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Study of InGaAsP/InP Quantum Well Structures Grown by Solid Source MBE and Their Application for Long Wavelength Infrared Light Detection

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School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
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SUMMARY

The energy band dispersion relations for InGaAsP/InP multi quantum well (MQW) structures were investigated using 8x8 $k \cdot p$ method. In this study, different strain cases in the well of the structures were investigated with well width and well doping concentration as parameters. The results give out the energy band structure for each case explicitly. To the best of our knowledge, it is the first study of InGaAsP/InPMQW energy band structure considering doping concentration, strain and well width effect at the same time.

Optical, structural and electrical properties of Silicon doped strained InGaAsP/InP multiple quantum well structures grown by solid source molecular beam epitaxy (SSMBE) with different Si-doping densities in InGaAsP wells and different well widths in the MQW structures were systematically studied. From the X-ray result, it is found that the centre satellite peak of the centre-enveloping peak should be the zero-order satellite peak. With increasing of well width, the number of satellite peaks in each enveloping peak will decrease. These were confirmed by simulation results. On the other hand, the relationship of well doping concentration and quantum well interface quality was investigated using x-ray and photoluminescence (PL). PL was also used to investigate the energy band in the MQW structures. It was found that higher doping concentration would degrade the interface quality.

Intermixing of the quantum wells structures was investigated using X-ray and PL as well. Under 700 °C, the strain in the well layer does not change significantly, but the well width decreases. At 700 °C, the strain increases with increasing of the annealing time. From the x-ray results, the intermixing was found dominated by the diffusion of group V

atoms. It was also found that the intermixing is also sensitive to the doping concentration in the wells. The PL peak blue shift became less for the samples doped with higher concentration.

Lattice matched InGaAsP/InP MQW structures were grown using SSMBE. PL and Fourier transform infrared (FTIR) spectroscopy were used to characterize the MQW structures. FTIR results show the relationship of IR light polarization degree and absorption intensity. At 0 degree (TE+TM), MQW structures has the maximum absorption intensity. The QWIP devices were fabricated using standard microelectronics process and their performance was characterized. High doping concentration in the well layer induces high dark current, which suppresses the absorption signal. For the low doping concentration devices, we investigated the photoresponsivity spectrum at different bias voltages and temperatures.

InGaAsN/GaAsN MQW structures were also grown by SSMBE with RF N plasma source. X-ray, PL and FTIR were used to investigate the nitride MQW structures. Single band absorption theory was used to simulate the FTIR result and they are in good agreement with the experimental results. It is interesting to find that InGaAsN/GaAsN MQW structures absorb the normal incident.

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Chapter 1 Introduction

1.1 Infrared radiation

Infrared (IR) radiation is a form of electromagnetic energy. The intensity of the object's radiation is determined by a number of factors such as temperature, distance, the size of the object as well as its emissivity. Blackbody is a perfect emitting source. The radiation emitted by a blackbody is governed by the Planck equation according to the absolute temperature T [1]:

$$L(T, \lambda) = \frac{2c}{\lambda^4} \frac{1}{e^{hc/\lambda kT} - 1}, \quad (1.1)$$

where $L(T, \lambda)$ is the spectral radiance, defined as the photon flux per unit projected area per unit solid angle per unit wavelength. In the equation, $h = 6.6262 \times 10^{-34}$ Js is the Planck constant, $c = 2.9979 \times 10^8$ m/s is the speed of light in vacuum, $k = 1.3806 \times 10^{-23}$ J/K is the Boltzmann constant, T is the Kelvin temperature and λ is the wavelength.

Figure 1.1 shows the Blackbody spectral radiant at various temperatures. From Fig 1.1, it is clear that these blackbodies radiate most of their energy in the infrared range ($\lambda > 0.7 \mu\text{m}$). The peak position λ_m shifts to lower wavelengths as the blackbody temperature goes up. $\lambda_m \cong 10 \mu\text{m}$ for blackbodies at room temperature $T \cong 300$ K. At the same time, there is an atmospheric transmittance window between 8 to 12 μm . This point makes infrared detection a very powerful tool for observing distant objects at or around

300K. The infrared detection has many applications in fire fighting, volcanology, medicine, defense and astronomy.

Figure 1.1. Radiation of a blackbody as a function of wavelength at different temperatures.

1.2 History of the quantum well infrared photodetector research

To detect the IR radiation, one can use an IR photodetector to convert the light signal to an electrical signal [2]. Conventional interband optical absorption involves photoexciting carriers across the band gap E_g i.e., promoting an electron from the valence-band ground state to the conduction-band excited state. In a detector structure

these photocarriers are collected, thereby producing a photocurrent. Since the optical energy $h\nu$ is greater than the energy gap ($h\nu > E_g$), electrons and holes can be created and thus the semiconductor does not need to be doped. In fact, doping increases the dark current and reduces the sensitivity of such an interband absorption detector.

By controlling the bandgap of the material (e.g., using an alloy of varying composition such as $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$) [3], the spectrum of the absorption and hence the wavelength dependence of the detector response can be modified. For example, the detection of long-wavelength infrared radiation $\lambda \approx 10 \mu\text{m}$ requires a small gap $E_g \approx 0.1 \text{ eV}$. Such small-band-gap materials are well known to be more difficult to grow (due to the narrower growth parameter window), process, and fabricate into devices than the larger-band-gap semiconductors. These difficulties thus motivate the study of novel “artificial” low “effective” band-gap materials, which use quantum well (QW) in large-band-gap ($E_g > 1 \text{ eV}$) semiconductors [4, 5]. However, in order to employ these desirable large gap materials for long-wavelength optical devices, it is advantageous to use intersubband (i.e., intraband) absorption involving transitions within the same band, rather than the usual interband absorption mechanism (involving transitions between the conduction and valence bands).

In order to create these states within the conduction or valence bands, quantum wells are used. It is important to note, however, that unlike the usual interband transition, these quantum wells must be doped since $h\nu < E_g$ and thus the photon energy is not sufficient to create photocarriers. The infrared-absorption mechanism is, therefore, an excitation of an electron (hole) from the doped quantum-well ground state in the conduction (valence) band to an unoccupied excited state in the same band (see Fig. 1.1).

In the quantum-well infrared photodetectors, the quantum-well structure is designed so that this excited carrier can escape from the well and be collected as photocurrent. Thus, these QWIPs are somewhat analogous to extrinsically doped semiconductors but with much larger optical transition dipole moments $\langle z \rangle$ (since the size of the quantum well is 1-2 orders of magnitude larger than that of an impurity atom). Furthermore, the quantum-well parameters can be designed to vary the intersubband optical spectrum (peak wavelength as well as spectral width) whereas a particular extrinsic impurity has a fixed absorption.

Figure 1.2. (a) Interband transition, and (b) intersubband transition.

Intersubband absorption has been studied by many researchers for nearly 20 years [6], in both electron and hole Si space-charge layers as well as in III-V surface layers. This work has led to a detailed understanding of the quantum-well energy-level spacing including many-body effects, intersubband absorption selection rules, oscillator strengths, and line shapes. However, these optical transitions in surface space charge layers, which are in the far infrared ($\lambda \geq 50 \mu\text{m}$) spectral region, are not well suited for making intersubband detectors in the medium-wave ($\lambda \cong 5 \mu\text{m}$) or long-wave ($\lambda \cong 10 \mu\text{m}$)

infrared spectral regions. Furthermore, the optical absorption in a single layer is small ($< 1\%$) and the photoexcited carrier cannot readily escape from the deep quantum well induced by the surface space charge.

The first experimental measurement of the strong intersubband absorption in a series of MQW was performed by West and Eglash [7], who achieved large near-unity oscillator strength in a stack of 50 highly doped GaAs quantum wells. Following these results, in 1987, Levine *et al.* [8] demonstrated the first QWIP based on intersubband absorption between two bound quantum-well states and achieved a large peak responsivity of $R_p^0 = 0.52$ A/W at $\lambda = 10.8$ μm . In this MQW structure, the final QW state of transition was placed either slightly above or below the top of the barriers to obtain optimum sensitivity. By increasing the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ barrier thickness to reduce the tunneling current and using an intersubband transition between a bound ground state and a continuum excited state, Levine *et al.* [9] dramatically improved the QWIP's detectivity. In 1991, Bethea *et al.* obtained the first infrared image device using a 10-element linear scanning array. Large 128×128 high-sensitivity staring arrays have been demonstrated by several groups recently [10].

The advantages of QWIP compared with HgCdTe detectors include the mature III-V growth and processing technologies, which lead to high uniformity, excellent reproducibility, and thus large-area and low-cost staring arrays. In addition, the ability to accurately control the band structure, and hence spectral response, allows monolithically integrated multispectral infrared detectors as well as the potential for monolithic integration with high-speed GaAs multiplexers and other electronics.

1.3 Objectives

In the GaAs/AlGaAs system, transport properties of AlGaAs can be affected by oxygen related defects [11]. InGaAsP/InP material system, which is aluminum-free, has more advantages than the GaAs/AlGaAs system in optoelectronics field. The high-quality binary InP barriers and higher mobility of InP material give better transport properties compared with AlGaAs. The primary application of optoelectronics is presently in the well-established area of long-distance fiber-optic communication. Due to the potential large responsivity, longer wavelength detection and broad application area, the InGaAsP/InP material systems became attractive recently.

One of the major objectives of our project is to characterize the InGaAsP/InP multi quantum well structures grown by solid source molecular beam epitaxy (SSMBE) and optimize the structures for better performance of QWIP devices for long wavelength infrared detection. In this project, we investigated the InGaAsP/InP MQW structures with different well widths and with different well doping concentrations.

InGaAsN/GaAs structure has a conduction-band discontinuity of possibly more than 300meV at the interface of the heterostructure. This makes the InGaAsN/GaAs structures a very interesting research topic for the QWIP working at about 4 μm [12]. To find out the advantage of InGaAsN material in the QWIP application, the characterization was carried out for the InGaAsN/GaAsN multi quantum well structures grown by SSMBE.

1.4 Major contribution of this thesis

In this thesis, we investigated the quantum well energy band structures using 8×8 $k \cdot p$ method. In this study, the four strain cases in the well layer, compressive strain, lattice matched, small tensile strain and large tensile strain were covered. We investigated MQW structures with different doping concentrations for n-type MQW structures. We also investigated the intersubband transition of the n-type MQW structures with single band method. In addition, it was also found that in the large tensile strain case, the light hole could be the first energy level in the valence band of the well. It can be used to design a p-type QWIP with improved detectivity.

Si-doped InGaAsP/InP MQW structures were grown by SSMBE with different strain cases, well widths and well doping concentrations. Optical, physical and electrical properties were systematically investigated. From the x-ray diffraction (XRD) results, a new method to determine the zero-order satellite peak was developed. From the XRD and photoluminescence (PL) results with the relation of well doping concentration and well width, it is found that the heavy Si doping in the wells degraded abruptness and caused more inhomogeneity at the well-barrier interfaces. The PL results show the changes of peak energy and line width of the spectra with the doping concentration in the wells. On the other hand, the InGaAsP/InP was thermally treated to investigate the intermixing in the quantum wells. QWIP devices were fabricated in house. Responsivity was investigated under different bias voltages and different temperatures. It is found that by introducing narrow band gap contact layer, the dark current could decrease significantly.

InGaAsN/GaAsN MQW structures were grown using SSMBE with RF plasma nitride source. XRD, PL and FTIR were used to investigate the properties of the

structures. From the results of FTIR, we found that the intensity of the normal incident absorption was higher than that of in-plane incident absorption. It indicated that InGaAsN/GaAsN MQW structures could be a candidate for the normal incident absorption infrared photodetector.

1.5 Organization of this thesis

The thesis is composed of eight chapters. In Chapter 1, the infrared radiation and the roadmap of the QWIP research are introduced. The experimental methods are shown in Chapter 2. In Chapter 3, a brief theoretical review on the fundamental of quantum well physics is given firstly. Then the 8×8 $k \cdot p$ method is introduced and the calculation results of the InGaAsP/InPMQW structures with different strains in the well layer are shown. In Chapter 4, Si-doped InGaAsP/InP MQW structures are extensively investigated. The quantum well intermixing effect of this system is characterized and the results are discussed in Chapter 5. In Chapter 6, the optical and electrical properties of the InGaAsP/InP MQW structure and photodetector are reported. GaInAsN/GaAsN MQW structures are characterized and discussed in Chapter 7. Finally, the conclusion and recommendation are presented in Chapter 8.

The source code for the 8×8 $k \cdot p$ method using FORTRAN language is listed in Appendix A.

Chapter 2 Experimental methods

2.1 Molecular beam epitaxy

Molecular beam epitaxy (MBE) was developed in the early 1970s as a means of growing high-quality epitaxial layers of semiconductors, allowing precise control of layer thickness, doping and chemical composition. Since then, it has evolved into a popular technique for growing III-V compound semiconductors and several other materials. Because of the high degree of control with MBE, it is a valuable tool in the development of sophisticated electronic and optoelectronic devices [13, 14].

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

Layers are grown at the rate of approximately $1 \mu\text{m/hr}$ or about one mono-layer per second.

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

Figure 2.1. Schematic diagram of the MBE growth chamber.

Figure 2.1 shows the schematic diagram of the MBE growth chamber. The key components of MBE growth chamber are:

(1) A vacuum pumping system and a chamber to create a clean, ultra-high vacuum (UHV) environment. The pumping system comprises of a rough pumping, which consists of a dry diaphragm pump and three sorption pumps which can pump down to

about 5×10^{-3} Torr, a fine pumping which consists of an ion pump and titanium sublimation pump. The base pressure of the liquid nitrogen cooled growth chamber is about 2×10^{-11} Torr.

(2) Molecular beam sources with their individual shutters or valves.

(3) A substrate heating station supplies enough thermal energy to achieve epitaxial growth and atomically clean substrate surfaces. During the growth, substrates can be rotated to ensure thickness and compositional uniformity throughout the wafer.

(4) A reflection high-energy electron diffraction (RHEED) system for in situ surface characterization.

(5) The ionization gauges to measure the vacuum and the flux of molecular beams.

(6) A quadrupole mass spectrometer for residual gas analysis and leak detection.

The reflection high-energy electron diffraction (RHEED) is one of the most useful tools for *in situ* monitoring of the growth. It can be used to calibrate growth rates, observe removal of oxides from the surface, calibrate the substrate temperature, monitor arrangement of the surface atoms, determine the proper arsenic overpressure, give feedback on surface morphology, and provide information about growth kinetics. As shown in Figure 2.1, the RHEED gun emits high-energy electrons of which strike the sample surface at a shallow angle, making it a sensitive probe of the semiconductor surface. Electrons reflect from the surface and strike a phosphor screen forming a pattern consisting of a reflection and a diffraction pattern from which characterize the surface crystallography.

For a successful MBE growth, it is important to prepare substrates with a “contamination-free” and “defect-free” surface prior to the growth. Once contaminants

absorb on substrate surfaces during the handling of wafers, many of them could not be removed without damaging the surface. Hence, it has become a common practice to grow the substrate with a very thin oxide film immediately after the initial chemical etching and then load in the UHV chamber just prior to the growth.

2.2 X-ray diffraction:

Conventional high resolution X-Ray diffraction has been developed into a powerful tool for the nondestructive *ex-situ* investigation of epitaxial layers, of heterostructures and superlattice systems [15]. The information that is obtained from diffraction patterns concerns the composition and uniformity of epitaxial layers, their thicknesses, the built-in strain and strain relaxation, and the crystalline perfection related to their dislocation density. Furthermore information on interfaces like interdiffusion and intermixing can be obtained under certain circumstances as well.

Modern computer-controlled diffractometer systems use automatic routines to measure, record and interpret the unique diffractograms produced by individual constituents in even highly complex mixtures. A crystal lattice is a regular three-dimensional distribution (cubic, rhombic, etc.) of atoms in space. These are arranged so that they form a series of parallel planes separated from one another by a distance, which varies according to the nature of the material. For any crystal, planes exist in a number of different orientations - each with its own specific d spacing.

Any measurement of lattice spacing is in principle determined by Bragg's Law is given by the following formula:

$$2d_{hkl} \sin \theta_B = n\lambda \quad (2.1)$$

where d_{hkl} is the spacing of lattice planes with Miller indices (hkl) and θ_B is the corresponding Bragg angle. This equation follows from kinematic diffraction theory and neglects the fact that the refractive index of matter for X-Rays is less than 1 by a few parts in 10^{-6} and so the incident beam is refracted to an internal angle slightly smaller than the external one.

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

Figure 2.2. Bragg's Law

Artificially structured multilayers have become an important class of new materials that offer within certain limits unique electronic, optical, magnetic and mechanical properties. Along growth direction, usually two layers of different chemical

composition are alternatively deposited. The one-dimensional periodicity with period D is the origin of a one-dimensional periodic potential, which is superimposed on the three-dimensional crystal potential, the period of which is determined by the lattice constants of the materials. For all properties listed above the structural perfection of a multilayer system is decisive. The x-ray diffraction pattern of such a periodic structure consists of a series of satellite peaks accompanying the main zero-order diffraction peak along the direction of chemical modulation. Besides the position of the main superlattice peak and of the satellites, their intensities and FWHMs are experimentally accessible. The separation of satellite peaks corresponds to the period D .

With the triple-axis spectrometers, maps of a reciprocal lattice spot are measured in order to determine independently Bragg plane tilts from asymmetry effects and the substrate curvature induced broadening from film mosaicity. The use of triple-axis diffractometer offers the following advantages in the analysis of multilayer structures. Firstly, strain and strain gradients can be separated from structural imperfections such as tilts and mosaicity. In the reciprocal space maps, the intensity distribution along the strain influences the direction along the ω - 2Θ -scan (ω is the sample rotation angle and 2Θ is the detector rotation angle). This direction is called $q_{\perp}$ direction. Second, mosaic spread or bending is observed along the ω -scan in the reciprocal space maps. This direction is called $q_{\parallel}$ direction.

2.3 Photoluminescence

Of all optical techniques photoluminescence (PL) is perhaps the most widely used technique in characterizing III-V semiconductors and their alloy [16]. This is because PL

is a simple and an elegant technique that provides a wealth of information on the material for minimum investment in equipment and time. PL is employed both to understand the fundamental recombination process in the semiconductor as well as to characterize the quality of the material system. In this latter role, PL has become a valuable non-destructive technique for routine characterization of GaAs, InP and the alloy semiconductors based on them. PL is used to study bulk or epitaxial films for their inter- and intra wafer variation and to compare material grown by different techniques. Information obtained by PL on the optical quality of the semiconductor becomes relevant when it is going to be used to make an optoelectronic device.

Radiative recombination takes place when the semiconductor is under a nonequilibrium condition. That is, excess electron-hole pairs are created in the material by some external excitation to cause departure from equilibrium and the return to equilibrium occurs by the recombination of the excess carriers. When the excitation is achieved by optical means the resulting radiative recombination is photoluminescence. We can get the information about the band gap of the semiconductor materials from the spectrum of PL.

The PL transition energy of the strained MQW structures can be expressed as [17]

$$E_{PL} = E_{g0} + E_{cl} + E_{vl} + E_s - E_x, \quad (2.2)$$

where E_{g0} is the strain-free band gap of well layer material, E_{cl} and E_{vl} are the ground energy in the conduction band and the valence band, respectively. E_s is the energy shift due to the strain effect and E_x is the exciton binding energy. If the multi-quantum well

structure was capped with a narrow bandgap material, the narrow bandgap material need to be removed before measuring PL. Otherwise, it is difficult to get a strong signal.

For photoluminescence characterization, a chopped 514.5 nm Ar^+ laser line was used for excitation. Samples were cooled down to 5K in a closed-cycle helium cryostat. 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-sensitive lock-in amplifier system. The schematic diagram of the PL system is shown in Figure 2.3.

Figure 2.3. Schematic diagram of the photoluminescence setup

2.4 Fourier Transform Infrared Spectroscopy

To measure the spectrum in visible and ultraviolet spectral range, usually grating monochromator is used to disperse the radiation. In the infrared region, a different kind of spectroscopy has turned out to be advantageous and is used nowadays almost exclusively. In a Fourier Transform Infrared Spectroscopy (FTIR) the radiation from a broadband light source is divided into two parts by a beam splitter [18]. After reflection from a fixed and a movable mirror, respectively, the two partial waves are combined by the same beam splitter and focused on the detector.

Figure 2.4. Schematic diagram of the FTIR setup

Over there they interfere and yield the total intensity. For different positions of the movable mirror, the two partial waves get different phase shifts. Therefore, on the

detector the radiation field is superimposed with a time-delayed copy of itself. Hence what is basically measured when the detector signal is recorded while the mirror moves is the autocorrelation function of the radiation field (which is called the interferogram in FTIR spectroscopy). The Fourier transform of this autocorrelation function is the desired power spectrum in the frequency domain.

For our MQW structure samples, we use a sample holder shown in Figure 2.5. With such waveguide geometry, the incident radiation undergoes several total internal reflections in the samples, leading to an increased coupling strength.

Figure 2.5. Schematic diagram of (a) the FTIR sample holder and (b) the waveguide geometry.

In FTIR result, the maximum of the interferogram corresponds to equal distances of the two mirrors to the beam splitter, which causes constructive interference of the two partial waves for all wavelengths. For this reason the peak is called “White Light Position” (WLP). Outside this central structure the phase difference between the partial waves reflected at the two mirrors depends on the wavelength. For a broadband source their superposition to the interferogram contains less and less structure the further away

one gets from the WLP. From the Fourier transformation it follows that a narrow WLP correlates to a broad frequency distribution whereas a broad interferogram correlates with a narrow, “monochromatic” frequency distribution. The spectral resolution in FTIR is determined by the inverse of the total path of the movable mirror. No mechanical slits are required in contrast to conventional grating instruments.

FTIR spectroscopy makes use of the following two advantages in comparison to grating instruments. First one is the multiplex advantage. In Fourier transform spectroscopy, light from all spectral intervals contributes to the detector signal, which is not available in slit based grating instruments. However, grating instruments equipped with an Optical Multichannel Analyzer (OMA), which is commonly used in the visible, and the near infrared may exhibit this multiplex advantage, too. Second one is the throughput advantage. Since no slit is necessary in FTIR, large apertures can be realized resulting in a large throughput.

25 Secondary Ion Mass Spectrum

Secondary Ion Mass Spectrum (SIMS) is an analytical technique that can be used to characterize the surface and near surface (~ 30 nm) region of solids and the surface of some liquids [19]. The technique uses a beam of energetic (0.5-20 keV) primary ions to sputter the sample surface, producing ionized secondary particles that are detected using a mass spectrometer. The primary beam can be O_2^+ , O^- , Cs^+ , Ar^+ , Xe^+ , Ga^+ , or any of a number of other species that have been used successfully for various applications. The sample can intercept the primary beam at different angles of incidence, with a typical range from normal to 60 degrees from normal. The sputtering process is not just a surface

layer phenomenon but consists of the implantation of the primary species into the sample and the removal of surface atoms by the energy loss of the primary species in the form of a collision cascade. Many species are formed by the interaction of the beam with the sample, but the positive and negative secondary ions are the species of interest for SIMS. Most of the secondary particles are neutrals and can be detected by post ionization (Secondary Neutral Mass Spectrometry or SNMS). The secondary ions are extracted by electric fields and then energy and mass analyzed. Detection is by electron multiplier, Faraday cup, or ion sensitive image amplifier for imaging.

There are various kinds of SIMS instruments differing in their complexity, performance, and the ways in which they generate and detect secondary ions, but they all contain these basic components: 1) a device to produce energetic primary ions and direct a focused ion beam at the sample, 2) a chamber to mount the sample to analyzed, 3) a secondary ion energy analyzer, 4) a mass spectrometer to separate the secondary ions according to their mass/charge ratio, and 5) a detector. The ion optics used to transport the beam to the sample may be able to focus the beam to a diameter as small as 100 nm in some cases, but primary ion beam diameters of 10 to 100 μm are more commonly used.

Figure 2.6. Schematic diagram of SIMS equipment.

The shape of a SIMS depth profile is subject to several distortions. The true in-depth distribution of elements in the material analyzed can be altered by the physics of the sputtering process and by the shape of the sputtered crater.

Three different ion beam-mixing processes can be identified: recoil mixing, cascade mixing, and radiation-enhanced diffusion. Recoil mixing arises from direct collisions of the primary ions with sample atoms that are driven into the sample (anisotropic effect). Cascade mixing results from the motion and collisions of sample atoms with each other in the collision cascade; all memory of the primary impact is quickly lost and motion is isotropic, moving subsurface sample atoms toward the surface and vice versa. Radiation-enhanced diffusion (RED) is thermally activated diffusion,

enhanced by the higher-than-equilibrium concentration of vacancies and defects produced by the bombardment. The direction of diffusion depends on the in-depth distribution of vacancies. Depending on the material, RED can occur even at room temperature.

The mixing depth is related to the penetration depth or projected range of the primary ion species. The penetration depth increases with energy and decreases with angle of incidence with respect to the sample surface normal. Compared with a normal incidence beam, the beam at an oblique angle of incidence has a shallower penetration and more of the recoiled sample atom paths intersect the surface, which would result in a higher sputtering yield. Penetration of the primary species decreases with increasing mass or atomic number of the primary ion species.

In the presence of ion beam mixing, overlayer depth profiles characteristically exhibit two regimes with different slopes. An initial steep decay corresponds to the direct removal of overlayer species from the surface, either by sputtering, or by mixing into the subsurface layers. This steep decay is followed by a characteristic slow exponential decay of the overlayer signal, with a decay length (distance over which the signal drops by a factor $1/e$) on the order of the primary ion range. The slow decay arises because the overlayer material is mixed more-or-less homogeneously with the substrate material over the depth of primary ion penetration; only the small fraction of the overlayer material in the outermost surface layer is accessible to sputtering, while the remainder of the material is continuously mixed deeper into the sample as sputtering proceeds. The decay length can be defined as the depth over which a signal decreases by factor of e or:

$$I_{x_2} = I_{x_1} e^{-(x_2-x_1)/\lambda} \quad (2.3)$$

where λ is the decay length, I is secondary ion intensity, x_1 and x_2 are the depths between which the decay length is determined.

In microelectronics processing, structures composed of multiple layers on a substrate are common. Analysis of multilayer samples requires special attention to depth resolution, choice of species to monitor, quantification, and sputtering rate.

For superlattices and multi-quantum wells samples, the best depth resolution can be obtained with high mass primary beams at low energy and high angle of incidence, such as O_2^+ , Cs^+ , or Xe^+ primary beam energies of 2 to 4 keV. The resolution can be better than 7.5 nm/1 μ m or 0.75%. Note that use of a linear intensity scale is appropriate.

2.6 Summary

In this chapter, the experimental methods for compound semiconductor material growth and characterization were introduced. They are MBE, XRD, PL, FTIR and SIMS. These methods are powerful tools for III-V compound semiconductor research.

Chapter 3 Theoretical investigation of MQW structure and intersubband transition.

3.1 Quantum well structure

A typical QWIP is made of alternate layers of two different semiconductor materials. Since there is a difference in the conduction band alignment in these material layers, a series of potential barriers is formed analogous to the quantum barriers. Indeed, to the first approximation, one can ignore the underlying atomic potentials that produce the respective material band structures, and concentrate on the effects of the potential created by the band misalignment. This simplification can be brought about using envelope function approximation, in which the electrons can be treated as plane waves in free space. The effects of the atomic potentials are accommodated by substituting the mass of a free electron by the effective mass m^* of the material. It turns out that such a simplified approach is quite adequate in device design and modeling.

Schrodinger equation (3.1) is the most popular one and it usually gives satisfactory description to the energy levels in quantum wells [20].

$$\left[-\frac{d}{dz} \frac{1}{m^*} \frac{d}{dz} + V(z) \right] \Psi(z) = E \Psi(z), \quad (3.1)$$

where $m^* = m_w$ in the well and $m^* = m_b$ in the barrier region.

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Figure 3.1. A quantum well with a width L and a finite barrier height V_0 . The energy level $n=1$ and $n=2$ with their corresponding wave functions.

For a finite barrier quantum well, as shown in Fig 3.1, we have

$$V(z) = \begin{cases} V_0 & |z| \geq L/2 \\ 0 & |z| \leq L/2 \end{cases} \quad (3.2)$$

Using boundary conditions in which the wave function Ψ and its first derivative divided by the effective mass $(1/m^*)(d\Psi/dz)$ are continuous at the interface between the barrier and the well, that is,

$$\Psi\left(\frac{L^+}{2}\right) = \Psi\left(\frac{L^-}{2}\right) \quad \text{and} \quad \frac{1}{m_b} \frac{d}{dz} \Psi\left(\frac{L^+}{2}\right) = \frac{1}{m_w} \frac{d}{dz} \Psi\left(\frac{L^-}{2}\right). \quad (3.3)$$

Solving the Schrodinger equation, the eigenequations or the quantization conditions for even (3.4) and odd (3.5) wave functions, respectively, were obtained:

$$\alpha = \frac{m_b k}{m_w} \tan k \frac{L}{2} \quad (3.4)$$

$$\alpha = -\frac{m_b k}{m_w} \cot k \frac{L}{2}, \quad (3.5)$$

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where

$$k = \frac{\sqrt{2m_w E}}{\hbar} \quad (3.6)$$

$$\alpha = \frac{\sqrt{2m_b (V_0 - E)}}{\hbar} \quad (3.7)$$

The eigenenergy E can be found for even and odd wave function case by searching for the root in Equation (3.4) and (3.5) respectively, together with (3.6) and (3.7). The number of bound states N is determined by

$$(N-1)\frac{\pi}{2} \leq \sqrt{2m_w V_0} \left(\frac{L}{2\hbar} \right) < N\frac{\pi}{2} \quad (3.8)$$

The band structures of typical semiconductor quantum wells are shown in Figure 3.2.

Figure 3.2. Quantum well profiles for a semiconductor QW system

For a given quantum well potential and in the case of conduction band, we can replace $V(z)$ with

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$$V(z) = \begin{cases} V_0 (= \Delta E_c) & |z| \geq L_w / 2 \\ 0 & |z| < L_w / 2 \end{cases}, \quad (3.9)$$

In the case of valence band, $V(z)$ as

$$V(z) = \begin{cases} V_0 (= -\Delta E_v) & |z| \geq L_w / 2 \\ 0 & |z| < L_w / 2 \end{cases}, \quad (3.10)$$

where the energies are all measured from the edge of the conduction band or valence band.

The solution to Schrodinger equation mentioned above is for a single band **and** the coupling to other bands is negligible. Even with this simplicity, the results obtained here can be used to approximately estimate the band structure near the band edges.

3.2 The 8x8 $k \cdot p$ method for the quantum well structure

3.2.1 Theory background

In Section 3.1, the physics concept of a quantum well structure and a single band method are given. Using this method, we can only get the eigenvalue of the Schrodinger equation without the coupling of other bands. To find the band structures and wave functions for the quantum well structure with the effect of band coupling, more complete method must be introduced.

There are many numerical methods for the semiconductor band structure calculation, such as the effective mass, tight binding, the pseudopotential, the orthogonalized plane wave, the augmented plane wave, Green's function and the cellular

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methods [21, 22]. If our interest is near the band edges of direct band-gap, the $k \cdot p$ method is an effective method [23].

To explicitly investigate the energy band structure with the strain effect, one needs to do the calculation using $8 \times 8 k \cdot p$ Hamiltonian including the electron, heavy hole, light hole and spin-orbit splitting bands. R. People et al. investigated the energy band structure of bulk semiconductor layer with strain effect using $8 \times 8 k \cdot p$ matrix elements [24]. This method uses a basis consistent with the formalism of Luttinger and Kohn [21]. Craig P. compared the eight-band calculations of strained InAs/GaAs quantum dots with one-, four- and six-band approximations [25].

In our study, eight-band $k \cdot p$ Hamiltonian was used and strain effect was considered. The Hamiltonian for the QW is therefore given by [26]

$$H = \begin{bmatrix} E_g + \frac{\hbar^2 k^2}{2m_c} & 0 & pk_+ & -i\sqrt{\frac{2}{3}}pk_z & \frac{1}{\sqrt{3}}pk_- & 0 & \frac{1}{\sqrt{3}}pk_z & -i\sqrt{\frac{2}{3}}pk_- \\ 0 & E_g + \frac{\hbar^2 k^2}{2m_c} & 0 & \frac{i}{\sqrt{3}}pk_+ & \sqrt{\frac{2}{3}}pk_z & ipk_- & \sqrt{\frac{2}{3}}pk_+ & \frac{i}{\sqrt{3}}pk_z \\ pk_- & 0 & F & H & I & 0 & \frac{iH}{\sqrt{2}} & -i\sqrt{2}I \\ i\sqrt{\frac{2}{3}}pk_z & -\frac{i}{\sqrt{3}}pk_- & H^* & G & 0 & I & \frac{i}{\sqrt{2}}(G-F) & i\sqrt{\frac{3}{2}}H \\ \frac{i}{\sqrt{3}}pk_+ & \sqrt{\frac{2}{3}}pk_z & I^* & 0 & G & -H & -i\sqrt{\frac{3}{2}}H^* & \frac{i}{\sqrt{2}}(G-F) \\ 0 & -ipk_+ & 0 & I^* & -H^* & F & -i\sqrt{2}I^* & \frac{-iH^*}{\sqrt{2}} \\ \frac{1}{\sqrt{3}}pk_z & \sqrt{\frac{2}{3}}pk_- & \frac{-iH^*}{\sqrt{2}} & \frac{-i}{\sqrt{2}}(G-F) & i\sqrt{\frac{3}{2}}H & i\sqrt{2}I & -\delta + \frac{F+G}{2} & 0 \\ i\sqrt{\frac{2}{3}}pk_+ & -\frac{i}{\sqrt{3}}pk_z & i\sqrt{2}I^* & -i\sqrt{\frac{3}{2}}H^* & \frac{-i}{\sqrt{2}}(G-F) & \frac{iH}{\sqrt{2}} & 0 & -\delta + \frac{F+G}{2} \end{bmatrix} \quad (3.11)$$

where

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

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

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

$$G = Ak^2 - \frac{B}{2}(k^2 - 3k_z^2) \quad (3.12)$$

$$H = -Dk_z(k_x + ik_y)$$

$$I = \frac{\sqrt{3}}{2}B(k_x^2 - k_y^2) - iDk_xk_y$$

The strain part H_{str} can be obtained by the following substitution because of the same underlying symmetry: $A \rightarrow a$, $B \rightarrow b$, $D \rightarrow d$, $k_xk_y \rightarrow \varepsilon_{xy}$ etc. P_0 is the coupling between the conduction and valence bands, $E_p = 2m_0P_0^2 / \hbar^2$. Δ is the spin-orbit splitting. The γ_i s are modified Luttinger parameters defined in terms of the usual Luttinger parameters, γ_i^L , by [27]

$$\begin{aligned} \gamma_1 &= \gamma_1^L - \frac{E_p}{3E_g}, \\ \gamma_2 &= \gamma_2^L - \frac{1}{2} \frac{E_p}{3E_g}, \\ \gamma_3 &= \gamma_3^L - \frac{1}{2} \frac{E_p}{3E_g}, \end{aligned} \quad (3.13)$$

The strain enters through a matrix-valued potential that couples the various components, e_{ij} 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.

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3.2.2 Input parameters

In our work, we investigate the $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}/\text{InP}$ strained quantum wells grown on (001)-oriented InP substrates. The strain only exists in the $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ well region. The in-plane strain is $e_{xx} = (a_0 - a)/a$, where a is the unstrained lattice constant of $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ and a_0 is the unstrained lattice constant of InP. $e_{zz} = -2\frac{c_{12}}{c_{11}}e_{xx}$ [28], c_{11} and c_{12} are the elastic stiffness constants. We take the well layer's valence-band energy edge as the energy reference point.

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

$$P(\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}) = xyP(\text{GaAs}) + (1-x)(1-y)P(\text{InP}) + (1-x)yP(\text{InAs}) + x(1-y)P(\text{GaP}) \quad (3.14)$$

The band gap energy is calculated using [22]

$$E_g(\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}) = 1.35 + 0.668x - 1.068y + 0.758x^2 + 0.078y^2 - 0.069xy - 0.322x^2y + 0.03xy^2 \quad (3.15)$$

The electron effective mass is given by

$$m_e(\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y})/m_0 = (0.08 - 0.116x + 0.026y - 0.059xy + (0.064 - 0.02x)y^2 + (0.06 + 0.032y)x^2) \quad (3.16)$$

The material parameters for binary semiconductors can be found in Table 3.1. In the calculation, the band offset $Q_v = 0.58$ is used [22].

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Table 3.1. Parameters of GaAs, InAs, InP, GaP used in the calculation [22, 29].

	GaAs	InAs	InP	GaP
Lattice constant a_0 (Å)	5.6533	6.0584	5.8688	5.4505
Elastic stiffness C_{11} (10 GPa)	12.21	8.329	10.11	14.05
Elastic stiffness C_{12} (10 GPa)	5.66	4.526	5.61	6.203
Deformation potentials a_c (eV)	-7.17	-5.08	-6.0	-8.2
Deformation potential a_v (eV)	1.16	1.0	0.6	1.7
Deformation potential b (eV)	-2.0	-1.8	-2.0	-1.6
Luttinger parameter γ_1	6.98	20.0	5.08	4.05
Luttinger parameter γ_2	2.06	8.5	1.6	0.49
Luttinger parameter γ_3	2.93	9.2	2.10	2.93
Spin-orbit splitting energy Δ_0	0.341	0.39	0.108	0.08

The eight dimensional envelope wave function for the QWs can be expanded as [30]

$$\Phi_{n_v} = \{\Phi_{n_v}^j\}, (j=1, 2, \dots, 8), \quad (3.17)$$

where

$$\Phi_{n_v}^j = \exp[i(k_x x + k_y y)] \sum_m a_{n_v, m}^j \frac{1}{\sqrt{L}} \exp\left[i\left(k_z + m \frac{2\pi}{L}\right)z\right], \quad (3.18)$$

and $L=l+d$ is the period of the QWs, where l and d are the widths of the wells and barriers, respectively. n_v is the subband energy level index, k_x , k_y , and k_z are the wave vectors, and $a_{n_v, m}^j$ is the expanding coefficient.

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

$$\begin{aligned}
 P_{n_v}^{hh} &= \sum_{j=3,6} \sum_m a_{n_v,m}^{j*} a_{n_v,m}^j, \\
 P_{n_v}^{lh} &= \sum_{j=4,5} \sum_m a_{n_v,m}^{j*} a_{n_v,m}^j, \\
 P_{n_v}^{so} &= \sum_{j=7,8} \sum_m a_{n_v,m}^{j*} a_{n_v,m}^j.
 \end{aligned} \tag{3.19}$$

3.2.3 Results and discussion

3.2.3a Different well widths

For the well concentration and barrier width, the parameters listed in Table 3.2 were used in the investigation of four different strained or matched cases by changing the composition of well layer. For each composition, three well widths: 4 nm, 6 nm and 8 nm were used in the calculation of the energy band structures.

Table 3.2. Simulation parameters for different strain cases

Figure	The thickness of Barrier (nm)	The composition of the well layer (%)				Lattice Constant
		Ga	In	As	P	
3.3	30	39	61	93	7	Compressive
3.4	30	39	61	83	17	Matched
3.5	30	39	61	73	27	Tensile
3.6	30	39	61	63	37	Tensile

In the calculation, the first two energy bands in the conduction band and the first four energy bands in the valence band were estimated.

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1) Compressive strain

Figure 3.3. E-k dispersion relations for compressive strained MQW with different well widths.

Figure 3.3 shows three groups of in-plane energy dispersion curves of $\text{In}_{0.61}\text{Ga}_{0.39}\text{As}_{0.93}\text{P}_{0.07}/\text{InP}$ compressively strained MQWs with different well width. We distinguished the heavy hole (HH), light hole (LH) and split-off (SO) using Equation 3.19. From Fig 3.3, one can see the energy bands shift due to the change of well width. Along [100] and [110] directions, different E-k dispersion relations were given out. The first

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energy levels in the valence bands are HH1 and the second energy levels are LH1 for the three cases.

Figure 3.4. E-k dispersion relations for lattice matched MQW with different well widths.

Figure 3.4 shows the E-k dispersion relations for the lattice-matched case. From Figure 3.4, one can find that the difference of dispersion relation of 4 nm and 8 nm is more significant than that of Figure 3.5. The first levels of valence band are HH1 and the second bands are LH1 as well.

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Figure 3.5. E-k dispersion relations for small tensile strained MQW with different well widths.

Figure 3.5 shows the E-k dispersion relations for the small tensile strain case. From the results, it is found that the dispersion relations show indirect bandgap semiconductor when well width is 6 nm and 8 nm. This kind of energy band structure is not suitable for the light-emitting device due to low efficiency.

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Figure 3.6. E-k dispersion relations for large tensile strained MQW with different well widths.

Figure 3.6 shows the E-k dispersion relations for the larger tensile strain case. It is found that the three cases all become indirect bandgap semiconductor. On the other side, under large tensile strain, the light-hole will become the first energy level of the valence band when well width is 8 nm.

Xie et al. investigated the invert between the light-hole and heavy hole in the GaInAs/AlInAs strained MQWs using transfer matrix method (TMM) [31]. It was

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reported that the infrared absorption could be greatly enhanced when the light-hole was the first energy band. Since the demonstration of the p-type quantum well infrared photodetectors (QWIPs), the p-type QWIPs have been attracting great attention due to their advantage for normal incident detection via intersubband transition [32]. However, the performances of the p-type QWIPs are in general not as good as that of the n-type devices. This is due to the fact that in conventional p-type QWIPs free holes occur primarily in the heavy-hole ground state with large effective mass [33]. This leads to weak absorption because of the inverse relationship between the effective mass and the absorption coefficient. If the light hole can be the first energy level of valence band, the performance of p-type QWIP would be improved greatly.

To verify the stability of the larger tensile strained InGaAsP/InP MQW structures, the critical layer thickness was estimated using People Bean model [34]. For single layer, the critical layer thickness is given by the expression

$$d_c = \frac{b(1-\nu)}{32\pi f^2(1+\nu)} \left[\ln \left(\frac{d_c}{b} \right) \right], \quad (3.20)$$

where $b = \frac{a_f}{\sqrt{2}}$, a_f is the lattice parameter of InGaAsP film, ν (-0.3) is Poisson's

Ratio and $f = \frac{a_f - a_s}{a_s}$. a_s is the lattice parameter of InP.

For InGaAsP/InP MQW structures, the lattice parameter for the multi-quantum wells part are estimated using [35]

$$\frac{a_{InGaAsP} \times d_{InGaAsP} + a_{InP} \times d_{InP}}{d_{InGaAsP} + d_{InP}} \quad (3.21)$$

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where a_{InGaAsP} is the thickness of well layer and d_{InP} is the thickness of barrier layer. From (3.20) and (3.21), one can get the critical layer thickness of InGaAsP/InP MQW structures being 5273 nm. In the simulation, InGaAsP well layer thickness is 8 nm and InP barrier layer thickness is 30 nm. For 30 periods of such QWs in the QWIP devices, the total thickness is much less than the critical thickness and these structures are, therefore, stable.

From the simulation results, one can see that with the increasing of phosphorus composition in the well layers, the band gap of the well layers increases as well. At the same time, the energy difference of E_1 and E_2 increases with the increase of well width at certain composition. From this, one can choose the suitable well width and well layers composition to get certain wavelength of the n-type QWIP device. The band gap, lattice constant, E_2-E_1 energy ($k=0$) and wavelength for the four figures were listed in Table 3.3.

Table 3.3. Well layer band gap, lattice constant, E_2-E_1 energy ($k=0$) and wavelength

Figure	Band gap (eV)	Well layer lattice constant (Å)	E_2-E_1 (meV)	Wavelength
3.3 (Compressive)	0.740	5.887	136 (4 nm)	9.12
			178 (6 nm)	6.97
			169 (8 nm)	7.34
3.4 (Matched)	0.838	5.867	118 (4 nm)	10.51
			158 (6 nm)	7.85
			163 (8 nm)	7.61
3.5 (Tensile)	0.939	5.848	104 (4 nm)	11.92
			139 (6 nm)	8.92
			154 (8 nm)	8.05
3.6 (Tensile)	1.041	5.828	90 (4 nm)	13.78
			121 (6 nm)	10.25
			143 (8 nm)	8.67

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Table 3.4. Absorption wavelength (HH1-HH2)

Strain	Compressive			Matched			Small Tensile			Large Tensile		
Well width (nm)	4	6	8	4	6	8	4	6	8	4	6	8
Wavelength (μm)	9.8	16.5	19.7	10.6	20	31	11.6	21.4	24.4	13.5	23	NA

From Figure 3.3, the detected wavelengths based on the intersubband transition between E_{hh1} and E_{hh2} are 9.8, 16.5 and 19.7 μm for the MQWs with well width of 4, 6, and 8 nm respectively. These data for the four strain cases are also summarized in Table 3.4. On the other hand, one can see that the E-k relation of energy bands in the valence bands change with the strain in the well layer. Under tensile strain, the well layer material becomes an indirect band gap semiconductor. This effect increases with the increase of strain.

In our case, at a larger tensile strain, the light-hole became the first energy level of valence band in the InGaAsP/InP MQW structure. It is very helpful to design a p-type InGaAsP/InPQWIP devices with improved performance.

3.2.3b Doping effect

For n-type MQW structures, it is known that doping will induce the band gap narrowing [36]. The value of band gap will decrease with the increasing of doping concentration. It follows this equation:

$$\Delta E = (1.6 \times 10^{-8} \times D^{1/3}) \quad (3.20)$$

where D is doping concentration. To investigate the effect of doping concentration, three doping Silicon doping concentration, $1 \times 10^{17} \text{ cm}^{-3}$, $1 \times 10^{18} \text{ cm}^{-3}$ and $1 \times 10^{19} \text{ cm}^{-3}$ were

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assumed in the well layers. In the calculation, well widths of the MQW structures were fixed at 4 nm.

Figure 3.7. E-k dispersion relations of compressive strained MQWs with different well doping concentrations.

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Figure 3.8. E-k dispersion relations of lattice matched MQW with different doping concentration.

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Figure 3.9. E-k dispersion relations of small tensile strained MQW with different doping concentrations.

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Figure 3.10. E-k dispersion relations of large tensile strained MQW with different doping concentrations.

Doping induces band gap narrowing in the well layer. For the electron and hole, it means an increase of barrier height. From Figure 3.7 to Figure 3.10, one can see the doping effect on the electron and hole energy band structures. Due to the large effective mass of hole, the energy band structures of valence band did not change significantly. For electron with small effective mass, the energy band structures change with the doping concentration in the well layer. The band gap narrowing, E_2-E_1 energy difference (at $k=0$) and wavelength for the four figures are listed in Table 3.5.

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Table 3.5. Well layer band gap narrowing, E_2-E_1 energy ($k=0$) and wavelength

Figure	Doping concentration (cm^{-3})	Band gap Narrowing (meV)	E_2-E_1 (meV)	Wavelength (μm)
3.7 (Compressive)	1E17	7.4	137.5	9.02
	1E18	16	139.7	8.88
	1E19	34	144.2	8.60
3.8 (Matched)	1E17	7.4	120.9	10.26
	1E18	16	123.0	10.08
	1E19	34	127.4	9.73
3.9 (Tensile)	1E17	7.4	105.9	11.71
	1E18	16	107.9	11.49
	1E19	34	112.1	11.06
3.10 (Tensile)	1E17	7.4	91.9	13.49
	1E18	16	93.7	13.23
	1E19	34	97.6	12.70

From Table 3.5, one can see that with the increase of doping concentration, the absorption wavelength will decrease.

3.3 The intersubband absorption coefficient

3.3.1 Theory background

For a large number of identical quantum wells, the system is better described by periodic boundary condition. In this case, one obtains energy bands $E_n(k_z)$, where k_z is the wavevector component parallel to the growth direction, which is a good quantum number. Such a system is normally called superlattice if the barriers are so thin that strong coupling between different QWs occurs.

A superlattice can be described by the Kronig-Penney model of a one-dimensional lattice with periodic boundary conditions. The z -dependent part of the

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envelope wave function can be written as the product of Bloch part, which is periodic in the superlattice period, and a slowly varying plane-wave part

$$\varphi_n(z) = e^{ik_z z} u_n(z) \quad (3.21)$$

where $u_n(z) = u_n(z+d)$ and d is the superlattice period. At the same time, the free motion in the x and y directions can be expressed as $e^{i\vec{k}_\perp \cdot \vec{r}}$, where $\vec{k}_\perp$ denotes the two-dimensional vector (k_x, k_y) .

To calculate the absorption coefficient, we start from the Fermi's golden rule for the transition rate from a state i to a state f induced by an external electromagnetic field

$$W_{if} = \frac{2\pi}{\hbar} \left| \langle \psi_f | H' | \psi_i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega) \quad (3.22)$$

where H' is the interaction Hamiltonian, $H' = (e/2m^*)(\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A})$ (the electron charge is $-e$).

A linearly polarized plane electromagnetic wave is described by

$$\vec{E} = E_0 \vec{e} \cos(\vec{q} \cdot \vec{r} - \omega t) \quad (3.23)$$

where $\vec{E}$ is the electric field, $\vec{e}$ is the polarization vector, and $\vec{q}$ is the propagation vector. The corresponding vector potential, which is related to the electric field by $\vec{E} = -\partial \vec{A} / \partial t$, can be written as

$$\vec{A} = \frac{iE_0 e}{2\omega} e^{i(\vec{q} \cdot \vec{r} - \omega t)} + c.c. \quad (3.24)$$

Employing the dipole approximation, the $\vec{p}$ commutes with $\vec{A}$, which leads to $H' = (e/m^*) \vec{A} \cdot \vec{p}$.

From equation (3.21) and (3.22), only the term proportional to e , yields a contribution at finite frequency. The electrical field of the radiation must have a z

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component to couple to the intersubband transition. In practice, some effect will relax this rule, such as indirect-gap semiconductor, spatial variation of the effective mass and coupling to the valence band.

The absorption coefficient α is usually defined through the ratio of the absorbed electromagnetic energy per unit time and volume, $\hbar\omega \cdot W_{if} / V$, and the intensity of the incident radiation I , summed over all occupied initial and empty final states. By taking into account the state occupation via the Fermi-Dirac distribution function, and replacing the energy-conserving δ function by a normalized Lorentzian with half width at half maximum (HWHM) of Γ , α is obtained through integration over k_x , k_y and k_z . After integration through k_x and k_y (assuming parabolic bands), we get [37]

$$\alpha = \frac{e^2 kT}{\epsilon_0 c \eta \hbar^2 \pi n^* \omega} \int_0^{\pi/d} dk_z \left| \langle 1 | p_z | 2 \rangle \right|^2 \ln \left[\frac{1 + \exp([E_F - E_1(k_z)]/kT)}{1 + \exp([E_F - E_2(k_z)]/kT)} \right] \times \left(\frac{\Gamma / \pi}{(E_2(k_z) - E_1(k_z) - \hbar\omega)^2 + \Gamma^2} \right) \quad (3.25)$$

Using this equation, the absorption coefficient of the transition from E1 to E2 can be calculated. One can also change the start state and the final state to get the absorption coefficient between the other pair of states.

3.3.2 Results and discussion

We use the lattice matched $\text{In}_{0.61}\text{Ga}_{0.39}\text{As}_{0.83}\text{P}_{0.27}/\text{InP}$ multi quantum wells structure to do the simulation. In this work, the well width and barrier width are varied to see how the device parameters affect the absorption coefficient.

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- 1) The barrier width effect on the absorption coefficient.

Firstly, we set the well width to 5 nm and change the barrier width to see the effect on the absorption coefficient. Fig. 3.1.1 shows the absorption coefficient of E_1 -to- E_2 with different barrier widths. When the barrier width is 5 nm, this structure is a superlattice; the absorption coefficient reflects the absorption of miniband-to-miniband.

The doping levels in the well were adjusted to keep the Fermi level at 100 meV for the four different barrier widths. The quasi-Fermi level F_c for the electron can be determined using

$$N = \sum_{\substack{n=\text{occupied} \\ \text{subbands}}} N_n = \sum_n \int dE \rho_e^{2D}(E) f_c^n(E) \quad (3.26)$$

Here, $\rho_n^{2D}(E)$ is two-dimensional density of states and $f_c^n(E)$ is the Fermi-Dirac distribution for the electrons in the conduction band [20].

The Fermi energy lies above the top of the first miniband, i.e., the first miniband is "full". The two peaks in the absorption coefficient are corresponding to the absorption at $k_z = 0$ (high energy peak) and $k_z = \pi/d$ (low energy peak, d is the quantum well period), respectively. The asymmetry of the intensity for the two peaks is decided by the variation of the oscillator strength across the Brillouin zone. For the barrier width of 10 nm, the absorption peak at high energy is not so significant. When the barrier thickness of a superlattice increases, the coupling of the different wells can be neglected and the miniband widths below the barriers will decrease and eventually approach zero. When the barrier width changes to 20 nm, there are two energy levels in the well (see Table 3.6). The E_2 energy level is near to the edge of barrier conduction band. The absorption is bound-to-bound transition.

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Figure 3.11. Absorption coefficient of the structures with the same well width and different barrier widths.

Table 3.6. Parameters used in the calculation for Figure 3.11

Barrier Width (nm)	Barrier Height (meV)	E1 at $k_z = 0$ (meV)	E2 at $k_z = 0$ (meV)	Doping Level (cm^{-3})	Fermi Level (meV)	HWHM of Γ (meV)	Temperature (K)
5	214	62.3	259.5	$5.6\text{E}18$	100	10	70
10	214	65.8	221.9	$5.1\text{E}18$	100	10	70
20	214	66.1	210.2	$5\text{E}18$	100	10	70
30	214	66.1	208.5	$5\text{E}18$	100	10	70

2) Different well width but the same barrier width

We set the barrier width at 30 nm and change the well width to see the effect of the well width on the absorption coefficient. Table 3.7 lists the parameters used in the calculation.

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Table 3.7. Parameters used in the calculation for Figure 3.12

Well Width (nm)	Barrier Height (meV)	E1 at $k_z = 0$ (meV)	E2 at $k_z = 0$ (meV)	Doping Level (cm^{-3})	Fermi Level (meV)	HWHM of Γ (meV)	Temperature (K)
4	214	84.9	218.8	$2.9\text{E}18$	100	10	70
5	214	66.1	208.5	$5\text{E}18$	100	10	70
6	214	52.7	183.2	$5.9\text{E}18$	100	10	70
7	214	42.9	156.6	$6.1\text{E}18$	100	10	70

Figure 3.12: Absorption coefficients of the MQWs structures with different well widths and same barrier width.

From Figure 3.12 and Table 3.7, one can see that the changing well width induces the shift of energy levels of E1 and E2. This causes the shift of absorption peak. On the other hand, when the well width is larger, the absorption coefficient will be larger.

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Figure 3.13. Absorption coefficient of MQW structures with 4 nm well width and 30 nm barrier.

Figure 3.13 shows the overall absorption coefficient and the separated E_1 - E_2 , E_1 - E_3 , E_1 - E_4 and E_1 - E_5 of well width of 4 nm. In this case, there is only one energy level in the quantum well, so it is a bound-to-continuum (B-C) transition. It is in contrast to the miniband-to-miniband (M-M) transition and bound-to-bound (B-B) transition, the energy of B-C is not determined by the available final states of the structure but by the oscillator strength of each state in the continuum. It turns out that in this structure, there is a final state with which the absorption is a maximum. This final state is denoted by E_m . The position of E_m is determined by the quantum well parameters. Previously, when the second resonant E_2 is below the barriers, no matter it is a bound state of an isolated well or a miniband of a superlattice, E_m always coincides with E_2 . When the second resonant

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state is above the barrier height, however, E_m no longer necessarily occurs at the second resonant state or the second miniband. It is because E_2 can be originated from a resonant state in the barrier layers, and thus the state does not provide the correct parity and the large wave amplitude in the well region for efficient transition. From Figure 3.13, one can see that the absorption maximum occurs at the E_1 - E_3 . In this case, the transition energy requires further consideration.

We also calculated the other case, small well width with small barrier width. We used 4 nm well width and 4 nm barrier width. In this case, the second energy level E_2 will be above the barrier with a big value. At the same time, the coupling between the different wells is significant due to the small barrier value. The absorption coefficient is shown in Figure 3.14.

Figure 3.14. Absorption coefficient of MQW structures with 4 nm well width and 4 nm barrier.

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From Fig 3.14, one can see that the difference between the overall absorption and E_1 - E_2 absorption is very small. This shows that the absorption is mainly due to the E_1 - E_2 transition. It is very different from the results in Figure 3.13. At the same time, the absorption coefficient value in this case is very much greater than that in Figure 3.13. The results in Figure 3.13 and Figure 3.14 all came from a structure with 4 nm well width but different barrier widths. Figure 3.13 is 30 nm and Figure 3.14 is 4 nm. In Figure 3.13, the E_1 level is a bound level, and the absorption is a bound-to-continuum transition. In Figure 3.14, the E_1 level is a miniband, and it is a miniband-to-miniband transition. The shape of the absorption coefficient is similar to that 5 nm structure in the Fig 3.11 as it is also a miniband-to-miniband transition,

On the other hand, from Figure 3.12 one can see that the absorption coefficient increases with the well width. But in the design of QWIP device, one must keep in mind that if E_2 is too far from the barrier conduction band edge, the electrons that transit to this level are hard to transport out of quantum well. This will lead to the decreasing of the responsivity of QWIP device.

3.4 Summary

In this chapter, the quantum well structures and single band method were first introduced to investigate the energy levels in a quantum well structure. After that, the 8×8 $k \cdot p$ method was used to investigate the strain effect on the band structures of InGaAsP/InP multi-quantum wells. In this study, different well widths and different doping concentrations for each strain case were studied explicitly. To the best of our

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knowledge, it is the first study of InGaAsP/InP MQW energy band structure considering doping concentration, strain and well width effect at the same time.

For the intersubband absorption in MQW structures, we investigated the effect of well width, barrier width on the absorption coefficient. The information acquired is useful to design of the QWIP devices.

Chapter 4 Si-doped strained InGaAsP/InP MQW structures

4.1 Introduction:

Since observation of the intersubband transition in quantum wells, a great deal of work has been done in the quantum well infrared detectors [38]. AlGaAs/GaAs MQW is a commonly used system for QWIP device [39]. However, with the consideration of the oxidation in the AlGaAs system, the InGaAsP system has drawn more and more attention [40]. In addition to the application in QWIP device, InGaAsP material is also widely used in other optoelectronics devices, such as avalanche photodiode, modulator and Semiconductor Optical Amplifier [41-46].

At first, InGaAsP system was grown by liquid phase epitaxy (LPE) [47] or MOCVD [48]. With the introduction of P cracker cell, SSMBE became a versatile technique to grow the InGaAsP system on GaAs substrate or InP substrate [49].

We have recently reported successful growth of high quality quaternary InGaAsP materials on InP and GaAs substrates using all solid sources [50, 51]. In this part, we report characterization of n-type strained InGaAsP/InP quantum wells structures grown by SSMBE.

4.2 Samples growth

The samples studied are three InGaAsP/InP MQW structures with different InGaAsP well widths and five InGaAsP/InP MQW structures with different Si-doping

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concentrations in the InGaAsP wells grown on semi-insulating InP (100) substrates in a solid source Riber 32 molecular beam epitaxy (MBE) system. The group III elements, In and Ga, are from effusion cells while the group V elements, As and P, are from cracker cells. In the growth, a Si-doped bottom contact layer of 500nm thick was first grown. Then the MQW structures, which contained 30 periods of Si-doped InGaAsP wells separated by 27 nm wide undoped InP barriers, were grown. They were then followed by a 500 nm-thick Si-doped InP upper contact layer.

For the samples with different well widths, the nominal well widths of the three samples are 4 nm, 6.5 nm and 10 nm, respectively. The Si doping concentration was 10^{18} cm^{-3} in all doped layers.

For the samples with different Si-doping concentrations, the nominal well widths is 5 nm and the Si doping concentrations in the wells are $5 \times 10^{18} \text{ cm}^{-3}$, $1 \times 10^{18} \text{ cm}^{-3}$, $5 \times 10^{17} \text{ cm}^{-3}$, $1 \times 10^{17} \text{ cm}^{-3}$ and $5 \times 10^{16} \text{ cm}^{-3}$, respectively. The Si doping concentration of the contact layers was $1 \times 10^{18} \text{ cm}^{-3}$. The substrate temperature during growth was 480°C.

Figure 4.1. Diagram of the InGaAsP/InPMQW structures.

SIMS is a tool to monitor MQW structures growth. An IMF 6f SIMS system was used to measure the InGaAsP/InP MQW structures. O_2^+ , Cs^+ ions were used for the first ion source. P, Ga, As atoms were monitored. The InGaAsP/InP MQW sample's SIMS result is shown in Figure 4.2. In the figure, only the SIMS result of MQW part was shown, not including the contact layer. In the region of InGaAsP well layers, the ion counts of Ga and As increase with the ion count of P decreases. On the other hand, in the region of InP barrier layers, ion count of P increases with the ion counts of Ga and As decreases. From this result, one can clearly see the periodical component change of well layer and barrier layer. But it is difficult to directly get the exactly well width from the SIMS depth profile result due to sputter-induced roughness [52].

Figure 4.2. SIMS result of InGaAsP/InP MQW sample.

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4.3.1 X-ray diffraction

Figure 4.3 shows the (004) InP Bragg reflection rocking curves plotted on a logarithmic scale using the 5-crystals mode, the Bartels monochromator in the (220) setting and $\omega/2\theta$ geometry. The three pairs of spectra correspond to the three samples that are named as N487, N486 and N488 and whose well widths are 4 nm, 6.5 nm and 10 nm, respectively. In each pair, the solid curve shows the measured result while the dashed curve shows the simulated result.

From Figure 4.3, well-defined periodic satellite peaks up to the 20th-order, indicating very good layer periodicity, were identified. Their sharpness indicated abrupt interfacial coherently strained QWs [53]. To get improved diffraction profiles, we added an analyzer before the detector and then measured the rocking curves again. The results are shown in Figure 4.4. The pronounced Pendellosung fringes appear between the satellite peaks. It is the indication of the high crystalline quality of the layers too, since any interface imperfection, relaxation, or compositional inhomogeneity would cause loss of phase coherence and eliminate the satellite peaks and the Pendellosung fringes [54].

Figure 4.3. XRD results of three samples, which consisting of 30 quantum wells and grown at identical conditions. The nominal well widths of the three samples are 4 nm (N487), 6.5 nm (N486), and 10 nm (N488), respectively. The dashed lines are the simulation results.

Figure 4.4. XRD results with Pendellosung fringes of the three samples: N487 (4 nm), N486 (6.5 nm) and N488 (10 nm).

$\Delta\theta_0$ is the angular separation between the zero-order satellite peak and InP substrate (004) reflection. It gives the average mismatch of the MQW along the growth axis. To investigate the strain in the MQW structure, the most important thing is to determine the position of the zero-order peak. It is commonly assumed that the zero-order

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satellite peak is either the strongest satellite peak or the one next to the substrate peak. For complex MQW structure, however, this is not always the case [55,56].

To accurately determine the position of the zero-order satellite peak, simulation using dynamical x-ray theory was carried out. During the simulation, firstly, we changed the composition in the well layers to change the mismatch in the MQW structures. The parameters used in the simulation are listed in the first three rows of Table 4.1.

Table 4.1. Parameters used for simulation in Figure 4.5 and 4.6

	Thickness of Barrier (nm)	Thickness of well (nm)	Composition of the well material (%)			
			Ga	In	As	P
Fig4.5 (a)	25	8	39	61	63	17
Fig 4.5 (b)	25	8	39	61	73	27
Fig 4.5 (c)	25	8	39	61	83	37
Fig 4.6 (a)	25	4	39	61	63	37
Fig 4.6 (b)	25	6	39	61	63	37
Fig 4.6 (c)	25	8	39	61	63	37

The rocking curves in Figure 4.5 clearly show that the intensities of the satellite peaks are modulated by packet wave and the satellite peaks were grouped into the envelope peaks. In the three rocking curves (a), (b) and (c), all envelope pockets involve four satellite peaks except the zero-order packet which has nine satellite peaks (two group satellite peaks plus one center peak, marked using an upper arrow). The intensity of this peak is higher than other satellite peaks and its position is determined by the mismatch in the MQW structure. It is clearly seen that this peak moves towards the substrate peak

with the decrease of mismatch in the MQW structure and it overlaps with substrate peak when the mismatch becomes zero, as shown in Figure 4.5 (c).

Figure 4.5. Simulated rocking curves of the MQW structures with different lattice mismatch.

To investigate the effect of the well width on the rocking curve, another set of parameters were used, which are listed in the last three rows of Table 4.1, and the results are shown in Figure 4.6. As shown in this figure, the number of the satellite peaks in each group varies with the width of the well layer, but the position of the zero-order peak does

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not. This envelope phenomenon has been reported by Zhuang et al. and been well-explained using x-ray dynamical theory [57]. In this paper, it was found that the intensity of satellite peaks of XRD result was modulated by the wave function of each sublayer in one superlattice period. From the simulation using x-ray dynamical diffraction theory, it was discovered that the intensity of the satellite peak situated near the modulating wave node point of each sublayer is very sensitive to the layer thickness. X-ray kinematical diffraction theory was used to explain the modulation phenomenon as well.

Figure 4.6. Simulated rocking curves of the MQW structures with different well widths.

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Using the conclusion drawn from the above simulation, one can easily determine the position of the zero-order satellite peak for the three samples studied. The $\Delta\theta_0$ can then be easily worked out from the three rocking curves shown in Figure 4.3. From the position of zero-order satellite peaks, one can see that the three InGaAsP/InP MQW structures are all tensile strained.

As a confirmation for the tensile strain, we also did the (115) reciprocal space mapping of the three samples. The result of sample N488 is shown in Figure 4.7. As shown in the figure, the satellite peaks stay in a line normal to the x-axis, indicating a fully strained case. This is because that the InGaAsP wells and the InP substrate have the same lattice constants in the direction parallel to the interfaces. The strain relaxation will cause the peak-line to rotate clockwise, and in the case of full relaxation, the peak-line will parallel to the longer sides of the rectangle in the figure, which indicates the difference of the lattice constants of the two materials [58].

Figure 4.7. XRD (115) reciprocal space mapping of the sample N488.

The average mismatch of the MQW along the growth direction ($\frac{\Delta q}{q_{\text{InP}}}$) can be

described by the following expressions [59],

$$\frac{\Delta q}{q_{\text{InP}}} = -\frac{\Delta \theta_0}{\tan \theta_B} \quad (4.1)$$

$$q_{\text{InP}} = \frac{2\pi}{d_{\text{InP}}} \quad (4.2)$$

where θ_B ($= 31.6682$) is the Bragg angle for the (004) reflection of the InP substrate, d_{InP} is the lattice spacing of the InP (004) diffraction. Equation (4.1) is obtained by

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simplifying diffracting Bragg's law and making the small angle approximation for $\Delta\theta_0$. From the Bragg's law, $\Delta q / q_{\text{InP}} = -\Delta d / d_{\text{InP}}$, the strain perpendicular to the surface was directly determined from the position of the zero-order satellite peak of the (004) rocking curve of MQW structures. The extracted $\Delta\theta_0$ is listed them in the second column of Table 4.2. Using Equation 4.1 and 4.2, the mismatch in the direction perpendicular to the surface was calculated and listed them in the third column of Table 4.2. One can see that the mismatch values ($\Delta d / d_{\text{InP}}$) of the three samples are almost same.

Table 4.2. Data extracted from the X-ray rocking curves of the three samples.

Samples	$\Delta\theta_0$ (sec.)	$\Delta d / d_{\text{InP}}$	$\Delta\theta$ (sec.)	Period (nm)	FWHM of 0th-order peak (sec.)	Intensity of 1st-order peak (a. u.)
N487	2023.2	1.59×10^{-2}	604.8	33	51 sec.	52147
N486	1994.4	1.58×10^{-2}	561.6	35.5	51 sec.	122014
N488	2217.6	1.74×10^{-2}	511.2	39.1	50 sec.	371528

The XRD rocking curves were fitted using Philips X'pert Epitaxy and the fit parameters are listed in Table 4.3. From the fitted component, we calculated the lattice constant of $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$ using the following expression [60] and the parameters listed in Table 2.2:

$$a_0 = 0.4174x + 0.2021y - 0.0123xy + 5.4512 \quad (4.3)$$

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Table 4.3. Simulation parameters for the XRD results shown in Figure 4.3

	$\Delta d / d_{InP}$	Barrier thickness (nm)	Well thickness (nm)	Composition of well material (%)			
				Ga	In	As	P
N487	1.58E-2	27.5	4.2	39	61	60	40
N486	1.55E-2	26.5	6.4	39	61	60.5	39.5
N488	1.71E-2	27.5	10	39	61	58	42

Because of the epitaxy between the InGaAsP layers and the InP substrates, the InGaAsP layers are tetragonally distorted. If there is no strain relaxation in the MQW structures, the lattice parameter for an unstrained cubic $In_{1-x}Ga_xAs_yP_{1-y}$ layer, $a_0(x, y)$ can be found from the InP substrate lattice parameter, $a_{InP} = 5.8686 \text{ \AA}$ and the experimentally determined value $\Delta d / d_{InP}$ using the relation below [61]

$$\left(\frac{a_0(x, y) - a_{InP}}{a_{InP}} \right) = \left(\frac{C_{11}}{C_{11} + 2C_{12}} \right) \left(\frac{\Delta d}{d_{InP}} \right), \quad (4.4)$$

where C_{11} and C_{12} are the elastic stiffness constants obtained by interpolating from the values corresponding to the binary compound. Hence, based on the relation shown above, the mismatches of the MQW structures can be calculated and they are listed in the second column of Table 4.3. It is clearly seen that the mismatch extracted from the three rocking curves have no significant difference as the three samples grown at identical conditions except the well width. At the same time, one can see that the mismatch obtained from the zero-order satellite peak position is similar to that estimated from the simulation. It is evident that the position of the zero-order satellite peak what we choice is right.

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The angular spacing $\Delta\theta$ between the satellite peaks is a measure of the MQW period length, that is the sum of the InGaAsP well and InP barrier thickness. The period Λ of the MQW structures is straightforward determined from the $\Delta\theta$ through the following expression [62],

$$\Lambda = \frac{\lambda}{2\Delta\theta \cos(\theta_B + \Delta\theta_0)} \quad (4.5)$$

where $\lambda=1.54056\text{\AA}$ for the $\text{Cu}_{K\alpha 1}$ line, θ_B is the Bragg angle for the (004) reflection of the InP substrate. The $\Delta\theta$ of the three samples in the fourth column of Table 4.2 and the corresponding period are listed in the fifth column. It is seen that the period values derived are almost the same as designed.

For the MQW structure, the full width at half maximum (FWHM) of the zero-order peak is a parameter that represents the interfacial quality of multiplayer structures. The intensity of the first-order satellite peak, which is the characteristic of MQW structure rocking curves, is strongly dependent upon diffusion [63], which usually degrades the sharpness of interfaces of the heterostructures and thus results in reduced satellite peak intensities particularly for the higher orders. The FWHM of the zero-order peaks and intensity of the first-order peaks of the three samples are listed in the sixth and seventh columns of Table 4.2, respectively. It is seen that the FWHMs of the three samples (51, 51 and 50 sec.) are basically the same and relatively narrow, indicating high quality of the interfaces. As for the increase of the first-order peak intensity with well width of the MQW structures, it is due to that wider InGaAsP quantum well layers contribute more to the diffraction.

4.3.2 Photoluminescence

Photoluminescence measurement was performed using the setup described in the Section 2.3. Prior to the measurement, the upper contact layer of the MQW structure was first removed by wet etching to reveal the MQWs.

Figure 4.8.5K PL of three MQW structures with different well widths: N487 (4.2 nm), N486 (6.4 nm) and N488 (10 nm). Solid lines are experimental results and dash lines are fitting results.

Figure 4.8 shows the 5K spectra of the three InGaAsP/InP MQW structures with Si-doping density of $1 \times 10^{18} \text{ cm}^{-3}$ in the InGaAsP well. The well widths of the three samples are 4.2 nm (N487), 6.4 nm (N486) and 10 nm (N488), respectively. From the XRD result in Figure 4.7, it is clear that the InGaAsP/InP MQW structures are under fully strained lattice mismatch. The tension strain splits the fourfold degenerate multiplet at the valence-band edge into a pair of degenerate doublets, HH1 and LH1, which are of

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spin degeneracy. The electrons in the conduction band will recombine with the holes in the two energy levels to generate the radiation. So there should be two PL peaks in the PL spectra. The peak position, FWHM and intensity are listed in Table 4.4. All of the values were obtained from Gaussian function fit parameters of the PL spectra in Figure 4.8.

Table 4.4. The peak positions, FWHM and Intensity of the PL spectra in Figure 4.8

Sample	Peak	Peak position (eV)	FWHM (meV)	Intensity (a. u.)
N487	Low-energy	1.098	33	3521
	High-energy	1.115	19	7516
N486	Low-energy	1.041	40	2335
	High-energy	1.061	23	2821
N488	Low-energy	1.010	47	1831
	High-energy	1.040	34	1521

Figure 4.9. PL peak positions under various temperatures of the samples N487, N486 and N488.

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We also investigated the PL peak position shift as a function of temperature. In Figure 4.9, the high-energy PL peak positions under various temperatures of the three samples are plotted, and the Varshni's Equation is also introduced for comparison [64],

$$E(T) = E(0) - \alpha T^2 / (\theta + T), \quad (4.6)$$

where T is the absolute temperature in K, $E(0)$ is the band gap energy in eV at 0 K, and α and θ are fitting parameters. As indicated in the Figure 4.9, it is clear that the temperature dependence of the PL peak positions of the three samples agree well with the Varshni's relation.

Table 4.5 Experimental PL peak positions and simulation results of eight-band method

Sample	Peak	Peak position (eV)	Simulation peak position (eV)
N487	Low-energy	1.098	1.09
	High-energy	1.115	1.10
N486	Low-energy	1.041	1.03
	High-energy	1.061	1.05
N488	Low-energy	1.010	1.01
	High-energy	1.040	1.03

The experimental and simulation results using eight-band method (Section 3.2) were listed in Table 4.5. The parameters of quantum well structures are coming from Table 4.3. The 5 K InGaAsP band gap energy is calculated using [20]

$$\begin{aligned} \text{Eg}(\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}) = & 1.425 + 0.668x - 1.068y + 0.758x^2 + 0.078y^2 - 0.069xy - \\ & 0.322x^2y + 0.03xy^2 \end{aligned} \quad (4.7)$$

From this table, we can see that the simulation results of PL peak positions are close to the experimental results. It shows that experimental and simulation results using eight-band method give a good agreement.

4.4 InGaAsP/InP MQWs with different well doping concentrations

4.4.1 X-ray diffraction

Figure 4.10 shows the (004) InP Bragg reflection rocking curves for MQW structures with different well doping concentration. The five pairs of spectra in the figure correspond to five InGaAsP/InP MQW samples which have well doping concentration of $5 \times 10^{18} \text{ cm}^{-3}$, $1 \times 10^{18} \text{ cm}^{-3}$, $5 \times 10^{17} \text{ cm}^{-3}$, $1 \times 10^{17} \text{ cm}^{-3}$ and $5 \times 10^{16} \text{ cm}^{-3}$, respectively. In each pair, the solid curve shows the measured result while the dashed curve shows the simulated result. The data extracted for the XRD curves are listed in Table 4.6. The parameters used in simulation are summarized in Table 4.7.

Figure 4.10. XRD results of the five samples which, consisting of 30 quantum wells, have different well doping concentration. The dashed lines are the simulation results.

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Table 4.6. Data extracted from the X-ray rocking curves in Figure 4.10

Samples (doping)	$\Delta\theta_0$ (sec.)	$\Delta d / d_{InP}$	$\Delta\theta$ (sec.)	Period (nm)	FWHM of 0 th -order peak (sec.)	Intensity of 1 st -order peak (a. u.)
N529 (a) (5E18)	2084	1.64E-2	590.4	31.8	144	42678
N530 (b) (1E18)	2110	1.66E-2	604.8	31.1	140	46780
N531 (c) (5E17)	2005	1.58E-2	583.2	32.2	115.2	56176
N532 (d) (1E17)	1944	1.53E-2	554.4	33.9	90	83450
N533 (e) (5E16)	1984	1.56E-2	554.4	33.9	72	113506

Table 4.7. Simulation parameters for the XRD results shown in Figure 4.10

Doping	$\Delta d / d_{InP}$	The thick of Barrier (nm)	The thickness of the well (nm)	The component of the well (%)			
				Ga	In	As	P
5E18	1.71E-2	27.5	5.0	39	61	58	42
1E18	1.58E-2	26.5	5.0	39	61	60	40
5E17	1.45E-2	27.5	5.3	39	61	62	38
1E17	1.51E-2	28.7	5.3	39	61	61	39
5E16	1.58E-2	28.5	5.3	39	61	60	40

From the mismatch data extracted from XRD curve and the mismatch estimated from the simulation result, one could see that the five InGaAsP/W MQW structures are all tensilely strained. The mismatch values for the five samples from the XRD results are slightly different. From the simulated results, the well width is 5.3 nm for the three samples with lower doping and 5.0 nm for the two samples with higher doping. The slight difference (about 6%) in the well width maybe due to the difference in the Si

partial pressure at different doping, which may slightly affect the growth of the well material. As far as the compositions are concerned, they are basically the same for all the samples except a 2% variation in the group V elements. It should be pointed out that the simulation tool used (Philips X'pert epitaxy) could not include the doping concentration in the wells. Therefore, the effect of doping cannot be reflected from the simulated curves.

It is also seen from Figure 4.10 that well-defined periodic satellite peaks up to the 15th order are easily identified for the samples with the doping density of $1 \times 10^{17} \text{ cm}^{-3}$ and $5 \times 10^{16} \text{ cm}^{-3}$. The small value of the full width at half maximum (FWHM) of satellite peaks indicates the abrupt interface of the MQW structures. With increase of the doping density in the wells, the number of the satellite peaks observed becomes less; the peaks' FWHM increases and the interference intensity is also degraded. These observations indicate degradation in the abruptness of interfaces of the MQW structures.

Figure 4.11. FWHM of the zero-order peak and intensity of the first-order peak of the XRD curves versus doping concentration in the wells of MQW structures.

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Figure 4.11 (the left vertical axis) shows the FWHM, derived from the x-ray diffraction curves in Figure 4.10, as a function of doping concentration in the wells. As shown in the figure, the FWHM increases monotonically with the doping density. The broadening of the zero order peaks clearly indicates that the doping concentration in the wells deteriorates the interface abruptness of the MQW structures.

The intensity of the first-order satellite peak is strongly dependent on diffusion, which usually degrades the abruptness of interfaces of the heterostructures and thus results in reduced satellite peak intensities particularly for the higher order satellite peaks. The intensity data of the first-order peaks, extracted from the XRD curves, are also shown in Figure 4.11 (the right vertical axis). It is seen that the intensity of the first-order peak decreases with well doping concentration. This relationship is exactly the same as observed from the compressively strained p-type InGaAs/AlGaAs MQW structures [65]. It is understandable that the heavy doping in the wells will undoubtedly cause inhomogeneity in the well layer and degrade the interference abruptness.

4.4.2 Photoluminescence

Figure 4.12. 5K PL spectra of the five samples with different well doping concentrations: (a) $5\text{E}18\text{ cm}^{-3}$, (b) $1\text{E}18\text{ cm}^{-3}$, (c) $5\text{E}17\text{ cm}^{-3}$, (d) $1\text{E}17\text{ cm}^{-3}$ and (e) $5\text{E}16\text{ cm}^{-3}$.

Figure 4.12 shows the 5K PL spectra of the five n-doped InGaAsP/InP MQW structures with different well doping concentration. There are two luminescence peaks in each of the five samples, one peak with high intensity at high-energy end and the other peak with low intensity at low-energy end. They are corresponding to the transition between E_1 to LH_1 and E_1 to HH_1 . Comparing Figure 4.12 and Figure 4.8, one can find that the two peaks in Figure 4.12 are more significant than that of Figure 4.8. It is due to

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the difference of peaks' FWHM and different distances of the two peaks position. The peak position, FWHM and Intensity are listed in the Table 4.8. All of the values were obtained from Gaussian function fit parameters of the PL spectra in Figure 4.12.

Table 4.8. Peak positions and FWHM of the PL spectra in Figure 4.12

Sample	Peak	Peak position (eV)	FWHM(meV)	Intensity (a. u.)
(a) N529	Low-energy	1.087	52.8	579
	High-energy	1.117	30.3	1052
(b) N530	Low-energy	1.061	34.0	659
	High-energy	1.081	16.4	5132
(c) N531	Low-energy	1.035	24.9	317
	High-energy	1.070	20.1	3403
(d) N532	Low-energy	1.049	35.3	496
	High-energy	1.076	14.7	9028
(e) N533	Low-energy	1.060	34.1	637
	High-energy	1.080	12.8	7513

From the data shown in Table 4.8, we draw the PL peak positions as the function of doping concentration in the well layers in Figure 4.13.

Figure 4.13. PL peak positions in Table 4.8

When the doping concentration changes from $5 \times 10^{16} \text{ cm}^{-3}$ to $5 \times 10^{18} \text{ cm}^{-3}$, it is well known that high doping causes the band-gap narrowing due mainly to the carrier interaction [66]. On the other hand, the Fermi level of the electron in the conduction band goes up with the increase of the doping concentration due to the band filling effect [65]. When the doping concentration reaches $1 \times 10^{18} \text{ cm}^{-3}$, the energy increase effect due to the up-going of Fermi level may overcome the energy decrease effect due to the energy band-gap narrowing in the recombination, which result in the increase of the peak energy.

From Table 4.8, one can see the FWHM of the PL peaks increase with the doping concentration increase in well layer. It indicates more defects at interface and more dispersion of the quantum energy levels due to increase of dopants.

4.5 Summary

In this chapter, we investigated Si-doped strained InGaAsP/InP multiple quantum well structures with different InGaAsP well widths and with different Si-doping densities in InGaAsP wells.

The XRD results show that the InGaAsP/InP MQW structures are all fully tensile strained. From the simulation and experimental results, a method with which the zero-order peak position of strained MQW structures can be determined. This can be confirmed by the lattice constant difference between the strained well layer and barrier layer. In addition, the relation between the envelope peak width and well width was also found.

For the InGaAsP/InP MQW samples with different doping density in the wells, the FWHM of the zero-order satellite peaks of the XRD curves increases with the increase of the well doping density while the intensity of the first-order satellite peaks decrease with the doping concentration. These observations indicate that the higher doping concentration degrades the interface quality of the MQW structures.

Photoluminescence was used to investigate the electron energy band structures in the InGaAsP/InP MQW samples. Gaussian function was used to fit the PL results of InGaAsP/InP strained MQW structures. There are two PL peaks, one came from the E1-HH1 transition and the other came from E1-LH1 transition. PL peaks as a function of temperature can be well described by the Varshni's equation.

From the PL results of the MQW structures with different doping concentrations, the FWHM of PL peaks increased with the doping densities. This observation is similar to the XRD result, indicating the degradation of the interface quality. On the other hand,

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we found that PL peak position was related not only to the bandgap shrinkage effect, but also to the band filling effect.

Chapter 5 Annealing effect on InGaAsP/InPMQW structures

5.1 Introduction

Quantum well intermixing (QWI) is a very attractive topic in the recent years [68, 69]. Through QWI, one can postgrowth tune the energy band profile of the quantum well structures. It is very useful for the laser and quantum well infrared photodetector (QWIP), which use the quantum well structures [70, 71]. Through postgrowth control of the QW composition profiles, QWI offers unique opportunities to fine-tune various aspects of a photodetector's response [72]. This chapter will present the intermixing of the multi quantum well structures through annealing treatment. X-ray diffraction was used to investigate the annealing effect on the MQW structure and photoluminescence to investigate the energy band-gap shift due to the QWI.

5.2 Experiment

Annealing was carried out under a flowing nitrogen atmosphere using a halogen lamp rapid thermal annealing (RTA) system. All samples were covered with an InP substrate to protect the surface and minimize phosphorus evaporation during the RTA process [73]. The annealing was carried out with two different ways, one was to anneal the samples at fixed time but different temperatures and the other was at fixed temperature but various periods of time.

5.3 Intermixing at different temperatures

5.3.1 XRD

First, the InGaAsP/InP MQW structure with well doping concentration of $1 \times 10^{17} \text{ cm}^{-3}$ were annealed at different temperatures and the fixed annealing time of 10 min. Figure 5.1 shows the (004) InP Bragg reflection rocking curves for the annealed samples as well as the as-grown samples, plotted on a logarithmic scale using the 5-crystalsmode.

Figure 5.1. XRD of the samples annealed at different temperatures. The annealing time at each temperature was fixed for 10 min.

Table 5.1. XRD data extracted from Figure 5.1

Sample	$\Delta\theta_0$ (sec.)	0 th order peaks' FWHM (sec.)
As-grown	1944	90
500 °C 10 min	1890	48.9
550 °C 10 min	2070	53.8
600 °C 10 min	2124	52.4
650 °C 10 min	2124	99.7

Figure 5.2. $\Delta\theta_0$ for the samples with different annealing temperatures but fixed annealing time (10 min).

$\Delta\theta_0$ is the angular separation between the zero-order satellite peak and InP substrate (004) reflection. It gives the average mismatch of the MQW along the growth axis. From the position of the zero-order satellite peaks in Figure 5.1 (listed in Table 5. 1),

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it shows that the as-grown and annealed MQW samples are all tensile strained to the InP substrate. From the $\Delta\theta_0$ plotted in Figure 5.2, one can see that the $\Delta\theta_0$ for the annealed samples from 500 °C to 650 °C show a small increase. The intermixing only occurs at the interface regions of wells and barriers, leading to a small change in the lattice constant. It is reflected the small change in $\Delta\theta_0$.

5.3.2 Photoluminescence

The QWI changes the MQW structure and it can be reflected by the energy band shift of the MQW as well. To investigate this point, the PL spectra for the samples at different annealing temperature were measured and the results are shown in Figure 5.3.

Figure 5.3. 5K PL result of the samples in Figure 5.1.

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From Figure 5.3, one can see that the annealing of the MQW structures induces blue shift of the PL peak. It is due to the energy band profile change caused by QWI. At the same time, the intensity of PL is also dropped with the increase of annealing temperature. The intermixing changes the profile of the energy band of quantum well and induces less confinement of the carrier in the quantum well. This causes decrease of the PL intensity. On the other hand, the annealing causes roughness of the sample surface that also causes the PL intensity decreasing.

The electrons in the conduction band recombine with the holes in the two energy levels (HH1 and LH1) to generate the radiation. So there should be two PL peaks in the PL spectra. From Figure 5.3, it is clear that the PL peaks include two peaks for the samples. PL results were fitted with Gaussian function and the parameters were listed in Table 5.2. The high-energy peak position was plotted in Figure 5.4 as a function of annealing temperature.

Table 5.2. PL peak energy position, FWHM and integrity intensity of the spectrum in Figure 5.3.

Samples	Highenergy Peak (eV)	FWHM (meV)	Integrity Intensity (a. u.)	Low energy Peak (eV)	FWHM (meV)	Integrity Intensity (a. u.)
As-grown	1.074	15.6	208	1.057	42.4	61
500°C 10 min	1.074	15.9	128	1.053	39.2	33
550°C 10 min	1.090	16.9	122	1.065	35.5	28
600°C 10 min	1.117	17.9	117	1.089	36.5	24
650°C 10 min	1.161	17.6	72	1.127	38.0	20

Figure 5.4. PL peak position for the annealed samples as the function of annealing temperature.

5.4 Intermixing after annealing at a fixed temperature for different periods of time

5.4.1 XRD

To study the intermixing at 700 °C, annealing for the InGaAsP/InP MQW structures at this temperature were carried out for different annealing times. The results are shown in Figure 5.5.

Figure 5.5. XRD results of the samples annealed at 700 °C for different annealing times.

From Figure 5.5, the angle between InP peak and zero order satellite peak increase with the annealing time. The $\Delta\theta_0$ of the rocking curves are listed in Table 5.3. At the same time, the $\Delta\theta_0$ are plotted in Figure 5.6 as the function of annealing time.

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Table 5.3. XRD data extracted from Figure 5.5

Sample	$\Delta\theta_0$ (sec.)	0 th order peaks' FWHM (sec.)
As-grown	1944	90
700 °C 30 sec	1998	57.3
700 °C 1 min	2106	50.1
700 °C 5 min	2502	60.4
700 °C 10 min	2916	44.7
700 °C 20 min	3132	135.8

Figure 5.6. $\Delta\theta_0$ for the samples annealed at 700 °C for different annealing time.

From Figure 5.6, it is clear that the thermal treatment of the MQW structures at 700 °C causes the mean mismatch value increasing with the annealing time. Comparing Table 5.1 and Table 5.3, one can see that the $\Delta\theta_0$ for 650 °C is 2124 sec and the $\Delta\theta_0$ for

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700 °C is 2916 sec with the same annealing time (10 min). The point shows that the intermixing of the MQW structures is more significant at higher annealing temperature. At higher temperature, the lattice constant in the well layers changes a larger value due to the intermixing.

5.4.2 Photoluminescence

Figure 5.7.5K PL for the samples in Figure 5.5.

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Table 5.4. PL peak energy position, FWHM and integrity intensity of the spectrum in Figure 5.7

Samples	High energy Peak (eV)	FWHM (meV)	Integrity Intensity (a. u.)	Lowenergy Peak (eV)	FWHM (meV)	Integrity Intensity (a. u.)
As-grown	1.074	15.6	208	1.057	42.4	61
700°C 30 sec	1.085	15.9	69	1.060	36.5	18
700°C 1 min	1.105	17.8	77	1.076	34.2	15
700°C 5 min	1.132	17.1	51	1.105	35.7	11
700°C 10 min	1.161	14.5	38	1.138	48.5	14
700°C 20 min	1.189	15.9	4.7	1.162	50.0	4.4

PL spectrum as a function of annealing time at 700 °C is shown in Figure 5.7. From Figure 5.7, one can see that each PL results include two PL peaks. The PL peaks were fitted with Gaussian function and the fitting parameters were listed in Table 5.4. The high-energy peak position was plotted in Figure 5.8 as the function of annealing time.

From Figure 5.8, one can see that for the samples annealed at 700 °C with different times, the PL peak blue shifts continuously from the value of the as-grown sample. It has the similar trend to the result shown in Figure 5.6. From the XRD and PL results, it clearly shows that annealing at 700 °C will change the lattice constant and energy band structure constantly with the increasing of annealing time.

Figure 5.8. PL peak position of the annealed sample as the function of annealing time.

5.5 Discussion

InGaAsP/InP QWs diffusion has been actively investigated. Li et al [74] investigated the InGaAsP/InP quantum well interdiffusion using theoretical method. They found that group III or group V diffusion would change the well energy profile with mini-wells. Lee et al [73] investigated the interdiffusion of InGaAsP/InP structures with low-temperature grown InP layer. Enhanced band-gap blue shift was achieved compared with normal structures. It was due to the group V intermixing. Aimez et al [75] investigated InGaAsP/InP intermixing induced by low energy P ion implantation for the realization of photonic integrated circuits. Bollet et al. [76] investigated the diffusion behavior of lattice matched InGaAs/InP heterostructures using PL and XRD. They found

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that for temperatures up to 850 °C strain was developed in the well/barrier interface region. The data are consistent with the presence of a miscibility gap in the InGaAsP quaternary system [77] at temperatures as high as 850 °C.

For the intermixing of InGaAsP/InP MQW structures, the In and P atoms in the barrier diffuse to well layer. At the same time, the Ga and As atoms diffuse to barrier layers. From our XRD results, it is clear that intermixing increases the tensile strain of the InGaAsP/InP MQW structures. Our observation is in good agreement with the report of Bollet et al. They found that within 2400s annealing time at 800 °C, the tensile strain would develop due to the greater group V atoms diffusion. From this, it is clear that our intermixing results are due to the faster diffusion of As and P atoms compared with Ga and In atoms. The reason for the greater group V atoms is caused by the miscibility gap in the InGaAsP quaternary system.

5.6 Summary

XRD and PL were used to investigate the QWI of the MQW structures after thermal treatment with different conditions.

First, the samples were annealed with increasing temperature and fixed time. From the XRD results, one can find that the strain in the MQW structures increases slowly with the annealing temperature. From the PL results, PL peaks shift to higher energy and the PL peak intensity drop. Second, the samples were annealed at 700 °C with increasing annealing time, the strain in the MQW structure increases with the annealing time, PL peaks shift to higher energy and the PL peak intensity drop. The change of strain

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in the MQW structures and PL peak shift are due to the intermixing of well layers and barrier layers. Comparing the strain shifting value at different annealing temperature for 10 min, one can find that the intermixing at 700 °C is more significant. The increase of lattice mismatch and blue shift in the energy band gap can be explained by the greater group V atoms diffusion.

Chapter 6 Characterization of InGaAsP/InP QWIP Device

6.1 Introduction

Infrared photodetectors are essential in various applications such as aerospace observation, target discrimination, and temperature sensing. Since the InGaAsP/InP MQW structure is widely used for light source and detector in optical fiber communication [78] based on interband transitions, it is also likely that the InGaAsP/InP quantum well structures can be used for QWIP based on intersubband transitions [79].

In this chapter, QWIP devices fabricated by InGaAsP/InP multi-quantum wells structure were investigated. First, the InGaAsP/InP MQWs materials were characterized using x-ray diffraction, photoluminescence and FTIR. Next, the relation between the photocurrent spectra, and the applied voltage to the device as well as the temperatures under which the devices were measured were studied.

6.2 Sample design and growth

The samples studied are two InGaAsP/InP MQW structures with different Si-doping concentration in the InGaAsP wells, grown on semi-insulating InP (100) substrates in the same SSMBE system. In the growth, a Si-doped $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ bottom contact layer of 500 nm thick was first grown. It was then followed by 30 MQW structures, which contained Si-doped 8 nm thick $\text{In}_{0.70}\text{Ga}_{0.30}\text{As}_{0.65}\text{P}_{0.35}$ wells separated by 40 nm wide undoped InP barriers. From our design, there is one energy level in the well; the second level is just above the well. In this structure, the absorption wavelength is

designed to be about 11 μm (El -E2). A 500 nm thick Si-doped $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ layer was grown as an upper contact layer. The Si doping concentrations in the wells are $5 \times 10^{18} \text{ cm}^{-3}$ (sample N768) and $5 \times 10^{17} \text{ cm}^{-3}$ (sample N769), respectively.

6.3 MQW structure characterization

6.3.1 XRD analysis

Figure 6.1. XRD (004) results for the two InGaAsP/InP MQW structures. Si doping concentrations in the well layers are $5 \times 10^{18} \text{ cm}^{-3}$ (sample N768) and $5 \times 10^{17} \text{ cm}^{-3}$ (sample N769), respectively. The solid lines are experimental results and the dot lines are simulation results.

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Figure 6.1 shows the XRD (004) rocking curves of the two MQWs samples. The solid lines are experimental results and the dot lines are simulation results. The simulation parameters were listed in Table 6.1. From the XRD results, one can see that the InGaAsP/InP MQWs structures were almost lattice-matched to the InP substrate. From the number of the satellite peaks observed in the rocking curves, it is clear that the MQWs have high interfacial quality. These results indicate that high quality MQW structures can be grown with all solid sources.

Table 6.1. Simulation results for XRD in Figure 6.1

	The thick of Barrier (nm)	The thickness of the well (nm)	The component of the well (%)			
			Ga	In	As	P
N768	37.5	8.5	30	70	62	38
N769	37.5	8.5	30	70	62	38

From Table 6.1, one can see that the compositions of the well layer are diverged from the design parameter with a small value. At the same time, the well widths are also diverged from the design parameter as well. These points will cause the change of energy level structure of InGaAsP/InP MQW samples. Fermi levels were estimated using the method in Section 3.3.2 for the two doping concentrations. When doping concentrations is $5 \times 10^{17} \text{ cm}^{-3}$, Fermi level is 3 meV above E1. The energy difference from Fermi level to the top of barrier is 179 meV. The first excite state is located 35 meV below the top of barrier. When doping concentrations is $5 \times 10^{18} \text{ cm}^{-3}$, Fermi level is 52 meV above E1. The energy difference from Fermi level to the top of barrier is 132 meV. With better control of composition of well layer and the thickness of well layer and barrier layer, plus

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the consideration of Fermi level position, more precision detecting wavelength can be achieved in the future study.

6.3.2 Photoluminescence

Figure 6.2.5 K photoluminescence of the two samples. The solid lines are experimental results and the dot lines are fitting results of Gaussian Function.

For photoluminescence characterization, a chopped 514.5 nm Ar^+ laser line was used for excitation. The InGaAs upper contact layer was removed prior to doing the PL measurements.

The 5 K photoluminescence measurements were done on the samples and the results are given in Figure 6.2. The peak positions of the two samples are 0.864 eV and

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0.870 eV, respectively. There are two peaks in each PL spectrum, the high-energy peaks come from the E_1 to LH1 recombination and the low-energy peaks come from the E_1 to HH1 recombination. Comparing the intensity of the PL results, one can see that the intensity increases with the decreasing of doping concentration in the well layer. The high doping may generate more non-radiative recombination centers.

6.3.3 FTIR analysis

FTIR is a very powerful tool to characterize the absorption property of the MQWs structures before the fabrication of the device [80]. It can be used to confirm the absorption wavelength that we design for the device. One can use polarized infrared light to measure the relationship between absorption and polarization [81]. In the experiment, the infrared absorption spectra at room temperature were measured by using a Perkin Elmer Spectrum 2000 FTIR spectrometer. The samples were polished into multi-reflection waveguides with 45° facets in order to increase net absorption.

Figure 6.3 shows the diagram of the infrared beam under different polarization degree. Figure 6.4 and Figure 6.5 show the FTIR results under different polarization of incident light. During the measurements, the InP substrate was used as the background and the InP substrate absorption was removed in the FTIR results. The absorption peak wavelengths are 10 μm and 12 μm respectively. The wavelength difference comes from the different doping concentration induced energy shift. From the $\Delta\lambda/\lambda$ value is about 0.2, it is bound to continuum transition. Sample N768 (5E18) has higher doping concentration, so it has higher absorption intensity. At zero degree polarization (mixed

TM and TE modes), the MQW structures have the maximum absorption for the polarized infrared light.

Figure 6.3. Diagram of infrared beam under different polarizations.

Figure 6.4. FTIR result for Sample N768.

Figure 6.5. FTIR result for Sample N769.

6.4 Device Fabrication

To fabricate QWIP devices, the samples were first etched into mesas using standard photolithography and wet etching processes. The gold, nickel and germanium alloy was then evaporated onto the n^+ type contact layers, followed by an annealing to ensure an ohmic contact. The mesa area of the device that was measured in the experiment is $200 \times 200 \mu\text{m}^2$. The mesa top is taken as positive terminal. To get better infrared light absorption, the wafer edge was polished to 45 degree. Figure 6.6 shows the diagram for the QWIP device measurements.

Figure 6.6. Diagram for QWIP device measurement.

The device fabrication process chart is shown in Figure 6.7. In the process, we used mesa mask for the mesa etching. Due to the selective etching for the InGaAsP well layer and InP barrier layer, two kinds of etch solutions are needed for the two materials. The etch solution are $\text{HCl}:\text{H}_3\text{PO}_4 = 1:5$ for InP barrier layer and $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O} = 1:8:20$ for InGaAsP well layer. Another mask was used to do the lift off of the metal contact.

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Figure 6.7. Device processing flow chart

6.5 QWIP Device Measurement

6.5.1 Dark Current

A good understanding of the dark current is crucial for design and optimization of QWIP devices. It is because that dark current contributes to the detector noise. A lot of works were reported for the dark current study of QWIP devices [82].

Dark current result for Sample N769 (5E17) is shown in Figure 6.8. For the bias voltage of -1 V, the dark current is 1×10^{-5} A. This result is at the same level as reported by Donchev et al for the GaAs/AlGaAs QWIPs [83].

Figure 6.8. Dark current of Sample N769 (5E17) at 30 K.

Figure 6.9. Dark current of the Sample N768 (5E18) at 30 K.

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The dark current result of Sample N768 (5E18) is shown in Figure 6.9. When the bias voltage was -1 V, the dark current was 0.1 A. It is four orders larger than that of Sample N769 (5E17). This result indicates that higher doping concentration in the well layers will induce higher dark current level of QWIP devices [11]. From Figure 6.4 and 6.5, one can see that higher doping concentration can get better absorption performance in FTIR measurement. At the same time, it will induce high dark current compared with lower doping concentration QWIP device. It causes a high noise for the device, so there is a trade off for the doping concentration in the well layers.

6.5.2 Photocurrent

The photocurrent spectra were measured at four temperatures, 20 K, 40K, 60K and 80K. The infrared light is from an Oriel 6575 infrared light source. It was chopped before passing through a TRIAX 320 monochromator. A low noise current pre-amplifier was used to provide the bias voltage for the device and pre-amplify the current signal. At the same time, it converts the current signal to voltage signal. A lock-in amplifier was used to measure the voltage signal. In Figure 6.10 we show the diagram of the photocurrent spectra measurement system.

Figure 6.10. Photocurrent measurement system.

A pyroelectric detector was used to calibrate the responsivity of the QWIP device:

$$R = \frac{I_{QWIP}}{P_{QWIP}} = \frac{V_{QWIP} \cdot K_{amplifier}}{\frac{V_{ref}}{R_{ref}} \cdot \frac{S_{mesa}}{S_{ref}} \cdot T_{ZnSe}} = \frac{R_{ref} \cdot K_{amplifier}}{T_{ZnSe}} \cdot \frac{S_{ref}}{S_{mesa}} \cdot \frac{V_{QWIP}}{V_{ref}} \quad (6.1)$$

Where, V_{QWIP} is the photovoltage signal for QWIP sample, $K_{amplifier}$ ($\mu A/V$) is the

sensitivity of current amplifier for QWIP photocurrent,

V_{ref} is the photo voltage signal from pyrodetector,

$R_{ref} = 2000$ v/w, is the responsivity of the pyrodetector,

S_{mesa} is the mesa area of QWIP sample, around $200 \times 200 \mu m^2$,

S_{ref} is the area of slit image on the pyrodetector, equal to $5 \times 2 \mu m^2$,

T_{ZnSe} (=70%) is the transmission of the refrigerator's window.

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Due to the high level of dark current, we did not get the photoresponse spectra of Sample N768 (5E18). The photoresponse spectra of Sample N769 (5E17) at different temperatures were measured.

Figure 6.1 1. Photoresponse spectra of Sample N769 (5E17) at 20 K.

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Figure 6.11 shows the photoresponse spectra of Sample N769 (5E17) at 20 K. From Figure 6.11, one can see that the responsivity under positive bias is larger than that under negative bias at the same bias voltage. On the other side, the shape and peak position of the responsivity spectra under positive bias are different from that of under negative bias. It is synopsized and shown in Figure 6.15 and Figure 6.16.

The asymmetrical results under positive and negative bias conditions are coming from the asymmetrical structure of QWIP device [84, 85]. From Figure 6.8, one can see the asymmetry of dark current under positive and negative bias as well.

Figure 6.12 shows the photoresponse spectra of Sample N769 (5E17) at 40 K, Figure 6.13 shows the photoresponse spectra of Sample N769 (5E17) at 60 K and Figure 6.14 shows the photoresponse spectra of Sample N769 (5E17) at 80 K.

Figure 6.12. Photoresponse spectra of Sample N769 at 40K.

Figure 6.13. Photoresponse spectra of Sample N769 at 60K.

Figure 6.14. Photoresponse spectra of Sample N769 at 80K.

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From the photocurrent results at different temperatures, we can see that the photocurrent of the device increases with the increasing of applied voltage. At the same level of bias voltage, the FWHM of the photoresponse peaks at positive bias is narrower than that of negative bias. On the other hand, the peak wavelength values are different at positive and negative bias conditions.

Figure 6.15. Responsivity peak values at different bias voltages measured at four temperatures.

From Figure 6.15, we can see that the responsivity of QWIP device is asymmetrical under positive and negative biases. When the bias voltage absolute value is less than 1 V, the responsivity under positive bias and that of negative bias are almost symmetrical. With the increasing of bias voltage, the responsivity values at the positive bias are increased by a larger value compared with negative bias.

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On the other side, from the responsivity results of 40 K with different positive bias voltage (Figure 6.12), we can see that the quantum efficiency η at the peak position is above 100% when bias voltage is equal to 2 V. For GaAs/AlGaAs QWIP, the quantum efficiency is normally less than 30% [86].

To explain the asymmetrical responsivity results, one diagram was given out as below. Due to the asymmetrical doping profile, the quantum well structures are asymmetrical. In this case, we have different energy level positions under positive and negative biases [84]. From Figure 6.16, we can see that, under positive bias, the electrons that are excited to the excited level have larger potential energy compared with those of under negative bias.

Figure 6.16. Diagram of the asymmetrical conduction band and energy levels

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To explain the quantum efficiency larger than 100% when bias voltage is + 2 V, avalanche multiplication process must be considered.

Firstly, we evaluated the possibility of avalanche multiplication process in InP barrier layers. Mohammad A. et al. systemically studied the impact ionization of thin III-V material, such as InP, InAlAs, GaAs and AlGaAs [87]. They gave out a carrier multiplication model that incorporates the effect of dead space and multiplication regions of different widths. With the Dead-space multiplication theory (DSMT), they determined the parameters of width-independent exponential-ionization-coefficient models.

The dependence of the electron and hole ionization coefficients on the electric field is often modeled by the standard equation [88]:

$$\alpha(\varepsilon), \beta(\varepsilon) = A \exp \left[- \left(\frac{\varepsilon_c}{\varepsilon} \right)^m \right] \quad (6.2)$$

where A , ε_c , and m are parameters chosen by fitting measured excess-noise factor data [89]. The values for InP avalanche photodiodes were listed the Table 6.2.

Table 6.2 Parameters of the width-independent exponential-ionization-coefficient models for InP APD [87].

		Units	InP
α	A	cm^{-1}	3.01×10^6
	ε_c	V/cm	2.45×10^6
	m		1.08
β	A	cm^{-1}	4.29×10^6
	ε_c	V/cm	2.08×10^6
	m		1.12

Inside this article, the electron and hole effective ionization threshold energies that determined from the best fit using DSMT are 2.05eV for electron and 2.20eV for

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hole [87]. For our case, with the bias voltage of +2V and without considering phonon scattering loss: the energy of electron is less than the effective ionization threshold energy. From here, we can see that +2V bias voltage is not enough to initiate impact ionization in InP barrier layers.

The thickness of our MQW structures is 1420 nm. When bias voltage is +2V, the electric field is 1.41×10^4 V/cm. Using Equation 6.2 and parameters listed in Table 6.2, $\alpha(\epsilon)$ and $\beta(\epsilon)$ values were calculated for +2V bias voltage case. From the results, we found that $\alpha(\epsilon)$ and $\beta(\epsilon)$ values were very small and could be neglected.

A number of groups have studied avalanche multiplication due to impact ionization in superlattices and MQW structures [90-95]. When photogenerated electron is incident on the neighboring quantum well containing bound electrons in the ground state, via Coulomb potential, the incident electron loses energy and momentum and the bound electron is excited to the first excited state. This excited electron can create gain for the photocurrent. From a conceptual point of view this effect has some similarities with the impact ionization of deep levels in the sense that the quantum well may be treated as an artificial trap. In this ionization effect only one type of carrier is created so that the positive feedback of impact ionizing holes is eliminated, leading to the possibility of a quiet avalanche with small excess noise [92]. Levine et al. firstly demonstrated 10 μm intersubband absorption initiated avalanche gain process, which is due to impact ionization of electrons out of the quantum wells [93].

In order to initiate avalanche multiplication process, the kinetic energy accumulated by drifting electrons has to reach a threshold value before a ground state

electron can be scattered out into the continuum. It means that the bias voltage should reach a threshold voltage to initiate the impact ionization process.

Figure 6.17. Diagram of avalanche multiplication process.

To explain the avalanche multiplication process when temperature is 40K and the bias voltage is +2V, theoretical estimation was done using eight-band $k \cdot p$ method and the diagram was shown in Figure 6.17. From the calculation, we found, in quantum well A, the responsivity peak at $10.5 \mu\text{m}$ is according to the electron was excited from ground state to level a . With the effect of electric field, the electron in level a will drift to quantum well B. During this period, the kinetic energy of electron would be increased by 67 meV. When this electron reaches quantum well B, it will pass the energy to the other electron in the ground state of quantum well B through Coulomb potential. The total energy of first electron is about 190 meV (according to the ground state of quantum well

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B). This value is large enough to excite one electron from ground state to the first excited state, at the same time; the original electron can keep enough energy as well.

After the energy transfer process with the first electron, the newborn electron will tunnel out quantum well B and both of them will draft to left direction due to the electron field. From above discussion, we can see the avalanche multiplication process is due to the impact ionization in the multi-quantum well structure.

On the other side, in photoconductive QWIPs, photoconductive gain g_{ph} is equal to gM and noise gain g_n is equal to gM^2 . With increasing $M > 1$, the detectivity (D^*) will decrease due to the avalanche multiplication process [95].

From the discussion above, we can see that the asymmetrical responsivity results coming from asymmetrical energy band profile. At the same time, impact ionization process can give out a good understanding for the responsivity peak value at 40K and +2V bias voltage.

Beside the responsivity, the blackbody was used to measure the detectivity (D^*) of the QWIP device.

$$D^* = \frac{\sqrt{A_d}}{NEP} \quad (6.3)$$

$$NEP = \frac{\Phi_s V_N}{V_s \sqrt{\Delta f}} \quad (6.4)$$

$$\Phi_s = \frac{\sigma(T_b^4 - T_0^4)A_b A_d}{2\sqrt{2}\pi L^2}, \quad (6.5)$$

which $\sigma = 5.6697 \times 10^{-8} (W/m^2 \cdot K^4)$, A_d is the area of detector, A_b is the area of blackbody, V_N is the root mean square noise voltage within the measurement bandwidth

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Δf , and V_s is the root mean square signal voltage, T_b is the temperature of blackbody and T_0 is the temperature of detector, L is the distance between blackbody and detector.

With the measurement and calculation using Equation 6.3-6.5, it was found that the value of detectivity was about $1.19 \times 10^9 \text{ cm}\sqrt{\text{Hz}}/\text{W}$ (at $V_b = -2.5 \text{ V}$ and 20 K).

6.6 Summary

InGaAsP/InP MQWs structures with different doping concentration in the well layer were characterized using XRD, PL and FTIR. Dark current and photo response for the devices were also investigated. From the dark current and photocurrent results, one can see the asymmetrical results at positive and negative biases. At the same time, the responsivity peak changes with the temperature and bias voltage were investigated. Compared with other group's result, it is due to the asymmetrical quantum well structures. At the same time, impact ionization process can give out a good understanding for the responsivity peak value at 40 K and $+2 \text{ V}$ bias voltage.

Chapter 7 InGaAsN/GaAsN MQW structures

7.1 Introduction

Recently, a novel material InGaAsN with dilute nitrogen has been attracting considerable attention due to their unusual physical properties and their potential in optoelectronic device applications. It is known that the very small N content can greatly reduce the band gap due to the very large bowing factor of this material (as larger as 10-20eV) [96, 97]. InGaAsN/GaAs QWIPs may have the advantages over conventional GaAs/AlGaAs QWIPs [11]. First, it can achieve mid infrared response due to its larger conduction band discontinuity; Second, there is expected enhanced normal incident caused by the coupling between conduction and valence bands. In this chapter, we report the growth and characterization of the n-type InGaAsN/GaAsN multiple quantum wells.

7.2 Sample Growth

Nitride MQW structures were grown by a Riber-32P SSMBE equipped with an N RF plasma source. The samples were grown on double-side polished (100) semi-insulating GaAs substrates. For the two samples, the quantum well structures consist of 20 periods of 2.3 nm thick $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.99}\text{N}_{0.01}$ QWs and 14.5 nm $\text{GaAs}_{0.998}\text{N}_{0.002}$ barriers. The Si doping concentration in the QWs is about $1.5 \times 10^{18} \text{ cm}^{-3}$. The quantum well structures were sandwiched between a 0.7 μm buffer layer and a 0.7 μm cap layer, both doped with Si of $2 \times 10^{18} \text{ cm}^{-3}$. The InGaAsN/GaAsN QWs were grown at 460°C and

clear streaky RHEED patterns were observed for all samples. The shutter of the ignited N plasma source is opened during the GaInNAs well growth and closed during the barrier growth. However, a little bit N can still be incorporated into the GaAs layer to form GaAsN barrier due to the dispersive nitrogen. The difference of the two samples studied is that there exists an in-situ annealing at 600 °C for about 10 min in the sample MN180.

7.3 Characterization of InGaAsN/GaAsN MQW structures

Figure 7.1 shows the experimental HRXRD (004) rocking curves of the two InGaAsN/GaAsN MQW samples. The simulation was carried out to estimate the structural parameters listed in Figure 7.1. From the peak shape of the XRD curves, one can see that the MN180's crystal quality is better than that of MN181 due to the in-situ annealing. This two MQW structures are compressively strained.

Figure 7.1. XRD results of the InGaAsN/GaAsN MQW structures.

The samples were also characterized by room-temperature (300K) photoluminescence (PL) using 514.5 nm argon ion lasers and liquid nitrogen Ge detector with a standard lock-in technique. Figure 7.2 shows the PL spectra of the InGaAsN/GaAsN QWIPs at 300K. The two PL peaks are from the doped InGaAsN/GaAsN QWs and doped GaAs contact layers. Without *in-situ* annealing, the peak intensity of GaInNAs QWs in sample MN181 is just half of that of the doped GaAs. After 10 min *in-situ* annealing at 600 °C, the peak intensity of GaInNAs QWs in sample MN180 is increased greatly, up to about 4 times that of the doped GaAs because some N related defects are annealed out. Figure 7.3 shows the 5K PL result for the two samples, we can see that sample MN180 has a high PL intensity compared with MN181.

Figure 7.2. 300K PL results of the two InGaAsN/GaAsN MQW structures.

Figure 7.3. 5K PL results of the two samples.

The infrared absorption spectra at room temperature were measured by using a Pekin-Elmer FTIR spectrometer. The samples were polished into multi-reflection waveguides with 45° facets in order to increase net absorption (see Chapter 3). We found that sample MN180 could not get FTIR signal and MN181 could get strong FTIR signal. Present, it is not clear why there is no absorption for the annealed sample. Further work is needed.

Figure 7.4. FTIR result for sample MN181.

Figure 7.4 shows the measured infrared absorption spectra of the sample MN181 at room temperature. From this figure, it is interesting to find that 0 degree polarization has minimum absorption while and 90 degree has maximum absorption. This observation indicates that the InGaAsN/GaAsN MQW structure is a potential candidate for the

normal incident infrared photodetector. The experimental intersubband absorption peak of 10 μm is in good agreement with our calculated 9.7 μm shown in Figure 7.5. In the calculation using single-band effective mass theory the band-offset ratio $\Delta E_c/\Delta E_g$ of InGaAsN/GaAs was assumed to be 65% and the edge of light hole in the tensile strained GaAsN was assumed to align with the top of the valence band of GaAs to extract the ΔE_c of the InGaAsN/GaAsN. At the end of this work, we found Duboz *et al.*'s report [11] on the intersubband transition in InGaAsN/GaAs quantum wells. The differences are that the bound-to-continuum intersubband transitions are studied and the barriers are GaAsN in our study.

Figure 7.5. Calculated intersubband absorption spectrum of sample MN181.

7.4 Summary

HRXRD, PL and intersubband absorption were investigated in the two n-type $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}_{0.99}\text{N}_{0.01}/\text{GaAs}_{0.998}\text{N}_{0.002}$ quantum wells grown by SSMBE. The FTIR absorption peaked around $10\text{ }\mu\text{m}$ are observed in as-grown samples. The single band effective mass theory was used to calculate the intersubband absorption in the InGaAsN/GaAsN QWs. The experimental absorption curve is in good agreement with our calculation. The important finding is the normal incident absorption of the InGaAsN/GaAsN MQW structures, which may give birth to the normal incident n-type QWIPs.

Chapter 8 Conclusion and Recommendation

8.1 Conclusion

The energy band dispersion relations for InGaAsP/InP MQW structures were investigated using 8x8 $k \cdot p$ method. It was found that the light hole could be the first energy level in the valence band at large tensile strain condition. This shows that one may use the light hole's small effective mass property to increase the absorption efficiency of p-type QWIP devices.

Optical, structural and electrical properties of silicon doped strained InGaAsP/InP multiple quantum wells structures were systematically studied. From the X-ray result, it is found that the center satellite peak of the center-enveloping peak should be the zero-order satellite peak. With increasing of well width, the number of satellite peaks in each enveloping peak will decrease. These relationships were confirmed by experimental results and simulation results. On the other hand, it is found that higher well doping concentration will degrade the quantum well interface quality. This is confirmed by the X-ray result and photoluminescence results.

Intermixing of the quantum wells structures was investigated using X-ray and PL as well. It is found that at different temperatures but fixed annealing time, the strain in the well layer increases with temperature. The PL peaks shift to high energy with the temperature increasing. With annealing at 700 °C but different periods of time, the strain increases with the increasing of annealing time. PL results also show the blue shift of peak energy. From the x-ray result, we found that the intermixing mainly caused by Group V atoms.

Lattice matched InGaAsP/InP MQW structures were grown using SSMBE. From the dark current results, it was found that the high doping concentration in the well layers gave high dark current which suppressed the photocurrent signal. For the low doping concentration devices, it was found that the dark current and photocurrent were asymmetrical at different bias directions, due to the asymmetrical quantum well structures caused by doping.

From the FTIR results, it is interesting to find that InGaAsN/GaAsN MQW structures absorb the normal incident grown by SSMBE with RF N plasma source.

8.2 Recommendation for Future works

1. In this thesis, single band method was used to calculate the intersubband transition. Next step, 8x8 matrix can be used to do the calculation for the intersubband transition. Compared with single band, it can get more accurate results.
2. From the theoretical results, it is shown that light-hole will be the first energy band in the valence band wells under large tensile strain. Next step, large tensile strained p-type InGaAsP/InP MQWs may be grown to investigate the light-hole intersubband transition.
3. From FTIR results, InGaAsN/GaAsN MQW structures show the absorption of normal incident. Next step, QWIP devices using InGaAsN/GaAsN materials should be used to investigate the abnormal absorption for the normal incident.

Publications

Author's Publications

Journal Papers:

- 1, D. H. Zhang, L. Sun and S. F. Yoon, "Doping effect on the Intermixing in GaInAsP/InP Multiple Quantum Well structures grown using all solid sources", *Journal of Crystal Growth* **268**, p401-405, (2004).
- 2 L. Sun, D. H. Zhang. " Study of InGaAsP/InP multiple quantum well grown by solid source molecular beam epitaxy ", *Journal of Vacuum Science and Technology* **B 21**, p1940-1944 (2003).
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4. L. Sun, D. H. Zhang, H. Q. Zheng, S. F. Yoon, C. H. Kam. " High-resolution X-ray diffraction study of strained InGaAsP/InP multiple quantum well structures grown using all solid sources ", *Materials Science in Semiconductor Processing* **4**, p631-636 (2001).
5. L. Sun, D. H. Zhang, **K.H.** Yuan, S. F. Yoon, **K.** Radhakrishnan, "InGaAsP/InP long wavelength quantum well infrared photodetector", to be submitted.

Conference Papers:

1. L. Sun, D. **H.** Zhang, M. Huang, W. J. Fan and S. F. Yoon "Theoretical Investigation **Of** P-Type Strained InGaAsP/InP Quantum Wells Using ~~8x8~~ $k \cdot p$ Hamiltonian", International Conference on Materials for Advanced Technologies (ICMAT2003), Dec 7-12 (2003), Singapore.

Publications

2. L. Sun, D. H. Zhang, and S. F. Yoon. "Doping effect on the Intermixing in GaInAsP/InP Multiple Quantum Well structures grown using all solid sources". International Conference on Materials for Advanced Technologies (ICMAT2003), Dec 7-12 (2003), Singapore.
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Program of Eight band Solution of the energy band structures

```

C      SCH8.FOR      (26/03/2003)
C
C
C      DESCRIPTIONS OF THE PAPRAMETERS USED IN THE PROGRAMM:
C
C      T      i.e.  $e//=exx$ . lattice mismatch degree  $T=exx=(a-a_0)/a_0$ .
C               $a(= a \text{ of substrate})$  is strained lattice const of well.
C               $a_0$  is unstrained lattice const of well material.
C               $T<0$ , compressive;  $T>0$ , tensile.
C              Hydrostatic strain is not included, which is considered
C              in conduction band calculation.
C      DU(meV)  DU=b, shear strain potential constant.
C      SO(meV)  spin-orbit splitting energy.
C      VO(meV)  SL potential. Input postive value due to + hole energy.
C
C      WW(A),BW(A)      SL well and barrier width.
C      XS,YS,ZS(2PI/L)  wave vector  $k_x,k_y,k_z$ .
C      GAM1,GAM2,GAM3   L-K effective mass parameters.
C      L4 ( 6*ODD )      dimension of the matrix H.
C
C      FD          the seperate value between the  $i$ th and  $(i+1)$ th wave
C                  function.in order to draw the wavefunction on a sheet.
C      C11,C12      elastic moduli. using C11/C12 in programme.
C      AKMAX        the maximum of the  $k$  along [100] and [110] in graph.
C      NAK          the number of the  $k$ -points between 0 and AKMAX
C                  along [100] and [110] in graph.
C
C      EIJ          strain tensor
C      BU,DU(meV)   the shear deformation potentials b and d
C      |||negative input
C      AC(meV)      conduction-band deformation potential  $ac|||$ negative
C      input
C      AV(meV)      hydrostatic valence-band deformation potential  $av|||$ 
C      positive input
C      C11,C12      elastic constants
C      IMPLICIT REAL*8(A-H,O-Z)
C      COMPLEX H9,A
C      COMPLEX ESH,ESI
C      PARAMETER (L4=248, NK=248, N41=41)
C
C      L4 IS MAXIMUM DIMENSION NUMBER OF MATRIX H
C      NK IS MAXIMUM NUMBER OF  $K_x(K_y,K_z)$ 
C      N41 DOT NUMBER OF EACH WAVE FUNCTION CURVE.
C
C      DIMENSION E(L4),EVR(L4,L4),EVI(L4,L4),AR(L4,L4),AI(L4,L4)
C      DIMENSION A(8,8,NK,NK),B(NK),H9(L4,L4),AAA(L4)
C      DIMENSION XS(NK),YS(NK),ZS(NK),FV1(L4),FV2(L4),FM1(2,L4)
C      DIMENSION PH(L4),PL(L4),PS(L4),FX(N41),FY(L4,N41)
C
C      OPEN(15,FILE='strain.inp',STATUS='UNKNOWN')
C      OPEN(16,FILE='strain.eng',STATUS='UNKNOWN')
C      OPEN(17,FILE='strain.wav',STATUS='UNKNOWN')
C      OPEN(20,FILE='strain.hls',STATUS='UNKNOWN')

```

Appendix

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C      OPEN( 8, FILE='strain.dat', STATUS='UNKNOWN', FORM='UNFORMATTED')

      READ(15,*) VC, VB, EG, CM, EP, WW, BW, GAM1, GAM2, GAM3, SO
      READ(15,*) AC, AV, BU, DU, C11, C12, ESXX
      READ(15,*) NZ, (ZS(N), N=1, NZ)
      READ(15,*) NAK, AKMAX
      READ(15,*) NEIGV, IVEC, FD

C      WRITE(8) NAK*2

      PI=3.1415926535898D0
      BR=0.52917706D0
      AU=27211.652D0
      L2=L4/8
      L1=L2/2+1
      WBW=WW+BW
      BB=AU*2.D0*(PI*BR/WBW)**2
      V1=VC/(PI*BB)
      V2=VB/(PI*BB)
      V3=EG/(PI*BB)

      GAM1=GAM1-EP*1000/(3.D0*EG)
      GAM2=GAM2-0.5D0*EP*1000/(3.D0*EG)
      GAM3=GAM3-0.5D0*EP*1000/(3.D0*EG)
C      CM=1.0D0/CM-EP*1000/3.D0*(2.0/EG+1.0/(EG+SO))
C      CM=1/CM

      BK=2.D0*PI/WBW
      P0=SQRT(EP*1000*BB)/BK
      P=P0/BB
      BKB=0.5D0*BW*BK

      SO=SO/BB

      ESY=ESXX
      ESZZ=-2.D0*C12/C11*ESXX
      ES=ESXX+ESY+ESZZ
      ESF=-(AV*ES-BU*(ES-3.0D0*ESZZ)/2.0D0)
      ESG=-(AV*ES+BU*(ES-3.0D0*ESZZ)/2.0D0)
      ESH=0.D0
      ESI=0.D0

      AC=AC/BB
      ESF=ESF/BB
      ESG=ESG/BB
      ESH=ESH/BB
      ESI=ESI/BB

      DO 2 IA=1, NAK
      XS(IA)=AKMAX-(IA-1)*(AKMAX-0.D0)/(NAK-1)          ! [100]
      YS(IA)=0.D0                                         ! [100]
      XS(IA+NAK)=(IA-1)*(AKMAX/DSQRT(2.D0)-0.D0)/(NAK-1) ! [110]
      YS(IA+NAK)=XS(IA+NAK)                             ! [110]
2      CONTINUE

```


Appendix

```

DO 5 K=1,NZ
ETZ=ZS(K)
DO 10 I=1,NAK*2
ETX=XS(I)
ETY=YS(I)

CALL HMA(V1,V2,V3,CM,P,BKB,BK,GAM1,GAM2,GAM3,ETX,ETY,ETZ,
1 WW,BW,SO,L4,L2,L1,NK,H9,A,AAA,AC,AV,ESXX,ESZZ,ESF,ESG,ESH,ESI)
DO 40 N=1,L4
DO 40 M=1,L4
AI(N,M)=AIMAG(H9(N,M))
40 AR(N,M)=REAL(H9(N,M))
CALL CH(L4,L4,AR,AI,E,EVR,EVI,FV1,FV2,FM1,IERR)
IF (IERR.NE.0) THEN
WRITE(*,510)K,I,IERR
ELSE
END IF
DO 30 N=1,NEIGV
30 E(N)=BB*E(N)

ETXY=ETX**2+ETY**2
DETXY=DSQRT(ETXY)
C IF (I.LT.NAK) THEN
C WRITE( 8 ) -DETXY, NEIGV, L4
C ELSE
C WRITE( 8 ) DETXY, NEIGV, L4
C END IF
C IF (ETXY.EQ.0.D0) THEN
C WRITE( 8 ) (E(N),N=187,NEIGV,2)
C WRITE( 8 ) ((EVR(IA,N),EVI(IA,N),IA=1,L4),N=187,NEIGV,2)
C END IF

IF (I.LT.NAK) THEN
WRITE(16,520) -DETXY,(E(N),N=173,194,2) ! "2" double degeneracy
ELSE
WRITE(16,520) DETXY,(E(N),N=173,194,2)
END IF
60 IF(IVEC.EQ.0) GO TO 15
CALL WFEV(NEIGV,WW,BW,PH,PL,PS,FX,FY,
1 L4,L2,NK,N41,B,EVR,EVI)
IF (ABS(ETXY).EQ.0.D0) THEN
DO 148 IO=1,N41
148 WRITE(17,520)FX(IO),(FY(KO,IO)+FD*(KO-1)/2,
1 KO=181,194,2)
ELSE
END IF
IF (I.LT.NAK) THEN
WRITE(20,530)-DETXY,(PH(IK),PL(IK),PS(IK),IK=179,186,2)
ELSE
WRITE(20,530) DETXY,(PH(IK),PL(IK),PS(IK),IK=179,186,2)
END IF
15 CONTINUE
10 CONTINUE
5 CONTINUE

```


Appendix

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510 FORMAT(1X, '***STOP!*** AT K,I =', 2I4, ' IERR = ', I4)
520 FORMAT(2X, 30F13.4)
530 FORMAT(1X, F7.3, 3X, 24F10.5)
    STOP
    END

    SUBROUTINE HMA(V1,V2,V3,CM,P,BKB,BK,GAM1,GAM2,GAM3,ETX,ETY,EZZ,
1    WW,BW,SO,L4,L2,L1,NK,H9,A,AAA,AC,AV,ESXX,ESZZ,ESF,ESG,ESH,ESI)

    IMPLICIT REAL*8(A-H,O-Z)
    COMPLEX H9,A,S
    COMPLEX ESH,ESI,ESPLUS,ESMINUS
    DIMENSION A(8,8,NK,NK),S(8,8,NK,NK),H9(L4,L4),AAA(L4)

    PI=3.1415926D0
    WW=WW+BW
    PKL=PI*WW/WBW
    ET1=ETX*ETX+ETY*ETY
C    BK=2.D0*PI/WBW

    ESY=ESXX
    ES=ESXX+ESY+ESZZ

    ESPLUS=(ESXX*ETX+(0.D0,1.D0)*ESY*ETY)*BK/SQRT(2.D0)
    ESMINUS=(ESXX*ETX-(0.D0,1.D0)*ESY*ETY)*BK/SQRT(2.D0)

    DO 10 I=1,L4
    DO 10 J=1,L4
10    H9(I,J)=0.0D0

    DO 35 M=1,8
    DO 35 L=1,8
    DO 35 I=1,L2
    DO 35 J=1,L2
    A(M,L,I,J)=0.D0
35    S(M,L,I,J)=0.D0

    DO 117 KAD=1,L2
117    AAA(KAD)=DFLOAT(KAD-L1)

    DO 20 I=1,L2
    DO 20 J=1,L2
    ETZ=EZZ-L1+I
    ESZ=ESZZ*ETZ*BK

    IF(I.NE.J) THEN
        DGL=AAA(J)-AAA(I)

        A(1,1,I,J)=-V1*DSIN(DGL*PKL)/DGL
        A(2,2,I,J)=A(1,1,I,J)
        A(3,3,I,J)=V2*DSIN(DGL*PKL)/DGL
        A(4,4,I,J)=A(3,3,I,J)
        A(5,5,I,J)=A(4,4,I,J)

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Appendix

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A(6,6,I,J)=A(3,3,I,J)
A(7,7,I,J)=A(3,3,I,J)
A(8,8,I,J)=A(7,7,I,J)

S(1,1,I,J)=AC*ES*DSIN(DGL*PKL)/DGL/PI
S(2,2,I,J)=S(1,1,I,J)
S(3,3,I,J)=ESF*DSIN(DGL*PKL)/DGL/PI
S(4,4,I,J)=ESG*DSIN(DGL*PKL)/DGL/PI
S(5,5,I,J)=S(4,4,I,J)
S(6,6,I,J)=S(3,3,I,J)
S(7,7,I,J)=(ESF+ESG)/2.D0*DSIN(DGL*PKL)/DGL/PI
S(8,8,I,J)=S(7,7,I,J)
S(1,3,I,J)=-P*ESPLUS*DSIN(DGL*PKL)/DGL/PI
S(3,1,I,J)=CONJG(S(1,3,I,J))
S(1,4,I,J)=(0.D0,1.D0)/DSQRT(1.5D0)*P*ESZ*DSIN(DGL*PKL)/DGL/PI
S(4,1,I,J)=CONJG(S(1,4,I,J))
S(1,5,I,J)=-1.D0/DSQRT(3.D0)*P*ESMINUS*DSIN(DGL*PKL)/DGL/PI
S(5,1,I,J)=CONJG(S(1,5,I,J))
S(1,7,I,J)=-1.D0/DSQRT(3.D0)*P*ESZ*DSIN(DGL*PKL)/DGL/PI
S(7,1,I,J)=CONJG(S(1,7,I,J))

S(1,8,I,J)=(0.0,1.0)/DSQRT(1.5D0)*P*ESMINUS*DSIN(DGL*PKL)/DGL/PI
S(8,1,I,J)=CONJG(S(1,8,I,J))
S(2,4,I,J)=-
(0.0,1.0)/DSQRT(3.0D0)*P*ESPLUS*DSIN(DGL*PKL)/DGL/PI
S(4,2,I,J)=CONJG(S(2,4,I,J))
S(2,5,I,J)=-1.D0/DSQRT(1.5D0)*P*ESZ*DSIN(DGL*PKL)/DGL/PI
S(5,2,I,J)=CONJG(S(2,5,I,J))
S(2,6,I,J)=- (0.D0,1.D0)*P*ESMINUS*DSIN(DGL*PKL)/DGL/PI
S(6,2,I,J)=CONJG(S(2,6,I,J))
S(2,7,I,J)=-1.D0/DSQRT(1.5D0)*P*ESPLUS*DSIN(DGL*PKL)/DGL/PI
S(7,2,I,J)=CONJG(S(2,7,I,J))
S(2,8,I,J)=- (0.D0,1.D0)/DSQRT(3.D0)*P*ESZ*DSIN(DGL*PKL)/DGL/PI
S(8,2,I,J)=CONJG(S(2,8,I,J))
S(3,4,I,J)=ESH*DSIN(DGL*PKL)/DGL/PI
S(4,3,I,J)=CONJG(S(3,4,I,J))
S(3,5,I,J)=ESI*DSIN(DGL*PKL)/DGL/PI
S(5,3,I,J)=CONJG(S(3,5,I,J))
S(3,7,I,J)=(0.D0,1.D0)/DSQRT(2.D0)*ESH*DSIN(DGL*PKL)/DGL/PI
S(7,3,I,J)=CONJG(S(3,7,I,J))
S(3,8,I,J)=- (0.D0,1.D0)*DSQRT(2.D0)*ESI*DSIN(DGL*PKL)/DGL/PI
S(8,3,I,J)=CONJG(S(3,8,I,J))
S(4,6,I,J)=ESI*DSIN(DGL*PKL)/DGL/PI
S(6,4,I,J)=CONJG(S(4,6,I,J))
S(4,7,I,J)=(0.0,1.0)/DSQRT(2.0D0)*(ESG-
ESF)*DSIN(DGL*PKL)/DGL/PI
S(7,4,I,J)=CONJG(S(4,7,I,J))
S(4,8,I,J)=(0.D0,1.D0)*DSQRT(1.5D0)*ESH*DSIN(DGL*PKL)/DGL/PI
S(8,4,I,J)=CONJG(S(4,8,I,J))
S(5,6,I,J)=-ESH*DSIN(DGL*PKL)/DGL/PI
S(6,5,I,J)=CONJG(S(5,6,I,J))
S(5,7,I,J)=- (0.0,1.0)*SQRT(1.5)*CONJG(ESH)*DSIN(DGL*PKL)/DGL/PI
S(7,5,I,J)=CONJG(S(5,7,I,J))
S(5,8,I,J)=(0.D0,1.D0)/SQRT(2.0)*(ESG-ESF)*DSIN(DGL*PKL)/DGL/PI
S(8,5,I,J)=CONJG(S(5,8,I,J))
S(6,7,I,J)=- (0.0,1.0)*SQRT(2.0)*CONJG(ESI)*DSIN(DGL*PKL)/DGL/PI

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S(7,6,I,J)=CONJG(S(6,7,I,J))
S(6,8,I,J)=- (0.0,1.0)/SQRT(2.0)*CONJG(ESH)*DSIN(DGL*PKL)/DGL/PI
S(8,6,I,J)=CONJG(S(6,8,I,J))

ELSE

A(1,1,I,I)= (V3+AC*ES-AV*ES)*PI+(ET1+ETZ*ETZ)/CM+V1*BKB
A(2,2,I,I)= A(1,1,I,I)
A(3,3,I,I)=- (GAM1+GAM2)*ET1- (GAM1-2.0D0*GAM2)*ETZ*ETZ-V2*BKB
A(4,4,I,I)=- (GAM1-GAM2)*ET1- (GAM1+2.0*GAM2)*ETZ*ETZ-V2*BKB
A(5,5,I,I)= A(4,4,I,I)
A(6,6,I,I)= A(3,3,I,I)
A(7,7,I,I)= -GAM1*(ET1+ETZ*ETZ)-SO-V2*BKB
A(8,8,I,I)= A(7,7,I,I)
A(1,3,I,I)= P*(ETX*(0.D0,1.D0)-ETY)/DSQRT(2.0D0)*BK*(0.D0,-1.D0)
A(3,1,I,I)=CONJG(A(1,3,I,I))
A(1,4,I,I)= P*DSQRT(2.D0/3.0D0)*ETZ*BK*(0.D0,-1.D0)
A(4,1,I,I)=CONJG(A(1,4,I,I))
A(1,5,I,I)= P*(ETX*(0.D0,1.D0)+ETY)/DSQRT(6.0D0)*BK*(0.D0,-1.D0)
A(5,1,I,I)=CONJG(A(1,5,I,I))
A(1,7,I,I)= P*ETZ/DSQRT(3.D0)*(0.D0,1.D0)*BK*(0.D0,-1.D0)
A(7,1,I,I)=CONJG(A(1,7,I,I))
A(1,8,I,I)=P*(-ETY*(0.D0,1.D0)+ETX)/DSQRT(3.0D0)*BK*(0.D0,-1.D0)
A(8,1,I,I)=CONJG(A(1,8,I,I))
A(2,4,I,I)= P*(ETX*(0.D0,1.D0)-ETY)/DSQRT(6.0D0)*BK*(0.D0,-1.D0)
A(4,2,I,I)=CONJG(A(2,4,I,I))
A(2,5,I,I)= P*DSQRT(2.D0/3.0D0)*ETZ*BK*(0.D0,-1.D0)
A(5,2,I,I)=CONJG(A(2,5,I,I))
A(2,6,I,I)= P*(ETX*(0.D0,1.D0)+ETY)/DSQRT(2.0D0)*BK*(0.D0,-1.D0)
A(6,2,I,I)=CONJG(A(2,6,I,I))
A(2,7,I,I)= P*(ETX*(0.D0,1.D0)+ETX)/DSQRT(3.0D0)*BK*(0.D0,-1.D0)
A(7,2,I,I)=CONJG(A(2,7,I,I))
A(2,8,I,I)=A(1,7,I,I)
A(8,2,I,I)=CONJG(A(2,8,I,I))
A(3,4,I,I)= 2.0D0*GAM3*DSQRT(3.0D0)*(ETX*(0.D0,1.D0)+ETY)*ETZ
A(4,3,I,I)=CONJG(A(3,4,I,I))
A(3,5,I,I)=-DSQRT(3.0D0)*(GAM2*(ETX*ETX-ETY*ETY)-2.0D0*
1 GAM3*ETX*ETY*(0.D0,1.D0))
A(5,3,I,I)=CONJG(A(3,5,I,I))
A(3,7,I,I)= -DSQRT(6.0D0)*GAM3*(ETX-ETY*(0.D0,1.D0))*ETZ
A(7,3,I,I)=CONJG(A(3,7,I,I))
A(3,8,I,I)= (0.D0,1.D0)*DSQRT(6.0D0)*(GAM2*(ETX*ETX-ETY*ETY)
1 -2.0D0*GAM3*ETX*ETY*(0.D0,1.D0))
A(8,3,I,I)=CONJG(A(3,8,I,I))
A(4,6,I,I)= A(3,5,I,I)
A(6,4,I,I)=CONJG(A(4,6,I,I))
A(4,7,I,I)= (0.D0,1.D0)*DSQRT(2.D0)*GAM2*(ET1-2.D0*ETZ*ETZ)
A(7,4,I,I)=CONJG(A(4,7,I,I))
A(4,8,I,I)= -3.0D0*DSQRT(2.0D0)*GAM3*(ETX-(0.D0,1.D0)*ETY)*ETZ
A(8,4,I,I)=CONJG(A(4,8,I,I))
A(5,6,I,I)= -A(3,4,I,I)
A(6,5,I,I)=CONJG(A(5,6,I,I))
A(5,7,I,I)=-3.0D0*DSQRT(2.0D0)*GAM3*(ETX+(0.D0,1.D0)*ETY)*ETZ
A(7,5,I,I)=CONJG(A(5,7,I,I))
A(5,8,I,I)= A(4,7,I,I)
A(8,5,I,I)=A(7,4,I,I)
A(6,7,I,I)= (0.D0,1.D0)*DSQRT(6.0D0)*(GAM2*(ETX*ETX-ETY*ETY)

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1      +2.D0*GAM3*ETX*ETY*(0.D0,1.D0))
A(7,6,I,I)=CONJG(A(6,7,I,I))
A(6,8,I,I)= -DSQRT(6.0D0)*GAM3*(ETX+ETY*(0.D0,1.D0))*ETZ
A(8,6,I,I)=CONJG(A(6,8,I,I))

S(1,1,I,J)=AC*ES*PKL/PI
S(2,2,I,J)=S(1,1,I,J)
S(3,3,I,J)=ESF*PKL/PI
S(4,4,I,J)=ESG*PKL/PI
S(5,5,I,J)=S(4,4,I,J)
S(6,6,I,J)=S(3,3,I,J)
S(7,7,I,J)=(ESF+ESG)/2.D0*PKL/PI
S(8,8,I,J)=S(7,7,I,J)
S(1,3,I,J)=-P*ESPLUS*PKL/PI
S(3,1,I,J)=CONJG(S(1,3,I,J))
S(1,4,I,J)=(0.D0,1.D0)/SQRT(1.5)*P*ESZ*PKL/PI
S(4,1,I,J)=CONJG(S(1,4,I,J))
S(1,5,I,J)=-1.D0/DSQRT(3.D0)*P*ESMINUS*PKL/PI
S(5,1,I,J)=CONJG(S(1,5,I,J))
S(1,7,I,J)=-1.D0/DSQRT(3.D0)*P*ESZ*PKL/PI
S(7,1,I,J)=CONJG(S(1,7,I,J))
S(1,8,I,J)=(0.D0,1.D0)/SQRT(1.5)*P*ESMINUS*PKL/PI
S(8,1,I,J)=CONJG(S(1,8,I,J))
S(2,4,I,J)=- (0.D0,1.D0)/SQRT(3.0)*P*ESPLUS*PKL/PI
S(4,2,I,J)=CONJG(S(2,4,I,J))
S(2,5,I,J)=-1.D0/SQRT(1.5)*P*ESZ*PKL/PI
S(5,2,I,J)=CONJG(S(2,5,I,J))
S(2,6,I,J)=- (0.D0,1.D0)*P*ESMINUS*PKL/PI
S(6,2,I,J)=CONJG(S(2,6,I,J))
S(2,7,I,J)=-1.D0/SQRT(1.5)*P*ESPLUS*PKL/PI
S(7,2,I,J)=CONJG(S(2,7,I,J))
S(2,8,I,J)=- (0.D0,1.D0)/DSQRT(3.D0)*P*ESZ*PKL/PI
S(8,2,I,J)=CONJG(S(2,8,I,J))
S(3,4,I,J)=ESH*PKL/PI
S(4,3,I,J)=CONJG(S(3,4,I,J))
S(3,5,I,J)=ESI*PKL/PI
S(5,3,I,J)=CONJG(S(3,5,I,J))
S(3,7,I,J)=(0.D0,1.D0)/DSQRT(2.D0)*ESH*PKL/PI
S(7,3,I,J)=CONJG(S(3,7,I,J))
S(3,8,I,J)=- (0.D0,1.D0)*DSQRT(2.D0)*ESI*PKL/PI
S(8,3,I,J)=CONJG(S(3,8,I,J))
S(4,6,I,J)=ESI*PKL/PI
S(6,4,I,J)=CONJG(S(4,6,I,J))
S(4,7,I,J)=(0.D0,1.D0)/SQRT(2.0)*(ESG-ESF)*PKL/PI
S(7,4,I,J)=CONJG(S(4,7,I,J))
S(4,8,I,J)=(0.D0,1.D0)*DSQRT(1.5D0)*ESH*PKL/PI
S(8,4,I,J)=CONJG(S(4,8,I,J))
S(5,6,I,J)=-ESH*PKL/PI
S(6,5,I,J)=CONJG(S(5,6,I,J))
S(5,7,I,J)=- (0.0,1.0)*SQRT(1.5)*CONJG(ESH)*PKL/PI
S(7,5,I,J)=CONJG(S(5,7,I,J))
S(5,8,I,J)=(0.D0,1.D0)/SQRT(2.0)*(ESG-ESF)*PKL/PI
S(8,5,I,J)=CONJG(S(5,8,I,J))
S(6,7,I,J)=- (0.0,1.0)*SQRT(2.0)*CONJG(ESI)*PKL/PI
S(7,6,I,J)=CONJG(S(6,7,I,J))
S(6,8,I,J)=- (0.0,1.0)/SQRT(2.0)*CONJG(ESH)*PKL/PI
S(8,6,I,J)=CONJG(S(6,8,I,J))

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Appendix

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      END IF
20    CONTINUE
      DO 30 M=1,8
      DO 30 L=1,8
      DO 30 I=1,L2
      DO 30 J=1,L2
      II=L2*(M-1)+I
      JJ=L2*(L-1)+J
30    H9(II,JJ)=A(M,L,I,J)+S(M,L,I,J)
      RETURN
      END

      SUBROUTINE WFEV(NW,WW,BW,PH,PL,PS,FX,FY,
1      L4,L2,NK,N41,B,EVR,EVI)

      IMPLICIT REAL*8(A-H,O-Z)
      COMPLEX X
      DIMENSION EVR(L4,L4),EVI(L4,L4)
      DIMENSION B(NK),PH(L4),PL(L4),PS(L4),FX(N41),FY(L4,N41)

      Z00=0.D0
      PI=3.1415926
      NG=L2/2
      DO 25 I=1,L2
      I2=I-NG-1
25    B(I)=FLOAT(I2)
      DO 30 K=1,NW
      Z=-.5*(WW+BW)
      DO 10 I=1,N41
      X=0.0D0
      DO 20 J=1,L2
      DO 20 L=1,L2
      DGL=B(L)-B(J)
20    X=X+(CMPLX(EVR(J+0*L2,K),-EVI(J+0*L2,K))*
1      CMPLX(EVR(L+0*L2,K),EVI(L+0*L2,K))+
2      CMPLX(EVR(J+1*L2,K),-EVI(J+1*L2,K))*
3      CMPLX(EVR(L+1*L2,K),EVI(L+1*L2,K))+
4      CMPLX(EVR(J+2*L2,K),-EVI(J+2*L2,K))*
5      CMPLX(EVR(L+2*L2,K),EVI(L+2*L2,K))+
6      CMPLX(EVR(J+3*L2,K),-EVI(J+3*L2,K))*
7      CMPLX(EVR(L+3*L2,K),EVI(L+3*L2,K))+
8      CMPLX(EVR(J+4*L2,K),-EVI(J+4*L2,K))*
9      CMPLX(EVR(L+4*L2,K),EVI(L+4*L2,K))+
9      CMPLX(EVR(J+5*L2,K),-EVI(J+5*L2,K))*
9      CMPLX(EVR(L+5*L2,K),EVI(L+5*L2,K))+
8      CMPLX(EVR(J+6*L2,K),-EVI(J+6*L2,K))*
9      CMPLX(EVR(L+6*L2,K),EVI(L+6*L2,K))+
9      CMPLX(EVR(J+7*L2,K),-EVI(J+7*L2,K))*
9      CMPLX(EVR(L+7*L2,K),EVI(L+7*L2,K)))
9      *CEXP(CMPLX(Z00,Z*2*PI/(WW+BW))*DGL))
      FX(I)=Z
      FY(K,I)=X

```

Appendix

```

10 Z=Z+(WW+BW)/(N41-1)
C
C   CALCULATE THE HH, LH, AND SO COMPOSTION IN EACH STATE
C
    BPH=0.D0
    BPL=0.D0
    BPS=0.D0
    DO 60 J=1,L2
    BPH=BPH+(EVR(J+2*L2,K))**2+(EVI(J+2*L2,K))**2
1      + (EVR(J+5*L2,K))**2+(EVI(J+5*L2,K))**2
    BPL=BPL+(EVR(J+3*L2,K))**2+(EVI(J+3*L2,K))**2
1      + (EVR(J+4*L2,K))**2+(EVI(J+4*L2,K))**2
    BPS=BPS+(EVR(J+6*L2,K))**2+(EVI(J+6*L2,K))**2
1      + (EVR(J+7*L2,K))**2+(EVI(J+7*L2,K))**2
60 CONTINUE
    PH(K)=BPH
    PL(K)=BPL
    PS(K)=BPS
30 CONTINUE
    RETURN
    END

    SUBROUTINE CH(NM,N,AR,AI,W,ZR,ZI,FV1,FV2,FM1,IERR)
    IMPLICIT REAL*8(A-H,O-Z)
    DIMENSION AR(NM,N),AI(NM,N),W(N),ZR(NM,N),ZI(NM,N),
1      FV1(N),FV2(N),FM1(2,N)
C*
C*****
C*          DETERMINE THE EIGENVALUES AND EIGENVECTORS OF          *
C*          A COMPLEX HERMITIAN MATRIX                             *
C*****
C*
C*      NM,N          NM=N. N IS THE ORDER OF COMPLEX HERMITIAN COMPLEX.
C*      AR,AI        ARE THE REAL AND IMAGINARY PARTS OF THE COMPLEX
MATRIX.
C*          ONLY THE FULL LOWER TRIANGLE OF AR(AI) NEED BE
SUPPLIED.
C*      W            ARE EIGENVALUES.
C*      ZR,ZI(I,J)   ARE THE EIGENVECTOR OF THE JTH EIGENVALUE.
C*      FV1,FV2,FM1 ARE WORKING ROOMS.
C*      IERR         ARE CODE. CALCULATION IS CORRECT WHEN IERR=0.
C*
    IF (N.LE.NM) GOTO 10
    IERR=10*N
    GOTO 50
10  CALL HTRIDI(NM,N,AR,AI,W,FV1,FV2,FM1)
    DO 40 I=1,N
    DO 30 J=1,N
    ZR(J,I)=0.0
30  CONTINUE
    ZR(I,I)=1.0
40  CONTINUE
    CALL TQL2(NM,N,W,FV1,ZR,IERR)
    IF (IERR.NE.0) GOTO 50
    CALL HTRIBK(NM,N,AR,AI,FM1,N,ZR,ZI)
50  RETURN
    END

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SUBROUTINE HTRIBK (NM,N,AR,AI,TAU,M,ZR,ZI)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION AR (NM,N),AI (NM,N),TAU (2,N),ZR (NM,M),ZI (NM,M)
IF (M.EQ.0) GOTO 200
DO 50 K=1,N
DO 50 J=1,M
ZI (K,J)=-ZR (K,J)*TAU (2,K)
ZR (K,J)= ZR (K,J)*TAU (1,K)
50 CONTINUE
IF (N.EQ.1) GOTO 200
DO 140 I=2,N
L=I-1
H=AI (I,I)
IF (H .EQ. 0.0) GOTO 140
DO 130 J=1,M
S=0.0
SI=0.0
DO 110 K=1,L
S=S+AR (I,K)*ZR (K,J)-AI (I,K)*ZI (K,J)
SI=SI+AR (I,K)*ZI (K,J)+AI (I,K)*ZR (K,J)
110 CONTINUE
S=(S/H)/H
SI=(SI/H)/H
DO 120 K=1,L
ZR (K,J)=ZR (K,J)-S*AR (I,K)-SI*AI (I,K)
ZI (K,J)=ZI (K,J)-SI*AR (I,K)+S*AI (I,K)
120 CONTINUE
130 CONTINUE
140 CONTINUE
200 RETURN
END

SUBROUTINE HTRIDI (NM,N,AR,AI,D,E,E2,TAU)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION AR (NM,N),AI (NM,N),D (N),E (N),E2 (N),TAU (2,N)
C COMPLEX CMPLX
TAU (1,N)=1.0
TAU (2,N)=0.0
DO 100 I=1,N
100 D (I)=AR (I,I)
DO 300 II=1,N
I=N+1-II
L=I-1
H=0.0
SCALE=0.0
IF (L.LT.1) GOTO 130
DO 120 K=1,L
120 SCALE=SCALE+ABS (AR (I,K))+ABS (AI (I,K))
IF (SCALE.NE.0.0) GOTO 140
TAU (1,L)=1.0
TAU (2,L)=0.0
130 E (I)=0.0
E2 (I)=0.0
GOTO 290
140 DO 150 K=1,L
AR (I,K)=AR (I,K)/SCALE

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      AI(I,K)=AI(I,K)/SCALE
      H=H+AR(I,K)*AR(I,K)+AI(I,K)*AI(I,K)
150  CONTINUE
      E2(I)=SCALE*SCALE*H
      G=SQRT(H)
      E(I)=SCALE*G
      F=CABS(CMPLX(AR(I,L),AI(I,L)))
      IF (F.EQ.0.0) GOTO 160
      TAU(1,L)=(AI(I,L)*TAU(2,I)-AR(I,L)*TAU(1,I))/F
      SI=(AR(I,L)*TAU(2,I)+AI(I,L)*TAU(1,I))/F
      H=H+F*G
      G=1.0+G/F
      AR(I,L)=G*AR(I,L)
      AI(I,L)=G*AI(I,L)
      IF (L.EQ.1) GOTO 270
      GOTO 170
160  TAU(1,L)=-TAU(1,I)
      SI=TAU(2,I)
      AR(I,L)=G
170  F=0.0
      DO 240 J=1,L
      G=0.0
      GI=0.0
      DO 180 K=1,J
      G=G+AR(J,K)*AR(I,K)+AI(J,K)*AI(I,K)
      GI=GI-AR(J,K)*AI(I,K)+AI(J,K)*AR(I,K)
180  CONTINUE
      JP1=J+1
      IF (L.LT.JP1) GOTO 220
      DO 200 K=JP1,L
      G=G+AR(K,J)*AR(I,K)-AI(K,J)*AI(I,K)
      GI=GI-AR(K,J)*AI(I,K)-AI(K,J)*AR(I,K)
200  CONTINUE
220  E(J)=G/H
      TAU(2,J)=GI/H
      F=F+E(J)*AR(I,J)-TAU(2,J)*AI(I,J)
240  CONTINUE
      HH=F/(H+H)
      DO 260 J=1,L
      F=AR(I,J)
      G=E(J)-HH*F
      E(J)=G
      FI=-AI(I,J)
      GI=TAU(2,J)-HH*FI
      TAU(2,J)=-GI
      DO 260 K=1,J
      AR(J,K)=AR(J,K)-F*E(K)-G*AR(I,K)+FI*TAU(2,K)+GI*AI(I,K)
      AI(J,K)=AI(J,K)-F*TAU(2,K)-G*AI(I,K)-FI*E(K)-GI*AR(I,K)
260  CONTINUE
270  DO 280 K=1,L
      AR(I,K)=SCALE*AR(I,K)
      AI(I,K)=SCALE*AI(I,K)
280  CONTINUE
      TAU(2,L)=-SI
290  HH=D(I)
      D(I)=AR(I,I)
      AR(I,I)=HH

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      AI(I,I)=SCALE*SQRT(H)
300  CONTINUE
      RETURN
      END

      SUBROUTINE TQL2(NM,N,D,E,Z,IERR)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION D(N),E(N),Z(NM,N)
      AMACHEP=1.E-15
      IERR=0
      IF(N.EQ.1) GOTO 1001
      DO 100 I=2,N
100   E(I-1)=E(I)
      F=0.0
      B=0.0
      E(N)=0.0
      DO 240 L=1,N
      J=0
      H=AMACHEP*(ABS(D(L))+ABS(E(L)))
      IF (B.LT.H) B=H
      DO 110 M=L,N
      IF (ABS(E(M)).LE.B) GOTO 120
110   CONTINUE
120   IF(M.EQ.L) GOTO 220
130   IF(J.EQ.30) GOTO 1000
      J=J+1
      L1=L+1
      G=D(L)
      P=(D(L1)-G)/(2.0*E(L))
      R=SQRT(P*P+1.0)
      D(L)=E(L)/(P+SIGN(R,P))
      H=G-D(L)
      DO 140 I=L1,N
140   D(I)=D(I)-H
      F=F+H
      P=D(M)
      C=1.0
      S=0.0
      MML=M-L
      DO 200 II=1,MML
      I=M-II
      G=C*E(I)
      H=C*P
      IF (ABS(P).LT.ABS(E(I))) GOTO 150
      C=E(I)/P
      R=SQRT(C*C+1.0)
      E(I+1)=S*P*R
      S=C/R
      C=1.0/R
      GOTO 160
150   C=P/E(I)
      R=SQRT(C*C+1.0)
      E(I+1)=S*E(I)*R
      S=1.0/R
      C=C*S
160   P=C*D(I)-S*G
      D(I+1)=H+S*(C*G+S*D(I))

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DO 180 K=1,N
H=Z(K,I+1)
Z(K,I+1)=S*Z(K,I)+C*H
Z(K,I)=C*Z(K,I)-S*H
180 CONTINUE
200 CONTINUE
E(L)=S*P
D(L)=C*P
IF (ABS(E(L)).GT.B) GOTO 130
220 D(L)=D(L)+F
240 CONTINUE
DO 300 II=2,N
I=II-1
K=I
P=D(I)
DO 260 J=II,N
IF(D(J).GE.P) GOTO 260
K=J
P=D(J)
260 CONTINUE
IF(K.EQ.I) GOTO 300
D(K)=D(I)
D(I)=P
DO 280 J=1,N
P=Z(J,I)
Z(J,I)=Z(J,K)
Z(J,K)=P
280 CONTINUE
300 CONTINUE
GOTO 1001
1000 IERR=L
1001 RETURN
END
```