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Selective Area Epitaxy for Indium Phosphide Based Photonic Integrated Circuits

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ABSTRACT

The ability to integrate multiple photonic devices on a single substrate has turned out to be very advantageous in the fabrication of components for optical communication networks. For example, improved fiber coupling can be achieved by integrating a modulator with an optical mode converter. However, current technology is very limited in its ability to fabricate such photonic integrated circuits (PIC).

We report on a selective area epitaxy (SAE) process suitable for the fabrication of a PIC. The process includes a quantitative model, which for the first time, is capable of predicting the growth rate and composition of thin films selectively deposited by metalorganic chemical vapour deposition in areas close to the dielectric mask as well as areas several microns away. The accuracy of the model is demonstrated by comparing simulation results with experimental measurements of the thickness and composition profiles obtained by surface profilometry and energy dispersed X-ray respectively.

The process is applied to the fabrication of an elecroabsorption modulator and optical mode converter, monolithically integrated on an InP substrate. As part of the fabrication, quantitative modeling of the converter waveguide core deposition is employed to achieve a thickness profile previously designed by beam propagation calculations. Modeling is also used to predict the composition and strain shifts introduced by selective deposition, enabling the composition to be designed such that the maximum strain is minimized. Device measurements demonstrate that SAE is successfully used for the fabrication of a PIC with characteristics superior to those found in conventional devices.

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Résumé

La capacité d'intégrer les dispositifs photonic multiples sur un substrat simple est très avantageuse pour les réseaux de transmission optique. Par exemple, l'accouplement amélioré de fibre peut être réalisé en intégrant un modulateur avec un convertisseur optique de mode. Cependant, la technologie courante est très limitée dans sa capacité de fabriquer de tels circuits intégrés photonic (PIC).

Nous rendons compte d'un procédé sélectif de l'épitaxie de secteur (SAE) approprié à la fabrication d'un PIC. Le processus inclut un modèle quantitatif capable de prévoir le taux de croissance et la composition des couches minces sélectivement déposées en utilisant la déposition en phase vapeur metalorganic. L'exactitude du modèle est démontrée en comparant des résultats de simulation aux mesures expérimentales de l'épaisseur et les profils de composition obtenus par la profilométrie extérieure et l'énergie dispersées radiographient respectivement.

Le processus est appliqué à la fabrication d'un modulateur d'elecroabsorption et d'un convertisseur optique de mode, monolithiquement intégrée sur un substrat de InP. En tant qu'élément de la fabrication, modeler quantitatif est employé pour déposer la couche de guide d'ondes de convertisseur avec un profil d'épaisseur précédemment optimisé par des méthodes numériques pour guides d'ondes. Modeler est également employé pour prévoir la composition et des décalages de contrainte présentés par le dépôt sélectif et la composition est conçus tels que la contrainte maximum est réduite au minimum. Les mesures de dispositif démontrent que le SAE a été avec succès employé pour la fabrication d'un PIC avec des caractéristiques supérieures à ceux trouvées dans des dispositifs conventionnels.

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LIST OF ABBREVIATIONS AND SYMBOLS

a_s	substrate lattice constant
a_f	thin film lattice constant
c_{Ga}	gallium precursor concentration
C _{In}	indium precursor concentration
C_{O}	precursor concentration at the top of the stagnant layer
AFM	atomic force microscopy
CV	capacitance-voltage
D	diffusion constant
DFB	distributed feedback
DH	double heterostructure
DLTS	deep level transient spectroscopy
EA	electroabsorption
EDX	energy dispersed X-ray
g	growth rate
\overline{G}_s	growth rate due to surgace migration
h_i	height of the <i>i</i> th InP layer between InGaAs marker layers
HP	Hewlett-Packard
IV	current-voltage
k	incorporation constant
k_a	adsorption coefficient
k_B	Boltzmann's constant
k_d	desorption coefficient
k_{g}	molecular volume of InP
Ľ	diffusion length+
LCR	inductance capacitance resistance
LPE	liquid phase epitaxy
MOCVD	metalorganic chemical vapour deposition
MOMBE	metalorganic molecular beam epitaxy
MOW	multiple quantum well
n_s	precursor surface concentration
p	partial pressure
PIC	photonic integrated circuit
PL	photoluminescence
RC	resistance capacitance
R_{In}	indium growth rate enhancement
R_{Ga}	gallium growth rate enhancement
S	strain
SAE	selective area epitaxy
SIMS	secondary ion mass spectroscopy
SEM	scanning electron microscopy
TEG	triethylgallium
TMI	trimethylindium
UV	ultraviolet

- V gas velocity
- δ height of stagnant layer
- λ wavelength
- μ gas viscosity
- τ mean lifetime of an adatom impacted from the (111) β sidewall
- θ fraction of occupied atomic sites
- X average distance from reactor inlet to the wafer

•

Chapter 1

Introduction

1.1 Motivation

SAE is the process of locally depositing a semiconductor film on a substrate, which has been patterned with an inert masking material such as SiO_2 . During deposition by metalorganic chemical vapour deposition (MOCVD), the build up of precursors over the SiO_2 mask causes material to diffuse into the open areas leading to a growth rate increase. In the case of ternary and quaternary alloys, a composition shift occurs due to the difference in diffusivity of the precursor molecules. The nature of this modulation can be controlled by proper design of the mask. Notably, the magnitude of the modulation is proportional to the area of the mask.

Selective area epitaxy is an important technique for electronic and photonic device fabrication, and for the monolithic integration of these devices. MOCVD is capable of yielding device quality semiconductor films with a high degree of control over the composition, doping and thickness. However, this control is normally possible in the growth direction only. SAE offers the ability to control the film properties in the lateral direction, which is necessary for the monolithic integration of photonic devices. This thesis makes original contributions to knowledge in the areas of crystal growth modeling, the physiochemical nature of SAE and semiconductor processing for photonic devices. The value of the contributions is highlighted with the demonstration of the first integrated

electroabsorption modulator and optical mode converter operating at 50 GHz with a coupling loss of 4 dB and a polarization dependent loss of 0.4 dB.

1.2 The InP Material System

Indium phosphide (InP) is a semiconductor material. The bandgap energy is 1.423 eV and the lattice constant is 5.8697 Å.¹ The telecommunication industry relies heavily on InP, which can be manufactured from a melt consisting of indium and phosphorus starting material. Laser transmitters and photodiode receivers are typically made from thin films of $In_{1-x}Ga_xAs_yP_{1-y}$ deposited on InP substrates. $In_{1-x}Ga_xAs_yP_{1-y}$ is a quaternary semiconductor and therefore synthesizing substrates from a melt is not technologically possible. $In_{1-x}Ga_xAs_yP_{1-y}$ must be deposited on an InP substrate using thin film *epitaxy*. Epitaxy is a process in which a thin layer of single crystal material is deposited on a single crystal substrate. The growth occurs in such a way that the crystallographic structure of the substrate is reproduced in the growing material.

The $In_{1-x}Ga_xAs_yP_{1-y}$ bandgap and lattice constant is a function of the group III and group V composition, denoted by *x* and *y* respectively. The quaternary phase diagram is shown in Fig. 1.1. The shaded region represents all possible compositions. The white line represents the compositions with the same lattice constant as InP. The bandgap energies of those alloys range from 0.750 eV to 1.423 eV. Alternatively, the bandgaps can be expressed as the corresponding photon wavelength, 1.65 μ m and 871 nm respectively. The important wavelengths for the telecommunications industry are 1.3 μ m and 1.55 μ m. These are the wavelengths at which the silica based fiber optic cable exhibits minimal optical dispersion and transmission loss. Metalorganic chemical vapor deposition (MOCVD) is an epitaxial technique well suited for $In_{1-x}Ga_xAs_yP_{1-y}$ deposition. The alloy composition can be finely controlled allowing the quaternary to be grown lattice matched to InP. The film can also tolerate a certain degree of lattice mismatch. The lattice elastically deforms to match the InP lattice and strain is introduced. Strain is the displacement of atoms in the crystal lattice from a nominal position. Quantitatively, it is defined as

$$s = \frac{a_f - a_s}{a_s} \tag{1.1}$$

where a_f is the thin film lattice constant and a_s is the substrate lattice constant.



Fig 1.1 The InGaAsP phase diagram. The white line represents the lattice-matched alloys.

1.3 The MOCVD Reactor

An MOCVD system is composed of several functional subsystems. The subsystems include reactant storage, a gas handling manifold, a reaction chamber and an exhaust. A schematic of an MOCVD system is shown in Fig. 1.2. The reactant storage houses the growth precursor materials. These include the group III metalorganic precursor compounds in the solid and liquid phases, as well as hydrides, which are the most common group V source. For the InP material system, trimethylindium (TMI) and triethylgallium (TEG) are commonly used metalorganic precursors while arsine (AsH₃)



Fig 1.2 A schematic representation of an MOCVD system.

and phosphine (PH₃) are commonly used hydrides. Typically, precursors used for doping sources are also present.

The hydride gases are kept in high pressure cylinders but the metalorganics require less conventional storage. The metalorganic precursors are stored in containers designed to facilitate their controlled evaporation. For this purpose, a carrier gas is passed through the material via a dip tube under controlled flow, temperature and pressure. The carrier gas, usually hydrogen or nitrogen, is saturated with precursor vapour, thus transporting the material through the gas handling manifold and into the reaction chamber. The metalorganic containers are called *bubblers* because of their design.

Once inside the reaction chamber, the organometallic compounds react with the hydrides at elevated temperatures to produce a film of semiconducting material, which is deposited onto a substrate fixed to a temperature controlled susceptor. Heat from the susceptor provides energy to drive the chemical reaction forward. In addition, the substrate often acts as a catalyst and, ideally, precursors do not react until they are close to the semiconductor. The net reaction for the synthesis of InP by MOCVD can be expressed as,

$$(CH_3)_3 In + PH_3 \rightarrow InP + 3CH_4. \tag{1.2}$$

The mass flow controllers (MFC) within the gas handling subsystem control the quantity of growth precursors delivered to the reaction chamber and hence help determine the film growth rate. The composition of a given element within the growing film is determined by the partial pressure of the corresponding precursor within the reactor. The ratio of the total group V partial pressure and total group III partial pressure is called the

V-III pressure ratio. It is an important MOCVD parameter. The deposition temperature and pressure are also of importance to the film growth. Together with the film growth rate, they constitute the major MOCVD parameters. For InGaAsP films the latter is, in first approximation, dependent on the supply of group III precursors alone,

1.4 The History of MOCVD

Before the invention of MOCVD, liquid phase epitaxy (LPE) was the dominant method for III-V film deposition.² LPE, which still plays a role in today's industry, was relatively simple, straightforward and inexpensive. In essence, it was an extension of bulk crystal growth techniques. By the late 1960's, however, there were indications of the need for an alternative method. For example, despite the high quality of LPE films, the large distribution coefficients found in the indium and aluminum alloys made it difficult to produce films with uniform composition and properties.³ Furthermore, LPE was becoming incapable of growing the full range of alloys needed for the developing photonics industry.⁴ In particular, a miscibility gap was calculated for InGaAsP, which included the region for growth of the solid composition necessary for 1.55 micron lasers lattice matched to InP.⁵ LPE experiments by Stringfellow confirmed the calculations.⁶

LPE employs elemental precursors and is a process which occurs in thermodynamic equilibrium, meaning there is a careful balance between deposition and etching. As a result, there is a relatively narrow range of parameters where multiple compounds can be deposited. MOCVD, in contrast, uses volatile organometallic and hydride precursors to create a strongly forward driven reaction. The nature of the precursor decomposition is such that the reaction is nearly irreversible and reaction times

are very short. Since the growth rate is small (1 or 2 monolayers per second) and the switching speed between precursors is fast, finely tuned and ultra-thin films can be grown to meet today's demand for quantum well devices.

The first successful growth of III-V compounds from organometallic and hydride sources was reported in 1960 by Didchenko and co-workers.⁷ In their experiment, InP was grown from TMI and phosphine in a closed system. Eight years later, Manasevit and Simpson developed the first open tube reactor for chemical vapour deposition using organometallic sources and coined the term *MOCVD*.⁸ Manasevit and Simpson's apparatus was the forerunner to the modern day *vertical* reactor in which source materials flow vertically over the susceptor. Alternatively, reactors have been designed such that source materials flow horizontally above the susceptor.

Pioneering work on the pyrolysis of TMI at low pressure was done by Jacko and Price in 1963.⁹ Using a specially designed apparatus, they concluded that each of the three In-CH₃ bonds are broken one at a time through a homogenous reaction and that for complete pyrolysis, the ambient temperature should be above 480°C. Larsen and Stringfellow reported the first pyrolysis studies of TMI in an atmospheric pressure MOCVD reactor.¹⁰ They observed an enhanced decomposition of TMI in an H₂ ambient compared to an N₂ ambient. More recent studies have shown that pyrolysis under the conditions present during MOCVD are very complex, probably not purely homogenous and cannot be explained by any single known model.¹¹ Pyrolysis studies have also been carried out for the organometallic compounds involved in the growth of GaAs^{12,13} and other semiconductors.¹⁴

By the mid-eighties, multi-wafer MOCVD reactors were being developed to maximize production efficiency. In these reactors, several substrates can be simultaneously placed on the susceptor. Early work by Ikeda¹⁵ showed that uniformity over the entire group of substrates was the major stumbling block. However, by intense modeling of the flow dynamics inside the reactor chamber, growth conditions and reactor geometries were found to obtain good uniformity. Notably, Emcore corporation developed the turbo disc rotation technology and Aixtron developed planetary rotation.^{16,17}

As MOCVD matured, it began to produce the best InP films in terms of mobility and crystal quality.^{18,19} The technique produced GaAs films of equal quality to those grown by molecular beam epitaxy, MOCVD's chief rival.²⁰ Reducing the background silicon and carbon concentrations proved to be the essential step.²¹ In the next section, this thesis will explore the wide range of optoelectronic devices used in today's communication systems.

1.5 MOCVD for Long Wavelength Optoelectronic Devices

MOCVD has been used to fabricate all manner of optoelectronic devices. Dapkus and Dupuis were the first to demonstrate an MOCVD grown laser with state of the art performance.²² This demonstrated the potential of MOCVD at a time when LPE dominated the industry. Demonstrating that graded index lasers could reduce the threshold current by a factor of three, further showed the advantages of MOCVD.²³ LPE could not realize such thin and well controlled layers. Nelson and co-workers fabricated an InGaAsP double heterostructure laser for emission at 1.55 µm with a threshold current

of 800 A/cm².²⁴ Marthur and co-workers obtained a threshold current of 314 A/cm² by using strained active layers.²⁵ In addition, they learnt that a very narrow range of growth conditions exist which produce high quality strained layers. Using electron microscopy, the strained layers were seen to be wavy, without proper optimization of the temperature, pressure and V/III pressure ratio.

Electroabsorption modulators have been successfully fabricated using MOCVD.²⁶ These devices rely on the Stark effect to absorb photons in a *pn* junction when an electric field is applied to reduce the bandgap. Examples can be found in the literature for MOCVD grown detectors²⁷ and optical amplifiers.²⁸

An important area of MOCVD research is the monolithic integration of photonic devices.²⁹ A semiconductor chip integrating two or more photonic devices is called a photonic integrated circuit (PIC). Two main MOCVD monolithic integration technologies currently exist, quantum well intermixing (QWI)³⁰ and selective area epitaxy (SAE). In QWI, a multiple quantum well is irradiated with an ion beam. The induced damage and subsequent anneal in an MOCVD reactor lead to inter-diffusion at the well barrier interface causing an enhanced bandgap. QWI has been used to integrate four laser diodes, each with a different bandgap and therefore each operating at a different carrier frequency.³¹ A full discussion on SAE is deferred to chapter two.

1.6 Thesis Organization

Chapter two begins with a history of SAE research and an overview of its applications. The chapter also reports on experiments conducted to qualitatively understand the physiochemical nature of SAE. Specifically, the experiments were aimed at understanding the impact of the major MOCVD growth parameters. Chapter three addresses the physics of SAE on a quantitative level. Growth models found in the literature are critically discussed. Moreover, we present a methodology for applying SAE quantitative modeling to the fabrication of a photonic integrated circuit. This includes novel contributions to the art as well as computer software implementations.

In chapters four and five, we report on experiments that were designed to demonstrate the accuracy and usefulness of our quantitative models. Chapter four discusses InP selective growth while chapter five is concerned with the selective growth of InGaAsP. The former chapter highlights our original contributions to understanding the physics of surface diffusion. The latter chapter focuses on our contributions to the physics of the selective growth of semiconductors containing multiple group III elements.

A novel fabrication process for a photonic integrated circuit, compatible with the SAE technique, is comprehensively explained in chapter six. The process includes the use of the SAE modeling software developed in chapter three. Finally, chapter seven summarizes the electrical and optical characteristics of the PIC. We emphasize results that demonstrate the advantages of SAE and our novel fabrication process.

¹ I. Vurgaftman, J.R. Meyer and L.R. Ram-Mohan, J. Appl. Phys, 89, 5815 (2001)

² H. Nelson, RCA Rev., 19, 603 (1963)

- ³ G.B. Stringfellow, Annual Rev.Mat. Sci., 8, 72 (1978)
- ⁴ D. Effer, J. Electrochem. Soc., 112, 1020 (1965)
- ⁵ B. DeCremoux, P. Hirtz and J. Ricciardi, Inst. Phys. Conf. Series, 56, 115 (1981)
- ⁶ G.B. Stringfellow, J. Crys. Growth 65, 454 (1983)
- ⁷ R. Didchinko, J.E. Alix and R.H. Toeniskoetter, J. Inorg. Nuc. Chem., 14, 35 (1960)
- ⁸ H.M. Manasevit and W.I. Simpson, J. Electrochem. Soc., 116, 1725 (1969)
- ⁹ M.G. Jacko and S.J. Price, Can. J. Chem., 41, 1560 (1963)
- ¹⁰ C.A. Larsen and G.B. Stringfellow, J. Crys. Growth, 75, 247 (1986)
- ¹¹ N.I. Buchan, C.A. Larsen and G.B. Stringfellow, J. Crys. Growth, 92, 591 (1988)
- ¹² M. Yoshida, H. Watanabe and F. Uesugi, J.Electrochem. Soc., 132, 677 (1985)
- ¹³ M.C. Paputa and S.J. Price, Can. J. Chem., 57, 3178 (1979)
- ¹⁴ C.H. Cheng, K.A. Jones and K.M. Motyl, J. Elec. Mat., 13, 703 (1984)
- ¹⁵ M. Ikeda, S. Kojima and Y. Kashiwayangi, J. Crys. Growth, 77, 157 (1986)
- ¹⁶ H.Q. Hou, P.R. Sharps, N.S. Fatemi, N. Li, M.A. Stan, P.A. Martin, B.E. Hammons, F. Spadafora, IEEE Photovoltaic Spec., 28, 1173 (2000)
- ¹⁷ C. Von Eichel-Streiber, O. Schon, R. Beccard, D. Schmitz, M. Heuken, H. Jurgensen,
 J. Crys. Growth, 189, 344 (1998)
- ¹⁸ E.J. Thrush, C.G. Cureton, J.M. Trigg, J.P. Stagg and B.R. Butler, Chemtronics, 2, 62 (1987)
- ¹⁹ R.P. Shneider, R.P. Bryan, J.A. Lott and G.R. Olbright, J. Crys. Growth, 124, 763 (1992)
- ²⁰ M. Razeghi, F. Omnes, J. Nagle, M. Defour, O. Archer and P. Bove, Appl. Phys. Lett.,
 55, 1677 (1989)

- ²¹ A.T.R. Briggs and B.R. Butler, J. Crys. Growth, 85, 535 (1987)
- ²² R.D. Dapuis and P.D. Dapkus, Appl. Phys. Lett., 32, 406 (1978)
- ²³ W.T. Tsang, Appl. Phys. Lett., 40, 217 (1982)
- ²⁴ A.W. Nelson, S. Cole, S. Wong, M.J. Harlow, W.J. Devlin, D. Wake, P.M. Rodgers and M.J. Robertson, J. Crys. Growth 77, 779 (1986)
- ²⁵ A. Marthur, P. Grodzinski, J.S. Osinski and P.D. Dapkus, J. Crys. Growth, 124, 730 (1992)
- ²⁶ H. Tanaka, M. Horita, Y. Matushama and Y. Takahashi, Opt. and Quant. Elec., 28, 605 (1996)
- ²⁷ A. Eisenbach, A. Goldhorn, E. Kuphal, K. Mause, J. Cry. Growth, 170, 451 (1997)
- ²⁸ S. Kitamura, H. Hatakeyama, K. Hamamoto, T. Sasaki, K. Komatsu, M. Yamaguchi,
 IEEE J. Quant. Elec., 35, 1067 (1999)
- ²⁹ C. Simoneaux, Comp. Semiconductor, 7, 37 (2001)
- ³⁰ J.H. Marsh, Semiconductor Sci. Technol., 8, 1136 (1993)
- ³¹ A. McKee, C.J. McLean, G. Lullo, A.C. Bryce, R.M. de La Rue, J.H. Marsh and C. Button, IEEE J. Quant. Elec., 33, 45 (1997)

Chapter 2

MOCVD Selective Area Epitaxy

2.1 Introduction

Like many scientific advancements, SAE was discovered by accident. While conducting early MOCVD experiments with GaAs, Duchemin observed a growth rate enhancement when dielectrics were present on the substrate.¹ He noticed that the excess growth was equal to the growth that would have occurred on the masked area. Similar studies were later performed with InP.^{2,3} A physical explanation for this phenomenon could not be found until the same experiment was carried out with metalorganic molecular beam epitaxy (MOMBE).⁴ An MOMBE reaction chamber is an ultra high vacuum environment so mass transport of the metalorganic precursors is restricted to ballistic motion. The films grown over a masked substrate showed no growth enhancement and so it was concluded that the primary cause of the SAE effect, in MOCVD, is gas phase diffusion.

Subsequently, experimental studies of SAE were published to assess the impact of the MOCVD parameters on the growth rate enhancement.^{5,6} The experiments varied the pressure, temperature and V-III pressure ratio. The dielectric mask sizes were also varied. Azoulay and co-workers demonstrated the first device quality films grown by SAE .⁷

In the early nineties, studies on alloy composition modulation were performed by Kayser,⁸ and independently by Chang.⁹ For the selective growth of InGaAs films, both workers observed a different arrival rate for the In and Ga precursors. This was attributed

to the dissimilar diffusion constants caused by the unique mass of each molecule. In particular, using Auger spectroscopy, an indium enrichment was measured in regions of the film near the dielectric mask with larger masks causing a larger enrichment. Iberl and co-workers later confirmed these initial findings using spatially resolved x-ray measurements.¹⁰

To date, SAE has been successfully used in a number of integrated photonics applications. Figure 2.1 shows how SAE is employed to integrate double heterostructure Fabry-Perot (DH-FP) lasers operating at different wavelengths on a single substrate.¹¹ Oxide mask pair #2 is wider than pair #1 therefore the $In_xGa_{1-x}As_yP_{1-y}$ film grown between the second pair is more In rich than the film grown between the first pair. In a DH-FP laser, the $In_xGa_{1-x}As_yP_{1-y}$ layer constitutes the active section of the laser and its bandgap controls the operating wavelength. Since the second film contains more indium, the bandgap is smaller and the wavelength of the laser is larger.









stack # 2

Fig. 2.2 Demonstration of the SAE technique applied to the fabrication of monolithically integrated MQW lasers operating at different carrier wavelengths.

Using an oxide mask set, with varying widths, Zah and co-workers demonstrated an array of 30 laser diodes integrated side by side on a single wafer.¹¹ The lasing wavelengths were spaced 2 nm apart and centred about $1.55 \,\mu$ m. The array achieved stable wavelength outputs and optical cross-talk was eliminated by an on-chip passive waveguide circuit. Additional benefits included component sharing (such as a single thermoelectric cooler) and simplified testing. The threshold current was 25 mA for each laser and the power per channel launched into the fibre was –22 dBm.

Sasaki and co-workers made use of the SAE composition shift to laterally control the effective refractive index of the waveguide structure in the grating region to allow inplane lasing control without changing the grating pitch.^{12,13} An integrated 18 laser array was successfully fabricated and tested.

Integration of multiple quantum well lasers makes even better use of the properties of SAE. Figure 2.2 shows how two quantum well stacks could be grown between oxide mask pairs. The second pair uses wider oxide masks, therefore, the layers grown between that pair are thicker and more indium rich. In the case of a laser made from bulk material, the thickness of the active layer does not affect the wavelength but for an MQW laser made from $In_{1-x}Ga_xAs_yP_{1-y}$, the wavelength increases with increasing well thickness as well as increasing indium concentration.

Initial work on the selective growth of multiple quantum wells for application to laser fabrication was conducted by T.M. Cockerill *et al.*¹⁴ They demonstrated a laser made from a strained InGaAs/AlGaAs structure. For uncoated cleaved facets, threshold currents as low as 11 mA were demonstrated for a 540 μ m long, 4 μ m wide device. The devices operated at room temperature with more than 200 mW output power per uncoated facet and possessed 40 % quantum efficiency.

Mitsuo Yamamoto fabricated an MQW laser diode with an integrated optical mode converter.¹⁵ He obtained a room temperature threshold current and slope efficiency of 5.6 mA and 0.41 W/A respectively. The fiber coupling loss was less than 2.5 dB compared to 9 dB without the integrated mode converter. Ido and co-workers demonstrated a 40 GHz optical modulator by integrating a transparent waveguide with a 50 μ m modulation region.¹⁶ A semiconductor optical amplifier (SOA) was integrated with a transparent waveguide by Kim *el al.*¹⁷ Fiber to fiber gain was measured to be 22 dB at 200 mA. The waveguide was tapered to achieve a narrow beam divergence of 8° X 15°.

2.2 A parametric Study of InP Selective Area Epitaxy

The ability to tailor MOCVD semiconductor films to the needs of electronic and optoelectronic devices rests on a detailed knowledge of how all growth parameters impact the film growth rate and morphology as well as the electrical and optical properties. Each SAE study reported to date only examined the impact of a cross-section of the key growth parameters. Combining the results of all such studies is not realistic because of potential inconsistencies between pre-epitaxy wafer preparation, reactor design, post-epitaxy measurement techniques and dielectric mask geometry. It will be shown that by analyzing SAE grown films deposited over the broad range of parameters used in this study, the physics of SAE was explored to reveal brand new insight into previously unexplainable phenomena. Later chapters will report on the design of a novel photonic device fabricated using the knowledge gained from this examination.

The present work represents the first comprehensive study, which reports on the impact of all major growth parameters on SAE films. The study, which consisted of a large series of growth experiments, was designed to deliver design rules for the application of SAE to photonic integration. In each experiment, an InP film was deposited by MOCVD over a patterned InP substrate using unique growth conditions. The films were subsequently characterized by SEM and AFM imaging, and by DEKTAK surface profiling.

In all the experiments, 2'' sulfur doped (100) InP substrates were used. (The results are directly applicable to 3'' InP substrates). A 0.3 μ m thick SiO₂ film was deposited by plasma enhanced chemical vapour deposition (PECVD). No chemical treatment prior to PECVD was used since the wafers were procured "epi-ready".

Following PECVD, the oxide was patterned into a matrix of rectangle pairs separated by a semiconductor gap. The matrix consisted of pairs of rectangular oxide stripes as illustrated in Fig. 2.3(a). The mask widths and gap widths were altered from 7.6 μ m to 100 μ m and 5 μ m to 80 μ m respectively. The rectangle pairs were aligned to the [011] as well as the [011] crystallographic directions to study the impact of crystal orientation. To minimize experimental uncertainty, each structure was repeated several times on the mask so that multiple data points could be collected for each rectangle pair and for each set of conditions.



Fig 2.3(a) Photomask used to pattern the wafers for the parametric study. It consists of a matrix of rectangular oxide stripes separated by a gap.

Although dry etching techniques such as RIE generally allow for smaller line width variations, a wet etch solution composed of undiluted hydrofluoric acid was used for the oxide since dry etch processes have been shown to cause damage to the InP substrate, resulting in poor morphology after growth.¹⁸ These findings were experimentally confirmed in our lab as part of this study. To get the best of both worlds, Takemi and co-workers used a partial dry-etch to define the line widths and then removed the last remaining angstroms of oxide using HF.¹⁹ Hydrofluoric acid is a suitable etching agent since it has a huge etch selectivity between SiO₂ and InP.²⁰



Fig 2.3(b) The layer structure used for the parametric study.

The MOCVD reactor used for the SAE experiments was described in chapter one. During the course of its operation, a set of parameters was developed for optimal film deposition on unmasked substrates. These values were used for the first experiment (run S4788) and subsequently the parameters were varied around the initial conditions to access their impact on SAE. Table 2.1 lists the nominal growth parameter values as well as all other values employed. In addition, run S5891 was carried out using a substrate patterned with a different photomask. Run S5891 was used to study selective growth in very small gap openings. The gap sizes ranged from 1.0 to 5.0 μ m and the mask widths ranged from 10 to 40 μ m.

The same layer structure was used for all runs. It consisted of four layers of InP, 0.1 μ m thick, interspaced with 0.01 μ m InGaAs marker layers. The marker layers were very thin thus it can be assumed that they did not significantly affect any of the measurements.²¹ The structure is shown in Fig. 2.3(b). Prior to SEM cross-section

run	temperature	pressure	growth rate	V/III ratio	growth time	TMI molar flow	Total Flow	
<u>no.</u>	(°C)	_(torr)	$(\mu m/hr)$		(min)	(% H ₂)	(SLM)	
S4788	625	76	1.42	110	17	0.099	15	
S4922	625	76	1.42	55	17	0.099	15	
S4924	625	76	1.42	220	17	0.099	15	
S4926	625	76	0.71	110	34	0.050	15	
S4928	625	76	2.84	110	8.5	0.20	15	
S4934	625	76	1.42	110	76.5	0.099	15	
S5009	625	76	1.42	110	8.5	0.099	15	
S5010	625	76	1.42	110	4.2	0.099	15	
S5068	575	76	1.42	110	17	0.099	15	
S5070	600	76	1.42	110	17	0.099	15	
S5090	650	76	1.42	110	17	0.099	15	
S5093	625	150	1.42	110	17	0.099	15	
S5106	625	45	1.42	110	17	0.099	15	
S5891	625	76	1.42	110	17	0.099	15	

Table 2.1 A summary of the growths carried out as part of this study.
analysis, the wafers were cleaved and immersed for 10 sec in a 1:5:50 solution of H_2SO_4 : H_2O_2 : H_2O to selectively etch the InGaAs. (Etching enhances the contrast in the images). Since a native oxide forms on a cleaved (011) surface at room temperature²² and H_2 and H_2O are known to adsorb onto the cleaved surface,²³ etching was always performed immediately after cleaving to obtain the clearest possible resolution.

2.3 A parametric Study of InP Selective Area Epitaxy – Results

2.3.1 The Impact of the Major Growth Parameters

Figure 2.4 is an AFM image showing a typical morphology obtained in this study. Selective growth between two oxide stripes, aligned to the [011] direction, resulted in a mesa as shown in the figure. Near the oxide mask, the semiconductor surface was occasionally rough and irregular. Further away from the mask, however, surface morphology was always good and the films exhibited a clean, uniform and smooth surface.

Figure 2.5(a) and (b) show SEM cross-section images of selectively grown mesa structures from run S4788. In case (a), the ratio of the oxide mask width to the semiconductor gap width was large. The mask width was 80 μ m and the gap width was 20 μ m. In (b), the ratio was small. The mask width was 20 μ m and the gap width was 80 μ m. The thick layers are InP and the thin layers are InGaAs markers as indicated in Fig. 2.3(b). The time between successive marker layer depositions was always constant for a given sample. Therefore, the variation in distance between successive InGaAs layers is a direct measure of the variation in the growth rate.



Fig. 2.4 AFM image from run S4788. The morphology is typical of the mesa structures selectively grown in the gaps. The center is flat while "rabbit ears" are seen adjacent to the masks. The horizontal scaling is approximately 10 times the vertical scaling.



Fig. 2.5 SEM cross-section images of mesas aligned to [011]. The run number and mask geometry are indicated in the caption. (a,b) In run number S4788, the nominal growth conditions were used. (c,d) In S4924, the V/III ratio was doubled. (e,f) In S5068, the growth temperature was reduced.

MOCVD Selective Area Epitaxy

With the marker layers, it can be seen that the growth rate (in the [001] direction) is larger for the ridge fabricated using the larger mask to gap ratio. Also, notice that in (a), the surface contains a large bump, or "rabbit ear", near the oxide. In (b), the bump is not present (or insignificantly small). For both (a) and (b), a distinct sidewall plane is visible. This plane was present in every case of [011] alignment and its angle was measured to be 54 degrees and thus identified as the (111) β plane. The marker layers can be used to ascertain that no growth occurred on the (111) β crystal plane for S4788.

To study the effect of the V/III pressure ratio on the shape of selectively grown ridges, cross-section images taken from S4924 were examined and compared with those taken from S4788. Figures 2.5(c) and (d) show mesa sidewalls from S4924. In (c), the mask width is 80 μ m and the gap width is 20 μ m. For (d), the mask is 20 μ m and the gap is 80 μ m. In contrast to the standard growth conditions, rabbit ears did not occur for either of the two extremes of mask geometry. Moreover, for a mask pair consisting of a wide mask and thin gap, growth occurred on the (111) β plane. The InGaAs marker layers can be used to ascertain the relative growth rate on different crystal planes. From Fig. 2.5(c) it can be seen that the growth rate in the [111] direction was less than the growth rate in the [100] direction.

Figures 2.5(e) and 2.5(f) were taken from run S5068 (T = 575 °C). In (e) the mask width to gap width ratio is 80 μ m to 10 μ m. In (f), it is 20 μ m to 80 μ m. The former image illustrates an astonishing phenomenon for low temperature selectively grown mesas. The growth rate in the [111] direction is equal to the rate in the [100] direction. This occurred for ridges fabricated using a large mask to gap ratio. For small ratios, the growth rate is smaller than for the (100) plane. This can be seen in Fig. 2.5(f).

After examining SEM cross-section images from every run, it was found that sometimes a large ridge, shaped like a rabbit ear, formed adjacent to the oxide and other times it did not. When they occurred, rabbit ears were found to vary in size, being bigger for larger ratios of the mask width to the gap width. Moreover, when a rabbit ear formed, no growth was observed on the (111) β plane. Conversely, when rabbit ears were absent, a non-zero [111] growth rate was observed. Table 2.2 indicates which runs were found to posses rabbit ear formations on at least some of the mesas. Additional SEM cross-section images are not shown for runs where the pressure or growth rate was varied but the appearance of the ridges are similar to either Fig 2.5(a) or Fig 2.5(b).

run	temperature	pressure	growth rate	V/III ratio	growth time	rabbit-
no.	(°C)	(torr)	(µm/hr)		(min)	ears
S4788	625	76	1.42	110	17	yes
S4922	625	76	1.42	55	17	yes
S4924	625	76	1.42	220	17	no
S4926	625	76	0.71	110	34	no
S4928	625	76	2.84	110	8.5	no
S4934	625	76	1.42	110	76.5	yes
S5009	625	76	1.42	110	8.5	no
S5010	625	76	1.42	110	4.2	no
S5068	575	76	1.42	110	17	no
S5070	600	76	1.42	110	17	no
S5090	650	76	1.42	110	17	yes
S5093	625	150	1.42	110	17	no
S5106	625	45	1.42	110	17	yes

Table 2.2 A summary of the appearance of rabbit ears as a function of growth conditions

The impact of the growth time on the existence of rabbit ears can be determined with Figures 2.5(a) and (b). The InGaAs marker layers can be used to study the time evolution of the surface morphology. The first marker layer was deposited after 4.2 minutes of growth. The marker is flat in both figures. The subsequent markers remain flat for (b). For (a), each marker layer becomes increasingly more curved at the sidewall showing that the rabbit ear forms gradually over time.

2.3.2 The Effect of Orientation

For oxide stripes aligned to the $[01\overline{1}]$ direction, a unique shape was observed for the mesa sidewalls. Figure 2.6(a) shows an SEM cross-section image of a mesa in the $[01\overline{1}]$ direction from run S4788 produced using a large ratio of oxide stripe width to



Fig. 2.6 SEM cross-section images for mesas aligned to [011]. (a,b) In run number S4788, the nominal growth conditions were used. (c) In S5068, the growth temperature was reduced.

semiconductor gap width. Figure 2.6(b) shows an image for a mesa produced using a small ratio. The angle of the side wall was 54° and since InP has a zinc blend crystal structure, the planes were identified as (111) α planes. Using the InGaAs marker layers, it was determined that growth occurred on the sidewalls. Indeed, lateral growth caused the mesa to grow over the oxide surface.

Figure 2.6(c) shows an SEM image taken from run S5068. The stripe geometry was the same as for the structure in Fig. 2.6(b). For low temperature deposition, the growth rate in the horizontal direction further increased causing the mesa to cover the oxide with a peculiar formation. Examining the (111) α sidewalls in every run and for every geometry revealed that contrary to what occurred for the case of an exposed (111) β plane, growth took place in the horizontal direction for the entire spectrum of growth conditions. The ratio of horizontal growth rate to vertical growth rate was always close to unity.



Fig 2.7 SEM image of the dielectric mask from run number S5093 (elevated pressure). Polycrystalline deposits are visible.

2.3.3 The Dielectric Masks

After growth, the dielectric mask surfaces were smooth and untouched for all runs except S5093, the only run executed at 150 torr instead of 76 torr. Figure 2.7 shows an SEM image of a typical dielectric mask surface from S5093. Deposits were visible all over the oxide surface. The deposits were identified as being crystalline because of the facets that could be seen in the SEM. The deposits remained after etching the wafer in hydrofluoric acid.

2.3.4 Quantitative Results

Using the surface profiler, thickness profiles were obtained for every mesa in each run. Figure 2.8(a) shows the profile of a mesa from run S4788 grown between two 30 µm dielectric masks spaced 30 µm apart. The plot is a good representative of the other measurements. Adjacent to the mask, a super enhanced thickness was measured corresponding to the rabbit ears. In the center of the mesa, the profile takes on a parabolic shape. Some of the other measurements from run S4788 are summarized in Fig. 2.8(b) where the mesa height measured at the center of the gap between the oxide stripes is plotted as a function of mask width for four different gap widths. The growth rate enhancement can be seen to have increased for increasing mask width and decreasing gap width. For runs where the temperature or pressure was altered, the slope of the curves changed. For runs where the V/III was altered, the data points coincided exactly. These results will be used in section 2.4 to help interpret the SEM cross-section images however a full discussion on the quantitative aspects of SAE is deferred to chapter three.



Fig 2.8 (a) The film thickness profile of a mesa from run number S4788 (30 μ m mask, 30 μ m gap) as measured by surface profilometry. (b) The film thickness at the center of the mesa as a function of mask width for different gap widths.

2.3.5 Very Small Gap Openings

Figures 2.9(a)-(c) are from run S5891. Fig. 2.9(a) shows a mesa grown in a 2 μ m gap using 10 μ m oxide stripes. The gap width was not much bigger than the width of the rabbit ears and the rabbit ear formations on either side of the mesa have come into contact with one another. For the mesa shown in Fig. 2.9(b), the gap width was also 2 μ m but the mask width was 40 μ m. The width of the mesa top surface was reduced to 1.2 μ m and the two rabbit ears merged into one formation. Using the InGaAs markers, the rabbit ears could be seen to first approach one another as per Fig. 2.9(a) and then as growth proceeded, they merged. Figure 2.9(c) shows a very interesting phenomenon. The gap width was 1 μ m and the mask width was 20 μ m. Just after the second marker layer was inserted, the sidewalls reached an apex and the (100) surface disappeared. After the (100) surface disappeared, growth began on the (111) β surface, although at a slow rate. (The marker layers in (c,d) were digitally enhanced because otherwise they would not be easily observable in the reproduction). The sidewall reached an apex for several other runs. It occurred whenever the film thickness exceeded the value, (*gap_width)•tan*(55°).



Fig. 2.9 SEM cross-section images from run number S5891.

2.4 A parametric Study of InP Selective Area Epitaxy – Discussion

2.4.1 The Major Growth Parameters on Morphology

Conventional MOCVD growth of InP implies a linear dependency of the growth rate on the TMI partial pressure in the reactor. The partial pressure gradient that is formed above the semiconductor surface creates precursor transportation via gas phase diffusion. Upon reaching the surface, the precursors are incorporated into the solid. In contrast, the transport in selective area epitaxy is not solely determined by diffusion perpendicular to the surface. The localized consumption of material causes the formation of lateral concentration gradients leading to the diffusion of materials from the masked region towards the gaps. Thus in SAE, one has to expect accelerated growth compared to deposition on non-patterned substrates.

It has been well established that the additional material is supplied by two mechanisms, gas phase diffusion and surface migration.²⁴ The atomic force microscopy image in Fig. 2.4 identifies two distinct regions. In the center of the gap region, the morphology is smooth and uniform. This region was controlled by gas phase diffusion. The pile up of material near the oxide is attributed to surface migration. In the first studies of SAE, material landing on the mask was thought to migrate along the SiO₂ surface until it reaches the semiconductor.²⁵ Subsequently, the material migrates to the (100) surface, resulting in the formation of rabbit ears near the oxide.

In contrast to the initial model, in 1993 Sasaki proposed that surface migration stems only from the mesa sidewalls and material landing on the oxide completely returns to the vapour layer through evaporation.²⁶ A number of more recent papers used Sasaki's results to construct quantitative models for SAE,^{27,28} however, others continued to back

the initial model.^{29,30,31} The results of this study show that Sasaki's conclusions should not be generalized because of the small range of dielectric mask geometries employed in his study. In contrast to the present study, only 3 gap width sizes were used, ranging from 2.5 to 4.5 μ m at a fixed mask width of 8 μ m. The SEM images of Fig. 2.9 showed that the surface migration characteristics are unique in the small gap size limit and results should not assumed to be valid for larger dimensions. In addition, since mesas are bound by (111) planes, the effective gap width is reduced by $2h/tan(54^o)$ where h is the mesa height, and this amount is significant for gap sizes comparable to the mesa height.

The role played by the oxide in surface migration remained an unresolved issue in the science. This work is a landmark in the field due the unprecedented scale of the investigation. Never before has such a wide range of growth conditions and mask geometries been used in a single study. The discussion to follow will make original conclusions based on the large amount of collected data. In particular, it will be shown that rabbit ear formation is caused only by adatoms originating from the sidewalls and previous conclusions to the contrary were based on a confusion caused by the strong correlation between dielectric mask size and sidewall surface areas.

From the earlier examination of the time evolution of the InGaAs marker layer, it can be concluded that the rabbit ear size is determined, at least in part, by the nominal film thickness. For example, in Fig. 2.5(a), rabbit ear formations did not take place after the first marker but as growth proceeded, the formations took shape. Figure 2.10 is a graph of rabbit ear size versus dielectric mask width. It can be used to assess the mask width dependency on rabbit ear size. The size was measured by calculating the difference, $h_2 - h_1$, between the InP film thickness above the topmost InGaAs marker, h_2 ,

and the thickness of the InP between the substrate and the bottom most InGaAs marker, h_1 . Fig. 2.5(a) demonstrates the measurements schematically. The definition is justified because the formations were insignificantly small below the first InGaAs marker. The thickness measurements were obtained from the digitized SEM cross-section images using a calibrated standard. The graph was generated using several semiconductor gap widths. The graph shows that the rabbit ear height increases with increasing mask width and illustrates how previous works could falsely conclude that the rabbit ear material originated from the dielectric mask.



Fig. 2.10 Rabbit ear size versus mask width for five variations of gap width. The definition of rabbit ear size is described in the text using Fig. 2.5(a).

By analyzing the rabbit ear height as a function of both mask size and gap width, it was found that rabbit ear size can remain unchanged for increasing mask width if the gap width is correspondingly decreased. This is illustrated in Fig. 2.10 with the equal rabbit ear size line. Surface profile measurements showed that the mesa height for each mask set which lies along the line were approximately the same. The rabbit ear size is not, however, a function of the growth rate enhancement. This can be inferred from the results of runs S5009 and S5010 where the enhancements were equivalent. The size of the rabbit ears is therefore a function of the length of the (111) β mesa side wall which is directly proportional to the absolute mesa height by a factor of (sin 54°)⁻¹. This conclusion is supported by the absence (or insignificant size) of rabbit ears in the lower InGaAs marker layers observed in run S4788.

The same trends were observed for every run where rabbit ears were found to exist. Any rabbit ear height dependence on the oxide mask width was found to be insignificant compared to the dependence on the nominal mesa height. It can be inferred that the diffusion length on the sidewalls was greater than the sidewall length leading to migration to the (100) surface, which is known to have a very small surface diffusion length.³²

For some runs, rabbit ears did not form for any of the mesas and growth occurred on the (111) β plane, for example in the case of an elevated V/III pressure ratio (S4924). This can be explained by surmising that precursors impinged on the (111) β side-walls did not move into the gap via surface migration. Rather, the adatoms adsorbed to the sidewalls and were incorporated into the solid causing growth in the [111] direction, as seen in Fig. 2.5(c) and (d). Conversely, when rabbit ears formed, it was because material

impinging on the sidewall, migrated to the (100) plane. The graph of mesa height versus mask width shown in Fig. 2.8(b) can be used to prove that adatoms originating from the sidewalls, contribute to rabbit ear growth only and do not contribute to growth elsewhere on the (100) plane. The curve of mesa height (at the center of the mesa) versus mask width is linear for the entire range of widths indicating a constant growth mechanism. Since rabbit ears form for large ratios of gap width to mask width, one would expect a super-linear curve for large values of mask width if adatoms originating on the sidewalls were migrating to the mesa center. However, a super-linear region is not observed. Moreover, the mesa heights for S4924 (double V/III ratio) are identical to the heights measured on S4788, indicating that it is possible to suppress rabbit ear formation without impacting the film thickness at the center of the gap.

The (111) β sidewall and the (100) mesa top are distinct surfaces and therefore have different growth rates.³³ Reactants migrate from the slower growing (111) β surface to the faster growing (100) surface,³⁴ in order to reduce the total surface energy.^{35,36} Migration is believed to occur via transport along dangling bonds. Kayser suggested that an increased concentration of In vacancies with increasing PH₃ partial pressure reduces the migration length of the group III species on the (111) β planes.⁸ Indium species, therefore, reach the gap in far reduced numbers and growth on the sidewall planes is enhanced. However, Kayser did not expand his study to include the effects of growth rate or pressure.

It can be concluded that decreasing the growth temperature reduces the migration length on the $(111)\beta$ plane since the surface diffusion process is a strong function of temperature. For example, the (100) surface diffusion coefficient of Ga changes by a

factor of three over the temperature range 525 °C to 625 °C.³⁷ It can be seen from Table 2.2 that at 625°C, the surface diffusion length was greater than 0.5 μ m, corresponding to the length of the (111) β surface in run S4788. At 600 °C and at 575 °C (runs S5068 and S5070), however, the surface diffusion length must have been less than 0.5 μ m and adatoms were unable to migrate into the gap and cause the formation of rabbit ears.

Runs S4926, S4928, S5093 and S5106 demonstrated that the total pressure and growth rate also determined the formation of rabbit ears. The results were analyzed in the context of a sidewall surface migration model. Although classic diffusion theory is governed by Fick's law, it has been well established that for III-V semiconductors, the process is not nearly so simple.³⁸ For example, diffusion can be strongly affected by the concentration of defects.³⁹ Similarly, the state of the solid surface can have a great impact on surface migration. The most widely used approach to the quantitative treatment of the surface concentration is the Langmuir isotherm, which relates the surface coverage of a given species to its partial pressure in the gas phase.⁴⁰ The rule is expressed as follows,

$$\Theta = \frac{Kp}{1 + Kp} \tag{2.1}$$

where Θ is the fraction of sites occupied by the species, *p* is the partial pressure and *K* is the adsorption coefficient. Equation (2.1) shows that the growth rate affects the surface coverage by altering the TMI partial pressure. The absence of rabbit ears for run S4926 can thus be attributed to a reduction in the surface diffusion constant due to an increase in In vacancies on the (111) β plane.

From Table 2.2, a smaller diffusion constant can also be deduced for the run performed at an elevated total pressure (S5093). Possible explanations include an increased surface concentration of hydrogen, hydrocarbons or reduced metal-organics such as dimethylindium. Various species of the like are believed to exist on the surface during growth⁴¹ and at higher pressures, re-evaporation of adsorbed species, is reduced.

2.4.2 The Effect of Orientation

The growth evolution on the (111) planes was completely different for stripes aligned to the [011] direction compared to stripes in the orthogonal direction because in the zinc blend lattice, (111) α and (111) β are not identical surfaces. Figure 2.11 illustrates the two atomic configurations. From the SEM images in Fig. 2.6, it can be inferred that In is readily incorporated into the (111) α surface and migration to the (100) surface was inhibited. This accounts for the absence of rabbit ear formations in mesas aligned to [011]. The surface energies of the (100) and (111) α planes are similar whereas the (111) β plane has a higher surface energy and incorporation is less favorable.⁴²

Messmer and Lourdudoss have given descriptions of In incorporation for both (111) planes based on the atomic configurations of the respective planes.⁴² For the (111) α plane, an incoming In atom can bond directly with any of the steps over the surface and therefore has a relatively high probability of incorporation. For the (111) β surface, incoming In atoms can not bond with the [011] step until another In atom has first bonded with the (100) step otherwise an insufficient number of dangling bonds would be present to accommodate all the valence electrons of the incoming atom.



InP

Fig. 2.11 The atomic configuration of InP showing (a) the (111) β surface and (b) the (111) α surface.

2.4.3 The Dielectric Masks

Ideally, growth over a patterned substrate should be 100% selective. That is, semiconductor material should be deposited only in the regions between the oxide masks and no deposition should occur on the masked area. It has been shown that improper growth conditions lead to polycrystalline formations on the oxide.⁴³ Naturally, for post growth processing, the cleanest possible wafer is desired.

As a rule of thumb, factors promoting good selectivity include high temperatures, which enhance evaporation from the oxide, and low growth rates.⁴⁴ In addition, since metals stick to oxide more readily than metalorganics, it is important to delay pyrolysis until just moments before the precursors reach the semiconductor. This is accomplished via limiting gas phase reactions by lowering the pressure and by reducing the transit time of metalogranics through the stagnant layer by increasing the gas velocity.²³

Another way to prevent gas phase reactions is by choosing a more stable metalorganic precursor. Eckel compared TMI and

DimethylAminopropylDimethylIndium for use in the selective area epitaxy of InGaAs.⁴⁵ The nucleation density on the mask for the DADI grown samples was lower than the density for the TMI grown samples. This was attributed to a faster decomposition of the less stable TMI and its stronger tendency to undergo parasitic gas phase reactions. Huang and co-workers reported worse selectivity when using TEI compared to TMI,⁴⁶ and attributed the results to the lower stability of the former molecule.

Choosing a precursor containing chlorine has been used to promote selectivity since the chlorine based acid byproduct etches the polycrystalline formations.⁴⁷

DiEthylGalliumChloride has been used as a type III precursor⁴⁸ and arsenic trichloride has been used as a type V precursor,⁴⁹ both for this purpose.

The presence of elemental group V species can also eliminate the selectivity as they are presumed to enhance the deposition of In and Ga containing species,^{50,51} however since the sticking coefficient of group V precursors is virtually zero on dielectric surfaces,⁵² there is no effect of the V/III ratio on selectivity.

Finally, the mask itself is important when considering selectivity.⁵³ The reagent partial pressure (or reactant concentration) above the mask surface increases with increasing oxide area to open semiconductor area ratio. Deposition on the mask surface will occur once the partial pressure reaches the value needed to form stable nuclei for the polycrystalline formation. To counteract this effect, Yamaguchi and Okamoto used atom beam irradiation prior to growth to remove defects on the SiO₂ surface, which act as nucleation sites.⁵⁴

2.5 Design Rules

In this chapter, a parametric study of some of the qualitative characteristics of SAE was described. AFM and SEM were used to study the morphology and cross-sectional shape of selectively grown mesas and surface profilometry was used to measure the thickness profiles. The impact of an extremely large number of parameters was explored, making this an important and original contribution to the field of material science. Previous studies examined only a cross-section of the relevant growth parameters and used only a small set of dielectric mask sizes. This limited the amount of information that could be learned from the experimental results. Furthermore, the results of separate studies should

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not be combined because of the dissimilarity of reactor construction and sample preparation used in different labs.

From a practical standpoint, the purpose of any fundamental study on SAE is to deliver a set of design rules that can be applied to the fabrication of semiconductor devices. This study established a set of empirical rules as well as an understanding of the growth chemistry responsible for some of the experimental results. In particular, it has been established that pressure, growth rate, temperature and V/III partial pressure ratio can all be used to manipulate the formation of rabbit ears adjacent to the dielectric mask. Thus, the morphology can be tailored to a desired application and the needs of post-growth processing. Additionally, it was learnt that for stripes aligned to [011], the size of the mesa sidewall facet strongly determines the size of the formations for those growth conditions where the rabbit ears are encouraged to form. This is contrary to the popularly held belief that the dielectric mask width controls the size of the formations. The present study relied on its large range of mask size sets to show that while there is a strong correlation between mask width and sidewall facet size, the facet size is the only significant controlling parameter. A surface migration mechanism was responsible for delivering material adsorbed on the sidewall to the mesa top.

Traditionally, semiconductor optoelectronic device technology has made use of vertical variations in the material deposited onto the substrate. This has been made possible by growth techniques such as MOCVD and MBE, which offer excellent control over the film properties in the growth direction. This approach contrasts the more mature Si microelectronic industry, which has traditionally relied on an excellent control of the wafer properties across its surface. At present the optoelectronic industry is maturing and

it is beginning to require a certain degree of horizontal control over the wafer properties. In chapter six, it will be shown that the design guidelines delivered in this study, when combined with results presented in subsequent chapters, are essential to the successful fabrication of an active device with an optical mode transformer, and more generally, to the fabrication of any photonic integrated circuit using SAE.

- ¹ J.P. Duchemin, A. Bonnet, F. Koelsch and D. Huyghe, J. Crys. Growth, 45, 181 (1987)
- ² M. Oishi and K. Kuroiwa, J. Electrochem. Soc., 132, 1209 (1985)
- ³ C. Blauw, A. Szaplonczay, K. Fox and B. Emmerstorfer, J. Crys. Growth, 77, 326 (1986)
- ⁴ N.Vodjdani, A. Lemarchand and H. Paradan, J. Physique, 43, C5-339 (1982)
- ⁵ A.R. Clawson, C.M. Hanson and T.T. Vu, J. Crys. Growth, 77, 334 (1986)
- ⁶ N. Nakai, T. Sanada, S. Yamakoshi, J. Crys. Growth, 93, 248 (1988)
- ⁷ R. Azoulay, N. Bouadama, J.C. Bouley and L. Dugran, J. Crys. Growth, 55, 229 (1981)
- ⁸ O. Kayser, J. Cry. Growth, 107, 989 (1991)
- ⁹ J.S.C. Chang, K.W. Carey, J.E. Turner and L.A. Hodge, J. Elec. Mat., 19, 345 (1990)
- ¹⁰ A. Iberl, H. Göbel and H. Heinecke, J. App.Phys., D28, A172 (1995)
- ¹¹ C. Zah, M.A. Amersfoort, B.N. Pathak, F.J. Favire, P.S.D. Lin, N.C. Andreakis, A.W.

Rajhel, R. Bhat, C. Caneua, M.A. Koza and J. Gamelin, IEEE J. Sel. Top. Quant.Elec., 3, 584 (1997)

- ¹² T. Sasaki, M. Yamaguchi and K. Kitamura, Elec. Lett., 30, 785 (1994)
- ¹³ T. Sasaki, M. Yamaguchi and K. Kitamura, J. Crys. Growth, 145, 846 (1994)

- ¹⁴ T.M. Cockerill, D.V. Forbes, J.A. Dantzig and J.J. Coleman, IEEE J.Quant. Elec., 30,
 441 (1994)
- ¹⁵ M. Yamamoto, Y. Itaya and T. Sugie, 8th Proc. IPRM., 376 (1996)
- ¹⁶ T. Ido, H. Sano, M. Suzuki, S. Tanaka and H. Inoue, IEEE Phot. Tech. Lett., 7, 170 (1995)
- ¹⁷ J.R. Kim, J.S. Lee, S. Park, M.W. Park, J.S. Yu, S.D. Lee, A.G. Choo, T.I. Kim and Y.H. Lee, IEEE Phot. Tech. Lett., 11, 967 (1999)
- ¹⁸ J.E. Greenspan, X. Zhang, N. Puetz and B. Emmerstorfer, J. Vac. Sci. Technol. A., 18, 648 (2000)
- ¹⁹ M. Takemi, T. Kimura, D. Suzuki, T. Shiba, K. Shibata, Y. Mihashi, S. Takamiya and M. Aiga, Proc. IPRM, 8, 396 (1996)
- ²⁰ K. Akita, T. Kusunoki, S. Komiya and T. Kotani, J. Crys. Growth, 46, 783 (1979)
- ²¹ B. Garrett and E.J. Thrush, J. Crys. Growth, 97, 273 (1989)
- ²² P. Pianetta, I. Lindau, C.M. Garner and W.E. Spicer, Surf. Sci., 88, 439 (1979)
- ²³ A.J. Rosenberg, J.N. Butler and A.A. Meena, Surf. Sci., 5, 1 (1966)
- ²⁴ O. Kayser, R. Westphalen, B. Opitz and P. Balk, J. Crys. Growth, 112, 111 (1991)
- ²⁵ K. Yamaguci, M. Ogasawara and K. Okamoto, Jpn. J. Appl. Phys., 72, 5919 (1992)
- ²⁶ T. Sasaki, M. Kitamura and I. Mito, J. Crys. Growth, 132, 435 (1993)
- ²⁷ M. Gibbon, J.P. Stagg, C.G. Cureton, E.J. Thrush, C.J. Jones, R.E. Mallard, R.E. Pritchard, N. Collis and A. Chew, Semicond. Sci. Technol., 8, 998 (1993)
- ²⁸ A.M. Jones, M.L. Osowski, R.M. Lammert, J.A. Dantzig and J.J. Coleman, J. Elec.
 Mat., 24 1631 (1995)

- ²⁹ Y. Arituka, T. Umeda, J. Motohisa and T. Fakui, Mat. Res. Soc. Symp. Proc., 97, 570 (1999)
- ³⁰ Y. Sakata and K. Komatsu, 11th Proc. IPRM, 41 (1999)
- ³¹ T. Fujii, M. Ekawa and S. Yamazaki, J. Crys. Growth, 146, 475 (1995)
- ³² J.H. Neave, P.J. Dobson, B.A. Joyce and J. Zhang, Appl. Phys. Lett, 47, 100 (1985)
- ³³ H. Asai, J. Crys. Growth, 80, 425 (1987)
- ³⁴ B. Garret and E.J. Thrush, J. Crys. Growth, 97, 273 (1989)
- ³⁵ S.D. Hersee, E. Barbier and R. Blondeau, J. Crys. Growth, 77, 310 (1986)
- ³⁶ M. Hata, T. Isu, A. Watanabe, Y. Kajikawa and Y. Katayama, J. Crys. Growth, 114, 203 (1991)
- ³⁷ M. Kasu and N. Kobayashi, J. Crys. Growth, 170, 246 (1997)
- ³⁸ B. Tuck and M.A. Kadhim, J. Mat. Sci., 7, 585 (1972)
- ³⁹ F.C. Frank and D. Turnbull, Phys. Rev., 104, 617 (1956)
- ⁴⁰ I. Langmuir, J. Amer. Chem. Soc., 40, 1361 (1918)
- ⁴¹ J.H.G. Owen, K. Miki, D.R. Bowler, C.M. Goringe, I. Goldfarb and G.A.D. Briggs,
- Surf. Sci., 394, 91 (1997)
- ⁴² E. R. Messmer and S. Lourdudoss, J. Crys. Growth, 219, 185 (2000)
- ⁴³ C. Tomiyama, A. Kuramata, S. Yamazaki and K. Nakajima, J. Crys. Growth, 84, 115 (1987)
- ⁴⁴ J. Finders and J. Geurts, J. Crys. Growth, 107, 151 (1991)
- ⁴⁵ M. Eckel, D. Ottenwaelder, F. Scholz, G. Frankowsky, T. Wacker and A. Hangleiter,
 App. Phys. Lett., 64, 854 (1994)

- ⁴⁶ R.T. Huang, C.L Jiang, A. Appelbaum, D. Renner and S.W. Zehr, J.Elec. Mat., 19, 1313 (1990)
- ⁴⁷ V. Haerle, B. Rose D. Robein, Y. Gao, E. Landsbeck and F. Scolz, J. Crys. Growth,
 124, 260 (1992)
- ⁴⁸ T.F. Kuech, M.A. Tischler, N.I. Buchan and R. Potemski, J. Crys. Growth, 99, 324 (1990)
- ⁴⁹ R. Azoulay and L. Dugrand, Appl. Phys. Lett., 58, 128 (1991)
- ⁵⁰ R. Bhat, J. Crys. Growth, 120, 362 (1992)
- ⁵¹ H. Heinecke, A. Brauers, F. Grafahrend, C. Plass, N. Puetz, K. Werner, M. Weyers, H. Luth and P. Balk, J. Crys. Growth, 77, 303 (1986)
- ⁵² D.A. Andrews, M.A. Rejman-Green, B. Wakefield, G.J. Davies, Appl. Phys. Lett., 53, 97 (1988)
- ⁵³ Y.D. Galeuchet, P. Roentgen and V. Graf, J. Appl.Phys., 68, 560 (1990)
- ⁵⁴ K. Yamaguchi and K. Okamoto, Jpn. J. Appl.Phys., 28, L1489 (1989)

Chapter 3

Quantitative Modeling

3.1 Introduction

In chapter two, the SAE growth rate enhancement mechanisms were explained on a qualitative level. The magnitude of the enhancement was shown to be proportional to the width of the dielectric mask and inversely proportional to the open area between the masks. Similar observations are found in the literature.¹ Additionally, for an alloy such as InGaAsP, a non-uniform composition shift on the group III sub-lattice is established because each group III precursor has a different lateral diffusion length.² The group V sub-lattice composition is not significantly affected because group V precursors are available in excess under standard growth conditions.³

Understanding the relationship between mask geometry and the resulting thickness profile is essential for the design of a wide range of optoelectronic semiconductor devices employing SAE in the fabrication process. Examples include an integrated laser and optical modulator.⁴ The multiple quantum wells for both devices were deposited in a single growth step. A dielectric mask was used to generate thicker wells in the laser region. In addition, the well composition was perturbed by the presence of the mask. Together, the two effects led to a smaller bandgap in the laser section compared to the modulator section. Understanding the SAE process allows the designer to control the size of the shift. Similarly, an integrated semiconductor optical amplifier and optical mode converter has been demonstrated.⁵ The mode converter was fabricated from a vertical taper deposited in a single MOCVD growth step. A dielectric mask with a tapered width was used to control the growth rate enhancement. In this case, a

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quantitative model for SAE can be used to control the thickness profile of the mode converter to ensure adiabatic mode expansion.

Several quantitative SAE models exist in the literature. They compute the growth rate enhancement and composition shift as a function of mask size and shape by quantifying the physical processes involved in the deposition. Early studies on the growth mechanisms of SAE recognized the two components described in chapter two, a surface migration component and a vapor phase diffusion component.⁶ Section 2.2 demonstrated that for a gap width greater than 10 μ m between two dielectric masks, surface migration was responsible for the observed morphology in a region within 1 or 2 μ m of the mask while the growth mechanism responsible for the remaining region of the gap was dominated by vapour phase diffusion.

Coronell and Jensen presented a coupled volume and surface diffusion model.⁷ The model considered the precursor sticking probability, residence time and surface diffusion length on the masked substrate. No experimental results were offered in their work so the validity of their model was not demonstrated. Yamaguchi and Okamoto presented a model based on a process whereby precursors, which impinge on a SiO₂ mask, migrate along the surface for a characteristic diffusion length (about 1 µm) and then evaporate.⁸ After evaporation, a vapor phase diffusion mechanism, characterized by a separate diffusion length, carries the precursors into the open area of the substrate. However, compared to more recent papers, their report was beleaguered by very poor agreement between simulated curves and measured values. Fujii, Ekawa and Yamazaki took a different approach to develop a model for the growth rate enhancement, accounting for both vapour phase diffusion and surface migration.⁹ They analyzed

simultaneous 2-D differential equations for diffusion in the vapour state, migration on the surface and total particle flux into the surface. The mathematical domain for the vapour phase diffusion equation was perpendicular to the substrate while the domain for the surface migration equation was parallel to the surface and could account for non-uniform dielectric masks. Much analysis resulted in the following expression for the adatom concentration on the semiconductor surface, (Eq. (19) from ref. 9)

$$\nabla^2 P(x, y) = \frac{P(x, y)}{L^2} - \frac{P_o}{L^2}$$
(3.1)

where P(x,y) is the surface concentration, P_o is the surface concentration in the absence of a dielectric mask and *L* is the effective lateral diffusion length. The reference contains an equation for *L* in terms of the vapour phase diffusion constant, the surface migration constant for the mask and the rate of adsorption for the semiconductor surface. Measured values as well as a curve calculated using Eq. (3.1) were plotted together to show the excellent agreement between theory and experiment but measurements were only performed on parts of the semiconductor at least a few microns from the mask and that region is known to be insignificantly affected by surface migration.⁶ For infinitely long dielectric rectangle pairs, Eq. (3.1) can be simplified as follows,

$$\frac{d^2 P(x)}{dx^2} = \frac{P(x)}{L^2} - \frac{P_o}{L^2}.$$
(3.2)

Equation (3.2) predicts that the surface concentration across the gap between two rectangle pairs is

$$P(x) = A\exp(x/L) + B\exp(-x/L) + P_o$$
(3.3)

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where *A* and *B* are constants that would be determined by the boundary conditions at x = -W/2 and x = W/2 where *W* is the width of the gap. Although the model appears initially attractive because previous models could not offer a solution in algebraic form, it will soon become clear that the form of Eq. (3.3) is too simplistic to describe the measured results that will be presented in chapter four.

Gibbon and co-workers demonstrated that surface migration can be ignored for a wide range of circumstances, and presented a quantitative model for SAE based on Laplace's equation in 2-dimensions.¹⁰ The model used a single vapor phase diffusion parameter for each group III precursor and was solved numerically for the case of dielectric masks of uniform width. Alam and co-workers expanded the model to 3dimensions to simulate growth on a wafer patterned with masks of non-uniform width.¹¹ The equations were solved using a finite element method and calculated values were compared with experimental measurements of the growth rate enhancement and composition shift. Both reports demonstrated excellent agreement between the experimental measurements and the values predicted by the model for regions of the semiconductor at least a few microns from the dielectric mask. Further use of the model, was reported by Jones and Coleman.¹² In their experiments, the nominal thickness of the deposited films was 250 Å, much thinner than the films deposited in the other two studies. Excellent agreement between experimental measurements and theory was obtained including measurements of the semiconductor adjacent to the mask. In this chapter, an explanation for their success is given for the first time. Moreover, a quantitative model for SAE is developed to properly incorporate the effects of surface migration. Based on the results of chapter two, section 3.6 hypothesizes that precursors

originating from the mesa sidewall facets account for the thickness profile of the semiconductor film within a few microns of the mask. It follows that for very thin films, there is no discrepancy since the surface area of the sidewall is extremely small.

In subsequent sections, the SAE vapour phase diffusion model will prove itself to be the most important of the quantitative models and it will be dealt with in more detail. Section 3.2 will present an introduction to quantitative modeling in MOCVD and section 3.3 will detail aspects of quantitative modeling specific to SAE. Gibbon's model will be explained in detail along with original contributions to its application. Equation (3.17) will be presented for the first time as a means to eliminate one fitting parameter from the model. Sections 3.4 and 3.5 will outline numerical implementations of the model using MATLAB and the C programming language respectively.

3.2 The Boundary Layer Model

Given sufficient computing power, the gas flow pattern within the reactor can be well described by the laws of fluid dynamics. Furthermore, the chemistry of organometalics has received much attention over the past decade due to the importance of MOCVD to semiconductor manufacturing.^{13,14} Mountziaris and Jensen assumed a mass transport limited regime and developed a comprehensive model of the flow dynamics during growth.¹⁵ Numerical solutions were obtained for equations of conservation of mass, momentum, energy and species. The pyrolysis of precursor molecules was also accounted for such as the decomposition of trimethylindium to dimelthylindium and monomethylindium. Mazumder and Lowry accounted for deposition on the reactor walls, which deplete the carrier concentration.¹⁶ These approaches have been useful for

reactor geometry design. For example, detailed modeling was used to improve the gas inlet configuration of a horizontal MOCVD reactor,¹⁷ but this sort of modeling is too numerically cumbersome for growth experiments carried out in the course of process development.



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Fig. 3.1 A pictorial description of the boundary layer model used for MOCVD growth.

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Quantitative Modeling

In practice, the complex flow dynamics of MOCVD inhibits practical applications of complete and detailed modeling. Moreover, the chemical reactions taking place at the substrate surface during growth, a non-equilibrium process, are more complex than the reactions studied by *ex situ* experiments.^{18,19} As such, a successful quantitative model for SAE must only concentrate on the essential processes to obtain an approximate simulation of the key growth parameters. Fortunately, growth is diffusion rate limited and chemical kinetics produce secondary effects, which can be greatly simplified in a mathematical treatment.²⁰

The most widely used model for growth rate calculations is the boundary layer model. Early experimental work by Everstyn and co-workers revealed that the net velocity of gas molecules at the wafer surface during growth is zero.²¹ Surface friction was believed to be the cause. This conclusion was reached, at least in part, from the analogous phenomenon in general fluid dynamics.²² Since there is no gas flow near the surface, the model is also called the *stagnant layer* model. To apply the model, the MOCVD reaction chamber is divided into three sections as shown in Fig. 3.1. The top most section contains the gas phase molecules originating from the inlet at a concentration given by the flow rates. The middle, or stagnant layer, consists of the carrier and precursor gases in the volume directly above the semiconductor surface. The bottom layer consists of the molecules in contact with the semiconductor, where the word, "contact," implies the existence of interaction forces.

To generate an equation for the growth rate, a coordinate system must be established within the stagnant layer. Let the semiconductor surface lie within the xy plane as shown in Fig. 3.2. Let z = 0 be the semiconductor surface and $z = \delta$ be the top

of the stagnant layer. Since the net velocity is zero within the stagnant layer, the concentration of the *i*th group III precursor is given by Laplace's equation, $\nabla^2 c_i = 0$. The flow dynamics within the top layer (above the stagnant layer) are beyond the scope of this simple model. Likewise, details of the chemical reactions occurring in the bottom layer are unimportant. However, each layer makes one contribution. The top layer provides a uniform and steady supply of precursors to the stagnant layer so that for the *i*th group III precursor,

$$c_i(x, y, z = \delta) = c_{io}. \tag{3.4}$$

In actuality, a uniform supply of precursors is assured by rotating the substrate. It has been observed that for a horizontal flow reactor, the precursor supply is depleted along the direction of flow.²³ Traditionally, the consumption of precursors at the semiconductor surface is assumed to take place at an infinitely fast rate so that,²⁴

$$c_i(x, y, z = 0) = 0. (3.5)$$



Semiconductor surface

Fig. 3.2 Mathematical domain for the boundary layer. The wafer surface is the z = 0 plane.

Since there is no variation in the x- or y-directions, the problem is a 1-D boundary value problem with a simple solution,

$$c_i(z) = (c_{io} / \delta)z. \tag{3.6}$$

The diffusion flux of the reactant at the surface is

$$J_{i} = -D_{i} \frac{\partial c_{i}}{\partial z} \bigg|_{z=0}$$
(3.7)

where D_i is the diffusion coefficient of the *i*th gas moelecule. For InP, the growth rate is $g = -k_g J_{ln}$ where k_g is the molecular volume of InP. The growth rate can be expressed more explicitly as,

$$g = k_g D_{in} c_{io} / \delta. \tag{3.8}$$

The Ideal gas law, $P = c_{io}RT$, can be employed to obtain an approximate numerical value for c_{io} .²⁵ In early works, the height of the stagnant layer, δ , was assumed to be proportional to the *velocity boundary layer*, δ_V , a concept borrowed from fluid dynamics. The following expression was quoted,^{26,27}

$$\delta \propto \sqrt{\mu X \,/\,\rho V} \tag{3.9}$$

where μ is the gas viscosity, ρ is the gas density, X is the average distance from the reactor inlet to the wafer and V is the gas velocity at the inlet. For the special case of a horizontal flow reactor, Berkman and co-workers²⁸ obtained a more practical expression by assuming laminar flow and a uniform temperature distribution:

$$\delta = \sqrt{\pi D X / V} \,. \tag{3.10}$$

3.3 SAE Quantitative Modeling

The foundation for the SAE vapor phase diffusion model lies in stagnant layer theory, which states that the steady state concentration of each group III precursor is given by Laplace's equation,

$$\nabla^2 c(x, y, z) = 0, \tag{3.11}$$

where *c* is the concentration of the group III precursor. Figure 3.3 illustrates the (x,y,z) coordinate system. The boundary condition for the top of the stagnant layer is

$$c(x, y, z = \delta) = c_o, \tag{3.12}$$



Fig. 3.3 The stagnant layer model of SAE.

where δ is the height of the stagnant layer and c_o is a constant representing the steady supply of precursors from the reactor inlet. At the bottom of the stagnant layer, two surfaces exist, the dielectric mask and the open semiconductor area. For the mask, since there is no net flux, the boundary condition is

$$\left. \frac{\partial c}{\partial z} \right|_{z=0} = 0. \tag{3.13}$$

For the open area, the diffusive flux is equated to the growth flux, giving

$$\left. D \frac{\partial c}{\partial z} \right|_{z=0} = kc \tag{3.14}$$

where D is the vapor phase diffusion constant of the precursor and k is the incorporation rate of the semiconductor surface. The boundary conditions for the remaining surfaces are chosen by selecting L_1 and L_2 in Fig. 3.3 to be much larger than the lateral diffusion length so that

$$\frac{\partial c}{\partial x}\Big|_{x=-L1} = \frac{\partial c}{\partial x}\Big|_{x=L1} = \frac{\partial c}{\partial y}\Big|_{x=-L2} = \frac{\partial c}{\partial y}\Big|_{x=L2} = 0.$$
(3.15)

Equations (3.11) to (3.15), along with Laplace's equation, describe the lateral vapor phase diffusion of a group III precursor. To calculate the growth rate enhancement and the composition shift for InGaAsP, the system of equations must be solved separately for the In precursor and the Ga precursor. Each solution requires a unique value of D/k. The growth rate enhancement for the indium component is given by

$$R_{ln}(x,y) = c_{ln}(x,y,z=0)/c_{ln}$$
(3.16)

where c_{ln} is the solution to Laplace's equation when no mask is present. A closed form solution for c_{ln} can be found by solving Laplace's equation under the condition of no
dielectric mask, or equivalently by modifying the nominal stagnant layer theory by replacing Eq. (3.5) with Eq. (3.14). The solution is

$$c_{ln} = \frac{c_o}{(k/D)_{ln}\delta + 1}.$$
(3.17)

This equation has a similar form to Eq. (3.6). The additional parameter, k, appears because the approximation of zero precursor concentration on the semiconductor surface has been replaced by a kinetic factor, represented by Eq. (3.14), needed to describe the lateral vapor phase diffusion action of each group III precursor. The kinetic factor, k, disappears if Eq. (3.16) is used to calculate the growth rate in the absence of a dielectric mask. Chapter four will show that c_o and δ can be chosen such that R_{ln} is independent of their value, leaving $(D/k)_{ln}$ as the only model parameter. The need for only one parameter simplifies the model's use but the ability to calculate the absolute growth rate is lost. However, this value is typically well known from routine reactor calibrations.

A value can be found for R_{Ga} using an identical procedure. The growth rate enhancement for In_{1-s}Ga_sAs_tP_{1-t} is a linear combination of the two components,²⁷

$$R_{InGaAsP} = (1-s)R_{In} + sR_{Ga}.$$
(3.18)

The perturbed composition, s', can be found using a similar argument.²⁹

$$s' = \frac{sR_{Ga}}{(1-s)R_{In} + sR_{Ga}}$$
(3.19)

 R_{In} and R_{Ga} are functions of $(D/k)_{In}$ and $(D/k)_{Ga}$ respectively. R_{In} is calculated with Eq. (3.16). R_{Ga} is calculated with an analogous equation.

3.4 A Program for Solving the SAE Equations in 2-Dimensions

Equations (3.11) to (3.17) were implemented in 2-dimensions using the commercially available MATLAB computer software package. Figure 3.4 illustrates the domain used for simulating SAE with dielectric stripes of uniform width. For the case of two identical dielectric stripes, the domain was further simplified to contain only one stripe and half of the spacing between the stripes. The simplification arises from the problem's symmetry. The MATLAB Partial Differential Equation (PDE) Toolbox contains scripts that allow the user to define a boundary value problem graphically. The toolbox also contains scripts to generate a mesh, discretize the equations and obtain a numerical solution.



Fig. 3.4 A 2-D description of the SAE vapour phase model applicable to masks of uniform width.

A MATLAB script called SAEsolve.m, which makes calls to the PDE toolbox, was programmed with the following call format:

c = SAEsolve(stripe,gap,Dk,**xin**)

where *stripe* is the width of the mask stripe, *gap* is the width of the gap between stripes and *Dk* is equal to (*D/k*). *c* is the solution for the concentration in vector format where the *i*th component corresponds to $c_{in}(x_i,z=0)$ and x_i is the *i*th component of the input vector *xin*. Although the script computes the solution over the entire 2-D domain, only the solution on the z = 0 surface is passed to the output since only those values are necessary to compute the growth rate enhancement using Eq. (3.16). The flow chart for *SAEsolve.m* is illustrated in Fig. 3.5. To avoid unnecessary repetition, numerical methods will be dealt with in greater detail in section 3.5 when the 3-D problem is discussed.



Fig. 3.5 The Flow chart for *SAEsolve.m*.



Fig. 3.6 The mesh created by *SAEsolve.m* to solve Laplace's equation under the boundary conditions illustrated in Fig. 3.4. The mesh is more refined near the mask and near the gap.

Figure 3.6 illustrates the mesh created for the domain shown in Fig. 3.4. It was generated using the following call,

 $c = SAEsolve(50 \,\mu\text{m}, 100 \,\mu\text{m}, 40 \,\mu\text{m}, xin)$

The script created a finer mesh in the gap between the masks, where the solution is the most critical. Since the thickness of the dielectric mask (30 nm) is much less than the height of the stagnant layer, δ , the dielectric thickness was approximated as zero.

Figure 3.7 illustrates the preliminary solution for the gas phase precursor concentration. At the substrate surface, in the gap between the dielectric masks, the solution has a parabolic shape. Also, the concentration is largest above the dielectric mask due to the absence of growth material consumption. Far above the surface, the solution is linear and takes on the form of Eq. (3.6). A plot of *c* versus *xin* is shown in Fig. 3.8. The left half of the *x*-axis is included and the *y*-axis shows growth rate enhancement rather than concentration. The former was easily calculated using the symmetry relation, c(x) = c(-x) and the latter was calculated with Eq. (3.16), a function built into *SAEsolve*. In chapter four, *SAEsolve* will be used to obtain solutions for a wide variety of dielectric stripe widths and gap widths and the calculated values will be compared with experimentally obtained measurements. It will be seen that by varying the growth pressure and temperature, the value of *D/k* changes in accordance with basic stagnant layer theory.



Fig. 3.7 The raw output from *SAEsolve.m*. The concentration distribution is linear except for a perturbation in the vicinity of the dielectric mask.



Fig. 3.8 The finalized output from *SAEsolve.m*: a plot of growth rate enhancement versus distance along the wafer between a dielectric mask pair.

3.5 A Program for Solving the SAE Equations in 3-Dimensions

Equations (3.11) to (3.17) were implemented in 3-dimensions using a finite difference method. The algorithm was realized using the C programming language. The finite difference method is a powerful yet direct method for numerically solving a wide variety of boundary value problems. Figure 3.9 shows the flow chart for *SAE3D* and Table 3.1 summarizes the main variables and their definitions. The program's first task is to define a mesh within the boundary layer. The mesh point spacing is uniform in the *y*-direction and non-uniform in both the *x*- and *z*-directions. The mesh is fine near the dielectric mask, where the accuracy is critical, and coarse far away from the mask, where it is advantageous to trade accuracy for computation speed. A typical simulation takes two hours on a Pentium 500 MHz machine.



Fig. 3.9 Flow chart for the program SAE3D.

Table 5.1 Main variables used in SALSE	
Variable	Meaning
u[0Imax , 0Jmax , 0Kmax]	solution value at mesh point [i,j,k]
hx[0Imax]	mesh spacing in the x-direction
hy	(uniform) mesh spacing in the y-direction
hz[0Kmax]	mesh spacing in the z-direction
edge1[0Jmax]	left-hand boundary of the dielectric mask
edge2[0Jmax]	right-hand boundary of the dielectric mask
Dk	D/k
Lx	length of domain in the x-direction
Ly	length of the domain in the y-direction
Lz	δ
Со	Co





Fig. 3.10 A simplified non-uniform mesh created by *SAE3D*. The *y*-axis spacing is omitted for ease of viewing. The mesh spacing is smallest about the origin.

Quantitative Modeling

Figure 3.10 illustrates a simplified mesh. Grey lines have been drawn on the surface of the domain to illustrate the non-uniformity in the *x*- and *z*-directions. An illustration of the uniform mesh spacing in the y-direction was omitted to simplify the drawing. Notice that the mesh is finest near the line defined by the intersection of the x = 0 and z = 0 planes. The frame of reference is defined such that the dielectric mask is located near that line, and the semiconductor gap between the masks is centered about the line. Within *SAE3D*, two 1-D arrays, **hx[i]** and **hz[k]**, and one scalar, **hy**, are defined to specify the mesh point spacing. **hx[I]** is equal to the spacing from mesh points [*I*,*j*,*k*] to [*I*,*j*,*k*] to [*I*,*j*,*k*] (for all *j*,*k*) and **hz[K]** is equal to the spacing from points [*i*,*j*,*K*] to [*i*,*j*,*K*+1] (for all *i*,*j*).

After establishing the mesh, *SAE3D* determines which mesh points, [i,j,0] (on the z = 0 surface), fall within the dielectric mask boundary. This is done by rounding-off the dimensions of the dielectric mask edges to fit a polygon whose sides lie on mesh points. *SAE3D* contains the 1-D arrays, **edge1[j]** and **edge2[j]**, which define the mask edge closer to the x = 0 plane and further from the plane respectively. Boundary conditions are established on the $z = \delta$ plane by assigning the value c_0 to all mesh points, $[i,j,K_{max}]$. Equation (3.6), the solution to Laplace's equation for the special case of no dielectric mask, is used to assign initial guess values to the interior mesh points. This is reasonable since SAE increases the growth rate by less than an order of magnitude compared to the case of no masks and the increase occurs mostly at mesh points near the z = 0 surface, as seen in Fig. 3.7. In principle, the solution is independent of the initial guess but the computation time can be greatly reduced by an intelligent choice.

Next, *SAE3D* successively refines the solution using a finite difference implementation of Laplace's equation. For the reader not familiar with finite differences, let u(x) be a function. The first derivative can be approximated,

$$\frac{\partial u}{\partial x} \approx \frac{u(x) - u(x - h)}{h}$$
(3.20)

where h is a sufficiently small value; and similarly,

$$\frac{\partial^2 u}{\partial x^2} \approx \frac{u(x) - 2u(x-h) - u(x-2h)}{h^2}.$$
(3.21)

Let u[i,j,k] be a difference element where the integers [i,j,k] define a mesh point and $u[i,j,k] = u(ih_x,jh_y,kh_z)$. h_x,h_y , and h_z are the mesh spacing in the three directions. Using Eq. (3.21) and similar expressions for the partial derivatives in the y- and z-directions, a finite difference equation can be obtained for Laplace's equation,

$$\frac{u[i, j, k] - 2u[i - 1, j, k] - u[i - 2, j, k]}{h_x^2} + \frac{u[i, j, k] - 2u[i, j - 1, k] - u[i, j - 2, k]}{h_y^2} + \frac{u[i, j, k] - 2u[i, j, k - 1] - u[i, j, k - 2]}{h_z^2} = 0.$$
(3.22)

Notice that each term has the same form as Eq. (3.21). Solving the equation for u[i,j,k] gives

$$u[i,j,k] = (3.23)$$

$$\left(\frac{2}{h_x^2} + \frac{2}{h_y^2} + \frac{2}{h_z^2}\right)^{-1} \left(\frac{u[i+1,j,k] + u[i-1,j,k]}{h_x^2} + \frac{u[i,j+1,k] + u[i,j-1,k]}{h_y^2} + \frac{u[i,j,k+1] + u[i,j,k-1]}{h_z^2}\right)^{-1} \left(\frac{u[i,j,k] + u[i,j,k-1]}{h_z^2} + \frac{u[i,j+1,k] + u[i,j-1,k]}{h_z^2}\right)^{-1} \left(\frac{u[i+1,j,k] + u[i-1,j,k]}{h_z^2} + \frac{u[i,j+1,k] + u[i,j-1,k]}{h_z^2}\right)^{-1} \left(\frac{u[i+1,j,k] + u[i-1,j,k]}{h_z^2}\right)^{-1} \left(\frac{u[i+1,j,k] + u[i-1,j,k]}{h_z^2} + \frac{u[i,j+1,k] + u[i,j,k]}{h_z^2}\right)^{-1} \left(\frac{u[i+1,j,k] + u[i-1,j,k]}{h_z^2}\right)^{-1} \left(\frac{u[i+1,j,k]}{h_z^2}\right)^{-1} \left(\frac{u[i+1,j,k]}{h_z^2}\right)^{-1} \left(\frac{u[i+1,j,k]}{h_z^2}\right)^{-1} \left(\frac{u[i+1,j,k]}{h_z^2}\right)^{-1} \left(\frac{u[i+1,j,k]}{h_z^2}\right)^{-1} \left(\frac{u[i+1,j,k]}{h_z^2}\right)^{-1} \left(\frac{u[i+1,j,k]}{h_z^2}\right)^{-1} \left(\frac{u[i+1,j,k]}{h_z^2}\right)^{-1} \left(\frac{u[i+1,j,k]}{h_z^2}\right)$$

For the special case of $h = h_x = h_y$, $= h_z$, the approximation error in Eq. (3.23) is $O(h^4)$.³⁰

SAE3D performs the operation of Eq. (3.23) on each mesh point using three main loops. The first begins at the z = 0+ plane containing the points [i,j,1] and ends at the $z = \delta$ - plane containing the points $[i,j,K_{max}-1]$. For each value of k, two sub-loops handle the *i* and *j* indexes respectively. The sub-loops start in the middle of the plane and proceed outwards. Before proceeding to the second main loop, the boundary conditions at the wafer surface are dealt with. To this end, Eq. (3.13) for the dielectric and Eq. (3.14) for the semiconductor were implemented in finite difference form; for the dielectric,

$$u[i,j,0] = u[i,j,1]$$
(3.24)

and for the semiconductor,

$$u[i, j, 0] = \frac{u[i, j, 1]}{1 + (D/k)^{-1} h_z[0]}.$$
(3.25)

Sub-loops for the *i* and *j* indexes sweep through the points [i,j,0] and apply Eq. (3.24) or Eq. (3.25). For points [i,j,0] such that **edge1[j]** < *i* < **edge2[j]**, the former is used. For all other points, [i,j,0], the latter is used.

The second and third main loops sweep from the interior of the mesh outwards, starting at the plane defined by the set of points, $[i, J_{avg}, k]$, where J_{avg} is equal to the average of all values in both arrays, **edge1** and **edge2**, and is therefore approximately the middle of the dielectric mask. The main loops were designed to begin at mesh points with the largest residuals (the difference between solution values at successive iterations) since that will lead to convergence more quickly,³¹ however, rather then consume calculation time by calculating the residuals, the algorithm was designed using an intuitive knowledge of the particle flows and knowing that the dielectric surface is responsible for altering the solution from the initial guess values.

SAE3D iterates until the residual is less than the uncertainty in the experimental growth rate measurements. A proof for the convergence of u[i,j,k] to u(ih,jh,kh) as the number of iterations tends to infinity is given in ref. 31.



(100) InP substrate

Fig 3.11 A pictorial description of surface migration during SAE. The numbered arrows represent different processes described in the text.

3.6 A Quantitative Surface Diffusion Model

For a gap width greater than 10 μ m between two dielectric masks, chapter two demonstrated that surface migration was responsible for the observed morphology in a region within 1 or 2 μ m of the mask while the growth mechanism of the center region of the gap was dominated by vapour phase diffusion. The previous sections detailed a quantitative description of the contribution made by the latter component. In this section, the role of surface migration is quantified with an original model employing time dependent boundary conditions.

Figure 3.11 shows an InP mesa in the [011] direction. The (100) mesa top surface as well as the (111) β sidewall are shown. The black circles and arrows illustrate the surface migration process. Initially, adatoms are adsorbed onto the (111) β surface. In the figure, the process is denoted by arrow (1). (Of course, adatoms are absorbed onto the (100) surface as well but that was accounted for in the vapour phase model). Adsorbed adatoms can be desorbed, illustrated by arrow (4), or can migrate to the (100) mesa top, illustrated by arrow (2). The rate of adsorption is the product of the precursor partial pressure, the number of vacant atomic sites and an adsorption constant. The rate of desorption is equal to the product of the number of occupied sites and a desorption constant.³² Let N_{so} be the rate at which adatoms leave the (111) β surface via process (2). Without loss of generality, we assume a zero <111> growth rate and the following mass balancing equation can be stated

$$k_{a} p_{i} (1 - \Theta) - k_{d} \Theta - N_{so} = 0$$
(3.26)

where Θ is the percentage of occupied atomic sites. The rate constants can be expressed more explicitly,³³

$$k_a = \frac{\sigma \kappa}{\sqrt{2\pi M k_B T}} \tag{3.27}$$

 $k_d = v \exp(-E_b / k_B T)$

(3.28)

where *M* is the mass of the adsorbed molecule, σ its effective surface area and κ is the *sticking probability*, the probability that a gas molecule that has arrived at an adsorption center on the surface will become attached. In Eq. (3.28), E_b is the binding energy and ν is the pre-exponential constant.³⁴ It is safe to consider only the group III species since $\Theta_{\text{III}} << \Theta_{\text{V}}$ for typical V/III pressure ratios. For a planar surface, a (111) surface is not exposed so $N_{so} = 0$ and Eq. (3.26) reduces to Eq. (2.1).

The variables k_a , k_d , p_i and Θ depend strongly on the growth parameters. In chapter two, it was found that certain growth conditions, including the "nominal" conditions (run # S4788), lead to zero growth on the (111) β surface. Zero growth implies $\Theta \approx 0$ and Eq. (3.26) reduces to

$$n_s = k_a p_i. \tag{3.29}$$

At intermediate values of surface coverage, Θ is given by the Freundlich isotherm,^{35,36}

$$\Theta = b p_i^{1/n} \tag{3.30}$$

where *b* is a combination of the adsorption and desorption rate constants. N_{so} remains a function of only k_a , k_d and p_i . Similarly, Eq. (3.29) can be modified to account for a finite <111> growth rate.

The surface area of the sidewall is given by $S_A = l \ge h$ where, l, the mesa length and, h, the height are defined in Fig. 3.11. For $l \ll L_{(111)}$ where $L_{(111)}$ is the diffusion length, the total number of adatoms, per unit of width, arriving on the mesa top via the mechanism illustrated by arrow (3) is $n_{so} = hN_{so}$. Since $h = (sin 55^o)^{-l}r_g t$ where r_g is the mesa growth rate (due to vapour phase diffusion), t is the growth time and 55^o is the angle between the (100) and (111) planes, n_{so} can be expressed,

$$n_{so} = (\sin 55^{\circ})^{-1} r_g k_a p_i t.$$
(3.31)

When the Freundlich isotherm applies, the factor $k_a p_i$ must be replaced by a more complicated function of k_a , k_d and p_i .

Applying the continuity equation to the (100) surface results in the following equation,

$$\frac{\partial n_s}{\partial t} = D_s \frac{\partial^2 n_s}{\partial x^2} - \frac{n_s}{\tau}$$
(3.32)

where D_s is the surface diffusion constant. The y-axis coordinate has been removed due to symmetry. The second term on the right accounts for the loss of adatoms due to incorporation into the growing film.^{37,38} τ is the mean lifetime of an adatom injected from the (111) sidewall. Desorption is expected to be small since the reaction is heavily forward driven, however, a loss of surface density due to desorption could be accounted for by modifying τ to describe both processes. Equation (3.32) must be solved under the following conditions,

$$n_s(t, x = -w/2) = At$$
 (3.32a)

$$n_s(t, x = w/2) = At$$
 (3.32b)

$$n_s(0,x) = 0.$$
 (3.32c)

Equation (3.32a) follows from Eq. (3.31) where A has replaced the pre-time variable constants. Appendix A details the calculations leading to following solution for the surface concentration under the condition, $t \gg \tau$.

$$n_{s}(x,t) = At\left(e^{-\frac{x}{L}} + e^{-\frac{W-x}{L}}\right)$$
(3.33)

The two independent parameters, τ and D_s , have been replaced by a single parameter, L, the *surface diffusion length*, where $L^2 = D_s \tau$. The growth rate due to the SAE surface migration component is

$$G_s(x,t) = \frac{k_s}{\tau} n(x,t). \tag{3.34}$$

Finally, the overall film thickness after a growth time, T, taking vapour phase diffusion and surface migration into account, is

$$h'(x) = gTR_{ln}(x) + \int_{0}^{T} G_{s}(x,t)dt.$$
(3.35)

¹O. Kayser, R. Westphalen, B. Opitz and P. Balk, J. Cryst. Growth, 112, 111 (1991)

² J.S.C. Chang, K.W. Carey, J.E. Turner and L.A. Hodge, J. Elec. Mat., 19, 345 (1990)

- ³ M. Ida, N. Shigekawa, T. Furuta, H. Ito, T. Kobayashi, J. Cryst. Growth, 158 (1996) 437
- ⁴ R.M. Lammert, G.M. Smith, J.S. Hughes, M.L. Osowski, A.M. Jones and J.J. Coleman, IEEE Photon. Tech. Lett. 8, 797 (1996)
- ⁵ H. Hardtdegen, A. Kaluza, D. Gauer, M.V.D. Ahe, M. Grimm, P. Kaufmann and L. Kadinski, J. Cryst. Growth, 223, 15 (2001)
- ⁶ O. Kayser, J. Cryst. Growth, 107, 989 (1991)
- ⁷ K.F. Coronell and R. Jensen, J. Crystal Growth 114, 581 (1991)
- ⁸ K. Yamaguchi and K. Okamoto, Japan. J. App. Phys. 32, 1523 (1993)

⁹ T. Fujii, M. Ekawa and S. Yamazaki, J. Cryst. Growth, 146, 475 (1995)

¹⁰ M. Gibbon, J.P. Stagg, C.G. Cureton, E.J. Thrush, C.J. Jones, R.E. Mallard, R.E.

Pritchard, N. Collis and A. Chew, Semicond. Sci. Technol. 8, 998 (1993)

¹¹ M.A. Alam, R. People, E. Isaacs, C.Y. Kim, K. Evans-Lutterodt, T. Siegrist, T.L.

Pernell, J. Vandenberg, S.K. Sputz, S.N.G. Chu, D.V. Lang and L. Smith, App. Phys. Lett. 74, 2617 (1999)

¹² A.M. Jones and J.J. Coleman, J. Elec. Mat., 24, 1631 (1995)

¹³ G.B. Stringfellow in Semiconductors and Semimetals, Vol. 22, ed. W.T. Tsang,
 Academic Press, Orlando, Florida (1985)

¹⁴ K.L. Fry, C.P. Kuo, C.A. Larsen, R.M. Cohen, G.B. Strinfellow and A. Melas, J. Elec.
Mat., 15, 91 (1986)

¹⁵ T.J. Mountziaris and K.F. Jensen, J. Electrochem. Soc., 238, 2426 (1991)
 ¹⁶ S. Mazumder and S.A. Lowry, J. Cryst. Growth, 224, 165 (2001)

- ¹⁷ H. Hardtdegen, A. Kaluza, D. Gauer, M.V.D. Ahe, M. Grimm, P. Kaufmann and L.
 Kadinski, J. Cryst. Growth, 223, 15 (2001)
- ¹⁸ C.A. Larsen, N.I. Buchan and G.B. Stringfellow, J. Cryst. Growth, 85, 148 (1987)
- ¹⁹ N.I. Buchan, C.A. Larsen, G.B. Stringfellow, App. Phys. Lett., 51, 1024 (1987)
- ²⁰ D.H. Reep, S.K. Ghandi, J. Electrochem. Soc., 130, 675 (1983)
- ²¹ F.C. Everstyn, P.J.W. Severin, C.H.J. van der Brekel and H.L. Peel, J. Electrochem.
 Soc., 119, 925 (1970)
- ²² V.L. Streeter, Fluid Dynamics, McGraw-Hill, New York, New York, pp. 241-248(1948)
- ²³ A.S. Grove, Physics and Technology of Semiconductor Devices, Wiley Publishing, New York, New York, pp. 7-21 (1967)
- ²⁴ S.K. Ghandi and R.J. Field, J. Cryst. Growth 69, 619 (1984)
- ²⁵ R.J. Field and S.K. Ghandi, J. Cryst. Growth, 69, 581 (1984)
- ²⁶ M.R. Leys and H. Veenvliet, J. Cryst. Growth, 55, 145 (1981)
- ²⁷ S.E. Bradshaw, J. Electron., 23, 381 (1967)
- ²⁸ S. Berkman, V.S. Band and N. Goldsmith, Hetoroepitaxial Semiconductors for
- Electronic Devices, Springer Publishing, New York, New York, pp. 264-281 (1978)
- ²⁹ J.F. Kluender, A.M. Jones, R.M. Lammert, J.E. Baker and J.J. Coleman, J. Electron. Mater. 25, 1514 (1996)
- ³⁰ W.E. Milne, "Numerical Solution of Differential Equations", John Wiley and Sons, New York, NY (1953)
- ³¹ G.F.D. Duff and D. Naylor, "Differential Equations of Applied Mathematics", John
 Wiley & Sons, New York, NY (1966)

- ³² I. Langmuir, J. Am. Chem. Soc., 40, 1361 (1918)
- ³³ T. Wolkenstein, Electronic Processes on Semiconductor Surfaces During

Chemisorption, Consultants Bureau, New York (1991)

- ³⁴ S. Glasstone, K.J. Leidler and H. Eyring, The Theory of Rate Processes, McGraw-Hill, New York (1941)
- ³⁵ H. Freundlich, Capillary Chemistry, Verlag Academic Press, Leipzig (1922)
- ³⁶ W.S. Hobson, T.D. Harris, C.R. Abernathy and S.J. Pearton, App. Phys. Lett., 58, 77

- ³⁷ B.S. Swartzentruber, Phys. Rev., 76, 459 (1995)
- ³⁸ C. Pearson, N. Kobayashi and H. Yamaguchi, App. Phys. Lett., 63, 678 (1993)

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Chapter 4

Experiments on InP Selective Area Epitaxy

4.1 Introduction

The previous chapter established a theoretical framework for SAE quantitative modeling. The framework will prove critical for the successful fabrication of a photonic integrated circuit. A vapour phase diffusion component and a surface migration component were explored in detail. Partial differential equations were presented to describe the precursor distribution. Computer programs for solving the equations were also presented.

In the present chapter, we report on experiments designed to confirm the validity of the models and assess their accuracy. The experiments are restricted to InP film growth. Only one fitting parameter is necessary for the vapour phase model and two components are necessary for the surface migration model. Therefore, the modeling is simplified and the physics of SAE can be explored without parasitic effects caused by the presence of multiple group III precursors. Chapter five reports on InGaAs and InGaAsP film growth.



Fig. 4.1 Schematic of the surface profilometer used in this work.

4.2 Experimental Procedure

Using a Sloan DEKTAK surface profiler, a large series of thickness profile measurements were made of the selectively grown ridges. The workings of a DEKTAK can be explained with the aid of Fig. 4.1. The sample is mounted on a moveable stage controlled by a stepper motor. A needle is in contact with the sample as the motor pulls the stage. The other end of the needle is connected to a transformer coil mounted to a moveable support by a spring. The second transformer coil is fixed. As the sample moves under the needle, the needle's vertical displacement is translated into a change in the effective transformer turn ratio. The transformer and the stepper motor are wired into a computer so that a plot of film thickness versus stepper distance can be obtained as shown in the figure inset. An algorithm was used to correct for the tilt of the sample mounting. For the DEKTAK apparatus used in this work, the step height measurement error was 10 nm, the minimum stepper distance per sampling point was 100 nm and the slew rate was 2 μ m/ μ m.

Several profiles were obtained using atomic force microscopy. Excellent agreement was obtained with the DEKTAK traces and the latter apparatus was used for most of the study. SEM images were also studied in order to better characterize surface migration effects adjacent to the mask.

The InP films used for the present series of experiments were the same films used for the experiments of the previous chapter, listed in Table 2.1. This enabled the SAE vapour phase diffusion constant, D/k, to be determined as a function of pressure, temperature and V/III ratio. For a reminder of the details of the dielectric mask set used for these experiments, the reader may refer to Fig. 2.3. One additional InP film, S9246 was deposited at 675°C. The purpose of this experiment was to confirm a trend that was uncovered in D/k as a function of temperature. Other then temperature, the growth conditions for S9246 are identical to those of S4788.

4.3 A Study of the SAE Growth Rate Enhancement – Results

4.3.1 The Effects of Surface Migration

Use of a DEKTAK instrument to study SAE was introduced in chapter two. A typical example of the output is shown in Fig 2.8. In the figure, the dielectric mask is shown for illustrative purposes but in actuality it was removed with HF prior to the measurements so that an accurate thickness profile could be obtained. Note that the absolute film thickness is shown. The growth rate enhancement can be determined by dividing the film thickness inside the gap by the nominal film thickness. The latter value was determined by measuring the thickness at a point more than five hundred microns from the mask since the vapour phase diffusion length is typically on the order of 100 μ m or less.¹ This value was found to be in perfect agreement with values obtained from routine reactor calibrations. The run-to-run film thickness variation of the MOCVD apparatus was found to be less than ten percent.

Dielectric rectangle pairs aligned to [011] and $[01\overline{1}]$ were analyzed. The thickness profile in the center of the gap, where vapour phase diffusion is expected to dominate, was found to be invariant with mask orientation. Also, one growth experiment was conducted with a static susceptor and the results were found to be identical to the results obtained using a rotating susceptor. Therefore, only results from stripes aligned to [011] will be presented. Of course, the measured thickness profiles within a few microns of the mask were not the same as for stripes aligned to $[01\overline{1}]$, however, surface migration of adatoms originating from the (111) α sidewall were not analyzed quantitatively in the present work.



Fig. 4.2 Plot of the growth rate enhancement at the center of the mesa versus mask width for wafer S4788.

Figure 4.2 shows a plot of growth rate enhancement at the center of the mesa versus mask width for six gap widths from wafer S4788. The markers represent measured values obtained with the surface profiler and the solid curves are simulated values generated using the 2-D vapour phase model with $(D/k)_{In} = 40.0 \ \mu m$. Initially, simulations were run using different values of δ . It was found that the solution depended strongly on δ for $\delta \leq 0.5$ cm and was insensitive to its value for $\delta \geq 0.5$ cm. Similarly, it was found that for $c_o > 100 \text{ cm}^{-3}$, Eq. (3.17) could be used to eliminate the c_o dependency in R_{In} .

The simulation error is less than 5% (for the mesa center). To examine the accuracy of the vapour phase model over the entire width of the selectively grown mesa,

Fig. 4.3(a), a plot of growth rate enhancement versus distance between masks for a 30 μ m gap and 30 μ m masks, was created. The solid curve represents values measured with the surface profiler and the broken curve represents values calculated with the vapour phase diffusion model. The model accurately predicted the growth rate enhancement in the center part of the mesa but failed for regions of the gap within 2 μ m of the mask. Based on the results of chapter two, it was concluded that surface migration was responsible for delivering extra adatoms to the film adjacent to the dielectric. Figure 4.3(b) shows the growth rate enhancement profile for a 30 μ m gap between 30 μ m masks from S5010 (same growth conditions as S4788 but one quarter the growth time). Excellent agreement between the measured values and the simulated values can be seen throughout the entire gap. The shorter growth time led to the absence of a super enhanced region due to the lack of a large (111) β surface. Moreover, Fig. 4.3(b) is representative of the agreement between experimentally obtained thickness values from run S5010 and values calculated with the 2-D SAE vapour phase model for the entire range of mask geometries.



Fig. 4.3 Plots of the growth rate enhancement versus distance between masks in a dielectric mask pair. The gap width is 30 μ m and the mask width is 30 μ m for both plots. Plot (a) is from S4788 where the nominal thickness is 0.4 μ m. Plot (b) is from S5010 where the nominal thickness is 0.1 μ m.



Fig. 4.3 Plots of the growth rate enhancement versus distance between masks in a dielectric mask pair for S4788. (c) The gap width is 10 μ m and the mask width is 7.6 μ m. (d) The gap width is 80 μ m and the mask width is 40 μ m.

The surface migration model, represented by Eq. (3.35), was employed to account for the missing material in the mesa depicted in Fig. 4.3(a). Unlike for the case of the vapour phase diffusion model, two independent parameters were necessary to fit the model to the measured growth rate numbers; the surface diffusion length, *L*, and the constant *A* in Eq. (3.33). *A* was chosen such that the calculated thickness equaled the measured ridge thickness adjacent to the mask. (The position adjacent to the mask is represented by x = 0 in Eq. 3.33)

The dotted curve in Fig. 4.3(a) represents the solution to Eq. (3.35) with L = 0.92 µm. Figures 4.3(c)-(d) show plots of the growth rate enhancement profile for two limiting cases. The profile for a 10 µm ridge (7.6 µm mask) is shown in (c) and the profile for a 80 µm ridge (40 µm mask) is shown in (d). In the latter figure, the plot focuses on the region adjacent to the mask since surface migration effects do not extend into the center of the ridge. For both plots, L = 0.92 µm and D/k = 40 µm were used for the calculations and good agreement with the measured values was obtained. For the smaller gap sizes, it was necessary to shift the *x*-axis by $h'(\tan 55^{\circ})^{-1}$ in order to account for the slope of the (111) β sidewall. For the wider gaps, the adjustment was not necessary since $h' \ll$ (gap width), where h' is the ridge height adjacent to the mask.

Film thickness as a function of growth time was measured using SEM imaging and InGaAs marker layers. The data markers in Fig 4.4 show film thickness measured at the point where the mesa top intercepts the sidewall for a 30 μ m ridge. The solid curve was calculated using Eq. (3.35) with $L = 0.92 \ \mu$ m and $D/k = 40 \ \mu$ m while the dashed curve was calculated using only the vapour phase model represented by Eq. (3.16). The vapour phase model was sufficiently accurate for very thin films since the number of precursors available for surface migration is small but as the growth time increased, a surface migration component became evident.



Fig. 4.4 Plot of film thickness versus growth time for a 30 μ m ridge from S4788. The markers represent SEM measurements. The solid curve represents values calculated with the surface migration model. The dashed line represents values calculated using the traditional vapour phase diffusion model.

An important figure of merit for a thin film is the curvature. Ideally, a film should be completely flat before post-processing steps such as resist spinning and metalization. However, films deposited by SAE possess a curvature due to lateral vapour phase diffusion. Figure 4.3(a) is a good example. Figure 4.5 illustrates how the surface migration model is useful for estimating film thickness non-uniformity as a function of growth time. Surface profile curves were obtained for a 60 µm gap between 30 µm masks using Eq. (3.35) with D/k = 40 µm and L = 0.92 µm. The five curves represent growth after 4, 8, 12, 16 and 20 minutes respectively. The curvature at the center of the ridge is relatively constant but near the oxide, the surface becomes progressively more curved for thicker films. For each surface profile curve, the thickness change, η over a 5 µm lateral distance from the mask edge is indicated. For the first ridge, $\eta = 51$ Å/µm. For the topmost ridge, $\eta = 735$ Å/µm. The time evolution of the surface profile predicted by the model can be verified by monitoring the InGaAs marker layers visible in Fig. 2.5(a).

A single rectangular SiO₂ mask pattern was used to study the growth enhancement profile of an InP film over large lateral distances. The rectangle was 600 μ m long and 200 μ m wide. The nominal film thickness was 0.44 μ m and the growth conditions were identical to those of S4788. Figure 4.6 shows the normalized DEKTAK trace. The thickness was enhanced over a length of a few hundred microns. After removing the surface migration component, the trace was fitted with a function of the form *exp(-x,L_v)*, where *L_v* is an effective diffusion length due to vapour phase diffusion. A value of *L_v* = 30 μ m was found. The measurement was repeated for a film with a 0.2 μ m nominal thickness so that no surface migration component would be present. The

signal to noise ratio of the DEKTAK trace made determining the vapour phase diffusion constant impractical.



Fig. 4.5 Plot of the simulated growth rate enhancement as a function of distance between masks for five different growth times. The gap width is 60 μ m and the mask width is 30 μ m. The parameter, η , is defined in the text and is a measure of the surface curvature.



Fig. 4.6 Plot of film thickness versus distance for a single dielectric mask.



Fig. 4.7 Plot of the growth rate enhancement versus distance between masks in a dielectric mask pair from S5093 (P = 150 torr). The gap width is 30 μ m and the mask width is 30 μ m for both plots.

4.3.2 Growth Temperature and Pressure

The runs performed at different temperatures (S5068, S5070, S5090 and S9246) were used to determine the parameters, D/k and L as a function of temperature. Runs S5093 and S5106 were used to determine D/k as a function of pressure. L could not be determined as a function of pressure because the surface migration component was too small to measure for the film grown at 150 torr (S5093). For example, Fig. 4.7 shows a growth enhancement plot for a 30 µm ridge between two 30 µm masks from S5093. The solid curve was measured using the profilometer and the dashed curve was calculated using the vapour phase model. The difference between the experimental curve and the curve calculated using the vapour phase model is very small, making it impossible to accurately determine a component that can be attributed to surface migration. A vanishing value for the parameter, A, in the surface migration model is assumed to be responsible for the lack of injected adatoms from the (111) β sidewall.

Figure 4.8(a) shows *D/k* versus temperature and Fig. 4.8(b) shows *L* versus temperature. In plot (a), two additional data points are shown representing the growths at an elevated (150 torr) and reduced (45 torr) pressure respectively. For plot (b), the growth pressure was fixed (76 torr). The surface diffusion length activation energy was determined. Values of 0.23 eV and 0.66 eV were found for the high temperature and low temperature growths respectively. The level of agreement between measured thickness values and calculated values was found to be very good, and with one exception, comparable to the results of section 4.3.1. At a growth pressure of 150 torr (S5093), the vapour phase model failed to accurately predict the growth rate enhancement.



(b)

Fig. 4.8 (a) Plot of D/k versus temperature. The circular markers were obtained from runs conducted at 76 torr. The square marker was obtained from a run conducted at 45 torr. The triangular marker was obtained from a run conducted at 150 torr. (b) Plot of L versus reciprocal temperature. The activation energy for surface diffusion was calculated from the slope of the curve.



Fig. 4.9 A plot of growth rate enhancement at the center of the gap versus mask width for run S5093. The markers represent measured values, the solid curves were calculated using the standard vapour phase model and the broken curve was calculated with the vapour phase model and Eq. (4.1).

Figure 4.9 shows the measured and simulated growth rate enhancements versus mask width for a variety of ridge widths for S5093. The agreement between experimentally obtained numbers and calculated numbers, represented by the solid curves, is seen to be increasingly poor as the mask width increases. The experiments reported in chapter two showed that for selective area growth at 150 torr, crystalline deposits form on the dielectric mask and a finite precursor flux into the mask exists.⁵ The boundary condition for the mask surface, represented by Eq. (3.13) is thus modified accordingly:

$$\frac{\partial c}{\partial z} = q , \qquad (4.1)$$

(as opposed to $\partial c/\partial z = 0$ indicating the absence of a precursor flux) where q is a constant. The vapour phase model was found to accurately simulate the experimental findings with the proper choice of q. The broken curves in Fig. 4.9 illustrate the results.

4.4 A Study of the SAE Growth Rate Enhancement - Discussion

4.4.1 Vapour Phase Diffusion versus Surface Migration

The results of this chapter illustrate various characteristics of the two transport processes involved in SAE. Vapour phase diffusion controls the growth enhancement profile over the entire width of the selectively grown ridges whereas the effects of surface migration are confined to a lateral distance of a few microns from the mask edges. Measurements of the growth in the presence of a single rectangular mask showed that the effects of vapour phase diffusion extend over a distance of several hundred microns. The film deposition using a substrate with a mask rotated by ninety degrees showed that the profile created by vapour phase diffusion is invariant under rotation. By comparing ridges aligned to [011] with ridges aligned to $[01\overline{1}]$, it was shown that surface migration is heavily dependent on direction. An explanation for the opposing characteristics follows from the fact that surface migration is controlled by the surface atomic configuration while vapour phase diffusion is controlled by the precursor concentration gradient above the wafer.

Many modern optoelectronic devices are based on narrow ridge waveguides.^{2,3,4} The devices are fabricated from a ridge, a few microns wide, etched into the epi-layers. The impact of surface migration on device fabrication can therefore be reduced by selectively depositing the structure layers in a gap which is larger than the surface
diffusion length, L, and then defining the waveguide ridge in the center part of the gap. This will be the approach taken in chapter six, which outlines the fabrication of a photonic integrated circuit. The basic procedure is outlined in Fig. 4.10.



Fig. 4.10 A process for fabricating uniform ridges using selective area epitaxy. (a) A film is deposited in a wide $(30 \ \mu m)$ gap. (b) An etch mask such as SiO₂ is patterned in the center of each selectively grown film. (c) The films are selectively etched leaving only the center part.

More generally, the results of the previous section can be used to obtain rules on the relative impact of surface migration. Since the transport mechanism only affects locations in close proximity to the mask,⁵ wider gaps between masking pads can be modeled almost entirely with the vapour phase model. Figure 4.3(d) showed an example for an 80 μ m gap. Also, for the first time, the importance of surface migration was shown to depend on growth pressure and growth time. The latter, being equivalent to film thickness. The growth time dependency can be easily explained with the model presented in chapter three and specifically, with Eq. (3.31), which states that the number of adatoms available for surface migration is proportional to the growth time. It is advantageous to limit the role of surface migration since the process leads to greater thickness non-uniformities.⁶ Moreover, the physics is more difficult to model and perturbations in the growth conditions or pre-growth processing will potentially lead to unpredictable changes in the growth enhancement near the mask.

The application of the SAE vapour phase model to the simulation of film thickness measurements obtained with surface profilometry yielded values for D/kconsistent with values reported in other labs for low pressure MOCVD. Using a methodology similar to what was used in the present work, Alam and co-workers determined a value of 25 µm for TMI.⁷ Ida and co-workers⁸ obtained D/k = 63 µm for the same precursor and F. Sholz⁹ obtained 30 µm. Reported parameters for atmospheric pressure growth have a larger range. Gibbon and co-workers found D/k = 15 µm.¹⁰ In contrast, Jones and Coleman determined D/k = 238 µm.¹¹ The discrepancy in the data can be attributed, at least in part, to different growth conditions and reactor geometries. However, different approaches in extracting the model parameters from experimental

data must not be overlooked. In the present work, a wide range of mask sizes and gap sizes were used and modeling parameters self-consistent over the entire size range were obtained. Gibbon's approach was very similar to the present approach. In other reports, simulated curves were compared with measured thickness values for only one or two mask sets.

The stagnant layer height is an important parameter of the boundary layer model. It is instructive to use Eq. (3.10) to estimate the height. For the reactor in our lab, X = 10 cm and $V = (15 \ l/m) / (32 \ cm^2) = 27 \ cm/s$, where $15 \ l/m$ is the total flow rate and $32 \ cm^2$ is the reactor cross-sectional area. For TMI in H₂ at 630°C and 76 torr, $D = 0.29 \ cm^2/s$.¹² Replacing these values into the equation gives $\delta = 0.58 \ cm$. This number is similar to 0.5 cm, found in section 4.3 to be the critical value needed for stagnant layer height independency in the simulations. Hydrodynamic treatments of the MOCVD process have yielded values ranging from a few millimeters to several centimeters.^{13,14,15}

The precursor diffusion coefficient is a crucial value for calculating the height of the stagnant layer. In the previous calculation, the coefficient for $(CH_3)_3$ In (TMI) was assumed. In actuality, the diffusing precursor is unknown. Other possibilities include $(CH_3)_2$ In and CH₃In since the growth reaction is known to follow a series of subreactions which include TMI decomposition.^{16,17,18,19} Therefore, the diffusion coefficient represents an effective or average value. The same is true for the numerator in the parameter D/k. k is expected to be better defined since the temperature at the substrate is constant, however, Kim and Caneau have suggested that the precursor residence time on the mask surface may effect group III decomposition.²⁰

4.4.2 The Effects of Pressure and Temperature on Vapour Phase Diffusion

Figure 4.8(a) reveals a strong dependency on the reactor pressure and temperature in D/k. For the three different pressures used in the study, D/k increased as the pressure decreased. This is expected since the diffusion coefficient is known to increase for decreasing pressure and the rate of reaction, k, is not expected to have a strong pressure dependency. Interpreting the D/k versus temperature data requires more thought since both D and k depend on the temperature. For the diffusion coefficient,

$$D \propto T^n. \tag{4.2}$$

For the rate of reaction,

$$k \propto e^{-E_a/k_B T} \tag{4.3}$$

where E_a is the activation energy and k_B is Boltzman's constant. Therefore,

$$D/k = cT^n e^{E_a/k_B T} \tag{4.4}$$

where *c* does not depend on temperature. The power dependency on temperature, arising from the inherent MOCVD vapour phase diffusion mechanism, will cause an increase in D/k with increasing temperature. The exponential dependency, arising from the kinetic component, will lead to the opposite effect. This accounts for the local minimum in the plot of Fig. 4.8(a). The minimum occurs at approximately 630°C and Eq. (4.4) can be used to connect the two fundamental mechanisms of MOCVD. Taking the derivative of D/k with respect to temperature and equating the function to zero reveals information about the local minimum.

$$nT^{n-1}e^{E_a/k_BT} - \frac{E_a}{k_BT^2}T^n e^{E_a/k_BT} = 0$$
(4.5)

Equation (4.5) can be simplified and rewritten as follows,

$$\frac{E_a}{k_B T} = n. \tag{4.6}$$

At 630°C, $k_B T = 0.7742$ eV so that

$$E_a = (0.7742 \ eV)n. \tag{4.7}$$

n is a known quantity, ranging from 1.7 to $1.9.^{21,22}$ Hence, the activation energy can be calculated. The resulting value is consistent with a value of 1.68 eV for the reaction, $CH_3In \rightarrow CH_3 + In$, reported by Smith and Patrick.²³ In comparison, values of 2.05 eV to 2.34 eV have been reported for the reaction $(CH_3)_3In \rightarrow (CH_3)_2In + CH_3$. The reaction $(CH_3)_2In \rightarrow CH_3In + CH_3$ is known to be extremely rapid $(E_a \approx 0).^{22,24}$ The data supports the hypothesis that the diffusing species within the boundary layer is a reduced subprecursor such as CH_3In .

In the previous section, the surface diffusion activation energy was calculated. Sakata and Komatsu obtained similar values for selectively grown stripes using a different and much more indirect method to extract the surface diffusion length.²⁵ 0.24 eV was found for growth at 650°C to 600°C and 2.92 eV was found for growth at 600°C to 580°C. In their study, the diffusion length was found to decrease for higher growth temperatures in agreement with the experimental results shown in Fig. 4.8(b). Sakata attributed the smaller diffusion length at 580°C to less phosphorus on the semiconductor surface due to poor PH₃ decomposition.²⁶ Another obvious explanation is the fact that at reduced temperatures, adatoms have less kinetic energy to overcome the energy barrier between atomic sites. However, this explanation does not account for the increase in activation energy at lower temperatures. The smaller change in activation energy reported in the present study would suggest that a reduction in surface mobility due to poor PH₃ decomposition is less significant in our reactor.

- ¹ R. Bhat, J. Crys. Growth, 120, 362 (1992)
- ² R.E. Bartolo, S. Saini, T. Ren, Y. Zhu, M. Dagenais, H. Shen, J. Pamulapati, W. Zhou,
- O. King and F.G. Johnson, IEEE Phot. Tech. Lett., 11, 554 (1999)
- ³ S.Z. Zhang, Y.J. Chiu, P. Abraham and J.E. Bowers, IEEE Phot. Tech. Lett, 11, 191 (1999)
- ⁴ M.L. Osowski, R.M. Lammert and J.J. Coleman, IEEE Phot. Tech. Lett, 9, 158 (1997)
- ⁵ O. Kaysor, J. Crys. Growth, 107, 989 (1991)
- ⁶ O. Kayser, R. Westphalen, B. Opitz and P. Balk, J. Crys. Growth, 112, 111 (1991)
- ⁷ M.A. Alam, R. People, E. Isaacs, C.Y. Kim, K. Evans-Lutterodt, T. Siegrist, T.L.
- Pernell, J. Vandenberg, S.K. Sputz, S.N.G. Chu, D.V. Lang and L. Smith, Appl. Phys. Lett. 74, 2617 (1999)
- ⁸ M. Ida, N. Shigekawa, T. Furuta, H. Ito and T. Kobayashi, J. Crys. Growth, 158, 437 (1996)
- ⁹ F. Scholz, D. Ottenwalder, M. Eckel, M. Wild, G. Frankowsky, T. Wacker and A. Hangleiter, J. Crys. Growth, 145, 242 (1994)
- ¹⁰ M. Gibbon, J.P. Stagg, C.G. Cureton, E.J. Thrush, C.J. Jones, R.E. Mallard, R.E.

Pritchard, N. Collis and A. Chew, Semicond. Sci. Technol., 8, 998 (1993)

- ¹¹ A.M. Jones, M.L. Osowski, R.M. Lammert, J.A. Dantzig and J.J. Coleman, J. Elec. Mat., 24, 1631 (1995)
- ¹² T. Fujii and M. Ekawa, J. Appl. Phys., 78, 5373 (1995)
- ¹³ N. Shibata and S. Zembutsu, Jpn. J. App. Phys., 26, 1416 (1987)
- ¹⁴ W.G. van Sark, M.J. deCroon, G.H. Janssen and L.J. Giling, Semicond. Sci. Tech., 5, 291 (1990)

- ¹⁵ M.J. deCroon and L.G. Giling, J. Crys. Growth, 93, 932 (1988)
- ¹⁶ K.W. Benz, H. Renz, J. Wiedlien and M.H. Pilkuhn, J. Elec. Mat., 10, 185 (1981)
- ¹⁷ R.H. Moss and J.S. Evans, J. Crys. Growth, 55, 129 (1981)
- ¹⁸ A.H. Moore, M.D. Scott, J.I. Davies, D.C. Bradley, M.M. Factor and H. Chudzynska,
- J. Crys. Growth, 77, 19 (1986)
- ¹⁹ E.J. Thrush, C.G. Cureton, J.M. Trigg, J.P. Stagg and B.R. Butler, Chemtronics, 2, 62 (1987)
- ²⁰ M. Kim, C. Caneau, E. Colas and R. Bhat, J. Crys. Growth, 123, 69 (1992)
- ²¹ F. Rosenberger, "Fundamentals of Crystal Growth" Springer-Verlag, Berlin, Germany (1979)
- ²² H.K. Moffat and K.F. Jensen, J. Crys. Growth, 77, 108 (1986)
- ²³ G.P. Smith and R. Patrick, Int. J. Chem. Kinet., 15, 167 (1983)
- ²⁴ N.I. Buchan, C.A. Larsen and G.B. Stringfellow, J. Crys. Growth, 92, 591 (1988)
- ²⁵ Y. Sakata and K. Komatsu, 11th IPRM, 41 (1999)
- ²⁶ Y. Sakata and K. Komatsu, J. Elec. Mat., 29, 37 (2000)

Chapter 5

Experiments on InGaAsP Selective Area Epitaxy

5.1 Introduction

The previous chapter undertook an experimental investigation of the growth rate perturbation of InP films selectively deposited on (100) InP substrates. The measurements were used to assess the validity and accuracy of the SAE models developed in chapters two and three. In this chapter, selectively grown $In_{1-s}Ga_sAs_tP_{1-t}$ films are studied, both experimentally and theoretically. As discussed in chapter 3, in addition to a growth rate enhancement, an SAE composition perturbation occurs due to the presence of multiple group III atoms.

Films of varying composition were deposited on masked InP substrates using the selective area epitaxy technique. The growth rate enhancement and composition shift as a function of mask geometry were measured for each film and also calculated using the vapour phase diffusion model incorporating an indium diffusion parameter and a gallium diffusion parameter. The parameters were found to be a function of film composition. This is the first report on the phenomenon.¹ Consideration of the physical meaning of the parameters suggested that the gallium incorporation constant decreased in the low wavelength alloys. In the second part of the study, an InGaAs film was deposited on a substrate masked with a dielectric pattern of the type used in the fabrication of integrated photonic devices. An increase in modeling accuracy was obtained using knowledge of the alloy composition dependence in the modeling parameters.

5.2 Experimental Procedure

For the growth experiments, (100) S-doped InP substrates were used. To form the dielectric mask structures, a 300 nm SiO_2 film was deposited by CVD. The dielectric was patterned and etched using standard lithography and buffered HF. In the first set of experiments, an array of dielectric stripe pairs was formed. Each pair consisted of two rectangular masks separated by a gap, as shown in Fig. 2.3(a). The mask widths ranged from 7.5 µm to 100 µm and were oriented in the [011] direction. The gap widths ranged from 10 µm to 60 µm. The growths were carried out in a horizontal flow MOCVD reactor at 76 torr and 630°C with a susceptor rotation speed of 300 rpm. Trimethylindium (TMI), triethylgallium (TEG), PH₃ and AsH₃ were used as the source materials. InP and InGaAs films were deposited as well as several InGaAsP alloys. For InP, the V/III pressure ratio was 110 and the nominal growth rate was 1.5 μ m/h. For the InGaAsP films, the TMI and PH₃ flow rates were fixed and the TEG and AsH₃ flow rates were adjusted to achieve lattice-matched compositions in the unperturbed areas. For the InGaAs film, the V/III pressure ratio was 28 and the unperturbed growth rate was 2.9 μ m/h. The total flow rate was 15 SLM. The SAE composition shift did not lead to the observation of relaxed material in regions of the wafer used for the present study. Also, polycrystalline deposits were not observed on the dielectric masks.

Growth on the patterned substrates produced ridges within the gap openings.² The film thickness at the center of each ridge was measured using a DEKTAK surface profiler and the composition was measured using energy dispersed x-ray (EDX) with an electron beam focused to $1 \,\mu\text{m}^2$ in the center of the gap. The latter measurements were calibrated using the composition of the InGaAsP film very far from the mask, obtained

using photoluminescence and x-ray diffraction. The need for EDX, as opposed to x-ray diffraction within the gaps was due to their small widths. The minimum spot size for a conventional x-ray source is on the order of 1 mm and is therefore too large to characterize a selectively grown stripe. Growth spikes in the ridges were observed adjacent to the mask but the width of the spikes never exceeded 2 μ m so a flat surface for measurements was always available in the ridge center.

The films for EDX were grown with a nominal thickness of 1.0 μ m. The thickness was important and carefully chosen in light of the SAE composition shift. For overly thick films, a critical level strain exists, above which relaxation (leading to defects) occurs.³ Yet, the film thickness must not be less than the EDX electron beam penetration depth or the detected signal will contain interference from the substrate. A 0.1 μ m InP cap layer was deposited over quaternary films to protect the group V surface composition during the reactor cool-down cycle because the distribution coefficients of the group V precursors are highly temperature dependent.^{4,5} Prior to EDX, the InP cap layer was removed by immersing the sample in concentrated HCl for 3 sec.

In the second set of experiments, a dielectric mask of non-uniform width was deposited on an S-doped (100) InP substrate for selective area deposition of an InGaAs film. The mask was similar in shape to masks reported in the literature for the fabrication of integrated photonic devices. (The mask is shown in Fig. 5.5). A series of surface profile measurements was performed lengthwise down the ridge to characterize the growth rate enhancement profile. Similarly, a series of EDX measurements were made to assess the composition profile.



Fig. 5.1 The apparatus used to perform the EDX measurements. It consists of a Li doped Si detector embedded in a scanning electron microscope. Liquid nitrogen is used to cool the detector and minimize noise. SD is the *sample distance*.

5.3 Description of the EDX Equipment

The EDX apparatus consisted of a lithium doped Si detector embedded in a Joel field emission scanning electron microscope. A diagram of the apparatus is shown in Fig. 5.1. An electron beam emitted from the polepiece is focused onto the sample, giving valence electrons within the sample sufficient energy to escape their orbits. Higher energy electrons re-fill the vacancies causing the emission of characteristic X-rays. The emission spectrum from each element is a fingerprint from which the atomic number can be inferred.

X-rays enter through the thin beryllium window and produce electron-hole (e-h) pairs in the detector. The *e*-*h* pairs are accelerated to the contacts by an applied voltage. Each pair requires 3.8 eV at 77 K thus the number of pairs created by a photon of energy E_p is $E_p/3.8$.⁶ The charge produced by the photon is amplified by the low noise FET and fed to a pulse processor. The pulse peak intensity is measured by an analog to digital converter and this information is stored in the computer where the height of the spectrum is a measure of the input energy of the incident photon. From this, the computer plots X-ray count versus E_p .

For a given electron beam acceleration voltage and take-off angle, the detector efficiency must be calibrated using a sample of known composition.⁷ This was done using an aluminum standard. An acceleration voltage of 10 keV was used so that the electron beam would not penetrate the InP substrate. The penetration depth is proportional to the voltage.⁸ The absence of a phosphorus peak for InGaAs films thicker than 0.7 μ m confirmed that the excited volume was confined to the epi layer. Since the X-ray count is proportional to the electron beam current, a Faraday cup was used to

ensure stability. A carbon or gold thin film is sometimes deposited on low conductivity samples to avoid charge buildup⁹ but this was found to be unnecessary in the present set of experiments. Figure 5.2 shows a typical spectrum obtained for an InGaAsP film and Table 5.1 lists the line energies used to identify each of the four elements in the film. The largest energy line is the In $L_{\beta 2}$ line at 3.713 keV. As a rule of thumb, for accurate results, the largest energy line should be less than one third the value of the acceleration voltage.⁷ The computer software subtracts the background Bremsstahlung radiation and measures the intensity of each line peak.

The intensity, I, is proportional to the element concentration, c. When a standard is used, the concentration can be found with the following formula.

$$c_{sample} = ZAF \cdot c_{s \tan dard} \frac{I_{sample}}{I_{s \tan dard}}$$
(5.1)

The ZAF correction accounts for three material dependent phenomena. An atomic number correction (Z) is necessary because of the differences in the backscatter coefficient and electron stopping power of the various elements in a multi-element specimen. An absorption factor (A) corrects for the X-rays that were generated in the sample but absorbed before they were able to escape and a fluorescence factor (F) accounts for fluorescence generated by the electron beam. Equations to correct for absorption^{10,11} and fluorescence^{12,13} can be found in the literature. In the present work, a commercially available software package was used to compute the ZAF correction automatically.

Energy	Element	Principal	Less Intense
(keV)		Emission Line	Minor Lines
1.098	Ga	L_{α}	
1.282	As	L_{lpha}	
2.013	Р	$K_{\alpha 1}$	K _β @ 2.137
3.286	In	$L_{\alpha 1}$	$L_{\beta 1} @ \ 3.48 \ , L_{\beta 2} @ \ 3.713$

Table 5.1 Energies of X-rays for InGaAsP



Fig. 5.2 EDX spectra for an $In_{0.79}Ga_{0.21}As_{0.46}P_{0.54}$ sample. The characteristic energies for each of the four constituents are shown.

5.4 Results and Discussion

5.4.1. Uniform Mask Width

An InGaAs film was deposited on a masked substrate. The film was characterized using a surface profiler and EDX. Fig. 5.3(a) is a plot of the growth rate enhancement at the center of the ridge versus mask width for different gap widths. Fig. 5.3(b) is a plot of the composition at the center of the ridge. In order to determine values for $(D/k)_{ln}$ and $(D/k)_{Ga}$, multiple modeling solutions were calculated. A set of simulated curves, $\{R^i_{ln}\}$, was formed where the *i*th element was a solution to R_{ln} corresponding to $(D/k)^i_{ln}$. Similarly, the set, $\{R^j_{Ga}\}$, was formed. Every possible solution to the InGaAs growth rate enhancement, R^{ij}_{InGaAs} , was then determined as well as every possible solution to Eq. (3.19), s^{ij} . The optimal modeling parameters were chosen on the basis of minimizing the sum of the square errors between each data point and the associated simulated value. $(D/k)_{ln} = 36 \ \mu m$ and $(D/k)_{Ga} = 96 \ \mu m$ gave the best fit. These values agree reasonably well with the diffusion coefficients that have been determined in the past.¹⁴

In_{1-s}Ga_sAs_tP_{1-t} alloys of varying compositions were similarly deposited and characterized. The group V sub-lattice composition, measured by EDX, was found to remain constant within the precision of the tool. Others have made the same finding.¹⁵ For modeling purposes, the alloys were therefore treated similarly to InGaAs since only R_{In} and R_{Ga} needed to be considered. The optimal diffusion coefficients were found using the method described above. The results are summarized in Table 5.2.



Fig. 5.3 (a) Growth rate enhancement and (b) Ga mole fraction at the center of an InGaAs ridge as a function of mask width for different gap widths. Markers: experimental data. Curves: simulation results.

Diffusion coefficients for the alloys explored in this study					
Alloy	$(D/k)_{In}$	$(D/k)_{Ga}$			
	[µm]	[µm]			
InP	40	N/a			
Q1.10	40	150			
Q1.25	40	120			
Q1.62	36	96			
InGaAs	36	96			

Table 5.2

To determine the effect of varying the growth rate, two InP films were deposited with a growth rate of 0.75 μ m/hr and 3.0 μ m/hr respectively. Similarly, two InGaAs films were deposited at 1.4 μ m/hr and 5.8 μ m/hr respectively. InP and InGaAs represent the two compositional extremes of lattice-matched alloys. The parameters (*D/k*)_{*In*} and (*D/k*)_{*Ga*} were determined for each film. For a given composition, the parameters did not vary with growth rate. This confirms that the modeling parameters are dependent on alloy composition and not growth rate.

For the first time, a film composition dependence in the SAE diffusion coefficients has been shown to exist. Since the coefficient is made up of two elements, a diffusion component and a kinetic component, some thought is required in order to determine the root cause. It is highly unlikely that the diffusion component varies significantly with composition because the magnitude of the change in the gallium precursor concentration with film composition was relatively small, and the TMI flow rate was not changed at all. Cause lies with the incorporation constant, which, as shown in Table 5.2, decreases for Ga and decreases slightly for In with increasing In molar fraction. A possible physical explanation for the reduced Ga incorporation is the interaction of Ga and In precursor molecules at the substrate surface. When both methyl

and ethyl molecules were used as group III sources, a reduction in the group III atom incorporation from ethyl molecules was reported to occur because the CH_3 termination obstructs the bond formation of ethyl molecules to the atoms near the termination.¹⁶

Our contribution to the SAE model predicts that the composition dependency of the incorporation rate leads to a reduction in the strain shift. This is meaningful because elevated strain leads to film defects. Appendix B shows that Eq. (3.19) predicts a monotonic increase in the composition shift, *s*-*s*', for fixed values of R_{In} and R_{Ga} , as *s* varies from 0 to 0.5. Therefore the effect of smaller values of $(D/k)_{Ga}$ for the high wavelength alloys is to reduce the composition shift and hence reduce the strain by increasing R_{Ga} to a value more comparable with R_{In} .

In general, it was found that the calculated values of the growth rate enhancement depended more strongly on the value chosen for the indium diffusion coefficient than the gallium coefficient because the enhancement increases with decreasing diffusion coefficient and the coefficient of indium is smaller. Also, the alloys contain more indium than gallium making the indium contribution in Eq. (3.18) more significant. It was found that without the composition data, accurately determining both diffusion coefficients would have been impossible, partly due to the small contribution made by the Ga component. Likewise, the composition data alone would have been insufficient because two completely different sets of diffusion coefficients were found to exist which gave the same simulated composition. For example, Fig. 5.4 illustrates two calculated InGaAs composition curves for three gap widths. The solid curve was obtained using $(D/k)_{ln} = 36 \ \mu m$ and $(D/k)_{Ga} = 96 \ \mu m$ while the broken curve was obtained using $(D/k)_{ln} = 30 \ \mu m$ and $(D/k)_{Ga} = 76 \ \mu m$. The former set was ultimately chosen because it yielded the smallest

square error sum when growth rate enhancement was simultaneously considered. (The two different sets of modeling parameters yielded distinct curves for the simulated growth rate enhancements).

Similar SAE measurements have been reported in the literature. They can be used to further illustrate the difficulties associated with extracting modeling parameters from experimental data. Ida and co-workers varied the growth temperature rather than the nominal film composition of selectively grown films.¹⁷ For a fixed mask geometry, the composition shift of an InGaAs film changed significantly with temperature while the growth rate enhancement remained almost constant. Kim and co-workers measured the growth rate enhancements of InP, InGaAs and InGaAsP ($\lambda = 1.3 \mu m$) films.¹⁸ InP exhibited the largest enhancement while the enhancement of the ternary and quaternary films were almost identical, showing the need for composition shift measurements if it were desired to extract the modeling parameters.



Fig. 5.4 Simulation results for the Ga mole fraction in an InGaAs film. The solid curves were obtained using one set of diffusion coefficients and the broken curves were obtained using a different set. The values of the coefficients are shown.



Fig. 5.5 The dielectric mask used for the study presented in section 5.4.1. It is representative of a mask that could be used for fabricating a photonic integrated circuit.

5.4.1 Non-Uniform Mask Width

An InGaAs film was deposited on a substrate patterned with the mask structure shown in Fig. 5.5. This mask could potentially be applied to the fabrication of an integrated laser and optical modulator.¹⁹ The growth rate enhancement and the composition profile were experimentally characterized. Using the 3-D vapour phase diffusion model reported in chapter three, simulated curves were generated with the In and Ga diffusion coefficients for InGaAs listed in Table 5.2.

Very good agreement with the experimental data was obtained, illustrating the versatility of the model. Fig. 5.6 is a plot of the composition as a function of distance along the ridge, lengthwise. The markers represent values measured with the EDX tool and the solid curve represents the results of the simulation. At the first edge of the ridge (y = 0), the Ga mole fraction is nearly unperturbed. As y increases, the Ga fraction drops because excess In diffused from the large surrounding dielectric areas. As the end of the ridge $(y = 500 \ \mu m)$ is approached, the composition increases towards the nominal value because only part of the surrounding area was masked.

Simulated curves were also generated using the modeling coefficients for InGaAsP ($\lambda = 1.3 \mu m$) but the nominal gallium concentration for InGaAs (s = 0.47). Although the simulated growth rate enhancement was not found to significantly vary, the simulated composition shift difference was meaningful. To illustrate, the results are shown in Fig. 5.6 with the broken curve. The accuracy of the model has been compromised, suggesting that great care is needed when applying SAE modeling to the design of optoelectronic devices. In particular, the alloy composition dependency should be considered. Simulations of the composition profile for larger mask widths led to even bigger errors if the incorrect coefficients were used.



Fig. 5.6 Ga mole fraction along the ridge for an InGaAs film deposited using the mask shown in Fig. 5.5. Markers: experimental data. Solid curve: simulation results using InGaAs modeling parameters. Broken curve: simulation results using InGaAsP modeling parameters.

- ¹ J.E. Greenspan, J. Cryst. Growth, 236, 273 (2002)
- ² T. Sasaki, M. Mitsuhiro and I. Mito, J. Crystal Growth 132, 435 (1993)
- ³ B.A. Fox and W.A. Jesser, J. Cryst. Growth, 109, 252 (1991)
- ⁴ G.B. Stringfellow, J. Cryst. Growth, 55, 42 (1981)
- ⁵ P.D. Dapkus, H.M. Manasevit and K.L. Hess, J. Cryst. Growth, 55, 10 (1981)

⁶ M.H. Loretto, Electron Beam Analysis of Materials, Chapman and Hall, London,

England (1994)

⁷ J.P. Eberhart, Structural and chemical analysis of materials. X-ray, electron, and neutron diffraction; X-ray, electron, and ion spectrometry; electron microscopy, John Wiley and Sons, Chichester, UK (1991)

⁸ D. B. Williams, J. R. Michael, J. I. Goldstein and A. D. Romig, Jr., Ultramicroscopy, 47, 121, (1992)

⁹ T. Watanabe, A. Kawano, K. Ueda, N. Umesaki and H. Wakita, J. Synchrotron Radiation, 8, 334 (2001)

¹⁰ J. Philibert and R. Tixier, Br. J. App. Phys., 1, 685 (1968)

¹¹ J.I. Goldstein, J.L. Costley, G.W. Lorimer and S.J.B. Reed, Scanning Elec. Microsc., 1,
315 (1977)

¹² C. Nockolds, M.J. Nasir, G. Cliff and G.W. Lorimer, Inst. Phys. Conf. Ser., 52, 417 (1979)

¹³ A.W. Nicholls and I.P. Jones, J. Microscopy, 127, 119 (1982)

¹⁴ F. Sholz, D. Ottenwalder, M. Eckel, M. Wild, G. Frankowsky, T. Wacker, A. Hangleiter, J. Crystal Growth 145, 242 (1994)

¹⁵ M.A. Alam, R. People, E. Isaacs, C.Y. Kim, K. Evans-Lutterodt, T. Siegrist, T.L.

Pernell, J. Vandenberg, S.K. Sputz, S.N.G. Chu, D.V. Lang and L. Smith, Appl. Phys. Lett. 74, 2617 (1999)

- ¹⁶ M. Sato and M. Weyers, Jpn. J. App. Phys., 30, L1911 (1991)
- ¹⁷ M. Ida, N. Shigekawa, T. Furuta, H. Ito and T. Kobayashi, J. Crystal Growth 158, 437 (1996)
- ¹⁸ M. Kim, C. Caneau, E. Colas, R. Bhat, J. Crystal Growth 123, 69 (1992)
- ¹⁹ R.M. Lammert, G.M. Smith, J.S. Hughes, M.L. Osowski, A.M. Jones and J.J.

Coleman, IEEE Phot. Tech. Lett. 8, 797 (1996)

Chapter 6

Fabrication of a Photonic Integrated Circuit

6.1. Introduction

The transmitter is a key component for fiber optic networks. Semiconductor laser diodes operating at 1.55 μ m or 1.3 μ m are the de facto standard for implementing a transmitter light source. However, direct modulation of semiconductor lasers leads to frequency chirp.¹ An external modulator is therefore a very desirable component for fiber optic systems. Modulators based on the electroabsorption (EA) effect have been successfully demonstrated for this purpose.^{2,3} They exhibit high modulation speed and efficiency. Figure 6.1 illustrates a conventional EA modulator. It consists of a *p-i-n* semiconductor structure. The structure can be routinely deposited in an MOCVD reactor. In the InP material system, the p-layer is typically doped with Zn and the n-layer is doped with Si. The intrinsic (*i*) layer is made from InGaAsP. Its composition is based on the light source carrier frequency. Metal electrodes are in contact with both sides of the device.





During operation, a light beam is incident in the plane of the p-i-n junction. The transmission of light follows Lamberts' law,

$$I_{i} = I_{i} \exp\left(\int \alpha(x) dx\right)$$
(6.1)

 I_t is the transmitted intensity, I_i is the incident intensity and α is the absorption coefficient of the depleted intrinsic layer. Modulation is achieved by applying a modulating voltage across the junction. The absorption coefficient is a function of the electric field created by the applied voltage. Solutions for α in terms of the electric field can be found in the literature.^{4,5}

The device capacitance is given by,

$$C = \varepsilon_r \varepsilon_o \frac{A}{w} \tag{6.2}$$

where $\varepsilon_{\rm r}$ is the relative dielectric constant and $\varepsilon_{\rm o}$ is the dielectric constant of free space, *w* is the depletion width and *A* is area. Minimizing the area of the device is crucial to achieving high speed operation. The device dimension perpendicular to the light beam is typically 2 µm and chosen to optimize the waveguide properties. The dimension parallel to the beam is at least two orders of magnitude larger. To make handling the device practical, it should be at least 300 µm long.⁶ An integrated modulator and passive waveguide is therefore desirable for minimizing the capacitance while maintaining a large device length.

Additional shortcomings to the EA modulator exist as well. Earlier works have examined and solved many of these challenges. Polarization insensitivity was achieved by introducing strain into the modulator's active region.⁷ An open problem is matching the optical mode of an EA modulator to that of a single mode fiber. A solution can be

realized by integrating an optical mode converter and EA modulator. A mode converter can be made from a passive waveguide containing a tapered core.

Many demonstrations of an integrated laser and optical mode converter are given in the literature.^{8,9,10} Similarly, there have been several demonstrations of an integrated semiconductor optical amplifier and optical mode converter.^{11,12} In contrast, only three authoritative groups have demonstrated an integrated EA modulator and passive waveguide, and in these instances, the waveguide cores were not tapered.^{13,14,15} The passive element was included to reduce the length of the active section to increase speed.

The optical modes in semiconductor lasers and optical amplifiers for lightwave communications are larger than the mode for an electroabsorption modulator. For example, a typical near-field full width half-max (FWHM) for an InGaAsP buried heterostructure laser is 2.5 μ m x 2.1 μ m.¹⁶ The FWHM for the active section of our modulator is 0.86 μ m x 0.45 μ m and a typical value for a tapered single mode fiber is 2.0 μ m x 2.0 μ m.¹⁷ Clearly, matching an EA modulator to a fiber is more challenging because the integrated optical mode converter must produce a stronger mode change.

The effectiveness of the converter is determined by the ratio of the input and output core thickness values. For a mode converter integrated with a laser or semiconductor optical amplifier, the ratio is typically less than 3.0.¹¹⁻¹⁵ Section 6.6 shows that the required ratio is greater than 3.7 for this work. Such a large growth rate enhancement requires a very large dielectric mask and produces an unprecedented SAE composition shift. Challenges that are not present in past efforts must be overcome.

The integrated EA modulator and optical mode converter is depicted in Fig. 6.2. For illustrative purpose, the modulator section is on the right and the optical mode





Fig. 6.2 Schematic configuration of an integrated EA modulator and optical mode converter.

converter is on the left. An actual device is composed of an input and output mode converter and a modulator in the centre. From top to bottom, the modulator section consists of a metal electrode, a shared p-type InP cladding layer, an InGaAsP active section and a shared n-type InP cladding layer. The length of the metal electrode and the modulator section is minimized to decrease capacitance. The optical mode converter consists of a shared p-type InP cladding, a tapered InGaAsP core and an n-type InP cladding. The core is 500 Å thick at the device output and 2000 Å thick at the mode converter modulator interface. The optical mode size is therefore significantly larger at the output, as seen in the figure. The nominal composition of the core is chosen to optimize the dielectric constant at the output. Moreover, the bandgap should be about 100 meV larger than the active bandgap to prevent absorption under zero bias.

6.2 An Integrated EA Modulator and Optical Mode Converter

The steps to fabricate the integrated modulator and mode converter include several conventional semiconductor processes as well as several novel processes developed to address issues arising from the selective area epitaxy technique. For example, the fabrication process includes standard dielectric deposition and metalization steps. Similarly, conventional lithography using photoresist and ultraviolet exposure is employed. However, the multiple overgrowths associated with producing a photonic integrated circuit necessitated the development of several original chemical cleans to prepare the semiconductor surface for epitaxy. The various innovative processes that were developed as part of this work will be discussed in detail while the conventional process steps will be described much more briefly.



Fig. 6.3(a) The processing steps for the fabrication of an integrated EA modulator and optical mode converter. The arrows indicate the sequence. Each step is explained in the text.



Fig. 6.3(b) The SAE dielectric mask used to define the thickness profile of the optical mode converter Q1.3 core. The mask is also used to protect the Q1.47 active core during the InGaAsP etch step. The shape of the mask is given by the function f(x) as indicated.

The basic process is schematically outlined in Fig. 6.3(a). Initially, the n⁺InP cladding layer and In_{0.63}Ga_{0.37}As_{0.80}P_{0.20} active layers are deposited by MOCVD. (In_{0.63}Ga_{0.37}As_{0.80}P_{0.20} is often abbreviated as Q1.47 since the compound produces photoluminescence at 1.47 μ m). An InP cap layer is also present. These layers constitute the *first growth* structure. A 3000 Å SiO₂ layer is subsequently deposited over the wafer using plasma enhanced chemical vapour deposition.¹⁸ The SiO₂ layer is patterned using lithography.^{19,20} The pattern is shown in Fig. 6.3(b). The centre dielectric defines the active region of the modulator by protecting the underlying semiconductor material during the subsequent etching steps. The tapered sections of the dielectric constitute the

selective area growth mask. The shape of the taper is given by a third order exponential as shown in the figure. During SAE, the film growth rate enhancement will be largest near the areas where the dielectric mask has the largest surface area.

After lithography, the InP cap layer is etched using a solution of hydrochloric acid. HCl is well known for selectively etching InP over InGaAsP and InGaAs.^{21,22} Next, the Q1.47 layer is etched using one of two methods. Some samples were *wet etched* using a 5:1:1 solution of H₂SO₄:H₂O₂:H₂O to remove the InGaAsP.²³ Wet etching is relatively simple and leaves the semiconductor surface free of defects. However, it is not a suitable process for the fabrication of an integrated modulator made from a multiple quantum well (MQW). In an MQW, the well layers and barrier layers are made from distinct materials. However, the wet chemical etch rate is a function of the layer composition. To explore a more generic process, some samples were *dry etched* using a Cl_2-O_2 plasma.²⁴ After etching, the semiconductor material that was protected by the SiO₂ mask takes on the shape of a mesa as shown in Fig. 6.3(a). The mesa sidewall surface integrity is important for the subsequent SAE overgrowth.

The SAE overgrowth step is the heart and soul of the process. The sample is initially dipped in a series of chemical solutions to repair damage to the semiconductor surface sustained during the previous etching step. Next, the sample is loaded into the MOCVD reaction chamber and a thin $In_{0.72}Ga_{0.28}As_{0.61}P_{0.39}$ (Q1.3) layer is deposited using the SAE technique. This layer, which is part of the *second growth* structure, constitutes the core of the integrated passive waveguide. SAE is used to taper the core thickness thus the waveguide acts as an optical mode converter. A high quality lateral interface from the Q1.3 to the Q1.47 active section is obtained by suitably cleaning the

mesa sidewalls after InGaAsP etching. Since the patterned SiO_2 serves the dual purpose of etch mask and selective area growth mask, the two steps are conveniently selfaligning.

After SAE, the wafer is removed from the reaction chamber and the SiO₂ mask is etched with hydrofluoric acid (HF). The surface of the wafer is exposed to ozone to oxidize any Si contamination and then dipped again in HF to prepare the surface for the subsequent film deposition step. The wafer is loaded into the MOCVD reaction chamber for the last time and the p-type InP cladding layer and p⁺InGaAs contact layer are deposited using conventional MOCVD. These two layers form the *third growth* structure. Next, the integrated modulator and mode converter are patterned into a single ridge using lithography and a standard HBr plasma etch.²⁵ The ridge cannot be seen in Fig. 6.3(a) because it runs perpendicular to the cross-sectional view. Figure 6.4 shows two SEM images of the ridge taken from different angles. Finally, the lift-off technique is used to pattern the metal electrodes and the wafer is cleaved into bars. The finished PIC is shown in Fig. 6.5 where the input optical signal and output (modulated) signal are illustrated as well. Figure 6.6 is an SEM top view image of a final sample. A shadow left behind by the SiO₂ mask is visible. Additionally, the ridge defined by the HBr plasma etch step, and the metal electrodes can be seen. The electrode runs the full length of the Q1.47 active region that was protected by the mask and is connected to a bonding pad.



Fig. 6.4 SEM images of the waveguide ridge takes at different angles. The picture on the left is a cross-section. The picture on the right is an off-angle cross-section. The top dark layer is the electrode. The thin light shaded layer just under the electrode is the InGaAs cap. The light shaded layer in the ridge centre is the InGaAsP active core.



Fig. 6.5 Cross-section of the integrated EA modulator and optical mode converter showing the direction of the optical signal relative to the mode converter. A carrier signal is applied to the input. A modulated signal results at the output.



Fig. 6.6 SEM image of a completely fabricated integrated EA modulator and optical mode converter. The metal electrode over the ridge defines the active section. The ridges on each end of the active section constitute the optical mode converters. The shadow left behind by the SAE mask is also visible.

6.3 The First Growth Structure

The first growth structure is illustrated in Fig. 6.7. The bottom layer is a 0.5 μ m InP film. SiH₄ flows through the reaction chamber during growth making the layer silicon (n-type) doped. The impurity concentration is 1.0×10^{18} cm⁻³. The high impurity concentration is used to give the layer a low series resistance. High conductivity n-type substrates are also used for this purpose. Next, 2.75 μ m of 5.0×10^{17} cm⁻³ silicon doped InP is deposited. The lower doped InP material has less optical absorption (due to free carriers) and is therefore placed in proximity to the Q1.47 waveguide core.

The Q1.47 is grown with 0.055 % compressive strain to remove the light hole – heavy hole degeneracy in the valence band and reduce the polarization dependency of the absorption coefficient. A thin Si doped InP layer is present above the graded layers. The ionized Si impurities inhibit Zn atoms inserted in a subsequent growth step from diffusing from the p-InP cladding layers into the intrinsic region of the *pin* device.²⁶ Ideally, the Zn atoms compensate the Si impurities.

InP	0.03 µm	Si: 4 x 10 ¹⁷ cm ⁻³
Q1.47	0.29 µm	undoped
InP	2.8 µm	Si: 5 x 10 ¹⁷ cm ⁻³
InP	0.5 µm	Si : 1 x 10 ¹⁸ cm ⁻³

Fig. 6.7 The first growth structure for the integrated EA modulator and optical mode converter.

6.4 The Second Growth Structure

The second growth is the SAE overgrowth step. The structure is shown in Fig. 6.8. The growth occurs after the InGaAsP etch. Repairing damage sustained during the etching process is critical. This is especially true for the dry etched samples. III-V semiconductors are softer than Si. Damage to the lattice at the surface is inevitable.^{27,28} The surface must therefore be restored prior to epitaxy. Various techniques have been developed for this purpose. Henry and co-workers annealed their samples in P₂ at $525^{\circ}C.^{29}$ A more common approach is to perform a shallow wet etch after the dry etch.^{30,31} In the present work, several schemes were attempted before a successful restoration technique was found. It was found that removing approximately 200 Å of the InP cap layer from the first growth with a wet chemical etch leads to good quality material in the SAE overgrowth.

InP	30 nm	undoped		
Q1.3	46 nm	undoped		
InP	20 nm	undoped		
Etched First Growth				

Fig. 6.8 The second growth structure for the integrated EA modulator and optical mode converter.
Bromine diluted in methanol has long been known to etch InP. The etch rate can be controlled by adjusting the dilution and a smooth semiconductor surface can be obtained for relatively slow etch rates.^{32,33} Sulfuric acid was used to clean the surface and quench hydrocarbon contamination originating from the methanol. Figure 6.9 is an SEM cross-section image of a successful SAE overgrowth. Figure 6.10(a) shows the results of an insufficient surface restoration. For the latter sample, an attempt was made to clean the surface using a mixture of sulfuric acid and hydrogen peroxide. Figure 6.10(b) shows a sample with a second growth structure that was not optimized. The structure thickness was larger leading to parasitic growth enhancement due to surface diffusion (see Section 3.6). The result was an interface with a hockey stick formation.



Fig. 6.9 An SEM cross-section of an active core – passive core interface fabricated using the optimized process.



Fig. 6.10 SEM cross-section of active core – passive core interfaces fabricated before an optimized process was found. (a) Insufficient surface restoration after the InGaAsP etch step. (b) Non-optimized growth structure.

After the growth, polycrystalline deposits were consistently visible on one particular section of the dielectric mask. Figure 6.11(a) shows part of a 4 mm² mask. Its purpose was to protect mask alignment markers necessary for the lithography step. The mask was large enough to cause the precursor concentration to reach the critical value needed for nucleation on the mask surface. To remove the deposits, the sample was immersed in a beaker with HF and the beaker was agitated in an ultrasonic bath for 10 minutes. Figure 6.11(b) shows the 4 mm² mask after the treatment. A gross reduction in particle density is visible



Fig. 6.11 A microscope image of a section of the 4 mm^2 dielectric mask used for the lithography step (a) after the second growth step (b) after the ultrasonic HF treatment. A gross reduction in the number of polycrystalline deposits is visible.

InGaAs	0.2 µm	$Zn: 1.0 \times 10^{19} \text{ cm}^{-3}$		
InP	2.2 µm	Zn : 4.0 x 10 ¹⁷ cm ⁻³		
First and Second Growths				

Fig. 6.12 The third growth structure for the integrated EA modulator and optical mode converter.

6.5 The Third Growth

The third growth structure is shown in Fig. 6.12. It is composed of two layers. The bottom layer is the shared Zn doped (p-type) cladding. The top layer is the InGaAs contact layer. After deposition, the InGaAs is removed from the mode converter sections. The layer is highly doped so the metal electrode can make a good ohmic contact. The InP layer thickness is $2.2 \ \mu m$ to maintain sufficient spacing between the waveguide core and the highly absorbent InGaAs.

Prior to the third growth, the SAE dielectric mask was stripped with HF. HF does not damage the semiconductor like the plasmas used in dry etching so a wet etch to restore the surface was not necessary. However, initial samples suffered from a contamination problem that was solved by including extra steps at this stage of the processing sequence. Various airborne contaminants are known to adsorb to InP. These include S, O and Si.³⁴,³⁵ Samples were analyzed using secondary ion mass spectroscopy (SIMS) and contamination between the second and third growth layers was found. Figure 6.13 is the SIMS profile showing the Si and O concentrations as a function of layer depth. The Ga and Zn concentrations are also plotted so the relative positions of the other layers may be known. A silicon and oxygen interfacial layer is visible. The Si and O dose are indicated in the figure. (The dose is the integrated concentration profile). In particular, the Si concentration is much larger than the targeted value. No sulfur contamination was found. We conclude that Si and SiO₂ adsorbed to the sample surface between the second and third MOCVD growth steps.



Fig. 6.13 Plot of impurity concentration as a function of depth obtained by secondary ion mass spectroscopy (SIMS). A large amount of Si contamination and some oxygen contamination are visible at the MOCVD growth interface, just above the Q1.47 layer.

Chapter 7 will show that the interfacial layer has a large impact on the electrical performance of the modulator hence a series of experiments were performed, aimed at reducing the interfacial contamination. For each experimental trial, a first growth structure was deposited on an InP substrate. Subsequently, 3000 Å of SiO₂ was deposited using plasma enhanced CVD to simulate the SAE mask, which is a possible source of Si contamination. To further simulate the PIC process, the SiO_2 was removed using HF and ultrasonic agitation. Next, the sample was cleaned. For each trial, a different clean was attempted. Following the cleaning step, the sample was loaded into a quartz petri dish that was previously sanitized in aqua regia. Special precautions were developed to avoid Si contamination originating from the MOCVD reaction chamber walls. The walls were heated to 220°C and the susceptor was heated to 750°C for 50 minutes. No Si doping sources were pumped into the reactor once it was cleaned. Finally, the third growth structure was deposited and the samples were characterized using SIMS. The third growth layers were deposited on all the samples simultaneously using a multi-wafer MOCVD reactor. This way, the random effects of unknown contamination sources were reduced. It was not necessary to deposit the second growth structure because the passive waveguide sections of the PIC are not electrically biased and Si contamination is not an issue.

6.5.1 Clean A – UV Exposure

Exposing the sample to ultraviolet (UV) radiation ultimately proved to be the most successful method for removing interfacial contamination. It is known that UV radiation creates ozone to oxidize the Si on the sample surface. In our work, a sulfuric acid and

hydrofluoric acid treatment was used in conjunction with UV radiation. The process is similar to one described by Ingrey and co-workers.³⁶

6.5.2 Clean $B - H_2SO_4$

We attempted to prevent interfacial contamination by immersing some samples in a solution of sulfuric acid and hydrogen peroxide. Such solutions are commonly used to clean InP surfaces.³⁷

6.5.3 Clean C - CBr₄

Some samples were etched in-situ prior to the third growth using carbon tetrabromide (CBr₄). CBr₄ is known to etch InP.³⁸ The etch depth and etch rate were both varied, however, interfacial contamination was not prevented even for etch depths as large as $0.2 \,\mu\text{m}$.

6.5.4 Clean D – PH₃

Exposure to PH₃ at elevated temperatures is known to enhance Si evaporation from an InP surface.³⁴ Therefore, one sample was annealed in a 2.5 % PH₃ ambient (PH₃ flow = 800 sccm, H₂ flow = 32 slm,) at 700°C for 20 min. The temperature and PH₃ concentration were kept low enough to prevent thermal etching of the sample. Conventionally, samples are annealed in a 1.2% PH₃ ambient at 650°C for 15 min. Prior to the heat treatment, the sample was immersed in a solution of sulfuric acid and hydrogen peroxide.

6.5.5 Clean E – InGaAs Cap Layer

For some trials, the second growth structure included an InGaAs sacrificial cap. The cap was etched away immediately prior to growth using a 1:5:50 solution of H_2SO_4 : H_2O_2 : H_2O and no additional cleaning was done.

6.5.6. Results of the Cleaning Experiments

The trial results are summarized in Table 6.1. Each row represents the best result for the indicated cleaning method. The results demonstrate that "clean A" reduced the Si interfacial dose to below 4×10^{11} cm⁻². In contrast, samples with no clean had Si dose levels above 3×10^{12} cm⁻². "Clean B" led to similar levels.

Clean procedures C and D achieved some success. The oxygen contamination was reduced below the SIMS detection level and Si contamination was somewhat reduced. This suggests that oxygen is more readily removed from the surface. Furthermore, it is likely that some of the removed Si contamination was bonded to oxygen, facilitating its removal.

Using an InGaAs sacrificial cap did not reduce Si contamination. This would indicate that in addition to removing the contamination, an effective clean recipe must pacify the surface such that subsequent Si adsorption is inhibited. Yamamoto and co-workers demonstrated reduced Si interfacial contamination by using ammonium sulfide to pacify an InP surface with S atoms.³⁹ (The group achieved Si doses of 10^{12} cm²).

Table 6.1

Results of the Si contamination experiments					
Clean		Si Dose	O Dose		
		(cm ⁻²)	(cm ⁻²)		
А	UV	2.9×10^{11}	< 10 ¹¹		
В	H_2SO_4	2.9×10^{12}	2.0×10^{12}		
С	CBr ₄	6.7×10^{11}	< 10 ¹¹		
D	PH ₃	9.0×10^{11}	< 10 ¹¹		
Е	InGaAs Cap	3.1×10^{12}	< 10 ¹¹		

6.6 SAE Modeling for the Second Growth Structure

The purpose of the second growth is to fabricate the core of the optical mode converter. SAE was used to taper the core thickness. Quantitative SAE modeling was used to determine the mask dimensions required to deposit a waveguide core with an optimized thickness profile. Modeling was also used to predict the composition and strain shifts caused by growth in the presence of the dielectric masks, and to minimize the peak strain shift. Measurements using spatially resolved photoluminescence and surface profiling are reported to demonstrate the power and effectiveness of the model. The core was also tapered in the lateral direction using lithography, however, optical modeling predicted that the exact shape of the taper in the horizontal direction is unimportant.⁴⁰

The solid curve in Fig. 6.14 is the theoretically desired thickness profile of the mode converter core. The profile was calculated by the Nortel Networks optical modulator design team using a beam propagation method.^{41,42} A core thickness value of 500 Å at the interface with the fiber and a core thickness value of 2000 Å at the interface with the fiber and a core thickness value of 2000 Å at the interface with the modulator was determined. Additionally, the overall profile shape was theoretically established. It was optimized for adiabatic mode conversion, minimal loss for coupling to a single mode fiber operating near 1550 nm and minimum coupling loss at the interface with the EA modulator. Several dielectric mask shapes were simulated using SAE3D until the simulated thickness profile matched the required profile. The dashed curve in Fig. 6.14 is the simulation output for the final mask. Figure 6.3(b) shows the mask geometry. During the simulation trials, the gap width was fixed at 15 μ m and the shape and width of the dielectric was varied. 15 μ m is sufficiently wide to ensure that a 2 μ m ridge can be easily defined in the gap centre. The



Fig. 6.14 Thickness profile for the Q1.3 layer which composes the optical mode converter core. The solid curve was obtained by beam propagation calculations. The dashed curve is the output of a simulation performed with SAE3D. The dotted curve was measured from a fabricated sample using surface profilometry.



Fig. 615 Group III sub-lattice composition profile for the optical mode converter core. The dotted curve is inferred from the photoluminescence measurement and the solid curve is the simulated profile.

dotted curve in Fig. 6.14 is the measured thickness profile of a fabricated optical mode converter. The measured curve agrees very well with the simulated curve.

SAE3D was also used to predict the group III sub-lattice composition profile of the optical mode converter. The strain was subsequently calculated assuming a fixed group V composition. The calculation was made using a polynomial that relates strain to group III composition.⁴³ The mass flow controllers on the MOCVD reactor were adjusted to target a nominal composition for the selective area growth such that the peak strain would be minimized. To experimentally characterize the strain, a wavelength map of the spot size converter was measured using a high resolution photoluminescence apparatus. The group III sub-lattice composition and hence the strain was obtained using a polynomial from Ref. 42. Figure 6.15 shows the measured and simulated group III composition profiles and Fig. 6.16 shows the strain profile inferred from the measured wavelength map. The strain is centered about zero and the maximum absolute strain is less than 0.4%. It is well known that strain has deleterious effects on material quality and photoluminescence intensity is an excellent quality gauge.⁴⁴ Figure 6.17 shows the photoluminescence intensity profile measured for a fabricated spot size converter. The intensity is quite uniform. The intensity at the location of highest growth rate enhancement (interface with the modulator) is as high as 80 % of the nominal value. This is the first reported use of selective area growth modeling to minimize the maximum strain.



Fig. 6.16 Strain profile for the optical mode converter core. The absolute maximum is minimized by centering the strain at a zero.



Fig. 6.17 Photoluminescence intensity profile for the optical mode converter core. At the interface with the active core, the intensity is 80 % of the maximum intensity indicating good crystalline quality.

- ¹ K. Inoue, IEICE Trans. Communic. B, 81, 1197 (1998)
- ² K. Satzke, D. Baums, U. Cebulla, H. Haisch, IEE Elec. Lett., 31, 2030 (1995)
- ³ K. Yamada, K. Nakamura, Y. Matsui, T. Kunii, IEEE Phot. Tech. Lett., 7, 1154 (1995)
- ⁴ N. Bottka, Opt. Eng., 17, 530 (1978)
- ⁵ G. Mak, C. Rolland, K.E. Fox and C. Blaauw, IEEE Photon. Tech. Lett., 2, 10 (1990)
- ⁶ R.T. Sahara, M. Matsuda, K. Morito, H. Soda, Opt. Quant. Electron., 28, 599 (1996)
- ⁷ T. Aizawa, K.G. Ravikumar, S. Suzaki, T. Watanabe and R. Yamauchi, IEEE J. Quant. Elec., 30, 585 (1994)
- ⁸ H. Jeon, A. Mathur and M. Ziari, Electron. Lett., 34, 1313 (1998)
- ⁹ I. Moreman, M. D'Hondt, W. Vanderbawhede, G. Coudenys, J. Haes, P. De
- Dobbelaere, R. Baetes, P. Van Daele and P. Demeester, IEEE Phot. Tech. Lett., 6, 888 (1994)
- ¹⁰ N. Kalonji and J. Semo, Electron. Lett., 30, 892 (1994)
- ¹¹ S. Kitamura, H. Hatakeyama, K. Hamamoto, T. Sasaki, K. Komatsu and M. Yamaguchi, IEEE J. Quant. Elec., 7, 1067 (1999)
- ¹² J.R. Kim, J.S. Lee, S. Park, M.W. Park, J.S. Yu, S.D. Lee, A.G. Choo, T.I. Kim and Y.H. Lee, IEEE Phot. Tech. Lett., 11, 967 (1999)
- ¹³ F. Alexandre, D. Jahan, F. Devaux, A. Ougazzaden, F. Huet, E. Vergnol and E.V.K.Rao, Proc. IPRM, 9, 621 (1997)
- ¹⁴ T. Ido, H. Sano, M. Suzuki, S. Tanaka and H. Inoue, IEEE Phot. Tech. Lett., 7, 170 (1995)
- ¹⁵ U. Koren, R. Ben Michael, B.I. Miller, M.G. Young, M. Chien, H.H. Yaffe, G. Raybon and K. Dreyer, Electron. Lett., 30, 1852 (1994)

¹⁶ I. Moerman, M. D'Hondt, W. Vanderbauwhede, P. Van Daele, P. Demeester, W.

Hunziker, Electron. Lett., 31, 452 (1995)

¹⁷ Namiki Reference #354007-01

¹⁸ A.C. Adams, "Dielectric and Polysilicon Film Deposition" in VLSI Technology, ed.

S.M. Sze, McGraw Hill, New York, New York, 1983

¹⁹ R.C. Jaeger, "Introduction to Microelectronic Fabrication", Addison-Wesley, Reading, Massachusetts, 1988.

²⁰ R.A. Colclaser, "Microelectronics: Processing and Device Design", Wiley, New York, New York, 1980.

²¹ L.A. Coldren, K. Furuya, and B.I. Miller, J. Electrochem. Soc., 130, 1918 (1983)

²² R.D. Dupuis, D.G. Deppe, C.J. Pinzone, N.D. Gerrard, S. Singh, G.J. Zydzik, J.P. van der Ziel, and

C.A. Green, J. Cryst. Growth, 107, 790 (1991)

²³ H. Nishi, M. Yano, Y. Nishitani, Y. Akita, and M. Takusagawa, Appl. Phys. Lett., 35, 232 (1979)

²⁴ V.M. Donnelly, D.L. Flamm, C.W. Tu, D.E. Ibbotson, J. Elec. Chem. Soc., 129, 2533 (1982)

²⁵ S. Agarwala, I. Adesida, C. Caneau and R. Bhat, 37th Int. Symp. on Electron, Ion, Photon Beams, San Dieigo, California, June 1993.

²⁶ J.E. Haysom, R. Glew, C. Blaauw, R. Driad, D. MacQuistan, C.A. Hampel, J.E. Greenspan and T. Bryskiewicz, Proc. 14th IPRM, (2002).

²⁷ T.R. Hayes, M.A. Dreisbach, P.M. Thomas, W.C. Dautremont-Smith and L.A.
Heimbrook, J. Vac. Sci. Technol. B, 7, 1130 (1989)

- ²⁸ S.J. Pearton, U.K. Chakrabarti and F.A. Baiocci, Appl. Phys. Lett., 55, 1633 (1989)
- ²⁹ L. Henry, C. Vaudry, A. Le Corre, D. Le Crosnier, P. Alnot and J. Olivier, Electron. Lett., 25, 1257 (1989)
- ³⁰ B. Garrett and E.J. Thrush, J. Cryst. Growth, 97, 273 (1989)
- ³¹ V.S. Ban, G.C. Erikson, S. Mason and G.H. Olsen, J. Electrochem. Soc., 137, 2904 (1990)
- ³² F. Capasso, R.A. Logan, P.W. Foy, S. Sumski, and D.D. Manchon, Electron. Lett., 16, 241, (1980)
- ³³ T. Brenner and H. Melchior, J. Electrochem. Soc., 141, 1954, (1994)
- ³⁴ H. Ishikawa, S. Miwa, T. Maruyama and M. Kamada, J. App. Phys., 71, 3898 (1992)
- ³⁵ D.G. Knight, G. Kelly, J. Hu, S.P. Watkins, M.L.W. Thewalt, J. Cryst. Growth, 182, 23 (1997)
- ³⁶ S. Ingrey, W. M. Lau, and N. S. McIntyre, J. Vac. Sci. Technol. A, 4, 983 (1986)
- ³⁷ J.F. Wagner and C.W. Wilmsen, Physics and Chemistry of III-V Compound Semiconductor Interfaces, Plenum Press, New York, New York (1985)
- ³⁸ S. Arakawa, M. Itoh and K. Kasukawa, Proc. 13th IPRM, TuB2-3 (2001)
- ³⁹ N. Yamamoto, K. Kishi, Y. Kondo, S. Matsumoto, R. Iga, Y. Kadota, H. Okamoto and
- H. Mawatari, J. Cryst. Growth, 193, 16 (1998)
- ⁴⁰I. Moreman, G. Vermeire, M. D'Hondt, W. Vanderbawhede, J. Blondelle, G.
- Coudenys, P. Van Daele and P. Demeesester, Microelectron. J., 25, 675 (1994)
- ⁴¹ G.R. Hadley, IEEE Phot. Tech. Lett., 5, 1068 (1993)
- ⁴² I. Betty, Nortel Networks Internal Report (2000)
- ⁴³ K. Utaka, Y. Suematsu, K.I. Hawanishi, Jpn. J. Appl. Phys., 19, L137 (1980)

⁴⁴ C.J. Miner, C.J.L. Moore, EMIS Dat, Rev. GaAs, 16, 320 (1996)

Chapter 7

Electrical and Optical Characterization

7.1 Introduction

In this chapter, the electrical and optical properties of the integrated EA modulator and optical mode converter are examined. The current voltage relation (IV curve) and the capacitance voltage relation (CV curve) of the EA modulator are characterized. Measurements of the coupling loss are presented. It is important to characterize the coupling loss because a principal function of the optical mode converter is to facilitate coupling to a silica fiber. In addition, the frequency response of the photonic integrated circuit (PIC) is characterized. Decreasing the area of the active p-i-n junction and thereby increasing modulation speed are the second functions of the optical mode converter.

A key figure of merit for an EA modulator is the transmission loss, defined as,

$$L = 10\log\frac{P_{out}}{P_{in}}.$$
(7.1)

 P_{out} is the output optical power and P_{in} is the input optical power. Measurements of the transmission loss as a function of voltage will be presented for a variety of optical carrier wavelengths. The characterization was performed for both TE and TM polarized light.

We emphasize the results that can be connected with the developments of the previous chapters. It should be stressed that this is not a thesis on EA modulator physics. The important contributions of this work are in the areas of SAE modeling, semiconductor fabrication and materials science. With this in mind, the chapter has two main objectives. First, we will show that the SAE models developed in the initial

chapters were crucial to the fabrication of the optical mode converter. By tailoring the shape of the converter waveguide core, extremely low coupling losses have been achieved. Second, we will show the importance of controlling Si interfacial contamination. The Nortel Networks optical modulator design team performed the measurements presented in this chapter.

7.2 The IV curve

To verify the rectifying action of the *p-i-n* junction, an IV curve was measured for a large area EA modulator. The measurement was made using a Keithley 2400 source meter and the sample was mounted on a thermoelectric cooler ($T = 25^{\circ}C$). The large area device was fabricated by depositing all the layers that compose the EA modulator. The layers were deposited in a single growth step. After growth, metal electrodes were deposited and a small piece was cleaved from the wafer. The area of the piece was measured to be 7.77 mm². The IV curve is shown in Fig. 7.1. The measured data was fit to the following expression for a pn junction.¹



Fig. 7.1 IV curve of a large area EA modulator.

$$I = I_o \left(\exp\left(\frac{qV}{nkT}\right) - 1 \right)$$
(7.2)

 I_o is the saturation current, q is the Coulomb charge, kT is the thermal energy and n is the ideality factor. From the ideality factor, the current mechanism can be deduced. Fitting the data was accomplished by working with the natural logarithm so that n could be derived from the slope of the IV curve. An ideality factor of 1.9 was found indicating that the current is mostly controlled by recombination in the depletion region.² This can be explained by the relatively large width of the intrinsic region. Inside this region, the excess carrier concentration is large. Recombination occurs to restore intrinsic carrier levels.

Figure 7.2 shows the IV curves for several fully fabricated PICs under reverse bias. The breakdown voltage is clearly greater than 12 V and the reverse current is dominated by carrier generation in the depletion region. The reverse bias region is important because the EA modulator is operated in reverse bias during normal operation.



Fig. 7.2 Reverse bias IV curve for the EA modulator of a fabricated PIC.

7.3 The CV Curve

The capacitance of a *p-i-n* junction can be modeled after a parallel plate capacitor. The highly doped *p* and *n* semiconductor regions are likened to the metal plates and the depletion region is likened to the dielectric spacing. In a conventional *pn* junction diode, the width of the depletion region in reverse bias is proportional to the square root of the voltage. Once the width is known, Eq. (6.2) can be used to determine the capacitance. For our *p-i-n* structure at zero bias, the calculation can be further simplified because the width of the depletion region is approximately the width of the intrinsic layer. Using $\varepsilon_r = 13.0$, $A = 350 \ \mu\text{m}^2$ and $w = 0.30 \ \mu\text{m}$, we find $C = 0.13 \ \text{pF}$.

Figure 7.3(a) shows the CV curve for several fabricated integrated EA modulator and optical mode converter devices. For these devices, the length of the EA region is 175 μ m, the ridge width is 2 μ m and the area is 350 μ m². The zero bias capacitance is 0.13 pF as per the calculated value. The capacitance decreases with increasing voltage as the depletion region widens into the *p* and *n* regions. Since the intrinsic region dominates the total width, the change in capacitance is small. The capacitance at –1 V is shown in Fig. 7.3(b) as a function of small signal frequency. The capacitance is constant and behaves ideally for frequencies in the 5 MHz to 50 GHz range. Below 5 MHz, the capacitance increases. This sort of behavior is consistent with the existence of deep level traps within the intrinsic region. Carriers trapped within these centres cannot respond at high modulation frequencies and are inert. At lower excitation frequencies, the carriers can contribute to the effective carrier concentration and cause the depletion region to contract.³



Fig. 7.3 Capacitance of the integrated EA modulator and optical mode converter as (a) a function of voltage and (b) a function of modulation frequency.

The frequency response of a fabricated PIC is shown in Fig. 7.4. The -3dB frequency is 49.6 GHz. This is a best in class achievement.^{4,5} In this work, we achieved a very low RC time constant due to the small length of the active section. Such a length is only practical because the two integrated mode converters increase the total PIC length.



Fig. 7.4 Frequency response for a fabricated EA modulator and spot size converter. The -3 dB frequency is 49.6 GHz.

7.4 The Transmission Loss

To characterize the transmission loss, an optical signal from a fiber, was applied to a fabricated device. The light source was an Agilent 8164A lightwave measurement system equipped with a tunable laser. The polarization was controlled with an HP11896A polarization controller. The optical power was measured with an HP8153A light meter. Figure 7.5 shows the transmission loss for TE polarized light as a function of voltage measured from a sample fabricated using an initial version of the fabrication process. The transmission loss is shown for three different carrier wavelengths. The fabrication process for the sample was optimized in every way except that Si interfacial contamination had not been addressed. The plot makes it evident that the



Fig. 7.5 Transmission loss for TE polarized light. The device under test is an early sample. Interfacial contamination had not yet been addressed. A 2 V turn-on voltage is visible.

electroabsorption action of the modulator is functioning. At 6 V reverse bias, the transmission loss is -39 dB for 1530 nm. However, there is a 2 V turn-on voltage. State of the art EA modulators are known to turn-on near 1V.⁶ A larger turn-on voltage imposes stricter demands on the driver electronics.



Fig. 7.6 SIMS depth profile of the active section of an early device showing a large amount of Si interfacial contamination.

The cause of the large turn-on voltage can be traced to the impurity profile. Figure 7.6 is a SIMS plot of the Si and Zn concentration depth profile for the sample. The integrated Si impurity concentration (dose) measured for the *Si-spike* layer is 2.6×10^{12} cm⁻², double the target value. The effect of the increased dose on the internal electric field can be calculated with the aid of a simplified structure diagram, illustrated in Fig. 7.7(a). The internal electric field is governed by Gauss's law,

$$\frac{dF}{dx} = \frac{\rho}{\varepsilon_r \varepsilon_o},\tag{7.3}$$

where ρ is the charge density. Figure 7.7(b) is a plot of F(x) where the x-axis is normal to the *p-i-n* junction. It is instructive to calculate ΔF for the Si-spike region and for the intrinsic region. For the latter region,



Fig. 7.7 (a) Simplified structure diagram of the active section of the integrated EA modulator and optical mode converter. (b) Internal electric field.

$$\Delta F_i = \frac{N_i d_i}{\varepsilon_r \varepsilon_o} \tag{7.4}$$

where $N_i = 10^{15}$ cm⁻³ is the impurity concentration in the intrinsic region and $d_i = 0.3 \mu m$ is the layer thickness. For the former region,

$$\Delta F_{s_i} = \frac{\delta_{s_i}}{\varepsilon_r \varepsilon_o} \tag{7.5}$$

where δ_{s_i} is the integrated charge distribution. For the purposes of this exercise, the dielectric constant for InP and InGaAsP are similar enough so that,

$$\frac{\Delta F_{s_i}}{\Delta F_i} = \frac{\delta_{s_i}}{N_i d_i} = \frac{\delta_{s_i}}{3.0 \times 10^{10} \, cm^{-2}} \tag{7.6}$$

In the Si-spike region the impurities are compensated (both n-type and p-type impurities are present). The net charge density is therefore given by the difference of the Si and Zn concentration profiles, $N_{si} - N_{Zn}$. The SIMS plot shows that most of the Si in the Si-spike region is compensated. Nonetheless, we find the ratio is greater than unity explaining why a thin interfacial layer can have such a deleterious effect on the turn-on voltage. The Si contamination layer is, in effect, absorbing a large portion of the applied electric signal. E.H. Sargent and co-workers experienced a large turn-on voltage for lateral current injection lasers fabricated in a multi-growth process.⁷ The reference attributed the problem to interfacial contamination, however, a solution was not proposed.

In this work, a solution for eliminating the electrical problems caused by Si interfacial contamination was found and the details were presented in chapter six. Figure 7.8 is a plot of the transmission loss for a sample fabricated with the fully optimized process. The turn-on characteristics are greatly improved. Furthermore, the modulation efficiency is superior to samples suffering from Si interfacial contamination. Figure 7.9



Fig. 7.8 Transmission loss for TE polarized light. The device under test was fabricated using the fully optimized process.

is a plot of loss slope versus transparent state absorption for two PICs. The loss slope is the derivative of the transmission loss versus voltage plot at the turn-on voltage. It is a measure of the absorption change per unit of applied voltage. The triangle markers represent measurements of the sample made with the fully optimized process. The circle markers represent measurements of the sample fabricated with no Si clean step. It can be seen that eliminating the interfacial contamination resulted in a significant loss slope improvement. The above analysis shows that the interfacial layer absorbs a large portion of the electric field and therefore causes the decrease in loss slope.



Fig. 7.9 Loss slope for two PICs. The triangle markers represent a device fabricated with the fully optimized process. The circle markers represent a device fabricated before interfacial contamination had been addressed.

7.5 The Coupling Loss

The great achievement of SAE modeling in this work is the fabrication of a tapered core in the optical mode converter. Appropriate tapering is necessary for obtaining adiabatic low-loss mode conversion and low-loss coupling to an optical fiber. For a fabricated PIC, the zero bias transmission loss for a 1.55 μ m optical signal is 3.7 dB, as seen in Fig. 7.8. At zero bias, the absorption in the Q1.47 active region is negligible thus the losses are due to fiber coupling losses, mode expansion losses and reflection at the converter core active core interface.

The zero bias optical loss (P_{out}/P_{in}) for a 1.55 µm signal was extracted for a large number of samples. The loss per facet for all the tested structures is plotted in a bar graph, Fig. 7.10. For most samples, the loss is 1.5 dB and the mean total loss (both facets) is 3.96 dB.



Fig. 7.10 The coupling loss per facet for all tested PICs. The mean is 1.98 dB. (Each device has two facets).

For conventional EA modulators (with no integrated optical mode converter), the coupling loss is greater than 10 dB, and 15 dB is a typical value.⁸ The lower coupling loss achieved by integrating an optical mode converter is therefore extremely significant. Semiconductor optical amplifiers can be used to provide 15 dB of gain,⁹ however, eliminating an amplifier by improving the modulator results in a great cost savings to the optical module. Coupling loss reduction has been accomplished in the past for an electroabsorption modulator. Ido and co-workers integrated a passive waveguide with an electroabsorption modulator.¹⁰ However, the passive core was not tapered for optical mode conversion and the coupling loss was 7 dB. Koren and co-workers demonstrated a coupling loss of 10 dB.¹¹ In their integrated devices, the passive core was tapered for optical mode conversion. However, the taper was in the horizontal direction only. It was implemented by photolithography rather than epitaxy.

Previous state of the art coupling loss values for an active component, other than an optical modulator, integrated with a mode converter are in the range of 3 dB to 4 dB. Kitamura and co-workers reported such numbers for an integrated semiconductor optical amplifier.¹² In their work, the SAE growth rate enhancement of the vertical taper, which composes the optical mode converter core, was only 2.7, compared to 3.8 in this work. Vusirikala and co-workers obtained a coupling loss of 3.7 dB for an integrated laser and optical mode transformer.¹³ In their PIC, photolithography was used to taper the mode converter core in the vertical direction only. In conclusion, we have beaten the best reports of coupling loss for an EA modulator and demonstrated coupling losses equal to those of a laser PIC.

7.6 The Polarization Dependent Loss

The polarization dependent loss (PDL) is the difference in transmission loss for TE and TM polarized light. A small PDL is desirable so that the device can be easily used for both polarizations. The PDL at zero bias was obtained for a large number of devices by separately characterizing the TE and TM transmission loss at 1550 nm. The results are summarized in Fig. 7.11. The data are plotted as a function of transmission loss for TE polarized light. For most devices, the PDL is less than 0.2 dB. This is a world record value for an electroabsorption modulator.⁶ Two successes were necessary to achieve such low values. Proper design of the EA core, an effort that was not part of this thesis, and the fabrication of an interface between the EA core and the optical mode converter core, resulting in ultra-low optical dispersion and adiabatic mode conversion. The latter is attributed to two principal factors.



Fig. 7.11 The single side polarization dependent loss for a large sampling of PICs.

Firstly, SAE modeling is used to tailor the optical mode converter core thickness to match theoretically required values for effective optical coupling. The ability to accurately shape the properties of the core rests on the modeling theory and techniques developed in chapters three through five, which constitute a phenomenal contribution to the state of the technology. The maximum growth rate and composition uncertainty for top grade optoelectronic thin films is 10%.¹⁴ Modeling accuracy is crucial because 10 % is already very close to the control limits of conventional MOCVD.

The second factor contributing to our success is the novel fabrication process detailed in chapter six. Optimized epitaxy conditions and an optimized surface restoration procedure are used to fabricate growth interfaces with good crystal quality.

³ L.C. Kimerling, J. App. Phys., 45, 1839 (1974)

⁴ Y.J. Chiu, H.F. Chou; V. Kaman, P. Abraham, and J.E. Bowers, IEEE Phot. Tech. Lett., 14, 792 (2002)

⁵ N. Mineo, K. Nagai, T. Ushikubo, Intl. Meeting Microwave Photonics, MWP '01, 9 (2001)

⁶ R.E. Batrolo, S.S. Saini, T. Ren, Y. Zhu, M. Dagenais, H. Shen, J. Pamulapati, W. Zhou, O. King and F.G. Johnson, IEEE Phot. Tech. Lett., 11, 554 (1999)

¹ W. Shockley, Bell Syst. Tech. J., 28, 435 (1949)

² G.W. Neudeck, "The PN Junction Diode", Addison-Wesley, Reading, Massachusetts (1989)

⁷ E.H. Sargent, D.A. Suda, A. Margittai, F.R. Shepherd, M. Cleroux, G. Knight, N. Puetz,

T. Makino, A.J. Springthorpe, G. Chik and J.M. Xu, IEEE Phot. Tech. Lett., 10, 1536 (1998)

- ⁸ F. Devaux, Fifth Optoelec. Conf., 14A1 (1994)
- ⁹ J.R. Kim, J.S. Lee, S. Park, M.W. Park, J.S. Yu, S.D. Lee, A.G. Choo, T.I. Kim and
- Y.H. Lee, IEEE Phot. Tech. Lett., 11, 967 (1999)
- ¹⁰ T. Ido, H. Sano, M. Suzuki, S. Tanaka and H. Inoue, IEEE Phot. Tech. Lett., 7, 170 (1995)
- ¹¹ U. Koren, R. Ben Michael, B.I. Miller, M.G. Young, M. Chien, H.H. Yaffe, G. Raybon and K. Dreyer, Elec. Lett., 30, 1852 (1994)
- ¹² S. Kitamura, H. Katakeyama, K. Hamamoto, T. Sasaki, K. Komatsu and M. Yamaguchi, IEEE J. Quant. Elec., 7, 1067 (1999)
- ¹³ V. Vusirikala, S.S. Saini, R.E. Bartolo, R. Whaley, S. Agarwala, M. Dagenais, F.G.
- Johnson and D. Stone, IEEE Phot. Tech. Lett., 9, 1472 (1997)
- ¹⁴ E. Veuhoff, J. Crys. Growth, 195, 444 (1998)

Chapter 8

Conclusion

8.1 Thesis Summary

MOCVD Selective area epitaxy has been intensely studied and applied to the fabrication of a photonic integrated circuit. The study included both qualitative and quantitative elements. Qualitatively, we examined the effects of the major MOCVD growth parameters on the morphology of selectively deposited thin films. Precursors originating from the (111) β sidewalls were shown to be responsible for the formation of ridges adjacent to the dielectric masks. However, by tuning the temperature, pressure, V-III ratio and growth rate, the ridges could be suppressed.

A new approach for SAE quantitative modeling was presented. The model accounted for the effects of both vapour phase diffusion and surface migration. For the former component, Laplace's equation was employed to describe the precursor concentration density and only one fitting parameter per group III precursor was needed. For the latter component, time dependent boundary conditions were employed for the first time and two fitting parameters were required. The novel boundary conditions added physical insight and improved simulation accuracy. A closed form solution was found for the surface migration component.

Using a large array of different mask geometries, the vapour phase fitting parameters for In and Ga were extracted from surface profile and EDX measurements. The parameters were found to depend on the alloy composition. Similarly, the surface diffusion length was extracted. The size of the ridges formed by surface migration was

shown to be a strong function of the film thickness. For films thinner than 3000 Å, the ridges disappeared.

An integrated electroabsorption modulator and optical mode converter was fabricated using the SAE technique. The fabrication process included a novel wet chemical clean, designed to reduce Si interfacial contamination and minimize the modulator turn-on voltage. One of the demonstrated advantages of SAE was the ability to reduce the length of the modulator section and thereby reduce the capacitance. Moreover, SAE quantitative modeling was used to tune the MOCVD growth kinetics and tailor the film characteristics of the converter waveguide core to achieve state of the art device performance. Surface profile measurements confirmed that the core thickness profile matched the profile designed by beam propagation calculations. High resolution photoluminescence mapping confirmed the ability of our quantitative model to target the nominal composition such that the maximum strain was minimized.

The electrical and optical properties of the photonic integrated circuit were characterized to further demonstrate the benefits of our SAE process. The 3 dB frequency was 50 GHz, the polarization dependent loss was less than 0.4 dB and the coupling loss was 4 dB, representing an improvement on the order of 10 dB compared to the coupling loss of a conventional InP electroabsorption modulator.
8.2 Statement of Originality

The author claims the following aspects of the thesis to be original contributions of knowledge.

- A novel quantitative model for SAE surface migration, incorporating time dependent boundary conditions.
- (2) The extraction of the (100) InP surface diffusion length as a function of temperature from surface profile measurements of SAE grown films. The model of aspect (1) was used in the extraction.
- (3) A methodology for extracting (D/k)_{In} and (D/k)_{Ga}, the SAE vapour phase model parameters, from surface profile and EDX measurements. The methodology is based on minimizing the square error sum when a large array of simulated curves is fitted to a corresponding array of measured curves.
- (4) The recognition of the alloy composition dependency in $(D/k)_{In}$ and $(D/k)_{Ga}$.
- (5) The use of SAE quantitative modeling to minimize the maximum strain in MOCVD selectively grown layer. A method for minimizing the strain is necessary for counteracting the SAE composition shift and achieving high quality thin films.
- (6) A method for reducing the dose of Si interfacial contamination to a level below 3x10¹¹ cm⁻² and thereby reducing the turn-on voltage of a *pin* structure fabricated in multiple thin film deposition steps.
- (7) Experimental evidence to show that ridges which form adjacent to dielectric masks aligned to [011] during SAE are caused primarily by the surface migration

of precursors originating from the $(111)\beta$ sidewalls. The contribution of migrating precursors originating from the growth mask is negligible.

8.3 Outlook

Several possibilities for further research exist. The time dependent surface diffusion model presented in this work can be applied to a wide range of microstructures fabricated by SAE. For example, the gratings in a distributed feedback laser (DFB) can be deposited directly onto an appropriately patterned substrate. The width of the mask openings would have to be on the order of nanometers hence surface migration would determine the film morphology. The time dependent model can also be applied to the fabrication of quantum dots and quantum wires by MOCVD. Moreover, Khenner and co-workers have recently published a paper, which references this work, and uses time dependent boundary conditions to study surface migration in anisotropic epitaxial lateral overgrowth.¹

Further studies are warranted on the effects of multiple film deposition steps on a *pn* junction. This thesis has examined the enhanced turn-on voltage phenomenon, but there may be other effects that were not explicitly revealed in the course of characterizing the electroabsorption modulator. In chapter seven, the observed increase in capacitance at low frequencies was attributed to deep level traps. It is possible that the traps are interface traps at the overgrowth interface. One can learn more by growing structures with different interface conditions and performing CV or deep level transient spectroscopy (DLTS) measurements.

¹ M. Khenner, R.J. Braun and M.G. Mauk, J. Crys. Growth, 241, 330 (2002)

Appendix A

The following boundary value problem describes surface diffusion on the (100) surface

for ridges aligned to [011].

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} - \frac{n}{\tau}$$
(A.1)

$$n(0,t) = At \tag{A.1a}$$

$$n(W,t) = At \tag{A.1b}$$

$$n(x,0) = 0 \tag{A.1c}$$

A change of variable is made,

$$u(x,t) = e^{t/\tau} n(x,t).$$
 (A.2)

Substitution of Eq. (A.2) into Eq. (A.1) gives,

$$\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial x^2} \tag{A.3}$$

$$u(0,t) = Ate^{t/\tau}$$
(A.3a)

$$u(W,t) = Ate^{t/\tau} \tag{A.3b}$$

$$u(x,0) = 0 \tag{A.3c}$$

Equation (A.3) has the solution, †

$$u(x,t) = v(x,t) + u(0,t)$$
 (A.4)

with

$$v(x,t) = \sum_{n=1}^{\infty} \left(\int_{0}^{t} G_{n}(q) e^{n^{2} \pi^{2} D(q-t)/W^{2}} dq \right) \sin \frac{n \pi x}{W}$$
(A.5)

and

$$G_n(t) = \frac{2}{W} \int_0^W \left(-\frac{d}{dt} u(0,t) \right) \sin \frac{n\pi x}{W} dx.$$
(A.6)

[†] D. Trim, "Applied Partial Differential Equations", PWS-Kent Publishing, Boston, Massachusetts, 1990, pp. 133-135.

Evaluating gives,

$$v(x,t) = 2A \sum_{n=1}^{\infty} \frac{(-1)^n - 1}{n\pi} \left(\frac{\tau}{a} \right) \left(e^{t/\tau} \left[1 + \frac{t}{\tau} - \frac{1}{a} \right] + e^{-n^2 \pi^2 D t/W^2} \left[\frac{1}{a} - 1 \right] \right) \sin \frac{n\pi x}{W}$$
(A.7a) with

$$\frac{1}{a} = \frac{W^2}{W^2 + n^2 \pi^2 L^2}$$
(A.7b)

$$L^2 = D\tau. \tag{A.7c}$$

For $t/\tau >> 1$, the three terms within the first set of square brackets is approximately equal to t/τ since 1/a < 1 for all $n \ge 1$. Also, when considering the sum of the two exponential terms, the second summand is insignificantly small compared to the first. Therefore, to a good approximation, v(x,t) can be represented as,

$$v(x,t) \cong 2A \sum_{n=1}^{\infty} \frac{(-1)^n - 1}{n\pi} \left(\frac{te^{t/\tau}}{a}\right) \sin \frac{n\pi x}{W}.$$
(A.8)

Using Eq. (A.7b) to eliminate a and using Eq. (A.2) to perform the change of variable, gives,

$$n(x,t) = At \left(1 + 2\sum_{n=1}^{\infty} \frac{(-1)^n - 1}{n\pi \left[1 + n^2 \pi^2 \left(\frac{L}{W} \right)^2 \right]} \sin \frac{n\pi x}{W} \right).$$
(A.9)

The term on the right side of Eq. (A.9) can be recognized as the Fourier sine series representation of the function in Eq. (3.33).

Appendix **B**

We define the following function,

$$f(s) = s - s^{\prime}. \tag{B.1}$$

The function can be expanded as follows.

$$f(s) = s - \frac{sR_{Ga}}{(1-s)R_{In} + sR_{Ga}}$$
(B.2)

The derivative, f'(s), is

$$f'(s) = 1 - \frac{R_{Ga}}{\left[(1-s)R_{in} + sR_{Ga}\right]^2}.$$
(B.3)

For $R_{In} > R_{Ga}$, and 0 < s < 0.5, f'(s) is greater than zero therefore f(s) is monotonically increasing under those conditions.