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STUDY OF DILUTE NITRIDE BASED STRUCTURES FOR INFRARED PHOTODETECTION

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Abbreviations

ISBT	Intersubband transitions
QW	Quantum well
MQW	Multiple quantum well
LWIR	Long wavelength infrared
BAC	Band-anticrossing
NB	Nitrogen band
CB	Conduction band
VB	Valence band
E1	The ground electron state
E2	The first excited state
H1	The ground hole state
B-to-B	Bound-to-bound transition
B-to-C	Bound-to-continuum transition
FWHM	Full width at half maximum
SSMBE	Solid-source Molecular Beam Epitaxy
HRXRD	High-resolution X-ray diffraction
PL	Photoluminescence
FTIR	Fourier Transform Infrared Spectroscopy
SIMS	Secondary ion mass spectrometry
RTA	Rapid thermal annealing
TE	Transverse-electric
TM	Transverse-magnetic

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SUMMARY

Dilute nitride III-V compound semiconductor materials have attracted considerable interests in recent years owing to the unique nitrogen-driving physics that are attributed to the highly localized nature of perturbations induced by nitrogen (N) band. Most research activities were about interband transition physics and applications. However, limited research work has been done for dilute-N related intersubband transition (ISBT) physics. In this thesis work, the ISBT properties in various dilute-N quantum wells (QWs) have been investigated using modified multi-band **k·p** models systematically. The growth and characterization of n-type InGaAsN/GaAs QWs for 8–12 μm infrared absorption are also reported. In Addition, studies on $\text{InSb}_{1-x}\text{N}_x$ alloys with extended infrared detection ability to the long-wavelength infrared window are presented.

A theoretical method based on eight- and fourteen-band **k·p** Hamiltonians in combination with envelope-function Fourier expansions has been developed to study ISBTs in N-free QWs. Then the ten- and sixteen-band **k·p** models taking the high-lying N resonant bands into consideration were developed to study ISBTs in various dilute-N QWs. The complete momentum matrix elements are derived. The ISBT selectivities on subband order, wave vector and well width in finitely deep QWs are concluded.

The variations of ISBTs with well width and N content in n-type (In,Ga)AsN/(Al,Ga)As QWs have been analyzed. The coupling of N-band and conduction-band results in significant modifications in the ISBT properties,

which are consistent with experimental observations. The absorption energy is much larger than that of the equivalent N-free structure in the case of narrow wells, but such difference becomes small rapidly and even reverses with the increase of well width. In the case of moderate and wider wells where the ground to the first excited state transition dominates, the transition energy is insensitive to the increase of N content up to 3%, and even a redshift of the transition energy can occur.

ISBTs in InGaAsN/InGaAs/GaAs QWs with the asymmetric N incorporation are also analyzed. The results show significant in-plane (TE) polarized transitions, especially at narrow wells. The variations of subband structures and ISBTs with N and In diffusions in InGaAsN/GaAs QWs have also been investigated.

The successful growth of high quality InGaAsN/GaAs n-type multiple quantum wells (MQWs) with narrower well widths by solid-source molecular beam epitaxy (SSMBE) has been reported. The structural and material properties are characterized. The annealing-induced In and N diffusions are measured by SIMS, and their impact on PL and subband structures are analyzed. The intersubband absorption in the 8–12 μm infrared band has been achieved.

As an additional work, the incorporation of dilute N in narrow bandgap semiconductor material InSb has been studied, and the extended detection ability to the 8–12 μm long-wavelength infrared window has been realized. A set of $\text{InSb}_{1-x}\text{N}_x$ alloys with approximate N contents ranging from 0.4% to 8%

has been fabricated by multi-step high energy N^+ ion implantation followed by thermal annealing. Photoconductive and photovoltaic $InSb_{1-x}N_x$ detectors have been fabricated and tested. The redshifted photodetection band up to $\sim 11 \mu m$ with increasing N content has been observed in experiment.

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Chapter 1 Introduction

1.1 Semiconductor infrared photodetection technologies

Infrared (IR) detection technologies are very important for a wide range of military, scientific and commercial applications. Detection and processing of infrared radiation can provide a wealth of information about an object that is not available in other regions of the spectrum. Infrared detectors are usually classified into photon and thermal detectors. The absorption of long-wavelength radiation in photon detectors results directly in some specific quantum events, such as the photoelectric emission of electrons from a surface, or electronic interband or intraband transitions in semiconductor materials and structures. Photon absorption in thermal detectors leads to an increase in temperature, resulting in a measurable change in certain material properties. Compared to photon detectors, thermal detectors have been considerably less exploited in commercial and military systems. The main reason is that the response of thermal detectors is much slower (ms order) and the detectivity is much lower ($\sim 10^8 \text{cmHz}^{1/2}/\text{W}^{-1}$) in comparison with photon detectors due to reliance on heating of atomic structure [1.1].

The ability to detect light begins with the optical and electrical properties of candidate materials systems, and the most technologically important photodetector materials are the semiconductors. From a physics perspective, the presence of electronic bandgaps with energies comparable to those of photons makes the semiconductor an extremely capable material for detecting light by the photoelectric effect. Compound semiconductor materials with various direct

bandgaps become good candidates for the desirable optical detection bands. The narrow bandgap materials such as InSb, PbSnTe and HgCdTe have been employed for infrared detectors. The detection wavelength is inversely proportional to the bandgap of the material [1.2].

The atmosphere has a few important transmission windows in the infrared region. The short wavelength infrared (SWIR) window extends from the visible region up to 2.5 μm , the middle wavelength infrared (MWIR) window lies between 3 and 5 μm , and the long wavelength infrared (LWIR) window ranges from 8 to 14 μm . Detection of wavelengths larger than 14 μm , so called very long wavelength infrared (VLWIR), is mainly used for outer space application. The detection in LWIR window is especially important since room temperature objects have a peak wavelength round almost 10 μm [1.3].

Indium antimonide (InSb) is an important binary compound semiconductor with a direct bandgap for infrared detector applications in the 3-5 μm MWIR window, and there has been significant interest in large area InSb focal plane arrays (FPAs) [1.4, 1.5]. It has the smallest bandgap energy, 230 meV at 77 K, among developed III–V semiconductor materials. There are a few favorable features such as high atomic numbers, In:49, Sb:51, high density, 5.78 $\text{g}\cdot\text{cm}^{-3}$, and high mobilities of electrons and holes, and high mobilities of electrons and holes, about 78000 and 750 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ at 77 K. For MWIR detection, InSb offers important advantages over HgCdTe, and the other widely used infrared material,

such as relatively easy large area homogeneous growth and stronger covalent bonding.

For infrared detection in the LWIR and VLWIR windows, mercury-cadmium telluride ($\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ or MCT), an II–VI compound semiconductor, is the most widely used variable direct bandgap material at present [1.6, 1.7]. The HgCdTe detectors can possess very high quantum efficiency ($>70\%$) and detectivity ($>10^{12}\text{cmHz}^{1/2}/\text{W}^{-1}$). However, there are still motivations to replace HgCdTe due to some technological problems of this material. One problem is a weak Hg-Te bond that results in bulk, surface and interface instabilities. Uniformity and weak yield ability are another prominent problem. It is well known that these low band gap materials are more difficult to grow and process than large band gap semiconductors such as GaAs. These difficulties motivate the exploration of utilizing the intersubband transitions (ISBTs) in quantum wells (QWs), quantum wire (QWR) and quantum dot (QD) structures made of large bandgap semiconductors.

Rapid development in bandgap engineering by modern epitaxial technologies such as molecular beam epitaxy (MBE) and metal organic chemical vapor phase deposition (MOCVD) has led to the rapid development of quantum well infrared photodetector (QWIP) that opens up a new era in infrared technologies [1.8, 1.9]. The detection mechanism of QWIP involves photoexcitation of electrons or holes between ground and excited states of either conduction or valence bands in a multiple quantum well (MQW) structure. The parameters are

designed so that these photon-excited carriers can escape from the well and be collected as photocurrent. These quantum wells can be realized by placing thin layers of two different high bandgap semiconductor materials alternately where the bandgap discontinuity creates potential wells associated with conduction and valence bands. Since the first experimental observation of intersubband transitions by West and Eglash [1.10] and demonstration of the first GaAs/AlGaAs quantum well infrared photodetectors (QWIP) by Levine *et al.* [1.11], considerable work has been done in the development of high quality QWIPs for the detection of mid and long wavelength infrared. The large 128×128 and even 640×480 high-sensitivity staring arrays based on the GaAs/AlGaAs system, demonstrated by several groups, has now reached commercial stage [1.12, 1.13]. In addition to GaAs/AlGaAs, other strained and unstrained material systems such as InGaAs/(Al,Ga)As [1.14, 1.15], InGaAs/InAlAs/InP [1.16], InGa(As,P)/InP [1.17–1.19], GaAs/InGaP [1.20], SiGe/Si [1.21, 1.22] etc., have also been widely investigated. The ability to accurately control the band structure and the spectral response results in the studies of QWIPs for various advanced applications. In addition to the conventional single-color QWIPs with narrow response bandwidth, multi-color and broadband QWIPs employing complex quantum-well structures have also emerged in recent years [1.23–1.28]. For instance, Doboz *et al.* have studied the effect of asymmetric barriers on the performance of GaAs/AlGaAs QWIPs experimentally [1.23]. Jiang *et al.* have reported a high-performance three-stack, three-color InGaAs/AlGaAs QWIP for the mid, long, and very long wavelength infrared detection [1.24]. Jiang and Lee *et al.* have demonstrated systematically

multi-color, broadband QWIPs with multi-stack quantum-wells, digital graded superlattice barriers or linear graded barriers [1.25, 1.26].

Compared to the interband transition based infrared photodetectors such as InSb and HgCdTe detectors, the advantages of QWIPs lie in the matured material growth techniques, good material uniformity over large area, and flexible and multicolor detection ability. The wavelength of the peak response and bandwidth can be continuously tailored by varying the quantum-well parameters, i.e. well and barrier materials, composition and thickness, doping concentration, and quantum-well structural design, to allow infrared detection in almost the whole near-infrared (NIR) and mid-infrared (MIR) ranges.

However, QWIP has the weakness of low quantum efficiency, bad thermal property, and low working temperature, which restrict its commercial applications in comparison to MCT and InSb detectors.

1.2 Dilute nitride materials

Dilute nitrides such as $\text{GaAs}_{1-x}\text{N}_x$ and $\text{In}_y\text{Ga}_{1-y}\text{As}_{1-x}\text{N}_x$ have attracted considerable attentions because of the novel physical properties and applications [1.29–1.32]. The advantages in thin-film deposition technology have allowed these materials to be grown with improving crystal quality, which in turn improves their optical and electronic performances. This enables the fundamental study of the unusual properties of these materials. These include a reduction of the bandgap energy, a significant increase in electron effective

mass and a decrease in electron mobility. Incorporation of only one percent nitrogen (N) into GaAs induces a great reduction of >100 meV in the fundamental bandgap energy [1.33, 1.34]. The mechanism by which the addition of N changes the material properties appears to be fundamentally different from that in common III–V alloy systems such as $\text{In}_x\text{Ga}_{1-x}\text{As}$ and $\text{Al}_x\text{Ga}_{1-x}\text{As}$. This creates new opportunities for bandgap engineering and optoelectronic devices based on these dilute nitrides accessible to the near infrared (NIR), including the laser diodes emitting at $1.3\text{--}1.5$ μm optical communication window [1.35–1.38] and high-efficient solar cells etc. with $>70\%$ internal quantum efficiencies [1.39, 1.40].

The unexpected strong effect of the introduction of N in III–V compound semiconductors is related to the fact that replacement of atoms such as As with the small N atoms leads to a large, local perturbation of the crystal lattice potential. A series of first-principles calculations examined various aspects of the band structure for GaAsN, showing that the band-edge wave functions in GaAsN tend to be localized impurity-like states [1.41–1.43]. It is well known that an isolated N atom introduces a localized state with Energy E_N in conventional III–V materials [1.44]. In most cases, this level is located close to the conduction band edge. A pressure dependent study showed that the $\text{In}_y\text{Ga}_{1-y}\text{As}_{1-x}\text{N}_x$ samples exhibit a weak dependence of the bandgap energy at low pressures, and a tendency of the energy gap to saturate at high pressures, suggesting that it is a manifestation of an anticrossing behavior of two strongly interacting energy levels with distinctly different pressure dependences [1.45, 1.46]. Shan *et al.* have presented evidence for a strong interaction between the conduction band

and a narrow resonant band formed by N states in $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ described with a band-anticrossing (BAC) model [1.46]. The interaction leads to a splitting of the conduction band into two subbands, E_+ and E_- , and a reduction of the fundamental band gap, which were experimentally observed using photomodulated reflectance (PR) spectroscopy in conjunction with large hydrostatic pressure. The dispersion relation of the two interacting bands takes the form [1.47]

$$E_{\pm}(k) = 0.5 \left\{ (E_C(k) + E_N) \pm \sqrt{(E_N - E_C(k))^2 + 4\beta^2 \cdot y} \right\} \quad (1.1)$$

where E_C is the uncoupled conduction band energy at the Γ point, E_N is the energy of the N level, y is the N composition, and β is the off-diagonal term of the Hamiltonian describing the coupling between the N level and the Γ conduction band. Duboz *et al.* have examined the decrease of bandgap energy of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ with N content by precise absorption measurements and proposed a set of reasonable E_N and β values.

1.3 Motivation and objectives of the study

The dilute nitride semiconductor materials have attracted considerable attentions in recent years owing to the unique nitrogen (N)-driving physical properties which are attributed to the highly localized nature of perturbations induced by N-band [1.35–1.40]. The incorporation of dilute N in $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ based quantum-wells modified the electron states significantly, enabling the interband transition optical wavelength to redshift to the 1.3 μm optical communication window. The high-efficiency $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ based solar cells also benefit from the largely shrinked bandgap that enables lower-energy

photons to be absorbed. However, most research activities have been related to the interband transition physics and applications, and very limited investigations have been done for intersubband transitions in the conduction band of dilute-N quantum-wells. Actually, it is possible to achieve some significant optoelectronic applications with ISBTs in such dilute-N materials. With the increase of N content and hence the conduction-band discontinuity, the $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/(\text{Al,Ga})\text{As}$ quantum-well could allow photons with much shorter wavelengths to be absorbed through ISBTs in comparison with the equivalent N-free structure. This blue-shifted absorption band enables more flexible IR detecting ability without needing to introduce too much indium (In) in the well or involve aluminum (Al) in the barrier. Furthermore, the ISBT property in dilute-N structures may also take significant variations upon the N-band interaction, which deserve to be studied for both theoretical and experimental interests.

Conventionally, the single-band Schrödinger equation was employed to analyze ISBTs in conduction-band quantum-wells [1.48, 1.49]. The transverse-electric (TE) polarized ISBTs are forbidden with the single-band model due to the neglecting of the conduction and valence bands coupling. The multi-band $\mathbf{k}\cdot\mathbf{p}$ models based on the Kane's $\mathbf{k}\cdot\mathbf{p}$ theory [1.50, 1.51] have been used frequently to study the impact of interband coupling on ISBTs [1.52, 1.53]. Yang & Xu have revealed that the TE-mode ISBT exists in fact although the rate is lower than that of transverse-magnetic (TM)- mode ISBT based on an eight-band $\mathbf{k}\cdot\mathbf{p}$ model [1.52]. More recently, the fourteen-band $\mathbf{k}\cdot\mathbf{p}$ model with the introduction of six p -like conduction bands (Γ_{7c} and Γ_{8c}) has also been developed to examine

ISBTs [1.53–1.55]. However, limited research has been done to analyze in detail the variation rules of TM- and TE-polarized transitions with some critical parameters such as well width, well depth and structure symmetry. In dilute-N quantum-wells, the situation is complicated further due to the existence of high-lying N resonant state and its interaction with the other bands.

In this dissertation work, we aim to investigate the ISBT properties in dilute-N quantum-wells based on some modified multi-band models, i.e. ten-band and sixteen-band **k·p** models, and their dependences on some important structural and material parameters. Some experimental work on the growth and characterization of n-type InGaAsN/GaAs MQW structures are also done.

In addition, we also do some theoretical and experimental studies on the incorporation of dilute-N in the narrow bandgap semiconductor material InSb, and demonstrate extended infrared detection ability to the 8-12 μm LWIR window with InSb_{1-x}N_x alloys.

1.4 Major contributions

About ISBTs in dilute-N quantum-wells:

- (1) A theoretical method based on eight-band and fourteen-band **k·p** Hamiltonians in combination with envelope-function Fourier expansions has been developed to study the ISBTs in various N-free quantum-wells. The complete momentum matrix elements are derived and the ISBT selectivities

with subband order, wave vector and well width in finitely deep quantum-wells are concluded.

- (2) Based on the work in (1), the ten-band and sixteen-band **k·p** models taking the high-lying N resonant bands into account have been developed to study the ISBTs in various dilute-N quantum-wells. The ISBT selectivities on subband order, wave vector and well width in finitely deep quantum-wells are derived. The dependences of ISBTs on well width and N content in n-type (In,Ga)AsN/(Al,Ga)As quantum-wells are analyzed. The results show that the coupling of N-band and conduction-band induces some significant modifications in the ISBT property, which are consistent with experimental observations. The absorption peak energy is much larger than that of the equivalent N-free structure in the case of narrow wells, but the difference will become small rapidly and even reverse with the increase of well width. In the case of moderate and wider wells where the transition from the ground state to the bound first excited state dominates, the absorption energy shows insensitive variations with increasing N content up to 3% and an energy redshift can occur.
- (3) ISBTs in asymmetric InGaAsN/InGaAs/GaAs quantum-well structures are analyzed theoretically. The variations of subband structures and ISBTs with N and In diffusions in InGaAsN/GaAs quantum-wells have also been discussed in detail.
- (4) Some InGaAsN/GaAs n-type MQW structures with narrow well widths have been grown. The structure and material properties have been characterized using High-resolution X-ray diffraction (HRXRD), photoluminescence (PL), and Fourier Transform Infrared Spectroscopy

(FTIR). Very large blueshifts (>200 meV) of PL energies have been obtained with anneal-induced intermixing. Intersubband absorptions in the 8-12 μ m LWIR window for both TM and TE polarizations have been observed.

Some additional researches on infrared detection with $\text{InSb}_{1-x}\text{N}_x$ alloys:

- (1) The 10-band $\mathbf{k}\cdot\mathbf{p}$ model has been employed to analyze the energy band structures in $\text{InSb}_{1-x}\text{N}_x$ alloys. In addition, the theoretical study on $\text{InSb}_{1-x}\text{N}_x/\text{InSb}$ quantum-wells shows intense intra-conduction band transition rates due to the improved coupling effect associated with the very narrow bandgap.
- (2) A series of dilute-nitride $\text{InSb}_{1-x}\text{N}_x$ alloys with approximate N contents ranging from 0.4% to 8% have been fabricated by multi-step high energy N^+ ion implantation followed by thermal anneal. The N concentration distributions pre- and post- thermal anneal were measured using secondary ion mass spectrometry (SIMS). Photoconductive and photovoltaic detectors were fabricated and tested. The red-shifted photodetection band up to ~ 11 μm has been observed. The detection ability for the 8–12 μm LWIR window with the $\text{InSb}_{1-x}\text{N}_x$ detectors was demonstrated.

1.5 Organization of the thesis

This thesis is organized into eight chapters:

In Chapter 1, the research background, motivation, objectives and major contributions are introduced.

In Chapter 2, a theoretical method based on eight-band and fourteen-band **k·p** models in combination with envelop-function Fourier expansions is presented to analyze ISBTs in common quantum-well structures. The transition selectivities with subband order, in-plane wave vector and well width are discussed.

In Chapter 3, ISBTs in dilute-N quantum-wells are investigated systematically based on ten-band and sixteen-band **k·p** models that take the interaction of N-band and conduction-band into account. The ISBT selectivities with subband order, in-plane wave vector and well width are derived, the dependences of ISBTs with well width and N content are also analyzed and compared to reported experimental results.

In Chapters 4 and 5, ISBTs in some dilute-N structures with complex potential profiles are investigated theoretically, including asymmetric InGaAsN/InGaAs/GaAs quantum-wells and N and In interdiffused InGaAsN/GaAs quantum-wells.

In Chapter 6, the growth and characterization of some high quality InGaAsN/GaAs multiple quantum wells (MQWs) are presented. The effects of rapid thermal process on composition interdiffusion and photoluminescence are studied. The experimental measurement of intersubband absorptions in the 8–12 μm LWIR window is reported.

Chapter 1: Introduction

In Chapter 7, both theoretical and experimental studies on $\text{InSb}_{1-x}\text{N}_x$ alloys are presented. Firstly, the energy band structures, and inter- and intra-band optical transitions are analyzed based on the 10-band $\mathbf{k}\cdot\mathbf{p}$ model. Then the $\text{InSb}_{1-x}\text{N}_x$ growth, characterization, photodetector fabrication and measurement are reported in detail. Red-shifted infrared detection ability up to $\sim 11\ \mu\text{m}$ is demonstrated by photocurrent measurements at low temperature.

Finally, the major conclusion of this work and some necessary recommendations for future work are presented in Chapter 8.

Chapter 2 Theoretical methods and ISBTs in N-free quantum wells

2.1 Introduction

Conventionally, the intersubband transitions (ISBTs) in conduction-band quantum-wells (QWs) were analyzed using the time-independent Schrödinger equation [1.48, 1.49]. However, the solution with the wave functions derived from the Schrödinger equation is for a single band and the coupling to other bands is ignored. As a result, the transverse-electric (TE) polarized ISBT was considered to be forbidden.

In recent years, the multi-band $\mathbf{k}\cdot\mathbf{p}$ models have been used frequently to study the impact of interband coupling on ISBTs [1.50, 1.51]. The $\mathbf{k}\cdot\mathbf{p}$ method was introduced by Bardeen [2.1] and Seitz [2.2] based on a perturbation theory. It has been widely applied to analyze the band structures near the band edges of direct bandgap semiconductors [2.3, 2.4, 1.52-1.55]. Yang and Xu employed an eight-band $\mathbf{k}\cdot\mathbf{p}$ model to reveal that the TE-polarized ISBT exists actually although the rate is lower than that of the transverse-magnetic (TM) polarized ISBT [1.52]. It is also found that ISBTs would be contributed more by the interband coupling other than the intraband effect [1.53]. More recently, the fourteen-band $\mathbf{k}\cdot\mathbf{p}$ model with the introduction of six p -like conduction bands (Γ_{7c} and Γ_{8c}) has been developed to examine ISBTs in zinc-blendes semiconductors [1.53–1.55]. The analysis on ISBTs with a fourteen-band $\mathbf{k}\cdot\mathbf{p}$ model was first reported by Peng *et al.* to account for the large TE absorption in

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the experimental observation [1.53]. The debate about how much the amplitude of TE absorption could be improved raised later. Flatté *et al.* concluded that the upper limit for the ratio of TE to TM absorption is about 20% for the GaAs/AlGaAs system [1.54]. Cheah *et al.* also reported an analytical 14-band **k**·**p** method by including the six Γ_7 and Γ_8 conduction bands nonperturbatively [1.55]. Moreover, Ridene *et al.* have examined the inter-valence band optical transitions in p-type SiGe/Si quantum-wells using the 14-band **k**·**p** Hamiltonian [2.5].

In this chapter, we will introduce the theoretical model and calculation method in our study to analyze subband structures and ISBTs in quantum-wells. Then the ISBT selectivities with subband order, in-plane wave vector and well width in common N-free quantum-wells will be discussed (the studies on dilute-N quantum-wells will be presented in next chapter).

2.2 Theoretical methods

2.2.1 Schrödinger equation and k·p method

The time-independent Schrödinger equation is commonly used to calculate the band structures and the corresponding wave functions in semiconductor quantum structures, such as quantum-wells and superlattices. It takes the form of [2.6]

$$H\Psi(\mathbf{r}) = \left[-\frac{\hbar^2}{2m_0} \nabla^2 + V(\mathbf{r}) \right] \Psi(\mathbf{r}) = E(\mathbf{k})\Psi(\mathbf{r}), \quad (2.1)$$

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where H is the Hamiltonian, $\hbar$ is the Planck constant h divided by 2π , Ψ is the total wave function, $\mathbf{r}$ is the position vector, $E(\mathbf{k})$ is the eigen-energy at the electron wave vector $\mathbf{k}$, m_0 is the electron mass, and $V(\mathbf{r})$ is the potential energy function.

For an electron in a periodic potential satisfying the symmetry of the semiconductor crystals,

$$V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R}), \quad (2.2)$$

where $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$, and $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ are the lattice vectors, and n_1 , n_2 and n_3 are integers, the general solution of the electron wave function is given by

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \quad (2.3)$$

where
$$u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r}) \quad (2.4)$$

is a periodic function, and n refers to the band and $\mathbf{k}$ is the wave vector. This result is the Bloch theorem. Numeric methods to find the band structures and the wave functions include the tight-binding, the pseudopotential approach, the orthogonalized plan wave, Green's function, etc [2.7, 2.8]. In this work, we focus on the conduction and valence band structures near the band edges, where the wave vector $\mathbf{k}$ deviates by a small amount from a $\mathbf{k}_0$ where a local minimum or maximum occurs. Therefore, the standard model we used is the $\mathbf{k}\cdot\mathbf{p}$ method together with the envelope-function approximation. The $\mathbf{k}\cdot\mathbf{p}$ method is based on a perturbation theory description of band dispersion for semiconductors with a small set of near-edge bands identified as physical relevant [2.3]. In the

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envelope-function approximation, the form used for the wave function in the quantum-well structure assumes that envelope functions vary on a scale much larger than the lattice constant [2.9]. The computational effort is essentially independent of the number of atoms in the system. When written in terms of $u_{n\mathbf{k}}(\mathbf{r})$, the Schrödinger equation becomes

$$\left[\frac{\mathbf{p}^2}{2m_0} + V(\mathbf{r}) + \frac{\hbar^2}{m_0} \mathbf{k} \cdot \mathbf{p} + \frac{\hbar^2 k^2}{2m_0} \right] u_{n\mathbf{k}}(\mathbf{r}) = E_n(\mathbf{k}) u_{n\mathbf{k}}(\mathbf{r}) \quad (2.5)$$

This equation can be expanded near a particular point $\mathbf{k}_0$ where a local minimum or maximum occurs.

For quantum-wells, most $\mathbf{k} \cdot \mathbf{p}$ analyses with envelope-function approximation approaches are based on the formalism of Luttinger and Kohn [2.10], which treated the response of a homogeneous crystal to a weak, slowly varying external perturbing potential. Under flat band conditions, the well or barrier regions are assumed to be bulk-like, and the wave function takes the form

$$\Psi(\mathbf{r}) = \sum_{n=1}^N F_n(\mathbf{r}) u_n(\mathbf{r}) \quad (2.6)$$

where the $F_n(\mathbf{r})$ are envelope functions and $u_n(\mathbf{r})$ are the zone-center states. The sum runs over the N states retained in the $\mathbf{k} \cdot \mathbf{p}$ description, defining a multiband envelope-function approximation.

2.2.2 Eight-band $\mathbf{k}\cdot\mathbf{p}$ model

In Kane's model for direct band semiconductors, four bands – the conduction-band (CB), the heavy-hole (HH), light-hole (LH), and the spin-orbit split-off (SO) bands are taken into consideration (Fig. 2.1), which have double degeneracy with their spin counterparts. It is called as an eight-band $\mathbf{k}\cdot\mathbf{p}$ model. The lowest conduction-band states and the upper valence-band states at $\mathbf{k}$ near the Γ point are expanded in terms of the eight zone center eigenstates composed of $|S\rangle$ (s -like conduction-band Bloch state), and $|X\rangle$, $|Y\rangle$ and $|Z\rangle$ (p -like valence-band Bloch states) with spin up and down.

Figure 2.1. Schematic bulk band structures in the eight-band $\mathbf{k}\cdot\mathbf{p}$ model near the Γ point of the Brillouin zone. E_g defines the energy bandgap between CB and VB, and Δ defines the spin-orbit splitting energy.

Figure 2.2. Schematic coordinate axis in the quantum-well: x and y define the in-plane direction and z defines the quantum-well growth direction.

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The total wave function $\Psi(r)$ for the electron state in the quantum-well satisfies

$$H\Psi(r) = E\Psi(r). \quad (2.7)$$

The total Hamiltonian H is given by

$$H = H_k + H_s + U(z) \quad (2.8)$$

where H_k is the 8×8 $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian, H_s is the strain Hamiltonian, and $U(z)$ is the quantum-well potential function. $\Psi(r)$ can be written as

$$\Psi(r) = \sum_{j=1}^8 F_j(r) u_j(r) = \sum_{j=1}^8 \exp(ik_t \rho) \phi_j(z) u_j(r) \quad (2.9)$$

where $F_j(r)$ are the envelope functions in the eight-band model and $u_j(r)$ are the periodic part of the Bloch basis functions at the zone center. Since the carrier motion is free in the quantum well plane, $F_j(r)$ can be expressed as $\exp(ik_t \rho) \phi_j(z)$, where $k_t = (k_x, k_y)$ is the two-dimensional in-plane wave vector, $\rho = (x, y)$ is the two-dimensional in-plane space vector, and $\phi_j(z)$ is the growth direction-dependent envelope function. The result is that the Schrödinger equation can then be converted into a set of eight coupled differential equations for the envelope function. The eight basis functions of $u_j(r)$ we employed in the calculation are

$$u_1 = \phi_{c,\alpha} = |1/2, 1/2\rangle_c = |S \uparrow\rangle,$$

$$u_2 = \phi_{c,\beta} = |1/2, -1/2\rangle_c = |S \downarrow\rangle,$$

$$u_3 = \phi_{hh,\alpha} = |3/2, 3/2\rangle_v = -i\sqrt{1/2} |(X + iY) \uparrow\rangle,$$

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$$u_4 = \phi_{LH,\alpha} = |3/2, 1/2\rangle_v = i\sqrt{2/3}|Z \uparrow\rangle - i\sqrt{1/6}|(X + iY) \downarrow\rangle,$$

$$u_5 = \phi_{LH,\beta} = |3/2, -1/2\rangle_v = i\sqrt{2/3}|Z \downarrow\rangle + i\sqrt{1/6}|(X - iY) \uparrow\rangle,$$

$$u_6 = \phi_{HH,\beta} = |3/2, -3/2\rangle_v = i\sqrt{1/2}|(X - iY) \downarrow\rangle,$$

$$u_7 = \phi_{SO,\alpha} = |1/2, 1/2\rangle_v = i\sqrt{1/3}|Z \uparrow\rangle + i\sqrt{1/3}|(X + iY) \downarrow\rangle,$$

and $u_8 = \phi_{SO,\beta} = |1/2, -1/2\rangle_v = -i\sqrt{1/3}|Z \downarrow\rangle + i\sqrt{1/3}|(X - iY) \uparrow\rangle.$

(2.10)

The elements in the eight-band $k \cdot p$ Hamiltonian H_k are shown in Eq. (2.11).

Only the upper triangular block is displayed since the matrix is Hermitian.

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

$$H_k = \begin{bmatrix} C & 0 & -pk_+ & \sqrt{\frac{2}{3}}pk_z & \frac{1}{\sqrt{3}}pk_- & 0 & \frac{1}{\sqrt{3}}pk_z & \sqrt{\frac{2}{3}}pk_- \\ c.c. & C & 0 & \frac{-1}{\sqrt{3}}pk_+ & \sqrt{\frac{2}{3}}pk_z & pk_- & \sqrt{\frac{2}{3}}pk_+ & \frac{-1}{\sqrt{3}}pk_z \\ c.c. & c.c. & F & H & I & 0 & \frac{H}{\sqrt{2}} & \sqrt{2}I \\ c.c. & c.c. & c.c. & G & 0 & I & \frac{1}{\sqrt{2}}(G - F) & -\sqrt{\frac{3}{2}}H \\ c.c. & c.c. & c.c. & c.c. & G & -H & -\sqrt{\frac{3}{2}}H^* & \frac{-1}{\sqrt{2}}(G - F) \\ c.c. & c.c. & c.c. & c.c. & c.c. & F & -\sqrt{2}I^* & \frac{H^*}{\sqrt{2}} \\ c.c. & c.c. & c.c. & c.c. & c.c. & c.c. & \frac{F + G}{2} - \Delta & 0 \\ c.c. & c.c. & c.c. & c.c. & c.c. & c.c. & c.c. & \frac{F + G}{2} - \Delta \end{bmatrix}$$

(2.11)

where

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$$k_+ = (k_x + ik_y) / \sqrt{2}, \quad k_- = (k_x - ik_y) / \sqrt{2},$$

$$C = E_g + \frac{\hbar^2 k^2}{2m_0} \left[\frac{1}{m_e^*} - \frac{E_p}{3} \left(\frac{2}{E_g} + \frac{1}{E_g + \Delta} \right) \right],$$

$$F = Ak^2 + \frac{B}{2}(k^2 - 3k_z^2), \quad G = Ak^2 - \frac{B}{2}(k^2 - 3k_z^2),$$

$$H = -Dk_z(k_x - ik_y), \quad I = -\frac{\sqrt{3}}{2}B(k_x^2 - k_y^2) + iDk_xk_y,$$

$$A = -\frac{\hbar^2 \gamma_1}{2m_0}, \quad B = -\frac{\hbar^2 \gamma_2}{m_0}, \quad D = -\sqrt{3} \frac{\hbar^2 \gamma_3}{m_0},$$

$$\text{and} \quad p = (\hbar / m_0) \cdot P_0, \quad (2.12)$$

where $P_0 = i\langle S | \mathbf{p}_x | X_v \rangle = i\langle S | \mathbf{p}_y | Y_v \rangle = i\langle S | \mathbf{p}_z | Z_v \rangle$ is the momentum matrix, γ_i ($i = 1, 2, 3$) are the modified Luttinger parameters [2.11], Δ is the spin-orbit splitting energy, k_x and k_y is the in-plane wave vector, and k_z is the wave vector along the quantum well growth direction.

The strain Hamiltonian H_s can be obtained by the following substitution because of the same underlying symmetry [2.12]: $A \rightarrow a_v$, $B \rightarrow b$, $D \rightarrow d$, $k_\alpha k_\beta \rightarrow \varepsilon_{\alpha\beta}$ ($\alpha, \beta = x, y, z$), and $\hbar^2 k^2 / 2m_0 \rightarrow a_c$, where $\varepsilon_{\alpha\beta}$ is the strain tensor, b and d are the shear deformation potentials, a_v is the hydrostatic valence-band deformation potential, and a_c is the conduction-band deformation potential.

2.2.3 Fourteen-band $\mathbf{k}\cdot\mathbf{p}$ model

The fourteen-band $\mathbf{k}\cdot\mathbf{p}$ model takes the coupling of the p -like conduction bands (Γ_{7c} and Γ_{8c}), the s -like conduction bands (Γ_{6c}) and the p -like valence bands (Γ_{7v} and Γ_{8v}) in the zinc-blendes semiconductors that lack inversion symmetry into account [1.53, 1.54]. The total wave function for the electron state can be written as

$$\Psi(r) = \sum_{j=1}^{14} F_j(r) u_j(r) = \sum_{j=1}^{14} \exp(ik_t \rho) \varphi_j(z) u_j(r) \quad (2.13)$$

The Bloch functions $u_j(r)$ for the fourteen bands we used are

$$u_1 = \phi_{HE,\alpha} = -i\sqrt{1/2} |(X_c + iY_c) \uparrow\rangle,$$

$$u_2 = \phi_{LE,\alpha} = i\sqrt{2/3} |Z_c \uparrow\rangle - i\sqrt{1/6} |(X_c + iY_c) \downarrow\rangle,$$

$$u_3 = \phi_{LE,\beta} = i\sqrt{2/3} |Z_c \downarrow\rangle + i\sqrt{1/6} |(X_c - iY_c) \uparrow\rangle,$$

$$u_4 = \phi_{HE,\beta} = i\sqrt{1/2} |(X_c - iY_c) \downarrow\rangle,$$

$$u_5 = \phi_{SOE,\alpha} = i\sqrt{1/3} |Z_c \uparrow\rangle + i\sqrt{1/3} |(X_c + iY_c) \downarrow\rangle,$$

$$u_6 = \phi_{SOE,\beta} = -i\sqrt{1/3} |Z_c \downarrow\rangle + i\sqrt{1/3} |(X_c - iY_c) \uparrow\rangle,$$

$$u_7 = \phi_{C,\alpha} = |S \uparrow\rangle,$$

$$u_8 = \phi_{C,\beta} = |S \downarrow\rangle,$$

$$u_9 = \phi_{HH,\alpha} = -i\sqrt{1/2} |(X_v + iY_v) \uparrow\rangle,$$

$$u_{10} = \phi_{LH,\alpha} = i\sqrt{2/3} |Z_v \uparrow\rangle - i\sqrt{1/6} |(X_v + iY_v) \downarrow\rangle,$$

$$u_{11} = \phi_{LH,\beta} = i\sqrt{2/3} |Z_v \downarrow\rangle + i\sqrt{1/6} |(X_v - iY_v) \uparrow\rangle,$$

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$$\begin{aligned}
 u_{12} &= \phi_{HH,\beta} = i\sqrt{1/2} \left| (X_v - iY_v) \downarrow \right\rangle, \\
 u_{13} &= \phi_{SOH,\alpha} = i\sqrt{1/3} \left| Z_v \uparrow \right\rangle + i\sqrt{1/3} \left| (X_v + iY_v) \downarrow \right\rangle, \\
 u_{14} &= \phi_{SOH,\beta} = -i\sqrt{1/3} \left| Z_v \downarrow \right\rangle + i\sqrt{1/3} \left| (X_v - iY_v) \uparrow \right\rangle,
 \end{aligned}
 \tag{2.14}$$

where $|S\rangle$ indicates the s -like conduction-band Bloch state, $|X_c\rangle$, $|Y_c\rangle$ and $|Z_c\rangle$ indicate the p -like conduction-band Bloch states, and $|X\rangle$, $|Y\rangle$ and $|Z\rangle$ indicate the p -like valence-band Bloch states. HE (heavy electron), LE (light electron) and SOE (spin-orbit splitting) denote the three states of the p -like conduction-band, and C denotes the state of the s -like conduction-band, as shown in Fig. 2.3.

Figure 2.3. Schematic bulk band structures in the fourteen-band $\mathbf{k}\cdot\mathbf{p}$ model for zinc-blende semiconductors near the Γ point of the Brillouin zone. E_g defines the energy bandgap of Γ_{8v} - Γ_{6c} , E_{gc} defines the energy difference of Γ_{7c} - Γ_{6c} , Δ defines the spin-orbit splitting in the p -like valence-band, and Δ_c defines the spin-orbit splitting in the p -like conduction-band.

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The three momentum matrix elements in Fig. 2.3 are defined as

$$P_0 = i\langle S | \mathbf{p}_x | X_v \rangle = i\langle S | \mathbf{p}_y | Y_v \rangle = i\langle S | \mathbf{p}_z | Z_v \rangle, \quad (2.15)$$

$$P_1 = i\langle S | \mathbf{p}_x | X_c \rangle = i\langle S | \mathbf{p}_y | Y_c \rangle = i\langle S | \mathbf{p}_z | Z_c \rangle, \quad (2.16)$$

$$Q = i\langle X_c | \mathbf{p}_z | Y_v \rangle = i\langle X_c | \mathbf{p}_y | Z_v \rangle = -i\langle X_v | \mathbf{p}_z | Y_c \rangle, \quad (2.17)$$

where P_0 is the coupling of s -like conduction-band and p -like valence-band, P_1 is the coupling of p -like conduction-band and s -like conduction-band, and Q is the coupling of p -like conduction-band and p -like valence-band (see Fig. 2.3).

The 14-band $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian is given by

$$\mathbf{H} = \begin{bmatrix} \mathbf{H}_{\bar{p}} & \mathbf{H}_{\bar{p}-sp} \\ (6 \times 6) & (6 \times 8) \\ \mathbf{H}_{\bar{p}-sp}^* & \mathbf{H}_{sp} \\ (8 \times 6) & (8 \times 8) \end{bmatrix}, \quad (2.18)$$

where $\mathbf{H}_{\bar{p}}$ consists of the elements of the six p -like conduction-band states, $\mathbf{H}_{sp}$ is the eight-band $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian which consists of the elements of the two s -like conduction-band states and the six p -like valence-band states, $\mathbf{H}_{\bar{p}-sp}$ consists of the coupling elements between the p -like conduction-band and the s -like conduction-band and the p -like valence-band, and $\mathbf{H}_{\bar{p}-sp}^*$ at the down triangular block is the corresponding conjugation part of $\mathbf{H}_{\bar{p}-sp}$. $\mathbf{H}_{\bar{p}}$ and $\mathbf{H}_{\bar{p}-sp}$ take the form of

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$$\mathbf{H}_{\bar{p}} = \begin{bmatrix} E_{g2} + F_c & H_c & I_c & 0 & \frac{H_c}{\sqrt{2}} & \sqrt{2}I_c \\ c.c. & E_{g2} + G_c & 0 & I_c & \frac{G_c - F_c}{\sqrt{2}} & -\sqrt{\frac{3}{2}}H_c \\ c.c. & c.c. & E_{g2} + G_c & -H_c & -\sqrt{\frac{3}{2}}H_c^* & -\frac{G_c - F_c}{\sqrt{2}} \\ c.c. & c.c. & c.c. & E_{g2} + F_c & -\sqrt{2}I_c^* & \frac{H_c}{\sqrt{2}} \\ c.c. & c.c. & c.c. & c.c. & E_{g2} + \frac{F_c + G_c}{2} - \Delta_c & 0 \\ c.c. & c.c. & c.c. & c.c. & c.c. & E_{g2} + \frac{F_c + G_c}{2} - \Delta_c \end{bmatrix}, \quad (2.19)$$

$$\mathbf{H}_{\bar{p}-sp} = \begin{bmatrix} -p_1 k_- & 0 & 0 & \sqrt{\frac{2}{3}}qk_+ & \frac{1}{\sqrt{3}}qk_z & 0 & \frac{1}{\sqrt{3}}qk_+ & \frac{2}{\sqrt{3}}qk_+ \\ \sqrt{\frac{2}{3}}p_1 k_z & \frac{-1}{\sqrt{3}}p_1 k_- & -\sqrt{\frac{2}{3}}qk_- & 0 & 0 & \frac{1}{\sqrt{3}}qk_z & 0 & -qk_+ \\ \frac{1}{\sqrt{3}}p_1 k_+ & \sqrt{\frac{2}{3}}p_1 k_z & -\frac{1}{\sqrt{3}}qk_z & 0 & 0 & -\sqrt{\frac{2}{3}}qk_+ & qk_- & 0 \\ 0 & p_1 k_+ & 0 & -\frac{1}{\sqrt{3}}qk_z & \sqrt{\frac{2}{3}}qk_- & 0 & \sqrt{\frac{2}{3}}qk_z & -\frac{1}{\sqrt{3}}qk_- \\ \frac{1}{\sqrt{3}}p_1 k_z & \sqrt{\frac{2}{3}}p_1 k_- & -\frac{1}{\sqrt{3}}qk_- & 0 & -qk_+ & -\sqrt{\frac{2}{3}}qk_z & 0 & 0 \\ \sqrt{\frac{2}{3}}p_1 k_+ & \frac{-1}{\sqrt{3}}p_1 k_z & -\sqrt{\frac{2}{3}}qk_z & qk_- & 0 & \frac{1}{\sqrt{3}}qk_+ & 0 & 0 \end{bmatrix} \quad (2.20)$$

where

$$k_+ = (k_x + ik_y)/\sqrt{2}, \quad k_- = (k_x - ik_y)/\sqrt{2},$$

$$F_c = A_c k^2 + \frac{B_c}{2}(k^2 - 3k_z^2),$$

$$G_c = A_c k^2 - \frac{B_c}{2}(k^2 - 3k_z^2),$$

$$H_c = -D_c k_z (k_x - ik_y),$$

$$I_c = -\frac{\sqrt{3}}{2}B_c(k_x^2 - k_y^2) + iD_c k_x k_y,$$

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$$A_c = -\frac{\hbar^2 \gamma_{c1}}{2m_0}, B_c = -\frac{\hbar^2 \gamma_{c2}}{m_0}, D_c = -\sqrt{3} \frac{\hbar^2 \gamma_{c3}}{m_0},$$

$$p_0 = (\hbar/m_0) \cdot P_0, p_1 = (\hbar/m_0) \cdot P_1 \text{ and } q = (\hbar/m_0) \cdot Q.$$
(2.21)

where γ_{c1} , γ_{c2} and γ_{c3} are the modified Luttinger parameters of the p -like conduction bands [2.5]. The down triangular block in the matrix (2.17) is not shown since they are Hermitian.

2.2.4 Envelope-function Fourier expansion

The envelope-function Fourier expansion method is employed to calculate the eigen-states and eigen-functions for electron states in quantum wells [2.13–2.15]. The expansion of the envelope-function $F_{n,j}(r)$ takes the form of

$$F_{n,j}(r) = \exp[i(k_x x + k_y y)] \sum_m a_{n,j,m} \phi_m(z), \quad (2.22)$$

where

$$\phi_m(z) = \frac{1}{\sqrt{L}} \exp \left[i \left(k_z + m \cdot \frac{2\pi}{L} \right) \cdot z \right], \quad (2.23)$$

n is the subband order, m are a set of integers and L is the sum of well and barrier widths ($L = L_B + L_W$). This discrete Fourier series assumes that the overall structure is periodic with L along the growth direction. In the case of MQW structures usually employed in QWIPs, this is exactly what is wanted. Substituting Eq. (2.22) into the multi-band coupled differential equations

$$\sum_{j'=1}^i (\mathbf{H}_{j,j'} + U(z) \delta_{j,j'}) F_{j'}(r) = E F_j(r), \quad (2.24)$$

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where $U(z)$ is the electronic potential function, $\mathbf{H}_{j,j'}$ is the multi-band $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian, and i is the number of bands ($i = 8$ or 14). Then multiplying by $\phi_m^*(z)$ on both side of (2.24) and integrating over L , one gets

$$\sum_{j',m'} \mathbf{H}_{j,j'}(m,m') a_{j',m'} = E a_{j,m}, \quad j, j' = 1, \dots, i \quad (2.25)$$

where the matrix elements $\mathbf{H}_{j,j'}(m',m)$ are given by

$$\begin{aligned} \mathbf{H}_{j,j'}(m,m') &= \int_{-L/2}^{L/2} \phi_m^*(z) [H_{j,j'} + U(z) \delta_{j,j'}] \phi_{m'}(z) dz \\ &= \langle \phi_m | H_{j,j'} + U(z) \delta_{j,j'} | \phi_{m'} \rangle. \end{aligned} \quad (2.26)$$

$U(z)$ includes the quantum-well potential from the band discontinuity as well as the potential change induced by strain. For rectangular quantum-wells, the integration of $U(z)$ over the structure period L in Eq. (2.24) can be yielded analytically as

$$\begin{aligned} \langle \phi_m | U(z) | \phi_m \rangle &= V \cdot L_B / L \\ \langle \phi_m | U(z) | \phi_{m'} \rangle &= -V \cdot \frac{\sin(\pi L_W f)}{\pi f L} \quad (m \neq m') \end{aligned} \quad (2.27)$$

where V is the rectangular quantum well potential, L_W is the well width, L_B is the barrier width, and $f = (m - m')/L$. For the quantum wells with complex asymmetric potential profiles, the analytical integration is hard to derived, so numerical calculation is preferred. The eigen-energies and eigen-states can then be obtained by solving the giant algebraic set of coupled equations (2.25).

The following probability functions are introduced to decide the components of HH, LH, SOH, CB, HE, LE, and SOE bands in each subband states:

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$$P_n^{HE} = \sum_{j=1,4} \sum_m a_{n,j,m}^* a_{n,j,m} ,$$

$$P_n^{LE} = \sum_{j=2,3} \sum_m a_{n,j,m}^* a_{n,j,m} ,$$

$$P_n^{SOE} = \sum_{j=5,6} \sum_m a_{n,j,m}^* a_{n,j,m} ,$$

$$P_n^{CB} = \sum_{j=7,8} \sum_m a_{n,j,m}^* a_{n,j,m} ,$$

$$P_n^{HH} = \sum_{j=9,12} \sum_m a_{n,j,m}^* a_{n,j,m} ,$$

$$P_n^{LH} = \sum_{j=10,11} \sum_m a_{n,j,m}^* a_{n,j,m} ,$$

and

$$P_n^{SOH} = \sum_{j=13,14} \sum_m a_{n,j,m}^* a_{n,j,m} ,$$

(2.28)

These probability functions are particularly useful to identify the dominant character in a particular subband. Note that the following sum rule should hold:

$$\sum_i P_n^i = 1 \quad i = HE, LE, SOE, CB, HH, LH, SOH . \quad (2.29)$$

2.2.5 Momentum matrix elements and optical absorption

With the fourteen-band model, the momentum matrix element between subbands n and n' is

$$M_{nn'} = \langle \Psi_n | e_v \cdot \mathbf{p} | \Psi_{n'} \rangle = \sum_{j,j'=1}^{14} \langle F_{n,j} u_j | e_v \cdot \mathbf{p} | F_{n',j'} u_{j'} \rangle , \quad (2.30)$$

where $\mathbf{p}$ is the momentum operator and

$e_v = v_x e_x + v_y e_y + v_z e_z$ ($v_x^2 + v_y^2 + v_z^2 = 1$) is the photon polarization unit vector.

Substituting Eqs. (2.13) and (2.22) into (2.30), we obtain

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$$\begin{aligned}
 M_{nn'} &= \sum_{j,j'=1}^{14} \left\langle \sum_m a_{n,j,m} \phi_m(z) u_j \middle| e_v \cdot \mathbf{p} \middle| \sum_{m'} a_{n',j',m'} \phi_{m'}(z) u_{j'} \right\rangle \\
 &\approx \sum_{j,j'=1}^{14} \left[\left\langle \sum_m a_{n,j,m} \phi_m(z) \middle| e_v \cdot \mathbf{p} \middle| \sum_{m'} a_{n',j',m'} \phi_{m'}(z) \right\rangle \langle u_j | u_{j'} \rangle \right] \\
 &\quad + \sum_{j,j'=1}^{14} \left[\left\langle \sum_m a_{n,j,m} \phi_m(z) \middle| \sum_{m'} a_{n',j',m'} \phi_{m'}(z) \right\rangle \langle u_j | e_v \cdot \mathbf{p} | u_{j'} \rangle \right] \\
 &= \sum_{j=1}^{14} \left[\left\langle \sum_m a_{n,j,m} \phi_m(z) \middle| e_v \cdot \mathbf{p} \middle| \sum_{m'} a_{n',j,m'} \phi_{m'}(z) \right\rangle \right] \\
 &\quad + \sum_{j,j'=1}^{14} \left[\sum_m (a_{n,j,m}^* \cdot a_{n',j',m}) \langle u_j | e_v \cdot \mathbf{p} | u_{j'} \rangle \right].
 \end{aligned} \tag{2.31}$$

$M_{nn'}$ consists of seven parts as follows

$$\begin{aligned}
 M_{nn'} &= M_{nn'_{\text{int ra}}} + M_{nn'_{P0}}^{\uparrow} + M_{nn'_{P0}}^{\downarrow} + M_{nn'_{P1}}^{\uparrow} \\
 &\quad + M_{nn'_{P1}}^{\downarrow} + M_{nn'_{Q}}^{\uparrow} + M_{nn'_{Q}}^{\downarrow},
 \end{aligned} \tag{2.32}$$

where $M_{nn'_{\text{int ra}}}$ denotes the elements from the intraband contribution, i.e. the first term on the right of Eq. (2.31), $M_{nn'_{P0}}^{\uparrow}$, $M_{nn'_{P1}}^{\uparrow}$ and $M_{nn'_{Q}}^{\uparrow}$ denote the elements from the couplings between s -like conduction-band and p -like valence-band states ($\propto P_0$), between s -like conduction-band and p -like conduction-band states ($\propto P_1$), and between p -like conduction-band and p -like valence-band states ($\propto Q$), respectively, for the spin-up components, and similarly $M_{nn'_{P0}}^{\downarrow}$, $M_{nn'_{P1}}^{\downarrow}$ and $M_{nn'_{Q}}^{\downarrow}$ denote the elements for the spin-down components.

For TM-polarized transitions,

$$\begin{aligned}
 M_{nn',\text{TM}} &= M_{nn'_{\text{int ra}}} + M_{nn'_{P0},\text{TM}}^{\uparrow} + M_{nn'_{P0},\text{TM}}^{\downarrow} + M_{nn'_{P1},\text{TM}}^{\uparrow} \\
 &\quad + M_{nn'_{P1},\text{TM}}^{\downarrow} + M_{nn'_{Q},\text{TM}}^{\uparrow} + M_{nn'_{Q},\text{TM}}^{\downarrow}
 \end{aligned} \tag{2.33}$$

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where

$$M_{nn'_{\text{int}}ra} = \sum_{j=1}^{14} \left[\left\langle \sum_m a_{n,j,m} \phi_m(z) | e_v \cdot \mathbf{p} | \sum_{m'} a_{n',j,m'} \phi_{m'}(z) \right\rangle \right]$$

$$M_{nn'_{P0},\text{TM}}^{\uparrow} = \frac{P_0}{\sqrt{3}} \sum_m \left(\sqrt{2} a_{n,7,m}^* a_{n',10,m} - \sqrt{2} a_{n,10,m}^* a_{n',7,m} + a_{n,7,m}^* a_{n',13,m} - a_{n,13,m}^* a_{n',7,m} \right),$$

$$M_{nn'_{P0},\text{TM}}^{\downarrow} = \frac{P_0}{\sqrt{3}} \sum_m \left(\sqrt{2} a_{n,8,m}^* a_{n',11,m} - \sqrt{2} a_{n,11,m}^* a_{n',8,m} - a_{n,8,m}^* a_{n',14,m} - a_{n,14,m}^* a_{n',8,m} \right),$$

$$M_{nn'_{P1},\text{TM}}^{\uparrow} = \frac{P_1}{\sqrt{3}} \sum_m \left(\sqrt{2} a_{n,7,m}^* a_{n',2,m} - \sqrt{2} a_{n,2,m}^* a_{n',7,m} + a_{n,7,m}^* a_{n',5,m} - a_{n,5,m}^* a_{n',7,m} \right),$$

$$M_{nn'_{P1},\text{TM}}^{\downarrow} = \frac{P_1}{\sqrt{3}} \sum_m \left(\sqrt{2} a_{n,8,m}^* a_{n',3,m} - \sqrt{2} a_{n,3,m}^* a_{n',8,m} - a_{n,8,m}^* a_{n',6,m} - a_{n,6,m}^* a_{n',8,m} \right),$$

$$M_{nn'_{Q},\text{TM}}^{\uparrow} = -2i \cdot Q \sum_m \left[\frac{1}{\sqrt{12}} (a_{n,1,m}^* a_{n',11,m} + a_{n,11,m}^* a_{n',1,m}) + \frac{1}{\sqrt{6}} (a_{n,1,m}^* a_{n',14,m} + a_{n,14,m}^* a_{n',1,m}) - \frac{1}{\sqrt{12}} (a_{n,3,m}^* a_{n',9,m} + a_{n,9,m}^* a_{n',3,m}) - \frac{1}{\sqrt{6}} (a_{n,6,m}^* a_{n',9,m} + a_{n,9,m}^* a_{n',6,m}) \right],$$

$$M_{nn'_{Q},\text{TM}}^{\downarrow} = -2i \cdot Q \sum_m \left[\frac{1}{\sqrt{12}} (a_{n,2,m}^* a_{n',12,m} + a_{n,12,m}^* a_{n',2,m}) - \frac{1}{\sqrt{12}} (a_{n,4,m}^* a_{n',10,m} + a_{n,10,m}^* a_{n',4,m}) + \frac{1}{\sqrt{6}} (a_{n,4,m}^* a_{n',13,m} + a_{n,13,m}^* a_{n',4,m}) - \frac{1}{\sqrt{6}} (a_{n,5,m}^* a_{n',12,m} + a_{n,12,m}^* a_{n',5,m}) \right].$$

and

(2.34)

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For TE-polarized transitions,

$$\begin{aligned}
 M_{nn', \text{TE}} = & M_{nn' - P0, \text{TE}}^{\uparrow} + M_{nn' - P0, \text{TE}}^{\downarrow} + M_{nn' - P1, \text{TE}}^{\uparrow} \\
 & + M_{nn' - P1, \text{TE}}^{\downarrow} + M_{nn' - Q, \text{TE}}^{\uparrow} + M_{nn' - Q, \text{TE}}^{\downarrow}
 \end{aligned} \quad (2.35)$$

where

$$\begin{aligned}
 M_{nn' - P0, \text{TE}}^{\downarrow} = & P_0 \sum_m \left(-\frac{1+i}{\sqrt{6}} a_{n,8,m}^* a_{n',10,m} + \frac{1-i}{\sqrt{6}} a_{n,10,m}^* a_{n',8,m} \right. \\
 & + \frac{1-i}{\sqrt{2}} a_{n,8,m}^* a_{n',12,m} - \frac{1+i}{\sqrt{2}} a_{n,12,m}^* a_{n',8,m} \\
 & \left. + \frac{1+i}{\sqrt{3}} a_{n,8,m}^* a_{n',13,m} - \frac{1-i}{\sqrt{3}} a_{n,13,m}^* a_{n',8,m} \right),
 \end{aligned}$$

$$\begin{aligned}
 M_{nn' - P1, \text{TE}}^{\uparrow} = & P_1 \sum_m \left(-\frac{1+i}{\sqrt{2}} a_{n,7,m}^* a_{n',1,m} + \frac{1-i}{\sqrt{2}} a_{n,1,m}^* a_{n',7,m} \right. \\
 & + \frac{1-i}{\sqrt{6}} a_{n,7,m}^* a_{n',3,m} - \frac{1+i}{\sqrt{6}} a_{n,3,m}^* a_{n',7,m} \\
 & \left. + \frac{1-i}{\sqrt{3}} a_{n,7,m}^* a_{n',6,m} - \frac{1+i}{\sqrt{3}} a_{n,6,m}^* a_{n',7,m} \right),
 \end{aligned}$$

$$\begin{aligned}
 M_{nn' - P1, \text{TE}}^{\downarrow} = & P_1 \sum_m \left(-\frac{1+i}{\sqrt{6}} a_{n,8,m}^* a_{n',2,m} + \frac{1-i}{\sqrt{6}} a_{n,2,m}^* a_{n',8,m} \right. \\
 & + \frac{1-i}{\sqrt{2}} a_{n,8,m}^* a_{n',4,m} - \frac{1+i}{\sqrt{2}} a_{n,4,m}^* a_{n',8,m} \\
 & \left. + \frac{1+i}{\sqrt{3}} a_{n,8,m}^* a_{n',5,m} - \frac{1-i}{\sqrt{3}} a_{n,5,m}^* a_{n',8,m} \right),
 \end{aligned}$$

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$$\begin{aligned}
M_{nn'-Q, \text{TE}}^{\uparrow} = -iQ \sum_m \bigg(& -\frac{1-i}{\sqrt{3}} a_{n,1,m}^* a_{n',10,m} + \frac{1+i}{\sqrt{3}} a_{n,10,m}^* a_{n',1,m} \\
& -\frac{1-i}{\sqrt{6}} a_{n,1,m}^* a_{n',13,m} + \frac{1+i}{\sqrt{6}} a_{n,13,m}^* a_{n',1,m} \\
& + \frac{1+i}{3} a_{n,3,m}^* a_{n',10,m} - \frac{1-i}{3} a_{n,10,m}^* a_{n',3,m} \\
& + \frac{1+i}{3\sqrt{2}} a_{n,3,m}^* a_{n',13,m} - \frac{1-i}{3\sqrt{2}} a_{n,13,m}^* a_{n',3,m} \\
& + \frac{\sqrt{2}(1+i)}{3} a_{n,6,m}^* a_{n',10,m} - \frac{\sqrt{2}(1-i)}{3} a_{n,10,m}^* a_{n',6,m} \\
& - \frac{1+i}{3} a_{n,6,m}^* a_{n',13,m} + \frac{1-i}{3} a_{n,13,m}^* a_{n',6,m} \\
& - \frac{1+i}{\sqrt{3}} a_{n,2,m}^* a_{n',9,m} + \frac{1-i}{\sqrt{3}} a_{n,9,m}^* a_{n',2,m} \\
& + \frac{1-i}{3} a_{n,2,m}^* a_{n',11,m} - \frac{1+i}{3} a_{n,11,m}^* a_{n',2,m} \\
& + \frac{\sqrt{2}(1-i)}{3} a_{n,2,m}^* a_{n',14,m} - \frac{\sqrt{2}(1+i)}{3} a_{n,14,m}^* a_{n',2,m} \\
& - \frac{1+i}{\sqrt{6}} a_{n,5,m}^* a_{n',9,m} + \frac{1-i}{\sqrt{6}} a_{n,9,m}^* a_{n',5,m} \\
& + \frac{1-i}{3\sqrt{2}} a_{n,5,m}^* a_{n',11,m} - \frac{1+i}{3\sqrt{2}} a_{n,11,m}^* a_{n',5,m} \\
& + \frac{1-i}{3} a_{n,5,m}^* a_{n',14,m} - \frac{1+i}{3} a_{n,14,m}^* a_{n',5,m} \bigg),
\end{aligned}$$

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$$\begin{aligned}
M_{nn'-Q, TE}^{\downarrow} = & -iQ \sum_m \left(-\frac{1-i}{3} a_{n,2,m}^* a_{n',11,m} + \frac{1+i}{3} a_{n,11,m}^* a_{n',2,m} \right. \\
& + \frac{1-i}{3\sqrt{2}} a_{n,2,m}^* a_{n',14,m} - \frac{1+i}{3\sqrt{2}} a_{n,14,m}^* a_{n',2,m} \\
& + \frac{1+i}{\sqrt{3}} a_{n,4,m}^* a_{n',11,m} - \frac{1-i}{\sqrt{3}} a_{n,11,m}^* a_{n',4,m} \\
& - \frac{1+i}{\sqrt{6}} a_{n,4,m}^* a_{n',14,m} + \frac{1-i}{\sqrt{6}} a_{n,14,m}^* a_{n',4,m} \\
& + \frac{\sqrt{2}(1-i)}{3} a_{n,5,m}^* a_{n',11,m} - \frac{\sqrt{2}(1+i)}{3} a_{n,11,m}^* a_{n',5,m} \\
& - \frac{1-i}{3} a_{n,5,m}^* a_{n',14,m} + \frac{1+i}{3} a_{n,14,m}^* a_{n',5,m} \\
& - \frac{1+i}{3} a_{n,3,m}^* a_{n',10,m} + \frac{1-i}{3} a_{n,10,m}^* a_{n',3,m} \\
& + \frac{1-i}{\sqrt{3}} a_{n,3,m}^* a_{n',12,m} - \frac{1+i}{\sqrt{3}} a_{n,12,m}^* a_{n',3,m} \\
& + \frac{\sqrt{2}(1+i)}{3} a_{n,3,m}^* a_{n',13,m} - \frac{\sqrt{2}(1-i)}{3} a_{n,13,m}^* a_{n',3,m} \\
& + \frac{1+i}{3\sqrt{2}} a_{n,6,m}^* a_{n',10,m} - \frac{1-i}{3\sqrt{2}} a_{n,10,m}^* a_{n',6,m} \\
& - \frac{1-i}{\sqrt{6}} a_{n,6,m}^* a_{n',12,m} + \frac{1+i}{\sqrt{6}} a_{n,12,m}^* a_{n',6,m} \\
& \left. - \frac{1+i}{3} a_{n,6,m}^* a_{n',13,m} + \frac{1-i}{3} a_{n,13,m}^* a_{n',6,m} \right).
\end{aligned}$$

and

(2.36)

The absorption coefficient between subbands n and n' is calculated by [1.49]

$$\alpha_{nn'}(\hbar\omega) = \frac{\pi e^2}{n_r c \epsilon_0 m_0^2 \omega V} \sum_{k_z} \sum_{k_t} |M_{nn'}|^2 \delta(E_{n'} - E_n - \hbar\omega) (f_n - f_{n'}) \quad (2.37)$$

where $M_{nn'}$ is the momentum matrix element, f_n and $f_{n'}$ are the Fermi-Dirac distributions for electrons in respective subbands, k_t is the in-plane wave vector.

To take scattering relaxation into account, the delta function in Eq. (2.37) was replaced by a Lorentzian function:

$$\delta(E_{n'} - E_n - \hbar\omega) \rightarrow \frac{\Gamma/(2\pi)}{(E_{n'} - E_n - \hbar\omega)^2 + (\Gamma/2)^2} \quad (2.38)$$

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where the Lorentzian linewidth Γ represents the effective dephasing rate to interpret homogeneous broadening in absorption spectra. The Fermi-Dirac distribution function takes the form of

$$f_n = \frac{1}{1 + \exp[(E_n - E_F)/k_B T]}, \quad (2.39)$$

where k_B is the Boltzmann constant and T is the temperature. To know the Fermi energy level E_F in a quantum well, a determination of carrier density by numerically integrating over k -space can be done:

$$N = \sum_n \frac{2}{L_w} \int \frac{dk_x dk_y}{(2\pi)^2} f_n[E_n(k_x, k_y)] = \sum_n \frac{1}{2\pi^2 L_w} \int 2\pi k_t dk_t f_n[E_n(k_t)], \quad (2.40)$$

where the summation is over all the occupied subbands, and the non-parabolic energy dispersion can be taken into account. In a MQW structure, the coupling between well states is significant especially when the subband order is high and the barrier is thin, leading to the formation of extended minibands. The dispersion of energy subbands with k_z should be taken into account when evaluating the Fermi energy level. In this case, the carrier density can be decided by

$$N = \frac{1}{L} \int_0^L \rho(z, E_F) dz \quad (2.41)$$

$$\text{where } \rho(z, E_F) = \frac{1}{2\pi^2} \sum_n \int_0^\infty k_t dk_t \int_{-\pi/L}^{\pi/L} dk_z |\psi_{n,k_z}(z)|^2 f_n[E_n(k_t, k_z)], \quad (2.42)$$

and the single-particle Bloch wave function $\psi_{n,k_z}(z)$ should satisfy

$$\frac{1}{L} \int_0^L |\psi_{n,k_z}(z)|^2 dz = 1. \quad (2.43)$$

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If we assume a parabolic approximation for the energy band and hence

$E_n(k_t, k_z)$ can be written as $E_n(k_t, k_z) = E_n(k_t = 0) + \frac{\hbar^2}{2m^*} k_t^2 + \varepsilon_n(k_z L)$, Eq.

(2.41) becomes

$$N = \frac{m^* k_B T}{\pi \hbar^2 L} \sum_n \frac{1}{2\pi} \int_{-\pi}^{\pi} dx \ln \{1 + \exp[(E_F - \varepsilon_j(x))/k_B T]\} \quad (2.44)$$

At a lower doping concentration only the ground state (E1) is occupied mainly, so that the terms associated with the excited states ($n > 1$) can be ignored. Since the dispersion of E1 with k_z is minimum if the barrier is not too thin, Eq. (2.44) can be simplified to

$$N = (m_e k_B T / \pi \hbar^2 L) \ln [1 + \exp(E_F' / k_B T)]. \quad (2.45)$$

where $E_F' = E_F - E_1(k_t = 0)$. Levine has used Eq. (2.45) to estimate the Fermi level in GaAs/AlGaAs QWIPs and achieved good agreement with the experimental measurement by dark current spectra and cutoff wavelengths [1.9].

2.3 Analyses of ISBT selectivities

2.3.1 Parameters used in calculations

In the calculation, most parameters for the ternary compounds are obtained using a linear interpolation between the parameters of the relevant binary semiconductors except the bandgap energy and the electron effective mass. The basic material parameters are taken from Ref. [2.16-2.18]. Some important parameters of GaAs and AlAs used in this section are listed in Table 2.1.

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Table 2.1. Parameters of GaAs and AlAs at 0 K used in the calculation. The lattice constant of a is given in Å, the elastic stiffness constant c_{11} and c_{12} are given in 10 GPa, the deformation potential a_c , a_v , b and d are given in eV. The energy gap E_g , E_{gc} , spin-orbit splitting Δ and Δ_c , and the Kane energy E_{P0} , E_{P1} and E_Q are given in eV, where $E_{P0} = 2P_0^2 / m_0$, $E_{P1} = 2P_1^2 / m_0$ and

$$E_Q = 2Q^2 / m_0.$$

	a	c_{11}	c_{12}	a_c	a_v	b	d
GaAs	5.6533	12.21	5.66	-7.17	1.16	-2.0	-4.8
AlAs	5.6611	12.50	5.43	-5.64	2.47	-2.3	-3.4
	E_g	E_{gc}	Δ	Δ_c	E_{P0}	E_{P1}	E_Q
GaAs	1.519	3.04	0.34	0.16	25.7	5.9	13.5

Figure 2.4. Schematic quantum well structure showing the bandgap and band-edge discontinuity

Figure 2.4 shows the schematic quantum-well energy band structure. ΔE_c and ΔE_v are the band-edge discontinuities of conduction-band and valence-band, respectively. The conduction band offset ratio Q_C is defined as

$$Q_C = \frac{\Delta E_c}{\Delta E_c + \Delta E_v} \quad (2.46)$$

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In this subsection, we will analyze the selectivities of TM- and TE-polarized ISBTs with subband order, in-plane wave vector and well width based on the eight-band $\mathbf{k}\cdot\mathbf{p}$ model. The GaAs/Al_{0.25}Ga_{0.75}As MQW structures are chosen in the calculation. The barrier width is assumed to be 40 nm. The uniform doping concentration in the n-type wells is assumed to be $5 \times 10^{17} \text{ cm}^{-3}$. The conduction band offset ratio Q_C is assumed to be 0.66 [2.19]. A linewidth of 20 meV in the Lorentzian function Eq. (2.38) is assumed.

2.3.2 Results with the eight-band model

Figure 2.5. Subband energy dispersions along the [100] and [110] k_t directions in conduction band of GaAs/Al_{0.25}Ga_{0.75}As MQWs with well widths of (a) 3 nm and (b) 10 nm, respectively, calculated using the eight-band $\mathbf{k}\cdot\mathbf{p}$ model.

Figure 2.5 shows the calculated energy dispersions of the conduction subbands E1–E7 in the GaAs/Al_{0.25}Ga_{0.75}As MQWs with well widths (a) 3 nm and (b) 10 nm, respectively, at low temperature (0 K). The variation of subband energy

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with k_z is also taken into account in the computation. This is very necessary for those continuum states with relaxed quantum confinements in the quantum-well growth direction. The bulk VB edge of the GaAs well is regarded as the zero energy level. The valence subbands are not shown in this figure since they are not the focus here. In the case of small well width ($L_w = 3$ nm), all the excited states (E2–E5) are continuum states appearing to be minibands with relaxed quantum confinement effects. In the case of large well width ($L_w = 10$ nm), E2 lowers down to be a bound state, and E3 also becomes a quasi-bound state.

Figure 2.6. Squared optical transition matrix elements for TM-polarized ISBTs (E1 to E2–E7) as a function of k_t in [100] direction in the GaAs/Al_{0.25}Ga_{0.75}As MQWs with well widths of (a) 3 nm and (b) 10 nm, respectively, calculated using the eight-band $\mathbf{k} \cdot \mathbf{p}$ model. M_{TM} is given by Eq. (2.33).

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Figure 2.7. Squared optical transition matrix elements for TE-polarized ISBTs (E1 to E2–E7) as a function of k_t in [100] direction in the GaAs/Al_{0.25}Ga_{0.75}As MQWs with well widths of (a) 3 nm and (b) 10 nm, respectively, calculated using the eight-band $\mathbf{k} \cdot \mathbf{p}$ model. M_{TE} is given by Eq. (2.35).

The squared optical transition matrix elements

$$Q_{nn', TE \text{ or } TM} = 2|M_{nn', TE \text{ or } TM}|^2/m_0 \quad (2.47)$$

of the intersubband transitions from the ground to those excited states are calculated. The transition matrix elements for a serial of k_z values between $m \cdot (2\pi/L)$ to $(m+1) \cdot (2\pi/L)$, where m is an integer, are calculated and then integrated to obtain an overall outcome. It is observed from Fig. 2.6(a) that in the case of narrow well width ($L_w = 3$ nm), all the TM-polarized transitions have considerable magnitudes. The transition rates are maximum at $k_t = 0$ (zone center) and decrease slightly at finite k_t . No obvious selection rule appears there. The TE-polarized transitions showed in Fig. 2.7(a) have the similar phenomenon, except that the transition rates are minimum at $k_t = 0$ and

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increase with k_i rapidly. In the case of wide well width ($L_W = 10$ nm) in which E2 and E3 turn to bound states, the E1→E2 transition becomes dominant for TM-polarization while the other transitions are negligible as shown in Fig. 2.6(b). However, the E1→E3 transition becomes dominant for TE-polarization as shown in Fig. 2.7(b). The result for wide quantum wells is consistent to Yang & Xu' conclusion based on a simplified 8-band $\mathbf{k}\cdot\mathbf{p}$ model that in the case of the subband index differences (Δn) being even integers, ISBTs for both TE and TM polarizations are allowed for electrons at finite k_i , and the TE polarized transition is dominant; in the case of Δn being odd integers, intersubband transitions for both polarizations can occur at $k_i = 0$ and the TM polarized transition is dominant.

Figure 2.8. Peak absorption coefficients of ISBTs for (a) TM and (b) TE polarizations as a function of well width calculated with the eight-band $\mathbf{k}\cdot\mathbf{p}$ model.

In order to better observe the variation trend, the calculated peak absorption coefficients for both TM- and TE-polarized ISBTs as a function of well width are shown in Fig. 2.8. The abrupt variation of some data sites in the curves is

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associated with the conversion of certain subbands from continuum to bound states at certain well widths. It is clearly shown that the variations of the intersubband absorptions are tightly correlated to the change of different excited states from continuum to bound states, and the selectivity appears more and more apparently with the increasing of well width. The rules are summarized as follows:

- 1) In narrower quantum wells where all the excited states are continuum states, most bound-to-continuum (B-to-C) ISBTs have comparable rates, and the transitions to higher excited states are relatively strong in general.
- 2) In moderate or wider quantum wells where some lower excited states are bound states, the ISBTs from the ground to the even-order excited states (E2, E4...) are dominated by the B-to-B TM-polarized transitions, while the ground to the odd-order excited states (E3, E5...) transitions are dominated by the B-to-B TE-polarized transitions.
- 3) Generally, the rates of TM-polarized transitions are highest at $k_{\parallel} = 0$ and decrease with the increasing $k_{\parallel}$, while the rates of TE-polarized transitions are absent at $k_{\parallel} = 0$ and increase quickly with $k_{\parallel}$. The transitions from the ground to the higher-order continuum states are always much weaker than the dominant B-to-B transitions. The overall transition rate for TM polarization is larger than that for TE polarization by three to four orders of magnitude.

In general, our results are consistent to the ISBT rules in conduction-band quantum wells derived by Yang *et al.* with an analytic eight-band $\mathbf{k} \cdot \mathbf{p}$

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Hamiltonian treating all subbands as ideal bound states [1.52], but there are also some significant differences. This is because that the quantum confinement relaxation especially to the continuum states in real quantum wells is taken into reasonable consideration in our methodology. Consequently, the well width becomes a critical impact factor for the transitions from E1 to different excited states.

2.3.3 Results with the fourteen-band $\mathbf{k}\cdot\mathbf{p}$ model

In this subsection, the B-to-B and B-to-C ISBTs are to be analyzed with the fourteen-band $\mathbf{k}\cdot\mathbf{p}$ model. The n-type GaAs/Al_{0.25}Ga_{0.75}As structure is chosen again for the calculation, and the AlGaAs barrier width is assumed to be 40 nm.

Figure 2.9. Squared optical transition matrix elements for TM-polarized ISBTs as a function of k_t in [100] with well widths of (a) 3 nm and (b) 10 nm, respectively, calculated using the fourteen-band $\mathbf{k}\cdot\mathbf{p}$ model.

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Figure 2.10. Squared optical transition matrix elements for TE-polarized ISBTs as a function of k_t in [100] direction with well widths of (a) 3 nm and (b) 10 nm, respectively, calculated using the fourteen-band $\mathbf{k}\cdot\mathbf{p}$ model.

Figures 2.9 and 2.10 show the squared optical transition matrix elements of the transitions from the ground state E1 to the excited states E2-E7 for TM and TE polarizations, respectively. Note that the curves are shown with linear scale for the Y-axis in Fig. 2.9(a) and Fig. 2.10(a) but with logarithmic scale for the Y-axis in Fig. 2.9(b) and Fig. 2.10(b). It can be seen that in the case of narrow well ($L_w = 3$ nm), all the TM- and TE-polarized transitions have considerable rates and there is no obvious selectivity exhibited. The transitions from E1 to higher excited states (E5, E6 and E7) are relatively large. However, in the case of broad well ($L_w = 10$ nm), the B-to-B E1→E2 transition becomes dominant for both polarization cases, while the B-to-C transitions (E1→E4, E5...) become much weaker. The E1→E2 transition for TM polarization is larger than that for TE polarization. Furthermore, it is observed that the TM-polarized ISBTs always occur mainly around the zone center ($k_t = 0$), but the TE-polarized ISBTs are always almost absent at $k_t = 0$ and maximize at finite k_t rapidly.

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Figure 2.11. Calculated peak absorption coefficients of E1 to E2–E7 transitions as a function of the well width ranging from 2 to 18 nm for (a) TM and (b) TE polarizations calculated using the fourteen-band $\mathbf{k}\cdot\mathbf{p}$ model.

After working out the transition matrix elements, the optical absorption coefficients can be calculated with Eq. (2.37). We plot in Fig. 2.11 the peak absorption coefficients of different ISBTs as a function of well width ranging from 2 to 18 nm to better observe the ISBT selectivity upon the subband order. The ISBTs involving E1 and the first six excited subbands (E2–E7) are displayed. It can be seen that the variation trends of TM and TE absorptions are very similar. When the well width is very small (<5 nm) and all the excited states are continuum states, no obvious selectivity presents and all the B-to-C transitions have comparable magnitudes. However, the B-to-B $E1 \rightarrow E2$ absorption increases rapidly to be dominant while the other intersubband absorptions become negligible when the well width is larger than 5 nm. When the well width is larger than 8 nm E3 also becomes a bound state. The B-to-B $E1 \rightarrow E3$ absorption for TM-polarization decreases rapidly and is much less than

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that for TE-polarization. When the well width increases further to beyond 13 nm, the B-to-B $E1 \rightarrow E4$ absorption for both polarizations rises obviously although the intensity is still smaller than that of $E1 \rightarrow E2$.

Furthermore, it is found that the TE-polarized ISBT with k_t in the [110] direction is significantly stronger than that in the [100] direction but the TM-polarized ISBT is almost unchangeable. Figures 2.12(a) and (b) show the squared optical transition matrix elements of the $E1 \rightarrow E2$ transition as a function of k_t in the two directions, respectively, for the GaAs/Al_{0.25}Ga_{0.75}As MQW with well widths of 6 nm. The transitions to other excited states are not shown since they are negligible. It can be seen that the magnitude of TE-polarized transition in the [110] direction is about three times as large as that in the [100] direction. However, the TM-polarized transitions in the two k_t directions show little difference. This is because that the TE-polarized ISBTs are mostly induced by the coupling between the p -like conduction-band and the s -like conduction-band and the p -like valence-band (P1 and Q), which are much stronger in the [110] direction. The TM-polarized ISBTs are affected little since they are determined by P_0 mainly.

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Figure 2.12. Squared optical transition matrix elements of the E1→E2 transition as a function of k_t in [100] and [110] directions, respectively, for the GaAs/Al_{0.25}Ga_{0.75}As MQW with 6 nm well width.

From the preceding analyses based on the fourteen-band $\mathbf{k}\cdot\mathbf{p}$ model, the ISBTs in the conduction-band quantum wells with common zinc-blendes semiconductors that lack inversion symmetry are summarized:

- 1) In narrower wells where all the excited states are miniband-like continuum states, the major B-to-C ISBTs have considerable rates. In moderate and wider wells the B-to-B ISBTs from the ground (E1) to even-order excited states (E2, E4...) are dominant for both TM and TE polarizations. The B-to-C transitions are always much weaker than the dominant B-to-B transitions.
- 2) The TM-polarized ISBTs occur mainly at the zone center, while the TE-polarized ISBTs occur mainly at finite k_t and the rates increase rapidly with k_t . Therefore, the TE-polarized transition rate as well as the TE to TM absorption ratio would be improved with a higher Fermi level.
- 3) In the B-to-B ISBTs from the ground (E1) to the even-order excited states (E2, E4...), the TM-polarized transitions are dominant over the TE-

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polarized transitions. However, in the B-to-B ISBTs from E1 to the odd-order excited states (E3, E5...), the TE-polarized transitions are dominant over the TM-polarized transitions.

The ISBT selectivities on the subband order and the in-plane wave vector derived with the eight- and fourteen-band **k**·**p** models are compared as follows:

- 1) The overall TE-polarized transition rates derived with the fourteen-band model are about two orders of amplitude larger than those derived with the eight-band model. However, the TM-polarized transitions rates are almost unchangeable.
- 2) In the eight-band model, the B-to-B transitions between E1 and the even excited states (E2, E4...) are dominant for TM polarization, while the B-to-B transitions between E1 and the odd excited states (E3, E5...) are dominant for TE polarization. However, the transitions between E1 and the even excited states (E2, E4...) are dominant for both TM and TE polarizations with the fourteen-band model.
- 3) The TE-polarized transitions occur mainly at finite plane wave vector k_t but the TM-polarized transitions occur mainly at the zone center ($k_t = 0$) under the 14-band model. However, the trend with k_t depends on the subband orders under the 8-band model. For instance, the TE-polarized transitions between E1 and the odd excited states (E3, E5) rise dramatically at $k_t \neq 0$, but the TE-polarized transitions between E1 and the even excited states (E2, E4) occur mainly at the zone center. This difference is caused by the neglect of the coupling effect of *p*-like conduction-band with *s*-like conduction-band

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and p -like valence-band in the eight-band model and hence incomplete TE-polarized transitions in consideration.

- 4) The calculated TE-polarized transition rates in the $[110]$ k_z direction are significantly greater ($\sim$ three times) than those in the $[100]$ k_z direction with the fourteen-band model. However, it is not observed under the eight-band model.

It can be seen that the coupling between p -like conduction-band with s -like conduction-band and p -like valence-band states (P1 and Q) in the fourteen-band $\mathbf{k}\cdot\mathbf{p}$ model has resulted in significant changes to the rate and selectivity of TE-polarized ISBTs. The TM-polarized transitions are almost unchanged since they are determined by the coupling of s -like conduction-band and p -like valence-band states (P_0) chiefly.

2.4 Summary

In this chapter, the theoretical method based on multi-band $\mathbf{k}\cdot\mathbf{p}$ models in combination with the envelope function Fourier expansions has been introduced in detail. Then the ISBT selectivities with the subband order, in-plane wave vector and well width in common N-free quantum wells are discussed.

In general, our results based on the eight-band $\mathbf{k}\cdot\mathbf{p}$ model are consistent with those derived by Yang *et al.* for ISBTs in conduction-band quantum wells [1.52], but there are also some significant differences. This is because that the quantum confinement relaxation especially to the continuum states in real quantum wells is taken into reasonable consideration in our methodology.

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Consequently, the well width becomes a critical impact factor for the transitions from E1 to different excited states.

The analyses based on the fourteen-band **k·p** model for ISBTs in common zinc-blendes semiconductors show that the TE-polarized transitions are significant at finite k_z in fact, and are quite asymmetric in [100] and [110] k_z directions. The transitions from E1 to the bound even excited states (E2, E4...) are dominant for both TM and TE polarizations.

Chapter 3 Theoretical study on ISBTs in dilute-N quantum wells

3.1 Introduction

The dilute-nitrogen (N) materials especially (In,Ga)AsN have attracted considerable attention in recent years owing to the unique N-driving physical properties which are attributed to the highly localized nature of perturbations induced by N-band [3.1–3.5]. Most research activities on dilute-N materials have been related to the inter-band transition process. And some limited investigations on intersubband transitions (ISBTs) in the conduction-band of dilute-N quantum wells (QWs) have been reported so far [3.6–3.11]. Duboz *et al.* reported the observation of ISBTs in n-type InGaAsN/GaAs multiple quantum wells (MQWs) for the first time [3.6]. Luna *et al.* demonstrated double-barrier GaAsN/AlAs/AlGaAs quantum well photodetector operating in the near infrared [3.7]. Giehler *et al.* studied the influence of N on ISBTs in InGaAsN/AlGaAs MQWs and observed an unexpected redshift of main absorption band [3.9]. Liu *et al.* measured the absorptions in a set of $\text{In}_{0.77}\text{Ga}_{0.23}\text{As}_{0.99}\text{N}_{0.01}/\text{GaAs}$ MQWs with narrow well widths and found that the transition energy was very insensitive to the well width [3.10].

Because of the existence of highly localized N-band, the properties of intersubband transitions and absorptions in dilute-N quantum wells may also take significant changes that deserve to be studied theoretically. The conventional single-band or eight-band $\mathbf{k}\cdot\mathbf{p}$ models for common III–V quantum wells are no longer applicable for this case. However, only limited theoretical

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work based on simplified two-band, three-band $\mathbf{k}\cdot\mathbf{p}$ or analytical models have been carried out [3.9–3.11]. Although the ten-band $\mathbf{k}\cdot\mathbf{p}$ model has been proposed and some theoretical work has been done to study dilute-N quantum wells and lasers [3.12-3.15], little analysis was reported about the ISBT physics based on this model.

In this chapter, we will investigate ISBTs in dilute-N quantum wells based on ten-band and sixteen-band $\mathbf{k}\cdot\mathbf{p}$ models that take the interaction of the localized N-band with conduction- and valence-bands into consideration. The results are to be compared with those derived for N-free quantum wells in Chapter 2. The theoretical models will be elaborated firstly and then the analyses of ISBT selectivities on subband order and in-plane wave vector. Furthermore, the variations of subband structures and intersubband absorptions with well width and N content will be investigated in detail. Both quasi-strainless GaAsN/AlGaAs and compressive-strained InGaAsN/GaAs quantum wells are to be addressed.

Due to the difficulties in growing high quality dilute-N materials and structures with various dimension and composition parameters, the actual (In,Ga)AsN/(Al,Ga)As QWIP device doesn't work in current stage. Therefore, we will focus on predicting and verifying the quantum-well properties in this chapter work. The available experimental results in literature will be used for comparison.

3.2 Theoretical methods

3.2.1 Ten-band $\mathbf{k}\cdot\mathbf{p}$ model

Figure 3.1. Schematic bulk band structure near the Γ point of the Brillouin zone in the ten-band $\mathbf{k}\cdot\mathbf{p}$ model. E_g defines the energy bandgap of Γ_{8v} - Γ_{6c} , ΔE_{N0} defines the energy separation between the high-lying N-band (NB) and the conduction-band (CB), Δ defines the spin-orbit splitting in the p -like valence-band (VB).

The ten-band $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian that includes the interaction of the localized N-band (NB) with the conduction-band (CB) and valence-band (VB) (as shown in Fig. 3.1) can be written as

$$\mathbf{H} = \begin{bmatrix} \mathbf{H}_{sp} & \mathbf{H}_{sp-N} \\ (8 \times 8) & (8 \times 2) \\ \mathbf{H}_{sp-N}^* & \mathbf{H}_N \\ (2 \times 8) & (2 \times 2) \end{bmatrix} \quad (3.1)$$

where $\mathbf{H}_{sp}$ is the 8-band Hamiltonian as described in Chapter 2, $\mathbf{H}_N$ is the N-band Hamiltonian, and $\mathbf{H}_{sp-N}$ consists the terms coupling the conduction-band and valence-band to the N-band. $\mathbf{H}_N$ and $\mathbf{H}_{sp-N}$ take the following forms:

$$\mathbf{H}_N = \begin{bmatrix} E_{N0} + \alpha_N k^2 & 0 \\ 0 & E_{N0} + \alpha_N k^2 \end{bmatrix}, \quad (3.2)$$

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and

$$\mathbf{H}_{sp-N}^* = \begin{bmatrix} V_{NC} & 0 & -\sqrt{3}T_{N+} & \sqrt{2}Q_N & -T_{N-} & 0 & -Q_N & -\sqrt{2}T_{N-} \\ 0 & V_{NC} & 0 & T_{N+} & \sqrt{2}Q_N & -\sqrt{3}T_{N-} & \sqrt{2}T_{N+} & -Q_N \end{bmatrix} \quad (3.3)$$

respectively, where E_{N0} is the N level energy at the zone center, $V_{NC} = \beta\sqrt{x}$ describes the coupling between the conduction-band and the high-lying N-band with N composition x , k is wave vector and $k^2 = k_x^2 + k_y^2 + k_z^2$. The coefficient α_N is related to the effective mass of the N-band state. For the localized N state, a very flat dispersion is used, which corresponds to a very large effective mass [3.12, 3.13]. Therefore, α_N is regarded as zero in our calculation. The matrix elements $T_{N\pm}$ and Q_N should vary linearly with k , coupling the N-band to the valence-band. $T_{N\pm}$ and Q_N are in the forms of

$$T_{N\pm} = \frac{1}{\sqrt{6}} p_N (k_x \pm ik_y) \quad (3.4)$$

$$Q_N = \frac{1}{\sqrt{3}} p_N k_z \quad (3.5)$$

where $p_N = (\hbar/m_0) \langle s_N | \mathbf{p}_v | v \rangle = (\hbar/m_0) \cdot P_N$, $|s_N\rangle$ indicates a N-band Bloch state of s -like symmetry and $|v\rangle$ indicates a VB p -like state, with character $|v\rangle = |x\rangle$, $|y\rangle$ or $|z\rangle$.

In this ten-band model for dilute-N materials, the N component is described as a dispersionless band that is degenerate with the conduction-band of host material like GaAs. Since there are only a few N atoms in the crystal, they are locally well separated and only weakly coupled. Therefore, the electronic level of the N

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atoms do not show the formation of a dispersed band, but can be described by a dispersionless band at the energy of the degenerate states. The states forming this band strongly couple with the conduction-band states of the host material, resulting in an anticrossing between them.

There are two most important N-related band parameters in Eqs. (3.2) and (3.3), E_{N0} and β , which characterize the position of N energy level and the strength of NB-CB interaction, respectively. In Ref. 3.5 some reasonable values are given:

$$E_{N0} = 1.65 - 0.31x \text{ eV and } \beta = 2.4(1 - x) + 1.75x \text{ eV} \quad (3.6)$$

for a Ga-rich environment of N-bonding configuration, and

$$E_{N0} = 1.7125 - 0.31x \text{ eV and } \beta = 2.4(0.75 - x) + 1.75(x + 0.25) \text{ eV} \quad (3.7)$$

for an In-rich environment of N-bonding configuration.

In the ten-band scheme, the total wave function of the subband state n in the quantum well can be written as

$$\Psi_n(r) = \sum_{j=1}^{10} F_{n,j}(r) u_j(r), \quad (3.8)$$

where $F_j(r)$ is the envelope function, $u_j(r)$ is the periodic part of the Bloch basis function at the zone center, $k_t = (k_x, k_y)$ is the two-dimensional in-plane wave vector and $\rho = (x, y)$ is the two-dimensional in-plane space vector. The Bloch basic functions for the high-lying N-band (NB), conduction-band (CB), and the heavy hole (HH), light hole (LH) and spin-orbit split-off (SO) bands used here to derive the Hamiltonian are

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$$\begin{aligned}
u_1 &= \phi_{NB,\alpha} = |S_N \uparrow\rangle, \\
u_2 &= \phi_{NB,\beta} = |S_N \downarrow\rangle, \\
u_3 &= \phi_{CB,\alpha} = |S \uparrow\rangle, \\
u_4 &= \phi_{CB,\beta} = |S \downarrow\rangle, \\
u_5 &= \phi_{HH} = -i\sqrt{1/2} |(X_v + iY_v) \uparrow\rangle, \\
u_6 &= \phi_{LH,\alpha} = i\sqrt{2/3} |Z_v \uparrow\rangle - i\sqrt{1/6} |(X_v + iY_v) \downarrow\rangle, \\
u_7 &= \phi_{LH,\beta} = i\sqrt{2/3} |Z_v \downarrow\rangle + i\sqrt{1/6} |(X_v - iY_v) \uparrow\rangle, \\
u_8 &= \phi_{HH,\beta} = i\sqrt{1/2} |(X_v - iY_v) \downarrow\rangle, \\
u_9 &= \phi_{SOH,\alpha} = i\sqrt{1/3} |Z_v \uparrow\rangle + i\sqrt{1/3} |(X_v + iY_v) \downarrow\rangle, \\
u_{10} &= \phi_{SOH,\beta} = -i\sqrt{1/3} |Z_v \downarrow\rangle + i\sqrt{1/3} |(X_v - iY_v) \uparrow\rangle.
\end{aligned} \tag{3.9}$$

where $|S\rangle$ denote the s -like conduction-band Bloch state, $|S_N\rangle$ denotes the s -like N-band Bloch state, and $|X_v\rangle$, $|Y_v\rangle$ and $|Z_v\rangle$ denote the p -like valence-band Bloch states.

The momentum matrix elements P_0 and P_N are defined as

$$P_0 = i\langle S | \mathbf{p}_x | X_v \rangle = i\langle S | \mathbf{p}_y | Y_v \rangle = i\langle S | \mathbf{p}_z | Z_v \rangle \tag{3.10}$$

$$\text{and} \quad P_N = i\langle S_N | \mathbf{p}_x | X_v \rangle = i\langle S_N | \mathbf{p}_y | Y_v \rangle = i\langle S_N | \mathbf{p}_z | Z_v \rangle, \tag{3.11}$$

respectively.

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The envelope-functions are expanded as

$$F_{n,j}(r) = \exp[i(k_x x + k_y y)] \sum_m a_{n,j,m} \phi_m(z), \quad (3.12)$$

where

$$\phi_m(z) = \frac{1}{\sqrt{L}} \exp \left[i \left(k_z + m \cdot \frac{2\pi}{L} \right) \cdot z \right], \quad (3.13)$$

where m is a set of integers and L is the sum of the well and barrier widths [3.12–3.14]. Substituting Eq. (3.12) into the coupled differential equations of

$$\sum_{j'=1}^{10} (H_{j,j'} + U(z) \delta_{j,j'}) F_{j'}(r) = E F_j(r), \quad (3.14)$$

where $U(z)$ is the electronic potential function and $H_{j,j'}$ is the ten-band $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian, then multiplying by $\phi_m^*(z)$ and integrating over L , one gets

$$\sum_{j',m'} H_{j,j'}(m,m') a_{j',m'} = E a_{j,m}, \quad j, j' = 1, \dots, 10 \quad (3.15)$$

where the matrix elements $H_{j,j'}(m',m)$ are given by

$$\begin{aligned} H_{j,j'}(m,m') &= \int_{-L/2}^{L/2} \phi_m^*(z) [H_{j,j'} + \delta_{j,j'} U(z)] \phi_{m'}(z) dz \\ &= \langle \phi_m | H_{j,j'} + \delta_{j,j'} U(z) | \phi_{m'} \rangle. \end{aligned} \quad (3.16)$$

The following probability functions are introduced to determine the NB, CB, HH, LH and SO components in the quantum-well eigen-states:

$$P_n^{\text{NB}} = \sum_{j=1,2} \sum_m a_{n,j,m}^* a_{n,j,m}$$

$$P_n^{\text{CB}} = \sum_{j=3,4} \sum_m a_{n,j,m}^* a_{n,j,m},$$

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$$\begin{aligned}
 P_n^{\text{HH}} &= \sum_{j=5,8} \sum_m a_{n,j,m}^* a_{n,j,m} , \\
 P_n^{\text{LH}} &= \sum_{j=6,7} \sum_m a_{n,j,m}^* a_{n,j,m} , \\
 P_n^{\text{SO}} &= \sum_{j=9,10} \sum_m a_{n,j,m}^* a_{n,j,m} ,
 \end{aligned}
 \tag{3.17}$$

These probability functions are particularly useful to identify the dominant character in a particular subband. Note that the following sum rule should hold:

$$\sum_i P_n^i = 1 \quad i = \text{NB}, \text{CB}, \text{HH}, \text{LH}, \text{SO} .
 \tag{3.18}$$

The momentum matrix element between subband n and n' is

$$M_{nn'} = \langle \Psi_n | e_v \cdot \mathbf{p} | \Psi_{n'} \rangle = \sum_{j,j'=1}^{10} \langle F_{n,j} u_j | e_v \cdot \mathbf{p} | F_{n',j'} u_{j'} \rangle
 \tag{3.19}$$

where $\mathbf{p}$ is the momentum operator and

$e_v = v_x e_x + v_y e_y + v_z e_z$ ($v_x^2 + v_y^2 + v_z^2 = 1$) is the photon polarization unit vector.

Substituting Eqs. (3.8) and (3.12) into (3.19), we obtain

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$$\begin{aligned}
M_{nn'} &= \sum_{j,j'=1}^{10} \left\langle \sum_m a_{n,j,m} \phi_m(z) u_j | e_v \cdot \mathbf{p} | \sum_{m'} a_{n',j',m'} \phi_{m'}(z) u_{j'} \right\rangle \\
&\approx \sum_{j,j'=1}^{10} \left[\left\langle \sum_m a_{n,j,m} \phi_m(z) | e_v \cdot \mathbf{p} | \sum_{m'} a_{n',j',m'} \phi_{m'}(z) \right\rangle \langle u_j | u_{j'} \rangle \right] \\
&\quad + \sum_{j,j'=1}^{10} \left[\left\langle \sum_m a_{n,j,m} \phi_m(z) \left| \sum_{m'} a_{n',j',m'} \phi_{m'}(z) \right\rangle \langle u_j | e_v \cdot \mathbf{p} | u_{j'} \rangle \right] \\
&= \sum_{j=1}^{10} \left[\left\langle \sum_m a_{n,j,m} \phi_m(z) | e_v \cdot \mathbf{p} | \sum_{m'} a_{n',j,m'} \phi_{m'}(z) \right\rangle \right] \\
&\quad + \sum_{j,j'=1}^{10} \left[\sum_m (a_{n,j,m}^* \cdot a_{n',j',m}) \langle u_j | e_v \cdot \mathbf{p} | u_{j'} \rangle \right].
\end{aligned} \tag{3.20}$$

Substituting Eqs. (3.9) and (3.13) into (3.20), one obtains

$$\begin{aligned}
M_{nn'}^{\text{TM}} &= \sum_{j=1}^{10} \left[\left\langle \sum_m a_{n,j,m} \phi_m(z) | e_v \cdot \mathbf{p}_z | \sum_{m'} a_{n',j,m'} \phi_{m'}(z) \right\rangle \right] \\
&\quad + \frac{P_0}{\sqrt{3}} \sum_m \left(\sqrt{2} a_{n,1,m}^* a_{n',4,m} - \sqrt{2} a_{n,4,m}^* a_{n',1,m} \right. \\
&\quad \quad \left. + a_{n,1,m}^* a_{n',7,m} - a_{n,7,m}^* a_{n',1,m} \right) \\
&\quad + \frac{P_0}{\sqrt{3}} \sum_m \left(\sqrt{2} a_{n,2,m}^* a_{n',5,m} - \sqrt{2} a_{n,5,m}^* a_{n',2,m} \right. \\
&\quad \quad \left. - a_{n,2,m}^* a_{n',8,m} - a_{n,8,m}^* a_{n',2,m} \right) \\
&\quad + \frac{P_N}{\sqrt{3}} \sum_m \left(\sqrt{2} a_{n,9,m}^* a_{n',4,m} - \sqrt{2} a_{n,4,m}^* a_{n',9,m} \right. \\
&\quad \quad \left. + a_{n,9,m}^* a_{n',7,m} - a_{n,7,m}^* a_{n',9,m} \right) \\
&\quad + \frac{P_N}{\sqrt{3}} \sum_m \left(\sqrt{2} a_{n,10,m}^* a_{n',5,m} - \sqrt{2} a_{n,5,m}^* a_{n',10,m} \right. \\
&\quad \quad \left. - a_{n,10,m}^* a_{n',8,m} - a_{n,8,m}^* a_{n',10,m} \right),
\end{aligned} \tag{3.21}$$

for TM polarization, and

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$$\begin{aligned}
M_{nn'}^{\text{TE}} = & P_0 \sum_m \left(-\frac{1+i}{\sqrt{2}} a_{n,1,m}^* a_{n',3,m} + \frac{1-i}{\sqrt{2}} a_{n,3,m}^* a_{n',1,m} \right. \\
& + \frac{1-i}{\sqrt{6}} a_{n,1,m}^* a_{n',5,m} - \frac{1+i}{\sqrt{6}} a_{n,5,m}^* a_{n',1,m} \\
& \left. + \frac{1-i}{\sqrt{3}} a_{n,1,m}^* a_{n',8,m} - \frac{1+i}{\sqrt{3}} a_{n,8,m}^* a_{n',1,m} \right) \\
& + P_0 \sum_m \left(-\frac{1+i}{\sqrt{6}} a_{n,2,m}^* a_{n',4,m} + \frac{1-i}{\sqrt{6}} a_{n,4,m}^* a_{n',2,m} \right. \\
& + \frac{1-i}{\sqrt{2}} a_{n,2,m}^* a_{n',6,m} - \frac{1+i}{\sqrt{2}} a_{n,6,m}^* a_{n',2,m} \\
& \left. + \frac{1+i}{\sqrt{3}} a_{n,2,m}^* a_{n',7,m} - \frac{1-i}{\sqrt{3}} a_{n,7,m}^* a_{n',2,m} \right) \\
& + P_N \sum_m \left(-\frac{1+i}{\sqrt{2}} a_{n,9,m}^* a_{n',3,m} + \frac{1-i}{\sqrt{2}} a_{n,3,m}^* a_{n',9,m} \right. \\
& + \frac{1-i}{\sqrt{6}} a_{n,9,m}^* a_{n',5,m} - \frac{1+i}{\sqrt{6}} a_{n,5,m}^* a_{n',9,m} \\
& \left. + \frac{1-i}{\sqrt{3}} a_{n,9,m}^* a_{n',8,m} - \frac{1+i}{\sqrt{3}} a_{n,8,m}^* a_{n',9,m} \right) \\
& + P_N \sum_m \left(-\frac{1+i}{\sqrt{6}} a_{n,10,m}^* a_{n',4,m} + \frac{1-i}{\sqrt{6}} a_{n,4,m}^* a_{n',10,m} \right. \\
& + \frac{1-i}{\sqrt{2}} a_{n,10,m}^* a_{n',6,m} - \frac{1+i}{\sqrt{2}} a_{n,6,m}^* a_{n',10,m} \\
& \left. + \frac{1+i}{\sqrt{3}} a_{n,10,m}^* a_{n',7,m} - \frac{1-i}{\sqrt{3}} a_{n,7,m}^* a_{n',10,m} \right)
\end{aligned} \tag{3.22}$$

for TE polarization.

3.2.2 Sixteen-band $\mathbf{k}\cdot\mathbf{p}$ model

The sixteen-band $\mathbf{k}\cdot\mathbf{p}$ model introduces the six p -like conduction bands (Γ_{7c} and Γ_{8c}) in the zinc-blendes semiconductors that lack inversion symmetry into the ten-band $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian to take more coupling effects into consideration. It is reasonable to use this model to analyze TE-polarized ISBTs accurately.

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The sixteen-band $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian is given by

$$\begin{bmatrix} \mathbf{H}_{\bar{p}} & \mathbf{H}_{\bar{p}-sp} & \mathbf{H}_{\bar{p}-N} \\ (6\times 6) & (6\times 8) & (6\times 2) \\ \mathbf{H}_{\bar{p}-sp}^* & \mathbf{H}_{sp} & \mathbf{H}_{sp-N} \\ (8\times 6) & (8\times 8) & (8\times 2) \\ \mathbf{H}_{\bar{p}-N}^* & \mathbf{H}_{sp-N}^* & \mathbf{H}_N \\ (2\times 6) & (2\times 8) & (2\times 2) \end{bmatrix} \quad (3.23)$$

where $\mathbf{H}_{\bar{p}}$ consists of the elements of the six p -like conduction-band states, $\mathbf{H}_{\bar{p}-sp}$ consists of the elements coupling the p -like conduction-band to the s -like conduction-band and the p -like valence-band, $\mathbf{H}_N$ is the N-band Hamiltonian, $\mathbf{H}_{sp}$ is the eight-band $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian, and $\mathbf{H}_{sp-N}$ and $\mathbf{H}_{\bar{p}-N}$ consist the elements coupling the N-band to the conduction-band and valence-band. $\mathbf{H}_{\bar{p}-sp}^*$, $\mathbf{H}_{sp-N}^*$ and $\mathbf{H}_{\bar{p}-N}^*$ at the down triangular block are the corresponding conjugation part of $\mathbf{H}_{\bar{p}-sp}$, $\mathbf{H}_{sp-N}$ and $\mathbf{H}_{\bar{p}-N}$, respectively. The details of $\mathbf{H}_{\bar{p}-sp}$ and $\mathbf{H}_{sp-N}$ have been shown in Eqs. (2.11) and (3.3), respectively. In our calculation the interaction between N-band and p -like conduction-band is neglected, so $\mathbf{H}_{\bar{p}-N}$ is assumed to be null.

3.3 ISBT selectivities in dilute-N quantum wells

In this section, the ISBTs selectivities with subband order and in-plane wave vector as well as their variations with well width in the dilute-N $\text{GaAs}_{0.99}\text{N}_{0.01}/\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ quantum wells will be discussed based on the ten-band and sixteen-band $\mathbf{k}\cdot\mathbf{p}$ models. The barrier width is assumed to be 40 nm. The n-type doping concentration in the wells is assumed to be $5 \times 10^{17} \text{ cm}^{-3}$, and a linewidth of 20 meV in the Lorentzian function Eq. (2.38) is assumed. The results will be compared to those derived for the equivalent N-free structures in Chapter 2.

3.3.1 ISBT selectivities with the ten-band $\mathbf{k}\cdot\mathbf{p}$ model

Figure 3.2 shows the calculated energy dispersions of the conduction subbands E1–E6 along [100] and [110] k_t directions for the $\text{GaAs}_{0.99}\text{N}_{0.01}/\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ MQWs with well widths of 3 and 10 nm, respectively, at low temperature (0 K). In the calculation it is assumed that the high-lying N-band interacts with conduction-band only and the NB-VB coupling is negligible [3.12, 3.13, 3.16]. This $\text{GaAs}_{1-x}\text{N}_x/\text{Al}_{1-y}\text{Ga}_y\text{As}$ system is chosen for the analyses to minimize the strain-induced influence in the results. Compared to the equivalent N-free $\text{GaAs}/\text{AlGaAs}$ quantum wells shown in Figure 2.5, the CB-NB interaction results in obvious lowering of conduction subbands in the dilute-N quantum wells. Therefore, more bound states are located in the well. At $L_w = 3 \text{ nm}$, E2 is a bound state. At $L_w = 10 \text{ nm}$, the first five states E1–E5 are all bound states and E6 becomes a quasi-bound state, unlike the situation in Figure 2.5(b) where only E1–E3 are bound states.

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Figure 3.2. Energy dispersions of conduction subbands in the $\text{GaAs}_{0.99}\text{N}_{0.01}/\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ MQWs with well widths of (a) 3 nm and (b) 10 nm, respectively.

Figures 3.3 and 3.4 show the squared optical transition matrix elements for TM and TE polarizations, respectively, of E1 to E2–E6 transitions calculated using the 10-band $\mathbf{k}\cdot\mathbf{p}$ model. It can be seen that the E1→E2 transition at $L_w = 3$ nm is dominant and the other transitions are neglectable for TM polarization, as E2 is a bound state under the band-anticrossing (BAC) effect. This is unlike the situation of the equivalent N-free quantum wells shown in Fig. 2.6(a) where the transitions from E1 to those continuum states have comparable rates. At $L_w = 10$ nm, the transition from E1 to the even excited state E4 also shows considerable rate. Note that the peak transition rates for TE polarization in the dilute-N structures ($\sim 3 \times 10^{-2}$ in Fig. 3.4(a)) are almost one order of magnitude larger than those for the N-free structures ($\sim 2 \times 10^{-3}$ in Fig 2.7). The transitions of E1 to the odd excited states E3 and E5 are dominating at $L_w = 10$ nm for TE polarization, as shown in Fig. 3.4(b). Both N-containing and N-free quantum wells show similar dependences of B-to-B transitions on the wave vector k_t .

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For TM polarization, the dominant transitions are always maximal around the zone center ($k_t = 0$). For TE polarization, the transitions are almost absent in the zone center but arise dramatically at finite k_t .

Figure 3.3. Squared optical transition matrix elements for **TM** polarization as a function of k_t in $[110]$ direction of E1 to E2–E6 transitions in the $\text{GaAs}_{0.99}\text{N}_{0.01}/\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ MQWs with well widths of (a) 3 nm and (b) 10 nm, respectively, calculated with the ten-band $\mathbf{k}\cdot\mathbf{p}$ model.

Figure 3.4. Squared optical transition matrix elements for **TE** polarized ISBTs as a function of k_t in $[110]$ direction in the $\text{GaAs}_{0.99}\text{N}_{0.01}/\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ MQWs calculated with the ten-band $\mathbf{k}\cdot\mathbf{p}$ model. The abrupt variation of the curves at $L_w = 3$ nm is due to significant intermixing of some higher continuum states at finite k_t .

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Figures 3.5 and 3.6 show the calculated absorption spectra for TM and TE polarizations, respectively. The uniform doping concentration in the n-type wells is assumed to be $5 \times 10^{17} \text{ cm}^{-3}$. The Fermi level is estimated to be at 1482 meV when the well width is 3 nm, and 1421 meV when the well width is 10 nm. It can be seen that both the TM absorption spectra for $L_w = 3$ and 10 nm show narrow profiles as the B-to-B $E1 \rightarrow E2$ transition is dominant. The TE absorption spectrum for $L_w = 3$ nm is relatively broad due the comparable $E1$ to $E3$ – $E6$ (continuum states) transitions. The TE absorption spectrum for $L_w = 10$ nm shows two comparable peaks as the $E1$ to odd excited states $E3$ and $E5$ (bound states) transitions become dominant in the wider wells. Figure 3.7 shows the calculated peak absorption coefficients of respective ISBTs as a function of well width ranging from 2 to 20 nm. It can be seen that the $E1 \rightarrow E2$ absorption becomes dominating rapidly with increasing L_w beyond 2.5 nm for TM polarization. The absorptions from $E1$ to even excited states $E4$ and $E6$ are also observable when $L_w > 8$ nm. For TE polarization, the $E1 \rightarrow E3$ absorption becomes dominating rapidly with increasing L_w beyond 4 nm. The secondary absorption peak appeared when $L_w > 8$ nm comes from the B-to-B $E1 \rightarrow E5$ transition. The ISBT selectivity derived here are consistent with that for the N-free structures in chapter 2. The interaction of conduction-band and localized N-band results in more bound states in the well compared to the equivalent N-free structures, so the ISBT selectivity on the subband order is more obvious.

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Figure 3.5. Calculated TM absorption spectra of the $\text{GaAs}_{0.99}\text{N}_{0.01}/\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ MQW with well width of (a) 3 nm and (b) 10 nm using the ten-band $\mathbf{k}\cdot\mathbf{p}$ model.

Figure 3.6. Calculated TE absorption spectra of the $\text{GaAs}_{0.99}\text{N}_{0.01}/\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ MQW with well width of (a) 3 nm and (b) 10 nm using the ten-band $\mathbf{k}\cdot\mathbf{p}$ model.

Figure 3.7. Peak absorption coefficients vs. well width of respective ISBTs in the GaAs_{0.99}N_{0.01}/Al_{0.25}Ga_{0.75}As MQW calculated using the ten-band $\mathbf{k}\cdot\mathbf{p}$ model.

3.3.2 ISBT selectivities with the sixteen-band $\mathbf{k}\cdot\mathbf{p}$ model

Figures 3.8 and 3.9 show the ISBT squared optical transition matrix elements for TM and TE polarizations, respectively, at well widths of 3 and 10 nm calculated using the sixteen-band $\mathbf{k}\cdot\mathbf{p}$ model. Accordingly, Figures 3.10 and 3.11 show the calculated TM- and TE-polarized absorption spectra, respectively. Compared to the results with the ten-band $\mathbf{k}\cdot\mathbf{p}$ model shown in Figures 3.3 to 3.6, the TM-polarized transitions are quite similar, while the TE-polarized transitions show big differences. The transition rate increases by nearly one order of amplitude due to the coupling of p -like conduction-band with s -like conduction-band and p -like valence-band. At $L_w = 3$ nm, the B-to-B E1→E2 transition is relatively strong and the other B-to-C transitions are also observable. Accordingly, the calculated TE absorption spectrum in Figure 3.11(a) shows two peaks coming from E1→E2 and E1→continuum states

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transitions respectively. At $L_w=10$ nm, the $E1 \rightarrow E2$ transition is dominant and the $E1 \rightarrow E4$ transition is also observable.

Figure 3.8. Squared optical transition matrix elements for TM-polarized ISBTs as a function of k_t in $[110]$ direction for the GaAs/ $\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ MQWs with well widths of (a) 3 nm and (b) 10 nm, respectively, calculated with the sixteen-band $\mathbf{k} \cdot \mathbf{p}$ model.

Figure 3.9. Squared optical transition matrix elements for TE-polarized ISBTs as a function of k_t in $[110]$ direction for the GaAs/ $\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ MQWs with well widths of (a) 3 nm and (b) 10 nm, respectively, calculated with the sixteen-band $\mathbf{k} \cdot \mathbf{p}$ model.

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Figure 3.10. Calculated TM absorption spectra of the GaAs_{0.99}N_{0.01}/Al_{0.25}Ga_{0.75}As MQWs with well widths of (a) 3 nm and (b) 10 nm, respectively, using the sixteen-band **k**·**p** model.

Figure 3.11. Calculated TE absorption spectra of the GaAs_{0.99}N_{0.01}/Al_{0.25}Ga_{0.75}As MQWs with well widths of (a) 3 nm and (b) 10 nm, respectively, using the sixteen-band **k**·**p** model.

Figure 3.12 shows the calculated peak absorption coefficients as a function of well width ranging from 2 to 20 nm for different ISBTs. It can be seen that only at very narrow wells (<3 nm) all the B-to-C intersubband absorptions show comparable intensities. The E1→E2 absorption becomes dominant over the

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others rapidly with increasing L_w over 3 nm for both TM- and TE-polarizations, because E2 lowers down to be a bound state resulting from the NB-CB interaction. When L_w is larger than 8 nm, the TM-polarized absorptions from E1 to the even excited states E4 and E6 become 1–3 orders of magnitude greater than the E1→E3 and E5 absorptions. When L_w is larger than 12 nm, the TE-polarized absorption from E1 to the even excited state E4 shows greater rate than the others except the dominating E1→E2 absorption. This is consistent with the selectivity derived with the fourteen-band $\mathbf{k}\cdot\mathbf{p}$ model for N-free quantum wells that both TM- and TE-polarized ISBTs are dominated by B-to-B transitions from E1 to the even excited states.

Figure 3.12. Peak absorption coefficients vs. well width of respective ISBTs calculated using the sixteen-band $\mathbf{k}\cdot\mathbf{p}$ model.

3.4 Dependence of absorption energy on well width

In this section, we will analyze the dependence of ISBT absorption energy on well width in the N-containing quantum wells for TM polarization. The TE

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absorption is discussed here since they are considered to be significantly weaker than the TM absorption. Both quasi-strainless GaAsN/AlGaAs and largely compressive-strained InGaAsN/GaAs structures will be discussed and compared to the equivalent N-free structures to clarify the influence of N incorporation on the ISBT properties.

Since the well width is an important parameter to affect the ISBT properties, a clear judgment criteria for narrow, moderate and wide wells is helpful for our analysis and understanding:

Narrow well – only the ground E1 is a bound state in the well, while all the excited states are continuum states.

Moderate well – the first excited state (E2) becomes a bound state as the well width increases.

Wide well – more than one excited states (E2, E3, ...) are bound states when the well width is large enough.

3.4.1 GaAsN/AlGaAs system

Figure 3.13 shows the TM-polarized absorption peak energy as a function of well width ranging from 2 to 12 nm for the semi-strainless GaAs_{0.99}N_{0.01}/Al_{0.25}Ga_{0.75}As quantum wells calculated using the ten-band **k**·**p** model. The results for the N-free GaAs/Al_{0.25}Ga_{0.75}As quantum wells are also shown in the figure for comparison. It can be seen that in the case of narrower wells ($L_w \sim 2\text{--}4$ nm), the absorption peak energy of the N-containing quantum

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well is significantly larger than that of the equivalent N-free structure. For instance, the former is 194.4 meV at $L_w = 2$ nm, which is about 83 meV greater than the latter (110.9 meV). However, the former decreases quickly with increasing L_w beyond 3 nm, while the latter shows relatively slow variations with increasing L_w beyond 4 nm. Consequently, the absorption peak energy of the N-containing quantum well is even slightly smaller than that of the equivalent N-free structure in the case of wider wells ($L_w > 6$ nm).

Figure 3.13. Absorption peak energies as a function of well width for the $\text{GaAs}_{0.99}\text{N}_{0.01}/\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ and N-free $\text{GaAs}/\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ quantum wells based on ten- and eight-band $\mathbf{k}\cdot\mathbf{p}$ models, respectively.

To understand the underlying cause of the phenomenon above, we show in Fig. 3.14(a) and (b) the subband E1–E6 energies at the zone center ($k_t = 0$) as a function of well width, for the $\text{GaAs}_{0.99}\text{N}_{0.01}/\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ and N-free $\text{GaAs}/\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ quantum wells, respectively. As the TM-polarized transitions rates are always maximal around the zone center, the absorption peak energy should be very close the subband energy separations at $k_t = 0$.

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Figure 3.14. Calculated subbands energies at $k_t = 0$ as a function of well width for (a) the $\text{GaAs}_{0.99}\text{N}_{0.01}/\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ quantum well using the ten-band $\mathbf{k}\cdot\mathbf{p}$ model, and (b) N-free $\text{GaAs}/\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ quantum well using the eight-band $\mathbf{k}\cdot\mathbf{p}$ model, respectively.

It can be seen that the BAC interaction between N-band and conduction-band impacts the subband dispersions significantly. Firstly, the energy of the ground state E1 in the $\text{GaAs}_{0.99}\text{N}_{0.01}/\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ quantum well is much lower than that in the equivalent N-free $\text{GaAs}/\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ quantum well (1576 vs. 1672 meV) at $L_w = 2$ nm. Therefore, the absorption peak energy in the former is much larger compared to the latter (194 vs. 111 meV) at $L_w = 2$ nm. Secondly, the transforming of E2 from a continuum to a bound state occurs at narrower

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well width (~ 2.5 nm) in the dilute-N quantum wells compared to the case in the N-free quantum wells (~ 4 nm). The lowering of the excited states ($E_2, E_3 \dots$) with the increase of well width in the former is obviously quicker than that in the latter. For instance, E_2 lowers by 275 meV (from 1750 to 1475 meV) for the former, but only lowers by 153 meV (from 1750 to 1597 meV) for the latter, when L_w increases from 2 to 12 nm. However, the lowering of the ground state E_1 for the dilute-N and N-free quantum wells with increasing well width are comparable. E_1 lowers by 159 meV (from 1575 to 1416 meV) for the former, and by 135 meV (from 1672 to 1537 meV) for the latter, respectively, when L_w increases from 2 to 12 nm. As the $E_1 \rightarrow E_2$ transition dominates in wider wells, the quickly lowering of E_2 results in the quick reduction of absorption peak energy in the dilute-N quantum wells. It indicates that it is only effective for narrow quantum wells to blueshift the intersubband absorption energy by introducing N in the well.

Most of state-of-the-art QWIPs are based on B-to-C transitions to achieve larger responsivity working at lower bias voltage. Since the intersubband absorption peak energy of the GaAsN/AlGaAs quantum well is significantly larger than that of the equivalent N-free structure in the case of narrow wells, such dilute-N based QWIP device would allow infrared photodetection for much shorter wavelengths. For instance, in the case of 3 nm well width, the GaAs/Al_{0.25}Ga_{0.75}As quantum well shows an absorption peak at 127 meV corresponding to a wavelength of 9.8 μm (Fig. 3.13). In contrast, the GaAs_{0.99}N_{0.01}/Al_{0.25}Ga_{0.75}As quantum well shows an absorption peak at 200 meV corresponding to a much short wavelength of 6.2 μm . This blue-shifted

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absorption band enables the extension of infrared detection ability without introducing too much Al in the barrier material. Such merit will not show up in dilute-N quantum wells with wide wells.

3.4.2 InGaAsN/GaAs system

The structures to be analyzed are compressive-strained $\text{In}_{0.23}\text{Ga}_{0.77}\text{As}_{0.99}\text{N}_{0.01}/\text{GaAs}$ n-type MQWs. The conduction-band offset ratio between the InGaAsN well and the GaAs barrier is assumed to be 0.8 [3.17]. The GaAs barrier width is assumed to be 20 nm. The n-doping concentration N_D in wells is assumed to be $1 \times 10^{18} \text{ cm}^{-3}$. This enables us to directly compare the theoretical results with the available experimental observations [3.10].

Figure 3.15. Calculated absorption peak energies for the $\text{In}_{0.23}\text{Ga}_{0.77}\text{As}_{0.99}\text{N}_{0.01}/\text{GaAs}$ (open circles) and $\text{In}_{0.23}\text{Ga}_{0.77}\text{As}/\text{GaAs}$ quantum wells (open squares), and spectral FWHMs for the former (open triangles) as a function of well width. The solid squares and triangles are the experimental data of Ref [3.10].

Figure 3.15 shows the calculated absorption peak energies for the $\text{In}_{0.23}\text{Ga}_{0.77}\text{As}_{0.99}\text{N}_{0.01}/\text{GaAs}$ quantum well and the equivalent N-free

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$\text{In}_{0.23}\text{Ga}_{0.77}\text{As}/\text{GaAs}$ structure, and spectral FWHMs for the former as a function of well width. We can see that the absorption peak of the $\text{InGaAsN}/\text{GaAs}$ quantum well exhibits a blueshift firstly with increasing well width from 2 to 3.5 nm. This is because that all the excited subbands in the narrower wells are continuum states near the edge of the GaAs barrier and the increase of L_w only induces obviously lowering of the ground state E1. The absorption spectrum FWHM is wide due to the superposition of comparable E1-to-continuum states transitions. When L_w is larger than 3.5 nm, the transition energy tends to decrease as the first excited state (E2) starts to move downwards quickly. At the same time the absorption spectrum FWHM becomes narrow as the E1→E2 transition becomes dominating.

It can be seen that the absorption energy of the $\text{InGaAsN}/\text{GaAs}$ quantum well is much greater than that of the equivalent N-free quantum well in the case of narrower well widths (about 2–4.5 nm), but the difference becomes small quickly with the increasing of well width ($L_w > 4.5$ nm). To understand the reason, we show in Fig. 3.16 the subbands E1–E5 energies at the zone center as a function of well width in both dilute-N and N-free quantum wells. One can see that the coupling of N-band and conduction-band in InGaAsN results in two significant effects on the subband dispersions. Firstly, the energy level of the ground state E1 in the dilute-N quantum well is obviously lower than that in the equivalent N-free quantum well (1264 vs. 1363 meV). Secondly, the change of E2 from a continuum to a bound state occurs at narrower well width in the dilute-N quantum well compared to the N-free quantum well (~ 3.5 vs. 5 nm),

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and thereafter the lowering of E2 with increasing well width in the former is much quicker. For instance, the reduced energy of bound state E2 is 122 meV (from 1361 to 1239 meV) for the former when L_w increases from 3.5 to 8 nm, but is only 39 meV (from 1361 to 1322 meV) for the latter. Consequently, the absorption peak energy of the dilute-N quantum well can be 50–80 meV larger than that of the N-free structure in the case of narrower wells ($L_w < 4.5$ nm). However, such difference becomes very small for wider wells, as E2 moves downwards quickly under NB-CB interaction.

Figure 3.16. Calculated subband energies at $k_t = 0$ as a function of well width for the $\text{In}_{0.23}\text{Ga}_{0.77}\text{As}_{0.99}\text{N}_{0.01}/\text{GaAs}$ and equivalent N-free quantum wells.

Compared to the nearly lattice-matched $\text{GaAs}_{1-x}\text{N}_x/\text{Al}_y\text{Ga}_{1-y}\text{As}$ quantum wells analyzed in the preceding subsection, the decrease of absorption energy with L_w at wider wells in the compressive-strained $\text{In}_y\text{Ga}_{1-y}\text{As}_{1-x}\text{N}_x/\text{GaAs}$ quantum wells is relatively slow. For example, the absorption peak energy decreases by

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about 102 meV (from 199.9 to 97.7 meV) for the GaAs/AlGaAs quantum well, and by about 70 meV (from 152.9 to 82.4 meV) for the InGaAsN/GaAs quantum well, with the increasing of L_w from 3 to 8 nm. As a result, the absorption energy for the former is even slightly lower than the equivalent N-free GaAs/Al_yGa_{1-y}As when $L_w > 6$ nm (Fig. 3.13), while the absorption energy for the latter is still higher than the equivalent N-free In_yGa_{1-y}As/GaAs (Fig. 3.15). This difference is firstly due to the reverse proportional relationship between NB-CB coupling and In composition as shown in Eqs. (3.6) and (3.7). For instance, the coupling factor β is 2.4 eV for GaAs_{0.99}N_{0.01} and 2.25 eV for In_{0.23}Ga_{0.77}As_{0.99}N_{0.01}. The excited states (E2...) move downwards less due to the weaker NB-CB interaction in the InGaAsN/GaAs quantum wells. Secondly, the strong compressive strain (about -1.42% of in-plane strain) in the In_{0.23}Ga_{0.77}As_{0.99}N_{0.01}/GaAs quantum wells pushes high E2 significantly and hinders its falling with increasing well width.

The large absorption peak energy blueshift of the InGaAsN/GaAs quantum-well relative to the N-free InGaAs/GaAs quantum-well in the case of narrow well widths (Fig. 3.15) enables the infrared detection at the 8–12 μm LWIR window without introducing too much In in the barrier material. For instance, the In_{0.23}Ga_{0.77}As_{0.99}N_{0.01}/GaAs quantum-well with 3 nm well width shows an overall absorption peak at 137 meV corresponding to a wavelength of 9.1 μm . In contrast, the equivalent N-free In_{0.23}Ga_{0.77}AsN/GaAs quantum-well shows an absorption peak at 79 meV corresponding to a much longer wavelength of 15.7 μm (out of the LWIR window).

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Figure 3.17. Conduction subband structures as a function of k_t along [100] and [110] directions in the $\text{In}_{0.23}\text{Ga}_{0.77}\text{As}_{0.99}\text{N}_{0.01}/\text{GaAs}$ quantum wells with well widths of (a) 2.6, (b) 3.8 and (c) 5.0 nm, respectively.

To look into the ISBTs in the $\text{In}_{0.23}\text{Ga}_{0.77}\text{As}_{0.99}\text{N}_{0.01}/\text{GaAs}$ structures clearly, the calculated subband structures, squared optical transition matrix elements, and intersubband optical absorption spectra are plotted in Figs. 3.17, 3.18 and 3.19, respectively. The results for well widths of 2.6, 3.8 and 5.0 nm, are displayed. It can be seen that in the case of 2.6 nm well width, all the B-to-C transitions from E1 to E2–E5 have comparable rates (Fig. 3.17(a)). The superposition of E1 to E2–E5 absorptions results in a broad overall absorption spectrum (Fig. 3.18(a)).

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The spectral FWHM is 80.5 meV and the absorption peak energy is 146.1 meV. When the well width increases to 3.8 nm, E2 turns to a quasi-bound state and the E1→E2 transition rate is obviously larger than the others (Fig. 3.18(b)). Consequently, the FWHM of the overall absorption spectrum decreases to about 54.5 meV (Fig. 3.19(b)). The absorption peak energy is 151.1 meV that is determined by the E1→E2 transition. When the well width increases further to 5.0 nm, E2 goes down quickly to be a completely bound state as shown in Fig. 3.17(c). The E1→E2 transition is dominating and the other transitions have negligible rates. The overall absorption spectrum becomes very narrow since it is completely dominated by E1→E2 (Fig. 3.19(c)). The spectral FWHM is only about 34.1 meV and the absorption peak energy decreases to 132.3 meV due to the largely lowering of E2 level. The calculated peak absorption coefficients are 392.3, 927.2 and 1171.6 cm⁻¹ for well widths of 2.6, 3.8 and 5.0 nm, respectively. It can be seen that in the case of narrower well widths (2–5 nm), the absorption energy is relatively insensitive with the increase of well width while the absorption intensity increases and bandwidth decreases significantly, which is in good agreement with the reported experimental data [3.10]. The validity of our theoretical method for ISBT analysis in dilute-N quantum wells is proved here. In wider wells the absorption peak energy should keep decreasing with the increase of well width because of the quick lowering of E2 as shown in Fig. 3.16.

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Figure 3.18. Calculated ISBT squared optical transition matrix elements (TM mode) as a function of k_t in [110] direction in the $\text{In}_{0.23}\text{Ga}_{0.77}\text{As}_{0.99}\text{N}_{0.01}/\text{GaAs}$ quantum wells with well widths of (a) 2.6, (b) 3.8 and (c) 5.0 nm, respectively. “x100” indicates that the curve is shown one hundred times larger than reality.

Figure 3.19. Optical absorption spectra for the $\text{In}_{0.23}\text{Ga}_{0.77}\text{As}_{0.99}\text{N}_{0.01}/\text{GaAs}$ quantum wells with well widths of (a) 2.6, (b) 3.8 and (d) 5.0 nm, respectively. The solid curve is overall absorption and the dash curves are respective ISBT absorptions.

3.5 Dependence of absorption energy on N composition

In this section another interesting item, the dependence of ISBTs on N content (N_N), will be discussed. In General, it is considered that the incorporation of N in III–V materials will result in a great negative bandgap bowing and hence a great augment of conduction-band offset between well and barrier. Subsequently, a blue-shifted intersubband absorption band should appear in the deepened quantum well with N incorporation. However, some experiments show that the real situation is not in this case. For instance, Giehler *et al.* studied the influence of N on intersubband absorption spectra in (In,Ga)AsN/(Al,Ga)As MQWs and observed an unexpected redshift of main absorption band instead of a blueshift with incorporated N content up to 4% [3.9]. In this section, we will study the variations of intersubband absorption with N composition x in the GaAs_{1-x}N_x/AlGaAs and InGaAs_{1-x}N_x/GaAs quantum wells based on the ten-band **k**·**p** model.

3.5.1 GaAs_{1-x}N_x/AlGaAs system

The calculation was carried out on GaAs_{1-x}N_x/Al_{0.35}Ga_{0.65}As MQW structures with 6 nm well width and 20 nm barrier width. Figure 3.20 shows the calculated subbands E1–E3 energies at the zone center ($k_t = 0$) and the absorption energy at overall absorption peak as a function of N_N ranging from 0 to 3%. The valance-band edge of bulk GaAs_{1-x}N_x is regarded as zero energy level. It is found that in the 6 nm wide well, both E1 and E2 are bound states and the E1→E2 transition dominates in the overall intersubband absorption. Therefore, the theoretical absorption energy is very close to the energy separation between E1 and E2.

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One can see that the absorption peak energy shows relatively small variations (within 144–171 meV) with the increase of N_N up to 3%, although the N incorporation has narrowed the bandgap with a ratio of approximate 100 meV per 1% N. Furthermore, it can be seen that the absorption peak energy exhibits a moderate redshift with increasing N_N from 0 to 0.4% and then begins to blueshift gradually with N_N over 0.5%. This is because that the lowering of E2 is slightly quicker than that of E1 with increasing N_N as shown in Fig. 3.20(a). The largest redshift occurs at $N_N \approx 0.4\text{--}0.5\%$ and the corresponding absorption peak locates at 144 meV. The absorption peak energies with increasing N_N up to 2.1% are smaller than that for $N_N = 0$ (160 meV). The theoretical results are consistent with the measured absorption band redshifts in similar structures reported in Ref. 3.9.

Figure 3.20. Calculated (a) subbands E1–E3 energies at $k_t = 0$ and (b) absorption energy of at overall intersubband absorption peak as a function of N_N for the $\text{GaAs}_{1-x}\text{N}_x/\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ MQW with 6 nm well width.

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Figure 3.21. N-band and conduction-band components in E1 and E2 states at $k_t = 0$ as a function of N content (N_N) for the $\text{GaAs}_{1-x}\text{N}_x/\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ MQW.

To examine the admixing of N-band wave function in the electron wave function, we plot in Fig. 3.21 the N-band and conduction-band components in the E1 and E2 states at $k_t = 0$ as a function of N_N calculated using Eq. (3.17). It can be seen that the N-band component in E1 (P_{E1}^{NB}) increases quickly to 24.5% with increasing N_N to 1%, and further to 30.1% at $N_N = 3\%$. The N-band component in E2 (P_{E2}^{NB}) goes up rapidly to 37.0% with increasing N_N to 0.6% and then tends to saturate. At $N_N = 3\%$ P_{E2}^{NB} is about 39.5%. It clearly indicates that the intermixing of N-band and conduction-band wave functions in E1 and E2 intensifies with the increase of N_N . This intermixing effect should weaken the optical transition matrix element between E1 and E2, since the conduction-band and valence-band components in these states contributing to the ISBT rate are reduced. Figure 3.22(a) shows the calculated $Q_{E1,E2}$ for N contents of 0, 0.1%, 0.5% and 1%, respectively. One can see that the $Q_{E1,E2}$ value at $k_t = 0$ decreases from 7.2 to 5.6 and 4.6, respectively, with increasing N_N from 0 to

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0.1% and 0.5%. However, there is little reduction of $Q_{E1,E2}$ when N_N increases further to 1%. Consequently, the calculated absorption peak intensity shows an obvious decrease by about 31% (from 1806.8 to 1248.4 cm^{-1}) when only 0.4% N is incorporated, as displayed in Fig. 3.22(b). Indeed, the reduction of intersubband absorption intensities in (In,Ga)AsN/AlGaAs quantum wells compared to N-free structures has been observed in experiment [3.9]. Our analysis indicates that the admixing of the N-band wave functions in the subband states is an important reason.

Figure 3.22. Calculated (a) squared optical transition matrix elements vs. k_t at N contents of 0, 0.1%, 0.5% and 1%, respectively, and (b) absorption peak intensity (α_{peak}) as a function of N content for the $\text{GaAs}_{1-x}\text{N}_x/\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ MQW.

3.5.2 InGaAs_{1-x}N_x/GaAs system

Figure 3.23 shows the calculated energies of subbands E1–E3 at the zone center and the absorption energy at the overall ISBT absorption peak as a function of N_N up to 3% for $\text{In}_{0.23}\text{Ga}_{0.77}\text{As}_{1-x}\text{N}_x/\text{GaAs}$ MQW with 6 nm well width. Compared to the $\text{GaAs}_{1-x}\text{N}_x/\text{AlGaAs}$ system discussed in the preceding

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Subsection 3.5.1, a large compressive strain (the in-plane strain tensor $\mathcal{E}_{xx} \approx -1.42\%$) exists in the wells. In this structure both E1 and E2 are bound states and the E1→E2 transition dominates in the overall ISBT absorption. Therefore, the theoretical absorption peak energy is close to the E1 and E2 separation. Similarly to what is observed for the InGaAs_{1-x}N_x/AlGaAs MQW in Fig. 3.20, the E1 and E2 levels move down with comparable rates as N_N increases, resulting in a slow variation of the absorption peak energy. When N_N varies from 0 to 3%, the absorption peak energy only increases from 90 to 130 meV although the 3 % N content has increased the quantum well depth by about 200 meV in this In_{0.23}Ga_{0.77}As_{1-x}N_x/GaAs structure. This is because that the interaction of N-band and conduction-band has comparable repulsion effects on the ground and bound excited states. Figure 3.24 shows the N-band and conduction-band components in the E1 and E2 states at $k_t = 0$ as a function of N_N calculated using Eq. (3.17), to show up the intermixing of N-band and conduction-band wave functions in the electron states. It can be seen that the N-band component in E1 (P_{E1}^{NB}) increases quickly to 14.6% with increasing N_N to 1%, and further to 23.9% at $N_N = 3\%$. The N-band component in E2 (P_{E2}^{NB}) goes up to 17.1% with increasing N_N to 1.0%, and then reaches 28.3% at $N_N = 3\%$. It is clearly shown that the admixing of N-band wave function in E1 and E2 states intensifies with the increase of N_N , and the N-band admixing in E2 is even slightly stronger than that in E1, indicating that higher subbands are more interacted with N-band.

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Figure 3.23. Calculated (a) energies of subbands E1–E3 at $k_t = 0$ and (b) absorption energy at the overall ISBT absorption peak as a function of N content (N_N) for the $\text{In}_{0.23}\text{Ga}_{0.77}\text{As}_{1-x}\text{N}_x/\text{GaAs}$ MQW with 6 nm well width.

Figure 3.24. N-band and conduction-band components in E1 and E2 states at $k_t = 0$ as a function of N_N in the $\text{In}_{0.23}\text{Ga}_{0.77}\text{As}_{1-x}\text{N}_x/\text{GaAs}$ MQW.

By comparing Fig. 3.23 with Fig. 3.20, it can be seen that the phenomenon of the insensitive change of absorption peak energy with N content appears more obvious in nearly lattice-matched $\text{GaAs}_{1-x}\text{N}_x/\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ quantum wells in which In and In-induced large compressive strain are absent. The GaAs_{1-x}

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$x\text{N}_x/\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ structure has larger well depth and has no compressive strain in the well, and therefore the lowering of E2 state with the increase of N content is less hindered. This is the major reason why a redshift of absorption peak energy can show in the $\text{GaAs}_{1-x}\text{N}_x/\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ quantum wells but not in the $\text{In}_{0.23}\text{Ga}_{0.77}\text{As}_{1-x}\text{N}_x/\text{GaAs}$ quantum wells.

3.6 Summary

In this chapter we elaborated the ten-band and sixteen-band $\mathbf{k}\cdot\mathbf{p}$ models in combination with the envelop-function Fourier expansion method to analyze ISBTs in dilute-N quantum structures. The complete optical transition momentum matrix elements are derived. The subband dispersions, and intersubband transitions and absorptions as well as their dependences on well width and N composition in $(\text{In,Ga})\text{AsN}/(\text{Al,Ga})\text{As}$ quantum wells are analyzed and discussed in detail. It is found that some novel ISBT properties and phenomena exhibit due to the NB-CB coupling. The theoretical results are in good agreement with reported experimental observations. The major conclusions are listed in the following:

- 1) The interaction of conduction-band and localized N-band results in more bound excited states in the quantum wells compared to equivalent N-free structures. The transition from the ground to the first excited states ($E1 \rightarrow E2$) is almost always dominating in the overall ISBTs, because E2 is more easily to be a bound state with the CB-NB interaction even under very narrow well widths. The ISBT selectivities with subband order and in-plane wave vector for the dilute-N quantum wells are consistent with those derived for N-free quantum wells in Chapter 2 Section 2.3.

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- 2) The intersubband absorption energy of the dilute-N quantum well is much larger than that of the equivalent N-free structure in narrow wells because of the much lower ground state under the NB-CB interaction. However, this difference becomes small quickly in broader wells, and even the dilute-N quantum well shows smaller absorption energy compared to the equivalent N-free structure. This is not consistent to the usual understanding of large conduction-band discontinuity in quantum wells upon N-incorporation. Actually, this is because that the NB-CB coupling has comparable effects on both ground and excited states, The lowering of those bound states in wider wells upon N-incorporation are approximately equivalent, and E2 lowers even more quickly than E1. Therefore, the ISBT absorption energies of the N-containing and the equivalent N-free quantum wells become quite comparable. In the case of narrow well widths, the $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/(\text{Al,Ga})\text{As}$ based QWIP would allow photons with much shorter wavelengths to be absorbed by intersubband transitions compared to the equivalent N-free structure. This blue-shifted absorption band enables more flexible infrared detection ability without needing to introduce too much indium (In) in the well or aluminum (Al) in the barrier.
- 3) In the case of moderate and wider wells where both E1 and E2 are bound states, the ISBT absorption energy at the overall absorption peak is insensitive to the N composition because of the comparable impacts of NB-CB coupling on the subbands. In $\text{In}_{0.23}\text{Ga}_{0.77}\text{As}_{1-x}\text{N}_x/\text{GaAs}$ quantum wells, the absorption peak energy can only increase by about 40 meV with

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increasing N composition (N_N) up to 3% although the quantum-well depth increases by ~ 200 meV. In quasi-lattice-matched $\text{GaAs}_{1-x}\text{N}_x/\text{AlGaAs}$ quantum wells the absorption peak energy even shows a slight redshift with N_N up to 2% compared to the equivalent N-free structures. It is also shown that the admixing of N-band wave function in E1 and E2 states intensifies with the increase of N_N , and the N-band component in E2 is even slightly stronger than that in E1.

Chapter 4 Theoretical study on ISBTs in asymmetric dilute-N quantum wells

4.1 Introduction

Asymmetric quantum well structures designed purposely or formed by nonuniform doping are of considerable interest for various optoelectronic research and applications [4.1-4.6]. For example, Touse *et al.* have reported near- and mid-infrared detection using GaAs/In_xGa_{1-x}As/In_yGa_{1-y}As step quantum wells recently [4.5]. We have also investigated InGaAs/Al_xGa_{1-x}As MQW with linear-graded barrier for voltage-tunable broadband photodetection and revealed that the intersubband transitions (ISBTs) from the ground state to all bound and continuum excited states contribute to the overall absorption [4.6]. In this chapter, ISBTs in dilute-N quantum wells with asymmetric potential profiles will be studied theoretically.

Figure 4.1. Schematic of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ MQW with asymmetric N incorporation in the well layer. L_w is the well width and L is the structure period.

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Figure 4.1 shows the schematic $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ quantum well structure with N incorporation only in the left half of InGaAs well, resulting in an asymmetric quantum potential in the conduction band associated with the high-lying N-band. L_W defines both the InGaAsN and InGaAs well widths. In the calculation, the ten-band $\mathbf{k}\cdot\mathbf{p}$ model was modified to introduce the asymmetric BAC effect in the coupled differential equations (3.14). The conduction-band offset ratio of $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ is assumed to be 0.8 as the indium (In) composition x is larger than 30% [3.17].

4.2 Theoretical analysis

The conduction and valence subband structures at low temperature in $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}/\text{In}_{0.32}\text{Ga}_{0.68}\text{As}/\text{GaAs}$ asymmetric MQWs are calculated for $L_W = 1.5, 2, 3, 4, 5$ and 6 nm, respectively. The state variations with k_z (the normal-to-plane wave vector) due to quantum confinement relaxation are taken into account, especially for high order excited states. The results are shown in Fig. 4.2. The valence-band edge of bulk $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}$ is regarded as zero energy position. The interaction between N-band and valence-band is regarded as negligible in the calculation. It can be seen that the number of bound states in conduction-band increase quickly with well width, partially due to the intense BAC effect. At $L_W = 1.5$ or 2 nm, only the ground state is bounded. When L_W increases to 4 nm, there are three bound states with comparable energy separations. When L_W increases further to 6 nm, four bound states are observed.

The squared optical transition matrix elements (transition rates) of the ISBTs from the ground state E1 to the first four excited states (E2–E5), respectively, as

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a function of k_t are computed based on the ten-band $\mathbf{k}\cdot\mathbf{p}$ model (Fig. 4.3). Same as the method used in Chapters 2 and 3, the results are achieved by normalized integrating the calculated transition rates for various k_z (wave vector along the quantum well growth direction) values between $m \cdot (2\pi/L)$ to $(m+1) \cdot (2\pi/L)$, where m is an integer. This is quite necessary, especially for ISBTs involving continuum states associated with significant quantum confinement relaxation. It is interesting to observe that in the case of narrow well width, i.e. $L_W = 1.5$ nm, the TE-polarized transitions at finite k_t are considerably high. For instance, the peak transition rates of TE E1 $\rightarrow$ E2 are 0.53 and 1.10 in [100] and [110] k_t directions, respectively, at $k_t = 4.95$ ($2\pi/L$) as shown in Fig. 4.3(a). The corresponding TE/TM ratios are about 20% and 40%, respectively.

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Figure 4.2. Calculated conduction and valence subbands in the $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}/\text{In}_{0.32}\text{Ga}_{0.68}\text{As}/\text{GaAs}$ asymmetric MQWs with well widths (L_w) of 1.5, 2, 3, 4, 5 and 6 nm, respectively.

When the well width increases to 3 nm, E2 becomes a bound state and E3 is still a quasi-continuum state. Both B-to-B $E1 \rightarrow E2$ and B-to-C $E1 \rightarrow E3$ transitions for TE polarization show considerable rates (Fig. 4.3(b)). The peak $E1 \rightarrow E2$ transition rates are 0.25 and 0.48, and the peak $E1 \rightarrow E3$ transition rates are 0.68 and 1.34 at finite k_t in [100] and [110] directions, respectively. However, the overall TE/TM ratio degrades in some degree, as the TM-polarized $E1 \rightarrow E2$ transition rate increases to 5.5 at $k_t = 0$.

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When the well width increases further to 6 nm, it is observed that the ISBT selectivity derived in Chapter 3 doesn't hold here due to the broken structural symmetry, and consequently both B-to-B TE-polarized $E1 \rightarrow E2$ and $E1 \rightarrow E3$ transitions show considerable rates (Fig. 4.3(c)). It is also seen that the TE-polarized transitions decrease obviously compared to the narrower wells. This trend is similar to what we derived for the symmetric dilute-N quantum wells in Section 3.3. The peak transition rates for TE polarization are only about 0.11 and 0.23 at finite k_z in [100] and [110] directions, respectively. However, the TM-polarized transitions still show high rates of 3.56 for $E1 \rightarrow E2$ and 0.5 for $E1 \rightarrow E3$. As a result, the overall TE/TM ratio degrades to below 10%. It indicates that narrower well widths are favorable for TE-polarized ISBTs under the ten-band model.

It looks that the TE-polarized ISBTs in dilute-N quantum wells with asymmetric N incorporation are improved in some degree. The TE-polarized transition rate in [110] k_z direction is about two times of that in [100] k_z direction, while the TM-polarized transition rates are almost equivalent in the two directions. This is quite similar to the analysis result base on the fourteen-band $\mathbf{k} \cdot \mathbf{p}$ model for common zinc-blendes semiconductors that lack inversion symmetry (Subsection 2.3.3).

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Figure 4.3. TM and TE polarized squared optical transition matrix elements as a function of k_t in [100] and [110] directions for the $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}/\text{In}_{0.32}\text{Ga}_{68}\text{As}/\text{GaAs}$ asymmetric MQWs with well widths of (a) 1.5, (b) 3 and (c) 6nm calculated with the ten-band $\mathbf{k}\cdot\mathbf{p}$ model. L is the quantum well structure period.

4.3 Impact of electric field on ISBTs in asymmetric dilute-N quantum wells

It is known that the applied bias would impact ISBTs in asymmetric quantum well structures more evidently compared to common rectangular quantum wells because symmetry only allows a quadratic electric-field shift [1.9, 4.4]. In this section such electric field-dependent effect on the $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ quantum wells with asymmetric N incorporation will be elaborated theoretically (Fig. 4.4).

Figure 4.4. The $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ quantum wells under applied bias

The electronic potential function $U(z)$ in the coupled differential equations (3.14) consists of three parts:

$$U(z) = V_0 + V_s + q\xi z, \quad (4.1)$$

where V_0 is the quantum well potential induced by the band discontinuity between the barrier and well, V_s is the potential change induced by strain and $q\xi z$ is the potential change induced by applied electric field ξ , where q is the electronic charge and z is the growth direction.

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Figure 4.5. Calculated conduction subband dispersions in the InGaAsN/InGaAs/GaAs asymmetric MQW with well width of 2 nm, at applied biases of (a) 0 and (b) 2 MV/m. The schematic conduction band profiles with subband distributions are also shown for clarification.

Figure 4.6. Calculated TM-polarized squared optical transition matrix elements for ISBTs in the In_{0.32}Ga_{0.68}As_{0.984}N_{0.016}/In_{0.32}Ga_{0.68}As/GaAs MQW with $L_W = 2$ nm at applied electric fields of 0, 1 and 2 MV/m, respectively.

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Figure 4.7. Calculated TM intersubband absorption spectra for the $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}/\text{In}_{0.32}\text{Ga}_{68}\text{As}/\text{GaAs}$ MQW with $L_W = 2$ nm at applied electric fields of 0, 1 and 2 MV/m, respectively.

The $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}/\text{In}_{0.32}\text{Ga}_{68}\text{As}/\text{GaAs}$ MQW with $L_W = 2$ nm was chosen for the calculation (Fig. 4.4). The Fermi level is assumed to be aligned with the edge of E1. The conduction subband dispersions in the asymmetric MQW are computed with the 10-band model and the result is shown in Fig. 4.5. The calculated TM-polarized squared optical transition matrix elements and absorption coefficients at applied electric fields of 0, 1 and 2 MV/m, respectively, are shown in Figs. 4.6 and 4.7. At zero bias, E2 is a quasi-bound state and all the other excited states are continuum states. The $\text{E1} \rightarrow \text{E2}$ transition is dominant with a maximal rate of 3.85 at $k_t = 3.3$, and the $\text{E1} \rightarrow \text{E3}$ transition shows a maximal rate of 1.38 at $k_t = 0$. The overall absorption spectrum shows a main peak at 171 meV determined mainly by the $\text{E1} \rightarrow \text{E2}$ absorption. It is interesting to find that the $\text{E1} \rightarrow \text{E2}$ and $\text{E1} \rightarrow \text{E3}$ transitions show regular variations with the increase of electric field intensity. When an electric field of 1 MV/m is applied, the $\text{E1} \rightarrow \text{E2}$ transition drops obviously around the zone center,

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and the $E1 \rightarrow E3$ transition goes up dramatically with a maximal rate of 3.60 at $k_t = 0$. The calculated $E1 \rightarrow E3$ absorption peak is over twice as high as the $E1 \rightarrow E2$ absorption as shown in Fig. 4.7(b). When the electric field is increased further to 2 MV/m, the $E1 \rightarrow E3$ transition becomes dominant with a maximal rate of 4.48 at $k_t = 0$. Consequently, the $E1 \rightarrow E3$ absorption determines the overall absorption peak as shown in Fig. 4.7(c), while the other intersubband absorptions are much weaker. This can be explained by the change of E-k curves as shown in Fig. 4.5. At the 2 MV/m bias, both E1 and E2 appear to be quasi-bound states, and the exaggerated quantum potential asymmetry strengthens the $E1 \rightarrow E3$ transition that should be minimum in a symmetric structure.

4.4 Summary

The ten-band $\mathbf{k} \cdot \mathbf{p}$ method was applied to analyze the subband structures and ISBTs in asymmetric quantum well structures in this chapter. The calculation results on the InGaAsN/InGaAs/GaAs MQW with asymmetric N incorporation show significant TE-polarized transitions at finite in-plane wave vector k_t , especially for narrower well widths. The TE transition rate in [110] k_t direction is about two times of that in [100] k_t direction, while the TM transition rates in both directions are almost equivalent. Furthermore, the impact of applied bias on the ISBTs in such asymmetric MQW with InGaAsN and InGaAs well widths of 2 nm has also been analyzed. The results show that the ISBT properties would be modified significantly, and consequently the dominant ISBT changes from the $E1 \rightarrow E2$ transition to the $E1 \rightarrow E3$ transition gradually with the increasing electric field in this structure.

Chapter 5 Theoretical study on ISBTs in interdiffused dilute-N quantum wells

5.1 Introduction

A post-growth rapid thermal annealing (RTA) is often necessary for InGaAsN-based quantum wells (QWs) to ameliorate the poor crystal quality due to the incorporation of nitrogen and improve the material and optical properties. It has been commonly observed that InGaAsN/GaAs quantum wells show emission wavelength blueshifts after RTA [5.1–5.6], which is commonly attributed to the quantum potential reconfiguration with component interdiffusion. In this subsection, we would like to analyze the impact of interdiffusion on subband dispersions and intersubband transitions (ISBTs) based on the ten-band $\mathbf{k}\cdot\mathbf{p}$ model.

The original structure before component diffusion is the $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}/\text{GaAs}$ MQW structure in our analyses. The GaAs barrier width is assumed to be 35 nm. A classic expression was employed to model the composition profile upon interdiffusion as follows [5.6]

$$x'(z) = \frac{x}{2} \left[\text{erf} \left[\frac{L_w + 2z}{4L_d} \right] + \text{erf} \left[\frac{L_w - 2z}{4L_d} \right] \right] \quad (5.1)$$

Where x is the as-grown composition, z is the distance in the quantum well growth direction, L_w is the well width before interdiffusion and L_d is the diffusion length. Note that the component diffusion will in-turn change the quantum well potential profile as well as the strain distribution. The conduction-band offset ratio Q_C (Eq. (2.38)) of $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ is assumed to be 0.8 if x

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$\geq 30\%$, $0.65+0.5x$ if $30\% > x \geq 20\%$, $0.15+3x$ if $20\% > x \geq 10\%$, and 0.45 if $x < 10\%$ [3.18].

5.2 ISBTs in InGaAsN/GaAs quantum wells with N diffusion

5.2.1 ISBTs with N diffusion in narrow wells

Firstly, the dependence of ISBTs with N diffusion in narrow wells will be discussed, since it is most sensitive to composition interdiffusion. Figure 5.1(a) shows the calculated N composition distribution as a function of diffusion length $L_d(\text{N})$ up to 4.0 nm for the $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}$ well with a width of 2 nm. It can be seen that with $L_d(\text{N})$ increasing from 0 to only 0.8 nm, about half of the N content diffuses out of the well region. At $L_d(\text{N}) = 4$ nm, the remaining N composition in the well region is only about 0.0023, and the overall N distribution profile becomes very wide (from about -10 to 10 nm).

Figure 5.1(b) shows the impact of N out-diffusion on subband structures clearly. At $L_d(\text{N}) = 0$, the ground state E1 in the conduction band is as low as 1200 meV due to the strong band-anticrossing effect with the high N composition, while all the excited subbands are continuum states under the very narrow well width. At $L_d(\text{N}) = 2$ nm, E1 moves up to about 1280 meV because of N diffusion and hence the BAC effect is relaxed. Whereas, it is interesting to note that the first two excited states E2 and E3 in the conduction-band move downwards to be bound states at the same time (Table 5.1). Actually, this is resulted from the extended BAC effect out from the original 2 nm $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}$ well upon N out-diffusion. This out-diffused N

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generates a wide quantum well-like potential that tends to lower down the excited states. However, the energy of the ground state E1 is more influenced by the relaxed BAC effect with diluted N concentration distribution, and therefore it shows reverse trend relative to the excited states. When $L_d(\mathbf{N})$ increases further to 4 nm, it can be seen that E1 moves up further to 1312 meV. The energy of E2 at $k_i = 0$ almost doesn't change, while the subband curvature increases in some degree compared to the case of $L_d(\mathbf{N}) = 2$ nm, indicating a decreased electron effective mass resulted from more relaxation of the BAC effect. At the same time, E3 moves down to become a bound state and the electron effective mass also shows a slight decrease.

Table 5.1. Dependence of conduction subband energies at zone center with N diffusion length in the case of **2 nm** well width

Subband	Energy at zone center (meV)			Trend
	$L_d(\mathbf{N}) = 0$	$L_d(\mathbf{N}) = 2$ nm	$L_d(\mathbf{N}) = 4$ nm	
E1	1205	1278	1311	↑
E2	1435	1390	1392	↓
E3	1442	1424	1408	↓
E4	1464	1442	1437	↓

Figure 5.1(c) shows the squared optical transition matrix elements for $L_d(\mathbf{N}) = 0, 2$ and 4 nm. Only TM-polarized transitions are taken into consideration here since TE-polarized ones are much weaker in the symmetric structures. It can be seen that all the E1 to E2–E5 transitions have considerable rates at $L_d(\mathbf{N}) = 0$ nm, because all the excited subbands are continuum states. The maximum transition rates occur generally at finite k_i instead of at the zone center ($k_i = 0$), indicating different ISBT behaviors from the moderate and wide wells in which at least one excited state is bounded. At $L_d(\mathbf{N}) = 2$ nm, the E1→E2 transition

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becomes dominant with a maximum rate (~ 3.27) at the zone center, since E2 has lowered down to be a bound state. At $L_d(\mathbf{N}) = 4$ nm, the $E1 \rightarrow E2$ transition is still dominating, but the maximum rate at the zone center decreases obviously (~ 2.16). It indicates that N out-diffusion tends to reduce the ISBT intensity because of the broadened quantum well potential profile and hence relaxed quantum restriction. The $E1 \rightarrow E4$ transition becomes observable, as E4 has also been lowered down to be a quasi-bound state upon the great N out-diffusion. This phenomenon is consistent with the ISBT selectivity on subband order as derived for the symmetric square quantum wells in Chapter 3 that E1 to the even order excited states transitions should dominate.

Figure 5.1(d) shows the calculated ISBT absorption spectra for a set of N diffusion lengths $L_d(\mathbf{N})$ increasing from 0 to 4 nm. It is assumed that the Fermi energy level is aligned with the ground state E1 at $k_x = 0$ in the calculation. The results show clearly that absorption peak energy redshifts continually with the increasing $L_d(\mathbf{N})$, especially in the range of smaller $L_d(\mathbf{N})$. It can be seen when $L_d(\mathbf{N})$ increases from 0 to 0.4 and 0.8 nm, the absorption peak redshifts dramatically from 240 meV to 206 and 168 meV, respectively. This is caused by the quicker N out-diffusion in the earlier stage (Fig. 5.1(a)). The absorption spectrum is the broadest at $L_d(\mathbf{N}) = 0$ because of the superposition of comparable B-to-C E1 to E2, E3 and E4 transitions. A secondary absorption peak appears (at 117 meV) in the right side of the main peak (at 78 meV) in the case of $L_d(\mathbf{N}) = 4$ nm, which comes from the B-to-B $E1 \rightarrow E4$ transition. The absorption intensity increases with $L_d(\mathbf{N})$ up to 2 nm and thereafter it tends to

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decrease because of relaxed quantum restriction upon great N-diffusion as addressed in the preceding paragraph.

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Figure 5.1. (a) N distributions for various diffusion lengths $L_d(N)$ (Z is the quantum well growth direction), with original $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}$ well width of **2 nm**. (b) Subband structures and (c) TM-polarized squared optical transition matrix elements as a function of k_t at $L_d(N) = 0, 2$, and 4 nm, respectively. (d) Calculated absorption spectra at $L_d(N) = 0, 0.4, 0.8, 1.2, 2, 2.8$ and 4 nm, respectively.

5.2.2 ISBTs with N diffusion in moderate wells

Now let us look into the dependence of ISBTs on N diffusion in the case of moderate well width (4 nm) as shown in Fig. 5.2(a). It can be seen that the out-diffusion of N is not so rapid in the 4 nm wide well as in the 2 nm wide well discussed in last subsection. Over half of the N content still stays in the well

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region until $L_d(\text{N})$ is beyond 2 nm. When $L_d(\text{N})$ goes up to 4 nm, the remaining N composition in the well region is about 0.44%.

The calculated subband structures are shown in Fig. 5.2(b) for $L_d(\text{N}) = 0, 2,$ and 4 nm. When $L_d(\text{N})$ equals to zero, there are two bound states (E1 and E2) in the well. As summarized in Table 5.2, the energies of E1 and E2 at $k_t = 0$ are 1120 and 1302 meV, respectively, due to the intense BAC effect. The energies of the continuum E3 and E4 states at $k_t = 0$ are 1433 and 1440 meV, respectively. When $L_d(\text{N})$ increases to 2 nm, E1 moves up to 1183 meV, E2 only shifts slightly to 1315 meV, E3 moves down to 1382 meV to be a bound state, and E4 also lowers down to 1418 meV to be a quasi-bound state. When $L_d(\text{N})$ increases further to 4 nm, E1 and E2 continue to move up to 1229 and 1339 meV, while E3 and E4 lower down further to 1372 and 1398 meV, respectively. This indicates again that the ground state E1 is mostly impacted by the relaxed BAC effect, while the higher excited states are more influenced by the broadening quantum well potential upon N out-diffusion at the same time.

The squared optical transition matrix elements with k_t show that the B-to-B E1→E2 transition always dominates in the 4 nm wide well (Fig. 5.2(c)). The maximum transition rate occurs at the zone center that decreases continuously with the increase of N diffusion length, indicating the negative impact of broadening quantum well potential and hence relaxed quantum restriction on ISBTs upon N out-diffusion. The calculated absorption spectrum peaks at 178 meV for $L_d(\text{N}) = 0$, and then redshifts gradually to 127 meV with increasing

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$L_d(\text{N})$ to 2 nm (Fig. 5.2(d)). The changes of absorption peak position and profile are not so dramatic compared to the preceding 2 nm InGaAsN well. When $L_d(\text{N})$ is larger than 2.8 nm, the absorption peak position and intensity only show little change since the N out-diffusion saturates in this range.

(a)

(b)

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Figure 5.2. N distributions for various diffusion lengths $L_d(\mathbf{N})$ (Z is the quantum well growth direction), with original InGaAsN well width of **4 nm**. (b) Subband structures and (c) TM-polarized squared optical transition matrix elements as a function of $k_{\parallel}$ at $L_d(\mathbf{N}) = 0, 2$, and 4 nm , respectively. (d) Calculated absorption spectra at different $L_d(\mathbf{N})$.

Table 5.2. Dependence of conduction subband energies at zone center with N diffusion length in the case of **4 nm** well width

Subband	Energy at zone center (meV)			Trend
	$L_d(\mathbf{N}) = 0$	$L_d(\mathbf{N}) = 2 \text{ nm}$	$L_d(\mathbf{N}) = 4 \text{ nm}$	
E1	1119	1184	1229	↑
E2	1302	1315	1338	↑
E3	1431	1382	1373	↓
E4	1439	1418	1398	↓

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5.2.3 ISBTs with N diffusion in wide wells

In this subsection, the case of large well width ($L_W = 6$ nm) will be discussed. The N out-diffusion in this wide well is significantly less compared to the previous narrow and moderate wells at the same $L_d(\text{N})$. Over half of the N content stays in the 6 nm well region until $L_d(\text{N})$ goes up to 3.2 nm (Fig. 5.3(a)).

The calculated subband structures for $L_d(\text{N}) = 0, 2$, and 4 nm are shown in Fig. 5.3(b). Because of the large well width as well as the intense BAC effect, all the four subbands (E1–E4) are bound states inside the well when no N diffusion occurs ($L_d(\text{N}) = 0$). With increasing $L_d(\text{N})$ to 2 and 4 nm, E1 and E2 keep moving up, E3 is almost unchanged, and E4 keeps moving down as summarized in Table 5.3. The increasing curvatures of the E1–E4 states with $L_d(\text{N})$ are also observed, indicating clearly the decrease of electron effective masses with N-diffusion in these bound states.

Table 5.3. Dependence of conduction subband energies at zone center with N diffusion length in the case of 6 nm well width

Subband	Energy at zone center (meV)			Trend
	$L_d(\text{N}) = 0$	$L_d(\text{N}) = 2$ nm	$L_d(\text{N}) = 4$ nm	
E1	1081	1128	1178	↑
E2	1213	1245	1276	↑
E3	1341	1334	1341	→
E4	1425	1384	1366	↓

The squared optical transition matrix elements in Fig. 5.3(c) show that the dominating B-to-B E1→E2 transition is almost unchanged when $L_d(\text{N})$ increases from 0 to 2 nm, and then decreases slightly with $L_d(\text{N})$ further to 4

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nm. This reveals that the impact of N out-diffusion on ISBT rates in wide wells is not significant. The calculated absorption spectra in Fig. 5.3(d) show relatively slow variations with $L_d(\text{N})$ compared to the narrow and moderate wells in the preceding subsections. It is interesting to find that the absorption peak has a slight blueshift instead of a common redshift when N diffusion just begins to happen. For instance, the transition energy at the absorption peak is 128.3 meV when $L_d(\text{N})$ is zero, and then blueshifts to 130.7 meV when $L_d(\text{N})$ increases to 0.4 nm. Thereafter, it redshifts gradually to 112.6 meV at $L_d(\text{N}) = 2$ nm, and then 96.2 when $L_d(\text{N})$ goes up to 4 nm finally.

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Figure 5.3. N distributions for various diffusion lengths $L_d(N)$ (Z is the quantum well growth direction), with original InGaAsN well width of **6 nm**. (b) Subband structures and (c) TM-polarized squared optical transition matrix elements as a function of k_t at $L_d(N) = 0, 2$, and 4 nm, respectively. (d) Calculated absorption spectra at $L_d(N) = 0, 0.4, 0.8, 1.2, 2, 2.8$ and 4 nm, respectively.

5.2.4 Dependence of intra- and inter-band transition energies on N diffusion

In this subsection, we would like to discuss the variation trends of both intra- and inter-band transition energies caused by N diffusion. Figure 5.4 shows the calculated energies of conduction subbands E1–E4 and valence subbands H1–

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H4 at $k_t = 0$ as a function of $L_d(\text{N})$ for the $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}/\text{GaAs}$ MQWs discussed previously. The energies of valence subbands change little with $L_d(\text{N})$, because the NB-VB interaction is regarded as negligible in our calculation and the only influence comes from the strain re-distribution upon N diffusion. In the case of narrow well width ($L_w = 2$ nm), only E1 energy edge goes up quickly with $L_d(\text{N})$, while the energy edges of E2–E4 keep lowering down. In the case of moderate well width ($L_w = 4$ nm), the energy edges of E1 and E2 go up, while the energy edges of E3 and E4 lower down with $L_d(\text{N})$. In the case of large well width ($L_w = 6$ nm), E3 energy edge becomes unchangeable, and only E4 energy edge moves down with $L_d(\text{N})$.

Figure 5.4. Calculated subband energies at $k_t = 0$ as a function of N diffusion length $L_d(\text{N})$ for the InGaAsN/GaAs MQWs with well widths of (a) 2, (b) 4 and (c) 6 nm, respectively.

Here we define the interband (inter-conduction and valence bands) transition energy as E1-H1, and define the intraband (intra-conduction band) transition energy as E2-E1. The calculated E1-H1 and E2-E1 transition energies at $k_t = 0$

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as a function of $L_d(N)$ are plotted in Fig. 5.5(a) and (b), respectively. It is interesting to observe that the interband E1-H1 transition energy blueshifts with $L_d(N)$ at approximately equivalent rates whatever L_w equals to. The overall changes of E1-H1 are always about 100 meV with increasing $L_d(N)$ from 0 to 4 nm, in all cases of L_w (2, 4, or 6 nm). In contrast, the variation of the intraband E2-E1 transition is very sensitive to the well width. In the case of narrow well width ($L_w = 2$ nm), the E2-E1 transition energy redshifts dramatically from 230 to 81 meV when $L_d(N)$ increases from 0 to 4 nm. In the case of moderate well width ($L_w = 4$ nm), such redshift becomes relatively moderate (from 182 to 110 meV). In the case of large well width ($L_w = 6$ nm), the E2-E1 transition energy even shows a slight blueshift with increasing $L_d(N)$ from 0 to about 0.8 nm, and then begins to redshift slowly thereafter.

Figure 5.5. Calculated (a) interband (E1-H1) and (b) intraband (E2-E1) transition energies at $k_t = 0$ as a function of N diffusion length.

5.3 ISBTs in InGaAsN/GaAs quantum wells with In diffusion

In this subsection the influence of another diffusion behavior, In-Ga interdiffusion, on ISBTs will be studied in theoretically. Figure 5.6 shows the squared optical transition matrix elements with k_t at In diffusion lengths ($L_d(\text{In})$) of 0, 2 and 4 nm, respectively, calculated using the ten-band $\mathbf{k}\cdot\mathbf{p}$ model. The results for the three representative well widths, 2, 4 and 6 nm, are shown in the figures. The obvious correlation of ISBTs with In diffusion observed is the quick decrease of the squared optical transition matrix elements with the crease of $L_d(\text{In})$. It can be seen that in the case of 2 nm well width, the transition rates at $L_d(\text{In}) = 2$ nm of all the B-to-C ISBTs shown in Fig. 5.6(a) is only about half of those at $L_d(\text{In}) = 0$. Even in the case of 6 nm well width, the dominant E1→E2 transition rate at the zone center is reduced from 4.2 to 3.4 with the increase of $L_d(\text{In})$ from 0 to 2 nm, and then to 2.7 with $L_d(\text{In})$ further to 4 nm. This is most likely due to the quick relaxation of quantum restriction with the formation of a wide $\text{In}_x\text{Ga}_{1-x}\text{AsN}$ quantum potential profile with graded In distribution upon out-diffusion.

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Figure 5.6. Calculated TM-polarized squared optical transition matrix elements as a function of k_t at $L_d(\text{In}) = 0, 2$, and 4 nm, respectively, with original $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}$ well widths of (a) 2, (b) 4 and (c) 6 nm.

The calculated intersubband absorption spectra in conduction-band for the three representative well widths are shown in Fig. 5.7. It is assumed that the Fermi energy level is aligned with the edge of ground state in the calculation. In the case of narrow well width ($L_w = 2$ nm), all the ISBTs are B-to-C transitions. Unlike the impact of N diffusion on ISBTs in the narrow well, all the ISBTs are still comparable B-to-C transitions upon In diffusion. The superposition of these comparable ISBTs results in a wide absorption range. The absorption energy at main peak redshifts from 240 to 210 meV with the increasing of In diffusion

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length ($L_d(\text{In})$) from 0 to 0.8 nm. The absorption coefficient decreases obviously meanwhile, due to the large degradation of transition matrix elements as indicated in the preceding paragraph. However, the absorption spectrum is almost unchangeable when $L_d(\text{In})$ is beyond 2 nm, since most In has diffused out of the narrow well region. In the cases of moderate and large well widths ($L_w = 4$ and 6 nm), the B-to-B $E_1 \rightarrow E_2$ absorption always dominates and the absorption energy only shifts slightly with $L_d(\text{In})$ up to 4 nm as shown in Figs. 5.7(b) and (c). The absorption coefficient at the peak decreases continuously with $L_d(\text{In})$ because of the degraded ISBT rates associated with In out-diffusion as discussed previously. In the 6 nm wide well, the absorption energy at the peak even shows a small blueshift (from 128 to 132 meV) with the increasing In diffusion length from 0 to 0.8 nm. This is because that in the wide well, both E_1 and E_2 are deeply bound states which move up at comparable speeds with the In out-diffusion, and E_2 even moves slightly fast than E_1 when In just starts to diffuse as shown in Figs. 5.8 and 5.9 clearly.

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Figure 5.7. Absorption spectra at a series of $L_d(\text{In})$ with original $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}$ well widths of (a) 2, (b) 4 and (c) 6 nm, respectively.

The variations of conduction and valence subbands at the zone center with $L_d(\text{In})$ are shown in Fig. 5.8. The energy edges of the conduction subbands E1–E4 move up more or less with increasing $L_d(\text{In})$ for all the L_w cases, as the $\text{In}_x\text{Ga}_{1-x}\text{AsN}$ bandgap broadens and the effective conduction-band well depth decreases with In diffusion. At the same time the energy of ground state H1 in valence-band only changes slightly. Therefore, the interband E1–H1 transition energy keeps increasing with $L_d(\text{In})$ as shown in Fig. 5.9(a). The

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overall blueshifts are as large as 123, 152 and 142 meV in the cases of $L_w = 2, 4$ and 6 nm, respectively, with the increasing of $L_d(\text{In})$ from 0 to 4 nm,.

The intraband E1-E2 transition energy for the narrow well ($L_w = 2$) shows a very different trend with $L_d(\text{In})$ as shown in Fig. 5.9(b). It redshifts rapidly from 229 to 137 meV with increasing $L_d(\text{In})$ from 0 to 1.6 nm, as E1 moves up fast with In out-diffusion while the continuum state E2 only moves slightly. In the case of moderate or wide wells ($L_w = 4$ or 6 nm), The E1-E2 transition energy changes slowly with increasing $L_d(\text{In})$ up to 4 nm, because the bound states E1 and E2 move up with similar rates upon In diffusion as shown in Fig. 5.8(b) and (c).

Figure 5.8. Calculated subband energies at $k_t = 0$ as a function of In diffusion length $L_d(\text{In})$ for the InGaAsN/GaAs MQWs with original well widths L_w of (a) 2, (b) 4 and (c) 6 nm, respectively.

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Figure 5.9. Calculated interband (E1-HH1) and intraband (E2-E1) transition energies at $k_t = 0$ as a function of In diffusion length.

5.4 Summary

In this chapter, the variations of subband structures and ISBTs with N and In diffusions in InGaAsN/GaAs quantum wells are studied theoretically. The results show that lower subbands in conduction-band tend to move up, while higher subbands tend to move down with N diffusion. The electron effective masses in bound states decrease with the N diffusion. The N diffusion should induce comparable blueshifts of interband transition energies in all cases of well widths (narrow, moderate and wide wells). The ISBT transition energy in narrow wells should redshift dramatically with the increase of N diffusion length. Such change becomes much smaller in the case of wider wells. In diffusion should induce even more blueshifts of interband transition energies compared to N diffusion. However, the intersubband transition energy is not sensitive to the In diffusion in the cases of moderate and wide wells. It is also found that squared optical transition matrix elements decrease obviously with In diffusion because of the relaxation of quantum confinement effect.

Chapter 6 Experimental investigation on InGaAsN/GaAs quantum wells

6.1 Introduction

Since the observation of intersubband transitions (ISBTs) in GaAs/AlGaAs quantum wells (QWs), a great deal of work has been done for various material systems, InGaAs/(Al,Ga)As [6.1–6.3], InGaAsP/InP [6.4, 6.5], GaAs/InGaP [6.6], etc.. In recent years $\text{In}_{1-y}\text{Ga}_y\text{As}_{1-x}\text{N}_x$ alloys have received considerable attentions due to the novel physical properties of the dilute-N material and significant applications for laser diodes emitting at 1.3–1.5 μm optical fiber windows and high-efficiency solar cells [1.35-1.40, 1.45-1.47]. It is also possible to obtain some significant optoelectronic applications based on ISBTs in such dilute-N materials. With the increase of N composition x , the $\text{In}_{1-y}\text{Ga}_y\text{As}_{1-x}\text{N}_x$ /(Al,Ga)As quantum wells can allow the photons with shorter wavelengths to be absorbed through ISBTs due to the significantly increased conduction-band discontinuity. This blue-shifted absorption band enables the flexible infrared detecting ability without introducing too much indium (In) in the well or use aluminum (Al) in the barrier.

In this chapter, we present the successful growth of some high quality $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}$ /GaAs and $\text{In}_{0.7}\text{Ga}_{0.3}\text{As}_{0.99}\text{N}_{0.01}$ /GaAs multiple quantum wells (MQWs) by solid-source Molecular Beam Epitaxy (SSMBE). The structural and material properties are characterized using High-resolution X-ray diffraction (HRXRD), photoluminescence (PL), rapid thermal annealing (RTA),

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secondary ion mass spectrometry (SIMS), Fourier Transform Infrared Spectroscopy (FTIR), etc. The experimental measurement of intersubband absorptions in the 8–12 μm band will also be reported.

6.2 Sample growth and characterization

Molecular Beam Epitaxy (MBE) was developed in early 1970s as a means of growing high-purity epitaxial layers of compound semiconductors [6.7, 6.8]. MBE is a versatile technique allowing precise control of epitaxial layer thickness, doping and chemical composition. MBE has become a valuable tool in the development of sophisticated electronic and optoelectronic devices based on superlattice structure using III-V compound semiconductors [6.9, 6.10].

Figure 6.1 shows a schematic diagram of the MBE growth chamber. The key components of such system are:

- 1) A vacuum pumping system and a chamber to create a clean, ultra-high vacuum (UHV) environment.
- 2) Molecular beam effusion cells that are the key components of an MBE system. They must provide excellent flux stability and uniformity, and material purity. The cells are placed on a source flange, and are co-focused on the substrate heater, to optimize flux uniformity.
- 3) The substrate manipulator is capable of continuous azimuthal rotation (CAR) around its axis to improve uniformity across the wafer. The heater behind the sample is designed to maximize temperature uniformity and minimize power consumption and impurity outgassing.
- 4) The ionization gauges to measure the vacuum and the flux of molecular beams.

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- 5) Surface science techniques such as reflection high-energy electron diffraction (RHEED) system for in-situ surface characterization is compatible with the MBE.

Figure 6.1. The schematic diagram of a solid source MBE growth chamber.

Three $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}/\text{GaAs}$ n-type MQW samples, S1, S2 and S3 were grown on double-side polished (100) semi-insulating GaAs substrates by a Riber-32P SSMBE system. The schematic structure is shown in Figure 6.2 and the structure and composition parameters are listed in Table 6.1. In the growth the group III elements, In and Ga, are from effusion cells while the group V elements, As and P, are from cracker cells. The nitrogen was provided by a radio-frequency plasma source. The growth condition, structure parameters and doping concentrations of S1, S2 and S3 are the same except that their well widths are different. Each sample consists of eight periods of $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.986}\text{N}_{0.014}$ wells and GaAs barriers. The Si doping concentration in the wells is about $4 \times 10^{17} \text{ cm}^{-3}$. The well widths for S1, S2 and S3 are 2, 3 and 4 nm, respectively. The barrier widths are all 36 nm. The MQW structures were

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sandwiched between a 0.5 μm GaAs bottom contact layer and a 0.2 μm GaAs cap layer, both doped with Si of $5 \times 10^{18} \text{ cm}^{-3}$. The growth temperature is 440 $^{\circ}\text{C}$ for the quantum wells, and 590 $^{\circ}\text{C}$ for the buffer and cap layers. Clear streaky RHEED patterns were observed for all samples.

Figure 6.2. Schematic structure of the $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}/\text{GaAs}$ n-type MQWs.

Table 6.1. Structure and composition parameters for S1, S2 and S3

Sample	GaAs Barrier (nm)	Well width (nm)	Well component (%)			
			Ga	In	As	N
S1	35	2	0.68	0.32	0.984	0.016
S2	35	3	0.68	0.32	0.984	0.016
S3	35	4	0.68	0.32	0.984	0.016

High-resolution X-ray diffraction (HRXRD) characterization is measured using a Philips X'Pert Material Research Diffractometer after the growth. The information obtained from diffraction patterns concerns the composition and uniformity of epitaxial layers, the layer thickness, the built-in strain and strain relaxation, and the crystalline perfection related to their dislocation density [6.11]. The measurement of the diffraction is in principle determined by Bragg's Law with the following formula:

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$$2d_{hkl} \sin \theta_B = n\lambda \quad (6.1)$$

where d_{hkl} is the spacing of lattice planes with Miller indices (hkl) and θ_B is the corresponding Bragg angle. As shown in Fig. 6.3, when a monochromatic X-ray beam with wavelength λ is projected onto a crystalline material at an angle θ_B , diffraction occurs only when the distance traveled by the rays reflected from successive planes differs by a complete number n of wavelengths. By varying the angle θ_B , the Bragg's Law condition is satisfied by different spacing d_{hkl} in different materials. Plotting the angular positions and intensities of the resultant diffracted peaks of radiation produces a pattern which is called rocking curve. In artificial MQWs, X-ray diffraction patterns are dominated by the interference among the periodically repeated layer stack. Besides the Bragg peak of substrate, a series of so-called satellites are observed, which are a set of subsidiary maximum with the same angular spacing $\Delta\theta$.

Figure 6.3. Bragg's Law

The angular separation $\Delta\theta_0$ between the zero-order satellite peak and the Bragg peak of the substrate in X-ray rocking curve gives the average mismatch of the epitaxy-layers along the growth axis, which can be described by [6.12]

$$\frac{\Delta d}{d_{Sub}} = \frac{\Delta\theta_0}{\tan \theta_B} \quad (6.2)$$

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where θ_B ($\approx 33^\circ$) is the Bragg angle for the (004) reflection of GaAs substrate, d_{Sub} is the lattice spacing of the GaAs substrate (004) diffraction. Note that this formula is derived by simplified diffracting Bragg's law and small angle approximation for $\Delta\theta_0$. The lattice mismatch of the epitaxy-layers along the growth axis $\Delta d / d_{Sub}$ can be computed by [6.13]

$$\frac{\Delta d}{d_{Sub}} = - \left(\frac{C_{11} + 2C_{12}}{C_{11}} \right) \left(\frac{a_0(x, y) - a_{Sub}}{a_{Sub}} \right) \quad (6.3)$$

where C_{11} and C_{12} are the elastic stiffness constants obtained by interpolating from the values corresponding to the binary compound, $a_0(x, y)$ is the lattice constant of the unstrained cubic $\text{In}_{1-y}\text{Ga}_y\text{As}_{1-x}\text{N}_x$ well layer, a_{Sub} is the lattice constant of the GaAs substrate.

The angular spacing $\Delta\theta$ between the satellite peaks is a measure of the MQW period length, that is the sum of the InGaAsN well and GaAs barrier thickness. The period Λ of the MQW structures is straightforward determined from the $\Delta\theta$ through the following expression [6.14],

$$\Lambda = \frac{\lambda}{2\Delta\theta \cos(\theta_B + \Delta\theta_0)} \quad (6.4)$$

where $\lambda = 1.54056 \text{ \AA}$ for the $\text{Cu}_{K\alpha 1}$ line.

For a perfect superlattice-like MQW structure with homogeneous composition in individual layers and ideally abrupt interfaces, the number of satellites and their intensities are dominantly dependent on the difference in the lattice

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parameters and structure factors. A larger difference among the lattice parameters as well as the structure factors in individual layers results in a larger number of satellites and higher peak intensities. For a real MQW structure, the number of satellites and their peak intensities are strongly degraded by the imperfections of interfaces, the compositional inhomogeneity and the fluctuations from period to period.

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Figure 6.4. XRD (004) measurement results of three $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}/\text{GaAs}$ MQW samples with well widths of (a) 2 nm, (b) 3 nm and (c) 4 nm, respectively. The simulation curves shown with dash curves were shifted vertically for clarity.

Figure 6.4 shows the (004) GaAs Bragg reflection rocking curves in the $\omega/2\theta$ geometry measured using Philips X'Pert Material Research Diffractometer [6.15] for the three $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}/\text{GaAs}$ MQW samples. In each figure the solid curve is the experimental result, and the dash curve is the simulation based on the dynamical X-ray theory. The excellent agreement between them confirms the exact structural and composition parameters. The greatest peak at about 33° is from the GaAs substrate, and the satellite peaks are from the MQW structure. It can be seen that the well-defined periodic satellite peaks over the 10^{th} order can be identified, indicating good layer periodicity. The sharpness of the peaks represents the interface abruptness of the strained MQW. The angular spacing between the satellite peaks is directly determined by the period of the MQW. It is commonly assumed that the zero-order satellite peak is either the strongest satellite peak or the one next to the substrate peak. However, this is not the real case for largely strained MQW structures. Based on Eqs. (6.2) and

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(6.3), we can estimate the angular separation $\Delta\theta_0$ between the zero-order satellite peak and the Bragg peak of the GaAs substrate. The calculated results are shown in Table. 6.2. It can be seen that the derived $\Delta\theta_0$ is about -1.44° (on the left side of substrate peak $P0_{\text{GaAs}}$) for the three $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}/\text{GaAs}$ MQWs, which is purely determined by the strain and the Bragg diffraction angle of substrate (θ_B). In Figure 6.4, $P0_{\text{GaAs}}$ and $P0_{\text{InGaAsN}}$ show the positions of GaAs substrate (004) diffraction and the zero-order satellite peak, respectively. It is independent on the MQW structural periods. The different structural periods due to different well widths result in different angular spacing $\Delta\theta$ between the satellite peaks that can be obtained directly in Figure 6.4. The results are 504, 486 and 468 sec. for S1, S2 and S3, respectively, as shown in Table 6.2. Based on the values of $\Delta\theta_0$, $\Delta\theta$ and θ_B we can derived the MQW structural period Λ using Eq. (6.4). The computed results are 37.1, 38.4 and 39.8 nm for S1, S2 and S3, respectively, (Table 6.2 Column 6), which are very close to the designed periods of 37, 38 and 39 nm (Table 6.1).

Table 6.2. Structure parameters obtained from the XRD rocking curves in Fig. 5.4

Samples	θ_B (deg.)	$\Delta d / d_{\text{InP}}$	$\Delta\theta_0$ (deg.)	$\Delta\theta$ (sec.)	Calculated Period (nm)	Designed Period (nm)
S1	33.03	-0.0388	-1.445	504	37.1	37
S2	33.03	-0.0388	-1.445	486	38.4	38
S3	33.01	-0.0388	-1.444	468	39.8	39

Another InGaAsN/GaAs MQW sample (S4) has also been grown and characterized. The schematic structure is shown in Figure 6.5. This sample

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consists of 20 periods of 2.3 nm thick Si-doped $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.99}\text{N}_{0.01}$ quantum wells with a Si concentration of $1.5 \times 10^{18} \text{ cm}^{-3}$ and 14.5 nm wide undoped GaAs barriers. All layers in S4 were grown at the same temperature (460°C). The MQW structure was sandwiched between a $0.7 \mu\text{m}$ bottom contact layer and a $0.7 \mu\text{m}$ cap layer, both doped with Si of $2 \times 10^{18} \text{ cm}^{-3}$. The shutter of the ignited N plasma source was closed but not the valve during growth of barrier layers, which causes a composition of about 0.002 into the barriers. The measured (004) GaAs Bragg diffraction rocking curves in the $\omega/2\theta$ geometry is shown in Fig. 6.6. The annealed sample (10 min in-situ annealing at 600°C) shows relatively clear periodic satellite peaks up to the 7th order, likely due to removal of some N related defects.

Figure 6.5. Schematic structure of the $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.99}\text{N}_{0.01}/\text{GaAs}$ MQW (S4) with 2.3 nm well width and 14.5 nm barrier width.

Figure 6.6. The XRD (004) rocking curve of the $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.99}\text{N}_{0.01}/\text{GaAs}$ MQW sample (S4) with 2.3 nm well width and 14.5 nm barrier width. The solid and long dash curves show measured results for as-grown and annealed samples, respectively. The short dash curve show the simulation result based on the dynamical X-ray theory.

6.3 Photoluminescence study

Photoluminescence (PL) has been widely used to study fundamental recombination processes as well as the material quality of semiconductor bulk or epitaxial films. Radiative recombination takes place when the semiconductor is under a nonequilibrium condition. Excess electron-hole pairs can be created by external excitation (photons) to cause departure from equilibrium, and then these excess carriers will recombine to return to equilibrium and release photoluminescence at the same time. Therefore, we can get the information about the bandgap of the semiconductor materials from the PL spectrum.

For PL characterization, a chopped 514.5 nm Ar^+ laser line was used for excitation. Samples were cooled down generally in a cryostat or in liquid nitrogen. The luminescence signals from the sample passed through a Spex 0.75 m monochromator and were then detected by a Ge photodetector using a phase-

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sensitive lock-in amplifier system. The schematic diagram of the PL system is shown in Figure 6.7.

Figure 6.7. Schematic PL measurement system

Figure 6.8 shows the measured 77 K PL spectra of samples S1, S2 and S3. It can be seen that the emission peak shows an obvious redshift with the increase of well width. For S1 with 2 nm wide wells, the PL peak is at 1236 meV with a full width at half maximum (FWHM) of 62 meV. For S2 with 3 nm wide wells, the PL peak redshifts to 1187 meV with a FWHM of 50 meV. For S3 with 4 nm wide wells, the PL peak shifts further to 1079 meV with a FWHM of 54 nm. The clear and sharp PL peaks for the three dilute-N MQWs indicate good material quality. It is known that a post-growth rapid thermal annealing (RTA) is required usually for InGaAsN based quantum wells to ameliorate the poor crystal quality and improve the material optical properties. However, all the three as-grown samples show good PL performances without a post-growth annealing. This is likely because that the cap layer was grown at 590 °C as mentioned in Section 6.2, which resulted in an equivalent anneal process for the

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underlying layers although the MQW structure was grown at lower temperature (440 °C).

Figure 6.8. PL spectra measured at 77 K for the three $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}/\text{GaAs}$ MQW samples with well widths of 2, 3 and 4 nm respectively.

Figure 6.9. Calculated energy dispersions of conduction and valence subbands for the three $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}/\text{GaAs}$ MQW samples with well widths of 2, 3 and 4 nm respectively.

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Figure 6.9 shows the calculated energy dispersions of the first three conduction subbands (E1–E3) and valence subbands (HH1, HH2 and LH1) along [100] and [110] in-plane wave vector directions. The bulk valence-band edge of InGaAsN is regarded as zero energy position. It can be seen that for the 2 nm well width (S1), both the excited states E2 and E3 are continuum states closely to each other. E2 becomes a quasi-bound state and a bound state at the 3 and 4 nm well widths (S2 and S3), respectively. The large compressive strain for well layers, about -3.88% mismatch along the growth axis, splits the fourfold degenerate multiplet at the valence-band edge into a pair of degenerate doublets, HH1 and LH1, which are of spin degeneracy. Consequently, LH1 is pushed down to be about 200 meV lower than HH1. The calculated energies of the conduction and valence subband states shown in Fig. 6.9 at the zone center ($k_x = 0$) are listed in Table 6.3. The calculated energy separations between the ground state E1 in conduction-band and HH1 in valence-band are 1238.6, 1168.0 and 1105.3 meV for S1, S2 and S3, respectively, which are close to the measured PL peak energies shown in Fig. 5.8. The small deviations (<30 meV) between the theoretical and experimental results mainly come from the approximate estimation of material and structure parameters such as conduction-band offset, well width, N effect factor, etc.

Table 6.3. Calculated subband energies at $k_x = 0$ for samples S1, S2 and S3.

E1-HH1 is also listed to compare with measured PL peak energy.

	LH1	HH2	HH1	E1	E2	E3	E1-HH1 (meV)	Measured PL peak (meV)
S1	-132.6	-121.1	-28.2	1210.4	1391.3	1400.0	1238.6	1236
S2	-121.3	-111.1	-1.4	1167.6	1373.3	1392.5	1168.0	1187
S3	-101.3	-77.4	16.5	1121.8	1304.9	1391.0	1105.3	1079

6.4 Interdiffusion study

A post-growth rapid thermal annealing (RTA) is often necessary for InGaAsN-based quantum wells to ameliorate the poor crystal quality with the incorporation of nitrogen and improve the material properties. It has been commonly observed that InGaAsN/GaAs quantum wells show emission wavelength blueshifts after RTA processing [5.1–5.5, 6.16–6.19, 3.5]. However, the detailed fundamentals behind the blueshift phenomenon remain under debate, and several possible mechanisms have been proposed. For example, Sun *et al.* and Kageyama *et al.* suggested In-Ga interdiffusion [5.1–5.3], Albrecht *et al.* suggested N diffusion out of the wells [6.16], Pan *et al.*, Li *et al.* and Spruytte *et al.* observed both In and N diffusions [6.17–6.19], and Kurtz *et al.* and Duboz *et al.* supported the change in N-bonding configuration from a Ga-rich to an In-rich environment [3.5, 5.4]. In addition, Oye *et al.* have investigated In intra- and inter-diffusion mechanisms in InGaAs/GaAsN quantum wells with RTA and found that a lot of N atoms diffused from the GaAsN barriers into the InGaAs wells [5.5].

In this subsection, the RTA-induced interdiffusion in the $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}/\text{GaAs}$ MQWs is investigated. The samples were cleaved into $\sim 3 \times 3$ mm squares and then coated with 120 nm thick SiO_2 cap layers deposited by a PECVD system to prevent surface damage. The RTA was performed in a JETSTAR 100 system for 60 seconds at temperatures of 650, 700, and 750 °C, respectively. During thermal processing, the samples were kept in flowing nitrogen ambient for protection. For the PL measurement, a 532

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nm laser was used as the exciting source and an InGaAs photodetector was used to detect the PL signal.

Figure 6.10. PL spectra measured at 77 K for (a) S1 and (b) S3, with different thermal annealing conditions: (1) as-grown, (2) 650 °C, (3) 700 °C and (4) 750 °C . The annealing time is 60 s.

Figure 6.10 shows measured PL spectra of S1 and S3 under different annealing conditions. For S1, the as-grown sample exhibits an emission peak at 1236 meV. It shifts to 1337.6, 1419.6 and 1441.6 meV after RTA for 60 s at 650 °C, 700 °C and 750 °C, respectively. For S2, the as-grown sample shows an emission peak

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at 1078.9 meV. It shifts to 1173.1, 1316.5 and 1342.6 meV after annealing for 60 s at 650 °C, 700 °C and 750 °C, respectively. It can be seen that the blueshifts increase rapidly with the annealing temperature and then becomes relatively stable when the temperature is above 700 °C. The maximum blueshifts of 205.7 meV and 263.7 meV were observed with RTA processing at 750 °C for S1 and S2, respectively. To our knowledge, they are the largest blueshifts reported so far for InGaAsN-based quantum wells.

Figure 6.11. Composition profiles of Ga and In measured by SIMS for sample S3 with different RTA conditions: (a) as-grown, (b) 650 °C, (c) 700 °C and (d) 750 °C.

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Figure 6.12. Composition profiles of N measured by SIMS of sample S3 with different RTA conditions: (a) as-grown, (b) 650 °C, (c) 700 °C and (d) 750 °C.

To find the origin of the great blueshifts in the PL spectra, an analysis of the composition profile was performed using secondary ion mass spectrometry (SIMS). Figures 6.11 and 6.12 show the distributions of In, Ga and N along the growth direction with sample S3 for different annealing conditions. The non-square composition profile of the as-grown $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}/\text{GaAs}$ MQW is mainly due to the limited depth resolution and the ion beam mixing effect of SIMS. Although the composition profiles in SIMS are relatively rough, they clearly revealed that not only In-Ga interdiffusion but also N diffusion out from the wells have taken place. The peak In composition in the InGaAsN wells is about 32% in the as-grown sample, while it reduces to about 23%, 21% and 19% for samples annealed at 650, 700 and 750 °C, respectively. The diffusion of N is even more severe. Its average composition in the InGaAsN wells is about 1.6% in the as-grown sample. The peak composition decreases quickly to

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about 1.1%, 0.62% and 0.61% in the samples annealed at 650, 700 and 750 °C, respectively. We can also observe that the variations of In and N diffusions with increasing RTA temperature show different trends. Significant In-Ga interdiffusion occurs at 650 °C. When the temperature increases to 700 and 750 °C, the In-Ga interdiffusion shows little increase. However, the diffusion of N increases rapidly with the increase of temperature from 650 to 700 °C and slows down at 750 °C. It indicates that the N diffusion tends to dominate at higher temperatures in the InGaAsN/GaAs MQWs. Upon RTA, the SIMS results show that a lot of N atoms diffuse out from the InGaAsN wells into the GaAs barriers at higher anneal temperatures. This is consistent with the report by Pan *et al.* [6.17], suggesting that the interior defects generated in the growth of dilute-N material have assisted the diffusion of N and In atoms greatly.

It can be seen that the observed diffusion behaviors by SIMS in Figs. 6.11 and 6.12 show good consistence with the PL blueshifts in Fig. 6.10 for different annealing temperatures. The blueshift in the annealed sample at 650 °C should result from moderate In and N diffusions. The large increase of blueshift in the annealed sample at 700 °C is mainly due to the severe N diffusion. The slight increase of blueshift when the RTA temperature is increased further to 750 °C can be explained by the saturation of In and N diffusions.

The narrow well widths in our InGaAsN/GaAs MQWs enhance the RTA-induced blueshifts, as the In and N atoms can diffuse faster out of the narrower wells. To account to for this we employ a classic expression to model the diffused composition profile in the quantum well as follows [5.6]

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$$x'(z) = \frac{x}{2} \left[\operatorname{erf} \left[\frac{L_w + 2z}{4L_d} \right] + \operatorname{erf} \left[\frac{L_w - 2z}{4L_d} \right] \right] \quad (6.5)$$

where x is the as-grown composition, z is the distance in the growth direction, L_w is the well width before interdiffusion and L_d is the diffusion length. Figures 6.13(a) and (b) show the calculated In composition profiles at different diffusion lengths for 2 and 4 nm as-grown wide wells, respectively. It can be seen that at $L_d = 1$ nm, about half of the In content diffuses out of the original 2 nm well region, and about 31% of the In content diffuses out of the original 4 nm well region. At $L_d = 2$ nm, the diffusion ratios increase to about 73 % and 52 % for 2 and 4 nm well widths, respectively. Therefore, a larger increase of the effective well bandgap should occur in the narrower well at the same diffusion length, resulting in a more evident PL blueshift. The observed blue-shifted PL peak at 1441.6 meV for S1 after RTA at 750 °C is very close to the GaAs barrier bandgap at 77 K. Note that S1 showed a larger blueshift compared to S2 with RTA for 650 °C, but not for 700 and 750 °C. This is because that the ground state in as-grown S1 has already been promoted to a very high energy level with the very narrow well width (2 nm), and hence the possible maximum blueshift is limited.

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Figure 6.13. Calculated dependence of In composition profile with diffusion length L_d in the $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.994}\text{N}_{0.016}/\text{GaAs}$ quantum wells with well widths of (a) 4 nm and (b) 7 nm, respectively.

It is favorable to do a detailed theoretical analysis about the dependence of quantum well emission peak on the composition diffusion to account for the experimental results. Two important facts should be considered. One is the complex quantum well potential profile with the interdiffusion, and the other is the existence of high-lying N resonant state. Some theoretical work about the interdiffusion effects in InGaAsN/GaAs quantum wells has been reported [6.20, 6.21]. Chan *et al.* have investigated the group-III interdiffusion using a one-dimensional Schrödinger equation to calculate the electron and hole subband energies [6.20]. Dang *et al.* have also done a theoretical study on the In-Ga interdiffusion using an 8-band $\mathbf{k}\cdot\mathbf{p}$ model [6.21]. Here we employed the 10-band $\mathbf{k}\cdot\mathbf{p}$ model combined with the envelope function Fourier expansions to calculate the eigen-states in interdiffused InGaAsN/GaAs quantum wells.

We select S3 to do the calculation under different annealing conditions. The diffusions of In and N contents are characterized using Eq. (6.5), which in turn causes the variations of the quantum well potential profile as well as the strain

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distribution. By fitting theoretical peak compositions upon interdiffusions with Eq. (6.5) to the measured SIMS results in Figs. 6.11 and 6.12, the In diffusion lengths are estimated to be 1.3, 1.5 and 1.7 nm, and the N diffusion lengths are estimated to be 1.3, 2.8 and 2.9 nm, for annealing at 650, 700 and 750 °C, respectively.

Figure 6.14. Calculated energy dispersions of conduction and valence subbands in S3 with estimated In and N diffusion lengths: (a) as-grown, (b) $L_d(\text{In}) = 1.3$ nm and $L_d(\text{N}) = 1.3$ nm for RTA at 650 °C, (c) $L_d(\text{In}) = 1.5$ nm and $L_d(\text{N}) = 2.8$ nm for RTA at 700 °C, and (d) $L_d(\text{In}) = 1.7$ nm and $L_d(\text{N}) = 2.9$ nm for RTA at 750 °C.

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Figure 6.15. Comparison of the calculated E1-HH1 transition energies and the experimental PL emission peaks of S3 under different annealing conditions.

Figure 6.14 shows the calculated energy dispersions of the conduction and valence subbands as a function of k_i in [100] and [110] directions for S3. The lowest three states are displayed in the figure. The separation between the ground state E1 in the conduction-band and the ground state HH1 in the valence-band at the zone center ($k_i=0$) is regarded as theoretical PL emission energy. The calculated E1-HH1 transition energies for different RTA conditions are plotted in Fig. 6.15. The experimental PL emission energies are also shown for comparison. It can be seen that the computed results are 1095, 1186, 1304 and 1328 meV for the as-grown and annealed samples at 650, 700 and 750 °C, respectively. A good agreement of the theoretical and experimental results is achieved. The small difference (less than 20 meV) is likely due to the approximate estimation of the diffusion profiles using Eq. (6.5). The theoretical results confirm the impact of the In and N diffusions on the emission energies in our samples. The In-Ga interdiffusion increases the well bandgap directly, and the severe diffusion of N out of the well diminishes the band-anticrossing effect, resulting in an obvious blueshift in the PL.

6.5 Intersubband absorption

The FTIR absorption spectra of the InGaAsN/GaAs samples were measured by a Perkin-Elmer spectrometer at room temperature. The samples were polished into multi-reflection waveguides with 45° input and output facets in order to enhance the net absorption. A polarizer was to select the polarization state of incident IR to test the relationship between absorption and polarization state. Figure 6.16 shows the multipass waveguide geometry applied in the FTIR measurement for intersubband absorptions in MQWs. In the case of 0° -polarization, the incident IR contains both TM and TE components, because the photoelectrical field is not parallel or vertical to the quantum well plane, as shown in Fig. 6.16(a). However, in the case of 90° -polarization, the incident IR only contains the TE component, i.e. the photon electrical field parallel with the quantum well plane absolutely, as shown in Fig. 6.16(b).

(a) Incident IR beam with 0° polarization (TM+TE state).

(b) Incident IR beam with 90° polarization (TE state)

Figure 6.16. The multipass waveguide geometry applied to measure intersubband absorption of MQWs.

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Figure 6.17. Measured FTIR transmittance spectra of the $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.99}\text{N}_{0.01}/\text{GaAs}$ MQW sample (S4).

Figure 6.18. FTIR absorption spectra of S4 with baseline correction.

Figure 6.17 shows the FTIR transmittance spectra of the $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.99}\text{N}_{0.01}/\text{GaAs}$ MQW sample (S4) with 2.3 nm well width and 14.5 nm barrier width, measured at 0° , 45° and 90° polarizations. Figure 6.18 shows the absorption spectra after baseline correction. The broad spectral width reflects the contribution from comparable B-to-C ISBTs in the narrow wells. It is interesting to observe that the sample has maximum absorption peaking at

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about 9.6 μm for the 90°-polarized light, while has smaller absorption for the 0°-polarized light. This observation of the strong TE-polarized absorption is contrary to the well-known fact that TM-polarized intersubband absorptions should be dominant always. To double confirm the occurrence of TE-polarized absorption in the $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.99}\text{N}_{0.01}/\text{GaAs}$ MQW, the FTIR transmittance spectra for normal-incident IR has also been measured (Fig. 6.19). This was done by putting a large area sample across the optical path perpendicularly. A clear absorption band ranging from about 8 to 12 μm was observed, indicating that the purely TE-polarized light in the normal-incident geometry can be absorbed significantly by this InGaAsN/GaAs MQW sample.

Figure 6.19. Measured absorption spectra of S4 for normal incident IR.

Some work has been done to understand the possible reasons of the strong TE-polarized absorption:

- 1) A theoretical analysis on ISBTs in S4 was done based on the sixteen-band **k·p** method. The calculated squared optical transition matrix elements as a function of k_x are shown in Fig. 6.20. All the excited states (E2, E3...) are

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continuum states in this structure. It can be seen that the TE-polarized transitions do show considerable rates at finite k_t . Particularly, the TE-polarized E1→E2 transition goes up rapidly at $k_t > 2 \cdot (2\pi/L)$, where L is the period width of the MQW, and finally becomes larger than the TM-polarized E1→E2 transition at $k_t \sim 5.4 \cdot (2\pi/L)$. Figure 6.21 shows the theoretical absorption spectra for the two polarizations. The Fermi level is calculated to be at 1187 meV based on Eq. (2.41), which is very close to the edge of E1 (~1189 meV). The calculated peak absorption coefficient for TE polarization is about 15% of that for TM polarization (118 vs. 792 cm⁻¹). Because of the presence of BAC effect in the dilute-N quantum wells, it is possible that the actual Fermi level is even higher. If we assume that the doping concentration is high enough to push up the Fermi level above E1 and hence higher k_t states in E1 could be occupied significantly, an even stronger TE-polarized absorption may be achieved. In this case, the many-body effects like Coulomb interaction induced collective excitations and phase space filling cannot be ignored, which goes beyond the discussion scope of this thesis and some future work is needed. It should also be indicated that the observable TE absorptions in n-type quantum wells based on conventional III-V semiconductors have been reported by several groups, although the underlying physical mechanism remained a subject of ongoing debates. [6.33–6.38] In most cases the doping concentrations are high compared to what is normally used in QWIPs to maintain lower dark currents [6.33-6.37]. For instance, L. H. Peng *et al.* have observed comparable TM and TE absorptions in InGaAs/(In)AlAs quantum wells with a doping concentration of 10¹⁹ cm⁻³ [6.33].

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- 2) Another possible contribution is from the unevenness and imperfection of the well layers in S4. The cross-section image of the MQW layers obtained by transmission electron microscopy (TEM) is shown in 6.22. It does show obvious roughness of well-barrier interfaces and some local “bumps” in the thin well layers. This would induce overestimation of TE-polarized absorption in measurement, since the incident infrared is not really “TE-polarized” with respect the uneven and bumped well layers.

Figure 6.20. Squared optical transition matrix elements as a function of k_t in [110] direction for ISBTs in S4, calculated using the sixteen-band $\mathbf{k}\cdot\mathbf{p}$ method.

Figure 6.21. Calculated absorption spectra of S4 based on the sixteen-band $\mathbf{k}\cdot\mathbf{p}$ method.

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Figure 6.22. TEM image showing the MQW cross-section of S4.

6.6 Summary

In this chapter, the growth and characterization of a few $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}/\text{GaAs}$ and $\text{In}_{0.7}\text{Ga}_{0.3}\text{As}_{0.99}\text{N}_{0.01}/\text{GaAs}$ MQWs with narrower well widths have been reported.

The HRXRD measurement confirmed the good layer periodicity, the interface abruptness, and the consistence of designed structural and composition parameters with the actual values in the samples. The clear PL spectra at 77K have been observed, which are consistent with the theoretical results.

Interdiffusion in the MQW samples has been studied. RTA at different temperatures were performed for the $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}/\text{GaAs}$ MQW samples with well width of 2 and 4 nm, respectively, and maximum blueshifts of 206 and 264 meV in the PL peak were observed. SIMS spectrometry has

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shown that both great In-Ga and N-As interdiffusions play key roles for the large blueshifts. The significant In-Ga interdiffusion took place at about 650 °C while the N diffusion at about 700 °C. The experimental result is in good agreement with the theoretical analysis for subband structures with the diffusion modeling.

The intersubband absorptions in the 8–12 μm infrared window in S4 was observed using FTIR. Some work has been done to understand the possible root cause of the strong TE-polarized absorption. The theoretical calculation based on the sixteen-band $\mathbf{k}\cdot\mathbf{p}$ model shows the possibility of strong TE-polarized ISBTs at high k_z with high doping concentrations. It is pending future work to calculate the actual TE-polarized absorptions in heavily doped quantum wells with an incorporation of the many-body effects. Another possible reason is the unevenness of the well layers in S4, as shown in the TEM cross-section image.

Chapter 7 InSb_{1-x}N_x alloys and infrared detection

7.1 Introduction

The dilute-N correlated physics enables the bandgap of III-V alloys to be tuned to particular energies for some advanced applications. It is a good idea to introduce dilute-N into narrow-bandgap semiconductor materials to extend the detectable band to even longer wavelength range. The binary compound InSb has been widely utilized for photodetection in the 3–5 μm MWIR window. It is possible to redshift its cutoff wavelength to the 8–14 μm LWIR window if InSb_{1-x}N_x alloys can be made.

In fact, a limited number of studies about the growth and characterization of dilute InSb_{1-x}N_x alloys have been reported in recent years [7.1–7.8]. The growth and characterization of InSb_{1-x}N_x alloys was first reported in 2000 [7.1]. Murdin *et al* have revealed that the Auger recombination rate, which is the limiting factor in detector sensitivity and light emitting diode (LED) efficiency, is only about one third of that of the equivalent band gap MCT due to the high electron mass and conduction band nonparabolicity of the InSbN alloys [7.2]. The increase of electron effective mass in InSb_{1-x}N_x alloys has also been observed by cyclotron resonance [7.3]. Veal *et al* have presented an experimental evidence of negative bandgap occurrence in a thin InSbN layer fabricated by low-energy N implantation using high-resolution electron-energy-loss spectroscopy [7.4]. Merrick *et al* have observed ~10% redshift of the InSbN bandgap at room temperature using a Fourier transform infrared (FTIR) based photo-modulated

transmission spectroscopic technique [7.5, 7.6]. However, InSb_{1-x}N_x-based photodetection has not been reported so far to our knowledge.

In this chapter, both theoretical and experimental studies on InSb_{1-x}N_x alloys will be presented. Firstly, the energy band structures, and inter- and intra-band optical transitions are analyzed based on the 10-band **k·p** model. Then the growth and characterization of InSb_{1-x}N_x alloys, and the fabrication and measurement of InSb_{1-x}N_x photodetectors are reported in detail. Red-shifted infrared detection ability up to ~11 μm is demonstrated by photocurrent measurements at low temperature.

7.2 Theoretical study on InSb_{1-x}N_x

In this section, the energy band structures and their changes with N content in bulk InSb_{1-x}N_x alloy will be discussed firstly, to look into the bandgap narrowing resulted from dilute-N incorporation. It is significant to study quantitatively the possible redshift of cutoff wavelength as well as infrared photodetection band in the InSb_{1-x}N_x alloy. Then the InSb_{1-x}N_x/InSb quantum structures will be analyzed based on the theoretical calculations on both interband and intra-conduction band transitions. Some significant physical properties will be addressed.

7.2.1 InSb_{1-x}N_x bulk bands

The energy band structure of InSb_{1-x}N_x with small x is calculated using the ten-band **k·p** model developed for (In,Ga)As_{1-x}N_x in Chapter 3. The ten-band **k·p** Hamiltonian can be expressed simply as

$$\mathbf{H} = \begin{bmatrix} \mathbf{H}_{p\bar{s}} & \mathbf{H}_{p\bar{s}-N}^* \\ (8 \times 8) & (8 \times 2) \\ \mathbf{H}_{p\bar{s}-N} & \mathbf{H}_N \\ (2 \times 8) & (2 \times 2) \end{bmatrix} \quad (7.1)$$

where $\mathbf{H}_{p\bar{s}}$ is the 8-band $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian [7.10], $\mathbf{H}_N$ is the N-band Hamiltonian, and $\mathbf{H}_{p\bar{s}-N}$ consists of the coupling terms of two degenerate N bands (NB) with two s -like conduction-bands (CB) and six p -like valence-bands (VB). The energy of the localized N resonant level is given by $E_{N0} - \alpha_N x$, where $\alpha_N x$ describes the decrease of effective N level energy with the increase of N content x . The band-anticrossing effect between N-band and conduction-band is described as $\beta\sqrt{x}$. The interaction of N-band and valence-band is assumed to be negligible. In the calculation, the bandgap of InSb is assumed to be 235 and 180 meV for low temperature (0 K) and room temperature (300 K), respectively. The temperature dependence of InSb energy bandgap is

$$E_g(T) = E_g(0) - aT^2/(b+T) \quad (7.2)$$

where $a = 0.6 \text{ meV} \cdot \text{K}^{-1}$ and $b = 500 \text{ K}$. E_{N0} is assumed to be 470 meV above the InSb host conduction band edge, $\alpha_N = 2770 \text{ meV}$, and β is assumed to be 2200 meV [7.3, 7.4]. Basic InSb material parameters used in the calculation are listed in Table 7.1.

Table 7.1. Basic InSb material parameters used in the calculation

Parameter	Value
Γ bandgap (eV)	0.180 (300 K) 0.235 (0 K)
Spin-orbit splitting energy Δ (eV)	0.81
Optical matrix parameter $E_p = 2P_0^2 / m_0$ (eV)	23.3
Luttinger parameter γ_1	6.98
Luttinger parameter γ_2	2.06
Luttinger parameter γ_3	2.93
Elastic stiffness C_{11} (10 GPa)	68.47
Elastic stiffness C_{12} (10 GPa)	37.35
Deformation potentials a_c (eV)	-6.94
Deformation potential a_v (eV)	-0.36
Deformation potential b (eV)	-2.0

Figure 7.1 shows the calculated InSb_{1-x}N_x bulk energy bands at 300 K for three different N contents (N_N), 0, 1% and 2%. The valance-band edge is regarded as zero energy position. It can be seen that in N-free material the separation of electron band (EB) and heavy and light hole bands (HH and LH) at the zone center ($k_t = 0$) defines the basic InSb bandgap of 180 meV, which is interpreted to an approximate cutoff optical absorption wavelength of 6.9 μm . When dilute-N is introduced, the interaction of localized N resonant band and the InSb host conduction-band results in splitting of the electron state into two subbands, E_- and E_+ (Figs. 7.1(b) and (c)). At $N_N=1\%$, the separation of E_- and HH (or LH) decreases to 89.2 meV. It means that the cutoff optical absorption wavelength is red-shifted to about 13.9 μm . One can see that the curvature of E_- decreases compared to the electron state E in Fig. 7.1(a), indicating an increased electron effective mass upon N incorporation. At $N_N=2\%$, E_- lowers further to about 15 meV and becomes very close to the valance-band. If the N composition is

increased further, E_v is anticipated to go below valence-band edge to form a negative bandgap structure (a semi-metallic alloy). Actually, the negative bandgap phenomenon has been observed and confirmed in InSb_{0.94}N_{0.06} alloy by high-resolution electron-energy-loss spectroscopy [7.4].

Figure 7.1. Calculated bulk energy band structures along [100] and [110] k_t direction of InSb_{1-x}N_x with N composition x of (a) 0, (b) 0.01 and (c) 0.02, respectively, at room temperature (300 K).

In order to look into the impact of N content on E_- and E_+ , we plot the E_- and E_+ band edge energies (at $k_t = 0$) as a function of N_N ranging from 0 to 3% at temperatures of 30 and 300 K, respectively, in Figs. 7.2(a) and (b). The N-band energy is also shown as a reference. It can be seen that E_- energy decreases at an approximate rate of 80 meV per 1% N composition increase. Consequently the bandgap at 30 K decreases to 0 when $N_N > 3\%$, and the bandgap at 300 K decreases to 0 when $N_N > 2.2\%$. Therefore, it can be derived that if we want to red-shift the cutoff optical absorption wavelength to about 10 μm , the central of LWIR window, the incorporated N compositions should be 1.3% at low temperature (30 K), and 0.6% N at room temperature (300 K), respectively.

Figure 7.2. The E₊ and E₋ band edges and N level (E_N) in InSb_{1-x}N_x as a function of N composition at (a) 30 K and (b) 300 K, respectively, calculated using the ten-band **k·p** model

7.2.2 InSb_{1-x}N_x/InSb quantum well structures

It is possible to obtain an equivalent quantum well potential by epitaxially growing periodic InSb_{1-x}N_x/InSb thin films on an InSb substrate. Actually, an InSb_{1-x}N_x/InSb superlattice with 10.5 μm optical emission wavelength has been demonstrated using molecular beam epitaxy (MBE) techniques [7.7]. Here we

will do a theoretical investigation on the inter- and intra-band transitions in InSb_{1-x}N_x/InSb quantum well structures based on the 10-band **k**·**p** model.

Figure 7.3. Band edge lineup of the InSb_{0.99}N_{0.01}/InSb system at room temperature. The energy unit in the figure is meV.

The band lineup of the InSb_{0.99}N_{0.01}/InSb system is shown in Fig. 7.3. Due to the interaction of the conduction band and the high-lying N band with dilute N incorporated in the host InSb material, two subbands E₊ and E₋ will form associated with the band anti-crossing (BAC) effect. Since E₋ is 91 meV below the conduction band of the barrier InSb material (89 vs. 180 meV), an effective quantum well is formed.

Figures 7.4(a) and (b) show the calculated energy dispersions of conduction and valence subbands in an InSb_{0.99}N_{0.01}/InSb and an InSb_{0.985}N_{0.015}/InSb MQW structures, respectively. The InSbN well width is assumed to be 14 nm, and the InSb barrier width is assumed to be 25nm. The first two subbands in conduction-band (E1 and E2) and valence-band (H1 and H2) are shown. It can

be seen that these subband states appear to be minibands due to relaxation of quantum confinement in the growth direction, especially in the narrow-bandgap material with an small electron effective mass ($\sim 0.0135 m_0$ for InSb). It can be seen that the separation of conduction- and valence- ground states is about 125 meV at 1% N composition, corresponding to a cutoff wavelength of 9.9 μm . It is reduced further to about 98 meV when N composition increases to 1.5%, corresponding to a cutoff wavelength of 12.6 μm .

Figure 7.4. Calculated subband dispersions of (a) an InSb_{0.99}N_{0.01}/InSb MQW and (b) an InSb_{0.985}N_{0.015}/InSb MQW with 14 nm wide InSbN wells and 25 nm wide InSb barriers. The first two states are displayed.

To study the interband (between valence-band and conduction-band) and intraband (within conduction band) transition rates, we select the InSb_{0.99}N_{0.01}/InSb MQW structure with 14 nm well width and 26 nm barrier width to carry out the computation. Figure 7.5 shows the calculated optical transition matrix elements and absorption spectra of H1→E1 transition for this structure. Both in-plane (TE) and normal-to-plane (TM) polarized transitions

are plotted for comparison. It can be seen that the TE-polarized transition is over 3 times larger than the TM-polarized transition. This is consistent with the well-know fact that interband transitions are dominated generally by TE mode. The corresponding TE and TM absorption spectra peak at 9.3 and 9.1 μm , respectively, which are within the 8-12 μm LWIR window.

Figure 7.5. Calculated (a) squared optical transition matrix elements vs. plane wave vector k_t and (b) absorption coefficients vs. optical wavelength of interband H1→E1 transition for TE and TM polarizations, respectively, for the InSb_{0.99}N_{0.01}/InSb MQW.

Figure 7.6 shows the calculated intra-conduction band optical transition results of the InSb_{0.99}N_{0.01}/InSb structure. Only TM-polarized transitions are displayed since the TE-polarized ones are much weaker. It is found that the squared optical transition matrix elements show large amplitudes. For instance, the value is 8.9 at $k_t = 0$ for E1→E2, which is over one third of that (~24.1) of the interband H1→E1 transition (Fig. 7.5(a)). This value is also about 3 to 5 times greater than that of the B-to-B E1→E2 transition in GaAs/AlGaAs systems as discussed in Chapter 2. This feature should be attributed to the very narrow

bandgap of InSb_{1-x}N_x material and hence the improved coupling of valence-band and conduction-band. The B-to-C E1→E3 transition also shows considerable rate, about 1.6 at $k_t = 0$. The absorption spectrum shown in Fig. 7.6 (b) peaks at 25.8 μm and the absorption band expands to beyond 30 μm . It indicates that the InSb_{1-x}N_x/InSb system is potentially advantageous for photodetection at very long infrared wavelength band, possessing the intense ISBT rates in conduction-band. Also this system can gain another advantage, the broad absorption wavelength range due to the wide E2 miniband. For instance, the FWHM of the E1→E2 absorption is nearly 15 μm , ranging from 19.5 to 34.2 μm as shown in Fig. 7.6(b).

Figure 7.6. Calculated (a) squared optical transition matrix elements vs. plane wave vector k_t and (b) absorption coefficients vs. optical wavelength of intra-conduction band E1-E2 and E1-E3 transitions for TM polarization, respectively, for the InSb_{0.99}N_{0.01}/InSb MQW.

7.3 Experimental study on InSb_{1-x}N_x alloys and devices

In this section, the preparations of InSb_{1-x}N_x alloys with various N contents by N⁺ ion implantation to InSb (111) and (100) substrates are introduced firstly.

Then the fabrication and characterization of photoconductive and photovoltaic structural InSb_{1-x}N_x detectors are presented in detail. The red-shifted optical photodetection bands up to 10 μm at low temperature are realized.

7.3.1 Preparation of InSb_{1-x}N_x alloys

We employed N⁺ ion implantation and annealing to incorporate dilute nitrogen into InSb. Compared to the common epitaxial technologies like MBE to grow InSbN [7.1–7.3], the ion implantation method has some attractive merits such as simplicity and low-cost, wide and flexible N dose control range, and low-temperature operation which allow fast and cost-efficient production of InSb_{1-x}N_x alloys and detector arrays. Its weak points lie in inaccurate control of N layer thickness and concentration uniformity, and lower N substitutional incorporation ratio. The ion bombardment induced surface damage is another major concern, which can be alleviated by post-implantation annealing and sacrifice layer etching.

Firstly, a set of n-type InSb (111) wafers with a sheet carrier concentration of about $5 \times 10^{13} \text{ cm}^{-2}$ (at 77 K) were used to fabricate InSb_{1-x}N_x alloys by the method of N⁺ ion implantation. The implanted N depth and concentration profile was adjusted by bombardment energy and dose as listed in Table 7.2. The implantation process was simulated using the TRIM94 program. Six InSb_{1-x}N_x samples with approximate N compositions of 0.2%, 0.4%, 0.6%, 0.7% and 1% (labeled as A1–A6), respectively, were fabricated by the two-step N implantation method. The bombardment energies are 33 keV for a target depth of about 60 nm and 150 keV for a target depth of about 300 nm, respectively. A

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thermal annealing at 550 K for some hours was done on the N-implanted samples to remove radiation-induced damage and enhance the incorporation of substitutional N atoms in InSb. This anneal processing can also drive the implanted N atoms to diffuse and re-distribute to form a deeper and smoother concentration profile.

Table 7.2. Two-step N⁺ ion implantation scheme to obtain a set of InSb_{1-x}N_x alloys with different N contents on InSb substrates. R_p is the projected range (the position where the peak is), and ΔR_p is the standard deviation

Sample No.	A1	A2	A3	A4	A5	A6
Target N composition	0.2%	0.4%	0.6%	0.7%	1.0%	6.0%
Target implanted N depth (nm)	300	300	300	300	300	300
Target Implanted N concentration (cm ⁻³)	2.95×10^{19}	5.91×10^{19}	8.86×10^{19}	1.03×10^{20}	1.48×10^{20}	8.86×10^{20}
Bombardment energy (keV)	1) 33 2) 150	1) 33 2) 150	1) 33 2) 150	1) 33 2) 150	1) 33 2) 150	1) 33 2) 150
Dose (cm ⁻²)	1) 2×10^{14} 2) 8×10^{14}	1) 4×10^{14} 2) 1.6×10^{15}	1) 5.5×10^{14} 2) 2.4×10^{15}	1) 6.5×10^{14} 2) 2.8×10^{15}	1) 9.5×10^{14} 2) 4×10^{15}	1) 5.5×10^{15} 2) 2.4×10^{16}
N ⁺ R_p	1) 60.7 nm for 33 keV 2) 250.9 nm for 150 keV (Calculated by Trim94)					
N ⁺ ΔR_p	1) 54.5 nm for 33 keV 2) 143.4 nm for 150 keV (Calculated by Trim94)					

The N distribution profiles were measured using secondary ion mass spectrometry (SIMS). Figure 7.7 shows the measured N concentration as a function of depth for as-implanted A6, and three A6 samples annealed at 550 K for 3, 5 and 10 hours, respectively, to look into the annealing effect on N distribution. We can see that the as-implanted N distribution profile appears to be an obvious two-peak curve. The first peak at 26 nm depth was generated mainly by the 33 keV N⁺ ion implantation, while the second peak at 190 nm was

dominated by the 150 keV N⁺ ion implantation. They show approximately equivalent peak concentrations of $\sim 6.1 \times 10^{20} \text{ cm}^{-3}$. When 3 hours annealing was done, the N atoms diffused deeply and the two peaks migrated to the depths of about 53 and 270 nm, respectively. When the annealing time increased to 5 hours, the two peaks diffused further to the depths about 65 and 315 nm, respectively, and the concentration profile became much flatter than the as-implanted profile due to the long thermal diffusion time. The N concentration distribution in the 50–400 nm depth range shows an approximately uniform profile (3.2×10^{20} to $4.5 \times 10^{20} \text{ cm}^{-3}$). When the annealing time increased further to 10 hours, the second peak migrated to a depth of about 410 nm. It is also observed a large amount of N atoms assemble near the sample surface. This phenomenon of out-diffusion of N was also reported in some literatures [7.11, 7.12].

Figure 7.7. Nitrogen concentration distributions measured by SIMS in N⁺ implanted A6 sample, and three A6 samples annealed at 550 K for 3, 5 and 10 hours, respectively.

Figure 7.8 shows the measured N concentration profiles as a function of depth using for the samples of A2, A3, A5 and A6 that were annealed at 550 K for 5 hours. The target N compositions for the four N⁺ implanted samples are 0.4%, 0.6%, 1% and 6%, respectively, as described in Table 7.2. It can be seen that an approximately uniform N profiles at the depths range from about 50 to 350 nm were obtained after the two-step N⁺ implantation and thermal annealing. The post-annealing average N concentrations for A2, A3, A5 and A6 are about 5.0×10^{19} , 7.3×10^{19} , 1.15×10^{20} and 4×10^{20} cm⁻³, respectively. The real N concentration of A6 is remarkably lower than the target value 8.8×10^{20} cm⁻³, indicating the difficulty of implantation and incorporation of high concentration N in the InSb substrate.

Figure 7.8. N concentration distributions measured by SIMS in A2, A3, A5 and A6 annealed at 550 K for five hours.

Another set of n-type InSb (100) wafers with a sheet carrier concentration of about 2×10^{13} cm⁻² (at 77 K) were used to fabricate InSb_{1-x}N_x alloys with p-n junction structures by N⁺ and Mg⁺ ion implantations. In order to obtain a deep high-concentration N profile in the InSb substrate, a three-step N⁺ implantation

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scheme was used as shown in Table 7.3. The three-step bombardment energies are 90, 180 and 530 keV, respectively, to realize relatively uniform N concentration distribution up to 0.6 μm . The target N compositions for samples B1–B4 are 5%, 6%, 7% and 8%, respectively, by adjusting the implanted N⁺ dose between 8.0×10^{15} to $5.9 \times 10^{16} \text{ cm}^{-2}$ with different bombardment energies. Mg⁺ ions were implanted with an energy of 40 keV and a dose of $2.0 \times 10^{15} \text{ cm}^{-2}$ as the acceptors to form a thin p-type layer above the thicker n-type InSbN layer. The N and Mg concentrations profiles measured by SIMS for sample B1 after annealing process (550 K for four hours) are shown in Figure 7.9. It can be seen that the N concentration shows an approximate uniform distribution profile ($>1.6 \times 10^{20} \text{ cm}^{-3}$) in the depth range from about 50 to 700 nm. The N concentration decreases to below $1 \times 10^{20} \text{ cm}^{-3}$ at the depth beyond 820 nm. The Mg atoms distribute mainly at a shallower depth range after annealing. The Mg peak concentration is $5.6 \times 10^{20} \text{ cm}^{-3}$ at the depth of about 25 nm.

Table 7.3. The N⁺ and Mg⁺ ion implantation scheme to obtain InSb_{1-x}N_x alloys with p-n junction structure.

Sample No.	B1	B2	B3	B4
Target doped N composition	5%	6%	7%	8%
Target Doping depth (nm)	600	600	600	600
N ⁺ implantation energy (keV)	1) 90 2) 180 3) 530	1) 90 2) 180 3) 530	1) 90 2) 180 3) 530	1) 90 2) 180 3) 530
N ⁺ dose (cm ⁻²)	1) 8.0×10^{15} 2) 1.8×10^{16} 3) 3.7×10^{16}	1) 9.6×10^{15} 2) 2.2×10^{16} 3) 4.4×10^{16}	1) 1.1×10^{16} 2) 2.5×10^{16} 3) 5.2×10^{16}	1) 1.3×10^{16} 2) 2.9×10^{16} 3) 5.9×10^{16}
Mg ⁺ implantation energy and dose	40 keV $2.0 \times 10^{15} \text{ cm}^{-2}$

Figure 7.9. Measured N and Mg concentration distributions by SIMS of in a B1 sample annealed at 550 K for four hours.

7.3.2 Electrical characterization

Carrier concentration, electron mobility and sheet resistivity of the InSb_{1-x}N_x alloys fabricated by N⁺ implantation and thermal anneal are characterized with Hall effect measurements. The temperature condition was changed from about 90 to 300 K in a liquid nitrogen circulation chamber with a temperature controller.

Figure 7.10. Measured sheet carrier concentration as a function of temperature for InSb substrate and three InSb_{1-x}N_x samples.

Figure 7.10 shows the measured sheet carrier concentration for three InSb_{1-x}N_x samples, A3, A5 and A6 in comparison with the (111) InSb substrate. It can be seen that the N-free (111) InSb substrate shows a n-type carrier concentration of $1.6 \times 10^{15} \text{ cm}^{-2}$ at room temperature (300 K). It decreases fast to about $5 \times 10^{13} \text{ cm}^{-2}$ with the lowering of temperature to 150 K and then becomes stable. With the implantation of about 0.6% N, the n-type carrier concentration in A5 shows decrease, especially at temperature below 180 K compared to the N-free InSb substrate (A3). At 100 K, its carrier concentration is $2.68 \times 10^{13} \text{ cm}^{-2}$ that is only about half of the value for A3. With the implantation of more N (about 1% composition in A5), the n-type carrier concentration in A5 is reduced further. However, this trend reverses in A6 whose carrier concentration is nearly twice of that for the InSb substrate at low temperature (<170 K). These observations indicate that the implanted N ions appear to be acceptors at low and moderate implantation doses (A3 and A5), while appear to be donors at very large implantation dose (A6) likely due to a lot of N atoms existing as impurity states.

Figure 7.11 shows the measured electron mobilities of the three InSb_{1-x}N_x samples and the InSb substrate. It can be seen that the electron mobility keeps increasing almost exponentially with the temperature decreasing from 300 to 90 K, which is consistent with the common relationship for InSb as follows:

$$\mu_n(\text{InSb}) = 7.7 \times 10^4 (T/300)^{-1.66} \text{ cm}^2/\text{Vs} \quad (7.3)$$

Under most temperatures the N-free InSb substrate shows greater electron mobility compared to the N-implanted samples. This is understandable since the electronic effective mass should increase upon the incorporation of N atoms,

and the impurity carrier concentration and hence the scattering rate would also increase in InSb_{1-x}N_x alloys. An abnormal phenomenon observed is that A5 (about 1% N composition) shows greater electron mobility than the N-free InSb substrate at temperatures below 160 K.

Figure 7.11. Measured electron mobilities as a function of temperature for the InSb substrate and the three InSb_{1-x}N_x samples.

Figure 7.12 shows the measured sheet resistivity as a function of temperature ranging from 90 to 300 K for the three InSb_{1-x}N_x samples in comparison with the InSb substrate. It can be seen that the resistivity increases rapidly by over one order of amplitude with the lowering of temperature up to about 150 K. This is consistent with the trend of carrier concentration in this temperature range (Fig. 7.10), as the well-known inversely proportional relationship between them as follows

$$\rho = \frac{1}{qn\mu} \quad (7.4)$$

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where ρ , q , n and μ are the resistivity, the electronic charge, the carrier concentration and the mobility, respectively. However, the sheet resistivity at temperatures below 150 K shows a reverse trend when the temperature is lowered further. For instance, the sheet resistivity for A3 shows the maximum value of 2.47 ohm/sq at 150 K, but then decreases gradually to 1.92 ohm/sq at 90 K. This is because that the electron concentration is almost unchangeable at temperatures below 150 K as shown in Fig. 7.10, but the electron mobility still keeps increasing at the same time. Consequently, the sheet resistivity shows decrease since it is also inversely proportional to the electron mobility. It is also observed that A3 and A5 with moderate implanted N doses show larger sheet resistivities by 1–2 times than the N-free InSb. It is advantageous to use them for the fabrication of photoconductive detectors.

Figure 7.12. Measured sheet resistivities as a function of temperature for InSb substrate and three InSb_{1-x}N_x samples.

7.3.3 InSb_{1-x}N_x photoconductive detectors

The (111) InSb_{1-x}N_x wafers were cut into rectangular slabs having about 4 mm in length, 2 mm in width and 0.5 mm in thickness. Then the thickness was reduced properly by mechanical and chemical polishing. Indium contacts were soldered to the slabs as ohmic contact electrodes, and gold wires have been used as terminal leads. A photocurrent characterization system was used to measure the photoresponse spectra (Figure 7.13). This system was built of an infrared source, a monochromator (Jobin Yvon Triax 320), a lock-in amplifier, a chopper, a cryostat with temperature controller, some optical components, etc. The infrared source is an Oriel 6575 ceramic element mounted in a lamp house. The element has a cylindrical ceramic core with a platinum resistance wire wound around. The irradiation is similar to that of the blackbody at 1450 K. It has high output in a wide wavelength range from 1 to over 10 μm . A set of KRS-5 lens is used to focus the light from the radiation source on the input slit of the monochromator. The off-axis parabolic mirror pair is used to collect the output light from the exit slit of the monochromator and focus it to the sample inside the cryostat. The sample is fixed onto the cold finger of the cryostat. A close loop cycling helium gas is compressed and expanded based on the Gifford-McMahon thermodynamic cycle. A heater and a thermometer are installed on the cold finger and are employed to precisely control the sample temperature. The cryostat system can perform a wide range of temperature environment from 10 to 300K.

Figure 7.13. Schematic photocurrent measurement system

The measured photoresponse spectra of the three InN_xSb_{1-x} samples and the N-free InSb at 30 K are shown in Fig. 7.14. In order to prevent the second-order or any other high-order diffraction responses from the incident light below 5 μm appearing in the target wavelength observation range, a 5 μm high-pass filter was placed at the exit slit of the monochromator to ensure only infrared larger than 5 μm irradiating on the sample. As a consequence, the N-free InSb sample shows a narrow response curve peaking at 5.3 μm as shown in Fig. 7.14(a). This is consistent with the InSb bandgap of about 233 meV at 30 K that corresponds to a wavelength of 5.33 μm . For these InSb_{1-x}N_x samples fabricated by N⁺ ion implantation and thermal process, it can be seen that the photoresponse spectrum extends to longer wavelengths gradually with the increasing of N content as shown in Figs. 7.14(b), (c) and (d). The strongest photocurrent in the 5–6 μm range is mainly due to the response from the thick InSb substrate beneath the thin InSb_{1-x}N_x layer. The detection band tails coming from the thin InSb_{1-x}N_x layer redshift to about 7, 9 and 11 μm , respectively, for A2, A3, and

A5. It is proved that the energy bandgap of the N-implanted layer was decreased significantly. Compared to the reported observations in recent years for InSb_{1-x}N_x using some other measurement methods such as the FTIR-based photo-modulated transmission spectroscopy [7.8, 7.9], etc., our photodetection result is a direct demonstration of decreased bandgap of InSb_{1-x}N_x compared to N-free InSb. A new way to detect longer wavelength infrared beyond the limitation of convention InSb devices based on the InSb_{1-x}N_x alloys is realized here.

Figure 7.14. Measured photocurrent spectra of the N-free InSb and the three InSb_{1-x}N_x samples.

7.3.4 InSb_{1-x}N_x photovoltaic detectors

The p-n structural InSb_{1-x}N_x samples (B1–B4) made by Mg⁺ and N⁺ ion implantations were used to fabricate photovoltaic detectors (Fig. 7.15). The device fabrication process chart is schematically shown in Fig. 7.16 and the details are listed as follows.

Chapter 7: InSb_{1-x}N_x alloys and infrared detection Figure 7.15. Schematic InSb_{1-x}N_x photovoltaic detector structure Figure 7.16. Flow chart of InSb_{1-x}N_x photovoltaic detector fabrication process

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- 1) Wafer cleaning: put the samples into acetone and then IPA, and boil the solution at 200 °C for about 15 minutes to clean the sample contamination.
- 2) Mask cleaning: clean the mask surfaces with acetone and IPA.
- 3) The 1st photolithography step for mesa fabrication: drop 1518 photoresist onto the sample surface and then spin it for 30 seconds to form a uniform thin photoresist layer → bake the sample at 105 °C for 1 minute and 45 seconds to get rid of H₂O → expose the sample under the mesa mask under ultraviolet for 20 seconds.
- 4) Developing: Mix AZ solution and H₂O in the proportion of 1:2 into a beaker. Develop for 1–2 minutes and then bake the samples at 110 °C for 15 minutes.
- 5) Mesa wet etching: The etch solution is lactic acid (C₃H₆O₃): nitric acid (HNO₃) =10:1. The etching rate is about 300 nm per minute. The InSbN mesa with a height of ~2 μm was formed after 7 minutes etching (Fig. 7.17).
- 6) The 2nd photolithography step for metal electrode fabrication: Spin 5214 photoresist on the sample surface → bake the sample at 105 °C for 1 minute and 45 seconds → expose the sample covered with the metal-contact mask under ultraviolet (UV) for 5 seconds → bake the sample at 110 °C for 8-10 minutes → expose the sample under ultraviolet for 25 seconds → develop the sample using solution of AZ:H₂O = 1:2 for about 2 minutes.
- 7) Clean oxide: remove the oxide in the sample surface using solution of HCL (37%): H₂O = 1:10 for about 20 seconds and then rinse the sample in DI water.

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- 8) E-beam evaporation and lift-off: after the photoresist pattern for electrodes is realized with the 2nd photomask, the metal deposition is done using E-beam evaporation to coat the sample surface with 80 nm titanium and 250 nm gold layers. Then put the samples into acetone for 6 hours to lift-off useless metal area to form Au/Ti electrodes.
- 9) Wafer packaging and wire bonding.

Figure 7.17. The photograph of mesa-like InSbN devices. The diameter of the biggest mesa is 300 μm .

The I-V characteristics were measured using a Keithley 320 programmable current-voltage measurement unit. The I-V curve of one $\text{InSb}_{1-x}\text{N}_x$ p-n device fabricated with B2 is shown in Fig. 7.17 (measured at 30 K). It can be seen that at reverse bias up to -1.0 V the device shows very small current, indicating the formation of depletion region around the p-n junction.

Figure 7.18. Measured current-voltage (I-V) curve of one InSb_{1-x}N_x p-n device.

Figure 7.19. The photoresponse spectra of four p-n InSb_{1-x}N_x devices fabricated with B1, B2, B3 and B4, respectively, by Mg⁺ and N⁺ ions implantation,

The photoresponses of these InSb_{1-x}N_x p-n devices were tested using the photocurrent measurement system shown in Fig. 7.13. The device temperature was cooled down to about 30 K in the cryostat to suppress the thermal noise. A 5 μm high-pass filter was placed at the exit slit of the monochromator to remove the incident infrared light below 5 μm. It is mandatory to prevent responses from the second order and other high-order diffractions by the light below 5 μm to mix with the first order diffract response by the light in the 5–10 μm observation window. The measured photocurrent spectra for the InSb_{1-x}N_x p-n devices fabricated with B1–B4 are in Figs. 7.19(a) to (b), respectively.

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Compared to the N-free InSb with absorption band edge at about 6 μm as shown in Fig. 7.14(a), it can be seen that all the four InSb_{1-x}N_x p-n devices show red-shifting absorption band edges to around 8 μm . It is demonstrated that the implanted N contents do induce the shrinkage of material bandgaps. However, the redshift amplitudes of the photoresponse spectra show no clear correlations with the implanted N doses in B1–B4. The first three devices have similar spectral profiles although the target N compositions are 5%, 6% and 7%, respectively, while the device fabricated with B4 show much higher response intensity in the 6 to 8 μm range. This is unlike the continuously redshifting response band to longer wavelengths with increasing N composition for the photoconductive devices presented in Subsection 7.3.3. It is reasonable because high concentration Mg dopants (over $1 \times 10^{19} \text{ cm}^{-3}$) and hence the p-type region distribute from the sample surface to the depth of about 700 nm as shown in the Mg concentration distribution curve in Fig. 7.9. Therefore, the depletion region contributing most photogenerated carriers at reverse bias should locate at a depth close to ~ 700 nm and onward. In this deep region the N incorporation concentration and hence the photo response spectra is not sensitive to the change of overall N⁺ implantation dose. Moreover, the N concentration in this depth onward is remarkably lower than the peak concentration in shallower region (from 0 to about 600 nm depths) as shown by the N concentration distribution curve in Fig. 7.9. Therefore, the actual redshift of photoresponse spectrum is limited.

7.4 Summary

In this chapter, the dilute nitride InSb_{1-x}N_x alloys and their infrared detection have been investigated theoretically and experimentally.

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In the theoretical work, the 10-band **k·p** model was employed to analyze the changes of energy band structures under NB-CB coupling. It is derived that about 1.3% N should be incorporated at low temperature, and about 0.6% N should be incorporated at room temperature, respectively, to redshift the optical absorption wavelength to the 10 μm band. In addition, the study on InSb_{1-x}N_x/InSb quantum well structures shows that they have intense intra-conduction band transition rates due to the narrow bandgap of InSb_{1-x}N_x material and hence the greatly improved coupling effect between the valence and conduction bands.

In the experimental work, a set of InSb_{1-x}N_x alloys with various N contents (0.2%, 0.4%, 0.6%, 1%, 5%, 6%, etc.) has been made successfully based on the technique of multi-step N⁺ ion implantation into InSb substrates. The N distributions pre- and post-thermal process in some samples have been measured using SIMS, and approximately uniform N concentration distribution at the depths from about 50 to 350 nm was achieved. The electrical characterization based on Hall measurement revealed the significant changes of carrier concentration, electron mobility and sheet resistivity relative to the N-free InSb material. The fabricated InSb_{1-x}N_x photoconductive detectors show redshifting photoresponse band edges up to 11 μm at 30 K with the increase of N content up to 1%. Compared to the N-free InSb detector showing photoresponse band edges at about 6 μm at low temperature, the InSb_{1-x}N_x detectors show extra ability for photodetection in the 8–12 μm LWIR window. The InSb_{1-x}N_x p-n structural detectors fabricated by Mg⁺ and three-step N⁺ ion

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implantations also demonstrate redshifted photoresponse band edges to about 8 μm at 30 K.

Chapter 8 Conclusion and recommendation

8.1 Conclusion

A theoretical method based on the ten-band and sixteen-band $\mathbf{k}\cdot\mathbf{p}$ models involving the high-lying N resonant band has been developed to study ISBTs in dilute-N conduction-band quantum wells. The ISBT selectivities on subband order, wave vector and well widths in finitely deep quantum wells are derived. The quantum confinement relaxation especially for the continuum states is taken into reasonable consideration. Consequently, the well width becomes a critical impact factor to determine the actual ISBT properties and selectivities.

The variations of ISBTs with well width and N content in n-type (In,Ga)AsN/(Al,Ga)As quantum wells are analyzed. It is found that some novel ISBT properties and phenomena would exhibit due to the N-band and conduction-band coupling, which are in good agreement with reported experimental observations. The absorption energy is much larger than that of the equivalent N-free quantum well in the case of narrow wells, but such difference becomes small rapidly and even reverses with the increase of well width. In the case of moderate and wider wells where the ground to the first excited state transition dominates, the transition energy is insensitive to the increase of N content up to 3%, and a redshift of the transition energy can occur with increasing N content within a range for the $\text{GaAs}_{1-x}\text{N}_x/\text{AlGaAs}$ quantum wells.

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Also, ISBTs in asymmetric InGaAsN/InGaAs/GaAs quantum wells are analyzed theoretically. The results show that the TE-polarized transitions can be improved significantly with the asymmetric N incorporation, especially in the case of narrow well widths. The variations of subband dispersions and ISBTs with N and In diffusions in InGaAsN/GaAs quantum wells have also been studied. The transition energy in narrow well should redshift dramatically with the increase of N diffusion length. Such change becomes much smaller in wider wells. In diffusion induces more blueshifts of interband transition energies compared to N diffusion. However, the intersubband transition energy is not sensitive to the In diffusion, especially for moderate and wide wells. The optical transition rates decrease significantly with the In diffusion because of relaxed quantum restriction.

The successful growth and characterization of high quality $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.984}\text{N}_{0.016}/\text{GaAs}$ and $\text{In}_{0.7}\text{Ga}_{0.3}\text{As}_{0.99}\text{N}_{0.01}/\text{GaAs}$ n-type MQWs by SSMBE are reported. The anneal-induced In and N diffusions are measured by SIMS, and their impact on PL and subband structures are analyzed and discussed. The intersubband absorptions in the 8–12 μm infrared band are achieved.

The dilute nitride $\text{InSb}_{1-x}\text{N}_x$ alloys and their infrared detection are investigated theoretically and experimentally. The calculation on $\text{InSb}_{1-x}\text{N}_x/\text{InSb}$ quantum well structures shows that they have intense ISBTs due to the narrow bandgap of $\text{InSb}_{1-x}\text{N}_x$ material and hence the greatly improved coupling effect. A set of $\text{InSb}_{1-x}\text{N}_x$ alloys with various N contents (0.2%, 0.4%, 0.6%, 1%, 5%, 6%, etc.)

has been made successfully based on the technique of multi-step N^+ ion implantation into InSb substrates. The fabricated $\text{InSb}_{1-x}\text{N}_x$ photoconductive detectors show redshifting photoresponse band edges up to $11\ \mu\text{m}$ at 30 K with increasing N content. The $\text{InSb}_{1-x}\text{N}_x$ p-n detectors fabricated by Mg^+ and N^+ ion implantations also show redshifted photoresponse band edges to about $8\ \mu\text{m}$ at 30 K.

8.2 Recommendations for future research

There are some recommendations for future continual research on this topic:

- 1) To investigate the impact of many body effects on the intersubband absorptions in heavily doped quantum wells. In this thesis work our major focus is on lower and moderate doping concentrations ($\leq 1 \times 10^{18}\ \text{cm}^{-3}$), so the many-body effects like Coulomb interaction induced collective excitations and phase space filling can be ignored. In order to calculate intersubband absorptions in heavily doped quantum wells (generally $1 \times 10^{19}\ \text{cm}^{-3}$ or above), it is necessary to take some many-body effects into consideration. This is particularly important for further study on TE-polarized absorptions that occur mainly at finite k_z and hence can be boosted significantly by a high Fermi level under a high doping concentration.
- 2) To fabricate dilute-N QWIP devices with low noise and high responsivity. We found that the devices fabricated with the MQW samples we used in the experiment show high dark current, and consequently the photogenerated current cannot be detected effectively under the sensitivity limitation of our equipment. It is most likely due to the higher defect density in our InGaAsN

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- material. Therefore, an improved MBE dilute-nitride growth technique is needed to achieve high-quality InGaAsN-based MQWs for successful photodetector device demonstration.
- 3) To further understand the underlying physical mechanism of the large TE-polarized absorption observed in one InGaAsN/GaAs MQW sample. It is suggested to examine the possible impact of high doping concentrations and take the many-body effects into necessary consideration. It is also recommended to fabricate more dilute-N quantum wells with different designs and doping concentrations for experimental measurement.
 - 4) Since the theoretical analysis on $\text{InSb}_{1-x}\text{N}_x/\text{InSb}$ quantum well-like structures shows intense ISBTs associated with the narrow bandgap and hence the improved coupling effect, it is of interest to do some experimental work to confirm this hypothesis.
 - 5) It is suggested to further optimize N^+ implantation dose, energy, target depth and anneal condition to achieve $\text{InSb}_{1-x}\text{N}_x$ alloys with low surface damage, high N incorporation, and more uniform concentration profile. The responsivity in the 8–12 μm LWIR window of the fabricated $\text{InSb}_{1-x}\text{N}_x$ photodetectors needs to be improved.

Author's Publications

Journal Papers:

1. W. Liu, D. H. Zhang, W. J. Fan, X. Y. Hou, and Z. M. Jiang, "Intersubband transitions in InGaAsN/GaAs quantum wells", *Journal of Applied Physics* **104**(5), 053119 (2008).
2. W. Liu, D. H. Zhang, Z. M. Huang, and W. J. Fan, "Theoretical study of quantum well infrared photodetectors with asymmetric well and barrier structures for broadband photodetection", *Journal of Applied Physics* **101**(3), 033114 (2007).
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2. W. Liu, D. H. Zhang, "Modeling of intersubband transitions in quantum well infrared photodetectors with complex well-barrier structures", *6th International Conference On Numerical Simulation of Optoelectronic Devices (IEEE NUSOD06)*, TuB2 (31-2) (presentation), 11-14 Sept. (2006).
3. W. Liu, D. H. Zhang, Z. M. Huang, W. J. Fan, "Effect of N content on the intersubband transitions in (In,Ga)AsN/AlGaAs quantum wells", *4th*

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4. W. Liu, D. H. Zhang, Z. M. Huang, Y. Wang, "Characterization of high temperature InSb schottky barrier infrared detectors", *4th International Conference on Materials for Advanced Technologies (ICMAT2007)*, Singapore, 1-7 July (2007).
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Chapter 2

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