\text{GaAs}$ QW structure on the indium composition, the nitrogen composition, and the well width.	48

3.3	Dependence of subband energy and transition energy in the conduction band of the InGaAsN/GaAs QW structure on the barrier width and the temperature.	50
3.4	(a) The reported calculation result and (b) our calculated spectrum by the eight-band model of the $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}/\text{GaAs}$ QW structure.	51
3.5	(a) Experimental result and (b) calculated spectrum by the ten-band model of the $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.99}\text{N}_{0.01}/\text{GaAs}_{0.998}\text{N}_{0.002}$ QWIP structure. . .	52
3.6	Band structure of $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.99}\text{N}_{0.01}/\text{GaAs}_{0.998}\text{N}_{0.002}$ quantum well with well width of 25 Å at room temperature.	53
3.7	(a) Band structure and (b) absorption spectra of an $\text{In}_{0.6}\text{Ga}_{0.4}\text{As}_{0.95}\text{N}_{0.05}/\text{GaAs}$ quantum well with well width of 20 Å at room temperature.	54
4.1	Schematic conduction band potential diagram of one period of the DBQW at 82 K.	60
4.2	Dependence of subband energies and transition energies in the conduction band of the InGaAsN/AlAs/AlGaAs DBQW structures on indium and nitrogen compositions.	62
4.3	Dependence of subband energy and transition energy in the conduction band on the well width.	64

4.4	Dependence of subband energy and transition energy in the conduction band on the aluminum concentration and the temperature.	66
4.5	The calculated intersubband transition coefficients as a function of the transition energy.	67
4.6	Energy levels and absorption coefficients in a $\text{GaAs}_{0.99}\text{N}_{0.01}/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW.	70
4.7	Energy levels and absorption coefficients in a $\text{GaAs}_{0.993}\text{N}_{0.007}/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW with the well width of 30 Å.	72
4.8	Energy levels and absorption coefficients in a $\text{GaAs}_{0.993}\text{N}_{0.007}/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW with the well width of 55 Å.	73
4.9	Dependence of the squared wave functions on the N concentration. . . .	76
4.10	Dependence of the percentage of the components in the E_{1-} state on the N concentration.	77
4.11	Dependence of the percentage of the components in the E_{1+} state on the N concentration.	78
4.12	Dependence of the percentage of the components in the E_{2-} state on the N concentration.	78
4.13	Dependence of the percentage of the components in the E_{2+} state on the N concentration.	80

4.14	Dependence of energy dispersion curves for the subbands in the conduction band for an $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{1-y}\text{N}_y/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW on the N concentration.	81
4.15	Dependence of the subbands, the energy separation, and the absorption coefficients in the conduction band for an $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{1-y}\text{N}_y/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW on the N concentration.	82
4.16	Dependence of the subbands, the energy separation, and the absorption coefficients in the conduction band for an $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.985}\text{N}_{0.015}/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW on the well width.	83
4.17	Dependence of the subbands, the energy separation, and the absorption coefficients in the conduction band for an $\text{In}_x\text{Ga}_{1-x}\text{As}_{0.985}\text{N}_{0.015}/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW on the In concentration.	85
5.1	Comparison of the active region of the laser heterostructure at threshold bias between the results of our calculation and the reference.	91
5.2	Schematic conduction band diagrams and the modulus squared of the bound state wave functions of a single period of the $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.97}\text{N}_{0.03}/\text{AlAs}$ coupled quantum well.	93
5.3	Dependence of subband and transition energy for active regions on (a, b) well 1 widths, and (c, d) well 2 widths.	95

5.4	Dependence of subband energy and transition energy for active regions on (a, b) well 3 widths, (c) indium composition and (d) nitrogen composition.	98
5.5	Dependence of subband energy and transition energy for active regions on (a) barrier 1,2 widths, (b) barrier 3 widths, (c) electric field and (d) temperature.	102
5.6	Conduction band profiles of the active regions for an $\text{In}_{0.2}\text{Ga}_{0.8}\text{As}_{0.97}\text{N}_{0.03}/\text{AlAs}$ QCL structure at room temperature.	105
6.1	Dependence of electron, heavy hole, and light hole confinement potential for a $64 \text{ \AA}-\text{In}_{0.36}\text{Ga}_{0.64}\text{As}_{0.983}\text{N}_{0.017}/250 \text{ \AA}-\text{GaAs}$ QW on the diffusion length.	111
6.2	Dependence of (a) bulk band-gap energy profile, (b) the change of the band-gap due to strain, and (c) strained band-gap energy profile for a $64\text{\AA}-\text{Ga}_{0.64}\text{In}_{0.36}\text{N}_{0.017}\text{As}_{0.983}/250\text{\AA}-\text{GaAs}$ QW on the diffusion length.	112
6.3	Dependence of (a) heavy hole band edge profile, (b) $2 \times Q_{\epsilon}$ profile for a $64 \text{ \AA}-\text{In}_{0.36}\text{Ga}_{0.64}\text{As}_{0.983}\text{N}_{0.017}/250 \text{ \AA}-\text{GaAs}$ QW on the diffusion length.	114
6.4	Dependence of $e1\text{-HH1}$ transition energy for a $64 \text{ \AA}-\text{In}_{0.36}\text{Ga}_{0.64}\text{As}_{0.983}\text{N}_{0.017}/250 \text{ \AA}-\text{GaAs}$ QW on the diffusion length.	115
6.5	Low-temperature (4K) photoluminescence spectra of a $\text{GaAs}_{0.863}\text{Sb}_{0.13}\text{N}_{0.007}/\text{GaAs}$ QW as-grown sample and the samples after RTA.	117

6.6	Dependence of electron, heavy hole, and light hole confinement potential for a $\text{GaAs}_{0.863}\text{Sb}_{0.13}\text{N}_{0.007}/\text{GaAs}$ QW on the diffusion length.	118
6.7	Dependence of (a) bulk band-gap energy profile, (b) the change of the band gap due to strain, and (c) strained band-gap energy profile for a $\text{GaAs}_{0.863}\text{Sb}_{0.13}\text{N}_{0.007}/\text{GaAs}$ QW on the diffusion length.	119
6.8	Dependence of (a) HH band profile, (b) $2Q_\epsilon$ profile, and (c) LH band profile for a $\text{GaAs}_{0.863}\text{Sb}_{0.13}\text{N}_{0.007}/\text{GaAs}$ QW on the diffusion length. . .	121
6.9	Dependence of $e1\text{-HH1}$ transition energy for a $\text{GaAs}_{0.863}\text{Sb}_{0.13}\text{N}_{0.007}/$ GaAs QW on the diffusion length.	122
6.10	Dependence of calculated PL-peak shifts for a $\text{GaAs}_{0.863}\text{Sb}_{0.13}\text{N}_{0.007}/$ GaAs QW on the diffusion length.	123
6.11	Estimated diffusion constants D as a function of inverse temperature for a $\text{GaAs}_{0.863}\text{Sb}_{0.13}\text{N}_{0.007}/\text{GaAs}$ QW.	123

List of Tables

2.1	Parameters for binary compounds used in the thesis	24
2.2	Summary of reported conduction band offset ratio Q_C for $\text{In}_x\text{Ga}_{1-x}\text{As}/$ GaAs QWs.	29
2.3	The critical thickness (in unit of Å) obtained for $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ with respect to In (x) and N (y) compositions.	33
2.4	The conduction and the valence band edge related variables considering (a) compressive strain and (b) tensile strain.	36
2.5	The conduction and the valence band edge related variables considering all possible types of strains.	38
4.1	Comparison of theoretical transition energies by the eight-band $k \cdot p$ model with reported values.	59
4.2	Structures of the DBQWs for the comparison with the literature by the 10-band model and the comparison results	68

5.1	Comparison of theoretical transition energies of GaAs/AlGaAs by the eight-band $k \cdot p$ model with published values.	92
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Summary

III-V compounds consisting of nitrogen are candidates for interband transition applications because of their small band gap due to the nitrogen (N) incorporation. In addition, there is renewed interest in their possible applications in intersubband transition based devices owing to its large conduction band offset.

In this thesis, we have investigated the electronic band structures and optical properties for InGaAsN based quantum wells. The eight-band and the ten-band $k \cdot p$ models combined with an envelope function approximation have been used. Various quantum well types, including single quantum well, double-barrier quantum well, and coupled quantum well have been studied. The calculated intersubband transition energy ($e1 \rightarrow e2$ in the same well or $e1$ in one well $\rightarrow e1$ in another well) are in agreement with the published results. Based on the results of the energy band dispersion relations, the Fermi-level and the momentum matrix elements are determined. It leads to the study of the intersubband absorption coefficients. Utilizing the reliable calculation methods, we have successfully designed the GaAs based quantum well infrared photodetector (QWIP) structures operating at 1.31-1.55 and 8-12 μm . Appropriate

comparisons with the experimental results show the validity of our results. It is a good approach to design QWIPs for communication applications on economical GaAs substrates. In addition, the enlighten InGaAsN well combined with AlAs barrier also motivates us to design GaAs based quantum cascade laser (QCL) structures emitting within 3-5 μm range. Consequently, an optimized structure is obtained with 3.4 μm emission under electric field, which is very useful for the design of mid-infrared wavelength QCLs by the matured GaAs technology.

The effects of thermal annealing for a compressively strained 64 Å-In_{0.36}Ga_{0.64}As_{0.983}N_{0.017}/250 Å-GaAs quantum well have been investigated through eight-band $k \cdot p$ model considering the band anticrossing model for the description of the InGaAsN band gap variation. The modification of the In concentration profile due to In-Ga interdiffusion during thermal annealing is taken into account through the Fick's law. A good agreement is obtained between calculated and experimental energies of optical transitions. The corresponding curve of ground state transition ($e1 \rightarrow \text{HH1}$) energy dependent on the diffusion length is plotted. Subsequently, the effect of annealing on the photoluminescence (PL) in GaAsSbN/GaAs quantum well grown by solid-source molecular-beam epitaxy (SS-MBE) has been investigated. Low-temperature (4 K) PL peaks shift to higher energy sides with the increase of annealing temperature. An As-Sb atomic interdiffusion at the heterointerface is proposed to be one reason of this effect. The compositional profile of the QW after interdiffusion is modeled by an error function distribution and calculated with the ten-band $k \cdot p$ method. A good agreement is ob-

tained between calculated and experimental energies of optical transitions. Finally, the diffusion coefficient and the activation energy are given out.

Chapter 1

Introduction

1.1 Background and motivation

Over the last decade, a considerable number of studies have been made on N containing III-V alloys owing to the strong modifications exerted by N on the band structure of the III-V host. In contrast to that the band gap of the conventional III-V compound generally follows a linear interpolation of the binary constituents, the band gap of III-V-N decreases rapidly and non-linearly with the addition of small concentration of N [1–4]. It is well known that an isolated N atom introduces a localized state with energy level E_N in III-V materials. The band-anticrossing (BAC) model [5–8] has been successfully applied to interpret this N related state and hence the giant band gap reduction both theoretically and experimentally. As a result, the variation of band gap in the dilute nitride system is characterized by a very large “bowing” effect. In addition, a strong increase of the electron effective mass on the nitrogen concentration has been found by a variety of experimental works [9–14]. The decrease in the fundamental band gap and

the associated increase in the effective mass of electrons in the dilute nitride system have opened the new pathway to the potential applications of semiconductor device.

A quaternary dilute nitride alloy is more extensively used than a ternary so as to lattice match the dilute nitride alloy to the rest of the epitaxial device structure. It is due to the fact that the reduction in the lattice constant by nitrogen can be balanced by the co-incorporation of an atom of larger atomic radius, such as In or Sb. Thereby, studies of quaternaries such as InGaAsN and GaAsSbN are more common than those of ternary dilute nitrides.

Initially proposed by Kondow *et al.* [2], InGaAsN is the most popular III-V-N today. In the past decade, motivated by the need of low-cost sources for optical communications, InGaAsN/GaAs quantum well (QW) has exhibited its challenging advantages over conventional InGaAsP/InP system for emission at 1.3-1.55 μm wavelengths. The significant advantages of InGaAsN/GaAs system include: First, high performance is expected at high-temperature operation due to the larger conduction band offset (CBO) compared with that of InGaAsP/InP lasers. Second, InGaAsN active layer can be straightly combined with high reflectivity GaAs/AlAs Bragg mirrors. Third, from an economic viewpoint, GaAs substrate is cheaper and more robust compared to InP substrate. Thereby, InGaAsN/GaAs system could potentially increase the production yield. Finally, the removal of the thermoelectric cooler used to dissipate heat generated by the phosphide-based lasers can be expected by using the nitride system. Successful realizations of vertical cavity surface emitting lasers (VCSELs) and edge-emitting lasers

for use in local- and metro-area communications networks have been reported [15, 16]. Additionally, the InGaAsN alloy was also studied for solar cells in order to improve their efficiency [15, 17], and for heterojunction bipolar transistors (HBTs) in order to reduce their turn-on voltage [18, 19].

So far, a considerable number of studies on the device applications of the promising InGaAsN alloy have been restricted on the interband transitions (IBTs). On the other hand, research on the intersubband transitions (ISBTs) occurring in the large CBO of InGaAsN/(Al)GaAs system lags far behind with only a few reports [12, 20]. Nevertheless, the large CBO up to more than 1 eV makes this system very promising in GaAs-based short-wavelength ($<5 \mu\text{m}$) optoelectronic device applications, such as quantum well infrared photodetectors (QWIPs) and quantum-cascade lasers (QCLs). Thereby, the study of InGaAsN/(Al)GaAs QW structure as an alternative system grown on the more mature and economical GaAs substrates are motivated for short-wavelength ISBT device applications.

As-grown InGaAsN samples are usually annealed in order to reduce N-related defect states. Annealing increases the photoluminescence (PL) efficiency but it simultaneously blueshifts the PL peak emission wavelength of InGaAsN/GaAs QW. This has significant implication to the QW-laser design and processing, as the peak emission wavelength of as-grown InGaAsN/GaAs QW would need to emit at a longer wavelength than $1.3 \mu\text{m}$ to make provision for the annealing induced peak wavelength blueshift. It is believed that compositional changes across the interface, which are related to N

and In compositions in the InGaAsN, promote annealing induced blueshift.

GaAsSbN is a direct competitor to the more established InGaAsN system. Less nitrogen is required to reach a specific band gap in the antimonide than in the indium-containing quaternary. It has exhibited its potential in 1.55 μm GaAs-based IBT lasers [21] and HBTs [22]. However, like InGaAsN system, GaAsSbN also suffers from the poor optical properties due to the N related defects. When increasing the nitrogen composition in III-V-N semiconductors, the PL intensity is decreased and the PL full width at half maximum (FWHM) is increased. Rapid thermal annealing (RTA) has again been shown to significantly improve the optical quality of this material as of InGaAsN [22]. But there still exists a large amount of PL blueshifts. It leads us to investigate the possible reasons for this blueshift.

1.2 Objectives

As explained in the previous section, there are two major objectives of our project:

One of them is to investigate the ISBTs within the conduction band of the InGaAsN/(Al)GaAs QWs for QWIPs and QCLs.

For QWIPs, firstly, the band structures of InGaAsN/GaAs single quantum wells (SQWs) are to be understood by using the $k \cdot p$ model and then by varying the well width, concentration of the constituents etc., potential structures for QWIPs working at atmospheric window 3-5 and 8-12 μm are to be found out. With that, the stud-

ies on optical properties such as absorption coefficients are to be carried out for the realization of the design and to compare with the experimental work. Secondly, the band structures of InGaAsN/AlAs/AlGaAs double-barrier quantum wells (DBQWs) are to be understood by using the $k \cdot p$ model and then by varying the well width, concentration of the constituents etc., optimum structures for QWIPs operating at telecommunication wavelength 1.3-1.55 μm are to be explored, followed by the studies on absorption coefficients.

For QCLs, the band structures of InGaAsN/AlAs coupled quantum wells (CQWs) are to be known by using the $k \cdot p$ model and then by varying the well width, concentration of the constituents etc., optimum structures for the active regions of QCLs operating at mid-infrared wavelength 3-5 μm are to be obtained.

The other major objective is to study the mechanism of PL blueshifts of the annealed InGaAsN and GaAsSbN QWs.

For the InGaAsN alloy, the band structures of interdiffused InGaAsN/GaAs SQWs are to be obtained by using the $k \cdot p$ model with the Fick's law and then the dependence of the IBT energy on the diffusion length is to be understood. After that, the similar work is to be applied to the GaAsSbN SQWs so that the diffusion coefficients and the activation energy can be derived.

The $k \cdot p$ models used in our present work include the eight-band and the ten-band models.

1.3 Major contributions

In this work, for the theoretical basis on the design of ISBT structures and the study of the interdiffusion effect, extensive comparisons with theoretical and/or experimental results are conducted by using the $k \cdot p$ model combined with the BAC model. The results show the validity of this formalism in calculating the energy band structures of InGaAsN/GaAs SQWs, InGaAsN/AlAs/AlGaAs DBQWs, InGaAsN/AlAs CQWs, annealed InGaAsN/GaAs SQWs and annealed GaAsSbN/GaAs SQWs.

The major contributions of our work are as follows:

(I) An InGaAsN/GaAs QW structure for QWIP with intersubband absorption around $10 \mu\text{m}$ is designed and the calculation results agree with the characterization results.

(II) Theoretical studies reveal that QWIPs with absorption wavelengths around $3\text{-}5 \mu\text{m}$ by using InGaAsN/GaAs QWs require high In and N concentrations.

(III) Successful design of InGaAsN/AlAs/AlGaAs DBQW structures for QWIPs which correspond to 1.31 and $1.55 \mu\text{m}$ intersubband absorptions, respectively, have been achieved.

(IV) An emission wavelength as short as $3.4 \mu\text{m}$ has been achieved by utilizing an InGaAsN/AlAs CQW for the QCL active region. It could avoid introducing an upper lasing level beyond the X-minima of the AlAs barrier.

(V) The dependence of IBT energy on the diffusion length is obtained with an InGaAsN/GaAs SQW structure which can emit around $1.3\ \mu\text{m}$.

(VI) The effect of annealing on the PL in GaAsSbN/GaAs quantum wells grown by solid-source molecular-beam epitaxy (SS-MBE) has been investigated. Interdiffusion constant D and the activation energy are obtained.

1.4 Organization of the thesis

In **Chapter 1** of this thesis, we provide a brief introduction of the background and the motivation behind this study and present the objectives and contributions during this work. In **Chapter 2**, detailed theoretical models, band parameters, and optical properties are described. In **Chapter 3**, we look into the design of potential 3-5 and 8-12 μm QWIPs based on InGaAsN/GaAs QW structure. Design of DBQW photodetectors with absorptions at 1.31 and 1.55 μm by applying InGaAsN/AlAs/AlGaAs DBQWs are discussed in **Chapter 4**. **Chapter 5** is dedicated to the study of 3.4 μm InGaAsN/AlAs QCLs. The RTA-induced blueshifts of PL peak wavelengths in InGaAsN/GaAs and GaAsSbN/GaAs QWs are studied by applying the atomic interdiffusion mechanism in **Chapter 6**. Finally, concluding remarks are presented in **Chapter 7**.

Chapter 2

Theoretical models and calculations on the related parameters

2.1 Formalism and solution by the $k \cdot p$ method

The electronic states and energy levels of the semiconductor device are found in principle by solving the Schrödinger equation [23]:

$$H\Psi = [\frac{\mathbf{p}^2}{2m_0} + V(\mathbf{r})]\Psi = E\Psi, \quad (2.1)$$

where H is the Hamiltonian, Ψ is the total wave function, E is the total energy, $\mathbf{p}$ is the momentum operator, $\mathbf{r}$ is the position vector, m_0 is the free electron mass and $V(\mathbf{r})$ is the total three-dimensional atomistic potential, including all effects of the interfaces between material A and B for the A/B heterostructures. In a QW structure, the crystal composition and/or strain varies from region to region and approximations are needed in order to solve Eq. (2.1). Many such approximate methods are now well

known and extensively used, such as the LCAO (tight-binding), the Augmented Plane Wave, the Green's Function, the Orthogonalized Plane Wave, and the Pseudopotential methods [24].

In this thesis, we use the $k \cdot p$ method together with the envelope-function approximation (EFA). The $k \cdot p$ approach [25, 26] uses a perturbation theory description of band dispersion for pure alloy A or B of the A/B QWs within a small set of near-edge bands identified as physically relevant. In the EFA, the form used for the wave function in the heterostructure assumes that envelope functions vary on a scale much larger than the lattice constant of either A or B . The $k \cdot p$ method together with the EFA can be an extremely concise representation of QW electronic properties, usually require only material parameters for the bulk materials A and B and dimensions and orientations of the A and B regions. In particular, the computational effort is essentially independent of the number of atoms in the system. The model has been eminently successful in a variety of applications [27–36].

By using the $k \cdot p$ method and envelope functions, it means that in the QWs, the wave function for the n th level is assumed to be of the form

$$\Psi_n(z) = \sum_j \Phi_n^j(z) u_j, \quad (2.2)$$

where z is the coordinate in the growth direction, the $\Phi_n^j(z)$ are called envelope functions and the u_j are the periodic part of the Bloch basis functions at the zone center.

2.1.1 The eight-band $k \cdot p$ method

The choice of how many functions to solve the equation (2.2) will be needed is depending on the details of semiconductor material systems: For a III-V zinc-blende semiconductor, it is appropriate to include eight functions in the set, namely, the spin up and spin down zone center Bloch waves from the conduction band minimum, and the spin up and spin down functions from each of the three degenerate p-like states (heavy, light, and spin-orbit split off hole states) at the top of the valence band. It is called as an eight-band $k \cdot p$ model. The results of this approximation is that the Schrödinger equation is converted into a set of eight coupled differential equations for the envelope functions. In the eight-band model of the $k \cdot p$ theory approach, the lowest conduction band states and the upper valence band states at wave vector $\mathbf{k}$ near the Γ point are expanded in terms of the eight zone center eigenstates composed of the spatial $L=0$ conduction band basis function $|S\rangle$ and of the $L=1$ valence band basis functions $|X\rangle$, $|Y\rangle$, and $|Z\rangle$ plus sign. The spin-orbit coupling splits the sixfold degenerate valence band states into the fourfold degenerate $J = 3/2$ states at energy E_v and the twofold degenerate $J = 1/2$ split off states at energy $E_{so} = E_v - \Delta_{so}$, where Δ_{so} is the spin-orbit splitting energy. The conduction band edge (at $\mathbf{k}=0$) is located at $E_c = E_v + E_g$, where E_g is the energy gap. We choose the eight basis functions as follows:

$$u_1 = u_{c\uparrow} = |S \uparrow\rangle, \quad (2.3a)$$

$$u_2 = u_{c\downarrow} = |S \downarrow\rangle, \quad (2.3b)$$

$$u_3 = |3/2, +3/2\rangle = u_{hh\uparrow} = -\frac{i}{\sqrt{2}} |(X + iY) \uparrow\rangle, \quad (2.3c)$$

$$u_4 = |3/2, +1/2\rangle = u_{lh\uparrow} = -\frac{i}{\sqrt{6}} [(X + iY) \downarrow - 2Z \uparrow]\rangle, \quad (2.3d)$$

$$u_5 = |3/2, -1/2\rangle = u_{lh\downarrow} = \frac{i}{\sqrt{6}} [(X - iY) \uparrow + 2Z \downarrow]\rangle, \quad (2.3e)$$

$$u_6 = |3/2, -3/2\rangle = u_{hh\downarrow} = \frac{i}{\sqrt{2}} |(X - iY) \downarrow\rangle, \quad (2.3f)$$

$$u_7 = |1/2, +1/2\rangle = u_{so\uparrow} = \frac{i}{\sqrt{3}} [(X + iY) \downarrow + Z \uparrow]\rangle, \quad (2.3g)$$

$$u_8 = |1/2, -1/2\rangle = u_{so\downarrow} = \frac{i}{\sqrt{3}} [(X - iY) \uparrow - Z \downarrow]\rangle, \quad (2.3h)$$

where c , hh , lh and so indicate the conduction and the heavy, light, and split off hole states, respectively. The interaction with all other bands, away from the band gap, is taken into account perturbatively.

In adapting the eight-band $k \cdot p$ approach to a layered structure, the n th eigenstate $\Psi_n(z)$ in Eq. (2.2) can be written as

$$\Psi_n(z) = \sum_{j=1}^8 \Phi_n^j(z) u_j, \quad (2.4)$$

where the components of $\Phi_n^j(z)$ are the envelope functions which are given by

$$\Phi_n^j(z) = \exp[i(k_x x + k_y y)] \sum_m a_{n,m}^j \frac{1}{\sqrt{L}} \exp \left[i \left(k_z + m \frac{2\pi}{L} \right) z \right], \quad (2.5)$$

Figure 2.1: One period of a single quantum well structure along the growth direction.

where L designates the periodicity of the SQW, the DBQW or the CQW structure. For an SQW, $L = ww + bw$. We use ww to indicate the width of the well and bw to indicate the width of the barrier, as shown in Fig. 2.1. For a DBQW, $L = ww + 2bw1 + bw2$. We use ww to indicate the width of the central well, and $bw1$ and $bw2$ to represent the widths of the inner and outer barrier layers, respectively, as shown in Fig. 2.2. And for a CQW, $L = ww1 + ww2 + ww3 + bw1 + bw2 + bw3$. We use $ww1$, $ww2$ and $ww3$ to indicate the widths of wells and $bw1$, $bw2$ and $bw3$ to represent the widths of barrier layers, respectively, as shown in Fig. 2.3.

In Eq. (2.5), k_x , k_y , and k_z are the wave vectors, n is the index for the respective energy levels, $a_{n,m}^j$ is the expansion coefficient and z is the coordinate in the growth direction. The components of u_j are the Bloch basis function (2.3), and where we have

Figure 2.2: One period of a double-barrier quantum well structure along the growth direction.

Figure 2.3: One period of a coupled quantum well structure along the growth direction.

used the approximation that these basis functions are the same for each layer. Then the total wave function Ψ from Eq. (2.1) satisfies

$$H(z)\Psi(z) = E\Psi(z), \quad (2.6)$$

For a strained QW, the total Hamiltonian $H(z)$ is given by

$$H(z) = H_K(z) + H_s(z) + V(z), \quad (2.7)$$

where $H_K(z)$ is the 8×8 $k \cdot p$ Hamiltonian which we write in the following general form:

$$H_K(z) = \sum_{\alpha, \beta=x,y,z} k_\alpha D^{\alpha\beta}(z) k_\beta + \sum_{\alpha=x,y,z} F^\alpha k_\alpha, \quad (2.8)$$

where $k_z = -id/dz$, $D^{\alpha\beta}(z) = D^{\beta\alpha}(z)$ and F^α are 8×8 Hermitian matrices, which depends on the crystallographic growth direction. The matrices $D^{\alpha\beta}(z)$ depend on the conduction band effective mass m_e^* and on the effective mass at the valence band edges, expressed in terms of the Luttinger parameters that will be discussed later. The matrices F^α describe the coupling between conduction and valence band states and depend on the p -matrix element P .

In this thesis, we only consider the crystallographic growth direction z along the

(001) direction. The explicit 8×8 H_K along this direction takes the form [33]

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

“c.c.” denotes the complex conjugate of the corresponding symmetrical item along the diagonal line.

$$C = E_g + \frac{\hbar^2}{2m_0}(k_x^2 + k_y^2 + k_z^2)\tilde{\gamma}_c, \quad (2.10a)$$

$$H = \frac{\hbar^2}{2m_0}[-(k_x^2 + k_y^2)(\tilde{\gamma}_1 + \tilde{\gamma}_2) - k_z^2(\tilde{\gamma}_1 - 2\tilde{\gamma}_2)], \quad (2.10b)$$

$$L = \frac{\hbar^2}{2m_0}[-(k_x^2 + k_y^2)(\tilde{\gamma}_1 - \tilde{\gamma}_2) - k_z^2(\tilde{\gamma}_1 + 2\tilde{\gamma}_2)], \quad (2.10c)$$

$$S = \frac{\hbar^2}{2m_0}[-(k_x^2 + k_y^2 + k_z^2)\tilde{\gamma}_1] - \Delta_0, \quad (2.10d)$$

$$P_{\pm} = P(k_x \pm ik_y), \quad (2.10e)$$

$$P_z = Pk_z, \quad (2.10f)$$

$$\alpha = \frac{\hbar^2}{2m_0} 2\sqrt{3}[k_z(k_x - ik_y)\tilde{\gamma}_3], \quad (2.10g)$$

$$\beta = \frac{\hbar^2}{2m_0} \sqrt{3}[(k_x^2 - k_y^2)\tilde{\gamma}_2 - 2ik_x k_y \tilde{\gamma}_3], \quad (2.10h)$$

$$D = \frac{\hbar^2}{2m_0} [2k_z^2 - (k_x^2 + k_y^2)]\tilde{\gamma}_2, \quad (2.10i)$$

$$\tilde{\gamma}_c = \frac{1}{m_e^*} - \frac{E_P}{3} \left(\frac{2}{E_g} + \frac{1}{E_g + \Delta_0} \right), \quad (2.10j)$$

$$\tilde{\gamma}_1 = \gamma_1 - \frac{E_p}{3E_g}, \quad (2.10k)$$

$$\tilde{\gamma}_2 = \gamma_2 - \frac{E_p}{6E_g}, \quad (2.10l)$$

$$\tilde{\gamma}_3 = \gamma_3 - \frac{E_p}{6E_g}, \quad (2.10m)$$

and the p -matrix element P satisfies [37, 38]

$$E_P = \frac{2m_0}{\hbar^2} P^2. \quad (2.10n)$$

k_x , k_y and k_z are the wavevectors. E_g is the unstrained band gap 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 Eq. (2.10) are not identical to the Luttinger parameters (γ_1 , γ_2 , γ_3) normally used in the 6-band Hamiltonian [39–41], since the conduction band is now treated exactly in the 8-band Hamiltonian and must be subtracted off the original Luttinger parameters. These parameters are called modified Luttinger parameters [33, 42, 43].

The diagonal matrix $V(z) = \text{diag}[E_c(z), E_c(z), E_{hh}(z), E_{lh}(z), E_{lh}(z), E_{hh}(z), E_{so}$

$(z), E_{so}(z)]$ describes the potential profile in the z direction with discontinuities at the interfaces due to different E_g and Δ_{so} of adjacent layer materials. The Hamiltonian describing strain, H_s , can be derived by simply substituting $\varepsilon_{\alpha\beta}$ into k_α, k_β with $\alpha, \beta = x, y, z$.

In order to identify the electron (e), heavy hole (hh), light hole (lh), and spin-orbit split-off (so) band components in the energy states of the DBQW, we introduce the following probability functions:

$$P_n^e = \sum_{j=1,2} \sum_m a_{n,m}^{j*} a_{n,m}^j, \quad (2.11a)$$

$$P_n^{hh} = \sum_{j=3,6} \sum_m a_{n,m}^{j*} a_{n,m}^j, \quad (2.11b)$$

$$P_n^{lh} = \sum_{j=4,5} \sum_m a_{n,m}^{j*} a_{n,m}^j, \quad (2.11c)$$

$$P_n^{so} = \sum_{j=7,8} \sum_m a_{n,m}^{j*} a_{n,m}^j. \quad (2.11d)$$

By calculating $P_n^e, P_n^{hh}, P_n^{lh}$ and P_n^{so} , the constituting components of the electron, heavy hole, light hole, and spin-orbit split-off states in the QWs can be known. These probability functions are particularly useful in identifying the dominant character in a particular energy state. However, the following sum rule is valid:

$$\sum_i P_n^i = 1, \quad i = e, hh, lh, so. \quad (2.12)$$

The wave function can be classified into two categories. Φ_{n_c} and Φ_{n_v} belong to conduction band and valence band, respectively. They are determined according to the positions of the energy subbands and also the calculated probability functions.

2.1.2 The ten-band $k \cdot p$ method

From the reports of dilute nitride III-V material systems recently, it is found that the N level will interact strongly with the conduction band edge [8]. It leads to that the excited levels in the conduction band ($e2$, $e3$, $e4$ etc.) can not be accurately described by the eight-band $k \cdot p$ model [44]. Since then, a ten-band $k \cdot p$ model was extensively utilized by researchers [34, 35] to investigate the peculiarities induced by the nitrogen resonant state.

The variant of the ten-band Hamiltonian H_K is derived in the angular momentum Bloch basis

$$u_1 = u_{N\uparrow} = |S_N \uparrow\rangle, \quad (2.13a)$$

$$u_2 = u_{N\downarrow} = |S_N \downarrow\rangle, \quad (2.13b)$$

$$u_3 = u_{c\uparrow} = |S \uparrow\rangle, \quad (2.13c)$$

$$u_4 = u_{c\downarrow} = |S \downarrow\rangle, \quad (2.13d)$$

$$u_5 = |3/2, +3/2\rangle = u_{hh\uparrow} = -\frac{i}{\sqrt{2}} |(X + iY) \uparrow\rangle, \quad (2.13e)$$

$$u_6 = |3/2, +1/2\rangle = u_{lh\uparrow} = -\frac{i}{\sqrt{6}} |[(X + iY) \downarrow - 2Z \uparrow]\rangle, \quad (2.13f)$$

$$u_7 = |3/2, -1/2\rangle = u_{lh\downarrow} = \frac{i}{\sqrt{6}} |[(X - iY) \uparrow + 2Z \downarrow]\rangle, \quad (2.13g)$$

$$u_8 = |3/2, -3/2\rangle = u_{hh\downarrow} = \frac{i}{\sqrt{2}} |(X - iY) \downarrow\rangle, \quad (2.13h)$$

$$u_9 = |1/2, +1/2\rangle = u_{so\uparrow} = \frac{i}{\sqrt{3}} |[(X + iY) \downarrow + Z \uparrow]\rangle, \quad (2.13i)$$

$$u_{10} = |1/2, -1/2\rangle = u_{so\downarrow} = \frac{i}{\sqrt{3}} |[(X - iY) \uparrow - Z \downarrow]\rangle. \quad (2.13j)$$

In adapting the ten-band $k \cdot p$ approach to a layered structure, the n th eigenstate $\Psi_n(z)$ in Eq. (2.2) can be written as

$$\Psi_n(z) = \sum_{j=1}^{10} \Phi_n^j(z) u_j, \quad (2.14)$$

the components of u_j are the Bloch basis function (2.13), and where we have used the approximation that these basis functions are the same for each layer.

By taking into account the energy levels from nitrogen-induced band, the ten-band $k \cdot p$ Hamiltonian is formed from the eight-band Hamiltonian in Eq. (2.9). The most general form of the Hamiltonian includes k -dependent diagonal and off-diagonal matrix

elements, linking the nitrogen, conduction, and valence basis states, is given by:

$$\begin{bmatrix}
 N & 0 & V_{NC}\sqrt{y} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 c.c. & N & 0 & V_{NC}\sqrt{y} & 0 & 0 & 0 & 0 & 0 & 0 \\
 c.c. & c.c. & C & 0 & \frac{-1}{\sqrt{2}}P^+ & \sqrt{\frac{2}{3}}P^z & \frac{1}{\sqrt{6}}P^- & 0 & \frac{1}{\sqrt{3}}P^z & \frac{1}{\sqrt{3}}P^- \\
 c.c. & c.c. & c.c. & C & 0 & \frac{-1}{\sqrt{6}}P^+ & \sqrt{\frac{2}{3}}P^z & \frac{1}{\sqrt{2}}P^- & \frac{1}{\sqrt{3}}P^+ & \frac{-1}{\sqrt{3}}P^z \\
 c.c. & c.c. & c.c. & c.c. & H & \alpha & \beta & 0 & \frac{1}{\sqrt{2}}\alpha & \frac{1}{\sqrt{2}}\beta \\
 c.c. & c.c. & c.c. & c.c. & c.c. & L & 0 & \beta & -\sqrt{2}D & -\sqrt{\frac{3}{2}}\alpha \\
 c.c. & c.c. & c.c. & c.c. & c.c. & c.c. & L & -\alpha & -\sqrt{\frac{3}{2}}\alpha^* & \sqrt{2}D \\
 c.c. & c.c. & c.c. & c.c. & c.c. & c.c. & c.c. & H & -\sqrt{2}\beta^* & \frac{1}{\sqrt{2}}\alpha^* \\
 c.c. & c.c. & c.c. & c.c. & c.c. & c.c. & c.c. & c.c. & S & 0 \\
 c.c. & c.c. & c.c. & c.c. & c.c. & c.c. & c.c. & c.c. & c.c. & S
 \end{bmatrix}, \quad (2.15)$$

where the nitrogen-related elements N is defined as

$$N = E_N, \quad (2.16)$$

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 in Eq. (2.10).

The strain Hamiltonian H_s and the diagonal matrix $V(z)$ follow the same definitions for the eight-band $k \cdot p$ model.

In order to identify the nitrogen (N), e , hh , lh , and so band components in the

energy states of the QW, we introduce the following probability functions:

$$P_n^N = \sum_{j=1,2} \sum_m a_{n,m}^{j*} a_{n,m}^j, \quad (2.17a)$$

$$P_n^e = \sum_{j=3,4} \sum_m a_{n,m}^{j*} a_{n,m}^j, \quad (2.17b)$$

$$P_n^{hh} = \sum_{j=5,8} \sum_m a_{n,m}^{j*} a_{n,m}^j, \quad (2.17c)$$

$$P_n^{lh} = \sum_{j=6,7} \sum_m a_{n,m}^{j*} a_{n,m}^j, \quad (2.17d)$$

$$P_n^{so} = \sum_{j=9,10} \sum_m a_{n,m}^{j*} a_{n,m}^j. \quad (2.17e)$$

By calculating P_n^N , P_n^e , P_n^{hh} , P_n^{lh} and P_n^{so} , the constituting components of the nitrogen, electron, heavy hole, light hole, and spin-orbit split-off states in the QW can be known. These probability functions are particularly useful in identifying the dominant character in a particular energy state. However, the following sum rule is valid:

$$\sum_i P_n^i = 1, \quad i = N, e, hh, lh, so. \quad (2.18)$$

2.2 Calculation of band structure related parameters

2.2.1 Linear interpolation method

Not all parameters are known for all the semiconductor alloys of interest. Except for the quantities of band gaps, band offsets, effective masses in the conduction band, most parameters for the ternary or quaternary alloys are obtained by linear interpolations [37] between the widely accepted parameters of binary compound semiconductors. For $\text{In}_x\text{Ga}_{1-x}\text{As}$

$$P(\text{In}_x\text{Ga}_{1-x}\text{As}) = xP(\text{InAs}) + (1 - x)P(\text{GaAs}), \quad (2.19)$$

for $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$

$$\begin{aligned} P(\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y) = & x(1 - y)P(\text{InAs}) + (1 - x)(1 - y)P(\text{GaAs}) \\ & + xyP(\text{InN}) + (1 - x)yP(\text{GaN}), \end{aligned} \quad (2.20)$$

for $\text{GaAs}_{1-x}\text{Sb}_x$

$$P(\text{GaAs}_{1-x}\text{Sb}_x) = (1 - x)P(\text{GaAs}) + xP(\text{GaSb}), \quad (2.21)$$

for $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$

$$P(\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y) = (1 - x - y)P(\text{GaAs}) + xP(\text{GaSb}) + yP(\text{GaN}), \quad (2.22)$$

and for $\text{Al}_x\text{Ga}_{1-x}\text{As}$

$$P(\text{Al}_x\text{Ga}_{1-x}\text{As}) = xP(\text{AlAs}) + (1 - x)P(\text{GaAs}). \quad (2.23)$$

The parameters of binary alloys are listed in Table 2.1 [37, 45].

2.2.2 Calculation of E_g and m_e^* within the eight-band and the ten-band $k \cdot p$ regime

Recently, the BAC model has been employed to explain the modification to E_g [46], m_e^* [47], and pressure-induced shifting of conduction band edge [8] when nitrogen atoms are added into III-V matrices to form III-V-N alloys. The dependence of E_g on nitrogen composition has been predicted very well by the BAC model, which states that the large reduction of the fundamental band gap energy of III-V-N compounds is due to the repulsion between a localized nitrogen-related energy level (E_N) and the extended conduction band (E_C) of the III-V host matrix [8]. To date, the BAC model is used extensively and successfully in the prediction of E_g and m_e^* of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ and $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ [8, 45, 48]. We will apply the BAC model to calculate E_g and m_e^* by

Table 2.1: Parameters for binary compounds used in the thesis

Parameters	GaAs ^a	GaSb ^b	AlAs ^c	InAs ^d	GaN ^e	InN ^f
Lattice constant a_0 (Å)	5.6533	6.0959	5.6611	6.0584	4.50	4.98
Spin-orbit splitting energy Δ_0 (eV)	341	760	280	390	17	5
Optical matrix parameter E_p (eV)	28.8	27.0	21.1	21.5	25.0	17.2
Deformation potential constant a_c (eV)	-7.17	-7.50	-5.64	-5.08	-6.71	-2.65
Deformation potential constant a_v (eV)	1.16	0.80	2.47	1.00	0.69	0.70
Shear deformation potential b (eV)	-2.0	-2.0	-2.3	-1.8	-2.0	-1.2
Elastic constant c_{11} (Gpa)	122.10	88.42	125.00	83.29	293	187
Elastic constant c_{12} (Gpa)	56.60	40.26	53.40	45.26	159	125
Luttinger parameter γ_1	6.98	13.40	3.76	20.00	2.70	3.72
Luttinger parameter γ_2	2.06	4.70	0.82	8.50	0.76	1.26
Luttinger parameter γ_3	2.93	6.00	1.42	9.20	1.11	1.63
Conduction band effective mass $m_e^*(m_0)$	0.067	0.039	0.150	0.026	—	—
Unstrained band-gap energy E_g (T=300K) (eV)	1.422	0.727	3.003	0.354	—	—

^aRef. [37]^bRef. [37]^cRef. [37]^dRef. [37]^eRef. [45]^fRef. [45]

the eight-band model in this thesis.

The band gap energy of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ is calculated by the BAC model in the following form [8, 46]

$$E_g(\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y) = \left[\begin{array}{c} E_g(\text{In}_x\text{Ga}_{1-x}\text{As}) + E_N \\ -\sqrt{[E_g(\text{In}_x\text{Ga}_{1-x}\text{As}) - E_N]^2 + 4V_{NC}^2(1-y)} \end{array} \right] / 2, \quad (2.24)$$

where

$$E_g(\text{In}_x\text{Ga}_{1-x}\text{As}) = (1-x)(E_g(\text{GaAs}, T)) + x(E_g(\text{InAs}, T)) - 0.477(1-x). \quad (2.25)$$

And the effective mass m_e^* of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ as predicted by the BAC model are given by

$$m_e^*(\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y) = \frac{2m_e^*(\text{In}_x\text{Ga}_{1-x}\text{As})}{\left[1 - \frac{E_g(\text{In}_x\text{Ga}_{1-x}\text{As}) - E_N}{\sqrt{[E_g(\text{In}_x\text{Ga}_{1-x}\text{As}) - E_N]^2 + 4V_{NC}^2 y}} \right]}, \quad (2.26)$$

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

$$m_e^*(\text{In}_x\text{Ga}_{1-x}\text{As}) = (1-x)m_e^*(\text{GaAs}) + xm_e^*(\text{InAs}) - 0.0091x(1-x). \quad (2.27)$$

Note that the bowing factors 0.477 and 0.0091 in Eqs. (2.25) and (2.27), respectively, are recommended by Ref. [37]. In Eqs. (2.24) and (2.26), the E_N and V_{NC} can be

expressed as [45]

$$E_N = 1.65(1 - x) + 1.44x - 0.38x(1 - x), \quad (2.28)$$

$$V_{NC} = 2.7(1 - x) + 2.0x - 3.5x(1 - x). \quad (2.29)$$

The band gap energy of $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ by the BAC model is written as

$$E_g(\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y) = \frac{1}{2} \left[\frac{E_g(\text{GaAs}_{1-x}\text{Sb}_x) + E_N}{-\sqrt{[E_g(\text{GaAs}_{1-x}\text{Sb}_x) - E_N]^2 + 4V_{NC}^2 y}} \right], \quad (2.30)$$

where

$$E_g(\text{GaAs}_{1-x}\text{Sb}_x) = (1 - x) E_g(\text{GaAs}) + x E_g(\text{GaSb}) - 1.43x(1 - x). \quad (2.31)$$

And the effective mass m_e^* of $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ as predicted by the BAC model is given

by

$$m_e^*(\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y) = \frac{2m_e^*(\text{GaAs}_{1-x}\text{Sb}_x)}{\left[1 - \frac{E_g(\text{GaAs}_{1-x}\text{Sb}_x) - E_N}{\sqrt{[E_g(\text{GaAs}_{1-x}\text{Sb}_x) - E_N]^2 + 4V_{NC}^2 y}} \right]}, \quad (2.32)$$

where

$$m_e^*(\text{GaAs}_{1-x}\text{Sb}_x) = (1 - x) m_e^*(\text{GaAs}) + x m_e^*(\text{GaSb}) - 0.0252x(1 - x). \quad (2.33)$$

Note that the bowing factors 1.43 and 0.0252 in Eqs. (2.31) and (2.33), respectively, are recommended by Ref. [37]. In Eqs. (2.30) and (2.32), E_N is calculated as in Eq. (2.28)

instead that “ x ” represents the composition for Sb and V_{NC} is assumed to be 2.7 eV [45] for this case.

The band gap energy and effective mass of $\text{Al}_z\text{Ga}_{1-z}\text{As}$ can be calculated from the equations

$$E_g(\text{Al}_z\text{Ga}_{1-z}\text{As}) = (1 - z)(E_g(\text{GaAs}, T)) + z(E_g(\text{AlAs}, T)) - (1.31z - 0.127)z(1 - z), \quad (2.34)$$

and

$$m_e^*(\text{Al}_z\text{Ga}_{1-z}\text{As}) = 0.083z + 0.067, \quad (2.35)$$

respectively.

For the ten-band model, since all the band parameters are derived from the nitrogen-free host materials [44], the band gap energies and effective masses of $\text{In}_x\text{Ga}_{1-x}\text{As}$ and $\text{GaAs}_x\text{Sb}_{1-x}$ are given by Eqs. (2.25), (2.27), (2.31), and (2.33), respectively. Meanwhile, the quantities of E_N and V_{NC} for characterizing the position of the isolated nitrogen-induced energy level with respect to the valence band maximum are also calculated as mentioned above.

2.2.3 Strained band offset ratios Q_C and Q_V

Another important parameter which will strongly affect the band structure calculation is the strained CBO ratio (Q_C), which is defined as the ratio of the band discontinuity in the conduction band to the total discontinuity at the interface of an heterostructure. It is given by

$$Q_C = \frac{\Delta E_C}{\Delta E_C + \Delta E_V}, \quad (2.36)$$

where ΔE_C is the discontinuity in the conduction band and ΔE_V is the valence band offset (VBO) after considering the energy shifting caused by the strain. In the situation of compressive strain, ΔE_V is the VBO of the heavy hole state with respect to the valence band edge in the barrier, on the contrary, ΔE_V is the VBO of the light hole state with respect to the valence band edge in the barrier for tensile strain. The effect of strain on band edges will be discussed in the next section. Q_v is the VBO ratio of the heterostructure, it is derived by $Q_v = 1 - Q_C$.

Q_C for InGaAs/GaAs and InGaAsN/GaAs QWs

Table 2.2 shows the summary of Q_C for $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ QWs reported in the literature. From these data, we derive a relationship of Q_C versus indium composition as shown in Fig. 2.4.

It is strongly believed that since the BAC model is able to predict the lowering of conduction band edge of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ material, it should be able to aid in the

Table 2.2: Summary of reported conduction band offset ratio Q_C for $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ QWs.

In	R1 ^a	R2 ^b	R3 ^c	R4 ^d	R5 ^e	R6 ^f	R7 ^g	R8 ^h	R9 ⁱ	R10 ^j	R11 ^k	R12 ^l	R13 ^m	R14 ⁿ
0.02				0.4										
0.05			0.4	0.4		0.4	0.57			0.46				
0.08				0.4										
0.1								0.6						
0.11										0.5				0.64
0.13		0.698												
0.14										0.54				
0.15	0.679													
0.155												0.64		
0.17	0.677													
0.185												0.64		
0.19												0.64		
0.193		0.699												
0.2						0.6			0.7					
0.21					0.65					0.63				
0.215											0.64			
0.32													0.64	
0.5													0.64	

^aRef. [49]

^bRef. [50]

^cRef. [51]

^dRef. [52]

^eRef. [53]

^fRef. [54]

^gRef. [55]

^hRef. [56]

ⁱRef. [57]

^jRef. [58]

^kRef. [59]

^lRef. [60]

^mRef. [61]

ⁿRef. [62]

Figure 2.4: Dependence of Q_C for $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ QWs on the indium composition.

estimation of Q_C of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{GaAs}$ QWs from Q_C of $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ QWs. Thanks to the special characteristic of nitrogen atoms, a small amount of nitrogen incorporated affects the conduction band edge of the $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ alloy and leaves the valence band edge nearly unchanged [44]. Hence we propose the derivation of Q_c for $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{GaAs}$ from the $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ QWs, as shown in Fig. 2.4. Thereby, the explicit expression for Q_c of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{GaAs}$ QW is given by

$$Q_c(\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{GaAs}) = 1 - Q_v(\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{GaAs})$$

$$= 1 - \frac{\Delta E_g^s(\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs})Q_v(\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}) + \Delta_v^s(\text{In}_x\text{Ga}_{1-x}\text{As}/\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y)}{E_{g-\text{GaAs}}^s - E_{g-\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y}^s}, \quad (2.37)$$

where ΔE_g^s represents the difference of the strained band gap energy between the respective materials in the parenthesis, and Δ_v^s represents the difference of the amount

Figure 2.5: Dependence of Q_V for $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}$ heterostructures on the antimonide composition. References: a-Ref. [63], b-Ref. [64], c-Ref. [65], d-Ref. [66], e-Ref. [67], f-Ref. [68], g-Ref. [69], h-Ref. [70], i-Ref. [71], j-Ref. [72].

of valence band edge shift introduced by strain between the respective materials in the parenthesis. $E_{g,\text{GaAs}}^s$ and $E_{g,\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y}^s$ are the band gap energies of GaAs and $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ considering strain, respectively.

Q_V for GaAsSb/GaAs and GaAsSbN/GaAs QWs

Although the strained band offset ratio of GaAsSb/GaAs QW has been studied for a long time, it remains a matter for debate. The reported VBO ratios in the literature are summarized in Fig. 2.5. With the exception of Ref. [64], where a type-I band alignment was proposed for GaAsSb/GaAs QW, most researches supported a type-II alignment. Nevertheless, the reported strained VBO ratios Q_v were still divergent, which could be classified as either strongly type-II [63] or weakly type-II [71]. In our calculation we adopt a slightly type-II band lineup with a strained VBO Q_v of 1.05 for GaAsSb/GaAs

QW considering the results of Harmand *et al.* [67]. Following Eq. (2.37), the strained Q_v for the $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y/\text{GaAs}$ QW can be calculated as

$$Q_V(\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y/\text{GaAs}) = \frac{\Delta E_g^s(\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs})Q_V(\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}) + \Delta_V^s(\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y)}{E_{g-\text{GaAs}}^s - E_{g-\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y}^s} \quad (2.38)$$

Therefore, the strained Q_v for the $\text{GaAs}_{0.863}\text{Sb}_{0.13}\text{N}_{0.007}/\text{GaAs}$ QW is determined to be 0.66 which is comparable to the result of Ref. [73].

Q_C for InGaAs/AlGaAs and InGaAsN/AlGaAs QWs

We determine the band offset ratio of the $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{Al}_z\text{Ga}_{1-z}\text{As}$ QW from the summary in Ref. [74] and calculate the Q_c of the $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{Al}_z\text{Ga}_{1-z}\text{As}$ QW according to

$$Q_c(\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{Al}_z\text{Ga}_{1-z}\text{As}) = 1 - Q_V(\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{Al}_z\text{Ga}_{1-z}\text{As})$$

$$= 1 - \frac{\Delta E_g^s(\text{In}_x\text{Ga}_{1-x}\text{As}/\text{Al}_z\text{Ga}_{1-z}\text{As})Q_V(\text{In}_x\text{Ga}_{1-x}\text{As}/\text{Al}_z\text{Ga}_{1-z}\text{As}) + \Delta_V^s(\text{In}_x\text{Ga}_{1-x}\text{As}/\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y)}{E_{g-\text{Al}_z\text{Ga}_{1-z}\text{As}}^s - E_{g-\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y}^s} \quad (2.39)$$

2.2.4 Critical thickness

Critical thickness is defined as the stability of the structural integrity, which can be ensured up to a certain thickness. It means that for a thickness beyond a critical value,

Table 2.3: The critical thickness (in unit of Å) obtained for $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ with respect to In (x) and N (y) compositions.

y	$x=0.2$	$x=0.3$	$x=0.4$	$x=0.5$	$x=0.6$	$x=0.7$
0.005	157	91	62	45	35	2
0.010	173	97	65	47	36	2
0.015	193	104	68	49	37	30
0.020	216	111	71	51	39	30
0.025	245	120	75	53	40	31

it is energetically more favorable for the misfit dislocation to relieve the strain. And for a thickness below the critical value, the misfit strain can be accommodated without formation of the misfit dislocation. Misfit dislocation defects are greatly undesirable in many devices, such as QWIPs. We apply the model introduced by Ref. [76] to estimate the critical thickness (h_c)

$$h_c = \frac{a_0}{\sqrt{2}\pi\omega\epsilon_w} \frac{1 - \sigma/4}{1 + \sigma} \left[\ln \left(\frac{\sqrt{2}h_c}{a_0} \right) + 1 \right] \quad (2.40)$$

where a_0 is the lattice constant of the well material, σ is Poisson's ratio, ω is factor which is 2 for the QW structure, and ϵ_w is the amount of the in-plane strain which will be described in the next section. As a result, we have derived h_c for the $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ alloy grown on GaAs substrate, as shown in Table. 2.3.

2.2.5 Calculation of strain related parameters for different QW structures

For SQW and CQW structures

The band lineups for an SQW or a CQW structure considering strain are depicted in Fig. 2.6.

Figure 2.6: Potential profiles for a strained SQW or a CQW structure.

If the QW layer thickness is within the critical thickness range, the strain is twofold: a biaxial hydrostatic strain along two perpendicular directions in the interfacial plane, which is called the in-plane strain, and a uniaxial shear strain along the growth direction, which is perpendicular to the interfacial plane [75]. Assuming that the growth direction z is along $\langle 001 \rangle$, the in-plane strain is given by [75]

$$\epsilon_{\text{w}} = \frac{a_{\text{sub}} - a_{\text{w}}}{a_{\text{w}}}, \quad (2.41)$$

where a_{sub} and a_{w} are the lattice constants of the substrate and the well materials, respectively. The conduction band edge in the well is shifted by the hydrostatic strain

$$\delta E_{\text{c}} = 2a_{\text{c-w}} \left(1 - \frac{C_{12\text{-w}}}{C_{11\text{-w}}} \right) \epsilon_{\text{w}}, \quad (2.42)$$

where $a_{\text{c-w}}$ is the hydrostatic deformation potential in the conduction band. $C_{11\text{-w}}$ and $C_{12\text{-w}}$ are the elastic stiffness constants. The hydrostatic strain occurred in the valence band is given by

$$P_{\epsilon} = -2a_{\text{v-w}} \left(1 - \frac{C_{12\text{-w}}}{C_{11\text{-w}}} \right) \epsilon_{\text{w}}, \quad (2.43)$$

where $a_{\text{v-w}}$ is the hydrostatic deformation potential in the valence band. The shear strain in the valence band brings about the splitting of the heavy hole and light hole bands, which takes the form

$$Q_{\epsilon} = -b_{\text{w}} \left(1 + 2 \frac{C_{12\text{-w}}}{C_{11\text{-w}}} \right) \epsilon_{\text{w}}. \quad (2.44)$$

The definitions of all the band structure related variables depicted in Fig. 2.6 are summarized in Table. 2.4, where $E'_{\text{g-w}}$, $E_{\text{g-w}}$, $E_{\text{g-B}}$, and $\Delta E_{\text{g-w}}$ are the strained band gap of the well material, the unstrained band gap of the well material, the band gap of the barrier material and the strained band gap difference, respectively. ΔE_{C} , ΔE_{V} ,

Table 2.4: The conduction and the valence band edge related variables considering (a) compressive strain and (b) tensile strain.

Case	(a)	(b)
δE_c	+	-
P_ϵ	+	-
Q_ϵ	-	+
E'_{g-w}	$E_{g-w} + \delta E_c + P_\epsilon + Q_\epsilon$	$E_{g-w} + \delta E_c + P_\epsilon - Q_\epsilon$
ΔE_{g-w}	$E_{g-B} - E'_{g-w}$	$E_{g-B} - E'_{g-w}$
ΔE_C	$Q_C \times \Delta E_{g-w}$	$Q_C \times \Delta E_{g-w}$
ΔE_V	$(1 - Q_C) \times \Delta E_{g-w}$	$(1 - Q_C) \times \Delta E_{g-w}$
V_c	$\Delta E_C + \delta E_C$	$\Delta E_C + \delta E_C$
V_b	$\Delta E_V + P_\epsilon + Q_\epsilon$	$\Delta E_V + P_\epsilon - Q_\epsilon$

V_c , and V_b are the strained CBO, the strained VBO, the unstrained CBO and the unstrained VBO, respectively.

For DBQW structures

The band lineups for a DBQW structure considering strain are depicted in Fig. 2.7. The amounts describing shifts of the band edges are defined similarly to Eqs. (2.41-2.44). As can be seen from Table. 2.5, the definitions of the variables to describe the strained band edges are given out.

2.2.6 Effects of interdiffusion

For InGaAsN/GaAs QWs

Two types of interdiffusion are possible in InGaAsN/GaAs QW: (1) the interdiffusion between In and Ga atoms, and (2) the interdiffusion between N and As atoms [77, 78].

Table 2.5: The conduction and the valence band edge related variables considering all possible types of strains.

Case	(a)	(b)	(c)	(d)
δE_{c1}	+	+	-	-
δE_{c2}	-	+	-	+
$P_{\epsilon 1}$	+	+	-	-
$P_{\epsilon 2}$	-	+	-	+
$Q_{\epsilon 1}$	-	-	+	+
$Q_{\epsilon 2}$	+	-	+	-
E'_{g-w}	$E_{g-w} + \delta E_{c1} + P_{\epsilon 1} + Q_{\epsilon 1}$	$E_{g-w} + \delta E_{c1} + P_{\epsilon 1} + Q_{\epsilon 1}$	$E_{g-w} + \delta E_{c1} + P_{\epsilon 1} - Q_{\epsilon 1}$	$E_{g-w} + \delta E_{c1} + P_{\epsilon 1} - Q_{\epsilon 1}$
ΔE_{g-w}	$E_{g-B1} - E'_{g-w}$	$E_{g-B1} - E'_{g-w}$	$E_{g-B1} - E'_{g-w}$	$E_{g-B1} - E'_{g-w}$
ΔE_{c1}	$Q_C \times \Delta E_{g-w}$	$Q_C \times \Delta E_{g-w}$	$Q_C \times \Delta E_{g-w}$	$Q_C \times \Delta E_{g-w}$
ΔE_{v1}	$Q_V \times \Delta E_{g-w}$	$Q_V \times \Delta E_{g-w}$	$Q_V \times \Delta E_{g-w}$	$Q_V \times \Delta E_{g-w}$
V_{c1}	$\Delta E_{c1} + \delta E_{c1}$	$\Delta E_{c1} + \delta E_{c1}$	$\Delta E_{c1} + \delta E_{c1}$	$\Delta E_{c1} + \delta E_{c1}$
V_{b1}	$\Delta E_{v1} + P_{\epsilon 1} + Q_{\epsilon 1}$	$\Delta E_{v1} + P_{\epsilon 1} + Q_{\epsilon 1}$	$\Delta E_{v1} + P_{\epsilon 1} - Q_{\epsilon 1}$	$\Delta E_{v1} + P_{\epsilon 1} - Q_{\epsilon 1}$
E'_{g-B2}	$E_{g-B2} + \delta E_{c2} + P_{\epsilon 2} - Q_{\epsilon 2}$	$E_{g-B2} + \delta E_{c2} + P_{\epsilon 2} + Q_{\epsilon 2}$	$E_{g-B2} + \delta E_{c2} + P_{\epsilon 2} - Q_{\epsilon 2}$	$E_{g-B2} + \delta E_{c2} + P_{\epsilon 2} + Q_{\epsilon 2}$
ΔE_{g-B2}	$E'_{g-B2} - E'_{g-w}$	$E'_{g-B2} - E'_{g-w}$	$E'_{g-B2} - E'_{g-w}$	$E'_{g-B2} - E'_{g-w}$
ΔE_{c2}	$Q'_C \times \Delta E_{g-B2}$	$Q'_C \times \Delta E_{g-B2}$	$Q'_C \times \Delta E_{g-B2}$	$Q'_C \times \Delta E_{g-B2}$
ΔE_{v2}	$(1 - Q'_C) \times \Delta E_{g-B2}$	$(1 - Q'_C) \times \Delta E_{g-B2}$	$(1 - Q'_C) \times \Delta E_{g-B2}$	$(1 - Q'_C) \times \Delta E_{g-B2}$
V_{c2}	$\Delta E_{c2} + \delta E_{c1} - \delta E_{c2}$	$\Delta E_{c2} + \delta E_{c1} - \delta E_{c2}$	$\Delta E_{c2} + \delta E_{c1} - \delta E_{c2}$	$\Delta E_{c2} + \delta E_{c1} - \delta E_{c2}$
V_{b2}	$\Delta E_{v2} + P_{\epsilon 1} + Q_{\epsilon 1} - P_{\epsilon 2} + Q_{\epsilon 2}$	$\Delta E_{v2} + P_{\epsilon 1} + Q_{\epsilon 1} - P_{\epsilon 2} - Q_{\epsilon 2}$	$\Delta E_{v2} + P_{\epsilon 1} - Q_{\epsilon 1} - P_{\epsilon 2} + Q_{\epsilon 2}$	$\Delta E_{v2} + P_{\epsilon 1} - Q_{\epsilon 1} - P_{\epsilon 2} - Q_{\epsilon 2}$

However, recently Sun *et al.* discovered that the N-As interdiffusion mechanism is ruled out during thermal annealing due to the strong In-N bond [78]. Hence in our thesis, we exclude the N-As sublattice diffusion and only consider the diffusion between In and Ga atoms. We then consider an SQW with undoped $\text{In}_x\text{Ga}_x\text{As}_{1-y}\text{N}_y$ grown on GaAs substrate and set x' and $1-x'$ as the composition of In and Ga atoms after In-Ga interdiffusion, respectively. The interdiffusion of In and Ga atoms is characterized by a diffusion length L_d [79], which is equal to $(Dt)^{1/2}$, with the diffusion time t and the diffusion coefficient D . The In composition after interdiffusion is defined as [80]

$$x'(z) = \frac{x}{2} \left[\text{erf}\left(\frac{L_z + 2z}{4L_d}\right) + \text{erf}\left(\frac{L_z - 2z}{4L_d}\right) \right], \quad (2.45)$$

where z is the length along growth direction, x is the as-grown composition of In, and L_z is the QW well width before interdiffusion. Consequently, all the QW parameters related to the In concentration will vary accordingly, which firstly causes the variation of strain and subsequently affects the subband energy distribution across the QW.

For GaAsSbN/GaAs QWs

The experimental PL-peak shifts can be explained by the atomic interdiffusion across the interface of the QW, which is according to Ref. [81]. Two types of interdiffusion are possible in the GaAsSbN/GaAs QW: (1) the interdiffusion between As and Sb atoms and (2) the interdiffusion between N and As atoms. The second type N-As interdiffusion can be neglected as compared to As-Sb diffusion, because the Ga-N bond is much stronger than that of Ga-Sb [82], and the N-As interdiffusion has been ruled out as in the InGaAsN system by Sun *et al.* [78]. Therefore, we only consider the diffusion between As and Sb atoms. We model the GaAs_{1-x-y}Sb_xN_y/GaAs QW by setting x' and $1 - x' - y$ as the composition of Sb and As atoms after As-Sb interdiffusion, respectively. Since both As and Sb are group-V elements, the Sb composition x' after interdiffusion can be described as [79]

$$x'(z) = \frac{x}{2} \left[\operatorname{erf} \left(\frac{L_z + 2z}{4L_d} \right) + \operatorname{erf} \left(\frac{L_z - 2z}{4L_d} \right) \right], \quad (2.46)$$

where z is the length along the growth direction, x is the as-grown composition of Sb, and L_z is the QW width before interdiffusion. Consequently, all the QW parameters related to the Sb concentration will vary accordingly.

2.2.7 Effects of the electric field

Within the framework of the $k \cdot p$ model, the overall Hamiltonian taking electric field into account is given by

$$H'\Psi = E\Psi, \quad (2.47)$$

where

$$H' = H_0 + V_F(z), \quad (2.48)$$

where H_0 is the full Hamiltonian without electric field. In Eq. (2.48), we use $V_F(z)$ to indicate the electric field distribution along the growth direction, which can be expressed as

$$V_F(z) = -eFz, \quad (2.49)$$

where e is the electron charge, F represents the strength of an external electric field, z is the coordinate in the growth direction along the QW, and the origin of the electric field potential is taken as the midpoint of the central well. For convenience, throughout the work, the positive bias polarity corresponds to the conduction band potential being lowered along the growth direction z .

2.3 Mathematical formulation of the optical absorption in QW systems

The optical intersubband transition rate for the eight-band or the ten-band $k \cdot p$ model is proportional to the momentum matrix element (MME)

$$M_{nn'} = \langle \Psi_n | \vec{e}_v \bullet \vec{P} | \Psi_{n'} \rangle$$

$$= \sum_{j,j'=1}^{8 \text{ or } 10} \left[\langle \Phi_{nj} | \vec{e}_v \bullet \vec{P} | \Phi_{n'j'} \rangle \langle u_j | u_{j'} \rangle + \langle \Phi_{nj} | \Phi_{n'j'} \rangle \langle u_j | \vec{e}_v \bullet \vec{P} | u_{j'} \rangle \right], \quad (2.50)$$

where $\vec{e}_v = v_x e_x + v_y e_y + v_z e_z$ ($v_x^2 + v_y^2 + v_z^2 = 1$) is the unit vector in the direction of the electric field, $\vec{P}$ is the momentum operator, Φ is the envelope wave function and Ψ is the total electron wave functions derived from Eq. (2.1). Subscript n and n' are the index of the initial state and the final state of the intersubband transitions considered, respectively. u_j have been defined in Eqs. (2.3) and (2.13). In Eq. (2.50), the part before the plus sign represents the transitions occurring within the same Bloch basis states, namely, intraband transitions, while the other part represents the transitions occurring from the coupling of $|S\rangle$ and $|X\rangle$, $|Y\rangle$, $|Z\rangle$ Bloch basis states, which are known as interband transitions. The optical absorption coefficient $\alpha_{nn'}(\hbar\omega)$ can be obtained from

$$\alpha_{nn'}(\hbar\omega) = \frac{\pi e^2}{n_r c \varepsilon_0 m_0^2 \omega} \cdot \frac{2}{V} \sum_{k_t} |M_{nn'}|^2 \delta(E_{n'} - E_n - \hbar\omega) (f_n - f_{n'}), \quad (2.51)$$

where n_r is the refractive index, c is the light speed, ε_0 is the free-space dielectric constant, m_0 is the free electron mass, ω is the photon frequency, V is the volume of the integral space, $k_t=(k_x, k_y)$ is a two-dimensional in-plane wave vector, $\delta(E_{n'} - E_n - \hbar\omega)$ may be replaced by a Lorentzian function with a linewidth Γ when the scattering relaxation is taken into account, which becomes

$$\delta(E_{n'} - E_n - \hbar\omega) = \frac{\Gamma}{2\pi \left[(E_{n'} - E_n - \hbar\omega)^2 + \left(\frac{\Gamma}{2}\right)^2 \right]}, \quad (2.52)$$

and

$$f_n = \frac{1}{1 + e^{(E_n - E_F)/k_B T}} \quad (2.53)$$

is the Fermi-Dirac distribution function for the initial state, where E_n is the subband energy for the initial state and E_F is the quasi-Fermi level. A similar expression holds for the Fermi-Dirac distribution function for the excited state $f_{n'}$, where E_n is replaced by $E_{n'}$.

In order to investigate the absorption coefficients obtainable at certain carrier density, the corresponding quasi-Fermi levels must be determined from the integration of the density of states in the QWs. Considering the non-parabolic energy dispersion curves, a determination of carrier density by numerically integrating over k-space is more appropriate:

$$N = \sum_{n_c} \int \frac{1}{4\pi^2 w w} f_n[E_n(k_x, k_y)] dk_x dk_y, \quad (2.54)$$

where N is the electron density. f_n is the Fermi-Dirac distributions for electrons in the

conduction band which is given by Eq. (2.53).

Chapter 3

Study of 3-5 and 8-12 μm

intersubband transitions in

InGaAsN/GaAs quantum wells

3.1 Introduction

Ever since the first infrared (IR) detector was demonstrated in 1950s [83], many important applications, such as fire fighting, volcanology, medicine, defence, astronomy, have triggered extensive investigations of IR detectors. Early studies of the IR detectors are based on the IBTs, as shown in Fig. 3.1(a). The incoming photon excites an electron from the valence band to the conduction band, which can be collected to produce a photocurrent in the external circuit. Main alloys utilized are $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ [84, 85] and $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ [86–88], in which the energy gap can be controlled by varying x . The mechanism of IBTs gives rise to a problem, for example, when we need the detec-

Figure 3.1: (a) Interband transitions, and (b) intersubband transitions.

tion of a long wavelength IR $\lambda \approx 10 \mu\text{m}$, it requires a small band gap $E_g \approx 0.12$ eV. It is well known that these low-band-gap materials are more difficult to grow and process than large-band-gap materials such as GaAs. The difficulties in growing the low-band-gap material, encouraged the development of alternative detector technologies. The possibility of using ISBTs in QWs for infrared light detection was found by Smith *et al.* [89]. Later, Levin *et al.* [90] demonstrated the IR photodetectors based on multiple-quantum-well (MQW) structures made of large-band-gap semiconductors, the QWIPs, for the first time. Photoexcited electron (hole) from the fundamental state into the first excited state in the conduction (valence) band of a quantum well structure (Fig. 3.1(b)) can escape and be collected as photocurrent within a QWIP structure. When being compared to the usual IBT based IR detectors, ISBT based QWIPs offer: (1) the availability of a mature material and processing technology; (2) the flexibility of the approach for enhanced device functionality and for its ease to integrate with other devices; (3) the freedom of detection wavelengths tailoring and ultrafast carrier relaxation time.

During the past decade, tremendous progress has been made on QWIPs, which was well documented [91]. Recently, the novel material InGaAsN with dilute nitrogen has been attracting considerable attention due to their unusual physical properties and their potential optoelectronic device applications, as being discussed in the first chapter. In this chapter, we present a study on intersubband absorptions (ISAs) in InGaAsN/GaAs quantum wells for QWIPs to achieve the detection wavelength within the atmospheric window region (interest has centered mainly on the wavelengths of the two atmospheric windows 3-5 μm [middle wavelength IR] and 8-12 μm [long wavelength IR] region, since atmospheric transmission is the highest in these bands). Very few studies have been carried out on QWIPs in this system [12, 92, 93].

3.2 Experimental details

A RIBER-32P SS-MBE equipped with a nitrogen RF plasma source is used to grow two InGaAsN/GaAs QWIP samples. The substrates on which the samples are grown are double-side polished (100) semi-insulating GaAs substrates. Twenty periods of 2.5 nm thick $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.99}\text{N}_{0.01}$ QWs and 14.5 nm $\text{GaAs}_{0.998}\text{N}_{0.002}$ barriers form the QW structures. The QW structures are sandwiched between a 0.7 μm buffer with Si doping concentration of $2 \times 10^{18} \text{ cm}^{-3}$ and a 0.7 μm cap layer with Si doping concentration of $2 \times 10^{18} \text{ cm}^{-3}$. The GaAs growth rate is 0.78 $\mu\text{m/hr}$. The QWs are grown at 460 $^{\circ}\text{C}$ and clear streaky reflection high-energy electron diffraction (RHEED) patterns can be

observed for all samples. The difference between the two samples MN180 and MN181 is that an in-situ annealing at 600 °C for about 6 mins exists in the sample MN180.

3.3 Results and discussion

In this part, we use the ten-band $k \cdot p$ model to calculate the subband energy and the transition energy within an $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{GaAs}$ QW structure. We have also calculated the absorption coefficients to compare with the experimental results. All calculations presented are done with respect to the top of the valence band considering strain in this chapter, except for some case with special illustration.

We are firstly interested to know how the indium and the nitrogen compositions impact on the conduction band of the QW. The subband and the transition energy in the conduction band of the $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{GaAs}$ QW calculated as a function of the indium composition, the nitrogen composition and the well width are depicted in Fig. 3.2. The subbands are calculated with respect to the conduction band minimum. As can be observed from Fig. 3.2(a)-(c), with In increases from 10% to 30%, in a step of 10%, the first and the second electron states increase at the same time. It is due to the fact that with the indium composition increases, the effective mass of $\text{In}_x\text{Ga}_{1-x}\text{AsN}$ decreases. Electrons with smaller effective mass are to be localized in a higher level. Moreover, as In composition increases, the band gap of $\text{In}_x\text{Ga}_{1-x}\text{AsN}$ decreases, which results in that the bottom of the conduction band (zero point of

Figure 3.2: Dependence of subband energy and transition energy in the conduction band of the $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{GaAs}$ QW structure on the indium composition, the nitrogen composition, and the well width. All the calculations are under the conditions: the barrier widths are 200 Å and the temperature is 300 K.

energy) drops. Combining with the smaller effective mass, the subband energy increases with respect to the bottom of the well consequently. Also can be seen from Fig. 3.2(a)-(c), with the nitrogen concentration increases, the subband energy also increase. This is because that the incorporation of nitrogen atoms heavily affects the fundamental band gap energy of $\text{In}_x\text{Ga}_{1-x}\text{As}$ alloy and thus a deeper well forms. Due to that the zero point of the energy is taken as the bottom of the conduction band, it leads to the

rise of the electron states. As can be observed from Fig. 3.2(a)-(c), E_1 and E_2 reduce with well width in going from 20 to 80 Å. It is caused by that the subband drops with an increasing well width. As for the E_2 level, there are some interesting features that with the well width increases, it decreases slightly at first and then rapidly for all cases. It is due to the fact that E_2 drops from a level higher than the GaAs barrier edge (continuum state) to be lower than it (bound state) with an increasing well width.

Figure 3.2(d)-(f) presents how the indium, the nitrogen incorporation and the well width increasing affect the ground state transition ($E_1 \rightarrow E_2$) energy in the conduction band of the well. The $E_1 \rightarrow E_2$ transition energy increases with the indium and the nitrogen compositions. A straightforward reason is from Fig. 3.2(a)-(c) that the gap between E_1 and E_2 increases with In and N constituents increase, leading to a larger transition energy. Also can be seen from Fig. 3.2(d)-(f), the transition energy does not monotonically increase as the well width increases. Instead, it firstly increases to a peak value and then decreases with the well width. It is caused by that the transition occurs from a bound-to-continuum state for a narrower well and then it turns to be bound-to-bound for a wider well.

Turning now to consider the dependence of the subband energy and the transition energy in the conduction band of an $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.99}\text{N}_{0.01}/\text{GaAs}$ QW structure on the barrier width and the temperature. Figures 3.3(a) and (c) depict the curves of the subband energy and the transition energy versus the barrier width from 100 to 300 Å, respectively. E_2 decreases while E_1 keeps nearly unchanged with barrier width, which

Figure 3.3: Dependence of subband energy and transition energy in the conduction band of the $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.99}\text{N}_{0.01}/\text{GaAs}$ QW structure on the barrier width and the temperature. (a) and (b) are the curves of the subband energy E_1 and E_2 dependent on the barrier width and the temperature, respectively. (c) and (d) are the curves of the transition energy $E_1 \rightarrow E_2$ dependent on the barrier width and the temperature, respectively. All the calculations are under the well width of 25 Å.

leads to a decreasing $E_1 \rightarrow E_2$ with respect to the barrier width. From Figs. 3.3(b) and (d), due to that the band gap of $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.99}\text{N}_{0.01}$ alloy decreases with the temperature, E_1 and E_2 both decrease. It causes a negligible decrease of the transition energy (only about 6 meV with temperature rises from 0 to 300 K).

To calculate the intersubband absorption coefficients, firstly, we clarify the efficiency of our absorption program. Due to the lack of the theoretical study of the absorption by the ten-band $k \cdot p$ model, we compare our results with those by Cheah *et al.* [94] on an $\text{InGaAs}/\text{GaAs}$ QW. Fig. 3.4 shows the result of our comparison. The structure is a 40 Å- $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}/300$ Å- GaAs square QW. The QW analyzed are assumed to be

Figure 3.4: (a) The reported calculation result and (b) our calculated spectrum by the eight-band model of the In_{0.3}Ga_{0.7}As/GaAs QW structure.

n-type, uniformly doped in the well region at a concentration of $2 \times 10^{18} \text{ cm}^{-3}$ and undoped in the rest of the device. The offset in the conduction bands of the barrier and well regions is taken to be 65% of the total band gap difference. The absorption spectra are computed by taking five subbands into account, and a linewidth Γ of 20 meV in the Lorentzian function is assumed. The good agreement between our calculation and the published result shows the reliability of our algorithm for the absorption coefficients.

Finally, Fig. 3.5(a) shows the measured baseline-corrected infrared absorption spec-

Figure 3.5: (a) Experimental result and (b) calculated spectrum by the ten-band model of the $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.99}\text{N}_{0.01}/\text{GaAs}_{0.998}\text{N}_{0.002}$ QWIP structure.

tra of the sample MN180 (with in-situ annealing) and MN181 at room temperature. The insert shows the original absorption curves without baseline correction. Figure 3.5(b) shows the TM mode ISA result including five levels in the conduction band, which is calculated by the ten-band $k \cdot p$ model. The experimental ISA peak at $9.5 \mu\text{m}$ is in good agreement with our calculated $9.3 \mu\text{m}$.

One should note that in our work, we assume that the QW interface is abrupt for simplicity, so that the Lorentzian type line broadening is reasonable to describe the

Figure 3.6: Band structure of $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.99}\text{N}_{0.01}/\text{GaAs}_{0.998}\text{N}_{0.002}$ quantum well with well width of 25 Å at room temperature.

optical absorption [75]. But for the real device, the interface of the quantum well is not absolutely abrupt. If we take the fluctuations in the well and barrier widths in the planes on interfaces into account, it may leads to Gaussian type line broadening in optical transitions.

The conduction band structure of the above QWIP structure is illustrated in Fig. 3.6. From the graph we could observe clearly that there is a band nonparabolicity in the conduction band that is different from the simple effective mass theory. It results from band mixing with the valence band and the lack of inversion symmetry [95].

We have also done research on the possibility of InGaAsN/GaAs QW based QWIP to achive an absorption within 3-5 μm wavelength region by the ten-band $k \cdot p$ model.

Figure 3.7: (a) Band structure and (b) absorption spectra of an $\text{In}_{0.6}\text{Ga}_{0.4}\text{As}_{0.95}\text{N}_{0.05}/\text{GaAs}$ quantum well with well width of 20 Å at room temperature.

As shown in Fig. 3.7, only when In and N are as large as 60% and 5%, respectively, the absorption can reach the desired 5 μm . But an $\text{InGaAsN}/\text{GaAs}$ QW with such high In and N concentrations is known to be difficult to obtain. Experimental works may be carried out to further investigate on this.

3.4 Summary

In summary, the ten-band $k \cdot p$ model is applied to design a 8-12 μm QWIP based on the $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{GaAs}$ QWs. After comparison with the actual fabricated sample, a 25 Å- $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.99}\text{N}_{0.01}/145$ Å- $\text{GaAs}_{0.998}\text{N}_{0.002}$ QW structure with an ISA at around 10 μm is achieved. Following this work, we try to search an appropriate combination of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{GaAs}$ QW with a 3-5 μm ISA. As a consequence, it is likely that this system is not suitable for QWIPs operating within this range from our calculations.

Chapter 4

Study of intersubband transitions in InGaAsN/AlAs/AlGaAs double-barrier quantum wells for absorptions at 1.31 and 1.55 μm

4.1 Introduction

Over the past a few years, considerable number of studies have been made on GaAs-based QWIPs. One of the main advantages of QWIPs is the possibility of working in the 3-5 μm as well as 8-12 μm atmospheric transmission wavebands by changing their structures, which are well documented [91]. In view of optical fiber communications, the QWIPs designed for operating in 1.3-1.55 μm region are highly expected. Due to its inherently short carrier lifetime, the ISBTs based QWIPs may offer a higher

speed capability than the standard approach based on IBTs. Although there have been some reports on observations of the ISBTs in such a short wavelength region [96], a systematic theoretical study is still lacking.

The present chapter reports our attempts on achieving the 1.3-1.55 μm ISBTs by using a dilute nitride based material system grown on GaAs substrates. There are two routes to achieve the desired wavelengths based on GaAs substrates: one route is to seek a CBO as large as one can obtain and the other route is to make the excited state into a resonant state being confined by thin tunnel barriers. The first solution is extensively applied and known as an SQW structure by using the $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{Al}_z\text{Ga}_{1-z}\text{As}$ system in the early stage. The shortest wavelength that can be achieved by using this scheme is around 1.26 μm [97]. The second approach utilizes a DBQW structure [98–106]. Instead of a single layer as the barrier, this structure uses two thin layers with extremely large band gap and further separated by a layer with smaller band gap to form a combined-barrier. Devices based on such a design exhibit low dark current and also photovoltaic behavior due to the existence of unintentional asymmetries and internal electric field as compared to the SQW devices [107]. Luna *et al.* [20] have demonstrated QWIPs operating at a wavelength as short as 1.64 μm by applying this DBQW structure with $\text{GaAs}_{1-x}\text{N}_x/\text{AlAs}/\text{Al}_z\text{Ga}_{1-z}\text{As}$ system.

Here we further explore with the similar DBQW structure for the 1.3-1.55 μm operation. The material system investigated is $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{AlAs}/\text{Al}_z\text{Ga}_{1-z}\text{As}$ heterostructures. The peculiar properties of N atoms make the $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{AlAs}$

system very promising in the short wavelengths design, due to its large CBO up to 1.5 eV.

4.2 Results and discussion

4.2.1 Calculation with the eight-band $k \cdot p$ model

In this chapter, all calculations presented are done with respect to the valence band maximum without strain. In order to verify our theoretical model for the calculations on the DBQW structures, we have performed calculations based on the eight-band model and compared them with the results reported in the literature, which are summarized in Table 4.1 ([98–106]).

The good agreements with the literature show the validity of our eight-band model for N-free DBQWs. Fig. 4.1 shows our calculations on the GaAs/AlAs/AlGaAs DBQW structure which was demonstrated by Liu *et al.* [98]. As can be observed from the figure, the modulus squared wave functions of the first twenty subbands in the conduction band have been shown. In comparison with the SQW cases, it is noteworthy that not all the electron states of the system are confined in the well region, but some of the states are confined in the outer barrier region of the DBQW structure. For instance, as Fig. 4.1 indicates, the 1st, 2nd, 8th, 13th and 17th of all the electron states are confined in the well region, while all the other states are confined in the outer barrier region.

Table 4.1: Comparison of theoretical transition energies by the eight-band $k \cdot p$ model with reported values.

Material Systems	ww (Å)	bw1 (Å)	bw2 (Å)	Temperature (K)	Published Results (meV)	Calculation Results (meV)
GaAs/AlAs ^a /Al _{0.258} GaAs	92	11.1	269	82	$E_{21}=138$	$E_{21}=131$
GaAs/AlAs ^b /Al _{0.27} GaAs	88	13.5	260	82	$E_{21}=153$	$E_{21}=140$
GaAs/AlAs ^c /Al _{0.3} GaAs	45	20	250	300	$E_1=137$ $E_2=473$ $E_3=888$ $E_{21}=350$	$E_1=145$ $E_2=487$ $E_3=920$ $E_{21}=342$
GaAs/AlAs ^d /Al _{0.3} GaAs	50	20	250	300	$E_1=118$ $E_2=414$ $E_3=790$ $E_{21}=293$	$E_1=124$ $E_2=425$ $E_3=832$ $E_{21}=301$
In _{0.53} GaAs/AlAs ^e /In _{0.52} AlAs	44	15	300	77	$E_{21}=365$	$E_{21}=352$
In _{0.84} GaAs/AlAs ^f /In _{0.52} AlAs	80	23	220	300	$E_{21}=175$	$E_{21}=154$
In _{0.15} GaAs/GaAs ^g /Al _{0.15} GaAs	43	33	300	30	$E_{21}=134$	$E_{21}=128$
In _{0.2} GaAs/GaAs ^h /Al _{0.38} GaAs	25	5	300	10	$E_{21}=264$	$E_{21}=288$
In _{0.2} GaAs/GaAs ⁱ /Al _{0.4} GaAs	30	5	300	10	$E_{21}=276$	$E_{21}=284$
In _{0.28} GaAs/GaAs ^j /Al _{0.4} GaAs	25	5	300	10	$E_{21}=284$	$E_{21}=309$
In _{0.35} GaAs/GaAs ^k Al _{0.38} GaAs	24	5	300	77	$E_{21}=288$	$E_{21}=312$

^aRef. [98]^bRef. [98]^cRef. [99]^dRef. [99]^eRef. [100]^fRef. [101]^gRef. [102]^hRef. [103]ⁱRef. [104]^jRef. [105]^kRef. [106]

Figure 4.1: Schematic conduction band potential diagram of one period of the GaAs/AlAs/Al_{0.258}Ga_{0.742}As DBQW at 82 K. The GaAs well has thickness of 92 Å and are separated by two 11.1 Å AlAs barriers. The outmost barrier is 269 Å altogether. L is the length of one period along the growth direction z . The zero point is taken at the center point of the well. The conduction band edge profile is plotted with flat solid lines. Also shown are the positions of the calculated energy subbands and the corresponding modulus squared of the wave functions. The subband 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 dashed lines, respectively. The energy levels corresponding to the individual wave functions counted from the lowest to the highest are E_1 to E_{20} , respectively. The energies are in unit of meV. The calculated transition energy $E_1 \rightarrow E_2$ by the eight-band model is $E_{21}=131$ meV.

Therefore, the third level localized in the well is actually the eighth subband of all the subbands calculated for the DBQW system. The similar observation applies to higher levels being confined in the well region. It is due to the fact that the wave functions of the states being confined in the well region tunnel through the very thin inner barriers and couple with the states being confined in the outer barriers. As a result, the levels being confined in the well which are higher than the conduction band edge of the outer

barriers increase with the coupling strength arising from the adjacent levels localized in the outer barriers. Thereby, we may make use of this regime to obtain higher ISBT energy within the well region of the DBQW structures than by the SQW structures solely. Also can be seen from Fig. 4.1 and Table 4.1, the ISBT energy $E_1 \rightarrow E_2$ is calculated as 131 meV for the GaAs/AlAs/AlGaAs DBQW structure which is in close agreement with the measured 138 meV in Ref. [98].

For our study, we are firstly interested to know how the indium and nitrogen compositions impact on the conduction band of the DBQWs. The subband and transition energy in the conduction band of the $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW calculated as a function of the indium and nitrogen compositions are depicted in Fig. 4.2. As can be observed from Fig. 4.2(a), with In increases from 0 to 30%, in step of 10%, the first and the second electron states decrease at the same time. It is due to the fact that the CBO between $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{N}_y$ well and AlAs barrier increases with In concentration, leading to a deeper well. Therefore, there are more localized subband energy levels in the well, which results in lower energy states. Also can be seen from Fig. 4.2(a), with the nitrogen concentration increases, the subband energy also decrease. This is because that the incorporation of nitrogen atoms heavily affects the fundamental band gap energy of $\text{In}_x\text{Ga}_{1-x}\text{As}$ alloy and thus a deeper well forms. It leads to more localized subbands and hence the energy of the electron states decrease. Figure 4.2(c) presents how the indium and the nitrogen incorporation affect the ground state transition ($E_1 \rightarrow E_2$) energy in the conduction band of the well. The

Figure 4.2: Dependence of subband energies and transition energies in the conduction band of the $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW structures on indium and nitrogen compositions. (a) and (c) are results of the subband energies E_1 and E_2 , and the transition energy $E_1 \rightarrow E_2$, respectively, dependent on the In and N compositions with the well layer thickness of 30 Å. (b1), (b2) and (d) are results of the subband energy E_1 , the subband energy E_2 and the transition energy $E_1 \rightarrow E_2$, respectively, dependent on the In and N compositions with the well layer thickness of 60 Å. All the calculations are under the conditions: the inner barriers are 20 Å, the outer barrier widths are 200 Å and the temperature is 300 K.

$E_1 \rightarrow E_2$ transition energy decreases with indium composition increases. A straightforward reason is from Fig. 4.2(a) that the gap between E_1 and E_2 decreases with In constituents increases, leading to a smaller transition energy. Further consideration tells us that a lighter (heavier) effective mass (m_e^*) induces higher (lower) subband energy levels. As can be seen from the Figure 1 in Ref. [44], though the bulk band gap of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ decreases with the In concentration, which causes a larger CBO and thus leads to the drop of subband energy levels, the decrease of m_e^* with indium

content causes the levels to rise on the contrary. Furthermore, E_1 is affected more heavily than E_2 by the variation of the effective mass, hence E_2 decreases much faster than E_1 as the In constituent increases, which results in a lower transition energy, as shown in Fig. 4.2(c). It is also interesting to observe from Figure 4.2(c) that the transition energy does not monotonically increase as the N concentration increases, but it decreases at first and then increases as N is incorporated. It is for the reason that as the Figure 1 in Ref. [44] indicates, with an increasing N concentration, the bulk band gap of $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{N}_y$ decreases, which induces a larger CBO. Meanwhile, m_e^* increases rapidly with N composition at first. Due to the increase of m_e^* dominating the variation of the subbands at the initial stage, it causes a rapid drop of both E_1 and E_2 and hence a decreasing transition energy results. As N incorporation proceeds, the much slower increase of m_e^* results in a more slowly fall of the electron states. Then the CBO increasing dominates the variation of the subband energy and causes the gap between the first two subbands to be larger, as shown in Figure 4.2(a), so that the curve of the transition energy rises with the N concentration after it reaches the lowest point. The same discussions apply to the similar case when $w=60$ Å, as shown in Figs. 4.2(b1), (b2) and Fig. 4.2(d).

The next step is to investigate how the well width impacts on the energy levels of the $\text{GaAs}_{0.98}\text{N}_{0.02}/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW structure. The results are shown in Fig. 4.3. As can be observed from Fig. 4.3(b), E_1 and E_2 levels reduce with well width in going from 20 to 60 Å in step of 5 Å. It can be explained as: the energy levels

Figure 4.3: Dependence of subband energy E_1 , E_2 , and transition energy $E_1 \rightarrow E_2$ in the conduction band of (a) the $\text{GaAs}_{0.99}\text{N}_{0.01}/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ and (b) the $\text{GaAs}_{0.98}\text{N}_{0.02}/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW structures on the well width. All the calculations are under the conditions: the inner barriers are 20 Å, outer barrier widths are 200 Å and the temperature is 300 K.

drop with a wider well. As for the E_2 level, there are some interesting features that with the well width increases, it decreases markedly at first and then gently and finally rapidly again. A more detailed calculation tells us that the first electron state E_1 being confined in the AlGaAs barrier is localized at about 1705 meV. When well width equals to 35 Å, the energy of E_2 in the well region is just the same as that of E_1 in the AlGaAs barrier. That is, when the well width is smaller than 35 Å, the coupling effect between E_2 in the well and those subbands localized in the AlGaAs barrier will resist E_2 to be lower than the lowest subband in AlGaAs barrier. Thereby, as the well width approaches this boundary (35 Å), it drops more slowly. However, with well width increases to be larger than 35 Å, E_2 in the well drops to be even lower than E_1 in the AlGaAs barrier so that no coupling effects from the AlGaAs barrier impact on

E_2 in the well region and it follows that the dropping velocity of this state increases again. Taking into account that E_1 in the well region will never be impacted on by the level E_1 in the AlGaAs barrier, it steadily decreases with the well width. It illustrates why the variation of the transition energy $E_1 \rightarrow E_2$ in the well is similar to that of the E_2 level in the well, as shown in Fig. 4.3(b). In addition, we also calculate the case when $N=1\%$, all the other conditions are the same, as shown in Fig. 4.3(a). As we can see, the variation for this case are similar to the case when $N=2\%$, and we do not elaborate on it.

Turning now to investigate the dependence of $E_1 \rightarrow E_2$ transition energy on the Al composition of the $\text{Al}_z\text{Ga}_{1-z}\text{As}$ outer barrier by using a $\text{GaAs}_{0.98}\text{N}_{0.02}$ (25 Å)/AlAs (20 Å)/ $\text{Al}_z\text{Ga}_{1-z}\text{As}$ (200Å) DBQW structure. The Al content is changed from 0% to 45%, in step of 5%. As depicted in Fig. 4.4(a), E_1 decreases slightly while E_2 increases slowly with the aluminium composition. It is due to the fact that with Al increases, the band gap of AlGaAs increases, which results in a smaller AlGaAs band offset with respect to the AlAs barrier. Therefore, the subbands being confined in the AlGaAs barrier rise with more Al. Because of the coupling effects between the subbands in the AlGaAs barrier and those in the $\text{GaAs}_{0.98}\text{N}_{0.02}$ well, the subbands localized in the well which are higher than those in the barrier are caused to be lifted. This explains why E_2 in the well becomes higher as Al increases. Whereas with Al concentration being incorporated into the outer barrier, the actual CBO between the $\text{GaAs}_{0.98}\text{N}_{0.02}$ well and the AlGaAs barrier becomes larger, that's to say, a deeper virtual well forms. It

Figure 4.4: (a) Dependence of subband energy E_1 , E_2 , and transition energy $E_1 \rightarrow E_2$ in the conduction band of the $\text{GaAs}_{0.98}\text{N}_{0.02}/\text{AlAs}/\text{Al}_z\text{Ga}_{1-z}\text{As}$ DBQW structure on aluminum concentrations under the conditions: the well widths are 25 Å, inner barrier widths are 20 Å, outer barrier widths are 200 Å and the temperature is 300 K. (b) dependence of subband energy E_1 , E_2 , and transition energy $E_1 \rightarrow E_2$ in the conduction band of the $\text{GaAs}_{0.98}\text{N}_{0.02}/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW structure on the temperature under the conditions: the well widths are 25 Å, inner barrier widths are 20 Å, outer barrier widths are 200 Å.

induces a decreasing E_1 , as can be seen from Figure 4.4(a). From the analysis above, the transition energy $E_1 \rightarrow E_2$ increases with Al incorporation. However, the range is moderate, only about 30 meV (788-819 meV).

We have also done research on energy levels E_1 , E_2 and its separation as a function of temperature by using a $\text{GaAs}_{0.98}\text{N}_{0.02}$ (25 Å)/ AlAs (20 Å)/ $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ (200 Å) DBQW structure, as shown in Fig. 4.4(b). Both the E_1 and E_2 drop while the separation between them increases as the temperature increases. It can be explained as that the temperature sinking induces the band gap of $\text{GaAs}_{0.98}\text{N}_{0.02}$ to reduce, which leads to the decreasing subband energy. And due to that only E_2 is affected by the coupling effect from the levels localized in the outer barrier, it drops at a relatively slower speed with respect to E_1 . Thus the separation between E_1 and E_2 increases with temperature, as

Figure 4.5: The calculated intersubband transition ($E_1 \rightarrow E_2$) coefficients as a function of the transition energy for the $\text{GaAs}_{0.98}\text{N}_{0.02}/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW structure at room temperature. The $\text{GaAs}_{0.98}\text{N}_{0.02}$ well has a thickness of 25 Å and are separated by two 20 Å AlAs barriers. The outmost $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ barrier is 200 Å altogether. (a) and (b) are results of TM and TE mode transitions, respectively.

shown in the figure.

Figures 4.5(a) and (b) give out the calculated absorption curves for the combination of $\text{GaAs}_{0.98}\text{N}_{0.02}$ (25 Å)/AlAs (20 Å)/ $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ (200 Å) DBQW structure at room temperature. After calculating the density of states, a Fermi level of around 1500 meV is achieved with a doping concentration of $1 \times 10^{18}/\text{cm}^3$. The half linewidth is taken as 10 meV. The peak positions of the TM and TE absorption curves are both around

Table 4.2: Structures of the DBQWs for the comparison with the literature by the 10-band model and the comparison results

Structure No.	Structure	ww (Å)	bw1 (Å)	bw2 (Å)	T(K)	Experimental(μm)	Calculation(μm)
I	GaAs _{0.99} N _{0.01} /AlAs/ Al _{0.3} Ga _{0.7} As ^a	35	20	300	25	1.64(bias of 2V)	1.54
II	GaAs _{0.993} N _{0.007} /AlAs/ Al _{0.3} Ga _{0.7} As ^b	30	20	300	300	3	2.90
III	GaAs _{0.993} N _{0.007} /AlAs/ Al _{0.3} Ga _{0.7} As ^c	55	20	300	300	2.5	2.46

^aRef. [20]^bRef. [109]^cRef. [109]

795 meV (1.56 μm) which agree well with our calculated subband energy difference $E_1 \rightarrow E_2$ for this structure. From Fig. 4.5, we can observe that compared to the amplitude of TM mode absorption, TE mode absorption is neglectable, which obeys the selection rule [108].

4.2.2 Calculation with the ten-band $k \cdot p$ model

Verification of the 10-band $k \cdot p$ method

In order to verify our theoretical model, we have performed some calculations based on the ten-band model and compared them with the reported absorption results in the literature. Up to now, there are only a few studies on $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{AlAs}/\text{Al}_z\text{Ga}_{1-z}\text{As}$ DBQWs. We compared our calculations with the experimental results by Luna *et al.* [20, 109]. Table 4.2 gives out the detailed structures they studied and the results of our comparison.

Figure 4.6 illustrates our calculation results on the structure I shown in Table 4.2.

Luna *et al.* found a responsivity peak located at $1.64 \mu\text{m}$ under an applied bias of 2 V for this material system. Figure. 4.6(a) shows the squared wave functions. The first four wave functions coming from the GaAsN well are denoted by solid lines. It is interesting to note that two of them have one single peak and the other two have double peaks in the well region, rather than the normal case with a single peak for the ground level, double peaks for the first excited level and so on. We did not observe the similar features from the InGaAsN/GaAs QWs [44] with a low confinement, where both the ground and the first excited levels are below E_N . The interesting finding in the GaAsN/AlAs QW with a very deep well can be explained as follows: due to the fact that the nitrogen level is introduced between the ground level and the first excited level in the conduction band of the GaAsN/AlAs QW, the N repulsion leads to that the ground level E_1 splits into an S -like E_{1-} and an S_N -like E_{1+} , meanwhile, though the first excited level E_2 is much higher than the nitrogen state, it is still being affected by the strong repulsion of the N levels. The second level splits into a lower S_N -like E_{2-} and a higher S -like E_{2+} . It leads to the anticrossing effect to the dispersion curves, as observed from Fig. 4.6(b). The dispersion of E_{1-} exhibits flattening trend (S_N -like) near the nitrogen band as the wavevector increases, while the E_{1+} curve becomes flat (S_N -like) near the nitrogen band as the wavevector approaches zero. In addition, with the variation of the wavevector, the curve of E_{2-} is nearly flat-shaped (S_N -like), due to its strong interaction with the N band. From the analysis above, the actual S -like ground level E_1 ought to be E_{1-} while the S -like first excited level E_2 ought to be

Figure 4.6: Energy levels and absorption coefficients in a $\text{GaAs}_{0.99}\text{N}_{0.01}/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW with the well width of $35 \text{ \AA}$ (a) The corresponding squared wave functions. The wave functions being confined in the well region (GaAsN) are denoted by solid lines and those being confined in the outer barrier region (AlGaAs) are denoted by dashed dotted lines, respectively. (b) Dispersions of the subbands in the conduction band of the well (the ground and the first excited levels only). At $k=0$, the highest and the lowest subbands are identified as S -like and the other two states are identified as S_N -like. (c) The calculated intersubband transition coefficients as a function of the transition energy at 25 K. The detailed structure is for the structure I described in Table 4.2.

E_{2+} . Thereby, the ISBT of $E_1 \rightarrow E_2$ can be attributed to $E_{1-} \rightarrow E_{2+}$. Fig. 4.6(c) is a further evidence to support this rule. The absorption coefficient is calculated at an electron concentration of $1 \times 10^{18} \text{ cm}^{-3}$. The diagram shows us that the weak low energy transition is built on $E_{1-} \rightarrow E_{2-}$ while the strong high energy transition is built on $E_{1-} \rightarrow E_{2+}$. It can be explained as follows: the S -like E_{2+} contains much less N component (at $k=0$) than the S_N -like E_{2-} . Since the N component has no contribution to the transition, the amplitude of the oscillator strength decreases with N concentration. Hence the absorption coefficients decrease with more N component. A further discussion on the impact of the N component on the ISBTs will be presented later. Our views generally agree to those of Duboz [110]. However, we have found that though E_{2-} is very close to E_N (about 1650 meV), it is higher than E_N . The contrary case is found in Ref. [110]. It is due to the fact that although E_{2-} is shifted downward by the N repulsion, it is also lifted by the confinement potential of the AlGaAs barrier, as shown in the figure. Moreover, that the well width (35 Å) is narrower for the present calculation than the case in the reference (50 Å) may be another reason. Our calculated results show the energy of the ISBT based on the ground level $E_{1-} \rightarrow E_{2+}$ is 804 meV (1.54 μm) which is in good agreement with the responsivity peak (1.64 μm) [20], considering that the applied bias of 2 V leads to a redshift of the actual ISBT wavelength.

The comparison results of the structure II in Table 4.2 are shown in Fig. 4.7. From Fig. 4.7(a), a new order of E_{1+} and E_{2-} is discovered. Unlike the results we

Figure 4.7: Energy levels and absorption coefficients in a $\text{GaAs}_{0.993}\text{N}_{0.007}/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW with the well width of 30 Å (a) The squared wave functions corresponding to the subbands in the conduction band. The wave functions being confined in the well region (GaAsN) are denoted by solid lines and those being confined in the outer barrier region (AlGaAs) are denoted by dashed dotted lines, respectively. (b) The calculated intersubband absorption coefficients as a function of the transition energy at room temperature. The detailed structure is for the structure II described in Table 4.2.

have observed for the structure I, now E_{2-} is conversely above E_{1+} . The most likely explanation is that with the well width decreases as compared to the last case, the original E_2 level before split is pushed upward. When the nitrogen level couples with the higher E_2 level, E_2 also splits into higher E_{2-} and E_{2+} levels. Thus, the resulted E_{2-} level may be above the E_{1+} level. The ISA spectra shown in Fig. 4.7(b) allows to better understand the situation. A high energy peak at 778 meV (1.59 μm) with a larger amplitude than the one at low energy side (431 meV) appears. The former transition corresponds to the ISBT from the S -like ground level to the first excited level, $E_{1-} \rightarrow E_{2+}$. At the same time, the weak peak is resulted from the ISBT $E_{1-} \rightarrow$

E_{2-} , which corresponds to a $2.9 \mu\text{m}$ ISA. It matches the absorption peak observed in Ref. [109]. Since the experimental results did not cover ISA wavelengths below $2.5 \mu\text{m}$, we can not further draw conclusion on the calculated ISA feature at about $1.59 \mu\text{m}$.

Fig. 4.8 shows another comparison with the structure III described in Table 4.2. The width of the GaAsN well increases from $30 \text{ \AA}$ for the structure II to $55 \text{ \AA}$. As can

Figure 4.8: Energy levels and absorption coefficients in a $\text{GaAs}_{0.993}\text{N}_{0.007}/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW with the well width of $55 \text{ \AA}$ (a) The squared wave functions corresponding to the subbands in the conduction band. The wave functions being confined in the well region (GaAsN) are denoted by solid lines and those being confined in the outer barrier region (AlGaAs) are denoted by dashed dotted lines, respectively. (b) The calculated intersubband absorption coefficients as a function of the transition energy at room temperature. The detailed structure is for the structure III described in Table 4.2.

be observed from Fig. 4.8(a), all the levels in the conduction band drop with the well

width. Even the second excited level E_3 decreases to an energy below the band edge of the AlAs barrier. A similar case with the report in Ref. [110] is observed: due to the interaction of the original E_1 and E_2 with the nitrogen level, E_1 splits into E_{1-} and E_{1+} , while E_2 splits into E_{2-} and E_{2+} . Both the new levels E_{1-} and E_{2-} are below E_N (1650 meV) while the levels E_{1+} and E_{2+} are above it. Now E_{2-} is lower than the band edge of the AlGaAs barrier. The calculated ISA spectrum is shown in Fig. 4.8(b). There are three peaks presented in the figure, corresponding to the transitions of $E_{1-} \rightarrow E_{2-}$, $E_{1-} \rightarrow E_{2+}$ and $E_{1-} \rightarrow E_3$ from the low energy to the high energy portions. As the E_{2-} state is N-rich, while E_{2+} state contains less N content, the intensity of the transition based on E_{2-} is weaker than that of the transition based on E_{2+} . With respect to the AlGaAs barrier, the ISBT of $E_{1-} \rightarrow E_{2+}$ is bound to bound, while $E_{1-} \rightarrow E_3$ is bound to continuum. It follows that the ISA amplitude of the former transition is larger than the latter one, which is in agreement with the graph. As a result from the ISA curve, the transition of $E_{1-} \rightarrow E_{2+}$ corresponds to 503 meV ($2.46 \mu\text{m}$) which is in good agreement with the measured $2.5 \mu\text{m}$ peak. For the experimental results lack the wavelengths range ($<2 \mu\text{m}$ and $>5 \mu\text{m}$) covering the other two peaks from our calculations, the other two ISA peaks cannot be compared with the experimental results.

From the comparisons with the three samples above, we may, therefore, confirm the validity of the ten-band $k \cdot p$ method.

Theoretical design of the DBQW structures with ISAs at 1.31 and 1.55 μm

We now present the design procedure for the DBQW structures within which the ISBTs from the ground level to the second level corresponding to 1.31-1.55 μm . The band structures and absorptions of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW, with the inner barrier (AlAs) width of 15 Å and the outer barrier (AlGaAs) width of 130 Å are calculated by the ten-band model at the temperature of 20 K.

For our design, we are firstly interested to know how the N content impacts on the conduction band structure of the DBQW. For the current step, the In content is fixed at 30% and the well width is fixed at 20 Å.

Fig. 4.9 shows the variation of the squared wave functions of the ground level E_1 and the first excited state E_2 with the increasing N content. For simplicity, we have not included the states being confined in the AlGaAs barrier regions. As can be seen, as long as the N content being introduced in QWs with high confinement potentials, E_1 and E_2 will split into E_{1-} , E_{1+} , E_{2-} and E_{2+} , respectively. With E_N located at about 1610 meV, both the resulted E_{1+} and E_{2-} are adjacent to the N level but above it. We have seen the similar case earlier. The very narrow well width (20 Å) and the high confinement potential cause that these two levels keep at a relatively high energy. What's more interesting is that, at the beginning, E_{2-} is higher than E_{1+} , with the N content increases, E_{2-} drops while E_{1+} rises. When the N content increases from 0.6% to 0.9%, E_{1+} and E_{2-} swap their positions which leads to that E_{2-} is lower than E_{1+} .

Figure 4.9: Dependence of the squared wave functions corresponding to the subbands E_{1-} , E_{2-} , E_{1+} , E_{2+} in the well of an $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{1-y}\text{N}_y/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW on the N concentration. The well width is $20 \text{ \AA}$ and the temperature is 20 K .

The reason is that with N content increases, the increasing repulsion strength from the N level causes the separation between E_{1-} to E_{1+} and E_{2-} to E_{2+} being enlarged.

We shall now look more carefully into how the concentration of nitrogen atoms impacts on the components of nitrogen (N), electron (e), heavy hole (HH), light hole (LH) and spin-orbit split-off band (SO) in E_{1-} , E_{1+} , E_{2-} and E_{2+} states, respectively. Fig. 4.10 shows the dependence of the five components of the E_{1-} state on the nitrogen concentration. With k value decreases, the N component decreases while the electron component increases. As k approaches zero, the electron component becomes dominant. Considering the dominance of electron at $k=0$, the E_{1-} state is S -like. Also can be seen from Fig. 4.10, with nitrogen concentration increases from 0.3% to 1.5% , the N

Figure 4.10: Dependence of the percentage of the components of the N , electron, HH, LH and SO states in the E_{1-} state on the N concentration. The structure considered is an $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{1-y}\text{N}_y/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW. The well width is 20 Å and the temperature is 20 K.

component increases while the electron component decreases. We also find that there are still a very few percent of HH, LH, and SO components in the E_{1-} state due to the interaction effect between the valence band and the conduction band.

Figures 4.11 and 4.12 indicate the dependence of the five components of E_{1+} and E_{2-} states on the N concentration.

For these two subbands, the N component is dominant (S_N -like) near $k=0$ which shows the strong interaction between the two states and the N level. As can be seen from Fig. 4.11(a) and (b), with k increases, the N components generally increase while the electron components decrease. However, as the N concentration increases from

Figure 4.11: Dependence of the percentage of the components of the E_{1+} state on the N concentration. The structure considered is an $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{1-y}\text{N}_y/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW. The well width is 20 Å and the temperature is 20 K.

Figure 4.12: Dependence of the percentage of the components of the E_{2-} state on the N concentration. The structure considered is an $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{1-y}\text{N}_y/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW. The well width is 20 Å and the temperature is 20 K.

0.6% to 0.9%, the N components decrease while electron components increase and such a trend keeps towards higher N concentration. To explain this phenomenon, a comparison with Fig. 4.12 is helpful. Fig. 4.12(a) and (b) show a similar case with Fig. 4.11(c), (d) and (e). At the same time, Fig. 4.12(c), (d) and (e) are similar with Fig. 4.11(a) and (b). It is due to the fact that when N increases from 0.6% to 0.9%, E_{1+} alternates its position with E_{2-} , as previously shown in Fig. 4.9. At $N \leq 0.6\%$, E_{1+} is lower than E_{2-} , so that E_{1+} is closer to the N level than E_{2-} . It introduces larger N percentage into E_{1+} , as shown in Fig. 4.11(a) and (b). At $N \geq 0.6\%$, E_{1+} is above E_{2-} . The interaction between the N resonant state and E_{1+} is weaker. Though at $k=0$, the N occupation is still dominant, the electron becomes the major component for larger k , as shown in Fig. 4.11(c), (d) and (e). The similar explanation can be applied for the discussion on E_{2-} .

Figure 4.13 shows the variation of the five components of E_{2+} state in the InGaAsN well. We find that E_{2+} level is more like an electron state, because its N component is trivial. With the N content increases from 0.3% to 1.5% in the InGaAsN well, the N component increases. The dominant electron component in E_{2+} is another evidence confirming that it is the S -like E_2 level considering the N repulsion. In addition, it also explains why the amplitude of ISAs from E_{1-} to E_{2+} are much larger than E_{1-} to E_{2-} level, as previously illustrated in Figs. 4.6 to 4.8.

Now let us consider how the in-plane dispersion relations vary with the N content. We have calculated the energy dispersion curve along the $[100]$ and $[110]$ crystal di-

Figure 4.13: Dependence of the percentage of the components of the N , electron, HH, LH and SO states in the E_{2+} state on the N concentration. The structure considered is an $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{1-y}\text{N}_y/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW. The well width is 20 Å and the temperature is 20 K.

rections for conduction subbands of the DBQW structure using the ten-band model, as described in Fig. 4.14. We can observe that due to the band anticrossing, the conduction subbands are further flattened to be highly non-parabolic. The variation of the energy dispersions with k points follows such a rule: For a state contains more electron component (S -like), its dispersion curve is more parabolic. In contrast, for a state contains more N component (S_N -like), its curve tends to be flatter.

We present now the subbands and the transition energy in the conduction band of the $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{1-y}\text{N}_y/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW calculated as a function of the nitrogen composition, as illustrated in Fig. 4.15(a). As can be observed from the figure, with N increases from 0.3% to 1.5%, E_{1-} and E_{2-} decrease, while E_{1+} and E_{2+}

Figure 4.14: Dependence of energy dispersion curves for the subbands E_{1-} , E_{2-} , E_{1+} , E_{2+} in the conduction band along $[100]$ and $[110]$ crystal directions for an $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{1-y}\text{N}_y/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW on the N concentration. The well width is $20 \text{ \AA}$ and the temperature is 20 K .

increase at the same time. It is due to the fact that the repulsion strengths between the N level and the original E_1 and E_2 becomes stronger with the N content which leads to the separation between the split states increase. Such a variation of the discrete subbands directly results in the transition energy increases with the N content. The similar observation has been reported in Ref. [110], except for the crossing of the E_{1+} and the E_{2-} states with the N content. It can also be seen from Fig. 4.15(a), the discrete solid lines identified as B1 to B4 are the subbands localized in the AlGaAs barrier. They are nearly unchanged with N increases since the CBOs of AlGaAs/AlAs are constant.

We are now ready to consider the ISA spectra as a function of the N content calcu-

Figure 4.15: (a) Dependence of the subbands (E_{1-} , E_{2-} , E_{1+} , E_{2+}) and the energy separation between the ground and the first excited level ($E_{1-} \rightarrow E_{2+}$) in the conduction band for an $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{1-y}\text{N}_y/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW on the N concentration. The solid lines are the subbands being localized in the AlGaAs barrier ($E_1 \rightarrow E_4$ from bottom to top). (b) Dependence of the absorption coefficients for the DBQW on the N concentration. The well width is 20 Å and the temperature is 20 K.

lated by our model. The results are shown in Fig. 4.15(b) with a doping concentration at $1 \times 10^{18} \text{ cm}^{-3}$. Different with Fig. 4.6 to Fig. 4.8, where there are two peaks for the absorption spectra corresponding to the high energy and the low energy, respectively. The results show negligible feature at the low energy side for the $E_{1-} \rightarrow E_{2-}$ transition. We attribute this to the narrow-well-width effect. The E_{2-} level is pushed closer to the N level with the reduction of the well width so that the oscillator strength decreases. The energy of the ISBT increases from 521 meV to 727 meV with the N content changing from 0% to 1.5%, which shows an obvious blueshift.

We are now in a position to study how the InGaAsN well width impacts on the

Figure 4.16: (a) Dependence of the subbands E_{1-} , E_{2-} , E_{1+} , E_{2+} and the transition energy $E_{1-} \rightarrow E_{2+}$ in the conduction band of an $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.985}\text{N}_{0.015}/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW on the InGaAsN well width. The solid lines are the subbands being localized in the AlGaAs barrier ($E_1 \rightarrow E_4$ from bottom to top). (b) Dependence of the absorption coefficients for the DBQW on the InGaAsN well width. All the calculations are at the temperature of 20 K.

energy levels and the transition energy in the DBQW structure. The results are shown in Fig. 4.16(a). As can be seen, all the four levels E_{1-} to E_{2+} reduce with the well width in going from 20 to 50 Å. The highest level E_{2+} drops from above the fourth level in the AlGaAs barrier to a state lower than the first level in the AlGaAs barrier. As for the case considered here, the In content and the N content are equal to 30% and 1.5% in the well, respectively. E_{1+} is always above E_{2-} with the well width increases.

Now we discuss the ISA spectra as a function of the well width. The results are shown in Fig. 4.16(b) with a doping concentration at $1 \times 10^{18} \text{ cm}^{-3}$. When the well width increases, the amplitude of the peaks corresponding to the transition of

$E_{1-} \rightarrow E_{2+}$ (high energy one) reduces slightly. On the other hand, the lower energy peaks based on E_{1-} to E_{2-} transition become stronger with the well width. It can be explained as follows: due to that E_{2-} is pushed far away below the N level (around 1610 meV), by contrast, E_{2+} is pushed closer to the N level with a wider well, the oscillator strength of the ISBT $E_{1-} \rightarrow E_{2+}$ decreases while that of the ISBT $E_{1-} \rightarrow E_{2-}$ increases. It further explains why the low energy peak in Fig. 4.15 with narrow well width (20 Å) is trivial. Consequently, the ISBT energy redshifts from 727 meV to 482 meV with the increasing well width.

The subbands and the transition energy in the conduction band of the InGaAsN DBQW calculated as a function of the indium composition is illustrated in Fig. 4.17. When In increases from 0 to 30%, all the four levels E_{1-} to E_{2+} drop. The energy of the $E_{1-} \rightarrow E_{2+}$ transition decreases with In in the well. A straightforward reason is that the energy gap between E_{1-} and E_{2+} decreases with an increasing In, leading to a smaller transition energy.

Fig. 4.17(b) shows the ISA spectra at different In content with a doping concentration at $1 \times 10^{18} \text{ cm}^{-3}$. When In increases, the amplitude of the peaks corresponding to the transition of $E_{1-} \rightarrow E_{2+}$ (high energy one) increases, because the N component contained in E_{1-} decreases. When In < 10% and > 15%, the increase of the amplitude is slight. However, it increases greatly when In increases from 10% to 15%. This is due to the fact that the transition type changes from bound→bound to bound→continuum with respect to the AlAs barrier edge. There are other low energy peaks based on E_{1-}

Figure 4.17: (a) Dependence of the subbands E_{1-} , E_{2-} , E_{1+} , E_{2+} and the transition energy $E_{1-} \rightarrow E_{2+}$ in the conduction band of an $\text{In}_x\text{Ga}_{1-x}\text{As}_{0.985}\text{N}_{0.015}/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW on the In concentration of the InGaAsN alloy. The discrete dashed lines are the subbands being localized in the AlGaAs barrier ($E_1 \rightarrow E_7$ from bottom to top). (b) Dependence of the absorption coefficients for the DBQW on the In concentration. All the calculations are for $w=20$ Å and at the temperature of 20 K.

to E_{2-} transition which are negligible. They are resulted from the narrow-well-width (20 Å) effect mentioned above. As a result, the ISBT energy decreases from 1052 meV to 727 meV with the In concentration.

Finally, our design process by the ten-band model, as shown in Figs. 4.15 to 4.17, propose two structures. One is $\text{In}_{0.17}\text{Ga}_{0.83}\text{As}_{0.985}\text{N}_{0.015}/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW with the well width of 20 Å, the AlAs barrier width of 15 Å and the AlGaAs barrier width of 130 Å. Under the temperature of 20 K, it can achieve an ISA peak at about $1.31 \mu\text{m}$ (947 meV). The other one is with the In composition of 25% (the other

parameters are the same as above) which may achieve an ISA peak at about $1.55\ \mu\text{m}$ (800 meV).

4.2.3 Comparison of the results by the eight-band model with the ten-band model

We have also made use of the eight-band model to calculate the structures in Refs. [20, 109]. The resulted transition energies are far less than the experimental measured. From this view of point, the eight-band model are not as accurate as the ten-band model for our present calculations on the absorptions within InGaAsN/AlGaAs QWs. From the comparison of Figs. 4.2 calculated by the eight-band model with Figs. 4.17 by the ten-band model, we can conclude though the energy of ground levels (E_1) are comparable to each other, the excited level E_2 calculated by the eight-band model are much lower than those by the ten-band model. It is due to the fact that lacking the descriptions of the anticrossing characteristics from the N level, the eight-band model greatly underestimates the ground level transition energies especially for QWs with large CBO (N level is sandwiched between E_1 and E_2). It shows the consideration of E_{1+} and E_{2-} level is necessary in order to accurately calculate the $E_1 \rightarrow E_2$ transition energies and hence the absorptions.

4.3 Summary

In conclusion, a study of the $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW structures has been reported within the eight-band and the ten-band $k \cdot p$ scheme. This material system is very promising for the production of intersubband absorptions in the 1.3-1.55 μm optical communication wavelengths region thanks to its large CBO. After a careful comparison made between the results by the eight-band model and the ten-band model, the eight-band method is ruled out for the optimal design of the DBQW structures. From the calculations by the ten-band $k \cdot p$ model, we find that for the QWs with the N level being sandwiched between the ground and the first excited levels, the first two subbands are split. This effect is very useful to shorten the ISA wavelengths. We conclude that the energy of the ISBT within the QW increases with the N concentration, by contrast, it decreases with the well width and the In concentration, respectively. By a careful tailoring of the compositions, the optimal structures have been obtained to achieve ISA wavelengths at 1.31 and 1.55 μm , respectively.

Chapter 5

Study of inter-well intersubband transitions in InGaAsN/AlAs coupled quantum wells for emissions at 3-5 μm

5.1 Introduction

Ever since the first QCLs were demonstrated by a team of researchers at Bell Labs [111], tremendous progress in QCLs research has resulted in applications such as ultra-wide tunable sources, fs-pulse mode-locking, second-harmonic generation, and trace gas detection. In the early stage, the main material system used for the realization of QCLs was in the InP based InGaAs-AlInAs system [111], and a significant improvement of the device performance such as continuous wave (CW) operations above 5 μm at room

temperature have been demonstrated since [112, 113]. However, there has been no report of such high performance laser operation in the technologically important $\lambda \approx 3\text{--}5\ \mu\text{m}$ atmospheric window region by utilizing the same system. The obstacle in obtaining the short wavelength QCL operation originates from the relatively small CBO of the InGaAs-AlInAs heterostructure ($\sim 520\ \text{meV}$). Consequently, the main challenge of the $3\text{--}5\ \mu\text{m}$ QCL design is to seeking material systems with the highest possible CBO. Recently, the InGaAs-AlAsSb heterostructures grown on the InP substrates with CBO up to $1.6\ \text{eV}$ have been extensively studied [114], and a QCL emitting at $\lambda \approx 4.5\ \mu\text{m}$ up to at least $400\ \text{K}$ in pulsed mode has been achieved [115]. Another promising system for the development of QCLs is InAs-AlSb (CBO $\sim 2.1\ \text{eV}$) grown on GaSb or InAs substrates. $3.5\text{--}5.5\ \mu\text{m}$ emissions have been reported by utilizing this heterostructure grown on a GaSb substrate [116], however, no stable laser devices on such a specific substrate can be produced up to now.

In comparison to the systems discussed above, traditional GaAs based GaAs-Al(Ga)As system offers more growth flexibility. QCLs based on this system have been under extensive research for the past decade. The first GaAs-AlGaAs QCL with emission at $9.4\ \mu\text{m}$ was realized in 1998 [117], since then the radiation wavelengths of QCLs have been extended to as long as $160\ \mu\text{m}$ [118]. However, a QCL emitting below $5\ \mu\text{m}$ has not been achieved with this system. The limitation is set by the well depth of the GaAs-AlGaAs heterostructure. With up to 33% Al content, the conduction band discontinuity is no more than $0.3\ \text{eV}$. Though the GaAs-AlAs system has a much

larger CBO (~ 1 eV), the effective CBO in the GaAs/AlAs heterostructure is much smaller (~ 0.2 eV) in consideration of the Γ -X indirect discontinuity. Yet the emission wavelengths below $5\ \mu\text{m}$ with the GaAs/AlAs heterostructure are hard to achieve [119]. For applications of free space communications, stable laser devices emitting at the atmospheric transparent window are highly desirable. It leads to the design of active regions with as deep a well as one can obtain on the GaAs substrates.

If we restrict ourselves on GaAs based systems, a promising way to satisfy the requirements is by utilizing the $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{AlAs}$ heterosystems for the QCL active region design. Due to its large CBO (~ 1.5 eV), electrons being thermally activated into continuum states can be considerably suppressed, which results in the improvement of the temperature dependent threshold current characteristics [120]. In this work, we report a QCL active regions design based on GaAs substrates in order to achieve the goal of $3\text{-}5\ \mu\text{m}$ laser emissions.

5.2 Results and discussion

Though the eight-band model can not be accurately used to determine excited levels within InGaAsN/AlAs QWs, it is still reasonable to be utilized to calculate the ground levels in this system, as discussed in the previous chapter. Hence, in this chapter, we will apply this model in achieving optimum design of QCL structures based on InGaAsN/AlAs. All calculations presented are done with respect to the valence band

maximum without strain.

In order to verify our theoretical model for the calculations in the QCL structures, we have performed some calculations based on the eight-band model and compared them with the experimental and theoretical results reported in the literatures. The results are presented in Fig. 5.1 and Table 5.1, respectively.

Figure 5.1: Comparison of the active region of the laser heterostructure at threshold bias (at 48 kV/cm) between the results of our calculation and Ref. [117]. Shown are the positions of the calculated energy subbands and the corresponding modulus squared of the wave functions, denoted by flat solid lines and curved solid lines, respectively. The material system considered is GaAs/ $\text{Al}_{0.33}\text{Ga}_{0.67}\text{As}$ CQWs. Number 1, 2, and 3 indicate the sequence of electron states, E_1 , E_2 and E_3 , respectively. The sequence of the wells and barriers is in accordance with the definitions from Fig. 2.3. The thicknesses of the layers are in unit of nm. The calculated transition energy by the eight-band model are $E_{32}=143$ meV and $E_{21}=38$ meV.

Fig. 5.1 shows our calculation on the first GaAs/AlGaAs QCL structure which was demonstrated by Sirtori *et al.* [117]. The comparison is made on the first three principal

Table 5.1: Comparison of theoretical transition energies of GaAs/AlGaAs by the eight-band $k \cdot p$ model with published values.

Barrier layer composition (Al)	Well and Barrier width (well 1,2,3 and barrier 1,2,3) (nm)	External Electric Field (kV/cm)	Our Cal E_{32} (1) (meV)	Pub E_{32} (2) (meV)	Difference (1)-(2) (meV)
1 ^a	3.3, 6.8, 6.0	39	127	109	18
	0.5, 0.5, 3.0				
0.33 ^b	1.5, 4.9, 4.0	45	139	130	9
	2.0, 1.7, 11.4				
0.45 ^c	1.9, 5.4, 4.8	48	147	160	-13
	1.1, 1.1, 7.4				
0.45 ^d	4.3, 5.0, 5.4	30	35	43	-8
	0.94, 0.94, 2.84				

^aRef. [119]

^bRef. [121]

^cRef. [120]

^dRef. [122]

electron states that are confined in the active region, which comprises of the well 1 to the well 3 (equal to 15, 49, and 40 Å, respectively) and the barrier 1 to the barrier 3 (equal to 20, 17, and 92 Å, respectively). Our calculated transition energy from the upper lasing level (E_3) to the lower lasing level (E_2) for laser action, namely, E_{32} , equals to 143 meV. And the transition energy from the lower lasing level (E_2) to the ground level (E_1), namely, E_{21} , equals to 35 meV. These values are in agreement with the measured E_{32} (132 meV) and their calculated E_{21} (35 meV) in Ref. [117]. Also can be seen from Fig. 5.1, the respective squared wave functions calculated are also in accordance with the published results. In Table 5.1, the comparisons of our predicted transition energy E_{32} with the published results on GaAs/Al_xGa_{1-x}As QCLs establish the reliability of our method [119–122].

Figure 5.2: Schematic conduction band diagrams and the modulus squared of the bound state wave functions of a single period of the $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.97}\text{N}_{0.03}/\text{AlAs}$ coupled quantum well, which is the same as an active region of the quantum cascade laser structure, under zero bias. The InGaAsN wells have thicknesses of 40 Å, 60 Å and 80 Å from left to right, respectively, and are separated by 20 Å AlAs barriers (bw1 and bw2). The outmost barrier (bw3) is 200 Å altogether. The energy levels corresponding to the individual wave function counted from the lowest energy to the highest energy are E_1 to E_{15} , respectively. The temperature is 300K.

Fig. 5.2 illustrates the conduction band diagram of one period of the QCL active region in the laser core. It consists of three $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.97}\text{N}_{0.03}$ quantum wells closely coupled by AlAs barriers. The temperature and electric field strength being considered are 300 K and 0 kV/cm, respectively. As can be observed from the figure, there are overall fifteen subbands plotted, with fourteen bound states and one quasi-continuum state just above the barriers. In all cases, we express the n th subband in the w th well of the three-coupled wells in terms of “ C_n^w ”. For instance, the first subband confined in well 3 is expressed as C_1^3 . Thus, by applying the definition “ C_n^w ”, the first five states in

the TQWs are: $E_1 - C_1^3$, $E_2 - C_1^2$, $E_3 - C_1^1$, $E_4 - C_2^3$ and $E_5 - C_2^2$. Such an order of the levels is the consequence of the linear function form that the subband energy decreases as the well width increases. As the diagram indicates, the 80 Å well is the widest, thus the ground electron state of the whole CQWs is confined in this well. The second electron state is confined in the second widest, 60 Å central well, and the third state is confined in the narrowest well 1, and so forth. As In and N concentrations increase to 30% and 3%, respectively, the CBO of the heterostructure increases to 1.5 eV. At the same time, the conduction band effective mass of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ increases with the nitrogen concentration. Consequently, the subbands in the CQWs become closer and lower. By utilizing this regime, it is possible to design such a QCL structure, within which the upper lasing level will be lower than the X point in the CB of the barrier, in order to avoid the Γ -X inter-valley transition. Moreover, a deeper well leads to the freedom in enlargement of the separation between the upper lasing level (E_3) and the lower lasing level (E_2), which is promising for 3-5 μm QCL design.

The subband and transition energy of the QCL active region calculated as a function of the width of the well 1 (10-60 Å) is presented in Fig. 5.3(a). As can be seen from the figure, as well 1 grows, E_1 gradually increases from 1215 meV to 1228 meV, and E_2 slightly increases from 1246 to 1248 meV, nearly unaltered, whereas E_3 reaches a maximum at the well width of 40 Å, furthermore, a decrease at larger well widths is observed. The topmost curve shows that C_1^1 falls with the width of well 1, supporting the notion that the larger the well width, the lower the confined energy is. It is more

Figure 5.3: Dependence of subband and transition energy for active regions on (a, b) well 1 widths, and (c, d) well 2 widths. The subband energy are shown above the break, counted from bottom to the top, they are E_1 (solid line), E_2 (dashed line), E_3 (dashed dotted line) and the first subband being confined in the well 1 (dashed dotted dotted line, which are only for (a) and (b)). While below the break, the transition energy is shown. The bottom two curves are E_{21} (short dashed line) and E_{32} (short dashed dotted line). Note that there are some differences in the data points along the first two subband energy curves from the top of (c) and (d): (■) denotes the electron states are the second one of well 3, and (○) denotes they are the first energy levels of well 2. (a) and (c) are the results of $\text{In}_{0.1}\text{Ga}_{0.9}\text{As}_{0.99}\text{N}_{0.01}/\text{AlAs}$ CQWs, with (a) $\text{ww}2=70$ Å, $\text{ww}3=80$ Å, $\text{bw}1,2=20$ Å and $\text{bw}3=200$ Å, while (c) $\text{ww}1=20$ Å, $\text{ww}3=80$ Å, $\text{bw}1,2=20$ Å and $\text{bw}3=200$ Å. (b) and (d) are the results of $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.97}\text{N}_{0.03}/\text{AlAs}$ CQWs, with (b) having the same QW structure with (a) and (d) having the same QW structure with (c). All the calculations are under no electric field and room temperature.

interesting to note the trend of E_3 curve, which changes from an increase to a decrease when $ww1=40$ Å. It is due to the fact that when $ww1=40$ Å, C_1^1 alternates with C_2^3 to be E_3 . Another interesting thing to note is that with the widening of well 1, E_1 and E_2 does not decrease but increase instead. It can be explained as: the order of energy levels localized in the whole CQWs region is heavily impacted by the coupling effect, which causes the discrete levels localized in the well 2 and well 3 to rise slightly with the increasing well 1. On the contrary, the energy levels in well 1 drop with the increasing well 1. The trend continues until C_1^1 becomes even lower than C_2^3 , which pushes C_2^3 to rise slowly, it follows that C_1^3 in the same well as C_2^3 , e.g., E_1 increases. For the case of E_2 , since C_1^2 is lower than C_2^3 , while C_1^1 is close to C_2^3 , the drop of C_1^1 has negligible effect on C_1^2 . Moreover, since well 2 is located at the centre of the CQW, the two wells located on either side have contrary coupling effect on it, which means that C_1^3 , C_2^3 and C_1^1 will push the state to increase dramatically slower than the levels in well 3, and therefore, a nearly unchanged E_2 state results. Following the trend of the discrete levels versus the width of the well 1, the transition energy E_{32} first increases and then decreases, while the transition energy E_{21} declines with the increasing well 1 width, as Fig. 5.3(a) indicates. The points made so far apply in principle to Fig. 5.3(b), which is calculated with $In=30\%$ and $N=3\%$, all the other conditions are the same.

The subband and transition energy of the QCL active region calculated as a function of the width of the well 2 (30-70 Å) is depicted in Fig. 5.3(c). As sketched in the figure, with the widening $ww2$, E_1 is fixed, E_2 drops and E_3 decreases at first and then rises

slightly. The different symbols used in the same curve show that the electron states are not confined in the same well for the same energy level. For the E_2 curve, the first two points represent C_2^3 and the others represent C_1^2 . For the E_3 curve, the first two points represent C_1^2 and the others represent C_2^3 . This is a result of that: at first, C_1^2 is higher than C_2^3 , thus the former energy designates E_3 and the latter designates E_2 , with the well 2 width increases, C_1^2 drops until it is lower than C_2^3 . This leads to the exchanging of the levels localized in the whole CQWs region. If one only looks at the variation of C_1^2 with ww2 widens, it decreases straightly. While for the variation of C_2^3 , the amount is negligible. Because C_1^3 is far lower than the other states, it is unaffected by the other states as the well 2 width becoming larger, therefore E_1 is fixed all through the process. From the analysis above, the transition energy for E_{32} drops at first and then rises, while the transition energy for E_{21} decreases with the width of well 2 increases, as indicated in Fig. 5.3(c). So is the case in Fig. 5.3(d), when In=30% and N=3%.

Let us now examine how the width of the well 3 affects the CB structure of the $\text{In}_{0.1}\text{Ga}_{0.9}\text{As}_{0.99}\text{N}_{0.01}/\text{AlAs}$ CQWs. As illustrated in Fig. 5.4(a), E_1 decreases monotonously with the well 3 width owing to the fact that throughout the range of ww3, C_1^3 is E_1 of whole the system. As ww3 grows, C_1^3 (E_1) drops. The relationship between E_2 , E_3 and ww3 is a little more complicated. E_2 initially remains unchanged till ww3=70 Å, where it begins to decrease markedly. It could be explained with when ww3 is less than 70 Å, E_2 is localized in well 2. The fixed well width of well 2 results

Figure 5.4: Dependence of subband energy and transition energy for active regions on (a, b) well 3 widths, (c) indium composition and (d) nitrogen composition. Same legend from Fig. 5.3(c) and (d) applies. Note that there are some differences in the data points along the first two subband energy curves from the top of (a) and (b): (Δ) designates the ground state of the well 1, ($\circ$) designates that the electron states are the second ones of well 3 and ($\blacksquare$) designates the first energy levels of well 2. (a) and (b) are the results of $\text{In}_{0.1}\text{Ga}_{0.9}\text{As}_{0.99}\text{N}_{0.01}/\text{AlAs}$ and $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.97}\text{N}_{0.03}/\text{AlAs}$ CQWs, respectively, with $\text{ww1}=20$ Å, $\text{ww2}=30$ Å, $\text{bw1,2}=20$ Å and $\text{bw3}=200$ Å. (c) and (d) are $N_w=3\%$ and $\text{In}_w=10\%$, respectively, with $\text{ww1}=20$ Å, $\text{ww2}=30$ Å, $\text{ww3}=40$ Å, $\text{bw1,2}=20$ Å and $\text{bw3}=200$ Å. All the calculations are under no electric field and room temperature.

in an fixed E_2 energy. However, in the range that $ww3$ beyond 70 Å, E_2 turns to be C_2^3 , and with $ww3$ continues increasing, E_2 drops simultaneously. As for the case of E_3 versus $ww3$, with the latter grows, E_3 curve drops at first and then keeps flat. It happens because when $ww3=40$ Å, C_1^1 is E_3 . With an increase in $ww3$, the energy of C_2^3 falls below C_1^1 and substitutes its position for the whole system, which means, when the well 3 is larger than 50 Å, E_3 is localized in the well 3. As can be observed in Fig. 5.4(a), E_3 decreases with the increasing $ww3$, until $ww3$ equals to 70 Å, C_2^3 falls below C_1^2 . From then on, C_1^2 becomes E_3 . Because no variation of the well width occurs in the well 2 since then, the E_3 curve keeps flat. As a result of the variation of each subband with the $ww3$ increases, an initial increase followed by a decrease occurs in E_{21} and the contrary trend occurs in E_{32} , as depicted in Fig. 5.4(a). The same discussions apply to the similar case when $In=30\%$ and $N=3\%$, as shown in Fig. 5.4(b).

After investigating the impact of well widths on the band structure of $In_xGa_{1-x}As_{1-y}N_y/AlAs$ QCL active region, we are interested to know how the In and N concentration could impact on the band structure. The results are plotted in Fig. 5.4(c) and (d). As can be observed from Fig. 5.4(c), with indium atoms being added, the first three subband energies of the system monotonously decrease. It is due to the fact that as In content grows, the band gap of $In_xGa_{1-x}As_{0.97}N_{0.03}$ decreases which directly leads to the localized levels in the CB fall. With respect to the transition energy, we can see that E_{21} slightly decreases while E_{32} declines dramatically. One thing to note is that the energy level E_1 , E_2 and E_3 corresponding to all the In concentrations, are concen-

trated in ww3, ww2 and ww1, respectively. E_{21} corresponds to the energy difference between C_1^3 and C_1^2 , and E_{32} corresponds to the energy difference between C_1^2 and C_1^1 , respectively. There are two reasons why E_{32} drops faster than E_{21} : (1) The higher the energy, the faster it drops, hence, the dropping velocity of each subband is in the order of $E_3 > E_2 > E_1$, and (2) With a rise in the In content, the CBO becomes larger. As a result, more and more electron states are incorporated into the CBO, which pushes the other subbands to be further lowered. The amount of the decrease is in the order of $E_3 > E_2 > E_1$. The rule (1) and (2) make it clear that E_{32} falls more rapidly than E_{21} . Fig. 5.4(d) shows the dependence of band structure on the nitrogen composition. With an increasing N content, E_1 , E_2 and E_3 decrease simultaneously. It arises from the decline of InGaAsN band gap energy with increasing nitrogen atoms. However, this variation is not the same as that of the In concentration, which decreases nearly linearly. This is because our calculation is based on the BAC model, in which the band gap of InGaAsN does not decrease linearly but gradually with N concentration, as can be seen from our summary in Ref. [44]. The slow decreases of both E_2 and E_1 lead to a trivial increase of E_{21} . What's more interesting is that the energy separation between E_3 and E_2 slightly decreases at first and then increases sharply. This can be attributed to the special effect of the nitrogen related band, which is located at about 1500-1600 meV, near E_3 . Thus the impact of nitrogen band on E_3 is much more obvious than that on the E_2 band, which causes that E_3 declines more slowly than E_2 and E_1 , and results in an increase in E_{32} .

Our initial attempt on the design of 3-5 μm QCL emission with the $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{AlAs}$ CQW structure is based on: (1) In content ranging from 0% to 30%, (2) N content ranging from 0% to 3%, (3) ww1 ranging between 10 $\text{\AA}$ to 60 $\text{\AA}$, (4) ww2 ranging between 20 $\text{\AA}$ to 70 $\text{\AA}$, and (5) ww3 ranging between 30 $\text{\AA}$ to 80 $\text{\AA}$. At the same time, taking $\text{ww1} < \text{ww2} < \text{ww3}$, $\text{bw1} = \text{bw2} = 20 \text{ \AA}$, $\text{bw3} = 200 \text{ \AA}$, $T = 300 \text{ K}$ and $F = 0 \text{ kV/cm}$. However, the calculated results tell us that there is no combination within this range reaches the desired 3-5 μm laser emission. One should note that we have not yet attempted to design the QCL structures by taking $\text{ww1} < \text{ww2}$ and $\text{ww1} < \text{ww3}$, at the same time, allowing $\text{ww2} > \text{ww3}$. Such a combination has been adopted extensively in QCLs research over the past few years [111, 117]. Let us now try to extend our design by ranging: ww1 from 10 to 20 $\text{\AA}$, ww2 from 30 to 60 $\text{\AA}$, and ww3 from 25 to 55 $\text{\AA}$. All the other parameters are taken as in the first design plot mentioned above. As a result, though a large number of the calculations with In content below 20% can achieve the laser emissions within 3-5 μm , the corresponding E_3 level is either much higher than or close to the conduction band edge at X point of the AlAs barrier, which could deteriorate the QCL performance as electrons could transit from Γ valley in the well layers into X valley in the barriers. After a detailed investigation, we found that such a combination of $\text{In}_{0.2}\text{Ga}_{0.8}\text{As}_{0.97}\text{N}_{0.03}/\text{AlAs}$ CQW with $\text{ww1} = 10 \text{ \AA}$, $\text{ww2} = 35 \text{ \AA}$, $\text{ww3} = 27 \text{ \AA}$, $\text{bw1} = \text{bw2} = 20 \text{ \AA}$ and $\text{bw3} = 200 \text{ \AA}$ could reach the result of $E_{32} = 313 \text{ meV}$ (3.96 μm). Additionally, E_3 can be made equal to 1418 meV, which is below the conduction band edge in the X valley of AlAs barrier (1505 meV), satisfying our requirements.

Figure 5.5: Dependence of subband energy and transition energy for active regions on (a) barrier 1,2 widths, (b) barrier 3 widths, (c) electric field and (d) temperature. Same legend from Fig. 5.3(c) and (d) applies. Shown are the results of $\text{In}_{0.2}\text{Ga}_{0.8}\text{As}_{0.97}\text{N}_{0.03}/\text{AlAs}$ CQWs with $\text{ww1}=10 \text{ \AA}$, $\text{ww2}=35 \text{ \AA}$, $\text{ww3}=27 \text{ \AA}$. Meanwhile set (a) $\text{bw3}=200 \text{ \AA}$, (b) $\text{bw1,2}=22 \text{ \AA}$ and (c,d) $\text{bw1,2}=24 \text{ \AA}$, $\text{bw3}=250 \text{ \AA}$. (a), (b) and (c) are calculated at 300K, respectively, and (a), (b) are calculated under $F=0 \text{ kV/cm}$, while (c) is calculated under 100 kV/cm electric field.

The aim to achieve the shortest emission wavelength leads us further into a consideration of the dependence of transition energy on the barrier width, electric field and temperature, with the optimum combination so far derived. As shown in Fig. 5.5(a), we investigate how bw1 and bw2 will affect the transition energy. With the bw1(bw2) ranging from 10 to 30 Å, E_1 first rises and then falls slightly, E_2 decreases at first and then increases a little, and E_3 exhibits an increase. That is due to the order rearranging of the discrete subbands in different wells, and similar discussions have been made before. The variations in the subband energies lead to that E_{21} decreases quickly at first and then increases slightly, on the contrary, E_{32} grows at first and then drops slowly with bw1 (bw2). As a result, an optimal bw1 (bw2)=24 Å has been obtained, with the other parameters being mentioned in the figure caption. The corresponding E_{32} rises from 313 meV when bw1 (bw2)=20 Å to 331 meV when bw1 (bw2)=24 Å, as depicted in Fig. 5.5(a).

We have also plotted energy levels versus bw3 in Fig. 5.5(b). In the range of 100 to 350 Å, the trends of the energy curves are complicated due to the fast changing of their localized wells. Whereas, in addition to achieve the largest E_{32} , it is important to bear in mind that E_3 should be as low as possible. The compromise results in an optimal combination with bw3 being 250 Å (other parameters are the same as stated in the previous step). The increase of bw3 to 250 Å corresponds to an enhancement of E_{32} to 346 meV. Meanwhile, the calculated E_3 is 1454 meV (below CB edge of X valley in the AlAs layer).

Fig. 5.5(c) shows the calculated energy levels and separations as a function of the electric field strength for the CQW structures. To achieve a successful QCL emission, E_{21} should match the optical phonon energy in order to achieve the maximum population inversion. E_{21} corresponding to the best combination so far achieved is 23 meV, however, it is smaller than E_{Phonon} for $\text{In}_{0.2}\text{Ga}_{0.8}\text{As}_{0.97}\text{N}_{0.03}$ (36 meV). Therefore, we further investigate how the external electric field impacts on the band structure. As depicted in Fig. 5.5(c), as F increases, E_1 decreases, E_2 slightly decreases (nearly unchanged) and E_3 increases, respectively. Consequently, the curves exhibit linear stark effects, e.g., E_{21} increases dramatically while E_{32} increases slightly (both with respect to their extent) with the electric field strength. Thereby when $F=100$ kV/cm, a largest E_{32} of 362 meV is obtained. Additionally, E_{21} reaches 36 meV, which is just our desired value.

We have also done research on energy level and its separation as a function of temperature, as shown in Fig. 5.5(d). All of the first three electron states and the separation between the first two subbands drop, while the separation between the upper lasing level and the lower lasing level decreases as the temperature increases. It can be explained as that the temperature sinking induces the band gap of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ to reduce which leads to the decreasing subband energy.

Finally, the band structure of our optimized combination is plotted in Fig. 5.6. Fig. 5.6(a) is the structure under no external electric field and Fig. 5.6(b) is the structure at 100 kV/cm bias. As can be observed from Fig. 5.6(a), when no electric field

Figure 5.6: Conduction band profiles of the active regions for a $ww1=10$ Å, $ww2=35$ Å, $ww3=27$ Å, $bw1,2=24$ Å and $bw3=250$ Å $\text{In}_{0.2}\text{Ga}_{0.8}\text{As}_{0.97}\text{N}_{0.03}/\text{AlAs}$ QCL structure under applied electric fields of (a) 0 and (b) 100 kV/cm, respectively, at room temperature. The subband energy is sketched as the flat solid line. The moduli squared of the relevant wave functions are shown, counted from bottom to the top, they are E_1 (solid line), E_2 (dashed line), E_3 (dashed dotted line). The arrows in (a) and (b) indicate the lasing action related transition energy E_{32} . Dashed dotted dotted lines denote the conduction band at X point.

added, E_{21} and E_{32} are 23 and 346 meV, respectively. E_3 equals to 1454 meV, which is below X valley CB edge of the barrier. Fig. 5.6(b) tells us that the intersubband transition energy E_{21} (36 meV) is in accordance with E_{Phonon} and a 362 meV transition from E_3 to E_2 can be obtained under an electric field of 100 kV/cm. E_3 (1464 meV) is below the CB edge located in the X valley of AlAs barrier (1505 meV), which fulfills our design requirements.

5.3 Summary

In conclusion, the calculation and design of the active region of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{AlAs}$ QCLs has been reported within the eight-band $k \cdot p$ scheme. This material system is very promising for the production of QCLs operating in the $\lambda \approx 3\sim 5 \mu\text{m}$ atmospheric window thanks to its large CBO. The dependence of conduction band structure on well widths, barrier widths, In concentration, N concentration, electric field strength, and temperature have been investigated. A linear Stark effect occurs when an electric field is applied, which can be utilized for the fine tuning the emission wavelength and population inversion. By a careful tailoring of the layer thicknesses and compositions, an optimal structure comprising of $\text{In}_{0.2}\text{Ga}_{0.8}\text{As}_{0.97}\text{N}_{0.03}/\text{AlAs}$ CQW with $\text{ww1}=10 \text{ \AA}$, $\text{ww2}=35 \text{ \AA}$, $\text{ww3}=27 \text{ \AA}$, $\text{bw1}=\text{bw2}=24 \text{ \AA}$, and $\text{bw3}=250 \text{ \AA}$ has been obtained. As anticipated, this system can emit at a wavelength of $3.4 \mu\text{m}$ under an electric field of 100 kV/cm and at room temperature. The system could avoid the detrimental Γ -X intervalley interaction, because of its upper lasing level is lower than the conduction band edge in the X valley of the particular AlAs barrier. This work is useful for the $\text{InGaAsN}/\text{AlAs}$ QCLs design.

Chapter 6

Study of anneal-induced interdiffusion effects in InGaAsN/GaAs and GaAsSbN/GaAs quantum wells

6.1 Introduction

In recent years, a number of studies have been carried out on InGaAsN grown on GaAs substrate due to their potential applications in 1.3 and 1.55 μm optical fiber communication [2, 123–126]. The optical fiber attenuation at these wavelengths is low. Compared with the widely used InP substrates, GaAs would offer more cost-effectiveness, greater robustness, and better heat conductivity. In addition, the mature GaAs/AlAs Bragg mirrors with high refractive index contrast can be directly used to

fabricate VCSELs on GaAs substrates. Meanwhile, due to the smaller lattice constant of GaN, less strain exists in InGaAsN/GaAs QWs [127].

However, the performance of InGaAsN/GaAs lasers suffers from the poor crystal quality of InGaAsN, because of the incorporation of nitrogen [77, 128]. Nevertheless, the material quality and the optical properties of the QW can be improved greatly by RTA, which causes the constituent atoms to diffuse. The interdiffusion process can change the distribution of the constituent atoms across the interface of the QW, which in turn changes the band structure of the QW and leads to the blueshift of the emission wavelength [80]. Recently, a theoretical study on the interdiffusion effect of InGaAsN/GaAs QW was reported by Chan *et al.* [80, 129]. They used a parabolic band model and a four-band Pikus-Bir model for the conduction and valence band, respectively.

Although various devices operating near 1.3 μm wavelength based on InGaAsN/GaAs QWs have been demonstrated, including edge-emitting lasers [130], VCSELs [131], and laser diodes [132], to push the emission wavelengths of InGaAsN/GaAs systems to 1.55 μm still seems difficult. Because to achieve such wavelength, over 3% nitrogen is needed [133], which exceeds the most promising range of N composition 0%-3% [134] and leads to poor optical properties.

Recently, GaAsSbN was proposed by Ungaro *et al.* [21] as an alternative of InGaAsN for GaAs-based 1.3-1.55 μm optoelectronic devices with low N concentration. The reasons for this are not difficult to grasp: (i) strained InGaAs/GaAs has a large CBO

$\Delta E_c \approx 0.7\Delta E_g$, while GaAsSb/GaAs exhibits a large VBO $\Delta E_v \approx 1.05\Delta E_g$ (type-II band alignment). Considering that the band gap of $\text{GaAs}_{1-y}\text{Sb}_y$ is smaller than that of $\text{In}_y\text{Ga}_{1-y}\text{As}$ ($0 < y < 0.5$) and both compounds exhibit similar compressive strain when grown on GaAs, the cumulative effect leads to longer emission wavelengths for GaAsSb/GaAs QWs as compared to InGaAs/GaAs QWs. As the same amount of N is incorporated into the two ternaries respectively, GaAsSbN/GaAs QW (type-I band alignment) would therefore produce lower IBT energy than that of InGaAsN/GaAs QW. (ii) GaAsSbN/GaAs QW offers the possibility of tuning the CBO and VBO separately by altering N and Sb compositions, respectively [22]. (iii) The only group III element-Ga exists in GaAsSbN leads to that the group V elements can only be bonded to Ga, which minimizes the compositional modulation due to phase segregation, as compared to InGaAsN [135]. It follows from the above advantages that PL emissions approaching $1.55 \mu\text{m}$ with a low N composition ($< 2\%$) of GaAsSbN/GaAs QWs have been reported by several groups [73, 136]. Like InGaAsN system, GaAsSbN is usually annealed in order to enhance the quality. But there still exists a large discrepancy in the literature on the amount of PL blueshifts. In the recent reports of Peake *et al.* [137] and Bian *et al.* [138], 55 meV and 9 meV blueshift were observed in the GaAsSbN/GaAs QWs, respectively, while the result of Harmond *et al.* showed a much larger one (116 meV) [22]. According to the theoretical prediction that GaAsSbN would be less sensitive to thermal treatment than InGaAsN [22] and a 50 meV blueshift was reported for InGaAsN system [139], the amount of blueshift reported by Peake *et al.*

and Bian *et al.* seems more reasonable.

In this chapter, firstly, since the eight-band model is approximate to the ten-band model for calculating on ground levels [44], the realistic eight-band $k \cdot p$ method is used to investigate the interdiffusion mechanism of InGaAsN/GaAs QW. Secondly, we report detailed investigations on the annealing effects of GaAsSbN/GaAs QW structure through PL measurements and simulations using the ten-band $k \cdot p$ model.

6.2 Results and discussion

6.2.1 Effects of interdiffusion in InGaAsN/GaAs quantum well structure emitting at $1.3 \mu\text{m}$

In this chapter, the zero point of the potential is taken at the valence band maximum after strain. In this part, a $64\text{\AA}\text{-In}_{0.36}\text{Ga}_{0.64}\text{As}_{0.983}\text{N}_{0.017}/250\text{\AA}\text{-GaAs}$ QW structure is considered, similar to the structure investigated in Ref. [140] to achieve $1.3 \mu\text{m}$ emission. The temperature is taken to be 300 K in our study.

Fig. 6.1 shows the dependence of the electron, HH and LH confinement profiles of the $64\text{\AA}\text{-In}_{0.36}\text{Ga}_{0.64}\text{As}_{0.983}\text{N}_{0.017}/250\text{\AA}\text{-GaAs}$ strained QW structure along the growth axis with the diffusion length varying from 0 to 1.5 nm in step of 0.5 nm. The confinement profiles change gradually near the interface due to the In-Ga interdiffusion.

The profile of the unstrained band gap $E_g(x')$ after In-Ga interdiffusion is shown in

Fig. 6.2(a). The In atoms in the well diffuse into the GaAs barrier and the Ga atoms diffuse into the well layer, so that a new InGaAsN/InGaAs graded interface occurs (the As-N interdiffusion is omitted). Considering that the bulk band gap of GaAs is greater than that of InAs, as the interdiffusion proceeds, the unstrained band gap of InGaAsN gradually increases with z approaching the interface in the well region while that of InGaAs decreases with z approaching the interface in the barrier region. The room-temperature strained band gap $E_g(x')$ is calculated as

$$E_g^s(x') = E_g(x') + \Delta E_c(x') + \Delta E_{hh}(x') + Q_\varepsilon(x') \quad (6.1)$$

To illustrate how the unstrained band-gap is modified by strain, we define $E_{gs}(x')$

Figure 6.1: Dependence of electron, heavy hole, and light hole confinement potential for a 64 Å-In_{0.36}Ga_{0.64}As_{0.983}N_{0.017}/250 Å-GaAs QW on the diffusion length: $L_d = 0$ nm (solid line), $L_d = 0.5$ nm (dashed line), $L_d = 1$ nm (dotted line), and $L_d = 1.5$ nm (dash-dot line), with well center at $z=0$.

Figure 6.2: Dependence of (a) bulk band-gap energy E_g profile, (b) the change of the band-gap due to strain E_{gs} , and (c) strained band-gap energy E_g^s profile for a 64Å-Ga_{0.64}In_{0.36}N_{0.017}As_{0.983}/250Å-GaAs QW on the diffusion length: $L_d = 0$ nm (solid line), $L_d = 0.5$ nm (dash line), $L_d = 1$ nm (dot line), and $L_d = 1.5$ nm (dash dot line), with well center at $z=0$.

as

$$E_{gs}(x') = \Delta E_c(x') + \Delta E_{hh}(x') + Q_\varepsilon(x') \quad (6.2)$$

Thereby, Eq. (6.1) can be re-written as

$$E_g^s(x') = E_g(x') + E_{gs}(x') \quad (6.3)$$

The profiles of $E_{gs}(x')$ and $E_g^s(x')$ with interdiffusion are shown in Figs. 6.2(b), and 6.2(c), respectively. As the figures indicate, for the numerical case $L_d=1.5$ nm, at the well center ($z=0$ nm), the corresponding ΔE_c , ΔE_{hh} , and Q_ε are 125, 21, and -71

meV, respectively, resulting in $E_{gs}=75$ meV; while at a point in the well region near the interface ($z=3.1$ nm), the corresponding ΔE_c , ΔE_{hh} , and Q_ε are 69, 12, and -38 meV, respectively, leading to $E_{gs}=43$ meV.

Thereby, $|E_{gs}(x'(z=3.1)) - E_{gs}(x'(z=0))|=32$ meV, while $|E_g(x'(z=3.1)) - E_g(x'(z=0))|=126$ meV. It shows that strain produced in the diffused QW reduces the depth of the band gap profile in the well, as depicted in Fig. 6.2(c) with comparison to Fig. 6.2(a). The same explanation applies to the profile of the band gap after strain in the barrier. We define the band offsets of the conduction band and valence band after strain as $E_{c_offset}^s(x')$ and $E_{v_offset}^s(x')$, respectively, which satisfy

$$E_{c_offset}^s(x') + E_{v_offset}^s(x') + E_g^s(x') = E_g(\text{GaAs}(300\text{K}))$$

$$\frac{E_{c_offset}^s(x')}{E_{v_offset}^s(x')} = \frac{75\%}{25\%} = 3 \quad (6.4)$$

In going from the well center to the interface, $E_g^s(x')$ increases, so that the potential of the electron profile increases while that of the HH profile decreases. The converse holds for the case along the direction from the barrier to the interface, as shown in Fig. 6.1. However, for the case of the LH confinement profile, we observe an interesting structure. The as-grown GaAs valence band actually lies above the as-grown InGaAsN LH band, forming a potential barrier in the InGaAsN layer and a potential well in the GaAs layer, which is contrary to the normal case. This type of the LH band configuration is verified to be possible for InGaAs/GaAs (Ref. [49]). Fig. 6.1 also tells

us that the diffused LH profile is reversed from the diffused HH profile, in contrast to the result of Ref. [80]. The relationship between $E_{hh}^s(x')$ and $E_{lh}^s(x')$ is given as

$$E_{lh}^s(x') = E_{hh}^s(x') + 2 \times Q_\varepsilon(x') \quad (6.5)$$

The profiles of $E_{hh}^s(x')$ and $2 \times Q_\varepsilon(x')$ are shown in Fig. 6.3(a) and (b), respectively. As the figures indicate, the HH band edge of the as-grown profile lies about 120 meV

Figure 6.3: Dependence of (a) heavy hole band edge profile, (b) $2 \times Q_\varepsilon$ profile for a 64 Å-In_{0.36}Ga_{0.64}As_{0.983}N_{0.017}/250 Å-GaAs QW on the diffusion length: $L_d = 0$ nm (solid line), $L_d = 0.5$ nm (dash line), $L_d = 1$ nm (dot line), and $L_d = 1.5$ nm (dash dot line), with well center at $z=0$.

higher above the valence band edge (VBE) of GaAs, while the profile of $2 \times Q_\varepsilon(x')$ in the well region lies about 167 meV lower than the VBE of GaAs. Consequently, it causes the as-grown LH band edge to be pushed below the VBE of GaAs and form a weakly type-II structure for the LH band profile. Considering the interdiffusion effect,

Figure 6.4: Dependence of $e1$ -HH1 transition energy for a 64 Å- $\text{In}_{0.36}\text{Ga}_{0.64}\text{As}_{0.983}\text{N}_{0.017}/250$ Å-GaAs QW on the diffusion length: $L_d=0, 0.5, 1$, and 1.5 nm.

for the case $L_d=1.5$ nm, at the well center ($z=0$ nm), E_{hh}^s and $2 \times Q_\varepsilon$ are -9 and -142 meV, respectively. It follows that $E_{lh}^s=-151$ meV, which is below the VBE of GaAs (-122 meV). As z approaching the interface in the well region ($z=3.1$ nm), E_{hh}^s and $2 \times Q_\varepsilon$ are -33 and -75 meV, respectively, leading to $E_{lh}^s=-108$ meV, which is above the VBE of GaAs. It reveals that the increase of $2 \times Q_\varepsilon$ is faster than the reduction of E_{hh}^s in the well region. The same observation applies to the case in the barrier region. As can be seen from the above, the shear strain produced in the disordered QW structure combining with a small valence band (HH band) offset forces the LH confinement profile being reversed from the HH confinement profile. This explains the LH band curves of Fig. 6.1.

The variation of $e1$ -HH1 transition energy with interdiffusion for a 64 Å- $\text{In}_{0.36}\text{Ga}_{0.64}\text{As}_{0.983}\text{N}_{0.017}/250$ Å-GaAs QW structure is shown in Fig. 6.4. As the interdiffusion

proceeds, a strong blueshift is obtained. The emission wavelength of the as-grown structure is $1.29\ \mu\text{m}$ (961 meV) calculated by the eight-band $k \cdot p$ method, which is in good agreement with the experimental result ($1.27\ \mu\text{m}$) given in Ref. [140]. As L_d increases to 1.5 nm, the wavelength can be shifted to $1.225\ \mu\text{m}$ (1012 meV).

6.2.2 Effects of interdiffusion in GaAsSbN/GaAs quantum well structure

The GaAsSbN/GaAs QW structure was grown by SS-MBE in conjunction with N plasma source, As and Sb valved cracker source. The sample was grown at $1\ \mu\text{m/hr}$ growth rate, with As_4 overpressure of 9×10^{-6} Torr beam equivalent pressure (BEP) throughout the growth. At $580\ ^\circ\text{C}$ substrate temperature, approximately $5000\ \text{\AA}$ thick GaAs buffer was grown. Subsequently, after 10 mins of growth interruption, $60\ \text{\AA}$ GaAsSbN layer was grown at $460\ ^\circ\text{C}$. In the growth of the well layer, Sb flux of 1×10^{-7} Torr BEP was applied as well as the N plasma with 500 W plasma power and 10 sccm pure N_2 gas flow. $500\ \text{\AA}$ GaAs cap was grown at $580\ ^\circ\text{C}$ following 10 mins growth interruption to pump out the remaining N. The growth was monitored using RHEED, with 2×4 surface reconstruction observed throughout the growth. The nominal Sb and N compositions in the QW were about 13% and 0.7%, respectively, which were measured via XRD system. RTA was carried out on the sample at temperatures between 650 and $750\ ^\circ\text{C}$ for 5 mins to investigate the annealing effect on PL.

The PL spectra of the $\text{GaAs}_{0.863}\text{Sb}_{0.13}\text{N}_{0.007}/\text{GaAs}$ QW ($L_z=60 \text{ \AA}$) measured at low temperature (4 K) for the as-grown and annealed samples (650-750 °C at 5 mins) are shown in Fig. 6.5. A blueshift of the PL peak energy and a large increase of the PL

Figure 6.5: Low-temperature (4K) photoluminescence spectra of a $\text{GaAs}_{0.863}\text{Sb}_{0.13}\text{N}_{0.007}/\text{GaAs}$ QW as-grown sample (dashed line) and the samples after RTA at 650 °C (dotted line), 700 °C (solid line) and 750 °C (dashed dotted line) for 5 minutes. The optimum annealing temperature is 700 °C.

intensity after annealing are observed. Meanwhile, a large decrease of the FWHM is also found. For the as-grown sample, there exist two weak peaks in the PL spectra, one peak around 1028 nm and the other around 1170 nm, which show poor optical properties. The peak around 1170 nm may be induced by the N and Sb related defects. The fundamental PL peak of the as-grown sample should be the one located at 1028 nm (1206 meV) with a FWHM of about 70 meV. It is also observed from Fig. 6.5 that the optimum annealing temperature is 700 °C, the FWHM is reduced to 24 meV

Figure 6.6: Dependence of electron, heavy hole, and light hole confinement potential for a $\text{GaAs}_{0.863}\text{Sb}_{0.13}\text{N}_{0.007}/\text{GaAs}$ QW on the diffusion length: $L_d=0$ nm (solid line), $L_d=0.5$ nm (dashed line), $L_d=1$ nm (dotted line), $L_d=1.5$ nm (dashed dotted line), with well center at $z=0$.

and a largest PL intensity among the three annealing temperatures is obtained. This enhancement of the PL intensity is due to the reduction of the density of the defects in the sample by thermal annealing [139]. Fig. 6.5 presents another important PL characteristic that after annealing under the optimum condition (700 °C for 5 mins), the PL peak energy is blueshifted about 36 meV which is close to the result of Peake *et al.* [137] and supports the prediction that the PL blueshift for GaAsSbN would be smaller than that of InGaAsN [134].

Fig. 6.6 shows the dependence of the electron, HH and LH confinement profiles of a 60-Å $\text{GaAs}_{0.863}\text{Sb}_{0.13}\text{N}_{0.007}/200\text{-Å GaAs}$ strained QW structure along the growth axis with the diffusion length varying from 0 to 1.5 nm in steps of 0.5 nm. The confinement

profiles change gradually near the interface due to the As-Sb interdiffusion. The profile of the unstrained band gap $E_g(x')$ after As-Sb interdiffusion is shown in Fig. 6.7(a). The Sb atoms in the well diffuse into the GaAs barrier and the As atoms diffuse into

Figure 6.7: Dependence of (a) bulk band-gap energy E_g profile, (b) the change of the band gap due to strain E_{gs} , and (c) strained band-gap energy E_g^s profile for a $\text{GaAs}_{0.863}\text{Sb}_{0.13}\text{N}_{0.007}/\text{GaAs}$ QW on the diffusion length: $L_d=0$ nm (solid line), $L_d=0.5$ nm (dashed line), $L_d=1$ nm (dotted line), $L_d=1.5$ nm (dashed dotted line), with well center at $z=0$.

the well layer, so that a new $\text{GaAsSbN}/\text{GaAsSb}$ graded interface appears (the As-N interdiffusion is omitted). Considering that the bulk band gap of GaAs is greater than that of GaSb, as the interdiffusion proceeds, the unstrained band gap of GaAsSbN gradually increases with z approaching the interface in the well region, while that of GaAsSb decreases with z approaching the interface in the barrier region.

The strained band gap $E_g^s(x')$ is calculated as Eq. (6.1). The profiles of $E_{gs}(x')$ and $E_g^s(x')$ defined in Eq. (6.2) and (6.3), respectively, are shown in Figs. 6.7(b) and 6.7(c). As the figure indicates, for the numerical case $L_d=1.5$ nm, at the well center

($z=0$ nm), the corresponding ΔE_c , ΔE_{hh} , and Q_ε are 55, 8, and -27 meV, respectively, resulting in $E_{gs}=36$ meV; while at a point in the well region near the interface ($z=2.9$ nm), the corresponding ΔE_c , ΔE_{hh} , and Q_ε are 29, 5, and -15 meV, respectively, leading to $E_{gs}=19$ meV. Thus, $|E_{gs}(x'(z=2.9)) - E_{gs}(x'(z=0))|=17$ meV, while $|E_g(x'(z=2.9)) - E_g(x'(z=0))|=65$ meV. It shows that the strain produced in the diffused QW reduces the depth of the band-gap profile in the well, as depicted in Fig. 6.7(c) with comparison to Fig. 6.7(a). The same explanation applies to the profile of the band gap after strain in the barrier. We define the band offsets of the conduction band and the valence band after strain as $E_{c_offset}^s(x')$ and $E_{v_offset}^s(x')$, respectively, which satisfy

$$E_{c_offset}^s(x') + E_{v_offset}^s(x') + E_g^s(x') = E_g(\text{GaAs}) \quad (6.6)$$

$$\frac{E_{c_offset}^s(x')}{E_{v_offset}^s(x')} = \frac{34\%}{66\%} = 0.51$$

In going from the well center to the interface, $E_g^s(x')$ increases, so that the potential of the electron profile increases, while that of the HH profile decreases. The converse holds for the case along the direction from the barrier to the interface, as shown in Fig. 6.6. However, the effective barrier heights of LH in the valence band are reduced much more slightly than that of HH band, causing the profile of LH band to ultimately result in an almost flat-bottomed well. The relationship between $E_{hh}^s(x')$ and $E_{lh}^s(x')$ is described as in Eq. (6.5). The profiles of $E_{hh}^s(x')$ and $2 \times Q_\varepsilon(x')$ are shown in Figs. 6.8(a) and 6.8(b), respectively. Considering the interdiffusion effect, for the case $L_d=1.5$ nm, at the well center ($z=0$ nm), E_{hh}^s and $2 \times Q_\varepsilon$ are -14 and -55 meV, respectively, so that

$E_{lh}^s = -69$ meV. As z approaches the interface in the well region ($z=2.9$ nm), E_{hh}^s and $2Q_\varepsilon$ are -45 and -29 meV, respectively, leading to $E_{lh}^s = -74$ meV. It reveals that the increase of $2 \times Q_\varepsilon(x')$ (26 meV) is slower but comparable to the reduction of $E_{hh}^s(x')$ (31 meV) in the well region. The same observation applies to the case in the barrier region. As can be seen from the observation given above, though both the LH and HH band keep a uniform trend of variations, the adjacent extent of change between the twice shear strain $2 \times Q_\varepsilon(x')$ and the valence band (HH band) offset results in the shape of LH band becomes more flatter than that of the HH band.

By considering the interdiffusion effect, the dependence of transition energy on the diffusion length for the $\text{GaAs}_{0.863}\text{Sb}_{0.13}\text{N}_{0.007}/\text{GaAs}$ QW structure calculated by the ten-band $k \cdot p$ method is shown in Fig. 6.9. The calculated emission wavelength of

Figure 6.8: Dependence of (a) HH band profile, (b) $2Q_\varepsilon$ profile, and (c) LH band profile for a $\text{GaAs}_{0.863}\text{Sb}_{0.13}\text{N}_{0.007}/\text{GaAs}$ QW on the diffusion length: $L_d=0$ nm (solid line), $L_d=0.5$ nm (dashed line), $L_d=1$ nm (dotted line), $L_d=1.5$ nm (dashed dotted line), with well center at $z=0$.

Figure 6.9: Dependence of $e1-HH1$ transition energy for a $\text{GaAs}_{0.863}\text{Sb}_{0.13}\text{N}_{0.007}/\text{GaAs}$ QW on the diffusion length: $L_d=0-2.5$ nm.

the as-grown structure is $1.03 \mu\text{m}$ (1204 meV) which is very close to our experimental result $1.028 \mu\text{m}$ (1206 meV). As L_d increases, a blueshift can be observed. Subsequently, the calculated transition energy shift ΔE as a function of L_d is shown in Fig. 6.10. The experimental data are fitted with the theoretically calculated ones, as shown in Fig. 6.10, corresponding diffusion lengths are 1.2, 1.4, 2.2 nm for the temperature 650, 700, 750 °C, respectively.

The estimated values of diffusion coefficient D in the above temperatures are ranging from 10^{-17} to 10^{-16} which are plotted against inverse temperature in Fig. 6.11, from which an activation energy E_a of 1 ± 0.4 eV is yielded. The values of D obtained in this work are similar to those reported for $\text{GaAsSb}/\text{GaAs}$ QW structure [81, 141]. The value of E_a agrees with the reported 1.5 ± 0.4 eV for $\text{GaAsSb}/\text{GaAs}$ QW [81].

Figure 6.10: Dependence of calculated PL-peak shifts for a $\text{GaAs}_{0.863}\text{Sb}_{0.13}\text{N}_{0.007}/\text{GaAs}$ QW on the diffusion length: $L_d=0\text{-}2.5$ nm.

Figure 6.11: Estimated diffusion constants D as a function of inverse temperature for a $\text{GaAs}_{0.863}\text{Sb}_{0.13}\text{N}_{0.007}/\text{GaAs}$ QW, obtained from the data shown in Fig. 6.10.

6.3 Summary

The interdiffusion effect of a compressively strained 64 Å-In_{0.36}Ga_{0.64}As_{0.983}N_{0.017}/250 Å-GaAs QW has been studied by using an error function to model the compositional profiles. Ga-In interdiffusion causes the formation of a InGaAsN/InGaAs interface, while the N-As interdiffusion is ruled out by recent researches. As diffusion proceeds, it can result in a wider effective well width and a lower effective barrier of the confinement profiles. We would like to note that the LH confinement profile is reversed from the HH confinement profile, indicating that the interdiffusion-dependent strain effects can modify some band-edges significantly. The ground state (*e*1-HH1) transition energy calculated by the eight-band $k \cdot p$ method is 961 meV, which corresponds to an emission wavelength of 1.29 μm and agrees very well with the reported 1.27 μm . Finally the dependence of the *e*1-HH1 transition energy on the diffusion length is obtained, which shows a 51 meV blueshift as the diffusion length increases to 1.5 nm.

In addition, the effect of annealing on the optical properties of GaAs_{0.863}Sb_{0.13}N_{0.007}/GaAs QW structure prepared by SS-MBE is investigated by low-temperature PL measurements. The results show that the optical quality of QW can be improved in terms of PL intensity and FWHM under the optimum condition (700 °C for 5 mins). A PL blueshift (36 meV) under the optimum annealing condition is also observed, which is modeled by As-Sb atomic interdiffusion in our study. The interdiffusion causes the formation of a GaAsSbN/GaAsSb interface, while the As-N interdiffusion is ruled out

in our model. As diffusion proceeds, it can result in a wider effective well width and a lower effective barrier of the confinement profiles. The ground state transition energy of the as-grown structure calculated by the ten-band $k \cdot p$ method is 1024 meV, which corresponds to an emission wavelength of 1.03 μm and agrees with the measured 1.028 μm . As L_d increases to 1.4 nm, a blueshift of 36 meV can be derived which agrees with our PL results under the optimum condition. As a consequence, As-Sb diffusion coefficients D and activation energy E_a are determined to be 10^{-17} - 10^{-16} cm^2/s and 1 ± 0.4 eV, respectively, both of which are in agreement with the results reported for a similar structure.

Overall, the present study supports that it is possible to explain the PL blueshifts of both the InGaAsN/GaAs and the GaAsSbN/GaAs QWs by atomic interdiffusion mechanism.

Chapter 7

Conclusion and recommendations

7.1 Conclusion

First, the energy band dispersion relations and ISBT energy for InGaAsN/GaAs QWs are studied with the ten-band $k \cdot p$ model. When compared with other GaAs-based dilute-nitride material system, it has a relatively deeper well. Hence, the possibility of achieving 3-5 μm ISBT absorptions in this system emerges. However, final design results by varying the well width, the barrier width, and the concentration of constituents show that it is difficult to find a combination with absorption wavelengths within this mid-infrared region, with the exception of enhancing In and N to be larger than 60% and 5%, respectively. It is well known that such a high-N containing III-V compound with good quality is difficult to obtain. Therefore, we only manage to achieve a 25 Å-In_{0.3}Ga_{0.7}As_{0.99}N_{0.01}/145 Å-GaAs_{0.998}N_{0.002} QW structure with an ISA at around 10 μm by using this system. Based on GaAs substrate, it might be a useful alternative for the conventional GaAs/AlGaAs system for ISAs around 8-12 μm .

Secondly, to increase the ISBT energy drives us into further increasing the confinement energy in the conduction band. Therefore, a barrier material with larger band gap is desired. AlAs becomes a good candidate. The CBO of InGaAsN/AlAs QWs can reach in theory ~ 1.5 eV. With such a deep well, it should be easy to support an absorption wavelength of ISBT ($e1 \rightarrow e2$) below $5 \mu\text{m}$. Moreover, due to the peculiar when adding nitrogen into the III-V matrix, from the calculation with the ten-band $k \cdot p$ scheme, we discover that the ground level in the conduction band splits into two levels, one is below the nitrogen level and the other is above the nitrogen level. The similar observation applies to the first excited state in the conduction band. This feature has not been found for InGaAsN/GaAs QWs, where the first excited level lies below the N level. The rule is in close agreement with a recent report. It is very useful to further enlarge the ISBT energy when the second subband in the conduction band is localized above the nitrogen state. By adding an outer barrier of AlGaAs to the InGaAsN/AlAs QW, it is even possible to push the ISA wavelength of $e1 \rightarrow e2$ to be as short as $1.3\text{-}1.55 \mu\text{m}$. Consequently, by a careful tailoring of the compositions, an $\text{In}_{0.17}\text{Ga}_{0.83}\text{As}_{0.985}\text{N}_{0.015}/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW with the well width of $20 \text{ \AA}$, the AlAs barrier width of $15 \text{ \AA}$ and the AlGaAs barrier width of $130 \text{ \AA}$ can achieve an ISA peak at about $1.31 \mu\text{m}$. The other design result is an $\text{In}_{0.25}\text{Ga}_{0.83}\text{As}_{0.985}\text{N}_{0.015}/\text{AlAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ DBQW with the well width of $20 \text{ \AA}$, the AlAs barrier width of $15 \text{ \AA}$ and the AlGaAs barrier width of $130 \text{ \AA}$, which can achieve an ISA wavelength at about $1.55 \mu\text{m}$.

Thirdly, the large CBO of InGaAsN/AlAs QW offers the pathway to design mid-infrared QCLs structures. We apply the widely used three-quantum-well active region to design CQW structures with emission wavelengths as short as possible. The calculations based on the eight-band $k \cdot p$ model result in an $\text{In}_{0.2}\text{Ga}_{0.8}\text{As}_{0.97}\text{N}_{0.03}/\text{AlAs}$ CQW with $\text{ww1}=10 \text{ \AA}$, $\text{ww2}=35 \text{ \AA}$, $\text{ww3}=27 \text{ \AA}$, $\text{bw1}=\text{bw2}=24 \text{ \AA}$, and $\text{bw3}=250 \text{ \AA}$, which can supply an emission at $3.4 \mu\text{m}$ under an electric field of 100 kV/cm at room temperature.

Fourthly, the intermixing effect of the InGaAsN/GaAs QWs is investigated using the eight-band $k \cdot p$ model. The as-grown $64 \text{ \AA}-\text{In}_{0.36}\text{Ga}_{0.64}\text{As}_{0.983}\text{N}_{0.017}/250 \text{ \AA}-\text{GaAs}$ QW is experimentally determined to emit at $1.27 \mu\text{m}$ in the literature. The compositional profile of the QW after interdiffusion is modeled by an error function distribution. Varying the diffusion length, the effects of interdiffusion on the unstrained band-gap, in-plane strain, and confinement profiles are studied. The curve of ground state transition ($e\text{-HH}$) energy dependence on the interdiffusion length is obtained. Our work shows that the interdiffusion effect on the strain can greatly change the confinement profile of the LH which is confined in GaAs layer, not in the InGaAsN layer. From the transition energy curve, a blueshift of 51 meV is derived which is attributed to the In-Ga intermixing. This interdiffusion mechanism can be utilized in the tuning of laser operation wavelength by InGaAsN/GaAs QWs.

Finally, the intermixing effect of the GaAsSbN/GaAs QWs grown by SS-MBE has been investigated. The annealing time and the temperature are 5 minutes and 650

$^{\circ}\text{C}$ -750 $^{\circ}\text{C}$, respectively. Low-temperature (4 K) PL peaks shift to higher energies with the annealing temperatures. An As-Sb atomic interdiffusion at the heterointerface is proposed to model this effect. The compositional profile of the QW after interdiffusion follows the Fick's law and is calculated by the ten-band $k \cdot p$ method. The estimated interdiffusion constants D are $\sim 10^{-17}$ - 10^{-16} cm^2/s in the above temperature range and an activation energy of 1 ± 0.4 eV is obtained. This study is useful for the design of GaAsSbN/GaAs QW lasers taking the interdiffusion effect into account.

7.2 Recommendations for future research

To make the study more complete, the following research could be done:

- 1) Grow and fabricate the designed InGaAsN/GaAs QWIP structure for 3-5 μm ISA and check the working stability of this system within this wavelength range.
- 2) Grow and fabricate the 1.3-1.55 μm DBQW QWIPs and take further steps to fine tuning the components of the designed structure according the the characterization results. Then study their performance for real applications.
- 3) To model the optical gain for QCLs within the conduction band and compute the optical gain peak with the designed structure for ISBT wavelength around 3.4 μm . Subsequently, grow and fabricate the QCL structure, followed by studying its performance for applications.

Author's Publications

1. **Y. X. Dang**, W. J. Fan, S. T. Ng, S. F. Yoon, and D. H. Zhang, “Study of interdiffusion in GaInNAs/GaAs quantum well structure emitting at 1.3 μm by eight-band $k \cdot p$ method” *Journal of Applied Physics*, **97**, 103718 (2005).
2. **Y. X. Dang**, W. J. Fan, S. T. Ng, S. Wicaksono, S. F. Yoon, and D. H. Zhang, “Study of interdiffusion in GaAsSbN/GaAs quantum well structure by ten-band $k \cdot p$ method” *Journal of Applied Physics*, **98**, 026102 (2005).
3. **Y. X. Dang**, W. J. Fan, F. Lu, H. Wang, D. H. Zhang, and S. F. Yoon, “Study of the interdiffusion effect on the band structures of $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ quantum wells” *Journal of Applied Physics*, **99**, 076108 (2006).
4. **Y. X. Dang**, W. J. Fan, S. T. Ng, S. Wicaksono, S. F. Yoon, and D. H. Zhang, “Interdiffusion effect on GaAsSbN/GaAs quantum well structure studied by ten-band $k \cdot p$ model” *Thin Solid Films*, **515**, 4435 (2007).
5. **Y. X. Dang** and W. J. Fan, “Design of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{GaAs}$ quantum cascade structure for 3.4 μm intersubband emission” *Journal of Applied Physics*,

- 101, 084504 (2007).
6. S. T. Ng, W. J. Fan, **Y. X. Dang** and S. F. Yoon, “Influence of $k \cdot p$ formalisms on the band structure of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{GaAs}$ quantum well-a comparison of 8-band and 10-band models” Japanese Journal of Applied Physics, **44**, L658 (2005).
 7. S. T. Ng, W. J. Fan, **Y. X. Dang**, and S. F. Yoon, “Comparison of electronic band structure and optical transparency conditions of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{GaAs}$ quantum well calculated by 10-band, 8-band, and 6-band $k \cdot p$ models” Physical Review B: Condensed Matter and Material Physics, **72**, 115341 (2005).
 8. F. Lu, W. J. Fan, **Y. X. Dang**, D. H. Zhang, S. F. Yoon, and R. Wang “Band structure investigation of strained $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ coupled quantum wells” International Journal of Nanotechnology, **4**, 431 (2007).
 9. B. S. Ma, W. J. Fan, **Y. X. Dang**, W. K. Cheah, and S. F. Yoon, “Annealing effects on the optical properties of a GaInNAs double barrier quantum well infrared photodetector” Applied Physics Letters, **91**, 041905 (2007).
 10. B. S. Ma, W. J. Fan, **Y. X. Dang**, W. K. Cheah, W. K. Loke, W. Liu, D. S. Li, S. F. Yoon, D. H. Zhang, and H. Wang, “A GaInNAs double-barrier quantum well infrared photodetector with the photo detection at $1.24 \mu\text{m}$ ” Applied Physics Letters, **91**, 051102 (2007).

11. ***Y. X. Dang*** and W. J. Fan, “Dilute nitride based double-barrier quantum wells for intersubband absorption at 1.31 and 1.55 μm ” submitted.

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