GaAs/AlGaAs (111)A-based and InGaAsP based quantum well infrared photodetectors

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GaAs/AlGaAs (111)A-based and InGaAsP based Quantum Well Infrared Photodetectors

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School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
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SUMMARY

Intersubband transitions in quantum wells and superlattices are widely investigated in present years due to the potentially technological applications, especially for quantum well infrared photodetectors (QWIPs). The advantages of QWIP compared with HgCdTe detectors include the mature III-V compound semiconductor epitaxial growth and processing technologies based on GaAs, which lead to high uniformity, excellent reproducibility, and thus large-area and low-cost focal plane arrays (FPAs). 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. However, the study of QWIP so far is mainly based on the (100)-oriented GaAs substrate which has led to maturity of devices. In the meanwhile, other efforts using non-(100) oriented GaAs substrates or non-GaAs materials are also invested in order to explore novel properties. In this thesis, a (111)A-oriented GaAs/AlGaAs QWIP and an InGaAsP/InGaAsP/InGaAs step QWIP on InP substrate have been investigated.

The matrix method based on the effective approximation has been employed to study the subband states and intersubband transitions in the arbitrary shape quantum wells. The (111)-oriented four band k-p method has also been used to calculate the subband states in valence band, Orientation-dependent properties of the subband structure have been also discussed.

The crystal quality, doping and optical properties of Si-doped GaAs/AlGaAs QWIP structure grown on GaAs (111)A substrate by molecular beam epitaxy (MBE) have been

investigated. Enhancement of epitaxial growth rate, reduction in Al incorporation and acceptor conduction type of Si doping in (111)A oriented growth have been observed. The smooth surface morphology and enhanced photoluminescence emission intensity of GaAs (111)A layer grown by MOVPE with N₂ carrier gas have been achieved too.

The p-type (111)A GaAs/AlGaAs QWIP has been fabricated and characterized. Intersubband absorption, I-V characteristics and the spectra photocurrent responses have been investigated. Strong polarization dependence of photoresponse have been observed, for which the normal incidence transition is dominant. The highest responsivity is around 1 mA/W with a detection wavelength at about 7 μm under TE mode incidence at 25 K and a bias of 4.3 V.

A near lattice-matched In_yGa_{1-y}As_zP_{1-z}/In_wGa_{1-w}As_vP_{1-v}/In_xGa_{1-x}As asymmetric step quantum well infrared photodetector (ASQWIP) grown by low-pressure metalorganic vapor phase epitaxy (MOVPE) technique using N₂ carrier with tertiarybutylarsine (TBA) and tertiarybutylphosphine (TBP) has been reported. The spectral responsivity of the detector has its peak at a wavelength of 10.7 μm with a peak responsivity of 0.19 A/W under 0.8 V bias at 25 K. A maximum peak detectivity of $1.9 \times 10^9 \text{ cmHz}^{1/2} / \text{W}$ has been achieved under 0.6 V bias at 25 K. The measured activation energy by analyzing thermionic emission of carriers is found to be at about 81 meV. This work demonstrates the fabrication of InP based quantum well infrared detectors using MOVPE with TBA and TBP sources with performance comparable to that achieved using MBE.

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Chapter 1 Background and Introduction

1.1 Brief review on infrared detectors

Many interests in military, industry, scientific research and daily life such as night vision, process control, earth resource survey, medical diagnostics, and so on, have required advanced infrared imaging technology. As the “heart” of the infrared system, infrared detector is constantly afforded the most prominent position in the focal plane array (FPA) technology. Infrared detectors are based on passive detection of thermally emitted electromagnetic radiation as described by the well-known Planck's law. The Planck's radiation law states that every object at a temperature above absolute zero emits electromagnetic radiation, and the higher the temperature, the higher is the emitted intensity. Tremendous efforts have been spent on developing the technology and capability of infrared detectors for night vision and under obscured visibility conditions.

Infrared detectors are usually classified into thermal and photon detectors. The absorption of light in thermal detectors raises the temperature of the devices, which in turn changes some temperature-dependent parameters such as electrical conductivity. Thermal detectors may be thermopile, bolometer, or pyroelectric detectors. In contrast to photon detectors, thermal detectors typically operate at room temperature. They are usually characterized by moderate sensitivity and slow response but they are cheap and easy to use. They have found widespread use in low cost applications that do not require high performance.

The absorption of infrared radiation in photon detectors results directly in some specific excitation event, such as the photoelectric emission of electrons from a surface, or electronic

interband transitions in semiconductor materials. The most important photon detectors are intrinsic detectors, extrinsic detectors, photoemissive (metal silicide/Schottky barriers) detectors, and quantum well detectors. Depending on how the electric or magnetic fields are developed, there are various modes such as photoconductive, photovoltaic, photoelectromagnetic, and photoemissive ones. These detectors exhibit both better signal-to-noise performance and a very fast response as compared to the thermal detectors. The primary mechanism of the infrared photon detector is interband transition based on the excitation of electrons across a semiconductor bandgap. The narrow bandgap materials such as InSb, PbSnTe and HgCdTe have been employed for infrared detector. The detection wavelength is proportional to the bandgap of the material.

Indium antimonide (InSb) is the first narrow bandgap material used to make infrared detectors [1.1]. The metal-silicide/silicon Schottky-barrier detectors, which use free-carrier absorption, have achieved great progress [1.2]. In the near and middle infrared region (1~5 mm), platinum silicide has good sensitivity (at temperature as low as 50 mK) and excellent stability [1.3].

Neither InSb nor PtSi detector can extend their detection to long wavelength infrared (LWIR) range due to the relatively large bandgap or the Schottky barrier height. Difficulties in growing HgCdTe material, which is significantly due to the high vapour pressure of Hg, has encouraged the development of alternative detector technologies over past years. One of these was PbSnTe, a compound material system was vigorously pursued in parallel to HgCdTe in late 1960s and early 1970s. PbSnTe was comparatively easy to grow and good

quality diodes with alloy compositions tailored for the 8–12 μm spectral regions were readily demonstrated. However, The PbSnTe detector work was abandoned due to its high dielectric constant compared with HgCdTe and its large temperature coefficient of expansion (TCE) mismatch with Si [1.4].

Table 1.1 The comparison of the thermal and photon detectors [1.6].

Detector type		Advantages	Disadvantages
Thermal (thermopile, bolometers, pyroelectric)			
IV–VI(PbS, PbSe, PbSnTe)		Light, rugged, reliable, and low cost Room temperature operation Easier to prepare More stable materials	Low detectivity at high frequency Slow response(ms order) Very high thermal expansion coefficient
Photon			
Intrinsic	II–VI (HgCdTe)	Easy band gap tailoring Well developed theory & experiment Multicolor detectors	Nonuniformity over large area High cost in growth and processing Surface instability
	III–V (InGaAs, InAs, InSb, InAsSb)	Good material and dopants Advanced technology Possible monolithic integration	Heteroepitaxy with large lattice mismatch Long wavelength cutoff limited to 7 μm at 77 K
Extrinsic (Si:Ga, Si:As, Ge:Cu, Ge:Hg)		Very-long-wavelength operation Relatively simple technology	High thermal generation Extremely low-temperature operation
Free carriers (PtSi, Pt2Si, IrSi)		Low-cost, high yields Large and close-packed 2D arrays	Low quantum efficiency Low-temperature operation
Quantum wells	Type I (GaAs/AlGaAs, InGaAs/AlGaAs)	Matured material growth Good uniformity over large area Multicolor detectors	High thermal generation Complicated design and growth
	Type II (InAs/InGaSb, InAs/InAsSb)	Low Auger recombination rate Easy wavelength control	Complicated design and growth Sensitive to the interfaces
Quantum dots (InAs/GaAs, InGaAs/InGaP, Ge/Si)		Normal incidence of light Low thermal generation	Complicated design and growth

Infrared detection in HgCdTe begins with electrons being excited from the valence band into the conduction band. The minimum photon energy required is equal to the bandgap, E_g . The bandgap of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, which is a function of the alloy composition ratio “ x ” of CdTe to HgTe, provides a degree of freedom on both MWIR and LWIR detector design. With its high quantum efficiency, flexibility in the spectral response over a wide span of the infrared regions of interest, single HgCdTe detector has excellent performance in detection.

However, the problems emerging in interband transition based HgCdTe detector are that such a small bandgap material has always difficulties to grow, process, and fabricate into devices in comparison to the large bandgap semiconductors for detection of the long wavelength [1.5]. Serious technological difficulties in mass production make uniformity and yield for the larger area staring array remain to be unsolved issues. The weak Hg–Te bond results in bulk, surface, and interface instabilities. A comparison of various thermal and photon detectors are summarized in the Table 1.1 [1.6], in which usage of low-dimensional intersubband photodetectors such as quantum well (QW), quantum wire (QWR) and quantum dot (QD) have renewed the research interest as the replacement of HgCdTe detectors.

1.2 QWIP research and development

Rapid development in bandgap engineering by modern epitaxial technologies such as molecular beam epitaxy (MBE) and metal organic vapor phase epitaxy (MOVPE) has realized quantum well infrared photodetector (QWIP) [1.7]. The basic component of a

QWIP device is the multi-quantum wells (MQWs) which are artificially fabricated by placing thin layers of two different, large bandgap semiconductor materials alternately. The bandgap discontinuity of two materials creates quantized subbands in the potential wells in conduction band or valence band. The QWIP has the similar mechanism to the extrinsically doped semiconductor photodetector in that carrier in doped quantum wells are excited from the ground states to unoccupied states within the same band (i.e. intersubband transition). However, by tuning the material bandgaps, QWIP can adapt to operation in both MWIR and LWIR regions (3~5 and 8~12 μm). Furthermore, QWIPs have higher quantum efficiency and higher detectivity. Compared with HgCdTe, QWIPs have relatively lower responsivity and have to operate at lower temperature. As compared with well-developed HgCdTe and InSb detectors, QWIPs has advantages, such as the mature technology of material growth and processing for III-V group compound semiconductors, which have led to high uniformity, excellent reproducibility, and thus large-area, low-cost focal plane array (FPA). In addition, the flexibility of QWIP approach for enhancing device functionality and its easiness for monolithically integration with other devices [1.8, 1.9] allows it to be very promising technology.

As the fundamental physics of QWIP, strong intersubband absorption was first experimentally measured in a series of MQWs by West and Eglash [1.10]. A large near-unity oscillator strength was achieved in a stack of 50 n-type highly doped GaAs quantum wells. Following these results, Levine *et al.* [1.11] demonstrated the first n-type GaAs/AlGaAs QWIP based on intersubband absorption between two bound quantum-well states with peak detection wavelength of 10.8 μm . In MQW structures, the final QW state

for transition was placed either slightly above or below the top of the barriers to obtain optimum sensitivity. In 1991, Bethea et al. achieved 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 [1.12].

Since the emergence of QWIP, great progress has been made in developing device and FPA for infrared detection. To improve the QWIP performance, several configurations of QWIP structure were proposed based on transitions from bound-to-extended states [1.13], and bound-to-quasibound states [1.14]. The major advantage of the bound-to-continuum QWIP in which the excited state is above the barrier edge is higher efficiency and lower bias required for collection of photoelectron without tunneling through the barrier. Moreover, the barrier thickness can be increased to reduce the ground state sequential tunneling and thus decrease the dark current. The advantage of the bound-to-quasibound QWIP over the bound-to-continuum QWIP is its lower dark current and accordingly desirable to operate at higher temperature. The dark current is thoroughly dominated by the classical thermionic emission of ground-state electron directly out of the well into the continuum at a temperature above 45K [1.15]. As shown in Figure 1.1, the bound-to-quasibound QWIP has the energy barrier to thermionic emission is roughly the same as it to photo-ionization since the first excited state is dropped to the barrier edge as compared with the bound-to-continuum QWIP. For the later one, the first excited state is about 10~15meV than the barrier height. By increasing barrier thickness to about 50 nm for long wavelength bound-to-quasibound QWIPs, the dark current is reduced by an order of magnitude, thus enable the signal-to-noise ratio.

Figure 1.1 Schematic diagram of the flat conduction band of bound-to-quasibound QWIP and bound-to-continuum QWIP

Meanwhile, multicolor infrared detection is becoming an area of active research because it can be used for various applications such as aerospace observation, target discrimination, and remote temperature sensing [1.16]. So far three main approaches have been developed for such an application: (1) multiple lead-based approach. The detector involves contacting each intermediate conduction layer for a QWIP grown in the multistack [1.17]. Each stack is designed to detect a different wavelength. The advantage of this approach is its simplicity in QW structure design and its negligible electrical crosstalk between colors. The drawback is the difficulty in fabricating a many color version because the several separate leads are required in contacting intermediate layers. (2) Voltage switched approach. This kind of QWIP has a switchable response. One such example is realized by stacking the usual one-color QWIP separated by thin conducting layers [1.18, 1.19]. (3) Voltage tunable approach. Voltage tunable two-color detectors have been proposed in the past based on two main physical mechanisms. The first approach is to change the energy level structure and wave functions of excited states under bias by using asymmetric coupled QWs [1.20], graded barriers [1.21], or asymmetric step wells [1.22]. The second approach is based on electron

transport between ground states of adjacent QWs under a voltage bias and later used to achieve voltage tunable two-color detection [1.23].

However, the requirement for the optical coupling schemes such as diffraction grating stems from the MQW intersubband selection rule that only allows the absorption of infrared radiation having an electric field component perpendicular to the MQW layers [1.24]. The grating requirement is satisfied in the conventional QWIP by a metal surface relief grating or crystallographically etched through a cap layer on top of MQW. Linear gratings [1.25], two-dimensional periodic gratings [1.26, 1.27] and random reflectors [1.28] have demonstrated efficient light coupling to QWIP and have made QWIP imaging arrays feasible. These gratings diffract normal incident radiation into non-normal, higher order, transverse magnetic (TM) modes that have an electric field component perpendicular to the MQW layers. Other optical coupling schemes such as Enhanced QWIP [1.29] and Corrugated QWIP [1.30] were also reported.

The diffraction-based coupling scheme, however, has certain disadvantages. For example, the diffraction wavelength of the grating must match precisely with the material intrinsic absorption wavelength to obtain maximum efficiency. Each QWIP material wafer therefore needs a different grating geometry. Secondly, the fabrication of the gratings requires precision electron-beam lithography, which severely increases the cost and reduces the throughput of FPA production. Thirdly, for very short or very long wavelength detection, the design and fabrication of the corresponding grating may be difficult. Lastly, the

wavelength dependence of diffraction renders it unsuitable for broad-band or multicolor detection.

To overcome these difficulties, researchers have proposed and studied alternative approaches. There is an increasing interest in studying the less common p-type QWIPs [1.31~1.33]. The main advantage of the p- over n-type QWIP is their ability to absorb normal incident light without the need for gratings or other means to couple the light, this provides a significant simplification in the fabrication of a large focal plane array. This advantage makes optimization of *p*-QWIP structures a very promising undertaking. The first p-type QWIP has been successfully demonstrated by Levine et al [1.34] and also p-type GaInAs/InP QWIP gives the wavelength response of 2.7 μm by S. D. Gunapala [1.35], other p-type QWIPs using valence intersubband transitions in GaAs/AlGaAs and GaInAs/InAlAs material systems [1.36~1.41] have been investigated too.

P-QWIPs have more complicated energy band structure due to light hole and heavy hole coupling and, therefore are more interesting in device physics. Also due to the small gain and large capture probability of holes in p-QWIPs, the dark current is small and thus enables long signal integration time. Likewise, the current noise should be reduced as the capture probability grows [1.42, 1.43].

Recently, it has been actually observed that structures grown on (111) substrates exhibit special or enhanced electrical and optical properties over those grown on conventional (100) substrates. For example, a significant reduction in the lasing threshold current density was

achieved in GaAs/AlGaAs lasers grown by MBE on slightly misoriented (111) substrates [1.44]. Also, strained (111) layers exhibit the piezoelectric (PE) effect as well as the pyroelectric effect [1.45] and an enhanced quantum confinement Stark shift due to the PE field. These effects can be exploited for novel device applications [1.46]. The (111) orientations may also allow the fabrication of high electron mobility transistors or lasers with extended characteristics [1.47]. The (111)-oriented p-type GaAs/AlGaAs QWIP has been theoretically investigated by Tachee Cho et al [1.48]. And its low dark current and high detectivity have been estimated. The p-type Si-doped AlGaAs/GaAs and AlGaAs/InGaAs QWIPs were grown on (311)A substrates and the dark current performance were compared with the Be- doped p-type QWIP grown on (100) substrate [1.49]. The much larger effective mass of holes permits the use of much higher doping levels in the p-type (111) QWIP than that of (100) QWIP does. It has been expected that p-type (111) QWIP should take the advantages of both normal incidence detection and attractive electronic and optical properties to extend the performance of QWIP technology.

So far lattice matched GaAs/AlGaAs QWIPs have been well developed and widely used for 8~12 μ m wavelength detection using MBE technology. However, further shortening the detection wavelength is difficult for GaAs/AlGaAs material system due to the limited direct conduction band offset and inferior performance of device with high Al molar ratio. The strained material system of $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{In}_y\text{Ga}_{1-y}\text{As}$ has been employed to detect a wavelength from 2 to 35 μ m by changing the material composition and thickness [1.50]. An alternative approach is to put the final transition state into a resonance state by adding two ultra thin AlAs barriers to the basic QW structure and to form the double barrier quantum well (DBQW). The AlAs barriers must be thin enough to have the Γ -band edge forming the

high barrier [1.51]. AlGaAs/AlAs/InGaAs DBQW had performed a detection wavelength of 1~5 μm with various In content [1.52~1.53]. A 3.4 μm photodetector operating at 205 K has been demonstrated by using lattice-matched $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{AlAs}/\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ DBQW to InP substrate. [1.54]. A near-infrared detection (i.e. $\sim 1.67 \mu\text{m}$) has been recently performed for an AlGaAs/AlAs/ $\text{Ga}_{0.99}\text{AsN}_{0.01}$ DBQW photodetector [1.55].

Because of the extensive scientific and commercial exploration of the AlGaAs–GaAs material system over the past decades, the application of this technology to infrared MQW detectors has rapidly reached commercial maturity. Nonetheless, further improvements to detector performance through increasing responsivity and reducing dark currents have led to studies of other material systems such as GaAs–InGaAs [1.56], GaInP–GaAs [1.57,1.58], and InP–GaInAsP [1.59, 1.60]. These Al-free III-V group material systems are immune to aluminum oxidation problems that restrict fabrication methods, and oxygen-related defects that degrade electrical properties. Therefore, growth at lower temperatures, which minimizes undesirable dopant diffusion, can be adopted.

1.3 Objectives of the study

The development of conventional GaAs/AlGaAs QWIP has greatly benefited from advances in MBE technology and the widely utilized (100) oriented substrates due to the relatively large window of good epitaxial growth conditions, and the well-developed processing technology. To date, increasing interests in further research of QWIP still remain. Due to the attractive properties of QW grown on (11N) substrate, some pioneering efforts in (11N)-oriented QWIPs have been demonstrated in previous Section 1.2(See reference [1.48],

[1.49]). In this dissertation, we study the growth of Si-doped GaAs/AlGaAs QWIP structure on GaAs(111)A substrate by MBE technology to understand the epitaxial property, structural characteristic and Si incorporation behavior. Then the performance such as infrared absorption, current–voltage characteristic, photocurrent response of the (111) QWIP are investigated. We hope by this interesting work we can understand the (111)-oriented QWIP for potential application of normal incidence detection. As a good complement, the surface morphology and photoluminescence emission properties of GaAs (111) layer grown by MOVPE technique are studied for the preparation of development of (111)-oriented QWIP based on more productive MOVPE.

Quaternary materials especially InGaAsP are extremely important among these Al-free III-V group material candidates. InGaAsP is currently employed in commercial optoelectronic (especially semiconductor lasers emitting at 1.3 and 1.55 μm) and electronic (especially high-electron-mobility transistor) devices. It is of considerable interest due to the wide range of achievable bandgaps and the possibility of fabricating them on commercially important GaAs and InP substrates. MOVPE technology is from time to time applied to the QWIP growth owing to its ever-increasing advances and comparable performance of microstructure device as MBE technology does. As innovative work, we investigate the growth, structure performance of $\text{In}_y\text{Ga}_{1-y}\text{As}_z\text{P}_{1-z}/\text{In}_w\text{Ga}_{1-w}\text{As}_v\text{P}_{1-v}/\text{In}_x\text{Ga}_{1-x}\text{As}$ asymmetric step QWIP (ASQWIP) grown by low-pressure MOVPE technique with less poisonous precursors of TBA, TBP in safer nitrogen ambient.

1.4 Major contributions

The major contributions of this work are summarized as follows:

- (1) Designing and modifying the growth parameter on (111)A-oriented GaAs surface such as the growth temperature T_g , and V/III flux ratio to grow AlGaAs/GaAs epilayers by MBE.
- (2) The p-type Si-doped GaAs/AlGaAs QWIP structure have been successfully grown on GaAs (111)A substrate by MBE. The epitaxial property and structural characteristic have been investigated. The epitaxial growth rates of GaAs and AlGaAs were found to be enhanced and the Al incorporation was reduced in (111)A orientation.
- (3) By modifying the growth condition and source temperature of Silicon dopant, Si has been successfully incorporated as acceptor in p-type (111)A QWIP. The doping level is comparable to n-type Si doping in (100)-oriented GaAs layer. The outdiffusion of Si during the growth is negligible as judged from the symmetrical dark current characteristics of the QWIPs.
- (4) The p-type GaAs/AlGaAs (111)A QWIP device has been successfully fabricated and characterized. Dominant normal incident spectra photocurrent response for p-type (111)A QWIP has been discovered. The peak responsivity of (111)A QWIP is around 1.3 mA/W with a detection wavelength at 7 μm under TE mode incidence at 25 K and bias of 4.3 V.
- (5) A near lattice-matched $\text{In}_y\text{Ga}_{1-y}\text{As}_z\text{P}_{1-z}/\text{In}_w\text{Ga}_{1-w}\text{As}_v\text{P}_{1-v}/\text{In}_x\text{Ga}_{1-x}\text{As}$ asymmetric step quantum well infrared photodetector (ASQWIP) grown on InP(100) substrate by low-pressure metalorganic vapor phase epitaxy (MOVPE) technique using N_2 carrier with tertiarybutylarsine (TBA) and tertiarybutylphosphine (TBP) have been investigated. The

spectral responsivity of the detector has its peak at a wavelength of 10.7 μm with a peak responsivity of 0.19 A/W under 0.8 V bias at 25 K. A maximum peak detectivity of 1.9×10^9 $\text{cmHz}^{1/2}/\text{W}$ is achieved under 0.6 V bias at 25 K. The measured activation energy using thermionic emission of carriers is found to be about 81 meV. This work demonstrates InGaAsP based asymmetric QWIP using low pressure MOVPE with TBA and TBP sources has a comparable performance to that achieved using MBE.

1.5 Organization of the thesis

This thesis is organized into six chapters. Chapter 1 gives an introduction to the thesis, where the research background, motivation, objectives, and major contributions are briefed.

Chapter 2 presents the analysis of subband structure and intersubband transitions in quantum wells using the transfer matrix method under the framework of the effective mass approximation. The (111)-oriented 4 x 4 k-p method is also used to calculate the subband states in valence band. Orientation-dependent properties of the subband structure are discussed.

Chapter 3 discusses the basic epitaxial growth of (111)A-oriented GaAs by MBE technique. Then the structural, Si incorporation characteristics of Si-doped (111)A-based GaAs/AlGaAs QWIP growth by MBE are discussed. At last the surface morphology and photoluminescence emission properties of GaAs (111)A layer grown by MOVPE with N_2 carrier gas are investigated as a good complement.

In chapter 4, the device measurement of (111)A-GaAs/AlGaAs QWIP are performed. Intersubband absorption, dark-current characterization and spectral photocurrent response are discussed.

Chapter 5 demonstrates the near lattice-matched $\text{In}_y\text{Ga}_{1-y}\text{As}_z\text{P}_{1-z}/\text{In}_w\text{Ga}_{1-w}\text{As}_v\text{P}_{1-v}/\text{In}_x\text{Ga}_{1-x}\text{As}$ asymmetric stepped QWIP grown by low-pressure metalorganic vapor phase epitaxy (MOVPE) technique using N_2 carrier gas with tertiarybutylarsine (TBA) and tertiarybutylphosphine (TBP). The dark current characterization and spectral responsivity of the detector are presented.

Finally, Chapter 6 summarizes the major findings of this work and puts forth necessary recommendation for future work.

Chapter 2 Subband structure and intersubband transitions in quantum wells

2.1 Transfer matrix method

QWIPs operate by photoexcitation of electrons between the ground and the first excited state subbands of multi-quantum wells (MQWs) which are artificially fabricated by stacking thin layers of two different bandgap semiconductor materials alternately. The band alignment in these material layers forms a series of potential wells and barriers. The quantized subband states are created in conduction bands or valence bands. The subband states are analyzed with simplification in envelope function approximation. Indeed, to the good 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 band misalignment. The effects of the atomic potentials are accommodated by substituting the mass of a free electron with the effective mass m^* in the material. It turns out that such a simplified approach is quite adequate in device design and modeling.

Using the electron effective mass, which is different for different materials, the envelope wave function $\varphi(z)$ can be determined by the one-dimensional time-independent Schrödinger equation as follows:

$$\left[-\frac{d}{dz} \frac{1}{m^*} \frac{d}{dz} + V(z) \right] \varphi(z) = E \varphi(z), \quad (2.1)$$

where m^* is the effective mass, z is along the growth direction of quantum wells, $V(z)$ is the potential of the conduction band edge and E is the eigen state energy of electron.

Within the envelop function approximation, there are several popular methods in calculating the energy level structures and corresponding wavefunction. Comparing with Kronig-Penney model and tight-binding model, transfer matrix method (TMM) [2.1] is the most versatile method in solving problem related to quantum well structure with an arbitrary potential based on PC-level computer.

In the TMM approach, the wave function is assumed to be in a form of plane wave in each layer with a forward- and a backward-going component. After multiple reflections from the structure at the interfaces, parts of the waves transmit through the structure while the lefts are reflected back. By applying continuity conditions at each interface, a matrix can be set up to transfer amplitudes of the waves from one layer to the next.

In general, the wave function in the n^{th} layer of thickness d_n can be expressed as

$$\varphi_n = A_n e^{ik_n z} + B_n e^{-ik_n z}, \quad (2.2)$$

where $k_n = \frac{\sqrt{2m_n(E - V_n)}}{\hbar}$, m_n is the effective mass of electron. For the wave function to be mathematically well behaved, we require that they be finite, single valued and continuous.

This leads to the continuity conditions at each interface

$$\varphi_n = \varphi_{n+1} \quad (2.3)$$

and

$$\frac{1}{m_n^*} \frac{\partial \varphi_n}{\partial z} = \frac{1}{m_{n+1}^*} \frac{\partial \varphi_{n+1}}{\partial z}. \quad (2.4)$$

By substituting (2.2) into (2.3) and (2.4), we get

$$\begin{bmatrix} A_{n+1} \\ B_{n+1} \end{bmatrix} = M_{n+1} \begin{bmatrix} A_n \\ B_n \end{bmatrix}, \quad n = 1, \dots, N-1,$$

$$\text{where } M_{n+1} = \begin{bmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{bmatrix} = \frac{1}{2} \begin{bmatrix} (1 + \gamma_{n+1,n}) e^{-i(k_{n+1} - k_n)z_n} & (1 - \gamma_{n+1,n}) e^{-i(k_{n+1} + k_n)z_n} \\ (1 - \gamma_{n+1,n}) e^{i(k_{n+1} + k_n)z_n} & (1 + \gamma_{n+1,n}) e^{i(k_{n+1} - k_n)z_n} \end{bmatrix}, \quad (2.5)$$

$$\text{and } \gamma_{n+1,n} = \frac{m_{n+1}k_n}{m_nk_{n+1}}$$

Figure 2.1 Conduction band energy potential profile of arbitrary multilayer quantum well structure.

Figure 2.1 shows the conduction band energy potential profile of an arbitrary multilayer quantum well structure. The energy levels can be investigated by the global transmission coefficient T_G . If we assume that A_0, B_0 are the coefficients of wave function in the first layer and A_N, B_N are the ones in the last nth layer, the following relationship can be given:

$$\begin{bmatrix} A_N \\ B_N \end{bmatrix} = M_N \dots M_{n+1} M_n \dots M_1 \begin{bmatrix} A_0 \\ B_0 \end{bmatrix} = M_g \begin{bmatrix} A_0 \\ B_0 \end{bmatrix} = \begin{bmatrix} m_{g11} & m_{g12} \\ m_{g21} & m_{g22} \end{bmatrix} \begin{bmatrix} A_0 \\ B_0 \end{bmatrix} \quad (2.6)$$

Considering that there are no reflection in the last layer, we can suppose $B_N = 0$. The transmission coefficient is defined as the transmitted flux to the incident flux:

$$T_G = \frac{v_N \varphi_N^* \varphi_N}{v_0 \varphi_0^* \varphi_0} = \frac{m_0^*(E) k_N(E) |A_N|^2}{m_N^*(E) k_0(E) |A_0|^2} = \frac{m_0^*(E) k_N(E)}{m_N^*(E) k_0(E)} \left| \frac{1}{m_{g11}} \right|^2, \quad (2.7)$$

Where v is the electron group velocity and m_{g11} is the first diagonal element of M_g . The local maxima in T_G determine the locations of eigen energies. The energy eigen values can be obtained at minima of $|m_{g11}|$. Calculation of coefficients A_N , B_N at the maxima of T_G will yield the wave function.

As an example, the eigen energies of $300\text{\AA}$ $\text{In}_{0.95}\text{Ga}_{0.05}\text{As}_{0.11}\text{P}_{0.89}$ / $70\text{\AA}$ $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}_{0.41}\text{P}_{0.59}$ / $35\text{\AA}$ $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$ step quantum well are obtained by calculation of $|m_{g11}|$ as shown in Figure 2.2. The first bound states under the edge of barrier are demonstrated, which indicate the bound-to-bound transition in the step quantum well.

Figure 2.2 Eigen energies in a $300\text{\AA}$ $\text{In}_{0.95}\text{Ga}_{0.05}\text{As}_{0.11}\text{P}_{0.89}$ / $70\text{\AA}$ $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}_{0.41}\text{P}_{0.59}$ / $35\text{\AA}$ $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$ step QW calculated by the minima of $m_{g11}(E)$. The figure indicates the bound-to-bound transition in the quantum well. V_b is the barrier height of the QW. E1 and E2 are the two bound states in the QW.

From the above example, it can be seen that the transfer matrix approach provides a convenient way to obtain the eigen values and wavefunctions for a finite quantum well. However, further consideration has to be made to reveal the subband structure of periodic multiple quantum wells which are often used in the application of QWIP.

According to Bloch Theorem, in a periodical potential field, the wave function has the form as a product of a periodic wavefunction $u(q, z)$ and a plane wave. $u(q, z)$ has the same period length as the periodic multiple quantum well and is named Bloch function. That is

$$\varphi(z) = u(q, z)e^{iqz}, \quad (2.8)$$

where q is the wave vector of the plane wave.

If the quantum well period is L , then the wave function has the property:

$$\varphi(z + R_m) = e^{iqR_m} \varphi(z) \quad (2.9)$$

and $R_m = mL$, where m is an integer and its maximum is the number of period.

As a result, the wave function at the same locations in adjacent periods are identical except a phase shift factor. There should be:

$$A_N = A_0 e^{i\phi}, B_N = B_0 e^{i\phi}, \quad (2.10)$$

where $\phi = qL$.

For N period quantum wells, we can use the cyclic boundary conditions to find the number of states in each miniband (*i.e.* $\varphi(z + NL) = \varphi(z)$). Therefore, replacing m with N in Eq. (2.9) yields $e^{iqNL} = 1$, so

$$q = \frac{2l\pi}{NL}, \quad (2.11)$$

where l is an integer and has values $l = 0, 1, \dots, N-1$.

Substitute Eq. 2.10 into Eq. 2.6 we get

$$\begin{bmatrix} m_{g11} - e^{i\phi} & m_{g12} \\ m_{g21} & m_{g22} - e^{i\phi} \end{bmatrix} \begin{bmatrix} A_0 \\ B_0 \end{bmatrix} = 0. \quad (2.12)$$

The solution exists only if the determinant of the matrix is zero.

$$(m_{g11} - e^{i\phi})(m_{g22} - e^{i\phi}) - m_{g12}m_{g21} = 0.$$

We can deduce the following equation

$$m_{g11} + m_{g22} = e^{i\phi} + e^{-i\phi} = 2\cos\phi. \quad (2.13)$$

Therefore, the range of energies which satisfies the above condition can be found numerically by solving

$$|m_{g11} + m_{g22}| \leq 2. \quad (2.14)$$

In multiple quantum wells, energy minibands instead of discrete energy levels are formed for those energy values which satisfy Eq. 2.14. The minibands below the barrier top are narrower than those above and tend to degenerate as the barrier thickness increases. Figure 2.3 shows the miniband energies in a $50\text{\AA}$ $\text{In}_{0.89}\text{Ga}_{0.11}\text{As}_{0.16}\text{P}_{0.84}/60\text{\AA}$ $\text{In}_{0.62}\text{Ga}_{0.38}\text{As}_{0.78}\text{P}_{0.22}/40\text{\AA}$ $\text{In}_{0.56}\text{Ga}_{0.44}\text{As}$ step superlattice calculated by plotting absolute value of $(m_{g11} + m_{g22})$ versus energy. The first two bound states are below the barrier top.

Figure 2.3 The miniband energies in a $50\text{\AA}$ $\text{In}_{0.89}\text{Ga}_{0.11}\text{As}_{0.16}\text{P}_{0.84}/60\text{\AA}$ $\text{In}_{0.62}\text{Ga}_{0.38}\text{As}_{0.78}\text{P}_{0.22}/40\text{\AA}$ $\text{In}_{0.56}\text{Ga}_{0.44}\text{As}$ step superlattice calculated by the minima of $|m_{g11} + m_{g22}|$. V_b is the barrier height of the QW. E1~E4 are the miniband states in the QW.

From Eq. (2.12), we get the coefficient of wave function in the first layer:

$$A_0 = m_{12}; B_0 = e^{i\phi} - m_{11}. \quad (2.15)$$

Then the coefficients (A_n , B_n) and the wave function in each layer can be obtained using transfer matrix for each interface.

2.2 Electron intersubband transitions in quantum wells

For the quantum well structure in a QWIP, intersubband transition between quasi-two-dimensional electronic states in semiconductors occurs due to the confinement of the electron wavefunction in one dimension. The number of works on intersubband transition in quantum well has been ever-increasingly studied due to its high technological potential for

novel infrared detectors, emitter and nonlinear elements since 1985 when the intersubband absorption was firstly observed in GaAs/AlGaAs quantum well by West and Eglash [2.2].

In this section, we will briefly describe the expression for intersubband absorption based on Fermi's golden rule. Considering an n-type quantum well, the initial state E_i and final state E_f in quantum well under the approximation of envelop wave function, ψ_i and ψ_f can be given as

$$\begin{aligned}\psi_i(\mathbf{r}) &= \frac{e^{ik_{\perp i} \cdot \mathbf{r}}}{\sqrt{A}} \varphi_i(z) u_i(\mathbf{r}), \\ \psi_f(\mathbf{r}) &= \frac{e^{ik_{\perp f} \cdot \mathbf{r}}}{\sqrt{A}} \varphi_f(z) u_f(\mathbf{r}),\end{aligned}\tag{2.16}$$

where $k_{\perp i, f}$ denotes the two-dimensional vector (k_x, k_y) and A is the sample area. $u_{i, f}(\mathbf{r})$ are Bloch functions. $\varphi_{i, f}(z)$ are the envelop wave functions for the quantized state in z direction.

In an n-type QWIP, photocurrent is initiated through an external electromagnetic field by dipole transitions of electrons between two quantum well states E_i and E_f within the conduction band. The optical transition rate

$$W_{if} = \frac{2\pi}{\hbar} \left| \langle \psi_i | H | \psi_f \rangle \right|^2 \delta(E_i - E_f - \hbar\omega),\tag{2.17}$$

where $\hbar\omega$ is energy of incident photon, ψ_i , ψ_f are electron wave functions for ground and excited states, respectively, and H is interaction Hamiltonian and H has form under the dipole approximation [2.3] as

$$H = \frac{e}{2m^*} (\epsilon \cdot \mathbf{p}) = \frac{eE_0}{2m^*\omega} (\epsilon \cdot \mathbf{p}) \quad (2.18)$$

where ϵ is the polarization vector, $\mathbf{p}$ is momentum operator.

The absorption coefficient is determined by the oscillator strength $f_{i,f}$ and the joint density of states $\rho_{i,f}$. The relationship between these quantities is given by [2.4]

$$\alpha(\hbar\omega) = C \sum_{i,f} f_{i,f} \rho_{i,f} \quad (2.19)$$

where $C = \frac{\pi e^2 \hbar \sin^2 \theta \cos \theta}{2L \eta c \epsilon_0 m^*}$, in which c is velocity of light, e is electron charge, ϵ_0

is the permittivity of vacuum and η is the refractive index.

The oscillator strength for such optical transition can be defined as

$$f_{i,f}(\hbar\omega) = \frac{2}{m^* \omega \hbar} \left| \langle \psi_i | \epsilon \cdot \mathbf{p} | \psi_f \rangle \right|^2 = \frac{2}{m^* \omega \hbar} \left| \langle \psi_i | e_z p_z | \psi_f \rangle \right|^2 \quad (2.20)$$

For intersubband transition in the conduction band, due to the orthogonality of the envelop functions, $\int \varphi_f^*(z) \varphi_i(z) dz = 0$, for $i \neq f$, there is

$$f_{i,f}(\hbar\omega) = \frac{2}{m^* \omega \hbar} \left| \langle \psi_i | e_z \cdot p_z | \psi_f \rangle \right|^2 = \frac{2}{m^* \omega \hbar} \left| \langle \varphi_i | e_z \cdot p_z | \varphi_f \rangle \right|^2 \quad (2.21)$$

For all possible transitions from the bound state to excited states, the total oscillator strength should obey the sum rule ($\sum_f f_{i,f} = 1$). Since the wave function is not fully confined in the well, this effective mass will be slightly different from the effective mass in the well. The result of oscillator strength is overestimated if only one electron effective mass in the well is adopted. Since the place where the wave probability is high is assumed to contribute more

to the transition, the following formula is used to estimate an average m^* for numerical consideration,

$$m^* = \frac{\sum_{i=1}^n m_i \int_L \varphi_i^* \varphi_i dz}{\int_L \varphi_i^* \varphi_i dz}. \quad (2.22)$$

For a MQW/SL structure, one can obtain an expression for the joint density of states (JDOS) using [2.5]

$$\rho_{i,f} = \frac{g_s}{2\pi} \left| \frac{d\phi}{d(E_f - E_i)} \right|, \quad (2.23)$$

A main feature of intersubband transitions is their delta-function-like density of states. There will be a number of singularities in the function of the density of states, and this will cause problems in the numerical calculation. But then broadening effects such as impurity scattering, lattice scattering, and the fluctuation of layer thickness usually smooth the effect of singularities. Considering these broadening effects, we can use the Lorentzian function to represent the joint density of states,

$$\rho(\hbar\omega) = \sum_{i,f} \rho_{i,f} = \sum_{i,f} \frac{1}{\pi} \frac{(\Gamma_f/2)}{(E_f - E_i - \hbar\omega)^2 + (\Gamma_f/2)^2}, \quad (2.24)$$

where Γ_f is full width at half maximum and is equal to $2\hbar/\tau$, τ is the lifetime of the electron in the state E_f .

2.3 Design of the InGaAsP-based QWIP

Using the transfer matrix method mentioned above, we discuss an $\text{In}_y\text{Ga}_{1-y}\text{As}_z\text{P}_{1-z}/\text{In}_w\text{Ga}_{1-w}\text{As}_v\text{P}_{1-v}/\text{In}_x\text{Ga}_{1-x}\text{As}$ asymmetric step quantum well on (001) InP substrate for long

wavelength detection. The structural diagram of the active region in the InGaAsP QWIP is shown in Figure 2.4. It consists of an $\text{In}_y\text{Ga}_{1-y}\text{As}_z\text{P}_{1-z}$ barrier layer, an $\text{In}_w\text{Ga}_{1-w}\text{As}_v\text{P}_{1-v}$ step layer and an $\text{In}_x\text{Ga}_{1-x}\text{As}$ well. E_1 and E_2 are the first two ground states of the quantum well.

Figure 2.4 The structural diagram of $\text{In}_y\text{Ga}_{1-y}\text{As}_z\text{P}_{1-z}/\text{In}_w\text{Ga}_{1-w}\text{As}_v\text{P}_{1-v}/\text{In}_x\text{Ga}_{1-x}\text{As}$ asymmetric step quantum well.

Compared to square quantum well, the consideration of asymmetric quantum well in our design is that the asymmetric potential profile breaks the symmetry of wavefunction in square quantum well structure and wavelength-tunable transition using bias-modulation is expected.

2.3.1 Material parameters

For InGaAsP and InGaAs materials, the parameters such as lattice constant energy bandgap, effective mass, etc are collected in Table 2.1 and Table 2.2, respectively.

Table 2.1 The collection of parameters of InGaAsP used in the calculation [2.6].

Parameters	$\text{In}_y\text{Ga}_{1-y}\text{As}_z\text{P}_{1-z}$
Energy band gap E_g (eV)	$0.418+1.10(1-y)+1.005(1-z)-0.493y(1-y)-0.180z(1-z)-0.265y(1-y)-0.030(1-y)(1-z)z+0.347(1-y)(1-z)+0.875yz(1-y)(1-z)$
Lattice constant a_0 (Å)	$5.6533(1-y)z+6.0583yz+5.4505(1-y)(1-z)+5.8687y(1-z)$
Electron effective mass $m_e^*(m_0)$	$0.0665(1-y)z + 0.023yz + 0.17(1-y)(1-z) + 0.08y(1-z)$
Elastic stiffness c_{11} (GPa)	$12.33(1-y)z+8.33yz+14.39(1-y)(1-z)+10.22y(1-z)$
Elastic stiffness c_{12} (GPa)	$5.71(1-y)z+4.53yz+6.5(1-y)(1-z)+5.76y(1-z)$
Conduction band deformation potential a_c (eV)	$8.06(1-y)z+5.88yz+9.45(1-y)(1-z)+6.18y(1-z)$
Valence band deformation potential a_v (eV)	$1.16(1-y)z+yz+1.7(1-y)(1-z)+1.27y(1-z)$

These parameters in Table 2.1 and Table 2.2 are obtained by linear interpolation, except for the energy gap which is assumed to achieve by

$$E_g = xE_{gA} + (1-x)E_{gB} - Cx(1-x), \quad (2.25)$$

where E_{gA}, E_{gB} are bandgaps of binary materials such as GaAs, AlAs and InAs, $C=0.37$ for $\text{Al}_x\text{Ga}_{1-x}\text{As}$, and $C=0.475$ for $\text{In}_x\text{Ga}_{1-x}\text{As}$ [2.8].

The bandgap equations of $\text{In}_y\text{Ga}_{1-y}\text{As}_z\text{P}_{1-z}$ and $\text{In}_x\text{Ga}_{1-x}\text{As}$ materials without considering strain effect have been given in Table 2.1 and Table 2.2. For any $\text{In}_x\text{Ga}_{1-x}\text{As}$ and $\text{In}_y\text{Ga}_{1-y}$

$y\text{As}_z\text{P}_{1-z}$ layers grown on InP substrate, we have the in-plane strain and the perpendicular strain described by the following expressions, respectively [2.9]

$$\varepsilon_{xx} = \varepsilon_{yy} = \frac{a_0 - a_{\text{epi}}}{a_{\text{epi}}}$$

and

$$\varepsilon_{\perp} = \varepsilon_{zz} = -2 \frac{c_{12}}{c_{11}} \varepsilon_{xx}, \quad (2.26)$$

where $a_0 = 5.8688 \text{ \AA}$ is the lattice constant of the InP, a_{epi} is the lattice constant of $\text{In}_x\text{Ga}_{1-x}$

As or $\text{In}_y\text{Ga}_{1-y}\text{As}_z\text{P}_{1-z}$ alloy. c_{12} and c_{11} are the elastic stiffness constants.

Table 2.2 The collection of parameters of GaAs, InAs, AlAs, InP and InGaAs used in the calculation [2.7, 2.8].

Parameters	GaAs	InAs	AlAs	InP	$\text{In}_x\text{Ga}_{1-x}\text{As}$
Lattice constant a_0 (Å)	5.6533	6.0583	5.6611	5.8697	$5.6533+0.405x$
Band gap E_g (eV)	1.519	0.417	3.099	1.424	$1.519-1.577x+0.475x^2$
Electron effective mass m_e^* (Γ)	0.067	0.026	0.15	0.08	$0.0667-0.041x$
Conduction band deformation potential a_c (eV)	-7.17	-5.08	-5.64	-6	$-7.17+2.09x$
Valence band deformation potential a_v (eV)	-1.16	-1.00	-2.47	-0.6	$-1.16+0.06x$
Elastic stiffness c_{11} ($\times 10^{11} \text{ dyn/cm}^2$)	12.21	8.329	12.5	10.11	$12.21-3.88x$
Elastic stiffness c_{12} ($\times 10^{11} \text{ dyn/cm}^2$)	5.66	4.526	5.34	5.61	$5.66-1.134y$

The strains in the epilayers shift the conduction and valence band-edge energy. The modify energy bandgap is given

$$E_g^s = E_g^0 + \Delta E_c - \Delta E_v = E_g^0 + 2(a_c - a_v)\left(1 - \frac{c_{12}}{c_{11}}\right) \frac{a_0 - a_{\text{epi}}}{a_{\text{epi}}}, \quad (2.27)$$

where a_c and a_v are deformation potentials for conduction band and valence band,

respectively.

The conduction band offset for $\text{In}_y\text{Ga}_{1-y}\text{As}_z\text{P}_{1-z}/\text{In}_x\text{Ga}_{1-x}\text{As}$ heterostructure is adopted as 0.4 [2.10, 2.11]. Once the band nonparabolicity is taken into account, the effective mass for $\text{In}_x\text{Ga}_{1-x}\text{As}$ and $\text{In}_y\text{Ga}_{1-y}\text{As}_z\text{P}_{1-z}$ can be expressed as

$$m_e^*(E) = m_e^* \left(1 + \frac{E - \Delta E}{E_g^s} \right), \quad (2.28)$$

where E is the energy, ΔE is the band offset of $\text{In}_y\text{Ga}_{1-y}\text{As}_z\text{P}_{1-z}/\text{In}_x\text{Ga}_{1-x}\text{As}$ QW.

2.3.2 Calculation of InGaAsP asymmetric QWIP structure

For detail, the active region of our InGaAsP QWIP consists of 30 periods of step quantum wells. The periodic step quantum well is designed to be latticed-matched to the InP substrate. It consists of a doped $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ well, an undoped $(\text{InP})_y(\text{In}_{0.53}\text{Ga}_{0.47}\text{As})_{1-y}$ step and an undoped $(\text{InP})_z(\text{In}_{0.53}\text{Ga}_{0.47}\text{As})_{1-z}$ barrier.

The calculated peak wavelength of intersubband absorption against the compositions for $300 \text{ \AA}$ $(\text{InP})_z(\text{In}_{0.53}\text{Ga}_{0.47}\text{As})_{1-z}/44 \text{ \AA}$ $(\text{InP})_y(\text{In}_{0.53}\text{Ga}_{0.47}\text{As})_{1-y}/25 \text{ \AA}$ $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ matching to the InP substrate are shown in Figure 2.5. The values of y and z varied from 0.05 to 0.95 and they satisfy $y \leq z$ as shown in Figure 2.5 (a). The peak absorption wavelength is determined by the numerical spectral absorption coefficient. It can be observed that the peak absorption wavelength distributes within a wide range from $9.3 \text{ \mu m}$ to more than $20 \text{ \mu m}$.

Figure 2.5 (b) plots the first excited state energy E_2 relative to the barrier top H of the InGaAsP QWIP. Both bound-to-bound (B-B) and bound-to-continuum (B-C) transitions are obtained. The QWIP should be B-B detector once its parameter satisfy the relation of $y < 0.4$ and $z > 0.75$. Otherwise, it becomes the B-C detector.

Figure 2.5 The calculated peak absorption wavelength (a) and the location of the first excited state relative to the barrier height (b) as a function of y and z for $300 \text{ \AA}$ $(\text{InP})_z(\text{In}_{0.53}\text{Ga}_{0.47}\text{As})_{1-z}$ / $44 \text{ \AA}$ $(\text{InP})_y(\text{In}_{0.53}\text{Ga}_{0.47}\text{As})_{1-y}$ / $25 \text{ \AA}$ $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ asymmetric quantum well.

An ideal design is to have the excited state in resonance with the barrier top. The large electric field must be applied for good photoelectron transport in B-B transition detector, especially when the excited state is too deep below the barrier top. However, the excited state should not be too high above the barrier top. Otherwise, the thermionic emission dark current will increase drastically due to the reduced activation energy. Thus the so-called bound-to-quasibound (B-QB) transition configuration simultaneously gives a strong absorption like B-B transition and a rapid carrier transport in the excited states like B-C transition, and helps maintain low dark current.

Based on the above discussion, a multiple periodic symmetric step QW consisting of 300Å $(\text{InP})_{0.85}(\text{In}_{0.53}\text{Ga}_{0.47}\text{As})_{0.15}$ barrier, 44Å $(\text{InP})_{0.55}(\text{In}_{0.53}\text{Ga}_{0.47}\text{As})_{0.45}$ step and 25Å $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ well is selected for the long wavelength detection. The structure is designed to have the final state just several meV above the top of $(\text{InP})_{0.85}(\text{In}_{0.53}\text{Ga}_{0.47}\text{As})_{0.15}$ barrier to reserve the tolerance allowing a small amount of parameter fluctuation during the epitaxial growth.

Figure 2.6 Calculated miniband dispersion relations in multiple period InGaAsP-based step QW. The solid and dash lines are bound state and barrier height, respectively (a). The oscillator strengths of the transitions from the bound state (E1) to the several lowest excited states (b).

Figure 2.6 (a) shows the miniband dispersion relations in multiple periods of InGaAsP-based step QWs. The minibands below the $(\text{InP})_{0.85}(\text{In}_{0.53}\text{Ga}_{0.47}\text{As})_{0.15}$ barrier top are extremely narrow and degenerated into single state localized in the quantum well due to the thick barrier. The first excited state is just several meV above the barrier top. Above the top of the barrier, the minibands form quasi-continuum band structure. Figure 2.6 (b) displays the oscillator strengths of the transitions from the bound state (E1) to the several lowest excited states above the top of the barrier. The oscillator strength are distributed in a range

of transition energy and the peak absorption has to be determined by considering all transitions.

The JDOS versus the energy in the periodic InGaAsP step quantum well is calculated as shown in Figure 2.7. The singularities of JDOS are smoothed out by a broadening parameter of $\Gamma=10$ meV according to Eq. 2.24. The simulated normalized absorption spectrum is shown in Figure 2.8. A detection wavelength of $11.5\ \mu\text{m}$ for the InGaAsP-based multiple step quantum well is demonstrated. The detail experimental characterization of QWIP device will be discussed in Chapter 5.

Figure 2.7 The joint density of states in the periodic InGaAsP step quantum well versus the energy.

Figure 2.8 The simulated normalized absorption spectrum of the periodic InGaAsP-based step quantum well.

2.4 Hole subband state for (111)A-oriented quantum well

So far we have discussed the intersubband transitions of electron in conduction band of QW. In the similar way, valence band intersubband transitions can be handled in p-type QW. However, it is difficult to give subband structure with reasonable accurateness due to the complexity of the valence band. But it is also incapable of explaining these phenomena, especially related to normal-incidence absorption. To find band structure and wavefunction of quantum wells, we focus our interest near to the valence-band edge maximum of direct band gap semiconductor. As a useful technique for analyzing the band structure near the extremum, the k - p method has been used to explain the optoelectronic properties of a variety of III-V compound superlattice structure with a view toward exploring the material physics underpinning the infrared detectors, lasers and so on.

During the last few years, the growth of GaAs and the related ternary alloys $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and $\text{In}_x\text{Ga}_{1-x}\text{As}$ in the non-conventional (111) crystallographic directions have attracted increasing attention due to their special physical and structural properties and their applicability to novel optoelectronic devices [2.12, 2.13]. According to the substrate orientation, the anisotropy in the interband optical transitions is changed reflecting the inherent anisotropy of the materials and the quantum confinement of electronic systems. Moreover, the anisotropy reveals the crystal direction which generates the most intense optical transitions. This information is very important for optical device applications. For the interpretation of the physical phenomena in these heterostructures grown on high-index substrates, a detailed understanding of the valence band mixing is needed. Effective mass theory is widely used to calculate the energy band structures in semiconductor systems. The 4×4 and 6×6 Luttinger-Kohn models [2.14~2.16] have been used for the heterostructures grown on (001)-oriented substrate. Xia has proposed an effective mass theory for superlattices grown on (11 $\bar{N}$)-oriented substrates based on Luttinger's theory with a 4×4 matrix including the coupling between the heavy and light holes [2.16]. In this section, Xia's model is employed to study the subband energies in (111)A quantum wells. The calculation is based on the effective mass approximation and using plane wave approximation to describe the subband states. By introduction of the probability functions, we can quantitatively estimate the respective components of the heavy hole, light hole in the MQW substrate. The calculation is the prototype for (100) orientation after coordination transform to the high index (111)-orientation. It can be used to calculate the subband states in QW structure on other (11 $\bar{N}$)-orientated surface. The calculation can be more

sophistically updated to 8 x 8 k.p model by considering the perturbation of split-orbit split-off band (SO) and the conduction subband.

The hole motion equation in the QW can be described by the Schrödinger equation as follows:

$$H\Phi_{n_v} = E\Phi_{n_v} \quad (2.25)$$

where Φ_{n_v} is the hole envelop wave function, and the 4 x 4 Hamiltonian H for (111)-oriented GaAs/AlGaAs MQW has the following format

$$H = \frac{\hbar^2}{2m_0} \begin{bmatrix} P+Q+V(z) & S & R & 0 \\ S^* & P-Q+V(z) & 0 & R \\ R^* & 0 & P-Q+V(z) & -S \\ 0 & R^* & -S^* & P+Q+V(z) \end{bmatrix}, \quad (2.26)$$

where P, S, R, Q are presented as:

$$\begin{aligned} P &= -\gamma_1 k^2 \\ Q &= -\gamma_3 (k_1^2 + k_2^2 - 2k_3^2) \\ R &= -\frac{\sqrt{3}}{3} (\gamma_2 + 2\gamma_3) (k_1 - ik_2)^2 - \frac{2\sqrt{6}}{3} (\gamma_2 - \gamma_3) (k_1 + ik_2) k_3 \\ S &= -\frac{\sqrt{6}}{3} (\gamma_2 - \gamma_3) (k_1 + ik_2)^2 + \frac{2\sqrt{3}}{3} (2\gamma_2 + \gamma_3) (k_1 - ik_2) k_3 \end{aligned}$$

$V(z)$ is the periodic potential of the QW. S^*, R^* are the conjugated format of S and R . $\gamma_1, \gamma_2, \gamma_3$ are the so-called Luttinger parameters and describe the influence of remote bands on valence band. They can be obtained from the experiments and used as empirical parameters.

Now we pay our attention to the calculation of the subband energy states in QWs. The real hole wavefunction of valence subband is the product of the hole envelop wavefunction and the Bloch wave functions near the top of the valence band. The band-edge Bloch functions are explicitly given by

$$\begin{aligned}
 \text{Heavy hole band} &= \left| \frac{3}{2}, \frac{3}{2} \right\rangle = \frac{1}{\sqrt{2}} |(X + iY) \uparrow\rangle \text{ and} \\
 &\quad \left| \frac{3}{2}, -\frac{3}{2} \right\rangle = \frac{1}{\sqrt{2}} |(X - iY) \downarrow\rangle \\
 \text{Light hole band} &= \left| \frac{3}{2}, \frac{1}{2} \right\rangle = \frac{i}{\sqrt{6}} [(X + iY) \downarrow - 2Z \uparrow] \\
 &\quad \left| \frac{3}{2}, -\frac{1}{2} \right\rangle = \frac{i}{\sqrt{6}} [(X - iY) \uparrow + 2Z \downarrow],
 \end{aligned} \tag{2.27}$$

where $|X\rangle$, $|Y\rangle$, and $|Z\rangle$ are the orbital wave functions of the top of the valence band.

In the 4 x 4 effective mass Hamiltonian scheme, the four dimensional hole envelope wavefunction for the QWs can be expanded as [2.17]:

$$\Phi_{n_v} = \{\Phi_{n_v}^j\}, (j=1, 2, 3, 4), \tag{2.28}$$

where $\Phi_{n_v}^j$ is the j th hole envelope function and can be described using plane-wave expansion method:

$$\Phi_{n_v}^j = \exp[i(k_x x + k_y y)] \sum_m a_{n_v, m}^j \frac{1}{\sqrt{L}} \exp\left[i\left(k_z + m \frac{2\pi}{L}\right)z\right], \tag{2.29}$$

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.

For the purpose of distinguishing the heavy hole (HH) and light hole (LH) components in the energy states of the QWs, we introduce the following probability functions [2.17]:

Table 2.3 Summary of the parameters used to calculate the hole subband energies for (111)-oriented $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ QW structure. ΔE_c is the conduction-band offset, and ΔE_v is the valence-band offset [2.8, 2.18].

Parameters	GaAs	$\text{Al}_x\text{Ga}_{1-x}\text{As}$
Energy bandgap E_g (eV)	1.519	$1.519+1.21x+0.37x^2$
Electron effective mass $m_e^*(m_0)$	0.067	$0.067+0.083x$
Heavy hole effective mass $m_{hh}^*(m_0)$	0.952	$0.952+0.41x$
Light hole effective mass $m_{lh}^*(m_0)$	0.117	$0.117+0.033x$
Band offset $\Delta E_c / \Delta E_v$	0.33/0.67

Figure 2.9 The wave functions of hole subband energy levels at $k=0$ of $\text{GaAs}/\text{Al}_{0.32}\text{Ga}_{0.68}\text{As}$ QW with barrier $80 \text{ \AA}$ and a series of well widths: (a) $W=30 \text{ \AA}$, (b) $W=60 \text{ \AA}$, (c) and $W=100 \text{ \AA}$. The barrier height is 140 meV . Only the confinement subbands are demonstrated.

$$P_{n_v}^{hh} = \sum_{j=1,2} \sum_m a_{n_v,m}^{j*} a_{n_v,m}^j,$$

$$P_{n_v}^{lh} = \sum_{j=3,4} \sum_m a_{n_v,m}^{j*} a_{n_v,m}^j, \quad (2.30)$$

From $P_{n_v}^{hh}$, $P_{n_v}^{lh}$, we can estimate the respective components of heavy hole and light hole states in QW states $\Phi_{n_v}^j$. The following sum rule holds

$$\sum_i P_{n_v}^i = 1, \text{ where } i=\text{HH, LH.}$$

The eigen hole energies can be obtain from the secular equation by inserting Eq.2.26, 2.27, and 2.28 into Eq. 2.25. Table 2.3 gives the summary of the parameters used to calculate the

Figure 2.10 The in-plane dispersion curves for hole subband energy levels of GaAs/ $\text{Al}_{0.32}\text{Ga}_{0.68}\text{As}$ QW with barrier 80 Å and a series of well widths: (a) $W=30$ Å, (b) $W=60$ Å, (c) and $W=100$ Å. $k_{||}$ is in-plane wave vector. L is the sum of one period of well width and barrier thickness. Only the confinement subbands are demonstrated.

hole subband energies for (111)-oriented $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ QW structure.

The hole subband energies and wavefunctions in a (111)-oriented $\text{GaAs}/\text{Al}_{0.32}\text{Ga}_{0.68}\text{As}$ QW have been calculated. Figure 2.9 displays the wave functions of hole subband energy levels at $k=0$ in the $\text{GaAs}/\text{Al}_{0.32}\text{Ga}_{0.68}\text{As}$ QW with barrier of 80 and a series different well widths. Figure 2.10 shows the hole subband energy dispersion relations in the $\text{GaAs}/\text{AlGaAs}$ QW along the k_z direction. The energy order of the HH and LH bands is determined by the barrier confinement and quantum well width. Only the confinement subbands are demonstrated. For case (a), HH1=24 meV, LH1=84 meV and HH2=89 meV are below barrier top. For case (b), HH1=8 meV, LH1=32 meV, HH2=46 meV, HH3=70 meV and HH4=119 meV are below the barrier top. For case (c), HH1=3 meV, LH1=13 meV, HH2=24 meV, HH3=29 meV, HH4=52 meV, HH5= 85 meV, LH2= 97 meV, HH6= 128 meV are below the barrier top. The HH and LH hole subbands under the barrier height are not coupled to each other at the $k=0$ and can be identified as HH and LH states, respectively. For the subband states above the barrier height, the HH band and LH band strongly mix. The ground state subband is labeled as HH1 and is followed by subbands LH1, HH2 and so on according to Eq. 2.30.

The confined subband energies in a (111)-oriented 38 Å $\text{GaAs}/563$ Å $\text{Al}_{0.18}\text{Ga}_{0.82}\text{As}$ QW have also been calculated using the four band k-p model. Since the well become narrow and quantum confinement is weaker, only HH and LH bound states are observed in the well. Actually the four-band k-p model has given a good description of subband energies in valence band. In the following chapters, the growth and characterization of (111)A-based

GaAs/AlGaAs QWIP device will be investigated. The four band k-p model will be employed to analyze the hole band energy levels in QWIP as well.

Figure 2.11 The hole subband energy levels diagram of 38 Å GaAs/563 Å Al_{0.18}Ga_{0.82}As QW. Only the confinement subbands are demonstrated.

2.5 Summary

The matrix method based on the effective approximation is employed to study the subband states and intersubband transitions in quantum wells in this chapter. Based on this, the design of an In_yGa_{1-y}As_zP_{1-z}/In_wGa_{1-w}As_vP_{1-v}/In_xGa_{1-x}As asymmetric QWIP has been discussed. It has been proved such a simplified approach is quite adequate in n-type QWIP device design and modeling. On the other hand, as a good description of hole subband states in QW of valence band, the 4x4 k-p model used to calculate the hole subband states in (111)A-oriented GaAs/AlGaAs QW has been described. In the following chapters, the experimental work for the designed InGaAsP and GaAs/AlGaAs QWIP structures will be discussed.

Chapter 3 Growth and Characterization of (111)A-oriented GaAs/AlGaAs QWIP

In this chapter, the basic epitaxial growth, doping characteristics of (111)A-oriented GaAs by molecular beam epitaxy (MBE) technique have been investigated. Then the structure characteristics of Si-doped (111)A-based GaAs/AlGaAs QWIP structure growth by MBE are discussed. At last, the surface morphology and photoluminescence emission properties of GaAs (111)A layer grown by MOVPE with TBA precursor and N₂ carrier gas are discussed too.

3.1 An outline on MBE technology

Molecular Beam Epitaxy (MBE) was developed in early 1970s as a means of growing high-purity epitaxial layers of compound semiconductors [3.1, 3.2]. Since then it has evolved into a popular technique for growing III-V compound semiconductors as well as several other materials. MBE is a versatile technique for growing high-quality epitaxial layers of semiconductors, allowing precise control of layer thickness, doping and chemical composition. MBE has become a valuable tool in the development of sophisticated electronic and optoelectronic devices based on QW and superlattices structure using III-V compound semiconductors and several other materials [3.3, 3.4].

Figure 3.1 shows a schematic diagram of the MBE growth chamber. The key components of MBE reactor system are:

Figure 3.1 The schematic diagram of the solid source MBE growth chamber.

(1) A vacuum pumping system and a chamber to create a clean, ultra-high vacuum (UHV) environment. The pumping system comprises a rough pumping, which consists of a dry diaphragm pump and three sorption pumps which can pump down to about 5×10^{-3} Torr, and 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 effusion cells are the key components of an MBE system, because they must provide excellent flux stability and uniformity, and material purity. Furthermore, being the parts that must withstand the highest temperatures (up to 1400°C) for the longest periods, they are often responsible for machine downtime. Therefore a careful choice of elements, materials and geometry must be taken. The cells (usually six to ten) are placed on a source flange, and are co-focused on the substrate heater, to optimize flux uniformity.

- (3) The substrate manipulator is capable of continuous azimuthal rotation (CAR) around its axis to improve uniformity across the wafer and from wafer to wafer in multiwafer systems. The heater behind the sample is designed to maximize temperature uniformity and minimize power consumption and impurity outgassing.
- (4) Surface science techniques such as reflection high-energy electron diffraction (RHEED) system for in-situ surface characterization is compatible with the MBE.
- (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.

MBE is a semiconductor growth technique in which thermal beams of atoms are directed onto a heated substrate under ultra high vacuum conditions. Pressure is generally of the order of 10^{-10} Torr. This prevents inadvertent doping of samples by ambient atoms/molecules like oxygen and leads to high performance devices. Under UHV conditions, the beams do not interact and can be easily controlled. Therefore, unobstructed (molecular) flow of species can be deposited on the substrate of chemical cleanliness and surface highly controlled growth of ultra-thin epitaxial layers is possible. The elementary growth process in the case of GaAs MBE growth can be described as follows; Ga and As source beams from effusion cell arrive directly on the growing surface without scattering in their paths. There are some atoms or molecules directly reflected by the substrate but most of them are adsorbed physically or chemically on the surface. On atomically rough surface, the arriving Ga atoms are incorporated at the position where they arrived. On atomically flat

Figure 3.2 The elemental processes in MBE growth [3.5].

surfaces, the arrival atoms or molecules diffuse until they enter the steps which are mostly originated from 2D nuclei or a misoriented substrate. If the step edge is atomically rough, the entering atoms are fixed or detached without further diffusion along the step. On the other hand, if the step edge is atomically smooth, the entering atoms move along the step to find a kink. The overall stages involved in MBE are illustrated in Figure 3.2.

3.2 Non (100)-oriented epitaxial growth

By far most studies of III-V semiconductor quantum well, superlattices and heterostructures have concentrated on the conventional (100) oriented substrates because of the wide range of growth condition, resulting in good epitaxial layer quality, the well-developed processing technology for this orientation, and the natural cleavage planes normal to each other. However, the possibility of changing and improving the fundamental material properties,

growth mechanisms, surface kinetics and impurity incorporation by growing on non-(100) plane substrate has strongly motivated to study these aspects [3.6~3.8]. Quantum wells grown on (111) B substrates possess an enhanced optical transition, and a reduced threshold current density of laser diode has been demonstrated [3.9, 3.10]. More than one order of magnitude of photoluminescence (PL) intensity enhancement was measured for samples grown at temperature of 600°C [3.11~3.13]. Improved electron mobility in Si-doped (111) B AlGaAs to that of (100) has also been observed [3.14]. The improved optical property and electron mobility are attributed to the increased quantum confinement and reduced alloy scattering by the long-range ordering. Advantages have also been observed for heterostructures grown on (111)A substrates. Similar to strained (111)B heterostructures [3.15], coherently strained (111) A layers possess a large built-in field, and the quantum confined Stark shift due to the piezoelectric effect can be used for novel device application[3.16,3.17]. Most of the reports on good-quality GaAs/AlGaAs heterostructures on (111) GaAs have dealt with the growth by MBE. Relatively high growth temperature (~700°C) are required to obtain GaAs/AlGaAs quantum wells by MBE on (111) B and (111) A with good structural and optical quality [3.18, 3.19]. Nevertheless, *Watanabe et al* [3.20] have obtained high-quality QWs on (111) A GaAs at 540°C by MBE. Facts imply that the complicated growth mode in (111) surface which results in various optimization condition for different MBE systems. It is rather difficult, however, to grow high quality material on (111) A substrate. While the (100) surface always has two dangling bonds available for group-III surface adatoms, the (111) A surface has three dangling bonds. The larger number of dangling bonds to group-III adatoms reduces the surface migration velocity of adatoms and increases the density of defects in the material.

The nucleation and 2D-dimensional island growth on the semiconductor surface are fundamental to the epitaxial growth. The growth mechanism for GaAs (100) surface has been extensively studied because it is the one most widely used for epitaxial growth [3.21~3.27]. By combining the first principle calculations and electron counting model [3.28], it is clear that (100)-oriented growth is maintained by the microscopic self-organizing process. The MBE-grown GaAs (100) surface generally contains either missing dimer rows or excess As ad-dimer. The well-known GaAs (100) surface exhibits the As-rich (2 x 4) structure during the MBE growth.

For the GaAs (111)A surface, it is experimentally known that fairly high As pressure is needed in order to obtain a good epitaxial layer [3.29]. The surface structure is much different from (100) ones. A reconstructed GaAs (111)A surface has a (2x2) structure. Analysis of low-energy electron-diffraction (LEED) measurement led to the proposal of a Ga-vacancy structure, in which one of the four Ga atoms in (2x2) surface unit cell is missing. For the case of (111)A-oriented growth, its mechanism is still not clear. Under the conventional growth conditions of the MBE method, the stable reconstructed surface is a Ga-vacancy surface [3.30~3.32].

Tanguchi et al [3.33] proposed a growth mechanism for GaAs (111)A surface, which is characterized by the formation of a stable $\{Ga_{v_{Ga}} - As_{trimer}\}$ micro-structure and coalescence of that structure, the subsequent Ga adatom adsorption and final growth island formation. On the GaAs (100) surface, the number of growth islands decreases monotonically as the

island size increases. However, on the GaAs (111)A surface the size distribution has a peak, indicating the existence of critical size for the growth island formation [3.34,3.35].

On a (100) surface, Ga and As adatoms basically adsorb at GaAs lattice sites. Thus every adsorption site could potentially become a starting site for epitaxial growth. This results in a large number of smaller growth islands. Once the growth islands are formed, the epitaxial growth is achieved by the incorporation of adatoms at the step edge of the island. For Ga and As adatoms to occupy lattice sites, it is necessary to form a stable $\{Ga_{V_{Ga}} - As_{trimer}\}$ on the (111)A surface. A subsequent coalescence of the structure is needed for epitaxial growth. This process suggests the existence of the critical size to achieve the growth. Consequently, it shows the smaller probability of growth island formation and results in a small number of large growth islands.

3.3 Sample growth

The GaAs/AlGaAs QWIP structure was grown on an undoped semi-insulating GaAs (111)A substrate by a solid source Riber MBE 32P system. As shown in Figure 3.3, the MQW structure consists of 30-period GaAs wells and AlGaAs barriers, sandwiched by GaAs top and bottom contact layers. For a comparison study, a GaAs (100) substrate was placed together with the (111)A substrate during the epitaxial growth. The arsenic was supplied in the form of As_4 from a valved cracker cell and its beam equivalent pressure was fixed at 1.0×10^{-5} Torr during the growth. The substrates were outgassed in a preparation chamber before the oxide desorption were performed by heating up the substrates to 590°C with As_4

flux irradiation in the growth chamber. Silicon was incorporated as p-type dopant in the (111)A oriented QWIP sample, and in order to maintain smooth morphology, the growth temperature was set at 650 °C and As-rich growth condition (As_4/III flux ratio of $\sim 23:1$) was used. The Si cell temperature was fixed at 1020 °C during the growth of the GaAs well and contact layers. A 100 nm-thick GaAs buffer layer was grown before the growth of the QWIP structure.

Figure 3.3 The schematic diagram of GaAs/AlGaAs QWIP structure.

3.4 Material characterization and analysis

X-ray Diffraction (XRD) characterization is measured in a Philips X’Pert Material Research Diffractometer after the growth. The diffraction rocking curves were fitted by a computer program based on dynamical diffraction theory of XRD. To assess the material quality of the QWIP structure, the photoluminescence (PL) were measured at a temperature of 5K. The electrochemistry capacitance-voltage profile was measured to determine the type and concentration of carriers in the GaAs cap layer.

3.4.1 XRD measurement

Nowadays conventional high resolution X-ray diffraction has been developed into a powerful tool for the nondestructive *ex-situ* investigation of epitaxial layers, heterostructures and superlattice systems [3.36]. The information 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. The measurement of the diffraction is in principle determined by Bragg's Law with the following formula:

$$2d_{hkl} \sin \theta_B = n\lambda \quad (3.1)$$

where d_{hkl} is the spacing of lattice planes with Miller indices (hkl) and θ_B is the corresponding Bragg angle. 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_B , the Bragg's Law condition is satisfied by different spacing d in different materials. Plotting the angular positions and intensities of the resultant diffracted peaks of radiation produces a pattern which is characteristic of the sample and called rocking curve.

The angular separation between the zero-order satellite peak and the Bragg peak of the substrate in X-ray rocking curve gives the average mismatch of the epilayers along the growth axis. The perpendicular lattice mismatch of epilayer structure, which gives fingerprint of the average strain present in the artificial structure, is obtained from the

angular separation $\Delta\theta_0$ between the $n=0$ order peak and the substrate peak in the X-ray rocking curve simply according to

$$\frac{\Delta a_{\perp}}{a} = -\Delta\theta_0 \coth \theta_B, \quad (3.2)$$

In artificial superlattice, X-ray diffraction patterns are dominated by the interference among the periodically repeated layer stack. Besides the Bragg peak of substrate, a series of so-called satellites are observed, which are a set of subsidiary maximum with the same angular spacing $\Delta\theta$. The period of superlattice L can be determined as follows [3.37]:

$$L = \frac{\lambda |\gamma_H|}{\Delta\theta_p \sin(2\theta_B)} \quad (3.3)$$

where $\gamma_H = \sin(\theta_B + \varphi)$ is the direction cosines of diffracted beams, θ_B is the Bragg angle of the substrate, φ is the angle between reflecting plane and the sample surface (for symmetric reflection, $\varphi = 0$), $\Delta\theta_p$ is the angular separation of adjacent satellite peaks of the SL.

For a perfect SL with homogeneous composition in individual layers and ideally abrupt interfaces, the number of satellites and their intensities are dominantly dependent on the difference in the lattice parameters and structure factors. A larger difference among the lattice parameters as well as the structure factors in individual layers results in a larger number of satellites and higher peak intensities. For a real SL, the number of satellites and their peak intensities are also strongly degraded by the imperfections of interfaces, the compositional inhomogeneity and the fluctuations from period to period.

In X-ray measurement, the rocking curve from a sample is numerically simulated using dynamical theory described by the Takagi-Taupin equations [3.38, 3.39]. This approach takes multiple scattering, reflection and absorption of x-rays into account and gives the correct reflectivity. For lattice-matched GaAs/AlGaAs multi-quantum well structure, the simulation is more accurate than strain-relaxed one owing to the complicated strain and relaxation mechanisms [3.40].

Figure 3.4 The typical schematic structure of Philips XRD system [3.39].

Our measurement is implemented with a Philips X'Pert Material Research Diffractometer (X'Pert MRD). The system is configured with a hybrid monochromator or a high-resolution monochromator. Data collector software is to conduct and plot measured XRD profiles in X'Pert MRD systems. Figure.3.4 displays the typical schematic structure of Philips XRD system [3.41]. Incident Beam Part consists of X-ray Tube and Incident Beam Optics. The X-ray tube emits a Cu $K\alpha_1$ radiation with wavelength $\lambda=1.54 \text{ \AA}$. The incident beam optics is composed of beam attenuator, monochromator and filters. Diffracted beam part consists of diffracted beam optics and detectors. The diffracted beam optics consists of Triple Axis Attachment for the reciprocal space mapping (RSM) or Rocking Curve Attachment for rocking curve measurements. X'Pert Epitaxy software provides functionality to analyze rocking curves, reciprocal space maps and wafer maps.

Figure 3.5 shows the measured (solid lines) and simulated (dashed lines) X-ray rocking curves of GaAs/AlGaAs QWIP structure grown on (111)A (sample A) and (100) (sample B) GaAs substrates. $\Delta\theta_0$ is the angular separation between the Bragg peak of the substrate θ_B and the first order satellite peak of epilayers in X-ray rocking curve. For QW layers grown on symmetry planes such as (100) and (111), the lattice of epilayer will be distorted with different lattice parameter along the growth axis. $\Delta\theta_0$ gives the feature of the average lattice mismatch of the QW epilayers to substrate along the growth axis. It exists unless the QW epilayer is perfectly lattice matched to the substrate. The average effective perpendicular strain present in the QW structure $(\varepsilon_{QW})_{\perp}$ can be obtained from the X-ray rocking curve according to $(\varepsilon_{QW})_{\perp} = \frac{(\varepsilon_B)_{\perp}B + (\varepsilon_W)_{\perp}W}{B + W} = -\Delta\theta_0 \coth \theta_B$, where $(\varepsilon_B)_{\perp}, (\varepsilon_W)_{\perp}$ are the individual particular strains of barrier and well epilayers along growth axis, respectively. B and W are the thickness of barrier and well layers in the QW structure, respectively. For the (100)-oriented sample B, the $\omega/2\theta$ scan around the 400 reflection were record. While for the (111)A-oriented samples, we used $\omega/2\theta$ around 333 reflection. The zero-order satellite peaks (S_0) are clearly seen on the lower-angle side of the substrate peak. A set of high-order satellite peaks are discernible on the X-ray rocking curves for both samples but with diminutive intensities which usually result from the small difference in lattice parameters between layers and the small thickness of GaAs wells compared with the AlGaAs barriers for lattice-matched GaAs/AlGaAs QWIP structure. The average MQW period thickness is derived from the angular spacing of the satellite peaks which are about 601 Å and 377 Å, separately according to Eq. 3.3. Table 3.1 shows the structural parameters for (111)- (sample A) and (100)-oriented (sample B) GaAs/AlGaAs MQW structure extracted by XRD

measurement. The difference of period thicknesses results from the MBE growth dependence on substrate orientation. Under the same growth conditions, the average growth rates of AlGaAs and GaAs were calibrated to be about 1.18 $\mu\text{m/h}$ and 0.88 $\mu\text{m/h}$ on (111)A substrate and 0.78 $\mu\text{m/h}$ and 0.66 $\mu\text{m/h}$ on (100) substrate, respectively. Inherently, the epitaxial growth on (111)A surface has higher rate because there are three dangling bonds for each group III adatom on (111)A surface and only two on (100) surface. Different from the growth rate on (100) surface which is simply determined by Ga flux, the growth rate on (111)A surface is associated with both the As_4/Ga flux ratio and the substrate temperature in a complex relation above 550 $^\circ\text{C}$ due to the limited dissociative chemisorption of As_4 [3.42].

Figure 3.5 Experimental X-ray rocking curves and simulated results for a 30-period GaAs/AlGaAs QWIP structure grown on (111)A (sample A) and (100) (sample B) substrates.

Table 3.1 The structural parameters for (111)- (sample A) and (100)-oriented (sample B) GaAs/AlGaAs MQW structure extracted by XRD measurement.

Samples	Period (Å)	Angular spacing of satellite peak s(°)	Bragg diffraction angle (°)		FWMH (arc second)	
			AlGaAs (0 th -order satellite peak)	GaAs substrate	AlGaAs (0 th order-satellite peak)	GaAs substrate
Sample A	601	0.021°	45.18	45.21	61.2	50.4
Sample B	377	0.019°	33.17	33.19	36.0	32.4

3.4.2 PL analysis

The PL measurement data are incorporated to determine the well thickness and the Al fraction of AlGaAs barriers. As shown in Figure 3.6, the PL spectra measured at 5 K for sample A and B have linewidths of 12.6 meV and 6.1 meV, respectively. The transition between the ground states of electron and heavy hole, i.e. E1-HH1 transition, in (111)-oriented QWs is enhanced due to the larger heavy-hole mass in (111) orientation [3.43] and therefore sample A has much higher PL intensity than sample B. The E1-HH1 transition energy as a function of the barrier height and the well width is obtained by calculating the electron states which in turn are calculated using the transfer matrix method under the effective mass approximation except HH states for (111)A QW using 4×4 effective mass Hamiltonian model [3.44]. The parameters of bandgap, effective mass and band offset for (111)A and (100)-oriented AlGaAs and GaAs epilayers were adopted from references [3.45~3.47].

Figure 3.6 The PL spectra for sample A and sample B measured at temperature of 5K.

The well thickness and the barrier composition of QW were determined from the PL peak energy and the X-ray rocking curving simulation. The structural parameters are listed in Table 3.2. Moreover, it is observed that the Al compositions in AlGaAs epitaxial layers on (111)A and (100) surfaces are different under the same growth conditions. For example, the Al composition on (111)A epilayer is 0.18 while that on (100) surface is 0.22. It confirms the reduction of Al fraction in AlGaAs epitaxial layer on (111)A surface. The detail mechanism is still not very clear and similar phenomenon has been reported by A. Sanz-Hervás et al [3.48] and Toshilhide Watanabe et al [3.49]. This may result from the poorer efficiency of Al atom adsorption to Ga atom site under Ga-predominant (111)A surface.

Table 3.2 The structural and optical values obtained by XRD measurement and PL spectra for GaAs/AlGaAs QWIP structures on (111)A and (100) substrates. L_w and L_b are the well and barrier width, respectively. x is the aluminium fraction in the barrier. E_p is the PL emission energy.

Samples	A: (111)A MQW	B: (100) MQW
x (%)	18	22
L_b (Å)	563	346
L_w (Å)	38	31
PL FWHM (meV)	13	6
E_p (eV)	1.64	1.66

3.4.3 Si doping behavior in GaAs (111)A layer

The Si doping concentrations and the conduction types on GaAs (111)A surface were examined from the electrochemical capacitance-voltage(C-V) profiles. The Electrochemical C-V Profiler employs electrochemical etching to determine the electrical carrier concentration as a function of depth in compound semiconductors. By making use of a well-defined electrochemical dissolution reaction, the semiconductor can be profiled to any depth at a controlled rate. The semiconductor/electrolyte interface behaves as a Schottky diode across which C-V measurements are performed. By using the electrolyte to both etch and form a Schottky contact with the semiconductor, one can obtain the depth profile of the carrier concentration in the semiconductor. The advantage of such a contact is that one can make measurements with negligible bias, etch the material a tiny amount and continue to repeat the measurement cycle to unlimited depth. This is important for III-V epi-structures, which can have very complex layers of various epi-films. Taken together, this stack can measure up to several microns in thickness.

Figure 3.7 shows electrochemical C-V profiles of the Si-doped GaAs top contact layers of the two samples. A carrier concentration of about $1.4 \times 10^{18} \text{ cm}^{-3}$ is reached in both samples but the dopants are p-type for sample A and n type for sample B.

Figure 3.7 The electrochemical C-V profiles of the Si-doped GaAs cap layer in sample A and sample B.

Earlier work [3.50] has shown that Si acts as an acceptor in GaAs grown on (11n)A substrates during MBE when $n \sim 3$, but behaves as a donor on (n11)A for $n \geq 5$ and (11n)B for all values of n . The conduction type of incorporated Si atoms on (111)A surface can be controlled by the growth conditions, such as the substrate temperature and V/III flux ratio [3.51].

Employing Riber 32P MBE, we verified the n-type Si-doping behavior under low temperature ($\sim 480^\circ\text{C}$) and higher V/III ratio (~ 35) with the electron carrier concentration range of $1 \sim 5 \times 10^{18} \text{ cm}^{-3}$.

Si atoms preferentially occupy Ga sites on GaAs (100) surface that is terminated with double dangling bonds of both As and Ga atoms, and thus behave as donors under the arrival of excess As atoms. On GaAs (111)A surface, each Ga atom has three bonds appending the surface while each As atom has only one. Therefore, Si atoms replace more easily the weakly bonded As atoms and behaves as acceptors. However, the incorporation behavior of Si in the (111)A samples was found to be strongly dependent on the growth conditions. The layers are uncompensated p-type when grown at high substrate temperatures and low As_4/Ga flux ratio, and become increasingly compensated as the growth temperature is further decreased and the As_4/Ga flux ratio is further increased. Once the temperature becomes lower, and As_4/Ga flux ratio become higher, the layers eventually become uncompensated n-type. It has been speculated that this changing carrier behavior occurs as the preferential location for the Si atoms switches from As lattice sites (Si_{As}) to Ga lattice sites (Si_{Ga}). If Si incorporation is closely related to the incorporation of arsenic, the carrier concentration in Si doped GaAs layers should be a function of the critical flux ratio. Figure 3.8 shows a summary of the Si incorporation behavior in relation to the growth temperature and the As_4/Ga flux ratio with the critical flux ratio marked. Growth at less than the critical flux ratio always produces uncompensated p-type layers, which suggests that excess Ga atoms existing on the surface of the layer during growth under these conditions play an important role in determining whether a Si atom occupies an As site. As the As_4/Ga flux ratio is increased above the critical flux ratio the layers become more compensated and finally n-type. For growth with an $\text{As}_4:\text{Ga}$ flux ratios of more than 5 times of critical flux ratio, the layers are uncompensated n-type.

Figure 3.8 A summary of the Si incorporation behavior and the surface morphology of GaAs layers grown on GaAs (111)A. The solid line shows the critical flux ratio at each growth temperature. Growth below the critical flux ratio gives p-type layers with poor surface morphology. Above the critical flux ratio the morphology becomes good and the films initially become more compensated and then progressively more n-type [3.51].

3.5 Characterization of (111)A GaAs epilayer by MOVPE

As the complement to (111)A-oriented GaAs epilayer grown by MBE technique, metalorganic vapor phase epitaxy (MOVPE) growth process of GaAs epitaxial layer on both (111)A and (100) GaAs substrates using horizontal AIX 200 MOVPE in N_2 ambient with tertiarybutylarsine (TBA) as the group V source were also investigated and the work are briefly described [3.52]. The growth of GaAs epitaxial layers on (111)A and (100) oriented GaAs substrate have been investigated for various growth conditions. The growth temperature was varied from 530 to 750 °C, while the V/III ratio was varied from 4.8 to 64

optimize the growth conditions for receiving the best epitaxial layers on (111)A GaAs substrate.

Figure 3.9 The surface morphologies of GaAs epilayers on (111)A GaAs substrates. (a) Triangle pyramid defects on samples grown at 680°C and $V/III=40$. (b) Hexagonal pyramids on samples grown at 620°C and $V/III=40$ [3.52].

In contrast to highly smooth growth on the (100) GaAs substrate, the GaAs surface morphology on (111)A-oriented GaAs substrates showed a strong dependence on the combination of V/III ratio and growth temperature. Surface defects with different shapes were observed on the GaAs epitaxial layers' surfaces for different growth temperatures as shown in Figure 3.9. For growth at higher temperatures, a higher V/III ratio is required to produce a smooth surface. At lower growth temperatures, a mirror-like shine surface of the (111)A GaAs samples can be obtained with a lower V/III ratio.

Figure 3.10 The summary of (111)A-oriented GaAs epilayer surface morphology related to the growth conditions by a solid source MBE machine [3.53].

For growth on (111)A surface, it is notable that the surface morphologies of epilayers are also strongly growth-condition-dependent using MBE technique. Kenji Sato et al [3.53] investigated the growth dependence of the surface morphology of GaAs epilayer on GaAs (111)A substrate by MBE. Figure 3.10 shows their summary of (111)A-oriented GaAs epilayer surface morphology related to the growth conditions. Over a wide range of growth temperature and As_4/Ga flux ratios, pyramid defects are observed and their origin has been attributed to the presence of excess Ga atoms on the surface. Smooth layers can be obtained once growth condition above the critical region. It demonstrates that both MBE and

MOVPE techniques show the similar characteristic for epitaxial growth of (111)A GaAs layer in which the good quality of GaAs (111) epilayer is strongly condition-dependent.

Figure 3.11 PL spectra for (111)A GaAs epilayer grown at 650°C and V/III ratio of 48. The intensity of the RT PL spectrum of (100) GaAs layer is multiplied by 67 [3.52].

PL results show that under optimum growth conditions for GaAs layers on (111)A GaAs substrates, the PL emission of GaAs layers on (111)A GaAs is much stronger than that grown on (100) GaAs, especially at room temperature as shown in Figure 3.11. This result corresponds to that of MBE growth as shown in Figure 3.6. The optimal growth conditions for the (111)A GaAs epilayers are a growth temperature of 650°C for a V/III ratio of 48. It is likely that the optimized growth conditions for (111)A GaAs epilayers are not well suited for (100) GaAs epilayers. From the mirror-like surface and good optical quality of GaAs (111)A epilayer, MOVPE technique is proved to be also a good candidate to develop the

(111)-oriented material and structure since it performs the comparable characteristics as MBE does.

3.6 Summary

The crystal quality, doping and optical properties of Si-doped GaAs/AlGaAs QWIP structure grown on GaAs (111)A substrate by MBE is investigated. The epitaxial growth rates of GaAs and AlGaAs were enhanced and the Al incorporation was reduced in (111)A orientation. The positive conduction type was achieved using Si-doping in (111)A-oriented GaAs layer with comparable doping level to n-type Si doping in (100)-oriented GaAs layer. The smooth surface morphology and enhanced PL intensity of GaAs (111)A layer by MOVPE was obtained.

Chapter 4 Fabrication and Characterization of QWIP device

In this chapter, the photocurrent measurement system is introduced first and the discussion is made on the fabrication and characterization of (111)A-oriented GaAs/AlGaAs QWIP device. Wet etching of (111)A substrate using H_3PO_4 -based solution as an important device processing step is also investigated. The infrared absorption of (111)A QWIP device is characterized using Fourier Transform Infrared Spectrometer. The temperature-dependent current-voltage characteristics and spectral photocurrent response of the QWIP device are investigated using the photocurrent measurement system.

4.1 Photocurrent spectrum measurement system

The photocurrent measurement system is the most important setup to characterize the QWIP detector. The spectrum response, responsivity, and the peak detection wavelength can be conveniently measured by such a system. The photocurrent measurement system used in our work consists of an infrared source, a monochromator, a lock-in amplifier, a cryostat and temperature controller, and a series of optical components such as lens, chopper, mirror, etc. Figure 4.1 shows the schematic diagram of the photocurrent measurement system.

In order to achieve the maximum output of the photocurrent measurement system from IR source, the light coupling should be optimized. The basic design rules demand all the optical number ($f/\#$) of relevant component to be matched. The filament of the infrared lamp should be conjugated to the position of the entrance slit and its image must cover the input slit. A Jobin Yvon Triax 320 monochromator offers wavelength scanning in our system. The

input and output optical numbers of the monochromator are 4.1. We use a lens KRS-5 lens to focus the light from the radiation source on the input slit of the monochromator. The off-axis parabolic mirror pair is used to collect the output light from the exit slit of the monochromator and focus the light normally on the 45° facet of the QWIP sample fixed on a copper holder inside the cryostat.

Figure 4.1 The schematic diagram of the photocurrent measurement system.

The IR source used in our system is an Oriel 6575 ceramic element mounted in a lamp house. The element has a cylindrical ceramic core with a platinum resistance wire wound around it. The IR source has high output within the $1\sim 5\ \mu\text{m}$ range. The irradiation is similar to that of the blackbody at the same temperature of 1450K.

To calibrate the spectral nonuniformity of the system and the power of the IR source, an Oriel pyroelectric detector (Model 70124) is employed as the reference detector.

A ZnSe wire-grid polarizer is placed in the infrared beam path, allowing us to separate the contributions of the 90° -polarized light (equivalent to normal-incident radiation) or TE mode and 0° -polarized light (TE and TM polarization modes in equal shares) to the photocurrent spectra.

When monochromatic light comes out from the monochromator and is focused to the sample's surface or the pyroelectric detector, the photocurrent signal of the device are pre-amplified by the current pre-amplifier and then fed into the lock-in amplifier. A computer is employed to control the monochromator and collect data. The photocurrent responsivity for QWIP sample is calibrated by

$$R = \frac{I_{QWIP}}{P_{QWIP}} = \frac{V_{QWIP} \cdot K_{amplifier}}{\frac{V_{ref}}{R_{ref}} \cdot \frac{S_{mesa}}{S_{ref}} \cdot T_{ZnSe}} = \frac{R_{ref} \cdot K_{amplifier}}{T_{ZnSe}} \cdot \frac{S_{ref}}{S_{mesa}} \cdot \frac{V_{QWIP}}{V_{ref}}, \quad (4.1)$$

where

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

$K_{amplifier}$ (μ A/V) is the sensitivity of current amplifier for QWIP photocurrent;

R_{ref} is the responsivity of the pyroelectric detector (=2000 V/W);

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

S_{ref} is the area of slit image on the pyroelectric detector, equal to $5 \times 2 \text{mm}^2$;

V_{QWIP} is the photovoltage signal for QWIP sample;

V_{ref} is the photovoltage signal for pyrodetector.

4.2 Characterization of wet etching of GaAs (111)A substrate

In processing some III-V semiconductor electronic and optoelectronic devices, some part of semiconductor sample or layer often has to be etched away from the wafer surface according to pre-defined patterns. As a common approach, the selective removal is mostly performed by opening windows on a masking layer to allow chemical reaction with wet etchants. Up to date, most studies of wet etching on III-V semiconductor, typically GaAs have concentrated on the conventional (100) oriented substrates because of the wide range of epitaxial growth conditions, well-developed processing technology for (100) wafer, and the natural cleavage planes normal to each other. So far a lot of chemical solutions have been reported as the selective etching systems for GaAs(100) substrate, which include $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2\text{-H}_2\text{O}$ [4.1~4.3], $\text{NH}_4\text{OH- H}_2\text{O}_2\text{- H}_2\text{O}$ [4.1, 4.4, 4.5], $\text{H}_3\text{PO}_4\text{-H}_2\text{O}_2\text{-H}_2\text{O}$ [4.1, 4.6], $\text{HF-HNO}_3\text{-H}_2\text{O}$ [4.1, 4.7], $\text{Br}_2\text{-CH}_3\text{OH}$ [4.1, 4.8] and so on. However, the possibility of changing and improving the fundamental material properties, growth mechanisms, surface kinetics and impurity incorporation by growing on non-(100) plane substrate has motivated strong effort to study these aspects [4.9~4.11]. Among these works, there is few report on the wet etching of non-GaAs (100) orientation for potential application in novel electric and optoelectronic device [4.12~4.14]. Although *T. Takebe et al* [4.15] has studied the properties of wet etching of GaAs (111)A by $\text{HF-H}_2\text{O}_2\text{-H}_2\text{O}$ solution, there are still no adequate information on the basic etching characteristics for $\text{H}_3\text{PO}_4\text{-H}_2\text{O}_2\text{-H}_2\text{O}$ solution. In this section, wet etching GaAs (111)A substrate based on $\text{H}_3\text{PO}_4\text{-H}_2\text{O}_2\text{-H}_2\text{O}$ solution is investigated. H_3PO_4 -based solution has good properties for reproducible and controllable

etching process. *Yoshifumi Mori et al* [4.16] has made a fundamental study on the $\text{H}_3\text{PO}_4\text{-H}_2\text{O}_2\text{-H}_2\text{O}$ system for selective etching of GaAs (100) wafer. As referred to Figure 4.2, they found that the solution rate in region A can be accurately and reproducibly controlled.

Figure 4.2 The ternary diagram of the etching rate on GaAs (100) surface as a function of the composition of H_3PO_4 - H_2O_2 - H_2O solution. The solid lines divide the diagram into four regions: A, B, C, D [4.16].

The GaAs single crystal employed in our experiments are undoped semi-insulating (111)A and referred (100) substrates. After being degreased in organic solution, rinsed in DI water, and dried by N₂ gas, the GaAs wafers were coated by selective etching pattern through photolithography process using photoresist as the masking layer. The selective etching experiments are performed at room temperature. After substrate etching in H₃PO₄-H₂O₂-H₂O etchant and photoresist removed by acetone, the etched samples were cleaved with a razor blade along their natural cleavages. For zinc-blende substrates, the natural {111} cleavage planes are the very convenient reference to define the etching profiles. Figure 4.3

shows the top view for (100) and (111)A substrate orientations, indicating the directions of {n11} cleavage planes. The natural cleavages of GaAs (111)A wafer form a 60°-slop-angle diamond, in contrast to orthogonal direction for that of GaAs (100).

Table 4.1 The wet etching profiles for GaAs (100) and GaAs (111)A by H_3PO_4 - H_2O_2 - H_2O solution.

Composition ratios k (H_3PO_4 - H_2O_2 - H_2O) (region A)	GaAs (001) substrate (cross-sectional view)		GaAs (111)A substrate (cross-sectional view)	
	$[\bar{1}10]$	$[110]$	$[\bar{1}10]$	$[0\bar{1}1]$
k=3:4:13 Etching Rate =1.9 $\mu\text{m}/\text{min}(20^\circ\text{C})$

Figure 4.3 The stereographic projection for (100) and (111)A substrate orientations, the dash lines are the direction of {n11} cleavage planes.

Several typical points locating in region A were selected for the experimental conditions. The etching profiles for both GaAs (111)A and GaAs (100) wafer inspected by optical microscopy are shown in Table 4.1. Comparable etching rates of two (100) and (111)A

substrates are always observed under the same composition ratio indicated by a surface profiler.

For GaAs (100) substrate, it demonstrates the reverse-mesa and ordinary mesa shaped structures from the view of the (011) cleavage planes. The planes of the reverse-mesa and the ordinary-mesa plane form angles of about 115° and 55° respectively with respect to the (001) surface. On the other hand, the etch-profile from the view of the $(\bar{1}10)$ cleavage planes shows only outward sidewall. The etch-revealed planes form an angle of 55° with respect to (100) surface plane. This characteristic of profile is summarized in Figure 4.4 (A). As the experimental results demonstrate, in contrast to the GaAs (100) substrate, y-axis symmetric well-defined profiles for GaAs (111)A are displayed with good uniformity and reproducibility. From the view of two $(1\bar{1}0)$ and $(2\bar{1}\bar{1})$ cleavage planes, the profiles are just

Figure 4.4 The schematic presentation of profiles with defined θ and major low-index surfaces appearing as possible sidewalls for GaAs (001) substrate (A) and (111)A substrate (B)

180° - reverse symmetric. As the photos in table 4.1 show, one side of the profile is similar to that of the (01 $\bar{1}$) cleavage plane for GaAs (100) substrate with ordinary sidewalls except the greater slope angle and the other side is similar to that of the (011) cleavage plane for GaAs (100) substrate except its much smaller reverse sidewall and larger ordinary sidewall. Figure 4.4 (B) shows the typical etching profiles for (111) A substrates obtained in our experiments.

The zincblende crystalline nature of GaAs lattice leads to the anisotropic etching property in almost all cases in which mask material is used to pattern the wafer. The anisotropic etching behavior derives from the lack of symmetry in the GaAs lattice and dependence of etching rate on orientation. The shape of the edge profile produced by wet etching can be understood on the different etch rate of specific crystalline planes. If the relative etch rate of these planes can be determined, the edge profile can be predicated. The orientation of a sidewall is determined dominantly by the plane of the lowest etching rate R.

4.3 Device fabrication processing flow

The fabrication of QWIP devices utilizes standard compound semiconductor process technology. Photodiode devices are prepared for the dark and photocurrent measurements. A two-photomask process is employed. Firstly, the device mesa is fabricated using photolithography with photomask I and wet etching process. After the photoresist pattern for lift-off is transferred with photomask II, the metal deposition is done using E-beam evaporation on the diode surface.

Figure 4.5 The fundamental fabrication process flow for QWIP device. Photolithography I is used to define the mesa area of device. Photolithography II is used to define the metal deposition area for electrode contact.

After that, the bottom and top electrodes are formed using lift-off process and metal alloying is done in rapid temperature processor. Finally, a 45° facet is polished at the edge of the substrate. The substrate is fixed to the chip carrier and the photodiodes are wire-bonded to the leads. Figure 4.5 show the fundamental fabrication process flow for QWIP device.

4.4 Infrared absorption measurement

Infrared absorption is one of the most important characteristics of QWIP structure. Fourier Transform Infrared Spectrometer (FTIR) is widely used as a means to investigate the intersubband absorption in quantum well structures. The enhanced sensitivity in FTIR spectroscopic techniques allows weak signals to be measured with high precision. However, in the standard transmission geometry, the light is incident perpendicularly to the sample surface, and the electric field has components only in the QW plane, whereas we know that intersubband transitions in QWs is polarization-dependent. Furthermore, the absorption is

very small due to the small thickness of QW layers. Thus the waveguide geometry has to be used so that the incident light can pass QW layers several times and the polarization can be controlled using a polarizer.

Infrared absorption measurements were done using Perkin Elmer Spectrum 2000 Fourier transform infrared spectrometer (FTIR) at room temperature with a 45° polished multipass wave-guide geometry as shown in Figure 4.6. A ZnSe wire grid polarizer was used to define the polarization of infrared radiation.

Figure 4.6 The 45° polished multipass waveguide geometry applied to measure intersubband absorption of MQWs.

The normalized infrared absorption spectra of GaAs/AlGaAs QWIP versus the polarization angle were measured at room temperature in Figure 4.7. The peak absorptions of QW are closely related to the polarization of infrared radiation. The n-type (100) QWIP under 0° -polarization case has maximum absorption as shown in Figure 4.7 (a). For 0° -polarization, i.e. a mixture of TE and TM polarization, it contains a component of photon electrical field along the growth direction which maximizes the peak absorption of n-type QWIP. The result agrees to the quantum mechanical selection rule of intersubband transition in the Γ -symmetry conduction band. The peak absorption is close to $11.2\mu\text{m}$ with absorption with a linewidth ($\Delta\lambda/\lambda_p$) of 24.3% denoting typical bound-to-continuum QWIPs. As indicated in Figure 4.7 (b), for the p-type (111)A QWIP under 90° angle polarization (i.e. TE mode only),

which is equivalent to the normal incidence, the sample displays the strongest absorption.

The peak absorption wavelength is around $7\mu\text{m}$. The broadened spectra with absorption

Figure.4.7 Measured absorption spectrum at 300 K as a function of wavelength with baseline Correction(refer to the inserted figures) using a waveguide structure for (a) the p-type (111)A and (b) the n-type (100) GaAs/AlGaAs QWIPs.

linewidth(40.6%) of the p-type (111)A QWIP under 90°-polarization (TE mode only), implies the final excited state in the continuum subband further above the barrier top.

4.5 Dark current characteristics

A good understanding of the electron transport in the dark is crucial for the QWIP design and optimization, because it contributes to the detector noise and determines the operating temperature. The dark current in the typical QWIP device is controlled by the flow of electrons above the barriers, by the emission and capture of electron in the wells. There are mainly three physical mechanisms that contribute to the dark current, and these are described in Figure.4.8. The ground state sequential tunneling component involves electrons scattering from the localized state in one quantum well into the next. This current is only weakly temperature dependent, and it is observed at temperature low enough to suppress thermionic emission. The second component is called field induced emission or thermally assisted tunneling, in which the thermalized carriers in the higher momentum states of the quantum well tunnel through the top (triangular) part of the barriers and into the continuum. The third component, thermionic emission refers to the excitation of carriers from the well and into the continuum. These processes occur under the influence of an applied field.

Extensive amounts of experimental and theoretical efforts have covered the carrier transport mechanism. A 3D carrier drift model which only considers the drift contribution of carriers on top of the barriers and fits the experiments quite well under a low applied electric field was first presented by Kane [4.17]. Liu et al [4.18] published the widely used emission-capture model. The model quantitatively considers contributions of various scattering

Figure 4.8 The dark current mechanisms in a QW under applied electric field. The direct sequential tunneling component (a), the thermally assisted tunneling component (b) and the thermionic emission component (c) are demonstrated, respectively.

mechanisms and trapping and gives an adequate result for a large range of applied field. For more sophisticated study, a lot of numerical models have been investigated. Self-consistent emission-capture model has been developed by Thibaudau et al [4.19]. The main feature emerging from the model is the redistribution of the electric field along the structure in order to maintain current conservation. The calculated dark current, electrical noise, responsivity, and detectivity of different QWIP structures are compared with experimental measurements and the agreement is found to be fairly good. This model may be considered as a step toward more powerful simulation tools for QWIPs.

Ryzhii [4.20] constructed an analytical model by solving Poisson equation and an equation governing the electron balance in the quantum well. Interesting functional dependence of responsivity on the number of wells and the photon excitation power were found. A self-

consistent ensemble Monte Carlo model [4.21] is used to study the ultra fast electron transport in QWIPs.

Although several models have been established with varying degree of complexity and good agreement between models and experiments, the formulation of a true first-principle QWIP model is a very tough task. The situation becomes even more complicated for *p*-type QW structure because of the mixing of heavy hole and light hole subbands in the valence band. A hot-carrier-temperature model was proposed by P. Man et al [4.22] to calculate the dark current of a *p*-type GaAs/GaAlAs QWIP. Hot-carrier effects are incorporated inside both the mobile-carrier concentration and the drift velocity. Results of their calculations are in good agreement with experimental data at four different lattice temperatures and for the entire measured range of applied electric field. The increase of mobile-carrier concentration at a hot-carrier temperature is found to be the prevalent cause of the rise in dark current at higher applied electric fields. After that, the current from a *p*-type quantum well caused by the hole tunneling in applied electric field, is calculated by Petrov et al [4.23] for semiconductors with the valence band described by the Luttinger's Hamiltonian, where the heavy hole based bound state contains the admixture of heavy hole and light hole states with a low effective mass and high probability of tunneling through the barrier. They found this fact increased the dark current by several orders of magnitude, as compared with a primitive theory assuming light and heavy holes as independent particles. The current-voltage characteristic was calculated and its dependences on quantum well parameters and doping level were discussed.

In this section, the dark current characteristic of (111)A-oriented GaAs/AlGaAs QWIP are demonstrated. Current–voltage (I–V) characteristic measurements were carried out using a Keithley 320 programmable current-voltage measurement unit. When measuring the dark current characteristics, the sample is fixed onto the cold finger of a cryostat, which provides cooling sample down to 17K. A close loop cycling helium gas is compressed and expanded based on the Gifford-McMahon thermodynamic cycle. A heater and a thermometer are installed on the cold finger and are employed to precisely control the sample temperature. The cryostat system can perform a wide range of temperature environment from 17K to 300K.

The dark current as a function of applied bias voltage at different temperatures is given in Figure 4.9 for (111)A-based and (100) GaAs/AlGaAs QWIP diodes, respectively. The symmetrical I-V characteristics are due to the symmetry between the growth of GaAs on AlGaAs and the growth in reverse sequence, as well as negligible Si dopant migration in the growth direction, whereas Be doping always encounters fast outdiffusion issue [4.24]. Figure 4.9(b), its I-V characteristic always shows a temperature-dependent property within the measured temperature range and saturate at very high temperature. Although dark currents are relatively insensitive to the temperature, they depend much on bias voltage once they are under the temperature below 60K. However, the external field has more impact on the dark current increase for the sample at low temperature than high temperature. Under the dark condition, the thermionic emission due to carrier emission out of doped QW is dominant at low bias and higher temperature. The reduction of the dark current at low temperature is mainly due to the decrease of thermionic emission from the doped quantum

wells to the continuum states above the barrier. While at low temperature, tunneling-assisted current mainly controls the transfer process in quantum well region and leak currents increase accordingly once the bias voltages increase.

Since the dark current at low bias under high temperature conditions is dominated by thermionic emission[4.25], which follows $I(T)/T \propto \exp(-E_{ac}/k_B T)$, the activation energy E_{ac} can be extracted from the slope of the plot of the normalized dark current (I_d/T) versus the normalized inverse temperature $1000/T$ in semi-log scale and is given as a function of bias in Figure 4.10. The activation energies for both (111)A and (100) QWIPs and the bias voltage can be fitted quite well with the relation $E_{ac} = E_{ac0} \exp(-V/C)$ that is related to the energy bending due to the increased bias [4.26], where V is the bias voltage and C is a constant. As the bias increases, the energy bands are not symmetric any more and start to bend gradually. Thus the barrier height over which the holes are excited for conduction also become lower. Accordingly the activation energy due to biased field could drop. The extrapolated zero-bias activation energies E_{ac0} for thermal equilibrium and flat band condition are 58 meV and 74 meV for (111)A and (100) QWIP diodes, respectively.

Figure 4.9 The I-V characteristics of (a) the p-type (111)A and (b) the n-type (100) GaAs/AlGaAs QWIPs versus bias voltage under a series of temperatures.

Figure 4.11 show the energy subbands in (111)A and (100) QW structure. The energy levels of heavy hole states (HH) and light hole states (LH) in (111)A-oriented GaAs/AlGaAs QWs are determined as $HH1 = 36$ meV, $HH2 = 81$ meV, $LH1 = 57$ meV and higher levels like $LH2$ and $HH3$ are continuum states using a 4×4 effective mass Hamiltonian model for SL grown on (111) substrate [4.27], whereas the barrier height in the valence is around 82 meV. The energy levels of electron states in (100) GaAs/AlGaAs QWs are determined as $E_1 = 110$ meV and $E_2 = 222$ meV using the transfer matrix method under the effective mass approximation [4.28], whereas the barrier height in the conduction band is about 203 meV.

Figure 4.10 Measured activation energies of QWIP versus bias voltage. The y-axis is in log scale.

These experimental results of activation energies are in agreement with the calculated values 61 meV and 81 meV using $E_{ac} = V_b + E_{ex} - HH1 - E_F$ for p-type QWs and $E_{ac} = V_b - E_1 - E_F$ for n-type QWs, where V_b is the barrier energy height, E_F is the Fermi energy of 2D carrier gas referenced to the ground state, the exchange energy E_{ex} ($= 17\text{eV}$) due to the exchange effect in quantum well [4.29]. The heavy hole ground state $HH1$ in p-type QWs and the ground state electron energy E_1 in n-type QWs are derived using the QW structural parameters in Figure 4.11.

Figure 4.11 The schematic diagram of energy band of (111)A QW (sample A) and (100) QW (sample B).

Dissimilar to that in the n-type (100) QWIP, the low temperature dark current in (111)A QWIP has no abrupt increase under high bias. Such a difference may be caused by different tunneling behaviors due to the difference in the masses of electron and hole.

4.6 Photocurrent spectral response measurement

The spectral response of photocurrent is the key characterization of the QWIP device. The spectral dependence of the photoresponse was measured at low temperature using an Oriel 6575 infrared source coupled by an infrared lens to a Jobin Yvon Triax 320 monochromator as shown in Figure 4.1. Figure 4.12 shows the configuration of QWIP device for photocurrent measurement.

Figure 4.12 Schematic diagrams for the photocurrent measurement of QWIP.

The photoresponse spectra measured at 25K under several bias voltages are shown in Figure 4.13. The n-type (100) QWIP has an average spectral linewidth ($\Delta\lambda/\lambda_p$) of 24 % with a detection wavelength of near 11 μm , which is a typical linewidth value of bound-to-continuum QWIPs, while the broadened spectra with average spectral linewidth (49 %) of the p-type (111)A QWIP implies the final excited state in the continuum subband further above the barrier top as shown in Figure 4.11. In our experiment, the photocurrent spectrum exhibits peak responsivity of about 1 mA/W, which is relatively low compared with typical p-type QWIPs. The low peak responsivity is mainly due to the low doping concentration (equivalent 2D density, $N_D = 5.7 \times 10^{11} \text{ cm}^{-2}$) and the large spectrum width $\Delta\lambda/\lambda_p$. Regardless of its broader photoresponse spectrum, this (111)A p-QWIP has comparable peak responsivity to that of a low doping sample (sample A, $N_D = 1 \times 10^{12} \text{ cm}^{-2}$) under the same bias in a study of doping density effects for (100) GaAs/AlGaAs p-QWIPs [4.30].

Figure 4.13 The measured photocurrent spectra at 25 K for different bias voltages for (a) the p-type (111)A and (b) the n-type (100) GaAs/AlGaAs QWIPs.

Figure 4.14 The measured photocurrent spectra at 25 K for different polarization angles for (a) the p-type (111)A and (b) the n-type (100) GaAs/AlGaAs QWIPs. Infrared light is incident from a 45° facet polished on the substrate. 0° polarization refers to p-polarization (TE + TM) and 90° polarization refers to s-polarization (TE mode). The non-polarized spectra are also presented.

Figure 4.14 shows the photocurrent spectra of (111)A and (100) QWIP for different polarization angles. The photoresponse spectra of both QWIPs show very strong polarization dependence. In opposite to the polarization dependence in n-type QWIP that follows the intersubband transition selection rule [4.31,4.32], as seen in Figure 4.7(b) and Figure 4.14(b), the transition in p-type (111)A QWIP is the strongest in response to in-plane (x-y) polarized light. The peak responsivity is 1.3 mA/W for 90°-polarization (s-polarization), while it is only 0.44 mA/W for 0°-polarization (p-polarization).

Figure 4.15 The responsivity and peak absorbance normalized to their s-polarized counterparts versus the polarization angle for the p-type (111)A and the n-type (100) GaAs/AlGaAs QWIPs.

Normal incident response is usually expected in p-QWIPs due to the interactions between components of s-symmetry states in the LH(SO) subbands and p-symmetry states in the HH subbands [4.33] while in the present (111)A QWIP, we have observed the strongest response at normal incidence. Figure 4.15 shows that absorption and the photocurrent

spectra of the p-type (111)A QWIP exhibit polarization dependence opposite to that in n-type QWIPs which follow the intersubband transition selection rule [4.34,4.35]. The peak responsivity is 1.3 mA/W for 90° polarization (s-polarization, TE mode only), but only 0.4 mA/W for 0° polarization (p-polarization, TE+TM modes). Therefore, the transition of in-plane (x-y) polarization is stronger than that of z polarization. In a p-type quantum well, transitions between heavy hole states should be mainly sensitive to light polarized in z direction, similar to the case of an n-type quantum well [4.36]. Transitions of in-plane (x-y) polarization are expected to be strong between different hole bands (i.e., HH to LH) [4.33, 4.37]. For example, Szmulowicz et al.[4.37,4.38], Liu et al.[4.39,4.40] and Shen et al.[4.30] investigated a series of p-type GaAs/AlGaAs QWIPs and found the optimized p-type GaAs/AlGaAs QWIP for the strongest normal incident absorption has the final state for transition in resonance with the top of the barrier. By aligning LH₂ in resonance with the top of the barrier in the (100) p-QWIPs, Liu et al. obtained higher photoresponse of s-polarization than p-polarization [4.39]. However, in the (111)A QWIP the peak normal incident response occurs when the final states are about 95 meV above the top of the barrier. This indicates the highly mixed nature of the excited states far above the valence barrier and the interband processes that are allowed between p-symmetry and s-symmetry components [4.33, 4.41]. The heavy hole has much larger effective mass along (111) than (100), while the light hole has slightly smaller effective mass along (111). This might also be a reason for the dominant normal incident response in the (111) p-QWIP, since the lighter excited state mass should give a better absorption and responsivity depending on the carrier transport.

4.7 Summary

A p-type GaAs/AlGaAs QWIP structure on GaAs (111)A substrate was successfully fabricated and measured. The outdiffusion of Si during the growth is negligible as judged from the symmetrical dark current characteristics of the QWIPs. The (111)A GaAs/AlGaAs p-QWIP gave the strongest photoresponse at normal incidence, indicating the strong mixing of conduction and valence band Bloch states. The present QWIP sample has a peak responsivity of about 1 mA/W, but the responsivity can be further improved by optimizing the quantum well parameters and increasing the doping concentration to around 10^{19} cm^{-3} which is the level typically used in p-type QWIPs.

Chapter 5 Study of InGaAsP based asymmetric quantum well for infrared detection

In this chapter, an InGaAsP-based asymmetric QWIP grown by low pressure Metalorganic Vapour Phase Epitaxy (MOVPE) with less poisonous TBA, TBP sources in pure N₂ ambient has been demonstrated. The I-V characteristic and spectral photocurrent response have been investigated for the device fabricated using standard processing technology.

5.1 Introduction to MOVPE technology

The MOVPE technology was first reported in the scientific literature in 1968 by Manasevit [5.1]. Since then, the MOVPE technology for the growth of III–V compound semiconductors has developed quickly over the past years. Because of the economy and flexibility of the process, the quality of the materials produced, and the scalability of the technology, the MOVPE process has become an important element in the fabrication of a wide variety of high-performance semiconductor devices.

The advantages of this technology are high throughput and flexibility. It allows reproducible growth of thick (7~10 μm) and very thin (3 nm) layers for a wide range of strained and unstrained materials. In addition to the standard growth on planar substrates, growth on structured surfaces and selective area growth for laterally localized growth on the surface also provide perspectives for the development of new optoelectronic devices.

In MOVPE growth, atoms are deposited by decomposing organic molecules (precursors) as they pass over a hot substrate. The undesired remnants are removed or deposited on the walls of the reactor. The growth at the heated substrate surface is based on the chemical

reaction of gas molecules containing the constituent atomic species. MOVPE involves a series of surface reactions occurring as shown in Figure 5.1 with growth of III-nitride as an example, including adsorption and desorption of the precursor molecules, surface diffusion, nucleation and growth, and desorption of reaction products.

Figure 5.1 The basic growth process by MOVPE [5.2].

A basic MOVPE process begins with mixing the liquid or solid metalorganic (MO) compounds and hydride together and transporting them into the reaction zone with a carrier gas. Pd-purified H_2 is commonly used carrier gas in the MOVPE process for diluting of the reactants and transporting of the metalorganic compounds towards the reaction zones. The high substrate temperature results in the decomposition of the sources, forming film precursors. The film precursors transport and adsorb on the growth surface, and then diffuse and incorporate to the growth site. The by-products of the surface reactions desorb from substrate surface.

Figure 5.2 The schematic low pressure horizontal MOVPE system [5.3].

Figure 5.2 shows a typical low pressure MOVPE machine which consists of a reactor system, a vacuum exhaust system, a MO source, a gas handling system and a control system. Trimethylindium (TMIn), trimethylgallium (TMGa) and trimethylaluminium (TMAI) are used as Group III sources. TMGa, TMAI and TMIn are all liquids that have high vapour pressure at room temperature. In general, AsH₃ and PH₃ are used as Group V sources and require a sophisticated scrubbing system due to the high toxicity of these materials. In case of PH₃, which is not easily decomposed, this group V source is transferred to the reactor after thermal decomposition via a special furnace. From the academic point of view, a detailed understanding of the process mechanism is desirable, while for device application point of view, the exact control of growth rate, homogeneity, semiconductor composition and interface sharpness between semiconductors of different alloy composition is essential

[5.4]. To achieve high quality layers, the influence of the basic process parameters on the layer properties should be known.

A typical temperature dependence of the growth rate is shown in Figure 5.3. In an Arrhenius plot of the growth rate, usually three regimes are distinguishable [5.5]. The growth process is thermally activated at low temperature where the growth rate increases exponentially with increasing temperature. Here the layer quality tends to deteriorate. At higher temperature, the rate may drop again due to the desorption of reactants from the surface or enhanced parasitic prereactions, which may lead to a significant depletion of the precursor concentration along the substrate holder resulting in inhomogeneous. Usually an intermediate temperature range exists in which the rate is independent of temperature and determined by the supply of source material to the surface. Under most conditions the process is governed by the diffusion of the Group III species and thus called diffusion- or transport-controlled growth regime. In the diffusion-controlled regime the growth rate is linearly proportional to the molar flow of the Group III species. The V/III ratio is an important growth parameter for the electrical (i.e. doping or mobility) and optical properties [5.6~5.8].

Figure 5.3 Schematic of the Arrhenius plot of the growth rate versus reciprocal temperature in MOVPE process [5.5].

However safety is an important issue in MOVPE process for both research and production because of the use of high toxic group V sources such as arsine (AsH_3) and phosphine (PH_3) in the epitaxy process. In recent years, the less hazardous, liquid tertiarybutylarsine (TBA) and tertiarybutylphosphine (TBP) have been used as the substitutes for the highly toxic, hydride gas AsH_3 and PH_3 for MOVPE process. TBA and TBP offer some crucial advantages, i.e. the reduced vapour pressure and the improved growth of device structures, enhanced cracking efficiency, reduced amounts of waste material, and reduced toxicity. Therefore, a significant improvement in the overall safety is achieved for the entire epitaxial growth processes. A laser device with good performance has earlier been demonstrated by using TBA and TBP in MOVPE growth [5.9~5.12]. Since TBP decomposes more completely than phosphine at normal growth temperatures, it is easier to control the compositions of InGaAsP films during growth by using TBP. Furthermore, high quality materials can be grown at lower V/III ratios than that adopted for using phosphine and arsine counterparts [5.13].

Another improvement in safety for the MOVPE process is the replacement of the explosive hydrogen carrier gas by an inert nitrogen gas. For decades, purified H_2 has been widely used as the carrier gas for MOVPE. However, recently, nitrogen has been demonstrated to be excellent carrier gas in MOVPE for the growth of GaAs- and InP-based semiconductors [5.14~5.16], especially due to remarkable improvement in epitaxial layer uniformity in terms of thickness and PL wavelength [5.17].

5.2 MOVPE growth of InGaAsP QWIP structure

Due to the success of extensive exploration of the AlGaAs/GaAs material system over the past decades, high-performance long wavelength QWIPs have been realized and exploited in various applications. In parallel to these efforts, studies in material systems other than GaAs/AlGaAs have also progressed as motivated by concern regarding the quality of AlGaAs barriers which affects the performance of QWIPs. Carrier transport in AlGaAs barriers is influenced by oxygen-related defects [5.18] and undesirable dopant diffusion as a result of elevated growth temperatures [5.19]. The Al-free materials such as GaAs [5.20], GaInP [5.21, 5.22] and InP [5.23] were studied as potential barrier candidates. In these material systems, InGaAsP is of considerable interest due to the wide range of bandgaps achievable and the possibility of fabricating them on commercially important GaAs and InP substrates. It has been reported that the InGaAs/InP ternary [5.24] and InGaAsP/InP quaternary [5.25] long wavelength QWIPs grown by metalorganic molecular beam epitaxy have larger responsivities than GaAs/AlGaAs QWIPs for long wavelength detection.

The advances of MOVPE technique have also attracted many efforts in research of QWIP technology. Hoff et al [5.26] investigated *p*-type GaAs/Ga_{1-x}In_xAs_yP_{1-y} QWIP grown by MOVPE and verified the strong 2~5 μm photoresponse of these QWIPs was due to a much stronger coupling to the spin-orbit split-off components in the continuum state. M. Razeghi [5.27] reported the preliminary n-type InGaAsP/InP QWIP by low pressure MOCVD with group V source materials of 100% AsH₃ and PH₃, and the group III source materials of trimethylindium and triethylgallium. It has a detection wavelength up to 14.2 μm with peak responsivity of 1.09A/W at a bias of 2 V. Y. Paltiel et al [5.28] have recently reported high performance long wavelength Zn doped *p*-type GaAs/AlGaAs QWIPs grown by MOVPE with a peak wavelength of 8.2 μm and a peak detectivity $D^* = 0.97 \times 10^{10} \text{ cmHz}^{0.5}/\text{W}$ at 80 K and a bias of 2 V.

MOVPE has been proven to be an important technology for the growth of InGaAsP/InP-based optoelectronic components [5.29]. The composition and thickness uniformities of InGaAsP layer are of great importance in the fabrication of InGaAsP-based QWIP and focal array plane. However, the compositional uniformity of quaternary material is mainly dependent on gas phase reactions, diffusion processes, reactor flow conditions, i.e. total pressure, and temperature gradients especially on the wafer. Particularly the latter has a large impact on the As/P ratio uniformity of the epitaxial layer. While wafer rotation can provide excellent thickness uniformity [5.30], As/P variations continue to be the major source of compositional nonuniformity [5.31, 5.32]. Experimental techniques designed to improve As/P uniformity in the past have involved maintaining a uniform susceptor

temperature [5.33], using a nitrogen carrier gas [5.34], and employing Group V sources with similar decomposition properties [5.31], such as tertiary-butyl phosphine (TBP) and AsH₃.

The MOVPE system we used in the investigation of the growth of InGaAsP QWIP structure is a low pressure horizontal AIXTRON AIX 200 MOVPE reactor. Modern MOVPE systems adopt the high-speed rotating disk reactor planetary for the deposition of high-quality uniform films of a variety of materials. In AIXTRON MOVPE reactors, the substrate rotation is performed by the gas foil rotation, which is different from the mechanical rotation as adopted by Emcore system. In-situ monitoring of the growth process by reflectometry or Reflectance Anisotropy Spectroscopy helps to reduce the development time and costs considerably, hence improving innovation cycles and the time-to-market of novel devices since the growth of the material can be monitored in real time [5.35]. Nitrogen purified by a monoTorr phase II purifier was used as the carrier gas in the MOVPE process.

For In_xGa_{1-x}As_yP_{1-y} quaternary alloys, group III and group V compositions, denoted by x and y , respectively, determine both bandgap (wavelength) and the lattice constant. It is essential to precisely grow an In_xGa_{1-x}As_yP_{1-y} layer with desired Ga and As compositions to obtain the target wavelength whilst lattice matched to GaAs or InP substrate. For MOVPE system used in our experiment, the relationships between the alloy's compositions (x , y) and Ga/III and As/V source flow ratios have been studied by Huang and Zhang [5.36, 5.37]. It shows that the incorporation of Ga and In into the In_xGa_{1-x}As_yP_{1-y} epilayer is linearly proportional to the inlet partial pressures of TMGa and TMI_n sources, respectively. With

this linearly dependence, the Ga composition of the alloy can be controlled easily. The dependence of As composition on the As/V ratio appears exponential-like growth and becomes saturated when the As/V ratio is more than 0.4. In As composition range of 0.2–0.6, the As composition is very sensitive to the As/V ratio. This makes it very difficult to control the As composition in $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ layers. This arsenic incorporation in MOVPE growth of $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ films can be explained by an AsH surface adsorption trapping adsorption-trapping model [5.38].

Figure 5.4 The schematic structure of $\text{In}_y\text{Ga}_{1-y}\text{As}_z\text{P}_{1-z}/\text{In}_w\text{Ga}_{1-w}\text{As}_v\text{P}_{1-v}/\text{In}_x\text{Ga}_{1-x}\text{As}$ ASQWIP.

The InGaAsP based asymmetric QWIP (ASQWIP) structure grown by MOVPE is shown in Figure 5.4 The ASQWIP structure consists of 30 periods of step quantum wells and barriers sandwiched between two 0.5-μm-thick InP layers doped with Si to $1 \times 10^{18} \text{ cm}^{-3}$ for ohmic contacts. The step quantum well is designed to be latticed-matched to the InP substrate and consists of a 25-Å-thick $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ well doped with Si to $1 \times 10^{18} \text{ cm}^{-3}$, a 44-Å-thick undoped $(\text{InP})_{0.55}(\text{In}_{0.53}\text{Ga}_{0.47}\text{As})_{0.45}$ step and a 300-Å-thick $(\text{InP})_{0.85}(\text{In}_{0.53}\text{Ga}_{0.47}\text{As})_{0.15}$ barrier.

The step well structure provides an opportunity to explore the effects of layers with multiple compositions on the structural and optical properties.

The QWIP structure was grown on a semi-insulating InP (100) substrate. The n-type doping of the quantum wells was achieved using SiH₄. The reactor pressure during growth was set at 100 mbar. Before the growth of the QWIP structure, a 0.1- μ m-thick InP buffer layer was grown on the substrate at a temperature of 630 °C. The V/III ratios used in the growth of InP, InGaAs and InGaAsP step and barrier epilayers are 38, 23, 42 and 68, respectively. The TMIn/Group III ratios for the InGaAs well, InGaAsP step and barrier are 0.584, 0.831 and 0.906, respectively. The TBP/Group V ratio for the InGaAsP well and barrier layers are 0.952 and 0.984. Figure 5.7 shows the schematic energy band diagram of the ASQWIP structure where the layer thicknesses have been adjusted according to the individual epilayer growth rates *in situ* monitored by a Filmetrics F30 thin-film measurement system.

5.3 XRD characterization

The high-resolution X-ray diffraction measurements were carried out using a Philips X'Pert material research diffractometer, which is equipped with 4-crystal Bartels monochromator in the high-resolution (220) scattering and a 0.65mm slit in front of the detector to decrease the background intensity. The intense, sharp satellite peaks appeared in the X-ray rocking curve shown in Figure 5.5. For the symmetric (004) reflection, well-defined periodic oscillations are seen on both sides of peaks based on InP substrate. The high intensity and sharp peak of satellites are the merits of high crystalline quality and abrupt interface of the

MQW structure. Any imperfection, relaxation, or compositional inhomogeneity would cause loss of phase coherence and eliminate the satellite peaks. The period of the fabricated multiple quantum well structure is estimated to be 344 Å according to the relation of Eq.3.3 and agrees reasonably well with the designed value of 369 Å.

The angular separation between the zero-order satellite peak and InP substrate in X-ray rocking curve gives the average mismatch of the MQW along the growth axis. The perpendicular lattice mismatch of MQW structure, which gives fingerprint of the average strain present in the MQW structure, is obtained from the angular separation $\Delta\theta_0$ between the $n=0$ order peak and the substrate peak of the X-ray rocking curve according to the following [5.39]:

$$\varepsilon_{MQW} = -\Delta\theta_0 \coth \theta_B = \frac{\varepsilon_b b + \varepsilon_w w + \varepsilon_s s}{b + w + s}, \quad (5-1)$$

where θ_B is the Bragg angle, ε_{MQW} , ε_b , ε_w and ε_s are average strain for quantum well, barrier layer, well layer and step layer, respectively. b , w , s are the thickness for barrier, well and step layers, respectively. The X-ray rocking curve also indicates a slight lattice mismatch along the growth axis ($\sim 0.11\%$) of quantum well layers estimated from the angular separation between the zero-order satellite peak and the substrate peak given in above equation. Table 5.2 collects the ASQWIP structural parameters extracted from XRD rocking curve.

Table 5.1 The structural parameters for the ASQWIP extracted from XRD measurement.

Period (Å)	Substrate Position θ_B (degree)	Separation of 0 th -order peak S_0 and substrate peak $\Delta\theta_0$ (degree)	Angular spacing of satellite peak $\Delta\theta_p$ (degree)	FWHM of 0 th -order peak S_0 (sec.)
344	31.63	0.039	0.15	37

Figure 5.5 The X-ray rocking curve of the quantum well structure grown on InP (001) substrate. The slight separation of the S_0 and substrate peaks indicates the presence of small amount of stress in the quantum well layers. θ_B is the Bragg angle for InP substrate. The dashed curve shows the simulation result.

The reciprocal space mapping (RSM) by high resolution X-ray diffraction is ideally suitable for a detailed structural characterization of crystalline layered structures such as quantum

well and superlattice. The RSM of $\text{In}_y\text{Ga}_{1-y}\text{As}_z\text{P}_{1-z}/\text{In}_w\text{Ga}_{1-w}\text{As}_v\text{P}_{1-v}/\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ ASQWIP structure are achieved by running $(\omega+\omega_0)/2\theta$ scans for different offset angles ω_0 and the recorded intensities were drawn in two-dimensional reciprocal space mapping. Since a symmetric diffraction is only sensitive to the lattice plane spacing perpendicular to the sample surface, an asymmetric diffraction, such as (115) and (224) based reflections, whose diffraction planes lie inclined to the sample surface, is needed for obtaining the information about the in-plane lattice spacing, and thus residual strains.

Figure 5.6 Reciprocal space mapping around (224) reflection of the ASQWIP structure. The dashed line connecting main peaks indicates the almost full strained status of the structure.

The (224) based reflections of RSM of InGaAs/InGaAsP/InGaAsP SQWIP structure is shown in Figure 5.6. As shown in the figures, the satellite peaks of the structure stay in a line normal to the X-axis, showing a fully strained case. The peaks of InGaAs, InGaAsP epilayers allocate at the same line parallel to Q_y direction as the InP substrate peak, indicating full strain or slight mismatch ($\sim 0.11\%$) of epilayer lattice constants with substrate. The strain relaxation will cause the peak-line to rotate clockwise, and in the case of full relaxation, the peak-line will be parallel to the longer sides of the rectangle in the figure, which indicates the difference of the lattice constants of the two materials.

5.4 Dark current and spectral photocurrent response

To analyze the intersubband transition, the electron energy states and their corresponding envelope wave functions in the quantum well were calculated using a transfer matrix method within the framework of effective mass approximation [5.40]. The bandgap energy of $(\text{InP})_{1-z}(\text{In}_{0.47}\text{Ga}_{0.53}\text{As})_z$ was calculated using $E_g = 1.4236(1-z) + 0.816z + 0.13z^2$ ($T = 0\text{K}$), and the conduction band offset was taken as 43% of the total band offset [5.41]. The electron effective mass was taken as $m_e^* = 0.0795 - 0.0365z$ based on Vegard's law [5.42]. The band nonparabolicity was also incorporated in the calculation similar to that described in reference [5.40]. Figure 5.7 shows the energies of the ground state as well as the midpoints of the continuum minibands calculated using the above approach. The Fermi energy of the bound electrons was estimated using $E_F = N_D \pi \hbar^2 L_w / m_w^*$, where N_D , L_w and m_w^* are the doping density, the well width and the electron effective mass in the quantum

well, respectively. The calculated oscillator strengths (i.e. O.S.) for the transitions from the ground state to the first three minibands in the continuum are 0.22, 0.34, and 0.22.

Figure 5.7 Schematic energy band diagram of the ASQWIP structure. The composition z for $(InP)_{1-z}(In_{0.47}Ga_{0.53}As)_z$ for each layer is given. The lines above the barrier indicate the midpoints of the minibands and the numerical values indicate the edges of the minibands. O.S. is oscillator strength.

To measure dark current and photocurrent characteristics, mesa diodes of $150 \times 150 \mu m^2$ were fabricated using standard photolithography techniques and wet chemical etching by HCl/H₃PO₄/H₂O solution. The top and bottom contacts were formed by evaporating NiGeAu/Ni/Au and rapid thermal annealing at 420 °C. Finally a 45° facet on the substrate was polished for coupling IR radiation to the quantum well structure. The spectral dependence of the photoresponse was measured at low temperature using an Oriel 6575 infrared source coupled by an infrared lens to a Jobin Yvon Triax 320 monochromator. The photon flux of the system was measured using a calibrated Oriel 70124 pyroelectric detector. The photocurrent signal from the ASQWIP sample was amplified before sending it to the lock-in amplifier.

Figure 5.8 shows the measured dark current versus the applied bias voltage for a set of temperatures between 25 and 175 K, with the positive electrode placed on the top contact layer. The dark current shows an asymmetric characteristic for different bias polarities due to the asymmetric nature of the step quantum wells. Under the dark condition, the measured current is mainly due to temperature-dependent thermionic emission and field-assisted tunneling. The thermionic emission current is dominant at high temperatures and increases with rising temperature. The thermionic emission current can be estimated by calculating the number of electrons having energies larger than the barrier potential and has the dependence $I(T)/T \propto \exp(-E_A/kT)$, where $E_A = H - E_1 - E_F$ is the activation energy and H is the barrier potential [5.43]. The activation energy can be extracted from the plot of the normalized dark current I_d/T versus $1/T$ at high temperatures (above 80 K). Figure 5.9 shows the extracted activation energies plotted in log scale as a function of bias voltage. It can be seen from Figure 5.9 that the activation energy decreases exponentially with the increasing bias voltage, which is due to the decrease of the effective barrier height under the external bias. The two lines for the different bias polarities have different slopes due to the asymmetry of the quantum well structure, but they merge when extrapolated to zero bias voltage, which gives an activation energy of 81 meV under the flat band condition. This is in good agreement with the calculated value of about 78 meV.

Figure 5.8 The I-V characteristic as a function of bias voltage under a series of temperatures from 25 K to 175 K.

Figure 5.9 The plot of activation energy estimated using thermionic current versus bias voltage. Note that the y-axis is in log scale.

Figure 5.10 shows the spectral responsivity of the detector under a set of bias voltages measured at 25 K. The responsivity peak was found to be at about 10.7 μm with 0.19 A/W at 0.8 V bias. The responsivity spectrum has a linewidth ($\Delta\lambda / \lambda_p$) of about 15%, indicating the bound-to-continuum nature of the transition [5.44]. The calculated peak position is around 11.6 μm based on the intersubband transition from the ground state to the second miniband in the continuum, which has the highest oscillator strength. The difference between the measured and calculated peak position may be due to experimental uncertainty in the actual layer thickness and compositions.

Figure 5.10 The measured photocurrent responsivities as a function of wavelength for a set of bias voltages.

Figure 5.11 The peak responsivity and detectivity of the detector as a function of bias voltage.

From the peak responsivity R_p and the dark current I_d , the peak detectivity can be calculated using $D_\lambda^* = R_p \sqrt{A} / (i_n / \sqrt{\Delta f})$, where A is the detector area, Δf is the bandwidth, and i_n is the noise current. The noise current can be estimated using $i_n / \sqrt{\Delta f} = \sqrt{4eI_d g}$, where I_d is the dark current and g is the photoconductive gain which is estimated to be about 0.5 [5.45]. The peak responsivity and detectivity versus bias voltage are plotted in Figure 5.14. A maximum detectivity of $1.9 \times 10^9 \text{ cmHz}^{1/2}/\text{W}$ is achieved at a bias of 0.6 V. By taking into account the activation energy of 81 meV and the Fermi level of 13 meV, the actual position of the ground state is 94 meV below the barrier edge. Since the peak response occurs about 116 meV from the ground state, the maximum responsivity corresponds to an energy state 22 meV above the barrier. Therefore, by optimizing the quantum well structure, the activation energy for thermionic emission can be raised by about 20 meV to make an

appreciable reduction of the dark current which can further enhance the detectivity. The drop of the peak detectivity for the bias voltage beyond $\pm 0.8\text{V}$ is due to the rapid increase of the dark current in the ASQWIP sample. In the case of bound-to-continuum QWIPs, the responsivity is linearly proportional to the bias across the device [5.44].

The responsivity of the ASQWIP versus bias shown in Figure 5.11 also demonstrates the asymmetric behavior, and the responsivity is relatively large under the forward bias (i.e. the positive voltage applied to top contact) compared to the reverse bias. This is most likely due to the dependence of oscillator strength of intersubband transition in asymmetric quantum wells to the direction of the applied field [5.46]. The forward field contributes much more to the enhancement of the oscillator strength of ASQWIP than the backward field does [5.47]. Similar behavior has also been observed in other material systems due to the asymmetrical growth of different interfaces and dopant diffusion along the growth direction [5.48].

5.5 Summary

In this chapter, a long-wavelength ($\lambda = 10.7\text{ }\mu\text{m}$) near lattice-matched $\text{In}_y\text{Ga}_{1-y}\text{As}_z\text{P}_{1-z}/\text{In}_w\text{Ga}_{1-w}\text{As}_v\text{P}_{1-v}/\text{In}_x\text{Ga}_{1-x}\text{As}$ ASQWIP grown on (001) InP substrate by MOVPE has been successfully performed. This work demonstrates the fabrication of InP based asymmetric quantum well infrared detectors using MOVPE with TBA and TBP sources with performance comparable to that achieved using molecular beam epitaxy (MBE).

Chapter 6 Conclusions and Recommendations

The conclusions of the study are given with some highlighted recommendation for future work in this chapter.

6.1 Conclusions

The structural, electrical and optical properties of Si-doped (111)A-oriented GaAs/AlGaAs QWIP structure grown on GaAs (111)A substrate by MBE have been investigated.

Enhancement of epitaxial growth rate has been observed in (111)A GaAs/AlGaAs QW. The growth rate on (111)A surface is faster than (100) one because there are three dangling bonds for each group III adatom on (111)A surface and only two on (100) surface. Moreover, the growth rate on (111)A surface is associated with both the As_4/Ga flux ratio and the substrate temperature in a complex relation which is different from the growth rate on (100) surface which is simply determined by Ga flux. The reduction of Al composition in AlGaAs layer on (111)A surface has been obtained. This may result from the poor efficiency of Al atom adsorption to Ga atom site under Ga-predominant (111)A surface. Much stronger PL emission intensity has been achieved in (111)A GaAs/AlGaAs QW. The stronger optical transition should owe to the larger anisotropy of heavy-hole band in the host GaAs along the [111] direction. The conduction type of incorporated Si atoms on (111)A surface can be either donor or acceptor. It is found to strongly depend on the growth conditions, such as the substrate temperature and V/III flux ratio. P-type QWIP has been successfully demonstrated by incorporating Si as acceptor on (111)A-oriented substrate. The doping level is comparable to that of n-type Si doping in (100)-oriented GaAs layer.

The p-type GaAs/AlGaAs (111)A QWIP device has been successfully fabricated and characterized. Si shows a very low diffusion coefficient as compared with the traditional p-type dopant Be. Accordingly, the outdiffusion of Si during the growth is negligible as judged from the symmetrical dark current characteristics of the QWIPs. Strong polarization dependence of spectra photocurrent response for p-type (111)A QWIP has been observed, where intersubband transition at normal incidence is dominant. The peak responsivity of (111)A QWIP is around 1 mA/W with a detection wavelength at 7 μm under TE mode incidence at 25 K and bias of 4.3 V. The characteristic of intersubband transition for the (111)A-oriented QWIP should make it the promising candidate for the normal incident detection.

A near lattice-matched $\text{In}_y\text{Ga}_{1-y}\text{As}_z\text{P}_{1-z}/\text{In}_w\text{Ga}_{1-w}\text{As}_v\text{P}_{1-v}/\text{In}_x\text{Ga}_{1-x}\text{As}$ asymmetric step quantum well infrared photodetector (ASQWIP) grown by low-pressure MOVPE technique using N_2 carrier with less toxic TBA and TBP is reported. The matrix method based on the effective approximation has been employed to study the subband states and intersubband transitions in the InGaAsP-based ASQWIP. It turns out that such a simplified approach is quite adequate in device design and modeling. The spectral responsivity of the detector has its peak at a wavelength of 10.7 μm with value of 0.19 A/W under 0.8 V bias at 25 K. A maximum peak detectivity of $1.9 \times 10^9 \text{ cmHz}^{1/2}/\text{W}$ has been achieved. This work demonstrates the feasibility of fabricating InGaAsP based quantum well infrared detectors using MOVPE with TBA and TBP sources with performance comparable to that achieved using MBE.

6.2 Recommendations for future research

Some of the important points from this work are recommended here.

1. The optimization of structural parameters for the (111)A-oriented p-QWIP to further improve the performance of its photocurrent responsivity and peak detectivity. In our experiment, the photocurrent spectrum exhibits peak responsivity of about 1 mA/W (at bias $V_b = 4.3V$), which is relatively low compared with the typical p-type QWIPs. The lower peak responsivity is mainly due to the low doping concentration (equivalent 2D density, $N_D = 5.7 \times 10^{11} \text{ cm}^{-2}$) and the large spectrum width $\Delta\lambda/\lambda_p$. Regardless of its broader photoresponse spectrum, this p-QWIP should have higher doping density within the range of $1 \sim 2 \times 10^{12} \text{ cm}^{-2}$, which is expected for the maximum of the background limited infrared performance temperature and dark current limited detectivity [6.1]. From the peak of photocurrent response, the final state is far above the barrier top which should lead to the increase of the dark current and reduction of the responsivity. Further optimization of (111)A QWIP, for example, well thickness and barrier height is substantially necessary.

2. More sophisticated theoretical analysis is necessary for better understanding the dominant normal incident response phenomenon in (111)-oriented QW. We have observed strong polarization dependence of intersubband transition which responds to normal incidence polarization dominantly. The four-band model adopted in this work does not take into account the band mixing effects from spin-orbit split-off (SO) band and conduction band, and thus can not reveal further detail on polarization sensitivity of intersubband transitions. A more sophisticated multiple band k-p model such as eight-band one can be used for such

an application. However, this work is out of the scope since the current work mainly focuses on experimental work. A skeleton of the formulism is given in the appendix as a reference for possible future investigation.

3. Nowadays the crystallographic orientation of the QW can be another important degree of freedom in designing optical devices. Besides, valence-band engineering in semiconductor QWs is an attractive interest for developing novel performance optoelectronic devices. The use of strained layers for valence-band engineering on the non-(100) substrate has proven to be able to modify the optical properties. Development of strained AlGaAs/InGaAs QW on (111) substrate for infrared detector should put forth a prospective topic.

4. The applicable performance of InGaAsP ASQWIP grown by safer and productive MOVPE in comparison to similar one by MBE has been investigated in our work. However, further work to improve the performance of QWIP is still necessary. Generally, the InGaAs or InGaAsP based QWIP has superior responsivity. For example, the responsivities of InGaAsP/InP QWIPs are five times larger than that of similar GaAs/AlGaAs QWIPs [6.2]. The InGaAsP/InP QWIPs have approximately twice times as larger as the responsivity of similar GaAs/AlGaAs QWIPs [6.3]. These results clearly demonstrate the excellent hot electron transport in this material system. In fact, our InGaAsP asymmetric QWIP has approximate photocurrent responsivity of 0.19A/W compared to the maximum value around 2.5~6.5 A/W for the typical InGaAsP-based one. On other hands, the peak detectivity is still lower due to the relatively higher dark current. The further improvement of structural and optical quality is necessary to reduce the carrier

scattering and thus enhance the performance of responsivity and detectivity. Besides, the peak response from maximum responsivity of our sample corresponds to an energy state 22 meV above the barrier. Therefore, by optimizing the quantum well structure, the activation energy for thermionic emission can be raised by about 20 meV to make an appreciable reduction of the dark current which can further enhance the detectivity.

Notably, Stark shift of intersubband transition is strongly expected in the asymmetric QW. For example, Wu et al [6.4] have reported the bias-induced tuning of the peak wavelength of the photocurrent response in an $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{Al}_y\text{Ga}_{1-y}\text{As}/\text{Al}_z\text{Ga}_{1-z}\text{As}$ symmetric QWIP. The large Stark shift has not been actually observed in our InGaAsP asymmetric QWIP. We contribute it to the rapid increase of the dark current in our sample for the bias voltage beyond $\pm 0.8\text{V}$. Further improvement of the structural and optical quality of our QWIP should make it to be a competitive candidate for a bias-tunable detector.

Author's Publications

1. **H. Li**, T. Mei, J. Arokiaraj, D. Nie, D.H. Zhang and W.J. Fan, "Optical properties of Si-doped GaAs/AlGaAs quantum well infrared photodetector structure grown on GaAs (111)A substrate", International Conference on Materials for Advanced Technologies, Singapore, December 7~12, 2003.
2. **H. Li**, T. Mei, K. P. Lantz and G. Karunasiri, "Growth of InGaAsP based asymmetric quantum well infrared photodetector using metalorganic vapor phase epitaxy", J. Appl. Phys., 96, 6799 (2004).
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6. **H. Li**, T. Mei, D. H. Zhang, W. J. Fan, S. F. Yoon and W. K. Loke, "Infrared absorption and current-voltage characteristic of GaAs/AlGaAs multiple quantum wells grown on GaAs (111)A substrate by solid source molecular beam epitaxy", Journal of Crystal Growth 288 (2006) 36–39.

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Chapter 1

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Chapter 6

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Appendix

In chapter 2, we briefly discussed the calculation of hole subbands in GaAs/AlGaAs QW was based on a four-band effective-mass approximation using the Luttinger–Kohn valence-band Hamiltonian. There, only the HH and the LH bands were taken into account while the spin-orbit split-off (SO) band, the conduction band was neglected. More accurately, the hole subband structure in GaAs/AlGaAs QW should be solved in the envelope approximation by using the general eight-band model including the HH, LH, OS and conduction band. This evaluation should enable us to find distinctly the different properties of optical intersubband transitions dependent on selection rule and polarization [A.1].

The widely used eight band k-p Hamiltonian H is based on (001)-orientation and has been well discussed [A.2~A.6]. The Hamiltonian for (111) crystallographic orientation H' can be derived by rotating the angular and crystal momentum of (001) ones using the relationship of

$$X' = RX, \quad (\text{A-1})$$

where X, X' are the prime and desired wave vector ($k(k_x, k_y, k_z)$ and $k'(k'_x, k'_y, k'_z)$) and the angular momentum ($J(J_x, J_y, J_z)$ and $J'(J'_x, J'_y, J'_z)$) matrix, respectively. And R is the transformation matrix and given as [A.7, A.8].

$$R = \begin{bmatrix} \cos \phi / \sqrt{2} & \cos \phi / \sqrt{2} & -\sin \phi \\ -1/\sqrt{2} & 1/\sqrt{2} & 0 \\ \sin \phi / \sqrt{2} & \sin \phi / \sqrt{2} & \cos \phi \end{bmatrix}, \quad (\text{A-2})$$

where $\cos \phi = 1/\sqrt{3}$, $\sin \phi = \sqrt{2}/3$ in the case of (111) orientation relative to (001) coordinate system as shown in Figure A.1.

Figure A.1 The relationships of the $[111]$ coordinate system to the conventional $[001]$ crystal coordinate system.

In quantum wells, the z-component of the wave vector k'_z , is replaced by the differential operator $-i\partial/\partial z'$.

Using time-independent Schrödinger Equation, the eigen states satisfy:

$$H'\Psi(\mathbf{r}') = E\Psi(\mathbf{r}'), \quad (\text{A-3})$$

where $\Psi(\mathbf{r}')$ is the wavefunction of the eigenstate and given as

$$\Psi(\mathbf{r}') = e^{i(k'_x x' + k'_y y')} \sum_{s=1}^8 \varphi_s(z') u_s(\mathbf{r}'), \quad (\text{A-4})$$

where the components $\varphi_s(z')$ ($s = 1, 2 \dots 8$) are the envelope functions, the components $u_s(\mathbf{r}')$ ($s = 1, 2 \dots 8$) are the Bloch basic function. The eigenstates can be obtained by solving Schrödinger Equation using either finite difference method [A.6] or finite element method [A.8].

Once the eigen energy and wavefunction have been achieved, the intersubband transition matrix is

$$M = \langle \Psi_n | \mathbf{e} \cdot \mathbf{p} | \Psi_{n'} \rangle = \sum_{j,j'=1}^8 \left\langle e^{i(k'_x x' + k'_y y')} \varphi_{n,j} u_j | \mathbf{e} \cdot \mathbf{p} | e^{i(k'_x x' + k'_y y')} \varphi_{n',j'} u_{j'} \right\rangle, \quad (\text{A-5})$$

where $\mathbf{e}$ is the unit vector of the electric polarization of the incident light and $\mathbf{p}$ is the momentum operator $\mathbf{p} = -i\hbar \left(\frac{\partial}{\partial x'} + \frac{\partial}{\partial y'} + \frac{\partial}{\partial z'} \right)$, and subscript n, n' is the index of subbands.

The intersubband transition elements for polarization in z' direction and in (x', y') plane can be further obtained as well from above.

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