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Auteur: Author:	Xiaobin Hao
Date:	1995
Type:	Mémoire ou thèse / Dissertation or Thesis
Référence: Citation:	Hao, X. (1995). Selective area growth of InP/InP and IngaAs/Inp structures by metal organic vapor phase epitaxy [Master's thesis, École Polytechnique de Montréal]. PolyPublie. https://publications.polymtl.ca/32182/

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SELECTIVE AREA GROWTH OF InP/InP AND InGaAs/InP STRUCTURES BY METAL ORGANIC VAPOR PHASE EPITAXY

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MÉMOIRE PRÉSENTÉ EN VUE DE L'OBTENTION
DU DIPLOME DE MAÎTRISE ÈS SCIENCES APPLIQUÉES (M.Sc.A.)
(GÉNIE PHYSIQUE)

JUILLET 1995

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ISBN 0-612-08201-6

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ÉCOLE POLYTECHNIQUE

Ce mémoire intitulé:

SELECTIVE AREA GROWTH OF InP/InP AND InGaAs/InP STRUCTURES BY METAL ORGANIC VAPOR PHASE EPITAXY

présenté par: Xiaobin HAO
en vue de l'obtention du diplôme de: Maîtrise és Sciences Appliquées
a été dûment accepté par le jury d'examen constitué de:

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ACKNOWLEDGMENTS

I would like to express my deepest gratitude to Professors Remo Masut and John Currie, for their excellent guidance, their encouragement and their patience. Their experience in semiconductor science and technology has been very valuable to me. I also do appreciate their help in my personal life.

Many other individuals have participated in this work with technical help and more importantly their enthusiasm. I am greatly indebted to,

Mario Caron for his training in the SEM and EDX measurements.

Prof. Richard Leonelli of the University of Montreal, for the PL measurements.

Dr. Chetlur S. Sundararaman for the PECVD training.

Pierre Mihelich and Mihai Taslananu for SiN_X deposition.

Dr. Maleck Tabbal for his French translation of the abstract.

Dr. Mario Beaudoin, Dr. Ahmed Bensaada, Laurent Isnard, Yahya Ababou, Hugues Marchand, Marc Suys, Raymond Yip and Patrick Desjardins of the MOCVD group for their team-support.

Dr. Alain Champange for many discussions on lateral vapor diffusion.

SUMMARY

Selective area metalorganic vapor phase epitaxy (MOVPE) is an attractive technique to produce monolithic integration of electronic and optoelectronic devices and fabricate low dimensional semiconductor heterostructures, such as quantum wires and quantum dots.

In this thesis we report, for the first time, the selective area epitaxy (SAE) of InP and InGaAs/InP heterostructure with silicon nitride (SiN_X) as a mask using teriarybutylarsine (TBAs) as an As source. We studied stripe patterns of widths between 3 to 12 μm separated by 50 μm in both [110] and [$\bar{1}$10] orientations. We present the difference in optimized growth conditions and behaviour observed between growth over patterned and unpatterned InP substrates. Our results show that the optimized growth conditions on patterned and unpatterned substrates are different, and that the growth conditions optimized for patterned substrates will have to be changed as the mask geometry is changed. The experimental results also show that for a given growth temperature and reactor pressure the input gas concentration of group III elements in the vapor phase has a maximum limit in order to guarantee selectivity and epilayer quality.

A dependence of the InGaAs composition on the mask geometry is also found in SAE using TBAs. The In content increases when decreasing the width of the mask openings as is observed using AsH_3 as an As source.

We observe no effect of the SiN_X thickness on the selectivity and perfect selectivity is obtained for different SiN_X thickness ranging from 40 to 200 nm.

Due to the difference in growth rates for different families of crystallographic planes, facets such as the {111} A, {111} B, {110} and {100} can be developed in our selectively grown structures. Which facets are actually observed depends on the relative mask stripe orientation because the orthogonal $[\bar{1}10]$ and [110] directions are not equivalent in the zincblende structure.

RÉSUMÉ

La croissance sélective de couches minces par épitaxie à partir de la phase vapeur aux organo-métalliques (MOVPE) est une technique de choix pour l'intégration monolithique de dispositifs électroniques et opto-électroniques ainsi que pour la fabrication d'hétéro-structures de dimensions réduites comme des fils ou des points quantiques.

La fabrication de dispositifs à semiconducteurs consiste essentiellement en deux procédés: croissance des films et définition latérale des motifs. Cette dernière est réalisée, en général, en utilisant des techniques de lithographie conventionnelles après la croissance des films. Cependant, cette méthode peut contaminer ou même endommager les interfaces. L'épitaxie sélective par MOVPE est une technique qui permet le contrôle vertical et latéral des dimensions de la croissance. L'épitaxie sélective utilise une combinaison de masques définis par lithographie et l'anisotropie intrinsèque aux taux de croissance pour ainsi former des structures tri-dimensionelles en une seule étape d'épitaxie tout en réduisant la contamination ou les dommages à l'interface.

Plusieurs caractéristiques du MOVPE sélectif des systèmes InP/InP et InGaAs/InP ont déjà été étudiées, notamment la dépendance de la forme de la couche épitaxiale sur l'orientation du masque, l'influence de la taille des motifs sur la qualités des couches et le taux de croissance ainsi que l'effet de l'épaisseur de la couche diélectrique sur la sélectivité.

En général, l'oxyde de Silicium (SiO_2), est utilisé comme masque diélectrique sur les substrats d'InP et la source d'hydrure traditionnelle, l'AsH_3 est utilisée pour le dépôt de couches contenant de l'As comme l'InGaAs. Cependant, certains des problèmes reliés à cette technique n'ont pas encore été résolus, notamment (1) une augmentation du taux de croissance aux extrémités du masque causant ainsi une non-uniformité de l'épaisseur de la couche épitaxiale d'InP ou d'InGaAs, (2) la non-uniformité de la composition des couches d'InGaAs pendant la croissance, (3) l'influence du rapport surface du semiconducteur exposée sur la surface du masque diélectrique sur la qualité et la croissance de la couche formée sélectivement et finalement (4) la relation entre la forme de la couche épitaxiale et l'orientation du masque. Une uniformité latérale de l'épaisseur de la couche épitaxiale est nécessaire pour, par exemple, l'intégration d'un laser à un guide d'onde optique, puisque la région active du laser doit être couplée d'une façon optimale au guide d'onde optique. De plus, la croissance de l'InGaAs sur InP avec des paramètres de mailles correspondants est importante pour la fabrication de laser parce qu'une différence au niveaux des paramètres de maille produirait des dislocations qui, par conséquent, réduiront l'efficacité d'émission du laser.

Dans ce mémoire, nous rapportons, et ce, pour la première fois, la croissance épitaxiale sélective d'homostructures InP/InP et d'hétérostructures InGaAs/InP en utilisant, comme masque, le nitrure de

Silicium (SiN_x) et comme source d'As, le TBAs. Nous présentons ainsi les différences observés aux niveaux des conditions optimales de croissance et de comportements entre la croissance épitaxiale sur des substrats d'InP masqués ou non-masqués. Les problèmes que l'on a étudié particulièrement sont: (1) l'influence de la largeur des ouvertures dans le masque sur le taux de croissance, (2) le contrôle de l'uniformité de l'épaisseur des couches, (3) l'effet de l'épaisseur de la couche de SiN_x sur la sélectvité et finalement (4) la croissance des couches épitaxiales d'InGaAs et des hétérostructures InGaAs/InP ayant des paramètres de mailles correspondant à ceux de l'InP.

Des couches amorphes de SiN_x, ayant des épaisseurs variant entre 40 nm et 200 nm ont été déposées par dépôt assisté par plasma à partir de la phase gazeuse (PECVD) sur des substrats (001) InP:Fe. Le silane (SiH_4) et l'ammoniaque (NH_3) furent utilisés comme gaz précurseur pour les dépôts et le rapport des débits de SiH_4 et NH_3 fut fixé à 1:12 de telle façon à obtenir des films stoéchiométriques. Ces films furent déposés à une pression de 200 mTorr et à des températures entre 250 et 300 °C. Le taux de dépôt est de 0,8 nm/min, tel que déterminé à partir du temps de dépôt et de l'épaisseur des films mesurée par interférométrie. Des tranchées ayant une largeur variant entre 3 à 12 μm et séparés de 50 μm furent ouvertes dans le SiN_x, le long des orientations [110] et [$\bar{1}$ 10], en utilisant la lithographie UV et la gravure chimique en phase liquide. Les substrats sont ensuite dégraissés avec des solvants organiques, rincés dans de l'eau

dé-ionisée (H_2O DI) et gravés pendant deux minutes dans une solution de H_2SO_4:H_2O_2:H_2O (4:1:1 en volume). Finalement, ils sont rincés dans l'H_2O DI pour être ensuite séchés dans un jet d'azote pur et placés dans le réacteur.

Les croissances furent accomplies à 600°C et 640°C et à une pression de 40 Torr en utilisant comme précurseurs le Triméthylgallium (TMGa), le Triméthylindium (TMIn), le Tertiarybutylarsine (TBAs) et la Phosphine (PH_3). Pour éliminer la couche d'oxyde natif de la surface des substrats, un recuit pré-croissance de dix minutes a été fait à la température de la croissance sous une atmosphère de PH_3. La morphologie de la surface des échantillons fut examinée par Microscopie électronique à balayage (MEB) et microscopie optique. L'épaisseur de la couche épitaxiale fut mesurée par MEB après clivage des échantillons. Des mesures de spectroscopie des rayons-X (EDX) et de photoluminescence à basse température ont été effectuées afin de déterminer les compositions locale et moyenne des couches épitaxiales de InGaAs. La photoluminescence a aussi permis d'estimer le désaccord (*mismatch*) des paramètres de maille des couches épitaxiales de InGaAs avec les substrats d'InP ainsi que l'évolution de la qualité des couches épitaxiales.

Nous avons démarré l'épitaxie sélective des systèmes InP/InP et InGaAs/InP avec les conditions de croissance optimisées pour une croissance planaire. Nos résultats expérimentaux indiquent, pour les deux

systèmes étudiés, une augmentation du taux de croissance par rapport aux taux de croissance sur des substrats sans motifs. Cette augmentation devient plus importante avec la diminution de la largeur des motifs. L'observation au MEB des homostructures InP/InP montre une mauvaise morphologie ainsi qu'une mauvaise sélectivité. Pour les structures InGaAs/InP, une augmentation de l'incorporation d'In est détectée sur les échantillons de croissance épitaxiale sélective par rapport à la croissance planaire. Cette incorporation varie aussi avec la largeur des motifs. Les hétérostructures InGaAs/InP montrent aussi une mauvaise morphologie.

Les conditions pour la croissance épitaxiale sélective furent optimisées pour l'homostructure InP/InP en augmentant la température de croissance de 600 à 640°C et en diminuant la pression partielle de TMIn et de PH3 dans la phase vapeur. Ces conditions menèrent à une sélectivité parfaite et à une très bonne morphologie de la surface.

Pour optimiser la croissance épitaxiale sélective des hétérostructures InGaAs/InP , la pression partielle de TMIn a été réduite, sans toutefois changer la pression partielle du TMGa. Une croissance épitaxiale avec une bonne correspondance des paramètres de maille peut être obtenue quand le rapport de la pression partielle de TMIn sur les pressions partielles de TMIn et de TMGa est égale à 0,103. Comme pour l'homostructure InP/InP, une diminution du taux de croissance est nécessaire pour obtenir des couches épitaxiales de bonne qualité. Les hétérostructures obtenues en utilisant ces conditions optimales pour la

croissance épitaxiale sélective montrent une bonne morphologie. Les mesures de photoluminescence à basse température montrent un pic d'énergie à 0,803 eV avec une largeur à mi-hauteur de 8 meV, indiquant ainsi une très bonne correspondance des paramètres de maille.

On peut ainsi déduire que les conditions de croissances optimales pour des substrats avec motifs sont différentes de celles pour des substrats sans motifs et ces conditions optimales varient avec la géométrie des motifs. Pour une température et une pression du réacteur données, les résultats expérimentaux montrent que la concentration initiale des éléments du groupe III dans la phase vapeur a une limite maximale qui garantit la sélectivité et la qualité des couches épitaxiales.

Une non-uniformité latérale en épaisseur des couches réalisée par croissance épitaxiale sélective a été détectée. En effet, la présence de la surface de SiN_x, sur laquelle aucune croissance n'a lieu, résulte en une gradient de concentration des réactants. Ce gradient de concentration mène à une diffusion latérale et engendre une non-uniformité latérale des taux de croissance sur la surface exposée du semiconducteur. L'uniformité de l'épaisseur dépend ainsi de la largeur des ouvertures dans le masque, de l'orientaion des tranchées du masque par rapport aux directions cristallographiques et des conditions de dépôt. Des taux de croissance réduits favorisent une meilleure uniformité latérale.

Aucun effet de l'épaisseur de la couche de SiNx (de 40 à 200 nm) n'a été détecté sur la sélectivité.

La différence des taux de gravures détectée pour différentes familles de plans cristallographiques permettrait de développer des facettes, telles que le {111} A, le {111} B et le {100}, dans les structures obtenues par épitaxie sélective. La facette effectivement observée dépend de l'orientation relative de la tranchée du masque parce que les directions orthogonales [110] et [110] ne sont pas équivalentes dans la structure zincblende.

Contrairement aux observations lors de l'utilisation de l'AsH_3, nos résultats indiquent la croissance de l'InGaAs sur les plans {111} en utilisant le TBAs. Ainsi la possibilité de contrôler les dimensions latérales pour former des fils quantiques enfouis de InGaAs (tel que suggéré dans la littérature) en utilisant le TBAs comme source d'As est remise en question.

Dans notre procédé de croissance epitaxiale sélective, une dépendance de la composition des couches de InGaAs sur la géométrie des masques a aussi été détectée. Comme pour les résultats obtenus en utilisant l'AsH_3 comme source d'As, le contenu d'In dans les couches augmente en diminuant les ouvertures dans le masques. Par conséquent, pour les applications futures, les paramètres de croissance de l'épitaxie sélective

par MOVPE pour le systèmes InGaAs/InP doivent être adaptés aux motifs du masque.

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INTRODUCTION

Selective area epitaxy (SAE) is an important technique for the integration of electronic and optoelectronic devices and for the fabrication of low dimensional semiconductor structures,such as quantum wires. Two frequently used epitaxial techniques used in SAE are metal organic vapor phase epitaxy (MOVPE) and chemical beam epitaxy (CBE). In CBE, the thickness and composition of the grown film are independent of the mask width and the surrounding mask pattern [1]. In MOVPE, however, the growth rate and composition of the grown film vary not only with the opening width, but also with the mask width [2]. Therefore uniformity in composition and structure has easily been obtained in CBE, but not in MOVPE. The cost of CBE operation is however much higher than that of MOVPE. MOVPE has been shown to be capable of yielding III-V compound films with a high degree of control on composition, doping and thickness, with the thickness being controllable down to the monolayer scale [3]. It is therefore important to develop SAE in MOVPE growth.

The fabrication of semiconductor devices mainly includes two processes: film growth and lateral pattern. Current III-V semiconductor epitaxial growth techniques, such as molecular beam epitaxy (MBE), MOVPE and their variations allow growth of device quality films. These techniques, which have the ability to control the growth process in the

direction normal to the substrate surface and result in structures with controlled vertical anisotropy which are laterally uniform, are well established at present. Lateral patterning of semiconductor devices [4], however, has set new challenges to nanofabrication and crystal growth technologies due to the resolution limitation of the lithography process and damage and contamination induced by the etching process.

SAE has been used in the fabrication of quantum wires [5], production of monolithic integrated circuits [6], integration of a DFB laser and a ridge waveguide [7], fabrication of a quantum well laser with different quantum well thickness [8] and a circuit grating distributed-Bragg-reflector laser [9]. In spite of all this progress, however, the detailed mechanisms of SAE are only beginning to be understood and the performance of these integrated devices is poorer than that of individual components. Furthermore, the integration of a wide variety of optoelectronic components largely remains undone [10].

The objective of this project is to develop a complete SAE process of InP and InGaAs on InP substrates, to establish the optimized growth conditions and to study the characteristics of selective area MOVPE. The conditions of plasma enhanced chemical vapor deposition of SiN_X on InP, photolithography and wet chemical etching to obtain the masked substrates and MOVPE selective area growth on these masked substrates are

optimized. Facet growth, growth rate enhancement, lateral thickness uniformity and deviation in composition of InGaAs are discussed.

In chapter one, we introduce some notions and the current status of SAE and our study topics as well as highlights of our results. The experimental methods used for this research are given in chapter two. Chapter three presents the results, analysis and discussion followed by the conclusions and suggestion for further efforts in chapter four.

CHAPTER 1

SELECTIVE AREA MOVPE

SAE is a technique for controlling growth in the lateral dimensions as well as the vertical dimension. SAE can use a combination of lithographically defined masks and the naturally occurring anisotropy in growth rate to achieve three dimensional patterned structures with a single epitaxial growth step. In order to obtain the control of the growing films in lateral dimensions, selective area MOVPE has been investigated since 1971 [11-17]. The early studies were done exclusively on GaAs and AlGaAs and concentrated on defining the growth conditions necessary for achieving SAE and controlling the cross-sectional shape of the deposits. Subsequently, the studies were extended to InP [18], GaInAs [19-22], and GaInP [23].

The basic characteristics of selective area MOVPE of the InGaAs/InP material system have been studied, such as the necessary conditions for selective deposition, the dependence of the shape of epilayer on the mask orientation and the influence of mask patterning size on the epilayer quality and selectivity. Previous SAE work on InP substrates used silicon dioxide as a dielectric mask and the traditional source AsH_3 for the deposition of layers containing As, such as InGaAs. There are problems which have not yet been well resolved. The first problem is the control of

the shape of SAE growth. For this reason the growth habit at the edges of the deposits has been given considerable attention in the early studies [15-17]. It is a striking feature of the structures that they are bounded by well-defined crystallographic planes. However, the factors determining the shape of the epilayer are not yet fully known and the previous studies[14,24] presented apparently contradictory results. This characteristic is very important because it determines whether SAE can be used for fabrication of quantum wires or not.

A second problem is the influence of the ratio of the exposed semiconductor area to the dielectric mask area on the selectivity and quality of the epilayer. Previous studies[2] showed that (a) reduced total reactor pressure and higher velocity in MOVPE must be used to obtain perfect selectivity and (b) the flux of impinging group III species has to be sufficiently low to prevent deposition on the dielectric mask. It is also mentioned that, for selective growth of InGaAs, a higher growth temperature is required compared to SAE of InP. Starting from conditions for latticed matched growth on InP, the nucleation on the dielectric layer is more sensitive to an increase of the TMIn partial pressure than to that of the more stable TMGa. Therefore, it is important to establish a set of growth conditions (temperature and flow rates) in MOVPE for a given mask pattern where selective growth of both InP and InGaAs is possible. This allows deposition of InGaAs/InP heterostructures.

It is also important to guarantee high quality material with the growth parameters necessary for selective deposition.

A third problem is the composition deviation of InGaAs in SAE. Initial studies of selective area epitaxy concentrated on homoepitaxy of the binaries GaAs and InP. In all of these studies, lattice mismatch between the epitaxial layer and the substrate was not a problem. Studies of selective area growth of ternary compounds such as InGaAs, however, have indicated that substantial compositional deviation can occur[2,10]. Differences in either the surface diffusion rates on the mask or the gas phase diffusion rates of the various species have been invoked to account for the deviations in composition. For technological applications it is important to know how to obtain lattice matched growth of InGaAs to InP.

In this thesis we report, for the first time, the selective area growth of InP and GaInAs structures on InP substrates by low pressure metal organic vapor phase epitaxy through silicon nitride (SiN_X) stripe patterned masks using the alternative organometalic Tertiarybutylarsine (TBAs) as an As source. The choice of the dielectric layer is determined by the intended application and the required device performance. For example, in the fabrication of high voltage power devices, it is important to prevent the entry of oxygen during high temperature device processing [25]. Thus oxide-masking processes are not employed in the manufacture of these

devices. Therefore, silicon nitride-masking techniques are to be preferred in these cases. If only selectivity of the deposition is considered, SiO_2 and SiN_X probably perform the same function. However, the deposition of SiN_X on InP is more difficult than that of SiO_2 because a larger stress is present. As to TBAs and AsH_3, it is difficult to predict a priori difference in growth behaviour although some of our results, such as the InGaAs growth on {111} planes, show differences with those found in the literature. The advantages of TBAs are its low toxicity and vapor pressure which make it a promissing substitute for AsH_3.

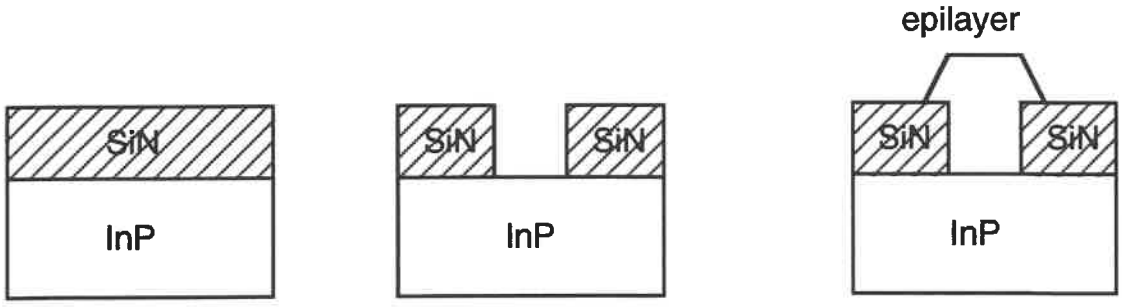
In this study we describe the differences observed in the optimized growth conditions obtained over unpatterned and patterned substrates. A detailed description to optimize SAE for a given mask pattern is presented. Due to the enhancement of the growth rate observed on patterned substrates compared to that on unpatterned substrates we found it necessary to adjust the growth condition lowering the growth rate in order to improve selectivity and epilayer quality. Lower growth rate also favor thickness uniformity. We found no influence of SiN_X thickness on selectivity, while stripe orientation and growth conditions determine the shape of epilayers. Concerning the growth of InGaAs/InP heterostructures we found that we could obtain near lattice match by adjusting the input concentration of TMIn and TMGa in the vapor phase.

CHAPTER 2

EXPERIMENTAL METHODS

SAE using a dielectric layer as a mask implies that the epitaxial growth only occurs at the exposed semiconductor areas, while there is no deposition on the surface of the mask.

The process of selective area MOVPE using a SiN_X dielectric layer as a mask includes three steps as shown in figure 2.1. The first step is plasma enhanced chemical vapor deposition (PECVD) of SiN_X on InP. Photolithography and wet chemical etching to obtain the masked substrates is the second step, and MOVPE selective area growth on these masked substrates is the third step.



SiN_X deposition Masked substrate fabrication MOVPE growth

Figure 2.1 Steps involved in the process of selective area MOVPE.

2.1 Plasma Enhanced Chemical Vapor Deposition

PECVD is an energy-enhanced CVD method, because plasma energy is added to the thermal energy of a conventional CVD system. The substrate temperature, the deposition rate and film uniformity, the morphology, and the chemical composition are basic considerations in the deposition of SiN_X on InP. The deposition temperature is usually limited below 300°C due to the evaporation of P element leading to a deviation in chemical composition. Lower deposition rate and thinner thickness of SiN_X are used because a larger stress between InP and SiN_X is present. The stoichiometric composition corresponds to good surface morphology, high density and low etching rate. Unfortunately, SiN_X deposited by PECVD is not stoichiometric and has a lower density.

In this study, the SiN_X films are deposited by an indirect plasma system [26]. The 100 kHz RF signal is applied to the bottom electrode. The reactant gases, SiH_4 and NH_3 are introduced into the chamber through a gas distribution ring. The chamber is pumped to a base pressure of 2-3 x 10^{-6} Torr before deposition begins.

An initial NH_3 discharge is used to clean any residual oxygen from the chamber. The ratio of flow rate of SiH_4 to NH_3 is maintained at 1:12 in order to obtain near stochiometric films. The films are grown at a pressure of 200 mT and temperatures between 250°C-300°C. The

thickness of the SiN_X layer deposited is measured by an optical interference fringe method. For our study we use a silicon nitride thickness which ranges between 40 to 200nm.

2.2 Photolithography and Wet Chemical Etching

The formation of the two dimensional pattern on the wafer is realized by lithography and etching processes. Semi-insulating (001) InP:Fe substrates with a deposited SiN_X layer were patterned with stripes 3-12μm wide and 50μm apart oriented along [110] and [$\bar{1}$10] crystallographic directions. InP substrates with the SiN_X layer were first cleaned with organic solvents (Trichorethane, Acetone and Propanol). The photoresist was then coated on the SiN_X surface at 3000/min spinning speed for 30 seconds. Pre-bake was performed at 90^{o}C for 30 minutes and exposure time is about 7 seconds. The development time is 30 seconds and post-bake treatment is done at 130^{o}C for 30 minutes. Finally a 5% HF solution is used to etch the SiN_X layer. The etching rate is about 4nm/sec at room temperature. Figure 2.2 presents an optical microscope picture of the masked substrate.

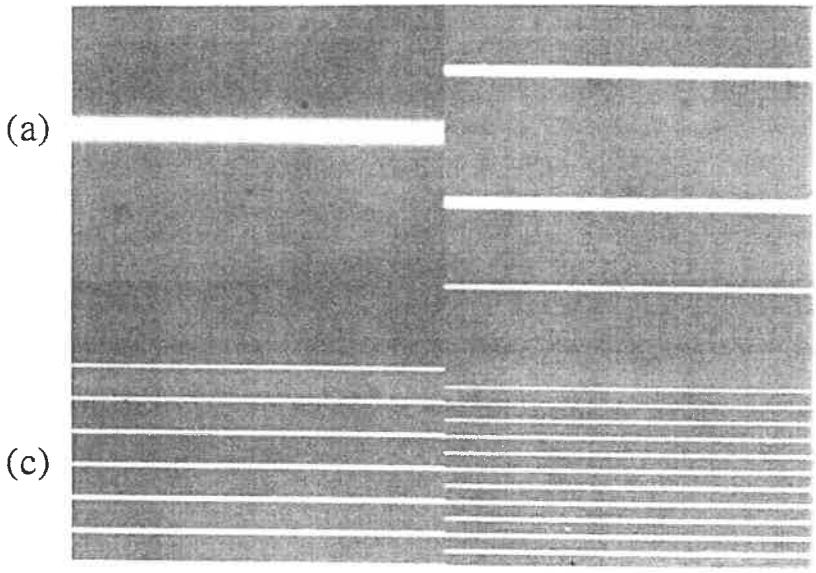


Figure 2.2. Optical microscope picture of a masked substrate (magnification: (a) 50x, (b) 200x, (c) 400x and (d) 1000x)

2.3 Low Pressure Metal Organic Vapor Phase Epitaxy

In 1969, H.M.Manasevit first proposed a epitaxial technique for compound semiconductors such as InP, InGaAs and InGaAsP using metal organic compounds of TMIn and TMGa as gas growth sources. This epitaxial technique, called MOVPE, has some advantages over chloride and hydride VPE methods, such as the elimination of multi-temperature zones and growth of multi-layer materials with sharp interfaces. It can easily grow quantum well, quantum wire and superlattice structures for device applications. The materials grown by MOVPE have been used to fabricate field effect transistors (FET) [27], heterostructure bipolar transistors (HBT) [28,29] and lasers [30-32].

2.3.1 Low Pressure Metal Organic Vapor Phase Epitaxy System

Our low pressure MOVPE system mainly consists of gas sources, reactor chamber, fast gas switching manifold and automated control system and exhaust gas treatment. Trimethylgallium (TMGa), Trimethylindium(TMIn), Phosphine(PH_3), Tertiarybutylarsine (TBAs), Silane(SiH_4) and (DEZn) are used as gas sources. The gas flow rate is electronically controlled by mass flow meters. The quartz chamber reactor contains a graphite susceptor heated by an infrared (IR) source. The computer controlled fast switching run-vent gas manifold is an important feature of this low-pressure MOVPE system as it allows the fabrication of heterostructures with thickness control of the order of a monolayer and with abrupt interfaces.

2.3.2 Selective Area MOVPE Growth of InP/InP and InGaAs Structures

Prior to growth, the patterned substrates were degreased with electronic grade standard organic solvents. They were abundantly rinsed in deionized water and etched in an H_2SO_4:H_2O_2:H_2O(4:1:1 solution by volume) for 2 minutes at room temperature and rinsed again with deionized water. Finally they were blown dry with N_2, and loaded into the reactor. Growth was performed at 600^oC and 640^oC and a reactor pressure of 40 Torr with TMGa, TMIn, TBAs and PH_3 as precursors. A pregrowth annealing at the growth temperature under PH_3 was performed

for 10 minutes to remove the native oxide from the patterned substrate surface.

2.4 Sample Characterization

The surface morphology of the samples was examined by scanning electron microscope (SEM) and optical microscope. The epilayer thickness was measured using SEM after the samples were cleaved and stain etched. Energy dispersive x-ray (EDX) and high resolution x- ray diffraction (HRXRD) were used for the determination of the local and average composition of InGaAs epilayers. Low temperature photoluminescence (PL) measurements give the average lattice mismatch between the InGaAs epilayers and the InP substrates and characterize epilayer quality.

CHAPTER 3

RESULTS, ANALYSIS AND DISCUSSION

As previously mentioned we focus mainly on the difference in optimized growth conditions and behaviour observed between growth over patterned and unpatterned (001) oriented substrates. In this chapter, we present the experimental results of SAE developed in our laboratory and analyze and discuss these results.

This chapter is organized in the following way: we first present, in section 3.1, the results of SAE growth of InP/InP and InGaAs/InP structures grown with conditions optimized for unpatterned substrates; in section 3.2 we discuss the growth conditions favoring perfect selectivity and the influence of SiN_X thickness on selectivity; the characteristics of SAE, including facet growth, growth rate enhancement, lateral thickness uniformity and deviation in composition in InGaAs are discussed in section 3.3; and finally, the optimization of InP/InP SAE is given in section 3.4 followed by optimization of InGaAs/InP SAE in section 3.5.

3.1 Selective Area Growth of InP/InP and InGaAs/InP Structures Grown With Conditions Optimized for Unpatterned Substrates

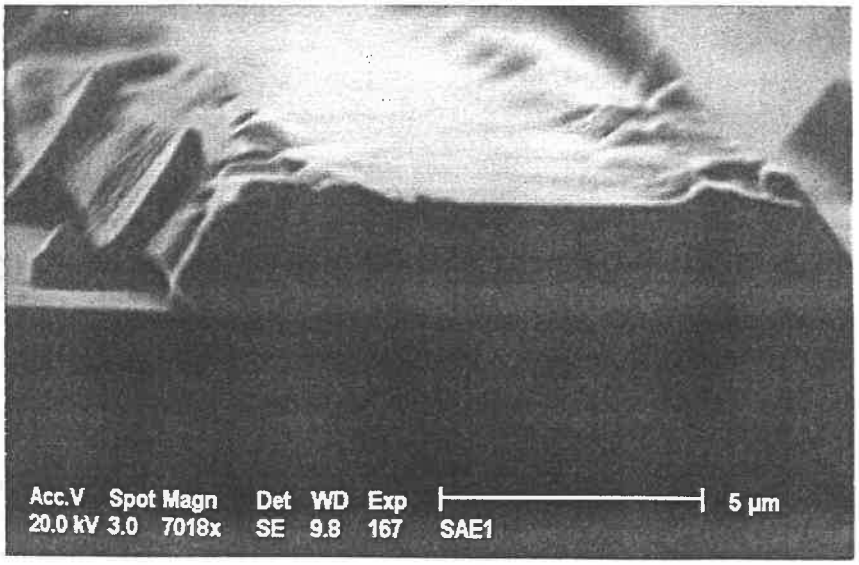
We started the SAE of InP/InP and InGaAs/InP with the growth conditions optimized for planar growth which are summarized in Table1. This table shows the growth temperature and partial pressures of reactants for InP/InP homostructures and InGaAs/InP heterostructures grown over patterned and unpatterned substrates. The partial pressures of reactant species are expressed in Torr. All samples were grown at 40 Torr reactor pressure.

Table 1. Growth temperature and reactants partial pressure (In Torr).

	InP/InP		InGaAs/InP	
	Unpatterned	Patterned	Unpatterned	Patterned
Growth Temperature(°C)	600	640	640	640
TMIn	2.3×10^{-3}	$<6.0\times10^{-4}$	8.3×10^{-4}	$< 1.8\times10^{-4}$
TMGa			3.3×10^{-3}	$<1.5\times10^{-3}$
PH3	0.607	0.307	0.04	0.023
TBAs			0.032	0.032

Figure 3.1 presents the surface morphologies of epilayers grown by selective area MOVPE under growth conditions optimized for unpatterned

(a)



(b)

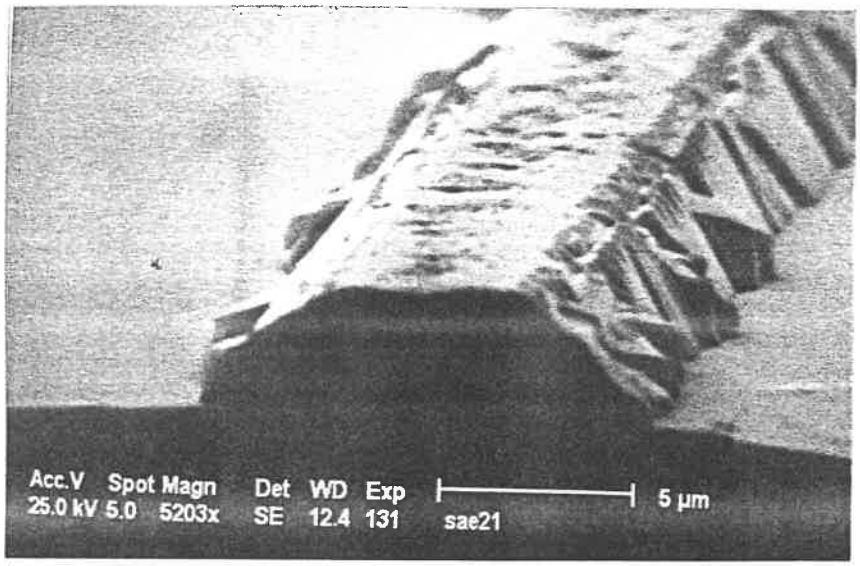


Figure 3.1 Surface morphologies of epilayers grown by selective area MOVPE under growth conditions optimized for unpatterned substrates: SEM pictures of : (a) InP/InP homostructure and (b) InGaAs/InP heterostructure.

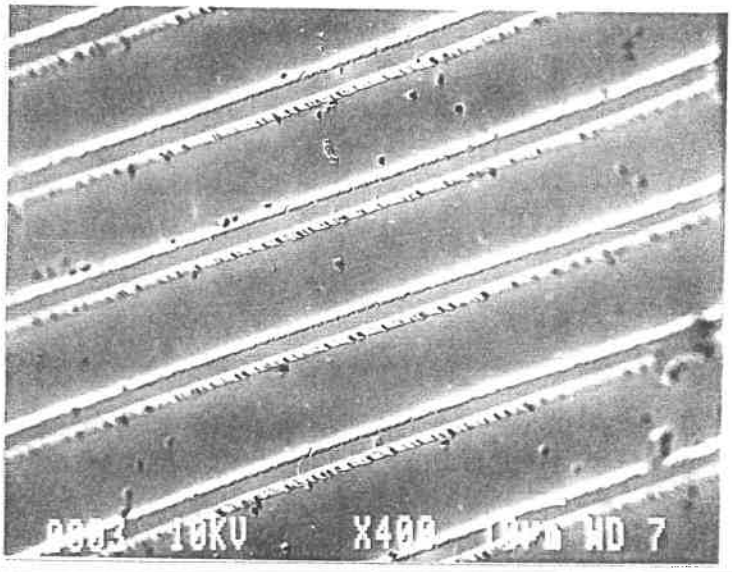
substrates. Our results show that an enhancement effect of the growth rate is found in SAE for both materials compared to the growth rate on unpatterned substrates. Moreover, this enhancement increases when decreasing the window width. SEM observation shows not only poor surface morphology, but also not perfect selectivity and non-uniform growth thickness across the windows for InP/InP homostructures. For InGaAs/InP heterostructures an enhancement of In incorporation is also found in SAE, compared to planar growth. This incorporation varies with the window width. As a general trend, In incorporation increases with decreasing width of the mask openings. SEM observation also shows poor morphology for the InGaAs/InP heterostructures, although perfect selectivity has been obtained. These results indicate that the optimized growth conditions on patterned and unpatterned substrates are different and show the need to optimize the SAE conditions. The presence of the silicon nitride makes the growth features of epitaxial growth change. In what follows, we will discuss in detail the characteristics of SAE and how to optimize growth conditions for SAE growth of InP/InP and InGaAs/InP structures.

3.2 Selectivity

Selective area growth using a dielectric layer as mask implies that the vapor phase sources are consumed in the exposed semiconductor areas, while they are not deposited on the surface of the mask.

Figure 3.2 presents SEM pictures of InP/InP structures grown under two different reagent fluxes, while keeping other growth parameters the same. The picture of figure 3.2 corresponds to higher reagent fluxes as optimized for growth on unpatterned substrates and the one in figure 3.2 (b) corresponds to reagent fluxes as optimized for growth on patterned substrates. These conditions are summarized in Table 1. Here we see that even if selectivity for the higher reagent is not perfect, there is no continuous growth on the mask surface. The reduction of the reagent flux leads to perfect selectivity, which means there is no deposition on the surface of SiN_X. This experimental result shows that the growth conditions favoring perfect selectivity for InP/InP structures are lower reagent fluxes than for growth on unpatterned substrates. Lower reagent fluxes are necessary due to the added mass transport of species not deposited on the mask. Perfect selectivity has also been obtained for the InGaAs/InP structures, in the entire range of the chosen growth conditions. Our results also show that selectivity is not influenced by the thickness of the dielectric layer (40-200 nm) and that perfect selectivity has been obtained for this range of thickness. These results show that selectivity is rather easily achieved in low pressure (LP) MOVPE.

(a)



(b)

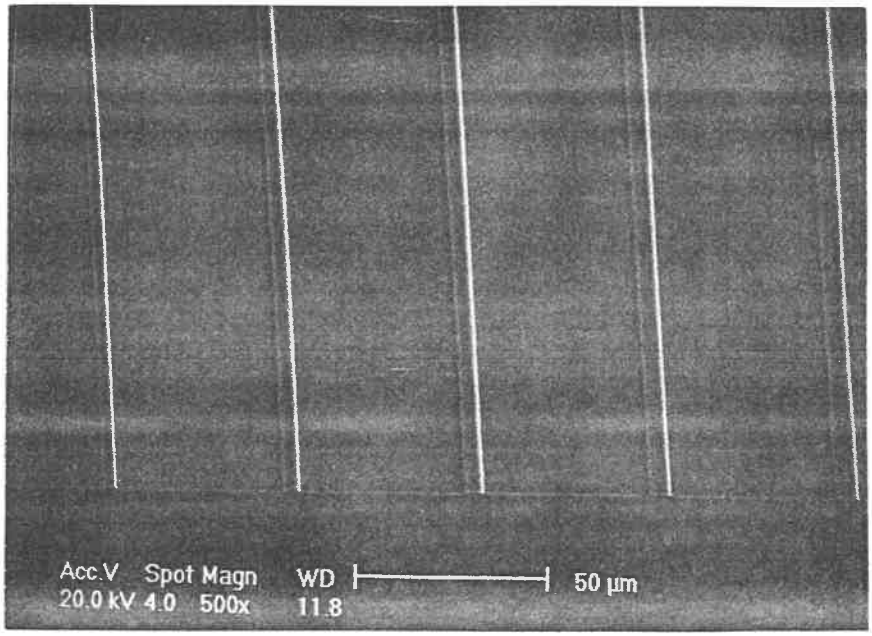


Figure 3.2 SEM pictures of InP/InP structures under two different reagent fluxes: (a) higher reagent fluxes (optimized for unpatterned substrates) and (b) lower reagent fluxes (optimized for patterned substrates).

The reasons leading to selectivity are not well known at present, and the explanation for this issue varies from one report to another [10]. Currently, there are two schools of thought for the mechanisms responsible for selectivity, one which proposes that diffusion on the mask surface [24] is the main cause and the other which proposes that the main cause is desorption and gas phase diffusion [2]. According to the later, selective deposition is due to the fact that there is no nucleation site on the surface of dielectric layers. Therefore, the molecules or atoms of reactant species impinging on the mask surface desorb.

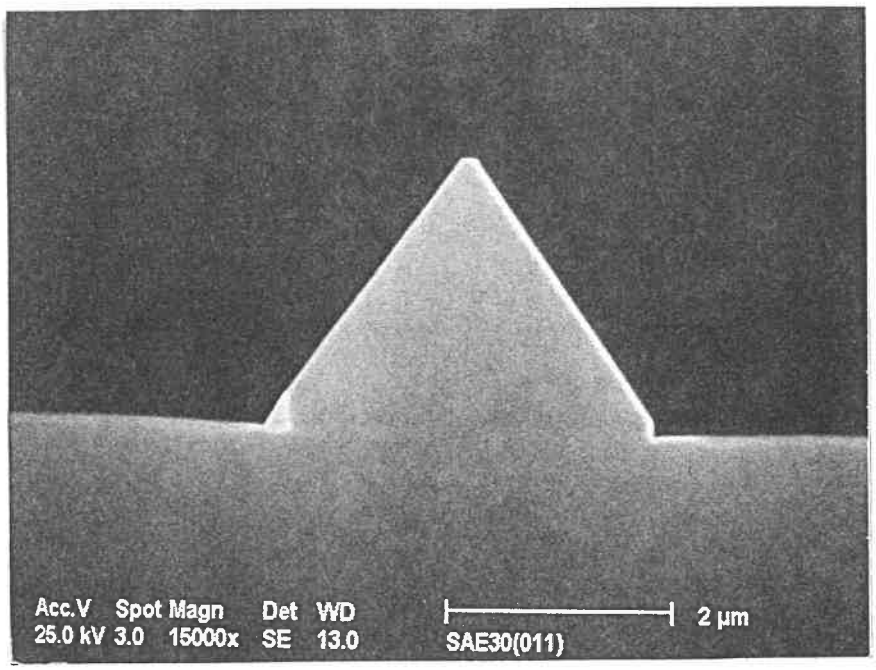
Generally speaking, the formation process of a new film on the surface of the solid mainly includes the adsorption of reagent species and chemical reactions on the surface of the wafer. A decrease in the adsorption or reevaporation of adsorbed species on the SiN_X surface has as a consequence a very low probability for reactions leading to no growth on the dielectric layer. This leads to lateral concentration gradients above the mask surface and selectivity is generated. According to this mechanism responsible for selectivity, higher growth temperature also favors selectivity since it promotes the reevaporation of adsorbed reagent species. Our experimental results also corroborate that the input gas concentration of group III elements in the vapor phase for a given growth temperature and reactor pressure has a maximum limit in order to guarantee perfect selectivity for InP/InP which was already observed in Kayser's study [2]. This is because a high concentration of group III

elements may lead to nucleation on the mask surface. Because our reactor pressure and mask pattern are different from his conditions, it is not possible to make a direct quantitative comparison his results. We observe, however, that we obtain selective growth for values of the TMIn partial pressure larger than his limit at 640°C, but the morphology is not optimized.

3.3 Characteristics of Selective Area Metal Organic Vapor Phase Epitaxy

3.3.1 Facet Growth

In figure 3.3 we present several kinds of shapes observed in InP/InP structures grown selectively together with their schematic drawings. Figure 3.3(a) and (b) show results on [110] mask stripe orientation and figure 3.3(c) on [$\bar{1}$10]. We observe two kinds of shapes of InP/InP structures for the [110] mask stripe orientation: one is bounded by the {111} and {100} families of crystallographic planes shown in figure 3.3(a), the other is bounded by the {111}, {110} and {100} families shown in figure 3.3(b). These two samples are grown with the same growth conditions except the growth time. If we increase the growth time for the sample shown in (b), we expect the final shape of the epilayer to be the same as that of the sample shown in (a).



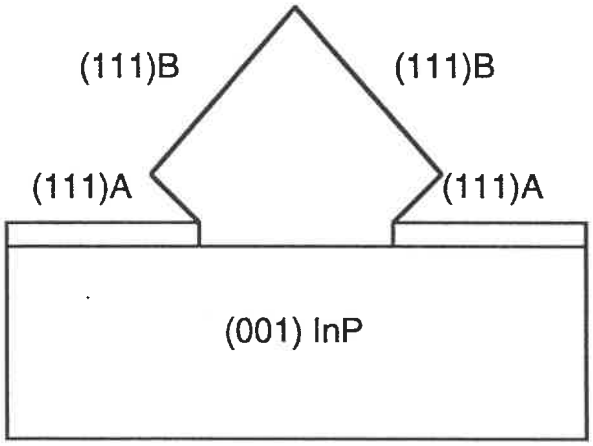
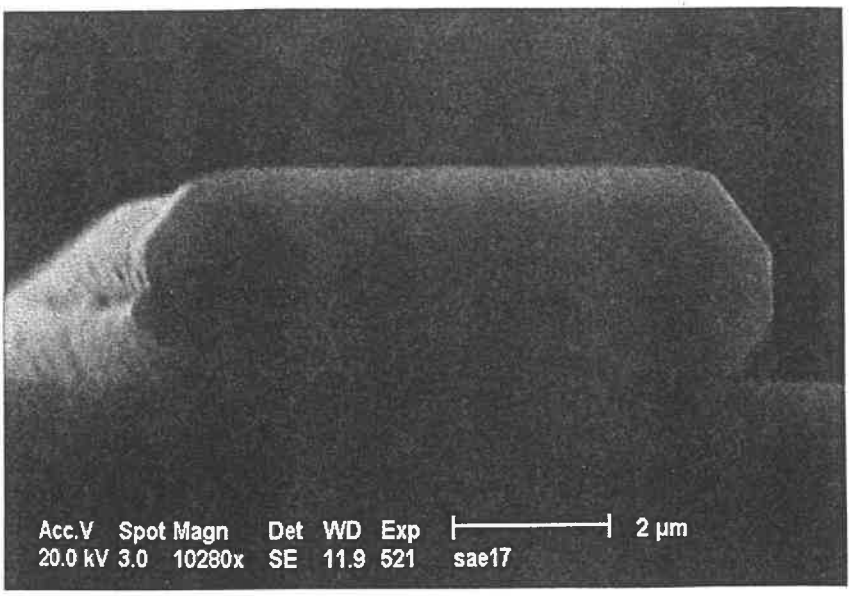


Figure 3.3(a) SEM picture of InP/InP structure selectively grown on [110] mask stripe orientation and its schematic drawing.



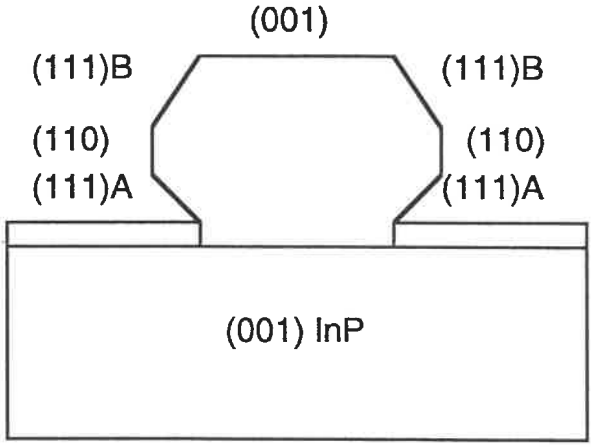
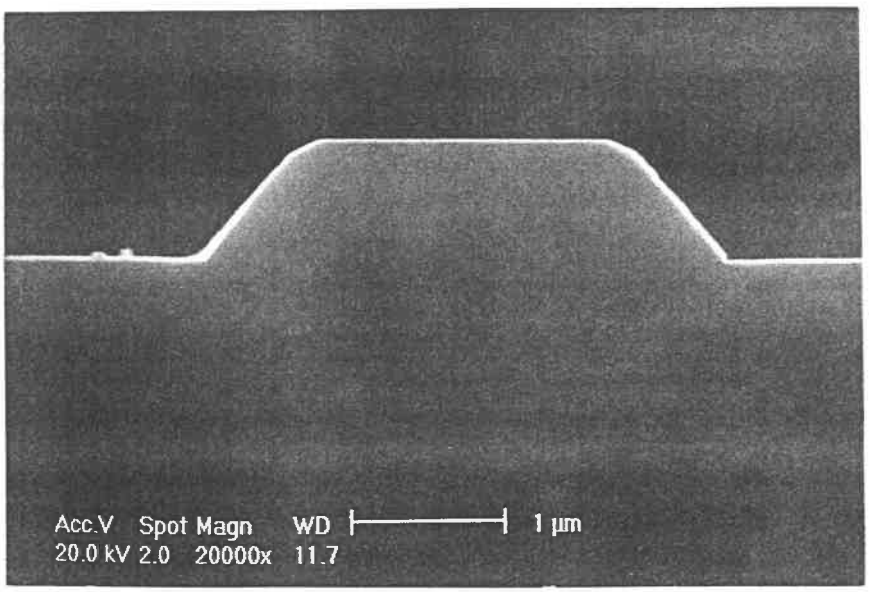


Figure 3.3(b) SEM picture of InP/InP structure selectively grown on [110] mask stripe orientation and its schematic drawing.



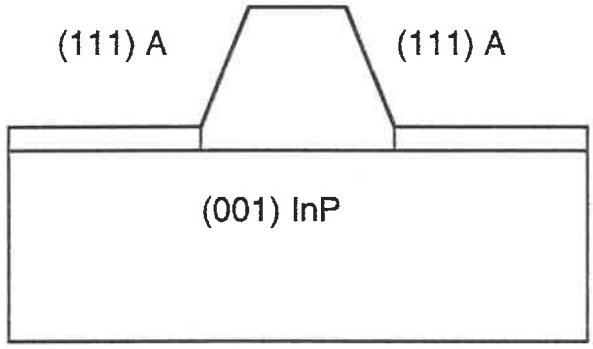
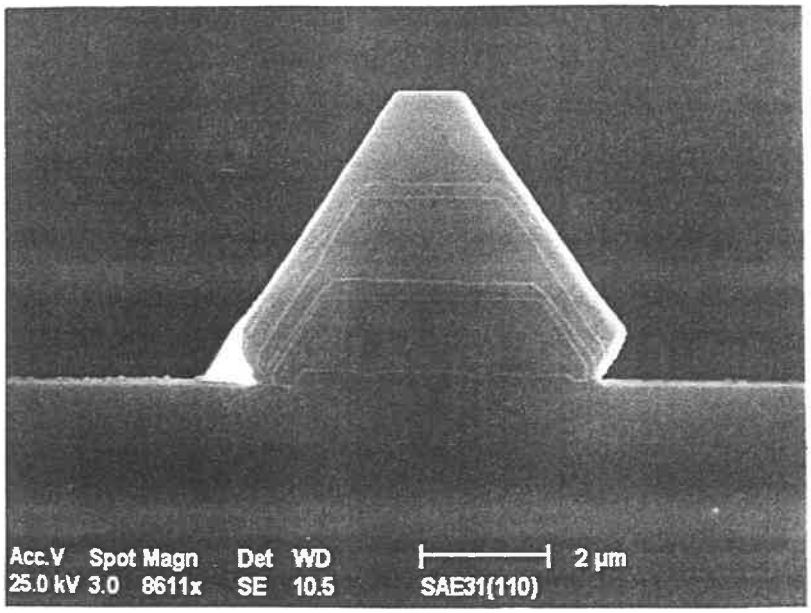


Figure 3.3(c) SEM picture of InP/InP structure selectively grown on [$\bar{1}$10] mask stripe orientation and its schematic drawing.

This is because the growth rate on the [110] orientation is faster than that on the [111] orientation. Therefore, as the growth proceeds, {110} planes will finally disappear. For the [$\bar{1}$10] mask stripe orientation, the shape of InP/InP structures that we obtained is bounded by the {111} A planes shown in figure 3.3(c).

Figure 3.4 presents SEM pictures of InGaAs/InP structures grown selectively and their schematic drawings. Figure 3.4 (a) shows typical



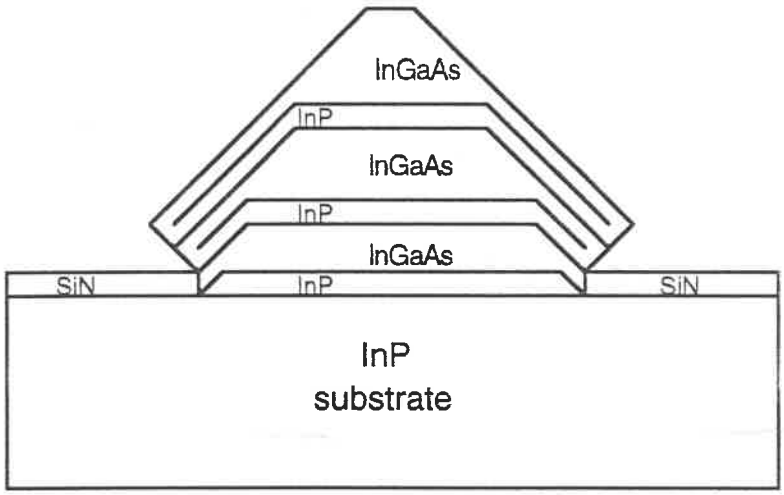
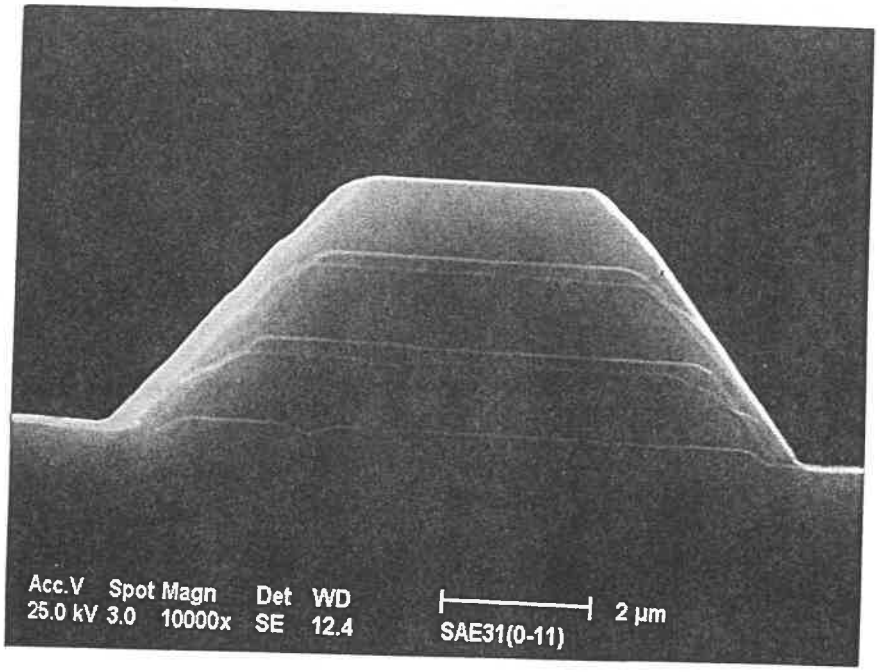


Figure 3.4(a) SEM picture of InGaAs/InP structures selectively grown on [110] mask stripe orientation and it schematic drawings.



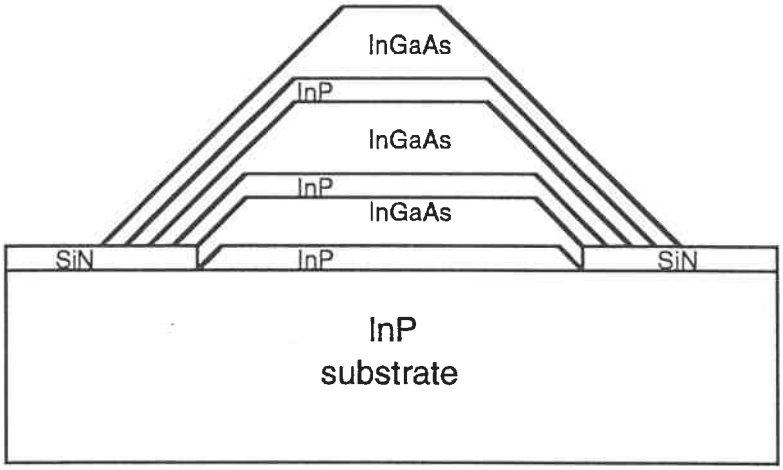


Figure 3.4(b) SEM picture of InGaAs/InP structures selectively grown on [$\bar{1}$ 10] mask stripe orientation and its schematic drawings.

results obtained on the [110] mask stripe orientation while figure 3.4(b) corresponds to the [$\bar{1}$10] mask stripe orientation. For the [110] mask stripe orientation, the shape of the epilayer is bounded by the {111}A and {111}B families of crystallographic planes. The growth on [$\bar{1}$10] orientation is apparently only bounded by the {111}A planes. Note that, from SEM observation, there is InGaAs growth on the {111} planes and that the growth rate on {111} planes is much smaller than on {100} planes. Galeuchet et al [24,33] reported no InGaAs growth on {111} planes using AsH_3. Different growth conditions, such as the reactor pressure and the concentration of reactants as well as V source may contribute to this difference.

As to the facet growth, Galeuchet et al [33] explain that surface catalyzed reactions dominate the growth in selective area MOVPE. Slow surface reactions in low growth rate planes block the adsorption and local redistribution of arriving species. Therefore, a difference in growth rates for different crystallographic facets can be observed.

Our results, to be presented later, show that the growth rate on [001] orientation is nearly linear with the partial pressures of group III elements, indicating the growth rate in this orientation is mass transport limited. The occurrence of facet growth in SAE also indicates that the growth mechanism on {111} and {110} planes, with lower growth rates, is limited by surface reactions.

There are two kinds of facet growth, one is a growth normal to the growth surface, which is also called normal growth, the other is growth along the growth surface, also called lateral growth. Different crystallographic facets have different atomic density. It is found that the facets with higher atomic density have faster lateral growth rate, but slower normal growth rate. Due to this difference in growth rate, these facets gradually annex neighbouring facets with faster normal growth rate during growth. The final shape of the grown crystal is then bounded by these facets under a free growth environment. This rule can be illustrated by figure 3.5. Crystalline facet A with a faster normal growth rate, being between facets B1 and B2 with a slower normal growth rate, is gradually annexed, abstracts and will finally disappear, while facets B1 and B2 expand and expose to the surface of the crystal. For III-V compound semiconductors belonging to the zincblende structure, the highest atomic density planes observed correspond to the {111} family while the {110} family is second and the {100} family is third. Therefore, the order of vertical growth rate for these three families of crystallographic planes is {100} > {110} > {111}. The final shape of epitaxial growth should be bounded by the {111} family of crystallographic plane under free growth environments. There are two kinds of {111} family planes for InP, one is the {111} A family containing In atoms, the other is the {111} B containing P atoms. Both two kinds of facets have different electronic structures. There are two antibinding electrons on the {111} B surface, while there is one empty orbit on the {111} A surface.

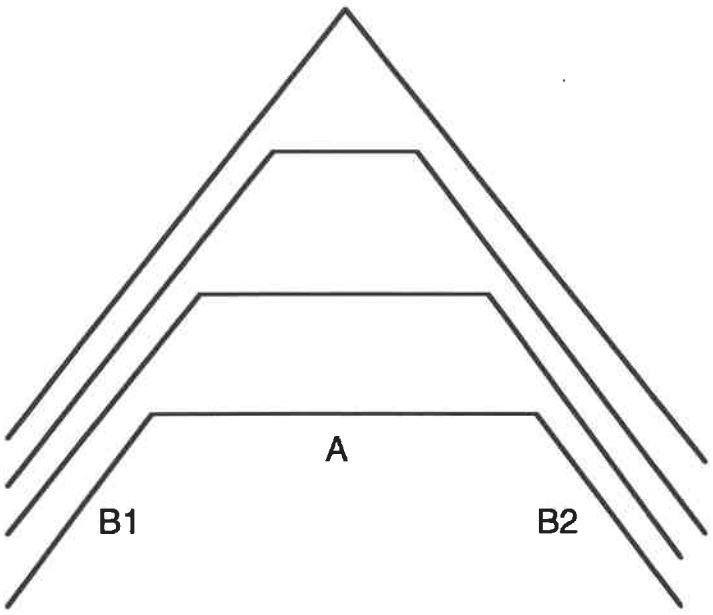


Figure 3.5 Process of crystalline plane growth

Therefore, the growth rates of these two {111} families would not be the same. Kayser [2] suggested that the {111} B planes have a slower growth rate than the {111}A planes. For the {110} family, the growth rates on [110] and [$\bar{1}$10] orientations are not equivalent and they are determined by the concentration of group V element [3]. Our results show that, under our chosen growth conditions, the growth rate on the [$\bar{1}$10] direction is faster than on the [110] direction. Please note that the growth in [$\bar{1}$10] direction is observed in our SAE pictures for the case of [110] mask stripe orientation.

Figure 3.6 shows the spatial arrangement of low index crystallographic planes for the [110] mask stripe orientation (i.e. the direction coming out of the page). Hence for this orientation, the shape of epilayers should be bounded by {111} A, {111} B and {110} planes shown in figure 3.3(a). As the growth proceeds, the final shape of the epilayer will bounded by {111}A and {111} B planes because the growth rate on the [$\bar{1}$ 10] direction is faster than the [111] orientation, as shown in figures 3.3(b) and 3.4(a).

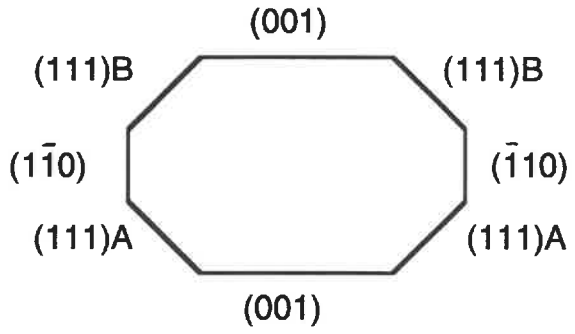


Figure 3.6 Spatial arrangement of low index crystallographic planes of [110] mask stripe orientation.

Figure 3.7 shows the spatial distribution of low index crystallographic planes for the [$\bar{1}$ 10] mask stripe orientation. Hence, for this orientation, the final shape of epilayers should also be bounded by

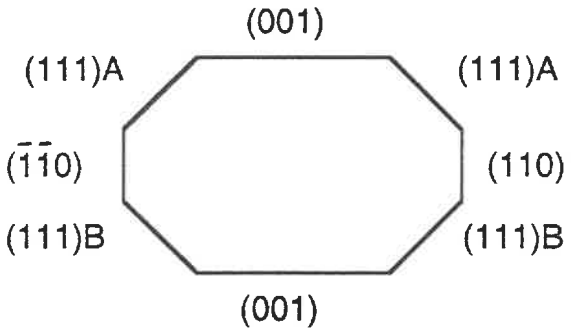


Figure 3.7 Spatial distribution of low index crystallographic planes of [$\bar{1}$10] mask stripe orientation.

{111}B and {111}A planes. Because the growth rate on the [110] direction is slower than on the [$\bar{1}$10] direction, the {111} B planes can not be clearly seen . Therefore, the shape of the epilayers shown in figures 3.3 (c) and 3.4 (b) is usually observed. The {111] B planes can be occasionally observed on some epilayers grown in this stripe orientation for longer growth times. The differences between {111}A, {111}B, {110} and {$\bar{1}$10} planes make the shape of III-V semiconductor selective area vapor phase growth complicated. As we have shown, however, all the details of the shape of the epilayers observed under different growth conditions and mask stripe orientations can be explained taking into account differences in growth rates imposed by the limiting growth mechanism in selective area MOVPE.

3.3.2 Growth Rate Enhancement Effect and Lateral Thickness Non-uniformity

In order to compare the difference in the growth rate on patterned and unpatterned substrates, the growth on both substrates was performed in the same run. Figure 3.8 presents the dependence of the InP relative growth rate on [001] orientation (the ratio of the growth rate on patterned substrates to the growth rate over unpatterned substrates) on the base width of the mask openings for the [110] mask stripe orientation. The mask spacing for this measurement is 50μm. As mentioned previously, facet growth is observed in SAE. Therefore, the measurement of the growth rate must be indicated with the shape of the epilayer. These data are measured with the shape of the epilayer shown in figure 3.3(a). There is an enhancement of the InP growth rate in SAE, compared to that over unpatterned substrates, as was reported in the literature. An enhancement of growth rate for InGaAs using TBAs is also observed compared to the growth on planar substrates. For example, in InGaAs/InP optimized structures, the [001] growth rate on a patterned substrate with a 6μm stripe width is about three times higher than on unpatterned substrates, which is comparable to that observed in InP Again, In order to observe the detailed growth process of InGaAs, we incorporate InP layers as "markers" during InGaAs growth.

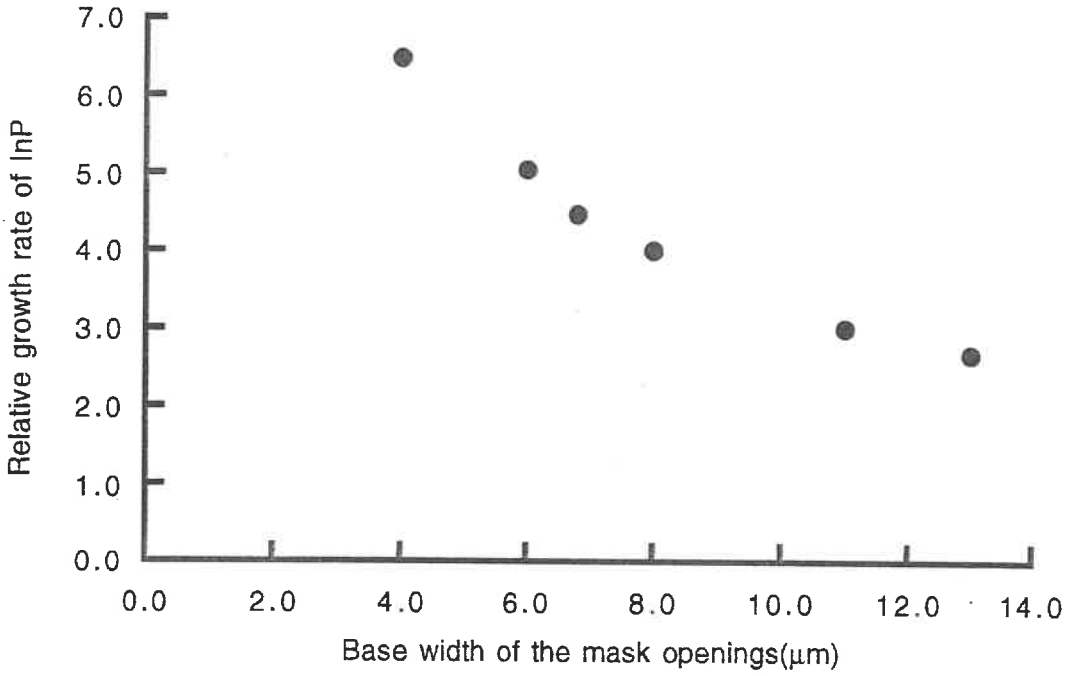


Figure 3.8 Dependence of the InP relative growth rate (the ratio of the growth rate on patterned substrates to the growth rate over unpatterned substrates) on the base width of the mask openings for the [110] mask stripe orientation. Error bars are ±5% of the measured values.

Figure 3.9 presents the SEM picture of the InGaAs/InP heterostructures selectively grown with the growth conditions optimized for SAE. The thin lines on the SEM photographs are InP markers. It is also observed that the growth rate of InGaAs increases for narrow line width of window openings by comparing for example figures 3.4(a) and

3.9. It is clear that the thickness of epilayers with different base width of mask openings is different and thicker for a narrow width.

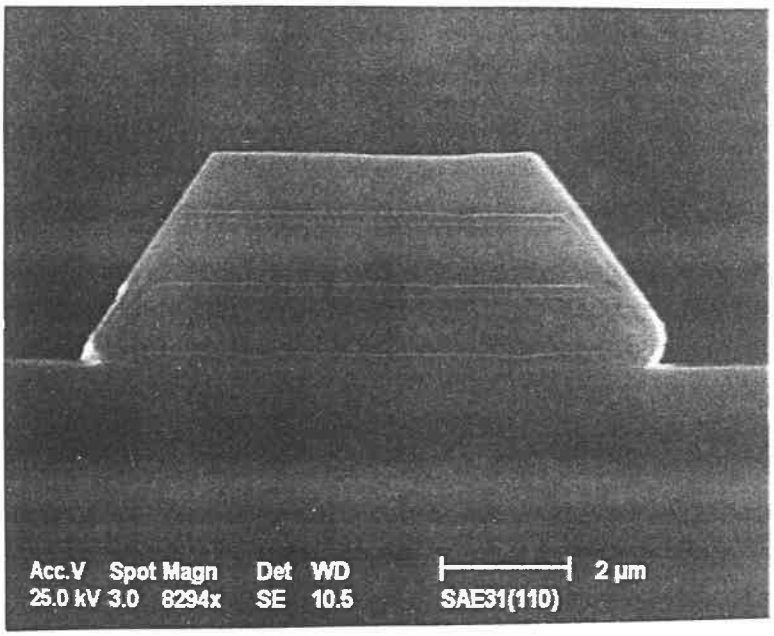


Figure 3.9 SEM picture of a selectively growth InGaAs/InP heterostructures

In summary, an enhancement of growth rate for InP and InGaAs materials was observed in SAE, compared to the growth on unpatterned substrates and this enhancement increases with the decrease in base width of openings. This phenomena has been observed by Galeuchet et al [24] for InGaAs/InP using AsH_3. They found that the growth rate of InP and InGaAs depends on the so called fill factor, which is related to the mask spacing and the facet growth on the side walls and top surface. The growth

rate increases with increase in mask spacing and decreases in the base width of the openings.

Our results presented in figure 3.8 and figure 3.9 show that the growth rates of InP and InGaAs increase with a decrease in base width of window openings. Wide base width corresponds to a wide top width. Therefore, our results basically agree with their results. It is difficult to make quantitative comparison between our data and theirs. This is because the growth conditions, such as growth temperature, reactor pressure and the concentration of reactants, are different. The exact functional dependence of the growth rate enhancement on the mask geometry is unknown because the growth rate in SAE is controlled by growth parameters such as reactor pressure and partial pressure of group III elements. Hence, different growth conditions will lead to different relationship between growth rate and mask geometry. Even for a given reactor pressure and concentration of reactants, facet growth in SAE leads to a slightly varying shape of the epilayer. Hence, the accurate relationship between growth rate and width of mask openings is difficult to assess. Therefore, the curve presented in figure 3.8 and the value of InGaAs growth rate only provide data on the growth rate enhancement as a function of the mask geometry for our particular set of growth parameters. It is nevertheless clear that there is an enhancement of growth rate for InGaAs and InP materials in SAE, compared to corresponding

growth on unpatterned substrates which depends on the base width of the mask openings.

We have also measured the growth rate on [001] orientation as a function of group III elements partial pressure. Our results show that the growth rates of InP and InGaAs increase linearly when increasing the partial pressures of group III elements TMIn and TMGa, which indicates that the selective area MOVPE growth on [001] orientation is still mass diffusion controlled.

In order to explain this growth rate enhancement effect in SAE, it is necessary to discuss the mechanism of selective area MOVPE. During SAE using a dielectric layer masks the growth only occurs at the exposed semiconductor areas, while there is no deposition taking place on the surface of mask areas. In mass transport controlled planar MOVPE, only vapor phase diffusion of reactant species normal to the substrate surface contributes to epitaxial growth. But in selective area MOVPE, since the reactant species arriving on mask areas can not be adsorbed or desorb by reevaporation, the consumption of reagents exclusively in mask openings results in a lateral concentration gradient in addition to the gradient normal to the sample surface that is present in diffusion controlled planar growth. This process is shown in figure 3.10. Since the growth rate on [001] orientation in typical growth conditions of selective area MOVPE is determined by the supply of group III species, it may be expected that

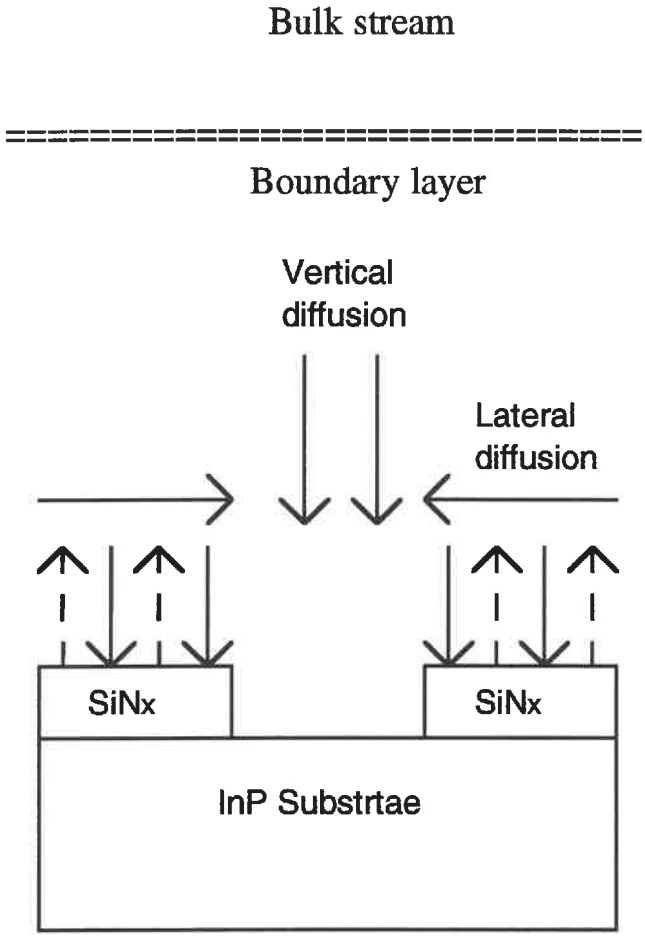


Figure 3.10 Mass transport of reactants in selective area MOVPE.

an additional supply of these species would enhance the growth on the semiconductor areas. The growth rate in openings is, therefore, higher than the growth rate on unpatterned substrates and the enhancement is greater, when the ratio of the opening width to the mask width is smaller. It is also obvious that this mechanism may cause nonuniform lateral growth rate. The growth rate near the edges of the mask maybe larger than in the middle areas.

The faster growth rate in SAE under growth conditions optimized for planar growth leads to the poor quality of the SAE epilayers. Therefore, the growth rate must be decreased in order to improve the epilayer quality. Since the growth on [001] orientation is mass transport limited, the growth rate can be decreased by decreasing the partial pressure of group III elements.

The enhancement of the growth rate in SAE is mainly due to the lateral vapor phase diffusion of reactant species. The consumption of species exclusively in the mask openings results in a lateral concentration gradient above the mask surface. This lateral concentration gradient may cause the non-uniform growth rate across the exposed semiconductor areas. The extent of non-uniform growth rate across the exposed semiconductor areas is related to the growth conditions and the width of mask openings. This will be discussed later. Yamagnchi et al [34] verified the occurrence of lateral vapor phase diffusion in SAE by solving a two dimensional diffusion equation in the steady state. They found that there is a lateral gradient of concentration in the presence of the non-growth surface and this lateral gradient becomes steep at the mask edges. Their analysis clearly shows that the lateral concentration gradient is strongly affected by the presence of the non-growing dielectric regions and it increases when increasing the mask width and decreasing the width of mask openings. In turn, this lateral concentration gradient will usually lead to non-uniform growth thickness across the epilayers.

Figure 3.11 presents the SEM pictures of InP/InP structures selectively grown on different base width in the same run. We see a nearly uniform lateral thickness for the mask opening with narrow width and a non-uniform lateral thickness for the mask opening with the wider width. Figure 3.11(b) shows a ridged tail of about 3μm for a mask width of 50μm and a opening width of 11.4μm. The uniformity of the thickness enhancement of the selective deposit depends on the relative values of the migration length of the reactant species in the vapor phase and the width of the mask openings. When the migration length is large compared to the width of the opening in the mask, the thickness enhancement via vapor phase diffusion is uniform. The migration length is determined by the growth conditions and has the same value(estimated between 2-3 μm value) for both cases shown in figure 3.11.

Figure 3.12 compares InP/InP structures for two concentrations of the reactant species while the other growth conditions are kept the same. We observe uniform (non-uniform) thickness for lower (higher) concentration. The migration length depends on the growth conditions, such as reactor pressure, growth temperature and the concentration of reactants. It increases for conditions leading to a reduced growth rate. It is possible that reactant species adsorbed on substrate surfaces are more mobile at low growth rates and can move away from the mask edge before reaction and incorporation in the lattice. Therefore, epilayers with better lateral thickness uniformity can be grown with conditions favoring lower

growth rates. Lower growth rate should then be used for wide mask openings.

(a)

(b)

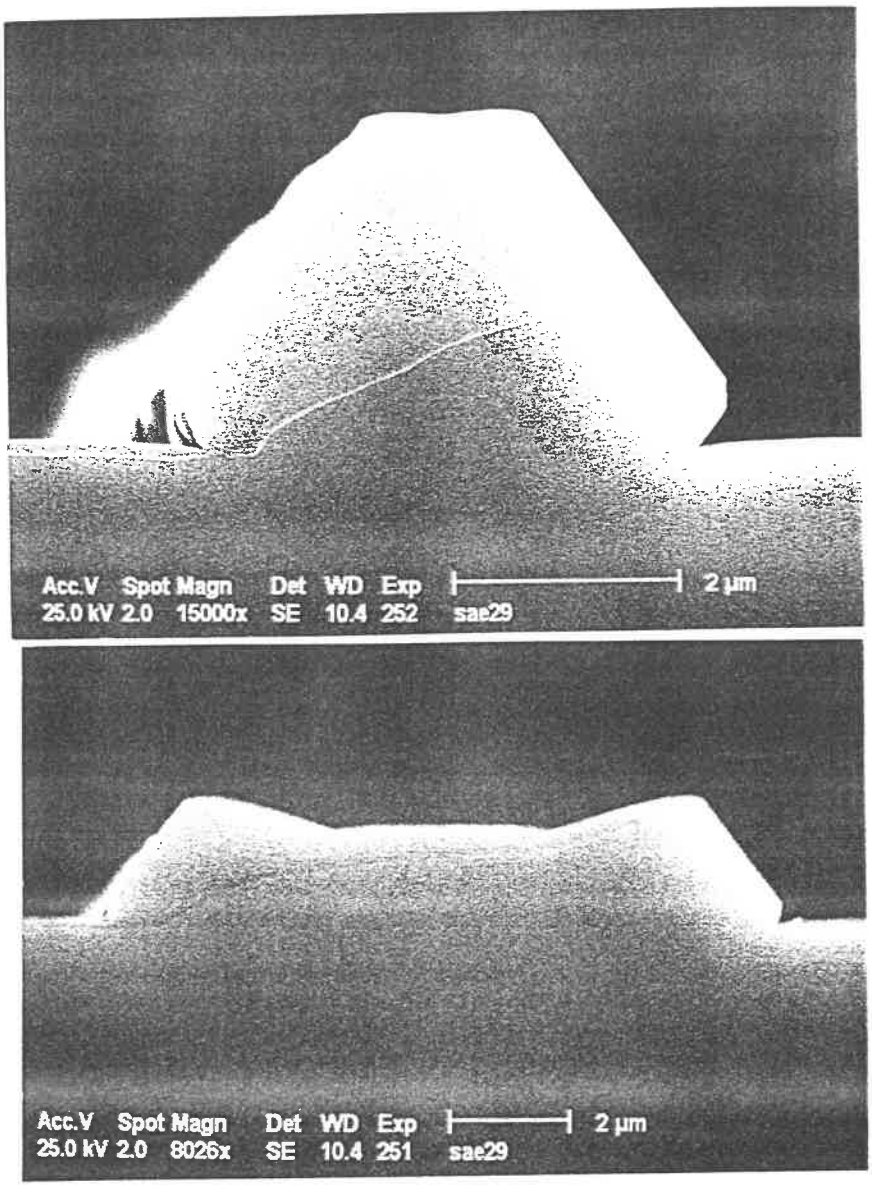
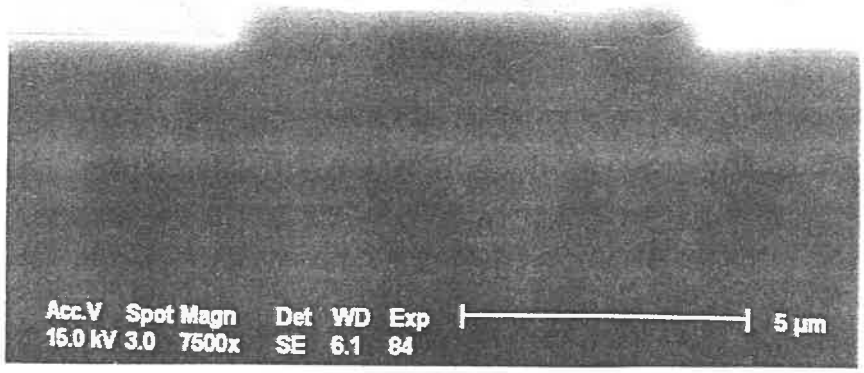


Figure 3.11 SEM pictures of InP/InP structures selectively grown during the same run: (a) narrow width of mask opening and (b) wide width of mask opening.

(a)



(b)

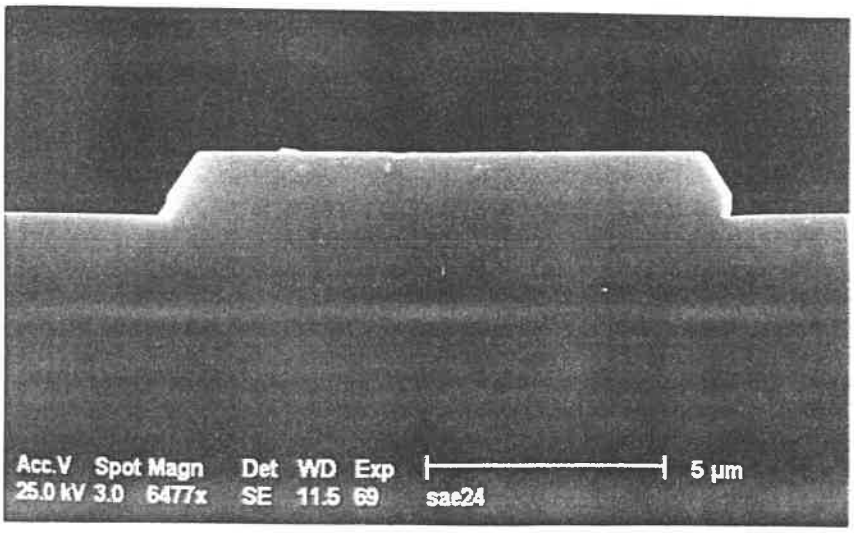


Figure 3.12 SEM pictures of InP/InP structures selectively grown with different concentration of reactant species: (a) TMIn partial pressure slightly lower than for planar growth and (b) TMIn partial pressure optimized for SAE growth.

Migration length also increases with increasing growth temperature and decreasing reactor pressure. Therefore, higher growth temperature and lower reactor pressure also favor better uniformity. However, the thickness at the edges of the mask openings is also influenced by the surface diffusion from the mask and from the surface of the facets formed at the edges of the deposit [10,34]. The control of the lateral thickness profile, therefore, can be difficult.

3.3.3 Compositional Effects in Selective Area Growth of InGaAs

For the selective area growth of InGaAs, selectivity and growth rate enhancement present similar problems as those observed in InP homostructure growth. There are, in addition, problems with the lattice mismatch between InGaAs and InP. The lattice constant of InGaAs is determined by the ratio of the In/Ga composition. Therefore, precise control of the composition and homogeneity across the epilayer is important.

To compare the composition deviation between SAE and planar epitaxy, the parameters corresponding to the lattice matching conditions for unpatterned substrates are used to grow films on both unpatterned and patterned substrates in the same run. EDX and HRXRD measurements for these two samples show an In concentration incorporation enhancement

effect in SAE, compared to the growth on unpatterned substrates. Bhat [10] suggested that in the case of SAE, TMIn decomposes into dimethylindium and methylindium in proportions different from that occurring above planar substrates and thus give rise to In rich layers, as these species have higher vapor phase diffusion rate than TMGa. Figure 3.13 shows the indium concentration in solid InGaAs, measured by EDX for a 6 μm width of mesa top, as a function of In fraction in the vapor phase. Here we see that, like planar MOVPE growth, In content in solid

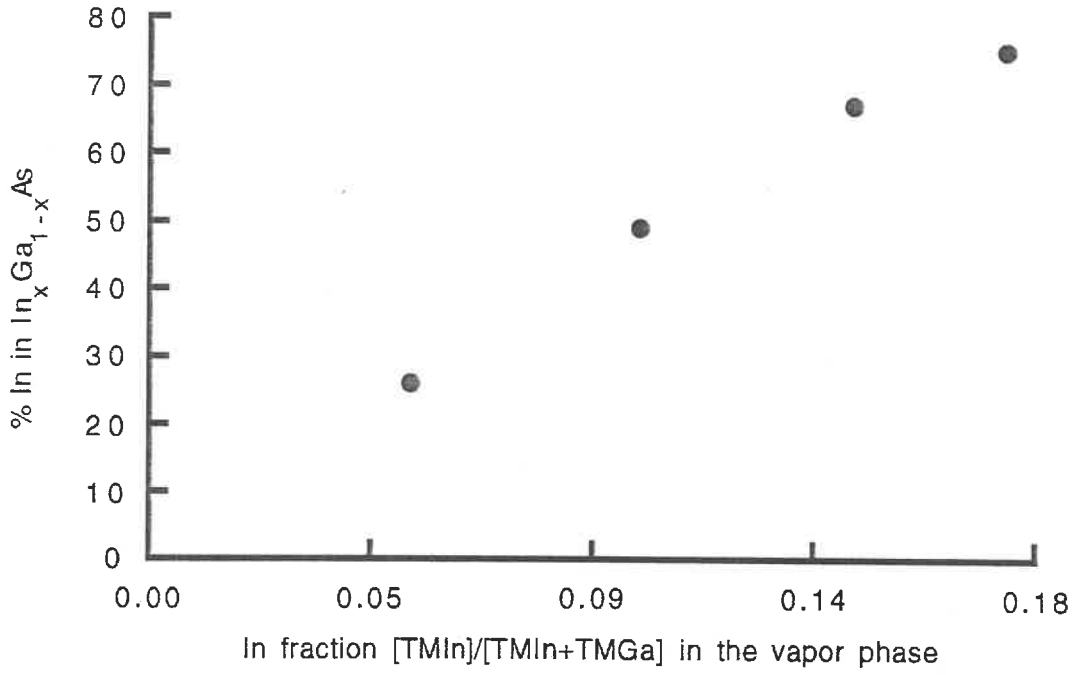


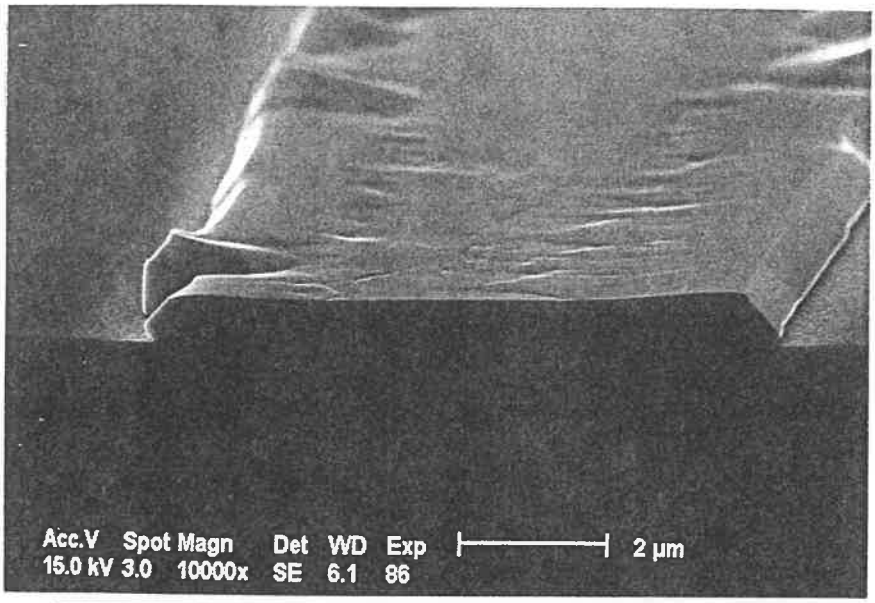
Figure 3.13 Solid In concentration x, of selectively grown $In_xGa_{1-x}As$ epilayers, versus the vapor composition [TMIn]/[TMIn+TMGa] for 6 μm width of mesa top and [110] mask stripe orientation. Error bars are ±3% of the measured values.

InGaAs is linearly determined by the ratio of the partial pressure of TMIn to the sum of partial pressures of TMIn and TMGa in the vapor phase. The segregation coefficient is 5, which is higher than that in planar growth since there is an enhancement of the In concentration incorporation in SAE. We should mention that this curve only corresponds to 6μm wide pattern and optimized growth conditions were used. Our results using TBAs also show an enhancement of the In concentration incorporation with the decrease in the width of openings in agreement with previous studies using AsH_3 [2,10,21]. These results indicate that the selective area MOVPE growth of InGaAs lattice matched to InP can be achieved with adjustment of the growth conditions with respect to masked substrates containing structures of a single size. The growth conditions therefore need to be adjusted for each width. To guarantee full control, mask width with openings of one fixed size should be deposited in a single epitaxial step.

3.4 Optimization of InP/InP Growth

Based on the discussion presented in section 3.2 and 3.3.2, we see that it is necessary to increase the growth temperature and decrease the partial pressures of TMIn and PH_3 in order to optimize the growth conditions for SAE of InP/InP homostructures. Figure 3.14 shows the SEM photographs of InP/InP homostructures selectively grown at two (a) different partial pressures of TMIn while the growth temperature, reactor

(a)



(b)

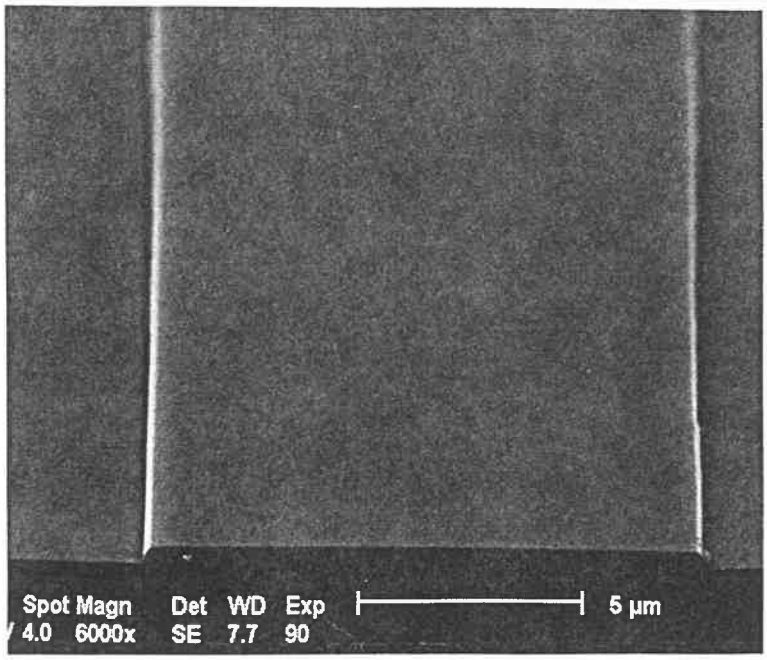


Figure 3.14 SEM pictures of InP/InP homostructures selectively grown at two different partial pressures of TMIn: (a) 1.03x 10^{-3} Torr and (b) 6.01x10^{-4}Torr.

pressure and the concentration of PH_3 are the same. Figure 3.14(a) shows a high partial pressure of TMIn while (b) shows a lower partial pressure of TMIn. We see that it is possible to obtain perfect selectivity as in figure 3.14(a) with a moderate growth rate. Yet, in order to obtain good epilayer quality as in figure 3.14(b), a lower growth rate is required. Here we also see, by comparing the surface morphologies of figures 3.1(a) and 3.14(b), that perfect selectivity and good surface morphology have been obtained after increasing the growth temperature and reducing the input gas concentration of reactant species. Figure 3.15 presents the SEM picture of InP/InP structures selectively grown with the optimized growth conditions for patterned substrates showing an excellent surface morphology. The optimized growth conditions are summarized in Table 1.

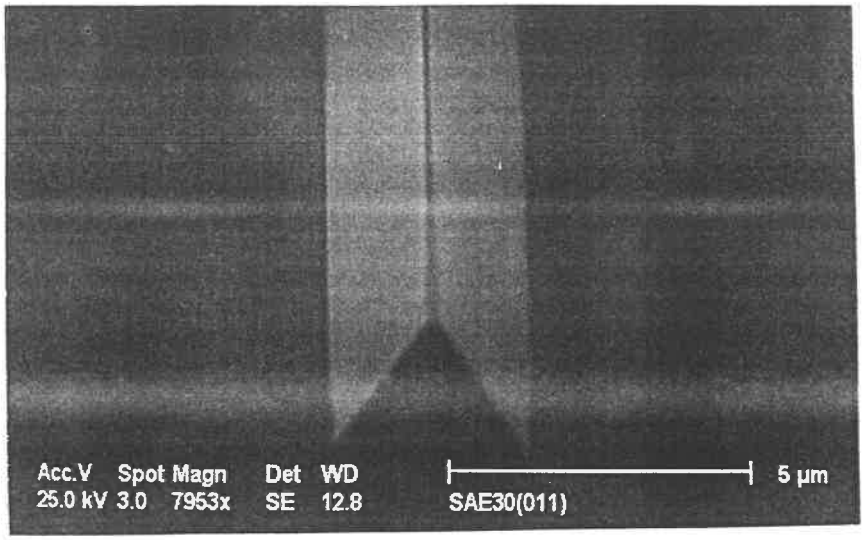


Figure 3.15 SEM picture of InP/InP structures selectively grown with the optimized growth conditions for patterned substrates(see Table 1).

3.5 Optimization of InGaAs/InP Growth Using TBAs

Based on the discussion presented in part 3.3.3, in order to obtain lattice matching of the selectively grown InGaAs/InP structures, the ratio of the partial pressure of TMIn to the partial pressure of TMGa has to be reduced. Figure 3.13 shows that nearly lattice matched growth can be achieved when the ratio of TMIn partial pressure to the sum of the partial pressures of TMIn and TMGa in the vapor phase is around 0.103. This is strictly true only for our mask pattern.

The enhancement of the growth rate also has to be considered in order to obtain high quality epilayers. Figure 3.16 shows the optical microscope photographys of three samples for different partial pressures of TMIn and TMGa in the vapor phase. These three samples were grown with the same growth conditions except for the difference in the partial pressures of TMIn and TMGa. Note that the ratio of the partial pressures of TMIn to TMGa in the vapor phase is kept approximately constant. Growth temperature is 640°C and reactor pressure is 40 Torr. The surface morphology is clearly improved as we decrease the partial pressures of TMIn and TMGa in the vapor phase. Table 2 gives the full width at half maximum (FWHM) and peak energy of the low temperature (7.4K) photoluminescence (PL) for these three samples. Here we observe that the FWHM becomes narrower when decreasing the partial pressures of TMIn and TMGa in the vapor phase.

(a)

(b)

(c)

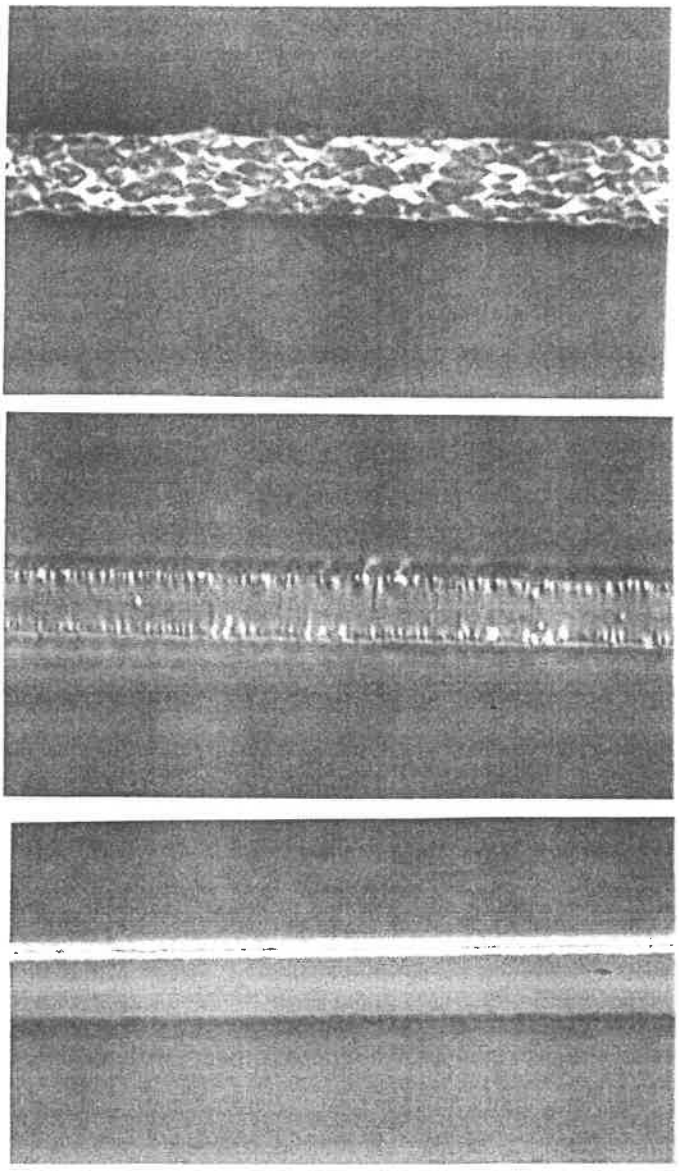


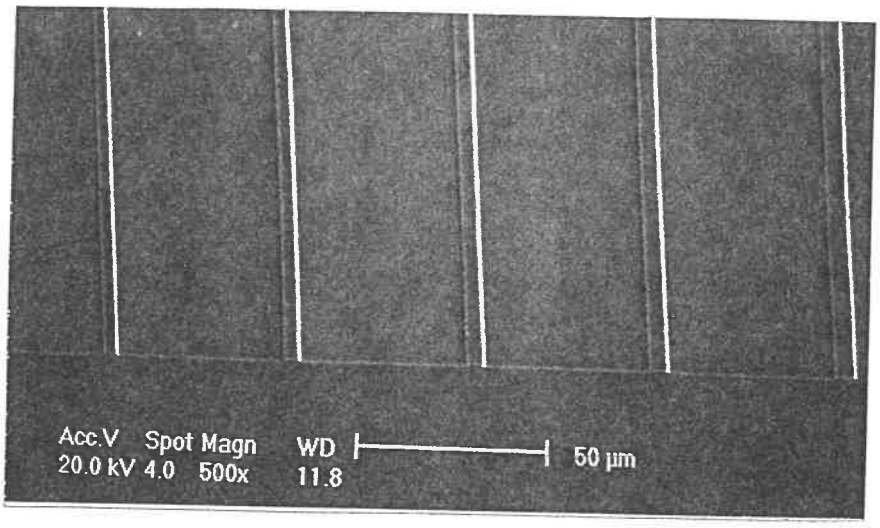
Figure 3.16 1000 optical microscope photographys of InGaAs/InP structures for different input partial pressures (In Torr) of TMIn and TMGa:
(a) 3.59×10^{-4} (TMIn) and 2.63×10^{-3} (TMGa), (b) 2.61×10^{-4} (TMIn) and 1.91×10^{-3}, and (c) 1.96×10^{-4} (TMIn) and 1.46×10^{-3} (TMGa).

It is thus clear that both the surface morphology and the optical property of the epilayers can be improved by decreasing the input gas concentration of TMIn and TMGa, compared to the growth over unpatterned substrates.

Table 2. 7.4K photoluminescence FWHM and peak energy

Partial pressures of TMIn (10^{-4}Torr)	TMGa (10^{-3}Torr)	Peak Energy (eV)	FWHM (meV)
3.59	2.63	0.8	85
2.61	1.91	0.81	18
1.96	1.46	0.803	10

Figure 3.17 presents the SEM pictures of an InGaAs/InP epilayer selectively grown on InP with growth conditions optimized for patterned substrates summized in Table 1. Good surface morphology and perfect selectivity are observed.



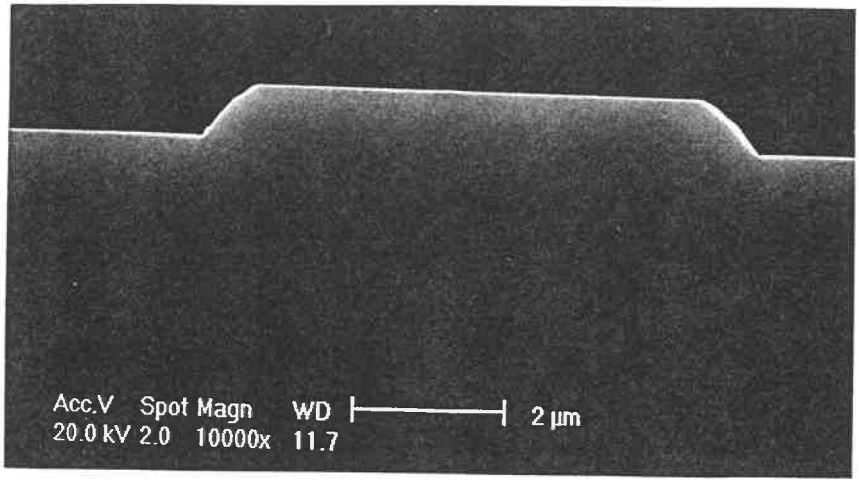


Figure 3.17 SEM pictures of InGaAs/InP heterostructures selectively grown on InP with growth conditions optimized for patterned substrates.

The composition of an InGaAs epilayer can be determined by measuring the photoluminescence peak energy since this is dependent on the epilayer composition. In turn, the InGaAs composition determines both the bandgap and the degree of lattice mismatch to the InP substrates. The low temperature photoluminescence (7.4K) of InGaAs/InP heterostructures grown with optimized growth conditions for patterned substrates was also measured. The measured InGaAs epilayer includes 19 windows oriented along [110] with 3-12 μm wide openings which an 50 μm apart. The PL measurement gives an average composition of the 19 InGaAs windows because the exciting laser beam area is about 2 mm. Figure 3.18 shows the 7.4 K PL spectrum which has a peak energy of about 0.803 eV and a FWHM of about 8meV. According to Bassignana et al [35], the 7K PL energy of zero mismatch InGaAs on semi-insulating InP substrates was 0.804 ± 0.002 eV. Therefore, our PL results indicate that the InGaAs epilayer is: (1) lattice matched and (2) of good structural quality. Please note that there is a low intensity peak at lower energy than that of the main peak. Its peak energy is about 0.79 eV. As we mentioned before, there is a difference in composition for different width of mask openings. EDX measurements can determine the composition of each InGaAs window and show that the In content increases when decreasing the width of windows. This lower intensity peak is caused then by deposits on narrower openings, due to the non-uniform composition of the InGaAs epilayer within the whole area of the measurement.

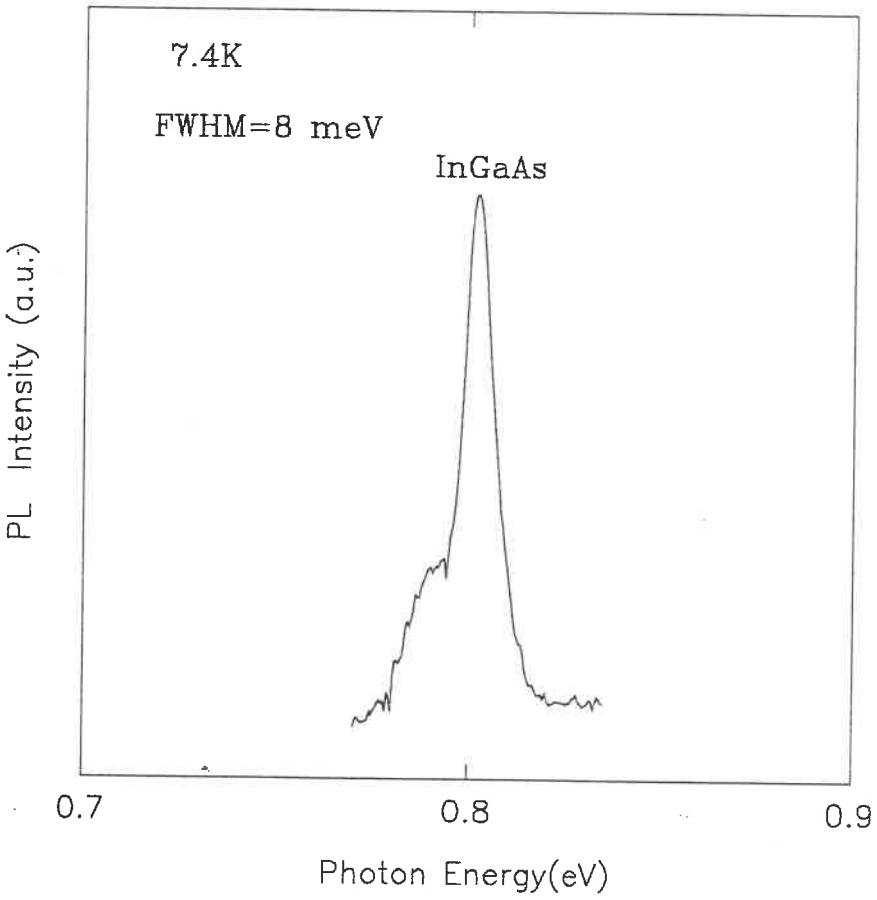


Figure 3.18 Low temperature (7.4K) photoluminescence spectra of InGaAs/InP heterostructures selectively grown at growth conditions optimized for patterned substrates.

CHAPTER 4

CONCLUSIONS AND FUTURE EFFORTS

4.1 Conclusions

Selective area MOVPE using a dielectric layer as mask is an important technique for the electronic, optoelectronic and photonic device fabrication, and for the integration of these devices on a single substrate. Therefore, development of the growth conditions optimized for selective area MOVPE and a better understanding of selective area MOVPE mechanism are vital for future integration of a wide variety of optoelectronic and electronic devices.

In this thesis, SAE of InP and InGaAs/InP structures on InP (001) oriented substrates by low pressure MOVPE through a SiN_X stripe patterned mask using TBAs as an As source have been studied for the first time. The objective is to investigate the difference in growth conditions and growth characteristics observed between SAE and planar MOVPE growth and find the growth conditions optimized for SAE growth with a given mask pattern. The complete SAE process, which includes PECVD of SiN_X, photolithography and wet chemical etching of (001) substrates and low pressure MOVPE growth of InP/InP and InGaAs/InP structures on InP patterned substrate has been developed.

Our experimental results show that the selectivity can be easily obtained in LPMOVPE and that there is no influence of the SiN_X thickness on the selectivity as perfect selectivity is obtained for different thicknesses, ranging from 40 to 200nm.

The SAE of InP/InP and InGaAs/InP structures on InP (001) substrates by low pressure MOVPE through SiN_X stripe patterned mask was compared to planar growth of the same materials in order to optimize SAE. Our experimental results show that the growth conditions optimized for patterned and unpatterned substrates are different, and that the growth conditions optimized for patterned substrates will probably have to be changed as the mask geometry is changed. An enhancement of growth rate for InP and InGaAs materials was observed in SAE, compared to the growth on unpatterned substrates and this enhancement increases with the decrease in the base width of the mask openings. A faster growth rate in SAE under growth conditions optimized for planar growth leads to the poor quality of the SAE epilayers. Therefore, the growth rate must be decreased in order to improve the epilayer quality. The growth mechanism of selective area MOVPE for our used mask pattern and growth parameters is still mass transport limited in the [001] orientation. Hence, the growth rate can be decreased by decreasing the partial pressure of group III elements. Our results clearly reveal that the growth conditions favoring SAE are lower input gas concentration of the group III species, compared with the growth on unpatterned substrates.

The input gas concentration of group III elements in the vapor phase had to be reduced simultaneously in order to guarantee selectivity and epilayer quality.

For the InGaAs/InP heterostructures, an In enrichment is found in SAE, compared to the growth on unpatterned substrates. A dependence of the composition on the mask geometry for SAE of InGaAs is also found. The In content increases with decreasing width of mask openings. Therefore, for practical applications the growth parameters of selective area MOVPE for InGaAs lattice matched to InP have to be adapted to the mask pattern. InGaAs layers lattice matched to InP can be obtained by precisely controlling the ratio of TMIn to TMGa partial pressure in the vapor phase for a given mask geometry.

The presence of a non-growing dielectric layer leads to non-uniformly lateral thickness across the growth areas. The uniformity of the lateral thickness depends on the width of mask openings and the migration length of element III species which is determined by the growth conditions. The use of a lower growth rate favors better lateral thickness uniformity.

Due to the difference in growth rates for different families of crystallographic planes, facets such as the {111} A, {111} B, {110} and {100} can be developed in our selectively grown structures, Which facet

are actually observed depends on the relative mask stripe orientation studied because the orthogonal [$\bar{1}$10] and [110] directions are not equivalent in the zincblende structure.

Contrary to what was observed with AsH_3, our results clearly show non-zero InGaAs growth on {111} planes using TBAs. Therefore the ability to control lateral dimensions to achieve InGaAs buried quantum wires, as proposed in the literature, is in question using TBAs as a As source.

4.2 Future Efforts

Although considerable progress has been made in being able to get good selectivity and in the understanding of the process since the first attempts at selective area epitaxy by MOVPE in 1971, the selective area epitaxy of ternary and quaternary alloys sets considerable challenges due to a large compositional deviation, non-uniformity of the lateral thickness profiles and formation of facets at the edges. As we have mentioned before, one of the most important applications of selective area epitaxy is the integration of a wide variety of optoelectronic devices. The performance of these integrated devices is poorer than that of the individual components. Therefore, the performance and the level of integration have to greatly increase to justify integration using selective area epitaxy. In order to make further progress, such as the fabrication of

quantum wire and quantum dot lasers, and to make large scale optoelectronic integration by selective area epitaxy a reality, a better understandings of the MOVPE process itself and the selective growth mechanisms are essential. We will, in the following, give some suggestions for further efforts in this direction:

1. Growth of quantum wires and quantum dots.

The elimination of InGaAs growth on the {111} planes is the key problem to grow quantum wires and quantum dots using TBAs. What are the reasons leading to growth of InGaAs on the {111} planes using TBAs? Can we eliminate this growth by adjusting the growth conditions?

2. Control of lateral thickness uniformity of epilayers.

Can we improve the lateral thickness of epilayers by reducing the reactor pressure?

3. Control of the shape of the epilayer.

We have observed the effect of mask stripe orientation, but the effect of the V/III ratio in the vapor phase and other growth parameters on the shape of the grown structure has not yet been studied.

REFERENCES

[1]. T. NISHIDA, H. SUGIURA AND T. TAMAMURA, "InGaAs/InP quantum wire selectively grown by chemical beam epitaxy", J. Crystal Growth 132(1993), pp.91-98.

[2]. O. KAYSER," Selective growth of InP/InGaAs in LP-MOVPE and MOMBE/CBE", J. Crystal Growth 107(1991), pp.989-998.

[3]. G.B. STRINGFELLOW, "Organometallic Vapor Phase Epitaxy: Theory and Practice", (Academic Press, New York, 1989).

[4]. E. KAPON, "Quamtum wire laser", Proc. IEEE 80(1992), pp.398-410.

[5]. E. KAPON, C.P. YUN, D.M. HWANG, M.C. TAMARGO, J.P. HARBISON AND R. BHAT, " Lateral patterning of semiconductor superlattice heterostructures by epitaxial growth on nonplanar substrates," Proc.SPIE 994(1988), pp.80-91.

[6]. J. THOMPSON, N. CARR, A.K. WOOD, N. MAUNG, P.J. WILLIAMS, P.M. CHARLES AND A.J. MOSELEY, " Selective area MOVPE growth for device integration", J. Crystal Growth 126(1993), pp317-324.

[7]. T.M. COCKERILL, D.V. FORBES, H. HAN, B.A. TURKOT, J.A. DANTZIG, I.M. ROBERSTSON AND J.J. COLEMA, "Wavelength tuning in strained layer InGaAs-GaAs-AlGaAs quantum well lasers by selective area MOCVD", J.Electron. Mater. 23(1994), pp.115-119.

[8]. H. KANBER, S.X. BAR, P.E. NORRIS, C. BECKHAM AND M. PACER, " Optimization of selective area growth of GaAs by low pressure MOVPE for monolithic integrated circuits", J. Electron. Mater.23 (1994), pp.159-166.

[9]. D.G. KNIGHT, C.J. MINER, B. WATT, C.M. WU, K. FOX, B. EMMERSTORFER, C. MARITAN AND J. HENNESSY, "Optimization of selective area epitaxy for fabrication of circular grating distributed-Bragg-reflector surface-emitting lasers", J. Crystal Growth128(1993), pp.19-26.

[10]. R. BHAT, " Current status of selective area epitaxy by OMCVD", J. Crystal Growth120(1992), pp.362-368.

[11]. P. RAI-CHOUDHURY AND D.K. SCHRODER, "Selective area growth of GaAs by CVD", J. Electrochem. Soc.118(1971), pp.107-110.

[12] J.P DUCHEMIN, M. BONNET, F. KOELSCH AND D. HUYGHE, " Selective area growth of GaAlAs/GaAs by VPE", J. Crystal Growth45 (1978), pp. 81-84.

[13]. S. ANDO AND T. FUKUI," Facet growth of AlGaAs on GaAs with SiO_2 gratings by MOCVD and application to quantum well wire", J. Crystal Growth 98(1989), pp.646-652.

[14]. S. Tsukamoto, Y. Nagamune, M. Nishiioka and Y. Arakowa, "Fabrication of GaAs quantum wires on epitaxially grown V grooves by metal-organic chemical vapor deposition", J.Appl.Phys. 71(1992), pp.533-535.

[15]. C. TASI, J.A. LEBENS, C.C. AHN, A. NOUHI AND K.J. VAHALA, "Facet modulation selective epitaxy-a technique for quantum-well wire doublet fabrication", Appl. Phys. Lett. 60(1992), pp240-242.

[16]. R. NOTZEL, L. DAWERITZ AND K. PLOOG, " Surface structure of high- and low-index GaAs surfaces: direct formation of quantum dot and quantum wire structures", J.Grystal Growth 127(1993), pp.858-862.

[17]. A. CATANA, R.F. BROOM, R. GERMANN AND P. ROENTGEN," Regrowth of InP by MOVPE on dry-etched

heterostructures of InP-GaInAsP", J.Crystal Growth 129(1993), pp.779-782.

[18]. R. MATZ, H. HEINECKE, B. BAUR, R. PRIMIG AND C. CREME, "Facet growth in selective area epitaxy of InP by MOMBE", J. Crystal Growth 127(1993), pp.230-236.

[19]. H. SUGIURA, T. NISHIDA, R. IGA, T. YAMADA AND T. TAMAMURA, "Facet growth of InP/InGaAs by chemical beam epitaxy", J. Crystal Growth 121(1992), pp. 579-586.

[20]. O. KAYSER, P. OPITZ, R. WESTPHALEN, U. NIGGEBRUGGE, K. SCHNEIDER AND P. BALK, "Selective embedded growth of InGaAs by low pressure MOVPE", J. Crystal Growth 107(1991), pp. 141-146.

[21]. E.J. THRUSH, M.A. GIBBON, J.P. STAGG, C.G. CURETON AND C.J. JONES, "Selective and non-planar epitaxy of InP, InGaAs and GaInAsP using LP-MOCVD", J. Grystal Growth124(1992), pp. 249-256.

[22]. T. ARAKAWA, S. TSUKAMOTO, Y. NAGAMUNE, M. NIAHIOKA, JIN-HEE LEE AND Y. ARAKAWA, " Fabrication of InGaAs strained quantum wire structures using selective area MOVPE", Jpn. J.Appl.Phys.32(1993), pp. L 1377-1379.

[23]. M. MAASSEN, O. KAYSER, R. WESTPHALEN, J. FINDERS, F.E.G. GUIMARAES, J. GEURTS AND P. BALK, "Localized deposition of GaAs/GaInP heterostructures using LP-MOVPE", J. of Electron. Mater.21 (1992), pp.257-263.

[24]. Y.D. GALEUCHET, P. ROENTGEN AND V. GREAF, "Metal organic vapor phase epitaxy on patterned substrates for the fabrication of In situ buried GaInAs/InP nanostructures", J.Appl. Phys. 68(1990), pp.560-568.

[25]. S. K. GHANDHI, " Semiconductor power devices", (A Wiley - Interscience Publication, 1977).

[26]. CHETLUR S. SUNDARARAMAN, " Self-aligned insulated gate FET technology for InP: an interface engineering approach", PhD Thesis, Ecole Polytechnoque de Montreal, May,1993.

[27]. M.M. HASHEMI, J.B. SHEALY, S.P. DENBAARS AND U.K. MISHRA, " High-speed P GaInGAs-n InP heterojunction JFET's grown by MOCVD", IEEE Electron Device Lett.15(1993), pp.60-62.

[28]. L.M. LUNARDI, S. CHANDRASEKHAR AND R.A. HAMM, "High-speed, high-current-gain P-n-p InP/InGaAs heterojunction bipolar transistors", IEEE Electron Device Lett.14(1993), pp19-21.

[29]. HIN-FAI CHAU AND E.A. BEAM, "High-speed InP/InGaAs heterojunction bipolar transistors", IEEE Electron Device Lett.14(1993), pp388-340.

[30]. R. BHAT, E. KAPON, J. WERNER, D.M. HWANG, N.G. STOFFEL AND M.A. KOZA, "Organic metal chemical vapor deposition of InP/InGaAsP on nonplanar InP substrates: application to multiple quantum well lasers", Appl.Phys. Lett.56(1990), pp.864-865.

[31]. S. SIMHONG, E. KAPON, E. COLAS, R. BHAT, N.G. STOFFEL AND D.M. HWANG, "Double quantum wire GaAs/AlGaAs diode lasers grown by MOVPE on grooved substrates", Phot. Tech. Lett.2(1990), pp305-306.

[32]. R. BHAT, E. KAPON, D.M. HWANG, M.A. KOZA AND C.P. YUN, "Patterned quantum well heterostructures grown by MOCVD on non-planar substrates: applications to extremely narrow SQW laser", J. Crystal Growth93(1988), pp.850-856.

[33]. Y.D. GALEUCHET, P. ROENTGEN AND V. GRAF, " Buried GaInAs/InP layers grown on nonplanar substrates by one-step low pressure metalorganic vapor phase epitaxy", Appl. Phys. Lett.53(1988), pp. 2638-2640.

[34]. K. YAMAGUCHI AND K. OKAMOTO, " Lateral supply mechanisms in selective MOCVD", Jpn.J.Appl.Phys.32(1993), pp.1523-1527.

[35]. I.C. BASSIGNANA, C.J. MINER AND N. PUETZ, "Photoluminescence and double-crystal x-ray study of InGaAs/InP: effect of mismatch strain on band gap" J.Appl. Phys.65(1989), pp.4299-4305.

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