Implementation of multiple band gaps of quantum wells/dots based on inductively-coupled argon plasma technique

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**IMPLEMENTATION OF MULTIPLE BAND GAPS
OF QUANTUM WELLS/DOTS BASED ON
INDUCTIVELY-COUPLED ARGON PLASMA
TECHNIQUE**

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SCHOOL OF ELECTRICAL & ELECTRONIC ENGINEERING

2008

Implementation of Multiple Band Gaps of Quantum Wells/Dots Based on Inductively-Coupled Argon Plasma Technique

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SUMMARY

Recently, defect-enhanced interdiffusion, known as intermixing, has been extensively investigated on a wide range of III-V semiconductor quantum well (QW) and quantum dot (QD) structures as a postgrowth process to implement multiple band-gap energies across a single substrate for monolithic integration of optoelectronic devices. In addition, defect-enhanced interdiffusion provides a unique opportunity to study the interdiffusion of semiconductor heterostructures and the role of defects in the interdiffusion. In this thesis, defect generation using inductively coupled argon (Ar) plasma (Ar-ICP) exposure, defect-enhanced intermixing and multiple band-gap implementations have been investigated for both InP- and GaAs-based QW and QD structures. In this technique, the mobile point defects are generated at the near surface region of a structure due to exposure to ICP Ar plasma and enhance intermixing in the subsequent rapid thermal annealing (RTA) process, whereas band-gap halftones can be achieved in several approaches.

Multiple band-gap energies have been realized across a single InP substrate in an InGaAs/InGaAsP five QWs laser structure through the control of local defect concentrations. With multistep plasma exposure using 200 nm SiO₂ as an exposure mask, different levels of near-surface point defect concentrations are established in different areas, which lead to different extents of band gap modification in a single step RTA. The material quality is preserved as no intensity reduction and linewidth broadening in the photoluminescence (PL) are observed after the process.

Band gap redshift has been observed experimentally on an undoped InGaAsP/InP QW structure and explained using theoretical calculations of interdiffused QWs. After plasma exposure, a band gap redshift as large as 50 nm is induced at RTA temperature below 650 °C and the interdiffusion rate on the group III sublattice is four times as fast as that on the group V sublattice, annealing at 700 °C leads to band gap blueshift. This annealing temperature dependent interdiffusion is not affected too much by the cap layer composition. The influence of doping type in the cap layer on the ICP Ar plasma exposure-enhanced interdiffusion has been studied.

Improved crystal quality has been achieved with a QD infrared photodetector structure consisting of 20 stacks of InGaAs/GaAs QD layer by ICP Ar plasma exposure. The PL peak intensity is enhanced by 1.7 times without change in the peak position immediately after plasma exposure, due to the reduction in the amount of low temperature grown-in defects, which is experimentally confirmed by the improved thermal stability and increased carrier life time. In addition, the ICP Ar plasma exposure-induced intermixing suppression has been used in association with SiO₂ cap induced intermixing enhancement to produce large differential band gap modification.

Large differential band gap blueshift against negligible thermal shift has been obtained with an InAs/InP QD structure. The small thermal shift is ascribed to the low RTA temperature, while the large differential band gap blueshift is attributed to the separation of the plasma exposure step and the RTA step. The nature of the mobile point

defects responsible for the enhanced interdiffusion is identified to be P vacancies by combining the analysis of x-ray photoelectron spectroscopy data and the exposure time dependent band gap blueshift. Band gap halftoning has been achieved by controlling the defect concentrations through wet chemical etching to partially remove the plasma-exposed InP cap.

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1. INTRODUCTION

1.1 RESEARCH BACKGROUND

1.1.1 Development of photonic integrated circuit technologies

Since the recognition by H. Welker in 1951 [1] that compound materials made up of group III and group V elements possess semiconductor characteristics, tremendous research efforts have been devoted to these III-V compound semiconductor material systems for optoelectronic device applications. This is due to their direct band gap structure and high electron mobility which are suitable for high speed and high efficient light emission and detection. Among various III-V compound semiconductors, GaAs- and InP- based materials are the most technologically important compounds, especially in the field of optical fiber telecommunications. GaAs-based devices have been well-developed in short-haul optical data links, while InP-based devices are promising for long-haul optical communication as the emission wavelength lies in the low loss window of optical fibers [2].

Due to the continuous technological advancement in the growth techniques, i.e., molecular beam epitaxy (MBE) and metalorganic vapor phase epitaxy (MOVPE), the structures of optoelectronic devices have evolved significantly for better performances. Taking the semiconductor laser as an example, it has evolved from a homojunction structure [3] to quantum confined heterostructures, i.e., the one-dimensional confined quantum well (QW) [4] and the three-dimensional confined quantum dot (QD) [5], resulting in significant improvement in device performances, such as the reduced

threshold current, higher quantum efficiency, lower temperature sensitivity, and etc. These improvements in the performance of optoelectronic devices have boosted their application for optical fiber communications.

Since the first proposal by S.E. Miller in 1969 [6] on monolithic integration of optoelectronic devices with specific functionalities on a single substrate as optoelectronic integrated circuits (OEICs) or its subset, photonic integrated circuits (PICs), OEICs and PICs have attracted considerable research interests for the development of optical fiber communications. The major driving force for monolithic integration is their advantages over discrete devices connected by wires or fibers in terms of compactness, cost effectiveness, and high reliability.

The major challenge in the realization of PICs is the lateral selective band gap control across a single substrate because different types of optoelectronic devices demand different band edges. Figure 1-1 (a) illustrates a generic PIC module integrating a laser, an electro-absorption (EA) modulator and a passive waveguide. As illustrated in Figure 1-1 (b), the band gap energy of the EA modulator (E_{g1}) should be higher than that of the laser (E_{g0}). When the operating wavelength of the laser is λ_{op} and the forward bias on the EA modulator is OFF, light passes through the modulator section without being absorbed. When the forward bias on the EA modulator is ON, the absorption edge of the modulator shifts towards lower energy side due to the quantum confined stark effect. Light from the laser is absorbed when it passes through the modulator section. Therefore, by switching ON/OFF the forward bias on the EA modulator, the light intensity is modulated. To

minimize the band-to-band absorption loss in the passive waveguide section, the band gap energy should be as high as possible. Therefore, the band gap energy of the original epitaxial grown structure should be engineered to three different levels in order to realize this PIC module.

Figure 1-1. (a) Schematic illustration of a generic PIC module monolithically integrated with a laser, EA modulator and waveguide, with band gap energy at E_{g0} , E_{g1} and E_{g2} , respectively. (b) Absorption spectra for the laser, EA modulator (with forward bias OFF and ON) and passive waveguide. The operating wavelength of the laser is λ_{op} .

A number of local band gap engineering technologies have been investigated and developed for monolithic photonic integration. Among them, the most mature and extensively utilized technologies are growth and re-growth [7], selective area growth [8] and quantum well intermixing (QWI) [9]. The growth and re-growth approach involves alternative growth and etch processes. It is the most versatile, complicated and expensive technology. In addition, it suffers from some disadvantages such as mode mismatch in

optical propagation coefficient and dimension mismatch resulting in scattering and back-reflection loss at the re-grown interface. In selective area growth, the growth rate is controlled locally by the widths of opened areas in a dielectric mask layer, such as SiO₂. The advantage of this approach is the reduction in the total number of processing steps. It works well under a precisely controlled set of parameters but it is difficult to control and manipulate in more generic situation. In contrast, QWI enables band gap energy control at a post-growth stage based on the inherent metastable material property of heterostructures due to the existence of a large composition gradient of constituent atomic species across interfaces. Annealing at an elevated temperature causes interdiffusion of atomic species and the change of compositional profile, resulting in the shift of band edges in low dimensional structures. In view of the desire for a low cost band gap energy technology, QWI has more potential than growth and re-growth and selective area growth technologies for fabricating commercially viable PICs.

The key of an intermixing technique applicable to photonic integration is the capability of selective local band gap tuning. Defect-enhanced QWI [10] has to be adopted and the defect creation and control are very important. It is well known that in quantum-confined heterostructures, the extent of intermixing and thus the degree of band gap modification can be characterized using the interdiffusion coefficient of certain atomic species D_{QW} as a function of the total number of mobile point defects as follows [11]:

$$D_{QW} = \sigma \lambda_D^2 \Gamma_D = (\sigma_0 + \sigma_E) \lambda_D^2 \Gamma_D, \quad (1.1)$$

where Γ_D and λ_D are the hopping frequency and the mean free path of the point defects, respectively. σ_0 is the number of thermal equilibrium mobile point defects; σ_E is the number of non-equilibrium mobile point defects that are either grown in the structure during structure growth or introduced into the structure externally after growth. The density of thermal equilibrium defects and the grown-in defects can be assumed to be uniform across a whole structure, while the number of externally introduced defects can be selectively controlled. Therefore, by introducing a certain amount of mobile point defects into a desired section of a structure, as schematically illustrated in Figure 1-2, the interdiffusion coefficient and thus the extent of band gap modification can be selectively enhanced. By controlling the amount of introduced defects in different areas, multiple band gaps across a single structure can be realized.

Figure 1-2. Schematic illustration of defect-enhanced selective QWI for multiple band gap creation across single chip. (a) as-grown structure, (b) defects introduction, and (c) after annealing.

Defect-enhanced selective QWI involves processes of defect creation and interdiffusion promoted by introduced defects, both of which are performed at the postgrowth stage. This makes it a simple yet effective approach to band gap tuning in

QW-based PIC application [12]-[14]. QDs in nature are also metastable system with composition gradient. Intermixing techniques obtained in QW research can be naturally extended to QD applications [15], which is a further advantage over growth-regrowth and selective area growth approaches. In addition, defect-enhanced intermixing provides a unique opportunity to study the interdiffusion mechanism of semiconductor heterointerfaces [16],[17] and the role of defects in the interdiffusion [18].

1.1.2 Historical review of defect-enhanced intermixing techniques

In 1980, N. Holonyak, Jr. and his student W. D. Laidig observed band gap blueshift in an AlAs/GaAs superlattice (SL) structure using Zn diffusion [19]. This impurity-induced layer disordering (IILD) was the first QWI technique. Since then, various physical processes capable of defects generation have been investigated and a number of defect-enhanced QWI techniques have been developed, including the impurity induced disordering (IID) [20],[21], ion implantation induced disordering (IIID) [22]-[25], impurity free vacancy-induced disordering (IFVD) [26]-[31], laser induced disordering (LID) [32]-[35], anodic oxidation induced QWI [36],[37], sputtered silica induced QWI [38],[39], low temperature grown-in defect-enhanced QWI [40],[41], and recently argon plasma induced QWI [42].

In IIID, high energetic ions are implanted into the QW structure thereby generating mobile point defects, such as interstitials or vacancies, or clustered defects, due to the violent collisions of the energetic ions with the host atoms in the crystal lattice. These generated defects might locate within the QW region or far away from the QW

region depending on the parameters adopted in the ion implantation [43]. During subsequent rapid thermal annealing, the mobile point defects can diffuse through the QW region to enhance the interdiffusion rate and thus the extent of intermixing. IIID is a relatively simple and repeatable QWI technique. However, the impurities introduced into the structures and the residue damages caused by high energetic ions bombardment can degrade the material quality and the device performances [44]. In addition, it requires a relatively complicated, specialized and expensive facility.

IFVD has been considered as an extremely successful QWI technique in GaAs/AlGaAs system. It involves the use of a SiO₂ dielectric cap to induce Ga out diffusion into the SiO₂ cap at high annealing temperature, thereby creating Ga vacancies at the near surface region of the QW structure. These Ga vacancies then diffuse down to the QW region to enhance the Al-Ga interdiffusion rate leading to enhanced extent of band gap modification. A major disadvantage of the IFVD technique is its lack of reproducibility. SiO₂ cap prepared under different deposition conditions, such as the deposition temperature [45] and gas flowrate [46] can result in significantly different extent of intermixing. In addition, the high annealing temperature required to initiate IFVD limits its application for InP-based material system. Significant thermal shift can lead to limited selectivity due to its poor thermal stability [47].

The LID has evolved from simple LID [48] through photo-absorption induced disordering (PAID) [49] to pulsed PAID (P-PAID) [50] with significant improvement in the spatial resolution. The P-PAID technique uses high energy laser pulse to irradiate

sample surface. Absorption of these laser pulses causes transient heating in the crystal. Rapid thermal expansion causes the bond breaking and disruption of the crystal lattice, leading to the localized increase in the density of point defects. During subsequent high temperature annealing, these point defects diffuse to the QW region to enhance intermixing. LID is potentially impurity free and offers the capability of direct writing. However, the poor spatial resolution limits its application in monolithic integration [50], especially in the InP-based material system.

It is widely known that the exposure of semiconductor materials to plasma leads to the generation of mobile point defects at the near-surface regions [51]. During the plasma exposure process, positively charged energetic ions and free radicals are accelerated to the earthed substrate electrode. This high accelerating potential provides the ions with sufficient energy to break atomic bonds close to the sample surface, thereby creating mobile point defects in the form of vacancies and interstitials. A number of experiments have confirmed that defects generated from low energy ion processes can penetrate deeply more than 100 nm into the substrate [52],[53]. Upon annealing, these mobile point defects can diffuse towards the QW regions to enhance the atomic interdiffusion rate.

Plasma exposure-enhanced QWI was initially investigated on a GaAs/AlGaAs QW structure using H₂ plasma generated in a reactive ion etcher (RIE). After eight cycles of H₂ plasma exposure and annealing, a maximum band gap blueshift of about 24 nm had been achieved [54]. This technique was then applied to an InGaAs/InGaAsP QW

structure using Ar plasma generated in an electron cyclotron resonance (ECR) etcher [55] and a RIE system [56]. Recently, Ar plasma generated in the inductively coupled plasma (ICP) etcher has been utilized for enhancing QWI [57].

As Ar is a noble gas with heavy atomic mass, large amount of surface defects can be generated due to pure physical bombardment. The separate control of ion energy and density by RF power and ICP power in the ICP system makes it possible to produce high density low energy ions, large amount of defects can be generated without significantly degrading the material quality. Therefore, the ICP Ar plasma exposure-enhanced intermixing is expected to be universally applicable to a wide range of III-V semiconductor QW and QD structures and effective in enhancing intermixing while preserving QW/QD lattice quality. In addition, ICP machine is a common facility that is widely used in the semiconductor industry for etching a wide variety of materials including dielectrics and III-V semiconductors. Therefore, no additional cost is involved. Hence, the ICP Ar plasma exposure-enhanced intermixing is a very promising technique for postgrowth band gap engineering for PIC applications.

1.2 MOTIVATIONS

The existing defect-enhanced QWI techniques have their individual advantages and shortcomings, and none of them is universally applicable to various material systems with equal success. The ICP Ar plasma exposure-enhanced intermixing is a relatively new technique as compared to IID, IFVD and LID. It is apparent that there is a big room to explore and exploit this technique, and further understand it as well. By the time of the

start of this project, this technique has been primarily investigated on InGaAs/InGaAsP QW structures and major results achieved include large differential band gap modification [58] with improved photoluminescence after intermixing [59]. In addition, the role of ICP power in intermixing enhancement has been investigated [60], and PIC application has been demonstrated with an extended cavity laser [61].

However, we are still eager to know the answers to several questions. For example, how versatile is the Ar-ICP intermixing for multiple band gap implementation? What else can it do apart from blue shifting band gaps? Furthermore, QD structures become more appealing in the research of PICs, while the interdiffusion behavior in QDs is much more complicated than that in QWs due to the large surface area to volume ratio and the strain effect. Therefore, there is a need to re-examine this technique in QD applications.

1.3 OBJECTIVES

The objectives of this project are to investigate the various technological aspects of the ICP Ar plasma exposure-enhanced intermixing for multiple band gap implementations not only in QW structures but also in QD structures. More specifically, they include the followings:

- Investigate the nature of the defects generated during ICP Ar plasma exposure that is responsible for the observed enhanced intermixing.

- Study the role of the plasma exposure generated surface defects in intermixing and the effect of the cap material composition and cap doping type on the resulting band gap modification.
- Study the effect of ICP Ar plasma exposure process on the material quality of processed structures.
- Implement multiple band gap energies across a single substrate consisting of either a QW or QD active regions.

1.4 MAJOR CONTRIBUTIONS

With the completion of this project, a better understanding of the ICP Ar plasma exposure-enhanced intermixing technique has been achieved and the major contributions including the followings have been made:

Multiple band gap energies have been demonstrated with good material quality preservations across a single InP substrate on an InGaAs/InGaAsP five-QW laser structure using a process involving a multiple step plasma exposure followed by a single step RTA.

Band gap redshift has been observed experimentally on an undoped InGaAsP/InP QW structure and explained theoretically with calculation results of interdiffused QWs. It is found that after plasma exposure, band gap redshift can be induced at low RTA temperature and the interdiffusion rate on the group III sublattice can be four times as fast as that on the group V sublattice. Meanwhile, annealing at high temperature leads to band

gap blueshift. This annealing temperature dependent intermixing is not affected too much by the cap layer composition. The effect of doping type in the cap layer on the resulting intermixing has been further recognized.

Improved crystal quality has been achieved with a QD infrared photodetector structure consisting of 20 stacks of InGaAs/GaAs QD layer by ICP Ar plasma exposure. It is found that, after plasma exposure only, the PL peak intensity can be enhanced by 1.7 times without peak shift due to the reduction in the amount of low temperature (LT) grown-in defects, which is experimentally confirmed by the improved thermal stability and increased carrier life time. The suppressed intermixing after ICP Ar plasma exposure indicates that the extent of intermixing is determined by two competing processes occurred during plasma exposure: the generation of surface defects and the reduction of grown-in defects. In addition, the ICP Ar plasma exposure-induced intermixing suppression has been used in association with SiO₂ cap induced intermixing enhancement to produce large differential band gap modification.

Large differential band gap blueshift on top of negligible thermal shift has been obtained with an InAs/InP QD structure. The nature of the mobile point defects responsible for the enhanced QDI is identified to be P vacancies by combining the XPS analysis and the band gap blueshift analysis. Band gap halftoning is achieved by wet etching to partially remove the plasma exposed InP cap. Therefore, the defect generation, defect amount control and defect-enhanced intermixing are implemented in three

independent processes. This is especially advantageous for process optimization for QD-based PIC applications.

1.5 ORGANIZATION OF THE THESIS

The thesis is organized into six chapters. Chapter 1 gives an introduction to the thesis, where the research background, motivation, objectives, and major contributions of the thesis are presented. The actual work that has been done is arranged from chapter 2 to chapter 5. In each chapter, the research background related to the topic presented in that chapter is introduced first, followed by the experimental details, results and discussions, and summary.

In chapter 2, the multiple band gap creation on a single InP substrate consisting of an InGaAs/InGaAsP five-QW laser structure using the ICP Ar plasma exposure-enhanced QWI is presented. The thermal stability of the structure, the plasma exposure time dependent QWI, the selective QWI using SiO₂ as exposure mask are studied first. The multiple band gap creation using a process involving a multistep plasma exposure followed by a single step RTA is implemented.

In chapter 3, the role of near-surface mobile point defects generated due to ICP Ar plasma exposure in enhancing intermixing is studied using an undoped InGaAsP/InP QW structure. Band gap redshift is observed and explained theoretically. Effect of cap layer composition and doping on the resulting intermixing are discussed.

In chapter 4, the effect of ICP Ar plasma exposure on the crystal quality of a QD infrared photodetector structure consisting of 20 stacks of InGaAs/GaAs QD layer is studied. 77 K PL measurement, excitation dependent PL measurement and time resolved PL measurement are used to characterize the change in the optical properties and thermal stability after ICP Ar plasma exposure. Multiple band gap creation using ICP Ar plasma exposure-induced intermixing suppression in association with SiO₂ dielectric films-induced intermixing enhancement is demonstrated.

In chapter 5, the ICP Ar plasma exposure-enhanced intermixing has been applied to tune the emission wavelength of an InAs/InP QD structure. The thermal stability of this structure is studied first to determine the critical temperature. The exposure time dependent band gap modification is investigated in association with XPS analysis to identify the nature of the defects generated during plasma exposure that are responsible for the enhanced QDI. The RF power and ICP power are optimized to achieve maximum differential band gap modification. Band gap halftoning is finally demonstrated via defect concentration control by wet etching to partially remove the plasma exposed InP cap.

In Chapter 6, conclusions are made based on all of the achieved results presented in the thesis and future works are recommended.

2. MULTIPLE BAND GAPS CREATION IN InGaAs/InGaAsP QW

In this chapter, the inductively coupled argon plasma-enhanced quantum well intermixing (QWI) technique is employed to implement multiple band gap energy on a single chip with an InGaAs/InGaAsP quantum well (QW) laser structure. The thermal stability of the structure is studied first to determine the critical annealing temperature for defect-enhanced QWI. The plasma exposure time dependent band gap modification is then investigated. Selective QWI is demonstrated using SiO₂ layer as exposure mask. Finally, three band gap energies across a single chip are implemented by controlling the defects concentration using a multistep plasma exposure approach.

2.1 INTRODUCTION

Defect-enhanced QWI has attracted great research interest in recent years. One of the major driving forces is its capability of post-growth selective band gap modification for multiple band gap energy creation across a single chip with great simplicity and cost effectiveness, as compared to alternative techniques such as re-growth and selective area growth. This enables the realization of monolithic integration of different optoelectronic devices with specific functionalities on a chip as a photonic integrated circuit (PIC) module [1],[2], leading to compactness, cost effectiveness, high reliability, and improved robustness, as compared to discrete devices connected by wires or fibers. A typical PIC module may demand at least three different band gap energies for amplification, detection, modulation, and low-loss transmission of optical signals.

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In defect-enhanced QWI, the extent of band gap modification is solely dependent on the amount of mobile point defects under fixed annealing temperature and time. Therefore, to implement multiple band gaps across a single chip, a lateral distribution of mobile point defects has to be established in a controllable fashion. To date, several defect-enhanced QWI techniques have been developed for implementing multiple band gaps, such as gray mask technique [3] based on ion implantation induced disordering (IID) [4], selective intermixing in a selective area (SISA) technique [5] based on impurity free vacancy-induced disordering (IFVD) [6], and ultraviolet light technique [7] based on pulsed photo-absorption induced disordering (P-PAID) [8]. However, the effectiveness of these techniques in practical PIC application is affected by several existing disadvantages. In the IFVD-based SISA technique, the pattern preparation in the mask may restrict the flexibility of process optimization. Furthermore, the poor thermal stability of InP materials limits the utilization of the IFVD-based SISA technique as well as the P-PAID-based ultraviolet light technique for the InGaAs/InP material system. In the IID-based gray mask technique, the photo-resist thickness control in photolithography and the subsequent pattern transfer in dry etching are crucial. These processes may result in poor repeatability of the controlled band gap levels both within a wafer and between wafers. Besides, the gray mask is also much more expensive than the standard mask.

In the inductively coupled argon plasma-enhance QWI technique, the control of the local concentration of mobile point defects and thus the extent of band gap modification on different areas of a single chip have been investigated through several

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approaches, including dielectric thickness modulated intermixing (DTMI) using gray mask technique [9], and spatial defect modulated intermixing (SDMI) using dielectric layer with different coverage [10]. These two approaches can be implemented with a single plasma exposure process followed by a single RTA process. However, the preparation of the desired dielectric layers is very complex and this can result in poor repeatability of the band gap control. In this chapter, we present results of multiple band gaps creation through a multi-step plasma exposure process. This approach releases the extra demands on masks, such as patterned or gray-leveled features, so that not only the mask cost increase can be avoided, but also no restraint in process optimization is present in the mask preparation stage. Since the band gap levels are controlled by a more controllable processing parameter - plasma exposure time, each band gap level can be well controlled with good accuracy and repeatability. Furthermore, the separation of the processes of band gap difference control and intermixing provides more flexibility for the process optimization.

2.2 EXPERIMENTAL DETAILS

The lattice-matched InGaAs/InGaAsP quantum well laser structure used in this work (as shown in Figure 2-1) was grown by MOVPE on a (100) oriented n^+ -type sulfur-doped InP substrate with an etch-pit density less than 1000 cm^{-2} . The QW active region consists of five 5.5 nm thick $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ quantum wells and six 12 nm thick $\text{In}_{0.77}\text{Ga}_{0.23}\text{As}_{0.49}\text{P}_{0.51}$ barriers. The active region is sandwiched by a step-graded index (GRIN) waveguide core consisting of 50 nm thick $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}_{0.38}\text{P}_{0.62}$ and 80 nm thick $\text{In}_{0.90}\text{Ga}_{0.10}\text{As}_{0.21}\text{P}_{0.79}$ confining layers. The upper and lower cladding layers are a 1370

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nm thick InP layer doped with zinc to $7.3 \times 10^{17} \text{ cm}^{-3}$ and a 1000 nm thick InP layer doped with sulphur to $2.5 \times 10^{18} \text{ cm}^{-3}$, respectively. The top contact consists of a 50 nm thick $\text{In}_{0.82}\text{Ga}_{0.18}\text{As}_{0.38}\text{P}_{0.62}$ layer doped with zinc to $2 \times 10^{18} \text{ cm}^{-3}$ and a 100 nm thick $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ layer doped with zinc to $1.8 \times 10^{19} \text{ cm}^{-3}$. The doped cladding layers and the undoped waveguide core consisting of the QW and the GRIN layers form a PIN laser structure. The sample results in a photoluminescence (PL) peak at $1.51 \pm 0.02 \text{ } \mu\text{m}$ at room temperature (RT). At 77 K, the PL peak wavelength is around $1.41 \sim 1.43 \text{ } \mu\text{m}$.

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

Figure 2-1. A schematic structure of the InGaAs/InGaAsP five QWs laser structure.

The plasma source generator ICP 180 used for the plasma exposure process was a Plasmalab System 100, which was built by Oxford Instrument. This system employs an inductive coil to generate high density remote plasma with no direct contact between the plasma and the substrate. The 13.56 MHz radio frequency (rf) and ICP power supply

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provide an independent control on the ion bombardment energy and the ion current density with the powers up to 500 and 3000 W, respectively. The high plasma density plays an important role in enhancing QWI, as the application of ICP power induces more damage due to the plasma radiation together with high ion current density on the samples. The chamber base pressure is maintained at 5×10^{-5} Torr. The ICP chamber is equipped with a water circulator to maintain the table temperature at 60 °C. The ICP system is also equipped with a He-back side cooled electrode with the quartz as a wafer susceptor. The samples were placed at the silicon substrate to provide fairly large heat conduction. The ICP parameter settings for the experiments were optimized by the Taguchi's method [11], i.e., 100 sccm Ar flowrate, 80 mTorr chamber pressure, 480 W RF power, and 500 W ICP power corresponding to a 730 V rf-induced dc bias.

After the plasma exposure process, samples were subjected to rapid thermal annealing (RTA) process in flowing nitrogen ambient to activate intermixing. During annealing, the samples were sandwiched between two fresh pieces of GaAs proximity caps to provide As overpressure environment and further protect the sample surface from As out-diffusion. To assess the extent of band gap modification and material quality change, PL spectra were measured at 77 K on samples before and after the QWI process using a Nd:YAG laser (1.064 μm , ~10 mW) for excitation, a monochromator, and a TE-cooled InGaAs photodetector associated with a SR-830 lock-in amplifier.

In the following sections, the thermal stability of the laser structure will be firstly studied using unexposed samples to determine the critical temperature for defect-

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enhanced intermixing. The band gap modification using plasma exposure time as controlling factor will then be investigated. Selectivity of the plasma-enhanced QWI technique will be studied using a 200 nm thick SiO₂ layer prepared by *e*-beam evaporation as plasma exposure mask to block defects generation on selected areas. Creation of three band gaps on single chip was finally demonstrated using multi-step plasma exposure followed by single step RTA process.

2.3 RESULTS AND DISCUSSIONS

2.3.1 Thermal stability studies

For defect-enhanced QWI techniques, a step of RTA at a sufficient high temperature is necessary to activate intermixing on the defect-introduced areas, as well as to recover the crystal quality after the QWI process. However, improperly high temperature may lead to the thermal decomposition of the structure. The high concentration of thermal equilibrium lattice defects over the whole structure can cause unwanted intermixing on areas without defect introduced externally, leading to reduced differential band gap blueshift that is undesirable for PIC application. In addition, an excessively high temperature annealing might cause thermal damage to the material quality and dopant redistribution in active device structures. Therefore, it is crucial to determine the RTA process temperature to maximize the effect of controllable intermixing process subjected to the externally introduced mobile point defects only.

The thermal stability of a structure is primarily determined by the properties of the material system. For example, the GaAs/AlGaAs system requires an annealing

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temperature normally higher than 800 °C to activate intermixing [12], while for the InGaAs/InGaAsP system, significant thermal intermixing can be induced at an annealing temperature above 650 °C [13]. Another factor that can influence the thermal stability of a structure is the etch pit density (EPD) of the substrate on which the structure is grown. Larger EPD often results in higher interdiffusion activation energy and thus higher thermal stability [14]. Since the EPD is different from wafer to wafer, it is necessary to perform a thermal stability study on each new wafer to determine the critical temperature, i.e., the highest annealing temperature at which no thermal intermixing is induced.

Figure 2-2. 77 K band gap blueshift of an InGaAs/InGaAsP 5 QWs laser structure against annealing temperature for unexposed annealed only samples.

The thermal stability study was performed on the unexposed as-grown samples. Four samples were annealed at four different temperatures at 580 °C, 600 °C, 620 °C and 650 °C, and the annealing time was fixed at 2 min, which is short enough to minimize the surface decomposition while promoting QWI. Figure 2-2 shows the band gap blueshift as

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a function of RTA temperature for the InGaAs/InGaAsP five QWs laser structure. It can be seen that, for samples annealed at 580 °C and 600 °C for 2 min, no band gap blueshifts are observed. This is in accordance with the reported annealing study on the influence of defect density in sulfur doped InP substrates [15] and the effect of thermal stability on the QWs [16]. With the increase in the annealing temperature to 620 °C, a 8 nm band gap blueshift is induced due to the grown-in defects in the epi-layers and the substrate. When the annealing temperature increases to 650 °C, a significant thermal shift of 55 nm is observed, owing to the large concentration of point defects in thermal equilibrium. A very large band gap shift obtained at a too high temperature may sign thermal damage due to the possibility of thermally induced material decomposition.

From the thermal stability study, the annealing temperature of 600 °C is determined for promoting QWI due to argon plasma exposure while avoiding thermal damage as well as large thermal shift in areas not being exposed to plasma. However, the suitability of this annealing condition for defect-enhanced QWI is still subjective to whether sufficient amount of band gap blueshift can be achieved on plasma exposed areas when annealing at this condition and whether the optical property can be recovered. This will be examined in the next section.

2.3.2 Plasma exposure time dependent QWI

In the argon plasma-enhanced QWI process, defects are generated at the near-surface region during the plasma exposure process and diffuse to enhance intermixing at the QW region during the subsequent annealing process. The extent of band gap

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modification is determined by the interdiffusion coefficient of the constituent species that is a function of the local amount of defect concentration at the surface region [17]. Intuitively, the amount of surface defects during argon plasma bombardment is controllable through the plasma exposure time. Therefore, the plasma exposure time can be utilized to control the extent of band gap modification while keeping other process parameters fixed.

The plasma exposure time dependent band gap modification was investigated using as-grown samples. The samples were exposed to Ar plasma first for 2-5 min. After plasma exposure, all the samples were annealed together at 600 °C for 2 min followed by PL measurement at 77 K. Figure 2-3 shows the band gap blueshift as a function of the plasma exposure time. It can be seen that significant band gap blueshifts are induced after plasma exposure and annealing at 600 °C for 2 min, in contrast with the results observed from the thermal stability studies where no band gap blueshift is induced after annealing only at the same condition. This result confirms that the defects introduced into the near-surface region by argon plasma irradiation have indeed enhanced the interdiffusion rate of the constituent atoms and thus the extent of band gap modification. In addition, this result also corroborates that the annealing conditions are properly determined such that the observed band gap modification is mainly ascribed to the defect-enhanced QWI rather than purely thermal intermixing.

Figure 2-3. 77 K band gap blueshift against plasma exposure time for samples exposed and annealed at 600 °C for 2 min (square symbols) and 2 min + 2 min (circle symbols).

Figure 2-3 also shows that the extent of band gap modification increases with plasma exposure time. This is expected since the amount of mobile point defects generated during plasma irradiation increases with plasma exposure time. The band gap blueshift increases very quickly with exposure time from 2-3 min, after which it increases with slowed speed or saturates. This phenomenon can be caused by several possible reasons. Firstly, it is possible that the RTA process time is not sufficiently long to drive all of the mobile point defects introduced into the near-surface region after long time plasma exposure down to the QW regions to enhance intermixing and thus the band gap blueshift. To verify this possibility, a second round of RTA process at 600 °C for 2 min was performed for all of the samples and the results are included in Figure 2-3. Compared with the large blueshift in the first round of RTA process, only several nanometers of additional blueshift is obtained in the second round of RTA process, which could be

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caused by purely thermal intermixing. This result indicates that the RTA process time, 2 min, is long enough to drive the mobile point defects down to the QW regions to make their contribution in enhancing intermixing and the extent of band gap modification. Secondly, theoretical calculation of interdiffused QWs for this structure has predicted that the band gap blueshift increases quickly with diffusion length at the initial stage of interdiffusion, and finally saturates at a value of ~140 nm after sufficient interdiffusion [18]. The maximum band gap blueshift observed here is around 80 nm, far less than the theoretical saturation value. Thirdly, during the argon plasma exposure, defects are generated and accumulated at the near-surface region with exposure time, due to the bombardment of energetic argon ions with the sample surface. Meanwhile, the sputtering process can remove a certain amount of the surface material, thereby removing the mobile point defects accumulated in the surface layer [19]. As the plasma exposure proceeds, these two competing processes finally reach equilibrium state and the amount of mobile point defects will not increase with exposure time. This mechanism is believed to explain the observed saturation of band gap blueshift after plasma exposure for 3~5 min most reasonably.

2.3.3 Selective QWI

Defect-enhanced QWI as a viable technology for monolithic photonic integrated circuit (PIC) application relies on its capability of selective band gap modification. In the inductively coupled argon plasma-enhanced QWI, defects are generated at the near-surface region due to the bombardment of the energetic argon ions with the sample surface. To achieve selective QWI, some area of the sample surface should be protected

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from the plasma exposure by some masking layers, such as SiO_2 or Si_xN_y . Good selectivity requires that the mask used possesses the capability of completely blocking the defect introduction to the masked areas. This is crucial for some PIC applications, such as the integration of active laser with passive waveguide. To minimize the absorption loss in the passive waveguide section, the band gap on this section should be blue shifted as much as possible. This requires sufficient amount of mobile point defects to be created on this section. In contrast, to avoid any negative effects produced by the QWI process on the section where the active laser is intended to be fabricated, this section should be protected against any defects introduction so that the optical properties on this section can be preserved. In addition, the employed mask layer itself should not bring any additional defects and thus enhanced QWI effect to the masked areas.

The selectivity of the inductively coupled argon plasma-enhanced QWI technique was studied using one as-grown sample. The maximum vacancy depth created by argon ions in SiO_2 films is predicted using SRIM simulation to be less than 10 nm under bombardment ion energy of 0.8 keV (corresponding to ~kV DC bias) [20]. The sample surface was firstly covered with a 200 nm thick SiO_2 layer prepared by *e*-beam evaporation, followed by photolithography process and wet chemical etching using buffer HF solution such that only half of the sample surface was masked with SiO_2 . The patterned sample was then exposed to argon plasma for 5 min. Before RTA process, the SiO_2 layer was removed to avoid IFVD effects during annealing. The sample was then RTA processed at 600 °C for 2 min. PL measurements were done at 77 K on the as-grown sample and the two sections of the same sample after selective QWI process.

Figure 2-4. 77 K PL spectra measured from one as-grown sample, one sample masked with 200 nm SiO₂ and subjected to plasma exposure and annealing, one bare sample exposed and annealed. Annealing was done at 600 °C for 2 min.

Figure 2-4 presents the normalized PL spectra. Compared with the PL spectrum measured from the as-grown sample, the PL spectrum measured from the masked area shows only 4 nm blueshift, possibly due to purely thermal intermixing. This small thermal shift proves that the 200 nm thick SiO₂ layer is very effective in blocking the defects generation during plasma exposure and thus the enhanced intermixing during subsequent RTA process. In contrast, the area exposed to argon plasma for 5 min and annealed shows a band gap blueshift of 76 nm, due to the significant enhancement in the diffusion coefficient by the large amount of mobile point defects introduced to the near-surface region during plasma exposure process. A differential band gap blueshift of 72 nm between the exposed area and masked area is achieved, which is sufficient for the band gap energy difference required for monolithic integration of optoelectronic devices.

2. Multiple band gaps creation in InGaAs/InGaAsP QW

In addition, no PL linewidth broadenings are observed on both the masked area and the exposed area. This indicates the optical property of the structure is not degraded after the selective QWI process.

2.3.4 Multiple band gaps QWI

Figure 2-5. Schematic illustration for (a) the first step and (b) second step of Ar plasma exposure. Different levels of surface defect concentration are depicted on three areas.

The process for implementing three band gaps over a single substrate involves photolithography, wet etching, plasma exposure and RTA. A 200 nm thick SiO₂ layer was first deposited on the substrate by *e*-beam evaporation. An AZ 5214 positive photo-resist layer was then spin-coated, exposed to ultraviolet light with a photo-mask, and developed to a pattern which was used as a mask for wet etching the SiO₂ layer in a solution of HF: NH₃F: H₂O (1:7:5). The windows corresponding to the areas designed for the maximum band gap modification were thus opened in the SiO₂ layer. The photo-resist residual was removed, and a new layer of photo-resist was coated and patterned to only cover the areas designed for no band gap modification. The substrate with the patterned SiO₂ and photo-resist layers was exposed to the Ar plasma, as shown schematically in

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Figure 2-5 (a). The photo-resist pattern was then transferred to the SiO₂ layer using wet etching, and subsequently the second plasma exposure was performed (see **Figure 2-5 (b)**). After the removal of the photo-resist and SiO₂ residuals from the substrate, the substrate was then annealed at 600 °C for 2 min. Finally, PL spectra were measured at 77 K to assess the band gap modification and material quality change on the three areas experienced different plasma exposure duration of the processed samples.

Figure 2-6. 77 K PL spectra measured from (a) as-grown sample, and different areas in the same sample having experienced plasma exposure and annealing, which are (b) unexposed in either exposure step, (c) exposed only in the second exposure step (3 min), and (d) exposed in both the first step (2 min) and the second step (3 min).

The interdiffusion coefficient of the constituent species is a function of the total number of near-surface point defects that are accumulated with time during the process of plasma exposure [18]. Therefore, with multi-step plasma exposure, the lateral control of defect concentration can be established over a single substrate. The areas having tolerated

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plasma exposure for more steps and thus longer time will have larger band gap blueshift.

Figure 2-6 shows the three band gaps achieved over a substrate resulting from a two-step plasma exposure followed by a single annealing step. With a duration of 2 min for the first step of plasma exposure and 3 min for the second step, band gap blueshifts of 66 nm and 84 nm were obtained in the areas being exposed once and twice, respectively, with respect to that directly measured from an un-annealed as-grown sample, whereas only 3 nm band gap blueshift was detected for the masked unexposed area. Although an interruption exists between the two plasma exposure steps due to the wet etching of SiO₂, the differential blueshift of 81 nm between the blocked areas and twice exposed area is very close to the result [21] obtained using continuous plasma exposure with duration of 5 min in the same process conditions. This shows that the interruption does not affect the achievable band gap modification.

Figure 2-7. 77 K band gap blueshift measured from the three areas on the samples vs the time duration for the second plasma exposure step. The time duration for the first plasma exposure step was fixed at 2 min.

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As investigated in section 2.3.2, the extent of the intermixing degree is associated with the plasma exposure time. The time duration of the exposure steps can be used as a parameter to control the respective band gap blueshifts. Figure 2-7 shows the curves for band gap blueshifts in the areas exposed once and twice with a fixed time duration for the first exposure, i.e., 2 min, and a varied time duration for the second exposure, i.e., from 1 min to 3 min. Two required band gap levels can be obtained with the combination of the time durations of exposure. The nonlinear relation between the band gap blueshift and the plasma exposure time shown in Figure 2-7 (c) is due to the trend of time saturation, in agreement with the assumption that the lattice can only accommodate a certain maximum number of concentrations of defects [22].

Figure 2-8. 77 K PL linewidth broadening and the PL peak intensity normalized to that from the as-grown sample vs the time duration for the second plasma exposure step from the three areas on the samples.

The material quality preservation, as a concern for any intermixing technology, was investigated via the PL study for samples before and after the process. The PL linewidth broadening and the PL peak intensity, as a good indicator to the preservation of lattice quality are plotted in **Figure 2-8**, where the time duration for the first plasma exposure is fixed at 2 min and the duration for the second exposure ranges from 1 min to 3 min. No appreciable change in the linewidth was found, and about 40% increase in the peak intensity was found for long plasma exposure. Such a PL enhancement effect has been observed and discussed in previous work [23]. These results implied that the material quality is well preserved during the multiple band gaps QWI process using a multistep plasma exposure followed by a single RTA process.

2.4 CHAPTER SUMMARY

In this chapter, the inductively coupled argon plasma-enhanced QWI has been investigated for multiple band gaps creation on a single chip with an InGaAs/InGaAsP five QWs laser structure. From the thermal stability study, the RTA condition has been determined to be 600 °C and 2 min, where negligible thermal shift has been induced. In contrast, more than 80 nm band gap blueshift has been observed after plasma exposure and annealing at the same condition due to the enhanced QWI by the mobile point defects introduced during the plasma exposure. In addition, the extent of band gap modification is controllable by the plasma exposure time. For selective QWI, a 200 nm SiO₂ layer prepared by *e*-beam evaporation has been proved to be able to completely block the defect generation and thus the enhanced band gap modification on the masked area.

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Three band gaps on a single substrate has been achieved using a two-step plasma exposure followed by a single-step RTA. The interruption in the plasma exposure process does not affect the achievable band gap modification. This QWI process is scalable for realizing more band gaps by increasing plasma exposure steps without manipulating the critical annealing processing step; therefore, the process is easy to control. The process causes no degradation to the crystal quality of samples, as is evident from the experimental data of PL linewidth and intensity. The achieved results, together with the availability of the process in the III-V industry, support this technique as a practical method for implementing multiple band gaps in the InP-based PIC application.

3. PLASMA EXPOSURE-ENHANCED QWI IN UNDOPED InGaAsP/InP QW

QWI as a powerful postgrowth band gap engineering technology not only provides a practical approach for multiple band gap energies creation on a single chip for photonic integrated circuit applications, but also provides a unique opportunity for fundamental interdiffusion studies, such as the role of mobile point defects in the interdiffusion of semiconductor heterostructures. In this chapter, the role of defects generated during ICP Ar plasma exposure in enhancing the extent of intermixing in an *undoped* InGaAsP/InP QW is investigated by varying the RTA temperature. The band gap redshift observed is explained in association with a theoretical calculation of interdiffused QWs. The effect of cap layer composition and cap layer doping on the plasma exposure-enhanced intermixing is discussed.

3.1 INTRODUCTION

QWI in InGaAs(P)/InP QWs is more complicated than that in InGaAs/GaAs or GaAs/AlGaAs QWs where interdiffusion occurs only on the group III sublattice [1]. In InGaAs(P)/InP QWs, composition gradients between the well and barrier layer exist on both the group III (In and Ga) and group V (As and P) sublattices. During the rapid thermal annealing (RTA) process, interdiffusion process may occur on both sublattices [2],[3], as schematically illustrated in Figure 3-1. The interdiffusion coefficients of atoms belonging to the same group are usually assumed to be identical. Therefore, atoms on the group III (or group V) sublattice have the same interdiffusion rate and the extent of interdiffusion can be characterized by one diffusion length $L_d^{\text{III}} = \sqrt{D^{\text{III}} t}$ (or $L_d^{\text{V}} = \sqrt{D^{\text{V}} t}$),

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where D^{III} (or D^V) is the interdiffusion coefficient for group III (or V) atoms and t is the interdiffusion time normally associated with the RTA time. The interdiffusion rates on each sublattice, however, depend on the details of interdiffusion process and may not necessarily be equal. The final potential profile modification and thus the band gap variation after interdiffusion process is dependent on the interdiffusion ratio k between the two sublattices, i.e., $k = L_d^V / L_d^{III}$ [4].

Figure 3-1. Schematic illustration of interdiffusion process in an InGaAsP/InP QW structure.

A number of theoretical studies have been done for the interdiffusion in the InGaAs(P)/InP QW system that can be broadly categorized into three cases:

- i) $k = 1$ [4], identical interdiffusion rates on both group III and V sublattices. A lattice matched QW structure remains lattice matched after QWI. Band gap blueshift is induced;
- ii) $k > 1$ [5], dominant interdiffusion on the group V sublattice. A lattice matched QW structure becomes tensile strained in the well and compressively strained in the barrier. Band gap blueshift is induced;

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iii) $k < 1$ [6], dominant interdiffusion on group III sublattice. A lattice matched QW structure becomes compressively strained in the well and tensile strained in the barrier. Band gap redshift can be induced within a range of interdiffusion length if k is sufficiently small.

In defect-enhanced QWI, it is widely accepted that the group III (V) defects dominantly enhance the extent of intermixing of atoms on the group III (V) sublattice [7],[8]. Therefore, the k parameter in defect-enhanced QWI process is subjective to the nature of introduced defects, the method used for defects introduction, the annealing temperature and the annealing time. So far, band gap blueshift in InGaAsP/InP QWs is often observed experimentally as reported in a number of defect-enhanced QWI techniques. Particularly, in experiments such as phosphor-doped silica cap enhanced QWI [9], phosphor ion implantation enhanced QWI [10], and low temperature grown-in defect enhanced QWI [11], the k values were deduced to be around 1.4, 1.7 and 2, respectively, denoting dominant interdiffusion on the group V sublattice, which is enhanced by the phosphor interstitial via a kick-out mechanism. In contrast, not many reports have presented results of dominant interdiffusion on the group III sublattice and the resulting band gap redshift in InGaAsP/InP QWs. Band gap redshift was observed in an InGaAsP/InP QW structure by Zn diffusion [12],[13], and also GaAs/InGaP multiple QWs by thermal annealing [14] or fluorine implantation followed by annealing [15]. However, the k parameter under the case of band gap redshift has never been determined quantitatively.

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In this chapter, we investigate the role of defects generated at the near-surface region during ICP Ar plasma exposure in enhancing the extent of intermixing of atoms on the group III and group V sublattices of an *undoped* InGaAsP/InP QW structure. The structure is intentionally undoped to avoid the influence of dopant on the defect diffusion as is observed in impurity diffusion process [16],[17]. It is found that, the plasma exposure generated near-surface defects can enhance the extent of intermixing of atoms on both group III and group V sublattices during RTA. At lower annealing temperature, the enhancement occurs mainly on the group III sublattice, leading to a group III dominant interdiffusion process and band gap redshift. In association with theoretical calculations of interdiffused QWs, the interdiffusion on the group III sublattice is found to be four times as fast as that on the group V sublattice.

3.2 EXPERIMENTAL DETAILS

Figure 3-2 shows the schematic layer structure of the lattice-matched InGaAsP/InP QW structure used in this work, which was grown by metal organic chemical vapor deposition on a (100)-oriented n-type sulfur-doped InP substrate. After the deposition of a 300 nm InP buffer layer, a 3.5 nm $\text{In}_{0.71}\text{Ga}_{0.29}\text{As}_{0.61}\text{P}_{0.39}$ well layer was grown followed by a 500 nm InP barrier layer. The structure was completed by a 500 nm $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ cap layer. All epilayers were grown at a growth temperature of 620 °C without doping. The as-grown sample presents a PL spectrum peaked at 1078-1087 nm at 77 K, which is around the designed value of 1084 nm.

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No.	Composition	Thickness (Å)	Layer
4	In _{0.53} Ga _{0.47} As	5000	Buffer/cap
3	InP	5000	Barrier/cap
2	In _{0.71} Ga _{0.29} As _{0.61} P _{0.39}	35	Well
1	InP	3000	Barrier
(100) oriented n-type sulfur-doped InP substrate			

Figure 3-2. The layer structure for the undoped InGaAsP/InP single quantum well.

To study the effect of cap layer composition on the surface defect generation and thus the intermixing process, two sets of samples were prepared for experiments. The samples with the top InGaAs layer removed by wet etching using H₂SO₄: H₂O₂: H₂O (1: 4: 40) are referred to as InP cap samples, whereas the samples keeping the as-grown structure are referred to as InGaAs cap samples. In experiment, samples were exposed to argon plasma first under different RF powers and ICP powers for different durations. The RTA process was then performed in several steps with each duration fixed at 120 s and temperature raised consecutively. In RTA process, flowing nitrogen ambient was adopted, and each sample was sandwiched between two fresh pieces of InP or GaAs proximity caps to prevent out-diffusion of P and As for InP cap samples and InGaAs cap samples, respectively. After each RTA step, photoluminescence (PL) spectra were examined at 77 K using an argon ion laser ($\lambda = 488$ nm) as excitation source to assess the band gap modification.

3.3 RESULTS AND DISCUSSIONS

3.3.1 Plasma exposure induced band gap redshift

Figure 3-3 (a) shows the PL spectra of one InP cap sample before plasma exposure and after plasma exposure followed by several RTA processes. The argon plasma process was done for 1 min under the following parameters: 480 W RF power, 300 W ICP power, 80 sccm argon flow rate and 60 mTorr chamber pressure. The annealing was done repetitively in five steps with temperatures set at 580 °C, 600 °C, 620 °C, 650 °C, and 700 °C for the five steps, respectively. As a reference, one unexposed InP cap sample was also subjected to the above RTA processes. The PL peak wavelength shift as a function of the RTA temperature for the plasma exposed and unexposed samples are presented in Figure 3-3 (b). It can be seen that, the unexposed and annealed-only sample presents band gap blueshifts at all RTA steps, mainly due to the grown-in defects in the epilayers and substrate [18]. In contrast, for the plasma exposed sample, band gap redshifts were observed at several RTA steps for annealing temperatures below 650 °C, whereas a blueshift was obtained after the last RTA step at 700 °C. The PL peak intensity is extremely low as compared to that of the as-grown sample when there is a redshift, and starts to recover when a blueshift appears in the annealing step at 700 °C. The reduction in PL peak intensity after band gap redshift at low annealing temperature and its recovery after band gap blueshift at high annealing temperature were also observed by other researchers in GaAs/InGaP QW samples [15].

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Figure 3-3. (a) PL spectra for one InP cap sample before plasma exposure and after plasma exposure followed by annealing at (i) 580 °C, (ii) 600 °C, (iii) 620 °C, (iv) 650 °C and (v) 700 °C. (b) PL peak wavelength shifts after each annealing step for the plasma-exposed (square) and the unexposed (circle) samples. The samples were with the InP cap layer throughout the experiment. The annealing time was fixed at 120 s at each step.

To interpret the above observations of band gap modification, theoretical calculation of interdiffused QWs is performed using a finite difference method [19]. The interdiffusion process is assumed to obey Fick's model [20] with constant interdiffusion coefficients which are *un-identical* for group III and group V atoms [5],[6]. Therefore, the extent of the band gap modification is characterized by two diffusion lengths, L_d^{III} and L_d^V . Alternatively, it can be characterized by the k parameter ($k = L_d^V / L_d^{III}$) with one diffusion length, e.g., L_d^{III} (or L_d^V). Under certain k value, for a given diffusion length L_d^{III} , the composition profiles for both group III and V atoms are determined by solving the equation of Fick's law of diffusion [20]. Consequently, the profiles for the band gap energy, effective mass, strain and its effect on band gap energy, confinement potential are

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determined. The sub-band energies in the interdiffused QWs are calculated separately for electron, heavy hole and light hole by solving the one-dimensional Schrodinger-like Ben Daniel Duke's equation [21]. The ground-state transition energy and thus the band gap modification are determined. The detailed procedure for the theoretical calculation of interdiffused QWs and the material parameters used for the calculation have been documented in [appendix A and B](#), respectively. With the variation in the diffusion length L_d^{III} , a theoretical curve of band gap modification vs diffusion length under one k parameter is thus determined. This theoretical curve can also be obtained for different k parameters.

Figure 3-4. (a) The calculated wavelength shift of the ground state transition energy as a function of the group III diffusion length under different k parameters. (b) The calculated maximum band gap redshift as a function of the k parameter. The group III diffusion lengths to obtain the maximum band gap redshifts are labeled in the parentheses.

Figure 3-4 (a) shows the calculated PL peak wavelength shift as a function of group III diffusion length L_d^{III} under different k parameters. It can be seen that, in this

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QW structure, observable band gap redshift can be obtained only when $k < 0.6$ roughly, i.e., atoms sitting on the group III sublattice must interdiffuse about twice as fast as that on the group V sublattice. In addition, the maximum achievable band gap redshift is subjective to the k parameter rather than the diffusion length, as plotted in [Figure 3-4 \(b\)](#). Therefore, after plasma exposure and annealing at 600 °C, the observed maximum band gap redshift of 34 nm, as shown in [Figure 3-3 \(b\)](#), reveals that a minimum k of less than 0.35 had ever been achieved in the history of the temperature-raising RTA process, as a result of dominant group III sublattice interdiffusion. However, for the unexposed annealed-only sample, the band gap blueshift at all RTA steps indicates that the k parameter is larger than 0.6.

The obvious difference in intermixing behaviors of the plasma exposed and unexposed samples implies different intermixing mechanisms. For the unexposed sample, band gap blueshifts at various temperatures denote that there are not sufficient group III grown-in defects to cause appreciable interdiffusion on group III sublattice that exceeds interdiffusion on group V sublattice. However, during argon plasma exposure, both group III and V defects are generated at the near-surface region due to the physical bombardment by high-density energetic argon ions. These defects can diffuse down towards the QW regions during the subsequent annealing to enhance interdiffusion on both group III and V sublattices. It has been determined that the group V sublattice diffusion is characterized by higher activation energy than that of the group III sublattice diffusion, and the diffusion of each atomic species proceeds through its own sublattice [\[22\]](#). The diffusion of group V defects may require more energy than the diffusion of

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group III defects, since the former involves the removal of five electrons from the bond system while the latter involves the removal of only three electrons. Therefore, for annealing at low temperature after plasma exposure, the group III defect diffusion is first activated to enhance intermixing primarily on the group III sublattice, resulting in a group III dominant intermixing process and a band gap redshift. The activation of interdiffusion on the group III sublattice at lower temperature than group V sublattice is also supported by the reported intermixing results on the GaAs-based material with a GaAs/InGaP QW [15] and the InP-based material with an InGaAs/InP QW [23]. With the increase in the annealing temperature, the group V defect diffusion is activated to enhance intermixing primarily on the group V sublattice, increasing the k value and shifting the band gap redshift towards blueshift.

3.3.2 Effect of cap layer composition

For this *undoped* InGaAs/InP QW structure, the different behavior of intermixing in the plasma-exposed sample from that of the as-grown sample is due to the introduction of near-surface defects in both sublattices, which is simply a result of physical ion bombardment. This nature should not be affected by the composition of the cap layer. For this regard, similar experiments were conducted using InGaAs cap samples. The argon plasma exposure process was performed for 2 min under the following parameters: 480 W RF power, 500 W ICP power, 100 sccm argon flow rate and 60 mTorr chamber pressure. The annealing was done in four steps at temperatures of 560 °C, 600 °C, 650 °C and 700 °C, consecutively.

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Figure 3-5. PL peak wavelength shifts after each annealing step. Plasma exposure was done on the InGaAs cap. In the curve with triangle symbols, the samples kept the InGaAs cap layer in all annealing steps, whereas in the curve with square symbols, the InGaAs cap layer was removed after the first annealing step and thereafter, the InP layer was on the top.

Figure 3-5 shows the results obtained from the InGaAs cap samples. For the curve with square symbols, the InGaAs cap layer was removed by wet chemical etching after the first annealing step at 560 °C, such that in the subsequent annealing steps the sample had InP as its cap layer without existence of the near-surface defects. For the curve with triangular symbols, the samples were annealed with the InGaAs cap that contained the plasma-induced defects through all annealing steps. Four samples were used to obtain this curve because one had to be taken out after each annealing step to remove the thick InGaAs layer by wet chemical etching for PL signal sampling. The two curves show the similar trend as that seen in the plasma-exposed sample in Figure 3-3 (b), denoting that the defect introduction into both sublattices by plasma exposure and thus the temperature

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dependence of the resulting band gap shift are not much affected by the composition of the cap layer. Redshift was seen in the beginning since the dominant group III sublattice interdiffusion was activated at low temperature. The maximum band gap redshift of ~50 nm reveals that a minimum k parameter of less than 0.25 was achieved in the history of annealing. In other words, the group III sublattice interdiffusion that is approximately four times as fast as that on the group V sublattice was remarkably induced by the argon plasma exposure-introduced defects. However, by removing the InGaAs cap layer and thus the plasma-introduced near-surface defects after the first annealing step at 560 °C, the intermixing process slowed down, resulting in slower change from redshift to blueshift. This observation further confirms the role of plasma generated surface defects in enhancing intermixing and thus band gap blueshift at higher RTA temperatures.

It is interesting to note that the maximum band gap redshift obtained from the InGaAs cap samples, ~50 nm as shown in [Figure 3-5](#), is larger than that obtained from the InP cap sample, ~35 nm as shown in [Figure 3-3 \(b\)](#). The InGaAs cap samples were exposed to argon plasma with a higher ICP power and higher argon flowrate for a longer duration. This will result in the generation of a larger amount of mobile point defects on both the group III and group V sublattices at the near-surface region for the InGaAs cap samples than the InP cap sample. Under similar RTA process conditions, a larger diffusion length on both sublattices will result for the InGaAs cap samples. However, the maximum achievable band gap redshift is not determined by the diffusion length, but by the diffusion length ratio, i.e., the k parameter, as shown in [Figure 3-4 \(b\)](#). The larger maximum band gap redshift obtained on the InGaAs cap samples must be caused by a

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smaller k parameter compared to the InP cap sample. This is possible only when the group III diffusion length increases with a larger extent than the group V diffusion length at low annealing temperature. This is consistent with the fact that the group III defects diffusion is activated at lower temperature than the group V defects diffusion. In addition, the larger band gap redshift observed from the InGaAs cap samples implies that, by optimizing the plasma exposure and RTA process conditions, even larger band gap redshift could be obtained.

3.3.3 Effect of cap layer doping

Previously, using the same argon plasma-enhanced QWI technique on InGaAs/InP QW laser structures with a p-i-n doping profile, enhanced band gap blueshift has been observed from exposed and annealed samples as compared to annealed only samples [24]. Here, using a QW structure with an *undoped* cap layer, band gap redshift is induced after plasma exposure and annealing at low temperature. After annealing at high temperature, a reduced band gap blueshift is observed as compared to the blueshift from the annealed only sample (Figure 3-3 (b)). We therefore ascribe the difference to the doping in the cap layer, which might have a different impact on the group III and V defects diffusion in annealing.

It has been reported that a P-type doped material has a high concentration of group III interstitial, while during the argon plasma exposure, vacancies might have been generated on both the group III and group V sublattices at the near-surface region as the argon ions sputter away the constituent atoms from the sample surface. The group III

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interstitial in the P-type doped cap layer can annihilate with the group III vacancies generated by plasma exposure, thereby reducing the amount of group III defects and diminishing the extent of intermixing on group III sublattice. As a result, band gap blueshift is induced due to the enhanced intermixing on the group V sublattice by the group V vacancies. Similar doping effect on intermixing has been reported by other researchers, where the intermixing on group III sublattice is suppressed due to reduced amount of group III vacancies by group III interstitial existing in P-typed doped material [25],[26].

3.4 CHAPTER SUMMARY

In this chapter, the effect of mobile point defects generated at the near-surface region during argon plasma exposure on QWI has been investigated with an *undoped* InGaAsP/InP QW structure. It is found that the enhanced QWI by the plasma generated surface defects is dependent on the RTA temperature. Without plasma exposure, band gap blueshift is induced at all RTA temperatures. While after plasma exposure, both band gap blueshift and redshift can be achieved depending on the RTA temperature. After plasma exposure and annealing at temperatures below 650 °C, interdiffusion on the group III sublattice can be four times as fast as that on the group V sublattice, resulting in an appreciable band gap redshift as large as 50 nm in the experiment. The group V sublattice interdiffusion is activated at higher annealing temperature and band gap blueshift is obtained at 700 °C accompanied with recovery of PL intensity. This annealing temperature dependent QWI is not affected too much by the cap layer composition. The different band gap modification observed on this *undoped* QW structure from that

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observed previously on practical device structures with a p-i-n doping profile suggests that the doping in the cap layer has a strong influence to the inductively coupled argon plasma-enhanced QWI technique. Hence, the results observed in this study are of practical relevance to better understand this QWI technique in controlling the band gap modification for practical monolithic photonic integration applications.

4. AR PLASMA IRRADIATION EFFECT ON InGaAs/GaAs QDs

Quantum dot (QD) structures provide superior device performances for optoelectronic applications due to their three-dimensional carrier confinement and atomic-like density of state as compared to the one dimensional carrier confinement and step-like density of state of quantum well (QW) structures. Recent technological advancements in the growth techniques by molecular beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD) have enabled extensive studies for achieving high quality QD structures for practical QD-based optoelectronic device applications to be carried out. In addition, defect-enhanced QD intermixing (QDI), in the similar way as what has been performed on QW structures, has been investigated for postgrowth band gap engineering of QD structures.

In this chapter, the effect of argon (Ar) plasma irradiation on the crystal quality of a quantum dot infrared photodetector (QDIP) structure consisting of 20 stacks of InGaAs/GaAs QD layers will be studied first. In the second section of this chapter, multiple band gap creation using ICP Ar plasma exposure-induced intermixing suppression in association with SiO₂ dielectric films-induced intermixing enhancement will be presented. In the next chapter, selective and multiple band gap modification in an InAs/InP QD structure using the ICP Ar plasma-enhanced QDI technique will be investigated.

4.1 CRYSTAL QUALITY IMPROVEMENT OF InGaAs/GaAs QDs

4.1.1 Introduction

Continuous advancement in the growth technique of QD structures, using either Stranski-Krastanov (SK) deposition or cycled submonolayer/monolayer deposition, has enabled practical QD-based optoelectronic devices with superior performance, such as low laser threshold, high quantum efficiency, low temperature-dependent characteristics, etc. [1],[2], due to the three dimensional confinement and atomic-like density of state of QDs. However, in either SK growth or cycled submonolayer/monolayer growth, a low temperature (LT) deposition is required for the self-assembly of QDs. Growth of III-V materials at LT normally leads to the incorporation of grown-in defects [3],[4] due to the reduced diffusivity of the constituent atomic species. The presence of these LT grown-in defects at the QD regions [5] can act as non-radiative recombination centers, degrading the optical emission efficiency of the QD structures and limiting the performances of QD-based optoelectronic devices.

In order to reduce the amount of LT grown-in defects and improve the performance of QD-based optoelectronic devices, thermal treatment has been used during the overgrowth of cap layers on top of the QDs [6] and at the postgrowth level [7] with the penalty of significant band gap blueshift due to the enhanced interdiffusion of QDs with their surrounding barriers by the LT grown-in defects. Enhanced interdiffusion by LT grown-in defects in cap layers has been widely studied with QW structures [3],[4]. This interdiffusion effect is more pronounced for QD structures than for QW structures because of the larger interface area to volume ratio between QDs and the surrounding

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barriers as compared to QW structures [8] and the proximity of the LT grown-in defects at the QD regions. This significant band gap blueshift will modify the original emission wavelength of QD structures. In the view of monolithic integration of QD-based optoelectronic devices where large differential band gap energy is desired by selective QDI [9], such a low thermal stability limits the net differential band gap shift. In addition, self-organized QDs are highly strained structures [10], especially for QD stack structures where large strain is accumulated with the increase in the number of QD layers. Thermal annealing may induce strain relaxation [11] and dislocation formation [12],[13] at the QD regions, further degrading the crystal quality of QD structures. In some cases, high temperature annealing can result in the dissolution of QDs into the surrounding matrix [14],[15].

Alternatively, there are some reports on the reduction of grown-in defects and photoluminescence enhancement of QD structures by proton implantations followed by annealing [16],[17]. The mechanisms underlying the enhanced optical emission efficiency are hydrogen passivation due to the proton implantation and the carrier capture efficiency enhancement due to intermixing in the subsequent annealing. During the proton implantation, a number of non-radiative recombination centers are passivated by combining the hydrogen atoms with the defects, leading to the reduction in the amount of defects. However, at the same time, a large number of point defects are generated due to the proton implantation, leading to enhanced band gap blueshift. Therefore, the enhanced optical emission efficiency is accompanied with a degraded thermal stability of the QD structure. Others have reported the enhanced optical emission efficiency of QD structures

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by hydrogen plasma process due to the hydrogen passivation effect [18],[19]. However, the benefits brought about by the hydrogen passivation can be reduced or lost during subsequent processing at high temperatures due to the removal of hydrogen and thus the passivation effect [18]. Therefore, although this method can improve the optical emission efficiency at lower temperatures, it cannot improve the thermal stability of QD structures at higher temperatures.

Enhanced photoluminescence has been observed in inductively coupled argon plasma process with an InGaAs/InP QW structure [20] and GaAs/AlGaAs QW structure [21], which has been explained as the reduction in the amount of grown-in defects at the epitaxial layer interfaces. It is expected that this effect will be more pronounced with QD structures due to the presence of LT grown-in defects around the QD regions. In this section, a QD infrared photodetector (QDIP) structure consisting of 20 stacks of InGaAs/GaAs QD layers is used to study the effect of the inductively coupled Ar plasma exposure on its optical emission efficiency and thermal stability. Low temperature photoluminescence (PL) measurement, excitation-power dependent PL measurement and time-resolved PL (TRPL) measurement will be used to confirm the improvement in the crystal quality after the ICP Ar plasma exposure.

4.1.2 Experimental details

The InGaAs/GaAs QD structure used in this work, as shown in Figure 4-1, is a QD infrared photodetector structure grown by molecular beam epitaxy on a Si-doped n^+ (100)-oriented GaAs substrate. A 300-nm-thick undoped GaAs buffer layer was first

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grown and subsequently a 1000-nm-thick, Si doped ($n=2 \times 10^{18} \text{ cm}^{-3}$) GaAs bottom contact layer. 20-stacks of InGaAs QD layers were then consecutively grown, separated by 50-nm-thick GaAs layers which were doped with Si ($n=1 \times 10^{18} \text{ cm}^{-3}$) within a thickness of 10 nm in the center of each layer. On the top is a 600-nm-thick, Si doped ($n=2 \times 10^{18} \text{ cm}^{-3}$) GaAs contact layer. For each QD layer, five pairs of alternating InAs and GaAs monolayers were grown under a constant As flux with interruption after each monolayer in order to stabilize the surface. The growth temperature was 515°C for the QD layers and 600°C for other layers.

Si: $2.0 \times 10^{18} \text{ cm}^{-3}$	n++ GaAs	600nm	} X 20
undoped	GaAs	20nm	
Si: $1.0 \times 10^{18} \text{ cm}^{-3}$	n+ GaAs	10nm	
undoped	GaAs	20nm	
undoped	In _x Ga _{1-x} As QD (x = 0.5)	10ML	
undoped	GaAs	20nm	
Si: $1.0 \times 10^{18} \text{ cm}^{-3}$	n+ GaAs	10nm	
undoped	GaAs	20nm	
Si: $2.0 \times 10^{18} \text{ cm}^{-3}$	n++ GaAs	1000nm	
undoped	GaAs	300nm	
Si: $1-6 \times 10^{18} \text{ cm}^{-3}$	GaAs substrate	EPD < 70000 cm^{-2}	

Figure 4-1. The schematic structure of the quantum dot infrared photodetector (QDIP) consisting of 20 stacks of InGaAs/GaAs QD.

The plasma exposure was carried out using an ICP180 plasma source generator for 1~5 min under the following parameters: 100 sccm Ar flowrate, 60 mTorr chamber

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pressure, 480 W RF power and 500 W ICP power with a RF-induced DC bias of ~900 V. The annealing was performed at 700~750 °C for 30~120 s under flowing N₂ ambient using GaAs proximity caps. The PL spectra were measured at 77 K using a green crystal laser ($\lambda=532$ nm, ~100s W/cm²) for excitation, a monochromator and a TE-cooled Ge photodetector associated with a lock-in amplifier. TRPL measurements were carried out using a femtosecond self-mode locked Ti-sapphire laser pumped by a 532 nm green crystal laser. The excitation wavelength was selected at 800 nm with an output power of 15 mW. The repetition rate was 82 MHz with a pulse width of 150 fs. The detection wavelength was selected at the PL peak wavelength of the ground state emission from the QD samples. The time resolution of the TRPL system was 30 ps.

4.1.3 Results and discussions

4.1.3.1 Enhanced PL intensity

Figure 4-2 (a) shows the PL spectra taken from samples exposed to argon plasma only and without annealing, with exposure time for 1 min, 2 min and 3 min, respectively. The PL spectra taken from one as-grown sample and one as-grown sample with its top 300 nm GaAs cap removed by wet chemical etching using H₃PO₄: H₂O₂: H₂O (10: 8: 120) for 80 s, are also shown as reference (curve (i) and (v) in Figure 4-2 (a), respectively). The normalized PL peak intensity of the exposed samples as a function of the plasma exposure duration is presented in Figure 4-2 (b). It can be seen that, compared with the as-grown sample, the PL peak intensity of the sample exposed for 1 min is slightly decreased. After the first 1 min, increasing the exposure duration up to 3 min leads to a steady increase in the enhancement of PL peak intensity up to 2.7 times. Further increase

4. Ar plasma irradiation effect on InGaAs/GaAs QDs

in the exposure duration up to 5 min results in a decreased enhancement in the PL peak intensity. It should be noted that no discernible PL peak wavelength shift is involved in this process as seen in Figure 4-2 (a), denoting no change in the composition profile of QDs.

Figure 4-2. (a) PL spectra at 77 K taken from (i) as-grown sample, samples exposed only to Ar plasma for (ii) 1 min, (iii) 2 min and (iv) 3 min, respectively, and (v) as-grown sample with 300 nm GaAs cap removed by wet etching. (b) The PL peak intensity as a function of plasma exposure time.

During the high-energy high-density argon plasma exposure, two phenomena that have opposite impacts to the PL peak intensity will occur to the surface of the QD samples. Firstly, the bombardment of the argon ions will cause surface defects generation and surface roughening, resulting in the decrease of the PL peak intensity, as can be seen from curve (ii) in Figure 4-2 (a) after 1 min plasma exposure. Secondly, the bombardment of the argon ions will sputter away a certain amount of the top GaAs cap material, with a sputter rate around 100 nm/min under the adopted plasma process

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conditions. Since the GaAs cap can absorb the incident photons from the excitation source, the reduction in the GaAs cap thickness will lead to an enhanced PL peak intensity. After 3 min plasma exposure, the QD region is very close to the damaged surface layer and therefore the extent of enhancement in the PL peak intensity starts to decrease. The surface defects generation and sputtering effect seem to be able to qualitatively explain the observed evolution of the PL peak intensity with plasma exposure duration; however, they cannot quantitatively explain the observed phenomena. For the sample exposed for 3 min, the sputtered thickness of GaAs cap is ~300 nm, and the PL peak intensity is enhanced by 2.7 times. However, direct wet chemical etching to remove 300 nm GaAs cap from one as-grown sample can only improve the PL peak intensity by 1.2 times (curve (v) in [Figure 4-2 \(a\)](#)). This comparison clearly confirms that the sputtering effect is not the dominant factor leading to the significant enhancement in the PL peak intensity after plasma exposure.

Another phenomena that may occur during a high-density plasma exposure process is that the electrode temperature might increase with exposure time. This creates in-situ annealing effect to the QD samples, hence reducing the amount of grown-in defects and enhancing the PL peak intensity. The actual temperature of the electrode during an ICP argon plasma exposure process is unknown for us. However, the in-situ annealing effect due to the increased electrode temperature has been simulated by annealing the as-grown QD samples for 2 min at different temperatures, i.e., 200°C, 300°C, 500°C, and 600°C. No enhanced PL peak intensity has been observed. This result

excluded the possibility of in-situ annealing effect to the QD samples during the ICP argon plasma exposure process.

Enhanced PL peak intensity after ICP argon plasma exposure observed previously with an InGaAs/InP QW structure [20] and GaAs/AlGaAs QW structure [21] was explained as the reduction in the amount of grown-in defects at the epitaxial layer interfaces. In this QDIP sample structure, QD layers were grown at 515°C, which is much lower than the optimal temperature required for growing high quality lattice. As a result, an appreciable amount of LT grown-in defects might have been incorporated into the QD layers [5] and may behave as non-radiative recombination centers. The enhancement in the PL peak intensity after ICP argon plasma exposure indicates the amount of LT grown-in defects around the QD regions has been reduced. This explanation will be examined in the following sections by excitation power dependent PL measurement, time resolved PL measurement, and thermal stability examination.

4.1.3.2 Excitation power dependent PL studies

Due to the three dimensional confinement in QD structure and its atomic-like density of state, a striking phenomena that can be observed is the state filling effect [22]. When a QD structure is excited with low excitation power, carriers will firstly populate the ground state and no emission from the excited states can be observed due to the quick relaxation of carriers into the ground state of QDs. With the increase in the excitation power, the emission intensity from the ground state will increase accordingly and approach saturation. Further increase in the excitation power will result in the emergence

of emission from the first excited state. Emission from higher excited states will gradually emerge with the continuous increase in the excitation power when the lower excited states are fully populated. In addition, the intensity ratio of emissions between the excited states and the ground state will increase with the excitation power. The unique characteristic of this state filling effect has been widely used to verify the existence of QD structure after various thermal treatments [8],[23].

Figure 4-3. Excitation power dependent PL spectra for (a) as-grown sample and (b) sample exposed to argon plasma for 5 min. PL spectra shown in short dash are Gaussian fits of the PL spectrum measured at 668 W/cm².

Since the state filling effect is closely related to the amount of carriers available at the QD regions, the existence of point defects at the QD regions will diminish the intensity or delay the emergence of emission from the higher excited states because a number of carriers will recombine non-radiatively through these defects. In contrast, the reduction in the amount of defects at the QD regions will enhance the emission from the excited states. To verify the reduction of LT grown-in defects after ICP Ar plasma

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exposure, excitation dependent PL measurements were carried out on one as-grown sample and samples exposed to argon plasma for different times.

Figure 4-3 presents the typical results measured from (a) one as-grown sample and (b) one sample after plasma exposure for 5 min. The solid curves are the measured PL spectra at different excitation power, while the curves in short dash are the Gaussian fits of the PL spectrum measured at the highest excitation power, 668 W/cm². It can be seen that with the increase in the excitation power, the emissions from the excited states gradually emerge. At the highest excitation power, the measured PL spectrum can be well fitted by three Gaussian peaks denoting the emission from the ground state, the 1st excited state and the 2nd excited state, respectively. Under each of the excitation power, the intensities from each excited state for the sample after plasma exposure for 5 min are much stronger than that from the corresponding excited state for the as-grown sample. This observation indicates that under the same excitation power, more carriers are available at the QD regions for the plasma exposed sample than for the as-grown sample.

The effect of argon plasma exposure on the PL intensity of the excited states can be seen more clearly from Figure 4-4, where the PL peak intensities from the ground state and the 1st and 2nd excited states measured at an excitation power of 668 W/cm² are plotted as a function of plasma exposure time. A similar trend for the variation of PL intensity with plasma exposure time is obtained for the excited states as that for the ground state. The reduction in the amount of grown-in defects is equivalent to the increase in the excitation power for the emergence of emission from excited states of

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QDs and the increase of its intensity. Since all the PL measurements are done at a fixed excitation power, the quicker increase in the PL intensity with plasma exposure time for the excited states as compared to that of the ground state supports the reduction of the LT grown-in defects around the QD regions.

Figure 4-4. PL peak intensity as a function of plasma exposure time for the emissions from the ground state, the 1st and 2nd excited states. The PL peak intensities of each state are normalized to that of the as-grown sample. PL measurements are carried out with a fixed excitation power of 668 W/cm².

4.1.3.3 Increased carrier lifetime by TRPL studies

The presence and the amount of defects in III-V semiconductor materials can be assessed by the carrier lifetime deduced from time-resolved PL (TRPL) measurements [24]. In a TRPL measurement, a sample is excited by a beam of optical pulse leading to the generation of a certain amount of electrons and holes. These carriers can recombine radiatively to emit PL signal corresponding to the characteristic transitional energy of the sample under test. On the time scale, the radiative recombination leads to a super fast

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increase in the PL intensity until it reaches a maximum intensity value at some time point, after which the PL intensity gradually decays due to the reduced amount of electrons and holes available for radiative recombination until it approaches zero when all of the carriers are consumed [25]. Since defects can act as non-radiative recombination centers through which a lot of carriers may be consumed without giving any contribution to the PL intensity, the presence of defects in III-V materials can reduce the maximum PL intensity, the presence of defects in III-V materials can reduce the maximum PL intensity and accelerate the decay speed of the PL intensity in the TRPL spectra [26],[27]. The more the defects, the faster the decay speed of the PL intensity, and the shorter the carrier lifetimes.

Figure 4-5. TRPL spectra at 100 K for (a) as-grown and (b) 3-min exposed samples. No annealing was performed. The lines indicate the best fittings from the experimental data.

To further confirm the reduction in the amount of LT grown-in defects around the QD regions by argon plasma exposure, TRPL measurements were performed on one as-grown sample and one sample exposed to plasma for 3 min. The results are plotted in

Figure 4-5, where the points denote the experimental data, and the lines are the best fittings of the experimental data using the following formula:

$$I_{PL}(t) = a_0 + a_1 e^{-\frac{t-t_0}{\tau_d}} + a_2 e^{-\frac{t-t_0}{\tau_r}}, \quad (4.1)$$

where τ_r and τ_d are the PL rise time and decay time, denoting the effective carrier capture time into the QDs and the effective carrier lifetime in QDs, respectively. The carrier lifetimes deduced by fitting the experimental data using the above formula are 735 ps and 1140 ps for the as-grown sample and the sample exposed to plasma for 3 min, respectively. The increased carrier lifetime after plasma exposure clearly confirms the reduction in the amount of LT grown-in defects around the QD regions. Therefore, more carriers can recombine radiatively leading to slower decay of the PL intensity in the TRPL spectra and enhanced PL peak intensities in time integrated PL spectra for samples exposed for 2-5 min.

4.1.3.4 Thermal stability improvement

A natural inference of the reduction in the amount of grown-in defects in the QD structure, or the improvement of the crystal quality, is the reduction in the amount of band gap blueshift upon annealing, or the improvement of the thermal stability, which is fairly important when the net differential band gap blueshift is pursued in selective intermixing for monolithic photonic integration. To investigate the thermal stability of the QD structure, thermal annealing was performed at 750 °C for 60 s for samples exposed to Ar plasma with different durations, and the observed band gap blueshifts were compared with the thermal shift from one unexposed and annealed only sample.

Figure 4-6 (a) shows the 77 K PL spectra measured from one as-grown sample, one annealed-only sample and one sample that was exposed to Ar plasma for 3 min and annealed. Compared with the annealed-only sample, the plasma exposed and annealed sample produces smaller band gap blueshift and much stronger PL intensity. The band gap blueshifts and the PL intensity after plasma exposure and annealing versus the plasma exposure duration are shown in Figure 4-6 (b). It can be seen that the band gap blueshift decreases with increasing Ar plasma exposure duration, and a maximum band gap blueshift suppression of 20 nm is obtained. This observation is consistent with the improvement of QD crystal quality and thus the thermal stability.

Figure 4-6. (a) PL spectra at 77 K from (i) as-grown, (ii) control, and (iii) 3-min exposed and annealed samples. The control sample was annealed without being exposed to plasma beforehand. Annealing was carried out at 750°C for 60 s. (b) The band gap shifts and the PL peak intensities as a function of the plasma exposure durations measured after annealing.

The trend of PL intensity versus the plasma exposure duration is similar to that shown in Figure 4-2 (b), except that the PL peak intensity after annealing is higher. This is because the PL spectra of QDs are less diverse after intermixing, such that the summed PL peak becomes narrower but higher. In addition, the recovered sample surface quality after annealing can also contribute to this enhanced PL intensity. Comparison between the PL spectra of the annealed-only sample and the as-grown sample shown in Figure 4-6 (a) shows insignificant change in PL peak intensity, denoting that the conventional RTA process is not as efficient as the Ar plasma exposure in diminishing grown-in defects in the crystal.

The suppressed band gap blueshift after ICP Ar plasma exposure and annealing shown in Figure 4-6 is different from our previous studies with an InGaAs/InP QW structure where enhanced band gap blueshifts were observed after plasma exposure and annealing [28]. It is well known that in a quantum-confined heterostructure, the extent of intermixing and thus the degree of band gap blueshift is mainly determined by the amount of mobile point defects present at the vicinity of the heterostructure. The point defects can either be grown into the heterostructure during structure growth [3],[4] or be diffused from external source into the heterostructure during the post-growth RTA process. During ICP Ar plasma exposure, a certain amount of point defects is introduced in the near surface region but at the same time, the grown-in defects in the active region microns under the surface are reduced. Whether intermixing can be enhanced or suppressed is determined by the net effect of these two factors. The suppressed band gap blueshift after plasma exposure observed here shows that the reduction of grown-in

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defects at the active region is more prominent than the increase of point defects at the surface region. This is possible because the 20 stacks of QD layers grown at LT can incorporate a large quantity of grown-in defects at the active region, while the surface defects creation during plasma exposure is less efficient for GaAs-based materials than for InP-based materials because the bond strength of GaAs is stronger than that for InP [29]. The band gap blueshift decreases almost linearly within the first 3 min of plasma exposure. However, this trend gradually vanishes beyond 3 min of exposure because the defects introduced near the surface of the top layer keep accumulating while the grown-in defects have been sufficiently reduced.

Figure 4-7. (a) 77 K PL peak shifts and (b) normalized PL peak intensities after consecutive annealing cycles at 700°C for (i) as-grown and (ii) 3-min exposed samples.

The improved thermal stability of the QD structure can be more clearly seen in Figure 4-7. Two samples, one as-grown, while the other experienced 3 min plasma exposure, underwent repetitive annealing cycles at 700°C with 30 s for each cycle, whereas the band gap blueshift and PL peak intensity after each cycle were collected. The

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consecutive annealing cycles result in a monotonic increase in band gap blueshift for both samples. Compared with the unexposed sample, the 3-min exposed sample produces a smaller band gap blueshift after each annealing cycle. After annealing for 120 s, a suppressed band gap blueshift of 26 nm is achieved between the 3-min exposed sample and the control sample. Significant PL peak intensity enhancement is maintained after each annealing cycle in the plasma-exposed sample, as compared to the low PL intensity observed in the control sample.

4.1.4 Section summary

In this section, the effect of ICP Ar plasma on the crystal quality of an InGaAs/GaAs QD structure has been studied. The PL peak intensity can be enhanced by 1.7 times immediately after plasma exposure without discernible band gap shift. Excitation power dependent PL measurement shows stronger emission from excited states for plasma exposed sample than for as-grown sample. Time-resolved PL measurement shows an increase in carrier lifetime by 55% indicating the reduction in the amount of LT grown-in defects around the QDs region. The thermal stability is also improved and suppression of band gap blueshift can be clearly observed. All of these observations support that the crystal quality of the QD structure has been improved by ICP Ar plasma exposure as a result of reduction in the amount of LT grown-in defects. This result indicates a more efficient approach to improving the crystal quality of QD structures than the conventional RTA process, which is beneficial to QD-based optoelectronic device applications.

4.2 MULTIPLE BAND GAP CREATION IN InGaAs/GaAs QDs

4.2.1 Introduction

Defect-enhanced intermixing techniques have recently extended their application to QD structures for band gap engineering at a postgrowth stage [9],[30]-[33], in contrast to the selective area growth technique [34]. The major challenge in defect-enhanced quantum dot intermixing (QDI) for multiple band gap implementation is the poor thermal stability of QD structures, due to the presence of strain [10], low temperature grown-in defects [5] and the three-dimensional atomic interdiffusion process in the QDs [8], which results in significant thermal intermixing on unwanted sections in rapid thermal annealing and reduces the achievable differential band gap modification. This is not favorable for monolithic integration where large differential band gap modifications are required for multiple band gap creation across a single chip.

To suppress the thermal intermixing, strain compensation in QD structures [35] and dielectric cap deposition [36],[37] have been studied. In the first method, it has been reported that a thin layer of GaP, when grown several tens of angstrom below the QD layer, can be used as a strain compensation layer in an InGaAs/GaAs QD structure. The GaP layer is in tensile strain with respect to GaAs, with a lattice mismatch of 4%, while the InGaAs dots are in compressive strain. The strain caused by the GaP layer can partially compensate the strain caused by the dot layer. This can stabilize the system during annealing and thus suppress the thermal intermixing. In the second method, it has been reported that the titanium dioxide (TiO₂) film can be used to suppress thermal intermixing in an InGaAs/GaAs QD structure. Due to the different thermal expansion

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coefficients between TiO₂ film ($\sim 8.2 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) and GaAs ($\sim 6.8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$), the TiO₂ film is under compressive stress and the GaAs is under tensile stress during RTA. In this situation, vacancies will be trapped at the TiO₂/GaAs interface making little contribution to the interdiffusion [38]. In addition, the tensile stress on the GaAs surface can stabilize the QD structure by partially compensating the strain field around the dots and thus suppress the thermal interdiffusion.

The ICP Ar plasma exposure has demonstrated its capability of eliminating low temperature grown-in defects at the QD regions and suppressing the thermal intermixing during annealing. Compared with the reported intermixing-suppressing techniques using strain compensation during structure growth and TiO₂ dielectric film deposition after structure growth, the ICP Ar plasma exposure is a much simpler technique for intermixing suppression. This can be exploited to achieve large differential band gap modifications in conjunction with some intermixing-enhancing technique such as impurity free vacancy-induced disordering utilizing SiO₂ dielectric films. In this section, three different band gap energies are demonstrated in a single RTA process. The minimum band gap modification is produced on the ICP Ar plasma exposed sample and the maximum band gap modification is produced on the sample capped with SiO₂ dielectric films, while the unexposed bare sample produces band gap modification in between.

4.2.2 Experimental details

The same sample structure as shown in **Figure 4-1** was used in this experiment. For intermixing suppression, samples were exposed to the ICP Ar plasma for 3 min at 400 W RF power, 500 W ICP power, 100 sccm Ar flowrate and 60 mTorr chamber pressure. For intermixing enhancement, 400 nm SiO₂ dielectric films were deposited at the surface of some samples by plasma-enhanced chemical vapor deposition (PECVD) with the following deposition conditions: 30 W RF power, 30 sccm SiH₄ (4% in N₂) flowrate, 300 sccm N₂O flowrate, 500 mTorr chamber pressure, 300 °C deposition temperature. The small SiH₄/N₂O flowrate ratio was used to increase the porosity and oxygen content of the SiO₂ dielectric films for better IFVD effect [39]. Rapid thermal annealing was performed for 30 s at several temperatures from 750-850 °C under flowing N₂ ambient with two fresh pieces of GaAs as proximity cap to prevent As out-diffusion during annealing. At each annealing temperature, one plasma exposed sample, one SiO₂ capped sample and one unexposed bare sample were loaded together into the annealing chamber. Before the PL measurements, SiO₂ films were removed from samples by diluted HF solution. PL spectra were measured at 77 K using a green crystal laser ($\lambda=532$ nm, ~ 100 s W/cm²) for excitation, a monochromator and a TE-cooled Ge photodetector associated with a lock-in amplifier.

4.2.3 Results and discussions

4.2.3.1 Multiple band gap creation

Figure 4-8. 77 K PL spectra taken from (i) as-grown sample, and samples annealed for 30 s at (ii) 750 °C, (iii) 800 °C, and (iv) 850°C for (a) bare samples annealed only, (b) samples exposed to argon plasma for 3 min and annealed, and (c) samples capped with 400 nm SiO₂ and annealed. For curve (ii)-(iv) in (c), 300 nm GaAs cap layer was removed by wet chemical etching before PL sampling. The band gap blueshift vs annealing temperature for the three different processes are summarized in (d).

Figure 4-8 (a)-(c) presents the 77 K PL spectra for samples after three different processes, i.e., annealing only, plasma exposure followed by annealing, and SiO₂

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deposition followed by annealing. The annealing was performed at 750-800-850 °C for 30 s at each temperature. It can be seen that the PL intensity of the annealed samples decreases with the increase in the annealing temperature for all of the three processes. Since QD structures are highly strained structure, annealing at high temperature may induce strain relaxation and dislocation formation leading to diminished PL intensity [11]-[13]. In addition, significant interdiffusion after annealing at high temperature weakens the confinement potential of QDs, making it easier for carriers to escape away from the QDs to the wetting layer or barrier matrix, resulting in low PL intensity [40]. For the three different processes, the ICP Ar plasma exposure followed by annealing produces the strongest PL intensity at each annealing temperature due to the significant reduction of grown-in defects around the QDs, while the IFVD process (SiO₂ deposition followed by annealing) produces the weakest PL intensity. The PL intensities of the QD samples after IFVD process are very low and the spectra presented in Figure 4-8 (c) were collected after removing 300 nm GaAs cap layer by wet chemical etching. Interestingly, the PL spectrum for the sample after IFVD process at 750 °C for 30 s exhibits a double-peak-like broad spectrum. The very weak PL intensity and broad PL linewidth after IFVD process will be discussed later.

Figure 4-8 (d) summarizes the band gap blueshift versus the annealing temperature for the samples that had been processed in the three different methods. Three different band gap energies are achieved at each annealing temperature. The minimum band gap blueshift is produced on the ICP Ar plasma exposed samples due to the reduced net amount of mobile point defects available at the QD region. The maximum band gap

blueshift is produced on the samples capped with SiO₂ dielectric films due to the increased amount of mobile point defects at the SiO₂/GaAs interface as a result of Ga out-diffusion during annealing [9], [31]. The unexposed bare samples produced band gap blueshift between the above two cases. The differential band gap blueshift between the SiO₂ capped samples and the ICP Ar plasma exposed samples obtained at 750 °C is 65 nm and it reduces to 40 nm at 850 °C. This is expected because with the increase in the annealing temperature, the contribution from thermal interdiffusion will gradually increase [32]. It is worthy to note that the method used here for multiple band gap creation is simple and capable of selective intermixing, and therefore has the potential for photonic integration application.

4.2.3.2 Double-peak-like broad PL spectrum with low PL intensity

Figure 4-9 (a) presents the PL spectra taken from one sample after IFVD process at 750 °C for 30 s (ii) and followed by wet chemical etching to remove the 300 nm GaAs cap layer (iii). Compared with the PL intensity of the as-grown sample (i), the PL intensity of the IFVD processed sample was extremely low. Annealing induced low PL intensity from QD structure has been reported due to the relaxation of strain and the formation of dislocation at the QD regions [11]-[13]. In IFVD process, the presence of the SiO₂ encapsulating films on the GaAs cap might exacerbate the strain relaxation. Since the thermal expansion coefficient of SiO₂ ($\sim 0.52 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$) is smaller than that of GaAs ($\sim 6.8 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$), during annealing the surface of GaAs is under compressive stress. This can strengthen the strain field around the QD regions and expedite the process of strain relaxation and dislocation formation, resulting in very low PL intensity. In addition,

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it has been reported that the defect diffusion in (Al)GaAs-based material is lower than that in InP-based material [41]. When annealing at 750 °C for 30 s, a number of vacancies generated at the SiO₂/GaAs interface may not diffuse away and still reside in the thick GaAs cap. These residual defects can make a strong contribution to the extremely low PL intensity. This possibility is verified by the fact that, after wet chemical etching to remove 300 nm GaAs cap from the IFVD processed sample, the PL intensity is significantly recovered as shown in curve (iii) of Figure 4-9 (a), while direct wet etching of the same thickness of GaAs from one as-grown sample can only improve the PL intensity by 20% (see Figure 4-2 (a)).

Figure 4-9. (a) 77 K PL spectra taken from (i) as-grown sample, and sample capped with 400 nm SiO₂ and annealed at 750 °C for 30 s, before (ii) and after (iii) wet chemical etching to remove 300 nm GaAs cap layer. (b) 77 K PL spectra taken from (i) as-grown sample, and sample capped with 400 nm SiO₂ and annealed at (ii) 750 °C for 15 s, (iii) 750 °C for 30 s, (iv) 750 °C for 60 s, (v) 800 °C for 30 s, (vi) 850 °C for 30 s. PL spectra for curve (ii)-(vi) in (b) were collected after wet chemical etching to remove 300 nm GaAs cap layer.

The double-peak-like broad PL spectrum after IFVD process at 750 °C for 30 s can easily be related to the coexistence of radiative emissions from both the ground state and excited states of QDs. However, excitation-dependent PL measurement does not give any changes in the PL shape except for the PL intensity, suggesting that the broad PL spectrum cannot be explained by state filling effect. To better understand the underlying mechanism responsible for this broad PL spectrum, two more IFVD processes were conducted at 750 °C for 15 s and 60 s, and the measured PL spectra are plotted together with other spectra collected from IFVD processed samples, as shown in [Figure 4-9 \(b\)](#). It can be seen that, similar to the result after IFVD process at 750 °C for 30 s, double-peak-like broad PL spectra are observed on the two samples after IFVD processes at 750 °C for 15 s and 60 s. In addition, with the increase in the annealing time at 750 °C, the double peaks shift simultaneously towards shorter wavelengths. They finally evolve into one single peak after annealing at 800 °C for 30s. This observation rules out the possible origin of the extra peak from the PL system, and confirms that the double peaks indeed come from the QD ensembles.

Double PL peaks from as-grown QD structure have been reported due to the coexistence of QD ensembles of different sizes [\[42\]](#). Larger dots produce a PL peak at lower energy or longer wavelength side, while smaller dots produce a PL peak at higher energy or shorter wavelength side. Upon thermal annealing, the PL peak from smaller dots will blueshift faster than that from larger dots due to the larger surface area to volume ratio of smaller dots [\[43\]](#), resulting in more and more separation of the two PL

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peaks and a broad overall PL spectrum. In defect-enhanced QDI, however, the extent of interdiffusion is determined not only by the QD size, but also by the amount of defects available at the QD region. When defects are introduced directly to the QD region to enhance intermixing, for example, proton implantation-induced QDI in an InGaAs/GaAs QD stack structure, broad PL peak after intermixing has been observed and explained with the above mechanism [32]. However, in IFVD process where defects are introduced far away from the QD regions to enhance intermixing, a different scenario may arise. When defects diffuse down from the surface to QD regions to enhance intermixing, larger dots may acquire more point defects leading to larger extent of interdiffusion than smaller dots. This will reduce the separation of the two PL peaks after intermixing resulting in a narrow PL spectrum [44].

In this work, the double-peak-like broad PL spectra observed after annealing at 750 °C for 15-30-60 s cannot be explained by any of the above mechanisms because no bimodal emission is observed from the as-grown sample. The QDIP structure consists of 20 stacks of InGaAs dot layer uniformly embedded in a GaAs matrix which is 1000 nm thick. Since the defects are generated at the near-surface region in IFVD process, it may take some time for defects to diffuse down and reach every QD layer to enhance intermixing [33]. The slow diffusion rate of defects is supported by the extremely low PL intensities of samples after IFVD process and their significant recovery after the removal of 300 nm GaAs cap by wet etching. Under such a situation, the interdiffusion of QDs in the upper QD layers may be enhanced by the diffusing mobile point defects at an earlier time and to a larger extent than that in the lower QD layers. The different extents of

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interdiffusion of QDs in different QD layers located at different depth results in the double-peak-like broad PL spectrum, with PL signals of shorter wavelength (left peak) from the upper QDs and that of longer wavelength (right peak) from the lower QDs. This explanation is further supported by the similar PL peak position of the right peak of curve (iii) in **Figure 4-9 (b)** (marked by a black arrow) with the PL peak position of curve (ii) in **Figure 4-8 (a)**. This comparison indicates that the shift of the left peak results from the IFVD enhanced interdiffusion, while the shift of the right peak results from thermal interdiffusion only. When the defects diffused through the 20 stacks of QD layer after annealing at 800 °C for 30 s, QDs in different layers are interdiffused to similar extents and a single PL peak is obtained.

So far, IFVD process has achieved great success with QW structures for monolithic photonic integration applications, and is considered as one of the most promising post-growth band gap engineering techniques for QD-based photonic integration applications. For practical QD-based optoelectronic device applications, QD stacks, rather than a single QD layer, is required to achieve sufficient optical gain [45]. The results observed here demonstrate that if IFVD process is adopted for QDI of a QD stack structure for monolithic integration application, great care in the structure design, growth, and the selection of QDI process conditions should be taken to avoid this non-uniform intermixing and the resultant double-peak-like broad PL spectrum. However, for QD-based superluminescence application [46], this non-uniform intermixing can be intentionally exploited to achieve a PL spectrum with a large full width at half maximum.

4.2.4 Section summary

In this section, three band gap energies have been demonstrated in a single RTA process with an InGaAs/GaAs QDIP structure using an intermixing-suppressing technique in association with an intermixing-enhancing technique. The minimum band gap modification is produced on the ICP Ar plasma exposed sample and the maximum band gap modification is produced on the sample capped with SiO₂ dielectric films, while the unexposed bare sample produces band gap modification in between. After the IFVD process, the PL intensity is extremely low, due to the possible strain relaxation and dislocation formation around the QDs. The residue defects in the GaAs cap layer have significantly contributed to the low PL intensity. Double-peak-like broad PL spectra are observed and explained as a result of non-uniform intermixing of QDs in different QD layers located at different depths.

5. BAND GAP HALFTONING OF InAs/InP QD

In this chapter, the ICP Ar plasma-enhanced QDI has been performed on an InAs/InP QD structure for large differential band gap blueshift on top of negligible thermal shift with good material quality preservation. The optimum RTA conditions are firstly investigated, followed by the argon plasma exposure time dependent band gap blueshift. The surface defects accumulation with plasma exposure time is analyzed by x-ray photoelectron spectroscopy (XPS) measurements. To maximize the achievable band gap blueshift, the RF power and ICP power are optimized. Finally, selective QDI and band gap halftoning are implemented.

5.1 INTRODUCTION

InAs quantum dots (QDs) grown on InP substrates have attracted great interests as its emission wavelength at room temperature can be tuned to $\sim 1.55 \mu\text{m}$ [1],[2] for potential applications in optical fiber telecommunications. Due to recent technological advancement in the growth technique, defect-free InAs/InP QDs with high dot density and high dot uniformity have been obtained, showing strong PL intensity with narrow linewidth [3],[4]. InAs/InP QD-based practical optoelectronic devices, such as laser [5], semiconductor optical amplifier [6] and detector [7], have been fabricated and superior performances, such as low threshold current, low temperature sensitivity, wide bandwidth and high detectivity have been demonstrated.

For monolithic integration of InAs/InP QD-based optoelectronic devices on a single chip as photonic integrated circuits (PICs) to be realized, selective and controllable band gap modification also need be achieved in InAs/InP QD-based structures. Post-growth band gap engineering using thermally driven interdiffusion has shown its effectiveness to tailor the optical properties of InAs/InP QDs [8], while for PIC application, selective band gap modification is expected to be realized by defect-enhanced quantum dot intermixing (QDI). Several techniques for selective QDI, such as impurity free vacancy-induced disordering (IFVD) [9]-[11], ion implantation induced disordering [12]-[14], laser induced disordering [15],[16], and low temperature grown-in defect-induced disordering [17], have been effectively applied to In(Ga)As/GaAs QD structures. Comparatively, selective intermixing of InAs/InP QD structures is far more challenging. IFVD has been reported to tune the band-gap energy of an InAs/InP QD structure [18], whereas the relatively high annealing temperature required for activating intermixing leads to a large amount of unwanted thermal shift on unintended regions, owing to the poor thermal stability of InP-based materials [19], in addition to the large surface area to volume ratio of QDs [20]. The large thermal shift results in a reduced differential band-gap blueshift and thus reduced band-gap tuning range, which is unfavorable for monolithic integration applications. A practical method to reinforce the thermal stability of InAs/InP QDs is to reduce the As/P exchange. This can be achieved by inserting an ultra thin layer such as GaAs [21], GaP [22] or InGaAs [23] between the InAs dot and the InP buffer layer, or capping the InAs dot with InGaAs [24] or InGaAsP [25] instead of InP. Large differential band gap blueshift with small thermal shift has been demonstrated by adopting these measures [26].

The inductively coupled argon plasma-enhanced intermixing technique has achieved large differential band-gap blueshift with negligible thermal shift in an InGaAs/InP quantum well (QW) structure [27]. In this section, we investigate the band-gap modification of an InAs/InP QD structure using the inductively coupled argon plasma-enhanced intermixing. This technique utilizes mobile point defects generated at the near-surface region during plasma exposure to promote intermixing at relatively low annealing temperature and thus there is no appreciable thermal shift as encountered in other techniques. More than 100 nm enhanced blueshift on top of 10 nm thermal shift was achieved without degrading the crystal quality as evidenced by the preserved PL intensity. The accumulation of near-surface defects due to plasma exposure is studied using x-ray photoelectron spectroscopy (XPS). Selective band gap modification is realized using a SiO₂ layer as plasma exposure mask. Band-gap halftoning is demonstrated by controlling the amount of mobile point defects using wet chemical etching to partially remove the plasma exposed InP cap.

5.2 EXPERIMENTAL DETAILS

Figure 5-1 shows the layer structure for the InAs/InP QDs used in this study, which was grown by metalorganic chemical vapor deposition (MOCVD) on an InP (100) substrates [18]. After oxide desorption, a 100 nm thick InP buffer layer was grown at 610 °C. The temperature was then reduced to 480 °C and the 5 monolayer (ML) of InAs QDs were deposited. After 10 s of growth interruption, the QDs were capped with 10 nm of

5. Band gap halftoning of InAs/InP QD

InP layer at the same temperature. The temperature was then raised to 610 °C and a 1 μm thick InP layer was grown to complete the structure.

No.	Layer	Growth T (°C)	Thickness (Å)
4	InP cap	610	10000
3	InP cap	480	100
10 s growth interruption			
2	InAs dot	480	5 ML
1	InP buffer layer	610	1000
(100) oriented n-type sulfur-doped InP substrate			

Figure 5-1. The layer structure for the InAs/InP QD.

For InAs/InP QDs, multiple PL peaks are often observed, which can be ascribed either to emission from the ground state of QD ensembles with different dot size [28] or to emission from different states of a single QD ensemble [29]. This can be differentiated by excitation power dependent PL measurements. Figure 5-2 presents the excitation dependent PL spectra for the InAs/InP QDs measured at 77 K. The saturation of the emission from the ground state and the emergence of the emission from the excited state with the increase of the excitation power confirm that there is only one QD ensemble. The emission peak from the ground state of this structure is around 1310 nm, which is significantly shorter than the normal value. This is possibly caused by As/P exchange [30] due to the in-situ annealing effect during the long time growth of the 1 μm thick InP cap layer at 610 °C. However, the observation of the excited state proves that the InAs/InP QD still retain its three dimensional confinement after the in-situ annealing.

Figure 5-2. Excitation power dependent PL spectra of the InAs/InP QD structure measured at 77 K.

The argon plasma exposure was carried out using an ICP180 plasma source generator at varied RF power from 200~450 W and ICP power from 0~700 W, while the argon flow rate and the chamber pressure were fixed at 100 sccm and 60 mTorr, respectively. XPS analysis was done using a monochromatic Al $K\alpha$ x-ray as excitation source to study the accumulation of the near-surface defects during plasma exposure by analyzing the surface composition change after argon plasma exposure. Selective intermixing was studied using a 300 nm thick SiO₂ layer deposited on the sample surface by plasma-enhanced chemical vapor deposition (PECVD) to block the defects generation due to plasma exposure. For band-gap toning, the amount of defects in the InP cap are controlled after plasma exposure by wet chemical etching for different times using HCl : H₂O (1:2) solution. The annealing was performed under flowing N₂ ambient using InP proximity caps to prevent the out-diffusion of P atoms. Photoluminescence (PL) spectra

were measured at 77 K using a green crystal laser (532 nm, $\sim 25 \text{ W/cm}^2$) for excitation. The excitation power was selected at a very low level to assure that only the ground state emission was collected.

5.3 RESULTS AND DISCUSSIONS

5.3.1 RTA condition studies

Similar to defect-enhance selective QWI, a step of thermal annealing at a sufficient high temperature for sufficient duration is required for defect-enhanced selective QDI to drive introduced defects towards the QDs regions to induce enhanced intermixing as well as to recover the crystal quality of the intermixed structure after defects introduction. However, annealing at an improper high temperature might induce significant thermal intermixing on the controlled areas leading to reduced differential band gap modification, or even cause thermal damage to the structure, leading to diminished PL intensity. The selection of the annealing temperature and duration is therefore critical for achieving large differential band gap modification without degrading the crystal quality by defect-enhanced selective QDI, especially for the InAs/InP QD structures.

In this section, the optimal annealing condition for the InAs/InP QD structure will be investigated. Two batches of samples, one as-grown, the other subjected to argon plasma exposure for 2 min with 300 W RF power and 500 W ICP power, are loaded into the annealing chamber simultaneously. The annealing was performed at four different temperatures, i.e., 580 °C, 600 °C, 625 °C and 650 °C. At each annealing temperature,

samples were repetitively annealed for four cycles, 30 s for each cycle. After each annealing, PL measurements were conducted to determine the band gap blueshift and PL intensity variations.

Figure 5-3. Band gap blueshift vs RTA time under different RTA temperatures at (i) 580 °C, (ii) 600 °C, (iii) 625 °C, and (iv) 650 °C for the unexposed annealed only samples (open symbols) and exposed and annealed samples (filled symbols).

Figure 5-3 presents the band gap blueshift as a function of annealing times under different temperatures for the two batches of samples. It can be seen that at all annealing conditions, the argon plasma exposed samples produce a much larger band gap blueshift than the unexposed samples, owing to the enhanced intermixing by the near-surface defects generated during the plasma exposure. With the increase in the annealing temperature or duration, band gap blueshift induced on the two batches of samples increase but with different rates. The band gap blueshift for the unexposed annealed only samples increases faster than that of the plasma exposed samples. This means that when annealing at lower temperature or shorter duration, the plasma exposure induced defects

dominate the intermixing process, while at higher temperature or longer duration, the thermal defect-induced intermixing gradually catches up, resulting in reduced differential band gap blueshift. The optimal annealing condition is thus determined to be 600 °C for 30 s for the purpose of large differential band gap blueshift.

5.3.2 Plasma exposure time dependent QDI

Figure 5-4. (a) 77 K PL spectra taken from one as-grown sample, one annealed only sample and one sample exposed to argon plasma for 45 s and annealed. (b) Band gap blueshift versus argon plasma exposure time for samples exposed to plasma and annealed at 600 °C for 30 s.

It has been demonstrated that the plasma exposure time can be used to control the extent of band gap blueshift in an InGaAs/InP QW structure, where the band gap blueshift increases firstly with the exposure time and saturates for longer exposure time [31]. Since intermixing occurs at the interface of heterostructure and the surface area-to-volume ratio for QDs is much larger than that for QWs, QDs structure is expected to be

more sensitive to defect-enhanced intermixing than QWs [20], and the plasma exposure time dependence of band gap modification might be different. For this investigation, the InAs/InP QD samples were exposed to argon plasma for different times from 10 s to 120 s under 200 W RF power and 500 W ICP power and annealed at 600 °C for 30 s.

Figure 5-4 (a) shows the 77 K PL spectra taken from one as-grown sample, one unexposed and annealed only sample and one sample exposed to argon plasma for 45 s and annealed. Compared with the emission peak from the as-grown sample, the emission peak from the annealed only sample is blueshifted by 10 nm due to thermal intermixing. This small thermal shift is mainly attributed to the relatively low annealing temperature and short duration. To our knowledge, the annealing temperature adopted in this work is the lowest among those ever reported for defect-enhanced QDI process [9]-[18],[26]. In contrast, the emission peak from the sample exposed to argon plasma for 45 s and annealed is blueshifted by 102 nm, leading to a differential band gap blueshift of 92 nm. Figure 5-4 (b) presents the plot of band-gap blueshift versus plasma exposure time for samples exposed to argon plasma and annealed. The 10 nm thermal shift level obtained from an unexposed and annealed-only sample is also marked for reference. It can be seen that the band-gap blueshift increases with plasma exposure time at the initial stage due to accumulation of point defects in the near-surface region and slightly decays for long plasma exposure duration. This exposure time dependent band gap blueshift is also observed recently with InGaAs/InP QW structures and will be explained in the next section by analyzing the exposure time dependent defects accumulation at the near-surface region using XPS analysis.

5.3.3 Surface defects accumulation studies

During plasma exposure, the highly energetic argon ions can knock the constituent atoms at the near-surface region out of their crystal sites or even sputter them away from the sample surface, resulting in surface compositional change and the formation of residual defects, such as interstitials and vacancies. During the subsequent annealing, these defects diffuse and promote intermixing between the dots and their surrounding barriers, modifying the QD potential profile and thus the band gap energy. Therefore, the evolution of band gap blueshift with exposure time as plotted in **Figure 5-4 (b)** reflects the evolution of surface composition and defect accumulation during the plasma exposure. To gain more knowledge on this, XPS analysis was used to characterize the surface compositions for one as-grown sample and samples exposed to argon plasma for different durations, i.e., 1 min and 2 min, and without annealing.

Figure 5-5. XPS spectra measured from the InP cap layer for (i) as-grown sample, and samples exposed to Ar plasma for (ii) 1 min and (iii) 2 min without annealing. The counts from In 3d5 and P 2p core levels for the three samples are labeled as well.

Figure 5-5 shows the XPS spectra measured from the three samples where the numbers are the counts from the In 3d5 and P 2p core levels. To determine the surface composition change, the In 3d5 and P 2p core level counts of the plasma exposed samples are normalized to those of the as-grown sample. With this treatment, the surface composition of the InP layer varies from that of the as-grown sample and becomes $\text{In}_{0.51}\text{P}_{0.43}$ for the 1 min exposed sample and $\text{In}_{0.388}\text{P}_{0.375}$ for the 2 min exposed sample with P/In ratios of 0.84 and 0.97, respectively. It can be seen that P atoms are preferentially sputtered away; resulting in the formation of a P deficient surface and more P vacancies. This is expected due to the mass difference between the In and P atoms with the surface binding energies of secondary importance [32]. In addition, the P deficiency is mitigated after 2 min of plasma exposure as compared to that after 1 min, leading to a reduction in the amount of P vacancies at the near-surface region. The surface composition of an InP layer under ion bombardment is governed by an interplay of several competing processes, mainly preferential sputtering and radiation-enhanced diffusion and segregation [33], whereas it has not reached the equilibrium state within the plasma exposure times employed in the experiment (see Ref. 32 as a reference). The competing processes may be dominant at different stages before the steady state is reached. It is therefore possible that the surface P deficiency is mitigated once the radiation-enhanced diffusion becomes dominant after a long time of plasma exposure. The experimental evidence of P deficiency and the correlation between the reduction of P deficiency and the slight decay of band-gap shift shown in Figure 5-4 (b) for long plasma exposure collectively support that P vacancies are the dominant defects responsible for promoting the intermixing.

5.3.4 RF and ICP power optimization

Figure 5-6. (a) Band-gap blueshift and (b) DC bias versus RF power under different ICP power levels at (i) 0 W, (ii) 300 W, (iii) 500 W, and (iv) 700 W. The plasma exposure time was fixed at 30 s. RTA was performed at 600 °C for 30 s.

In an inductively coupled plasma (ICP) system, the RF power and ICP power collectively determine the ion energy and ion density in the plasma and thus the amount of mobile point defects generated at the near-surface region. To maximize the amount of mobile point defects and thus the achievable band-gap blueshift, the RF power and ICP power have been further optimized. Figure 5-6 (a) shows the band-gap blueshifts for samples exposed to argon plasma for a fixed duration of 30 s at varied RF powers and three ICP power levels followed by annealing at 600 °C for 30 s. Except for the data collected at 300 W ICP power, the band gap blueshift increases with RF power up to 300 W under all ICP power levels due to the increased DC bias and thus the amount of near-surface mobile point defects. Although the application of ICP power reduces the DC bias as shown in Figure 5-6 (b) and thus the argon ion energy, the increased ion density leads

to more defects generation and thus larger band gap blueshift up to 500 W ICP power. At high RF power (above 300 W) or high ICP power (above 500 W), however, the band gap blueshift decreases. This might be caused by the increased sputtering rate leading to effective etching of the InP cap layer and removal of the near-surface defects [34]. A maximum band-gap blueshift of 116 nm is achieved at 300 W RF power and 500 W ICP power after optimization. This translates into a differential band-gap blueshift of 106 nm by taking into account the 10 nm thermal shift obtained from sample unexposed and annealed only at 600 °C for 30 s.

The effectiveness of the inductively coupled argon plasma-enhanced intermixing technique for InAs/InP QD structures can be seen from the achieved large differential band-gap blueshift with small thermal shift, in contrast to the results reported in Ref. 18 where the IFVD technique was adopted and the differential band-gap blueshift was significantly reduced by the large thermal shift in a similar InAs/InP QD structure. We ascribe the large differential band gap blueshift mainly to the separation of the two processes for defect generation and defect diffusion for promoting intermixing. A large amount of mobile point defects, dominantly the P vacancies, have already existed after plasma exposure without a demand on annealing temperature such that intermixing can be promoted in annealing at a relatively low temperature. However, in the IFVD technique, defects have to be firstly generated in annealing requiring a higher temperature than is desirable, hence increasing the thermal intermixing process. As a result, significant thermal shift is induced on unintended sections. This issue is more critical for cases where the materials have less thermal stability, such as InAs/InP QDs.

5.3.5 Selective QDI and band gap halftoning

For monolithic PIC applications, it is important not only to selectively alter the band-gap on intended areas, but also to halftone the band-gap into several levels to satisfy band-gap energy demands of various types of devices, such as emitter, modulator and waveguide. In several approaches, the plasma-enhanced intermixing technique can control the amount of near-surface point defects laterally to obtain multi-levels of band-gap in QW structures [35],[36]. Here, multiple band gap energies are achieved via defect control by partially removing the plasma exposed InP cap layer using wet chemical etching. Therefore, the defect creation, defect amount control, and intermixing promotion by defects are implemented in three thoroughly independent processes, i.e., plasma exposure, wet chemical etching and annealing.

Figure 5-7. PL spectra measured at 77 K from (i) an as-grown sample, (ii) an sample exposed to argon plasma and annealed with a 300-nm-thick SiO₂ layer (SiO₂ layer was removed before PL measurement), and bare samples exposed to argon plasma, chemically wet-etched in HCl : H₂O (1:2) solution for (iii) 0 min, (iv) 3 min, (v) 5 min, and (vi) 7 min, and finally annealed.

A piece of the sample was firstly covered by a 300 nm SiO₂ layer prepared by plasma-enhanced chemical vapor deposition (PECVD), which is thick enough to block the plasma bombardment effect, and subsequently divided into several smaller samples. The SiO₂ layer was preserved on only one sample, whereas for the rest of the samples, the layer was removed with diluted HF solution. All samples, including the SiO₂ covered sample, were exposed to argon plasma for 30 s under 300 W RF power and 500 W ICP power. The exposed bare samples were then subjected to wet chemical etching for 0 min, 3 min, 5 min and 7 min individually, using HCl : H₂O (1:2) with an etch rate of ~10 nm/min to control the amount of defects in the InP cap layer. Finally all the samples were annealed at 600 °C for 30 s in one run. Before the PL measurements, the SiO₂ layer was removed.

Figure 5-7 presents the measured PL spectra. Compared with the as-grown sample, the emission peak from the SiO₂ covered sample has been blueshifted by 10 nm only, which is just the same as the thermal shift as marked in Figure 5-4 (a). This observation indicates that the 300 nm thick SiO₂ layer has completely blocked the surface defects generation during plasma exposure, and that the deposited SiO₂ layer has not induced additional shift as a result of IFVD [9]-[11] due to the low annealing temperature. Compared with the SiO₂ covered sample, the emission peaks from the exposed bare samples have been blueshifted far beyond the thermal shift. In addition, the emission peaks from the exposed and etched samples lie between the thermally-shifted and completely-shifted peaks, showing halftones of band gap due to effective control on the amount of point defects by wet chemical etching. The wet chemical etching itself brings

negligible amount of defects, as being verified from an unexposed sample subject to wet chemical etching for 5 min which showed only thermal shift. In addition, there is no crystal quality degradation caused by the process as evidenced by the preserved PL intensity.

5.4 CHAPTER SUMMARY

In summary, inductively coupled argon plasma-enhanced intermixing has been shown to modify the band-gap energy of InAs/InP QDs effectively. A maximum differential band-gap blueshift of 106 nm has been obtained after plasma exposure and annealing at 600 °C for 30 s with a thermal shift of 10 nm only. The small thermal shift is ascribed to the low annealing temperature while the large differential blueshift is attributed to the separation of the defect generation and defect diffusion processes. The QDI can be done selectively using a SiO₂ layer as the plasma exposure mask, whereas band-gap halftones can be obtained by controlling the amount of introduced mobile point defects, dominantly P vacancies, in the InP cap via wet chemical etching. The QD crystal quality is not degraded in the process as evidenced by the preserved PL intensity. Defect creation, defect amount control, and intermixing promotion by defects are implemented in three independent processes, which are practically advantageous for process control in device fabrication.

6. CONCLUSIONS AND RECOMMENDATIONS

In this chapter, the major findings in this study are summarized and the recommendations for future works are given.

6.1 CONCLUSIONS

The Ar plasma exposure-enhanced interdiffusion (intermixing) using inductively coupled plasma (ICP) system has been investigated for multiple band gap energy creation as well as fundamental interdiffusion studies on both InP- and GaAs-based quantum wells (QWs) and quantum dots (QDs). The ICP Ar plasma exposure process results in the generation of mobile point defects at the near-surface region of a QW or QD structure. During the subsequent rapid thermal annealing (RTA) process, these defects can diffuse towards the QWs or QDs region to enhance the extent of quantum well intermixing (QWI) or quantum dot intermixing (QDI).

Multiple band gap energies have been realized across a single InP substrate consisting of an InGaAs/InGaAsP five QWs laser structure through the control of local defect concentrations. With multistep plasma exposures using 200 nm SiO₂ as exposure mask, different levels of point defect concentrations are established in different areas, which lead to different extents of band gap modification in a single step RTA. The extent of band gap modification on each area is controllable through the plasma exposure time in each exposure step. The material quality is preserved as no intensity reduction and linewidth broadening in the photoluminescence (PL) are observed after the process.

Band gap redshift has been observed experimentally on an undoped InGaAsP/InP QW structure. It is found that the enhanced intermixing by the plasma exposure generated surface defects is dependent on the RTA temperature. Without plasma exposure, band gap blueshift is induced at all RTA temperatures, whereas after plasma exposure, a band gap redshift as large as 50 nm is induced at temperatures below 650 °C with the interdiffusion rate on the group III sublattice four times as fast as that on the group V sublattice based on the experimental data and theoretical calculations, and band gap blueshift is observed at 700 °C with recovery of PL intensity. This annealing temperature dependent interdiffusion is not affected too much by the cap layer composition. The influence of doping type in the cap layer on the ICP Ar plasma exposure-enhanced interdiffusion has been recognized.

Improved crystal quality has been achieved with a QD infrared photodetector structure consisting of 20 stacks of InGaAs/GaAs QD layer by ICP Ar plasma exposure. The PL peak intensity is enhanced by 1.7 times immediately after plasma exposure without change in the peak position due to the reduction in the amount of low temperature grown-in defects. This is experimentally confirmed by the improved thermal stability and increased carrier life times. After plasma exposure, the band gap blueshift is suppressed by ~26 nm in RTA, and the carrier lifetime is increased by 55%. The suppressed interdiffusion by ICP Ar plasma exposure has been used to produce large differential band gap modification in association with impurity free vacancy-induced disordering process, which enhances the extent of interdiffusion.

Large differential band gap blueshift on top of negligible thermal shift has been obtained with an InAs/InP QD structure. The small thermal shift of 10 nm is ascribed to the low RTA temperature and short duration, which are 600 °C and 30 s, respectively. The large differential band gap blueshift of ~106 nm is attributed to the separation of the plasma exposure step and the RTA step. The nature of the mobile point defects responsible for the enhanced interdiffusion is identified to be P vacancies by combining the x-ray photoelectron spectroscopy analysis and the band gap blueshift analysis. Band gap halftoning has been achieved by controlling the defects concentration through wet etching to partially remove the plasma-exposed InP cap.

6.2 RECOMMENDATIONS

Defect-enhanced intermixing technique has been extensively investigated with a major goal for monolithic integration of optoelectronic devices on a single chip as photonic integrated circuits. The ICP Ar plasma exposure-enhanced intermixing has demonstrated its effectiveness in multiple band gap energy creation across single substrates with good material quality preservation. However, an undesirable side effect concurrent in the ICP Ar plasma exposure process, the **sputtering effect**, can damage or remove the cap (contact) layer which is heavily doped for good ohmic contact for active device structures. To avoid this shortcoming, a **sacrificial layer** with sufficient thickness is required to be grown on top of the complete device structures for defects introduction during the ICP Ar plasma exposure process. Similar procedure has been widely adopted

in ion-implantation-induced QWI [1]-[3]. Consequently, two issues related to the sacrificial layer need to be resolved:

1. The *doping type* for the sacrificial layer. The ICP Ar plasma exposure-enhanced intermixing can result in both band gap blueshift [4] and redshift [5] in the InGaAs(P)/InP QW structure. A systematic study of the effect of the doping type in the cap layer on the resulting intermixing is important not only for practical PIC applications but also for a better understanding of the ICP Ar plasma exposure-enhanced intermixing process. For this purpose, cap layers with different doping type (p-type, i-type or n-type) grown on an identical QW structure can be used.
2. The *composition* for the sacrificial layer. As has been reported in ion-implantation-induced QWI [6], the amount of mobile point defects and thus the extent of band gap modification are dependent on the composition of the cap layer. A systematic study of the effect of the cap layer composition on the ICP Ar plasma exposure-enhanced intermixing is thus necessary to maximize the achievable band gap modification for PIC applications.

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APPENDICES

A. PROCEDURE OF THEORETICAL CALCULATION OF INTERDIFFUSED QWs

Figure A-1 presents the flow chart for the calculation of interdiffused QWs with $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ system. The details are explained in the following sections.

Figure A-1. Flow chart for the calculation of interdiffused QWs with $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ system.

A.1 Coordinate system for the calculation of interdiffusion

A lattice matched InGaAs/InGaAsP 5 QW structure with a semi-infinite InP substrate is used to demonstrate the procedure of theoretical calculation of interdiffused QWs for the $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ system. The QWs coordinate is shown in Figure A-2. z is the interdiffusion direction (the structure growth direction) and the QWs are centered at $z = 0$. L_{QB} and L_{QW} are the thickness for the barrier and well layer, respectively. x_{QB} (y_{QB}) and x_{QW} (y_{QW}) are the initial In (As) composition in the barrier and well layer, respectively. $x(z)$ ($y(z)$) is the In (As) composition profile along the z direction after interdiffusion.

Figure A-2. The coordinate system used for the calculation of interdiffused QWs with the $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ system.

A.2 Composition profile after interdiffusion

The interdiffusion of atoms across the QWs region is usually assumed to obey the Fick's law of diffusion in the direction of crystal growth [1]

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2}, \quad (\text{A.1})$$

where C denotes the fractional concentration of the atoms in the $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ system, i.e., either $x(z)$ or $y(z)$, t is the interdiffusion time, normally associated with the RTA time, D is the diffusion coefficient for either group III atoms (D^{III}) or group V atoms (D^{V}). By

solving the diffusion equation A.1, the In composition profile after interdiffusion can be derived in term of superposition of error functions [1] as follows:

$$x(z, L_d^{III}) = x_{QW} + \frac{\Delta x_{QW}}{2} \left[2 - \operatorname{erf}\left(\frac{z-c_1}{2L_d^{III}}\right) + \operatorname{erf}\left(\frac{z-c_2}{2L_d^{III}}\right) + \sum_{i=1}^{N-1} \left[\operatorname{erf}\left(\frac{z-a_i}{2L_d^{III}}\right) - \operatorname{erf}\left(\frac{z-b_i}{2L_d^{III}}\right) \right] \right], \quad (\text{A.2})$$

where $L_d^{III} = \sqrt{D^{III}t}$ is the diffusion length on the group III sublattice. $\Delta x_{QW} = x_{QB} - x_{QW}$,

N is the number of QW layers and

$$c_1 = -c_2 = -(L_{QW} \frac{N}{2} + L_{QB} \frac{N-1}{2}); a_i = c_1 + L_{QW} + (i-1)(L_{QW} + L_{QB}); b_i = a_i + L_{QB}. \quad (\text{A.3})$$

The As composition profile after interdiffusion, $y(z, L_d^V)$, can be formulated by

substituting $L_d^V = \sqrt{D^V t}$, y_{QW} and y_{QB} into equation A.2.

A.3 Potential profile after interdiffusion

By assuming certain values for the diffusion lengths on the group III sublattice (L_d^{III}) and group V sublattice (L_d^V), the In and As composition profiles across the QWs region after interdiffusion, $x(z)$ and $y(z)$, are determined using equation A.2. Consequently, the profiles for the effective mass, $m^*(x(z), y(z))$, bulk bandgap energy, $E_g(x(z), y(z))$, strain, $\varepsilon(x(z), y(z))$ and its effect on the band edge, are all determined and vary continuously along the z direction. The formula used for the calculation of these material parameters as a function of In and As composition profiles are summarized in Appendix B. When the interdiffusion rate on the group III and group V sublattices is identical, i.e., $k = L_d^V / L_d^{III} = 1$, a lattice matched QW structure remains lattice matched and the unstrained confinement potential profile $V_r(x, y)$ is expressed as [2]:

$$V_r(x, y) = Q_r [E_g(x, y) - E_{g0}], \quad (\text{A.4})$$

where the subscript r represents either the conduction band (CB) for electron (E) or the valence band (VB) for heavy hole (HH) and light hole (LH), respectively. E_{g0} is the unstrained bandgap energy at the well center after interdiffusion. Q_r is the bandgap offset, which is 0.6 used here for the CB [2].

When the interdiffusion rate is not identical on the group III and V sublattices, i.e., $k < 1$ or $k > 1$, strain will be developed with interdiffusion [3]. As the QW layer is within the critical thickness regime, the QW structure is assumed to be coherently strained after interdiffusion, with a biaxial hydrostatic strain parallel to the interfacial plane, and a uniaxial shear strain perpendicular to the interfacial plane. Since strain can modify the band edge of both CB and VB, it is necessary to incorporate the effect of strain on the potential profiles for CB and VB for an accurate calculation of the confined energy states and the transitional energy.

The in-plane strain across the QWs region, $\varepsilon(x, y)$, is defined to be negative for compressive strain and is given by [4]:

$$\varepsilon(x, y) = \frac{a_s - a_e(x, y)}{a_e(x, y)}, \quad (\text{A.5})$$

where a_s is the lattice constant of the substrate, $a_e(x, y)$ is the unstrained lattice constant of the epilayers. The change in the bulk bandgap due to the biaxial hydrostatic strain is given by [5]:

$$S_{biaxial}(x, y) = -2a(x, y) \left[1 - \frac{c_{12}(x, y)}{c_{11}(x, y)} \right] \varepsilon(x, y), \quad (\text{A.6})$$

where $c_{ij}(x, y)$ are the elastic stiffness constants, and $a(x, y)$ is the hydrostatic deformation potential calculated from [5]

$$a(x, y) = -\frac{1}{3} [c_{11}(x, y) + 2c_{12}(x, y)] \frac{dE_g}{dP}(x, y), \quad (\text{A.7})$$

where $\frac{dE_g}{dP}(x, y)$ is the hydrostatic pressure coefficient of the lowest direct energy gap E_g . The splitting energy between the heavy hole (HH) and light hole (LH) band edges induced by the uniaxial shear strain is given by [5]:

$$S_{uniaxial}(x, y) = -b(x, y) \left[1 + 2 \frac{c_{12}(x, y)}{c_{11}(x, y)} \right] \varepsilon(x, y), \quad (\text{A.8})$$

where $b(x, y)$ is the shear deformation potential. The coupling between the LH and the split-off band gives rise to asymmetric HH to LH splitting [6], so that

$$\begin{aligned} S_{uniaxial}^{HH}(x, y) &= S_{uniaxial}(x, y) \\ \text{and } S_{uniaxial}^{LH}(x, y) &= -\frac{1}{2} [S_{uniaxial}(x, y) + \Delta_0(x, y)] + \\ &\quad \frac{1}{2} \sqrt{9[S_{uniaxial}(x, y)]^2 + [\Delta_0(x, y)]^2 - 2S_{uniaxial}(x, y)\Delta_0(x, y)} \end{aligned} \quad (\text{A.9})$$

where $\Delta_0(x, y)$ is the spin-orbit splitting. By taking into account the strain effect, the modified potential profile is therefore given by [2]:

$$V_r(x, y) = Q_r [E_g(x, y) - E_{g0} - S_{biaxial}(x, y)] \pm S_{uniaxial}^r(x, y), \quad (\text{A.10})$$

where r represents either E, HH, or LH, respectively. The positive sign represents the confined HH profile, the negative sign represents the confined LH profile, and for the confined electron profile, $S_{uniaxial}^E(x, y)$ is zero.

A.4 Numerical calculation of interdiffused QWs

With the profiles for the effective mass and confinement potential, the bound states at Γ valley can be obtained by solving the Schrödinger equation

$$H\Psi_r = E\Psi_r, \quad (\text{A.11})$$

where Ψ_r is the envelope function for E, HH or LH. Quantum mechanism requires the probability current density of the carrier to be conserved, i.e., $(\partial\psi/\partial z)/m^*(z)$ and ψ are both continuous along the growth direction z . Since the effective mass is not isotropic in most heterostructures, it requires the modification of the Schrödinger equation to the Ben Daniel-Duke's equation [7]

$$-\frac{\hbar^2}{2} \frac{\partial}{\partial z} \left[\frac{1}{m_r^*(z)} \frac{\partial \psi_m(z)}{\partial z} \right] + V_r(z) \psi_m(z) = E_m \psi_m(z), \quad (\text{A.12})$$

where $m_r^*(z)$, $\psi_m(z)$, $V_r(z)$, E_m are the local carrier effective mass, wave functions, potential functions and the confined bound state energies. $n = 1, 2, \dots$ are the QW sub-band levels for E, HH and LH.

In order to solve the equation numerically, finite difference method is used to transform the differential equation A.12 into the following eigen value matrix equation:

$$[H][\Psi_r] = E[\Psi_r], \quad (\text{A.13})$$

where $[H]$ is a $n \times n$ Hamiltonian matrix (n is the number of mesh points used in the above transformation). The eigen values and eigen vectors of $[H]$ are the confined sub-band energies E_m and the associated wave functions ψ_m , respectively.

The electron-heavy hole transitional energy (E_{EmHHn}) and the electron-light hole transitional energy (E_{EmLHn}) for a given diffusion length can be calculated from the following formula:

$$\begin{aligned} E_{EmHHn}(eV) &= E_{g0} + E_{Em} + E_{HHn} ; \\ E_{EmLHn}(eV) &= E_{g0} + E_{Em} + E_{LHn} . \end{aligned} \quad (\text{A.14})$$

The transitional energy from the 1st electron subband to the 1st heavy hole subband, E_{EmHHn} , corresponds to the PL peak energy measured experimentally. With variation of the diffusion lengths on the group III and V sublattices, the relation of the transitional energy vs diffusion length is determined. This theoretical relation can be used for various interdiffusion studies.

B. FORMULAE FOR THE MATERIAL PARAMETERS OF $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ SYSTEM

The formulae listed in the following table are taken from [Ref 8](#).

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	Band gap energy	$1.5194(1-x)y+0.418xy+2.895(1-x)(1-y)+1.4236x(1-y)+x(x-1)(0.51y+0.7(1-y))+y(y-1)(0.3(1-x)+0.23x)$	eV
Δ_0	Spin-orbit splitting	$0.341(1-x)y+0.38xy+0.082(1-x)(1-y)+0.108x(1-y)$	eV
m_c^*	Electron effective mass	$0.0665(1-x)y+0.023xy+0.17(1-x)(1-y)+0.08x(1-y)$	m_0
$m_{HH\perp}^*$	Heavy hole effective mass perpendicular to QW layer	$0.34(1-x)y+0.3413xy+0.4464(1-x)(1-y)+0.472x(1-y)$	m_0
$m_{LH\perp}^*$	Light hole effective mass perpendicular to QW layer	$0.0951(1-x)y+0.027xy+0.162(1-x)(1-y)+0.0958x(1-y)$	m_0
a_0	Lattice constant	$5.6525(1-x)y+6.0584xy+5.4512(1-x)(1-y)+5.8688x(1-y)$	$\text{\AA}$
C_{11}	Elastic stiffness constant	$12.23(1-x)y+8.33xy+14.39(1-x)(1-y)+10.22x(1-y)$	10^{11} dyn/cm ²
C_{12}	Elastic stiffness constant	$5.71(1-x)y+4.53xy+6.52(1-x)(1-y)+5.76x(1-y)$	10^{11} dyn/cm ²
dEg/dp	Hydrostatic pressure coefficient	$11.3(1-x)y+10.2xy+10.7(1-x)(1-y)+8.4x(1-y)$	10^{-6} eV/bar
b	Shear deformation potential	$(-1.7)(1-x)y+(-1.8)xy+(-1.8)(1-x)(1-y)+(-2.0)x(1-y)$	eV

$$1 \text{ eV} = 1.6021892 \times 10^{-19} \text{ J}$$

$$1 m_0 = 9.109534 \times 10^{-31} \text{ kg}$$

$$1 \text{ \AA} = 10^{-10} \text{ m}$$

$$1 \text{ dyn/cm}^2 = 10^{-6} \text{ bar}$$