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Metalorganic Vapor Phase Epitaxy Growth
of $\text{Al}_x\text{In}_{1-x}\text{P}$ Alloys and its CuPt
Type Atomic Ordering

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SUMMARY

The phenomenon of atomic scale ordering in III-V semiconductor alloys, which modifies their electronic and optical properties, is observed to occur spontaneously during epitaxial growth of semiconductor and attracts much interest. $\text{Al}_x\text{In}_{1-x}\text{P}$ alloy provides wide bandgap energy in the non-nitride III-V semiconductors and has been wide applied in electronic and photonic devices.

In this thesis, high quality AlInP epilayers have been successfully grown by metalorganic vapor phase epitaxy (MOVPE) using tertiarybutylphosphine (TBP) as phosphorus precursor in pure nitrogen (N_2) ambient. Effects of MOVPE growth conditions, such as growth temperature and V/III ratio, on the aluminum (Al) incorporation into AlInP alloys have been investigated. The experimental data agreed well with the simulation result using adsorption-trapping model. These results enable us to accurately control the Al solid composition during MOVPE growths.

The CuPt-B type atomic ordering in the AlInP epilayer grown by MOVPE was studied and characterized by using transmission electron diffraction (TED), photoluminescence (PL), X-ray diffraction (XRD), and polarized Raman. The MOVPE growth conditions, including growth temperature, V/III ratio, growth rate, reactor pressure, and carrier gas, were found to strongly affect the degree of order. The results provide a feasible way of controlling the degree of order by using MOVPE growth. Post-growth techniques, rapid thermal anneal (RTA) and inductively coupled plasma (ICP), were found to reduce the degree of order for AlInP layers, indicating these techniques can also be used to tailor the degree of order for AlInP.

Uni-compositional AlInP quantum wells (QWs), which profits from the bandgap reduction induced by the CuPt-B ordering in AlInP layers, were produced and

demonstrated by using PL, XRD and transmission electron microscopy (TEM). These results highlight the readiness of the atomic ordering application in bandgap engineering and optoelectronic devices.

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1 Introduction

1.1 III-V Semiconductor and MOVPE

Semiconductor research at the present time is mostly focused on the study of silicon (Si) and III-V compound semiconductors. It is clear that silicon technology has dominated the overall microelectronics market. Nevertheless, III-V compound semiconductors, used primarily in high speed and optoelectronic components, open up new dimensions in electronic and photonic technology and have a much larger impact than indicated by their current relatively small market share. For example, GaAs-based Metal Semiconductor Field Effect Transistors (MESFETs) are the basis of many wireless communication systems; InP/InGaAsP long wavelength lasers are used as light sources in fiber-optic communications, for sending cell phone signals and data; GaAs/AlGaAs High Electron Mobility Transistors (HEMTs) are used for low noise amplifiers in a host of applications, including direct broadcast satellite TV antenna receivers; and GaAs, InP based light emitting diodes cover a spectrum from the visible to the infrared range.

III-V compound semiconductors are attractive because they exhibit physical properties that are in some ways superior to group IV elementary semiconductors such as Si and germanium (Ge). First of all, unlike the indirect bandgap materials Si and Ge, most III-V semiconductors have direct energy bandgap so that the electrons and holes can recombine directly to create photons without involving phonons. This makes them favorable in the fabrication of highly efficient optoelectronic devices,

such as light emitting diodes (LEDs) and laser diodes. In addition, many III-V semiconductors have high electron mobility due to their small electron effective mass; therefore, they can be used to produce high-speed electronic devices. Table 1-1 shows a comparison of the physical properties between III-V semiconductors and Si. It can be seen that the electron mobilities of III-V materials are much higher than that of Si, which makes the III-V semiconductors suitable for high speed electronic devices.

Table 1-1: A comparison between the material properties of III-V semiconductors and Si.

	Si	GaAs	In _{0.53} Ga _{0.47} As	InAs	InSb
Electron mobility (cm ² V ⁻¹ s ⁻¹)@ns=1x10 ¹² /cm ²	600	4,600	7,800	20,000	30,000
Electron saturation Velocity (10 ⁷ cm/s)	1.0	1.2	0.8	3.5	5.0
Ballistic mean free path (nm)	28	80	106	194	226
Energy bandgap (eV)	1.12*	1.42	0.72	0.36	0.18

* indirect bandgap

Another attractive feature of III-V semiconductors is that the individual III-V binary alloys may be extended by combining two or more compounds to form ternary or quaternary alloys. These multinary alloys allow tailoring the physical properties, such as bandgap energy and lattice constant of the materials for specific applications. Figure 1-1 shows a plot of bandgap energy versus lattice constant of various III-V compound semiconductor materials. For binary compounds at a given temperature, the bandgap energy and lattice constant are both fixed. However, for a ternary or quaternary alloy, either the bandgap energy or the lattice constant can be varied within

a limited range by varying the solid composition resulting from the advanced epitaxial technology. Especially for quaternary alloys, the energy bandgap and lattice constant can be varied independently. Therefore, we can grow quaternary alloys with a specific desired energy bandgap having, at the same time, a lattice constant which is matched to that of the substrate to avoid the imperfections or defects due to lattice mismatch.

Figure 1-1: Bandgap energy vs lattice constant of III-V semiconductor at room temperature.

The interface that occurs between two layers or regions which have unequal bandgap energy forms a heterojunction. Many heterostructures composed by III-V materials have been widely applied in optoelectronic and electronic devices. For example, AlGaP/GaAs, InGaAs/InP, GaInP/GaAs, and InGaAsP/InP have been used for light emitting diodes (LEDs), laser diodes, solar cells, heterojunction bipolar transistors (HBTs), HEMTs, and photodetectors. High-brightness blue and blue-green InGaN/AlGaN LEDs have also become commercially available.

During the fabrication of optoelectronic and electronic devices employing III-V semiconductors, the critical layer (such as the active layer of a semiconductor laser diode) thickness, solid composition and abrupt interface of heterostructures must be controlled very accurately in order to get the expected results and reproduction. Under this circumstance, the epitaxial growth technique for III-V semiconductors is turned into the bridge which connects the theoretical design goal with the real device performance. Metalorganic vapor phase deposition (MOVPE) is the epitaxial growth technique mainly used in both research and industry of the epitaxy of materials, especially III-V compound semiconductors. MOVPE is capable of producing an almost atomically abrupt interface. The purity of InP grown by MOVPE is higher than that grown by other techniques, and the purity of GaAs grown by MOVPE is comparable with by other techniques, such as molecular beam epitaxy (MBE). For example, the Hall mobility reaches to $1.50 \times 10^5 \text{ cm}^2/\text{Vs}$,¹ and the impurity concentrations is below $\text{mid-}10^{14} \text{ cm}^{-3}$ for InP epilayer grown by MOVPE.² The most important advantage of MOVPE over other epitaxial techniques including molecular beam epitaxy (MBE), liquid phase epitaxy (LPE), and chloride vapor phase epitaxy (VPE) is the economical and mature epitaxial growth technique for industrial production, suitability for large-scale production, and the ability to grow a wide range of III-V materials with good quality, abrupt interfaces, and good uniformity. Although there still are safety and toxicity concerns during MOVPE growth, these problems have been alleviated with less toxic and commercial metalorganic sources used.^{3,4} By far, MOVPE has become the most versatile epitaxial technique for III-V semiconductor materials and devices, such as LEDs, LDs, photodetectors, and high speed transistors.

1.2 AlInP for Semiconductor Devices

AlInP is a ternary compound semiconductor material, which has many attractive properties for optoelectronic and high speed electronic devices. $\text{Al}_x\text{In}_{1-x}\text{P}$ has a direct energy gap for $x < 0.44$, and at the crossover composition the Γ -valley value of $E_g^\Gamma \approx 2.4\text{eV}$ is the largest of any non-nitride direct-bandgap III-V semiconductor. This makes AlInP to be of interest for laser diodes and light-emitting diodes emitting in the green and blue range. The large bandgap energy of AlInP also makes it suitable as a barrier layer material in semiconductor laser diode structures. In AlGaInP laser diodes emitting in the 630 nm band, AlInP is used as a barrier layer to reduce carrier leakage which leads to less temperature sensitivity and improves device performance.⁵ AlInP is also used as a window layer in InGaP/GaAs based tandem solar cells which demonstrate efficiency improvement up to 30%.⁶

Additionally, the large bandgap energy of AlInP offers a large conduction or/and valence band offset with a low bandgap material, indicating potential applications in electronic and photonic devices. For example, quantum cascade lasers (QCLs) are semiconductor lasers for which laser emission is achieved through the use of intersubband transitions. The wavelength of QCL can be extended to mid-infrared range, ranging from ~ 3.5 to $13\ \mu\text{m}$, which attracts a lot of attention for trace-gas sensing applications. Namjou *et al.*⁷ used pulsed QC-DFB lasers at near-RT conditions to measure mid-IR ($\lambda \sim 7.8\ \mu\text{m}$) absorption spectra of N_2O and CH_4 diluted in N_2 using a measurement technique known as wavelength-modulation spectroscopy. The noise equivalent sensitivity limit of the measurement was 50 ppm. Webster *et al.*⁸ reported the first atmospheric measurements using QC-DFB lasers. The devices were flown on NASA's ER-2 high-altitude aircraft to monitor stratospheric methane and

nitrous oxide over North America, Scandinavia and Russia. The sensitivity limit for methane was ~ 2 ppb. The large conduction band offset, ΔE_c , may extend the emitting wavelength of a quantum cascade laser to the near-infrared range which is quite important for the military, medical applications and is still under study due to small ΔE_c of the current, mature, material system. The conduction band offset of $\text{Al}_{0.44}\text{In}_{0.56}\text{P}/\text{In}_{0.52}\text{Ga}_{0.48}\text{As}$ can be extended to 1.0 eV. Moreover, GaInP/GaAs structures for Npn heterojunction transistors (HBTs) have received much attention recently over AlGaAs/GaAs structures, due to the large valence band offset, ΔE_v , of GaInP with respect to GaAs. Similarly, the AlInP/GaAs system is an interesting alternative. AlInP lattice matched to GaAs is expected to have an even greater ΔE_v than its GaInP counterpart. With a greater ΔE_v in the emitter junction, less base current due to back-injection of holes from the base into the emitter is likely to occur. Therefore, the AlInP/GaAs system appears very promising for Npn HBT applications.

1.3 CuPt Atomic Ordering in III-V Semiconductors

It had long been believed that at a certain range of temperatures the bandgap energy (E_g) of a III-V ternary compound alloy, such as for $\text{A}_x\text{B}_{1-x}\text{C}$ or $\text{AB}_x\text{C}_{1-x}$, is solely determined by the solid composition (x) of the alloy. During research work on the MOVPE growth of III-V semiconductor materials, an interesting experiment result of abnormal bandgap deduction of GaInP grown by MOVPE was reported.⁹ Later, it has been revealed that this bandgap reduction resulted from the change of the crystal lattice structure of the alloy—an atomic-scale phenomenon called CuPt-type spontaneous atomic ordering. For example, in a

GaInP alloy which shows such bandgap reduction, gallium (Ga) and indium (In) atoms are distributed periodically on face-centered-cubic (f.c.c.) sublattices and form a monolayer superlattice of Ga-and In- planes in the $[-111]$ or $[1-11]$ direction. A schematic of normal and CuPt-type atomic ordering structure models of III-V alloy $A_xB_{1-x}C$ is shown in Figure1-2. It can be seen that the A-atom plane and B-atom plane are distributed alternately in $[-111]$ direction in the CuPt-type atomic ordering alloy $A_xB_{1-x}C$. In the real epitaxy III-V alloy studied so far, the atomic ordering is partial, which means there is no purely A-atom plane or B-atom plane but A-atom-rich or B-atom-rich planes.

Figure1-2: Structure models of random alloy (a) and CuPt-type atomic ordering (b) in III-V alloy $A_xB_{1-x}C$. Light purple balls indicate group V atoms. Orange and gray balls indicate group III1(A) and group III2(B) atoms. (b) illustrates the CuPt-B atomic ordering in which A and B atoms distribute alternately in $[-111]$ direction.

Atomic ordering is a naturally occurring phenomenon during epitaxial growth and has been widely observed in III-V semiconductor alloys.

Table 1-2 lists some examples of III-V semiconductor materials which show the CuPt atomic ordering. It can be found that the atomic ordering exists in both mix-cation and mix-anion ternary or/and quaternary III-V semiconductors. A common feature among the above-listed growth methods is that they are all vapor-phase epitaxy (VPE); MBE can be regarded as a kind of extremely low-pressure VPE.

Table 1-2: Summary of CuPt atomic ordering in III-V semiconductor alloys.

MATERIAL	GROWTH TECHNIQUE	SUBSTRATE ORIENTATION	ORDERING TYPE	REFERENCE
GaInP	MOVPE	(001)	CuPt	10
GaInP	MBE	(001)	CuPt	11
AlInAs	MOVPE	(001)	CuPt	12
AlInAs	MBE	(001)	CuPt	13
GaInAs	MOVPE	(001) 6°C to (111)	CuPt	14
GaInNP	MOVPE	(001)	CuPt	15
AlInP	MOVPE	(001)	CuPt	16
GaAsP	MOVPE	(001)	CuPt	17
GaAsSb	MBE	(001), (111)A	CuPt	18
InAsP	MOVPE	(001)	CuPt	19
InSbP	MOVPE	(001)	CuPt	20
InAsSb	MBE	(001)	CuPt	21
AlGaInP	MOVPE	(001)	CuPt	22

Theoretical calculations,^{23,24} which ignore the effect of the free surface present during growth, show that the CuPt atomic ordering in a III-V semiconductor alloy is thermodynamically unstable in both bulk crystals and epitaxial III-V alloys.²⁵ One more phenomenon of atomic ordering in III-V alloys which cannot be explained solely by bulk crystal theory is the observation of two kinds of asymmetry in the

variant appearances.^{26,27} Combined with the findings mentioned above that the growth techniques of all the reported III-V semiconductor alloys in which ordering exist are vapor phase, such as MOVPE and MBE, all of the research results lead us to relate the CuPt atomic ordering in III-V alloys to the surface process during epitaxial growth. Moreover, CuPt ordering is calculated to be thermodynamically stable at and near the growth surface.^{28,29} The CuPt atomic ordering in III-V semiconductor alloys occurs at the surface during the vapor phase epitaxy growth and relates to the surface reconstruction induced subsurface stress.^{30,31}

Due to the extra periodicity in group III atoms sub-plane along the [1-11] direction, the unit cell is doubled, the Brillouin zone is reduced by half, and the point-group symmetry reduces from T_d to C_{3v} in CuPt-type ordered III-V alloys. These differences result in a series of changes in material physical properties,³² such as bandgap reduction, valence band splitting, optical anisotropy, changes in electron effective mass, and phonon property. Ordering may change the phonon property in the following ways: (1) doubling the number of phonon branches due to the doubling of the number of atoms in a unit cell; (2) introduction of anisotropy depending on the phonon wave vector with respect to the ordering axis; and (3) changing of the phonon frequencies because of different local arrangement of atoms.

Symmetry reduction in CuPt ordered III-V alloys also changes the selection rule for the optical transition of the materials. The symmetry effect has been demonstrated in polarized PL measurement,^{33,34,35} photoluminescence excitation (PLE) measurement,^{36,37} reflectance difference,³⁸ electroreflectance,³⁹ electroabsorption,⁴⁰ photocurrent,⁴¹ second harmonic generation,⁴² and birefringence.^{43,44,45}

1.4 Motivation

Since the first report on the spontaneous atomic ordering in III-V compound semiconductor materials, this topic has attracted much interest.

Both the theoretical simulation and experimental results have demonstrated the changes in the electronic and optical physical properties of the CuPt atomic ordered III-V semiconductor alloys. Valence band splitting, band gap reduction, optical birefringence, effective mass anisotropy, and electron spin polarization are examples of such atomic ordering induced modifications in the past investigations. As we know, the above mentioned physical properties of semiconductor alloys play key roles in the electronic and optoelectronic devices. For example, the laser diode emission wavelength is mainly determined by the active semiconductor alloy's bandgap energy and active region structure. If the atomic ordering is ignored in the ordered active alloy, there would be a shift between the theoretical calculation result and the emission peak position of the actual laser diode. Therefore, it is critical to understand and control the atomic ordering in semiconductor alloys during design and fabrication of devices.

Because of the unique physical property modifications induced by CuPt ordering and their potential application in electronic and photonic devices, it is important and necessary to investigate how to control, or tailor the atomic ordering degree in III-V semiconductors. By far, most of the research work on the atomic ordering in III-V semiconductors focuses on one particular alloy – GaInP grown on GaAs substrate. A universal application rule or conclusion about the growth effect on atomic ordering in III-V semiconductors is still absent (if it does exist). It is essential to put effort into the studying how growth parameters (such as growth temperature, growth rate) influence

the degree of order for III-V alloys, such as AlInP which is another ternary end material of $\text{Al}_x\text{Ga}_{1-x}\text{In}_y\text{P}_{1-y}$. On the other hand, we may expect to obtain valuable information on the detailed microscopic process of MOVPE growth from the study of atomic ordering since it relates to surface process at monolayer scale. For example in the GaInP epilayer grown by MOVPE, the reported occurrence of CuPt-B ordering is far more than the CuPt-A type. However, the eight [111] directions are equivalent in zincblende semiconductor materials and the probability of CuPt-A and CuPt-B type atomic ordering should be theoretically the same. The CuPt-B preference which affects the step growth rate in [110] and [1-10] directions is different. This difference is unlikely to be detected directly by the current monitoring equipment in MOVPE system and may lead us to new findings.

Additionally, since the ultimate target of novel III-V semiconductor materials is applications in devices which involve different kinds of fabrication process in addition to the epitaxial growth, it is meaningful to study the influence of post growth techniques on the atomic ordering in III-V semiconductor alloys. Rapid thermal annealing (RTA) and inductively coupled plasma (ICP) are two widely used post-growth techniques for material quality improvement and etching process, respectively. Within a whole process flow of semiconductor device fabrication, it may undergo RTA and ICP several times. So, it is necessary to study if these processes have an influence on the atomic ordering of III-V alloys.

Lastly, the atomic ordering also has potential applications in novel optoelectronic devices. Low dimensional structures such as quantum well rather than bulk III-V alloys occupy chief position in semiconductor devices. In order to apply atomic ordering in real devices, it is important to explore the heterostructure and low

dimensional structure by taking advantage of atomic ordering phenomenon in III-V semiconductor alloys.

1.5 Objectives

The objectives of this research focus on:

1. Developing MOVPE growth of the high quality AlInP alloy and studying the aluminum (Al) incorporation in the AlInP epilayer during the MOVPE growth. The effects of growth temperature and the gas phase ratio of TMAI on the Al incorporation are investigated. A theoretical model is created to simulate the process of the Al incorporation into AlInP process during the MOVPE growth.
2. Investigating the MOVPE growth effect on the atomic ordering degree in the grown AlInP epilayers. The growth conditions, such as the growth temperature, V/III ratio, growth rate, carrier gas, pressure, and substrate orientation, etc have been studied. The bandgap energy reductions induced by the atomic ordering of the AlInP samples are experimentally examined.
3. Studying the effect of post growth treatments, such as RTA and ICP, on the degree of order of the AlInP epilayer grown by MOVPE. Polarized Raman scattering spectroscopy and temperature dependent PL spectroscopy have been used to characterize the degree of atomic order of the AlInP samples.
4. Last but not least, investigating the AlInP uni-composition quantum well structures using the atomic ordering.

1.6 Organization of the Thesis

The thesis is organized as follows: some background information on the MOVPE growth, post growth techniques, and characterization techniques used in this study are discussed in Chapter 2. This chapter briefly describes MOVPE growth, and two kinds of post growth treatments: RTA and ICP. The characterization techniques such as XRD, PL, atomic force morphology (AFM), TED and Raman scattering are also described.

Chapter 3 deals with the MOVPE growth of AlInP and focuses on the result and analysis of aluminum incorporation into the AlInP epilayer.

A detailed study of effects of both MOVPE growth conditions and post growth treatments on the atomic ordering in AlInP is presented in Chapter 4. The examined MOVPE growth conditions contain growth temperature, growth rate, V/III ratio, carrier gas, pressure, and substrate orientation. The result of RTA and ICP effects on atomic ordering in AlInP is also presented in this chapter.

Design, growth, and characterization of the AlInP uni-composition quantum well are shown in Chapter 5. This chapter also includes RTA effect on the PL spectra of quantum well structures.

Chapter 6 gives the conclusions and further work. It includes the physical property change induced by atomic ordering and how to the tailor atomic ordering degree in AlInP grown by MOVPE. The potential applications of atomic ordering of AlInP in optoelectronic devices are also discussed.

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2 Experimental Procedures

In this chapter the background to the MOVPE technology, including the fundamental principles of MOVPE, the design and structure of the MOVPE system used in this research are introduced. Some post-growth techniques and characterization tools used to assess the epitaxial samples for this study are also introduced.

2.1 Metalorganic Vapor Phase Epitaxy (MOVPE)

2.1.1 Principles of MOVPE Process

Metalorganic Vapor Phase Epitaxy (MOVPE) is a chemical vapor phase deposition method for epitaxial growth of materials from the surface reaction of organic compounds or metalorganics and metal hydrides containing the required chemical elements. Since the late 1960s when Manasevit and coworkers started the pioneering research work,¹ efforts for MOVPE research, development and production have grown tremendously. The early doubts concerning the purity of the materials grown by MOVPE have been eliminated by the report of high-purity GaAs with extremely high mobility exceeding about $1 \times 10^5 \text{ cm}^2/\text{V}\cdot\text{s}$ at low temperature¹ and the demonstration of the first continuous-wave (CW) quantum-well (QW) injection laser operating at 300 K.² MOVPE can produce well-defined interfaces and has greater flexibility. Also, the design of the MOVPE system lends itself well to large-scale production. In general, high growth rates and very uniform grown films can be achieved by MOVPE with high repeatability. By far, MOVPE has been demonstrated

to be one of the favored epitaxial growth techniques for both commercial production and research work.

The general reaction in an MOVPE process of growing a III-V semiconductor alloy is given simply by:³

where M is the group III element (such as Indium, Aluminum, Gallium), E is the group V element (such as Arsenide, Phosphorus), R is Alkyl radical (such as CH_3 or C_2H_5), and H is hydrogen. In Equation (2-1), R_3M and EH_3 represent metalorganic (MO) group III and hydride group V sources, respectively. This equation only describes the overall growth process and does not take into account many intermediate reaction steps that occur in MOVPE growth process. The nature of these intermediate reactions depends on the precursors used in the growth, the growth conditions and the individual MOVPE system configurations used. Because of this, it is very difficult to identify all the steps involved in a particular MOVPE growth process, and attempts to model MOVPE systems have met with varying degrees of success.

Figure 2-1 depicts the basic processes included in a MOVPE growth. There are several steps involved in the growth process: (1) mass transport of the reactants to the surface; (2) absorption and reaction of the precursors on the surface; (3) incorporation of these reaction products into the growing film; and (4) desorption of by-products. The above description of reaction process is simplified. For example, homogeneous reactions may occur during the process of mass transport. The surface reactions and the nucleation for forming the thin film during a MOVPE growth are much more complicated. Substrate temperature (growth temperature), reactor pressure, V/III ratio

and substrate orientation, etc, affect the material growth rates and the grown film's element incorporation.

Figure 2-1: Basic processes associated with MOVPE growth. (1) mass transport of reactants to the surface; (2) adsorption and reaction of precursors on the surface; (3) incorporation of reaction products into the growing film; and (4) desorption of by-products. The slowest of these processes will determine the rate limiting step of the reaction.

Deposition of a solid thin film from the vapor phase involves many fundamental processes. In developing an overall growth model for MOVPE, the fundamental processes occurring during the crystal growth are commonly subdivided into two components: thermodynamics and kinetics.³ Thermodynamics determines the driving force for the overall growth processes, controls the maximum growth rate, solid composition of alloys, and microscopic rearrangement on the surface, such as surface reconstruction. Kinetics, which mainly includes physical surface processes, mass and heat transport, and chemical reactions, etc., defines the rates at which the various processes occur.

2.1.2 Thermodynamics in MOVPE Growth

Thermodynamics plays a very important role in the MOVPE growth since MOVPE is simply a highly controlled phase transition from vapor to solid. Thermodynamics determines completely the driving force and, hence, the maximum growth rate for all growth processes. Furthermore, a thermodynamic understanding of epitaxy allows the determination of alloy composition as well as the solid stoichiometry.

The thermodynamics of the mixing of III-V semiconductor alloys determines many characteristics of the epitaxial growth process as well as the properties of the resultant materials. For example, thermodynamic factors may limit the mutual solubility of the two (or more) components of an alloy. III-V semiconductor alloys are normally expected in a random or totally disordered state. However, when the sizes of the constituent atoms are sufficiently different, microscopic structures or spontaneous atomic ordering exists. Atomic ordering, which has natural superlattices, with a monolayer periodicity along a particular crystallographic direction in the lattice, is produced in III-V alloys during epitaxial growths. Interest in the formation of these ordered structures is more than academic, since the band-gap energy, phonon properties, effective mass, and free carrier mobilities may be significantly different between the disordered and ordered semiconductor alloys. Thus, specification of the composition of a semiconductor alloy does not completely determine the properties. The microscopic arrangement of the atoms, which relates to the thermodynamics during the epitaxial growth, must also be considered.

In addition to the traditional treatment of the thermodynamics of the bulk semiconductors, it has become clear in recent years that the thermodynamics of the

surface must also be considered in any effort to understand the growth processes as well as the characteristics of the epitaxially grown materials. Thus, this section will also cover the thermodynamics of the surface, including the bond rearrangement driven by the reduction in surface energy that leads to the various surface reconstructions.

In an MOVPE growth, there are the vapor and solid phases within the system. The basic goal of thermodynamics, applied to MOVPE, is to define the relationship between the composition of the various phases in an equilibrium system at constant temperature and pressure. Equilibrium of a system at constant temperature and pressure is defined as the state where the Gibbs free energy per mole is a minimum. The free energy change for any given reaction is given by:³

$$\Delta G = \Delta H - T\Delta S \quad (2-2)$$

Where $G=H-TS$ is the Gibbs free energy per mole, $H=E+PV$ is enthalpy, S is entropy, T is temperature, E is the internal energy, V is the volume, and P is the pressure of the system.

For a two phase, α and β , system, the total free energy is $G' = G'_\alpha + G'_\beta$, where the prime denotes the total free energy as opposed to the free energy per mole. The chemical potential, μ_i , is defined as the partial derivative of G' with respect to n_i , mole of component i . For a reversible perturbation of the system, μ_i is shown as:³

$$dG' = V' dP - S' dT \quad (2-3)$$

For an ideal gas ($PV' = nRT$) at constant temperature T , Equation (2-3) is written as:

$$dG' = nRT d(\ln P) \quad (2-4)$$

For a single ideal gas

$$\mu = RT \ln P = \mu^0 + RT \ln(P/P^0) \quad (2-5)$$

where μ^0 and P^0 are the chemical potential and pressure of an arbitrary standard state.

For an ideal gas mixture,

$$\mu_i = \mu_i^0 + RT \ln(p_i/p_i^0) \quad (2-6)$$

where p_i is the partial pressure. For an ideal liquid or solid solution, the same expression holds with p_i/p_i^0 replaced by x_i/x_i^0 , where x_i is mole fraction. Equation (2-6) is still successful for a nonideal solution with x_i replaced by the activity a_i :

$$\mu_i = \mu_i^0 + RT \ln a_i \quad (2-7)$$

Then for each component in the system, the equilibrium condition, $\mu_i^\alpha = \mu_i^\beta$, may be expressed as:

$$\mu_A^0 + RT \ln a_A^e = \mu_B^0 + RT \ln a_B^e \quad (2-8)$$

where a^e is the activity at equilibrium.

When the system is not at equilibrium, the thermodynamic driving force to restore equilibrium is:

$$\Delta\mu = \mu_B - \mu_A = \mu_B^0 + RT \ln a_B^e - \mu_A^0 - RT \ln a_A^e \quad (2-9)$$

Figure 2-2 shows the estimated thermodynamic driving force for several epitaxial growth processes.⁴ All estimations are for the growth of GaAs. It can be seen that the input vapor has much higher chemical potential than the solid produced for MOVPE. In this case, the powerful thermodynamic factors still control much of the MOVPE growth processes because even for a system with a high supersaturation of the input vapor phase, near-equilibrium conditions may prevail near the vapor-solid interface. However, it is necessary to consider the thermodynamic properties of the surface phases in addition to the vapor and bulk solid phases.

Figure2-2: Estimated thermodynamic driving force, Gibbs free energy difference between reactants and products, for several epitaxial growth processes.⁴

The importance of bulk thermodynamics for semiconductors grown epitaxially has been known for decades. In recent years, it has become apparent that the thermodynamics of the surface often plays the dominant role in many aspects of the MOVPE growth process. After all, the growth occurs entirely at the surface, and diffusion in the solid is slow. Thus, the vapor and solid at the surface are nearly in equilibrium for MOVPE growth of semiconductor materials under most conditions. The importance of surface thermodynamics for III-V alloys is the effect of the surface on the microscopic arrangement of the atoms in the solid, such as the production of spontaneously ordered structures during MOVPE growth.

Figure2-3 : (a) atomic configurations on (001), (110), and (111)A zincblende surfaces without reconstruction. (b) and (c) are the models for (2×4) surface reconstruction on (001)-oriented GaAs.

If the entire system were completely at equilibrium, it would not be important to consider the surface, since the bulk solid would also be in equilibrium with the vapor at the interface. However, the diffusion coefficients in these highly stoichiometric solids, where the vacancy concentrations are extremely low, are so small that the bulk solid is often not able to attain equilibrium with the surface. In this case, the stoichiometry of the solid is determined by the thermodynamics of the surface phase.

The surfaces created by termination of a model zincblende solid are shown in Figure2-3(a).³ For the (100) surface, commonly used for the epitaxial growth of III-V semiconductors, two of the four sp^3 bonds in the bulk are unsatisfied for the atoms on the surface. This would be expected to result in very strong binding of adatoms on the

surface, resulting in very low surface mobilities and, consequently, very rough surfaces. This appears to be contrary to experimental observations of large diffusion lengths and the ability to grow quantum well structures with abrupt and smooth interfaces.⁵ These are the first indications that each surface atom does not have two dangling bonds. Elementary thermodynamic considerations suggest that the surface atoms will rearrange to lower the surface energy by reducing the number of dangling bonds as well as changing the bonding geometries. In recent years, first-principles calculations have given detailed information about the way in which this might occur.⁶ Surface reconstruction during the MOVPE growth of GaAs has also been observed experimentally. Figure2-3(b) and Figure2-3(c) show the most commonly observed reconstruction for GaAs during epitaxial growths, (2×4) reconstruction, a terminology that refers to the periodicity of the (001) surface in the two <110> directions orthogonal to the (001) growth axis. As shown in Figure2-3(c), the (2×4) reconstruction surface is covered by [-110]-oriented As-As dimers arranged into [110] rows.

The surface reconstruction pattern is controlled by the extensive thermodynamic variables of the system. Thus, thermodynamic factors will determine much of what occurs at the surface during the growth processes and most of the properties of the grown materials.

2.1.3 Kinetics in MOVPE Growth

The thermodynamic equilibrium concepts discussed in Section 2.1.2 determine the state of a closed system. However, MOVPE process is not a perfect equilibrium but a near-equilibrium process. Therefore, thermodynamics, which is concerned only

with the energy of the system in the initial and final, equilibrium states, can only define certain aspects for the growth process, such as the driving force, maximum growth rate in the bulk or on the surface. It is unable to provide any information about the time required to attain equilibrium, the actual steps involved in obtaining the lowest energy state, and the rates of the various processes occurring during the transition from the initial input gases phase to the final semiconductor solid alloy. These problems can only be accessed in terms of kinetics.

The description of the kinetics of the MOVPE growth process contains several major processes: physical surfaces processes, chemical reactions, mass and heat transport. Physical surface processes try to describe the microscopic surface features, such as surface reconstruction, step size and spacing, adatom and step motion. Heat and mass transports in MOVPE control the transporting rates of materials to the growing solid/vapor interface. The rates of the chemical reactions occurring during a growth, either homogeneously in the gas phase or heterogeneously at the growing interface, also play a role. Each of these factors will affect some aspect of the overall growth process.

Figure2-4 shows the schematic overview of the MOVPE growing surface which has been believed to consist of atomically flat regions separated by steps.³ The surface during growth is visualized as somewhat rough due to entropic effects, with equilibrium concentrations of adatoms and advacancies. The adatoms and advacancies can also condense into two-dimensional clusters. The steps themselves may also be rough because of the kinks. In this mode, growth occurs by the propagation of steps as well as by the formation and propagation of two- and three-dimensional islands.

Figure2-4 : Schematic overview of the MOVPE surface process.

With the aid of the advanced surface measurement techniques, such as scanning tunneling microscope (STM), reflection high-energy electron diffraction (RHEED), observation of the atomic-scale features on the growing surface becomes possible. The physical processes occurring during the MOVPE growth consist of adatom adsorption and desorption, surface diffusion, incorporation of adatoms into the solid and surface reconstruction. The surface reconstruction has the primary effect on essentially all of these processes. Therefore, it plays a major role in determining the solid composition, atomic-scale microstructure, and the microscopic morphology of the surface. Reconstruction of step edges is also expected, which will affect the adatom attachment at steps and kinks.

Several types of reactions may occur during the MOVPE growth process. Homogeneous reactions refer to those that occur entirely in the gas phase. Reactions that occur at a solid surface are defined heterogeneous. Normally both types of reactions are either unimolecular, a process undergone by an energetically activated species without interaction with other species, or bimolecular, which requires the

collision of two species, producing an activated complex that may then undergo a unimolecular reaction.

For homogeneous unimolecular reactions, the type considered earlier, the reaction rate is proportional to the first power of the concentration of the species reaction. For a homogeneous bimolecular process, the reaction rate is the rate constant multiplied by the concentration of the complex, which is, in turn, proportional to the product of the partial pressures of the two reaction species.

Normally, several types of homogeneous, unimolecular reactions are involved in the pyrolysis of precursors during a MOVPE growth. The most common reaction for the $M(CH_3)_n$ -type precursors is simple homolysis, such as hemolytic fission:

The pyrolysis processes are frequently highly complex, so the process occurring in a particular reactor will depend on variables such as reactor pressure, temperature, precursor concentration, and the exact flow conditions.

The epitaxial growth process for MOVPE involves the interaction of the vapor with the surface of the solid phase, so the heterogeneous reactions occurring there often dominate the overall process. The first step in considering heterogeneous reactions is the adsorption of a molecule onto the surface and its' desorption. In the Langmuir isotherm model, which is the simplest and most intuitive approach to a quantitative treatment of adsorption, it is assumed that the surface is composed of a fixed number of sites on which species can absorb, a fraction of which are occupied. The remainders are vacant in this model. It is also assumed that there are no interactions between adsorbed species. This treatment implicitly assumes that a chemical bond is formed between the adsorbate and the surface (i.e., it applies to

chemisorbed species). It is widely believed that the chemisorption consists of two steps. First, the molecule is physisorbed – that is, bound to the surface only by weak, van der Waals forces. The physisorbed molecules can then either be desorbed, since the bond attracting the molecule to the surface is weak, or find a site where it can form a chemical bond to the surface. The rate of a unimolecular heterogeneous reaction is directly proportional to the concentration of reacting species on the surface, which is a linear function of the partial pressure.

The least understood aspect of the entire MOVPE growth process is probably the array of surface reactions and physical phenomena occurring at the solid/vapor interface during growth. Two reasons for this are the complexity of the system and the lack of tools for directly measuring the state of the surface (i.e., the structure and chemical composition) during the growth process.

Heat and mass transport in an MOVPE reactor can occur by a variety of mechanisms including diffusion and forced thermal convection. However, to provide well controlled growth, the reactor geometry and flow conditions are designed so that the system is free of turbulence and convection of the gas flow inside the MOVPE reactor during epitaxial growths. This choice of conditions improves the uniformity and efficiency of the growth process. In addition, this allows the diffusion mechanism to dominate the transport of material in the growth region.

2.1.4 Source Flux in a MOVPE Reactor

The characteristics of gas flow in a MOVPE system affect many properties of the grown epilayer, including uniformity of growth rate, composition, growth efficiency, and abruptness of interfaces. Most conventional MOVPE reactors operate in a

pressure regime where gas flow is best described as fluid in nature. This is in contrast to low pressure deposition techniques such as MBE and CBE where molecular flow is the dominant mechanism.

The gas flow in a MOVPE reactor is often tailored to eliminate or reduce some of the effects that cause the material non-uniformities described above. The two main processes with which to be concerned are turbulence and thermal convection. Turbulence can cause local changes in the flow of gases above the substrate, resulting in a variation of the film thickness or alloy composition in the deposited epilayer. Thermal convection currents result from the expansion of gases above the heated susceptor. This increases the residence time of the reactants above the substrate and makes it difficult to grow well-defined interfaces.

Most MOVPE reactors are designed to eliminate turbulence by the formation of a laminar flow pattern. This type of flow occurs when all of the gas velocity stream lines are aligned parallel to the direction of gas flow. The length of the reactor that the gas must travel before the flow becomes laminar is given by:⁷

$$L_e = 0.16a_r N_{Re} \quad (2-11)$$

where a_r is the radius of the reactor tube and N_{Re} is the Reynolds number. The Reynolds number is specific to a particular reactor geometry and can be expressed as:⁷

$$N_{Re} = VL\rho/\eta = VL/\nu \quad (2-12)$$

where V is the gas stream velocity, L is the reactor diameter, ρ is the gas density, η is the gas viscosity, and ν is the kinematic viscosity. Once laminar flow is initiated in a reactor cell, it can be theoretically maintained as long as there are smooth transitions between areas of differing geometry.

However, thermal convection currents are difficult to predict and can disrupt the flow pattern. The tendency for convection currents to form in a system can be predicted by the Rayleigh number for certain geometry:

$$N_{Ra} = \alpha g c_p h^3 \rho^2 \Delta T / \eta \kappa \quad (2-13)$$

where α is the thermal expansion coefficient, c_p is the specific heat of gas, h is the free height of the top wall above the substrate, $\Delta T = T_{hot} - T_{cold}$, κ is the thermal conductivity of gas, and g is the gravitational constant. A high value of the Rayleigh number will generally result in the formation of convection currents. Therefore, these effects can be reduced by avoiding large distances above the heated substrate, or by increasing the velocity of the gas flow.

2.1.5 Metalorganic Sources in MOVPE Growth

In an MOVPE growth of III-V semiconductor alloys, metalorganic and hydrides are normally used as the group III and group V material sources, respectively. Dopant sources are either metalorganic or hydride depending up the doping impurity type. Metalorganic sources usually include the molecules MR_n , where M represents the group II, III, IV, V and VI elements, and R usually indicates methyl or ethyl radicals. In the MOVPE community, M and E are used to denote methyl and ethyl radical, respectively. M (mono-), D (di-), and T (TRI-) are used to denote the number of specific radicals. For example, TMGa refers to trimethylgallium and TEGa refers to triethylgallium.

At the beginning ten- to fifteen-year development period for MOVPE, one of the limiting factors was in the source molecules, since there were no materials which

were manufactured particularly for the MOVPE process. The ideal molecular source has sufficient pyrolysis efficiency which widens the range of growth temperature. The unintentional impurity (such as carbon and oxygen) doping which results from the source precursors should be low.

Table 2-1: Comparison of properties of group III precursors for MOVPE

CHEMICAL NAME	NOTA TION	CHEMICAL FORMULA	PRESSURE (298K) (TORR)	MELTING POINT (°C)	VAPOR PRESSURE*	
					A	B
Trimethylaluminum	TMAI	(CH ₃) ₃ Al	14.2	15.4	2134	8.22
Triethylaluminum	TEAl	(C ₂ H ₅) ₃ Al	0.041	-52.5	3625	10.78
Trimethylaluminum	TMGa	(CH ₃) ₃ Ga	238	-15.8	1703	8.07
Triethylaluminum	TEGa	(C ₂ H ₅) ₃ Ga	4.79	-82.5	2530	9.19
Trimethylaluminum	TMIn	(CH ₃) ₃ In	1.75	88.4	3014	10.52
Trimethylaluminum	TEIn	(C ₂ H ₅) ₃ In	0.31	-32	2615	8.94

$$* \log_{10}(P[\text{Torr}]) = A - B/T$$

Table 2-1 lists the properties of group III precursors for MOVPE. It can be seen that the trimethyl sources (TMAI, TMGa, and TMIn) have higher vapor pressure and have greater stability than the triethyl ones.

Figure2-5 shows the decomposition of TMIn (left) and TMGa (right) versus temperature.⁸ It can be seen that the decomposition of TMIn is lower than that of TMGa. The TMIn molecule is planar with sp² bonding. The In-CH₃ bond is fairly weak, so homolysis occurs at fairly low temperatures, which results in lower decomposition temperature. The lower decomposition temperature of the MO source also helps to reduce the MOVPE growth temperature.

Figure2-5: Decomposition of TMIn (left) and TMGa (right) versus temperature. Experimental result for TMIn: (■) in D₂, (□) in H₂, (Δ) in He, and (—) in toluene.⁸ The lines are numerical calculations. Experimental result for TMGa: (■) in N₂, (□) in H₂, (◇) in He, (◆) in D₂, and (--) in toluene. The lines are numerical calculations.

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Arsine (AsH₃) and phosphine (PH₃) have been the most used group V precursors since the beginning stage of MOVPE development. These two precursors not only provide As and P elements but also produce H radicals to the surface reaction and removing the carbon-containing radicals which are generated from pyrolysis of the

group III precursors. In addition to their easy availability, AsH₃ and PH₃ provide high purity level. However, AsH₃ and PH₃ are extremely toxic and have high pyrolysis temperatures compared with that of group III precursors. AsH₃ and PH₃ have lethal doses (LD₅₀) well below 50 ppm.⁹ This puts stringent demands on the safety equipment, adds to the production costs.

In order to reduce the hazard during MOVPE growth and improve the growth efficiency, much effort has been made to explore other group V precursors. Among these new group V precursors, tertiarybutylarsine (TBAs) and tertiarybutylphosphine (TBP) produce outstanding performance.¹⁰ These precursors are less toxic (LD₅₀=70 ppm for TBAs, and >1100 ppm for TBP), and decompose upon air exposure to form relatively harmless solid oxides.¹¹ Liquid TBP and TBAs can be stored in bubblers at room temperature and mounted directly onto the MOVPE system. This reduces the danger to workers and researchers, since liquid materials disperse at rates several orders of magnitude slower than gases.¹⁵ In addition, TBP and TBAs exhibit higher incorporation efficiencies than the hydrides, so that growth can be carried out at the lower V/III ratios and substrate temperatures. One of the main obstacles to the use of TBP and TBAs at the early stage has been the presence of oxygen impurities in AlInP and AlInGaP at levels equal to or above 10¹⁷ cm⁻³.^{12,13} Nevertheless, recent developments in precursor purification may have overcome these drawbacks, suggesting that it is worthwhile to use and study these sources for III-V semiconductors. It has been found that impurity concentrations below mid-10¹⁴ cm⁻³ for InP and 10¹⁶ cm⁻³ for AlInP could be achieved at relatively low growth temperature and V/III ratio.¹⁴ TBP and TBAs have been shown the ability to replace PH₃ and AH₃ because of their lower pyrolysis temperature, much less toxicity, high

vapor pressure, and no additional carbon contamination. Therefore, in this study, we choose TBP for the phosphorus element and TBAs for the arsenic element in the group V sources.

The group III sources are trimethylaluminum (TMAI) for the aluminum element, triethylindium (TMIIn) for the indium element, and triethylgallium (TMGa) for the indium element.

2.1.6 MOVPE Growth System

As in the above introduction, there are a large number of parameters to be precisely controlled in the MOVPE system since it involves multi-phase and multi-component during growth. All the AlInP epilayers described in this study were grown in a horizontal IR lamp-heated low pressure MOVPE reactor equipped with both nitrogen and hydrogen carrier gas lines. The MOVPE reactor is an Aixtron AIX-200 system with gas foil substrate rotation to achieve uniform deposition. The schematic diagram of the system is shown in Figure2-6. The whole system is subdivided into four major parts: gas handling system, switching manifold, reactor chamber, and exhaust system. Figure2-7 shows the Aixtron AIX-200 system used in this study.

In this study, all the group III and group V sources are contained in stainless steel bubblers which are immersed in temperature baths. The temperature bath is capable of operating from -30 to 130 °C with a precision of 0.1 °C and stability of 0.01 °C at 20 °C to maintain a constant vapor pressure during epitaxial growth. The relation between the bubbler temperature and the equilibrium vapor pressure over the liquid or solid source phase is shown in:³

$$\text{Log}_{10} P_v = A - B/T \quad (2-14)$$

where P_v is the vapor pressure of metalorganic source at equilibrium in the unit of mmHg, T is the absolute temperature of the bubbler in the unit of K , and A , and B are constants determined by material properties. Equation (2-14) shows that the vapor pressure is exponentially proportional to the negative multiplicative inverse of bubbler temperature, and it is critical to control the bubbler temperature accurately and maintain the bubbler temperature steady.

The gas switching manifold in the AIX-200 system consists of stainless steel 3-way bellow valves to control the source gases either into the reactor when the sources are needed for growth or into the exhaust system when the sources are not required for the epilayer or the growth is in an idle state. The group III and group V sources are led into the inlet of the quartz reactor through separate gas lines in order to avoid any possible adduct formation.

The schematic of the bubbler immersed in a temperature bath is shown in Figure2-8. With the help of carrier gas (high purity nitrogen (N_2) or hydrogen (H_2)), the source is carried to the reactor from the bubbler. The carrier gas is led into the bubbler filled with a source or bubbles through the source to collect source molecules from the bubbler and deliver them into the reactor. It is very important to control the bubbler temperature accurately and maintain the bubbler temperature steady.

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Figure2-6: Schematic diagram of a MOVPE system. The whole system consists of four major parts: gas handling system, switching manifold, reactor chamber, and exhaust system.

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Figure2-7 : The photo of an Aixtron AIX 200 MOVPE system (left) and the schematic diagram of the MOVPE reactor.

Figure2-8: Schematic diagram of a bubbler immersed in a temperature bath.

The reactor chamber of the AIX-200 consists of a quartz reactor, a graphite susceptor, and an infrared strip heating system. All the source gases are fed into the reactor chamber nearly parallel to the wafer surface. The wafer is put on a graphite susceptor heated by infrared (IR) strip heaters. The susceptor is capable of high speed rotation in order to maintain a uniform growth rate and composition over the whole wafer. The power of the IR strip heater is driven by a power controller which drives

operating power from the control signal monitored by a temperature controller. The substrate temperature is monitored by a thermocouple inserted into the reactor chamber. The IR heater, temperature monitor, and temperature controller compose a feed-back loop to make it possible to maintain a desired set point substrate temperature.

The exhaust system of the MOVPE system not only filters out the residual toxic and reactive gases but also maintains a consistent reactor chamber pressure. During MOVPE growths, not all the sources join the real epitaxial film growth to react and adhere to the substrate surface; the remainder of the un-reacted sources and the byproducts formed during growth should be exhausted from the reactor chamber. After that, they are fed into the toxic gas burn system which burns and oxidizes the residual toxic and reactive gases. They are converted into solid wastes which are removed by the filters as harmless gaseous byproducts. The other function of the exhaust system is to maintain the reactor pressure at a certain specified value during the growth process. Since the growth pressure plays an important role in the properties of the epitaxial layers, a stable, non-fluctuating constant pressure is critical to obtain high quality and uniform epitaxy layers and devices.

2.2 Post-Growth Techniques

2.2.1 Rapid Thermal Annealing

Rapid thermal processing (RTP) is used for a wide variety of applications in semiconductor manufacturing including material recovery, dopant activation, thermal oxidation, and so on. Rapid thermal annealing (RTA) is a kind of RTP but with

shorter annealing time (normally shorter than 3 minutes). Compared with the conventional furnace annealing process, the advantage of RTA includes short annealing time, precise control of the annealing profile, and minimization of dopant redistribution and out-diffusion.¹⁷

Figure2-9: The RTA machine and the capping configuration for annealing process.

In this study, we use the basic mechanism in RTA, thermal excitation, to increase the vibrational amplitude of the atoms in the grown AlInP epilayer. With the high annealing temperature, the activation energy for the atoms may be overcome by the thermal excitation and the grown AlInP epilayer is expected to transform from the atomic ordered state which is metastable to the thermodynamically stable state, the normal random structure.

A RTA system consists of four major parts: (1) thermal energy source, (2) process chamber, (3) temperature measurement apparatus, and (4) temperature control.

Figure2-9 shows a typical RTA system which uses tungsten halogen lamps as

heaters. The process chamber is normally made of quartz, silicon carbide or stainless steel. The chamber also has quartz windows for the optical radiation to illuminate samples. The sample temperature in an RTA system can be measured by a non-contact optical pyrometer (for temperature higher than 700 °C) or a thermocouple (for temperature lower than 700 °C). The temperature measurement system is set in a temperature feedback and control loop to control the sample annealing temperature. The sample temperature is controlled with a high accuracy of ± 1 °C. In order to prevent surface contamination, the annealing process is in N₂ atmosphere.

2.2.2 Inductively Coupled Plasma (ICP)

ICP has been widely used in the semiconductor industry for etching the silicon dielectrics and III-V semiconductors. The plasma etch machine may cause damage to the sample, which is undesirable since it results in degradation in the electrical properties of the sample. However, this property damage can be recovered by the thermal annealing process after exposure to the plasma.

Plasma is an ionized gas with equal numbers of free negative and positive charges. The free charges are produced by the passage of electric current through discharge. The positive charge is mostly of singly ionized neutrals from which single electrons have been stripped. The majority of negatively charged particles are usually free electrons. ICP is a type of plasma source in which the energy is supplied by electrical currents which are produced by electromagnetic induction, that is, by time-varying magnetic fields.

Figure 2-10 shows an ICP reactor, which consists of parallel plate electrodes in a chamber that can be maintained at low pressure (0.01 to 1 Torr). When high

frequency voltage is supplied between the electrodes, the current flows and the plasma is formed which emits a characteristic glow. Reactive radicals are generated by this electrical discharge. This system uses an inductive coil to generate high-density 'remote' plasma with no direct contact between the plasma and the substrate. During the exposure to the plasma, 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 sample is placed on the silicon substrate to provide a fairly large (168 W/mK) heat conduction.

Figure2-10: Schematic diagram of an ICP reactor.

The RF-induced DC bias decreases with the increase in ICP power and the decrease in RF power during the exposure to the Ar plasma. The measurement of the plasma densities, thus ion current density, under various plasma conditions is made with Langmuir probes. Higher ICP power may be applied in order to obtain higher ion fluxes if needed.

2.3 Characterization Techniques

This section discusses the various techniques to characterize the properties of III-V epitaxy alloys, such as crystal structure, crystal quality, surface morphology, and optical properties. Both the basic principles and measurement mechanism of each technique are introduced.

2.3.1 X-Ray Diffraction

X-Ray Diffraction (XRD) is a very powerful ex-situ and non-destructive characterization technique to study the crystalline quality, solid composition, interface quality, and thin film strain of all sorts of crystalline materials. Every crystal which has periodic structures is accompanied a reciprocal space which is basically a three dimensional Fourier transform of the real-space periodicity. Like all other diffraction techniques, XRD probes the reciprocal space associated with a periodicity. In addition, the very short wavelength of an X-ray photon (typically, $\lambda=1.54 \text{ \AA}$) allows it to scan the reciprocal space points corresponding to a very short crystalline period ($<5.0 \text{ \AA}$). For single-crystal diffractometry, either Bragg's law, or the more elaborate Ewald sphere analysis is the most convenient description of the XRD technique. In the Ewald sphere approach in which the X-ray source and detector are set at a certain angle, the system is basically probing a certain point in the reciprocal space of the crystal under measurement given by the Laue equation:¹⁸

$$\vec{k}_i - \vec{k}_r = \vec{G} \quad (2-15)$$

where $\vec{k}_i$ is the wave-vector of the incident beam, $\vec{k}_r$ is the wave-vector of the reflected beam and $\vec{G}$ is the vector pointing towards the reciprocal space point being probed. A detailed analysis of these formulations can be found in many text books on solid-state physics.¹⁸

For the characterization of semiconductor materials, a symmetric ω -2 θ XRD scan can be used to determine the lattice constant based on Bragg's law¹⁹

$$2d_{hkl} \cdot \sin \theta_B = n\lambda \quad (2-16)$$

where d_{hkl} is the spacing of lattice planes with Miller indices (hkl), θ_B is the corresponding Bragg angle – the angle between the normal to the periodic planes and the source or the detector, and λ is the X-ray wavelength of Cu K $_{\alpha}$ (1.5406 Å). If measured on a crystalline alloy of two components, the lattice constant can be used to determine the alloy composition. Normally the best way to analyze the ω -2 θ scan data of a sample is to compare with Takagi-Taupin dynamic XRD simulation data. Commercial software is now readily available to provide such simulation data, and also to automatically fit the measured result with a proposed structure by varying a number of structural descriptions such as alloy solid composition, film thickness, relaxation percentage. Detailed description of dynamic XRD can be found in the textbook referred to among others.²⁰

Given a perfectly periodic structure of 3D delta functions in an infinite array, then in the corresponding Fourier space, each of the reciprocal space points will also be perfect delta functions with infinite height and zero spread. However, when considering crystal structure in real samples, these peaks in the reciprocal space will be broadened due to a number of factors such as finiteness of the crystal structure, presence of defects, and break of periodicity. The spread in any reciprocal space point

can thus be a good indication of the degree of perfection of the crystal, acting to indicate material quality. The full-width at half-maxima (FWHM) of ω - 2θ scan or a rocking curve is often used to compare material quality in the III-V compound materials.

Figure2-11: (a) Illustration of Bragg's Law. When $n\lambda=AB+BC$, constructive interference occurs. (b) Scattering geometry.

Bragg's law as illustrated in Figure2-11(a) describes how constructive interference of waves reflected from successive planes occurs when the path difference is an integral number n of wavelengths λ . So the diffraction peaks at Bragg angles which correspond to the perpendicular lattice constants of each set of planes are expected. By measuring the diffraction angle separation between the substrate peak and the epitaxial layer peak, the lattice constant of the epitaxial alloy can be determined by:

$$d_{epi(h,k,l)} = \frac{\lambda}{2 \sin(\theta_{epi(h,k,l)})} \quad (2-17)$$

where $d_{epi(hkl)}$ denotes the spacing of lattice plane with Miller indices (hkl) of epilayer.

For (004) diffraction plane, the lattice constant for a cubic crystal is written as:

$$a_{\text{epi}} = 4d_{\text{epi}} \quad (2-18)$$

So the mismatch between the epitaxial film and substrate is given by:

$$\frac{\Delta a}{a} = \frac{a_{\text{epi}} - a_{\text{sub}}}{a_{\text{sub}}} \quad (2-19)$$

Figure2-12: Basic features of a typical XRD system.

Figure2-13: Philips X'pert Materials Research Diffractometer.

Figure2-11(b) shows the scattering geometry for a crystal. ϕ is the angle between the lattice plane (hkl) and the surface; $\mathbf{k}_i$ and $\mathbf{k}_s$ are the incident and scattered wave

vectors, respectively. Bragg's diffraction is 'symmetric' when $\varphi=0$, i.e. the reflecting lattice planes are parallel to the crystal surface. Otherwise, Bragg's diffraction is called 'asymmetric'. Normally a symmetric ω - 2θ XRD scan is used to measure the c-direction lattice constant of the epitaxial layer.

The schematic of XRD setup is shown in Figure2-12. X-rays are produced whenever high-speed electrons collide with a metal target. The generated X-rays are incident on the surface of the sample which is mounted on the susceptor. Opposite to the X-ray tube, a detector is used to collect the diffracted X-rays. Figure2-13 shows the Philips XRD system used in this study.

2.3.2 Photoluminescence Spectroscopy

Photoluminescence (PL) provides a powerful non-destructive technique for study of the fundamental recombination processes in the semiconductors, for characterization of the optical quality of bulk or epitaxial III-V films. When a semiconductor material is under a non-equilibrium condition, radiative recombination will occur. A free electron and a free hole are created whenever a photon of energy greater than the band gap is absorbed in the semiconductor. This electron and hole can then be bound together by an attractive Coulombic attraction force to form an electron-hole pair (ehp), which is known as exciton. Excitons are unstable with respect to radiative recombination in which the electron combines with the hole in the valence band (VB), accompanied by the emission of a photon. The exciton recombination can also occur without the release of a photon as non-radiative recombination. In the application of the semiconductor as an optical device, the

fraction of non-radiative recombination should be less when compared with the radiative recombination.

Figure2-14 (left) shows different electron-hole radiative recombination paths in which the excess carrier density decays.¹⁸ The recombination of an electron in the conduction band (CB) with a hole in the VB gives a band-to-band transition (a). Similarly, the recombination between a captured electron and a free hole in the VB produces a donor-to-valence transition (c). On the other hand, the recombination between a free electron in the CB and a captured hole gives rise to a conduction band-to-acceptor transition (b). Both donor-to-valence and conduction band-to-acceptor transitions are referred to as free-to-bound transitions. If two bound particles recombine with each other, a donor-to-acceptor pair transition ensues (d).

Figure2-14: (left) various electron-hole recombination paths in a direct bandgap semiconductor. (right) illustration of Fermi level distributions at different temperatures.

PL measurement is usually performed below room temperature as it produces a sharper and smoother profile. At a lower temperature, the linewidth or the full-width at half-maximum (FWHM) of the profile is generally smaller. This is due to less

phonon vibration in the crystal at a lower temperature. The less phonon scattering, the less sideband intensity is obtained. At room temperature, the large concentration of phonons and the exciton levels merge into the continuum absorption spectrum. Therefore, the absorption spectrum from excitons can hardly be separated from the continuum absorption spectrum and this broadens the linewidth. Also, at a lower temperature, the charge carrier density decreases and reduces the sideband intensity. The decrease in the charge carrier density is due to the change of the Fermi level to a more abrupt profile at a lower temperature, as shown in Figure2-14(right).

Figure2-15: The schematic diagram of a home-made low temperature PL measurement setup.

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

$$E_g = E_{g0} - \frac{\alpha T^2}{(\beta + T)} \quad (2-20)$$

where E_g is the bandgap energy at temperature T in Kelvin, E_{g0} is bandgap energy at 0- K, and α and β are empirical constants of the III-V alloys.²¹ This equation governs the temperature and bandgap difference for III-V compounds. The decrease in phonon vibration at a lower temperature also affects the shift in the PL peak emission energy. Although the mean value of the vibration is always equal to zero, there exists a root-mean-square value that decreases as temperature decreases, thus raises the PL peak energy.

Besides the homogeneous broadening of FWHM of PL spectra such as caused by measurement temperature, there is also inhomogeneously broadening. For example, the excitonic recombination is inhomogeneously broadened, because of the disorder due to interface roughness including the island growth in a quantum well structure. Moreover, because of the alloy disorder, mixed crystals are characterized by exciton linewidths broader than those in the pure components. The atomic ordering gives rise to a typical domain structure, which is possible to be studied by the inhomogeneous broadening of FWHM of PL spectra from the ordered AlInP sample.

In this study we use a homemade PL system for characterization. Figure2-15 shows the main part of the system. The source is an Ar⁺ laser operating on its blue 488 nm line which produces photons at 2.54 eV. These photons can be generated at a continuous power of hundreds of milliwatts which is adequate to produce a good

signal. An optical chopper is used to modulate the laser beam such that signals can be processed by the lock-in amplifier. The PL signal passes through a 1200 groove/mm monochromator which selects a wavelength to transmit to a Si detector. The output signal from the detector is then transferred to a lock-in amplifier. Lastly, the processed signal is transferred from a lock-in amplifier to a computer and displayed as the PL spectrum. The wavelength sensitivity is around 0.1nm.

2.3.3 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a powerful technique that is used for microstructural and crystallographic analyses of compound semiconductor materials and devices. In this study, we use high resolution TEM image to check the microstructure in the grown AlInP epilayer at atomic level. The transmission electron diffraction (TED) pattern is used to investigate the superstructures along [1-11] direction in atomic ordered AlInP alloys.

In the TEM system, the electrons emitted from a hot-cathode or field-emission source are accelerated to high energy and projected through a high-vacuum column to obtain structural information from solid samples prepared as thin foils (normally less than one micrometer).

Figure2-16 illustrates the different TEM operational modes: bright-field, dark-field, and selected-area diffraction pattern. Diffraction and imaging operational modes differ primarily in post-specimen lens/aperture configurations. The selected diffraction pattern (TED) is viewed by positioning a SA in the image plane with supplementary optics. The pattern is often acquired on a low-index zone axis to reveal

the crystal symmetry from the spot positions; it can also be viewed off-axis to obtain a particular diffraction condition for BF and DF imaging.

Figure2-16: Simplified TEM operational modes: (a) bright field, (b) dark field, and (c) selected-area diffraction pattern.

The incident beam is a plane wave when illuminated parallel and ignores back-scattered beams:

$$\psi(r) = e^{2\pi i k \cdot r} \quad (2-21)$$

The exit wave function below a perfect crystal is a series of diffracted beams:

$$\psi(r) = \sum_g \Psi_g e^{2\pi i (k+g+s_g) \cdot r} \quad (2-22)$$

where S_g is the excitation error. The diffracted wave vectors satisfy the elastic-scattering condition $K=|k+g+s_g|$. One may collect divergent diffraction-beam (spot) intensities without interference:

$$I_g = |\Psi_g|^2 \quad (2-23)$$

Figure2-17: (a) Schematic drawing of the [110] TEM diffraction pattern of a perfectly CuPt atomic ordered $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$. (b) [110] electron diffraction pattern of a $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ epitaxial layer.

The TED symmetry and scale, rather than quantitative measurement of integrated spot intensities, are often sufficient for the determination of simple crystal structure.

The theoretical [110] TEM diffraction pattern of a perfectly CuPt ordered $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ is shown in Figure2-17(a).²² The large circles represent the fundamental zincblende diffraction maxima; the small ones show the CuPt atomic ordering diffraction spots. The theoretical simulation suggests that the CuPt atomic ordered structure results in additional diffraction spots determined by the reciprocal vectors $k_I = [\frac{\bar{1}}{2} \frac{1}{2} \frac{1}{2}]$ and $k_{II} = [\frac{1}{2} \frac{\bar{1}}{2} \frac{1}{2}]$ that are observable in the [110] cross-sectional diffraction patterns obtained by TEM. This is also confirmed by the experimental evidence, which is shown in Figure2-17 (b). The TEM diffraction was taken from a $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ epitaxial layer.²²

2.3.4 Raman Scattering Spectrum

In this study, Raman Scattering spectroscopic analysis provides the information on lattice dynamics and electronic properties. Lattice dynamics reflects structural information such as the identification of materials, including reacted phases at interfaces, but also aspects such as the composition of mixed compounds, layer orientation, stress, and crystalline perfection. The information mentioned above is obtained from scattering by phonons through the evaluation of the phonon frequencies, half width, lineshape and their intensities in the Raman spectrum.

Figure2-18: (a) Energy level diagram which includes the states involved in a Raman signal. (b) Raman spectrum with Stokes and anti-Stokes scatterings.

In the process of Raman scattering, the energy of an incoming photon ($\hbar\omega_i$) is altered by non-linear interaction with phonons, carriers, or impurities in the material, to produce a frequently-shifted outgoing photon with energy $\hbar\omega_s$.¹⁸ The amount of transferred energy corresponds to the eigenenergy $\hbar\Omega_j$ of an elementary excitation

labeled ' j ' in the sample, such as a phonon. A simplified energy diagram that illustrates these concepts is shown in Figure2-18. Figure2-19 schematically shows a Raman system setup.

Figure2-19: Principle of a conventional Raman spectrometer.

A Raman spectrum provides the eigenfrequencies of the elementary excitations through the analysis of the peak frequencies ω_s in the scattered light, as the frequency of the incident light ω_i is defined by the use of a laser light source. Energy conservation yields:

$$\hbar\omega_s = \hbar\omega_i \pm \hbar\Omega_j \quad (2-24)$$

where the '-' sign represents so called 'Stokes processes' in which an elementary excitation is generated. The '+' sign corresponds to so called 'anti-Stokes processes' in which an elementary excitation is annihilated. In most experimental Raman spectrum investigation only Stokes process is studied.

2.3.5 Atomic Force Morphology

Atomic force microscopy (AFM) is a characterization tool that provides a three-dimensional image of surfaces with sub-nanometer resolution. A schematic set up of AFM is shown in Figure2-20. During the AFM measurement, an atomically sharp tip (made from Silicon) is scanned over a surface. A feedback mechanism allows the piezoelectric scanner to maintain the tip at a constant force, which makes it possible to obtain the height of the contoured surface morphology. A laser beam is focused on the back of a reflective cantilever and is deflected toward the series of photodetectors, which measure the deflected light intensities and convert the cantilever motion into a voltage signal which is transferred to height information.

Figure2-20: The schematic diagram of an AFM system.

In this study, the tapping mode of an AFM system is employed. The tapping mode is non-destructive and allows high-resolution topographic imaging of sample surfaces.

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3 MOVPE Growth of AlInP and the Aluminum Incorporation

This chapter describes the MOVPE growth of AlInP and study of the aluminum (Al) incorporation into the AlInP epilayers in MOVPE growth. The MOVPE growth conditions for the AlInP epilayer have been optimized. Effects of the MOVPE growth conditions on the aluminum incorporation into AlInP epilayers during the growth have been investigated. A theoretical model has been developed to simulate the aluminum incorporation behavior in the MOVPE growths.

3.1 Introduction

As we know, the solid composition of cation, x , in a III-V semiconductor alloy, $A_xB_{1-x}C$, determines the material's electrical and optical properties, such as the bandgap energy, lattice constant, and effective mass. In order to obtain the expected III-V materials and the device performance which matches the design target, it is very important to precisely control the solid composition in the III-V semiconductor alloy during the epitaxial growth.

Moreover, in the study of the following chapters, we will focus on the mechanism of MOVPE grown III-V alloys' atomic ordering, the effects of the growth conditions on the grown epilayer's degree of order and the changes of the atomic ordering through post-growth processing. In order to make the atomic ordering degree

in the AlInP epilayers comparable,¹ the Al solid compositions in the grown AlInP epilayers in this study should be kept unchanged under different growth conditions. Thus, it is necessary to know how to control the Al composition during MOVPE growths.

Al solid composition in an AlInP epilayer can be tailored by varying the input aluminum source gas-phase flux ratio, TMAI/(TMAI+TMIn), while keeping the other conditions fixed during the MOVPE growth. As discussed in Chapter 2, MOVPE growth is a multi-phase and multi-component reaction process. Several types of reactions occur during the epitaxial growth. The heterogeneous reactions occur directly between the MO sources of group III elements and those of group V elements on the solid surface. The homogeneous reactions occur entirely in the gas-phase, such as the pyrolysis of the MO sources. An example of the pyrolysis reaction of a group III MO source can be written as:

where M represents the group III element. Both the heterogeneous and the homogeneous reactions are controlled by the growth conditions, such as the growth temperature, and reactor pressure. Therefore, a variation of growth conditions will result in change of the solid composition even with the same gas-phase ratio. So, it is essential to study the relationship between the Al solid composition in AlInP and the growth conditions for the applications of AlInP in optoelectronic devices as forms the research work in the following chapters.

3.2 Experiment Details

In this study, all the AlInP epilayers were grown in a horizontal, IR-heated MOVPE reactor with gas foil rotation in an AIX-200 system, which has been described in Chapter 2. The reactor pressure was set at 20mbar. The substrate rotation speed was set at 50 rpm. The metalorganic precursors used were TMAI, TMIn, and TBP. The carrier gas was purified nitrogen with the dew point of below -100 °C. Semi-insulating GaAs epi-ready wafers with exact (100) orientation were used as substrates. Before the growth of a 0.5 μm -thick AlInP layer, a GaAs buffer layer of 0.2 μm -thick was grown on the GaAs substrate.

Group A, group B, and group C of AlInP epilayers were grown for the study of the effect of the growth temperature, input TMAI source flux ratio, and the V/III ratio on the Al incorporation, separately. During the growths of AlInP epilayers in group A, the input V/III ratio was kept at 40. The growth temperature (monitored as ‘substrate temperature’) varied from 580 to 720 °C. For the AlInP samples in group B, the growth temperature was set at 630°C and the V/III ratio was 40. The input TMAI flux ratio was varied from 0.29 to 0.42. Since group C was grown to study the input V/III ratio effect on Al incorporation into AlInP, the input V/III ratio changed from 34.5 to 45.0 during the MOVPE growths. The growth temperature of group C samples was kept at 630 °C.

PL measurements were employed to investigate the optical properties of the AlInP epitaxial layers. The crystal quality and Al solid composition, x , of the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer, were characterized by the high resolution X-ray diffraction. By using Vegard’s law, lattice constant of the grown $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer can be calculated using the formula:

$$a(x) = x \cdot a_{AlP} + (1-x) \cdot a_{InP} \quad (3-3)$$

where $a_{AlP}=5.4672 \text{ \AA}$ and $a_{InP}=5.8688 \text{ \AA}$ are the lattice constants of AlP and InP, respectively.²

Figure 3-1: A typical X-ray double crystal rocking curve (004) of an $Al_xIn_{1-x}P$ epilayer grown on a GaAs (001) substrate

Figure 3-2: The 77K photoluminescence spectrum of an $Al_xIn_{1-x}P$ epilayer grown on a GaAs (001) substrate.

In the high-resolution XRD measurement, the lattice constant of an $Al_xIn_{1-x}P$ epilayer can also be calculated as:

$$a(x) = a_{GaAs} (1 - \Delta\theta) / \tan \theta_B \quad (3-4)$$

where $\Delta\theta$ is the separation between the diffraction angle of the epilayer and that of the substrate, and θ_B is the Bragg angle of the substrate material GaAs (004). The solid composition of an $Al_xIn_{1-x}P$ epilayer is obtained from combination of equation (3-3) and (3-4).

For example, Figure 3-1 shows a typical double-crystal X-ray rocking curve (004) of an $Al_xIn_{1-x}P$ sample. Two X-ray diffraction peaks are observed: one is from the GaAs substrate and the other originates from the AlInP epilayer, as indicated. The lattice constant, $a(x)$, of the $Al_xIn_{1-x}P$ epilayer calculated by using Equation (3-4) is about 5.75Å. Combined with Equation (3-3), the Al solid composition of the epilayer is determined as 0.37. The PL spectrum, measured at 77K, of the $Al_xIn_{1-x}P$ sample is shown in Figure3-2. The measured near band edge transition energy in Figure3-2 is 1.967eV, which is close to the calculated bandgap of $Al_{0.37}In_{0.63}P$, 1.970eV.³

3.3 Results and Discussion

3.3.1 Effect of the Growth Temperature

In this section, the effect of the growth temperature on the aluminum incorporation in the MOVPE grown AlInP alloy has been experimentally studied. Furthermore, the adsorption-trapping model⁴ is applied to investigate the kinetics of Al incorporation into AlInP epilayers during the MOVPE growth at different growth temperatures.

3.3.1.1 Experimental Results and Discussion

In order to study the growth temperature effect on the Al incorporation into

AlInP alloy during MOVPE growth, the growth temperature was varied from 580 to 720 °C.

Figure3-3: X-ray double crystal rocking curves (004) of $\text{Al}_x\text{In}_{1-x}\text{P}$ samples grown on GaAs (001) substrate at different temperatures: 610 °C, 630 °C, 660 °C, and 580 °C for S1, S2, S3, and S4, respectively.

Figure3-3 shows the XRD rocking curves of $\text{Al}_x\text{In}_{1-x}\text{P}$ samples grown at different temperatures. Sample S1 was grown at 610 °C and S2 was grown at 630 °C. Sample S3 and S4 were grown at 660 °C and 580 °C, respectively. The lattice constant of sample S1 is calculated at 5.715 Å by using Equation (3-3). Substituting this result into Equation (3-2), the aluminum composition of sample S1 is calculated as 0.383. Aluminum compositions of the other samples were calculated similarly. It shows that aluminum compositions of the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayers are different when the growth temperatures change, although the flow fluxes of the MO sources were kept the same during the MOVPE growths.

Figure3-4: Photoluminescence spectra (77K) of AlInP films grown at 610 °C (S1) and 630 °C (S2).

Figure3-4 shows the PL spectra of sample S1 and S2 which were grown at 610 °C and 630 °C. Strong emission with narrow width of PL spectra from samples S1 and S2 have been recorded, indicating good crystal quality of the epilayers. Moreover, when the growth temperature was higher, the sample's emission peak shifted to higher energy, which means the larger bandgap energy of the epilayer. There was no PL signal detected from S4 which was grown at 660 °C. This is because sample S4 is indirect bandgap material since Al composition in S4 is higher than the value of direct-indirect crossover. So the PL signal of sample S4 is too weak to be detected. The reason for the absence of the PL signal from S3 may be the poor quality of the epilayer since the growth temperature of S3 was too low.⁵

Figure3-5: Aluminum solid compositions of the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayers change with the substrate temperatures during the MOVPE growths.

Keeping the gas phase ratio of TMAI MO source at a constant in the MOVPE growths, it has been found that the Al solid composition in AlInP epilayers is different when the substrate temperature changes. Figure3-5 shows the Al solid composition in the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayers grown at different temperatures with the same TMAI gas-phase ratio of 0.58. The dots in Figure3-5 indicate the experimental data and the solid line is the fitting curve. It can be seen that the Al composition of the grown $\text{Al}_x\text{In}_{1-x}\text{P}$ films increases with increasing growth temperature from 580 to 660 °C. However, the Al composition in the grown $\text{Al}_x\text{In}_{1-x}\text{P}$ films saturates when the growth temperature is higher than 660 °C. The XRD peak's full width at half maximum (FWHM) of fully relaxed epilayers grown at different temperatures is shown in Figure3-6. The FWHM decreases when the growth temperature increases from 580 to 660 °C, and stops decreasing further when the growth temperature is above 660 °C. It shows that the crystal quality of AlInP alloy is improved with the increase of growth temperature during the range from 580 to 660 °C.

Figure3-6: FWHM of the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayers' XRD peaks as a function of the MOVPE growth temperature. The dotted line is the fitting curve.

The efficiency of incorporation of Al into the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer during the MOVPE growth is suspected to be affected mainly by three factors: (1) temperature-dependent decomposition of the MO source TMAI;^{6,7} (2) re-evaporation of the indium from the growth surface;⁸ and (3) the strain between the grown $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer and the GaAs substrate.⁹

During the MOVPE growth of $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayers, monomethylaluminum (MMAI) and monomethylindium (MMIn), which are generated by the pyrolysis of TMAI and TMIn molecules shown as Equation (3-1), react with PH which is generated by the pyrolysis of the TBP source. It is assumed that aluminum phosphide (AlP) and indium phosphide (InP) stay on the surface lattice sites long enough to be trapped into the epilayer's lattice structure.¹⁰ Then, the growth of the subsequent layer commences. Since the GaAs substrate is [001] oriented, the alternating planes of

group III atoms (Al, In) and group V atoms (P) are aligned with [001] orientation in the zincblende structure of the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer. The plane of group V atoms and that of group III atoms consist of the same and fixed number of sites. So the Al composition in $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer is proportional to the ratio of the adsorbed Al atoms on the growth surface to the surface atom density of the lattice, named N_s^0 . MOVPE growth is considered as a near-equilibrium dynamic system where adsorption of Al and In atoms, decomposition of Al-P and In-P bond, and re-evaporation of Al and In atoms occur at the same time on/from the growth surface.

When the growth temperature ranged from 580 to 660 °C, re-evaporation of both In atoms and Al atoms occurs at the growth surface. As we know, the group III elements can have significant volatility, which allows group III elements to re-evaporate from the growing surface.⁸ Since indium is the most volatile of the common group III elements used in III/V semiconductors,¹¹ the re-evaporation rate of In atoms was greater than that of Al atoms at higher growth temperature. The number of In atoms adsorpted onto the growth surface decreased accordingly, which increases the ratio of the Al atoms to the surface density, N_s^0 , on the growth surface and, therefore, the Al solid composition of the grown $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer increases correspondingly.

Another reason for the increase of the Al solid composition in the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer with the higher growth temperature is the higher pyrolysis temperature of the TMAI source than that of the TMIn MO source. The bond enthalpy of the TMAI and the TMIn molecules are 68 kcal/mol and 48 kcal/mol, respectively.¹² Thus, TMAI is more stable than TMIn. The TMIn MO source is decomposed completely by pyrolysis at 580 °C,^{13,14} but the TMAI MO source is only partially decomposed at this

temperature. Therefore, the decomposition rate of TMAI increases and more MMAIs are generated from the pyrolysis of TMAI MO source when the growth temperature increases within the range from 580 to 660 °C. Consequently, more Al atoms occupy the adsorption sites on the growth surface and the Al solid composition in the deposited $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer increases with the growth temperature.

Figure3-7: AFM images of top morphology for the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayers grown at different substrate temperatures: (a) grown at 630 °C; (b) grown at 680 °C.

The Al solid composition of the grown $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer saturates when the growth temperature reaches above 660 °C as shown in Figure3-5. This is attributed to an extra barrier for the incorporation of the atoms on the growth surface. This incorporation barrier is generated because of the lattice-mismatch strain between the grown $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer and the GaAs substrate. The strain changes the epitaxy growth mode from a quasi-two-dimension (quasi-2D) mode to a three-dimension (3D) growth mode.¹⁵

During a MOVPE growth, if the epilayer's lattice mismatches to that of the substrate material, such as the $\text{Al}_x\text{In}_{1-x}\text{P}$ ($x \neq 0.53$) epitaxially grown on the GaAs

substrate, the initial growth is a quasi layer-by-layer 2D mode.¹⁵ When the thickness of the epitaxial film exceeds the critical thickness, In-rich clusters start to be formed and the growth mode transfers from 2D to the 3D mode accordingly.¹⁵ Similar In-rich clusters and the 3D growth mode have been reported in MOVPE growth of strained GaInP on GaAs substrate.¹⁶ Figure 3-7 shows the AFM images of the surface morphology for the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayers which were grown at (a) 630 °C and (b) 680 °C, respectively. The root mean square (RMS) of surface roughness of the sample grown at 630 °C and 680 °C are 2.465nm and 0.368nm, respectively.

The indium composition of the grown $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer and the strain in the epilayer decreases, when the growth temperature increases from 630 to 680 °C. The number of In-rich clusters and the diameter of the cluster also decrease. Consequently, in the area which is occupied by In-rich clusters, more indium atoms are adsorpted into the adsorption centers on the growth surface and are incorporated into the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer. Adsorption of more In atoms results in the decrease of less aluminum atoms adsorpted into the growing surface, and reducing the Al solid composition in the AlInP epilayer consequently.

Therefore, when the growth temperature reaches or is above 660 °C, the three main factors: indium re-evaporation, TMAI decomposition, and the lattice mismatch strain of the grown $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer are expected to achieve a dynamic balance state. This balance produces a dynamic steady state on the growth surface where the ratio of the number of Al atoms to that of In atoms kept unchanged. Therefore, the Al solid composition in the final $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer does not increase further and the Al composition of the epilayer saturates.

3.3.1.2 Theoretical Simulation

In Section 3.2.1.1, we studied experimentally the relationship between the Al solid composition in $\text{Al}_x\text{In}_{1-x}\text{P}$ and the MOVPE growth temperature. In this section, the Al solid composition as a function of the growth temperature is studied quantitatively. The adsorption-trapping model⁴ was applied to describe the process of Al incorporation into $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayers during the MOVPE growth.

All the $\text{Al}_x\text{In}_{1-x}\text{P}$ samples studied in this section were grown on GaAs (001) substrates. The growth temperatures were set at 610 °C and 630 °C.

Figure3-8: Aluminum solid compositions of $\text{Al}_x\text{In}_{1-x}\text{P}$ films versus the gas-phase ratio of TMAI during the MOVPE growths. Squares represent the samples grown at 630 °C and dots represent the results of the samples grown at 610 °C.

Figure3-8 shows the relationship of Al composition, x , of the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayers with the input gas-phase ratio at different growth temperatures. The samples were grown at 610 °C and 630 °C, respectively. When the growth temperature was set at

630 °C, the Al solid composition of the grown $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayers varied from 0.387 to 0.560 with the changing of the gas-phase ratio, $\text{TMAI}/(\text{TMAI}+\text{TMin})$, from 0.295 to 0.426. With the growth temperature at 610 °C, the aluminum solid composition increased from 0.383 to 0.590 when the gas-phase ratio changed from 0.380 to 0.452.

Figure3-9: A schematic diagram showing the aluminum incorporation process on (100) AlInP surface grown on GaAs (100) substrate during epitaxial growth.

In the following, we will simulate the process of aluminum incorporation into the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayers during the MOVPE growth by adopting the surface adsorption-trapping model.⁴ During the MOVPE growth of $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayers, a phosphorus (P) atom stabilized surface is obtained by providing overpressure of the TBP, which prevents decomposition of $\text{Al}_x\text{In}_{1-x}\text{P}$ on the growth surface. Also, the epitaxial growth rate is controlled by the number of group III adatoms arriving on the liquid-solid interface because of the overpressure of group V source.

In the surface adsorption-trapping model, it is assumed that AlP and InP can stay on the surface lattice sites long enough to be trapped in the bulk lattice till the growth

of the subsequent layer commences. Since the substrate was [100] GaAs, the alternating group III (Al, In) and V (P) atom planes were aligned with [100] orientation in the zincblende lattice structure of the AlInP alloy. The planes of group III elements in the AlInP crystal structure consist of Al and In atoms. For a cubic lattice, the surface atomic density, N_s^0 , of the epilayer is given by n/a^2 , where a is the lattice constant and n is the number of atoms per square.⁴ Since the lattice constant of $\text{Al}_x\text{In}_{1-x}\text{P}$ is written as in Equation (3-2) and n is equal to two, we had $N_s^0 = \frac{n}{a^2} = 6.13 \times 10^{14} \text{ cm}^{-2}$ for the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer with $x = 0.383$. The planes of group V elements of the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer lattice are assumed to consist of the same number of P atoms.

The adsorption process during $\text{Al}_x\text{In}_{1-x}\text{P}$ epitaxial growth, as schematically shown in Figure 3-9, was described by introducing two parameters: the capture radius R_c , and the adsorption time τ_c .⁴ The capture radius R_c was defined such that either MMAI or MMIn within the range of radius R_c around the PH adsorption center would be captured by the PH during the AlInP epitaxial growth. The MMAIs generated by the pyrolysis of the incoming TMAI molecules diffused on the growth surface. The probability of the MMAI appearing within the range of R_c was proportional to the diffusivity of the MMAI molecule. With the assumption that each PH adsorption center can only adsorb one MMAI molecule, the capture radius R_c can be described by the diffusivity of MMAI D_a or by:⁴

$$R_c = R_0 \exp(-Q_d / kT) \quad (3-5)$$

where Q_d is the activation energy for the surface diffusion of an MMAI molecule.

The adsorption time, τ_c , was defined as the lifetime of the captured MMAI before desorbing from the HP adsorption center and can be written as:⁴

$$\tau_c = \tau_0 \exp(Q_{des} / kT) \quad (3-6)$$

where Q_{des} is the activation energy for desorption. It is assumed that the aluminum incorporation process in each atomic layer is a terminated adsorption-desorption process during the growth time for each layer, Δt . All the captured MMAIs would be buried and form the AlInP epitaxial layer if τ_c is larger than Δt ; the probability of the captured MMAI being buried in the growing layer was thus $\tau_c / \Delta t$ if τ_c is smaller than Δt . The adsorption rate was also related to the probability of MMAI compacting with the adsorption center which is N_s^* / N_s^0 , where N_s^* is the density of surface adsorption center and N_s^0 is the surface atomic density. Introducing N_s as the adsorbed aluminum atoms in unit area at time t on the surface, the adsorption rate equation can be written as:⁴

$$\frac{dN_s}{dt} = \frac{N_s^*}{N_s^0} R_c \delta\left(\frac{\tau_c}{\Delta t}\right) F_i (N_s^* - N_s) \quad (3-7)$$

where F_i is the incoming flux of MMAI molecules.

The Reynolds number for our MOVPE reactor, R_e , can be written as:¹⁷

$$R_e = uh\rho / \mu \quad (3-8)$$

where u is the mean flow rate of the carrier gas which is nitrogen in our MOVPE system, h is the height of the reactor, ρ is the density of N_2 gas, and μ is the dynamic viscosity of N_2 . For the presented work where the N_2 carrier gas flow rate was at 3.1 l/min and the susceptor temperature was at 610 °C, R_e is calculated to be ~38, which indicates a laminar flow in the reactor with the growth conditions.¹⁸ The impinging flux F_i can be calculated from the partial pressure using statistical thermodynamics and neglecting the mean flow velocity due to the high thermal velocity of TMAI molecules at the growth temperature. The impinging flux is given by:⁴

$$F_i = Cf_{Al} \quad (3-9)$$

where C is the flux factor which is defined as the number of MMAI molecules

impinging on a unit area of substrate surface per sccm flow of the source gas, and f_{Al} is the TMAI flow rate. The MMAI partial pressure is proportional to f_{Al} .

The solution of Equation (3-6) is given by:

$$N_s = N_s^* (1 - e^{-\alpha f_{Al} t}) \quad (3-10)$$

where

$$\alpha = \frac{N_s^*}{N_s^0} R_c \delta(\tau_c / \Delta t) C \quad (3-11)$$

The adsorption-desorption process for each atomic layer proceeded in only a short time period, Δt , which is the time interval for the growth of one atomic layer. Substituting Δt for t in Equation (3-9), the MMAI concentration incorporated on the surface is written by:

$$N_s = N_s^* (1 - e^{-\alpha f_{Al} \Delta t}) \quad (3-12)$$

The Al concentration in the grown $Al_xIn_{1-x}P$ epilayer is defined by $x = N_{Al}/N^0$, where N^0 is the number of group III atoms in unit volume of AlInP alloy, and $N_{Al} = N_s/d$ is the bulk aluminum atomic density of the epilayer. $d = a/2$ is the atomic layer thickness and a is the lattice constant. So, the Al concentration could be written as:

$$x = \frac{2 N_s^*}{a N^0} (1 - e^{-\alpha f_{Al} \Delta t}) \quad (3-13)$$

In the MOVPE growth of AlInP, the epilayer growth rate is determined by the incorporation of group III elements during the growth.¹⁹ The growth time was inversely proportional to the total flux of group III: $\Delta t = C/f_{III}$, where f_{III} is the total flux of group III sources; $C' = d/C_2$, where $C_2 = V_g/f_{III}$, V_g is the epilayer growth rate. Thus, the aluminum composition of the $Al_xIn_{1-x}P$ epilayer grown by MOVPE is:

$$x = \frac{N_s^*}{a N^0} (1 - e^{-\alpha C' \xi}) \quad (3-14)$$

where $\xi = f_{Al}/f_{III} = TMAI/(TMAI + TMIn)$ is the ratio of TMAI flux to the total group III

flux during the MOVPE growth. The aluminum composition of the grown $\text{Al}_x\text{In}_{1-x}\text{P}$ could be approximated as:

$$x \approx \frac{N_s^*}{aN^0} \alpha C' \xi \quad (3-15)$$

From Equation (3-14), a linear relationship between the aluminum composition of the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer and the gas-phase ratio of TMAI has been observed. The aluminum incorporation coefficient during the MOVPE growth was the slope of the straight line in Equation (3-14), which is:

$$k = \frac{N_s^*}{aN^0} \alpha C' \quad (3-16)$$

Figure3-8 shows a linear increase of the aluminium composition of the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayers with the input gas-phase ratio of TMAI at the growth temperatures of 610 and 630 °C, respectively. The aluminium incorporation coefficient was different at different growth temperature. The ratio of the incorporation coefficients k at 630 °C to that at 610 °C could be calculated as:

$$\frac{k_{630}}{k_{610}} = \left(\frac{N_{s630}^*}{a_{630} N_{630}^0} \alpha_{630} C'_{630} \right) / \left(\frac{N_{s610}^*}{a_{610} N_{610}^0} \alpha_{610} C'_{610} \right) \quad (3-17)$$

Substituting $\alpha = \frac{N_s^*}{2N_s^0} R_c \delta(\tau_c / \Delta t) C$ into equation (3-16), it could be written as:

$$\frac{k_{630}}{k_{610}} = \left(\frac{N_{s630}^*}{a_{630} N_{630}^0} \frac{N_{s630}^*}{N_{s630}^0} R_{c630} \frac{\tau_{c630}}{\Delta t} C_{630} C'_{630} \right) / \left(\frac{N_{s610}^*}{a_{610} N_{610}^0} \frac{N_{s610}^*}{N_{s610}^0} R_{c610} \frac{\tau_{c610}}{\Delta t} \alpha_{610} C_{610} C'_{610} \right) \quad (3-18)$$

Under the over pressure of the group V source during the MOVPE growth, the surface adsorption centers, N^* , and the group III atom density, N^0 , are constant.

Equation (3-17) could be simplified as:

$$\frac{k_{630}}{k_{610}} = \left(\frac{1}{a_{630}} R_{c630} \frac{\tau_{c630}}{\Delta t} C_{630} C'_{630} \right) / \left(\frac{1}{a_{610}} R_{c610} \frac{\tau_{c610}}{\Delta t} C_{610} C'_{610} \right) \quad (3-19)$$

During the MOVPE growths of the two samples, the total group III source flux,

f_{III} , was kept the same. Equation (3-18) is as follows:

$$\frac{k_{630}}{k_{610}} = \left(\frac{1}{a_{630}} R_{c630} \frac{\tau_{c630}}{\Delta t} C_{630} \frac{d}{V_{g630} / C_{630} f_{III}} \right) \left/ \left(\frac{1}{a_{610}} R_{c610} \frac{\tau_{c610}}{\Delta t} C_{610} \frac{d}{V_{g610} / C_{610} f_{III}} \right) \right. \quad (3-20)$$

Ignoring the variation of R_c and τ_c , equation (3-17) could be written as:

$$\frac{k_{630}}{k_{610}} = \left(\frac{C_{630}}{C_{610}} \right)^2 \left(\frac{V_{g610}}{V_{g630}} \right) \quad (3-21)$$

The flux factor C is written as:²⁰

$$C = \frac{1}{4} n v = \frac{1}{4} n \sqrt{\frac{8k_B T}{\pi M}} \quad (3-22)$$

where v is the mean thermal velocity, M is molecular weight of TMAI, and n is the density of TMAI molecules in the source flux. Assuming the gas temperature, T , right above the substrate is the same as the substrate temperature, n is inversely proportional to T due to expansion. Therefore, C is proportional to $1/\sqrt{T}$. Equation (3-20) is written as follow:

$$\frac{k_{630}}{k_{610}} = \frac{610 \times V_{g610}}{630 \times V_{g630}} \quad (3-23)$$

The MOVPE growth rate of the AlInP epilayer, V_{g630} and V_{g610} , at temperatures 630 °C and 610 °C were measured of 1.378 $\mu\text{m/h}$ and 0.781 $\mu\text{m/h}$, respectively. Thus, the ratio of aluminum incorporation coefficient between the growth temperature of 630 °C and 610 °C could be calculated as:

$$\frac{k_{630}}{k_{610}} \approx 0.548$$

In Figure3-8, the experimental data of the AlInP epilayer's aluminum composition versus the source flow flux with the growth temperature at 630 °C and 610°C were linearly fitted respectively. It has been shown that the aluminum incorporation coefficients at the two growth temperatures were $k_{630} = 1.384$ and k_{610}

=2.852 respectively. The incorporation coefficient ratio between the two growth temperatures from the experimental data is:

$$\frac{k_{630}}{k_{610}} = \frac{1.384}{2.852} \approx 0.486$$

The calculated incorporation coefficient ratio, $\frac{k_{630}}{k_{610}} \approx 0.548$, agreed with the experimental result, 0.486, well.

3.3.2 Input TMAI Gas-Phase Ratio

In the MOVPE growth of an AlInP alloy, it is expected that the grown epilayer's aluminum composition only depends on the input aluminum MO source flux, so that the grown AlInP epilayer's composition can be precisely controlled. In this study, we investigate the dependence of the Al solid composition of the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer on the input TMAI gas-phase ratio. The substrate temperature was kept at 630 °C during all the MOVPE growths in this study and the input V/III flux ratios of these growths were higher than 35. The grown AlInP epilayer's aluminum content was changed only by changing the input TMAI flux ratio, $\text{TMAI}/(\text{TMAI}+\text{TMin})$.

Figure3-10 shows the measured Al solid composition of the grown AlInP epilayer versus the input gas-phase ratio of TMAI, $\text{TMAI}/(\text{TMAI}+\text{TMin})$, during the MOVPE growths. It shows that the Al solid composition in the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer increases linearly from 0.38 to 0.56 while the gas-phase ratio of TMAI changes from 0.29 to 0.42. The linearly relationship between the grown film's solid composition and the gas-phase ratio of MO source indicates that the growth is with the mass-flow control.⁸

Figure3-10: The aluminum solid composition of $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayers versus the input TMAI gas-phase ratio, $\text{TMAI}/(\text{TMAI}+\text{TMIn})$, during the MOVPE growths. The growth temperature was set at 630°C .

Under the mass flow control growth conditions, the partial pressure of phosphorous source inside the reactor is extremely high compared with those of group III components, and the input vapor is highly supersaturated.⁸ Thus, the partial pressures of both group III components at the liquid-solid interface are nearly zero. Theoretically, all the group III atoms reaching the growing solid surface are incorporated. The solid composition of group III (Al or In) element is proportional to the rate of mass transport of each group III element to the growth interface. Therefore, the Al solid composition showed a linear relationship to the gas-phase ratio of TMAI, as displayed in Figure3-10.

3.3.3 Effect of the Input V/III Ratio

In MOVPE growths of III-V semiconductor alloys, the input V/III ratio,

normally referred to as simply the V/III ratio, is the ratio of total input group V element source flux to the total group III element sources flux. The input V/III ratio during the MOVPE growth is very important to the grown epilayer's properties and crystal quality.²¹ In this section, effect of the V/III ratio to the aluminum incorporation of the grown AlInP epilayer has been investigated. The AlInP epilayers were grown with different input V/III ratio while the other growth conditions were kept unchanged.

Figure3-11: The aluminum solid composition of the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer versus the V/III ratio during the MOVPE growth. The growth temperature was set at 630 °C.

Figure3-11 shows the dependence of the measured aluminum compositions in the grown $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayers changes with the input V/III ratio during the MOVPE growths. All the samples shown in Figure3-11 were grown at 630 °C and the input group III gas-phase ratio of $\text{TMAI}/(\text{TMAI}+\text{TMin})$ was kept at value of 0.35.

It was found that the Al solid composition of the grown AlInP epilayer decreases from 0.48 to 0.34 when the V/III ratio increases from 34.5 to 45.0. This indicates that the Al incorporation efficiency of the MOVPE growth of AlInP alloy decreases with

the increase of the V/III ratio.

The effect of the V/III ratio on the Al incorporation in the MOVPE growth of AlInP epilayer is attributed to the growth mode transition. It has been reported that the epitaxial growth mode of MOVPE growth changes from quasi-2D to 3D mode depending on the growth conditions, such as V/III ratio and growth temperature.⁹ By increasing the V/III ratio during the MOVPE growth process, mass-transport on the growth surface and, hence, the adatoms' surface migration length are reduced.⁸

The reduction of the surface migration length prevents the growing surface reaction from reaching equilibrium and consequently reduced the formation of 3D In-rich clusters. Reduction of the number of 3D In-rich clusters formation increases the density of indium adsorption centers on the growth surface which enhances the indium incorporation into the grown AlInP film. The enhancement of In incorporation reduces the Al atoms being trapped in surface adsorption sites. This results in the decrease of the Al solid composition in the AlInP layer.

3.4 Summary

In this chapter, high-quality AlInP films were grown successfully by MOVPE using TBP in pure N₂ ambient. The aluminum incorporation in the Al_xIn_{1-x}P epilayers during the MOVPE growth was investigated. It was observed that when TMAI gas-phase ratio was kept unchanged, the Al solid composition in Al_xIn_{1-x}P films increased with the increase of the growth temperature from 610 to 660 °C, and it saturated at the growth temperature higher than 660 °C. This was attributed to the integrated influence of TMAI decomposition, indium re-evaporation and the lattice

mismatch between the AlInP epilayer and the GaAs substrate. When grown at a constant temperature of 630 °C, the Al solid composition of the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer increased linearly with the TMAI gas-phase ratio: $\text{TMAI}/(\text{TMAI}+\text{TMIIn})$. The effect of the V/III ratio on Al incorporation in the AlInP film was also studied. The aluminum solid composition was found to decrease with the increase of the V/III ratio at the growth temperature of 630 °C.

The kinetics of aluminum incorporation during the MOVPE growth of $\text{Al}_x\text{In}_{1-x}\text{P}$ has been studied using a theoretical model based on MMAI surface adsorption trapping. By using this model, it has been demonstrated that the aluminum composition of $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayers increased linearly with the $\text{TMAI}/(\text{TMAI}+\text{TMIIn})$ source flow ratio in MOVPE growth. The ratio of the incorporation coefficient between 630 °C and 610 °C was theoretically calculated. The calculated result agreed well with the experimental result. The results are useful to precisely control the aluminum composition in MOVPE growths of high quality $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayers.

3.5 References

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4 CuPt-B Atomic Ordering in AlInP Grown by MOVPE

In this chapter, spontaneous CuPt-B atomic ordering in the MOVPE grown AlInP epilayers are studied and the changes of the atomic ordering of the epilayers after the post-growth processing, e.g. rapid thermal annealing (RTA) and exposing to the inductive coupling plasma (ICP), have also been investigated. The polarized Raman spectroscopy of the atomic ordered AlInP epilayers are investigated.

4.1 Introduction

4.1.1 Mechanism of CuPt Atomic Ordering

Figure 4.1 shows schematically the lattice structure of a III-V semiconductor, $A_xB_{1-x}C$, with the CuPt-B atomic ordering in the $[-111]$ direction. In the diagram, directions of $[-111]$ and $[1-11]$ are two of the four equivalent $\langle -111 \rangle_B$ directions ($[-111]$, $[1-11]$, $[11-1]$, and $[-1-1-1]$) in the zincblende structure of the III-V semiconductor alloy. We call these $[-111]$ and $[1-11]$ directions, the B_+ and B_- directions, respectively, or B directions for both. Similarly, the $[11-1]$, and $[-1-1-1]$ are called A_+ and A_- directions, or A for both. The CuPt ordering structures along the B_+ (A_+) and B_- (A_-) direction are called B_+ (A_+) and B_- (A_-) variants, respectively, or B (A) variants for both.

Figure 4-1: Structure models of CuPt-type atomic ordering in a III-V alloy $A_xB_{1-x}C$. Light purple balls indicate group V atoms. Orange and gray balls indicate group III₁(A) and group III₂(B) atoms. It illustrates the CuPt-B atomic ordering in which A and B atoms distribute alternatively in $[-111]$ direction.

The existence of B variants with non-existence of ‘A’ variants is called ‘BA asymmetry’. The BA asymmetry is a characteristic feature of CuPt-B ordering,^{1,2} indicating that the CuPt-B ordering is surface-induced because all four variants of CuPt ordering would be equally expected if the ordering occurs in the bulk of the layers. Moreover, the evidence for monolayer abrupt changes in the ordering structure along the [001] direction such as APBs and order-twin boundaries were observed in the diffraction patterns,³ also suggests that the ordering is induced at the surface during growth. In addition, theoretical calculation shows that the CuPt-B type atomic ordering in a III-V semiconductor alloy is thermodynamically unstable.⁴⁻⁷ All of the above information leads us to relate the

CuPt-B atomic ordering in III-V semiconductor alloys to the surface process during an epitaxial growth.

Later, the theoretical calculations demonstrate that the presence of dimer bonds at the reconstructed growth surfaces plays a key role in the formation of the CuPt-B atomic ordering.⁸ For the most commonly observed $(2 \times n)$, typically (2×4) , reconstruction on group V-terminated (001) surfaces, the valence force field (VFF) calculations indicate that the B variants of the CuPt structure with ordering on (-111) and (111) planes are the most stable in the layers just beneath the (001) surface. These calculations are in good agreement with the experimental observations.^{9,10}

It is believed that during the MOVPE growth of III-V alloys, the growth surface normally terminates with group V atoms.¹¹ On a (001)-oriented surface, two of the four sp^3 bonds of the group V atom bond with the group III atoms which are in the bulk alloy, the other two are unsatisfied and are described as ‘dangling bonds’. Figure 4-2(a) schematically shows a (001)-oriented surface terminated with P atoms with two dangling bonds. However, both theoretical calculations¹² and experimental results^{13,14} suggest that this dangling-bond state is unstable. Moreover, the surface atoms tend to rearrange to achieve a lower surface energy by reducing the number of dangling bonds as well as the bonding geometries, which corresponds to the process of surface reconstruction. In recent years, first-principle calculations have shown the details about the way in which surface reconstruction might occur.¹²

Figure4-2: Schematic of CuPt-B ordering mechanism: (a) Group V atoms terminated surface with each surface atom having two dangling bonds; (b) Surface energy minimization induced group V dimer formation and (2x4) surface reconstruction; (c) CuPt-B ordering formation with group III atoms distribute periodically in the [-111] direction driven by the surface reconstruction induced subsurface stress.

Figure4-3 schematically shows the (2×4) surface reconstruction during the MOVPE growth of GaAs. Here, (2×4) surface reconstruction refers to the periodicity of the (001) surface in the two $\langle 110 \rangle$ directions orthogonal to the (001) growth axis.¹¹ It can be seen from Figure4-3 that in the (2×4) reconstruction, three of the four sites in a unit cell of the growing epilayer's lattice are occupied by the $[1-10]$ group V dimers (As-As dimer for GaAs, P-P dimer for AlInP). The $[110]$ rows of $[1-10]$ oriented group V dimers distribute on the (2×4) reconstructed surface.

Figure4-3: Models for (2×4) surface reconstruction on (001) -oriented III-V alloy.

For the convenience of the following discussion, we adopt the convention that the surface atom layer during growth is layer one, the first subsurface layer is layer two, the second subsurface layer is layer three, etc. as shown in Figure4-2(b). The formation of dimers of group V atoms on the growth surface introduces the subsurface stresses in III-V semiconductor alloys. With the presence of the subsurface stresses, atomic sites in layer three and layer four are segregated alternately into two types: one is under compression and is directly below the dimers; the other is under tension or

dilated and is below the gaps between dimers along the [1-10] direction, as shown in Figure4-2(b). For the epitaxial growth of AlInP in which the group III atom sizes are different, indium atoms with the larger atom size tend to diffuse to and occupy the [110] direction rows in layer four under tension stress, while the aluminum atoms with the smaller size will diffuse to and occupy the [110] rows of sites under compression in the layer four.

This segregation between Al and In atoms, which profits from the formation of the group V dimers on the growth surface, makes it possible to incorporate the different-sized group III atoms beneath the reconstructed surface, and therefore minimizes the strain energy. For example, during a epitaxial growth of GaInAs with (2×4) surface reconstruction, VFF calculations show that the preferential occupation of the [110] rows of atomic sites which are beneath the gaps between dimers by the larger In atoms reduces the strain energy by ≈ 100 meV/dimer site over the less favorable arrangements.¹⁵ This is necessary for an ordered sub-plane along [1-11] direction observed in CuPt-B type atomic ordering structure. Since the diffusion coefficient of group III atoms in bulk alloys is very low,¹¹ disordering of the meta-stable CuPt-type atomic ordering in the bulk alloy during the following growth process is kinetically suppressed. Thus the surface dimers induced CuPt-B atomic ordering will be frozen into the bulk III-V alloy, as shown in Figure4-2(c).

4.1.2 Effect of CuPt Ordering on the Bandgap of III-V Alloys

As shown in Figure 4-1, an extra periodicity in the sub-planes of group III atoms is introduced in along the [1-11] direction of a CuPt-B ordered III-V alloy's lattice structure. Because of the extra periodicity of the lattice structure, unit cell size of an

ordered alloy is doubled, the Brillouin zone of the alloy's lattice is reduced by half in the reciprocal space, and its point-group symmetry reduces from T_d to C_{3v} .¹⁶ Furthermore, in an ordered alloy's lattice, two zinc-blende $\mathbf{k}$ -points (and states associated with them) fold into a single $\mathbf{k}$ -point in the CuPt-B Brillouin zone. The folded states that have the same superlattice symmetry interact with each other. This coupling leads to a series of changes in the optical properties of the alloys near the band edge.^{17,18} In this section, the bandgap energy reduction in a CuPt-B type ordered III-V alloy is introduced.

Figure4-4 shows the energy band structure near the band edge of a disordered zinc-blende III-V alloy (left) and a CuPt ordered III-V alloy (right). The states at $\bar{\Gamma}$ of an ordered alloy are constructed from the states at Γ and L^{11} of a disordered alloy.¹⁷ The coupling between the $\bar{\Gamma}_{3v}(\Gamma_{15v})$ and $\bar{\Gamma}_{3v}(L_{3v})$ states and the coupling between the $\bar{\Gamma}_{1c}(\Gamma_{1c})$ and $\bar{\Gamma}_{1c}(L_{1c})$ states causes the alloy's valence band maximum (VBM) shift upwards and its' conduction band minimum (CBM) shift downwards.¹⁸ The Γ_{15v} state splits into $\bar{\Gamma}_{3v}(\Gamma_{15v})$ and $\bar{\Gamma}_{1v}(\Gamma_{15v})$ while the Γ_{1c} splits into $\bar{\Gamma}_{1c}(\Gamma_{1c})$ and $\bar{\Gamma}_{1c}(L_{1c})$ in an ordered alloy. This results in a splitting at the VBM and a lowering of the bandgap relative to that of the disordered alloy, as shown in Figure4-4.

The bandgap reduction of a CuPt-B ordered III-V alloy relative to a disordered one can be written as:¹⁷

$$\Delta E_g(\eta) = E_g(\eta) - E_g(0) \quad (4-1)$$

where η is the ordering degree of the alloy. For a completely ordered alloy, $\eta=1$, and $\eta=0$ corresponding to a totally disordered alloy.

Figure 4-4: Schematic plot of the band structures near the band edge for (left) disordered zinc-blende III-V alloy and (right) CuPt-type ordered III-V alloy. E_{gd} and E_{go} are the bandgap energy of disordered and ordered alloy respectively.

The valence-band splitting in a CuPt ordered III-V alloy can be described by:

$$\Delta E_{12}(\eta) = E_1(\bar{\Gamma}_{4,5v}) - E_2(\bar{\Gamma}_{6v}^{(1)})$$

$$\Delta E_{13}(\eta) = E_1(\bar{\Gamma}_{4,5v}) - E_2(\bar{\Gamma}_{6v}^{(2)}) \quad (4-2)$$

where $|1\rangle = \bar{\Gamma}_{4,5v}$ is a heavy hole $\left|\frac{3}{2}, \frac{3}{2}\right\rangle$ state, $|2\rangle = \bar{\Gamma}_{6v}^{(1)}$ and $|3\rangle = \bar{\Gamma}_{6v}^{(2)}$ states are mixtures of the light hole $\left|\frac{3}{2}, \frac{1}{2}\right\rangle$ and split-off $\left|\frac{1}{2}, \frac{1}{2}\right\rangle$ states. $\bar{\Gamma}_{6c}\left|\frac{1}{2}, \frac{1}{2}\right\rangle$ is the conduction band minimum at Γ .

Based on the quasi-cubic model,¹⁹ the valence-band splitting at the top of the valence band of a CuPt ordered III-V alloy can be written as:

$$\Delta E_{12}(\eta) = \frac{1}{2}[\Delta_{so}(\eta) + \Delta_{cf}(\eta)] - \frac{1}{2} \left\{ [\Delta_{so}(\eta) + \Delta_{cf}(\eta)]^2 - \frac{8}{3} \Delta_{so}(\eta) \Delta_{cf}(\eta) \right\}^{1/2}$$

$$\Delta E_{13}(\eta) = \frac{1}{2}[\Delta_{so}(\eta) + \Delta_{CF}(\eta)] + \frac{1}{2} \left\{ [\Delta_{so}(\eta) + \Delta_{CF}(\eta)]^2 - \frac{8}{3} \Delta_{so}(\eta) \Delta_{CF}(\eta) \right\}^{1/2} \quad (4-3)$$

where $\Delta_{so}(\eta)$ is the spin-orbit splitting and $\Delta_{CF}(\eta) = \bar{\Gamma}_{3v} - \bar{\Gamma}_{1v}$ is the ordering-induced crystal field splitting in the absence of spin-orbit coupling.

The quantities of the ordering degree that are accessible experimentally are $\Delta E_{12}(\eta)$, $\Delta E_{13}(\eta)$, and $\Delta E_g(\eta)$ for a partially CuPt-type ordered III-V alloy and for a disordered alloy. These values can be used to derive:

$$\begin{aligned} \Delta_{so}(\eta) - \Delta_{so}(0) &= [\Delta_{so}(1) - \Delta_{so}(0)]\eta^2 \\ \Delta_{CF}(\eta) &= \Delta_{CF}(1)\eta^2 \\ \Delta E_g(\eta) &= \Delta E_g(1)\eta^2 \end{aligned} \quad (4-4)$$

However, since a completely CuPt-ordered ($\eta = 1$) alloy is very difficult to realize and the CuPt ordering degree η of a given sample usually cannot be determined from any measurement independently, one cannot find $\Delta_{so}(1)$, $\Delta_{CF}(1)$, and $\Delta E_g(1)$ by this fitting procedure either.²⁰ But Equation (4-4) shows that the bandgap reduction of a CuPt-type ordered alloy is proportional to the square of the CuPt ordering degree of the alloy. By experimentally measuring $\Delta E_g(\eta)$, the ordering degree of a III-V semiconductor alloy may be determined.

4.2 CuPt-B Ordered AlInP Alloy Grown by MOVPE

In this section, a systematic study of the effects of the MOVPE growth conditions on the spontaneous CuPt-B atomic ordering in the grown AlInP epilayers is carried out. Changes of the ordering degree of the AlInP epilayers through the post-growth

processes: rapid thermal annealing (RTA) and exposure to inductive coupling plasma (ICP) have also been investigated.

4.2.1 Growth Temperature Effect

It has been observed that the spontaneous atomic ordering of the grown semiconductor alloys depend on the epitaxial growth conditions. In this investigation, the dependence of the CuPt-B ordering in the AlInP epilayer on the growth temperature has been studied. Three AlInP samples, S1, S2 and S3, were grown for this study. The reactor pressure was set at 20mbar during all the MOVPE growths. Sample S1 was grown at 580 °C. Sample S2 and S3 were grown at 630 °C and 720 °C, respectively.

Figure4-5 shows the (a) XRD rocking curves and (b) the PL spectra of the three as-grown samples. Aluminum solid composition of the three AlInP samples were calculated based on the XRD results by using Vegard's law. The aluminum compositions are 0.42, 0.41, and 0.42 for sample S1, S2 and S3, respectively. The broad FWHM of sample S1's PL spectrum shows the poor crystal quality of the epilayer because of the low growth temperature.²¹

The bandgap energy of a relaxed disordered $\text{Al}_x\text{In}_{1-x}\text{P}$ alloy can be calculated by using equation:²²

$$E_g = 1.35 + 1.83x + 0.38x^2 \quad (4-5)$$

where x is the aluminum solid composition of the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer.

(a)

(b)

Figure 4-5: (a) X-ray double crystal rocking curves (004) and (b) PL spectra at 77 K from $\text{Al}_x\text{In}_{1-x}\text{P}$ films grown at 580 °C (S1), 630 °C (S2), and 720 °C (S3).

Using the above formula, the bandgap energy of the samples S1, S2 and S3 are calculated as 2.18eV, 2.16eV, and 2.18eV, respectively.²² However, as shown in Figure 4-5(b), the measured PL emission peak energy of the sample is smaller than the calculated bandgap energy of the AlInP alloy by using Equation (4-5). The PL emission-peak energies of the samples have large red-shifts from the calculated bandgap energies, which corresponds to bandgap energy reduction of the AlInP

epilayers. Figure4-6 shows the bandgap energy reduction of the AlInP epilayers versus the sample's growth temperature. The maximum bandgap energy reduction has been measured up to 260 meV for the sample S2 grown at 630 °C.

Figure4-6: PL red-shift between the calculated AlInP bandgap and the PL peak at 77 K versus growth temperature (T_g) of S(1), S(2) and S(3) is shown as solid square. PL blue-shift between the PL peak of as grown AlInP and the PL peak of AlInP after RTA is shown as solid dot. Inset shows the AlInP growth rate versus growth temperature from 630 to 720 °C.

The energy bandgap reduction measured from the PL peak red-shift of the AlInP epilayer is attributed to the CuPt-B type atomic ordering in the AlInP epilayer's lattice structure.²³ It is described in Section 4.1.2 that the bandgap energy of an ordered III-V ternary alloy, $A_xB_{1-x}C$, changes with its atomic ordering degree, η , which can be expressed by:²⁴

$$E_g(x, \eta) = E_g(x, 0) - \eta^2 [E_g(x, 0) - E_g(x, 1)] \quad (4-6)$$

where $E_g(x, 0)$ is the bandgap energy of the disordered III-V alloy, while $E_g(x, 1)$ is the bandgap energy of the perfectly ordered III-V alloy. The higher the degree of order is, the smaller the energy bandgap of the material is.

As shown in Figure4-6, an upside down “U” curve has been observed for the

bandgap energy reduction of the sample versus the MOVPE growth temperatures. The degree of CuPt atomic order of the grown AlInP epilayer increases when the growth temperature is increased from 580 to 655 °C. However, the degree of order is reduced with the further increase of the growth temperature from 655 to 720 °C.

When the growth temperature reduces from 655 to 580 °C, there are two factors may cause the reduction of the degree of the CuPt-B order of the grown AlInP epilayer.²⁵

First, when the growth temperature is lower, the diffusion coefficient of atoms on the growth surface is reduced.²⁶ During the MOVPE growth of the AlInP alloy, the growing top surface is terminated by group V atoms, phosphorus (P), as shown in Figure4-2(a). Each P atom has two dangling bonds. The state with two dangling bonds is not stable.²⁶ Two adjacent P atoms on the top surface can be bonded together to form a P-P dimer in order to reduce the surface energy, as shown in Figure4-2(b). The [110] rows of [1-10] oriented P-P dimers which form the (2×4) reconstruction which results in the alternating [110] rows of compressive and tensile strain in the 3rd buried layer (the top surface is assigned as 1st layer). This will generate the [110] rows of alternating group III atoms and the CuPt-type variants are formed in the lattice as shown in Figure4-2(b).²⁷ In this case, the (2×4) surface reconstruction induced by the P-P dimers plays a key role for the formation of CuPt-B atomic ordering in the AlInP epilayer during MOVPE growths.

It is known that during an epitaxial growth, the surface diffusion coefficient is proportional to the growth temperature.¹¹ When the growth temperature is lower, such as 580 °C, some P adatoms on the growth surface may not be able to move close to each other to form the P-P dimers due to the low diffusion coefficient, which causes

the decrease of the number of the P-P dimers formed on the growing surface. Thus, the driving force to reallocate the group III atoms (Al and In) at 3rd sub-layer to form [-110] oriented periodic structure is reduced, resulting in the reduction of the degree of CuPt-B atomic order in the grown AlInP epilayer.

The second possible cause of the reduction of the grown epilayer's ordering with the lower growth temperature is related to the (4×4) (or (2×2)) surface reconstruction during the MOVPE growth of AlInP. Since there is a competition between the (4×4) and the (2×4) surface reconstruction, occurrence of (4×4) surface reconstruction may reduce the possibility of the (2×4) surface reconstruction during the growth. An isotropic surface photoabsorption (SPA) peak at 480nm is observed besides the anisotropic peak at 400nm from the GaInP epilayer when the growth temperature decreases from 620 to 520 °C.²⁸ The anisotropic peak at 400nm indicates the (2×4) surface reconstruction which consists of [-110] oriented P-P dimers during the epitaxial growth. However, the anisotropic peak at 480nm indicates the (4×4) reconstruction surface covered by [110] oriented P-P dimers. Both the isotropic and anisotropic SPA peaks show that not only the (2×4) but also the (4×4) surface reconstruction, which resulted from the P-P dimers, exist on the growth surface at a lower growth temperature.

Moreover, theoretical calculations show that the (4×4) surface reconstruction on the growing surface favors the CuPt-A atomic ordering in the grown epilayer.⁷ So, the CuPt-A atomic ordering may be expected in the sample S1 if the (4×4) surface reconstruction happens during the epitaxial growth. In order to check whether the (4×4) surface reconstruction occurred during the MOVPE growth of sample S1, we took the [-110] zone TED of sample S1 which was grown at 580 °C.

Figure4-7: (a) $[110]$ zone TED pattern of S2 grown at 630°C. Extra diffraction spots indicate superstructures caused by the CuPt-B ordering. (b) $[-110]$ zone TED pattern of S1, grown at 580 °C. No extra diffraction spot corresponding to CuPt-A type ordering.

Figure4-7(a) shows the $[110]$ zone transmission electron diffraction (TED) of S2 and Figure4-7(b) shows the $[-110]$ zone TED of S1. It is noticed that in addition to the normal diffraction pattern of the f.c.c. structure, extra superstructure diffraction spots (indicated by arrows) are observed in the TED pattern, which is believed to be induced by the CuPt-B atomic ordering in the epilayer's lattice structure of the sample S2.

As shown in Figure 4-7 (b), no extra superlattice spots either at $(1/2, 1/2, 1/2)$ or $(-1/2, -1/2, 1/2)$ position is observed from the TED of sample S1, which indicates no CuPt-A ordering variants in the grown AlInP epilayer.²⁹ This confirms that there is no (4×4) surface reconstruction formation during the MOVPE growth of the sample S1. Only the (2×4) surface reconstruction happened in the MOVPE growth. Therefore, there are only CuPt-B variants of atomic ordering in the sample S1.

The reduction of the degree of CuPt-B atomic order with the decreasing of the growth temperature from 630 to 580 °C is mainly caused by the lower surface diffusion coefficient of the P adatoms. At the lower growth temperature, the lower surface diffusion coefficient of P adatoms produces fewer P-P dimers formed on the epitaxial growth surface, which results in the reduction of the degree of atomic order of the grown AlInP epilayer consequently.

As shown in Figure 4-6, the degree of the CuPt-B order of the AlInP epilayers decreases when the growth temperature increases from 655 to 720 °C. This is because of the higher growth rate when the substrate temperature is increased.

The inset in Figure 4-6 shows the MOVPE growth rate of the AlInP epilayers versus the growth temperature while the input group III fluxes were kept unchanged. The MOVPE growth rate of AlInP increases from 0.58 to 0.87 $\mu\text{m/h}$ when the substrate temperature is raised from 630 and 720 °C. The average growth time for growing one atomic layer of AlInP is reduced around 33% by increasing the growth temperature from 630 to 720 °C. Due to the higher MOVPE growth rate, some P adatoms are incorporated into the grown epilayer and covered by the adatoms for the following growing layers. The P adatoms have less time to move around to form the $[-110]$ oriented P-P dimers and the (2×4) reconstructed surface. Some P adatoms may

have been incorporated in the epilayer and covered by the following atomic layers before they reconstruct. With less P-P dimers on the growing surface, the degree of order decreases consequently with the increase of the growth temperature.

4.2.2 The V/III Flux Ratio Effect

In order to investigate the grown AlInP epilayer's atomic ordering changes with the input V/III ratio during the MOVPE growth, the V/III ratio was changed from 20 to 80 with an increasing step of 20. So there are four samples to be used to study the effect of the input V/III ratio on the CuPt-B atomic ordering of grown AlInP epilayers: samples S4, S5, S6, and S7 were grown with the input V/III ratio set at 20, 40, 60, and 80 respectively. The reactor pressure for all the growth was set at 20mbar. In order to obtain the highest CuPt-B atomic ordering degree in the AlInP, the growth temperature was set at 630 °C for all of the four samples.

Based on the XRD measurement results, the aluminum solid composition of sample S4, S5, S6 and S7 are calculated by using Vegard's law as 0.40, 0.43, 0.41 and 0.42, respectively. With these aluminum compositions, the energy bandgap of the sample S4, S5, S6 and S7 are calculated as 2.14eV, 2.20eV, 2.16eV and 2.19eV, respectively.³⁰ The results show that sample S5 with the highest Al solid composition should have the widest bandgap. However, as shown in Figure4-8, the PL emission-peak energy of sample S7 was the maximum and sample S6 had the minimum bandgap energy. Moreover, the measured PL emission-peak energies were all much smaller than the calculated bandgap energy of the samples by using Equation (4-5). The value of x in Equation (4-5) is the Al solid composition of the epilayer measured by using XRD. This discrepancy, which is between the measured PL peak

emission energy and the calculated epilayers' bandgap energy based on the XRD result, is attributed to the bandgap reduction induced by the CuPt-B type atomic ordering in AlInP.²³

Figure4-8: PL spectra at 77 K of $\text{Al}_x\text{In}_{1-x}\text{P}$ films grown with V/III of 20, 40, 60, and 80 on GaAs (001) substrates.

Figure4-9 shows (a) the [110] direction TED pattern and (b) the high resolution (HR) TEM image taken from the sample S6. Besides the fundamental diffraction spots from the zincblende lattice structure of the disordered AlInP epilayer, superstructure diffraction spots from $(-1/2, 1/2, 1/2)$, $(1/2, -1/2, 1/2)$, and equivalent positions were also observed in the TED pattern. The superstructure diffraction spots are demonstrated by arrows in Figure4-9(a). These spots indicated the CuPt-B atomic ordering in sample S6 in which the periodicities in the real space along $[-111]$ and $[1-11]$ directions were doubled. This is similar to the so-called double-variant CuPt-B atomic ordering (with both $[-111]$ and $[1-11]$ variant) structure in the GaInP epilayer.³¹ The elongation of the ordering-induced diffraction spots may be caused by the

imperfect (or partial) spatial periodicity of the lattice structure and domain boundaries induced by CuPt-B atomic ordering in the AlInP epilayer.³² This correlation was supported by the HR TEM image of S6 shown in Figure4-9 (b).

Figure4-9: (a) $[110]$ cross section TED pattern and (b) high resolution TEM image of AlInP sample S6. The arrows in (1) indicate the extra superstructure diffraction spots caused by CuPt-B atomic ordering.

Figure4-10: The bandgap energy reduction of AlInP induced by the CuPt-B ordering versus the V/III ratio during MOVPE growth.

In Figure4-9(b), the double periodicity in $[-111]$ and $[1-11]$ directions were clearly seen in area (A) and area (B). However, the AlInP epilayer contained more microstructure patterns than these two. There were also area (C) where no ordering structure occurs and area (D) where both $[-111]$ and $[1-11]$ oriented ordering structures coexist.

Moreover, in a partial CuPt-type ordered AlInP epilayer, the $(-1/2, 1/2, 1/2)$ or $(1/2, -1/2, 1/2)$ lattice plane does not contain aluminum atoms only or indium atoms only, but is aluminum-rich or indium-rich. Even the distribution of such aluminum-rich or indium-rich plane is not uniform in the AlInP epilayer. Therefore, both the imperfect CuPt-type ordering and the non-uniform distribution contribute to the elongation of the extra diffraction spots.³³

Figure4-10 plots the measured bandgap reduction of the as-grown AlInP

epilayers versus the input V/III ratio during MOVPE growth. It is clearly shown that the degree of the CuPt-B order increased when the V/III ratio was increased from 20 to 40 during the epitaxy growths. The degree of the CuPt-B order decreased when the V/III ratio during the growth further increased from 60 to 80. The fitting curve shows a downward parabolic relationship between the degree of order of the grown AlInP epilayer and the V/III ratio during MOVPE growths. The AlInP epilayer was expected to achieve the maximum degree of order when the V/III ratio is around 53.

Figure4-11: Terrace reconstruction model of the (2×4) reconstructed AlInP [001] oriented surface projected on [110] plane.

As mentioned in Section 4.1, each P atom has two dangling bonds on the group V atom terminated surface during the MOVPE growth of the AlInP alloy. This state with two dangling bonds is unstable and the surface energy will be reduced by forming [110] rows of [-110] oriented P-P dimers.³⁴ The P atoms terminated surface form the (2×4) surface reconstruction, as schematically shown in Figure4-11. The

[110] rows of [-110] oriented P-P dimers result in alternating [110] rows of Al and In atoms in the layer beneath. The driving force of this unique structure is the accommodation of the two group III atoms with the minimum strain energy. The consequence of it is the formation of the CuPt-B atomic ordering in the epitaxial AlInP layer. By theoretical calculation and also using the surface photo absorption (SPA) technique which measures the surface structure, the close correspondence between the formation of [-110] oriented group V dimers and the CuPt-B atomic ordering in GaInP layers have been clearly demonstrated.^{35,36} It shows that group V dimer and surface reconstruction structure on the top surface during III-V alloy growth are very critical for the formation of the ordering structure.³⁷

During the MOVPE growth of the AlInP sample with V/III ratio at 60, the MO source flow rate of group V element provided enough P atoms to form P-P dimers on the growing surface. When the group III atoms (aluminum and indium) arrive on the surface, they may be physically absorbed into the absorption sites. Then they move and diffuse further to form alternative aluminum and indium rows in [-110] direction after the surface reconstruction formation on the next group V top surface layer.

When the V/III ratio (or the group V partial pressure in this study) was reduced in the MOVPE growth, the surface coverage of P atoms decreased accordingly. When the surface coverage of P atoms decreases to certain level that there are insufficient P atoms to form P-P dimers, the ratio of P-P dimers to the overall P atoms on the growth surface will decrease.³⁵ Without the driving force to distribute Al and In atoms alternatively in the [-110] direction, more and more group III atoms would be absorbed with P atoms randomly. The atomic ordering degree in the AlInP epilayer was reduced accordingly.

As shown in Figure 4-10, the bandgap energy reduction of the grown AlInP epilayer decreased from 266 to 182 meV when the V/III ratio was reduced from 60 to 20 in the MOVPE growths. However, when the V/III ratio was increased from 60 to 80, the degree of order for the grown epilayer reduced. This was because the group III atoms' diffusion coefficient is reduced when the V/III ratio is too high. The higher group V partial pressure and excess P-P dimers on the growth surface may result in such a decrease of diffusion coefficient.¹¹ In this case, even though there are sufficient P-P dimers on the growth surface, the group III atoms, Al and In, do not have enough time to diffuse to the lower energy configuration, which forms the ordered structure in the AlInP alloy. Therefore, the reduction of Al and In adatoms' diffusion coefficient under the higher V/III ratio prevented Al and In adatoms from distributing alternately along $[-110]$ direction and forming the CuPt-B atomic ordering structure. Consequently, the degree of order for the AlInP sample decreased with the higher V/III ratio, such as 80 in this study.

4.2.3 Effect of the Growth Rate

As introduced in Chapter 2, the mechanisms of MOVPE growth include thermodynamics and kinetics. In Section 4.2.1 we have discussed the effects of thermodynamic factors on the CuPt-B ordering in the grown AlInP epilayer during MOVPE growths. In this section, the effect of dynamic factor, material growth rate, on the CuPt-B atomic ordering in AlInP epilayers grown by MOVPE will be discussed.

It is known that the diffusion coefficients of group III atoms in a bulk III-V material are quite low.³⁷ The group III atoms rearrangement from the random

distribution given by incident precursors to the ordered structure must occur on the growth surface or subsurface during the MOVPE growth. Since the kinetic components, which defines the rates at which the various steps occur, control the rate of reaction on the growing surface and the physical surface process, the kinetic factors, such as growth rate, are expected to have important influences on the microstructure of atoms on the growth surface, and also the arrangement of atoms in the epitaxial layers.³⁸

Two groups of the AlInP samples, group A and group B, were grown for this study. Each group has three AlInP samples, which were grown at different temperatures: 630 °C, 680 °C, and 720 °C, respectively. The difference between group A and group B is the growth rate. The reactor pressure was set at 20mbar for all the growths. The AlInP material growth rate was changed by adjusting the flow rate of the input group III sources during the MOVPE growth. The group A, which contains samples S8, S9, and S10, were grown with the low growth rate and were grown at 630, 680, and 720 °C, respectively. The group B, which contains samples S11, S12, and S13, were grown with high growth rate and the growth temperatures were set at 630, 680, and 720 °C, respectively. The total flow rate ratios of group III MO sources between the group B (with higher rate) and the group A (with lower growth rate) were 1.94, 1.95, and 1.98 with the growth temperature of 630, 680, and 720 °C, respectively. The group V source flow rate was raised accordingly when the input group III source flow rate was increased so as to keep the V/III ratio for the MOVPE growth around 40 to 45.

The epitaxial film thickness was measured by using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The growth rate was

then calculated by the film thickness divided by the growth time. The measured growth rates for S8, S9 and S10 were 0.63, 0.93, and 1.13 $\mu\text{m/h}$, respectively. The measured growth rate S11, S12 and S13 were 0.90, 1.22, and 1.72 $\mu\text{m/h}$, respectively.

Figure4-12: PL spectra at 77 K of AlInP epilayers with different growth rates. S8 and S10 were grown with lower growth rate, S11 and S13 were grown with higher growth rate. S8 and S11 were grown at 630 °C. S10 and S13 were grown at 720 °C.

The measured low temperature PL spectra of the AlInP epilayers grown with different growth rates at different temperatures are shown in Figure4-12. It shows that the two samples with the higher growth rates (dot lines for S11 and S13) had the higher PL peak emission energy when compared with the two samples (solid lines for S8 and S10) grown with the lower growth rates at the same substrate temperature. As for the samples grown at different temperatures, we explained it by using the study result of the growth temperature effect on the ordering in AlInP in Section 4.2.1: when the growth temperature is greater than 630°C, the higher the growth temperature, the lower the degree of CuPt-B order in AlInP and the lower the value of the bandgap energy reduction caused by the CuPt-B atomic ordering is.²⁵ The lower energy

shoulder in the PL spectrum of S10 is suggested to be caused by atomic ordering. This energy shoulder disappears after the sample is disordered, having been annealed at 900°C for 30seconds.

Figure4-13: The bandgap energy reduction caused by the CuPt-B atomic ordering versus the MOVPE growth rate of AlInP. Samples indicated by squares and dots were grown at 630 °C and 720 °C, respectively.

The bandgap energy reduction induced by the CuPt-B atomic ordering versus the growth rate is shown in Figure4-13. When the growth temperature was 630°C, the bandgap energy reduction decreased from 255meV to 216meV with the sample's material growth rate increasing from 0.63 to 0.90 μm/h. The bandgap energy reduction of sample S11 which was grown at 720 °C was only 80meV because the degree of order for AlInP decreases with increasing the growth temperature,²⁵ Keeping the growth conditions of S11 unchanged except for raising the growth rate, the bandgap energy reduction induced by CuPt-B ordering of sample S13 dropped to

0meV, indicating that the degree of order of sample S13 was zero. Figure4-13 clearly reflects that the degree of order for the AlInP epilayers changed with the growth rate of MOVPE growth: the higher growth rate suppressed the ordering formation on the growth surface.

The growth rate of sample S8 was measured around 0.63 $\mu\text{m/h}$ or 1.75 $\text{\AA/s}$. During the MOVPE growth of sample S8, it takes around 3 seconds for a group III atom on the growth surface to be incorporated and form a surface atomic layer. The growth rate of sample S11 was 0.90 $\mu\text{m/h}$ or 2.5 $\text{\AA/s}$, the time for the group III atoms on the growth surface to diffuse to be incorporated before being covered by the next following layer is only about 2.1s. Keeping other growth conditions of S11 the same as those of sample S8, the group III atoms diffuse on the growth surface during growing sample S11 in a shorter time than the atoms diffuse on the surface for growing sample S8. So, the atoms may have not enough time to form the ordering structure along the $[-110]$ direction for S11. Then less CuPt-B ordered structures were formed in sample S11. Since the diffusion coefficient of atoms which locate quite far away from the surface is significantly lower than that of the top few surface layers, the surface atom arrangement may not change obviously after being merged into the bulk material.³⁹ So the less CuPt-B atomic ordered structure would be retained in the bulk AlInP layer. After the MOVPE growth was completed, the ordering degree in the AlInP film decreased correspondingly. The similar process was expected to occur in the sample S13 which was grown at 720 °C with a higher growth rate.

4.2.4 Effect of the Reactor Pressure

To study the effect of the reactor pressure during the MOVPE growth on the grown AlInP epilayer's CuPt-B atomic ordering, three groups of samples were grown with the reactor pressure setting at 20, 60, and 100 mbar, respectively. Each group consists of two AlInP samples which were grown at different temperatures: 630 and 720 °C, respectively. The samples and the corresponding growth conditions are listed in Table 4-1. Except for the growth temperature (T_g) and reactor pressure (P), other growth parameters remained unchanged.

Table 4-1: The growth conditions of AlInP samples used for study of the growth pressure effect on the atomic ordering in AlInP.

	$P = 20 \text{ mbar}$	$P = 60 \text{ mbar}$	$P = 100 \text{ mbar}$
$T_g = 630^\circ\text{C}$	S14	S16	S18
$T_g = 720^\circ\text{C}$	S15	S17	S19

Figure4-14: PL spectra at 77K of AlInP epilayers grown under different reactor pressures. The solid, dash, and dot line represent the sample under 20, 60, and 100

mbar, respectively. The upper part corresponds to the samples grown at 630 °C, and the lower part shows the results of samples grown at 720 °C.

Figure4-14 shows the low temperature PL spectra of the AlInP samples grown with different reactor pressures and at different temperatures. It shows that the PL emission peak of the grown AlInP epilayer shifted to the higher energy with the increase of the reactor pressure. The aluminum solid compositions in S15 and S19 are calculated the same: 0.420. However, the PL peaks of these two samples were different and produced a difference up to 27meV.

Figure4-15: PL red-shift value of AlInP caused by CuPt-B atomic ordering versus reactor pressure during MOVPE growth.

Figure4-15 shows the bandgap energy reduction of the AlInP samples versus the reactor pressure during the MOVPE growth. The sample's bandgap energy reduction decreased when the reactor pressure increased from 20 to 100 mbar with the growth

temperature at either 630 °C (squares) or 720 °C (dots) during the MOVPE growth.

When grown at 630 °C, the sample's bandgap energy reduction reached at about 255 meV with the reactor pressure of 20 mbar; while the bandgap energy reduction of the sample grown at the same temperature with reactor pressure of 100 mbar was 138 meV. The bandgap energy reduction induced by the CuPt-B ordering was reduced by almost 46% when the reactor pressure increased from 20 to 100 mbar at 630 °C. The bandgap energy reduction of the sample reduced from 80 to 58 meV as the reactor pressure was raised from 20 to 100 mbar with the growth temperature at 720 °C.

As discussed previously, larger diffusion coefficient, or longer diffusion length in lateral directions of the adatoms during the MOVPE growth increases the degree of order for the grown epilayer. It has been demonstrated that the higher reactor pressure reduces the diffusion length of the adatoms of the MOVPE growth in the direction parallel to the substrate surface.^{40,41} In this case, the diffusion ability of group III atoms decreased and some of group III atoms could not arrive in the minimum energy favored sites before the next layer growth commenced.

At the same time, higher reactor pressure raises the pyrolysis rate of the group V source for the MOVPE growth.⁴² With the same MO source flow rates, the V/III ratio inside the reactor under the higher reactor pressure will be higher than that with the lower reactor pressure because of the higher pyrolysis rate with the higher reactor pressure. As learned from Section 4.2.2, the degree of CuPt-B order in the AlInP epilayer decreased with the increase of the V/III ratio when the V/III ratio was larger than 53. Since the V/III ratios of all of these six samples (S14-S19) were in the range from 60 to 65, the higher V/III ratio value would depress the CuPt-B ordering formation.

Therefore, it is speculated that the decrease of the degree of order for the AlInP alloys grown with the higher reactor pressure was mainly affected by both the decreasing of diffusion length and the increasing of V/III ratio under the higher reactor pressure.

4.2.5 Effect of the Carrier Gas

In MOVPE growths, MO sources are carried out from the source containers by hydrogen or nitrogen gas into the reactor where at high temperature the MO source molecules decomposed and are incorporated into the growth material and make the epitaxy growth done. So the carrier gas plays an important role in an MOVPE growth. MOVPE pioneers normally used hydrogen (H_2) as the carrier gas because H_2 gas has high thermal conductivity, high purification, and relatively low cost.⁴³ The disadvantage of using hydrogen gas as the carrier gas is the safety concern: H_2 is explosive. In order to improve the safety in MOVPE growth, H. Hadrtdegen started using nitrogen (N_2) gas to replace the H_2 as the carrier gas for MOVPE growth in the 1990s.⁴⁴ It has been reported that less carbon concentration in epilayers by using carrier nitrogen in MOVPE growths.^{45,46} In this study, we investigate the effect of different carrier gases (H_2 and N_2) in the MOVPE growths on the CuPt-B ordering in the grown AlInP epilayers.

Two samples, sample S20 and S21, were grown in a H_2 ambient (H_2 as carrier gas) at 630 °C and 720 °C, respectively. While samples S22 and S23 were grown in a N_2 ambient and at 630 °C and 720 °C, respectively. The reactor pressure was set at 20 -mbar.

The low temperature PL spectra of these samples are shown in Figure4-16. It

can be seen that the PL peaks of the samples grown in a H_2 ambient had higher photon energy than that of those grown in a N_2 ambient at both growth temperatures of 630 °C and 720 °C. Based on the XRD results, Al solid composition of the sample S20 was calculated as the same as that of S22. The Al solid composition of sample S21 was the same as that of sample S23. So, the PL peak difference was attributed to the CuPt-B atomic ordering in the AlInP epilayers of the samples grown in different carrier gas ambient. Within the examined range of growth temperature, the degree of CuPt-B order for the AlInP layer grown in the H_2 ambient was smaller than that of the AlInP grown in the N_2 ambient.

Figure4-16: PL spectra at 77K of AlInP epilayers grown in hydrogen (dot lines) and nitrogen (solid line) ambient.

In order to understand the carrier gas effect on the CuPt-B ordering of the AlInP

epilayer, we need to know the role of carrier gas in MOVPE growth. During the MOVPE growths, carrier gas transports gas phase group III MO sources and group V sources to the reactor where both homogenous and heterogeneous reactions occur.¹¹ After the growth, both the carrier gas, side-products of reaction and un-reacted sources are all drained out from the reactor. So the properties of carrier gas, such as viscosity, density and heat conductivity, have influence on the reactions during the MOVPE growth.

Since N_2 has larger molecular weight than that of H_2 (molecular weight of 28g/mole of N_2 compared with 2g/mole of H_2), its impact number is almost seven times higher than that of H_2 .⁴³ Therefore, the group V sources decompose more completely in a N_2 ambient.⁴² More P atoms are provided on to the growth surface in a N_2 ambient compared with H_2 during the MOVPE growth. Thus there were more P-P dimers on the growth surface to facilitate the formation of atomic ordering structure by using N_2 as the carrier gas. The provision of P-P dimers prompted the CuPt-B atomic ordering formation in the AlInP epilayer. Consequently, the degree of CuPt-B order of the AlInP epilayer grown in N_2 was greater than that in the AlInP epilayer grown in a H_2 ambient, given the other growth conditions were unchanged.

4.2.6 Optimization of the Growth Conditions on Atomic Ordering in AlInP

As discussed above, more than one MOVPE growth conditions affect the CuPt-B atomic ordering in the grown AlInP epilayer. It's important to understand which growth condition parameter contributes more on the CuPt-B ordering and if there is interaction between these parameters.

Design of Experiment (DOE)⁴⁷ is a structured, organized method for determining the relationship between factors (X_s) affecting a process and the output of that process (Y). Properly designed and executed experiments will generate more-precise data while using substantially fewer experimental runs than alternative approaches. They will lead to results that can be interpreted using relatively simple statistical techniques, in contrast to the information gathered in observational studies, which can be exceedingly difficult to interpret.

Table4-2: Summary of growth conditions and bandgap reduction of AlInP samples used in the DOE analysis.

NO	Temperature (°C)	Growth Rate (µm/h)	Pressure (mbar)	Eg reduction (meV)
1	-	-	-	250
2	+	-	-	88
3	-	+	-	216
4	+	+	-	31
5	-	-	+	207
6	+	-	+	52
7	-	+	+	153
8	+	+	+	0
- : 630		- : 0.5~0.8	- : 20	
+ : 720		+ : 0.75~1.2	+ : 100	

In this section, we use DOE method to analyze the experiment data and find out the most important MOVPE growth condition parameters affecting the atomic ordering in the grown AlInP epilayer. The examined growth parameters are growth temperature, growth rate, and reactor pressure. The atomic ordering in the AlInP epilayer was characterized by the value of bandgap reduction induced by the CuPt-B atomic ordering.

Table4-2 lists the DOE table and the measured bandgap energy reduction. The growth temperature was set at 630 °C (-) or 720 °C (+). The growth rate was changed

by variation of the group III flow rate. The lower growth rate varied from 0.5 to 0.8 $\mu\text{m/h}$ and the higher growth rate varied from 0.75 to 1.2 $\mu\text{m/h}$. The reactor pressure was set at 20 mbar (-) or 100 mbar (+). The substrates were GaAs (001) and the carrier gas was pure N_2 .

In this study, we choose the bandgap reduction induced by CuPt-B ordering in the AlInP epilayer as the output, Y . The growth temperature, growth rate, and reactor pressure are the three examined factors. Here we use the ‘factorial design’⁴⁷ in which experiments are run for all combinations of levels for all of the factors. With such a study design, testing will reveal what the effect of one variable would be when the other factors are changing. The affect of each factor can be characterized by using the coefficient of main effect and coefficients of interaction effect. The DOE result is written as:⁴⁷

$$Y = Y_0 + a_1 \cdot X_T + a_2 \cdot X_P + a_3 \cdot X_V + a_4 \cdot X_P \cdot X_T + a_5 \cdot X_V \cdot X_T + a_6 X_P \cdot X_V + a_7 \cdot X_P \cdot X_V \cdot X_T \quad (4-7)$$

where

Y is the measured bandgap reduction of the grown AlInP caused by the CuPt-B atomic ordering.

X_T , X_P , and X_V represent the growth temperature, reactor pressure, and the growth rate, respectively.

a_1 , a_2 , and a_3 are the coefficient of the main effect for growth temperature, reactor pressure, and growth rate, respectively.

a_4 is the coefficient of the interaction effect between growth temperature and reactor pressure.

a_5 is the coefficient of interaction effect between growth temperature and growth rate.

a_6 is the coefficient of interaction effect between reactor pressure and growth rate.

a_7 represents the interaction effect between all the three growth parameters.

The average main effect of changing reactor pressure from low (20mbar) to high (100mbar), P_m , can be calculated as the average response at the high level (P_h) minus the average response at the low level (P_l):

$$P_m = P_h - P_l = (207+52+153+0)/4 - (250+88+216+31)/4 = -43.25$$

The main effect of growth rate (V_m) and growth temperature (T_m) can be calculated similarly:

$$V_m = V_h - V_l = (216+31+153+0)/4 - (250+88+207+52)/4 = -49.25$$

$$T_m = T_h - T_l = (88+31+52+0)/4 - (250+216+207+153)/4 = -163.25$$

The factorial design makes it possible not only to determine the main effects of each variable, but also to estimate the interaction between the two factors, or three factors. For example, the interaction effect of pressure-growth rate, $P \times V$, is the average difference between the effect of reactor pressure at the high level of growth rate and the effect of reactor pressure at the low level of growth rate:

$$P \times V = [(153+0-216-31)/2 - (207+52-250-88)/2]/2 = -3.75$$

The interaction effect of pressure-growth temperature and growth rate-temperature can also be calculated as:

$$P \times T = [(52+0-88-31)/2 - (207+153-250-216)/2]/2 = 9.75$$

$$V \times T = [(31+0-88-52)/2 - (216+153-250-207)/2]/2 = -5.25$$

The interaction effect of pressure-growth rate-growth temperature, $P \times V \times T$, is the average difference between the effect of reactor pressure-growth rate at the high level of growth temperature and the effect of reactor pressure-growth rate at the low level of growth temperature:

$$P \times V \times T = [((0-31)-(52-88))/2 - ((153-216)-(207-250))/2]/2 = 6.25$$

The output value Y_0 is the average of the bandgap reduction:

$$Y_0 = (250+88+216+31+207+52+153+0)/8 = 124$$

These constants (a_1 to a_7) are obtained from the result in Table4-2:

$$Y_0 = 124;$$

$$a_1 = T_m/2 = -81.88; \quad a_2 = P_m/2 = -21.63; \quad a_3 = V_m/2 = -24.63;$$

$$a_4 = (P \times T)/2 = 4.88; \quad a_5 = (V \times T)/2 = -2.63; \quad a_6 = (P \times V)/2 = -1.88;$$

$$a_7 = (P \times V \times T)/2 = 3.13$$

$$X_T = (T - (T_+ + T_-)/2) / ((T_+ - T_-)/2) = (2T - 1350) / 90;$$

$$X_P = (P - (P_+ + P_-)/2) / ((P_+ - P_-)/2) = (2P - 120) / 80;$$

$$X_V = (V - (V_+ + V_-)/2) / ((V_+ - V_-)/2) = (2V - 1.65) / 0.55.$$

a_1 is the biggest among the main effect coefficients of the three examined growth parameters, indicating that the growth temperature is the most important parameter among the three growth condition parameters to affect the CuPt-B atomic ordering in the grown AlInP epilayer.

Substituting the value of the constants into equation (4-7), the bandgap reduction induced by the CuPt atomic ordering in AlInP will be determined by the three MOVPE growth parameters: X_T , X_P , and X_V . For example, given the conditions of a MOVPE growth, which means the values of X_T , X_P , and X_V are fixed, the bandgap reduction induced by the CuPt ordering in AlInP can be calculated by using Equation (4-7).

4.3 Influence of Post Growth Processes on the CuPt-B Ordering in AlInP

Theoretical simulation shows that the CuPt-B atomic ordering in III-V semiconductor alloys is metastable.⁸ Under certain conditions, this metastable state in the semiconductor materials will be changed. In this section, changes of the CuPt-B atomic ordering in AlInP after gone through rapid thermal annealing (RTA) and exposing to inductive coupled plasma (ICP) has been investigated.

4.3.1 Rapid Thermal Annealing of AlInP

4.3.1.1 Changes of the CuPt ordering in AlInP after RTA

In this study, all the AlInP epilayers described were grown at 630 °C and with the reactor pressure set at 100 mbar. The V/III ratio of the source flow during the MOVPE growth was set at 40. The samples were cleaved from the same wafer and were annealed for 30 second at 610 °C, 710 °C, 900 °C, and 950 °C respectively. The annealing process was carried out in an RTA chamber with atmospheric nitrogen ambient. During the annealing process, the sample temperature was raised from room temperature to the set annealing point in 40 seconds (s), then, kept the temperature at the setting point for 30 s and cooled down the sample temperature to room temperature in 30 s. To prevent the surface evaporation of the sample during the annealing process, the sample was covered with a fresh GaAs substrate wafer.

Figure4-17 shows the measured XRD rocking curve of the as grown $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer. And the PL spectra of the sample before and after the thermal annealing are shown in Figure4-18. The Al solid composition x of the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer is calculated

as 0.38 by using Vergad's law. Using Equation (4-5), the direct bandgap energy of the disordered $\text{Al}_{0.38}\text{In}_{0.62}\text{P}$ is calculated as 2.187eV. However, the PL measurement result shows that the bandgap energy of the as grown $\text{Al}_{0.38}\text{In}_{0.62}\text{P}$ epilayer was only 1.993eV, which is around 200 meV smaller than the calculated bandgap energy. This large bandgap energy reduction of the AlInP epilayer is attributed to the CuPt-B atomic ordering.

Figure4-17: XRD rocking curve of the $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer grown on GaAs (001) substrate.

Figure4-18: Photoluminescence spectra at 77K of the as-grown $\text{Al}_x\text{In}_{1-x}\text{P}$ sample (solid line) and the samples after annealing at 610°C (dot line, ...), 710 °C (dash line, ---), 900 °C (dash dot line, -.-.), and 950 °C (dash dot dot line, -.-.-) for 30 seconds.

The measured PL spectrum of the sample shows that after being annealed at 610 °C for 30 seconds, the sample's PL peak position shifts to 1.994eV. A minor peak position blue shift is observed. The PL peak position shifts to 2.093eV and 2.165eV, respectively, when the annealing temperatures is increased to 710 and 900°C. The measurement result shows that the PL emission peak of the sample after being annealed at 945°C is still 2.165eV. The blue-shift of the PL emission peak of the sample saturates when the annealing temperature reaches above 900°C. The maximum blue-shift of the sample after RTA is measured to be about 165meV. The PL measurement results show that the bandgap energy of $\text{Al}_{0.38}\text{In}_{0.62}\text{P}$ increases after annealing the sample at higher temperatures.

Figure4-19: PL emission peak of the $Al_xIn_{1-x}P$ samples versus the annealing temperatures.

Figure4-19 shows the measured PL emission peak of the $Al_{0.38}In_{0.62}P$ sample versus the annealing temperature. When the annealing temperature reaches 950°C or higher, the PL peak energy of the $Al_{0.38}In_{0.62}P$ sample saturates at around 2.165eV, which is quite close to the theoretically calculated bandgap energy of the disordered $Al_{0.38}In_{0.62}P$ alloy.⁴⁸ The experimental results are well fitted by using a second-order polynomial expression which agrees with the energy bandgap of an ordered III-V semiconductor alloy changes with its ordering degree $\eta^{2,34}$.

This increase of the bandgap energy of the $Al_{0.38}In_{0.62}P$ samples after going through the RTA annealing shows that the CuPt-B atomic ordering degree in the MOVPE grown $Al_{0.38}In_{0.62}P$ sample has been reduced. As the annealing temperature increases, the ordering degree of the $Al_{0.38}In_{0.62}P$ epilayer, η , reduces, the $Al_{0.38}In_{0.62}P$ alloy becomes more disordered. When the annealing temperature reaches 900 °C and above, the $Al_{0.38}In_{0.62}P$ alloy becomes completely disordered which means the CuPt-B

atomic ordering degree reduces to $\eta = 0$.

The reduction of the degree of CuPt-B order for the MOVPE grown AlInP sample with the thermal annealing temperature has been confirmed by using the TED pattern. Figure 4-20 shows the [110] zone transmission electron diffraction patterns of the as-grown AlInP sample (a) and that of the sample after being annealed at 900 °C for 30 second (b), respectively. For the as-grown sample as shown in Figure 4-20(a), in addition to the fundamental scattering spots from the AlInP zinc-blende lattice structure, superstructure scattering spots are observed in its TED pattern at $(-1/2, 1/2, 1/2)$, $(1/2, -1/2, 1/2)$ and the equivalent planes. This superstructure scattering in the TED pattern indicates the CuPt-B ordering in the as-grown AlInP epilayer's lattice structure in which the real-space periodicities along the $[-111]$ and $[1-11]$ directions are doubled.⁴⁹ The Al and In atoms occupy the crystal planes alternatively perpendicular to the $[-111]$ and $[1-11]$ crystallographic directions.⁵⁰ The imperfect spatial periodicity in this sample induces the elongation of the ordering-induced superlattice superstructure diffraction spots into lines.²³

Figure4-20: [110] zone TED patterns for (a) as-grown $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer and (b) after annealing at 900 °C for 30 seconds. The arrows in (a) indicate the superstructure scattering from the as-grown $\text{Al}_x\text{In}_{1-x}\text{P}$ epilayer.

As shown in Figure4-20(b), no ordering-induced superstructure diffraction spot is observed in the [110] zone TED pattern from the sample after being annealed at 900 °C or above. This indicates that no more CuPt-B atomic ordering in the AlInP

epilayer's lattice structure after the annealing. Only the diffraction spots from the AlInP zinc-blende lattice structure are seen in the TED pattern. This verifies the transition of the as-grown AlInP epilayer from a partial CuPt-B atomic ordering phase to a completely disordered phase by the rapid thermal annealing.

Figure4-21: Annealing temperature dependence of photoluminescence peak shift caused by CuPt-B atomic ordering of three AlInP epilayers in which the ordering degree is different. The CuPt-B ordering degree in S2 (dot) is the maximum among them.

In the above study, the sample used was grown at 630 °C. The sample's atomic ordering degree changes when it is annealed in the temperature range from 610 °C to 900 °C. The sample becomes completely disordered when it is annealed at 900 °C or above. This ordering degree change of the AlInP sample after thermal anneal has also been studied with the samples grown at different temperatures.

Three samples, S1, S2, and S3, were grown at 580 °C, 630 °C, and 720 °C, respectively. And then these AlInP samples were annealed at the temperature from

650 to 950 °C. The bandgap energy reductions of the three samples are shown in Figure4-6. It shows that the CuPt-B ordering degree in S2 is the maximum.²⁵

Figure4-21 shows the blue-shifts of the PL peak position of the samples grown at different temperature after the thermal annealing versus the annealing temperatures. Sample S2 which was grown at 630 °C had the largest blue-shift of PL peak after the thermal annealing. The PL peak blue shift after thermal annealing saturated at the annealing temperature of around 900 °C for S2. While the saturation annealing temperature for samples S1 and S3 were around 740 °C and 780 °C, respectively. The PL peak blue shifts of these two samples were also much smaller. As discussed in Section 4.2.1, the degree of CuPt-B order for sample S2 is greater than that in S1 and S3. Combined with the result in Figure4-21, it indicated that the higher the degree of CuPt-B order, the higher the saturation annealing temperature was. It shows that the annealing saturation temperature was proportional to the degree of CuPt-B order of the AlInP epilayer, and the annealing saturation temperature could be used to characterize the degree of order in III-V semiconductor alloys.

4.3.1.2 Temperature Dependent PL spectrum of the CuPt-B ordered AlInP

The measured temperature dependent PL spectra of the as grown CuPt-B ordered AlInP samples and the annealed disordered AlInP samples are shown Figure4-22. The annealing temperature was 900 °C and annealing time was 30 seconds. For the PL measurement, the sample temperature was changed from 15 K to 100 K.

Figure4-23 shows the temperature dependence of the PL peak of the as grown and after annealed AlInP sample. The PL emission peak position of the as grown sample blue shifted from 1.982eV to 2.005eV when the measurement temperature

increased from 15K to 100K. However, the peak position of the annealed sample red shifted from 2.162eV to 2.133eV with the same variation of the measurement temperature. The temperature dependence of PL spectrum of the as grown and the annealed samples displayed opposite trend.

Figure4-22: Temperature dependence of photoluminescence spectra of the as-grown ordered (solid line) and the annealed disordered (dot line,) AlInP epilayers.

The annealed sample displayed the normal trend of a totally disordered alloy that the PL peak shifts to the lower energy with the increase of measurement temperature. The temperature dependence of PL spectrum of the annealed sample indicates the absence of the CuPt-B ordering, which confirms the disordering of the sample after being thermal annealed. On the other hand, the PL peak of the as grown AlInP sample which was with CuPt-B atomic ordered lattice structure showed a clear blue-shift when the measurement temperature was increased within the studied range. This

abnormality of the PL emission peak shift suggests carrier (exciton) localization effects,^{51,52,53} indicating a spatially indirect recombination of the carriers at the boundaries of domains in the CuPt-B ordered AlInP epilayer.

Figure4-23: Temperature dependence of photoluminescence peak of the as-grown ordered (dot) and the annealed disordered (triangle.) AlInP epilayer. The dash lines are the fitting curves. The natural log of the integrated intensity of as grown and annealed samples as a function of inverse temperature is shown in the inset.

With an increase of the temperature the localized carriers gain enough thermal energy to overcome the barriers between the boundaries of the microscopic domains and the high-energy states become thermally populated at higher temperature, leading to a blue-shift of the transition energy. The localized states may originate at the boundaries of the domains with different lateral extension and degree of order. Another source of carrier localization may be the formation of microscopic domains

with different alloy composition which comes from the phase separation.

The occurrence of domains was attributed to two distinct and coexisting effects: one is the tendency of alloy phase separation during the MOVPE growth, and the other is the presence of CuPt-B atomic ordering.⁵⁴ As shown in Figure4-9 (b), the superstructures which are caused by the CuPt-B atomic ordering distribute unevenly in the epilayer. The uneven distribution results in several domains such as areas A, B, C, and D shown in Figure4-9(b). The sample contains domains with different ordered sizes and domains with different ordered directions. Moreover, the ordered domains adjacent to or are surrounded by the disordered domains. Since the bandgap energy of the ordered AlInP alloy is lower than that of the disordered one, the localized states form in the partially CuPt-B ordered AlInP alloy and the carriers were in the localized states in the real space. When the temperature increased, the localized carriers are prompted to populate higher energy states,⁵⁴ leading to a blue-shift of the transition energy in the as grown sample shown in Figure4-22.

The natural log of the integrated intensity of as grown and annealed AlInP samples as function of inverse temperature is shown in the inset of Figure4-23. According to the approach of Lambkin et al.⁵⁵: the PL emission efficiency (η) can simply be described by

$$\eta = [1 + C \exp(-E_A / kT)]^{-1} \quad (4-8)$$

where E_A is the thermal activation energies and $C = P_{nro}/P_r$. P_{nro} and P_r are prefactors independent of temperature. C represents effectively the ratio of nonradiative to radiative recombination probabilities at room temperature. The experimental result good fits to the model. The fitting activation energies for the as grown and annealed samples are $24 \pm 3(meV)$ and $13 \pm 3(meV)$. Here the activity energy is characteristic

of trapped excitations or carriers thermalizing from localized regions of atomic ordering induced band-edge fluctuations followed by nonradiative recombination. The increase in temperature merely enables the carriers to gain sufficient kinetic energy to diffuse to the vicinity of a nonradiative recombination center.

4.3.1.3 Polarized Raman Spectrum of The CuPt-B Atomic Ordered AlInP

Raman spectroscopy is widely used to study properties of semiconductor material such as the crystalline quality and lattice dynamics through the evaluation of the phonon frequencies, half widths, line-shape and intensities of the Raman spectrum.⁵⁶ In this study, we study the effect of CuPt-B ordering on the polarized Raman spectrum of the MOVPE grown AlInP epilayer.

In a CuPt-B atomic ordered AlInP epilayer, the doubling size of the unit cell of the lattice structure along the ordering axis doubles the number of atoms per unit cell and breaks the cubic symmetry of the zinc-blende structure of a disordered alloy. The CuPt-B atomic ordered structure has a trigonal symmetry with the point group $C_{3v}=3m$, which is a subgroup of point group $T_d=\bar{4}3m$ for the disordered alloy with the cubic zinc-blende structure. The new crystal symmetry should lead to phonon spectrum differences, due to the different atomic arrangement in the ordered alloy, and to modified selection rules for first order Raman scattering.^{57,58} Two modes, $\Gamma_1+\Gamma_3$ associated with the folding of the acoustic $L(LA)$ and $L(TA)$ zincblende phonon branches, and the splitting of the optic phonon energies are expected.⁵⁹ So far, however, the phonon spectra appeared not to be significantly influenced by CuPt-B ordering effects, due to the fact that samples are only partially ordered under present growth techniques.^{60,61,62}

The Raman studies of ordered GaInP₂ made previously have concentrated on line-shape analysis of the InP- and GaP-like Raman peaks.^{63,64,65} The ratio b/a , of the valley depth between the GaP- and InP-like LO-phonon peaks (b) to the InP-like LO-phonon peak height (a) has been found to be correlated with the PL peak energy, hence with the degree of ordering. The b/a value varies between 0.2 and 0.6 with the smaller values indicating the presence of higher degree of order. It has been reported that samples exhibiting a greater degree of order display larger deviations from the expected selection rules for materials with T_d symmetry.^{66,67} In addition, Shina et al. have shown that the difference in the resonance Raman profiles for polarization of the incident radiation along the [110] and [1-10] directions, enables the determination of the crystal-field splitting in these alloys.^{68,69}

Bearing all these in mind, we have performed polarized inelastic light scattering measurements on both the as-grown CuPt-B ordered and the annealed AlInP samples, to clarify the influence of CuPt-B atomic ordering on the phonon spectrum. The sample was grown on (001) GaAs substrate with growth temperature at 630 °C. The rapid thermal annealing was processed in N₂ ambient. The annealing temperature was 900 °C and the annealing time was 30 seconds.

The Raman configuration follows Porto's notation where $k_i(e_i, e_s)k_s$ refers to the scattering configuration in which k_i and k_s are the propagation directions of the incident and scattered photons, respectively, and e_i and e_s are the polarization directions of the incident and scattered photons, respectively. The directions used in the following discussion are shown in Figure 4-24.

Figure4-24: Sample geometry and the coordinate system. The axes X, Y, and Z refer to the two cleavage directions of the samples and the growth direction, respectively.

Figure4-25(a) shows the measured Raman spectra for the as-grown and the annealed AlInP samples. The Raman configuration was $\bar{Z}(X,X)Z$. The low temperature PL spectra of the as grown and the annealed AlInP samples are also shown in Figure4-25(b). The sample was annealed at 900 °C for 30 s. The PL peak positions of the as-grown and annealed AlInP epilayers were 1.960eV and 2.076eV, respectively. The measured PL peak photon energy agrees with the calculated bandgap energy of the disordered AlInP alloy of the sample, which indicates that, the CuPt-B atomic ordering completely disappears after being annealed.

Figure4-25: (a) Raman spectra taken in the described backscattering geometry and (b) photoluminescence spectra at 77K of as grown (solid line) and after-annealed (short-dash-dot line, -.-) AlInP samples. The annealing condition was 900 °C for 30s.

Figure4-25(a) shows that the measured polarized Raman spectrum of the annealed or disordered AlInP sample had three peaks which are identified as an

AlP-like LO phonon peak at 451 cm^{-1} , an InP-like LO phonon peak at 346 cm^{-1} , and a broad feature of InP-like TO phonon peak at around 325 cm^{-1} as defined in the figure. The TO phonon modes are forbidden in the (001) backscattering for crystals with the T_d symmetry, but was detected here due to the fluctuation in the distribution of the cation in the AlInP epilayer. The peak at $\sim 290\text{ cm}^{-1}$ originates from the GaAs-like LO mode.

Compared with that of the disordered AlInP sample, the following were observed in the Raman spectrum of the CuPt-B atomic ordered AlInP sample:

(1) Appearance of an additional peak at 267 cm^{-1} . The frequency of this peak is close to the simple mean of the L -point longitudinal acoustic (LA) phonon frequencies of AlP and InP. This phonon peak was suspected as resulting from the folded LA phonon branch in the CuPt-B ordered AlInP.

(2) The higher InP-like LO mode to the InP-like TO mode intensity ratio of the ordered AlInP sample. The higher InP-like LO mode to the InP-like TO mode intensity ratio of the disordered AlInP sample was around 0.7, while for the CuPt-B atomic ordered AlInP sample, the ratio increased to 1.0. A disordered AlInP alloy has a zinc-blende lattice structure under the T_d group, with this lattice structure no InP-like TO mode is observed in its Raman spectrum. However, for a CuPt-B atomic ordered AlInP sample, its crystalline structure symmetry is reduced from T_d to C_{3v} , where the trigonal C_3 axis is oriented along the [111] axis of the CuPt ordered variant. The selection rule for phonon transition changes and some forbidden modes are allowed in the atomic ordering material, such as the InP-like TO mode.⁷⁰

(3) The shifting of the AlP-like LO phonon peak to the higher frequency in the CuPt-B atomic ordered AlInP epilayer. The AlP-like LO phonon peak was around 453

cm^{-1} and the shift value was 2 cm^{-1} with respect to that in the disordered sample. Considering the difference of the degree of order between these two samples, the shift of AIP-like LO phonon peak was related to the CuPt-B atomic ordering. The increase of AIP-like phonon peak intensity in the annealed sample was attributed to the crystal quality recovery and the decrease of domain boundary induced by CuPt-B atomic ordering.

Performing polarized Raman scattering measurements in both the as-grown CuPt-B atomic ordered and after annealed AlInP epilayers, we are able to identify the vibrational modes in the trigonal ordered phase induced by the CuPt-B ordering.

4.3.2 Inductively Coupled Plasma Exposure of AlInP

In a plasma exposure process, high energy ions bombard semiconductor samples, the material can be removed under the plasma exposure. Exposed to the plasma, the sample is somehow damaged. However, these damages can be recovered by going through thermal annealing after exposure to the plasma. Plasma exposure, such as Inductively Coupled Plasma (ICP) exposure, has been widely used in semiconductor industry for the etching process. In this section, changes of the CuPt-B atomic ordering in the AlInP epilayer after going through the ICP plasma exposure and followed by RTA annealing has been investigated.

All the samples were cleaved from the same AlInP wafer which was grown at 630°C with the reactor pressure of 20 mbar. The PL measurement and XRD measurement show the as-grown sample is highly CuPt-B ordered. During the exposure to ICP plasma, the forward RF power for the plasma exposure was 400 W

and the ICP power was set at 500 W, the plasma exposure time was 30 seconds. After the plasma exposure, the samples were sent for RTA annealing process together with as-grown samples without the plasma-exposure. The RTA time was 30 seconds and the temperature varied from 650 °C to 900 °C.

Figure4-26: Photoluminescence at 77K of AlInP epilayers at different annealing temperatures: samples with plasma exposure and rapid thermal annealing (solid line), samples with rapid thermal annealing only (dash line, ---). The dot line in (a) is the PL spectrum of as-grown AlInP epilayer.

Figure4-26 shows the PL spectra of the AlInP samples after the ICP plasma exposure and having gone through the RTA annealed at different temperature. The dot lines represent the results of the AlInP samples with only the RTA annealing. With the annealing temperatures varied from 650 to 850 °C, the PL peaks of the plasma-exposed sample had lower photon energy than that of the RTA only samples. The PL peaks of both the plasma-exposed and the as-grown samples shifted to the same energy after being annealed at/above 900 °C.

Figure4-27: The rapid thermal annealing temperature dependence of PL peak energy of AlInP samples undergo (a) plasma exposure and rapid thermal annealing (squares), (b) rapid thermal annealing only (dots).

Figure4-27 plots the PL peak positions of both the plasma-exposed and the as grown samples versus the annealing temperatures. The large PL peak energy difference between the ICP exposure and the without ICP exposure samples was observed after being annealed at the temperature range between 650 °C and 840 °C. The largest PL peak position difference, ~71 meV has been observed after the samples were annealed at 750 °C. When the annealing temperature reached 900 °C, the PL peaks of both the ICP exposure sample and the without ICP sample approached ~2.046 eV which is very close to the bandgap energy of the disordered AlInP alloy. It indicates that the CuPt-B ordering degree in both the (ICP+RTA) and the RTA only AlInP sample decreased to zero after the rapid thermal annealing at 900 °C.

The large PL peak offset between the ICP plasma-exposed and the non-ICP exposed samples is 71 meV when being annealed at 750 °C might be attributed to the

competition of thermal energy between the defects drive-in created by the ICP plasma inside the AlInP sample and the transform from the Al/In atoms CuPt-B ordering to the less ordered or disordered state.

The plasma exposed samples in ICP system process undergo two consecutive steps: (1) defect introduction at low ion energy by plasma exposure and (2) defects drive-in. With the lower ion energy during the ICP process, most of the impinging ions of Ar plasma are stopped within the first few atomic monolayers of the material.⁷¹ Ar ions may knock atoms off from their crystal sites near the sample surface to produce either a single isolated vacancy or group of vacancies. After plasma exposure and without annealing, there was no observable shift in the PL spectra as compared to the as-grown sample. This indicates that the near surface point defects were created during low Ar ion energy (100s of eV) exposure and stayed within the surface region. However, during the subsequent annealing process, the plasma ions generated point defects effectively propagate from one lattice site to another in a random walk motion. One of the phenomena to prove the defect's drive-in is the ICP induced quantum well (QW) intermixing, where the diffusion of surface point defects down to the active QW region promotes intermixing between the QWs and its barriers to form alloy semiconductors.^{72,73} One thing needed to be pointed out is that the ICP induced surface defects will drive into the deeper region only if the annealing temperature is above the threshold value.⁷²

It is known that there is a critical annealing temperature above which the sample's atomic ordering degree decreases after the rapid thermal annealing process.²³ The Al and In atoms in the CuPt-B ordering phase region need extra energy to be activated to break loose from the surrounding bonds. After breaking the bonds, the Al

and In atoms may recover to the disordered structure which is the stable state in a bulk material. Since activation and drive-in of the Ar ions may share the thermal energy with Al and In atoms, the effective thermal energy absorbed by Al and In atoms might have become less when the annealing temperature was below 900 °C. Some Al and In atoms might have insufficient thermal energy to break the surrounding bonds and recover to the disordered structure. This might depress the phase transition from the CuPt-B ordering to the disordering in the AlInP epilayer, and prevent the increasing of bandgap energy of the AlInP epilayer to the value of the disordered one. When the annealing temperature was higher, such as at 900 °C, the thermal energy could meet the need to activate both the Ar ions and the Al/In atoms in the CuPt-B ordering phase. The Al and In atoms had enough thermal energy to break through the surrounding bonds and prompt the AlInP epilayer back to the stable phase in bulk material – disordered state. So after being annealed at 900 °C, the CuPt-B ordering degrees in both the (ICP + RTA) and the RTA only samples were zero, and the bandgap energies of both of them were the same as the value of the disordered one.

4.4 Summary

Spontaneous CuPt-B atomic ordering in AlInP epilayers grown by MOVPE has been investigated in this chapter. The dependences of the CuPt-B atomic ordering in the AlInP epilayer on the MOVPE growth conditions, such as the growth temperature, material growth rate, input MO source flux V/III ratio, reactor pressure, and the type of carrier gas, etc, have been studied. It has been observed that the CuPt-B ordering degree in the AlInP epilayer increases with the growth temperature from 580 to 655 °C, and then the ordering degree decreases when the growth temperature further

increases from 655 to 720 °C. This change of the ordering degree of the grown epilayer with the growth substrate temperatures is attributed to the reduction of group III atoms surface diffusion coefficient with decreasing the growth temperature and the presence of (4×4) surface reconstruction pattern on the growing surface at low temperature.

Within the certain material growth rate range, the CuPt-B atomic ordering degree in the grown AlInP has been found inversely proportional to the material growth rate. This is because the shorter monolayer growth time depresses the formation of (2×4) surface reconstruction which is the required to CuPt-B atomic ordering.

The results show that the CuPt-B ordering degree of the grown AlInP epilayer have an inverted “U” shape when the V/III ratio increases from 20 to 80 during the MOVPE growths. The maximum ordering degree of the epilayer is expected when the V/III ratio was set at 53 during the MOVPE growth. Increasing the reactor pressure from 20 to 100 mbar caused the reduction of the CuPt-B ordering degree in the grown AlInP epilayer. It has been observed that grown AlInP epilayer’s CuPt-B atomic ordering degree is higher when it was grown by using N₂ as the carrier gas than that of the epilayer grown in a H₂ ambient. All the effects of growth conditions on the CuPt-B ordering degree in the AlInP epilayer have been explained by thermodynamics, kinetics, and surface processing during MOVPE growth.

By using the DOE method, the most effective factor of the MOVPE growth conditions on the grown AlInP epilayer’s CuPt-B atomic ordering degree has been determined among the growth temperature, growth rate, and reactor pressure. It has been found that the grown AlInP epilayer’s atomic ordering degree is most sensitive to growth temperature during the MOVPE growth among the examined growth

factors. An equation has been presented which can be used to estimate the bandgap energy reduction induced by the CuPt-B atomic ordering in the AlInP epilayer given the MOVPE growth conditions.

The CuPt-B atomic ordering degree in the MOVPE grown AlInP epilayer changes by post-growth process, e.g. RTA and ICP. Changes of the epilayer's atomic ordering degree after thermal annealing at different temperatures and after exposing to ICP plasma have also been investigated. Since the CuPt-B ordering state is meta-stable in the bulk III-V alloys, rapid thermal annealing destroys the ordering structures in the CuPt-B atomic ordered AlInP. It has been found that the CuPt-B ordering degree in the AlInP alloy decreased with increasing of the annealing temperature given the same annealing time and was reduced to zero when the annealing temperature reached the saturated value. The saturated value of the annealing temperature was found to be proportional to the CuPt-B atomic ordering degree in the as-grown AlInP epilayer.

Both the temperature dependent PL and the polarized Raman were used to characterize the as grown CuPt-B ordered and the being annealed (disordered) AlInP epilayers. The abnormal temperature dependent photon energy in the as-grown CuPt-B ordered AlInP is suspected to relate with the carrier localization effect induced by ordering structure. The appearance of extra phonon peak at 267 cm^{-1} has been found and is attributed to the folded LA phonon branch in the CuPt-B ordered AlInP where the lattice symmetry transforms from T_d to C_{3v} .

Lastly, the ICP effect on the CuPt-B ordering degree in the AlInP alloy was studied. The ICP process showed different effects within different rapid thermal annealing temperature ranges. When the annealing temperature was below $900\text{ }^{\circ}\text{C}$,

with both the plasma-exposure and the rapid thermal annealing, the ordering degree in the AlInP sample with both ICP and RTA processes was higher than that in the sample with RTA process only. The transition from CuPt-B ordering to a less ordered state was depressed compared with the one without plasma-exposure. This difference is attributed to the competition of thermal energy consumption between the drive-in process of surface defects and the transformation process from ordering to less-ordering. When the annealing temperature was higher than 900 °C, CuPt-B atomic ordering in the AlInP samples was completely destroyed in both the plasma exposed sample and the sample without plasma exposure. This is suspected to result from the provision of sufficient thermal energy to both the drive-in process and transforming process from ordering to less-ordering.

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5 AlInP Uni-compositional Quantum Well Structure

5.1 Introduction

With the development of epitaxial growth techniques and semiconductor fabrication technologies, III-V semiconductor quantum well (QW) structures have attracted much interest in fundamental semiconductor physics studies and industrial devices fabrication. Quantum well structures have been widely used in novel semiconductor photonic and electronic devices structures to enhance the device performance. For example, a semiconductor photodetector with a quantum well structure in its active region demonstrates a dramatic reduction of the device's dark current, and the detection wavelength of the detector can be adjusted by changing the quantum well thickness of the device. In this chapter, we report on the spontaneous CuPt-B atomic ordering based uni-compositional AlInP quantum well structures grown by MOVPE, which explores the applications of atomic ordering in semiconductor devices.

In a semiconductor quantum well structure, a thin layer (<20nm) of a narrow energy bandgap semiconductor is sandwiched between two layers (or barriers) of wider bandgap semiconductors (shown in Figure 5-1(a)). The thin narrow bandgap layer is called the “well layer” of the QW structure, while the two wider bandgap semiconductors are called and the ‘barrier layers’ of the QW structure. When the well layer is thin enough, less than 20 nm, the motion of carriers in the well layer in the

direction perpendicular to the hetero-interface are quantized which means that the motions involve discrete (quantum) energy level in the growth direction. The discrete energy levels shown in Figure 5-1(b) are determined by the well layer thickness, the offset between the energy bandgap of the well and barrier layers and the effective mass of electrons and holes.

Figure 5-1: (a) Schematic diagram of a quantum well structure. (b) Bandgap structure of a quantum well structure.

The prerequisite to form quantum well structure is the bandgap offset between well and barrier layer, ΔE_g , which can be written as:

$$\Delta E_g = E_{g2} - E_{g1} = \Delta E_c + \Delta E_v \quad (5-1)$$

where E_{g1} and E_{g2} are the bandgap energy of well and barrier layers, respectively; and ΔE_c and ΔE_v are the energy offsets between the well and barrier layers' conduction and valence band of the QW structure, respectively.

As discussed in Chapter 4, CuPt-B atomic ordering results in the bandgap energy reduction of AlInP epilayers. We have also investigated that the CuPt-B atomic ordering degree in the AlInP epilayer can be controlled by changing the MOVPE growth conditions.^{1,2} These results encourage us to design a novel quantum well structure using the bandgap offset resulting from the bandgap reduction of a CuPt-B

ordered AlInP epilayer. In such a quantum well structure, the well layer and the barrier layers are all AlInP epilayers and have the same Al solid composition. The AlInP epilayer which has the higher atomic ordering degree is used as the well layer and the less ordered epilayers are used as the barrier layer.

The results in Section 4.2.1 show that the degree of order is remarkably changed by growth temperature, which suggests that the quantum well structure can be produced using a difference in the order parameter resulted from a change in the growth temperature. However, using a change in temperature to produce the desired degree of order is inconvenient in a practical process. The growth must be interrupted for several minutes to allow the growth temperature to be adjusted and stabilized at each interface. Contamination of the interface is suspected to appear because of this. Further more, when one of the layer is grown at a higher temperature, the TMAI gas phase ratio must be adjusted during the interruption to compensate for the increase in the Al solid incorporation. This increases the complexity of growth. Lastly, the previous layer which is grown at low temperature may undergo a RTA like process during the growth of the layer grown at high temperature. This process will cause reduction of degree of order in the layer grown at low temperature.

The degree of order in the AlInP epilayer is also found to be a function of the input V/III ratio during MOVPE growth as shown in Section 4.2.2. The V/III ratio is changed by varying the flow rate of group V precursor with fixed flow rates of group III precursors. Thus a much more practical approach would be to change the input V/III ratio to produce the desired change in degree of order, even though the bandgap reduction is typically smaller than for reduction in growth temperature.

This chapter reports the investigations of the uni-compositional AlInP quantum

well structures produced by changing the degree of order in AlInP at a growth temperature of 630 °C using a change in the input V/III ratio.

5.2 AlInP uni-composition QW structure

The quantum well structures were grown on singular (100) GaAs substrates at a substrate temperature of 630 °C with a reactor pressure of 20 mbar. The group V precursor was TBP and the group III precursors were the conventional TMAI and TMIIn. Both the ordered (well) and less ordered (barrier) layers in the QWs were grown at the same group III flow rates. The well and barrier layers were grown with the V/III ratio of 60 and 20, respectively, by reducing the TBP flux rate from 2.487×10^{-3} mol/min to 8.201×10^{-4} mol/min. At every interface there was a 30 second interruption of growth induced by 'switching off' the group III precursors (here the 'switching off' means switching group III precursors from the growth chamber into the exhaust lines. This interruption is provided to change the group V flow rate between 2.487×10^{-3} mol/min and 8.201×10^{-4} mol/min. 'Switching off' the group III precursors during the interruption was applied in order to avoid the growth of a transition layer between barrier and well layers. Before growing the QW structure, a 200 nm GaAs buffer layer was grown at 680 °C.

In Section 4.2.2, it has been reported that the CuPt-B ordering degree of the grown AlInP epilayer was much higher when the V/III flux ratio was set at 60 than that of the epilayer grown at V/III ratio of 20. Two AlInP uni-compositional disordered/ordered/disordered quantum well samples, sample (A) and sample (B), were grown for this study. The only difference between growths of these two samples was growth time of well layer: for sample (A), the well layer was grown for 30

seconds, while for sample (B), it was grown for 60 seconds. In other words, only the thickness of the well layer of the QW structure was different since all the other growth conditions were same.

The crystalline quality and the aluminum composition of the grown AlInP epilayers and quantum well structures were characterized by using XRD. The direct energy band gap of the AlInP single layer and the band to band transition energy of the AlInP unicompositional quantum well structure were determined by using PL. Ar⁺ laser (line at 488nm) was used as the exciting light for the PL measurement. To investigate the changes of the quantum well structures after going through thermal annealing, RTA process was carried out on the samples in nitrogen ambient. The annealing temperature was 900 °C and the annealing time was 30 seconds. To prevent surface decomposition, the samples were covered with fresh GaAs wafers during annealing

5.3 Results and Discussions

Figure5-2 shows surface morphologies of the two AlInP quantum well samples taken by a Nikon optical microscope. Image (a) and (b) were taken from the center area of sample (A) and (B), respectively. Image (c) and (d) were taken from the edge area of sample (A) and (B), respectively. Images in Figure5-2 show mirror like surface morphologies of both two AlInP quantum well samples. There were no hillock, pot, or other defects presented on the sample surfaces.

Figure5-3 shows the [110] TEM dark-field image of AlInP quantum well sample (A). The sample consists of a 140 nm bottom barrier layer grown with V/III ratio of 20, a 6.0 nm well layer grown with V/III ratio of 60, and a 140 nm top barrier layer

grown at the same conditions with that of bottom barrier layer. The well layer which has higher CuPt-B atomic ordering degree is indicated in Figure5-3. The interfaces between the different layers of the QW structure were well defined.

Figure5-2: The images taken from a Nikon optical microscope shows the mirror like surface of both two AlInP quantum well samples. Image (a) and (b) were taken from the center area of sample (A) and (B), respectively. Image (c) and (d) were taken from the edge area of sample (A) and (B), respectively.

Figure5-4 shows XRD rocking curves of the two quantum well samples. XRD peaks from the epilayers of two quantum well samples were almost at the same position. It can be seen that the aluminum (Al) solid compositions of the AlInP layers of the two samples were the same.

Figure5-3: Dark-field TEM image for the 6.0 nm AlInP less-ordering/greater-ordering/less-ordering quantum well. The well layer area is indicated as the arrow.

Figure5-4: High resolution XRD results of the AlInP unicompositional quantum well structure sample (A) and sample (B).

Figure5-5(a) plots the measured PL emission spectrum of the AlInP single layer grown with the same growth conditions as that for growing the well layer of the QW

structure, and the PL spectra of the QW sample (A) and sample (B). It shows that the AlInP bulky well layer had the peak emission energy at 1.90 eV, while for the QW sample (A) and QW sample (B), the peak emissions were at 2.002 eV and 1.966 eV, respectively.

(a)

(b)

Figure5-5: (a) PL spectra at 77K of the AlInP well single layer, AlInP unicompositional quantum well sample (A) and sample (B) grown on GaAs (001) substrate. (b) Calculated PL emission energy of quantum well sample (A) and (B).

The large emission blue-shifts of sample (A) and (B) compared with that of the single AlInP well layer show strong quantum confinement effect of the QW structures. Sample (A) with a shorter well layer growth time in the QW growth consisted of a narrower quantum well layer than that in sample (B). Its PL emission peak had higher energy because of the stronger quantum confinement. With the calibrated growth rate of the AlInP epilayer under the growth conditions, the well layer thicknesses of sample (A) and (B) were ~10 nm and ~20 nm, respectively. Based on investigations in Section 4.2.2, the bandgap energies of AlInP layers grown at 630 °C with the V/III ratio of 60 and 20 were 1.965 and 2.095 eV, respectively. So the bandgap difference between the well layer and barrier layers is calculated as 0.130 eV with the V/III ratios of well and barrier layers as 60 and 20.

The transition energy of the quantum well structure can be calculated by solving the Schrodinger equation:³

$$-\frac{\hbar^2}{2m_{e(h)}^*} \frac{d^2\psi_n(x)}{dx^2} + U(x)\psi_n(x) = E_n\psi_n(x) \quad (5-2)$$

where $m_{e(h)}^*$ is the effective mass of electron or hole. $U(x)$ is the band offset between well and barrier layers. The transition between the ground electron (*EI*) and heavy-hole (*HHI*) states was obtained by estimating electron states using a transfer-matrix method within the effect-mass approximation, and HH states using a 6×6 Hamiltonian model for the QW.⁴ The ratio of conduction to valence band offset is 6 to 4. The parameters of effective mass were adopted from Ref 5. Here the effective mass is taken the value corresponding to disordered material which is observed to be 3% larger than that of ordered one.⁶

Using the potential profile of QW structure, $U(x)$, as shown in Figure5-5 (b), the

$E1-HH1$ transition energies of sample (A) and (B) quantum well structure are calculated as 1.998 eV and 1.958 eV, respectively, by solving Equation (5-2). The theoretical transition energies agreed with the measured PL peak emission energies of sample (A) and (B), as shown in Figure5-5 (a), where the emission peaks of sample (A) and sample (B) were ~ 2.000 eV and 1.953 eV, respectively.

Figure5-6: PL spectra at 77K of both AlInP unicompositional QW and AlInP single barrier layer before and after the thermal annealing. The PL spectra of the as grown and the thermal annealed sample are indicated as the dotted line and solid line, respectively. The band gap alignment of AlInP quantum well structure is plotted in the inset. The solid and dotted line in inset represent band gap alignment of as-grown and after annealed AlInP quantum well structure, respectively.

It has been discussed that the spontaneous CuPt-B type atomic ordering of the grown semiconductor epilayers is reduced after going through thermal annealing.⁷ In this investigation, the AlInP unicompositional QW structure sample (A) was annealed at 900 °C for 30 seconds. Figure5-6 shows the low temperature PL spectra of both

sample (A) unicompositional QW structure and that of a single AlInP layer before and after being annealed. The AlInP single layer was grown with the same conditions as that for growing the QW's barrier layers. After thermal annealing, the PL emission peak of sample (A) shifted from 2.002 eV to 2.16 eV, a blue-shift of up to 0.158 eV was observed. The results show that after being annealed at 900 °C for 30 seconds, both the QW sample (A) and the AlInP single layer emitted at the same photon energy.

The QW structure of sample (A) was formed because of the band gap offset between AlInP layers with different degrees of CuPt-B atomic order. Since the barrier layer was grown with the V/III ratio of 20, the degree of order was lower and the barrier layer had consequently larger bandgap energy. While the well layer was grown with the V/III ratio of 60, it had narrower energy bandgap energy because of its higher degree of order.

After being annealed at 900 °C for 30 seconds, the spontaneous CuPt-B atomic ordering of the AlInP epilayer reduces to zero.⁷ The band offset between the well and the barrier layers in the QW disappeared accordingly. The QW structure became a single AlInP layer after the RTA annealing. The inset in Figure 5-6 shows the bandgap energy diagram of transition processes for sample (A) before (solid lines) and after being annealed (dot lines). After being annealed at 900 °C for 30 seconds, the CuPt type atomic ordering of AlInP epilayers disappeared, the QW structure became a disordered AlInP single layer. Therefore, after being annealed, the measured PL spectrum of the uni-compositional AlInP QW structure was the same as that of a single AlInP layer.

5.4 Summary

In conclusion, the disorder/order/disorder unicompositional AlInP quantum well structures have been grown by MOVPE. The energy bandgap offset of the unicompositional QW structure was achieved by changing the V/III flux ratio during the MOVPE growth. The low temperature PL spectra show that the PL peak energy from the QWs increases with a decrease in the thickness of the order well layer. This is due to the quantum size effect on the thin ordered well layers in the QWs. Strong quantum confinement effects of the QW structure have also been confirmed by the measured higher PL emission peak of the QW structure comparing with that of an AlInP single epilayer. After being annealed at 900 °C for 30 seconds, the bandgap offset of the QW structure disappeared, the uni-compositional quantum well structure became an AlInP single layer. This is because the CuPt atomic ordering of the AlInP epilayer is eliminated during high temperature annealing. This work provides the possibility of using atomic ordering of the semiconductor epitaxial layers in semiconductor devices.

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6 Summary and Future Work

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

6.1 Summary

High quality non-nitride based wide energy bandgap III-V alloy, AlInP epilayers, have been successfully grown by MOVPE using MO sources, TMAI, TMIn and TBP, as precursors and pure N₂ as the carrier gas. Effects of growth conditions on the Al incorporation into AlInP alloys have been investigated. Keeping the gas phase ratio of TMAI as a constant, it has been found Al solid compositions of AlInP epilayers were increased with increasing the growth temperature from 580 to 660 °C, and Al compositions saturated when the growth temperature was higher than 660 °C. The Al solid composition of the grown AlInP epilayer was linearly proportional to the gas phase ratio of TMAI source and it decreased with the increase of V/III flux ratio during MOVPE growths at 630 °C. The Al incorporation into the AlInP epilayer during the MOVPE growth has been theoretically analyzed using an adsorption-trapping model. The experimental data were well supported and explained by the theoretical model.

The spontaneous CuPt-B type atomic ordering in the AlInP epilayer grown by MOVPE has been studied in detail. The effects of MOVPE growth conditions on ordering have been explored. The superstructures induced by CuPt-B ordering were demonstrated using TED to measure the extra diffraction spots. PL and XRD measurements were used to determine the bandgap reduction induced by ordering.

The degree of order was observed to decrease markedly with decreasing the growth temperature from 630 to 580 °C and increasing growth temperature from 630 to 720 °C during the MOVPE growth of AlInP on singular (001) GaAs substrate. It shows an upside down “U” relation between the degree of order of the grown AlInP epilayer and the growth temperature. The reduction in ordering at low temperature was attributed to the low surface diffusion coefficients of group III atoms. The degree of order decreased when the growth temperature was increased beyond the optimum value of ordering and was caused by the loss of the (2×4) reconstruction. The degree of order versus the V/III ratio shows a similar relation to that of growth temperature. The degree of order decreased with decrease of V/III ratio from 45 to 20. The reduction in degree of order was attributed to the loss of the [-110]-oriented P-P dimers on the growing surface. When the V/III ratio was increased beyond the optimum value for CuPt-B ordering, the degree of order also decreased markedly. The decrease in the degree of order in this range was suspected to originate from the decrease of surface diffusion coefficients of group III atoms with high V/III ratios. The carrier gas has also been found to affect the CuPt-B atomic ordering in the AlInP epilayer. Compared with hydrogen, nitrogen facilitated the formation of CuPt-B ordering in the AlInP epilayer. A variation of the growth rate from 0.5 to 1.2 μm/hr was seen to decrease the degree of order. The degree of order was also found to decrease with increasing the reactor pressure from 20 to 100 mbar. The growth conditions’ effects on the degree of order have been explained by using thermodynamics, dynamics and surface reconstruction process during MOVPE growths. The results show that the degree of order in the AlInP epilayer can be

controlled by adjusting MOVPE growth conditions, such as growth temperature, input V/III ratio, growth rate, and reactor pressure.

Dependences of the degree of order of the AlInP epilayer on some post-growth processes have also been investigated. It has been found that the degree of order decreased after rapid thermal annealing process. The degree of order decreased with increasing annealing temperature, and reduced to zero after being annealed at 900°C. Both temperature dependent PL and polarized Raman measurements have been used to probe the difference of optical and phonon properties between the as-grown (ordered) and annealed (disordered) AlInP layers. The decrease of degree of order resulted from RTA was retarded after being exposed to ICP. The slow down was attributed to the thermal consumption for activating defects which were induced by ICP process.

Disorder/order/disorder uni-compositional AlInP quantum well samples have been obtained. The QW structures were grown by MOVPE and were characterized by PL, XRD and TEM. The bandgap offset of the QW structure profited from the bandgap reduction which resulted from the higher degree of order in the well than that in the barrier layer. The difference of order parameter was determined by changing the V/III ratio during the MOVPE growth. The strong quantum confinement of the QW structure has been observed from the low temperature PL measurement. The PL peak emission of the QW structure was the same as that of the AlInP single layer sample after being annealed at 900 °C for 30s. This is because degrees of order in both well and barrier layers were reduced to zero and the quantum well confinement disappeared correspondingly after being annealed.

6.2 Future Work

High quality AlInP alloy has been grown by MOVPE in pure N₂ ambient. CuPt-B atomic ordering in the AlInP epilayer grown by MOVPE has been studied in this research. However, there still remain several interesting topic for future studies.

1) CuPt-B atomic ordering in semiconductor III-V alloy occurs on the growing surface during the epitaxial growth. Most of the reported CuPt orderings in III-V alloys grown by MOVPE are CuPt-B type. The CuPt-A type is seldom found. The tendency of CuPt-B type ordering is not well understood and is suspected to be determined by surface processes of MOVPE growth. Moreover, the in-situ characterization tool for MOVPE is not well equipped. Therefore, it may help to probe and understand the detailed surface process of MOVPE growth by studying the asymmetry between CuPt-A and CuPt-B ordering in the III-V alloys.

2) Chapter 5 demonstrated the uni-compositional AlInP QWs grown by MOVPE. It has also been reported the ordering-induced modifications of the electronic structure of AlInP lead to a strong polarization dependence of its optical properties. Zhang *et al*¹ also reported the polarization ratio for the band edge excitonic transition is found to be ~ 2.0 for an ordered GaInP sample. The polarization dependent optical interband transition, electronic-absorption are expected in the uni-compositional AlInP QWs. Therefore, it is very attractive to study the polarization effects in the optical properties of the uni-compositional AlInP QWs and their applications in the fabrications of polarization sensitive devices, such as detector, polarization-stable vertical cavity surface emitting lasers (VCSELs) and micro-cavity LEDs. For a basic p-i-n photodiode, the ordered AlInP can be used as the absorption

layer. The photocurrents for [011] and [01-1] polarized lights will be different, which is the direct consequence of the absorption anisotropy in the ordered material.

Figure 6-1: (a) Plasma exposure on the structure which contains ordered layer. The top gray layer is the mask to produce different plasma exposures. (b) The annealing step is carried out to induce different bandgap energy.

3) In chapter 4, post-growth techniques affect the ordering of AlInP epilayers. These results suggest novel ways for bandgap engineering. For example, Figure 6.1 shows a proposed process to produce different bandgap energy from an atomic ordered layer using the plasmas exposure and thermal annealing processes. As shown in Figure 6.1(b), different bandgap energy in areas with different plasma exposure conditions will be obtained. Combined with other semiconductor fabrication techniques such as deposition, lithography and etching, the bandgap difference from an atomic ordered sample can be achieved by controlling the plasma exposure and rapid thermal annealing conditions. These processes could be easily integrated into the current fabrication flow for optoelectronic devices.

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