Plasma induced quantum well intermixing for photonic integration

Hery Susanto Djie

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Plasma Induced Quantum Well Intermixing for Photonic Integration

Hery Susanto Djie

School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

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SUMMARY

Photonic integration brings numerous benefits to the optical communications system designer in terms of improved performance and reliability due to elimination of losses associated with coupling to fibres, increased packaging robustness, simple interconnect and alignment of monolithically each individual guided-wave photonic devices with high precision. Quantum Well Intermixing (QWI) has been found as a very useful method to achieve photonic integration due to its ability to selectively fine tune the energy bandgap in different regions within the same epitaxial layer structure, through interdiffusion.

In this thesis, Ar plasma induced intermixing has been developed with various plasma systems, including Inductively Coupled Plasma (ICP) machine. A plasma induced QWI technique has been demonstrated to successfully tune a wide range of III-V compound semiconductor materials for photonic integration applications. The parameters of plasma system affecting intermixing process were optimised and studied using the Taguchi's method, producing adequate bandgap shift after the process, for example 104 nm blue-shift in InGaAs/InGaAsP QW laser structure.

The material after intermixing has been investigated using various tools such as photoluminescence, micro-Raman spectroscopy, x-ray diffraction, and atomic force microscopy. The high plasma density with an application of ICP power has been found to enhance the intermixing rate. No appreciable linewidth broadening and the peak intensity enhancement in photoluminescence spectrum

have made this technique very promising for photonic integration purposes, which demand a high quality material.

The universal quantum well interdiffusion model with strain calculation has been developed to gain a further understanding of various QWI techniques and to further optimise QWI process for the long term goal of photonic integration purposes. Through the developed program, a simple qualitative understanding of the effects of the plasma-induced defects, the factors that affect the plasma induced QWI process, and the general correlations of the inductively coupled plasma exposure effect on QWs bandgap shift, has been understood.

The demonstration of plasma induced QWI capability, which offers i) an adequate high spatial resolution ($\sim 2.4 \mu\text{m}$), ii) single step multiple bandgaps creation in a simple way, and iii) process universality to a wide range of material system, such as InGaAs/InAlGaAs on InP substrate and GaAs/AlGaAs on GaAs substrate, has made this technique a promising way for high-density photonic integration. A tendency of lateral diffusion of shallow point defects during annealing could be minimised by using modulated stress-inducing dielectric cap as a barrier for the lateral defect diffusion. Monolithically multiple bandgaps creation has been demonstrated in a single step plasma induced QWI process using the innovative approaches based on the spatial defect modulated intermixing (SDMI) and dielectric thickness modulated intermixing (DTMI) with the combination of the gray mask technology. The selective intermixing was achieved using SiO_2 material as an intermixing mask and low-loss broad area external cavity laser was later fabricated with the measured waveguide loss as low as 2.3 cm^{-1} with $1200 \mu\text{m}$ long passive waveguide. These results highlight the readiness of the plasma induced QWI technique for photonic integration purposes.

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1. INTRODUCTION

1.1 MOTIVATION

Rapid development in optical communications and optoelectronics technology is crucial for expediting the transition from the industrial age to the information age. Higher performance photonic components are required to assist the transition from point-to-point optical communications systems to networks, such as more dynamic and flexible operation, better mechanical and temperature stability, etc. Among the III-V semiconductors, GaAs and InP based materials are the most technologically important compounds. The technology platform required to realise these advances successfully and cost-effectively needs to be extremely versatile for high-speed operation. In order to realise the cost-effective systems, interest in the photonic integration of active and passive devices like the semiconductor lasers, wavelength monitors, high-speed modulators, filters, couplers, amplifiers, low-loss waveguides, photodetectors, etc., in high-bit rate optical communication has increased. Photonic integration brings numerous benefits to the optical communications system designer in terms of improved performance and reliability due to elimination of losses associated with coupling to fibres, the increased packaging robustness, and relatively simple interconnect and alignment requirements. Today, we are at the threshold of another revolutionary development, that is, the integration of optical components into one single package, widely known as photonic integrated circuits (PICs). PICs offer the promise of cost reduction, dramatically reduced size, and increased packaging robustness. The main advantage is all the interconnections between the individual guided-wave optoelectronics devices are precisely and permanently aligned with respect to one another since the waveguides are lithographically produced. Taking the integration of a laser and a

passive waveguide for example, the bandgap energy of the waveguide needs to be higher than the laser section. This is because laser action usually occurs just above the semiconductor band edge and the passive waveguide section, which is electrically unpumped, will be highly absorbing at the laser emission wavelength if it is not bandgap tuned to higher energy.

Integration of different optical elements within a single device supports advances in functionality and has the potential to create a revolution in the optical communications industry similar to what occurred when the first integrated circuits (IC) appeared in the electronic industry. To monolithically integrate several photonic devices, precise tailoring of the optical properties such as bandgap energy, absorption coefficient, and refractive index is required. Quantum Well Intermixing (QWI) [1]-[3] is a post-growth bandgap tuning technique for quantum well material that offers simplicity and flexibility as compared to the epitaxial growth and regrowth technique [4],[5] and the selective area epitaxy technique [6],[7]. In literature, QWI is referred to an interdiffusion or disordering. Heterostructure intermixing has become a promising postgrowth technique used widely in quantum well (QW) devices and structures to modify the electrical and optical properties within the same epitaxial layer structure. The ability to control the bandgap profile in III-V semiconductor device structures is of prime importance for the development of photonic integrated circuits [8].

It is widely known that plasma causes damage in a semiconductor material, and particular damage is beneficial for inducing the intermixing between wells and barriers in QW system, enabling the bandgap modification of QW structure from abrupt to the graded profile. The idea of plasma induced QWI to tune material bandgap is attractive since 1) the low ion energy (30 eV-1 keV) ions generated in

plasma chamber minimise QW optical quality degradation with comparable bandgap shift for PICs; 2); short processing time (typically from 5-10 minutes); 3) relatively simple and low-cost plasma etch facilities; 4) temperature independent of plasma process. Plasma induced QWI technique has been developed using several plasma machines, including Reactive Ion Etcher (RIE), Electron Cyclotron Resonance (ECR) and Inductively Coupled Plasma etcher (ICP). The latter will be the major part of this work for investigation of its capability for photonic integration purposes, starting from the optimisation of related parameters, intermixed material quality, the high-density plasma effect, the spatial resolution of selective intermixing, a single step multiple bandgaps creation, universality for intermixing of various material systems, the demonstration of devices from plasma induced damage process, and the development of interdiffusion theoretical model to gain further understanding of the QWI process.

Practical PICs fabrication mandates high manufacturing yield, low manufacturing cost, and high reliability. The realisation of such a fabrication scheme must establish the most fundamental condition for integrating photonic devices of differing functionalities monolithically, which is material bandgap/wavelength compatibility among various devices. Although a number of such technologies already exists; i.e., the growth and re-growth technique and selective area growth, none possesses the advantages of the process yield, process simplicity, mass production capability, and low equipment costs as QWI technique. For example, growth and re-growth is complicated and expensive process, which involves growing, etching and then re-growing of QW layers at selected areas on the substrate. The process gives low manufacturing yield, and therefore it adds an additional cost to the final PICs product. As well as having low manufacturing yield

(due to difficulties of regrowing on a vertically etched surface, and regrowing with high precision), the material selection necessitates a compromise between the bandgap, refractive index and layer thickness of the passive waveguide. Moreover, there is inevitably a mode mismatch at the butt joint, resulting in scattering and back-reflection losses. Bandgap engineering through QWI technology will be expected as a catalyst for the PICs revolution. Plasma induced QWI technique is largely in its infancy. Important challenges seek innovative solutions and more developments before this technology is ready for PICs industry. The various stage of developing this technology should be carefully thought out in order to produce fruitful results, beneficial for entire photonic research community in the future.

1.2 OBJECTIVES

The objectives of this work are to investigate the plasma induced damage to the QW material for photonic integration purposes, especially for tuning the bandgap of QW at a postgrowth level. Most of the investigations are based on the experimental study on the ICP induced damage for the future fabrication of high-density photonic devices. As the ICP induced QWI is relatively new and provides a promising approach for photonic integration purpose, the major part of the work would be carried out to investigate and develop the plasma induced QWI using Argon plasma in the ICP system to tune the InP based material bandgap energy. The theoretical work of interdiffusion study was carried out to verify the results obtained from the experimental data of the plasma induced QWI.

In this thesis, the main focus of the work is divided into three main parts. They are: (i) experimental investigation of plasma induced QWI in ICP system, (ii) investigation of plasma induced damage to material quality and high quality

photonic device fabrication, and (iii) theoretical calculation of interdiffusion process of various QWI techniques.

1.3 MAJOR CONTRIBUTION OF THE THESIS

The QWI effect in InGaAs/InGaAsP QW structures using Ar plasma induced QWI has been investigated with various plasma systems. A plasma induced QWI has been demonstrated to successfully tune a wide range of III-V compound semiconductor material for PICs application. The parameters of plasma system affecting QWI process were optimised and studied using the Taguchi's method for the first time. Large bandgap shift of up to 104 nm in InGaAs/InGaAsP QW laser structure was observed after exposing to Ar plasma in ICP system using the optimised parameters. The high plasma density enhanced QWI with the application of ICP power has been reported, gaining the fundamental mechanism of plasma induced QWI in a high-density plasma as compared to low plasma density of RIE system. The small linewidth broadening and the peak intensity enhancement in photoluminescence spectrum have made this technique very promising for photonic integration purposes, which demand a high quality material.

The demonstration of plasma induced QWI capability, which offers i) an adequate high spatial resolution, ii) single step multiple bandgaps creation in a simple way, and iii) universal process to a wide range of QW material system, has underscored the technique as a promising way for high-density photonic integration devices, therefore is expected to create a significant impact to the photonic research community. A universal plasma induced QWI process in ICP system to other III-V compound semiconductors, such as InGaAs/InAlGaAs on InP substrate and GaAs/AlGaAs on GaAs substrate with sufficient bandgap shift for PICs application

has been demonstrated. The result suggests that the technique can be potentially used as a universal QWI process to induce intermixing in III-V compound structures. In GaAs/AlGaAs, a breakthrough of Ar plasma induced QWI in ICP system in producing a comparable bandgap blue-shift to the H₂ plasma induced QWI technique [9] has been achieved with only a single exposure-annealing step.

A tendency of lateral diffusion of point defects during annealing stage, which leads to a poor spatial resolution, has been minimised by the use of a vertical stress-inducing dielectric cap to act as a barrier towards lateral defect diffusion. Such improvement in the spatial resolution using a stress-inducing dielectric layer can be further adopted for other shallow defect induced QWI techniques, such as low energy ion implantation induced QWI, sputter silica induced QWI, anodic oxidation induced QWI, and excimer laser induced QWI.

The approach to achieve multiple bandgaps across a single substrate using plasma induced QWI has been proposed based on the spatial defect modulated intermixing (SDMI) with good controllability in a single step process across a single wafer. In addition to the SDMI approach, the gray mask technology, which has been established in a low energy IID process [10], adopted for the first time to the plasma induced QWI technique here for achieving the multiple bandgaps. By a precise control of mask thickness, the gray mask process in plasma induced QWI technique provides an alternative for multiple bandgaps creation. The selective intermixing using plasma induced QWI technique with a differential bandgap of 86 nm has been achieved using SiO₂ as intermixing mask. Low-loss broad area external cavity laser (ECL) has been fabricated with the measured waveguide loss as low as 2.3 cm⁻¹ with 1200 μ m long passive waveguide. These results demonstrate the capability of this technique for photonic integration purpose.

Eventually, the development of the interdiffusion model with strain calculation has gained momentum in the thesis by a further understanding of QWI processes, especially in the inductively coupled plasma enhanced QWI. The developed model does not only apply to the study of plasma induced QWI process, but also has shown to be applicable for studying various interdiffusion processes, such as the phenomenon of polarisation dependent QWI using low energy IID, annealing induced blue-shift in InGaAsN QW, and a doped sol-gel cap enhanced InGaAs/InGaAsP QWI.

1.4 ORGANISATION OF THE THESIS

This report is organised into seven chapters. Chapter 1 gives an introduction to the thesis, where the motivation, objectives, and major contributions of the thesis are documented. This chapter provides both the background and motivation for this research. The objectives specify the main focus of this research. The major contributions of the thesis state both the theoretical and experimental work developed in this study.

Chapter 2 describes the background information of III-V compound semiconductor, monolithic integration process on InP based material, review on the existing QWI techniques, the detail of experimental and characterisation techniques of this work. In addition, advantages and disadvantages of each technique are also highlighted. Chapter 3 presents a design of experiment for optimisation of related parameters using Taguchi's method for QWI process using ICP machine. The RIE parameters were optimised using similar design of experiments, enabling the comparison study of the QWI effect and various control parameters between the two systems of high and low density plasma.

Chapter 4 outlines a study of intermixing mechanism and a systematic investigation of material property after plasma induced QWI process using ICP machine. The material investigation includes photoluminescence spectroscopy, X-ray diffraction measurement, atomic force microscopy, scanning electron microscopy, and micro-Raman spectroscopy. For the first time, the impact of high plasma density to improve optical quality, or at least to preserve optical quality, and the impact of ion energy reduction at high density causing the intermixing enhancement were reported.

Chapter 5 presents the general theoretical account of interdiffusion in quantum wells and numerical method for electronic structure calculation for the quantum well. A description of the finite difference method to calculate the band structure of the interdiffused QW including the strain effect is documented. The semi-empirical model of plasma induced defect has been validated, giving a further understanding of inductively coupled plasma enhanced QWI using Ar plasma.

Chapter 6 documents the feasibility of plasma induced QWI in ICP system for the application of photonic integrated circuits. The investigation of spatial resolution is described with the proposal to improve the spatial resolution using simple approach. Multiple bandgaps creation in plasma induced QWI is presented using single step process. The extension study of plasma induced QWI to other systems is described for universal approach demonstration using this technique. This chapter highlights the simple photonic device demonstration using Ar plasma induced intermixing to monolithically shift the bandgap of the material in the form of extended cavity laser (ECL) diode. Finally, Chapter 7 summarises the major findings of this work and puts forth necessary recommendation for future work.

2. BACKGROUND INFORMATION

In this chapter, the background information of III-V compound semiconductors and the need for monolithic integration are presented. The existing QWI techniques, advantages and disadvantages of each technique and requirement of intermixing masks are also discussed. A brief introduction to the main experimental tools and characterisation techniques of the semiconductor material is documented.

2.1 III-V COMPOUNDS SEMICONDUCTOR

Silicon is by far the most commonly used crystal material for integrated circuits, though a significant volume of semiconductor devices and circuits employs III-V technology. Semiconductor laser technology has been becoming a big and important activity since the demonstration of epitaxial III-V heterojunction as early as 1906 followed by the first realisation of lattice matched double heterojunctions (DHs) in GaAs/AlGaAs system in 1967 [1]. For electronic applications, the III-V semiconductors offer the basic advantage of higher electron mobility, which translates into higher operating speeds and benefits of direct bandgap property. In addition, devices made with III-V compounds provide lower voltage operation for specific functions, radiation hardness (especially important for satellites and space vehicles), and semi-insulating substrates (avoiding the presence of parasitic capacitance in switching devices).

Numerous compound semiconductors are composed of two or more elements. Gallium arsenide (GaAs), for example, is a binary III-V compound, which is a combination of gallium (Ga) from column III and arsenic (As) from column V. Ternary compounds can be formed by elements from three different

columns, as, for instance, mercury indium telluride (HgIn_2Te_4), a II-III-VI compound. They can also be formed by elements from two columns, such as aluminum gallium arsenide ($\text{Al}_x\text{Ga}_{1-x}\text{As}$), which is a ternary III-V compound, where both Al and Ga are from column III and the subscript x is related to the composition of the two elements from 100 percent Al ($x=1$) to 100 percent Ga ($x=0$) or other III-V compound semiconductors, *e.g.* gallium arsenide phosphide ($\text{GaAs}_{1-y}\text{P}_y$), aluminum gallium arsenide ($\text{Al}_x\text{Ga}_{1-x}\text{As}$), aluminum gallium indium phosphide [$\text{In}_y(\text{Al}_x\text{Ga}_{1-x})_{1-y}\text{P}$], aluminum gallium indium arsenic [$\text{In}_y(\text{Al}_x\text{Ga}_{1-x})_{1-y}\text{As}$], and gallium indium arsenide phosphide ($\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$). For quaternary solid solutions such as $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$, the x represents the percent of group III elements, while the y represents the percent of group V elements. Pure silicon is the most important material for integrated circuit application, while III-V binary and ternary compounds are the most significant for the application of light emission, modulation, and detection.

For efficient emission or detection of photons, it is often necessary to constrain the process to very thin semiconductor layers. These epitaxial thin layers are grown on top of bulk semiconductor wafers and the resultant structure is called a heterostructure. Most of the continuously operating semiconductor lasers consist of heterostructures, a simple example consisting of 1000 Å thick GaAs layers sandwiched between somewhat thicker (about 10000 Å) layers of AlGaAs; all grown epitaxially on a GaAs substrate. The sandwiching and repeating of very thin layers of a semiconductor between layers of a different composition allow one to modify the bandgap of the sandwiched layer. This technique, called bandgap engineering, permits the creation of semiconductor materials with properties that cannot be found in nature.

2.2 MONOLITHIC INTEGRATION OF PHOTONIC DEVICES

The monolithic integration of several optoelectronics devices in optoelectronic integrated circuits (OEICs) was first proposed by Miller [2]. OEICs are of considerable interest for the development of telecommunication system. In OEICs, optical devices such as lasers and electronic devices such as transistors are integrated on a single chip for high speed operation since the parasitic resistance in electrical connections can be minimised from the closely packed devices.

Figure 2-1. InP based material is the most promising candidate for monolithic integration of optical functions as well as electronic functions [2].

The move of OEICs and PICs out of the research laboratory into the marketplace has been made possible by the availability of high-quality epitaxial growth techniques for building up lattice-matched crystalline layers. The monolithic InP based ternary (InGaAs) or quaternary (InGaAsP and InAlGaAs) PICs has become increasingly interesting for four important reasons in optical telecommunication. The first driving force is the attractive application for long-haul optical communication, such as trans-ocean submarine cable, since the signal dispersion and loss windows in optical fibre medium are minimal in the 1.3 μm and 1.55 μm wavelength ranges. The second motivation is to reduce the complexity of next-generation optical communication links, networking architectures and

switching systems for the multi-channel wavelength division multiplexing (WDM) systems. In a photonic integrated transceiver chip for WDM systems, the photonic integration of laser sources, low-loss passive waveguides, filters and photo-diodes lead to the compactness and improved performance of WDM systems, as compared to that of the discrete devices. The next principal stimulus is the inception of the fibre optic technologies and networks, with the movement of the line terminals from the Fibre to the Curb (FTTC) toward the Fibre to the Home (FTTH). Thus, it creates the need for reduced terminal costs and alternative module concepts. Finally, an important point is that the technology of the monolithic integration on InP substrate has achieved a maturity level at which PICs fabrication with a reasonable yield becomes feasible.

Figure 2-2. An illustration of photonic integration circuits with active and passive devices across single chip.

In the photonic integration process, each photonic component needs different material structure at very different in functionality to achieve the optimised performance. As a result, the ability to modify the bandgap energy and the refractive index of materials are important in order to realise PICs. The ability to control the bandgap across an InP-based semiconductor wafer is a key requirement for the fabrication of monolithic PICs. To monolithically integrate

optoelectronic devices, precise tailoring of the optical properties such as bandgap energy, absorption coefficient, and refractive index is required.

Figure 2-2 gives an illustration of photonic integration of a semiconductor laser with an internal electro-absorption (EA) modulator, low-loss passive waveguides, and photodetector as power and/or wavelength monitor. With current injection, the laser will be lasing at just above the energy band-edge. The lasing band-edge is below that of the energy band of the EA modulator so that the electro-absorption effect can be greatly utilised for modulation. The photodetector needs the highly absorbing band energy, while the passive waveguide and combiner will be highly absorbing at the lasing wavelength if it has similar energy bandgap, and thus it requires the operation at transparent region of material. In addition, the monolithic integrated wavelength tunable laser diode mainly consists of an active gain region, a wavelength selective tunable reflector, and/or tunable phase shifter across a device. Each section of wavelength tunable laser diode requires different bandgap energies and wavelength transparencies. As a result, it is essential to modify the bandgap energy and other material characteristics on the single substrate in order to realise the PICs on single chip.

Figure 2-3. Epitaxial growth and regrowth process (a) epilayer grown on semiconductor substrate (b) etch away portion of the epilayer (c) regrow a new epilayer in the etched region.

A number of bandgap engineering techniques have emerged for photonic device integration, and commonly used approaches are the growth and regrowth, selective area growth and QWI. Epitaxial growth and regrowth is the most versatile,

complicated and expensive technique which involves growing, etching and regrowing of QW layers at selected area on a bulk material as depicted in Figure 2-3. These layer structures are overgrown with the same upper cladding but with a different active region. This approach always suffers from a mode mismatch at the butt joint in the optical propagation coefficient or dimensions of a waveguide at regrown interface resulting in scattering and back-reflection losses. In addition, this process gives complex process steps and technology, low yield (due to difficulties of regrowing on a vertically etched surface and regrowing with high precision) and low throughput, and therefore adds cost to the final product.

Figure 2-4. Selective area growth process (a) Dielectric patterned onto bulk semiconductor (b) epilayer is grown (c) dielectric is removed

A different technique, selective area growth, utilises differences in epitaxial layer composition and thickness produced by growth through a mask to achieve spatially selective bandgap variation with basic process steps as shown in Figure 2-4. After epitaxy growth, the substrate is coated with a dielectric mask such as SiO_2 , in which slots with different widths are defined. The growth rate in the opened areas depends on the width of the opening and the patterning of the mask. No growth can take place on top of the dielectric cap. However, surface migration of the species can take place for some distance across the mask to the nearest opening. The advantage of this approach is the reduction in total number of processing steps. This process works well under a precisely controlled set of parameters but is difficult to manipulate in a generic fashion. The technique is quite limited with regards to the bandgap changes that can be achieved, it cannot be used to pattern the bandgap

across a wafer in two dimensions, and it suffers from the potential mismatch at the interface (Figure 2-5).

Figure 2-5. Typical butt-joint selective area growth of a regrown active-passive region view on (011) plan active area (a) in the centre and (b) on the top [3].

A third technique, which is generating considerable interest due to its simplicity, is quantum well intermixing. QWI is based on the fact that a QW is inherently metastable system due to the large concentration gradient of atomic species across the QWs and barriers interface. Hence, this allows the modification of the bandgap of QW structures in selected regions by intermixing (sometimes referred to disordering) the quantum wells with the barriers to form alloy semiconductors.

2.3 QUANTUM WELL INTERMIXING

QWI technique [4]-[6] has been found to be a very useful method to achieve photonic integration due to its ability to selectively fine tune the energy bandgap in different regions within the same epitaxial layer structure, through the interdiffusion between QW and adjacent barrier material. QWI is a post-growth technique in tailoring the energy bandgap across single chip, which generates a considerable interest due to its simplicity, compatibility, and effectiveness for many photonic applications. It enables various benefits such as excellent alignment, negligible reflection losses, and intrinsic mode matching. QWI has provided a very enticing vision for the future of optoelectronics.

Since the first demonstration of impurity-induced disordering in the AlAs/GaAs superlattice by W. D. Laidig et al [7] and in the InGaAsP material by W. E. Plano et al. [8], a number of QWI techniques have been developed. QWI has been extensively studied in III-V QW structures. The emerging technology of QWI, such as the techniques of impurity-induced disordering (IID) [7],[8] and impurity-free vacancy disordering (IFVD) [9], usually involves the introduction of the beneficial defects especially vacancies and interstitials to the QW material. During high temperature annealing, the impurities or created point defects alter the Fermi level and enhance the solubility of certain point defects [10], which result in an increase in atomic interdiffusion rate and promote QWI. The annealing process also recovers the crystal damage due to point defect creation for minimising optical and electrical degradation. This process causes graded QW bandgap profiles and, in general, results in an increase of the bandgap energy (as shown in Figure 2-6).

Figure 2-6. (a) Postgrowth bandgap engineering process using QWI technique and its QW energy band (b) unintermixed section (c) intermixed section

In general, QWI techniques need a precise control of parameters, which can affect to the final device performances. The proper design of QW heterostructure is required to achieve the desired characteristics of the intermixed devices, such as to the epilayer thickness, material composition, doping profile, the strain profile, etc.

Since they are based on a defect generation mechanism, the suitable annealing condition is necessary in restoring the crystallinity, while minimizing the surface out-diffusion and dopant redistribution from high temperature treatment, which may contribute to the significant intrinsic waveguide loss from free carrier absorption.

Using IFVD technique, no penetration of impurities is required and the degree of intermixing is controlled by the diffusion of vacancies at high annealing temperature. A QW structure capped with SiO₂ and annealed at these temperatures leads to the out diffusion of Ga and the vacancies that are created in the GaAs diffuse rapidly through the structure. When the vacancies cross QW interface, intermixing occurs. There are several IFVD techniques, namely dielectric cap induced intermixing [11], laser induced disordering (LID) [12], hydrogen plasma induced/suppressed intermixing [13],[14] and He-plasma-assisted InP defects induced intermixing [15]. The dielectric cap can be formed by the common deposition method of plasma-enhanced chemical vapour deposition (PECVD), anodic oxidation [16], sputtering process [17], and commercially spin-on-glass layer [18]. The IID techniques utilise surface doping diffusion or ion implantation of certain highly energetic ions to introduce impurities within the crystal to create point defects [10]. The IID techniques including the ion implantation induced disordering (IIID) using either active or neutral species [19],[20], focused ion beam implantation (FIB) [21]-[23], and proton irradiation [24]. The detail of various QWI techniques and their advantages and shortcomings will be described in the following paragraph.

2.3.1 Dielectric cap induced intermixing

This technique involves the formation of a dielectric capping material on the QW materials and subsequent high temperature annealing to promote the injection

of vacancies from the dielectric cap to materials and hence enhance the intermixing at selected area. For instance, in GaAs/AlGaAs QW materials, SiO₂ induces out-diffusion of Ga atoms during annealing and generates group III vacancies in the QW material. The thermal stress at the interface between the GaAs and the SiO₂ layer plays a major role. The thermal expansion coefficient of GaAs is ten times larger than that of SiO₂. During high temperature annealing, the bonding in the highly porous SiO₂ layer deposited using PECVD may be broken due to the stress gradient between the GaAs and SiO₂ film. Thus, the out-diffusion of Ga would help to relieve the stress in the GaAs. Nevertheless, As atoms may diffuse into SiO₂ during high temperature annealing. However the diffusion coefficient of As in SiO₂ is extremely low as compared to Ga. These Ga vacancies then propagate downward into the QW and enhance the interdiffusion rate of Ga and Al hence resulting in QWI [10]. After the intermixing process, the bandgap in the well materials becomes widened and the refractive index decreases.

The selectivity of this technique can be obtained using a Si_xN_y layer [25], a SrF₂ layer [26], other fluoride dielectric compounds [27], P-doped SiO₂ layer [28], Ga-doped spin-on-glass layer [29], and TiO₂ layer [30], as they inhibit the outdiffusion of Ga, hence suppress the QWI process. Using this technique, devices such as multiple wavelengths tuned laser and four channel waveguide photodetectors have been successfully demonstrated [31]. Although IFVD is one of the successful techniques employed in GaAs/AlGaAs system, this technique gives poor reproducibility in InGaAs/InGaAsP system. Furthermore, due the poor thermal stability of InGaAs/InGaAsP materials, IFVD process, which requires high temperature annealing, is found to give low bandgap selectivity in InGaAs/InGaAsP based QW structure. The poor reproducibility of IFVD is commonly originated

from several causes, such as fluctuations in the quality and thickness of deposited dielectric cap layer and the surface condition of QW material before cap deposition.

A universal QWI technique by sputtering SiO₂ cap on various QW materials by subsequent annealing was proposed [17]. The processing steps of the technique are very similar to those of IFVD, in which a SiO₂ cap is used to enhance intermixing. However, it was found that the technique yielded large bandgap shift at significantly lower temperature than that required for IFVD. This implies that, despite the processing steps being similar, the fundamental intermixing mechanism is very different. It is believed that during the sputtering stage, the bombardments of Ar ions create point defects in the form of vacancies and interstitials, thus enhancing the atomic interdiffusion rate. Another possible contribution to the intermixing process could be atomic out-diffusion during the annealing stage, a mechanism similar to that responsible for the IFVD process in the GaAs-AlGaAs material. The presence of an increased concentration of point defects could lead to an enhancement in the rate of such out-diffusion, and provide an additional enhancement to the intermixing rate.

2.3.2 Laser induced disordering (LID)

The LID technique is first demonstrated by Epler *et al.*, by using a continuous wave (cw) Ar⁺ laser with a power density of $\sim 320 \text{ kWmm}^{-2}$ to introduce encapsulated Si into the epitaxial layers as a source for IID, which takes place during thermal annealing [32]-[34]. Laser induced disordering (LID) is a promising QWI process to achieve disordering in InGaAs-InGaAsP QW technique due to the poor thermal stability in InGaAsP material system.

Photoabsorption-induced disordering (PAID) is a laser induced QWI technique developed in the InGaAs/InGaAsP system. It involves a process of band-to-band absorption of the incident cw laser radiation in the active region. In the PAID technique, a cw laser irradiation is absorbed in the QW regions and generates heat to cause thermal induced intermixing. Although the resultant material is of high optical and electrical quality, the spatial selectivity of this technique is limited by lateral flow to around 100 μm [35]. A modification of the PAID method, known as pulsed-PAID (P-PAID), uses high-energy Q-switched Nd:YAG laser pulses to irradiate the InP-based material. Absorption of the pulses results in disruption to the lattice and increase in the density of point defects. These point defects subsequently interdiffuse into QW during high temperature annealing and hence enhance QW intermixing rate. Although P-PAID can provide spatial resolution higher than 2.5 μm [36] and direct writing capability [37], the intermixed materials give low quality due to the formation of extended defects [38].

2.3.3 Impurity induced disordering (IID)

The mechanism of IID in GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ system was proposed by Deppe and Holonyak [10]. Among all of the QWI methods, IID is the only process, which requires the introduction of impurities into the QW materials in order to realise the intermixing process. These impurities can be introduced through focused ion beam, furnace diffusion and also ion implantation induced disordering (IIID). IIID is a relatively simple and highly reproducible intermixing process. IIID has the ability to provide high spatial resolution for the integration of small dimension devices and bandgap shifts can be controlled through the implantation parameters. This technique is commonly used to achieve lateral electrical and optical confinement in

semiconductors such that low threshold current and single lateral-mode operation can be obtained [39].

In InP based material, the degree of intermixing is proportional to the number of point defects created in the material by ion implantation process [19]. Thus, The IIID technique enables variation of intermixing degrees across 2D photonic devices on single chip at single implant step using different dielectric mask thicknesses as illustrated in Figure 2-7 [40],[41] thus making PICs in reality, simple and efficient. For this reason, the IIID process is of considerable interest for the integration of WDM systems, such as the multiple wavelengths laser, low-loss waveguide, modulator and even the detector.

The use of IIID technique through relatively high energy ion implant (from 18 keV to 8.6 MeV) with electrically inactive implant species (10^{10} to 10^{16} ions/cm²); such as arsenic, phosphorus, argon, fluorine and boron; needs a relatively complicated, specialised and expensive facilities. The electrically active species can cause deleterious effects in which they lead to increase in free carrier absorption losses. In contrast, neutral impurities exhibit high electrical resistivity in the intermixed regions and result in insignificant free carrier absorption losses. The neutral impurities are commonly used in IIID technique to reduce optical losses and leakage current in grating section DBR laser.

Figure 2-7. Selective Intermixing using IIID (a) QW structure (b) ion implantation on patterned mask (c) masked removal and the selectively controlled intermixing degree upon annealing

It has been observed that the degree of lattice damage increases with an increase in the ion implant energy and causes a) the reduction of residual purity and crystalline quality [19], b) the degradation of electron transport properties due to the unintentionally implanted ions around QW region [42]. At high implantation energy of 2 MeV, it was shown that implanting directly in the QW region causes a significant drop in luminescence intensity, which suggest that implantation creates non-radiative recombination centres that cannot be annealed out. Hence, lower ion energy to create the defects on the vicinity of QW active region is preferred to minimise the direct QW degradation after QWI process [43]. A large bandgap shift in GaAs/AlGaAs system was achieved by irradiating proton at energy of 40 keV [23]. PL intensity of intermixed material exhibited less appreciable loss with 40 keV than 2 MeV implant energy. The use of low ion implant energy at 360 keV in InGaAs/InP system later showed a comparable bandgap shift of 76 nm with point defects mainly introduced in the cap layer or in the upper cladding [40]. A blue-shifted bandgap of 35 nm is also reported using 18 keV arsenic implant on the partly laser structure and subsequent multiple annealing cycles with interrupted growth of the complete laser structure [44]. The indirect creation of the defects to the active region with lower energy minimises the creation of complex defects and the generation of significant free carriers [45], thus preserving the material quality after intermixing process.

2.3.4 Plasma induced Quantum Well Intermixing

Plasma machines, such as RIE, ECR, and ICP, are widely used in the semiconductor industry for etching a wide variety of materials including dielectrics and III-V semiconductors. It is known that the plasma etch machine can cause damage to the substrate, which is undesirable as it can cause degradation in the

electrical properties of the substrate. However, these properties can be recovered by annealing the substrate after the plasma exposure. A number of experiments have confirmed that defects generated from low energy ion (with 100s eV of ion impact energy) processes can penetrate deeply more than 100 nm into the substrate [46],[47]. The beneficial defects, created in the form of mobile point defects, are often desirable for QWI as these defects can promote intermixing in QW substrates, as shown in Figure 2-8.

Figure 2-8. Selective QWI using argon plasma induced QWI

Initial work has been done using H_2 plasma glow discharge in a RIE system on GaAs/AlGaAs structures. Up to 8 cycles of H_2 plasma exposure and annealing is required to produce a maximum bandgap wavelength blue-shift of about 24 nm [13]. Using similar process in RIE, hydrogen plasma was used to suppress the intermixing on GaAs/AlGaAs system by the modification of native surface oxide of GaAs material to form Ga_2O_3 [14]. There is a potential use of the defect creation using plasma machine to promote QWI. The initial work has been done using ECR system [48], followed by ICP system [49] and RIE system [50]. The Ar plasma was adopted since Ar is a noble gas with an atomic weight of 39.938 g/mol. As Ar is electronically neutral in the QW material, the intermixing effect is expected not due to the diffusion of active impurities such as Si or Zn as the case of the IID technique. The noble property causes relatively deep damage [51] with literally no chemical interaction with the sputtered species. In addition, the relatively high

atomic weight is able to produce the surface damage on the semiconductor device [52], therefore the selective intermixing process using this technique can be achieved in a single exposure-annealing step, as depicted in Figure 2-8.

2.4 EXPERIMENTAL TECHNIQUES

The aim of the section is to present the operation of the hardware employed in preparing and characterising the various samples. The main elements comprising the experimental setup will be described in the order in which they are encountered by the samples. Among topics presented will be 1) the sample design and growth, 2) plasma machine, and 3) thermal processing using rapid thermal processor.

2.4.1 Quantum well structure

The study involved various samples designed and grown by different groups. A detailed summary of the QW material structure has been outlined in the Appendix A. The main structure for the Ar plasma induced QWI study is the InGaAs/InGaAsP five QWs structure grown by both the University of Sheffield and International Quantum Epitaxial (IQE) [53]. The structure was chosen as the technology of the InP-based material growth is matured covering a wide range of wavelength operation on the low-loss window of optical communication systems. A wide range of QW material including GaAs/AlGaAs and InGaAs/InAlGaAs QWs laser structure were employed to complete the universality of plasma induced QWI process. The plasma induced damage study was carried out using the GaAs/AlGaAs multiple widths QWs as a sensitive damage probe.

2.4.2 Plasma process

The plasma is an ionised gas with equal numbers of free negative and positive charges. The free charges are produced by passage of electric current

through the discharge. The positive charge is mostly of singly ionised neutrals from which single electron has been stripped. The majority of negatively charged particles are usually free electrons. A plasma reactor, as shown in Figure 2-9(a), usually consists of parallel plate electrodes in a chamber that can be maintained at low pressure (0.01 to 1 Torr). When a high frequency voltage is applied between the electrodes, the current flows and the plasma is formed which emits a characteristic glow. Reactive radicals are generated by this electrical discharge. Some of these reactive radical combine with the exposed substrate wafer in the chamber and form volatile products as an etching process. Plasma etching can proceed via physical sputtering, chemical reaction and ion-assisted mechanism. During sputtering process, substrate material is removed by purely physical process. Energetic ions crossing the sheath transfer large amounts of energy and momentum to the substrate, causing surface material to be ejected. This process requires high energy and thus provides the least selectivity etching solution. Other disadvantages are also encountered, low etching rate, surface trenching and damage to the substrate from ion bombardment and implantation.

Figure 2-9. A schematic diagram of (a) a simple plasma reactor and (b) ICP reactor.

Chemical and ion/chemical mechanism differ from sputtering such that the surface material is first converted into high vapour pressure products to facilitate removal. Mass loss is then evaporative, so that etching can be done at higher pressure when any sputtered material is scattered back onto the surface by gas collision. Volatility is essential for chemical and ion enhanced plasma etch process. Chemical etching is the most selective but it is usually isotropic or non-directional. Directional or anisotropic etch can be achieved with ion-enhanced etching. However, energetic ion-enhanced etching induces surface damage due to impinging ions.

An ICP reactor has been developed as high plasma density (10^{10} - 10^{12} cm⁻³), low gas pressure (<10's mTorr) sources for etching and deposition of semiconductor materials. The ICP sources are efficient because large RF currents can be circulated in the plasma for heating the plasma electrons and the plasma produced can be relatively uniform. Efforts has been carried out to reduce or control the amount of capacitive coupling of the input power compared with the inductive power coupling because only the inductive power will efficiently produce the high-density plasma. As shown in Figure 2-9(b), the ICP system used in the experiments was a Plasmalab System100 machine from Oxford Instruments Plasma Technology. The system uses an inductive coil to generate high-density "remote" plasma with no direct contact between the plasma and the substrate. The plasma is created by electromagnetic induction when an alternating high frequency current in the RF inductive coil causes a circulating current to flow in a low-pressure plasma. The plasma can be initiated by the induction coil or by the power applied to another system electrode, usually RF power to the substrate electrode. The 13.56 MHz radio frequency (RF) and ICP power supply can provide independent control on ion

bombardment energy and ion current density with the operating power up to 500 W and 3000 W, respectively. To create a high current in the RF coil in this non-resonant design without high reflected power, an RF tuning network with automatic matching is mounted close to the coil. The ICP power is supplied via a coaxial N-type 50 Ω connector on the matching unit. The matching unit contains motor-driven vacuum capacitors and a directional detection unit, which acts to make the load impedance presented to the RF generator as close as possible to 50 Ω . During plasma exposure, the chamber base pressure is maintained at $5 \cdot 10^{-5}$ Torr. The ICP chamber is equipped with a water circulator to maintain the table temperature at 60 °C. The measurement using thermocouple, which is attached on the chamber's wall, shows the increase up to 3 °C during the initial plasma strike and reaches the steady state temperature in less than 10 seconds. However, it should be noticed that the reading from the table temperature does not reflect the actual sample temperature during plasma exposure. The ICP system is equipped with a back side He-cooled electrode with quartz as a wafer susceptor. The QW samples were placed on the silicon substrate to provide a fairly large (168 W/mK) heat conduction.

From Figure 2-10(a), the RF-induced DC bias reduces with the increase in ICP power and the decrease in RF power during Ar plasma exposure. The rise on the pressure does not give effect to the RF-induced DC bias on the chamber significantly. High ion density in the order of 10^{16} m^{-3} can be generated in the ICP chamber with the different chamber pressures. The measurements of the plasma densities, thus ion current density, under various plasma conditions were made with Langmuir probes. The probes were biased at - 30 V for consistency to obtain the ion saturation behavior. The variation of the ion saturation current with voltage was then used to calculate the plasma densities based on an orbital ion motion model for

Langmuir probes [54]. Figure 2-10(a) shows a nearly linear increase in Ar ion current density with the increase in ICP power with the fixed RF power of 100 W. The lower working pressure provides higher ion current density generated in chamber. There is no sign of saturation behaviour (unlike ECR machine), so higher power can be used to get higher ion fluxes if required.

Figure 2-10. The ICP characteristics as an increase in ICP power to (a) RF-induced DC bias at 100 and 480 W RF power and (b) ion number density at 100 W RF power.

2.4.3 Annealing process in Rapid Thermal Processor (RTP)

Rapid thermal processing in the time regime of 1-5 minutes has received great attention in recent year as compared to the conventional furnace processing due to some spectacular advantages, such as minimisation of dopant redistribution and outdiffusion [55]. RTP system is a single-wafer reactor in which the thermal process is carried out. The RTP consists of four major components: (1) energy source, (2) process chamber, (3) temperature measurement apparatus, and (4) temperature control.

Figure 2-11. The RTP machine and the capping configuration for QWI process.

A schematic diagram of a typical RTP system using tungsten halogen lamps is shown in Figure 2-11. The process chamber is usually made of quartz, silicon carbide or stainless steel, and has quartz windows for the optical radiation to illuminate the wafer. A measurement system is placed in a control loop to set wafer temperature. The wafer temperature in an RTP system can be measured with a non-contact optical pyrometer or a thermocouple. After defects creation using the plasma exposure, the exposed materials are annealed using a Jipelec/Jetstar rapid thermal processor (RTP) in N_2 atmosphere to prevent contamination. The temperature was controlled by a thermocouple with a high accuracy of $\pm 1^\circ C$ (see Figure 2-12). Two fresh pieces of GaAs proximity caps were used to provide As over-pressure environment during the annealing process and further to prevent the sample surface from As outdiffusion. The annealing condition is chosen from the thermal stability test of the QW materials using RTP, at which the materials start to experience an appreciable bandgap shift induced by other mechanisms while avoiding thermal induced damage. The surface point defects diffuses down to the QW active region during high temperature annealing process and subsequently promotes intermixing between the wells and barriers to form alloy semiconductors. The end result of this process is an increase in the QW bandgap energy. In addition,

the annealing process also removes the crystal damage induced by the QWI technique.

Figure 2-12. The RTP temperature profile (a) during calibration on temperature range between 200 and 1200 °C and (b) during QWI process. The actual process (dotted line) deviates from the setting temperature (solid line) at about ± 1 °C.

2.4.4 Oxide deposition process for the intermixing mask

The oxide deposition is an important part in the common semiconductor process. In the plasma induced QWI technique, the oxide layer, such as SiO_2 and Si_xN_y , acts as the cap layer to prevent the damage creation on the sample surface during exposure. Utilising this approach, the spatial control of bandgap across the sample can be achieved. In the fabrication process of the devices, the oxide layer is used to be a common etch mask to provide selectivity of intermixing to the III-V compound material. In the active device process, good electrical insulation is provided by the oxide layer. In this work, the adopted oxide for the intermixing mask was deposited by either plasma enhanced chemical vapour deposition (PECVD) or electron beam evaporation.

In a PECVD system as shown in Figure 2-13(a), the plasma energy supplied by an external RF source takes the place of heating to generate species that

subsequently react and deposit on substrate surfaces. Significantly, excessive heating and degradation on the substrate can be avoided by using plasma electron kinetic energy instead of thermal energy. Besides the aspect of generating reactive species at much lower processing temperatures compared to conventional chemical vapour deposition (CVD) processing, the ion bombardment can be used to modify film characteristics. PECVD processes can be classified into many sub-processes, such as plasma evaporation deposition, plasma sputtering deposition, plasma ion plating, and plasma nitriding. PECVD processes for semiconductor processing are generally carried out at pressures of 1 mTorr to 20 Torr, substrate temperatures in the range of 100 to 500 °C, RF power densities $<0.5 \text{ Wcm}^{-2}$, electron densities of 1.0×10^8 to $1.0 \times 10^{12} \text{ cm}^{-3}$, electron mean free paths of $<0.1 \text{ cm}$, and average electron energies of 1 to 6 eV.

Figure 2-13. The schematic diagram of (a) PECVD reactor and (b) electron beam evaporator.

One of the major advantages of PECVD processing is its flexibility for depositing films with desirable properties. For conventional thermal CVD processing, physical and chemical properties of the deposited film pertaining to its stress, conformality, density, moisture resistance, and gap-fill properties can be

altered by changing the composition and/or type of reactive species. In PECVD, this can be accomplished by varying deposition parameters such as temperature, RF power, pressure, reactant gas mixture ratio, and type of reactant. For example, SiO₂ films coated with Tetra Ethyl Ortho Silicate (TEOS) generally show better step coverage or conformality than those deposited with silane in a PECVD process. For PECVD of SiO₂ films, properties can be modified not only by changing the type of reactive species, but also by the extent of ion bombardment.

The electron beam evaporator is utilised to evaporate various materials, including the metal and dielectric. As an alternative of oxide deposition using PECVD machine, the non-stoichiometric SiO₂ layer can be evaporated using the same machine. A simple evaporator configuration is shown in Figure 2-13(b). In this study, instead of SiO₂ mask, Au evaporation is used to provide an excellent intermixing mask during Ar exposure. The 50 nm thick gold layer is sufficient to block the radiation damage on the sample, thus minimises the damage creation for the spatial resolution study using plasma exposure. The p-type electrode (Ti/Au) and n-type electrode (Au/Ge/Ni) for laser devices were deposited using the electron beam evaporator. Initially, QW materials are loaded into a high vacuum chamber on the rotating holder with a controllable heater. The source material is loaded into a crucible, heated and melted by the high energy electron beam. An electron gun under the crucible ejects an intense, high-energy beam. A strong magnetic field bends the beam causing it to be incident on the surface of the solid charge. The beam is rastered across the solid charge to melt the material in the crucible and produce vapour. Low pressure in the chamber enables the vapour to travel in a straight line and strike the surface of the samples where they are deposited as a thin film layer.

2.5 CHARACTERISATION TECHNIQUES

In this section, two main characterisation systems undertaken are detailed, that are photoluminescence (PL) and micro-Raman spectroscopy. Both measurements are widely known as a non-destructive and indirect technique to study the material properties after intermixing process.

2.5.1 Photoluminescence spectroscopy

PL is used to study the fundamental recombination process in the semiconductors, to characterise the optical quality of material, and to study bulk or epitaxial films for the inter- and intra-wafer variation. When a piece of semiconductor is under a non-equilibrium condition, radiative recombination will take place. A free electron and a free hole are created whenever a photon of energy greater than the energy gap is absorbed in the crystal. This electron and hole can then be bound together by an attractive coulomb interaction force to form an electron-hole pair, which is known as exciton. Excitons are unstable with respect to radiative recombination in which the electron combines with the hole in the valence band (VB), accompanied by the emission of a photon. The exciton recombination can also occur without the release of a photon as non-radiative recombination. In the application of the semiconductor as an optical device, the number of non-radiative recombinations should be less when compared to the radiative recombinations [56].

Figure 2-14(a) shows the different electron-hole radiative recombination paths in which the excess carrier density decays. The recombination of an electron in the conduction band (CB) with a hole in the VB gives a band-to-band (B-B) transition. Similarly the recombination between a captured electron with a free hole

in the VB produces a donor-to-valence (D-V) transition. On the other hand, the recombination between a free electron in the CB with a captured hole gives rise to a conduction band-to-acceptor (C-A) transition. Both D-V and C-A transitions are referred to as free-to-bound (F-B) transitions. If two bound particles recombine with each other, a donor-to acceptor (D-A) pair transition ensues [57].

Figure 2-14. (a) Various electron-hole recombination paths in a direct bandgap semiconductor (b) Illustration of Fermi level distributions at different temperatures

In the case of QW structures, when the QW thickness is smaller than Bohr radius, the exciton binding energy will be the Rydberg value in two dimensions, R_{2D} , which is different from that in three dimensions, R_{3D} . The value of R_{3D} is 4.2 meV for bulk GaAs and 4 meV for bulk InP. The binding energy in the 2D limit is given by

$$R_{n,2D} = R_{3D} \left(n - \frac{1}{2}\right)^{-2}, \quad (1)$$

where n is the quantum level. The increase of the exciton binding energy in a 2D system implies that QW structures have their optical properties dominated by exciton effects even at room temperature. The recombination of the exciton in QW structures always occurs at the $n = 1$ electron-heavy hole (E_{1h}) transition since this level has the highest exciton binding energy. The exciton effects in the absorption spectra of an InP are illustrated in Figure 2-15.

Figure 2-15. (a) Absorption edge spectrum of an InP including exciton effects and bulk (3D) density of states. (b) Two dimensional energy band in a QW has a step function density of states. (c) Absorption edge spectrum predicted for an InP QW with a step function density of states is compared with that for bulk InP, including the contribution from exciton creation.

PL measurement is usually performed below room temperature as it produces a sharper and smoother profile. At lower temperature, the linewidth or the full-width at half-maximum (FWHM) of the profile is generally smaller. This is due to lesser phonon vibration in the crystal at lower temperature, the less phonon scattering, and thus the less sideband intensity is obtained. At room temperature, the large concentration of phonons and the exciton levels merge into the continuum absorption spectrum. Therefore, the absorption spectrum from excitons can hardly be separated from the continuum absorption spectrum and this broadens the linewidth. Also, at lower temperature, the charge carrier density decreases and reduces the sideband intensity. The decrease in the charge carrier density is due to the change of the Fermi level to a more abrupt profile at lower temperatures, as shown in Figure 2-14(b). Besides, the intensity of the PL spectrum is higher at

lower temperature owing to lesser phonon scattering, which leads to a higher recombination efficiency.

At lower temperature, the PL peak wavelength obtained is shifted to lower wavelength. This can be explained by the increase in the bulk energy bandgap at lower temperature, which is formulated as:

$$E_g = E_{go} - \frac{\alpha T^2}{(\beta + T)}, \quad (2)$$

where E_g is the bandgap energy at temperature T , E_{go} is bandgap energy at 0 K, T is the temperature in Kelvin, and α and β are empirical constants [56]. This equation governs the temperature and bandgap difference for ternary compounds. Quaternary compounds are also roughly governed by this equation with a certain degree of error. From the equation $E = hc/\lambda$, where c is the velocity of light and λ is the wavelength, the peak PL wavelength attained would be shorter. Besides, the decrease in phonon vibration at lower temperature also affects the shift in the wavelength peak. Although the mean value of the vibration is always equal to zero, there exists a root-mean-square value that decreases as temperature decreases, thus lowering the peak PL wavelength.

PL measurements were performed at room temperature (RT) and low temperature on the samples to assess the degree of intermixing. For low temperature measurement, the sample is mounted on a holder and immersed into liquid nitrogen for 77 K measurement. The excitation source is an Nd:YVO₄ laser with maximum power of 400 mW and peak wavelength at 1.064 μm for long wavelength (1.1-2 μm) measurement, while the Ar-ion laser source with a peak wavelength of 514.4 nm is used for short wavelength (0.6-1 μm) measurement. The laser beam is focused into a 3 dB fibre coupler. An optical chopper is used to modulate the laser

beam such that signals can be processed by the lock-in amplifier. The PL irradiation from the sample is collected by one end of the 3 dB coupler and guided into the monochromator. The PL spectrum is decomposed by optical grating in an Oriel monochromator and is detected by a thermo-electric (TE) cooled InGaAs photo-detector. A SR-830 lock-in amplifier processes the output signals from the detectors. Computer interface is used to control the PL measurement. This setup has the advantage of fast measurement as compared to loading sample into conventional low temperature measurement at 4 K using cryostat for cooling, which takes up to hours to ramp down to low temperature. However, in the initial study of the high density effect to the optical quality after intermixing process, the PL measurements were carried out at 4 K in order to minimise the effect of phonon vibration on the PL emission using an Ar-ion (514.5 nm) laser for excitation and a liquid nitrogen cooled Ge detector associated with a conventional lock-in technique.

Figure 2-16. The schematic diagram of the photoluminescence measurement setup

The PL mapping was done to get a spatial bandgap profile and its uniformity after selective QWI process at room temperature. The system scan has a resolution of 100 μm due to the limitation of stage controller. The illumination wavelength is at 1.064 μm using Q switch laser with a ~ 10 μm spot diameter of the focused laser

beam and 22.6 mW output power. The PL spectrum is decomposed by optical grating (150 g/mm) through a 0.5 mm slit width and a filter for 1.064 μm wavelength and is detected by a TE cooled InGaAs photo-detector. Thus, the spatial resolution of the PL map is 100 μm , which is limited to the stage controller.

2.5.2 Micro-Raman spectroscopy (MRS)

Among the various established characterisation techniques, MRS has been known as a non-destructive method to examine material properties based on the lattice vibration, especially QWs grown on binary, ternary or quaternary materials. Raman scattering is an interaction of light with the optical modes of lattice vibration. In a Raman scattering experiment, visible light from a polarised monochromatic laser is irradiated onto the sample. A small fraction of light is scattered by atoms and some of this fraction of light interacts with the sample to excite the vibrational mode. When this occurs the energy of the scattered light is reduced by an amount corresponding to the energy of the vibrational transition. This inelastic scattering is known as Raman scattering and is accompanied by the creation or annihilation of a phonon. The conservation of energy in the scattering process gives:

$$h\nu_s = h\nu_i \pm h\nu_p, \quad (3)$$

where subscripts s , i , and p represent the scattered radiation, incident radiation, and phonon respectively. The minus sign denotes emission of a phonon and the plus sign denotes absorption of a phonon [58],[59]. The two processes are termed as Stokes and anti-Stokes respectively. As can be seen in Figure 2-17, the intensity of Stokes is much higher than that of the anti-Stokes, and therefore, only they are recorded in the Raman spectrum.

Figure 2-17. Raman spectrum with Stokes and anti-Stokes lines

Raman spectroscopy is a non-destructive method for studying transformations between crystalline and amorphous phases, superlattice, and alloy structure. It has been used to investigate the structural and electrical damages after processing, the composition of mixed compounds, layer orientation, stress, and crystalline perfection [60]-[62]. The information provided by a MRS analysis includes lattice dynamics as well as electronic properties. The lattice dynamics reflects structural information such as the identification of materials and compounds, including reacted phases at interfaces. Information such as the composition of mixed compounds, layer orientation, stress, and crystalline perfection could also be obtained. The information is obtained through the evaluation of the phonon frequencies, half widths, lineshape and their intensities in the Raman spectrum [56]. Raman scattering experiments are usually carried out using Ar-ion or Kr-ion gas lasers. The laser light is focused on to the sample and the scattered light is collected normal to the sample surface and analysed with a double monochromator. The scattered intensity can be measured for different polarisation conditions of the incident and scattered light. The observation of the lattice vibration mode is determined by selection rules, which are dependent on the

sample orientation. Table 2-1 summarises the symmetry selection rules for backscattering geometry for crystals with diamond and zinc blende structures [63],[64].

Table 2-1. Symmetry selection rules for backscattering from ideal semiconductors with diamond and zinc blende structures.

Raman Active Mode	Surface Orientation		
	$\langle 100 \rangle$	$\langle 110 \rangle$	$\langle 111 \rangle$
LO	Allowed*	Forbidden	Allowed*
TO	Forbidden	Allowed*	Allowed*

* Allowed for at least one polarisation configuration

The Raman measurement technique has been proposed for characterising QWI processes with high spatial resolution through shifts in the Raman-mode energies and their linewidth [65]. MRS provides further information about the semiconductor lattice after QWI by studying other features of the mode spectra, such as relative-mode amplitudes and integrated-mode area. In this work, the Raman spectra were taken in backscattering configuration. An Ar laser of 514.5 nm wavelength, 20 mW, with a spot diameter from 0.4 to 1.2 μm was used as excitation source. The number of data set average was set at three for higher signal to noise ratio. The small spot size (0.4 μm) of excitation source provides a highly sensitive measurement of the in-plane spatial resolution in addition to the PL measurement.

3. OPTIMISATION OF PLASMA INDUCED QWI

In this chapter, a simple design of experiment (DOE) method using Taguchi's matrix to optimise the plasma system parameters is presented. With increasing understanding of the chemical and physical plasma processes, the optimisation aims to obtain the large bandgap blue-shift with minimum linewidth broadening using the ICP and the RIE machine to alter the material bandgap energy.

3.1 THE TAGUCHI'S DESIGN METHOD

The main parameters affecting the surface defects creation from the Ar plasma exposure involve a) gas flow rate, b) chamber pressure, c) RF power, and d) ICP power. Thus, the optimisation and characterisation of this process is complex. Experimenting with the process variables one at a time or by trial and error until a first feasible combination is found, is a common approach to attain optimisation. However, this approach can lead to a very long and tedious time span for completing the experiment. Varying one factor at a time requires experimental configurations. This "full factorial" approach, where all possible combinations of parameter values are tried, is prohibitive.

The Taguchi's robust design method is utilised for the optimisation of plasma induced QWI technique with the consideration of large bandgap shift and minimal linewidth broadening. Taguchi method [1], developed by Dr. Genichi Taguchi, attempts to identify and control critical variables that cause deviations to occur in the process quality. The entire concept can be described in two basic ideas:

1. Quality should be measured by the deviation from a specified target value, rather than by conformance to preset tolerance limits

2. Quality cannot be ensured through inspection and rework, but must be built in through the appropriate design of the process.

Taguchi methods emphasise the attainment of the specified target value and the elimination of variation. Through the proper design of a system, the process can be made insensitive to variations, thus avoiding the eventualities of rejection and/or rework. This technique provides a more systematic and efficient approach for determining near optimum settings and the inter-relationship of the process parameters. The robust design method uses orthogonal arrays (OA) to study the parameter space, usually containing a large number of process parameters, with a small number of experiments. Based on design of experiments (DOE) theory, Taguchi's orthogonal arrays provide a method for selecting an intelligent subset of the parameter space. Using orthogonal arrays significantly reduces the number of experimental configurations. The number of columns of an OA represents the maximum number of factors that can be studied using the array. Some of the commonly used orthogonal arrays are shown in Table 3-1.

Table 3-1. Common OA with number of equivalent full factorial experiments

Orthogonal Array	Factors & Levels	No. of Experiments
L4	3 Factors at 2 Levels	8
L8	7 Factors at 2 Levels	128
L9	4 Factors at 3 Levels	81
L16	15 Factors at 2 Levels	32,768
L27	13 Factors at 3 Levels	1,594,323
L64	21 Factors at 4 Levels	4.4×10^{12}

From Table 3-1, it is obvious that the number of experiment will be greatly reduced, especially when large number of factors and levels is involved. For example, using an L9 OA means that 9 experiments are carried out in search of the

81 control factor combinations, which gives the near optimal mean, and also the near minimum variation away from this mean.

3.2 THE OPTIMISATION PROCESS OF ICP PARAMETERS

Six basic steps are utilised in the optimisation process using Taguchi's method. The first four steps are used for planning the experiment. In the fifth step, the experiment is conducted. The experimental results are analysed and verified in the sixth step. The optimisation steps are to: (a) identify the main function, (b) identify the quality characteristics to be observed and the objective function to be optimised, (c) identify the control factors and their alternative levels, (d) design the suitable matrix experiment, and define the data analysis procedure, (e) conduct the matrix experiment, and (f) analyse the data and determine near optimum levels for the control factors.

1. Identify the main function

ICP machine which can provide the controllable beneficial point defects is utilised for the intermixing process. The InGaAs/InGaAsP QW laser structure on InP substrate was chosen for the optimisation as this material will be a major part of this work. The detail of epilayer structure has been given in Appendix A.1.

2. Identify the quality characteristics to be observed and the objective function to be optimised and studied

A large bandgap shift of InGaAs/InGaAsP QWs laser structure with no appreciable linewidth broadening after plasma exposure and subsequent annealing process is taken to be the quality characteristics to be observed. The main objective is to study and optimise the attainable bandgap shift with minimal linewidth broadening.

3. Identify the control factors and their alternative levels

In this experiment, Ar flow rates, chamber pressure, RF power, and ICP power are the control factors. In the optimisation process, three levels are selected for each factor. The level of a control parameter refers to the number of test values to be analysed. The first level is taken as the initial operating condition. The subsequent levels are taken sufficiently far apart to predict the non-linearity behaviour of the process parameters.

4. Design the matrix experiment and define the data analysis procedure

The selection of the appropriate orthogonal array to fit the experiment requires the calculation of the total degrees of freedom. This is done in order to find the minimum number of experiments that must be performed to reach a near optimum parameter set. One degree of freedom is associated with the overall mean regardless of the number of control factors such that the degrees of freedom are equal to the number of levels -1 . The tabulated values assigned to the different levels of each parameter are shown in Table 3-2.

Table 3-2. Values assigned to different levels of control parameters

Level	Ar flow rate (sccm) (F1)	Pressure (mTorr) (F2)	RF power (W) (F3)	ICP power (W) (F4)
1	10	10	100	1000
2	50	50	300	2000
3	80	80	480	2900

The tabulated values assigned to the different levels of each parameter are shown in Table 3-2. From Table 3-2, three levels for each of the four factors were set for this optimisation process. According to the calculation of the degrees of freedom, each factor contributes to 2 experiments. As a result, four factors with 8 experiments add up with an overall-mean experiment, at least 9 experiments are

required to be done in order to reach a near optimum case. This fits nicely into Taguchi's standard L9 array, as shown in Table 3-1. In order for an array to be a viable choice, the number of rows must be at least equal to the degrees of freedom required for the optimisation. L9 array is chosen as it has 8 degrees of freedom and it can handle four factors at 3 levels. The exposure combinations using ICP parameters are given in Table 3-3.

Table 3-3. L9 (3^4) Orthogonal Array

N ⁰ .	F1	F2	F3	F4
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

N^0 is the number of experiments

5. Conduct the matrix experiment

Table 3-4. The matrix experiment for optimisation in InGaAs/InGaAsP laser structure.

N ⁰	Setting level for each etching parameter			
	Ar flow rate (sccm) (F1)	Pressure (mTorr) (F2)	RF power (W) (F3)	ICP power (W) (F4)
1	10	10	100	1000
2	10	50	300	2000
3	10	80	480	2900
4	50	10	300	2900
5	50	50	480	1000
6	50	80	100	2000
7	80	10	480	2000
8	80	50	100	2900
9	80	80	300	1000

The matrix experiment given in Table 3-3 is conducted in search of the 81 control factor combinations, which gives the near optimum mean, and also the near minimum variation away from this mean. The InGaAs/InGaAsP QWs laser structure were cleaved at 2x2 mm size in order to observe the bandgap shift and linewidth broadening simultaneously using different variation of ICP parameters. Each sample was exposed under Ar plasma in ICP system for 5 minutes under the conditions as stated in Table 3-4 and was annealed at 600 °C for 2 minutes. The intermixed material was measured using PL spectroscopy before and after QWI process at room temperature.

6. Analyse the data and determine near optimum levels for the control factors

Table 3- 5. The bandgap shift and its linewidth broadening for each level.

Level	Bandgap shift / linewidth broadening (nm)			
	Ar flow rate (sccm) (F1)	Pressure (mTorr) (F2)	RF power (W) (F3)	ICP power (W) (F4)
1	10/14	29/12	13/11	51/25
2	29/14	28/27	35/17	26/8
3	52/20	46/13	60/26	16/14

Since the experimental design is orthogonal, it is possible to separate out the effect of each factor. The mean bandgap shift and the mean linewidth broadening for each level of the 4 control factors were measured and are tabulated in Table 3-5. The bandgap energy blue-shift and the corresponding linewidth broadening as a function of Ar flowrate, chamber pressure, RF power and ICP power were plotted and the results are shown in Figure 3-1(a) to (d). The dependency plots indicate that for large bandgap energy blue-shift and small linewidth broadening, the following process parameters are required: high Ar flowrate, high working pressure, high RF power and low ICP power.

Figure 3-1. Bandgap energy blue-shift (solid) and linewidth broadening (dashed) versus (a) Ar flowrate, (b) Chamber pressure, (c) RF power and (d) ICP power.

3.3 THE OPTIMUM BANDGAP TUNING OF ICP PROCESS

Figure 3-2. Bandgap energy blue-shift (solid) and the linewidth broadening (dashed) as a function of exposure time (Ar flowrate – 80 sccm, Pressure – 80 mTorr, RF power – 480 W and ICP power – 0 W)

From analysis of dependency plots in Figure 3-1, it is noted that the most-influential parameters that can increase the bandgap shift is to employ the small ICP

power. A subsequent experiment was carried out with an extreme condition without ICP application (ICP power = 0 W), with the other settings: Ar flowrate – 80 sccm, working pressure – 80 mTorr, and RF power – 480 W with exposure duration of 2, 2.5, 5, 10, and 15 minutes, respectively. The bandgap energy blue-shift is depicted in Figure 3-2. The bandgap saturation was observed after 5 minutes, in agreement with the previous study of saturation magnitude of created defects [2]. The optimum bandgap blue-shift as large as 80 nm has been achieved without ICP application.

Scaling down the low ICP power for optimising the bandgap blue-shift, further experiments were conducted with small ICP power from 0 to 500 W with other parameter settings fixed. As the ICP power increases, the ion induced bombardment energy decreases with the result of the bandgap enlargement. The result from Figure 3-3 shows that the bandgap of the QWs have been blue-shifted by as large as 104 nm after exposure to plasma for 5 minutes with ICP power of 500 W (corresponding RF induced DC bias was -730 V). This large bandgap shift with no appreciable linewidth broadening of intermixed sample is attributed to higher ion density to promote desirable point defects on the QWs surface than the bandgap shift obtained without ICP power application. The reproducible bandgap shifts were obtained with the bandgap shift variation of less than 5 nm obtained from the similar batch of samples using the optimised ICP process conditions as previously described. The wavelength discrepancy could be mainly due to lack of temperature control of the substrate, as the He-back side cooling system in the ICP system was not utilised.

Figure 3-3. (a) The optimum bandgap energy shift and the linewidth broadening versus ICP power; (b) The PL spectra of using 500 W ICP power for 5 minutes.

3.4 THE TAGUCHI'S OPTIMISATION OF THE RIE PARAMETERS

As the damage can be introduced by various plasma systems, a further exploration of plasma induced QWI using low density plasma from RIE machine is important to demonstrate the universality of plasma induced damage for QWI and to provide a comparative study to that of high plasma density from ICP machine. The study is expected to provide the comparison study of plasma induced damage nature due to the plasma properties using different control factors of plasma system, such as the pressure, RF power, and Ar flow rate. The machine used in this study was a conventional parallel-plate RIE. The 13.56 MHz RF power supply can provide up to 500 W. The Taguchi's method is similarly applied to optimise the RIE parameters for plasma induced QWI purpose.

Table 3-6. Values assigned to different levels of RIE control parameters

Level	Ar flow rate (sccm) (F1)	Pressure (mTorr) (F2)	RF power (W) (F3)
1	20	40	100
2	50	80	300
3	80	120	480

Adopting the similar steps of ICP optimisation, three levels are selected for each factor. Instead of 5 minute exposure, longer exposure duration at 8 minutes was added to provide the possible effect of longer exposure to the more damage creation, due to the pure highly energetic ion bombardment taking place in the RIE system with relatively low plasma density. From Table 3-6, three levels for each of the three factors were set for this optimisation process with 2 experiments in each factor.

Figure 3-4. Bandgap shift obtained using RIE machine for 5 minutes (dotted line) and 8 minutes (solid line) versus (a) flowrate, (b) pressure, and (c) RF power

Figure 3-4 (a) to (c) suggests that for large bandgap blue-shift from RIE systems, following process parameters are required: medium flowrate, low process pressure, and high RF power. At 8 minute exposure, the bandgap shift seems to saturate beyond RF power of 300 W, indicating the damage saturation. A subsequent experiment was carried out using the following parameters: 50 sccm flowrate, 30 mTorr pressure, and 480 W RF power with exposure time up to 8 minutes. This process conditions produces the RF-induced DC bias of -738 V, which is comparable to that of the optimised ICP parameters.

Figure 3-5(a) shows that the bandgap shift increases at the short exposure times less than 5 minutes and saturates, indicating the defect saturation has been

reached. The saturation of bandgap shift after long exposure times also was observed in the ICP system, indicating the similar defect creation process after long exposure. Slightly less amount of bandgap shift at 8 minute exposure as compared to 5 minute exposure was found to be similar to the pulsed LID [3] and boron IID [4] that increasing the amount of damage above the optimum value lead to the smaller bandgap shifts due to the extended defects in the form of dislocation loops inhibiting the atom interdiffusion [4],[5]. PL spectra of the intermixed sample using 5 minutes exposure has been shifted as large as 73 nm. The linewidth broadening is about 12 nm, indicating that the degradation in the QW from the QWI process is minimal.

Figure 3-5. (a) Bandgap shift and linewidth broadening using RIE system as a function of time (for flowrate – 50 sccm, pressure – 30 mTorr, and RF power – 480 W). (b) PL spectra of the as-grown sample and intermixed samples at 5 minute.

The amount of the bandgap shift achieved using RIE system is comparable with the ICP system without ICP power application (ICP power = 0 W), indicating that the low plasma density nature to promote intermixing on both RIE and ICP system is similar and various plasma systems can be further adopted for QWI purpose. This is very useful finding whenever the extension work using other plasma system to achieve the sufficient bandgap shift for photonic integration. In

this work, the low energy Ar plasma induced QWI can achieve relatively high or comparable bandgap shift of 104 nm in ICP system and 73 nm in RIE system as compared to the implantation-induced QWI using 360 keV-Arsenic ion [6], up to 50 KV-plasma immersion Ar ion [7],[8] and 30 keV-Ar ion [9] in InGaAs/InP QW. This bandgap shift is adequate for the use of photonic integration purpose at the postgrowth level.

3.5 SUMMARY

The effect of the ICP and RIE process parameters on the QWI degree has been investigated and optimised using the Taguchi method. The bandgap shift saturation after long exposure was observed in both systems, suggesting the similar plasma induced defect mechanism. A bandgap blueshift of as large as 104 nm and 73 nm in a InGaAs/InGaAsP QW laser structure have been obtained after 5 minutes exposure to Ar plasma in ICP and RIE machine, respectively. The application of ICP power results in the intermixing degree enhancement at lower RF-induced DC bias, which is ascribed to the high ion density to promote beneficial point defects on the QW surface.

4. PLASMA INDUCED QWI: MECHANISM AND MATERIAL STUDY

In the first part of this chapter, a systematic study to understand the mechanism of plasma induced damage into material including an examination of dynamic nature of the intermixing is presented. The damage study on defect generation mechanisms is carried out using a non-invasive way using QW probe heterostructures located on the near surface of material. Having an understanding of plasma induced QWI mechanism, a systematic study of the intermixing effect and its impact on QW material quality is discussed briefly in the second part of this chapter using low temperature PL measurement and micro-Raman spectroscopy (MRS). High resolution double-crystal x-ray diffraction (HRXRD) method was used to obtain the interdiffusion between epitaxial layers. The atomic force microscopy (AFM) was employed to assess the surface morphology.

4.1 THE PLASMA INDUCED QWI MECHANISM

Plasma induced QWI in ICP system process involves two consecutive steps: (a) defects introduction at low ion energy by plasma exposure and (b) defect's drive-in to promote the intermixing between wells and barriers. A systematic study of each step is therefore necessary, after the determination of thermal stability of QW material due to the RTP process.

4.1.1 Thermal stability of QW material

The annealing process significantly affects the bandgap energy of QWs related to the interdiffusion of QWs constituent atoms and material properties. The long defect migration from surface to the QW active region requires a sufficiently high annealing temperature to diffuse down promoting intermixing while repairing

the damaged region from Ar plasma. However, if the annealing temperature is very high, a large equilibrium of defects occurs in the non-exposed region, resulting in undesirable intermixing. Thus, it is important to investigate the thermal behaviour of as-grown material in order to properly select the optimum annealing condition. The study of annealing behaviour gives information about the thermal stability of the material system, which affects the thermal budget of subsequent device processing, and a baseline from which the effects of enhanced intermixing can be used.

Figure 4-1. (a) PL spectra with different annealing temperatures on the bare (uncapped) InGaAs/InGaAsP QWs. (b) PL peak shift versus annealing temperature without cap (line), with 250 nm thickness of SiO₂ (dotted), and Si₃N₄ caps (dashed).

In order to understand the influence of annealing process, a thermal stability study from 500 to 650 °C was carried out on the as-grown sample of InGaAs/InGaAsP QWs laser structure. The annealing time was fixed at 2 minutes with a rise time of 1 minute, which would be short enough to minimise the surface decomposition while promoting QWI and sufficient to propagate the created surface defects. Figure 4-1 shows the bandgap shifts by annealing the uncapped, SiO₂

capped, and Si_xN_y capped as-grown samples. The annealing duration is fixed at 2 minutes, which is sufficient to drive the created defects into the QW active region while maintaining smooth surface morphology against the thermal induced material decomposition. The uncapped sample annealed at 600 °C had a small blue-shift of 1 nm with minimal linewidth broadening, while the SiO_2 -capped and Si_xN_y -capped samples were shifted by 13 and 6 nm, respectively. Further increase in annealing temperature caused rapid changes in thermal shifts in the capped samples but whereas in the uncapped samples this trend occurred beyond 620 °C. The shifts that occurred after annealing on the uncapped samples were mainly attributed to the in-diffusion of point defects from the InP substrate. Larger bandgap shifts were observed in the dielectric capped samples because the dielectric caps affect the QWI results through IFVD effects [1] due to the vacancies generated at the dielectric-sample interface under stress gradient caused by the difference in the thermal expansion coefficients. The bandgap shift due to the thermal annealing effect is insignificant in the uncapped sample annealed below 620 °C. Only small linewidth broadening occurred implies that the material quality has been preserved after annealing process. This is in good agreement with the reported annealing study on the influence of the defect density in S-doped InP substrates [2] and the effect of thermal stability on the QWs [3]. Larger bandgap shifts in samples annealed at higher temperatures indicate the thermal damage due to the possibility of thermally induced material decomposition. From the thermal stability study, it can be concluded that the annealing process at 600 °C is suitable for intermixing process of InGaAs/InGaAsP QWs to avoid large thermal shift in the unintermixed area as well as to minimise the thermal induced damage to the material. The optimum annealing temperature for other QW systems are determined using a

similar methodology of thermal stability test for universality of plasma induced QWI study.

4.1.2 The Argon plasma-induced-near surface defects

At low ion energy, the majority of the impinging ions of Ar plasma is stopped within the first few atomic monolayer of material and may cause lattice disruption and damage up to a depth of a few tens of nm [4]. The creation of surface defects was investigated initially using $\sim 2\ \mu\text{m}$ thick strained $\text{In}_{0.47}\text{Ga}_{0.53}\text{As}$ and lattice-matched $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ bulk epilayers grown on InP substrate using metal-organic vapour phase epitaxy (MOVPE). A systematic decrease in the room temperature PL intensity of the band-to-band transition as the exposure time increases under Argon plasma was observed. This systematic drop in PL signal is attributed to the damage creation from the lattice dislocations generated to the InGaAs bulk material by Argon plasma in ICP system, leading to the creation of non-radiative recombination centres.

Precise detection of plasma induced damage is, in general, difficult because it is believed to occur within a few tens of nm from the surface, thus requiring a highly sensitive probing technique. The damage distribution from Ar plasma exposure was probed in a non-invasive way using a PL emission from the multiple widths QW structure as a sensitive damage probe. The idea of probing the ICP enhanced damage is to measure the PL emitted from QWs buried at selected depths in the material [5]-[6]. The decrease in PL as a result of damage resulting in the presence of non-radiative recombination centre at a particular QW depth, if compared with the PL of the undamaged material, gives an indication of the damage profile. Due to the material limitation of InP-based QW probe structure, the

GaAs/AlGaAs QW probe structure was adopted (Appendix A.2). Using such structure with similar Ar ion bombardment conditions, the damage in InP based material is expected to be greater [7] and the created defects penetrate deeper to initiate the interdiffusion in the QW region [8].

Figure 4-2. PL spectra of GaAs/AlGaAs QWs probe samples for damage detection. (a) PL wavelength peak shift at 77 K for each QWs after annealing with different temperatures. The inset shows corresponding amount of wavelength peak shift in the y-axis. (b) The 77 K PL spectra obtained (i) before, (ii) after plasma exposure, and (iii) subsequent annealing on the exposed sample at 765 °C for 2 minutes.

The damage detection using quantum well intermixing probe requires a thermal stability test of the sample to determine the thermal shift with respect to the annealing temperature. The annealing time was fixed at 2 minutes with similar reason for InGaAs/InGaAsP thermal test condition. Figure 4-2(a) summarises the thermal shift from the 77 K PL measurement of bare GaAs/AlGaAs QWs probe against the temperature annealing, which each QW having similar trend in PL shift. Increase in annealing temperature caused the PL blue-shifts indicating the thermal induced interdiffusion due to the presence of the as-grown defects during the

growth. For all QWs, rapid changes in thermal shift occurred at annealing temperature beyond 780 °C. At 800 °C annealing temperature, five QWs have been blue-shifted more than 20 nm as compared to the as-grown (unannealed) sample. The threshold temperature, which was determined from the negligible average bandgap shift, occurred at 675 °C. In this annealing condition, average bandgap shift from all QWs is as small as 2 nm. This annealing condition would be desirable for analysis of the QWs bandgap shifts at a particular depth by driving-in the created defects due to Ar plasma exposure.

The plasma induced damage distribution range after exposure and subsequent annealing was investigated and traced. Figure 4-2(b) shows the comparison of normalised 77 K PL spectra to the deepest QW after exposure at 500 W ICP power for 1 minute and subsequent annealing. Annealing condition was chosen below the thermal stability of QW probe at 765 °C for 2 minutes, which had no significant effect on overall shift of QWs. The bandgap blue-shifts were 3 nm and 2 nm for the shallowest QW (QW1) and the deepest QW (QW5), respectively. Figure 4-2(b-i) clearly exhibits six peaks for the as-grown QW probe structure, one for each QW and the GaAs substrate at 822 nm. The peak of QW4 from the as-grown samples are broader and lower than the other QW peaks, which is most likely due to the presence of grown-in defects and the non-uniformity of the QW composition during growth. After exposure [Figure 4-2(b-ii)], the PL intensity from the shallowest QW (2.5 nm width) is evidently reduced by 32 %, suggesting that the high-density plasma exposure generates the near surface damage at a depth of more than 0.4 μm , leading to an increase in non-radiative recombination centres and a decrease in PL intensity. Upon annealing [Figure 4-2(b-iii)], the PL intensity of the shallowest well is recovered similar to the as-grown with the shift of the PL peak

for all wells. The intensity recovery indicates the crystal damage restoration after the annealing process. The blue-shifts suggest that during annealing step, the surface defects propagate deeper to the deepest QW more than $2.32\text{ }\mu\text{m}$ and promote the intermixing between wells and barriers to form alloy semiconductors. It is worth pointing out that after plasma exposure, in contrast to the QW1, the normalised PL intensities from QW2, QW3, and QW4 were increased with the most pronounced effect in QW4 by nearly three folds. The enhancement in PL signals is a sign of the defect annihilation after exposure.

4.1.3 Annealing of near surface defects to promote intermixing

The effect of surface defect has been investigated in the previous discussion. The subsequent annealing treatment causes the created defects to migrate into the QW active region while recovering material quality. The arrival of point defects to the QW active region enhances the interdiffusion rate to promote intermixing, thereby resulting in the blueshift of PL emission. In order to study this effect, a set of bare QW samples were exposed under Ar plasma in the ICP chamber with the 480 W RF power only. The ICP power was turned off during plasma exposure. After plasma exposure, there was no observable shift in the PL spectra as compared to the as-grown sample. This indicates that the near surface point defects were created during low Ar ion energy (100s of eV) exposure, thus avoiding direct damage to the QW region which is located deeper than $1.6\text{ }\mu\text{m}$ below the sample surface. Ar ions may knock ions off its crystal site near the sample surface to produce either single isolated vacancy or group of vacancies. During the subsequent annealing, the created point defects can effectively propagate from one lattice to another lattice site in the random walk motion. The diffusion of point defects down to the active QWs region promotes intermixing between the QWs and its barriers to form alloy

semiconductors. This intermixing process results in an increase in the QW energy bandgap. In addition to the annealing process, the annealing treatment also recovers crystal damage on the sample surface induced by the QWI technique and the intermixed device does not suffer significant optical degradation.

Figure 4-3. (a) Plot of normalised 77 K PL spectra at various Ar plasma exposure times. The samples were exposed under 480 W RF power only. (b) The bandgap blue-shift (solid) and the corresponding linewidth broadening (dashed) versus the ICP power application up to 1000 W. The condition was taken at constant RF power of 480 W for up to 15 minutes exposure time.

The PL spectra at 77 K from the exposed samples after annealing versus exposure times were plotted in Figure 4-3(a). The control sample underwent a 6 nm bandgap shift and 5 nm linewidth broadening as compared to as-grown sample, which is mainly attributed to thermal shift after annealing. It can be observed that the bandgap of the samples subjected to longer exposure time have been shifted to higher energy. The degree of intermixing seems to saturate for samples exposed longer than 10 minutes. This can be understood that most of defects will be created in the early stage of Ar exposure. As the defects start to build up, there will be fewer defects created subsequently. No appreciable linewidth broadening in the

intermixed RT PL spectra was observed, thus indicating that no significant degradation of the optical properties since no direct damage creation occurs to the QWs region during exposure. This implies that the high temperature annealing minimises the ion bombardment induced damage in addition to the point defect propagation [9]. The bandgap shift has similar trends for both RT and 77 K and saturates after 10 minute Ar exposure at 80 nm and 70 nm, respectively with a linewidth broadening of ~ 2 nm. The bandgap shift achieved using pure RF mode in this experiment is comparable with the previous Ar plasma induced QWI using a conventional parallel plate RIE machine for similar QW structures in Chapter 3. With the absence of ICP power, the ionic species in plasma sheath region generated using pure RF power (without ICP power) is accelerated at normal incidence by electric field to obtain kinetic energy relative to the materials and is expected to dominantly induce highly energetic ion bombardment damage due to the high potential difference between the plasma and the sample. Hence from Figure 4-3(a), the bandgap shift is mainly attributed to relatively highly energetic ion bombardment effect.

After the ion bombardment induced QWI investigation, the QWI impacts with the presence of inductively coupled Ar plasma is investigated. Taguchi's optimisation indicated that low ICP power were required for high bandgap shifts with small linewidth broadening. Figure 4-3(b) shows the optimum bandgap blue-shift at RT and corresponding linewidth broadening versus ICP power with constant RF power at 480 W. At 0 W ICP power, the PL peak at RT was blue-shifted as large as 80 nm with -840 V RF-induced DC bias. The application of ICP power up to 500 W promotes higher degree of QWI (>80 nm) with a linear decrease in RF-induced DC bias with ICP power. The RF-induced DC bias reduction leads to less

energetic ion bombardment induced damage with higher ion current density. The presence of high plasma density from inductively coupled Ar plasma plays an important role in enhancing fast damage diffusion, thus promoting higher degree of QWI.

From Figure 4-3(b), the optimum bandgap shift using ICP power with minimum linewidth broadening was obtained at an ICP power of 500 W with the corresponding RF-induced DC bias of -730 V. The further increase in ICP power led to a blue-shift saturation with a small reduction in blue-shift and increased linewidth broadening, which can be attributed to the accumulation of damage clusters and extended defects [10],[11] due to high-density ion dose plasma after long plasma exposure. These types of defects are known to be stable and difficult to be fully annealed out causing the decrease in the interdiffusion rate in the QWs. The bandgap of the QW sample has been blue-shifted by a value as large as 104 nm with linewidth broadening of 11 nm after plasma exposure for 5 minutes at 500 W ICP power. The linewidth broadening is slightly higher than the pure RF power case, however this increase is not very significant as the broadening range is still relatively small at RT PL measurement. By comparison, the low energy Ar plasma induced QWI could achieve relatively high or comparable bandgap shift of 104 nm compared to the implantation-induced QWI using 360 keV-Arsenic ion [12], 30 keV-Argon ion [13], and 20 keV plasma immersion Argon ion [14] in InGaAs/InP QWs structure.

4.2 MATERIAL ASSESMENT AFTER PLASMA INDUCED QWI

Having no deleterious effects on the quality of intermixed material is important to improving the performance, reliability and the integration of photonic components.

4.2.1 The effect of high-density plasma application

To further explore the intermixing effect to the material quality, a low temperature PL measurement was carried out at 4 K in order to minimise the effect of phonon vibration. A comparative study was made to identify the intermixing effect on higher density plasma exposure with and without ICP power application, as depicted in Figure 4-4. A control sample, which was annealed at 600 °C for 2 minutes without plasma exposure, exhibited a negligible increase in bandgap energy mainly due to the thermal interdiffusion.

Figure 4-4. Plot of normalised PL at 4K spectra of intermixed samples without and with the application of ICP power at 500 W. For the intermixed samples, other parameters of ICP system and annealing process were fixed.

Increasing the ICP power to 250 W (with the RF power constant) results in the increase in ion flux and a decrease in ion bombardment energy. The two intermixed spectra show a comparable bandgap shift of 46 nm (29 meV) as compared to the as-grown spectrum after intermixing with 10 minutes exposure time. With the increase of ICP power at 250 W, the ICP machine produces higher ion current density and lower RF-induced DC bias operation. The RF-induced DC bias operation was -840 V at pure RF power and was reduced to -780 V when the ICP power was 250 W. The RF-induced DC bias reduction leads to less ion bombardment induced damage. At lower RF-induced DC bias, bombarding ions initiate less collision cascades leading to less extended damage formation. The comparable bandgap shift achieved using 250 W ICP power indicates that the high-density plasma application plays a strong intermixing role in the QW structures besides the pure ion bombardments. The application of ICP power induces more damage due to the plasma radiation together with high ion current density on the samples, similar to observation reported elsewhere using ECR system [15]. The broad shoulder peak observed in the intermixed materials at the lower energy could be due to the deep level radiative recombination of the defect states from the near surface region of QWs from Ar plasma exposure [16]. The linewidth broadening of main peak as compared to the as-grown samples was as low as 8 nm (6 meV) and 2 nm (3 meV) for ICP power at 0 W and 250 W, respectively. If compared with the control (annealed only) sample, there is no observable linewidth broadening (less than 1 meV) to the intermixed samples. The value is relatively lower than the reported linewidth broadening with similar bandgap shifts in InGaAs(P)/InP QWs structure using a high energy IIID at 1 MeV (with corresponding linewidth

broadening of ~ 3 meV) [17] suggesting a good optical quality preservation using ICP application.

4.2.2 The photoluminescence enhancement

A significant drop in PL intensity after intermixing may cause the detrimental effect of fabricated photonic device, related to the creation of non-radiative recombination centres that cannot be annealed out during intermixing, for example in the case of IID using high energy of 2 MeV [17]. Therefore, the evaluation of PL intensity is important to determine the optical quality after plasma induced QWI process.

Figure 4-5. (a) PL spectra at 77 K with normalised intensity with respect to as-grown sample were performed at different Ar exposure times: (i) as-grown, (ii) control, (iii) 2 minutes (iv) 3 minutes, and (v) 5 minutes. (b) The PL intensity of RT and 77 K versus the exposure time of another set of QW samples from different wafer measured from the top (solid) and back sample surface (dashed).

Figure 4-5(a) shows the PL intensity of intermixed samples under different Ar exposure times without further annealing step. A PL spectrum of control sample is included for comparison purpose. The small increase in PL intensity and 6 nm shifts were observed from the control sample, which had undergone annealing

treatment only at 600 °C for 2 minutes. During annealing, the thermal diffusion of grown-in defects within the heterostructure causes removal of some defects, hence it gives rise to small increase in PL intensity. For samples exposed for various durations to Ar plasma, (2, 3 and 5 minutes) there were no observable PL shifts and only a small amount of linewidth broadening. This indicates that point defects have been introduced to samples without damaging the QWs structures, which are located $\sim 1.6 \mu\text{m}$ below the sample surface. The increase in PL intensities as a function of Ar exposure time is attributed to reduction of non-radiative carrier recombination centres after plasma exposure. The increase in PL intensity was even evident from the samples selected from the periphery of the samples, which had low PL intensity before exposure. As summarised in Figure 4-5(b) on the different QW sample from another wafer, both RT and 77 K PL measurements retrieved from the backside of the exposed samples show the similar trend of the increase in PL intensity as a function of the exposure time up to 8 minutes. The PL intensities measured from QW samples with InGaAs/InGaAsP cap layer and without InGaAs/InGaAsP cap layer show the comparable level of PL intensity (not shown here). These evidences suggest that the photoluminescence enhancement after Ar exposure is not due to the changes in the cap properties.

Previous studies have shown that the role of Ar-assisted epitaxy of InGaAsP/InP has greater effect on the PL intensities with reduced line-width broadening. The plasma-assisted epitaxy, however allows the tensile strained layers to approach the quality of the lattice-matched layers by drastically reducing the LCM (lateral composition modulation), which give rise to relatively narrow linewidth and higher PL intensity [18]. Comparing the plasma-assisted epitaxy with the present post-growth plasma exposure, the remote plasma in the ICP creates a

high-density radiation regime in the vacuum ultraviolet (VUV) energy band of 4-30 eV, where most population are located above 9 eV, during Ar plasma exposure [19],[20]. This radiation at high-density can have a pronounced effect on the thin QW structure leading to annealing out of grown-in defects (*intrinsic* defects), and the reduction of interface roughness and compositional fluctuations [21], thereby enhancing the PL intensity, through the momentum and energy transfer from carrier recombination resulting in increased lattice vibration and local heating curing the non-radiative recombination centres. The improved PL efficiency could be mainly due to enhanced annealing of grown-in defects at the interface region between barriers and wells since an abrupt change in growing composition between the barriers and wells usually results in a high-density of point defects [22],[23] from low etch pit density of QWs material used here [2]. In addition, the dislocations in the InP substrate may extend during the growth process into the epilayers so that the dislocation density in the epilayer could be similar to that of the substrate [24]. Such defects appear to act as nonradiative recombination centres. Further experiments are required to verify the mechanism responsible for this observation in PL intensity enhancement. Since the emission is from the QWs, the effect of Ar exposure does not damage the QWs region, which is very important for any post-growth processing.

Figure 4-6. The PL spectra of (a) the intermixed QW samples at RT and (b) the intermixed sample partially masked with a 200 nm thick SiO₂ layer.

The point defects created near to the surface region are driven into the QW by rapid thermal annealing the samples at 600 °C for 2 minutes. Figure 4-6(a) shows the PL spectra of the intermixed sample using 500 W ICP power for 5 minutes exposure as compared to the PL spectra of the as-grown sample and control. The created point defects are mobile in nature causing QWI and hence the blue-shifts in PL peak with the consistency of PL improvement. The investigation was extended to the selective QWI across a sample with half of the surface area deposited with a 200 nm thick SiO₂ layer and 50 nm thick gold layers. The dielectric acts as exposure mask, which blocks ions from penetrating the structure during exposure, while the gold layer acts as a radiation protector and prevents the plasma radiation effect [25]. Figure 4-6(b) shows the 77 K PL spectra obtained from the partially masked sample after Ar plasma exposure and subsequent annealing treatment. As can be seen from the spectrum, the same phenomena occur in PL intensity after QWI between the masked and unmasked SiO₂ sections. The PL intensity is increased by three folds. The section which was masked with a layer of SiO₂ during plasma exposure, underwent a small amount of bandgap shift (6 nm),

which is mainly attributed to thermal shift after annealing. The portion exposed to the plasma had a much larger bandgap shift of 92 nm relative to the as-grown sample, thus producing a differential bandgap difference of 86 nm between masked and unmasked region with no appreciable linewidth broadening between two regions. This result strongly points to the high selectivity obtainable from the QWs samples using 200 nm SiO₂ and gold layer as a masking and a radiation shield layer, respectively, with the PL improvement on the intermixed region.

4.2.3 The x-ray diffraction investigation

Double-crystal x-ray diffraction has been used to study the lattice composition, strain between epilayers, material quality after growth, as well as composition interdiffusion in the QWs [26]-[28]. The HRXRD rocking curves in the (004) plane was investigated to further verify QW structural properties after plasma exposure and subsequent annealing. The measurements were performed using a Phillips x-ray diffractometer with a conventional x-ray generator with a copper target as the radiation source. The HRXRD rocking curves were recorded in the symmetrical (004) reflection.

As shown in Figure 4-7, the main peaks at 0 arcseconds are caused by (004) diffraction from the InP substrate and buffer layer and the equally spaced small peaks show the multilayer structure is matched to the (100)-oriented InP substrate. The as-grown QW structure with a lattice-matched structure to InP substrate, which consists of 5 periods (5.5 nm QW/12 nm Å barrier), shows a number of narrow and clear satellite peaks (fringes) located symmetrically on each side of the multilayer main peak. These satellite peaks indicate the periodically sharp and abrupt layer interfaces between epilayers with different lattice constants from that of InP

substrate. Due to the complexity of the investigated QW laser structure, the information from the QWs and barriers could not be easily resolved as the diffraction signal originated from the adjacent layer interfaces. The satellite peaks confirm the crystalline quality growth of the well-defined InGaAsP/InGaAs/InP layers in the as-grown sample. The exposed-only sample has a similar x-ray rocking curve with the main peak and clear satellite peaks. This confirms that most of the defects created during Ar exposure are located on the near sample surface. The defects created during Ar exposure are located on the near sample surface.

Figure 4-7. The high-resolution double X ray rocking curves for the QW samples (a) as-grown sample (b) exposed-only sample after Ar exposure for 5 minutes (c) intermixed sample after Ar exposure for 5 minutes and subsequent annealing.

The x-ray rocking curve of the intermixed sample just reveals only a broad peak on the high angle side of the substrate Bragg peak. The satellite peaks smear out after the intermixing process as compared to the as-grown sample. This shows that the compositional profile changes from abrupt to the graded interfaces as the intermixing occurs. The complete disappearance of satellite peaks clearly indicates

the interdiffusion occurred during annealing. A broad peak corresponds to InGaAsP alloy composition [27]. The result is in agreement to the calculation model that for increasing amounts of interdiffusion, the satellite fringes from superlattice structure are eroded away, leading to a uniform compositional alloy with no sharp periodicity [28]. As interdiffusion proceeds, the InGaAsP alloys are formed at the interfaces and local strain is developed but the average strain stills remains unchanged. Since the structure is lattice-matched to InP, it is rather difficult to obtain the first order peaks of QWs and scan beyond 800 arc-seconds did not reveal any additional fringes. The HRXRD result clearly indicates that the interdiffusion took place after intermixing causing the change from the sharp interfaces to form the alloy material.

4.2.4 The surface quality assesment

As most of the QWI techniques involve the defect creation and a subsequent annealing stage, the surface quality upon QWI is important as it gives an indication of the surface damage produced during the stage of introducing the defects. If the surface quality is being altered during the QWI stage, the subsequent devices fabricated using the intermixed material could very likely suffer from degradation in performance. Ar plasma is also known to produce very severe physical damage to the materials especially in III-V semiconductors [30] and a stronger physical sputtering effect due to its large atomic weight, it is necessary to investigate the surface quality and damage after Argon exposure in ICP machine. The surface morphology of intermixed samples was examined using a Park Scientific AFM in conjunction with the inspection under optical microscope and scanning electron microscopy (SEM).

Figure 4-8. The RMS surface roughness (solid line) and the corresponding maximum feature size (dashed line) from the intermixed samples using different exposure times. Insets show the AFM 3D profiles.

To examine the surface modification due to the sputtering effect, a set of QW samples were exposed using the optimised ICP parameters from Taguchi's study with the exposure time varying from 2 to 15 minutes. From inspection using optical microscope and SEM, it was found that there was no significant sputtering effect to the material surface roughness up to 10 minutes exposure time. The obvious change in surface colour was observed for intermixed samples with exposure duration more than 10 minutes, indicating the sputtering process took place in roughening the surface.

Figure 4-8 summarises the surface of the intermixed samples as the exposure time increases. The RMS roughness of the as-grown InGaAs/InGaAsP QW samples was observed to be 1 Å while the maximum feature size was found to be 2 Å. The control sample (annealed only without any plasma exposure) has a comparable roughness with the as-grown sample. A little increase in surface

roughness of the control sample could be due to the surface outdiffusion and decomposition during annealing step. The surface roughness reaches the maximum in the exposure for 10 minutes with RMS roughness of 14 Å and the maximum feature size of 55 Å. However, the previous optimum condition to achieve the large bandgap shift of 104 nm was at a 5 minute exposure with the measured surface roughness at 4 Å. As compared to the as-grown sample, the intermixed sample for 5 minutes exposure has a little increase in the surface roughness.

Figure 4-9. AFM picture of the intermixed InGaAs/InGaAsP QW samples using ICP power application of (a) 0 W and (b) 500 W at 5 minutes exposure time. The corresponding RF-induced DC bias was -840 V and -730 V, respectively.

The comparison was made to the intermixed samples with low plasma density without the application of ICP power during exposure. Figure 4-9 shows the comparison of surface morphology of the intermixed samples from AFM analysis between 0 W and 500 W ICP power at 5 minutes exposure time followed by subsequent annealing. The RMS surface roughness was 11 Å and 4 Å for the ICP power of 0 W and 500 W, respectively. A significant difference in the surface roughness of the intermixed sample at 0 W ICP power can be attributed to the sputtering effect from highly energetic ion bombardment with corresponding RF-induced DC bias of -840 V. The increase of ICP power at 500 W will decrease the

RF-induced DC bias operation to -730 V and leads the lower ion bombardment effect in ICP system, thus it can minimise the surface roughness of samples after exposure. The effect of energetic ions in ICP has been found to play a significant role in roughness degradation [31]. The AFM analysis performed at the samples exposed to 500 W ICP power indicates that the increase in the roughness is not very significant as the roughness is still relatively small and the surface could be still considered smooth. At this condition, the sputtering rate measured using Dektak surface profiler is about 18 Å/minute for plasma exposure up to 10 minutes. However, the quality of photonic device can still be improved by doing the regrowth after chemical etch removal of the InGaAs/InGaAsP contact layer with rough surface morphology. Another approach with the elimination of regrowth process is by incorporating the InP sacrificial layer on the top of InGaAs cap layer on the QW laser structure, which can be selectively using chemical etchant after the intermixing process.

4.2.5 The micro-Raman spectroscopy (MRS)

Raman spectroscopy is commonly used to study properties of semiconductor material such as the composition of compounds semiconductor, layer orientation, stress characteristics, and crystalline perfection through the evaluation of the phonon frequencies, half widths, lineshape and their intensities in the Raman spectrum [32]. Related to the intermixing effect, MRS has been used extensively to investigate the interdiffusion mechanism in QWs [25],[33] as well as damage assessment after implantation process [34],[35]. Particularly, in InGaAs/InP superlattices study, it was demonstrated that peak intensities and peak energies of InAs-, GaAs-, InP- like longitudinal optical (LO) phonon modes change with thermal annealing temperature and time [36].

Figure 4-10. Room temperature Raman spectra of the InGaAs/InGaAsP QW material at different conditions: (a) as-grown, (b) control, (c) intermixed at 5 minutes exposure, and (d) heavily intermixed at 10 minutes exposure.

As the Ar plasma exposure creates damage on the QW sample surface and the annealing process induced the surface decomposition, the material quality assessment of the potentially damaged area was determined using the MRS measurement. A Raman measurement in backscattering configuration has been carried out on test samples at room temperature in order to examine the material quality of the cap layer due to the point defects created after exposure and subsequent annealing. An argon laser of 514.5 nm wavelength, 20 mW, with a spot diameter of $< 1.0 \mu\text{m}$ was used as excitation source. Light penetration depth of ~ 90 nm and ~ 110 nm below the sample surface is predicted from the calculation of its absorption length directly within the potentially damaged area for InP and GaAs material, respectively [37]. According to the depth prediction, the Raman modes

with the largest signal-to-noise ratio were retrieved from the InGaAs/InGaAsP cap layers.

The Raman analysis in the cap layers, which are quaternary materials, are complicated as the layers exhibit two large groups of bands associated with LO phonons. Since the QW sample was grown on (100)-oriented InP substrate, only longitudinal optical (LO) phonons are allowed and the transverse optical (TO) phonons are forbidden by symmetric selection rules in the first order Raman scattering [38]. From Figure 4-10, the 210-270 cm^{-1} band corresponds to the InGaAs related LO and the 300-370 cm^{-1} band corresponds to the InGaP related LO mode were observed. The presence of these bands in the as-grown sample indicates the presence of InGaAs/InGaAsP cap layers, with the light penetration up to the InGaAsP layer. The InGaAs related LO mode is composed of InAs like (210-235 cm^{-1}) and GaAs like (240-270 cm^{-1}) LO peaks. The GaAs-like LO phonon peak exhibited a small shift from 270.2 cm^{-1} (as-grown sample) to 265 cm^{-1} (control and intermixed sample) and a decrease in peak intensity. Simultaneously the InAs-like LO phonon peak shifted to higher frequency. The decrease in GaAs-like LO phonon intensity in control sample (annealed only sample) as compared to the as-grown sample was attributed due to the outdiffused As and Ga species during annealing treatment from the cap layer [39]. The Raman spectra of control sample showed the similar Raman spectra to that of the as-grown sample except a slight frequency shift at the GaP-like LO phonon ($\sim 343.5 \text{ cm}^{-1}$) while no observable change in the peak of InP-like LO mode, indicating a little increase in P content, which may have been enhanced by the presence of the group V vacancies created due to As desorption at the surface during the annealing process. The thermal induced diffusion from MRS is consistent with the result of a small bandgap shift of 7 nm from PL

measurements. The intermixed sample shows a clear Raman shift towards GaP-like LO phonon at higher frequency (345.2 cm^{-1}) and the increase of InP-like LO phonon peak (304.3 cm^{-1}) [36], clearly indicating the increase in P composition in the observed layer associated with the Ar plasma exposure and subsequent annealing process [40]. The presence of high defect density from Ar plasma exposure on the sample surface may have favored higher level of P incorporation through diffusion process from InP upper cladding. The decrease in group V composition as evidenced by the decrease in GaAs-like LO phonon frequency and the increase in P atoms from MRS spectra, suggesting that the interdiffusion on the cap layers between group III and group V atoms has occurred to produce the InGaAsP alloys. In addition, no observable peak at about 430 cm^{-1} , assigned to P-P vibrations, on the intermixed sample provides an evidence of the diffused P atoms are substitutionally incorporated to the crystal lattice in the cap layers without creating the P clusters, as in the case of implanted InP material at high dose [36],[41]. The similar Raman spectra and intensity level of InGaP related LO peak as compared to as-grown sample implies that the surface properties of intermixed sample with 5 minutes exposure (bandgap shift of 109 nm) has been preserved after intermixing and the cap layer quality of the intermixed material remains good after QWI process. No appreciable difference of disorder activated longitudinal acoustic (DALA) mode at low frequencies after intermixing as compared to as-grown and control material indicates no activation of plasma induced disordering of transverse acoustic modes, further providing evidences of good crystal quality preservation of intermixed material. For the heavily intermixed sample with exposure of 10 minutes (bandgap shift of 112 nm), the Raman spectra was not clearly resolved on both InGaAs related LO mode and InGaP related LO mode with a flat plateau on each

band. The GaAs-, InAs-, and GaP-like modes have vanished and the intensity of the plateau has drastically reduced, indicating the possibility of the extended defects from structural disorder such as dislocation loops [10],[11] or the effect of rough surface after long exposure time. Such extended defects are stable and is difficult to be fully treated even after annealing step commonly used for QWI process. This damaged phenomenon is similar to the heavily disordered InGaAs/InP material after implantation above a critical defect level or ion dose [42],[43] due to amorphisation phase causing the defect trapping in the crystalline structure.

4.3 SUMMARY

From the thermal stability test of InGaAs/InGaAsP QW structure, the annealing process at 600 °C for 2 minutes is sufficient to promote QWI with plasma exposure while avoiding thermal damage as well as large thermal shift in the masked area. The Ar plasma induced surface damage mechanism has been studied using bulk material, resulting in the increasing non-radiative recombination centre. The increase in exposure time raises the amount of damage and saturates after 5 minute exposure time, leading to the saturation of intermixing degree. The presence of high plasma density from inductively coupled Ar plasma plays an important role in enhancing QWI. The saturation in blue-shift after long exposure time was ascribed to the accumulation of damage clusters and extended point defects due to high-density ion dose exposure, resulting in significant linewidth broadening of the PL spectra after annealing. Using QW probe structure as high sensitive damage detection, the detail plasma induced QWI mechanism has been revealed. The damage of more than 0.4 μm was observed after exposure. After annealing, the created damage is recovered in the form of mobile point defects, and propagates to a depth of more than 2.32 μm from sample surface and promoted the intermixing

between wells and barriers. The increase in normalised PL intensities from the QWs located deeper than the damage penetration depth further supports the PL improvement through defect annihilation in GaAs-based material.

The investigation of the material quality after plasma induced QWI effect has been carried out. Using 4 K PL measurements, the application of inductively coupled Ar plasma enhanced the intermixing degree with a minimal degradation of QW optical quality, as indicated by small linewidth broadening of 2 nm (3 meV) using ICP power of 250 W. The improvement of PL intensity was observed after Ar plasma exposure, which could be ascribed to the enhanced annealing of high-density grown-in defects from the inductively coupled Ar plasma radiation in VUV region. The x-ray diffractometry unambiguously shows the interdiffusion on the epilayers of material causing the change from the sharp interfaces to the alloy material. From AFM inspection, no significant sputtering to the surface quality takes place for exposure times up to 10 minutes. As compared to the pure RF power, the surface morphology of intermixed samples with the application of ICP power is better and considered smooth, due to the reduction of the highly energetic Ar ion bombardment. The micro-Raman spectroscopy revealed that the interdiffusion process of species takes place after annealing and the quality of the surface intermixed material being assessed remains good.

5. THEORETICAL MODEL OF INTERDIFFUSED QW

The interdiffusion of III-V heterostructures has been investigated for more than 20 years as the prime importance for the development of PICs via the interdiffusion mechanism between wells and barriers. The diffusion behaviour of point defects causing the intermixing in the QWs material often determines the final device properties. Therefore, the understanding of point defect diffusion mechanisms is of technological interest and is expected to be an important step towards the optimisation of various QWI processes and their exploitation for commercial photonic integration devices.

The objective of this chapter is to present a detailed theoretical model of interdiffusion process (also referred to as intermixing) in QW system needed for the calculation of various optical properties as well as to elucidate the mechanism by which interdiffusion modifies its properties. The interdiffusion model combined with the semi-empirical model of ICP induced damage will be presented here to give further understanding of plasma enhanced QWI process. An analytical model permits a simple qualitative understanding of the effects of the plasma-induced defects, the factors that affect the plasma induced QWI process and the general correlations of the inductively coupled plasma exposure effect on QWs bandgap shift through the diffusion coefficient enhancement of point defect propagation during annealing step.

It is worthy to point out that the strain incorporation in the interdiffused QW model has been implemented more generally to study various interdiffusion mechanisms, such as the polarisation dependent behaviour of low energy IID fabricated with gray mask technology [1],[2], annealing induced blue-shift

mechanism in the diluted nitride InGaAs(N)/GaAs QW [3], and the Ge-doped sol-gel cap induced QWI mechanism in InGaAs/InGaAsP system [4].

5.1 INTRODUCTION

QWI technology has positioned to be the promising postgrowth technique of tailoring the band gap. One of the first reported studies of the interdiffusion of an III-V material was on an AlAs/GaAs heterostructure by Chang and Koma in 1976 [5]. At present, the extensive study of the interdiffusion mechanisms will not be restricted to two constituent atoms, but it involves the two and multiple phases interdiffusion as well as multiple species. The present result has shown that the multiple species interdiffusion will have impact on the different interdiffusion mechanisms, such as the three cations only interdiffusion and two pairs of cation and anion interdiffusion with the same or different rates of diffusion [6]. As a result due to the interdiffusion effect of the materials, either compressive or tensile strained materials and either the blue-shift or the red shift in the band edge structure could be easily achieved depending on the type of interdiffusion. This advantage yields a highly controlled interdiffusion process with different rates of diffusion. QWI process itself involves the thermally induced interdiffusion of the constituent atoms across the quantum well and barrier interfaces, where the rate of interdiffusion process is described as a function of the nature and concentration of the impurity ions, and the annealing temperature and also the time. This process will further modify the compositional profile of the as-grown from abrupt QW to a graded profile.

The interdiffusion process provides a useful tool for tailoring the localised bandgap of quantum well. It is extremely important to understand the interdiffusion

mechanism. According to Li *et.al.*[6], interdiffusion mechanism in semiconductor heterostructure can be classified according to how the atomic constituents in the alloy take part in the intermixing process. In the perspective of material system, there are two major parts according to the number of different phases involved in the interdiffusion: i) the $A_xB_{1-x}C$ system and ii) the $A_xB_{1-x}C_yD_{1-y}$ system.

5.2 INTERDIFFUSION IN THE $A_xB_{1-x}C$ SYSTEM

The interdiffusion is relatively simple to be explained since it involves one phase process of the different materials. The thermal interdiffusion usually occurs at temperature above 850 °C for $Al_xGa_{1-x}As/GaAs$ and $In_xGa_{1-x}As/GaAs$ system. Intermixing of the lattice matched $A_xB_{1-x}C$ system results in the interdiffusion of only the group III atoms, which are In and As in the InGaAs/GaAs and the AlGaAs/GaAs QW material, respectively, due to the presence of the concentration gradient across the interface, as shown in Figure 5-1.

Figure 5-1. The existence of the chemical potential and the concentration gradient across the $A_xB_{1-x}C$ system after interdiffusion process

The single-phase interdiffusion process occurs in $Al_xGa_{1-x}As/GaAs$ and $In_xGa_{1-x}As/GaAs$ QWs structures. It is normally assumed that the interdiffused compositional profile can be well modeled by the Fick's law of diffusion [7]:

$$\frac{\partial C}{\partial t_a} = D_{QW} \frac{\partial^2 C}{\partial z^2}, \quad (1)$$

where, C is the concentration of one of the alloy, t_a is the interdiffusion time and D is the diffusion coefficient and z is the interdiffusion direction. Normally, the diffusion coefficient D_{QW} is assumed to be isotropic therefore constant across the interdiffusion region. The general solution for interdiffused QWs is given as [7]-[9]:

$$C(z) = C_1 + \frac{(C_2 - C_1)}{2} \left\{ 2 - \operatorname{erf} \left(\frac{z - c_1}{2 L_d} \right) + \operatorname{erf} \left(\frac{z - c_2}{2 L_d} \right) + \sum_{i=1}^{N-1} \left[\operatorname{erf} \left(\frac{z - a_i}{2 L_d} \right) - \operatorname{erf} \left(\frac{z - b_i}{2 L_d} \right) \right] \right\}, \quad (2)$$

where C is the fractional Al concentration across the well, C_1 and C_2 are the concentrations of Al in the well and at the barriers respectively, N is the number of wells and $L_d = \sqrt{D_{QW} \cdot t_a}$ is the diffusion length, which characterises the extent of interdiffusion of the QW.

Figure 5-2. The concentration profile after interdiffusion process in the $A_xB_{1-x}C$ system

It has been reported recently that the Fick's diffusion equation may not properly describe the interdiffusion in the InGaAs/GaAs QW with strain. The strain, caused during interdiffusion process, is believed to introduce changes in crystal defect concentration and thus influencing the diffusivity. Taking the strain effect into account, the Fick's equation is therefore modified to be [10]:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z} \left(D_0 e^{\kappa C} \frac{\partial C}{\partial z} \right), \quad (3)$$

where C is the Indium concentration, D_0 is the diffusion coefficient when no stress is applied, κ is the parameter indicating the degree of strain enhancement and is also a function of In concentration. This equation has included the effects of strain empirically. The equation can explain the experimental PL shifts as a function of annealing time. The diffusion coefficients in InGaAs/GaAs QW eventually can be found using this equation.

5.3 INTERDIFFUSION IN THE $A_xB_{1-x}C_yD_{1-y}$ SYSTEM

In the $A_xB_{1-x}C_yD_{1-y}$ system of III-V compounds, A and B are the representation of the group III sublattices while the C and D represent the group V sublattice. The interdiffusion processes in the $A_xB_{1-x}C_yD_{1-y}$ system are relatively more complex since the possibility of interdiffusion can occur for both group III (such as In, Al, and Ga) and group V (such as As, P, and N) atoms, which in turn are determined also by the impurity used to enhance the material interdiffusion.

In this system, the interdiffusion process may result in a large strain generation during the early stage of the intermixing process, so that it differs from that of the interdiffused in the $A_xB_{1-x}C$ system. There is a possibility that the final interdiffused structure is not lattice matched to the substrate, so that a strained structure may result after the process. On the other side, the type of impurity can produce either a blue-shift or a red-shift in the band absorption edge. The strain buildup effect in the interdiffused InGaAs(P)/InP system has been verified experimentally by cross-sectional scanning tunneling microscopy (XSTM) [11],[12], cross-sectional scanning transmission electron microscopy (TEM) [13],

and HRXRD [14],[15]. Comprehensive understanding of the interdiffusion process in this system has been of great of interests among researchers as the subject of active investigation in various intermixing processes.

5.3.1 One phase, Group III interdiffusion only in the $A_xB_{1-x}C_yD_{1-y}$ system

Cation interdiffusion results in the formation of an $A_xB_{1-x}C_yD_{1-y}$ abrupt interface from an as-grown material. When the interdiffusion process only on the group III sublattice is considered, a large build-up of strain resulted during the early stage of the intermixing. This process produces a compressive strained quantum well layer and tensile quantum barrier layers. Theoretical analysis indicates that a large strain was built up across the well during the early stage of the interdiffusion, the strain and its effect on the bandgap profile of the disordered structure produces a distinctive quantum confinement profile which remains abrupt even after significant interdiffusion. This phenomenon, together with a diffused well width, which is equal to that of the as-grown QW, is in contrast to the intermixed $A_xB_{1-x}C$ system. The effect of strain results in a potential build-up in the barrier near the interface at the top of the wells. The heavy holes (HH) and light holes (LH) band-edge splitting results in two distinct HH and LH confinement profile with different depths.

From experimental view, the diffusion effects in the intermixed InGaAs/InP QWs [10]-[18] and the annealing effect in the InGaAsN/GaAs QWs [19]-[23] have been explained as the group III interdiffusion only. The more dominant interdiffusion of In and Ga atoms than interdiffusion of As and P atoms in InGaAs(P)/InP system during intermixing process theoretically results in the decreasing bandgap energy, so-called red-shift phenomena [9]. However, later reports showed the possibility of blue-shift achievement in the InGaAsP material

using constant P/As ratio with only group III interdiffusion process [17],[18], similar mechanism to GaAs/AlGaAs, InGaAs/InAlGaAs [24], and InGaAs/GaAs systems. In InGaAs(N)/GaAs system, the group III interdiffusion only calculation results in the increasing bandgap energy [25] relevant to experiments of the annealing induced blue-shift [19]-[23].

5.3.2 One phase, Group III and V interdiffusion in $A_xB_{1-x}C_yD_{1-y}$

This type of interdiffusion may preserve a lattice matching condition or produce either a compressive or tensile-strained QWs after the process. Interdiffusion on both group III and V sublattices can be categorised into two major parts on both group III and group V sublattices: the identical and the unidentical interdiffusion rate. A comprehensive review and discussion on the different diffusivities on each sublattice in alloys of InGaAsP system can be found in [26].

In general, the impurity-free induced QWI results in the identical interdiffusion between group III and V sublattices. The final structure would remain lattice matched, the confinement profile changed to graded profile, and the ground state transition energy shifts to shorter wavelengths. Gillin *et al.* reported the identical interdiffusion between group III and group V sublattices within experimental sensitivities, using different experiments allowing the group III and V interdiffusion assessments separately in constant composition of group V and III sublattices, respectively [27],[17]. The group III and group V sublattices in InGaAs(P)/InP system has been verified experimentally to diffuse at a similar rate after intermixing process using Raman spectroscopy [28], the secondary ion mass spectroscopy (SIMS) [29], and HRXRD measurement [30]. The theoretical interdiffusion in the confinement profile of the InGaAs/InGaAsP quaternary

systems has been recently reported to perform the optical properties modification after intermixing [9],[31].

In unidentical interdiffusion, the decrease in wavelength is attributed to the interdiffusion of both group III and group V sublattices at different interdiffusion rates, since this process only produces either a compressive or tensile strained quantum well. In contrast, strained QW system was resulted after this intermixing process. The strain buildup due to the unidentical interdiffusion has been observed experimentally in the grown-in defect annealing [12],[15] and IID process using P ions [11],[13],[32] and As [2] ions. Theoretical results showed that when the cation interdiffusion rate is faster than that of the anion, the ground state (E1-HH1) transition shifts to longer wavelengths [33]. For prolonged interdiffusion, this shift to longer wavelengths saturates and then decreases. This is in good agreement with the reported experimental results of Si-IID [34], Zn-IID [35] as well as thermal annealing of InGaAs/InP QWs [36]. When the anion diffusion rate is faster, results showed that the effective bandgap of the diffused QW would be the E1-LH1 ground state transition, which shifts to shorter wavelength with interdiffusion. The tensile strain that is induced under this disordering condition moves the LH ground state above the HH ground state. Results obtained from these calculations showed that the control of relative extent of cation and anion interdiffusion offers different possibilities for optoelectronics device fabrication.

5.3.3 Two phase, Group V in $A_xB_{1-x}C_yD_{1-y}$ system

This type of interdiffusion is only governed by a two-phase interdiffusion process, where the well is under tensile strain while the barrier is compressively strained. The single as-grown lattice matched InGaAs/InP model has been reported

for a two-phase group V interdiffusion [7]. Mukai [37] has derived a formula that describes the two-phase interdiffusion mechanism of the quaternary material system, which includes the different diffusion coefficients between layers and interfacial discontinuity of interdiffused species. The formula was applied to analyse the dependence of an interdiffusion induced energy shift on annealing time, annealing temperature and QW width. Good agreement was achieved between the calculated and measured values. Two-phase group V sublattice interdiffusion in InGaAs/InP QW was also theoretically investigated [33] using the same formulation with pseudo-time dependence. This model has been validated with an even better agreement with experiment data. However, perfect fitting cannot be obtained and further work has to be pursued.

5.3.4 Multiple species, Group III

The recent analysis on multiple cations interdiffusion in InGaAs/InAlAs is performed using a model based on the expanded form of Fick's second law:

$$\frac{\partial C_i}{\partial t} = \sum_{j=1}^{n-1} D_{ij} \nabla^2 C_{ij}, \quad (4)$$

where n is the number of the diffusible species, and C is the indium concentration. The model is fitted to the measured concentration data in order to determine their diffusion coefficients. It was found that the diffusion coefficient of Ga-Ga is relatively large in comparison to the other rates so that the Ga concentration profiles show a more broadened distribution after annealing. The In-Ga diffusion is found to be negative which gives rise to the inverse process of diffusion, causes sudden abrupt change in the In profiles at the interfaces.

5.4 THEORETICAL MODEL FOR THE $A_xB_{1-x}C_yD_{1-y}$ SYSTEM

In the $A_xB_{1-x}C_yD_{1-y}$ system of III-V compound semiconductor material, A and B are the representation of the group III sublattices while the C and D represent two group V sublattices. In the $A_xB_{1-x}C_yD_{1-y}$ system the concentration of group III and group V is represented independently as x and y respectively. In the $A_xB_{1-x}C_yD_{1-y}$ system, the interdiffusion can be characterised by parameter $k = L_{dV} / L_{dIII}$ (known as the diffusion length ratio), where L_{dIII} and L_{dV} denote the diffusion lengths of the group III and group V sublattices respectively. There are two models based on the rate of interdiffusion of group III and group V sublattices:

1. Identical interdiffusion ($L_{dIII} = L_{dV}$), the lattice matched condition is maintained.
2. Unidentical interdiffusion ($L_{dIII} \neq L_{dV}$), the strain is introduced to QW structure.

In this model, the lattice-matched $\text{In}_x\text{Ga}_{1-x}\text{As} / \text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ QW to semi infinite InP substrates are considered for the prime structure in the theoretical model. The QWs coordinate system is shown in Figure 5-3.

Figure 5-3. The coordinate system used in the simulation of the $A_xB_{1-x}C$ system

The interdiffusion process can be described by a linear diffusion equation as for a heterojunction or a QW structure. In the QW structure, the InGaAs well layers are sandwiched by the InGaAsP quantum barriers and if the diffusion coefficients are assumed to be different for the QWs and the barriers, the diffusion equations will be given as:

$$\frac{\partial C_r(z,t)}{\partial t} = D_r \frac{\partial^2 C_r(z,t)}{\partial z^2}, t \geq 0, \quad (5)$$

where $C(z,t)$ is the atom's concentration and D is the corresponding diffusion coefficient, $r=B$ (denotes barrier) when $|z| \geq 0.5 L_{ZI}$ and $r=W$ (denotes well) when $|z| \leq 0.5 L_{ZI}$. Then, the boundary conditions to fulfill Equation (5) are

$$C_B(z,t) = kC_W(z,t), \text{ for } z \rightarrow c_1, a_1, b_1, \dots, a_N, b_N, c_2 \quad (6)$$

$$D_B \frac{\partial C_B(z,t)}{\partial t} = D_W \frac{\partial C_W(z,t)}{\partial z}, \text{ for } z \rightarrow c_1, a_1, b_1, \dots, a_N, b_N, c_2 \quad (7)$$

where the C_B and C_W are the concentrations of the diffusing species on each side of the QW/barrier interface, and k is the concentration ratio of diffused species at the QW/barrier.

The error function profile after interdiffusion process is obtained from summing the effects of a series of line sources representing an extended source of limited extent, each yielding a Gaussian distribution. The group III concentration in the active layer profile after interdiffusion can be expressed as:

$$x(z, L_{dIII}) = x_{QB} + \frac{\Delta x_{QW}}{2} \left[2 - \operatorname{erf}\left(\frac{z-c_1}{2L_{dIII}}\right) + \operatorname{erf}\left(\frac{z-c_2}{2L_{dIII}}\right) + \sum_{n=1}^{N-1} \left[\operatorname{erf}\left(\frac{z-a_i}{2L_{dIII}}\right) - \operatorname{erf}\left(\frac{z-b_i}{2L_{dIII}}\right) \right] \right] \quad (8)$$

where

$$c_1 = -c_2 = -\left(L_{QW} \frac{N}{2} + L_{QB} \frac{N-1}{2}\right); a(i) = c_1 + L_{QW} + (i-1)(L_{QW} + L_{QB}); b(i) = a_i + L_{QB} \quad (9)$$

$x(z, L_{dIII})$ is the group III concentration, x_{QB} is the concentration at the quantum barrier, Δx_{QW} is the difference in the concentration between the QW and the barrier, L_{QW} is the QW width, L_{QB} is the barrier width, N is the QW layer number and z is the direction along QW growth (QW is centred at $z=0$). The group V

concentration can be formulated using the analogy of Equation (9). For a given interdiffusion length the group III and group V concentrations (x and y , respectively) and hence the band edge interdiffusion profile can be calculated.

The compositional profiles imply that the carrier effective mass, the bulk bandgap, the strain, and its effects, will vary continuously across the QWs. Consequently, those parameters will be z -dependent. Thus, the carrier effective masses, $m_r^*(z)$ is z dependent and is obtained from $m_r^*(z) = m_r^*(x, y)$, where $m_r^*(x, y)$ is the respective bulk carrier effective mass, and the subscript- r denotes E, HH, and LH. The potential function of the QW after interdiffusion process can be calculated by considering both the unstrained and strained profile, which varies across the well.

5.4.1 Identical interdiffusion ($L_{dIII} = L_{dV}$; $k=1$)

Figure 5-4. The in-plane strain variation of identical interdiffusion at (a) well centre, (b) well-close to interface, (c) barrier-close to interface, and (d) barrier centre. The inset shows the strain as a function of growth direction (z).

The identical interdiffusion commonly occurs during interdiffusion due to the impurity-free induced intermixing, such as the dielectric cap encapsulant, which

there is no introduction of impurity or implanted atoms to initiate the interdiffusion of QWs. The lattice-matched conservation of QW system is resulted after the interdiffusion process as evidenced from various measurements using Raman spectroscopy [28], SIMS [29], and HRXRD measurements [30]. From Figure 5-4, a small tensile strain (<0.0018%) after interdiffusion is present at different positions across QWs structure. However, both of the tensile strain in the barrier near interface and the wells show that the lattice-matching condition of the QWs is maintained for intermixed structure (less than the lattice-matching condition, 0.032%). For longer interdiffusion length, the strain will be smaller across the wells and barriers since the compositional profile tends to be uniform, so-called bulk like profiles.

The lattice-matched bandgap across QWs structure $E_g(x,y)$ is also a function of the compositional profile, and the unstrained potential confinement profile $V_r(x,y)$ is expressed as:

$$V_r(z) = Q_r [E_g(z) - E_{go}] + zq_e E_{Field}, \quad (10)$$

where the subscript r represents either E or V for the conduction and the valence bands respectively. E_{go} is the minimum bandgap between the conduction and the valence bands in the well, Q_r is the bandgap offset of the QW, E_{Field} is the applied external field, and q_e is the electron charge.

5.4.2 Unidentical interdiffusion ($L_{dIII} \neq L_{dV}$; $k \neq 1$)

When the diffusion length of group III and group V sublattice is different, the strain is introduced in the model. Strains have an important influence on the physical properties of semiconductor films, because they change the electronic states, which result in an electronic energy-band structure via the strain-orbital

deformation potential interaction. The presence of internal strain not only shifts the band edge energies but also modifies the effective masses associated with individual bands. Hence, the carrier confinement profile and the sub-band structure have to consider the presence of strain after interdiffusion.

The necessity in modeling strained QW structure is the coherent pseudomorphic condition. The lattice mismatch can be taken up totally by the tensile or compressive strain inside the epilayer, and one then has a coherent interface. During interdiffusion, the critical layer thickness of QW structure continues to vary since the abrupt alloy compositions and thus the induced strain profiles have been redistributed to be a smooth one in the structure. The QW layer thickness is assumed within the critical thickness regime, the QW structure will be coherently strained after intermixing [38], with:

a. Biaxial hydrostatic strain parallel to the interfacial plane

A compressive hydrostatic strain will induce an increase in bandgap energy, while a tensile hydrostatic strain will induce a decrease in bandgap energy. Assuming that the growth direction z is along [001], then for the biaxial hydrostatic stress parallel to the interface strain components, after interdiffusion, are given by [39]:

$$\varepsilon(x, y) = \frac{a_s(x, y) - a_e(x, y)}{a_s(x, y)} \quad \text{with} \quad (11)$$

$$e_{xx} = e_{yy} = \varepsilon(x, y); e_{zz} = -\frac{2C_{12}(x, y)}{C_{11}(x, y)}\varepsilon(x, y); e_{xy} = e_{yz} = e_{zx} = 0, \quad (12)$$

where a_e and a_s are the lattice constant of the interface regions after interdiffusion respectively and $\varepsilon(x, y)$ is defined to be negative for compressive strain. $C_{ij}(x, y)$ are the elastic stiffness constants of the QW structure.

Figure 5-5. An (x,y) in-plane biaxial strain effect on the energy band structure

The biaxial strain in the heterostructure layer can split the fourfold valence band degeneracy into twofold LH and HH bands due to lattice deformation interactions. In Figure 5-5, it can be seen schematically that the biaxial strain effects on the electronic energy-band structure near the Γ point for zinc blende type. The directions are defined as follows: k_x lies in the growth plane (i.e., plane of biaxial strain), and k_z lies along the growth plane (i.e., perpendicular to the plane of biaxial strain). The biaxial strain in the material lowers its crystal symmetry which results in a change in the bandgap [an increase (decrease), when material is in compression (tension)] and a splitting of LH and HH valence bands. [The higher lying band is the HH (LH) band for a biaxial compression (tension)].

In the spherical model, the Luttinger-Kohn Hamiltonian calculations for strained bulk materials show that at small k_x , the band mass that is heavy along the strain direction is comparatively light perpendicular to that direction or vice versa. For biaxial compression, the highest valence band ($|J=3/2, m_j=\pm 3/2\rangle_z$) has heavy mass along k_z and comparatively light mass along k_x . For biaxial tension, the highest valence band ($|J=3/2, m_j=\pm 1/2\rangle_z$) has heavy mass along k_x and comparatively light mass along k_z . The HH band then acquires a “light” in-plane mass, and the LH

band, a “heavy” in-plane mass. The change in the bulk bandgap due to the biaxial component of strain, $S_{biaxial}(x, y)$, is expressed as

$$S_{biaxial}(x, y) = -2a(x, y) \left[1 - \frac{C_{12}(x, y)}{C_{11}(x, y)} \right] \varepsilon(x, y), \quad (13)$$

$$\text{and } a(x, y) = -\frac{1}{3} [C_{11}(x, y) + 2C_{12}(x, y)] \frac{dE_g}{dP}(x, y), \quad (14)$$

where $a(x, y)$ is the hydrostatic deformation potential and $\frac{dE_g}{dP}(x, y)$ is the hydrostatic pressure coefficient of the lowest direct energy bandgap E_g .

b. Uniaxial shear strain perpendicular to the interfacial plane.

The shear strain disrupts the cubic symmetry of the material and lifts the degeneracy of the HH and the LH band edges at the Brillouin zone centre Γ . The HH band shifts toward the conduction band and the LH moves away from the conduction band or vice versa. In addition, this shear strain causes the LH band to couple with the spin orbit split-off band. The splitting energy, $S_{uniaxial}(x, y)$, between the HH and LH band edges induced by the uniaxial component of strain is given by:

$$S_{uniaxial}(x, y) = -b(x, y) \left[1 + \frac{2C_{12}(x, y)}{C_{11}(x, y)} \right] e(x, y), \quad (15)$$

where $b(x, y)$ is the shear deformation potential. The coupling between the LH and split-off band gives rise to asymmetric HH-LH splitting, so that:

$$S_{HH\text{ uniaxial}}(x, y) = S_{uniaxial}(x, y), \quad (16)$$

$$\text{and } S_{LH\text{ uniaxial}}(x, y) = -\frac{1}{2} [S_{uniaxial}(x, y) + \Delta_0(x, y)] + \frac{1}{2} \sqrt{9[S_{uniaxial}(x, y)]^2 + [\Delta_0(x, y)]^2 - 2S_{uniaxial}(x, y)\Delta_0(x, y)}$$

with $\Delta_0(x, y)$ denoted as the spin-orbit splitting.

By modifying the bulk post processing confinement potential profile with variable strain effects (Figure 5-6), the strained confinement profiles calculation is expressed as:

$$V_r(z) = Q_r [E_g(z) - E_{go} - S_{r \text{ biaxial}}(x, y)] \pm S_{r \text{ uniaxial}}(x, y) + zq_e E_{\text{Field}} \quad (17)$$

where the subscript r represents either E, HH, or LH, respectively. $S_{r \text{ biaxial}}$ is the change in the bulk bandgap due to the biaxial component of strain, and the $S_{r \text{ uniaxial}}$ is the potential corresponding to the HH and LH band edge splitting induced by the uniaxial component of strain. The positive sign represents the confined HH profile, the negative sign represents the confined LH profile, and for the confined electron profile, $S_{C \text{ uniaxial}}$, is equal to zero. The QW parameters are assumed to obey the Vegard's law, so that their respective values depend directly on the compositional profile across the QW, depending on the material system detailed in Appendix B.

Figure 5-6. The conduction and valence band edge profile at various diffusion lengths in the $A_xB_{1-x}C_yD_{1-y}$ system

In a QW structure, the effective mass of carriers (electrons or holes) varies across different layers. In an intermixed QW, the effective mass depends on the alloy composition that in turn depends on the spatial position z . The Schrödinger equation is used to solve the bound states at Γ (zone centre) valley:

$$H \Psi_r = E \Psi_r, \quad (18)$$

where Ψ_r is the envelope wave function for E, HH or LH, respectively. Quantum mechanics requires the probability current density of the carrier to be conserved, i.e. the $\frac{1}{m^*(z)} \frac{\partial \psi}{\partial z}$ and ψ are both continuous along z . Since in most heterostructure the effective mass is not isotropic, it requires the modification of the Schrödinger's equation to a so-called Ben Daniel-Duke's equation [40]:

$$-\frac{\hbar^2}{2} \frac{\partial}{\partial z} \left[\frac{1}{m^*(z)} \frac{\partial \psi_n(z)}{\partial z} \right] + V(z) \psi_n(z) = E_n \psi_n(z), \quad (19)$$

where $m^*(z)$, $\psi_n(z)$, $V(z)$, E_n are the local carrier effective mass, eigen wave functions, potential function (in this case the band edge of either the conduction or the valence band) and the eigen energies respectively. $n=1,2,\dots$ are the QW sub-band levels for either E or HH/LH.

In order to solve the equation numerically, the differential equation is represented as finite difference equations along the QW growth direction (z), divided into n mesh points. The finite difference equations are derived from the 4th order Taylor series:

$$\begin{aligned} \frac{\partial \Psi(z_i)}{\partial z} &\approx \frac{\Psi(z_{i-2}) - 8\Psi(z_{i-1}) + 8\Psi(z_{i+1}) - \Psi(z_{i+2})}{12\Delta z} \text{ and} \\ \frac{\partial^2 \Psi(z_i)}{\partial z^2} &\approx \frac{-\Psi(z_{i-2}) + 16\Psi(z_{i-1}) - 30\Psi(z_i) + 16\Psi(z_{i+1}) - \Psi(z_{i+2})}{12\Delta z^2}. \end{aligned} \quad (20)$$

Now the Ben-Daniel Duke's equation at every mesh point (z_i) becomes:

$$C_1(z_i)\Psi(z_{i-2}) + B_1(z_i)\Psi(z_{i-1}) + [A(z_i) - E]\Psi(z_i) + B_2(z_i)\Psi(z_{i+1}) + C_2(z_i)\Psi(z_{i+2}) = 0, \quad (21)$$

where

$$\begin{aligned}
 C_1(z_i) &= \frac{\hbar^2}{24 m^*(z_i) \Delta z^2} \left[\frac{1}{m^*(z_i)} \frac{\partial m^*(z_i)}{\partial z} + 1 \right]; \\
 B_1(z_i) &= -\frac{\hbar^2}{24 m^*(z_i) \Delta z^2} \left[8 \frac{1}{m^*(z_i)} \frac{\partial m^*(z_i)}{\partial z} + 16 \right]; \\
 A(z_i) &= \frac{5 \hbar^2}{4 m^*(z_i) \Delta z^2} + V(z_i); \\
 B_2(z_i) &= -\frac{\hbar^2}{24 m^*(z_i) \Delta z^2} \left[-8 \frac{1}{m^*(z_i)} \frac{\partial m^*(z_i)}{\partial z} + 16 \right]; \\
 C_2(z_i) &= \frac{\hbar^2}{24 m^*(z_i) \Delta z^2} \left[-\frac{1}{m^*(z_i)} \frac{\partial m^*(z_i)}{\partial z} + 1 \right].
 \end{aligned} \tag{22}$$

Each of the coefficients above involves the term $\frac{\partial m^*(z_i)}{\partial z}$, which is represented in the finite difference equation as:

$$\frac{\partial m^*(z_i)}{\partial z} \approx \frac{m^*(z_{i-2}) - 8m^*(z_{i-1}) + 8m^*(z_{i+1}) - m^*(z_{i+2})}{12 \Delta z}. \tag{23}$$

For bound states, the boundary condition is such that the wavefunction must vanish at both ends and expressed as follows:

$$\Psi(z_{-1}) = \Psi(z_0) = 0 \text{ and } \Psi(z_{n+1}) = \Psi(z_{n+2}) = 0. \tag{24}$$

The finite difference equations for all mesh points will form a generalised eigen value matrix equation:

$$[H] [\Psi] = E [\Psi]. \tag{25}$$

The elements of the Hamiltonian matrix can be expressed as:

$$H_{mn} = C_1(z_n) \delta_{m,n-2} + B_1(z_n) \delta_{m,n-1} + A(z_n) \delta_{m,n} + B_2(z_n) \delta_{m,n+1} + C_2(z_n) \delta_{m,n+2} \tag{26}$$

where $\delta_{m,n}$ is the usual Kronecker delta function with $\delta_{m,n} = 1$, if $m = n$ or else $\delta_{m,n} = 0$.

As shown in Figure 5-7, the finite difference equation for every mesh point is coupled to each other. A matrix equation can be constructed to represent the whole system. The matrix equation obtained is an eigen value system where $\mathbf{E}$ is the eigen value and Ψ is the eigen vector representing the wave function.

$$\begin{pmatrix} A(z_1) - \mathbf{E} & B_2(z_1) & C_2(z_1) & 0 & 0 & 0 & \dots & 0 \\ B_1(z_2) & A(z_2) - \mathbf{E} & B_2(z_2) & C_2(z_2) & 0 & 0 & \dots & 0 \\ C_1(z_3) & B_1(z_3) & A(z_3) - \mathbf{E} & B_2(z_3) & C_2(z_3) & 0 & \dots & 0 \\ 0 & C_1(z_4) & B_1(z_4) & A(z_4) - \mathbf{E} & B_2(z_4) & C_2(z_4) & \dots & 0 \\ 0 & 0 & C_1(z_5) & B_1(z_5) & \dots & \dots & \dots & 0 \\ 0 & 0 & 0 & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & 0 & 0 & C_2(z_n) & B_1(z_n) & A(z_n) - \mathbf{E} \end{pmatrix} \begin{pmatrix} \Psi(z_1) \\ \Psi(z_2) \\ \Psi(z_3) \\ \Psi(z_4) \\ Y(z_5) \\ \dots \\ \Psi(z_n) \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad (27)$$

All mesh points construct $N \times N$ matrix equation [Equation (27)] representing eigen values problem that can be solved numerically. The eigen values of this matrix equation are the eigen energies (E_n) and their eigen vectors are the corresponding wavefunctions (Ψ_n).

Figure 5-7. Fourth order finite difference method to solve the Schrödinger equation

Now, the interband transitions energy can be determined, as well as the overlap integral $\langle \Psi_{v_n} | \Psi_{c_m} \rangle$ between the m -th conduction subband and the n -th valence subband envelope wavefunctions, where

$$\langle \Psi_{V_n} | \Psi_{C_m} \rangle = \int_{z_{-1}}^{z_{n+2}} \Psi_{V_n}^* (z) \Psi_{C_m} (z) dz \quad (28)$$

with the boundary is taken from Equation (24).

The electron-heavy hole transition energy (E_{EmHHn}) and the electron-light hole transition energy (E_{EmLHn}), can then be calculated from the following formula:

$$E_{EmHHn} (eV) = E_{gHH}[x(0),y(0)] + E_{Em} + E_{HHn} ; \quad (29)$$

$$E_{EmLHn} (eV) = E_{gLH}[x(0),y(0)] + E_{Em} + E_{LHn} , \quad (30)$$

respectively, where $E_{gHH}[x(0),y(0)]$, $E_{gLH}[x(0),y(0)]$ are the lowest bandgap of the E-HH and E-LH at Brillouin zone centre after intermixing.

5.5 THE SEMI-EMPIRICAL MODEL OF PLASMA INDUCED QWI

Intermixing process in crystalline materials can be generally understood in terms of the diffusion behaviour of point defects and their interaction with each other or with crystal atoms. The plasma enhanced QWI using ICP machine has been studied in the previous chapter for tuning the bandgap of InGaAs/InGaAsP as well as GaAs/AlGaAs QWs system [41]. The application of ICP power, thus high-density plasma, has been found to enhance the interdiffusion of point defects resulting in higher degree of intermixing.

The majority of the impinging ions of Ar plasma is stopped within the first few atomic monolayer of material and causes lattice disruption and damage up to a depth of a few tens of nm. When Ar ions are introduced to the semiconductor material, they create point defects, including vacancies, interstitials, vacancy-interstitial (Frenkel) pairs, and antisite defects. The generation of the atoms on the wrong sublattice, called the antisites, is negligible during Ar plasma exposure to promote the intermixing between barriers and QWs as the annealing temperature

used in common QWI process. An increase of ion bombardment energy greatly raises the formation probability of surface defects, which is sufficient to cause surface damage to a semiconductor.

A number of experiments have confirmed that defects generated from low energy ion (with 100s eV of ion impact energy) processes can penetrate deeply more than 100 nm into the substrate [42],[43]. The very short duration of plasma exposure (less than 10 minutes) is sufficient to raise the formation probability of surface defects and thus cause surface damage to a semiconductor substrate even with very small ion bombardment energy from 10 to 100 eV [44]. Instead of the radiation-enhanced motion defects [45], the channeling mechanism at this small ion bombardment energy has been identified to be the primary mechanism causing defects deep within the plasma-exposed crystalline material, with diffusion possibly modifying the final defects distribution [46]. From the previous experimental and reported results, the plasma-induced defects on the near surface of samples, which contributes to the raise of nonradiative recombination centres, can be summarised as follows: (i) the magnitude of the created defects increases with the plasma exposure time but the damage depth remains constant [47],[48]; (ii) The magnitude of created defects is expected to saturate after a long exposure time to the plasma; (iii) The amount of created defects is higher in the low etch rate process than that in the higher etch-rate process [49]; (iv) the magnitude of the created defects is higher in the high-density plasma rather than in the low-density plasma.

The beneficial defects in the form of mobile point defects created during plasma exposure near the sample surface propagate into QW region during annealing step. The arrival of point defects in the QW region enhances the

interdiffusion of the group III and group V species, widens the bandgap and results in the blue-shift of PL emission. In the unexposed samples, annealing step contributes a small bandgap shift, which could be attributed to the presence of the grown-in defects from the substrate. These defects propagate into the QW active region to promote the intermixing during annealing process. Our semi-empirical interdiffusion model is based on the plasma-induced defects model that the amount of point defects that can induce the QWI process are limited and saturate exponentially with the plasma exposure time. The point defects density created during the plasma exposure is assumed to be uniform in the vicinity of the QWs upon annealing. This approximation is made based on the fact that the QW width layers are very thin, i.e. 5.5 nm, as compared to the distance of the QW region from the sample surface. It is known that interdiffusion of the defects in plasma process is strongly affected by temperature. For the analysis performed in our model, the total amount of defects generated on the sample surface are taken into account, thus the defect distribution due to temperature variation during plasma exposure will not affect our model.

The extent of the quantum well intermixing can be characterised using the diffusion coefficient of certain atomic species D_{QW} as a function of the total number of created mobile point defects, σ_D [50]:

$$D_{QW} = \sigma_D \lambda_D^2 \Gamma_D = (\sigma_0 + \sigma_E) \lambda_D^2 \Gamma_D, \quad (31)$$

where σ_0 is the equilibrium number concentrations of mobile point defects, σ_E is the excess number concentrations of mobile point defects created by the high-density plasma application, Γ_D is the hopping frequency of the point defect, and λ_D is the mean free path of the point defect. Since the point defect creation is a random

interaction with atomic lattice, the probability of defects creation is proportional to the number of possible defects that can be created. Assuming that the lattice can only accommodate a certain maximum number concentrations of defects (σ_{sat}) [51], the rate of point defect creation due to high-density plasma enhancement can then be expressed as:

$$\frac{d\sigma_D}{dt} = k(\sigma_{sat} - \sigma_E), \quad (32)$$

where t is the plasma exposure time and k is point defect creation constant, which indicate the rate of defects creation per unit exposure time. This parameter k depends on the plasma radiation intensity. Solving this differential equation from Equation (32) gives:

$$\sigma_E = \sigma_{sat}(1 - e^{-kt}). \quad (33)$$

This relationship intuitively shows that rate of number concentrations of defects decreases as the exposure time increases. Most of point defects will be created in the early stage of exposure. As the point defects start to build up, there will be fewer point defects created subsequently. This agrees with the experimental observation that the degree of intermixing is not so much dependent on plasma exposure time after long exposure in the plasma enhanced QWI process. The saturated amount of mobile point defects depend on nature of plasma, including the RF-induced DC bias condition, such that the value will be different with the change of inductively coupled plasma power.

Considering the above points, Equation (31) can be expressed as:

$$D_{QW} = \sigma_0 \lambda_D^2 \Gamma_D + \sigma_{sat} \lambda_D^2 \Gamma_D (1 - e^{-kt}) = D_0 + D_E (1 - e^{-kt}), \quad (34)$$

where D_0 is the diffusion coefficient in thermal equilibrium and D_E is the diffusion coefficient enhanced by the excess mobile point defects due to plasma exposure. Both parameters are associated with the QW material, annealing condition, and plasma properties. D_{QW} is also temperature dependent and can be approximated using Arrhenius equation.

Assuming an identical interdiffusion length of group III and group V atoms using plasma induced QWI technique, the lattice matching condition is conserved after interdiffusion process [27]-[30]. The value of the diffusion coefficient and their related parameters can be deduced from the PL measurement results after solving the interdiffused QW ground state transition energy (E1-HH1). The ground state transitional energy (E1-HH1) that corresponds to the peak excitonic wavelength were fitted to the measured PL peak energies of intermixed samples by adjusting the value of L_d , thus L_d and D_{QW} can be determined.

5.6 THE MODEL VALIDATION WITH EXPERIMENTS

The amount of bandgap shift after plasma induced QWI process correlates to the changing of QW potential profile from abrupt to the graded profile. Solving the interdiffused QW transitional energies, the ground state E1-HH1 and E1-LH1 transition energies as the function of the single interdiffusion length are shown in Figure 5-8. The E1-HH1 calculation of the bound states transition energy is related to the PL emission of the QWs samples as a result of compositional profile change. The plot gives very important information related to the maximum possible bandgap or wavelength shift that can be obtained from this QWs structure by intermixing process.

Figure 5-8. Calculated ground state exciton transition energy (E1-HH1 and E1-LH1) with respect to PL peak of as-grown sample as a function of single interdiffusion length, L_d . The inset shows the corresponding confinement profile for both CB and VB.

From Figure 5-8, as the interdiffusion length increases the E1-HH1 transition energy also increases, known as blue-shift phenomenon, reported recently for the same material of interdiffused InGaAs/InGaAsP QW using existing QWI techniques such as IID, IFVD, and LID. It can be noted that significant intermixing occurs up to a interdiffusion length of 40 Å. For longer interdiffusion length, the intermixing effect is less pronounced due to the change of QW shape to the bulk-like profile. This effect can be observed in the experiment as the saturation phenomena i.e., there are fewer shifts in the exciton peak at high degree of intermixing. This result agrees with the previous observations in Chapter 3 and 4, which samples exposed to Ar plasma approach a steady state bandgap shift upon longer exposure time. It can be observed that both E1-HH1 and E1-LH1 excitons are shifted to the shorter wavelength; this shift is much larger for the E1-HH1 than for the E1-LH1. A change in interdiffusion length from 0 to 50 Å corresponds to a

change in the E1-HH1 transition energy of about 85.5 meV, which represents a shift to shorter wavelength of about 140 nm with respect to the E1-HH1 transition energy of the as-grown sample. Whereas the corresponding light hole transition energy changes by about 58 meV, representing a shift to shorter wavelengths of about 92 nm with respect to the E1-LH1 transition energy of as-grown samples. The inset shows the corresponding confinement profiles of electrons and holes in the QW region. The change from abrupt profile to graded profile indicates that there is a small amount of confinement loss.

From the E1-HH1 ground state transition energy curve in Figure 5-8, the corresponding interdiffusion length and the diffusion coefficient can be deduced from the experimental data of the intermixed samples without and with ICP application. The deduced diffusion coefficient was fitted to the semi-empirical model of diffusion coefficient in Equation (34) upon annealing to promote the intermixing. From Equation (34), the diffusion coefficients of point defect propagation increase with the Ar exposure time qualitatively. Figure 5-9(a) shows the comparison of diffusion coefficients between the experiments data and the curve-fitted results using our semi-empirical model. The diffusion coefficients from experimental data can be fitted well with our model with the parameters as shown in the inset. The small increase of k with respect to the ICP application is as expected, which is attributed to the increase in the radiation intensity from the high plasma density. At a short exposure time, the diffusivity increases rapidly corresponding to the most of defects created in the early stage of Ar exposure. The diffusion coefficient saturates after long exposure times at the interdiffusion value at $D_{QW} \sim 1.5 \cdot 10^{-16} \text{ cm}^2/\text{s}$ and $D_{QW} \sim 3.0 \cdot 10^{-16} \text{ cm}^2/\text{s}$ for ICP power at 0 W and 500 W, respectively. This diffusivity saturation implied that the amount of bandgap shift

saturates for a very long exposure time. The application of 500 W inductively coupled plasma enhances the defect diffusion coefficient by a factor of 2, if compared to the case of with no ICP power. The rate of interdiffusion is thus significantly increased by the use of inductively coupled plasma, promoting more intermixing degree in the QW material during annealing. The intermixing enhancement using ICP could be due to the presences of the high ion density and the high intensity of plasma radiation.

The experimental data of intermixed samples are then interpreted using the model in order to identify the enhanced QWI process with the application of inductively coupled Ar plasma. Figure 5-9(b) shows a comparison between the best fitted-theoretical model and the experimental results of blue-shift in wavelength as a function of Ar plasma exposure time. The interdiffusion model is curve fitted to the existing data implying that the intermixing processes obey the behaviour that the model assumes. For the exposure time of 5 minutes or below the relationship between the bandgap energy shift and time is linear. However, for longer exposure time, this relationship becomes non-linear. Preliminary interdiffusivity calculations have ruled out the possibility of this saturation effect being due to the complete intermixing induced by the propagation of mobile point defects and thus imply that the interdiffusion mechanisms takes on a different behaviour in this regime. The inclusion of enhanced defects interdiffusion due to inductively coupled plasma according to the semi-empirical model, even at very simple level, seems to provide good agreement with the experimental results.

Figure 5-9. The interdiffusion coefficients (left) and the corresponding bandgap shift (right), deduced from the experiments, versus plasma exposure times without (open circle) and with inductively coupled plasma of 500 W ICP power (open triangle). The solid line represents the best fitted from the theoretical model. The inset shows the deduced confinement profile of both CB and VB.

Earlier work reported that the defect enhancement takes place due to a radiation-enhanced diffusion process [52] and the high-density of atomic ions in the discharge during exposure [44]. Chen *et al.* recently found that the damage depth seemed to increase with the illumination intensity and attributed this to enhance the defect diffusion on top of any channeling effect [53]. It was determined that the generation of high energy photons in vacuum ultraviolet (VUV) range (4-30 eV) as high as $1 \text{ mW}/\text{cm}^2$ is possible to introduce radiation damage on semiconductor devices in the plasma chamber [54]. This radiation-enhanced damage can be attributed to the net effect of both electron-hole recombinations via electron phonon coupling and an excess flux of phonon or due to the net effect of the plasma radiation and ion bombardment. The radiation damage in VUV range to affect the intermixing was investigated by exposing the sample to plasma without the application of RF-induced DC bias. The samples exposed up to 15 minutes using

ICP power of 500 W and subsequent annealing resulted in no observable PL peak shift.

Figure 5-10. (a) The measured Ar ion current density (dashed line) at 100 W RF power and RF induced bias at 480 W RF power (solid line) versus chamber pressures. (b) The calculated Ar ion current density (dashed line) and sheath voltage (line) as a function ICP Power at 80 mTorr and a fixed RF power of 480 W.

The ion current density from inductively coupled Ar plasma with setting parameters at RF power 100 W and ICP power between 0 to 1000 W was plotted in Figure 5-10(a), as measured by ICP 180 manufacturer, showing a nearly linear increase from 0.03 to 1.0 mA/cm² with a small variation between 7 mTorr and 60 mTorr chamber pressure. There is no sign of saturation behaviour, so higher powers could be used to get higher ion fluxes with the decrease in the RF induced DC bias, hence less energetic ion bombardments to the sample. At RF power of 480 W, increasing ICP power from 0 to 1000 W causes the linear decrease in the RF induced DC bias by about 220 V.

To further estimate the inductively coupled plasma properties at optimum intermixing parameters (480 W RF power and 500 W ICP power), a collisional

sheath global discharge cylindrical model [55] is adopted to calculate the Ar plasma properties in ICP discharge. The steady-state ion current density (J_i) and the sheath voltage (V_s) is calculated at constant RF power of 480 W. It should, however, be pointed out that the plasma density is slightly overestimated in the calculation here as it is assumed that all the RF power is fully absorbed by the plasma. The ion bombardment voltage is roughly equal to V_s , and RF-induced DC bias decreases with the increase in ICP power from 0 W to 500 W as a result of, ranging from $V_s = 840$ V to 620 V, as depicted in Figure 5-10(b). The J_i increases linearly from about 0.36 to 1.2 mA/cm², which is at about 0.2 mA/cm² less than the actual ion current using RF power of 100 W, as measured by the ICP 180 manufacturer. This corresponds to a dose rate of $6.7 \cdot 10^{17}$ to $2.2 \cdot 10^{18}$ ions/cm² for a 5 minute plasma exposure, which is several orders larger than the traditional ion-implantation technique [56],[57]. The impact intensity by high ions dose at ICP power of 500 W is about 550 mW/cm² for 5 minute plasma exposure, which is three-orders of magnitude higher than the typical VUV Ar irradiance level of 0.96 mW/cm² with the integrated photon flux of $3.64 \cdot 10^{14}$ cm⁻²s⁻¹ in the ECR chamber [54]. Thus, it is postulated that the high dose atomic ion exposure due to the ICP application plays more significant effect in enhancing the mobile point defects level and thus the degree of intermixing in ICP chamber as compared to the presence of plasma radiation in the discharge. This is similar to a relevant report for damage enhancement in the ECR machine at higher ion dose as compared to RIE machine [58],[59].

5.8 SUMMARY

The interdiffusion model with strain induced confinement profile modification to investigate various mechanisms of QW has been presented. The

plasma induced-defect model predicts that the magnitude of defects is higher for the high-density plasma with the application of the ICP. Using the semi-empirical model of interdiffused QW, a substantial progress has been made in understanding the mechanism of the increase in the material bandgap energy using inductively coupled plasma exposure. The experimental data were well supported and explained by our theoretical model. According to the model, the degree of intermixing increases and saturates as the exposure time increases, in good agreement with the observation from experiments. Adopting a simple collisional sheath global discharge cylindrical model, the inductively coupled Ar plasma properties can be estimated, indicating several orders larger dose rate than the ion-implantation technique and leading to the more dominant factor than the plasma radiation intensity to intermixing enhancement.

The theoretical model serves as a good simulation program to study the intermixing mechanism and further to optimise the plasma enhanced QWI process for the long-term goal of photonic integration purposes. Through the developed program, the optical properties of the QW materials can be understood and evaluated, which eventually leads to their improvement and exploitation in commercial photonic integration devices.

6. PHOTONIC INTEGRATION STUDY

The photonic integration research community views QWI technology as a promising approach **only** for two/three-section photonic devices but not for multiple sections as the process becomes tedious and complicated. On the other hand, various QWI techniques have limitations to tune a wide range of material system. The development of the revolutionary QWI technology has proven that the application of QWI is not limited to two sectional devices with more cost effective, higher throughput, and of higher yield compared to selective area epitaxy. The impurity-free nature from Ar plasma induced QWI is expected to give a low loss waveguide operation in the intermixed area at the peak wavelength operation in the unintermixed area, as compared to the IID process, which commonly suffers from the significant free carrier absorption from the intermixed waveguide.

The capability of plasma induced QWI technique for high-density photonic integration devices, offers i) an adequately high spatial resolution, ii) single step multiple bandgaps creation in a simple way, and iii) universal process for a wide range of QW material system, and is therefore expected to create a significant impact to the photonic research community. In this chapter, a systematic study to figure out the feasible plasma induced QWI technique for photonic integration purposes is presented. Eventually, a simple photonic integrated device using Ar plasma induced QWI to monolithically shift the material bandgap is demonstrated in the form of extended cavity laser diode, where an active laser is integrated with a low-loss waveguide.

6.1 HIGH SPATIAL RESOLUTION STUDY

Recently, there has been increasing interest in scaling the PICs monolithically on a single wafer. In order to achieve high-density photonic integration, the QWI process must be capable of tuning the material bandgap with high spatial selectivity. For example, the spatial resolution requirement of quasi-phase-matching grating for second harmonic generation would be in the micrometer range [1]-[4]. The use of low-ion energy from Ar plasma exposure tends to have low spatial resolution as the highest concentration of mobile point defects on the top surface spread-out in the lateral direction as they propagate to the QW region during annealing. The spatial resolution here is defined as the lateral change of compositional interdiffusion from QW active area due to the QWI process.

In this section, the spatial resolution using Ar plasma induced QWI on InGaAs/InP system is investigated. In addition, a technique to improve spatial resolution of the Ar plasma-based QWI process using the stress-inducing dielectric cap will be demonstrated. PL spectroscopy was employed to investigate the selective intermixing results, the spatial resolution across the InGaAs/InGaAsP QW material, and the effect of stress-inducing dielectric cap during annealing. Aside from PL measurement, MRS was employed to investigate the interdiffusion process across the boundary of selectively intermixed material and to further provide a spatial resolution comparison with PL spectroscopy.

6.1.1 Experimental details

Two sets of lattice-matched InGaAs/InGaAsP five quantum well samples, as detailed in Appendix A.1, were grown by University of Sheffield and IQE with 77 K PL peak at $1.42 \pm 0.02 \mu\text{m}$ and $1.45 \pm 0.02 \mu\text{m}$, respectively. To study the effect of

stress-inducing dielectric cap with the variable grating period, two samples from IQE in dimensions of $8 \times 8 \text{ mm}^2$ were coated with 300 nm thick Si_xN_y layer using PECVD. The standard lithography was performed using 700 nm thick TSMR-CR B2 positive photoresist from Tokyo Ohka Kogyo Co. Ltd. after spin coating at 5000 rpm for 35 seconds. The 4 distinct arrays of mask pattern were aligned onto the sample and UV light was exposed for 5 s, containing variable mask stripes (50, 20, 10 and 5 μm stripe). Each array of mask was $2 \times 2 \text{ mm}^2$. The resist was then developed for 30 s. After postbaking at 120 °C for 2 minutes, the resist pattern was transferred to the Si_xN_y layer using the CF_4/O_2 RIE process for 6 minutes, followed by the wet etch ($\text{HF}:\text{DI}$ water) solution to minimise the RIE damage effect, which may contribute to the intermixing process. Figure 6-1 shows 4 distinct pattern stripes of Si_xN_y layer on the QW material after resist removal using acetone. The patterned samples were exposed in ICP system to Ar plasma for 5 minutes for defect introduction. The oxide pattern was removed for a sample using diluted HF solution, while another sample was kept with patterned oxide. Prior to annealing, the nitride pattern was removed in one sample using diluted HF solution, while it was preserved in another sample. The annealing process was carried out using a single step rapid thermal processor (RTP) at 600 °C for 2 minutes under a flowing nitrogen ambient. Two fresh pieces of GaAs proximity caps were used to provide As over-pressure environment during the annealing process and further to prevent the sample surface from outdiffusion. During high temperature annealing, the stress field on the film/QW material interface is modified due to the mismatch of the linear thermal expansion coefficient between Si_xN_y layer ($\sim 2.8 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$) and InP-based material ($\sim 4.6 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$). As a result, the QW material directly under the Si_xN_y layer is under compressive strain during annealing, while the QW material

under the trench is under tensile strain. This generates the modulation of the stress field distribution under Si_xN_y masked region oriented in a direction perpendicular to the sample surface. The amplitude of stress is modulated strongly between masked and unmasked region and enhanced compressive stress exists at the Si_xN_y pattern edges. PL measurements at 77 K were taken for each patterned area using a 50 μm multimode fibre optic as a probe. Due to the spot size dimension, the PL spectra from patterned sample exhibited the luminescence from both masked (unintermixed) and unmasked (exposed thus intermixed) area. From this way, the spatial resolution can be analysed between sample with and without stress-inducing dielectric cap during annealing process.

Figure 6-1. The Si_xN_y patterns with variable stripes after lithography and subsequent dry etch process using RIE machine, containing widths of (a) 50 μm , (b) 20 μm , (c) 10 μm , and (d) 5 μm .

Due to the limited availability of narrow pattern stripe mask and QW sample, PL mapping resolution and Raman line scanning was done to verify the PL measurement. A sample from University of Sheffield in dimensions of 4 x 2 mm² were selectively patterned with Au/ Si_xN_y (40 nm/300 nm) layers as an intermixing mask with a 800 μm wide pattern stripe with variable open area ranging from 500 μm to 2 mm. A 200 nm thick Si_xN_y layer was initially deposited of the QW samples using PECVD. A 40 nm thick gold mask was then evaporated using e-beam evaporator and defined on the Si_xN_y layer surface using photolithography and lift-off. This Au layer serves as a reflective layer to prevent further possible damage from high-density plasma radiation to the masked samples. The Si_xN_y layer on the

unpatterned Au section was then removed using CF_4/O_2 based plasma etch using RIE for 6 minutes, followed by the wet etch ($\text{HF}:\text{DI water}$) solution to minimise the RIE damage effect, which may contribute to the intermixing process. The subsequent intermixing processes were similar to the previous IQE samples. The annealing was done with stress-inducing Si_xN_y cap, as shown in Figure 6-2. PL map was then taken on the uniformity evaluation of selectively intermixed sample at room temperature.

Figure 6-2. Samples preparation for selective intermixing and spatial resolution study using MRS: (a) Ar plasma exposure step; annealing step to induce bandgap shift under unmasked section (b) without and (c) with the vertical stress-inducing dielectric cap

MRS has been used to investigate the microscopic nature of the disordered alloy due to its compositional fluctuation and to analyse many parameters of semiconductor crystals including lattice diffusion. *Helmy et al* [5] found that the MRS is suitable for characterising QWI processes with high spatial resolution by studying features of the Raman-mode spectra, such as relative mode amplitudes and integrated mode area. The Raman resolution is limited to the laser spot size, since the scattered light is produced only from the part of lattice illuminated by the laser excitation, serving as a sensitive technique for detecting and assessing the compositional interdiffusion.

Following the PL mapping measurement, the room temperature MRS map was carried out using Renishaw model inVia Reflex on the selectively intermixed

sample. The spectroscopy line mapping across intermixing boundary was taken in the backscattering configuration using the Argon laser of 514.5 nm as excitation source with $\times 100$ objective (Leica 100 $\times$ Nplan), giving a spot diameter of ~ 0.4 μm . The scanning was with interval distance of 0.2 μm across 8 μm spatial distance, which is the resolution limit of the high-precision x - y - z translation stage. A uniform penetration depth of ~ 90 nm and ~ 110 nm below the top surface is predicted from the calculation of its absorption length directly for InP and GaAs material, respectively [6]. To obtain a meaningful information of compositional intermixing across the interface boundary on the QW region, the selective wet chemical etchants ($\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2\text{:H}_2\text{O}$ solution and $\text{HCl:H}_3\text{PO}_4$ solution) were used to remove the InGaAs/InGaAsP cap layers and the InP upper cladding, respectively. This procedure aims to reduce photon absorption of laser source from the InGaAs/InGaAsP cap and InP upper cladding layers. Thus, the Raman modes with the largest signal-to-noise ratio was dominantly from the InGaAsP graded index (GRIN) layers of QW active region, rather than the previous study of spatial resolution using Raman spectra taken from the cap layers of QW laser structure [7]. The wet etching removal was controlled carefully with the routine check procedure on unprocessed QW sample measured using surface profiler to ensure adequate chemical etch depth to the region around the QW waveguide core. Thus, the Raman modes with the largest signal-to-noise ratio was dominantly from the InGaAsP GRIN layers of QW active region, rather than the previous study of spatial resolution using Raman spectra taken from the from the cap layers of QW laser structure [7]. After subsequent top section removal, 77 K PL measurement with 50 μm diameter fibre optic probe was performed on the interface boundary to check the compositional interdiffusion of QWs after intermixing.

6.1.2 Results and discussion

According to the previous thermal stability test of the QW structure using different dielectric cap layers, the Si_xN_y cap showed the less bandgap blue-shift after annealing if compared with the SiO_2 cap. The Si_xN_y dielectric layer was chosen to define the intermixing mask as well as a stress-inducing dielectric cap due to the less solubility of group III atoms to the nitride layer, thus minimising the species outdiffusion in the area patterned with the dielectric cap [8]. A 300 nm thick Si_xN_y layer was chosen as a QWI mask to prevent the point defects creation into the sample. Point defects diffusing inwards during plasma exposure are blocked by the Si_xN_y layers. Therefore, only very small amount of damage or ions is expected to reach the sample under masked (patterned) section as described earlier. On the unmasked section, the plasma exposure will create near surface point defects, which will then diffuse during high temperature annealing and enhance the QWI rate. By using variable pattern stripes, the sum of intermixed and unintermixed PL spectra can be collected as indication of its spatial resolution. The 300 nm-thick Si_xN_y mask patterned on the sample surface is expected to block the point defect creation during the plasma exposure in the masked region and minimizes the defect diffusion in the lateral direction due to the stress effect during the annealing process. In the unmasked region, the plasma exposure introduced near-surface point defects, which would diffuse during high temperature annealing and enhance the QWI rate. By varying the width of the patterned stripes, the sum of intermixed and unintermixed PL spectra can be collected as a direct evidence of spatial resolution.

Figure 6-3 shows the comparison of PL spectra from arrays with and without stress-inducing dielectric cap using different stripe widths. The masked and unmasked PL spectra referred to the luminescence probed from relatively large area

of masked and unmasked portion from the same substrate, respectively, were included for comparison. The diameter of fibre optic probe at 50 μm enables the sum of collected PL signals from two areas. The differential bandgap shifts between masked and unmasked area were 74 nm and 66 nm for annealed sample with and without stress-inducing dielectric cap, respectively. The sample with stress-inducing dielectric mask exhibited a larger bandgap shift due to the interdiffusion enhancement caused by the group V out diffusion from the presence of a small gap between sample and GaAs proximity cap during annealing.

Figure 6-3. The PL spectra of intermixed samples at different grating periods as intermixing mask: (a) annealed without cap and (b) annealed with cap. The 50 μm diameter multimode fibre was used as a probe during PL measurement.

The PL spectra from patterned sample exhibited two peaks corresponding to the masked and unmasked area. As the intermixing occurred, the created surface defects vertically propagate and the spatial resolution made the two peaks merge into one broad spectrum. With the given narrow stripe and the appearance of single peak corresponding to the masked PL spectra, the spatial resolution of the process can be determined spatially. The appearance of well resolved dual peak suggested

that high selectivity is obtainable in QW samples using dielectric layers as an intermixing mask. For the sample annealed without cap, the separation of two peaks is clearly observed for 50, 20 and 10 μm stripe width while at the stripe width of 5 μm , the PL spectrum only had single peak, similar to the masked PL spectrum. Thus, it is concluded that the amount of spatial diffusion is more than 2.5 μm , but less than 5 μm . The interesting finding here was the sample annealed with stress-inducing dielectric cap showed the dual peak of PL even at a stripe width of 5 μm , with a little blue-shift for the longer wavelength peak. From these observations, the spatial selectivity is determined to be 2.5 μm , which is half of the narrowest stripe width at the dual peak spectra.

Figure 6-4. (a) The two dimension image quality PL peak maps taken at room temperature across selectively intermixed samples. (b) The one dimension map of PL peak across the Y-position.

The intermixing of QWs under the masked region could be due to the combined effects: (a) lateral spread of surface defects during Ar plasma exposure and (b) lateral diffusion of defects during annealing due to the effect of stress. The improvement of spatial resolution observed here is ascribed to the existence of the stress-inducing dielectric mask, which provided the modulated stress field across the mask interface during annealing [9],[10]. The edges of the dielectric mask cause the modulation of the material stress during the annealing stage due to the large

difference in the thermal coefficient expansion between the Si_xN_y layer and the QW material. The compressive state of the QWs material under Si_xN_y masked region generates a higher compressive strain at the pattern edge and thus forming the stress field lines oriented in a direction perpendicular to the sample surface. The vertical stress field lines act as a barrier to limit the point defect diffusion in the lateral direction, since it is difficult for the mobile point defects to move across the vertical stress field lines due to the presence of the stress-inducing dielectric mask. As a result, the vertical stress will minimise the lateral diffusion of point defects underneath the mask during annealing, thus giving rise to a higher spatial resolution of $\sim 2.5 \mu\text{m}$ from the PL measurements.

Figure 6-5. (a) The PL spectrum from the intermixing boundary taken using $50 \mu\text{m}$ diameter fibre optic as PL probe and its deconvolution using Gaussian line profiles. (b) The Raman spectra taken from masked and unmasked sections.

PL map was then taken on the selectively intermixed sample at room temperature. As shown in Figure 6-4, the 2D map profile and 1D line profile of PL peak distribution across the selectively intermixed sample revealing the distinct

dual bandgap across the sample with a good uniformity across the selectively intermixed sample with dimension of 1.2 x 1.2 mm. Two distinguished bandgaps were revealed with a sharp contrast of colour indicating that an intermixing spatial resolution between two sections is below the resolution of the system, which is below 100 μm . The pitting on the edge of sample with non-uniform luminescence is caused by the use of proximity cap during annealing. It is worthy noting that the linewidth distribution of PL spectra (not shown here) was distributed evenly further supporting the low temperature PL measurement related to the optical quality preservation of the intermixed QWs. However, the precise spatial resolution cannot be deducted from the PL mapping due to the limitation of the stage controller from the PL system. MRS is utilised later to check the precise spatial resolution of the intermixing process using stress-inducing dielectric cap.

Prior to wet etching removal, PL spectra was taken around intermixing boundary as shown in Figure 6-5(a) using 50 μm diameter fibre optic as PL probe. A well-separated dual peak spectrum from the sum of intermixed and unintermixed signals was observed indicating the presence of QW active region after wet etch and showing that the spatial resolution of the process is smaller than the fibre optics diameter, which is 50 μm . The PL peak at 1441 nm was attributed to the unintermixed section while PL peak at 1366 nm was from the intermixed section. The as-grown sample resulted in PL peak at 1456 nm, indicating the thermal shift of 15 nm on the masked section due to annealing treatment. The dual peak PL spectra deconvoluted using Gaussian spectra to provide more accurate linewidth comparison, indicating the absence of any appreciable linewidth broadening between two sections and indicating no significant degradation on the intermixed section.

Table 6-1. Comparison of observed and reported Raman peaks for InGaAs(P)/InP.

Raman peak	Observed wavenumber (cm ⁻¹)	Reported wavenumber (cm ⁻¹)	Phonon mode designation
1	173	<200 [11],[12], [13]	DALA band
2	228	232 [14], 232.2 [15], 233 [16], 234 [17]	InAs-like LO mode
3	250-265	263.5 [15], 264 [17], 269 [14], 270 [16], 270.5 [18]	GaAs-like LO mode
4	326	325[14], 326.9 [13], 328.2 [15], 331.6 [13], 336 [17]	InP-like LO mode
5	345	348 [17], 350.8 [15]	GaP-like LO mode

Figure 6-5(b) depicts the Raman spectra from masked and unmasked sections using the stress-inducing dielectric cap from the QW waveguide core, with most of signals from the InGaAsP quaternaries from GRIN layers. The instrument confocality was optimised to improve the spatial resolution of the map, which was further enhanced by using a x100 objective. The mapped line was 8 μm long, and used a step size of 0.2 μm . Since the sample was grown (100)-oriented InP substrate, only longitudinal optical (LO) phonons are allowed and the transverse optical (TO) phonons are forbidden by symmetry selection rules.

The Raman spectra consists of three main groups of bands from InGaAsP layers [19]-[21] with each peak designated and summarised in Table 6-1 with a comparison of the reported values. The frequency mode difference noticed is due to the presence of strain, different phonon confinements, and interface epilayer properties [22]-[24]. The 200-270 cm⁻¹ band corresponds to the InGaAs related LO mode, which consists of InAs-like and GaAs-like LO modes. The 300-360 cm⁻¹ second band appears for InGaP related LO band, which comprises both the InP-like and GaP-like LO modes. The GaP-like LO mode appears as a shoulder at the higher side of the InP-LO mode because of the presence of Ga from the InGaAsP GRIN alloys (~0.10-0.18). The last band, at (< 200 cm⁻¹), was assigned to the DALA band

that could be found in III-V alloy crystal. Sharp peaks at 345 cm^{-1} have been observed from the masked section, whereas no clear peak arises for the unmasked section. For the masked section, the Raman peak at 345 cm^{-1} was attributed to the lattice matched InGaAsP layers to InP substrate as indicated from the material growth in Appendix A.1, which was of good quality as evidenced from the sharp PL spectra. However, the Raman spectra with no peak from masked samples were ascribed to the lattice interdiffusion occurred within the QW waveguide cores after the intermixing process. The spectra with no peak further supported that the InP upper cladding has been fully removed by wet chemical etching and the laser source does not penetrate to the InP lower cladding layer as predicted earlier. The bands corresponding to the InGaAs LO modes of unmasked sample were very strong as compared to those of masked sample. This phenomenon was ascribed to a strong depletion of As in the QW region due to a small gap between the unmasked area and GaAs proximity cap, enhancing the outdiffusion of As species during annealing [15].

The clear redshift and the increase in GaAs-like to InAs-like LO peak ratio was interpreted as due to the the compositional change in the InGaAsP GRIN layers caused by the outdiffused As and Ga species from wells increasing the As and Ga contents on the barriers and GRIN layers [11],[15],[21]. This observation is further substantiated by a marked decrease in the GaAs-like mode linewidth from the intermixed area as compared to the unintermixed are. The intermixing process suggests group III atom interdiffusion through the In content reduction in the GRIN layers as a consequence of the outdiffused Ga atoms from wells [25], similar to the relevant report in GaAs/AlGaAs system [1]. From the InGaP related LO band, the sharp peaks corresponding to the InP- and GaP-like LO modes were observed in the

masked spectra corresponding to the high fraction of P atoms in the GRIN layers. However, these peaks disappeared in the unmasked region due to the decrease in effective P fractions related to the indiffusion process of P atoms to wells as a consequence of As atom outdiffusion [39],[14]. Hence, the interdiffusion of both group III and group V atoms occurred between barriers and wells can be determined from the Raman study. As the end result, the InGaAsP quaternary alloy was formed [21] in the intermixed section.

Figure 6-6. (a) 3-D view of the line map Raman spectra, with the intermixed boundary clearly revealed from the spectra transition. (b) The Raman-mode amplitude from InAs-like LO peak and GaP-like LO peak across 8 μm scan line.

The lines are for the guide to the eyes, using average of 5 data points.

The interdiffusion of atoms in InGaAsP alloys has been reported to produce a remarkable variation in the amplitude-peak mode, related to the relative density of

corresponding bonds [19]-[21]. The change in Raman peak intensity between the intermixed and unintermixed regions between two consecutive Raman spectra indicates the spatial resolution of the process due to compositional alterations because such changes modify the vibrational properties of the crystal lattice. Figure 6-6(a) showed a unique feature of Raman spectra transition across the samples resembling both the intermixed and unintermixed region taken from 3.6 to 6 μm spatial distances, unambiguously indicating the interdiffusion process has started beneath the masked section due to the lateral diffusion of the QWI process.

The resulting line map Raman spectra were further analysed, by monitoring the amplitude-mode of InAs-like and GaP-like mode peaks and the amplitude-mode ratio to reveal the amount of lateral diffusion across intermixing boundary, as depicted in Figure 6-6(b). The similar lateral transition trends were obtained for GaAs- and InP-like LO phonon amplitude modes with lower amplitude-mode contrasts, not shown here for maintaining the clarity. An obvious decrease in the GaP-like LO mode amplitude with an increase in the InAs-like LO mode amplitude at a separation of 2.4 μm was observed, similarly to the amplitude-mode ratio transition across map line. These transitions unambiguously indicated the spatial resolution from the laterally compositional interdiffusion at about 2.4 μm . The value from MRS study was consistent to the spatial resolution obtained using PL measurements, indicating that the stress-inducing dielectric cap improves the spatial resolution of Ar plasma induced QWI to $\sim 2.4 \mu\text{m}$.

6.2 SINGLE STEP MULTIPLE BANDGAPS CREATION

The lateral control of bandgap across a single chip is crucial for the implementation of PICs because different optical components on a PIC module

usually have different bandgap requirements. Although QWI technique has great advantages over growth and regrowth and selective epitaxial growth technique for the bandgap engineering process, the spatial control of the existing QWI techniques is indirect and complicated. For example, using varying thickness of SiO₂ layer, as intermixing sources of IFVD or implant mask of IIID, to provide spatial control of the bandgap increases the number of processing steps of lithography and dielectric cap deposition. Annealing temperature in IFVD process can be controlled to achieve different intermixing degree in InGaAs/InGaAsP system, however this approach only limit the creation of two bandgaps across a substrate [1]. To overcome this shortcoming, for example, a one-step spatially controlled QWI technique based on IFVD has been developed in GaAs/AlGaAs system [27],[28] using a very small patterned area (~1 μm) of SrF₂ followed by coating the sample with SiO₂ layer as the intermixing source. The intermixing degree using selected intermixing in selected area (SISA) was found to depend on the area of semiconductor surface in direct contact with the SiO₂ layer, which causes different number of generated vacancies from Ga outdiffusion. However, it requires the deposition of two different materials for bandgap control (for instance, SiO₂ and SrF₂) and the requirement of electron beam lithography for SrF₂ layer patterning, which will decrease the process throughput and increase the design complexity. The SrF₂ layer could cause the surface damage after annealing process due to large different thermal coefficient expansion with SiO₂ layer and III-V material. Moreover, the SISA technique finds its difficulty to be applied to the InP-based material, for example InGaAs/InGaAsP system due to its poor thermal stability and InGaAs/InAlGaAs system due to the non-reproducible suppression effect in contrast behaviour to GaAs/AlGaAs system [29]. Another example, the gray mask

technology using IIID technique seems to be a successful way to achieve multiple bandgaps process in InGaAs/InGaAsP system, but it is an expensive approach, which requires the iso-etch rate pattern transfer capability with precise control using RIE process [30].

One common approach to get the arbitrary number of bandgap is through multiple masks thickness to modulate the concentration of defects on the selected area [31]-[33]. Varying the implantation dose, energy and time has been demonstrated with a limited range of wavelength control using Ar plasma immersion ion implantation in InGaAsP system, however such approach is not practical [34]. The similar approach in plasma induced QWI process suffered from the requirement of several cycle of photolithography-etching-exposure steps with poor controllability of the bandgap shift [35] due to the non-linear nature of plasma induced damage thus intermixing degree with respect to the time exposure. Hence, the innovative approach to achieve multiple bandgaps across a single substrate with good controllability and reproducibility in a single step process is demanding. The multiple bandgaps creation possibilities of plasma induced QWI with an effective and simple approach in a single step process is explored.

Figure 6-7. The three-bandgap creation across a single substrate using multiple exposure-lithography-etching steps.

6.2.1 Dielectric thickness modulated intermixing (DTMI) using gray mask technology

DTMI using gray mask process was initially implemented in the IIID process selective area intermixing, by modulating the ion reaching the sample. The intermixing degree depends on the amount of ions penetrating to the samples after annealing step. While the standard to achieve multiple thicknesses of implant mask requires the standard UV lithography, it still requires repeated cycles of lithography-SiO₂ deposition-etching processing steps. To overcome these shortcomings, the gray mask technology was adopted to achieve the different thicknesses of SiO₂ in a single step of lithography. The resist pattern was then transferred using plasma process in a single etching step, producing the multiple SiO₂ thicknesses. This technique simply requires a single lithography and etching step to produce different thicknesses of SiO₂ simultaneously in selected regions in order to achieve selective area intermixing for monolithic multiple bandgaps integration. This simple and cost effective technique is used to demonstrate 12-section energy bandgap on a single InGaAs/InGaAsP heterostructure using IIID technique [37].

6.2.2.1 Experimental details

The complete DTMI using gray-mask process in plasma induced QWI, as shown in Figure 6-8, consists mainly of three different processing steps of SiO₂ mask deposition, photolithography and dry etching in a single cycle, as compared with the other conventional processes to achieve different thicknesses [32],[33], which require these steps in multiple repeated cycles. The innovation of this process has been due to the use of these three steps consecutively with an improvement of different SiO₂ thicknesses (as exposure mask) at the selected regions in a single UV

lithography step [Figure 6-8(a)], through a gray-mask design and because of the transfer of a graded pattern by means of a dry etching procedure [Figure 6-8(b)]. After this, a one-step Ar plasma exposure process [Figure 6-8(c)], followed by an annealing stage [Figure 6-8(d)], for selective area intermixing has been done.

Figure 6-8. The DTMI process using gray mask to modulate the concentration of surface defects to achieve multiple bandgaps creation across a single substrate

The InGaAs/InGaAsP QW structure sample (see for detail in Appendix A.1) was firstly evaporated with ~ 600 nm thick of SiO_2 . The thickness was chosen due to the relatively easy pattern transfer process from resist to SiO_2 , that is thicker as predicted by the Stopping and Range of Ions in Matter 2000 simulations (see Appendix. C). In addition, the wide range of SiO_2 enables to define the optimum mask, which totally block the sample from surface damage creation. Then, a photolithography step has been employed in transferring the gray patterns onto the samples. The TSMR-CR positive photoresist was used to provide a ~ 700 nm thick pattern after spin coating at 5000 rpm for 35 seconds.

Table 6-2. Twelve gray mask levels for multiple bandgaps generation

Gray level												
Level	1	2	3	4	5	6	7	8	9	10	11	12
OD	—	1.00	0.70	0.60	0.52	0.39	0.30	0.22	0.15	0.10	0.05	0.00
T(%)	0	10	20	25	30	40	50	60	70	80	90	100

The gray mask was designed to have 12 gray tone levels, i.e. with UV light transmittance levels, ranging from 0 % (Level 1) to 100 % (Step 12) as tabulated in Table 6-2. 12 different thicknesses of photoresist could be obtained after development. The thickness of the developed photoresist after the UV exposure has

a linear relationship with the optical density. The iso-etch rate condition has been optimised using Taguchi's method to transfer the positive photoresist to the SiO₂ layer evaporated by electron beam [36].

Figure 6-9. (a) The optimisation process of RIE iso-etching rate parameters using CF₄/O₂ mixture. The RIE parameters were: 60 W RF power, 2 sccm O₂ flow rate and 100 mTorr chamber pressure. (b) The pattern transfer from resist to SiO₂ using gray mask with 12 levels.

As shown in Figure 6-9(a), the iso-etch rate parameters can be obtained using the CF₄ flow rate between 80 and 100 sccm, giving the etch rate of ~59 nm/minute and 55 nm/minute for SiO₂ and resist, respectively. A CF₄/O₂ plasma based RIE process then was performed in producing a graded photo-resist pattern onto SiO₂ such that 12 different thicknesses of SiO₂, ranging from 0 nm to 600 nm (denoted as Levels 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2 and 1 respectively) across the planar wafer, as depicted in Figure 6-9(b). Level 12 with 0 nm thickness of SiO₂ implies that the concentration of the surface defects introduced is the highest. The small difference between resist and SiO₂ final thickness could be due to the little

difference of etch rate using the optimised RIE parameters. The sample was then exposed under Ar plasma with the optimised ICP parameters. The intermixing step was then carried out using a RTP at 600 °C for 2 minutes. PL measurement at 77 K was then carried out to assess the effect of different SiO₂ thicknesses ranging from 0 nm to 600 nm on the bandgap shift.

6.2.2.2 Results and discussion

From PL measurement on the intermixed samples in Figure 6-10(a), the level 1 to level 8 exhibited no significant bandgap shift as compared to the control sample (not shown for clarity of the figure). This indicates that 230 nm thick SiO₂ thickness and thicker effectively blocked the sample from the defect creation, thus inhibiting the intermixing process. The extracted bandgap shift from level 6 to 12, as shown in Figure 6-10(b), suggests that the amount of bandgap shift has a non-linear dependence on the SiO₂ thickness below 170 nm. The non-linear nature could be due to many factors, such as the nature of plasma induced defect creation, the possible sputtering process on the SiO₂ material during exposure, or the process control of pattern transfer with thin layers below 200 nm. However, the non-linearity of the SiO₂ thickness dependency strongly points out the possible development of DTMI technique using gray mask to achieve more controllable shift provided a good control of dielectric thickness which can provide the modulation of the defects to promote the different QWI levels. The PL linewidth of intermixed levels shows no significant broadening, indicating the minimal optical quality degradation using plasma induced QWI process with the combination of DTMI approach using a gray mask.

Figure 6-10. (a) The PL spectra at 77 K at different gray levels. Only levels from 8 to 12 are plotted for clarity. (b) The correlation between bandgap shift as compared to the PL peak sample from gray level 1 and linewidth versus SiO₂ thickness.

6.2.2 Spatial defect modulated intermixing (SDMI) technique

The use of Ar plasma-induced QWI is attractive since the low energy ions (with 100s eV of ion impact energy) generated in the plasma chamber generates mobile point defects on the near sample surface. Since the most defects are introduced on the near sample surface at low ion energy, the lateral diffusion of defects below the spatial resolution during annealing can be utilised to modulate the defect concentration reaching the QW region using spatial masked pattern, thus different degrees of the intermixing can be obtained. The SDMI process will be

demonstrated with the plasma induced QWI technique using variable percentage of window exposure area, below its spatial resolution as measured previously.

6.2.2.1 Experimental details

Figure 6-11. (a) Schematic representation of spatial control of intermixing degree using the surface defects modulation during plasma exposure with a 300 nm thick SiO_2 mask. (b) The micrograph of the 8 different exposed area coverages using $2.5 \mu\text{m}$ stripe SiO_2 layer, varying from 0, 30, 40, 45, 50, 75, 90 and 100 %.

The multiple bandgaps creation using spatial defect modulated intermixing was prepared on the InGaAs/InGaAsP QWs samples (see Appendix. A.1 for detail structure) using the process as shown in Figure 6-11(a). Two samples were cleaved into $8 \times 8 \text{ mm}^2$ and were subsequently coated by 300 nm thick SiO_2 layer by electron beam evaporation. The AZ 5214 positive photoresist from Clariant Japan of thickness $\sim 1.5 \mu\text{m}$ was coated onto the sample by spin coating for 35 s at 4000 rpm. The positive pattern was aligned onto the sample and UV light was exposed for 10 s, containing 8 distinct fractions of plasma exposure area with $2.5 \mu\text{m}$ stripe SiO_2 mask from 0 % to 100 %. The resist was then developed away for 70 s. After postbaking at 120°C for 2 minutes, the resist pattern was transferred to the SiO_2 layer using the CF_4/O_2 RIE process for 6.5 minutes followed by the resist removal using acetone. Figure 6-11(b) shows 8 distinct fractions of plasma exposure area with $2.5 \mu\text{m}$ stripe SiO_2 mask from 0 % to 100 %. The patterned samples were

exposed to Ar plasma for 5 minutes, followed by the SiO₂ removal using diluted HF solution and subsequent annealing in an RTP at 600 °C for 2 minutes. The SiO₂ removal before annealing was intended to allow stress relaxation on the patterned mask, resulting in the uniform distribution of intermixing across the substrate. PL measurements at 77 K were taken and the results were analysed.

6.2.2.2 Results and discussion

The high mobility of mobile point defects on the near sample surface leads to the uniform distribution at the QW active region for modulated area of smaller than the lateral diffusion length. Figure 6-12 summarises the achievement of SDMI technique in InGaAs/InGaAsP QW laser structure to the bandgap shifts and the corresponding linewidths. Only small variation of the linewidth was observed as the exposure coverage increases and the PL spectra did not appear to be double peaked (not shown here), suggesting that the intermixing process is uniform with 2.5 µm period of exposure mask. The area with 0 % exposed was found to be almost fully inhibited from intermixing, whilst the area with 100 % exposed was intermixed by about 66 meV. The degree of intermixing increases linearly as the exposed percentage area increases indicating the correlation between the amount of created mobile defects on the surface and the achieved bandgap shifts, similar with the ion implantation case using As ions [38]. The linear dependency underscores the achievement of multiple bandgaps process, which is easy, simple, and promising in controlling multiple wavelengths across single substrate with compatible semiconductor process technology.

Figure 6-12. (a) The PL spectra at 77 K and (b) the correlation between bandgap shift as compared to the as-grown sample and linewidth versus percentage of window exposure area (a – as-grown, b - 0 %, c - 30 %, d - 40 %, e - 45 %, f - 50 %, g – 75 %, h – 90 %, and i - 100 %) of the 2.5 μm wide stripe control mask.

The proposed SDMI technique seems to be useful for the fabrication of PICs in general, and WDM sources in particular, not only using plasma induced QWI technique, but also using the other shallow defect induced intermixing techniques, such as low energy ion implantation, sputter silica capl, anodic oxidation, excimer laser, etc. Since wavelength can be spatially controlled across a wafer, the plasma induced QWI technique with the combination of SDMI approach can also be potentially used to increase the efficiency of solar cells by increasing the absorption spectrum and to ease the fabrication and design process of superluminescent diodes (SLD) by expanding the gain spectrum to a maximum after epitaxial growth.

6.3 UNIVERSAL PLASMA DAMAGE-INDUCED QWI

The plasma induced damage to various semiconductor materials is not only restricted to InGaAs/InGaAsP material and has been extended to the study of the other material systems. This study allows the feasibility of the plasma induced QWI technique to be applied universally to various QW systems covering the full range of wavelengths. Several QW materials, such as InGaAs/InAlGaAs QW laser structure for long wavelength optical communication application and GaAs/AlGaAs QW laser structure for short wavelength optical communication application will be investigated.

6.3.1 GaAs/AlGaAs system

A GaAs/AlGaAs structure, which operates at wavelength of 0.65~0.9 μm , has been widely used for short haul optical communications due to the low loss and low dispersion in that wavelength region. GaAs/AlGaAs devices is the promising component for wide applications in both the microwave technology and the photonic technology, such as ultrafast devices with good radiation resistance, high-speed supercomputers, high power laser diode, and bi-directional communications at a lower cost, more robust, and less fragile as compared to InP based material. Thus, integration of discrete GaAs-based components is essential for high device yield, improvement in performance, and speed, increase in long term reliability and robustness, as well as offering a potential cost reduction. Initial work on GaAs/AlGaAs structures has been done using a low energy H_2 plasma bombardment in an RIE system with up to 8 cycles of H_2 plasma exposure and annealing to produce 42 meV bandgap shift [39].

GaAs/AlGaAs 25 QWs laser structure was grown by MOVPE. The GaAs/AlGaAs QWs active region was located at $\sim 1.7 \mu\text{m}$ below the sample surface. The complete structure has been detailed in Appendix A.3. The as-grown QWs material gave a 77 K PL peak at about $810 \pm 2 \text{ nm}$. The thermal stability test was done to determine the threshold of QWI annealing temperature at 30 seconds. The annealing duration was chosen as the common annealing process for this material to induce QWI using other techniques in our group, allowing the simplification of the analysis and its comparison [40]. The ICP parameter settings for the experiments were similar to the previous optimised parameters using Taguchi's method, i.e., 100 sccm Ar flow rate, 60 mTorr chamber pressures, and 480 W RF power. After Ar plasma exposure, the samples were annealed using one step RTP process in a flowing nitrogen atmosphere followed by PL measurements to assess the bandgap shift and linewidth after intermixing.

Using similar procedure of thermal stability study in InGaAs/InGaAsP QWs structure, a set of samples was annealed by RTP with temperatures between 800 °C and 900 °C for 30 seconds. From thermal stability test in Figure 6-13(a), a barely as-grown samples exhibited a negligible bandgap shift up to 825 °C annealing temperature while beyond 825 °C, the interdiffusion caused by the grown-in defects on the interface of heterostructure, results in the bandgap widening due to the thermal induced interdiffusion process. The threshold annealing temperature was found to be at 860 °C for 30 seconds with the thermal induced bandgap blue-shift at about 5 nm, suggesting the optimum annealing condition for promoting QWI while recovering the material from plasma induced damage after Ar plasma exposure.

Figure 6-13. (a) PL spectra at 77 K from the thermal stability test of GaAs/AlGaAs QWs laser structure versus annealing temperature. (b) The comparison of PL spectra at 77 K using Ar exposure with and without ICP power application.

The understanding of the inductively coupled plasma application to promote intermixing is necessary to obtain the detailed mechanism of the plasma induced intermixing in the GaAs/AlGaAs system as compared to the previous InGaAs/InGaAsP system. In order to study such ICP effect, GaAs/AlGaAs laser samples were exposed for 1 minute without (0 W) and with (500 W) ICP power application. The corresponding RF-induced DC bias was -840 V and -730 V at 0 W and 500 W ICP power application, respectively. Under a pure RF bias (ICP power = 0) condition, the ionic species in plasma sheath region is accelerated at normal incidence by electric field and is expected to dominantly induce highly energetic ion bombardment induced damage. The plasma exposure to the QW samples under this condition leads to intermixing caused by the effect of ion bombardment-induced damage.

Figure 6-13(b) shows that the PL spectra of intermixed sample has been shifted to shorter wavelength as compared to the control sample, which was annealed only and has not undergone the plasma induced damage. The control sample exhibited a 5 nm bandgap shift as compared to the as-grown sample, which is mainly attributed to thermal shift. The PL peaks were blue-shifted at 18 nm and 19 nm for sample exposed without and with ICP power application. Without ICP power application, a larger bandgap shift can be achieved only by increasing the energy of bombarding ions, while with ICP power application, the ion density plays as a factor for bandgap shift control. In the experiment, the application of ICP power was accompanied with a decrease in RF-induced DC bias at ~ 110 V, but a slightly higher degree of QWI (~ 1 nm or 2 meV more) was still achieved. The RF-induced DC bias reduction leads to less effect of bombarding ion energy to the induced damage, and thus the high plasma density plays an important role in QWI on a GaAs/AlGaAs QW structure, in similar to the effect observed in InGaAs/InGaAsP QWs laser structure. The observation of the ICP enhancement in both QW structure grown in the InP substrate and GaAs substrate strongly points out the universal plasma induced QWI process to tailor the material bandgap for wide application of PICs covering the wide range of optical communication band from $0.8\ \mu\text{m}$ to $1.7\ \mu\text{m}$.

The exposure time effect is further investigated to achieve the optimum bandgap shift of QW laser structure using 500 W ICP power ($\sim$ corresponding RF-induced C bias of -730 V). Figure 6-14 shows that the bandgap shift and the PL linewidth of QWs laser samples subject to longer exposure have been shifted to higher energy after annealing. The bandgap shift from PL spectra saturates after 0.5 minute exposure and shows the most blue-shifted after 1.5 minute exposure at 21

nm (~ 40 meV) using a single annealing step. A small linewidth broadening of 4 nm was observed in the intermixed samples, which suggests that no significant degradation of optical properties has occurred in the QWs samples after the ICP induced QWI process. The less amount of bandgap energy shift in GaAs/AlGaAs QW material as compared to that of InGaAs/InGaAsP QW material as achieved earlier shows that the long range defect propagation process is more efficient to promote the intermixing in agreement with the study of defect diffusion using IID process [38], in addition to the limitation of the band offset of the material system. The achieved bandgap shift in GaAs/AlGaAs system here is comparable to the reported results using well established QWI techniques for GaAs-based material, such as IFVD technique utilising the dielectric cap [28],[41] and IID technique [38],[42].

Figure 6-14. Plot of bandgap energy shift (diamond) and the PL linewidth (square) from the intermixed GaAs/AlGaAs QWs laser structure with different Ar exposure times. The line is obtained from the semi-empirical model of interdiffused GaAs/AlGaAs QW. The inset shows the PL spectra between the intermixed sample using 1.5 minute Ar exposure (dotted line) and as-grown sample (thin solid line).

With the application of an exposure step using high-density inductively coupled Ar plasma and a single annealing step, the achieved degree of bandgap shift in GaAs-based material is comparable to that obtained by the H₂ plasma induced QWI technique using an RIE machine with up to 8 cycles of exposure and annealing steps [39]. As the annealing process was similar between two processes, the comparable bandgap shift with only single exposure-annealing step could be ascribed to the presence of inductively coupled plasma to provide higher plasma density together with high plasma radiation intensity, as calculated in Chapter 5. As the Ar atomic weight is much higher than the H atomic weight, another reason can be postulated related to the heavy atomic weight of Ar ion causing more surface damage on the QW material [43].

6.3.2 InGaAs/InAlGaAs system

The InGaAs/InAlGaAs material system lattice matched to InP substrate is used for 1.55 μm long wavelength optical communications, as well as high speed Heterojunction Bipolar Transistors (HBTs), device offering advantages such as large index difference, easy epitaxy growth, and a high conductivity band offset [44]. It has been shown that the low threshold current lasers can be fabricated using InGaAs/InAlGaAs/InP separate confinement heterostructure multiple QWs material [45]. The photocurrent measurements showed that the material from which these lasers were fabricated also exhibit good quantum confined Stark shift characteristics, suggesting the possibility of changing the absorption at the particular wavelength by the application of an electric field across the intrinsic layer and could be useful for the fabrication of optical modulators. The large conduction band offset (~ 0.7) provides the stronger electron confinement than the InGaAs/InGaAsP QW system, leading to the high-temperature stability, good hole

transport through the laser side, low temperature sensitivity for lasers and high-speed modulation capabilities [46]. However, it should be noted that the presence of highly reactive material in Al based raises lifetime issue for devices.

The possibility of fabricating both lasers and modulators from single substrate make it a good material system for PICs application at long wavelength. In conjunction, PICs on the InGaAs/InAlGaAs/InP system would be necessary to produce a blue-shift in the exciton energy of QWs in the guiding regions in order to reduce the high absorption losses present at the lasing emission of laser. Plasma induced QWI has been demonstrated previously to promote the bandgap widening of InGaAs/InGaAsP and GaAs/AlGaAs material systems, which offer the advantage of the impurity free induced intermixing where the point defects were created on the sample surface without damaging the QW active region. Here, the plasma induced QWI study is extended to produce the bandgap shift in InGaAs/InAlGaAs system.

The InGaAs/InAlGaAs QW laser structure was grown by Molecular Beam Epitaxy (MBE) on a Si-doped InP substrate. The QW active region consists of six 7 nm wide $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ wells separated by 8 nm $\text{In}_{0.53}\text{Al}_{0.27}\text{Ga}_{0.2}\text{As}$ barriers. The detail of laser structure is documented in Appendix A.4. The as-grown materials gave a 77 K PL peak at about 1388 ± 2 nm. The thermal stability test was done to determine the threshold of QWI annealing temperature at 2 minutes between 550 °C to 750 °C. The ICP parameter settings for the experiments were similar to the previous optimised parameters using Taguchi's method, i.e., 100 sccm Ar flow rate, 60 mTorr chamber pressures, 480 W RF power, and 500 W ICP power. The RF induced bias using these parameters was -730 V. After Ar plasma exposure, the samples were annealed using one step rapid RTP process in a flowing nitrogen

atmosphere followed by PL measurements to assess the bandgap shift and linewidth after intermixing.

Figure 6-15. (a) Bandgap shift of PL spectra at 77 K as a function of annealing temperature to achieve thermal stability condition for intermixing study for exposed sample to Ar plasma for 1 minute (solid triangle) and unexposed sample (solid square). (b) PL peak shift and the linewidth as the exposure time increases. The annealing temperature was fixed at 650 °C for 2 minutes.

The dependence of the bandgap shift on the annealing temperature was investigated from PL measurement at 77 K. Two set of samples, one exposed under Ar plasma for 1 minute and another is unexposed were annealed at temperatures between 600 °C to 700 °C for 2 minutes in a RTP. The bandgap shifts are depicted in Figure 6-15 (a); sample exposed for 1 minute exhibited more pronounced bandgap shifts as compared to the shifts from unexposed samples. This illustrates that the plasma enhanced QWI process induces higher bandgap shift in InGaAs/InAlGaAs material system. Adopting the use of dielectric cap as intermixing mask, the potentially selective intermixing while providing, at the same

time, a differential bandgap shift between the exposed area and the masked area, can be realised using the annealing temperature of 625 °C.

To further achieve the pronounced bandgap shift, a set of samples was exposed under Ar plasma with varying the exposure time from 0 minute to 3 minutes, followed by the subsequent annealing at 625 °C for 2 minutes. The result of bandgap shifts as a function of exposure time was plotted in Figure 6-15 (b), resulting in the large bandgap shift of 75 nm (~42 meV) after 2 minutes exposure time. Increase in the exposure time results in the saturation phenomena, similar to the cases of InGaAs/InGaAsP and GaAs/AlGaAs system, suggesting the similar mechanism of defects creation induced by Ar plasma. The optimum blue-shift achieved here using InAlGaAs barriers was less than using InGaAsP barriers in previous result. The similar case was reported using IIID process using F ion implantation, which gave a smaller bandgap shift to intermixed QW structure with InAlGaAs barriers as compared to that with InGaAsP barriers. The bandgap shift achieved using Ar plasma induced QWI is however comparable to intermixed InGaAs/InAlGaAs material using F ion IIID technique [47]. The linewidth increases with respect to the amount of bandgap shift at particular exposure time, causing the reduction of the optical confinement as the change of the compositional profile from abrupt to the graded profile. However, the linewidth broadening is as small as 11 nm at the bandgap shift of 75 nm, indicating the minimal damage creation to the optical quality after intermixing process. The produced bandgap shift of intermixed sample underscores the possibility of fabricating both laser and bandgap shifted modulators from single substrate to serve integrated photonic devices for long wavelength optical communications. Further careful optimisations

of ICP parameters and the QW design are possible to achieve higher bandgap shift in this material system.

6.4. FABRICATION OF EXTENDED CAVITY LASERS USING PLASMA INDUCED QWI TECHNIQUE

The monolithic integration of active laser and low-loss passive waveguide is an essential step toward the realisation of PICs technology [48],[49]. The integration of narrow linewidth semiconductor lasers with passive optical waveguide sections, which are transparent at the laser wavelength, is of great importance for integrated photonic circuits. Integration of a short active region of the order of hundreds micron in length with a single long passive waveguide blue-shifted using intermixing techniques enables lower dimension of integrated devices to be achieved, which is around a factor of four shorter than the equivalent air cavity. It is well known that a laser with an extended cavity can effectively reduce the linewidth [50], which can be estimated by using the Schawlow-Townes formula [51]. The integration is thus required [49] for monolithically integrated tunable laser diode, low-loss distributed Bragg reflector laser, laser integrated with optical modulators, high power grating coupled emission laser and integrated extended cavity mode-locked lasers. The use of QWI techniques to carry out such photonic integration promises excellent mode matching, excellent geometrical compatibility, and virtually no optical reflection between the active and passive waveguides. Since the Ar plasma induced QWI is an impurity free process, the demonstration of low loss waveguide is necessary. Losses in the intermixed area introduced by non-radiative recombination centres from free carriers, as in IID process using the electrically active implanted ions, are expected to be significantly reduced using Ar plasma process. In this section, broad area extended cavity lasers, which consist of

active regions integrated with passive low-loss waveguides, have been fabricated and studied in the InGaAs/InGaAsP QWs laser structures. The bandgap at passive waveguide sections were selectively widened using the inductively coupled Ar plasma induced QWI process in order to reduce the propagation loss at the lasing wavelength from the unintermixed active laser section.

6.4.1 Fabrication procedures

SiO₂ mask was chosen to define the protected section from Ar exposure. The maximum vacancy depth created by Ar ion in SiO₂ was predicted using SRIM simulation to be less than 10 nm under implantation ion energy of 0.8 keV (corresponding to ~kV RF-induced DC bias) [52]. A 200 nm thick SiO₂ layer was chosen as a QWI mask to prevent the penetration of both Ar ions and generated point defects in the sample. Point defects diffusing inwards will be trapped at the non-lattice matched interface between SiO₂ layer and the sample. Therefore, only very small amount of damage or ions is expected to reach the sample.

Figure 6-16. Selective intermixing result across a sample partially masked with a 200 nm thick SiO₂ layer during Ar plasma exposure. The differential bandgap shift was 86 nm between masked (solid line) and unmasked section (dashed line).

Figure 6-16 shows the normalised PL spectra at 77 K obtained from the partially masked sample after 5 minutes exposure and annealing. The masked section has 6 nm bandgap shift and 5 nm linewidth broadening, which is attributed to thermal shift. The unmasked section has a much larger bandgap shift of 92 nm, thus producing a bandgap difference of 86 nm with a small differential linewidth broadening of 0.3 nm. This result suggests that high selectivity is obtainable in QW samples using 200 nm thick SiO₂ layer as plasma induced QWI mask. This minimal linewidth broadening indicates good preservation of the crystalline quality.

Figure 6-17. A SEM picture of fabricated broad area ECL with 50 μm wide active window for current injection. All individual ECL was 400 μm wide, the length of active section was 800 μm , and the passive section lengths of lasers were varied.

Figure 6-17 shows the fabricated broad area ECLs with the unmasked sections as low-loss passive waveguide. The removal of the 150nm thick highly doped InGaAs/InGaAsP cap layer minimises current spreading into the passive section and the absorption of light in this section. A 200 nm thick SiO₂ was deposited using PECVD and a 50 μm contact window was defined using dry etch in RIE machine followed by wet etch. A p-contact of Ti/Au layers was defined over the laser active sections using lift-off process to ensure electrical isolation between active and passive sections. The sample was then thinned down and n-metal contact

of Au/Ge/Au/Ni/Au layers was formed. The details of fabrication procedure is documented in Appendix D.

6.4.2 Results and Discussion

In order to assess the amount of intermixing in the extended cavity region, lasers in the selected passive waveguide section have been fabricated. The fabricated lasers were tested at room temperature under pulsed current operation (1 % duty cycle). Figure 6-18 shows the plot of light output versus injected current (L-I) characteristics of 800 μm long active section lasers with passive section length of 1200 μm . For comparison, 800 μm long all active lasers (AAL) were cleaved from the same sample. The threshold current was increased by 18 % from 481 mA for AAL to 569 mA, which can be attributed to diffractive losses within intermixed passive section. The slope efficiency undergoes a little decrease by 9 %, from 0.174 W/A to 0.159 W/A per facet.

Figure 6-18. The L-I characteristics of an broad area ECL (dotted line) with active (passive) length of 800 μm (1200 μm) and AAL (solid line) with 800 μm cavity length. The measurement was done at RT with pulse driving current with 0.1 % duty cycle.

From the L-I characteristics, it is possible to define the relationship between AAL threshold current (I_{AA}), ECL threshold current (I_{ECL}), and the propagation loss in the passive section (α_P). The threshold currents are related by the formula [53]:

$$\ln\left(\frac{I_{ECL}}{I_{AA}}\right) = \frac{\alpha_P L_P + \ln(1/\kappa)}{\Gamma g_0 L_A}, \quad (1)$$

where L_A and L_P are length of active and passive section, g_0 is the gain of the active structure, κ is the optical transmission coefficient from active to passive section, and Γ is the overlap integral within the quantum wells. An estimated value of $\Gamma g_0 \sim 30 \text{ cm}^{-1}$ was used [54] and κ is calculated from the QWI-induced refractive index change with a step profile to be 0.999998. This value of κ confirms that negligible reflection occurs at the passive/active interface. Comparing ECL with active (passive) length of 800 μm (1200 μm) and AAL with 800 μm cavity length, α_P is calculated to be 2.98 cm^{-1} or 12.9 dBcm^{-1} , which corresponds to about 2.6 dBcm^{-1} per well.

Figure 6-19. The beam propagation method (BPM) calculation of light distribution on the ECL laser. The coordinate system used here: x -lateral direction, y -transverse direction, and z -longitudinal direction (along laser cavity).

The increase of threshold current density partly was ascribed to the divergence of the lasing mode within the extended cavity, as shown in Figure 6-19(left). This reduces the amount of light returning to the pumped laser region. Using our

improved theoretical calculation [55], which taking into account the interface reflectivity due to the spatially graded interdiffusion profile and lateral optical spreading loss of 7.9 % at the active-passive interface, the corrected value of waveguide loss α_p is 2.3 cm^{-1} indicating the clear discrepancy confirms that the effects of spreading are significant as depicted in Figure 6-19.

To further substantiate the contribution of free carrier absorption from both the p- and n- dopants in the InP cladding layers, the residual optical loss in the passive waveguide, which causes a threshold current increase of the composite device, is estimated. The total propagation loss in passive section is the resultant loss from several factors: band to band loss, scattering loss, evanescent coupling loss, and free carrier absorption loss in the upper and lower InP cladding layers [56]. The QW active region contributes negligible free carrier absorption loss due to the undoped design. The radiation leakage into highly doped InGaAs/InGaAsP cap layers was not taken into account as the cap layer of passive section has been removed by wet chemical etching during fabrication. After considering the wavelength dependent loss components, the estimated residual propagation loss of passive waveguide is reduced to 1.3 cm^{-1} , taking the estimated losses as 1.0 cm^{-1} resulting from the carrier diffusion and spreading into the cladding and the active layers on the unpumped passive section, as depicted in Figure 6-19(right) [57]. The residual loss here almost approached the limit of low loss InP passive waveguide in ECL laser fabricated using growth and regrowth process [58] and comparable to the multimode propagation losses summarised in [59]. However, this residual loss was less than the pure ridge waveguide loss of 2.1 cm^{-1} using Fabry Perot measurement which was the lowest reported in intermixed InGaAs/InGaAsP material using LID

process [60]. The quantum efficiency degradation in the presence of integrated passive section can be expressed as [61]:

$$\frac{\eta_{\text{ECL}}}{\eta_{\text{AA}}} = \frac{\alpha_A + \frac{1}{L_A} \ln \frac{1}{R}}{\alpha_A + \frac{1}{L_A} \ln \frac{1}{R} + \alpha P \frac{L_p}{L_A}}, \quad (2)$$

where R is the facet reflectivity, calculated to be 0.27 for this as-cleaved structure. The ratio calculated with the above equation is 0.87, which is in agreement with the measured value of 0.91 from the L-I characteristics. This small discrepancy can be explained by noting that the effective length of gain section is shorter than the physical active pumped section due to the graded bandgap interface region after intermixing, which can lead to increase in the threshold current without any contribution to the gain.

Figure 6-20. The wavelength emission at the pulse current injection of 120 % I_{th} from (a) as-grown (unprocessed) broad area laser with 800 μm cavity length, (b) broad area AAL with 800 μm cavity length, and (c) broad area ECL with active (passive) length of 800 μm (1200 μm).

As shown in Figure 6-20, the measured optical spectra of AAL and unprocessed (as-grown) laser with similar cavity length of 800 μm emit the wavelength peak at 1.542 μm and 1.546 nm, respectively. The small discrepancy of

4 nm wavelength peak emission is comparable with the PL shift obtained between the unprocessed (as-grown) sample and the annealed only (control) sample, suggesting that the thermal annealing induces the wavelength shift on the fabricated AAL laser. However, the optical spectrum of ECL exhibits an apparent blue-shift at 1.535 μm as compared to unprocessed AAL laser. The 7 nm blue-shift in wavelength emission seems likely due to the band filling effect from the increase in threshold current in the ECL rather than the graded bandgap on the passive-active interface [54]. This shift of the wavelength will cause the propagation losses to increase slightly, since the energy of the photons is now closer to the bandgap of the passive waveguide section. It is obvious that consideration of this blue-shift is very important when designing ECL for a predetermined laser wavelength, e.g. in distributed Bragg reflector lasers [62].

Table 6-3. The summary of fabricated AAL and ECL laser using Ar plasma induced QWI for photonic integration demonstration.

Active section length L_A (μm)	Passive section length L_P (μm)	Threshold current density J_{th} (kA cm^{-2})	Slope efficiency per-facet (W A^{-1})
800	0	1.20	0.174
800	1200	1.42	0.159
2000	0	1.12	0.022

Another advantage of the fabricated ECL was the lower threshold as compared to the AAL with the similar total cavity length, enabling the good performance of the laser characteristics across for mode-locked laser sources. Table 6-3 provides the comparison of the best threshold current density and the corresponding slope efficiency per-facet between an ECL and an AAL with total cavity length of 2000 μm measured under pulsed driving current. An improvement in the threshold current reduction in ECL as compared to ALL using similar cavity

length was noted. The increase in the threshold current density of 18 % for ECL is still favorable if compared to the increase of threshold current to 1136 mA for AAL with similar cavity length of 2000 μm .

6.5 SUMMARY

The capability of plasma induced QWI technique for high-density photonic integrated devices has been demonstrated, which offers three aspects of investigation: i) spatial resolution, ii) single step multiple bandgaps creation and iii) universal to a wide range of material systems. Using the stress-inducing dielectric cap, the lateral defect diffusion can be limited leading to the improvement of spatial resolution at 2.4 μm . Two approaches of single step multiple bandgaps creation have been presented using dielectric thickness modulated intermixing and spatial defect modulated intermixing, with each approach possessing its advantages and disadvantages. The demonstration of tuning the GaAs/AlGaAs and InGaAs/InAlGaAs system suggests the universal damage creation leading to the QWI process in a wide range of the GaAs-based and InP-based material.

The selective QWI using 200 nm thick SiO_2 layer in InGaAs/InGaAsP QW laser structure was achieved resulting in a differential bandgap shift of 86 nm with differential linewidth broadening of 0.3 nm. A low-loss ECL has been fabricated with the measured waveguide loss as low as 2.3 cm^{-1} with 1200 μm long passive waveguide. These results highlight the capability of plasma induced QWI technique in the application of photonic integration, such as monolithically integrated tunable laser laser diode, low-loss DBR lasers, lasers integrated with optical modulators, and integrated mode-locked ECLs.

7. CONCLUSIONS AND RECOMMENDATIONS

In this chapter, the summary of the study is given with some highlighted points for future work.

7.1 CONCLUSIONS

Ar plasma induced QWI using ICP system has been demonstrated to successfully tune a wide range of III-V compound semiconductor material, including InGaAs/InGaAsP and InGaAs/InAlGaAs on InP substrate and GaAs/AlGaAs on GaAs substrate. The plasma parameters affecting QWI process were optimised and studied using the Taguchi's method, producing a bandgap shift of up to 104 nm in InGaAs/InGaAsP QW laser structure. The high plasma density in ICP system has been shown to enhance intermixing with a small linewidth broadening and the preservation of optical quality as compared to the low plasma density in RIE system. In GaAs/AlGaAs system, a comparable bandgap blue-shift (~ 40 meV) of Ar plasma in a single exposure and annealing step to the H₂ plasma induced QWI technique indicating the highly efficient damage introduction for promoting the interdiffusion within QWs. The comparison between plasma induced QWI and other existing QWI techniques has been presented in Appendix E.

A systematic study of the material properties after intermixing has been carried out with low temperature PL measurement to check the optical property of the intermixed QW, high resolution double-crystal x-ray diffraction to observe the interdiffusion process between epitaxial layers, and atomic force microscopy for the assessment of surface morphology, and micro-Raman spectroscopy to study the recovery of created damage.

The theoretical model for the interdiffused QW with the strain calculation has been developed. In conjunction with the model, the semi-empirical model of plasma induced QWI has been used to understand the mechanism of the increase in the material bandgap energy using ICP exposure. The experimental data were well supported and explained by our theoretical model. The theoretical model serves as a good simulation program to study the intermixing mechanism and further to optimise the plasma enhanced QWI process for the long-term goal of photonic integration purposes.

The annealing step can induce the lateral diffusion of point defects, which has an effect on the low spatial resolution of this technique. This has been minimised by the use of a modulated stress-inducing dielectric cap to act as a barrier of lateral defect diffusion. The spatial resolution can be improved to 2.4 μm using the vertical stress-inducing layer, further substantiating the wide application of improvement to other shallow defect induced QWI techniques. One step multiple bandgaps creation across single substrate has been obtained using the spatial defect modulated intermixing and the dielectric thickness modulated intermixing with the combination of gray mask technology. In addition, broad area external cavity lasers were fabricated using the plasma induced selective QWI (~ 86 nm differential bandgap shift) with the measured waveguide loss as low as 2.3 cm^{-1} with 1200 μm long passive waveguide. The low-loss performance was attributed to the impurity free process in Ar plasma induced QWI technique with no contribution to an increase in free carrier absorption loss in the device.

7.2 RECOMMENDATIONS

Some of the important points from this project are recommended.

1. The use of an encapsulant layer as an annealing cap, such as Si_xN_y and evaporated SiO_2 . It is widely known that SiO_2 material evaporated by electron beam has a non-stoichiometric composition with relatively high refractive index [1], thus high material density. Si_xN_y layer in IFVD process is commonly employed for intermixing suppression due to the minimal Ga outdiffusion to the cap layer during annealing [2]. These annealing caps are expected to further minimise the surface contamination issue and group V atoms outdiffusion, providing an alternative annealing approach with common proximity cap using fresh GaAs substrate [2],[3]. In addition, the presence of annealing cap further minimises the structural defects, in the form of misfit dislocations, if a strained material was intermixed. The temperature threshold of the material could be higher by more than 40 °C, according to the preliminary results shown in Figure 7-2, suggesting that the achievement of better selectivity with the improvement of the differential bandgap shift. In addition, the evaporated SiO_2 is inexpensive and does not require complex processing, as it is commonly used in the semiconductor fabrication. This approach will further eliminate the routine use of GaAs substrate as annealing cap.

Figure 7-1. The schematic diagram of (a) common annealing process using GaAs proximity capping and (b) proposed annealing process using evaporated SiO_2 capping

The preliminary results are depicted in Figure 7-2(a) and (b), indicating the higher thermal stability condition with minimal thermal shift as compared to the previous annealing condition. Up to temperature of 640 °C, the annealed sample with cap exhibited a smaller bandgap shift. The higher annealing condition leads to the achievement of larger differential bandgap shift between exposed and

unexposed sample, gaining the advantage for PICs fabrication for the absorption loss reduction for waveguiding properties. Another interesting result was the linewidth of intermixed samples with cap annealing is relatively narrower than the unexposed samples, as shown in Figure 7-2(b). This phenomenon is such an interesting field to be explored as the additional point to further improve the optical material quality after plasma induced QWI process.

Figure 7-2. (a) PL spectra at 77 K from the control (line) and intermixed (circle) InGaAs/InGaAsP QW samples with RTP temperatures at (i) 580, (ii) 600, (iii) 620, and (iv) 640 °C. The annealing was done using a fresh evaporated SiO₂ to protect sample surface and prevent outdiffusion process. (b) The corresponding linewidth broadening versus temperature between control (square) and intermixed (triangle) samples.

Another recommendation is the investigation of selective intermixing mask for plasma induced QWI which has been effectively proven to suppress intermixing below the protected area, for example: Si_xN_y, P-doped SiO₂, SrF₂ etc.

2. A selectively-etch sacrificial layer can be used in the laser structure to preserve the cap quality after intermixing. The defects are created in the sacrificial layer. After annealing, thus intermixing in the QWs region, the layer can be selectively etch away. Using this process, the good surface morphology can be obtained for further device processing. For example, InGaAs/InGaAsP QW laser structure (detailed in Appendix A.1) with the top most InGaAs cap layer

can be added to an InP sacrificial layer. By using **plasma induced sacrificial layer intermixing**, as illustrated in Figure 7-3, the excellent surface morphology can be obtained for the demand of high quality photonic devices.

Figure 7-3. Plasma induced QWI process on a complete QW laser structure with additional layer as a sacrificial layer. The annealing steps carried out to induce QWI followed by the chemical etch for sacrificial layer removal.

3. The investigation of **plasma induced proximity QWI** on the partial laser structure, as shown in Figure 7-4. The overgrowth can be done after the QWI process. The proximity QW active region has two advantages: 1) the use of similar parameters leading to the higher intermixing degree and 2) the minimal lateral defect diffusion resulting in the high spatial resolution without the use of vertical stress-inducing dielectric layer if the multiple bandgaps was required. The spatial resolution study of shallow QWI is required for the future of high-density PICs and spatially submicron bandgap modification through the demonstration of quantum wire and even quantum dot structures.

Figure 7-4. (a) Plasma induced shallow QWI using partial laser structure for multiple bandgaps creation with gray mask process. The annealing step is carried out to induce QWI followed by the overgrowth step.

4. The demonstration of multiple bandgaps technique across a single substrate for plasma induced QWI, using gray mask process and spatial defect modulated intermixing process, paves a way to the fabrication of photonic integrated devices, such as simple cross point switches based on the passive waveguide integrated with modulator/amplifier [4], superluminescence diode (SLD) [5]-

[9], multiwavelength laser array, array waveguide grating (AWG) [3], laser diode integrated with modulator and amplifier, etc.

Figure 7-5. The schematic diagram of photonic integrated devices: (a) multiwavelength transmitter consisting multiwavelength laser, 10×1 multimode interference (MMI) waveguide as combiner/multiplexer and semiconductor optical amplifier (SOA), and (b) Distributed Bragg reflector (DBR) laser integrated with asymmetric MMI waveguide as a wavelength splitter and two photodiodes (PD). Each single device with different functionalities requires different specification post-tuned using plasma induced QWI.

5. The universal semi-empirical model of plasma induced QWI behaviour has been developed, related to the damage creation upon plasma exposure. The further work on the model development is recommended, including the application to other strained and unstrained material systems, such as GaAs/AlGaAs QW and InGaAs/InAlGaAs QW systems where the saturation behaviour was observed.
6. The realisation of bandgap modification followed by the demonstration of simple photonic integration using plasma induced QWI to other material system, such as InGaAs/GaAs, GaAs/AlGaAs, InGaAs/InAlGaAs, InGaAsN/GaAs, InGaP/InAlGaP, InGaAsNSb/GaAs, GaN/AlGaN, ZnO, SiGe etc can be pursued. An important work can be extended to the investigation of Ar plasma induced QWI to quantum well infrared photodetector (QWIP), quantum wire and quantum dot structures.
7. The study of the effects of plasma induced QWI on the strain properties of QWs. Strained QW system may be used to fabricate the polarisation insensitive devices, such as amplifiers, modulators, etc.

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CHAPTER 5

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CHAPTER 7

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APPENDIX A

QUANTUM WELL STRUCTURE

A.1 INGAAS/INGAASP QWS LASER STRUCTURE

$1.8 \cdot 10^{19} \text{ cm}^{-3}$ Zn-doped	$\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$	100 nm	Cap layer
$2.0 \cdot 10^{18} \text{ cm}^{-3}$ Zn-doped	$\text{In}_{0.82}\text{Ga}_{0.18}\text{As}_{0.38}\text{P}_{0.62}$	50 nm	
$7.3 \cdot 10^{17} \text{ cm}^{-3}$ Zn-doped	InP	1370 nm	Upper cladding
undoped	$\text{In}_{0.90}\text{Ga}_{0.10}\text{As}_{0.21}\text{P}_{0.79}$	80 nm	Graded index structure
undoped	$\text{In}_{0.82}\text{Ga}_{0.18}\text{As}_{0.38}\text{P}_{0.62}$	50 nm	
undoped	$\text{In}_{0.77}\text{Ga}_{0.23}\text{As}_{0.49}\text{P}_{0.51}$	12 nm	6 Quantum barriers
undoped	$\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$	5.5 nm	
undoped	$\text{In}_{0.77}\text{Ga}_{0.23}\text{As}_{0.49}\text{P}_{0.51}$	12 nm	5 Quantum wells
undoped	$\text{In}_{0.82}\text{Ga}_{0.18}\text{As}_{0.38}\text{P}_{0.62}$	50 nm	
$5.0 \cdot 10^{17} \text{ cm}^{-3}$ S-doped	$\text{In}_{0.90}\text{Ga}_{0.10}\text{As}_{0.21}\text{P}_{0.79}$	80 nm	Graded index structure
$2.5 \cdot 10^{18} \text{ cm}^{-3}$ S-doped	InP	1000 nm	
$3.8 \cdot 10^{18} \text{ cm}^{-3}$ S-doped	InP substrate		Lower cladding

Figure A-1. The schematic structure of InGaAs/InGaAsP five QWs laser structure

The lattice-matched InGaAs/InGaAsP QW samples, as shown in Figure A-1, were grown by MOVPE on (100)-oriented n^+ -type S-doped InP substrates with less than 1000 cm^{-2} etch-pit density. The laser structure consisted of five periods of 5.5 nm $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ QWs with 12 nm InGaAsP barriers. The active region was sandwiched by a step-graded index waveguide core consisting of InGaAsP confining layers. The thickness of these confining layers were 50 nm and 80 nm, respectively. The structure was completed by an upper cladding InP layer of 1.37 μm with Zn doping of $5 \times 10^{17} \text{ cm}^{-3}$. The contact layers consisted of 50 nm InGaAsP (Zn-doped of $2 \times 10^{18} \text{ cm}^{-3}$) and 100 nm InGaAs (Zn-doped of $2 \times 10^{19} \text{ cm}^{-3}$)

³), respectively. The samples produced a PL peak at $1.51 \pm 0.02 \mu\text{m}$ at RT and one at $1.43 \pm 0.02 \mu\text{m}$ at 77 K. The layer structure is summarised in Table A-1 and the graphical interpretation is shown in Figure A-1.

Table A-1. Detail epitaxial growth of InGaAs/InGaAsP five QWs laser structure.

Repeats	Thickness (nm)	Material	E _g (μm)	Dopant	Type	Conc. (cm ⁻³)	Remark
1	100	In _{0.53} Ga _{0.47} As	1.55	Zn	p	$1.8 \cdot 10^{19}$	cap layer
1	50	In _{0.82} Ga _{0.18} As _{0.38} P _{0.62}	1.18	Zn	p	$2.0 \cdot 10^{18}$	cap layer
1	1370	InP	-	Zn	p	$7.3 \cdot 10^{17}$	cladding
1	80	In _{0.90} Ga _{0.10} As _{0.21} P _{0.79}	1.05		u		GRIN
1	50	In _{0.82} Ga _{0.18} As _{0.38} P _{0.62}	1.18		u		GRIN
1	12	In _{0.77} Ga _{0.23} As _{0.49} P _{0.51}	1.26		u		barrier
5	5.5	In _{0.53} Ga _{0.47} As	1.55		u		QW
5	12	In _{0.77} Ga _{0.23} As _{0.49} P _{0.51}	1.26		u		barrier
1	50	In _{0.82} Ga _{0.18} As _{0.38} P _{0.62}	1.18		u		GRIN
1	80	In _{0.90} Ga _{0.10} As _{0.21} P _{0.79}	1.05	S	n	$5.0 \cdot 10^{17}$	GRIN
1	1000	InP	-	S	n	$2.5 \cdot 10^{18}$	Cladding/ buffer
-	-	InP Substrate	-	S	n	$3.8 \cdot 10^{18}$	

A.2 GAAS/ALGAAS QWS STRUCTURE FOR DAMAGE PROBE

The GaAs/AlGaAs multiple widths QW structure used in this experiment was grown using solid source Molecular Beam Epitaxy (MBE) on a GaAs substrate. The QW region consists of five QW separated by 300 nm of Al_{0.3}Ga_{0.7}As barrier, except the deepest two wells, which were separated by a 1 μm Al_{0.3}Ga_{0.7}As barrier. All the QW regions were undoped. The thickness of the QW closest to the substrate was greatest and the thickness of the subsequent QWs decreased gradually towards the surface. The thicknesses of the five QW were 9.5 nm, 7 nm, 4 nm, 3 nm and 2.5 nm respectively. The structure, which was lattice matched to GaAs throughout, was completed with a 300 nm upper cladding layer and a layer of 100 nm GaAs which functions as the contact layer. A 2 μm GaAs buffer layer was placed in between the GaAs substrate and the lower cladding. A designed

structure allows damage depth profile resolution from a depth approximately 0.4 μm , the position of 2.5 nm wide QW1, to approximately 2.321 μm , the depth of 9.5 nm wide QW5.

Figure A-2. The schematic structure of GaAs/AlGaAs multiple widths QWs laser structure located at different depth from surface.

A.3 GAAS/ALGAAS QWS LASER STRUCTURE

The structure was grown by MOVPE. The QW active region was undoped and consisted of 25 pairs of 10-nm-wide GaAs QW, sandwiched by 26 pairs of 10-nm $\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$ barrier. The top and bottom $\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$ layers were 100 nm thick to complete the waveguide core. Both upper and lower cladding $\text{Al}_{0.4}\text{Ga}_{0.6}\text{As}$ layers were 1500 nm thick and doped to a concentration of $8 \cdot 10^{17}\text{cm}^{-3}$ and $9 \cdot 10^{17}\text{cm}^{-3}$ using carbon and silicon, respectively. The top contact layer consists of 100 nm of GaAs doped with $1.3 \cdot 10^{19}\text{cm}^{-3}$ of zinc. This as-grown material gave a 77 K PL peak at about 810 ± 2 nm and a lasing wavelength from a broad-area laser at around 860 nm at RT.

$1.3 \cdot 10^{19} \text{ cm}^{-3}$ Zn-doped	GaAs	100 nm	Cap layer
$8.0 \cdot 10^{17} \text{ cm}^{-3}$ C-doped	$\text{Al}_{0.4}\text{Ga}_{0.6}\text{As}$	1500 nm	
undoped	$\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$	100 nm	Upper cladding
undoped	GaAs	10 nm	
undoped	$\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$	10 nm	Waveguide core
undoped	GaAs	10 nm	
undoped	$\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$	100 nm	25 Quantum wells
undoped	GaAs	10 nm	
undoped	$\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$	100 nm	26 Quantum barriers
undoped	GaAs	10 nm	
undoped	$\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$	100 nm	Waveguide core
$9.0 \cdot 10^{17} \text{ cm}^{-3}$ Si-doped	$\text{Al}_{0.4}\text{Ga}_{0.6}\text{As}$	1500 nm	
Si-doped	GaAs substrate		Lower cladding

Figure A-3. The schematic structure of GaAs/AlGaAs multiple QWs laser structure

A.4 INGAAS/INALGAAS QWS LASER STRUCTURE

The InGaAs/InAlGaAs QW laser structure was grown by MBE on a Si-doped InP substrate. The QW active region consists of six 7 nm wide $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ wells separated by 8 nm $\text{In}_{0.53}\text{Al}_{0.27}\text{Ga}_{0.2}\text{As}$ barriers. The QW was centrally placed between 100 nm $\text{In}_{0.53}\text{Al}_{0.27}\text{Ga}_{0.2}\text{As}$ waveguide cores with Zn to a concentration of $2 \cdot 10^{17} \text{ cm}^{-3}$. The structure was lattice matched to InP throughout. It was completed with a 100 nm thick InP upper cladding layer (Zn-doped of $7 \cdot 10^{17} \text{ cm}^{-3}$), a 50 nm thick InGaAsP etch stop layer (Zn-doped of $1 \cdot 10^{18} \text{ cm}^{-3}$), and a 1200 nm thick InP upper cladding layer (Zn-doped of $1 \cdot 10^{18} \text{ cm}^{-3}$). The contact layer consists of 50 nm InGaAsP (Zn-doped of $2 \cdot 10^{18} \text{ cm}^{-3}$) and 200 nm InGaAs (Zn-doped of $1.4 \cdot 10^{19} \text{ cm}^{-3}$). The thicknesses of InP buffer layer and lower cladding layer were 500 nm (Si doped of $1 \cdot 10^{18} \text{ cm}^{-3}$) nm and 300 (Si doped of $3 \cdot 10^{18} \text{ cm}^{-3}$), respectively. The QW area was undoped thus forming a P-I-N structure with intrinsic region restricted to the QW layers. The samples resulted in a PL peak at $1.55 \pm 0.02 \mu\text{m}$ at room temperature (RT) and $1.43 \pm 0.02 \mu\text{m}$ at 77 K.

$1.4 \cdot 10^{19} \text{ cm}^{-3}$ Zn-doped	$\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$	200 nm	} Cap layer
$2.0 \cdot 10^{18} \text{ cm}^{-3}$ Zn-doped	InGaAsP	50 nm	
$1.0 \cdot 10^{18} \text{ cm}^{-3}$ Zn-doped	InP	1200 nm	Upper cladding
$1.0 \cdot 10^{18} \text{ cm}^{-3}$ Zn-doped	InGaAsP	50 nm	Etch stop layer
$7.0 \cdot 10^{17} \text{ cm}^{-3}$ Zn-doped	InP	100 nm	Upper cladding
$2.0 \cdot 10^{17} \text{ cm}^{-3}$ Zn-doped	InAlGaAs	100 nm	Waveguide core
undoped	$\text{In}_{0.53}\text{Al}_{0.27}\text{Ga}_{0.20}\text{As}$	8 nm	} 7 Quantum barriers 6 Quantum wells
undoped	$\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$	7 nm	
undoped	$\text{In}_{0.53}\text{Al}_{0.27}\text{Ga}_{0.20}\text{As}$	8 nm	
$1.0 \cdot 10^{18} \text{ cm}^{-3}$ S-doped	InAlGaAs	100 nm	Waveguide core
$1.0 \cdot 10^{18} \text{ cm}^{-3}$ S-doped	InP	500 nm	Lower cladding
$3.0 \cdot 10^{18} \text{ cm}^{-3}$ S-doped	InP	300 nm	Buffer
$3.8 \cdot 10^{18} \text{ cm}^{-3}$ S-doped	InP substrate		

Figure A-4. The schematic structure of InGaAs/InAlGaAs multiple QWs laser structure with InGaAsP upper cladding and etch stop layer.

APPENDIX B

MATERIAL PARAMETERS FOR $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$

Symbol	Parameter	$\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$	Unit
$Q_c:Q_v$	Band offset splitting ratio	0.6:0.4	-
$E_g(x,y)$	Energy band gap	$1.35-1.17y+0.668(1-x)-0.069y(1-x)+0.18y^2+0.03(1-x)y^2+0.758(1-x)^2-0.322y(1-x)^2$	eV
$\Delta_0(X)$	Spin-orbit splitting	$0.34(1-x)y + 0.43xy + 0.10(1-x)(1-y)+0.10x(1-y)$	eV
$m_c^*(X)$	Electron effective mass	$0.0632(1-x)y + 0.0213xy + 0.17(1-x)(1-y)+0.077x(1-y)$	m_e
$m_{\perp HH}^*(X)$	Heavy Hole effective mass perpendicular to QW layer	$0.5(1-x)y + 0.41xy + 0.54(1-x)(1-y)+0.12x(1-y)$	m_e
$m_{\perp LH}^*(X)$	Light Hole effective mass perpendicular to QW layer	$0.088(1-x)y + 0.024xy + 0.16(1-x)(1-y)+0.12x(1-y)$	m_e
$m_{\parallel HH}^*(X)$	Heavy Hole effective mass parallel/transverse to QW layer	$0.11(1-x)y + 0.031xy + 0.19(1-x)(1-y)+0.15x(1-y)$	m_e
$m_{\parallel LH}^*(X)$	Light Hole effective mass parallel/transverse to QW layer	$0.23(1-x)y + 0.082xy + 0.34(1-x)(1-y)+0.29x(1-y)$	m_e
a_0	Lattice constant	$5.6533(1-x)y + 6.0584xy + 5.4512(1-x)(1-y)+5.8688x(1-y)$	Å
C_{11}	Elastic stiffness constant	$11.8(1-x)y + 8.329xy + 14.12(1-x)(1-y)+10.22x(1-y)$	10^{11}dyn/cm^2
C_{12}	Elastic stiffness constant	$5.38(1-x)y + 4.526xy + 6.253(1-x)(1-y)+5.76x(1-y)$	10^{11}dyn/cm^2
dE_g/dP	Hydrostatic pressure coefficient	$11.5(1-x)y + 10.0xy + 11.0(1-x)(1-y)+8.5x(1-y)$	10^{-6}eV/bar
b	Shear deformation potential	$-1.7(1-x)y -1.8xy -1.5(1-x)(1-y)-2.0x(1-y)$	eV
ϵ_{static}	Dielectric function	$0.11(1-x)y +0.031xy +0.19(1-x)(1-y)+0.150x(1-y)$	ϵ_0
A	Renewed strength of E_0 and $(E_0+\Delta_0)$ transitions	8.40-3.40y	-
B	Nondispersive contribution	6.60+3.40y	-

($m_0=0.91095\times 10^{-30}$ kg, and $\epsilon_0=8.85418\times 10^{-12}$ F/m)

APPENDIX C

THEORETICAL PREDICTION USING SRIM SIMULATOR

SRIM 2002 simulator,¹ was TRIM, is a program, which allow one to calculate the stopping and range of ions (10 eV-2 GeV/amu) into matter using a full quantum mechanical treatment of ion-atom collisions. This calculation has made very efficient by using Monte-Carlo statistical algorithms that allows the ions to make jump between calculated collisions and then averaging the collision results over the intervening gap.

In this work, the prediction of point defects concentration and maximum vacancy depth created after Ar plasma exposure was made to estimate the damage distribution on the exposed material and to determine the sufficient thickness of intermixing mask, which effectively can block the ion bombardment induced damage during plasma exposure. It should, however, be pointed out that the depth prediction, assuming the implantation process of the Ar ions with the energy equivalent to that of RF-induced energy bias using pure RF power, is underestimated using SRIM calculation as the plasma induced damage as in the case of ion implantation are assumed, without taking consideration into the damage penetration mechanisms of ion channeling and diffusion of the ion created defects.² Thus, the actual damage exceeds the calculated implantation depth of ions.

From Figure C-1., the Ar ion penetrates in the bare InGaAs/InGaAsP QW laser structure at less than 10 nm and the vacancies are created less than 10 nm from SiO₂ surface using implant energy up to 1000 eV. These ion distributions

¹ J. F. Ziegler, J. P. Biersack, and U. Littmark, *The stopping and Range of Ions in Solids*, New York: Pergamon, 1985.

accumulated on the InGaAs cap layer imply that no implantation damage is created directly to the QW active region. As the ion energy increases, the ions distribution tends to penetrate deeper and more uniform. The actual damage can be deeper as the incident ions, fortuitously scattered into a channeling direction, can penetrate into QW material.

Figure C-1. The SRIM 2002 simulation using different ion energies of (a) the predicted Ar ion ranges on the bare InGaAs/InGaAsP material and (b) the created vacancy distribution on the SiO₂ layer as a mask.

The created vacancies only accumulate within the 10 nm thick layer of SiO₂ and the highest concentration of vacancies is almost similar over the implant energy up to 1000 eV. Thus, considering the possible sputtering effect to the SiO₂ layer at high plasma density, a 200 nm thick SiO₂ layer was chosen as an intermixing mask to prevent the penetration of both Ar ions and generated point defects in the sample. No ion induced damage is later expected to reach the QW sample.

² E. L. Hu, C. H. Chen, and D. L. Green, "Low-energy ion damage in semiconductors: A progress report," *J. Vac. Sci. Technol. B*, vol. 14, pp. 3632-3636, 1996.

APPENDIX D

BROAD AREA EXTENDED CAVITY LASER PROCEDURES

- i) Cleave sample into size of $1.2 \times 1.2 \text{ cm}^2$.
- ii) Clean samples using the ultrasonic bath in
 - a) Acetone for 5 minutes.
 - b) IPA for 5 minutes.
 - c) DI water for 5 minutes followed by blow dry with nitrogen gun
- iii) Bake the sample at the hotplate using temperature of 120°C for 30 minutes.
- iv) Deposit 200-300 nm thick SiO_2 on sample.

PECVD condition: SiH_4 : 30 sccm N_2O : 35 sccm
Pressure: 450 mTorr RF:200 W
Temperature: 300°C Deposition time: 6.5 minutes
- v) Conduct photolithography to pattern the ECL stripe for intermixing mask.
 - a) Spun the AZ 5214 positive photoresist using spin coater at 4000 rpm for 35 seconds.
 - b) Place samples on the hot plate at 90°C for 90 seconds.
 - c) Align samples with the mask using mask aligner and expose to UV light for 5 seconds.
 - d) Develop the exposed resist using AZ developer for ~35-45 seconds.
 - e) Rinse in DI water for 60 seconds and blow dry out with an nitrogen gun
 - f) Inspect under microscope with yellow filter to check the properly developed pattern. Repeat developing if necessary.
 - g) Post bake on the hot plate at 120°C for 120 seconds.
- vi) Etch away SiO_2 layer at the ECL stripe window region.
 - a) RIE dry etch for 6 minutes
Condition: O_2 : 2 sccm CF_4 : 60 sccm
Pressure: 100 mTorr RF power: 60 W
 - b) Wet etch using HF : DI at 1 : 4 for about 10 seconds.
 - c) Remove the resist pattern using the acetone solution
- vii) Clean samples using the ultrasonic bath using similar procedure in point (ii)
- viii) Expose sample to process which promotes QWI in ICP chamber.
- ix) Anneal sample at thermal stability temperature of intermixing using GaAs proximity cap for 2 minutes. The annealing is done in RTP under flowing nitrogen ambient.

- x) Remove the highly-doped InGaAs/InGaAsP contact layers using chemical solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ with ratio of 1: 4: 40) for 1 minute.
- xi) Strip oxide using HF : DI solution in the ratio of 1:1.
- xii) Deposit a new layer of 200 nm SiO_2 on sample surface using PECVD with similar procedure in point (iv).
- xiii) Conduct photolithography and RIE dry etching to obtain the 50 μm wide oxide stripe for current injection using similar procedure in point (v) and (vi), respectively.
- xiv) Clean samples using the ultrasonic bath using similar procedure in point (ii). Deoxidise in 1:2 solution of NH_3 to H_2O for 60 seconds.
- xv) Coat P-contact using e-beam evaporator at deposition rate about 0.7-0.9 $\text{\AA}/\text{second}$. The chamber pressure has to be maintained at $<5 \cdot 10^{-6}$ Torr during the process. The substrate heater is set at 100 $^\circ\text{C}$.

P-contact: Ti Au
 40 nm 200 nm
- xvi) Lap the bottom side of the sample until the desired thickness.
 - a) Mount epilayer down on a stainless steel jig with brown wax.
 - b) Hand lap samples until approximately 200 μm thick using 5 μm alumina grit and water on the appropriate glass plate followed by further lap until 180 μm using 1 μm alumina grit.
 - c) Remove the lap damage approximately 30 μm from the n-side type of samples using $\text{HCl}:\text{H}_3\text{PO}_4$ with ratio of 1: 3 for 2 minutes.
 - d) Rinse in DI water for 60 seconds and blow dry out with the nitrogen gun.
- xvii) Coat N-contact using e-beam evaporator using similar procedure in point (xv).

N-contact: Au Ge Au Ni Au
 14 nm 14 nm 14 nm 11 nm 200 nm
- xviii) Anneal sample at 360 $^\circ\text{C}$ for 1 minute for contact annealing. The annealing is done in RTP under flowing nitrogen ambient.
- xix) Cleave the sample according to the desired ECL length.

APPENDIX E

COMPARISON OF DIFFERENT QWI TECHNIQUES

A comparison of QWI techniques is presented covering various aspects of the usage of impact energy for defect introduction, the photonic integration simplicity and the fabricated waveguide from the extended cavity laser.

E.1 ION ENERGY

Table E-1. Comparison of reported IIID techniques on InP based material.

IIID techniques	Implant species	Energy (keV)	Bandgap shift (nm)	Depth (nm)	Institutions
FIB	Ga	130	100	300	Universitat Wurzburg, ³ Germany
High energy IIID	P, As	2000	90	1880	National Research Council, ⁴ Canada
Low energy IIID	P	360	76	330	Sherbrooke University, ⁵ Canada;
	As, P	360	120	330	Nanyang Technological University (NTU), ⁶ Singapore.
Argon ion IIID	Ar	30	100	25	Universitat Wurzburg, ⁷ Germany
Very low energy IIID	As	18	35	45	Sherbrooke University, ⁸ Canada

³ J. P. Reithmaier and A. Forchel, "Focused ion-beam implantation induced thermal quantum well intermixing for monolithic optoelectronic device integration," *IEEE J. Select.Top.Quantum Electron.*, vol. 4, pp. 595-605, 1998.

⁴ S. Charbonneau, P. J. Poole, Y. Feng, G. C. Aers, M. Dion, M. Davies, R.D. Goldberd, and I.V. Mitchell, "Bandgap tuning of InGaAs/InGaAsP/InP laser using high energy ion implantation," *Appl. Phys. Lett.*, vol. 67, pp. 2954-2956, 1995.

⁵ V. Aimez, J. Beauvais, J. Beerens, D. Morris, H. S. Lim, and B. S. Ooi, "Low-energy ion-implantation-induced quantum-well intermixing," *IEEE J. Sel. Top. Quantum. Electron.*, vol. 8, pp. 870-879, 2002.

⁶ H. S. Lim, V. Aimez, B. S. Ooi, J. Beauvais, and J. Beerens, "A novel fabrication technique for multiple-wavelength photonic-integrated devices in InGaAs-InGaAsP laser heterostructures," *IEEE Photon. Technol. Lett.*, vol. 14, pp. 594-596, 2002.

⁷ J. Oshinowo, J. Dreybrodt, A. Forchel, N. Mestres, J. M. Calleja, I. Gyuro, P. Speier, and E. Zielinski, "Photoluminescence study of implantation-induced intermixing of In_{0.53}Ga_{0.47}As/InP single quantum wells by argon ions," *J. Appl. Phys.*, vol. 73, pp. 1983-1986, 1993.

⁸ M. Paquette, J. Beauvais, J. Beerens, P. J. Poole, S. Charbonneau, C. J. Miner, and C. Blaauw, "Blue shifting of InGaAs/InP laser diodes by low-energy ion implantation," *Appl. Phys.Lett.*, vol. 71, pp. 3749-3751, 1997.

Table E-1 summarises the comparison between the existing IIID techniques in term of ion energy to create point defects and the reported bandgap shift in InGaAs/InP system. The use of IIID technique through relatively high implant energy (from 18 keV to 8.6 MeV) with electrically inactive implant species (10^{10} to 10^{16} ions/cm²); such as As, P, Ar, F, and B; needs a relatively complicated, specialised and expensive facilities. The neutral impurities are commonly employed later to reduce optical losses and leakage current in active intermixed section, and device lifetime.

Table E-2. Comparison of plasma induced QWI technique on InP based material.

Parameters	RIE	ECR	ICP
Schematic diagram of plasma system
Ion	Ar	Ar	Ar
Bandgap shift	73 nm	106 nm	104 nm
Linewidth broadening	12 nm	17 nm	10 nm
Processing time	5 minutes	10 minutes	5 minutes
Operating pressure	5-150 mTorr	0.5-5 mTorr	1-100 mTorr
Plasma density	$\sim 5 \cdot 10^9 \text{ cm}^{-2}$	$\sim 5 \cdot 10^{11} \text{ cm}^{-2}$	$\sim 5 \cdot 10^{11} \text{ cm}^{-2}$
Institutions	NTU ⁹	NTU ¹⁰	NTU ¹¹

It has been observed that the degree of non-recovered damage on lattice structures increases with an increase in the ion implant energy and causes a) the

⁹ D. Leong, H. S. Djie, and L. K. Ang, "Quantum well intermixing using Argon plasma generated in a reactive-ion etching system on InGaAs/InGaAsP laser structures," in *Proc. Int. Conf. IEEE/LEOS Workshop Fibre and Optical Passive Components*, 2002, pp. 148-152.

¹⁰ T. C. L. Wee, B. S. Ooi, T. K. Ong, Y. L. Lam, Y. C. Chan and G. I. Ng, "Novel quantum well intermixing in InGaAs-InGaAsP laser structure using Argon plasma exposure," in *Conf. Digest of IEEE Lasers and Electro-Optics Europe*, 2000, pp. 234.

reduction of residual purity and crystalline quality⁸, b) the degradation of electron transport properties due to the unintentionally implanted ions around QW region.¹² The use of the defect introduction far away from the QW active region, including low energy IID and plasma induced QWI here, is preferable to minimise the device degradation. The intermixing is enhanced by long-range defect migration upon annealing. When the defects reached the QW region, the interdiffusion between the atoms of the QW and the barrier layer widens the bandgap and results in a blue-shift. The achievement using plasma induced QWI is summarised in Table E-2.

Conventional RIE technology is based on parallel plate reactor in which the plasma density is coupled with the ion energy and depends on the applied power and the process pressure. With the increased understanding of the plasma etch processes it became clear that such a configuration would not operate in the optimum processing range for high rates at low ion energies. Later, ECR machine is developed for the needs of high rates and low damage. However, there are some disadvantage of ECR machine, such as 1) the manual or "semi-automatic" matching of microwave energy; 2) "mode hopping" of ECR resonance; 3) plasma uniformity^{13,14}; 4) problem of microwave energy passing to the wafer at operation outside the resonance (at pressures > 2 mTorr). It turned out, that a much simpler technology as "Inductive Coupled Plasma" overcomes above ECR problems. The

¹¹ H. S. Djie, T. Mei, J. Arokiaraj, and P. Thilakan, "High-density plasma enhanced quantum well intermixing in InGaAs/InGaAsP structure using Argon plasma," *Jpn. J. Appl. Phys.*, vol. 41, pp. L867-L868, 2002.

¹² M. Itoh, T. Saku, and S. Tarucha, "High-mobility quantum wires fabricated by Ga focused ion beam shallow implantation," *Jpn. J. Appl. Phys.*, vol. 31, pp. 4487-4491, 1991.

¹³ J. Hopwood and T. D. Mantei, "Application-driven development of plasma source technology," *J. Vac. Sci. Technol. A*, vol. 21, pp. S139-S144, 2003.

¹⁴ R. J. Shul and S. J. Pearton, *Handbook of advanced plasma processing techniques*. Berlin: Springer, 2000.

independent control of ion energy and ion current density ICP is fully automatic with 2 RF automatch units. Moreover, the plasma density in most ICP cases increases linear with power even up to high power levels indicating the possible use of high plasma dose. The maximum bandgap shifts produced by ECR and ICP were 106 nm and 104 nm respectively with no appreciable linewidth broadening in PL spectra. The smaller shift from RIE machine may be due to the low-density plasma generated to introduce desirable defects for QWI. The optimum bandgap shifts by ECR and ICP was higher than the reported value using Ar ion implantation QWI at 30 keV.⁷

E.2 PROCESS SIMPLICITY IN PHOTONIC INTEGRATION

In order to apply a QWI technique successfully, the simplicity in processing the technique is a major concern that is closely related to the process yield. The complex process steps results in low process yield and low throughput, and therefore adds cost to the final commercial devices. In this section, the various process steps required for QWI is presented.

E.2.1 Wide area intermixing

In principal, the intermixing process includes the defect generation stage (which is ion implantation for IIID process, dielectric cap for IFVD technique, plasma exposure for Ar plasma intermixing process and laser irradiation for P-PAID process), followed by a thermal annealing stage. Thus, for wide area intermixing, the different QWI techniques are rather similar in terms of simplicity providing the uniform defect creation across the wafer. IFVD, IIID, LID utilising a beam expander or an ultra-fast beam stirrer and plasma induced QWI techniques show similar simplicity in process with good uniformity on the wide area of wafer, while FIB techniques have a limitation of the ion beam spot size, requiring

multicycle disordering process in order to achieve uniformly broad area of intermixing. This increases the processing time and gives a low throughput for mass production purpose. The ability to control the intermixing reproducibility evenly across the substrate for this technique might pose a problem.

E.2.2 Selective intermixing

In order to produce selective QWI, different masking methods have to be applied to generate bandgap shift on the selected area. The mask has to be sufficiently effective in preventing the defects generated from the various techniques from penetrating into the sample. For IID process, the general masking layer used is SiO_2 . The oxide has to be sufficiently thick in order to totally prevent the ions from penetrating into the sample surface. Patterning for selective intermixing requires a lithography step followed by an etching step to remove the oxide in the region where intermixing is desired.

In the IFVD technique, intermixing masks using P-doped silica, $\text{SrF}_2/\text{AlF}_3$, and Si_xN_y have been proven to be successful.^{15,16,17} The 5 % P-doped SiO_2 film can be deposited using a conventional PECVD equipped with a separate PH_3 flow line for P doping. On the other hand, the $\text{SrF}_2/\text{AlF}_3$ can be obtained by thermally evaporating a mixture of 92 % SrF_2 with 8 % AlF_3 from a tungsten boat. The AlF_3 is included to reduce the grain size of the evaporated dielectric layer. Si_xN_y films can be deposited using PECVD to act as an intermixing mask.

¹⁵ P. Cusumano, B. S. Ooi, A. Saher Helmy, S. G. Ayling, A. C. Bryce, J. H. Marsh, B. Voegelé, and M. J. Rose, "Suppression of quantum well intermixing in GaAs/AlGaAs laser structures using phosphorus-doped SiO_2 encapsulant layer," *J. Appl. Phys.*, vol. 81, pp. 2445–2447, 1997.

¹⁶ J. Beauvais, J. H. Marsh, A. H. Kean, A. C. Bryce, and C. Button, "Suppression of Bandgap Shifts in GaAs/AlGaAs quantum wells using strontium fluoride caps," *Electron. Lett.*, vol. 28, pp. 1670–1672, 1992.

For LID process, a good reflector is needed for the masking layer to reflect the laser radiation. Gold is used for this purpose. However, the issue of using gold as a masking layer is the difficulty in removing it after the intermixing process. Thus, instead of directly depositing the gold layer, a dielectric layer is grown in between the gold and the sample. The common dielectric layer for LID masking process is Si_xN_y layer with Au layer on the top of it due to its high selectivity.^{18,19} By doing this, the removal of the gold mask is simpler as the lift-off process can be used.

Table E-3. A comparison of process steps required for selective intermixing.

QWI technique	Mask	Process steps
IID	SiO_2	4
IFVD	SrF_2 , P-doped SiO_2 , Si_xN_y	5
Pulsed LID	$\text{Au/Si}_x\text{N}_y$	5
Plasma induced QWI	SiO_2 , Si_xN_y , Au, Ti, Cr	4

For Ar plasma induced QWI process, masking process is relatively easy as the low energy ion can be simply blocked from reaching the material surface using various dielectric layers (i.e. SiO_2 , Si_xN_y) and metal materials (i.e. Au, Ti, Cr). However, for dielectric material mask, the plasma irradiation in the VUV region could penetrate and cause the radiation effect to the QW active region. Thus, adopting the pulsed LID masking process, a metal layer can be used on the top of dielectric material to further protect the sample from plasma irradiation with the

¹⁷ J. H. Lee, S. K. Si, Y. B. Moon, E. J. Yoon, and S. J. Kim, "Bandgap tuning of $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{InP}$ multiquantum well structure by impurity free vacancy diffusion using $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ cap layer and SiO_2 dielectric capping," *Electron. Lett.*, vol. 33, pp. 1179–1181, 1997.

¹⁸ C. J. McLean, A. McKee, G. Lullo, A. C. Bryce, R. M. De La Rue, and J. H. Marsh, "Quantum well intermixing with high spatial selectivity using a pulsed laser technique," *Electron. Lett.*, vol. 31, pp. 1285–1286, 1995.

¹⁹ T. K. Ong, B. S. Ooi, Y. L. Lam, Y. C. Chan, Y. Zhou, A. Saher Helmy, and J. H. Marsh, "High spatial resolution quantum well intermixing process in $\text{GaInAs}/\text{GaInAsP}$ laser structure using pulsed photoabsorption induced disordering," *J. Appl. Phys.*, vol. 87, pp. 2775–2779, 2000.

ease of metal layer removal by removing the oxide layer. Table E-3 presents a comparison on number of steps required for selective intermixing process for the different techniques.

E.2.3 Multiple bandgaps creation

Various methods could be used to produce multiple bandgaps across a single substrate. Some of these methods are tedious and require many cycles of processing steps, whereas some of the methods are rather simple and could even be a single step process. Chapter 6.2 has discussed a partial comparison of the existing multiple bandgaps creation with the shortcoming. In the IFVD process, SISA could be used to spatially control the degree of the intermixing using small patterns of SrF_2 as a bandgap control mask. SISA is a promising technique in the GaAs/AlGaAs system but finds its difficulty to be applied to the InGaAs/InGaAsP system due to the poor thermal stability of material. In addition, it requires the electron beam lithography process, which involves high cost and low throughput.

As for pulsed LID technique, multiple wavelengths could be achieved by changing the energy density of the laser irradiation while scanning the laser across the sample. This method requires a good control of the wafer movements and the energy density of the laser irradiation, which could be achieved by using computers and motion controllers. However, control of laser power to obtain the specified bandgap shift has to be done carefully due to the non-linearity bandgap shift to the energy density of the laser irradiation.¹⁹

Conventionally, in order to produce multiple bandgap energies across a wafer using IIID technique, windows would be opened at areas where intermixing is preferred, and suitable implantation energy would be executed. The cycle would then be repeated with intermixing of different degree done onto different desired

areas. This process could be very tedious, as multiple cycles are required in order to produce many different wavelengths. To overcome these shortcomings, the DTMI process using the gray mask technology was adopted to achieve the different thicknesses of SiO_2 in a single step of lithography. The resist pattern was then transferred using plasma process in a single etching step, producing the multiple SiO_2 thicknesses. This technique simply requires a single lithography and etching step to produce different thicknesses of SiO_2 simultaneously in selected regions in order to achieve selective area intermixing for monolithic multiple bandgaps integration. This simple and cost effective technique is used to demonstrate multiple bandgaps on a single InGaAs/InGaAsP QW laser structure using IIID technique.²⁰ In plasma induced QWI, several methods have been presented in Chapter 6.2 to achieve multiple bandgaps, using (a) several cycle of photolithography-etching-exposure steps and (b) single step process with both TDMI and SDMI approach. The later approach provides a simple multiple bandgaps creation in a single step.

E.2.4 Universality

The conventional IFVD technique has been applied successfully to GaAs/AlGaAs system, however finds its difficulty to InGaAs/InGaAsP system due to its poor thermal stability.²¹ However, sputter silica based IFVD has been proven to be a universal technique to be applied to a wide range of material covering a

²⁰ S. L. Ng, H.S. Lim, Y. L. Lam, Y.C. Chan, B.S. Ooi, V. Aimez, J. Beauvais, and J. Beerens, "Generation of multiple energy bandgaps using a gray mask process and quantum well intermixing," *Jpn. J. Appl. Phys.*, vol. 41, pp. 1080-1084, 2002.

²¹ T. Miyazawa, H. Iwamura, and M. Naganuma, "Integrated external-cavity InGaAs/InP lasers using dielectric cap disordering," *IEEE Photon. Technol. Lett.*, vol. 3, pp. 421-423, 1991.

wavelength from 660 to 1600 nm.²² The use of IIID and pulsed LID to induce QWI in III-V material system has been successfully demonstrated. In the GaAs/AlGaAs system^{23, 24} and InGaAs/InGaAsP system,²⁵ tuning a material bandgap by pulsed LID to induce QWI has been reported. The demonstration of bandgap shift in Chapter 6.3 using plasma induced QWI technique to GaAs/AlGaAs, InGaAs/InGaAsP and InGaAs/InAlGaAs system has positioned the plasma induced QWI technique as a universal process to III-V compound semiconductor.

E.3 DEVICE PERFORMANCE

A great importance of PICs is the integration between active and passive device into the single substrate. The passive devices as the optical waveguide are required as interconnector among discrete devices across a substrate to be low loss at the wavelength operation of PICs module. We focus on the comparison of the fabricated waveguide after QWI process, which usually is integrated with the active laser in the form of ECL laser. In contrast with the impurity-free based QWI techniques, IIID process requires the introduction of impurities during ion implantation or impurity diffusion, which may contribute to some loss of the fabricated waveguide. The use of high power densities to melt the material in pulsed LID can introduce thermal shock damage if used in a pulsed mode and the

²² O. P. Kowalski, C. J. Hamilton, S. D. McDougall, J. H. Marsh, A. C. Bryce, R. M. De La Rue, B. Vogege, C. R. Stanley, C. C. Button and J. S. Roberts, "A universal damage induced technique for quantum well intermixing," *Appl. Phys. Lett.*, vol. 72, pp. 581-583, 1998.

²³ J. Ralston, A. L. Moretti, R. K. Jain, and F. A. Chambers, "Intermixing of Al_xGa_{1-x}As/GaAs superlattices by pulsed laser irradiation," *Appl. Phys. Lett.*, vol. 50, pp. 1817-1819, 1987.

²⁴ B. S. Ooi, C. J. Hamilton, K. McIlvancey, A. C. Bryce, R. M. De La Rue, J. H. Marsh, and J. S. Roberts, "Quantum-well intermixing in GaAs-AlGaAs structures using pulsed laser irradiation," *IEEE Photon. Technol. Lett.*, vol. 9, pp. 587-589, 1997.

²⁵ A. McKee, C.J. McLean, G. Lullo, A.C. Bruce, R.M. De La Rue, J. H. Marsh, and C. C. Button, "Monolithic integration in InGaAs-InGaAsP multiple quantum well structures using laser intermixing," *IEEE J. Quantum Electron.*, vol. 33, pp. 45-55, 1997.

intermixed materials give low quality due to the formation of extended defects.²⁶ A quantitative comparison of the low-loss waveguide for the IID, IFVD, pulsed LID, and plasma induced QWI techniques is given in Table E-4. The use of Ar plasma induced QWI technique produced a relatively low-loss in the InGaAs/InGaAsP material system as compared to other techniques, demonstrating the usefulness of the process to the photonic integration technology with low-loss waveguide.

Table E-4. Quantitative comparison of bandgap energy shift and absorption loss in the passive waveguide of InP based extended cavity laser

Techniques	Absorption loss from ECL device
IID	InGaAs/InGaAsP (F ion): 2.88 cm^{-1} . ²⁷ InGaAs/InGaAsP (P ion): 10 cm^{-1} . ²⁸
IFVD	InGaAs/InP: 7.8 cm^{-1} at 1410 nm. ²¹ InGaAs/InGaAsP (sputter silica): 4.1 cm^{-1} at 1555 nm. ²⁹
LID	InGaAs/InGaAsP (LID): 28.7 cm^{-1} at 1550 nm. ³⁰ InGaAs/InGaAsP (LID + Pulsed LID*): 3.8 cm^{-1} at 1556 nm. ³¹
Plasma induced QWI	InGaAs/InGaAsP (Ar plasma)**: 2.3 cm^{-1} at 1546 nm [as documented in Chapter 6.4]

*intermixing was achieved by irradiating with combination of pulsed and cw Nd:YAG laser

** waveguide loss is calculated after consideration of reflectivity and spreading loss on the interface.

²⁶ S. J. Fancey, G. S. Buller, J. S. Massa, A. C. Walker, C. J. Mclean, A. Mckee, A. C. Bryce, J. H. Marsh and R. M. De La Rue, "Time-resolved photoluminescence microscopy of GaInAs/InGaAsP quantum wells intermixed using pulsed laser technique," *J. Appl. Phys.*, vol. 79, pp. 9390-9392, 1996.

²⁷ S. A. Bradshaw, J. h. Marsh, and R. W. Glew, "Extended cavity lasers formed by fluorine induced quantum well disordering," *IEEE Colloquium on Applications on Quantum Well Technologies*, 1993.

²⁸ E. J. Skogen, J. S. Barton, S. P. Denbaars, and L. A. Coldren, "Quantum-Well-Intermixing Process for Wavelength-Agile Photonic Integrated Circuits," *IEEE J. Select. Top. Quantum Electron.*, vol. 8, pp. 863-869, 2002.

²⁹ S. D. McDougall, O. P. Kowalski, C. J. Hamilton, F. Camacho, B. C. Qiu, M. Ke, R. M. De La Rue, A. C. Bryce, and J. H. Marsh, "Monolithic integration via a universal damage enhanced quantum-well intermixing technique," *IEEE J. Select. Top. Quantum Electron.*, vol. 4, pp. 636-646, 1998.

³⁰ A. McKee, C. J. McLean, G. Lullo, A. C. Bryce, R. M. De La Rue, J. H. Marsh, and C. C. Button, "Monolithic integration in InGaAs-InGaAsP multiple-quantum-well structures using laser intermixing," *IEEE J. Quantum Electron.*, vol. 33, pp. 43-45, 1997.

³¹ B. C. Qiu, A. C. Bryce, R. M. De La Rue, and J. H. Marsh, "Monolithic integration in InGaAs-InGaAsP multiquantum-well structure using laser processing," *IEEE Photon. Technol. Lett.*, vol. 10, pp. 769-771, 1998.