METALORGANIC VAPOUR PHASE EPITAXY FOR ADVANCED III-V DEVICES

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ABSTRACT

Metalorganic vapour phase epitaxy (MOVPE) has proven to be a successful method for growth of structures for advanced optoelectronic semiconductor devices in III-V compounds. This thesis deals with technological and process related aspects of MOVPE from an experimental perspective. Special attention is given to three main questions: uniformity over large areas, p-type dopant diffusion and redistribution in structures for heterostructure bipolar transistors, and planar embedding of high mesas for buried heterostructure lasers.

A uniformity within a few per cents for thickness, alloy composition, and dopant incorporation over large areas is fundamental for growth of advanced device structures. We present a new horizontal reactor with a large width-to-height aspect ratio operating at reduced pressure, and with a rotating susceptor for single wafers with a diameter of up to 75 mm. The obtained uniformity over 40 mm diameter is within \( \pm 1 \% \) for thickness, composition and doping, and within \( \pm 1 \) nm for the wavelength of quaternary InGaAsP at \( \lambda = 1560 \) nm. The doping distribution has been used to estimate the temperature gradient over the wafer to a few tenths of a degree, and the uniformity is most probably limited by gas phase diffusion and depletion of the reactants.

Abrupt doping profiles are important for some devices. An example is the high frequency performance of the n-p-n heterostructure bipolar transistor (HBT), which is improved by a very narrow and highly doped p-type base. We have compared Zn and Mg for this application. The memory effect of Mg in the reactor gives doping tails towards the surface, but with Zn we obtained an abruptness of three decades over 60 nm at a maximum doping level exceeding \( 2 \times 10^{19} \) cm\(^{-3} \). However, a highly n-doped layer of AlGaAs adjacent to the Zn-doped region gives rise to a significant re-distribution of Zn into the AlGaAs layer. At a reduced growth temperature this effect is diminished and the maximum doping level is simultaneously increased.

Growth on partly masked and non-planar substrates has become an important field for realisation of devices designed in three dimensions. We have focused on planar regrowth of semi-insulating InP around high mesas of buried heterostructure lasers. Unwanted growth over the masked mesa top usually occurs. These depositions are reduced at high growth temperatures and for growth around low mesas (< 2 \( \mu \)m). Addition of CCl\(_4\) in the MOVPE process considerably improves the morphology, especially for growth around high mesas. When chlorine is provided to the growing surface nucleation is prevented on the phosphorus-faced \( \{111\}B \) lattice planes and the mask, and this effect permits reproducible planar regrowth not limited by the mesa height.

Descriptors.- Metalorganic vapour phase epitaxy (MOVPE), III-V compound semiconductors, epitaxial uniformity, p-type doping profiles, epitaxial regrowth, chlorine-MOVPE, buried heterostructure laser, heterostructure bipolar transistor.
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IL S'AGIT TOUT SIMPLEMENT DE TENER UNE PSYCHANALYSE DES CHOSES.

Jean-Paul Sartre: "L'être et le neant", 1943.

IN DER AUFFÄLLIGKEIT, AUFDRINGLICHKEIT UND AUFSASSIGKEIT GEHT DAS ZUHANDENE IN GEWISSE WEISE SEINER ZUHANDENHEIT VERLUSTIG. DIESE IST ABER SELBST IM UMGANG MIT DEM ZUHANDENEN, OBZWAR UNTHEMatisch, verstanden. SIE VERSCHWINDET NICHT EINFACH, SONDERN IN DER AUFFÄLLIGKEIT DES UNVERWENDBAREN VERABSCHEIET SIE SICH GLEICHSAM. ZUHANDENHEIT ZIEGT SICH NOCH EINMAL, UND GERADE HIERBEI ZIEGT SICH AUCH DIE WELTMÄSSIGKEIT DES ZUHANDENEN.

Martin Heidegger: "Sein und Zeit", 1927.

VI SKRIVER STIGARNAS, OCH STIGARNA BLIR KVAR, OCH STIGARNÄR KLOKARE ÅN VI, OCH VET ALLT DET VI VILLE VETA.

Lars Gustafsson: "Ballad om stigarna i Västmanland", 1980.
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Preface

In the late summer of 1987 I had ended my theoretical studies at KTH (Royal Institute of Technology), and started my employment at IM (Swedish Institute of Microelectronics), where I should work with materials for optoelectronic devices. The first day at my new work my colleagues taught me how to replace a broken hydrogen purifier in an MOVPE equipment and how to handle the helium leak detector. Quite soon I realised that the German existentialist philosopher Prof. Martin Heidegger was right when he said that you discover the world when your tools fail to work as expected. This was the way I learnt how to practise the art of MOVPE and the necessary methods for materials characterisation under perfect supervision of Michael Rask and with good help and encouragement from Åsa Lundberg.

Our manager and my supervisor of the Ph.D. work, Dr. Gunnar Landgren, always has many more or less realistic ideas but most of them have become realised sooner or later. The first two device projects I was involved in relied on very demanding structures, and they both became successful when I had left them, and Zoltan Paska, who usually finds the correct theory to solve most practical problems, became responsible for the epitaxy. One device was a quantum well IR detector, with Dr. Jan Andersson as project leader. He has always been ready to discuss most problems in chemistry, quantum mechanics and philosophy. The other device was the heterojunction bipolar transistor, a project led by Bo Willén, who has willingly explained the difficulties in device physics, process technology and house construction. For both these device projects Urban Westergren made extensive simulation work and for the transistor project Peter Ojala and Wim van Berlo evaluated the diffusion constant and revealed the diffusion mechanism for the highly diffusive p-type dopants in the structures. Margareta Linnarsson at KTH made the SIMS measurements for this project and others, and her wide experience from and interest in growth of III-V materials have made the collaboration easy.

After some years I got the opportunity to improve an MOVPE system and to start it. After a year most components had been regarded useless (from the reactor chamber to thermostats, valves and computer program), and they were modified or changed. My existentialist approach seemed to be successful and after this year I had learnt nearly everything about the function of an MOVPE system. Of course this work had been impossible if not Gunnar Andersson had made a lot of fundamental design and assembly work, e.g. the considerably improved reactor chamber and modifications of the gas system. His ability to identify the problem and repair most things that fail to work has also been invaluable, as well as his engagement in the safety arrangements in the laboratories. The access to the skilled personnel in the IM work-
shop, Nils-Erik Ahlstrand, Lars Engström, Glenn Gustafsson and Hans-Olof Larding, has also been of great importance for this project.

Finally this MOVPE system worked, and got the name MOVITZ. The control of planar layers and primarily the uniformity proved to be as good as expected and the next challenge was to also control three dimensional growth on non-planar substrates. Here Jan Borglind made important contributions in crystal growth and characterisation. His skill in scanning electron microscopy, and especially the preparation of our very demanding samples, has resulted in several astonishing micrographs. Dan Haga and Janos André did provide us with a lot of dry etched mesas for regrowth experiments and Olle Kjebon processed some excellent lasers. The discussions with Dr. Sebastian Lourdudoss about the chemical reactions gave us some understanding of the growth mechanisms and his suggestions to improve the growth morphology by introducing chlorine solved many problems.

The discussions with Johan Wallin and Dr. Klaus Streubel, whom both have a deep experience of a commercial MOVPE system and personal computers have been fruitful. It is obvious that also commercial systems give an opportunity to approach the world by the way M. Heidegger proposed.

The efforts made by these people have been invaluable for the results I will present here, and I wish to thank them specially. I also wish to thank the president of IM Prof. Peter Weissglass, and the manager of the optoelectronic department Dr. Kjell Björkqvist, who accepted me as an employee and created the economical prerequisites for my Ph.D. work. However, thanks are due to all persons working at IM, and specially those at the optoelectronic department, who have contributed to the atmosphere and large amount of collected knowledge, which made this work possible.

Finally I wish to thank Prof. Sture Petersson at KTH, who accepted me as a Ph.D. student and partly financed my studies.


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LIST OF PAPERS

The following papers are included in the thesis. They can be organised according to three main scientific questions. First, in paper A a new reactor design for improved layer uniformity is presented. Second, paper B treats p-type dopant diffusion and in paper C the results are applied to a heterojunction bipolar transistor. Third, regrowth for buried heterostructure lasers, i.e. embedding of laser mesas with semi-insulating material is studied in papers D - F and a laser prepared by this technique is presented in paper G. The papers are treated as references A - G in the thesis.


**INTRODUCTION**

Semiconducting III-V compounds, composed by elements from the group III and V columns in the periodic table, have during the last decades proven to be successful as materials for advanced electronic and optoelectronic devices, mainly due to their direct bandgap and high electron mobility. Most of them crystallise in the cubic zinc-blende lattice and generally allow a wide range of alloying. The possibility to grow epitaxially lattice matched layers of different compositions and hence different bandgaps opens the possibility for "bandgap engineering". This is the basis for three important device families, i.e. the semiconductor laser\(^1\), the heterostructure bipolar transistor (HBT)\(^2\) and the high electron mobility transistor (HEMT)\(^3\), but also for many other devices, e.g. optical modulators, detectors and solar cells.

The most extensively studied compound is Al\(_x\)Ga\(_{1-x}\)As, which happens to be lattice matched to GaAs for all Al contents \(x\) and can hence easily be grown on GaAs substrates without introducing lattice misfit dislocations. In\(_{1-x}\)Ga\(_x\)As\(_y\)P\(_{1-y}\) compounds grown on InP substrates are suitable for light emitting devices in the 1.0 - 1.7 \(\mu\)m wavelength range used for fibre optical communication. This wide bandgap range for lattice matched material is obtained by simultaneously changing the Ga content \(x\) and the As content \(y\) in a controlled manner. Other combinations of III-V compounds in use are e.g. In\(_{1-x,y}\)Ga\(_x\)Al\(_y\)As on InP, primarily for electronic devices and In\(_{1-x}\)Ga\(_x\)As\(_y\)P\(_{1-y}\) on GaAs for light emitting devices with wavelengths shorter than 1 \(\mu\)m. Sb containing semiconductors are suitable, e.g. for long wavelength (about 5 \(\mu\)m) detectors but not as widely used, due to the large lattice misfit to the most common substrates in combination with limited alloying possibilities.

The first successful method in use for growth of III-V crystals was liquid phase epitaxy (LPE)\(^4\), where growth occurs at a crystal - liquid interface from a supersaturated solution near thermodynamical equilibrium. Growth is often restricted to substrate areas smaller than a few square centimetres and it is only with difficulty possible to grow layers thinner than a tenth of a micrometre with this method. Another method for growth at thermodynamical equilibrium is chloride transport vapour phase epitaxy (VPE)\(^5\), where the group III elements are supplied to the substrate as chlorides and the group V elements either as chlorides or as hydrides. This method is also restricted to growth of relatively thick layers and it is difficult to find and maintain the reactor parameters for the near equilibrium growth conditions. Molecular beam epitaxy (MBE)\(^6\), performed by effusion of the elements towards a heated substrate in ultra high vacuum, is suitable for precision growth of very thin layers. Accurate thickness control of single monolayers is possible over large areas. The use of high vacuum based surface characterisation techniques such as reflection high energy electron diffraction (RHEED) makes MBE
attractive for many applications. However, the ultra high vacuum required makes the equipment expensive and the growth of compounds containing high vapour pressure elements (e.g. P) difficult. Nevertheless, some success has been experienced by supplying P as a hydride (i.e. gas source MBE). The epitaxial technology which during the last decade has proven to be the most flexible is metalorganic vapour phase epitaxy (MOVPE), first described by Manasevit and Simpson in 1968. This process has also been named metalorganic chemical vapour deposition (MOCVD) and the acronyms OMVPE and OMCD are also in use. In MOVPE the group III elements are supplied as metalorganic compounds and the group V elements usually as hydrides. Growth occurs at non-equilibrium conditions and the method provides excellent control of doping, thickness and alloy composition over large areas (reactors for several 100 mm diameter wafers are commercially available). Development of computer controlled gas handling systems, new reactor geometries and improved methods for purification of the precursors have provided high quality of the material as well as the structures. The main drawback of the MOVPE technology is the use of highly toxic and pyrophoric precursors, which demands extensive safety arrangements.

This thesis treats the MOVPE process and technology and compares the performance with the requirements set by the design of advanced opto-electronic devices. From general considerations particularly important areas are identified and some are treated in detail in the original research work, which is the basis of the thesis. When the work started in 1987, no commercially available MOVPE systems fulfilled our demands for growth of complex device structures and only rough guidelines for system design were available. Hence we had to improve the designs of reactor, gas delivery system and chemical reactions. The three specific subjects that were the aim of the efforts were improved layer uniformity, dopant diffusion control (with application to HBTs) and growth on non-planar substrates (primarily for embedding of laser mesas). These items will dominate the account, but in order to give a wide description of the performance of MOVPE, also other fields will be reviewed. While the recent improvements of the technology have been significant, the ultimate limits of the performance might now be set by the epitaxial structure itself and the chemical reactions.

The thesis is organised as follows. First, some important heterostructure devices are described and the main requirements set by the devices on the quality of the semiconductor crystals and epitaxial structures are presented. Next the MOVPE process will be analysed, hence the chemicals, the reactor, and the gas system are the important blocks. Some methods for characterisation of the crystals are also presented. Then the MOVPE process performance is reviewed and compared to the device requirements. Finally some aspects are given on important areas for future development.
HETEROSTRUCTURE DEVICES

The technique to fabricate high quality heterojunctions and multilayer structures give a new dimension to device design. While, in a homostructure the only variation is in doping level and type, the heterostructure also introduces the possibility to choose the bandgap. Hence the energy of the electron and hole carriers could be independently changed through the structure and the carriers will primarily be confined to regions with low bandgap. A quantum well (QW) structure consists of a layer with a thickness of a few nanometres of low bandgap (the well), surrounded by high gap material (the barriers). In the QW there might exist several energy levels, due to quantum mechanical confinement of the electron wave function, determined by the thickness of the well and the bandgap difference between the well and the barriers. A multiple quantum well (MQW) structure or superlattice (SL) consists of several quantum wells with relatively thin barriers in between. The energy levels are extended to subbands with the energies determined by the bandgaps and thicknesses of wells and barriers, and thinner barriers give a stronger coupling between the wells. Heterojunctions, QWs and SLS are the main blocks that combined with different dopings are used to build heterostructure devices.

The semiconductor laser.- A simple structure of a heterostructure laser is a p-n-junction coincident with a bulk active layer of about 0.1 μm thickness with a lower bandgap and a higher refractive index than the surrounding confinement layers. From these, carriers are injected and recombine in the active layer. Hence light is emitted with a wavelength corresponding to the bandgap of the active layer. The optical mode is guided by the high refractive index of the active layer and the cleaved edges of the wafer act as mirrors. In a QW laser the active layer instead consists of a few quantum wells, with the advantage of efficient radiative recombination and low optical losses. Their capability to trap carriers and confine the optical mode is less than the bulk.

![Figure 1. Flat surface buried heterostructure laser.](image-url)
layer and hence they are usually surrounded by a wider confinement layer of an intermediate bandgap.

In order to laterally confine the optical mode it is often necessary, particularly for high performance long wavelength lasers in InP based materials, to let the active layer to form a 1 - 2 \(\mu m\) wide stripe This is made e.g. by etching a stripe mesa through the laser structure followed by epitaxial regrowth, which embeds the mesa with a high bandgap material. Usually a reversed biased p-n-junction is sufficient to avoid leakage currents beside the active layer, but for lasers that are intended to be modulated at frequencies around 10 GHz a semi-insulating layer is necessary in order to reach sufficiently low parasitic capacitance\(^9\) (Fig. 1).

Vertical cavity surface emitting lasers\(^{10}\), which emit light perpendicular to and not parallel with the substrate surface are becoming an interesting candidate for optical interchip communication. These lasers have epitaxially grown dielectric mirrors on one or both sides of the active (QW) layer. The mirror reflectivity has to be extremely high at the emitted wavelength to obtain a gain high enough for lasing at room temperature.

An important parameter for laser characterisation is the threshold current, which is the threshold for stimulated emission, below this point the laser acts as a light emitting diode (LED). A high threshold current indicates high losses, e.g. due to current leakage beside the active region or a significant amount of non radiative recombination.

**The heterostructure bipolar transistor.** - The main advantage of an HBT as compared to the homostructure bipolar transistor is the use of a high bandgap emitter\(^3\). This enables a high injection rate of electrons from the emitter through the base and at the same time blocks the hole current from the base into the emitter (for an n-p-n structure). This is equivalent to a high

![Bandgap diagram](image)

Figure 2. Heterostructure bipolar transistor, epitaxial structure and bandgap diagram.
current gain. The high gap emitter also permits a high base doping, which therefore gives a low base resistance even for a base thinner than 100 nm. A narrow base lowers the base transit time, which together with a low base resistance is important for the high frequency performance. A grading of the bandgap through the heterojunction removes the "barrier spike", which occurs due to band bending at the emitter - base interface. A further bandgap grading through the base increases the electron velocity and hence the high frequency performance, due to a decreased base transit time (Fig. 2). Furthermore, it is important to keep the recombination probability in the base region low, which requires that the electron life time has to be at least an order of magnitude higher than the base transit time.

**The high electron mobility transistor.** The HEMT structure consists of a modulation doped heterojunction, which means that electrons have diffused from an n-doped high bandgap region to an undoped low bandgap region. Due to the band bending they form a "two-dimensional electron gas" close to the heterojunction where they have an extremely high mobility because they are spatially separated from the donor atoms and hence less affected by the Coulomb scattering. Drain and source contacts are usually made by diffusion or ion implantation to the electron gas, which forms the channel in a field effect transistor, while the gate contact is made by metallisation on the high bandgap material. In order to further reduce the influence from the Coulomb scattering a spacer layer of a few nanometres is usually left undoped in the high gap material close to the heterojunction (Fig. 3). The high frequency and current handling parameters of a HEMT are improved by a high transconductance, which in turn depends on e.g. the carrier concentration and mobility in the channel. Another important parameter is the threshold voltage, i.e. the gate voltage for which the channel opens.

![Figure 3. High electron mobility transistor.](image-url)
**Novel multiple quantum well devices.** - The possibility to grow QW structures of high quality have opened the field for entirely new concepts of optoelectronic devices. QWs both confine the electrons and introduce new energy levels, which facilitate design of photonic devices for a wide variety of wavelengths.

By excitation of electrons from the first to the second subband in a QW, infrared (IR) light with wavelengths of about 3 - 10 μm could be absorbed\(^{11}\). The absorbed wavelength depends on the exact QW design. If the second subband is approximately coincident with the conduction band, the excited electrons will increase the conductivity through the structure. This effect has successfully been used in long wavelength IR detectors\(^{12}\). About 50 QWs are needed for high detector efficiency (Fig. 4).

Light could also be absorbed by excitation of electrons from an MQW subband in the valence band to a subband in the conduction band\(^{13}\). When an electric field is applied perpendicular to the MQW layer the effective bandgap in the QWs decreases and the absorption wavelength increases. This effect is called the quantum-confined Stark effect. The intensity of light with a wavelength corresponding to the effective bandgap at applied bias, which propagates perpendicular to the structure, can be modulated with this device.

Electrons easily tunnel through barriers in MQW structures if the barriers are thin enough and the energy levels of the subbands on each side of the barrier are made to coincide by an applied bias\(^{14}\). This effect, known as resonant tunnelling, gives rise to negative differential resistance, which can be used for high frequency devices because of the fast tunnelling process.

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**Figure 4.** Multiple quantum well IR detector. Intersubband excitation is indicated in the band diagram to the right.
DEVICE REQUIREMENTS ON THE CRYSTAL STRUCTURES

From the brief device descriptions above it is evident that fabrication of advanced electronic and optoelectronic devices requires a precise control in each step of the process. This is important in epitaxy as well as in the following steps, e.g. lithography, etching, metallisation and passivation. However, the quality of the epitaxial material and structure usually (but not always) defines the ultimate limits of the device performance.

Uniformity and reproducibility.- The allowed span in device performance and the coupling between device performance and material parameters defines the limits for acceptable variations in doping, growth rate and composition both laterally over the wafer and from one time to another. Close examination of these requirements reveals that they are quite tough. Furthermore, for most advanced structures there are several layers that simultaneously have to fulfill all requirements on exactly the same point of the wafer. This is the main argument for accurate process control and lateral uniformity.

The emitting wavelength of high performance lasers for optical communication and spectroscopic measurements are usually specified within a nanometre, which to some extent might be adjusted in the following process, but the luminescence wavelength is usually not allowed to vary more than about 10 nm. For a laser with a bulk InGaAsP active layer grown lattice matched to an InP substrate this equals a composition variation of about 0.7 % in As/P-ratio or 0.3 % in In/Ga-ratio. In a QW laser a change in the thickness of the well of about 4 % will give the same wavelength shift. For MQW optical modulators the requirements are similar.

In epitaxially grown multilayer dielectric mirrors, the wavelength dependent reflectivity is determined by the thickness and refractive index of the layers (Fig. 5). These mirrors can be designed for specific wavelengths within a wide spectrum and have many applications, e.g. for making Fabry-Perot étalons for optical bistability experiments, and for vertical cavity surface emitting lasers. Usually high reflectivity is demanded for a wavelength determined by an active layer in the structure. For high performance surface emitting lasers this sets the requirements on thickness and composition variations within 1 %.

For HBT structures grown in AlGaAs on GaAs substrates the requirements on the Al content at the emitter - base junction limit the variations in the Al/Ga-ratio to at most 2 % in order to keep both current gain and cut-off frequency within 10 % of their maximum values. The HBT device performance is less sensitive to variations in doping levels and thicknesses but if an etch step is used in the process to reach the extremely thin base in
Figure 5. Simulated and measured reflected intensity as a function of wavelength for an aperiodic multilayer AlGaAs/AlAs mirror designed to obtain a broad reflectivity spectrum. The two curves are laterally displaced.

The SEM micrograph to the left shows a cross section of the epitaxial structure. Contrast is revealed by using a stain etch.

order to form the base contact problems might occur if the thickness uniformity is unsatisfactory.

On the other hand AlGaAs/GaAs HEMT structures are extremely sensitive to variations in doping (1 %), Al content (1 %) and thickness (10 %) in order to control the threshold current within the necessary 10 mV.

For IR absorption at around 10 μm wavelength in an AlGaAs/GaAs MQW structure the absorption wavelength shifts as much as 0.5 μm for a change in Al content with 1 % or in qw width with 0.3 nm.
**Thickness and junction abruptness.**- Beside the variations connected with uniformity and reproducibility it is important to control layer thicknesses in an absolute way. Of course the importance of absolute thickness control increases for thinner structures. In narrow QWs for example, where the typical distance is 1 nm, changes of composition have to be made within one monolayer (0.3 nm) in order to not affect the energy levels in the well. However, the intersubband absorption of IR in 8 nm thick QWs is not considerably shifted for a linear interface grading of some nanometres\textsuperscript{18}. But a rough heterointerface might deteriorate the performance of resonant tunneling structures\textsuperscript{14}, and affects the transconductance in HEMTs by increased alloy scattering.

The transconductance is also sensitive to the thickness of the undoped spacer layer between the highly doped part of the barrier and the HEMT channel\textsuperscript{19}. This sets the requirements both on the dopant distribution and on the heterojunction. A similar problem occurs in the HBT, where current gain and cut-off frequency could be degraded as much as 10\% for only 10 nm diffusion of the base dopant into the high gap emitter, depending on the exact structure\textsuperscript{17}. Furthermore, the base transit time and hence the high frequency performance is closely connected with the total thickness of the base layer, making the requirement on the interface abruptness and dopant distribution strong. From a doping level in the base of about $10^{19}$ cm\textsuperscript{-3} it has to fall below the emitter and collector doping levels of about $10^{17}$ cm\textsuperscript{-3} within ten nanometres and the total thickness of the doped layer has to be less than 100 nm\textsuperscript{C}.

**Doping level control.**- For most structures control of the exact doping level is uncritical within 10 - 50\% (with the exception of e.g. the HEMT structure as mentioned above). A more common problem is encountered when extremely high or low doping levels are required. The thin HBT base has to be doped to well above $10^{19}$ cm\textsuperscript{-3} and preferably to about $10^{20}$ cm\textsuperscript{-3} in order not to give a too large base resistance. High doping levels are also desired in contact layers in all devices to reduce the contact resistance. Low doping levels ($10^{14}$ - $10^{15}$ cm\textsuperscript{-3}) are used in e.g. high power devices\textsuperscript{20} where the breakdown voltage is increased at lower doping\textsuperscript{21} and in p-i-n detector diodes\textsuperscript{22}. In these cases the background doping level in the material, i.e. the amount of unintentionally incorporated dopants, will determine the device performance. A high background doping level also reduces the carrier mobility.

Dopant atoms giving deep levels in the bandgap, which act as traps for electrons and holes, might be introduced in the material in order to make it semi-insulating, e.g. for use in current blocking layers\textsuperscript{23,24}. Deep levels could also function as centres for recombination and are in that case deleterious for most devices.
**Crystal quality.**- Crystal defects in epitaxial material do often deteriorate the device performance, but the relation between defect density and device properties is not always clear. In lasers the dark line defects are associated with dislocations. These defects occur in the active layer as centers for non-radiative recombination, and are believed to cause enhanced device degradation. Dislocations do either emanate from the substrate or are formed during crystal growth, in the latter case often as misfit dislocations due to a too large lattice mismatch between two epitaxial layers or between one layer and the substrate. For InGaAs lattice matched to InP a misfit of between - 800 and 0 ppm at room temperature is acceptable for layer thicknesses up to 2 μm. This corresponds to a variation in Ga/In ratio of about 1 % and in As/P ratio of about 2 %. The problem of misfit dislocations is fundamental for growth of largely mismatched systems, e.g. when GaAs is grown on Si-substrates. For thin layers the strain introduced by misfit can be accommodated elastically, such strain changes the electronic states and could be used for increasing the performance, e.g. in qw-lasers.

Point defects, such as interstitials, vacancies and substitutionals could be electrically active. One example is the EL2 level in GaAs, a deep acceptor that might be due to a Ga vacancy or an As interstitial or antisite defect. They can also enhance dopant diffusion and act as recombination centres.

Large crystallographic defects, e.g. oval defects, consist of a misoriented crystal structure with a diameter up to about ten micrometers. They combine regions of high resistivity electron traps or recombination centres with low resistivity stacking faults and dislocations. Some of them located in an active region will most probably kill the device.

**Non-planar growth.**- Until now growth of planar layers on planar substrates has been discussed. However, an important extension is growth on patterned and etched substrates. This will become even more important as the devices are designed in three dimensions for improved performance and integration, e.g. of both electronic and photonic devices. Regrowth of current blocking layers around laser mesas is one application. Here the main requirements are selectivity (i.e. no growth over the mask) and planarity. The interfaces between the original and regrown material also has to be good in order not to affect the optical mode or to form an electrical shortcut.

Growth of quantum dots or wires might be accomplished by growth in quadratic or stripe openings in a mask when taking the advantage of growth rate differences between the lattice planes. Patterned growth has also been obtained by locally stimulated deposition. Hence irradiation with a laser or electron beam has been used.
THE MOVPE PROCESS

Growth of high quality devices by MOVPE relies on several process parameters such as the choice and amount of chemicals introduced into the reactor, the growth parameters (e.g. gas flow rate, reactor pressure and substrate temperature), the reactor design (which controls gas flow) and the overall design of the gas delivery system. During the history of MOVPE several designs have been tried and now most of the problems are identified and some are solved.

Chemical reactions.- The overall reaction for the most well studied case of MOVPE i.e. growth of GaAs from trimethylgallium, Ga(CH₃)₃, (TMGa) and arsine, AsH₃ is

\[ \text{Ga(CH₃)₃} + \text{AsH₃} \leftrightarrow \text{GaAs} + 3 \text{CH}_₄. \]

Despite its simplicity, little is known about the detailed reaction paths. A serious attempt has been made by Stringfellow\(^{36}\) to review the chemical aspects of MOVPE. As growth occurs far from equilibrium, thermodynamics defines only the outermost limits for the process, while kinetics and mass transport are the restricting parameters.

For growth on the (001) lattice plane at temperatures below 550°C the growth rate is increasing with the temperature because it is limited by decomposition of the reactants. In the temperature region of about 600 - 750°C the growth rate is independent of the temperature and restricted by diffusion of reactants through the gas to the surface. Above 800°C the desorption from the surface becomes important and the growth rate is falling with further rise in temperature\(^{37}\). Other temperature regimes might be valid for growth on other lattice planes. The growth temperature is usually chosen in the diffusion controlled regime, and hence such fundamental properties as growth rate and to some extent alloy composition are determined primarily by mass transport. However, kinetics plays an important role, e.g. in impurity incorporation and growth on non planar substrates.

The reaction paths have been investigated through studies of variations in growth rates\(^{38}\) and compositions\(^{39}\) at different growth conditions, and by mass spectrometry\(^{40}\) and infrared absorption spectrometry\(^{41}\) of reaction products, or by combinations of these methods\(^{42}\). Simultaneous introduction of hydrides and alkyls seems to catalyse decomposition of the precursors, as well as the presence of a III-V surface (e.g. a substrate)\(^{40,41}\). It is also believed that adducts of hydrides and alkyls are formed in the gas phase\(^{38,42}\). The fact that PH₃ decomposes at a higher temperature than AsH₃ results in larger incorporation efficiency of As than of P\(^{39}\). No distinct reports on relative incorporation efficiencies for the group III species exist. In the diffusion
controlled regime they are assumed to be equal, but most probably there are kinetically determined differences.

At the growth temperature the vapour pressure above the III-V surface is significantly higher for the group V elements than for the group III elements. This, and the relatively high decomposition temperature of the hydrides necessitates a higher molar fraction of group V than of group III species in the gas, i.e. a high V/III ratio.

For alkyls with loosely bound hydrocarbon chains it is evident that the homogeneous (gas phase) reactions and the formation of gas phase adducts are important, while for those with strongly bound chains the heterogeneous (surface) reactions are dominant. (Long hydrocarbon chains and heavy metal atoms result in weak bonds.) This affects the incorporation of C into the epitaxial layer, which most probably occurs through a surface reaction where hydrocarbon radicals are strongly adsorbed to group V atoms. Carbon incorporation hence becomes severe when trimethylaluminium (TMAI) is used but insignificant for use of triethylindium (TEIn).

The efficiency of dopant incorporation is dependent on the dopant element, the precursor and the doped material, as shown in the following examples. The most often used n-type dopant is Si, incorporated on a group III site. (As Si belongs to group IV, the type is determined by on which lattice site it is incorporated.) Supplied as SiH₄, which has a relatively high decomposition temperature, the doping efficiency is increased at elevated growth temperatures. It is also found that the incorporation efficiency depends on which lattice plane growth is performed and hence on the surface bond strength. Carbon, another group IV element, acts as p-type dopant in GaAs. CCl₄ is commonly used as C precursor. In InGaAs the C incorporation from CCl₄ decreases as the In content increases and for growth of InP CCl₄ acts as a pure etchant with no C incorporation at all. The most common p-type dopant is Zn, supplied as an alkyl. The Zn doping level decreases for increased susceptor temperatures, due to evaporation of the volatile Zn from the surface. Zn incorporation is also reported to be dependent on crystal orientation, and a model based on the influence of the crystal bonding geometry on the impurity adsorption has been proposed.

Growth on substrates with different orientations, on partly masked areas, or on substrates etched in three dimensional formations give the possibility to study growth behaviour on different lattice planes. It is found that high quality material is most easily grown on the (001) surface, and that nucleation on the group V faced (111)B planes relative to the (001) surface usually is sparse for GaAs, might occur for InGaAs, and is extensive for InP. The deposition rates on different lattice planes are hence sensitive to materials, but also to growth parameters and substrate geometries. The final crystal shape is dependent on the supply of reactants, surface mobility
and reaction probabilities on different lattice planes\cite{52,53,F}. In order to decrease the deposition on masked areas, Cl containing compounds have been added with great success\cite{55,56}. Furthermore, we have shown that Cl addition at InP growth considerably increases the importance of surface kinetics, and hence the growth behaviour on masked and non-planar substrates becomes less related to gas phase and surface diffusion\cite{F}.

Due to the great complexity and the large amount of possible species and reactions only a few computer simulations of MOVPE growth kinetics have been done\cite{57-60}. In the future these tools could be important for prediction of growth rates on different lattice planes and for the choice of proper precursors.

**Choice of chemicals.**- A chemical compound being a suitable precursor for MOVPE has to fulfil certain requirements. Most convenient to handle are gases. Liquids with suitable vapour pressure in the temperature range -10°C to +20°C for pick-up from a bubbler are also easy to use, while liquids with a vapour pressure so low that heating above room temperature is needed also require heated gas lines to avoid re-condensation in the lines. Sublimation of solids often is dependent on the area of the solid in contact with the carrier gas and hence the pick-up tends to depend on the amount consumed. The decomposition temperature should be sufficiently high to avoid prereactions with the other reactants before reaching the susceptor but low enough to allow decomposition at the growth temperature. It is therefore important that the precursors function together. Compounds that easily adsorb in the tubes or at the reactor walls give memory effects and should be avoided. The precursor should be cheap to produce and easy to purify and should not include elements that could deteriorate the crystal quality. If possible it should not be toxic or dangerous to handle. Most precursors used are compromises and none fulfil all these requirements.

The most extensively used group III precursors are the trimethyls (TMAI, TMGa and TMIn), which are relatively cheap to fabricate and to purify and have convenient vapour pressures. However, they are pyrophoric and some problems with material purity (especially TMAI) and supply control (TMIn) do occur. As group V precursors arsine (AsH₃) and phosphine (PH₃) are used. Their main disadvantages are that they are extremely toxic, and that they require relatively high temperature for decomposition.

The Al - C bond in TMAI is relatively strong and AlGaAs grown with TMAI usually contain C in the 10¹⁶ - 10¹⁸ cm⁻³ range, where high Al-contents are accompanied by high C-doping levels\cite{61}. Also TMGa gives some C incorporation in GaAs. The C incorporation has been successfully diminished by using triethyls (TEGa and TEAl) in stead of trimethyls\cite{62}. Hence the weaker C - metal bond facilitates C disengagement but simultaneously the decomposition
temperature is decreased, which results in some prereactions between the metal alkyls and the group V hydrides. Furthermore, the triethylenes have too low vapour pressures for convenient use in MOVPE. Another way to avoid the C-contamination in Al-alloys is the use of novel precursors without the direct Al - C bond. One of them is trimethylamine alane, AlH₃(N(CH₃)₃), which with TEGa gives AlGaAs with considerably reduced C-content⁶₃. With TMGa the C seems still to be incorporated but at reduced concentrations⁶⁴.

Growth of InP using TMIn does not give any deleterious impurity incorporation, but the source is a solid below 88°C. A liquid alternative is TEIn, which has the disadvantage of very low vapour pressure. It also exhibits tendencies to react with AsH₃ and PH₃ forming non-volatile polymers⁶⁵.

In order to find substitutes for the toxic group V hydrides, some different organic group V compounds have been investigated. The boundary condition is that the contamination of the layers shall be low. The main impurity is C from the methyl radicals, and formation of volatile CH₄ requires one H atom per methyl group supplied from the group V precursor (since H₂ used as carrier gas does not participate in the reaction⁶⁶). This disqualifies e.g. trimethylarsine (TMA) for growth of GaAs⁶⁷. The most extensively used alternatives today are tertiarybutylarsine, (CH₃)₃CASH₂, (TBAs) and tertiarybutylphosphine, (CH₃)₃CPH₂, (TBP). At least TBAs is still toxic, and the main advantage is that it is a liquid with a vapour pressure low enough to avoid the hazardous handling of a full gas bottle under high pressure. Both TBAs⁶⁸ and TBP⁶⁹ provide material of reasonable high quality and device performance is comparable to that obtained with AsH₃ and PH₃⁷⁰,⁷¹.

For n-type doping the most common dopant is Si, both for InP- and GaAs-based materials. The precursors used are silane, SiH₄ and disilane Si₂H₆. Silane is fully decomposed at temperatures considerably above those used at normal growth temperatures, which makes the incorporation strongly temperature dependent⁴⁴. However, for disilane the temperature for total decomposition seems to be lower and the incorporation less temperature dependent⁷². Si gives n-type doping up to mid 10¹⁸ cm⁻³ level, and then compensation and formation of precipitates occur. For higher doping levels Sn has been used, with tetraethyltin (TESn) as the precursor⁷₃.

For p-type doping the choice of dopant element and precursor has not been so obvious. From infinite source surface diffusion studies it has been found that Mg and Be are slowly diffusing elements in GaAs, while Zn diffuses fast⁷⁴. Because Be is extremely toxic, the reports on Be doping are rare, but diethylborylum (DEBe) has been used⁷⁵. A typical Mg precursor is bis-(cyclopentadienyl)magnesium, (C₅H₅)₂Mg, (C₅Mg), which has been found to interact with the internal surfaces in the reactor and hence give rise to memory effects, which makes abrupt turn on and turn off difficult⁷⁶,⁷⁷. Diffusion of Zn in epitaxial layers has proven to be smaller than expected⁸,
and Zn is used for materials based on both GaAs\textsuperscript{47,78} and InP\textsuperscript{79}. Both DMZn and DEZn have been used as precursors, where the lower vapour pressure of DEZn makes the doping level more easy to control. In recent years C has proven to be the most suitable dopant in GaAs/AlGaAs with respect to low diffusivity and high doping levels. Different C precursors have been used, e.g. CCl\textsubscript{4}\textsuperscript{80}, where the C incorporation is proportional to the CCl\textsubscript{4} molar fraction in the gas, and TMAs, where the dopant incorporation is facilitated by an increased TMAs/AsH\textsubscript{3} ratio and at low growth temperatures\textsuperscript{81}.

InP with a low n-type background doping level can be made semi-insulating for use in current blocking layers by introduction of a deep acceptor. Fe has proven to be a good choice and ferrocene, (C\textsubscript{5}H\textsubscript{5})\textsubscript{2}Fe, (Cp\textsubscript{2}Fe), could be used as the precursor\textsuperscript{82}. However, memory effects are known to occur, as for Cp\textsubscript{2}Mg.

In order to change the growth behaviour on patterned substrates and to inhibit deposition on masked areas, chlorine could be introduced into the reactor. Some different ways have been tried. Cl-based metalorganic precursors, such as diethylgalliumchloride (C\textsubscript{2}H\textsubscript{5})\textsubscript{2}GaCl and diethylaluminiumchloride (C\textsubscript{2}H\textsubscript{5})\textsubscript{2}AlCl, have been used\textsuperscript{56,83}. The disadvantage with these precursors is that the group III to Cl ratio can not be independently varied, hence Cl-based precursors, e.g. arsenictrichloride AsCl\textsubscript{3} has been used in addition to AsH\textsubscript{3} for growth of GaAs/AlGaAs\textsuperscript{55} and CCl\textsubscript{4} for growth of InP\textsubscript{EF}. HCl has also been used both at atmospheric\textsuperscript{84} and low\textsuperscript{85} pressure, but care should be taken because of the high reactivity with the gas tubing system.

**Reaction chamber.** - The MOVPE reactions preferably occur on a heated substrate in a reactor with cold walls. The geometry of the reactor chamber determines the uniformity of the epitaxial layers and to some extent also the interface abruptness. There are two main reactor concepts for growth on single wafers. In the horizontal reactor the gas flow is parallel to the substrate surface, which for convenience usually is horizontally oriented, and in the vertical reactor the gas flow is vertical, perpendicular to the horizontal substrate surface. There are also two reactor concepts for growth on multiple wafers. In the barrel reactor the substrates are mounted vertically on a rotating slightly conical barrel with the gas stream parallel to the surfaces, and in the planetary reactor the wafers are horizontally oriented and in planetary motion in a circle with the gas flowing from the centre to the periphery.

In order to diminish the memory effects, unpurged volumes must be avoided in all reactor designs. The gas flow has to be optimised in order to prevent vortices, which might conserve precursors for several minutes\textsuperscript{86} and also affect the uniformity. The vortices are most often due to the buoyancy.
forces, which tend to raise the gas heated by the susceptor and to press the cold gas down. These vortices are mainly suppressed by forced convection, i.e. high enough gas flow velocity to override the buoyancy driven (natural) convection. The uniformity can be further improved by a mixing device, attached at the reactor inlet, which will mix and spread the entering gas jet\textsuperscript{86,87}.

The horizontal geometry is the most common, and it has also been the most extensively simulated and documented. The growth rate in this reactor is primarily determined by the amount of growth rate limiting reactants (i.e. the group III reactants) transported through a diffusion boundary layer, assumed to be depleted of reactants\textsuperscript{88,89}. The thickness of the boundary layer decreases for higher gas velocities but increases along the susceptor, and as the thickness increases, the growth rate falls. It is hence possible to counteract the falling growth rate through increased gas flow velocity by lowering the reactor ceiling along the susceptor\textsuperscript{90}. Reactants are supplied from an infinite source as long as the top of the boundary layer has not reached the reactor ceiling, but then the growth rate begins to fall exponentially due to total depletion of reactants. Increase of the gas flow velocity is equal to keeping a "gas finger" cold enough to preserve the uncracked reactants above the susceptor\textsuperscript{91}.

In addition to the boundary layer approximation one has to consider the buoyancy effects. There are on one hand the longitudinal rolls, parallel to the flow, driven by the temperature difference between the cold walls and the heated susceptor\textsuperscript{92}, and on the other hand the transverse rolls, at the entrance to and exit from the heated region\textsuperscript{93}. The former will primarily result in transportation of material from the edges to the centre (for the case of adiabatic walls) and the latter in memory effects.

The ways to reduce the influence from buoyancy rolls is to reduce the reactor height, to move the side walls far away from the susceptor, to increase the gas velocity (by a lower reactor pressure or a higher gas flow rate) and to choose hydrogen rather than nitrogen as carrier gas\textsuperscript{93-95}. With a low reactor cell height it is a risk that the boundary layer reaches the ceiling, and a higher gas velocity is needed. By introducing susceptor rotation (Fig. 6), which provides a linear averaging of reactant supply and temperature field, the deposition uniformity could be further improved\textsuperscript{96-98, A}. The rotation speed has to be higher than one revolution per grown monolayer, and is usually about 100 r.p.m.. By careful design of the geometry of the horizontal reactor, the growth parameters (e.g. carrier gas flow rate and reactor pressure) could be varied at least a factor of two without deteriorating the layer uniformity\textsuperscript{A}. 

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Figure 6. Some methods for introducing susceptor rotation in horizontal reactors. Inductive RF (radio frequency) heating of a graphite susceptor is for simplicity assumed in all cases, but other methods, such as in-irradiation and resistive heating are also used. a) A horizontal rod is rotated and the rotation is transferred by gears to the susceptor (ref. 96). This method does not require a rotation feed through in the quartz outer cell, but some particles are likely to be generated by friction to the inner cell. b) This design combines the horizontal and vertical geometries (ref. 98). It is not likely to generate particles, but the absence of an inner cell might enhance the influence of buoyancy rolls. c) The simple vertical rotation has here been combined with an inner cell with low ceiling (paper A). In this design the rotation feed through is in the end of a quartz tube fastened perpendicular to the outer cell and the circular susceptor is aligned with a hole in the inner cell. Careful alignment prevents friction and particle generation. d) Most promising is the foil rotation (ref. 104). No mechanical rotation transfer is used, in stead gas is introduced through narrow channels under the upper disk of the susceptor and lifts it. The gas is forced to follow spiral grooves from the centre of the disk to the periphery and makes it to rotate. No particles are generated, but the function is sensitive to depositions on the susceptor.

In the vertical reactor the reactants are also assumed to reach the substrate by diffusion through a boundary layer. However, in this case the layer thickness is dependent on the susceptor rotation, which produces a pumping action on the gas and hence provides a lateral flow near the substrate surface towards the susceptor edge. A rotation speed of about 1500 r.p.m. is required to obtain laminar flow\(^9\). The buoyancy driven convection, which gives
memory effects, is diminished by the susceptor rotation and could be further reduced by high flow rate, low reactor pressure, and introduction of a gas distribution device. It has also been shown that the reactor geometry is important for suppression of vortices. The rule is to diminish the free volume between the susceptor and the gas inlet and to optimise the slope of the walls. However, it has been found that the growth rate uniformity is very sensitive to variations in the gas flow rate, which has to be optimised within a few per cents.

The barrel reactor could be regarded as a combination of the horizontal reactor (the gas flow is parallel to the substrate surfaces) and the vertical reactor (the gas enters into a relatively large volume where recirculation vortices easily occur). The buoyancy driven recirculation is again diminished by low pressure, high gas flow rates and a careful geometric design. However, the uniformity seems to be improved by balancing of natural and forced convection, i.e. to allow some vortices, which counteract the requirements on abrupt interfaces. Rotation of the susceptor is found to improve the uniformity between the wafers, does not influence the uniformity along the gas flow, but rotation speeds above 5 r.p.m. seem to be deteriorating for the uniformity across the wafer.

The planetary reactor has proven to be a very successful design for uniform growth of abrupt structures on multiple wafers. The concept is close to the horizontal reactor with laminar flow and substrate rotation. By a careful design of the gas inlet the flow could be perfectly radial and any horizontal vortices be avoided. Furthermore, the alkyls and hydrides are mixed just in front of the wafer, which eliminates the parasitic reactions.

**Gas system.** To control the MOVPE process is to a large extent to control gas flows and pressures, not only in the reactor, but also in the lines from the sources to the reactor.

The reactant supply from a gas source is easily controlled. A regulator that roughly controls the pressure close to the gas bottle and an electronic mass flow controller (MFC) could provide an exact flow rate (well within 1 %) over a span of about two decades.

The liquid bubbler requires some more complicated regulation equipment. An inert carrier gas flows through the liquid and for reasonably low flow rates the vapour pressure above the liquid could be assumed to be in equilibrium with the liquid surface. The source precursor is hence diluted in the carrier gas and the total precursor flow into the reactor is proportional to the carrier gas flow rate and the vapour pressure of the precursor in the bubbler, and inversely proportional to the total pressure in the bubbler. For exact precursor supply an MFC controlling the carrier gas flow is placed before the bubbler, an electronical upstream pressure controller (UPC) is placed after the
bubbler and the vapour pressure in the bubbler has to be held constant by accurate temperature regulation (Fig. 7).

![Diagram of bubbler configurations]

**Figure 7.** Some MO-bubbler configurations. a) In an atmospheric pressure system the pressure in the bubbler could conveniently be determined by the reactor pressure, and hence only the flow through the bubbler has to be controlled. b) In a low pressure system the desired bubbler pressure is usually higher than the reactor pressure, and a pressure drop is introduced over the UPC. c) With an MFC added, an increased gas flow rate through the vent/run line could be obtained. d) The extra MFC on the inlet to the vent/run line selects only a part of the flow and the rest is directed to the vent line through the UPC. This configuration is used for dilution, e.g. of dopant precursors, and increases the span of controllable doping levels with at least an order of magnitude compared to the other configurations.

Sublimation of a solid source is in theory controlled as evaporation from a liquid, but it has been found that the degree of gas saturation is dependent on the precursor surface area in contact with the gas, and the efficiency is usually decreasing as the source is consumed\textsuperscript{105}. One way to overcome the problem is to combine two bubblers in series and hence increase the total area of reactants\textsuperscript{106}. Another way is to use a diffuser, where the precursor diffuses through a capillary. The diffusion rate is only dependent on the pressure and the temperature in the container, and not on the carrier gas flow rate\textsuperscript{108}. A saturated solution of TMIn in an inert liquid has also been proposed to provide a stable output\textsuperscript{106}. However, the most reliable way is to measure the amount of reactants in the gas after the bubbler. This is possible with the use of an ultrasonic approach, measuring the variation in sound velocity due to composition changes in the gas\textsuperscript{107}. The carrier gas flow rate or the pressure in the bubbler could then be varied in order to provide a constant supply of reactants to the growth zone.
Abrupt heterointerfaces are formed by instant change of the reactant composition in the reactor. This is only possible if the different flows are established in advance and switched into the reactor when they are needed. To stabilise the flow from the TMIn bubbler could take more than 15 minutes\textsuperscript{107} and from liquid sources a few minutes. This motivates the necessity of the vent-run manifold, a block of three-way valves, one for each source, where the stabilised flow could be directed either into the reactor (run-line) or not (vent-line)\textsuperscript{108}. The abruptness in gas switching is also improved by a high gas flow velocity through the manifold, which might be obtained by high dilution flow rates\textsuperscript{109} or low pressure\textsuperscript{110}. The unpurged volumes and the distance between the manifold and the reactor have to be minimised in order to reduce memory effects and dispersion of the pulse of reactants\textsuperscript{111}. The nominal gas transport time from the vent-run valve to the reactor can be designed to be less than 0.1 s. An exact pressure balance between the vent- and run-lines has to be maintained to avoid initial gas pulses when a valve is switched (Fig. 8).

Figure 8. Configurations for control of pressure in the reactor chamber and pressure balance in the vent-run manifold. a) In an atmospheric pressure system both reactor exhaust and vent gases emanate to atmosphere and the \textit{UPC} on the vent line controls the pressure balance between vent and run lines. b) If the reactor is kept at low pressure and the vent-run manifold at atmospheric pressure the vent gases could emanate to the atmosphere and \textit{UPCs} are required on both vent and run lines, and between the pump and the reactor. c) With both vent and run lines connected to low pressure and the manifold kept at the reactor pressure, \textit{UPCs} are required on each MO source line. Furthermore the pressure drop in the vent and run lines could influence the pressure balance in the manifold.
To diminish the adsorption of reactants in the tubes, the surface area to length ratio should be small and unpurged volumes avoided in all the gas system. When gas bottles and metalorganic bubblers are changed, the opened tubes have to be easily purged, firstly to not contaminate the environment with the toxins and secondly not to allow oxygen and water to rest in the system and to contaminate the sources. Furthermore, leak tightness is important, both to hinder the toxic gases to come out and to reduce impurities entering into the system. Welded couplings with metal gaskets and bellow sealed valves gives the sufficient leak tightness with helium leak rates lower than $10^{-9}$ atm cm$^3$/s.

For reactors operating at low pressure the pump and pressure regulation system has to be designed with respect to depositions downstream the reactor. Furthermore, the pressure drop in the lines becomes more severe for narrow tubes and large flow rates, which makes the pressure balancing of the vent-run manifold difficult.

**Safety arrangements.**- The use of highly toxic and pyrophoric chemicals raises the need for extensive safety arrangements. Some part of the arsine and phosphine used in the process is undecomposed after the reactor and so are all the precursors directed into the vent line. A scrubber system, which hinders the reactants to be spread in the environment is hence needed. The most easily used is a charcoal container, where the toxins are adsorbed and possibly also oxidised$^{112}$. The hydrides and metalorganics could also be oxidised in HBrO$_3$,$^{113}$ or in a hydrogen flame (where air is added to the H$_2$ carrier gas),$^{114}$ forming phosphorus and arsenic acids.

Toxic gas monitoring systems can be used both to check the efficiency of the scrubber system and to detect leaks and hazardous discharges in the laboratory. When high levels are detected warning signals sound in the lab and the process in the reactor could be automatically stopped by resetting all valves, i.e. the sources are closed and nitrogen flushed through the reactor, and pumps and heaters are shut off.$^{112}$ These routines could also be triggered when other systems, e.g. the ventilation or cooling water, fails. The ventilation ought to be dimensioned at least for an arsine leak of the order of the maximum process flow. The gas bottle could be equipped with a flow limit shut of valve or an orifice$^{115}$, which restricts the flow in an emergency situation. Both gas bottles and metalorganic bubblers should be properly fastened so that no tension is transferred to the tubing when the sources are opened or changed.

There is also an extensive work in progress to find replacements for the most dangerous toxins, arsine and phosphine. TBAs$^{68}$ and TBP$^{69}$ are hence found to be acceptable for most applications$^{70,71}$. However, their extremely
high price makes them still not competitive, and we have to learn how to handle the toxic hydrides.

It is hence highly important to develop safe routines for handling toxic chemicals and cleaning the gas system downstream the reactor, where arsenic and pyrophorich phosphorus are deposited. For a reactor operating at low pressure also the pump will become contaminated and routines for changing oil and filters are needed.

Above all, the personnel working in the laboratory should be informed of the risks and the safety routines and trained to handle emergency situations.

**Process parameters.** The final choice of process parameters is often a compromise to obtain a reasonably material quality, layer uniformity and efficient use of the chemicals and time.

A high reactor pressure increases the probability of prereactions of the reactants, affects the uniformity due to low gas velocities, and deteriorates the gas switch performance. To obtain a significant improvement in these parameters, the pressure has to be reduced at least an order of magnitude, and 20 - 100 mbar are typical process pressures. For further decreased pressures the pumping capacity has to be considerably increased and it will be difficult to keep the pressure balance in the vent-run manifold. The gas flow also becomes less laminar. Implementation of reactors for low pressure is more complicated than for atmospheric pressure, because of the need of pressure regulation and pumping of toxic gases. However, these problems are now satisfactorily solved and low pressure reactors are common.

Closely connected to the reactor pressure is the total gas flow rate through the reactor. A high gas flow rate will improve the uniformity and reduce the memory effects, but it will also dilute the reactants and hence decrease the efficient use of them. Normally the carrier gas flow rate in single wafer reactors is 3 - 10 SLM (standard litres per minute), dependent on the volume of the reactor cell and which uniformities are required. As high flow rates as 15 SLM has been successfully used to obtain large area uniformity in an atmospheric pressure reactor without rotating substrate.

The substrate temperature is usually chosen in the range where the growth rate and group III alloy composition is determined by mass transport of the rate limiting reactants (i.e. the group III reactants) through the diffusion boundary layer, which means that these parameters will become temperature independent. The accurate temperature range is about 600 - 750°C, and within this range the temperature might be optimised to obtain the best material quality. As incorporation of C from CH₃ groups increase with the temperatures, the lowest possible temperature should be chosen to avoid unintentional C doping. Increased incorporation of Si impurities also occurs at elevated temperatures. The Si might originate from the reactor
quartz ware or residual impurities\textsuperscript{117}. The group V hydrides, and specially \( \text{PH}_3 \) have high decomposition temperatures (about 600\(^\circ\)C), which motivates a somewhat higher growth temperature\textsuperscript{39,40}. Growth of Al containing compounds requires even higher temperatures to reduce the incorporation of oxygen\textsuperscript{118}. In conclusion, growth of InP, GaAs and related materials are preferably performed at about 600 - 680\(^\circ\)C, and Al containing compounds at 680 - 720\(^\circ\)C.

The V/III ratio has to be large enough to avoid evaporation of the group V elements from the surface, and hence the required V/III ratio increases with the growth temperature. It has also been found that hillocks might appear at a too high V/III ratio, probably due to parasitic reactions between the alkyls and hydrides\textsuperscript{119}, but also at a too low V/III ratio\textsuperscript{120}. For GaAs and AlGaAs the C incorporation and hence the background doping level depends on the V/III ratio\textsuperscript{61}. For low V/III ratios C is incorporated at As sites, giving a p-type background, while high V/III ratios give an n-type background\textsuperscript{28,61}. This transition from p- to n-type is very sensitive on both the V/III ratio and the Al-content, but is not observed in growth of InP\textsuperscript{119}. The V/III ratio has to be optimised for each reactor individually and depends on the growth temperature, reactor geometry and carrier gas flow rate. Normally the V/III ratios are in the range 10 - 200.

The growth rate, proportional to the molar fraction of group III species in the carrier gas, is adjusted to a convenient level depending on the structure to be grown. For thick layers, growth rates up to 10 \( \mu \)m/h could be used, while to control thin layers and abrupt interfaces low growth rates (= 1 \( \mu \)m/h or 1 monolayer/s) are required. In order to further improve the interface abruptness, the sequence for changing the gas composition in the reactor has been optimised. Hence the reactor is flushed with a mixture of hydrides in the carrier gas that purges traces of undesired precursors and prepares it for the new layer to be grown. The flushing time has to be chosen so that the surface is not deteriorated by incorporation of impurities or loss of group V species\textsuperscript{121,122}. A low molar fraction of group III species has also proven to slightly improve the thickness uniformity over the wafer\textsuperscript{4}.  

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MEASUREMENT METHODS

Before growing a device structure important material parameters, e.g. thickness, doping concentration and material composition, are calibrated in separate growth runs and hence related to reactor dependent parameters such as gas flow, growth time, reactor pressure and temperature. In order to make reliable determinations of these parameters the following measurement methods have been used. The measured result is often strongly dependent on the epitaxial structure grown and it is hence important to choose calibration structures compatible with the respective measurement methods.

**Hall effect measurements.** - The Hall effect relies on the fact that charged particles moving in a magnetic field are deflected from a straight course. Hence if a current flows through a sample and a magnetic field is applied perpendicular to the current, a voltage builds up in a direction perpendicular both to the magnetic field and to the current. The polarity of the voltage is determined by the charge of the current carrying particles (holes or electrons), and from the magnitude and a known sheet resistivity the carrier concentration and mobility can be calculated. The accuracy of the measurement depends on the reproducibility of the contacts, while the geometry of the sample is regarded by the van der Pauw measurement method. With a mesa etched Greek cross structure and lithographically defined contacts the effects of differences in contact resistivity are eliminated.

As the Hall measurement weights the carrier concentrations and mobilities throughout the sample, measurements made on multi layer structures are not reliable. E.g. if a highly doped high bandgap material is grown with a junction to a material with lower gap, carriers are injected into the low gap region, a HEMT-effect occurs, and the mobility will be overestimated. In a sample with both positive and negative carriers only a weighted mean value of mobility and carrier concentration is obtained. However, the main error introduced in the Hall measurement is proportional to the unknown ratio between the Hall and conductivity mobilities, and can be up to 30%.

**C-V. etch profiling.** - A Schottky barrier applied to a semiconductor will deplete it of free carriers to some depth, determined by the carrier concentration, the applied voltage and material constants. Hence, the carrier concentration and type at the depletion depth can be calculated from the differential capacitance of the Schottky barrier. Usually the Schottky barrier is formed by a metal, but it might also be formed by an electrolyte with well-defined area to the semiconductor. It might act as an etchant of the semiconductor, and the carrier concentration can hence be determined as a function of depth. The total depth is the sum of the etch depth, determined
from the integrated etch current, and the depletion depth. Hence electrochemical capacitance - voltage (C-V) etch profiling gives a profile of the net doping level and type throughout the sample.

The depth resolution is theoretically limited by the diffusion of carriers out from the doped region and is hence determined by the Debye length. However, the surface roughness of the etched crater also limits the resolution, as well as the problems to accurately calculate the depletion depth for low doped regions. These problems become most severe for profiling across sharp concentration transitions and for thin highly doped layers, where tails might occur. Nevertheless, good results have been obtained, also for extremely demanding structures\textsuperscript{8}.

**X-ray diffractometry.**—X-ray diffractometry of crystals is based on the Bragg law, which states that incident X-rays are reflected by the crystal planes and interfere constructively. Diffracted beams are hence found in an angle determined by the spacing of the lattice planes and the wavelength of the X-rays. Hence X-ray diffractometry is used to measure the lattice parameter of a crystal. The resolution of the measurement method is limited by the monochromation of the beam and the accuracy of the goniometer used for choosing the diffraction angle. By using a four crystal monochromator, where the X-rays are monochromated by consecutive reflections in four perfect crystals in a given geometry, and a goniometer with a resolution of a few arc seconds, a resolution of relative lattice constants of $10^{-5}$ could be obtained\textsuperscript{126}. By measuring the diffracted X-ray intensity while the incidence angle is changed a "rocking-curve" is obtained. This method is called high resolution X-ray diffractometry, (HRXRD).

From simple measurements of the difference in lattice constant between the substrate and nearly lattice matched epitaxial layers, the composition, e.g. of AlGaAs on GaAs can be determined. Here linear interpolation of the lattice constants of AlAs and GaAs is assumed (Vegard's law) and furthermore, elastic deformation of the epitaxial layer is assumed if the lattice mismatch is so small that no misfit dislocations appear\textsuperscript{127}. By an intelligent choice of diffraction angles the three dimensional deformation of the strained crystal can be found\textsuperscript{127,128}.

For more complicated structures, involving several layers of different composition, the rocking-curve becomes complicated because of cross-interferences from all layers\textsuperscript{129}. One special case is the SL, which gives diffraction peaks with a periodic spacing, inversely proportional to the superlattice period\textsuperscript{130}. By the use of commercially available programs, rocking-curves could be simulated from given structures, which facilitate the interpretation of the curves (Fig. 9).
HRXRD is a fast and non-destructive measurement method for measurements of lattice mismatch within some ten ppm and layer thicknesses within a few tenths of a nanometre (for SLs). Easily interpreted rocking curves usually requires specially designed calibration structures, either consisting of a thick layer with a homogeneous composition or of a SL for thickness calibration. In order to facilitate extensive full wafer characterisation of epitaxial layers an equipment for automated HRXRD mapping of 50 mm diameter wafers has been developed in co-operation with PHILIPS.

![Image](image.png)

Figure 9. HRXRD rocking curve and simulation of a InGaAs/InP SL sample. The simulated structure is shown in the insert. An unexpected high intensity is obtained for satellite peaks of high order. The simulation indicates that this is due to thin and highly strained InGaAsP layers at the interfaces between InP and InGaAs. The InGaAsP layers are probably due to memory effects and can be eliminated by an optimised routine for the change of gases in the reactor.

**Photoluminescence.** Electron - hole pairs can be created in a semiconductor by absorption of light with a photon energy higher than the bandgap. The light emitted when the electron - hole pairs recombine again is called photoluminescence, PL. By recording the PL as a function of photon energy a spectrum is obtained, which correctly analysed could provide extensive information of the recombination paths and hence of the material. Many probable radiative transitions exist, e.g. directly from band to band, from band to impurities, by recombination of free excitons and excitons bound to an impurity or defect. PL peaks are most often associated with impurity
bound excitons. The impurities could hence be identified from the spectrum, if their characteristic PL energy levels are known. To some extent there is a relation between intensity and line width of the peak and the concentration of the related impurity, but the measurements should be regarded primarily as qualitative and not quantitative.

PL of QW structures gives information of the energy levels in the QWs (by the energy of the PL peak) and to some extent also to the interface roughness of the QWs (by the width of the peak)\textsuperscript{132,133}. Several QWs with different thickness could be grown in the same run and simultaneously analysed if the thinner wells are nearest to the surface, so they can not absorb the light emitted from the inner wells (the Frijlink structure\textsuperscript{132}).

As the line width increases with temperature, high resolution analysis has to be performed at low temperatures (4 K or 77 K), while at room temperature PL is a convenient method to measure the bandgap (and hence implicitly also the composition of ternary materials). For this purpose an equipment for automated mapping of 50 mm diameter wafers has been constructed, using a fiberoptic approach (Fig. 10). Compositions of quaternary materials require both HRXRD and PL measurements of lattice constant and bandgap in order to provide values for calculation of the group III and group V ratios.

![Diagram of scanning photoluminescence system]

Figure 10. Principle of the scanning photoluminescence system.

**Microscopy.** Observation of the epitaxial surface in an optical microscope gives immediate information of the defect density. By applying the Nomarsky technique for obtaining phase contrast\textsuperscript{134}, it is possible to resolve variations in the surface level of a few ten nanometres. This is of great importance for identification, e.g. of hillocks and etch pits. However, the lateral resolution is
limited by the light wavelength to about 300 nm, and the depth of field is less than one micrometer at higher magnifications, which limits the use of the optical microscope to inspection of large areas and to magnifications of up to 1,000 times.

In scanning electron microscopy (SEM) a beam of electrons is accelerated with a few keV and focused to a spot of some ten nanometres at the sample. The amount of electrons scattered from the sample surface are measured with an appropriate detector. An image is formed by scanning the beam over the sample and to simultaneously scan a cathode ray tube in a one-to-one correspondence. The intensity variations determined by the detector are transferred as intensity variations at the cathode ray tube and will hence give rise to an image. The resolution is to some extent determined by the electron - surface interaction, but is in the order of some ten nanometres, which allow magnifications of up to 100,000 times. The depth of field is also large compared to that of the optical microscope, e.g. up to 4 μm at a magnification of 10,000 times.

To observe a cross section through an epitaxial structure consisting of layers of different composition, selective etching might be used in order to obtain contrast between the layers. By this method thickness variations over the wafer could be resolved within a few per cent.

**Secondary ion mass spectrometry.** One of the most sensitive methods to determine the atomic composition in a sample is secondary ion mass spectrometry (SIMS). SIMS is based on the fact that ionised atomic and molecular species are ejected from a surface bombarded with particles. The sample is usually bombarded with O₂⁺ or Cs⁺ primary ions in the energy range of some keV, and the mass to charge ratio of the ejected (secondary) ions are detected in a mass spectrometer. While a crater is sputtered in the sample a depth profile is obtained as a function of time. This profile might be calibrated if the sputtering rate is known.

As the primary ions interact with the surface the lattice structure is destroyed, primary ions are implanted into the sample and atoms near the surface are moved into the sample due to a recoil effect. The depth resolution is limited to a few nanometres, mainly by ballistic mixing and the surface roughness of the sputtered crater. The detection limit of impurity elements is determined e.g. by their ionisation probability, the level of background impurities in the system, the sputtering rate, and interference from other ionised atoms and molecules with the same mass to charge ratio, and could be as low as 10¹⁴ cm⁻³. One complication when heterostructures are analysed is that the ionisation probability and sputtering rate might be strongly dependent of the bulk composition and hence change through the sample.

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MOVPE PROCESS PERFORMANCE

As previously implied, the overall performance of the MOVPE process is determined by the interplay of many elements. In spite of this and due to an extensive effort to improve every detail in the process, the greater part of the requirements set by very demanding device structures can now be fulfilled. In this section the obtained performance will be reviewed, with emphasis on the results of the original research work of this thesis. However, also important results from other fields, e.g. heterojunction abruptness and layer purity, are presented.

Reproducibility.- The run-to-run reproducibility has to be better than a few per mills for compositions and a few per cents for doping levels. These parameters are primarily determined by the supply of reactants from the sources, the total gas flow rate, and the substrate temperature. With the use of electronic MFCs and pressure controllers, the gas flows and the pressures in reactor and metalorganic bubblers can be accurately controlled. These controllers are usually specified to an accuracy of 2 % of full range. This is

![Graph](image)

Figure 11. Pick-up from a TMIn bubbler as a function of run number at atmospheric pressure for two different carrier gas flow rates through the bubbler, 250 and 600 standard cm³/minute (sccm) respectively. It is shown how the pick-up decreases with increased carrier gas flow rate and run number, i.e. at reduced TMIn area in contact with the carrier gas. The measurement was made with an ultrasonic concentration meter.
not sufficient for growth of InGaAsP with compositions lattice matched to InP, but the reproducibility normally obtained indicates that the accuracy is considerably better than specified. By keeping the bubblers for metalorganics in thermostat baths, which allow temperature stability within 0.1°C, the vapour pressure of the precursors could be maintained within acceptable limits. The whole bubbler has to be under water for sufficient temperature stability.

There is still a problem to control sublimation from solid sources and no final solution has yet been found (Fig. 11). However, the use of an ultrasonic concentration meter reduces the need of calibration runs to a minimum. We have successfully reproduced the same InGaAsP composition, grown with TMIn from a full and from a half full bubbler, only by keeping the product of gas flow and measured TMIn concentration constant. At a bubbler pressure below 500 mbar the ultrasonic signal becomes weak and the measurement fails, but simultaneously the TMIn output becomes more stable.

The substrate temperature strongly affects the dopant incorporation and the As/P ratio and has to be controlled within one Kelvin. By the use of a thermocouple in close contact with the susceptor and a stable temperature regulation this can be reproduced.

Uniformity.- As for the reproducibility, the uniformity has to be within one per cent for thicknesses, a few per mills for composition distributions and a few per cents for dopant distributions. As the commercially available reactors as long as until 1990 did not fulfil these requirements, it was necessary for us to make considerable improvements of the reactor design in order to grow advanced device structures. We did obtain acceptable overall layer uniformity for single wafers in a horizontal reactor with high width/height aspect ratio, rotating substrate, and at a relatively high carrier gas flow rate. This reactor and the results are in detail described in paper A. Thickness uniformities within ± 1 % over a 40 mm diameter of a 50 mm diameter wafer are routinely obtained, as measured from SLS with HRXRD. Both the group III and group V compositions vary within a few tenths of a per cent in ternary (AlGaAs and InGaAs), and quaternary (InGaAsP) layers. Furthermore they vary in correlation in such a way that the standard deviation of the PL wavelength (which is the most important parameter for laser fabrication) is about 2 nm, while the lattice mismatch varies from 0 ppm to 700 ppm. These figures refer to 40 mm diameter of a 50 mm diameter wafer and are well within the device requirements (Fig. 12). Dopant variations are also acceptable, and fall within ± 2 %, which is sufficient for most applications.

One important feature of this reactor is that all uniformity data has been obtained at standardised process conditions, without individual optimisation of the uniformity for each composition and dopant. In vertical reactors and
Figure 12. The uniformity of a) lattice mismatch and b) bandgap wavelength of an InGaAsP layer grown lattice matched to a 50 mm diameter InP substrate. The lattice mismatch is measured with high resolution X-ray diffractometry and the wavelength with room temperature photoluminescence. Both mappings were obtained automatically. The mismatch wary from 0 to -700 ppm and the wavelength within a few nanometres over a 40 mm diameter.
horizontal reactors with non-rotating substrate the uniformity profiles vary considerably and the process parameters have to be optimised for each layer.

The parameters that limit the uniformity in the high aspect ratio reactor are the temperature gradient, the differences in diffusion coefficients of the reactants, and to some extent parasitic reactions. The results are considerably improved by the substrate rotation, which linearly average both temperature profile and the reactant distribution profile. We have estimated the temperature gradient over the 40 mm diameter of the rotating substrate to a few tenths of a degree by comparing the incorporation of Zn and Si dopants from DEZn and SiH₄ and using the known temperature dependence of their incorporation. As the As/P incorporation ratio also is determined by the substrate temperature, these compositional variations could to some extent be attributed to temperature variations. However, since growth is performed in the diffusion limited regime, the variation in group III composition can not be due to temperature variations, rather we suggest that it is mainly due to differences in diffusion coefficient of the molecules that reside in the boundary layer. It is unknown exactly which these molecules are, because the high temperature above the susceptor initialises homogeneous reactions, but there are both decomposed and undecomposed precursors, and some complex molecules might also be formed. Furthermore, the differences in decomposition energies between the precursors will most probably result in differences in their depletion by parasitic reactions. By accurate measurements we also observed significant edge effects, extending about 5 mm from the wafer rim. These might be due to re-evaporation and diffusion from the susceptor. The non uniformity due to diffusion and depletion of reactants is fundamental and might be difficult to avoid also in other reactor designs.

For multiwafer growth the planetary reactor has proven to give a uniformity comparable to that of the horizontal single wafer reactor, i.e. variations in thickness within ± 1 %, in ternary composition within ± 0.1 %, and in PL wavelength within ± 3 nm. These figures represent the total variation over seven 50 mm diameter wafers from one growth run, with 3 mm of the edge omitted. A critical part of the design is an optimised gas inlet, which provides a laminar flow radially over the susceptor, and mixes the hydrides and alkyls near the growth zone.

**Heterojunction abruptness.** The possibility to promptly change the gas composition in the growth chamber is necessary in order to grow heterojunctions without introducing dislocations due to lattice misfit. The fundamental problems in this field were overcome by introduction of a pressure balanced vent-run manifold, which allows stabilisation of the gas flows before they are switched into the reactor, and by a relatively high rate of gas exchange in the reactor. In the mid 1980's alloy transitions of a
few nanometres were state of the art\textsuperscript{141}. However, the requirements on abrupt heterojunctions for thin QW structures increase, and now an abruptness within one or a few monolayers is possible to obtain\textsuperscript{142}. At these levels the degree of abruptness becomes a matter of definition and the averaging in the measurement\textsuperscript{133}.

To improve the heterojunction abruptness, growth interruptions are used. This method is most successful when only the group III elements have to be changed, e.g. in AlGaAs/GaAs QWs\textsuperscript{143}. In this case the substrate can be held under a constant group V pressure during the time when the residual group III species are flushed out. The time required (usually of the order of a second) is strongly dependent on the design of the MOVPE system.

Problems occur when also the group V species have to be changed, as in the case of InGaAs/InP\textsuperscript{121,142} and InGaAs/InGaAsP\textsuperscript{122} structures. Here the grown surface has to be protected under a group V over pressure, with a composition close to that used during growth, and the atmosphere in the reactor has to be changed to a composition close to that required for next layer to be grown. Furthermore, there are memory effects due to evaporation of group V species from the reactor walls and the susceptor. These might result in a systematic change in crystal composition during growth of a SL as the composition of the depositions changes\textsuperscript{122}. It has been shown that a short growth interruption is to be preferred and that the surface should be flushed with the new composition of group V material at most 1 s to avoid group V substitution\textsuperscript{121,122}.

Another effect that might influence the heterointerfaces in structures with very high doping is impurity induced disordering\textsuperscript{144}. When an impurity, e.g. a dopant, is diffused through a SL, the group III atoms are redistributed and the whole structure might be deteriorated. This mechanism has been used in post epitaxial device processing, e.g. to confine the active layer in QW lasers.

**Doping profiles.**- The ability to grow abrupt doping profiles is extremely important, e.g. for HBT and HEMT structures. The main problems that occur are memory effects of the dopant precursor (e.g. by accumulation on the reactor walls) and dopant diffusion in the layer after growth. These problems are not severe for n-type doping, when SiH$_4$ is used as the precursor\textsuperscript{145}. However, the choice of p-type dopant has proven to be difficult, especially for the base layer in the HBT structure, which has to be both extremely narrow and highly doped.

A p-type dopant with low diffusivity and high doping capability is Be. It has been excluded from MOVPE because of its high toxicity, which makes downstream depositions difficult to handle, and problems with doping tails extending towards the surface have occurred\textsuperscript{75}. More realistic choices of p-type dopants for device structures are Mg and Zn. In paper B we present a
study of Mg and Zn doping of GaAs and AlGaAs. As shown from infinite source diffusion experiments in GaAs at 900°C, the diffusion coefficient of Mg is $1 \times 10^{-13}$ cm$^2$/s, while it is $3 \times 10^{-8}$ cm$^2$/s for Zn$^{74}$. These data made us believe that Mg is the best choice of a dopant for the HBT base layer. However, we found that the precursor Cp$_2$Mg gives extensive problems with memory effects. This necessitates flushing of the reactor with AsH$_3$ and Cp$_2$Mg during 10 minutes before growth of the doped layer in order to saturate the walls with Cp$_2$Mg, and 40 minutes of growth at an extremely low growth rate after growth of the doped layer in order to get an abrupt turn-off$^{77}$. These structures were grown in an atmospheric pressure reactor. Slightly more promising results have been obtained at low pressure$^{146}$. Nevertheless, there were problems to reach doping levels in the vicinity of $1 \times 10^{19}$ cm$^{-3}$.

We found that dopant diffusion in epitaxially grown layers is only $7 \times 10^{-14}$ cm$^2$/s for Mg doped GaAs, and $2 \times 10^{-14}$ cm$^2$/s for Zn doped GaAs at 900°C furnace anneal, i.e. several orders of magnitude lower than expected from the infinite source diffusion experiments. The Zn doping saturated at a level of about $2 \times 10^{19}$ cm$^{-3}$, and an abruptness of three decades per 60 nm was obtained (which is close to the SIMS depth resolution). These facts together show that Zn, rather than Mg is to be preferred from all points of view. However, in the HBT structures a systematically larger broadening of the p-doped layer than expected from the diffusion study did occur. When we investigated the behaviour of Zn doped layers in heterostructures we found, quite unexpectedly, that a broadening of the as-grown Zn doped region occurred when it was grown adjacent to highly n-doped (1$\times 10^{18}$ cm$^{-3}$) Al$_{0.3}$Ga$_{0.7}$As.

Both the low diffusivity of dopants in epitaxial layers and the broadening of the dopant profile adjacent to highly doped Al$_{0.3}$Ga$_{0.7}$As can be explained by a modified interstitial - substitutional diffusion theory$^{147}$. It is assumed that the diffusivity of substitutional dopants (i.e. dopant atoms on Ga lattice sites) could be neglected, compared to diffusion of interstitial dopants. An equilibrium between dopant interstitials, $N_i$, dopant substitutionals, $N_s$, and group III vacancies $V_{III}$, is also assumed:

$$N_s \leftrightarrow N_i + V_{III}.$$  

The fact that dopants in infinite source experiments are primarily interstitials, while they during epitaxial growth are incorporated as substitutional, explains the dependence of measured diffusion constant on experimental conditions. Furthermore, in regions of highly n-doped layers the amount of $V_{III}$ is enhanced due to Fermi level pinning during growth. According to a model proposed by Deppe$^{148}$, this causes group III self interstitials to diffuse from the n-doped region to the p-doped region where
they kick out p-dopants to interstitial sites, where they diffuse fast. This indicates that the p-layer broadening is due to a structural effect, and that the layer thickness hardly could be further optimised by adjusting the growth parameters. This means that the broadening has to be taken into account and that an undoped spacer layer has to be introduced between the base and emitter.

In paper C, we present a SIMS profile of an HBT with this structure. The intended width of the p-doped base is here 0.1 μm, but it is broadened to about 0.3 μm. Nevertheless, with this structure we have obtained excellent device results of Zn-doped MOVPE grown HBTs. Extrapolated values for maximum oscillation frequency and current gain cut of frequency are 50 and 30 GHz respectively, at a current small signal gain of 60. (These figures have been obtained after publication of paper C, and the improvement is due to an optimised device process.) In paper C we also present a SIMS profile of an HBT structure where the base layer is grown at low susceptor temperature. This facilitates high Zn incorporation and simultaneously inhibits the profile broadening. The total width of this base layer is about 0.2 μm. Unfortunately, no devices with this structure have been evaluated.

![Graph showing atomic conc. vs depth](image)

Figure 13. Interdiffusion between Zn and Fe in InP, determined with SIMS. The intended depths of the doped regions are indicated with arrows. The concentration of Fe in the Zn doped region is severe, while the diffusion of Zn into the Fe doped region is more enhanced than expected, but still not detrimental.
In recent years C doping of GaAs/AlGaAs HBT base layers has become dominating, due both to the ability to obtain dopant concentrations of $1 \times 10^{20}$ cm$^{-3}$ and the extreme low diffusion ($<10^{-16}$ cm$^2$/s at 950°C). With the use of CCl$_4$ as C precursor, HBTs operating above 100 GHz has been grown$^{149}$. However, for InP HBTs Zn doping is still used and also here diffusion of Zn into Si doped layers has been observed$^{150}$.

There are also other areas where dopant interdiffusion is of large importance for device performance. In structures for high frequency InP lasers, an Fe-doped semi-insulating layer is usually grown around the laser mesa to confine the current. Here diffusion of Zn from the p-contact into the Fe-doped layer has been announced. This diffusion is believed to deteriorate the semi-insulating properties of the current blocking layer as Fe acts as a deep electron trap in InP and hence could not stop a hole current. The diffusion has proven to be minimised by introduction of an n-doped spacer between the Zn and Fe doped layers$^{151}$. However, from a SIMS profile we can show that the diffusion of Zn into the Fe doped region is of minor importance (Fig. 13). Nevertheless, the semi-insulating properties of this structure are considerably improved by an n-doped spacer. This is easily explained by hindered hole injection from the p-doped layer$^{152,153}$. The high Fe concentration in the Zn doped layer might either be due to diffusion or to a memory effect.

**Impurities and defects.** One important limitation of the crystal quality is the amount of impurities. Impurities are introduced from the precursor chemicals, from leaks and from residuals desorbing, e.g. from unpurged volumes and walls in the gas supply system. High purity material could be grown only if all these sources are eliminated, but the material quality is also sensitive to the growth conditions. Some common methods to characterise and prove high purity is Hall measurements, which gives the concentration of electrical active dopants and their mobility, and low temperature PL, which gives characteristic luminescence peaks from impurity levels in the bandgap.

For GaAs a lowest donor concentration of about $1 \times 10^{14}$ cm$^{-3}$ and an electron mobility of 200 000 cm$^2$/Vs at 77 K have been obtained$^{154,155}$. Si, Ge, Zn, and C have been identified as impurities. Both TEGa$^{154}$ and TMGa$^{155}$ have been used, the incorporation of C from the Ga-precursor might be reduced by using the former, but no significant difference in overall purity was seen. This indicates that residual impurities in the system and the precursors, and not the growth kinetics limits the layer purity. However, a low reactor pressure, and a carefully optimised susceptor temperature and group V partial pressure or V/III ratio, seems to be important for low impurity incorporation$^{155,156}$. The purity of the precursors does also vary between the bottles$^{155,156}$. In AlGaAs the incorporation of C from the methyl precursors increases with the growth
temperature and the Al content, and the C acceptor density could reach the \(10^{17}\) cm\(^{-3}\) level for an Al content above 80\%. With the use of trimethylamine alane and TEGa the C incorporation can be reduced about an order of magnitude\(^{63,64}\).

For InP a 77 K mobility of 130 000 cm\(^2\)/Vs and a donor level of \(3\times10^{14}\) cm\(^{-3}\) have been obtained\(^{157}\). C is not an important impurity, and hence the V/III ratio or group V partial pressure is of minor importance for the layer purity. However, Si has been identified and the Si concentration increases with temperature, while a low growth temperature is preferable\(^{117}\). For InGaAs lattice matched to InP an electron concentration of \(4\times10^{14}\) cm\(^{-3}\) and a 77 K mobility of 80 000 cm\(^2\)/Vs has been obtained\(^{157}\). In this case of not perfectly lattice matched layers it is probable that scattering due to lattice imperfection is more deleterious for the mobility than impurity scattering.

There are two main sources for dislocations in the epitaxial layer. Either they propagate from existing dislocations and micro defects in the substrate\(^{159}\), or they occur during growth due to lattice misfit between layers\(^{140}\). In both cases they might deteriorate the device performance\(^{25}\). One way to hinder dislocation propagation is to introduce a strained SL. Hence the total thickness and the thickness of each layer in the SL have to be below the critical thickness for misfit dislocations to occur\(^{160}\).

![Figure 14. SEM micrograph of a cross section of an oval defect. An AlGaAs/GaAs superlattice is introduced and stain etched to show how growth propagates. It is obvious that the defect origin is at the substrate surface.](image)

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One type of large defects in GaAs/AlGaAs is the oval defect, consisting of stacking faults in the four \( \{111\} \) planes, usually originating from the substrate surface\(^{161}\). They occur at low V/III ratios and at high temperatures, i.e. under As poor conditions\(^{120}\). This indicates that Ga clusters, As vacancies, or other microscopic defects are responsible for their formation. We have found that they more easily occur when the reactor has been out of operation for some weeks, which suggests that impurities from the tubing settle on the substrate surface. Furthermore, AlGaAs layers with high Al contents are most sensitive for oval defects, which might depend on the existence of aluminium oxide complexes. Fig. 14 shows a stain etched cleavage through an oval defect in an AlGaAs/GaAs SL.

**Non-planar growth.** Growth on masked and non-planar substrates is a relatively new area of MOVPE development. Most work has been made on fundamental investigations, and on efforts to grow quantum wires and quantum dots. Another related field is regrowth around mesa structures for embedding of devices. The common question to be answered in this field is how three dimensional growth geometries could be predicted and controlled.

Slow growing planes determines the final crystal shapes in convex geometries, and fast growing planes in concave geometries\(^{162}\). Hence the relative growth rates between different planes have to be known and preferably also controlled by changes in the process parameters or chemical reactions. As the reaction probability and surface diffusivity depend on the precursors, the composition of alloys is difficult to maintain when the geometry changes\(^{163,164}\).

Quite promising results have been obtained for growth of quantum wires and quantum dots, i.e. zero- or one-dimensional structures of low bandgap material surrounded by high bandgap material. Slow growing \( \{111\} \) and \( \{110\} \) planes have been used to limit pyramids, with low gap material embedded in the top, grown in mask openings\(^{31}\). The changes in relative growth rate between different lattice planes for changes in growth conditions\(^{32}\) and chemistry\(^{33}\) have also been used to control low dimensional structures. One problem is that the wires or dots grown hitherto are at least 0.1 \( \mu \)m apart, limited by the lithography. This distance is too long to fabricate efficient devices, e.g. quantum wire lasers, which need close packing of the wires\(^{165}\).

To realise the advanced optoelectronic integrated circuit (OEIC), designed in three dimensions, it is necessary to with precision handle etching and subsequent regrowth. A high performance etch method is reactive ion etch (RIE), which is more easy to reproduce than common wet etching. It is also anisotropic, and could hence produce nearly rectangular mesa profiles\(^{166}\). This makes it advantageous for high yield fabrication of OEICS. However, the etch is performed by bombardment of a surface with reactive ions, and hence
the surface becomes amorphous and losses volatile group V species\textsuperscript{167}. The surface damage has a depth of a few tenths of a nanometre and might be overcome, e.g. by annealing in a group V atmosphere\textsuperscript{168} or a shallow wet etch.

The most important device application for advanced regrowth is embedding of laser mesas with material of high bandgap and high refractive index. This will confine the optical mode and electrical current to the active region. For lasers operating at extremely high frequency (around 10 GHz) the capacitance of the regrown layer will limit the performance. Hence the layer should be thick and semi-insulating in order to reduce the capacitance. Furthermore, if the regrowth properties could be accurately controlled, a new era of three dimensional design of \textsc{oeics} could begin, e.g. involving monolithic integration of \textsc{hbt}s and advanced lasers.

By the use of hydride \textsc{vpe}, nearly perfect regrowth morphologies can be obtained. The embedding is planar, linearised with the top of the mesa, and selective, i.e. it does not cover the dielectric mesa cap\textsuperscript{169}. \textsc{vpe} also enables growth of Fe doped semi-insulating InP\textsuperscript{170}, and hence it is suitable for embedding of laser mesas. High performance high frequency lasers fabricated by \textsc{movpe} and regrown by hydride \textsc{vpe} have also been presented\textsuperscript{171}. However, regrowth with \textsc{movpe} has proven to be difficult, mainly because problems with growth covering mesas higher than a few micrometers, but highly desired, due to the wide possibilities in \textsc{movpe} to vary the structure and composition. Reports in this field were sparse in 1990, when we started our development, and most early reports focused on the importance of the mesa shape for planar regrowth\textsuperscript{172-174}.

In paper \textbf{D} we present an investigation of regrowth properties of InP around 1 - 4 μm high and 1 μm wide mesas, formed with \textsc{rie} and oriented along the \{110\} direction on (001) substrates. The samples were grown with doped marker layers, cleaved perpendicular to the mesas, stain etched and examined in \textsc{sem}. We could hence temporally resolve the propagation of growth. Reproducible regrowth without overgrowth is obtained at high substrate temperature (= 680°C) and low mesa height (< 2.5 μm). A low reactor pressure (= 100 mbar) does also to some extent improve the results. Guided by the marker layers we found that the overgrowth is due to extensive depositions on the \{110\} mesa walls, which give rise to nucleation near the top of the mesa. For high temperatures the growth rate on the mesa walls decreases in accordance with an investigation on GaAs\textsuperscript{175}, and for low mesas the wall depositions do not grow so large that overgrowth occurs.

Encouraged by the success of \textsc{vpe}, where the chemicals reaching the substrate are metal chlorides\textsuperscript{169}, we introduced CCl\textsubscript{4} into the reactor to provide Cl to the growing surface in an effort to improve the regrowth properties. The most astonishing results are presented in paper \textbf{E}, where we show that perfect embedding without overgrowth is routinely obtained.
around high mesas (up to 5.5 μm) oriented along the [110] direction. Changing the process parameters influences the overall growth behaviour, but does not deteriorate the selectivity. Good regrowth morphologies were obtained at temperatures as low as 580°C. Introduction of CCl₄ lowers the growth rate but does not influence dopant incorporation or semi-insulating properties⁸,¹⁷⁶.

A more complete investigation of the mechanisms of InP growth on non-planar substrates is presented in paper F. Here the mesa orientation as well as fundamental reactor parameters are varied and results from growth with and without CCl₄ addition are presented. For growth without CCl₄ a relatively high surface diffusion rate is observed on the P faced {111}B planes, but also a low probability of desorption from the plane, which results in substantial nucleation. This is in contrast to growth of InGaAs and GaAs, where the {111}B planes are reluctant to nucleation. A high reactor pressure results in low reactant diffusivity, and hence a growth morphology not restricted to exact lattice planes. At a high susceptor temperature the desorption probability increases, especially for P species. The nucleation becomes minor on the In faced {111}A planes, where P is weakly bound, and uncontrolled on other planes. The influence of variations of the V/III ratio and growth rate is limited. For most reactor parameters it is difficult to find a specific growth rate for each lattice plane. This indicates that the growth behaviour is determined by the crystal geometry and the supply of reactants, either by surface or gas phase diffusion, rather than by surface reaction probabilities.

However, when CCl₄ is added, the lattice plane specific growth rates are nearly constant and independent of sample geometry. The growth behaviour is hence most probably determined by surface reactions and not by the supply of reactants. When CCl₄ is added, growth is totally reluctant on the {111}B planes, which indicates that In either desorbs from the surface (in the form of volatile InCl) or is sterically hindered to nucleate by adsorbed Cl. At high reactor pressure the nucleation on high index planes is enhanced, probably due to low surface mobility. At a high effective V/III ratio competition between P and Cl about the group V lattice sites could explain the somewhat changed Cl influence on the crystal shapes. A completely different growth behaviour occurs when PH₃ is substituted by the less toxic TBP while CCl₄ is added (Fig. 15). Then growth is non-existing on the {111}B planes and slow on the {111}A planes, which give rise to deep grooves emanating from the mesa base. Acceptable regrowth morphologies do only occur for low mesas (< 2 μm).
Figure 15. Growth of InP around 4 μm high mesas formed on (001) oriented InP substrates. TBP was used instead of PH₃ as P precursor, the growth temperature was 580°C, the reactor pressure 100 mbar, the V/III ratio 70 and the Cl/In ratio 0.1.

For all growth conditions a higher growth rate on the walls of mesas oriented along the [110] than along the [-110] direction is observed. This is most probably due to the bonding configuration, where the growth rate limiting group III atoms are bound perpendicular to the [110] but parallel to the [-110] oriented mesa. Atomic steps will propagate out from the former mesa, but just be filled up parallel to the latter and eliminated. It is also obvious that the mesa has to be oriented along the [110] direction to obtain reproducible and well-behaved regrowth morphologies.

A laser with the mesa formed by RIE along the [110] direction, surrounded by semi-insulating InP grown by MOVPE is presented in paper G. Here the laser mesa is low (2.5 μm) and no CCl₄ was added. No wet etch was used to remove the surface damage from the RIE or to optimise the mesa shape. The laser exhibits a threshold current of 30 mA, a 3 dB bandwidth of 7.9 GHz at 10.5 mW optical power, and a wavelength of 1.46 nm. These data are comparable with those obtained with hydride VPE. Unfortunately, no optimised lasers with semi-insulating layers grown with addition of CCl₄ have yet been evaluated.
CONCLUSIONS AND SUGGESTIONS FOR FUTURE DEVELOPMENT

The recent years of intensive work to improve and verify the MOVPE process have made it an important tool for epitaxial growth of most III-V devices. The basic problems with gas handling have been solved by development of accurate controllers for mass flow and pressure and construction of high performance vent-run valves. Novel designs of both single and multiple wafer reactors provide the required uniformity for most devices of thickness, doping distribution and alloy composition. The possibility to grow abrupt heterointerfaces is facilitated by the design of the gas handling system, the reactor geometry and an optimised sequence for valve switching, while the abruptness of doping profiles in addition is strongly dependent on the device structure and the choice of dopant. Nevertheless, reasonable choices of dopant elements and precursors exist for most applications. A purposeful work on precursor purification and development of new precursors has improved the crystal quality and less toxic alternatives to AsH₃ and PH₃ have been presented.

However, there are still some problems that remain to be solved. The unstable supply from the solid TMIn source is the main reason for irreproducible growth of ternary and quaternary layers lattice matched to InP, and frequent calibrations are necessary. Despite that some solutions have been proposed none is without objections. The layer uniformity might be difficult to improve, since the limiting factor most probably is the diffusion rate of the reactants through the gas phase. Today the obtained uniformity is sufficient, but for extremely large scale production of large area devices entirely new concepts might be needed. For growth of HBTs based on GaAs carbon has proven to be the ultimate choice as base dopant, but for HBTs grown on InP Zn is still used and there is a lack of a less diffusive base dopant. Also interdiffusion between Zn and Fe might be a problem in InP based lasers with semi-insulating cladding. Growth of high purity material has failed for the case of Al containing compounds, where the C incorporation is deleterious. New precursors have been tried, and the C doping level has been lowered an order of magnitude, but still the C doping is too high at high Al concentrations. Here development of new precursors, which are totally free of C, or at least do not provide any C to the growth surface are needed. The abruptness of heterointerfaces where the group V element has to be changed is deteriorated by memory effects, and a new design with a separated gas inlet might to some extent overcome this problem. Despite that TBAs and TBP are powerful less toxic alternatives to AsH₃ and PH₃ for most applications, they are not suitable in all cases, e.g. InP regrowth around high mesas with the use of TBP seems to be difficult. This indicates that other alternatives to the hydrides will be requested.
The need of more complicated device structures, designed in three dimensions, will soon raise the demand for a much better control of etching and growth on patterned and non-planar substrates. For semiconductor lasers the possibilities of several consecutive steps of etch and growth have been widely used to realise three dimensional structures, not only for embedding of the mesa and gratings\textsuperscript{177}, but also for e.g. butt joint of the active layer with a passive waveguide\textsuperscript{178}. Similar advanced design methods will certainly become more common also in electronics. An HBT with two growth steps in order to improve the structure for high speed operation has been reported\textsuperscript{179}, as well as an FET with selectively grown source and drain\textsuperscript{180}. This development will become significant only if the regrowth morphologies can be predicted and accurately controlled. There is hence a need of a theory that can explain the experimental results and give an understanding of the combined effects of surface kinetics and diffusion, which determines the final crystal shape. In order to provide this understanding, the chemical reactions have to be understood in detail.

The growth process is complicated and is not easily monitored as in e.g. MBE, where the ultra high vacuum conditions allow in situ surface analysis, e.g. by RHEED. Some examination of reaction by-products and simulations based on these and chemical data for the reactants have been made for MOVPE. An exact knowledge of the surface reactions, which determines the incorporation of impurities, formation of defects, and growth behaviour on non-planar substrates, is still lacking. Some surface analysis methods that might provide information about the surface kinetics have been presented. Reflectance difference spectroscopy is a technique relying on the polarisation dependence of light reflected at the crystal surface. It is sensitive to step formation and surface coverage and it can be used also at atmospheric pressure\textsuperscript{181}. Other methods are in-situ X-ray scattering\textsuperscript{182} and infrared Fourier transform infrared spectroscopy\textsuperscript{183}, for monitoring of surface reconstruction and precursor decomposition reactions, respectively. These might be tools to obtain experimental data for further simulations and predictions of the growth behaviour on non-planar substrates under the special conditions that are present in an MOVPE reactor.
REFERENCES


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Design and Performance of a New Reactor for Metal Organic Vapor Phase Epitaxial Growth of Extremely Uniform Layers

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ABSTRACT

We have designed and built a new metal organic vapor phase epitaxy reactor for single wafer, low pressure operation employing a very large width-to-height aspect ratio to meet the demands on uniformity over a large area. The uniformity obtained under various growth conditions have been mapped using high resolution analytical techniques capable of sufficient accuracy in the determination of the significant material parameters. Doping uniformities are used to accurately evaluate temperature gradients across the susceptor. The results compare favorably with expectations, thereby confirming the design rules presented in the paper. Thickness uniformities of better than ±1% over full 50 mm diam are obtained and compositional deviations are within ±0.3 atomic percent over 40 mm diameter for all components in the AlGaAs as well as in the InGaAsP system. Over the same area the wavelength uniformity of quaternary InGaAsP is better than ±1 nm at λ = 1.56 μm. These numbers represent some of the best uniformity data ever reported.

Metal organic vapor phase epitaxy (MOVPE) has been established as a major production technology for device structures in III-V materials with applications in optoelectronics as well as high speed electronics. Hence, increasing attention has to be paid to establishing high yield epitaxial processes. A prime requirement is then the achievement of high uniformity in layer thickness, composition, and dopant concentration over a large area. Furthermore, tolerances are steadily decreasing as the epitaxial structures become more complex and more intimately related to device performance. This latter aspect also forces device research and development work to carefully consider the uniformity problem. The demands vary somewhat for different components. It is not unusual that a thickness uniformity of ±1% is required, particularly in quantum well structures. For typical thicknesses this corresponds to less than one molecular monolayer, representing an ultimate challenge for the crystal grower in terms of average layer thickness and growth surface morphology. In optical devices such as lasers the critical parameter is the wavelength uniformity where deviations of at most a few nanometers will be acceptable. Keeping lattice mismatch requirements of about ±500 ppm in mind, this translates to a compositional uniformity of ±0.005 or less for several constituents. A doping uniformity of about ±1% is required in order to keep the channel conductivity in field effect transistors uniform enough to allow fabrication of large scale integrated circuits.

It is obvious that demands such as those just mentioned are extremely difficult to fulfill simultaneously for all layers that may be present in a complicated structure. Large improvements in uniformity have recently been accomplished through the introduction of substrate rotation. However, stringent performance tests are still sparse, particularly for the InGaAsP/InP materials system. It is important to note that evaluation of layer quality and uniformity with the accuracy required is a tedious task, and in most cases necessitates the use of advanced structures and/or nonconventional analytical methods. This is particularly true for the thickness and doping measurements where the use of scanning electron microscopy or surface profilometry and coarse Hall measurements, respectively, do not meet the requirements. In addition, measurements ought to be made on structures that resemble the device structures as much as possible. Many previous reports have neglected these important aspects.

In recent years there has been an increase in theoretical papers on flow patterns and gas distribution in horizontal MOVPE reactors, based on detailed models and calculations made in powered computers. Propositions of new, optimized reactor configurations for uniform growth have also been made. However, the comparison with experimental uniformity data, obtained with accurate methods, is largely insufficient. In addition, such a comparison would most likely reveal large discrepancies due to poorly modeled nonidealities such as vapor phase preactions, geometry variations and edge effects. Since a quantitative modeling of these phenomena may still be far away, there seems to be a definite need for qualitative but detailed guidelines for reactor design.

The purpose of this paper is to report on the design and performance of a single wafer, horizontal MOVPE-reactor for low pressure operation and with a rotating susceptor which employs a very large aspect ratio to meet the demands on uniformity over large area. The uniformity obtained under various growth conditions is mapped with techniques which can sufficiently resolve small differences in the significant parameters. We also show that the results can be qualitatively well understood from the gas flow models.

Reactor Design

Gas flow models.—Early investigations of gas flow in horizontal reactor cells were made using light scattering particles such as TiO₂ (1, 2). In these works a double screw flow pattern was observed at high pressure and low flow rate,
i.e. where free convection flow dominates over forced convection. A particle freely, apparently stagnant layer with a thickness proportional to the inverse square root of gas flow velocity was also seen near the susceptor. This observation gave rise to the stagnant layer theory. By using interference holography to monitor flow patterns, Gilling modified the ideas on the stagnant boundary layer (3). It was found that light gases such as H₂ and He had an overall laminar flow, while the flow for more heavy gases, such as N₂ and Ar, was convective and unstable above a laminar region near the susceptor. The particle free region seen in the TiO₂ experiments has later been explained as being due to thermophoretic migration of the light particles from the heated surface (4). Despite these experimental results, the analytic model for diffusion limited growth partly based on the stagnant boundary layer theory has proven to be reasonably successful in predicting the growth rate under various growth conditions (5-7). In this model a boundary layer with thickness

$$\delta = \gamma (u D_v \sqrt{\nu})$$  

is assumed to be depleted of reactants, and the growth is limited by diffusion of reactants through this layer. In the formula, D is the diffusion coefficient of the rate limiting reactive component in the gas, z is the distance along the susceptor, and v is the average gas velocity. According to the theory the growth rate is proportional to the inverse square root of the distance downstream along the susceptor. When \( \delta \) exceeds the height of the reactor cell, the growth rate will drop exponentially along the susceptor due to depletion of the rate limiting component.

The flow pattern seen in the flow visualization experiments is due to buoyancy forces, which tend to raise the hot gas and press the cold gas down. Buoyancy forces are not easy to interpret analytically, but in recent years advances in computer aided modeling in both two- and three-dimensional have focused on their influence on growth uniformity (8-10). The buoyancy forces give rise to two different phenomena. On the one hand, the longitudinal screw rolls, parallel to gas flow, which is caused by temperature differences between the hot susceptor and the cold reactor walls, on the other hand, transverse rolls perpendicular to gas flow, occurring when the gas enters and exits the hot susceptor region. The magnitude of the longitudinal rolls, which mainly affects the growth uniformity by transport of reactants from the center of the reactor to the edges (for the case of adiabatic walls) are correlated to the dimensionless Rayleigh number

$$Ra = g \rho \beta \Delta T \theta /\nu \mu$$  

where g is the gravitational acceleration, \( \rho \) the specific heat, \( \beta \) the coefficient of thermal expansion, \( \Delta T \) the temperature difference between the susceptor and the reactor ceiling, \( h \) the reactor height, \( \mu \) the dynamic viscosity, and \( \alpha \) the thermal conductivity (3). Convection will occur when \( Ra \) exceeds 2056, but buoyancy driven rolls may be present also for lower \( Ra \).

The transverse rolls, which will result in recirculation at entrance to and exit from the susceptor and hence to memory effects and rough interfaces between layers of different material compositions (9, 11), are correlated to the ratio

$$Gr/Re^\alpha = g \mu \alpha /\nu \rho$$  

where Gr is the Grashoff number, Re is the Reynolds number, and T is the average gas temperature. Minimal transverse buoyancy effects are obtained for \( Gr/Re^\alpha < 0.3 \).

General design considerations.—From the analysis of gas flow it is clear that the vortices caused by buoyancy forces have to be suppressed to obtain good uniformity and sharp interfaces. This is obtained when the Ra-number and the Gr-Re^\alpha-ratio are low, which means low cell height and high gas velocity (obtained at low pressure and high flow rates). It also strongly favors hydrogen as a carrier gas. Given a susceptor of a given size, with high or low mass flow, the Ra number will be low enough that longitudinal screw rolls should never occur. The theory of diffusion limited growth demands that the height of the boundary layer is less than the cell height for any position on the wafer. This is equal to keeping the cold gas fingers observed by Giling (3) long enough, which again is achieved at high gas velocities. The impinging cold gas fingers have recently been theoretically analyzed (12, 13) and it is shown that it preserves reactants for downstream deposition and will hence contribute to the uniformity. The gas flows along the flow axis. In the perpendicular direction, a parabolic velocity profile will develop which can be interpreted as a thicker boundary layer at the edges than in the middle, resulting in a correspondingly smaller growth rate (6, 10). It is therefore important to make the reactor cell much wider than the wafer in order to eliminate the influence of the side walls. This in turn requires attention to the gas inlet stream, which must be thoroughly mixed and redistributed uniformly enough over the reactor cross-section area to allow laminar flow to be established before the susceptor is reached. This is typically accomplished by some kind of obstacle at the inlet which prevents a jet stream effect (14, 15). It may also be combined with a zone of exponential expansion at the entrance of the reactor cell (16).

When designing the reactor and flow parameters, a number of issues apart from the gas flow modeling are very important. Substrate temperature uniformity to better than ±1°C is required. The susceptor should therefore be large enough, and the wafer placed as close to the susceptor as possible, that temperature edge effects could be neglected. This consideration determines the reactor width. Susceptor rotation to average nonuniformities in the heating field would clearly be beneficial. Furthermore, the susceptor length in front of the wafer should be sufficient to allow a reasonably stable, vertical temperature gradient to be established. Second, it must also be possible to choose the growth parameters so that reasonable growth rates (about 1 µm/h) are reached while operating at convenient source conditions. Efficient use of chemicals is obviously desired, and in this case it is probably most important with respect to the group V materials. Unused group V chemicals cause unnecessary depositions on the reactor walls as well as strain on particle filters and gas scrubbers. In addition, large V:V:V:V ratios increase the rate of parasitic vapor phase reactions.

As to the actual choice of the reactor geometry and general growth conditions there seems to be no unique choice. Although some very good results have recently been obtained on static susceptors (17), averaging across the wafer area through susceptor rotation seems highly desirable in order to sufficiently average the modeled nonuniformities as well as nonuniformities due to imperfections in geometry or parasitic reactions. Linear averaging by spin coating has proven to be very successful in this respect (18-21) and in principle even better results should be obtainable with planetary rotation (22). Provided that longitudinal screw rolls are eliminated, further guidance is given by Eqs. [1] and [3] in the form

$$\sqrt{\gamma (u D_v \sqrt{\nu})} < 0.3 \sqrt{T} v^\alpha /\mu$$  

where \( z_{end} \) is the distance from the leading susceptor edge to the downstream wafer edge. The condition limits the allowed area in the h-v-plane and effects of changing flow or pressure can easily be established. Applying the less fundamental condition that the lowest possible gas velocity should be used to efficiently crack the group V molecules, the available parameter space is further reduced. The \( v_{max} \) obtained in this way is only weakly dependent on pressure (\( -p^{1/2} \)) and \( h \) becomes independent of pressure. Hence, we conclude that pressure is not a very important parameter as long as it is in the low pressure regime. The remaining parameter, the gas flow, can be chosen to give a convenient growth rate, i.e., typically a group III Molar fraction of about 10⁻⁴ for a flow of 20 standard liters per min (SLM), which settles the design. When analyzing the results of such a calculation one must be aware of the great uncertainty in many of the input parameters. On the other hand, the effect of any variable within a factor of two is not expected to significantly alter the performance of the reactor and relative comparisons should be quite reliable.
Specific features of our system.—We have designed and built a MOVPE system equipped with a double cell quartz reactor for low pressure operation. The inner cell has a rectangular cross section with a large aspect ratio (width to height = 12.5:1.3 cm) and a rotating, RF heated, disk-shaped graphite susceptor which accepts both 50 and 75 mm diameter wafers (Fig. 1). A cell height of 1.5 cm in combination with a carrier flow of 20 SLM at 100 mbar roughly satisfies the conditions given in the previous paragraph for a 50 mm wafer. To obtain uniform lateral gas distribution, the incoming gas stream is forced through a plate with several small holes. The outer cell is purged with a hydrogen flow of about 3.5 SLM and the pressure is kept the same in both inner and outer cells. No significant deposition in the outer cell had occurred during the first 100 runs. The vent-run manifold is kept at atmospheric pressure, which necessitates small valve volumes to avoid memory effects (23). The three way switching valves therefore have an unimpeded volume less than 0.1 cm³. A pressure control device is applied after the vent-run manifold in order to keep the same pressure in all organometallic bubblers, which enables good homogeneity in ternary and quaternary layers (24). One of the gas channels is also equipped with an ultrasonic organometallic concentration meter (25). In total there are seven organometallic channels and eight gas channels, distributed on four gas sources. Palladium diffused hydrogen is used as carrier gas.

Structures optimized for different measurements have been grown in this reactor. Source chemicals were trimethylgallium (TMG), trimethylaluminum (TMA), trimethylindium (TMI), arsine, and phosphine. Silane and dieethylzinc (DEZ) were used as n- and p-type dopant precursors, respectively. Susceptor rotation was 130 rpm, which corresponds to between 2 and 10 revolutions per monolayer. Growth temperature, measured with a thermocouple in the susceptor, was fixed to 700°C for GaAs and 625°C for InP. The temperature at the inner cell ceiling is high, and some deposition occurs, especially at low flow rates.

Uniformity Evaluation Techniques

Highly accurate determinations of the thickness variation over the wafer was achieved through the use of high resolution x-ray diffraction (XRD) to measure superlattice periods. The equipment (PHILIPS) employs a four crystal x-ray monochromator and a four-circle goniometer with ±25 mm x-y-motion capability. The structure typically consists of either 10 periods of 20-50 nm length consisting of alternating AlAs/GaAs or, for InGaAsP/InP layers, 10 periods of 100-150 nm length. The error in this determination is estimated to be less than ±10% and ±0.1% in relative thickness. The same equipment is used to measure lattice mismatch on InGaAsP/InP.

Optical properties were checked by photoluminescence. Measurements at 4 K with Ar-laser excitation and a 1.26 nm monochromator, which provides an accuracy of ±1 meV in determination of luminescence energy, was used to measure the Al content in thick Al,Ga,_,As layers and the exciton recombination energy in Al,Ga,_,As/GaAs and In,Ga,_,As/InP quantum well structures. Quaternary InGaAsP bulk layers were characterized using a novel novel room temperature photoluminescence wafer mapping equipment, utilizing a fiberoptic approach with GaAs-laser excitation and a spectrum analyzer which provides a resolution of about ±1 nm.

Measurements of dopant uniformity were carried out on processed Hall devices using the Hall-van der Pauw method at room temperature. The device structure was a mesa etched Greek cross (100 × 100 μm²) with lithographically defined contacts. Dopant concentrations were determined to within ±1%.

We have chosen to display the uniformity data as a function of radius across the wafer from the center to the edge. This has enabled us to carry out accurate measurements at high resolution within a reasonable time. Full circular symmetry was verified through automated mapping routines for the x-ray (100 points) and photoluminescence (400 points) measurements. The resulting slightly larger spread in data in these measurements could be attributed entirely to the somewhat lower resolution necessary in the mapping mode. The full mapping results will be presented elsewhere.

Experimental Results

Main growth conditions.—A series of Al,Ga,_,As superlattices were grown in order to investigate the influence of reactor pressure, total gas flow, and molar fraction of the reactants on the growth rate uniformity for wafer by wafer. In Table 1, the calculated Gr/Re²-ratios, Ra-numbers, and boundary layer thicknesses for front edge, middle, and back edge of the 50 mm diameter wafer are displayed for the combinations of gas flow and reactor pressure used in the experiments. For all combinations the Ra-number is well below the critical value of about 2000 for fully developed longitudinal rolls. This is primarily due to the fact that hydrogen was used as a carrier gas, but also to low cell height and low reactor pressure. Gr/Re² varies around 0.3, which is the critical value for appearance of transverse rolls. The boundary layer thickness is for most points greater than 0.2 cm and indicates that the growth rate will drop exponentially with the distance along the susceptor, z (z is here set to 0 at the entrance edge of the susceptor). Figure 2 shows the growth rate uniformity for three different reactor pressures at the same gas flow rate (7.0 SLM) and the same molar fraction of the reactants. The uniformity within the measurement errors is the same for the samples grown at 50 and 100 mbar. At 200 mbar the decrease of the growth rate towards the edge is more pronounced. This is probably due to the high value of Gr/Re²

<table>
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<tr>
<th>Gas flow SLM</th>
<th>Pressure mbar</th>
<th>Gas velocity m/s</th>
<th>Gr/Re²</th>
<th>Ra</th>
<th>Boundary layer thickness cm</th>
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<td>0.31</td>
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<td>1.24</td>
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</tr>
</tbody>
</table>

Table 1. Gr/Re²-ratios, Ra-numbers, and some boundary layer thicknesses for front, middle, and tail of a 50 mm wafer, calculated for the combinations of gas flow rate and reactor pressure used in the experiments. Mean gas temperature was assumed to be 625 K and the temperature difference between susceptor and reactor ceiling 300 K. The values of gas constants are from Ref. (3).
for that sample, which indicates backflow and increased parasitic reactions at the susceptor edge. The boundary layer thickness is the same for all samples in this series, which, together with only small buoyancy perturbations, explains the overall growth rate constancy (5, 9).

The uniformity differences obtained when the reactor pressure and gas flow through the organometallic bubblers were held constant, while the carrier gas flow and, hence, the molar fraction of the reactants, were changed, are shown in Fig. 3. In this case both GrRe and the boundary layer thickness are changed. For the samples grown at 14 and 7.0 SLM, the uniformity remains nearly the same, but at the very low flow rate of 3.5 SLM the growth rate is significantly increased towards the wafer edge. This is attributed to strong depletion, which cannot be linearly averaged by substrate rotation. For low gas flow, the GrRe also exceeds the critical value, and in Fig. 2 we saw a decrease of thickness towards the wafer edge for this case. This may moderate the effects of the exponential decline. The average growth rate seems to follow a square root dependence on carrier gas flow, as expected in diffusion limited growth (5).

In order to isolate the influence on uniformity of the molar fraction of reactants in the gas, a series of samples were grown on 75 mm substrates (Fig. 4). All samples were grown at a reactor pressure of 100 mbar. Two samples were grown at a total gas flow of 7.0 SLM and the molar fraction was halved in one of them by halving the flow through the organometallic bubblers. To compensate for the low growth rate at the low molar fraction, the growth time was doubled. The third sample was grown at a total flow rate of 14 SLM with the higher flow rate through the bubblers and at the shorter growth time. The sample grown at high flow rate is the most uniform (±2.6% over 30 mm radius), while the sample grown at reduced molar fraction at 7.0 SLM is significantly more uniform (±3.7%) than the one grown at high molar fraction (±6.6%). Parasitic reactions have proven to affect the composition uniformity (26, 27) and it is also probable that they affect thickness uniformity in this case. For the sample grown at a carrier gas flow of 14 SLM the uniformity has been further improved due to the thinner boundary layer.

Figure 5 compares two samples grown under similar conditions (carrier gas flow 14 SLM and reactor pressure 100 mbar). One of them is grown on a 50 mm wafer and the other on a 75 mm wafer. The thickness uniformity is about ±1% over a 20 mm radius for both the samples. The relative thickness variation of the AlAs and GaAs layers in the superlattices is later shown to be less than 0.6%, which is smaller than the overall uniformity discussed here. The growth rate is enhanced at about 5 mm from the wafers edge, which may be explained by surface migration of material from the heated susceptor to the colder substrate.

AlGaAs structures.—In order to investigate the composition variations in AlGaxAsy, a 0.5 µm thick layer was grown at a carrier gas flow of 7 SLM, a reactor pressure of 100 mbar, and high molar fraction of reactants. The aluminum content is determined from the energy of the bound exciton photoluminescence at low temperature (4 K), a method which gives an error in x of about 0.002 (28). Due to the small lattice parameter difference between AlAs and GaAs, XRD is not sufficiently accurate in this case. The data is presented in Fig. 6 and shows a monotonic increase in aluminum content from 0.365 to 0.371 over a
35 mm radius while the edge effect is restricted to at most 2 mm of the wafer edge. Compositional variations are due either to temperature gradients over the wafer or to different diffusion coefficients of the reactants. This case is mainly diffusion limited and we will show below that the difference in the diffusion coefficients of TMG and TMA are likely to give rise to the composition gradient.

A structure which is extremely sensitive to variations in both layer thickness and aluminum content is the narrow quantum well with high barriers. A 1.2 nm thick GaAs quantum well with $\text{Al}_x\text{Ga}_{1-x}\text{As}$ ($x = 51\%$) barriers was grown in order to determine the total influence of uniformity in gallium to aluminum ratio and in layer thickness. Quantum well luminescence energy increases from 1.961 to 1.967 eV from the middle to the edge of the 50 mm wafer (Fig. 7). This is also expected from the coincidence of higher barriers and narrower wells towards the edge. The full width at half maximum of the photoluminescence peaks were 10-12 meV, which indicates a reasonable interface quality.

Figure 8 shows the normalized dopant distribution of Si- and Zn-doped GaAs layers grown on 630 μm thick semi-insulating 75 mm wafers at 100 mbar and a carrier gas flow rate of 7 SLM. Si incorporation from silane is a kinetically governed process and is strongly enhanced at higher temperatures (29). Zn incorporation from DEZ is, on the other hand, decreasing at higher temperatures (30). By comparing dopant distribution of Zn and Si over the wafer, an estimation of the acceptor temperature profile can be made by two independent measurements with minimal influence from variations in gas composition and differences in diffusion coefficients. The small change in local $V_\text{III}/V_\text{II}$ ratio due to a temperature gradient of a few degrees would be insignificant with respect to dopant incorporation. In this case, the increase of the acceptor concentration for the Zn-doped sample is about 18% from a radius of 20 mm to the edge of the wafer, which corresponds to a temperature fall of about 1.5 K. For the Si doped sample, the donor concentration decreases 10% for the same distance, which corresponds to a temperature fall of about 2.0 K. For the inner 20 mm radius the dopant profiles are only slightly diverging, which indicates a temperature gradient of a few tenths of a degree. The accuracy in determination of the temperature variation is mainly limited by the errors in activation energy and the uncertainty in estimation of the depletion of the dopant precursors in the gas phase. The fact that the two measurements give coinciding results indicates that the determination of the temperature profile is reasonable within one degree or less. A stronger gradient was observed for Si-doping at a higher carrier gas flow rate. This is an indication that the temperature gradient is primarily due to cooling by the gas or, equivalently, to a short susceptor entrance length.

**InGaAsP/InP structures.**—Growth of ternary InGaAs and quaternary InGaAsP layers lattice matched to InP is complicated by the large change in lattice constant for a small change in composition. The demands on layer uniformity are stringent, both in terms of lattice match and in bandgap. Furthermore, the growth process is more complex than in the AlGaAs case, making it more difficult to optimize the growth parameters with respect to uniformity. All growths of InP based layers were performed at nonoptimized conditions (i.e. midpoint calibration only) with a carrier gas flow rate of 7 SLM and a reactor pressure of 100 mbar on sulfur doped InP substrates.

The variation of lattice mismatch and hence the Ga/In ratio measured with high resolution x-ray diffractometry for an In$_x$Ga$_{1-x}$As layer lattice matched to InP, is shown in Fig. 9a. The Ga content $x$ is calculated, assuming coherent growth and Vegard’s law, for each point and the variation is within ±0.2% over a radius of 20 mm. A significant indium depletion is seen near the edge of the wafer. Further evidence for this In/Ga distribution is obtained from the 4 K photoluminescence of the InGaAs/InP quantum well,
as shown in Fig. 9b. Since the independently measured thickness variation is less than ±1% (see below) the luminescence wavelength directly reflects the barrier height and thus the Ga/In ratio.

The lattice mismatch uniformity is similar for a In$_{1.1}$Ga$_{0.9}$As$_{0.5}$P$_{0.5}$ sample with a wavelength of 1560 nm (Fig. 10b). The variation of room temperature photoluminescence wavelength shown in Fig. 10b is within ±1 nm for a radius of 20 mm. We believe that this is the best uniformity value ever reported. Near the wafer edge the wavelength peak is flattened and the peak wavelength becomes more difficult to determine. This explains the rapid wavelength shift at 22 mm radius. From calculations of $z$ and $y$ presented in Fig. 10c it is seen that both the Ga/In ratio and As/P ratio are slightly increasing towards the wafer edge, this is the reason for the excellent wavelength uniformity while the lattice mismatch is affected. This behavior has also been observed by Mirescu et al. (19). The edge effect of the computed gallium and arsenic content is obscured by the uncertainty in the wavelength determination.

Finally, thickness variations of an InP/InGaAsP superlattice with a period length of about 135 nm measured with x-ray diffraction is shown in Fig. 11. This sample has a uniformity of ±1.5% over a radius of 20 mm, which is comparable to that for an AlAs/GaAs superlattice grown under similar conditions (see Fig. 2).

**Discussion**

The dependence of carrier gas flow rate and reactor pressure on thickness uniformity of GaAs/AlGaAs structures seems to be qualitatively well understood from models for diffusion limited growth and buoyancy forces. While the latter are effectively eliminated in our design, it may be somewhat surprising that excellent uniformities were obtained also when the boundary layer thickness exceeded the cell height by a factor of two. Although this may partly be explained by uncertainty in the exact figures, it is also clear that the exponential depletion will be quite well averaged by the rotation since it is of the form $\exp (-z_0z)$, where the characteristic distance $z_0$ is proportional to the gas flow rate and of the same magnitude as the water diam for reasonably high carrier gas flows. This has been confirmed for growth of a GaAs/AlAs superlattice with nonrotating susceptor at a flow of 7 SLM and a reactor pressure of 100 mbar (Fig. 12). Here, the point where the thickness of the depleted layer, $d$, exceeds the height of the cell, $h$, is also clearly seen (at a coordinate of about 10 mm, i.e. 40 mm from the edge of the susceptor). As a result, it is possible to operate the reactor with a somewhat lower flow, thereby making more efficient use of the chemicals.

The experimental optimum apparently lies somewhere between $h < s < 2h$, corresponding to a significant reduction in gas consumption. An advantage of low gas flow rate is also a reduction of the nonuniformities induced by the cooling effect and the parabolic velocity profile in the transverse direction.

**Fig. 10.** Data for an InGaAsP layer grown on InP of a reactor pressure of 100 mbar and a carrier gas flow rate of 7.0 SLM. (a, top) Measured lattice mismatch. (b, center) Measured room temperature photoluminescence wavelength. (c, bottom) Gallium and arsenic content calculated from the measured lattice mismatch and photoluminescence wavelength.

The composition gradients are more difficult to discuss due to the complexity in reaction kinetics, premature reactions in gas phase, and differences in diffusion coefficient and, hence, in gas depletion for the different materials. Nevertheless some conclusions can be drawn from our data. The substrate temperature gradient strongly affects dopant uniformity and probably also the As/P ratio. The influence of incorporation of the group III materials is not totally clarified but of minor significance. We could show that the temperature gradient on thick semi-insulating GaAs wafers is less than 9.5 K over a 20 mm radius and about 2 K for the entire wafer, and mainly due to cooling by the gas. This implies that the temperature variation on a thinner wafer with higher heat conductivity (e.g. InP) should be less than that.

Uniformity of growth rate and group III ratios are strongly connected to the diffusion of the group III metal organics through the boundary layer (Eq. [1]) and hence their depletion. In order to further clarify the mechanisms
that control the compositional uniformity, a layer of InGaAsP was grown with a nonrotating susceptor at the same conditions as the quaternary layer presented in Fig. 10 (100 mbar, 7 SLM). The result is presented in Fig. 13. Figure 13a shows the composition along the flow. The gallium content forms a plateau at about 39% at the first 20 mm of the wafer and then it increases linearly to about 44% at the tail of the wafer. Figure 13b shows the molar composition perpendicular to flow, and here the gallium content increases towards the edges from 41 to 42.5%, the edge effects omitted. Similar tendency has also been observed by other authors (27, 31). The averaging introduced by wafer rotation is likely to give the result presented in Fig. 10c. Here, as well as in Fig. 9a for the case of InGaAsSb and Fig. 8 for the case of AlGaAs, it is clear that the incorporation of the lighter element is enhanced towards the edge of the wafer. The expression

$$\frac{dx}{x} = \frac{b^2}{2} (D_x + D_y) x \Delta t - \frac{b^2}{2} (4x \Delta t^2)$$  \[4\]

for the relation between the diffusion coefficients for the reactants $D_x$ and $D_y$, the compositional variation $dx$, variation in velocity $\delta v$ and in length coordinate $\delta z$, can easily be obtained from the basic equations for diffusion limited growth for the case when the region of depletion of reactants in the gas has reached the ceiling of the cell (i.e., $d > h$) (7). The formula shows that the reactant with the largest diffusion coefficient will be depleted faster than the other in the direction of gas flow, $x$, but also in the direction of decreasing gas velocity, i.e., towards the edge of the wafer perpendicular to gas flow due to the parabolic gas velocity profile. An estimation of the composition gradient, based on the simple assumption that the diffusion coefficient for a heavy metal organic molecule is smaller than for a light molecule, should give a result opposite to that present. A possible explanation for this anomaly is related to the decomposition of the metal organic compounds in the gas phase. The energy required to break the first metal-carbon bond is 65, 59, and 47 kcal/mol for TMA, TMG, and TMH, respectively (32) and the probability for loss of a methyl group is hence larger for the heavier metal organics. The important parameter in the expression for interdiffusion between hydrogen and considerably heavier gases is the dimension of molecules, and not their molar weight (e.g. Ref. 31)). This indicates that if the difference between the heavier and lighter metal organics in probability to lose a methyl group is large enough, the relation between their diffusion coefficients will change and the molecule with the heavier metal atom will be the fastest depleted. This will explain the increase in Ga/In-ratio both perpendicular to and along the flow. The formation of reactive complexes (33) is another possibility. This will be a relevent explanation only if atoms of the lighter metals tend to nucleate in larger complexes with smaller diffusion coefficients than the heavier metals. Depositions in the reactor ceiling (30) and formation of stable complexes (26), which both will result in loss of the least stable compound, has been proposed as an explanation of the depletion of indium along the flow, but this may not explain the Ga/In-profile perpendicular to flow. Nevertheless, the presence of parasitic reactions is indicated by the increased thickness uniformity at lower molar fractions observed for AlGaAs/SbAs (Fig. 4). More work has to be carried out to elucidate the detailed nature of these parasitic reactions.

The phosphorus gradient, which in fact gives rise to the wavelength uniformity in the quaternary layer, cannot be explained by the diffusion relation above since it is not applicable for the group V materials which are supplied in excess. To check the influence of the temperature gradient we use the relation

$$E_x \gamma (1 - y) = E_x \gamma T (kT)$$  \[5\]

with an activation energy $E_x$ of 1 eV for the As/P competition on the group V sublattice (34). The temperature gradient necessary to obtain the variation in As/P-ratio shown in Fig. 13a is about 70 K and in Fig. 13b about 10 K, edge effects omitted. For the case of a rotating susceptor, the
variation in As/P-ratio correspond to a temperature gradi-
ent of about 3 K. In all these cases the direction of the As/P-gradient is as expected, i.e., lower As-content where the
temperature is supposed to be higher. However, the
magnitude of the temperature gradients calculated from the
theory are much larger than expected. The gradient for the
case of a rotating susceptor has been estimated with the
more sensitive method based on dopant incorporation to be
less than 0.5 K for the central 18 mm radius, and a cal-
culation of the temperature field for a nonrotating suscep-
tor at growth conditions similar to ours shows that the pro-
file is almost fully established in the region where our
substrate is placed (9), and, hence, the temperature varia-
tion along the flow should not be more than a few K.
Therefore, the As/P gradient is most probably not only due
to temperature variations on the substrate. The strong de-
pletion of arsenic along the flow could be explained by
both ceiling depositions, which are more enhanced for the
most reactive compound (AsH₃ and PH₃) has an average
bond strength of 99 and 77 kcal/mol, respectively (32),
and by formation of stable complexes, e.g., As₅, which are
creased by surface reactions at the susceptor (35). Parasitic
reactions between metal organics and the hydrides are not
likely to significantly deplete the hydrides because of the
high V/H ratio (>180 in this case).

Etch effects are more or less pronounced, depending on
substrate. The temperature effect is obvious outside the
20 mm radius, but only the dopant uniformity is clearly in-
fluenced by that. The significant increase in layer thick-
ness near the wafer edge, observed for both AlGaAs/GaAs
and InGaAsP/InP superlattices, as well as the enhanced
phosphorus and gallium incorporation at the edge of the
InGaAsP and InGaAs layers, respectively, could be due to
mass transport from the susceptor. Frjilink et al. has cal-
lculated the growth rate at the wafers edge and found an in-
crease due to the disturbance in pressure and, hence, in
arrival rate of the reactants at the step between the wafer and
the susceptor (38). This model predicts enhanced growth
near the edge which is also observed in our measurements.
The discrepancy between the ternary and quaternary lay-
ers in GaAsP ratio near the edge is expected, but may be
due to uncertainties in the wavelength measurement be-
cause of the flat photoluminescence peak. Differences in
reaction mechanisms in the presence of arsine and phos-
phine, respectively, could also affect the incorporation of
the elements.

Some structures have been grown twice or more in order
to determine the reproducibility. This is the case for the
quaternary bulk layer and some of the AlGaAs/GaAs super-
lattices (Fig. 5). At the central part of the wafer (about 5
mm of the edge excluded) the growth is reproduced mainly
within the measurement errors, while the edge ef-
fects may vary considerably.

Conclusion

In summary, we have presented a set of detailed qualita-
tive guidelines for the design of horizontal MOVPE
reactors and utilized them for the construction of a new re-
actor with a rotating substrate. The performance of this
machine has been scrutinized with respect to both the
AlGaAs/GaAs and the InGaAsP/InP systems. Particular
emphasis was given to the evaluation techniques. Differ-
ent physical and chemical contributions to the nonuni-
formities have been discussed. We have shown that the op-
timization of uniformity, which is drastically facilitated by
the substrate rotation, is mainly a function of the reactor
design and largely independent of material. The ultimate
performance limit for this type of reactor will probably be
set by a compromise between high carrier gas flow for re-
duced depletion of reactants and the increased cooling by the
higher work has resulted in some extremely uniform layers with respect to thickness, composition, and
dopant incorporation. The uniformity thus achieved should be sufficient for high yield fabrication of complex
quantum well and modulation doped device structures.

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REFERENCES
2. R. Takahashi, Y. Koga, and K. Sugawara, ibid., 119,
1406 (1972).
6. J. v.d. Ven, G. M. J. Butten, M. F. D. J. Raaijmakers, and
14. E. S. Johnson, G. E. Legg, and N. E. Schumaker,
15. I. Moerman, G. Coudenys, P. Demeester, B. Turner, and
17. C. G. Cureton, E. J. Thrush, and A. T. R. Briggs, ibid.,
18. A. Okamoto, H. Sunakawa, H. Terao, and H. Watanabe,
19. A. Mircea, A. Ougazzaden, P. Dasté, Y. Gao, C. Kaz-
mierski, J.-C. Bouley, and A. Carenco, ibid., 93, 235
(1988).
20. D. Schmitz, G. Strauch, H. Jürgensen, and M. Heyen,
24. A. Mircea, R. Mellet, B. Rose, P. Dasté, and G. Schia-
28. G. B. Stringfellow and R. Linnebach, J. Appl. Phys., 51,
2212 (1980).
29. J. P. Duchemin, M. Bonnet, P. Koelsch, and D.
Huyyge, This Journal, 136, 1134 (1979).
31. A. Mircea, R. Mellet, B. Rose, D. Robein, H. Thibierge,
G. Leroux, P. Dasté, S. Godfrey, P. Ossart, and
32. G. B. Stringfellow, "Organometallic Vapor-Phase Epita-
taxy, Theory and Practice," p. 21, Academic Press,
33. Y. Takahashi, T. Soga, S. Sakai, M. Umeno, and S. Hat-
34. L. Samuelsson, P. Omling, and H. G. Grimmeiss, J.
36. P. M. Frjilink, J. L. Nicolais, and P. Suchet, ibid., 107,
Paper B
Diffusion of Zn and Mg in AlGaAs/GaAs structures grown by metalorganic vapor-phase epitaxy

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The diffusion of thin, highly $p$-doped layers in AlGaAs/GaAs single- and double-heterostructures, grown by metalorganic vapor-phase epitaxy, was studied with C-V etch profiling and secondary ion mass spectroscopy. The effect of different post-growth heat treatments was investigated and diffusion coefficients for both magnesium and zinc were measured. It was found that Mg diffuses about twice as fast as Zn and that the order of magnitude of the diffusion coefficient is $10^{-14}$ cm$^2$ s$^{-1}$ at 900 °C, the exact value being process and concentration dependent. A model based on the interstitial/substitutional diffusion mechanism with suitable kinetic limitations was successfully used to simulate the observed dopant concentration profiles. We also found an anomalous strong diffusion of zinc from GaAs into highly $n$-doped AlGaAs. Detailed results on this and other structures are presented and implications for optimal design of heterostructure devices such as bipolar transistors are discussed.

I. INTRODUCTION

Despite the vast literature on diffusion of $p$-type dopants in III-V compounds, comparatively little data have relevance for growth of the thin layers that comprise devices of current interest. In particular, the differences between diffusion from an epitaxially grown profile and from an external source have been neglected. The observed discrepancies may be viewed as the result of different concentration of defects that participate in the diffusion reactions, which in turn may impose kinetical limitations to the diffusion process. Failure to appreciate these restrictions has led to erroneous predictions of diffusion constants as well as the lack of a reliable model for accurate simulation of doping profiles for thin layers. Furthermore, in a layered structure the diffusion can be dramatically influenced by composition, doping level, and crystal quality of the adjacent layers.

One of the most demanding devices from the point of view of $p$-type doping is the $n$-$p$-$n$ heterostructure bipolar transistor (HBT). On the one hand, the device performance will degrade severely with diffusion of the $p$-type dopant only a few nanometers across the heterojunction. On the other hand, the base doping level has to be at least $1 \times 10^{19}$ cm$^{-3}$ in order to reduce the base series resistance while keeping the base narrow for shortest possible transit time. So far, molecular-beam epitaxy (MBE) has been the most widespread method to grow HBT structures. In MBE, beryllium is almost universally used as a $p$-type dopant and a number of studies indicating very low diffusion coefficient and abrupt doping transitions over several decades have been published. However, some “surface tailing” has also been observed. Recently there has been considerable interest in the growth of HBT structures, also with the alternative technique metalorganic vapor-phase epitaxy (MOVPE). For MOVPE the choice of a $p$-type dopant has been less obvious. In part this is due to the somewhat higher growth temperatures typically used in MOVPE as compared to MBE (700 °C vs. 600 °C), which puts even tighter requirements on the properties of a potential dopant. The traditional $p$-type dopant has been zinc, which, however, for a long time was thought to have rather undesirable diffusion properties. Of the alternatives, use of Be has until recently been hampered by the lack of a readily available metalorganic source as well as by safety problems. Cadmium has been tried with some success for InP but the available doping range has been limited to below $1 \times 10^{18}$ cm$^{-3}$. Useful results also at higher doping levels have been obtained with Mg, despite problems with reactor memory effects.

In the course of realizing an HBT structure using MOVPE, several recent reports have indicated that the diffusion of Zn is much lower than expected, both during growth and during post-growth processing. To even further increase the usefulness of Zn, rapid thermal processing (RTP) has been proposed as a substitute for conventional furnace heat treatment in subsequent processing, e.g., annealing of contact implantations or alloying of ohmic contacts. Enquist and co-workers have presented some data on zinc diffusion in HBT structures grown by MOVPE. One of their main conclusions was that there seems to be a much stronger diffusion in an actual HBT structure than in a simple thin $p$-doped layer structure (“$p$-spike”). No satisfactory explanation could be given for this peculiarity. Furthermore, some of their results, e.g., the growth temperature dependence, could not be reproduced in our reactor. In summary, it is clear that although some qualitative data exist, a viable recipe for growth of HBT structures with MOVPE is still lacking. Hence, a more thorough investigation aiming at a better understanding of the fundamental aspects of dopant diffusion in this type of structure is needed.
In this paper we present the results of a systematic study of the behavior of Zn-doped MOVPE-grown GaAs and AlGaAs layers and structures as well as on the choice of method for heat treatment, RTP or furnace. In addition, we show a direct comparison between Zn and Mg as dopants in thin layers. Experimental values for the diffusion coefficient and the activation energy for diffusion are derived for the various cases. Simple model calculations are shown that explain the resulting profiles in terms of the substitutional-interstitial diffusion mechanism in conjunction with suitable kinetical limitations and boundary conditions. Finally, we discuss in some detail structures with particular interest to the HBT application and compare with actual HBT results.

II. EXPERIMENT

All the samples in this investigation were grown in a horizontal, atmospheric pressure MOVPE reactor, equipped with a vent-run manifold, at 700 °C using trimethylgallium (TMG), trimethylaluminum (TMA), and a 17% arsine hydrogen mixture. The V/III ratio was kept at 60 and 80 for GaAs and AlGaAs, respectively. Palladium purified hydrogen was used as carrying gas. The average gas velocity over the susceptor was about 0.4 m/s. Silane (SiH₄) was used for n-type Si doping. In the Zn-doped structures, diethylzinc (DEZ) was used and in the Mg-doped structures bis-cyclopentadienyl)-magnesium (Cp₂Mg) was used as the dopant precursor. The normal growth rate was about 2.5 μm/h for both GaAs and AlGaAs. The basic structure studied was a 0.2 μm p'-spike between two 0.7 μm undoped or n-doped layers with or without AlGaAs heterojunctions. In order to obtain an abrupt interface to the Mg-doped layer the growth was stopped during 400 s, while the reactor was flushed with Cp₂Mg and AsH₃ to saturate it with Cp₂Mg. The growth rate in the 0.2-μm-doped layer was 1.0 μm/h, followed by a 0.15-μm-thick layer grown at 0.2 μm/h to get an abrupt doping turn-off and the top 0.55 μm layer again grown at normal growth rate. The Zn-doped structures were all grown without interruption at normal growth rate. The spread in doping level across a 2-in. wafer was approximately a factor of 2, edge effects excluded.

All doping profiles were acquired with a Polaron electrochemical C-V etch profiler. Secondary ion mass spectroscopy (SIMS) was used to obtain the atomic depth profiles. The instrument used was a Cameca IMS 4f. Magnesium-doping profiles were obtained with oxygen primary beam and positive ion detection by monitoring Mg at mass 24. Zinc-doped profiles were obtained with cesium (Cs) primary beam and positive ion detection by monitoring CszZn at mass 197, the aluminum signal by monitoring Al, at mass 54, and silicon by monitoring Si at mass 28. In the figures the doping levels are calibrated by comparison with ion implantations in identical material and corrected to display the total atomic concentrations.

Heat treatment was performed both in a conventional diffusion furnace or in a Heatpulse 410 rapid thermal processing system (RTP) with incoherent light. The wafer temperature was monitored with a pyrometer. In order to avoid arsenic evaporation from the sample surface it had to be protected with some sort of cap. A brief discussion of the influence of the encapsulation is therefore necessary. The short processing times in the RTP permit a simple Si wafer as a cap whereas the longer annealing times in the furnace necessitate Si₃N₄ cap. Figure 1 shows a comparison between two RTP samples, both annealed at 900 °C for 90 s—one with a 120 nm Si₃N₄ cap layer deposited by plasma-enhanced chemical vapor deposition at 350 °C and the other capped with a Si wafer. There is nearly no difference in diffusion between the two samples. Figure 2 shows a Si₃N₄-capped sample annealed at 800 °C in 45 min and a sample annealed at the same temperature in 2 h in arsenic atmosphere. (The as-grown profile is shown for reference.) Although a slightly smaller diffusion coefficient can be derived for the case of AsH₃ over pressure, it is evident that the Si₃N₄ cap provides sufficient encapsulation for long-time furnace anneals. From the profiles in Figs. 1 and 2 we can conclude that the results presented below are not sensitive to the specific cap used but would be qualitatively valid for any reasonable heat treatment process.

III. RESULTS

A. Diffusion coefficients in homostructures

In order to determine the diffusion coefficients of Zn and Mg in epitaxially grown GaAs, three structures were grown. Each consisted of a 0.1- or 0.2-μm Zn- or Mg-doped...
layer, surrounded by 0.7 μm epitaxially grown GaAs. A structure with a 0.2-μm Zn-doped spike in AlGaAs was also grown to determine the diffusion coefficient in AlGaAs. The 0.7-μm epitaxially grown undoped layers on both sides of the doped layer diminish the influence from the surface and from the interface between the substrate and the epitaxial layer.

Two heat treatment series were made, one in a conventional diffusion furnace and the other in an RTP system. The temperature was varied between 750 and 950 °C. The annealing time was varied between 10 and 250 s in the RTP and between 20 and 80 min in the furnace. The temperatures and times were chosen in a range near that of the real process situation and at the same time wide enough to give significant differences in measured profile width.

Figures 3(a) and 3(b) show three doping profiles of the 0.1-μm Zn-doped spike as measured with SIMS and C-V, respectively. The as-grown profile is compared to two samples annealed at 850 °C, one for 90 s in the RTP, the other for 20 min in the conventional furnace. The general agreement between the SIMS and C-V profiles is quite good. The measured as-grown peak hole concentration is $8 \times 10^{19}$ cm$^{-3}$, which is somewhat lower than the nominal doping level of $2.4 \times 10^{19}$ cm$^{-3}$. SIMS data in combination with measurement of the Hall mobility (58 cm$^2$/V s) for uniformly doped 2-μm-thick layers indicate very high activation of Zn and almost no compensation. The discrepancy is therefore most likely related to difficulties in C-V etch profiling thin but highly doped layers. This effect may also explain a part of the large difference in apparent total doping between as-grown and annealed samples. However, the spread in doping level between samples does not permit a detailed comparison of sheet concentrations.

The as-grown SIMS profile spans more than three decades (restricted by the SIMS background level) with an abruptness of about three decades per 60 nm, a figure comparable to the SIMS depth resolution. The doping level seems to saturate at about $3 \times 10^{19}$ cm$^{-3}$, discussed above and not to the difference in doping element. The Mg memory effect in the reactor gives a tail towards the surface, decreasing the abruptness of the transition to about two decades which is an order of magnitude smaller than for Zn.

Finally, it is worthwhile to note that, for Zn as well as for Mg, the profile broadening per unit time is much larger for the RTP annealed samples than for the furnace annealed one, indicating different diffusion mechanisms.

The diffusion coefficient is determined by measuring the
width of the C-V profiles and applying simple diffusion theory for concentration independent diffusion. The result depends slightly on the choice of doping level at which the width is measured. Results discussed here are from measurements at $e^{-3}$ (≈ 5%) of the peak concentration. Since this point is typically below the defect controlled top part of the profile this procedure seems reasonably justified. The calculation is based on the assumption of gaussian-shaped profiles and concentration-independent diffusion, and an Arrhenius form of the temperature dependence of the diffusion coefficient. Although this model is simple, we believe that the magnitude, and especially the relative magnitude, of the derived quantities is correct. These values can then be used as starting approximations in more complex modeling such as described below. The samples were heated at a fixed temperature for different times, and for a fixed time for a series of temperatures. In Fig. 5 the measurements for determination of the diffusion coefficient

$$D = D_0 \exp\left(\frac{-E_a}{kT}\right)$$  

(1)

for the 0.2-μm Zn-doped spike in GaAs are shown. Here $D$ represents the diffusion coefficient, $D_0$, the frequency factor, $E_a$ the activation energy, $T$ the temperature, and $k$ Boltzmann's constant. Figure 5(a) shows the effective diffusion broadening $(Dt)^{0.5}$ at constant temperature (900 °C) vs $t^{0.5}$, where $t$ represents the annealing time. The diffusion constant $D$ is obtained from the slope of the straight line. Figure 5(b) shows $\ln(D)$ vs $1/T$, obtained from the broadening of the profiles for a 90 s RTP anneal. From this figure $E_a$ is given as the slope of the straight line. In all cases studied a straight line could be very well fitted to data. Derived values are listed in Table I.

<table>
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<th>Material</th>
<th>$D_{90}$ (cm²/s)</th>
<th>$E_a$ (eV)</th>
<th>$D_0$ (cm²/s)</th>
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<td>2.1</td>
<td>$4.6 \times 10^{-4}$</td>
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<td>1.8</td>
<td>$6.5 \times 10^{-3}$</td>
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<td>Zn-doped AlGaAs</td>
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<td>$1.5 \times 10^{-3}$</td>
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<table>
<thead>
<tr>
<th>Material</th>
<th>$D_{90}$ (cm²/s)</th>
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<td>$1.2 \times 10^{-6}$</td>
</tr>
<tr>
<td>Mg-doped GaAs</td>
<td>$6.8 \times 10^{-14}$</td>
<td>1.5</td>
<td>$1.9 \times 10^{-3}$</td>
</tr>
<tr>
<td>Zn-doped AlGaAs</td>
<td>$2.9 \times 10^{-14}$</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

To investigate the significance of the observed dopant and process dependence in a more realistic case a separate study was made using typical parameters for annealing of ion implantation damage induced by a shallow contact implantation. Typically, an RTP anneal at 900 °C in 10 s (Ref. 17) or furnace anneal at 800 °C in 20 min (Ref. 18) is necessary to activate the implanted material. Figures 6(a) and 6(b) compare 0.2-μm Mg and Zn spikes after those treatments, respectively. For reference, the as-grown profiles are displayed in Fig. 6(c). It is clear that the Zn profile is nearly undisturbed after the RTP treatment [Fig. 6(a)] while the Mg profile is broadened and exhibits increased tailing on the surface side. The anneal [Fig. 6(b)] shows a large broadening of both the Mg and Zn profiles, and shoulders at the 10⁻⁸ cm⁻³ level on both of the profiles indicate a concentration-dependent diffusion.

**B. Heterostructures**

In order to investigate the diffusion of the Zn-doped base in an HBT structure, we have also studied the influence of heterojunctions and $p$-$n$ junctions on the Zn diffusion. The structures grown with this purpose follow the same concept as those described above, i.e., a 0.2-μm Zn-doped spike surrounded by 0.7 μm Al₀.₃Ga₀.₇As or GaAs. Some of the surrounding layers were also $n$-type Si doped. Figure 7 shows an asymmetrical structure, where the undermost layer and the $p$-spike are grown in GaAs and the uppermost layer in Al₀.₃Ga₀.₇As. The as-grown profile is not influenced by the heterojunction, but after annealing an evident shoulder coincides with the heterojunction. This may be due to lower solubility for Zn in Al₀.₃Ga₀.₇As than in GaAs.

The most surprising result obtained is presented in Fig. 8, where a symmetric Al₀.₃Ga₀.₇As/GaAs/Al₀.₃Ga₀.₇As structure is shown as-grown. The Al₀.₃Ga₀.₇As layers are Si...
FIG. 6. C-V profiles of Zn and Mg spikes are compared after typical anneal treatments. (a) RTP at 900 °C for 10 s; (b) furnace anneal at 800 °C for 20 min; (c) as-grown.

FIG. 7. SIMS profile of an Al$_{0.5}$Ga$_{0.5}$As/0.2 μm p-GaAs/n-Al$_{0.5}$Ga$_{0.5}$As heterostructure. The Al signal is shown for depth reference only, its magnitude is not calibrated. The p-type dopant is Zn.

doped to $1 \times 10^{18}$ cm$^{-3}$ and the GaAs layer is Zn doped. The Al level in the figure is just for depth reference and not calibrated. A large Zn diffusion occurs below a concentration of $5 \times 10^{18}$ cm$^{-3}$. Figure 8 clarifies the origin of this effect. Three different as-grown GaAs p-doped spikes are shown in Fig. 8(a), they are all surrounded by Al$_{0.5}$Ga$_{0.5}$As with different Si doping (high doped $1 \times 10^{18}$ cm$^{-3}$, low doped $5 \times 10^{17}$ cm$^{-3}$, and nondoped). Here only the spike surrounded by highly doped material is substantially broad-
ened. There is no difference in broadening between the spikes surrounded by low-doped or nondoped material. Figure 8(b) shows in the same way three different as-grown GaAs Zn-doped spikes with adjacent Si-doped GaAs (high doped $5 \times 10^{13}$ cm$^{-3}$, low doped $2 \times 10^{13}$ cm$^{-3}$, and nondoped). In this case the spike surrounded by highly doped material is slightly broadened, while the others are undisturbed. In Al$_{0.5}$Ga$_{0.5}$As homostructures [Fig. 8(c)], where the layers surrounding the p-spikes are high n-doped $2 \times 10^{18}$ and nondoped respectively, the broadening of the p-spikes is comparable to that obtained in the heterojunctions showed in Fig. 8(a). It is obvious that high Si doping together with Al$_{0.5}$Ga$_{0.5}$As is the only condition where significant broadening of the as-grown profile is observed. Figs. 8(a)–8(c) also shows that the Zn solubility is indeed larger in GaAs than in Al$_{0.5}$Ga$_{0.5}$As.

IV. MODEL

In order to get a better understanding of the mechanism responsible for the effects which were observed in the experiments, we simulated the concentration profiles for some cases. An algorithm, which was originally developed for simulation of the activation process of implanted structures, was adapted for this case. The model, which will be described in more detail elsewhere, incorporates an interstitial substitutional mechanism, as is already established for the case of zinc diffusion in compound semiconductors. The algorithm is based on the rate equations for the chemical reaction

$$N_p = N_i + V_{Ga},$$

plus a diffusion equation for the interstitial atoms. Here $V_{Ga}$ denotes the gallium vacancy, $N_p$ the dopant, and subscripts $i$ and $s$ the interstitials and substitutionals, respectively. As-diffusion of the substitutional population (impurity atoms on gallium lattice sites) is expected to be much less than that of the interstitial population, it is neglected in this model. Diffusion of Ga vacancies is also ignored. The diffusion coefficient of interstitial dopant atoms was allowed to be concentration dependent and best results were achieved with a diffusion coefficient which was linearly dependent on the dopant concentration.

The rate of the reaction for the generation (forward reaction) and recombination (backward reaction) of interstitial impurity atoms is represented by two temperature-dependent time constants, $\tau_g$ and $\tau_r$, respectively, where the temperature dependence is given by the equations

$$\tau_g = \tau_{g0} \exp(E_g/kT),$$

$$\tau_r = \tau_{r0} \exp(E_r/kT),$$

where $\tau_{g0}$ and $\tau_{r0}$ are the frequency terms, and $E_g$ and $E_r$ the activation energy for the two processes. The time constants may be interpreted as the mean lifetime of the respective population. The energy barrier for the forward reaction is expected to be smaller than that for the backward reaction, i.e., $E_g > E_r$. In addition, for substitutional atoms to be the more stable population, their lifetime has to be larger than that of the interstitial atoms so that $\tau_g > \tau_r$. The final system of coupled differential equations arrived at then becomes

$$\frac{dN_p}{dt} = \frac{d(DN_p/dx)}{dx} + \frac{N_i - N_p}{\tau_g - \tau_r},$$

(4a)

$$\frac{dN_i}{dt} = \frac{N_i - N_p}{\tau_r},$$

(4b)

$$\frac{dV_{Ga}}{dt} = \frac{dN_i}{dt} - \frac{dN_p}{dt}.$$  

(4c)

A similar approach has been discussed by Tuck and Kadhim. However, they applied a slightly different formalism and their study focused on iso-concentration profiles with large penetration depths.

The diffusion process may be described as follows: Interstitials are generated in the spike region, diffuse, and ultimately recombine with a gallium vacancy to become electrically active again. It is clear that the diffusion length of impurity atoms is then determined by the diffusion coefficient and the time that the atom is at an interstitial position. If the profile broadening is represented by $x(t)$, then

$$x(t) = D_t \tau_r/(\tau_g + \tau_r),$$

(5)

where $t$ is the time and $D_t$ the intrinsic diffusion coefficient of interstitial atoms. The diffusion coefficient which is actually measured is given by

$$D_{meas} = D_t \tau_r/(\tau_g + \tau_r) \approx D_t \tau_r/\tau_g.$$  

(6)

The approximation is due to the requirement $\tau_g \gg \tau_r$. The temperature dependence of the measured diffusion coefficient is given by

$$D_{meas} = D_0 \exp[-(E_a + E_r - E_d)/kT],$$

(7)

where $D_0$ and $E_d$ denote the frequency factor and activation energy of $D_t$, respectively. As $E_a > E_r$, the measured activation energy will be larger than the energy of the intrinsic

---

FIG. 9. (a) Simulated and measured concentration profile for zinc diffusion in GaAs at 950°C for 20 min. (b) Simulated and measured concentration profile for magnesium diffusion in GaAs at 850°C for 20 min.
diffusion coefficient, $E_s$. The activation energy of pure interstitial diffusion is expected to be approximately 1 eV.\textsuperscript{22} The difference with respect to a measured value should then be an estimate for the difference between $E_s$ and $E_i$.

Equations (3a)–(3c) are solved numerically for several sets of input parameters. For the diffusion coefficients the measured values derived above were used. Results of the simulations in the case of zinc and magnesium spikes in GaAs subject to post-growth heat treatment are shown in Figs. 9(a) and 9(b), respectively. The as-grown profiles are depicted in Fig. 6(c). The best fits were achieved with the following input parameters:

\[ \begin{align*}
\text{Zn:} & \quad \tau_{\sigma} = 0.2 \text{ s}, \quad E_\sigma = 0.4 \text{ eV}, \quad \tau_{\pi} = 0.01 \text{ s}, \\
E_s &= 0.9 \text{ eV}; \\
\text{Mg:} & \quad \tau_{\sigma} = 0.2 \text{ s}, \quad E_\sigma = 0.4 \text{ eV}, \quad \tau_{\pi} = 0.05 \text{ s}, \\
E_s &= 0.9 \text{ eV}.
\end{align*} \]

Criteria for the selection of these parameters will be discussed elsewhere.\textsuperscript{18} The agreement between the measured dopant distributions and the simulations is remarkably good for both dopants, particularly at higher doping levels. Deviations in the low $10^{17}$ cm$^{-2}$ range is probably due to a combination of truncation errors in the calculation and measurement errors.

V. DISCUSSION

Several somewhat unexpected conclusions may be drawn from the data presented above. First, let us compare the diffusivities of zinc and magnesium. From infinite source surface diffusion studies, values for the diffusion constant at 900 °C of about $10^{-7}$ cm$^2$ s$^{-1}$ for Zn and $10^{17}$ cm$^2$ s$^{-1}$ for Mg would be expected. Since the diffusion proceeds via an interstitial–substitutional mechanism, an activation energy of about 1 eV would seem reasonable. Our findings indicate (i) a much smaller difference between Mg and Zn, both being of the order of $10^{-14}$ cm$^2$ s$^{-1}$, and (ii) much larger activation energies, around 2 eV. To explain this we assume that the transition of the dopant from a substitutional to an interstitial site occurs via reactions of the type (2). At the high $p$-doping levels (large $N_p$) studied in our experiments the above reaction is driven to the right. The ability of the crystal to generate the necessary native defects then becomes the rate-limiting step. The observed diffusivity and activation energy should therefore be characteristic of the defect generation rather than of the dopant species or its motion. A value of 2 eV is in good agreement with estimates of the defect formation energy. When the defect generation is limiting the diffusion, one may regard the region with higher dopant than defect concentration as an infinite source for diffusion which explains the sharp concentration change from the flat top of the peak to the shoulder. Outside this region, the regular concentration-dependent diffusion proceeds, giving rise to a shoulder at a doping level which thus can be interpreted as the concentration of the dominant native defect in the crystal as observed, e.g., in Fig. 6 (b). The very small but definite broadening of the part of the profile which is the remains of the original structure can readily be explained as the result of diffusion of the Ga vacancies. In this case the apparent activation energy is considerably higher, 3–4 eV. The differences observed between the values for Mg and Zn may be due to a different relative importance of the two main reactions illustrated above. In fact, regardless of reactor memory effects it seems as if zinc should be a better choice of dopant than magnesium in terms of profile control, quite contrary to earlier beliefs. It is interesting to note that the activation energy quoted for Be diffusion both in MOVPE- and in MBE-grown samples are in accordance with our findings (~1.8 eV). The substantially smaller $D_0$ in the case of Be as well as the factor-of-2 difference between Zn and Mg is attributed to the different defect kinetics and may also be related to the size of the dopant atom. With all necessary reservations in interpretation of the derived values of the diffusion constants due to application of a simplified model, we believe that our conclusions are qualitatively correct and quite general.

The above conclusions are substantiated by comparison between the profiles obtained after heat treatment using rapid thermal processing and furnace annealing. It is clear that the difference is not large and that it decreases with the doping level, just as expected if the influence of the interstitial diffusion is limited to the region below the shoulder corresponding to the native defect concentration. As seen in Table I the measured activation energy for RTP and furnace anneal are about the same the preexponential factor and hence also the diffusion coefficient is 20 times larger for RTP than for furnace anneal. Thus, the $D_0$ product does not vary by more than a factor of 2 for conditions typical for annealing of, e.g., ion implantations for ohmic contacts. The conclusion is that the choice of heat treatment process is not as important as is generally believed. However, at least for zinc, it seems as if RTP should have some advantages for suppressing tails in the diffusion profile. The reason for this difference in $D_0$ is probably due to different defect kinetics in the two processes.

Numerous attempts to model in particular Zn diffusion in III-V compounds have been made, the majority of them with modest success considering the complexity of the models used. It is therefore encouraging to note that we have achieved very good agreement with experimental data using such a simple model. One of the major drawbacks of our model is the neglect of electrical charge effects. However, as recently pointed out for the case of InP,\textsuperscript{23,24} the charge state of, e.g., the interstitial may not be as unique as is frequently assumed. In view of the relatively small differences in the final profiles that result from changes in assignment of the interstitial charge one can conclude that correct modeling of charge is much less important than correct modeling of the defect kinetics.

From an applied point of view, direct studies of various structures are most interesting since the influence of structure parameters may sometimes determine the "effective" diffusivity. Specifically we have tried to investigate the influence of the doping in adjacent layers and the presence of a heterojunction. The following conclusions can be drawn:

(i) It is quite feasible to grow thin highly $p$-doped layers at growth temperatures as high as 700 °C. We have not in any


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case observed the massive broadening already at 650 °C, reported by Enquist. 12
(ii) As long as the background doping is low (≤5 × 10^{17} cm^{-3}), broadening of a single p-doped layer does neither depend on the material composition (Al_{0.5}Ga_{0.5}As or GaAs), nor on the presence of a heterojunction. This fact is contrary to the conclusion reached in conventional Zn-diffusion studies in Al_{0.5}Ga_{0.5}As, where the diffusion is found to be significant greater in Al_{0.5}Ga_{0.5}As than in GaAs. 25 It is also an indication that the native defect level is about the same in the two materials.

(iii) There is a significant increase in Zn diffusivity for high Si doping of the surrounding layers. The effect is much stronger for Al_{0.5}Ga_{0.5}As than for GaAs. Currently we have no detailed explanation for this anomaly but suggest that it may be due to increased defect concentrations. Similar observations have been made on laser structures. 26 Our results are in contrast to those obtained by Enquist, who reported a decreasing diffusion with increasing Si doping and attributed that to a Fermi level effect in combination with a repulsive force due to the space charge at the p-n junction. In addition, we have not observed any tendency for accumulation of zinc at the interfaces to contact layers. We can speculate in the reason for these discrepancies and suggest that they may be related to the lower growth temperature used by Enquist (550 vs 700 °C). A lower growth temperature should increase the density of native defects, particularly for AlGaAs which is generally believed to deteriorate rapidly below 700 °C.

It should be noted that most of our studies have been done on homojunctions or double heterojunctions with a rather thin GaAs layer (0.2 μm). Just as Enquist we have noted a considerably larger diffusion in real HBT structures. Since we have shown above that this is neither due to doping differences (both emitter and collector are relatively low doped) nor to the heterojunction per se, the only parameters left seem to be the native defect concentration and strain introduced by the small lattice mismatch introduced by the heterojunction. The fact that a change in emitter composition influences diffusion into the collector as much as the diffusion into the emitter clearly is an indication that the strain may play a role in determining the doping profiles.

Using our experimental diffusion constants we can calculate the necessary thickness of the undoped spacer layer that normally is inserted between the base and emitter in the HBT structure to allow for some p-type dopant diffusion. For our standard MOVPE conditions (700 °C, 2–3 μm/h growth rate, continuous growth) a value of about 30 nm is then achieved. In contrast, the best HBT dc performance is typically reached for a spacer thickness of 100 nm, where typically current gains of about 70 are obtained. Finding new ways to minimize the strain associated with the heterojunction may be a possible way to lower the defect concentration, thereby reducing dopant diffusion and improving the HBT performance.

VI. CONCLUSION

Through a number of experiments and supported by simulation of dopant profiles, we have been able to reach

new insight and improved understanding of p-type dopants in thin layers of GaAs as well as in GaAs/AlGaAs heterostructures. Our main conclusions can be summarized as follows:

1. MOVPE can successfully be used for these types of structures. Contrary to expectations Zn is preferred over Mg as a dopant.
2. The diffusivity of Zn is a factor of approximately 2 smaller than that of Mg, independent of processing conditions.
3. The diffusivity measured with RTP heat treatment is larger than with conventional furnace anneal. This largely offsets the much shorter times used with RTP. Mainly due to the smaller tails in the diffusion profiles RTP should still be preferred for high-temperature post-growth processing.
4. There is no difference in Zn diffusivity between undoped Al_{0.5}Ga_{0.5}As and GaAs.
5. Si doping of adjacent layers does not influence the diffusion during growth, except for the case of very high n-doping in Al_{0.5}Ga_{0.5}As layers. Tentatively we suggest that this is due to the higher defect concentration present in these structures.
6. The diffusion is quite well modeled by an interstitial–substitutional mechanism when restrictions due to deviation from gallium vacancy equilibrium concentration are taken into account.

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Growth and performance of AlGaAs/GaAs heterostructure bipolar transistors


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AlGaAs/GaAs heterostructure bipolar transistors (HBTs) were grown using a standard MOVPE process at 700 °C, where the AlGaAs quality is known to be acceptable, with Zn as the base dopant. A maximum current gain of 200 has been achieved for large area devices and a maximum oscillation frequency of 31.8 GHz was obtained for devices with two emitter stripes, each 2.5 μm × 10 μm. An equivalent circuit model shows that the performance is mainly limited by the base transit time. An investigation of the growth temperature dependence on Zn migration in HBT structures shows a significant reduction of base broadening at lower temperatures.

1. Introduction

Heterostructure bipolar transistors (HBTs) are currently of great interest for high frequency devices with a demonstrated performance well over 100 GHz. Other favourable properties are the high power handling capacity, low 1/f noise and a well defined threshold voltage.

In an HBT structure the base–emitter p–n junction must coincide with the heterojunction to within a few nanometers. This requires an epitaxial growth technology with exceptional control over doping profiles and heterojunction placement. To date most HBTs have been grown using molecular beam epitaxy (MBE). Reports on metal organic vapor phase epitaxy (MOVPE) growth of HBT structures are often concerned with the problem of diffusion of the p-type base dopant. This problem does not seem so severe in the MBE process where lower growth temperatures are used. Common dopants in MOVPE are magnesium, carbon and zinc. The organometallic Mg precursors available show abnormal memory effects which necessitates several minutes of growth interruption before and after growth of the Mg-doped layer in order to achieve an abrupt turn on and turn off [1]. This interruption may damage the interface by impurity incorporation. Nevertheless device results have recently been reported [2]. A relatively new field is carbon doping. Carbon doping can be achieved either from the methyl groups in the group III organometallics (in, e.g., atomic layer epitaxy) [3], or from carbon containing precursors as trimethylarsenic (TMAs) [4] or CCl₄ [5]. Several investigations show sharp doping profiles and relatively high doping concentrations. A problem is the low growth temperature required which might degrade the quality of the AlGaAs. Zn is probably the most popular p-type dopant in MOVPE growth since it is possible to obtain high doping levels and sufficient abruptness at relatively high growth temperatures (700 °C) without reactor purging [6,7]. It has also been shown that the diffusion coefficient for Zn is not as high as usually claimed; in fact, we have shown [6] that it is lower than for Mg in this type of epitaxial structures. Microwave performance has been reported for HBTs grown by MOVPE at 700 °C where the AlGaAs quality is known to be acceptable [8–10]. Further reduction of the zinc diffusion by lowering the growth temperature for HBT structures has also been attempted [11].

Operation at microwave frequencies necessitates minimization of all parasitic resistances and capacitances. In the HBT case this translates to a base contact self-aligned to the emitter with a base–emitter separation of a few tenths of a micron. Such requirements put very high demands
on a precise etching and contact technology. Except for this self-alignment, all dimensions are compatible with optical lithography.

We report in this paper successful fabrication and high frequency evaluation of AlGaAs/GaAs HBTs using the standard p-type dopant zinc in an MOVPE process at the conventional growth temperature of 700°C. The device fabrication utilizes chemical wet etching and a self-aligned base contact. Further improvements of the epitaxial structure are also discussed.

2. HBT fabrication

The material was grown in a horizontal, atmospheric pressure MOVPE reactor [12] at 700°C using trimethylgallium (TMG), trimethylaluminum (TMA) and 100% arsine (AsH₃). The V/III ratio was kept at 60 and 80 for GaAs and Al₀.₃ Ga₀.₇As, respectively. Palladium purified hydrogen was used as a carrier gas. The average gas velocity over the susceptor was about 0.4 m/s. Silane (SiH₄) and diethylzinc (DEZn) were used as n- and p-type doping precursors, respectively. Normal growth rate was 2.5 μm/h, but it was lowered to 1.2 μm/h in base, spacer and emitter in order to reduce the memory effect of DEZn remaining in the reactor after growth of the Zn-doped base layer. The complete epitaxial HBT structure is described in table 1. A linearly graded aluminum concentration in the base and spacer (which together constitutes the effective p-doped base layer after Zn migration) is used to achieve a built-in electric field and hence an improved electron transport through the base. The spacer layer employed is relatively thick to ensure that the base doping does not penetrate into the emitter, which would considerably reduce the current gain.

The transistor fabrication process begins with device isolation by a deep proton implant. Wet etching down to the base layer defines areas for base contacts and for a shallow proton implant into the collector which reduces the extrinsic collector doping and hence the base–collector capacitance. Base contacts are formed by evaporation of Au/Ni/Ti/Pt/Au and capped by deposition of SiO₂. This self-aligned process relies on controlled underetching of the emitter mesa and offers a base to emitter distance of about 0.2 μm. The collector contact layer is reached by wet etching and evaporated AuGe/Ni/Ti/Au is used for both collector and emitter contacts. Si₃N₄ is deposited as protection and dielectric and sputtered TiW/Au and NiCr are used for circuit connections and resistances, respectively. The temperature during the process never exceeds 350°C to avoid damage of the structure.

3. Results

Common emitter I–V characteristics for an 80 μm × 80 μm device are depicted in fig. 1. The maximum current small signal gain β is about

![Fig. 1. Common emitter I–V characteristics for an 80 μm × 80 μm device. Iₜᵢₜ step: 10 μA.](image_url)
200. The dependence of gain on device size is illustrated in fig. 2, where $1/\beta_{\text{max}}$ is plotted as a function of inverse emitter width. Acceptable gain is provided even for devices as small as $0.6\ \mu\text{m} \times 10\ \mu\text{m}$ nominal emitter area. A plot of the small signal amplification as a function of collector current shows an ideality factor of 1.68 for the base-emitter junction, indicating a reasonable p–n junction quality. The microwave response of the transistors was evaluated using a Cascade high frequency wafer probe station and an automatic network analyser for frequencies up to 18 GHz. Values are extracted from $S$-parameter measurements. The high frequency gain curve is shown in fig. 3 for a device with two emitter fingers of $2.5\ \mu\text{m} \times 10\ \mu\text{m}$ area. The extrapolated values for maximum oscillation frequency, $f_{\text{max}}$, and current gain cut off frequency, $f_T$ are 31.8 and 24.6 GHz, respectively.

4. Discussion

In order to separate the various contributions to the time delays of the devices we use the simple equivalent circuit model shown in fig. 4. The estimated values of the parameters for a typical transistor with two emitter fingers with dimensions $2.5\ \mu\text{m} \times 10\ \mu\text{m}$ are given in table 2. The cut off frequencies can be expressed by

$$f_T = \frac{1}{2\pi\tau_F}, \quad f_{\text{max}} = \frac{1}{4\pi\sqrt{\tau_F\tau_{BC}}}$$  \hspace{1cm} (1)

where $\tau_F$ is the total emitter to collector delay time, expressed by

$$\tau_F = \tau_{\text{EC}} + \tau_B + \tau_C + \tau_{\text{CC}}.$$  \hspace{1cm} (2)

Here $\tau_{\text{EC}}$ is the emitter charging time, $\tau_B$ the base transit time, $\tau_C$ the depleted collector transit time and $\tau_{\text{CC}}$ the collector charging time. $\tau_{BC}$ is the base–collector charging time. The analysis reveals that the cut off frequency is mainly limited by the extrinsic base transit time $\tau_B$, which is linearly dependent on the total width of base and spacer. The analysis also clearly reveals the importance of the aluminum grading in the base. The calculated
Table 2
Extracted model parameters

\begin{align*}
R_b &= 22 \, \Omega \\
R_C &= 24 \, \Omega \\
\tau_C &= 1.20 \, \text{ps} \\
R_t &= 19 \, \Omega \\
\tau_E &= \tau_E C_{BE} = 0.41 \, \text{ps} \\
C_{BC} &= 0.04 \, \text{pF} \\
C_{BE} &= 0.25 \, \text{pF} \\
\tau_B &= \tau_B + \tau_C + \tau_{BC} + \tau_{EB} = 7.35 \, \text{ps} \\
\tau_{BC} &= R_C C_{BC} = 0.89 \, \text{ps} \\
f_T &= 1/(2\pi f_T) = 21.7 \, \text{GHz} \\
\nu_{max} &= 1/(4\pi \sqrt{\text{C}_{\text{BC}}}) = 31.5 \, \text{GHz}
\end{align*}

Base transport times without and with a built-in electric field are 12 and 4 ps, respectively. This is in accordance with measured DC gains of about 50 and 200 for large area devices. Without grading, the gain was not sufficient to allow high frequency evaluation of realistically small devices while structures including grading have consistently gained a high yield of transistors with 2.5 \, \mu\text{m} \times 10 \, \mu\text{m} emitters. The only way to further reduce \tau_B without increasing the base resistance is by growing a more highly doped and narrower base layer. Despite the fact that Zn-doped layers in GaAs homostructures exhibit only a moderate diffusion, they will be significantly broadened in realistic heterostructures, i.e. surrounded by Si-doped AlGaAs. This is due to higher defect concentration in this material [6,7]. The defect generation has been explained as being due to increased group III vacancy generation caused by Fermi level pinning at the growth surface [13]. This effect is strongly dependent on n-doping in adjacent layers and of growth temperature. It has been shown that either counterdoping the base layer with Si or omitting the contact layers effectively reduces the Zn migration [14]. This is clearly not a solution for a realistic device structure. Instead we suggest a lowering of the temperature during growth of the base while keeping the n-doped layers intact. Fig. 5 shows secondary ion mass spectroscopy (SIMS) profiles of base and emitter regions in two complete HBT structures. The Zn and Si levels are calibrated and depicted above noise level. The Al profile is shown as a depth reference. The only difference in growth conditions between the two samples was the susceptor temperature during growth of the base layer. It was constant at 700°C for the structure in fig. 5a, but for the structure fig. 5b it was graded down to 550°C without growth interruption before switching in DEZn and graded up again to 700°C after growth of the base. In the former structure the p-doped region is significantly broadened below a

Fig. 5. SIMS profiles of the emitter–base region. The Al concentration is not calibrated. The base growth temperature was in (a) 700°C and in (b) graded to 550°C. The other layers were grown at 700°C.
concentration level of $8 \times 10^{17} \text{ cm}^{-3}$ and the peak reaches a level of $1 \times 10^{19} \text{ cm}^{-3}$, while in the latter the peak reaches a level of $4 \times 10^{19} \text{ cm}^{-3}$ with a shoulder only at $8 \times 10^{16} \text{ cm}^{-3}$, which is an order of magnitude lower than in fig 5a. The shoulder seen in fig. 5a moves the p–n junction as much as 50 nm towards the high bandgap emitter which necessitates an equal broadening of the spacer layer to avoid loss in current gain. In fig. 5b it is particularly encouraging that the shoulder on the emitter side is down in the mid $10^{16} \text{ cm}^{-3}$, thus well below the desired emitter n-doping level of $(2–5) \times 10^{17} \text{ cm}^{-3}$. Furthermore this shoulder is absent on the collector side. The total width of the Zn profile is 0.19 μm measured at the doping level of the adjacent layers, i.e. at the p–n junctions. The base broadening is a factor of two smaller than for a base grown at 700 °C and within measurement errors the same that occurs for a single Zn layer in a nominally undoped GaAs structure as shown in fig. 6 where the temperature grading to 550 °C was performed in the same way as for the HBT base shown in fig. 5b (cf. ref. [6]). It is thus obvious that a lower temperature during growth of the base solves the problem with structure related zinc migration, which would lead to a 40% reduction in $\tau_b$. The fact that Zn incorporation is significantly higher at low growth temperatures makes it at the same time possible to reduce the base resistance. However, it is not clear if the material quality is unaffected. It is well known that the quality of AlGaAs decreases at low growth temperatures resulting in an increased recombination current and an associated reduction of the gain. Investigations to clarify this point are currently in progress.

5. Conclusion

In conclusion we have demonstrated the use of material grown by MOVPE at 700 °C for fabrication of HBTs working up to 32 GHz. An analysis of limitations of the cut of frequency reveals that it is mainly limited by the base transit time. Growth of the base layer at lower temperatures has been investigated and it is shown to be a possible way to reduce the base width by as much as 40% and at the same time increase the base doping level. These effects can further increase the cut of frequencies if material quality is unaffected.

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References

Paper D
MOVPE growth of InP around reactive ion etched mesas

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We present a study of temporally resolved metalorganic vapour phase epitaxial growth of InP around reactive ion etched mesas in InP substrates. The experiments were performed at substrate temperatures in the range 580 to 680°C and for reactor pressures between 30 and 300 mbar. The planarity is primarily affected by substrate temperature, but to some extent also by the pressure. Planar and selective embedding is obtained around 1 μm wide and 1–4 μm high mesas at reactor pressures of 100 mbar and below, and for temperatures above 650°C without formation of any mask overhang. Overgrowth at low temperatures is found to be due to high growth rate at the mesa walls.

1. Introduction

Reliable techniques for planar and selective growth of InP around the mesas are essential for fabrication of buried heterostructure lasers and optoelectronic integrated circuits (OEICs). High accuracy in width and height of the mesas is provided by mesa formation with reactive ion etch (RIE) which has proven to be non-selective and highly directional, contrary to the usually used wet etchants [1]. This makes the use of RIE preferable for many production processes. Metalorganic vapour phase epitaxy (MOVPE) is the most successful technology for large area growth of high performance OEICs and lasers for long wavelength applications. However, selective epitaxial regrowth of InP with MOVPE around mesas is non-trivial and only a few papers focusing on this problem have been published and then exclusively concerned with growth around wet etched mesas [2–4]. It has been claimed that a mask overhang of up to 1 μm is essential for planar growth and to avoid grooves beside the mesa [2,3]. The influence of mesa shape on the planarity of growth has also been investigated and it was shown that a re-entrant mesa easily gives rise to "rabbit ears" growing up at the mesa edge, contrary to the non-re-entrant mesa, at which planar growth more easily was obtained [3,4]. The demand for a large mask overhang should disqualify the use of mesas formed with RIE without further wet etch for MOVPE regrowth.

General investigations of growth on non-planar and masked InP substrates show that both reduced reactor pressure and increased substrate temperature will contribute to improved planarity and selectivity due to increased diffusion lengths in the vapour and probably also to higher surface mobilities [5,6]. InGaAs/InP superlattice (SL) structures have been used to temporally resolve growth and investigate the growth behaviour on different lattice planes [7–10]. Here it is observed that the phosphorus-rich [111]B planes are reluctant to grow, while reduced growth may occur at the indium-faced [111]A planes [8]. The growth behaviour at the {110} planes is not fully clarified, but some InP nucleation seems to occur, while InGaAs does not grow at these facets [8,10]. Furthermore, it is obvious that arsenic containing compounds show a higher degree of faceted growth, while InP forms more rounded profiles. This implies that growth of InGaAs/InP superlattices is not ideal for studies of the growth behaviour of pure InP.

In this paper we present an investigation of InP growth with MOVPE around nearly rectan-
2. Experimental

The mesa stripes used in the growth experiments were formed along the [110] direction on (001) S-doped InP substrates. Plasma-deposited Si₃N₄ was used as a mask for the RIE performed with CH₄ and H₂ as active gases at an etch rate of about 2 μm/h. Remaining polymers were removed in an O₂ plasma. Prior to growth, the samples were cleaned in organic solvents, semi-clean and H₂SO₄ and also baked in the MOVPE reactor for 40 min in PH₃/H₂ atmosphere in order to remove the oxide layer from the surface. The mesa shape was not changed by this treatment. Growth was performed in a horizontal MOVPE reactor constructed for low pressure operation with substrate rotation, in more detail presented elsewhere [11]. Growth precursors were trimethyl-indium (TMI) and phosphine (PH₃) while silane and ferrocene (Cp₂Fe) were used for n-type Si doping and semi-insulating Fe doping, respectively. The PH₃/TMI ratio was about 150 and the nominal growth rate 1.5 μm/h on the (001) plane.

The mesa width was fixed to about 1 μm, while the height was varied between 1.5 and 4 μm. The epitaxial structures, mostly grown without removing the nitride stripes, consist of superlattices with four to twelve periods, depending on mesa height, of alternating n-doped and semi-insulating InP. After growth the samples were cleaved perpendicular to the mesas, stain etched and examined in a scanning electron microscope (SEM).

3. Results and discussion

In order to study the dependence of morphology on temperature, samples were grown at 580,
625 and 680°C. Figs. 1–3 show the most typical growth behaviour at the three temperatures and clearly illustrates the trend in growth habit as a function of temperature. The overall variation with temperature is independent of the reactor pressure in the range examined (see below). Slight
differences between mesas on the same sample were observed and they are most probably due to small differences in mesa shape. Growth performed at the lower temperatures shows the “rabbit ears” previously reported [2–4], but the planarity is greatly improved at the highest temperature. At 580°C (fig. 1) the growth rate on the substrate (001) plane is lower than on the {111}B planes, forming edge of the “ears”. There is also a significant nucleation on the {110} planes which form the mesa wall. This causes the growth to creep up the wall, covering the mesa, and leaves a triangular hole, restricted by the {111}A stop planes, which occurs just above the nitride stripe. It is this behavior that has been prevented by the mask overhang demanded in previous reports. This figure also shows the formation of grooves beside the mesa between the (001) plane and the slow growing {111}A planes. The relation between the high growth rate on the {111}B planes and the low growth rate on the (001) plane determines the depth of the grooves, probably combined with enhanced gas depletion in the cavity. At 625°C (fig. 2) the growth rate at the (001) plane is clearly higher than at the {111}A and {110} planes, but still the growth on these planes is too high for overgrowth to be avoided. Fig. 3 shows the planarity obtained at a growth temperature of 680°C. In this case, also nucleation occurs at the mesa walls, but it is only of minor importance and no tendency to form “rabbit ears” is seen. A higher growth rate near the mesa top than at the base is observed in all the examples. In order to further clarify the differences in growth behavior at high and low temperature, growth was performed around 4.5 μm high mesas at 580 and 680°C (figs. 4 and 5, respectively). Here the silicon nitride cap has been removed prior to growth to avoid disturbance from the otherwise inactive surface at the mesa top. Fig. 4 shows growth at 580°C. The mesa has been totally embedded and a decrease in growth rate from being high at the {001} planes to being lower at the {110} and poor at the {111} planes can be seen. This trend has also been observed by Garrett and Thrush for growth at 650°C [8]. Furthermore, they make clear that the ratio between the growth rate at the different planes is affected by diffusion from less reactive planes and hence strongly dependent on the geometry present. At 680°C the behavior is quite different; fig. 5 is a representative example. Here growth at the {001} and {111}B planes is enhanced, while the deposition on the {110} planes is nearly non-existent. At the slightly concave mesa base, where the lattice planes are poorly defined and growth is determined by adsorption to atomic steps, the initial growth rate is higher than at the adjacent atomically well-defined planes. The figure also shows the reluctance of growth at the {111}A planes. This indicates a high “sticking coefficient” on the phosphorus {111}B planes compared to the indium {111}A planes, which is contrary to previous work [8]. However, in that case both {111}A and {111}B planes were not simultaneously exposed. To explain the higher probability to nucleate at the phosphorus-rich planes, one has to consider that both In (with three valence electrons) and P (with five valence electrons) are bound to three
underlying atoms at the \{111\} planes. Hence zero and two electrons are free in the case of In and P respectively, which makes the phosphorus surface more reactive. When the (001) and \{111\}B planes are exposed, but not the \{111\}A planes, growth solely occurs at the former (fig. 6), which agrees well with the previous reports. This clearly shows that the “sticking coefficient” is smaller and hence the diffusion length larger on the \{111\}A planes that on the (001) plane.

Growth around capped mesas formed along the [110] direction showed similar overgrowth at 580°C as on those formed along the [110] direction, while at 680°C the mesas were not embedded due the reluctance of growth at the \{110\} walls and at the \{111\}A planes.

A clear temperature dependence of growth at the mesa wall \{011\} planes has been observed for GaAs [12]. The phenomena were then explained as being due to the desorption of As from the \{011\} planes which increases exponentially with temperature and reduces the probability of Ga incorporation and hence lowers the growth rate. In this case the growth rate at the (011) plane is reduced by a factor of five when the temperature

Fig. 5. Growth around a high mesa without cap at 680°C and 100 mbar.

Fig. 6. Growth around a high mesa capped with Si$_3$N$_4$ at 650°C and 75 mbar, with the intended thickness of the epitaxial layer larger than the mesa height.
is raised from 700 to 800°C. The volatility of phosphorus is higher than that for arsenic, which might explain why the transition occurs at a lower temperature.

Some effort has been made to investigate the influence of reactor pressure on the growth habit. The combinations of temperature and pressure examined are shown in fig. 7, where the tendency of overgrowth has been indicated. Obviously the dependence of reactor pressure on growth habit is weak in the region we have been able to examine (35 to 300 mbar), but overgrowth seems to diminish to some extent at lower pressures. Previous studies of the dependence of reactor pressure on growth on masked substrates has focused on nucleation and polycrystalline growth on large masked areas, which is not applicable here. The migration length of the reactants is about 10 μm on the mask [6] and it is sufficient to avoid deposition on the masked stripes in this case. To lower the molar fractions of the reactants, and hence the growth rate, is also thought to enhance the selectivity. We have grown one sample at 625°C and 100 mbar at halved growth rate. This did not change the growth behaviour. Phosphorus desorption might also increase at lower pressures and growth rates, but the dependence is only linear, while the temperature dependence is exponential. A thorough investigation of the pressure dependence in the temperature region where the growth rate at the mesa walls is changing rapidly (i.e. 625 to 680°C) could probably give more information relevant to this matter.

Fig. 7. Growth morphology as a function of reactor pressure and substrate temperature.

Fig. 8. Growth around a high laser mesa capped with Si₃N₄ at 680°C and 100 mbar.
Superlattice regrowth around laser mesas has been performed adopting the 100 mbar and 680°C process (fig. 8). The growth near the mesa is different from that around the mesa shown in fig. 3, but quite similar to that seen in figs. 5 and 6. This might be due to the difference in mesa profile. The mesa in fig. 3 is low and with vertical walls which forms nearly a right angle with the(001) surface at the base. Those in figs. 5, 6 and 8 are higher, the lower halves slope outward and they are significantly rounded at the base. Nucleation follows this rounding and growth proceeds until a (111) plane is reached. The structure is later planarized due to the fact that the growth rate is higher on the (001) plane than on the (111) planes and that the nucleation of InP tends to form rounded surfaces. This process seems to be sensitive to disturbances such as variations in mesa shape, which may cause overgrowth even at high temperatures, but there is no particular problem with growth around mesas containing quaternary InGaAsP and ternary InGaAs layers such as the active and contact layers in the laser structure shown.

Lasers (presented in detail elsewhere [13]) regrown with solely semi-insulating iron-doped InP give a threshold current of 30 mA, an output power of 20 mW per facet and a quantum efficiency of 20% per facet. The 3 dB modulation bandwidth is 7.9 GHz at 10.5 mW output power and not limited by parasitic capacitances. This indicates that the regrowth process does not significantly affect the laser structure, despite the exposure at a comparatively high temperature for a long time (about 2 h).

4. Conclusion

Growth of InP around reactive ion etched mesas without mask overhang has been examined with respect to substrate temperature and reactor pressure. It was found that planarity is greatly improved at higher temperatures, mainly due to a lower growth rate at the (011) planes forming the mesa walls. The influence of reactor pressure is weak, but at higher pressure overgrowth might be enhanced. The mesa shape near the base and hence nucleation of the first layers of InP seems to be important for the overall growth, and a rounded profile is in this case thought to deteriorate the result, contrary to what was previously reported for the case of mask overhang. Growth at 680°C and 100 mbar gives sufficient planarity and selectivity for laser fabrication.

Acknowledgements

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References

Improved InP regrowth properties in metalorganic vapor phase epitaxy by addition of CCl₄

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Selective and planar regrowth of InP around stripe mesa up to 5.5 μm height formed with reactive ion etching in InP substrates has been made with metalorganic vapor phase epitaxy by adding CCl₄ to the process gases. CCl₄ seems to prevent nucleation on the phosphorous-rich {111}B lattice planes and on the silicon-nitride cap at the top of the mesa and hence permits reproducible regrowth with desired morphologies for integration of optoelectronic circuits at mesas oriented along the [110] direction. The addition of CCl₄ does not influence dopant capability or the semi-insulating properties of Fe-doped material, for which a resistivity of 1 × 10⁷ Ω cm has been obtained.

Selective epitaxial regrowth around mesa structures is of great importance for, e.g., integration of optoelectronic circuits and in fabrication of laser diodes for high speed operation. Good regrowth morphology (i.e., planar and selective growth) is routinely obtained with hydride vapor phase epitaxy (HVPE), while regrowth using the more common method of metalorganic vapor phase epitaxy (MOVPE) has proven to be very sensitive to the mesa shape, formation of mask overhang, and to require high growth temperatures. Introduction of chlorine containing precursors in MOVPE improves the selectivity on large masked areas and has been used for growth of quantum wires and quantum dots in GaAs. CCl₄ is acting as a carbon dopant precursor in MOVPE growth of GaAs, but it has been shown that it is etching InP and that it will not influence the background doping level in growth of this material. In this letter, we present an investigation on the use of CCl₄ in MOVPE regrowth of InP around InP mesa which provides morphologies comparable to those obtained with HVPE. The growth behavior at different V/III ratios and pressures are discussed and the material quality with respect to regrowth of semi-insulating material is presented.

The stripe mesas were formed along the [110] and [110] directions on (001) oriented S-doped InP substrates using reactive ion etching (RIE) with H₂, CH₄, and Ar as active gases. Remaining polymers were removed in an O₂ plasma. Silicon nitride was used as mask for both etch and epitaxy. Prior to growth the samples were rinsed in semiclean, H₂SO₄, and water. They were also heated to 250°C in 40 min in the reactor. The original RIE mesa shape was not changed by this treatment and hence there was no mask overhang. The samples were grown in a horizontal MOVPE reactor at reduced pressure and at a susceptor temperature of 625°C. Growth precursors were trimethyl indium (TMI) and phosphine, while silane and ferrocene (C₅H₅Fe) were added for growth of n-type and semi-insulating material, respectively. The CCl₄/TMI ratio was usually fixed to about 0.07. To follow how growth proceeds around the mesas over time, structures with alternating n-doped and semi-insulating InP layers were grown, stain etched, and examined in scanning electron microscope (SEM).

At our ordinary growth conditions, i.e., a reactor pressure of 100 mbar, a V/III ratio of about 200 and no CCl₄ added, mesas formed with RIE are usually overgrown due to a high growth rate at the mesa walls and a tendency of growth to creep up on the top of the mesa. This is especially significant when nucleation occurs close to the edge of the nitride cap. It appears that this nucleation is often hindered by formation of a mask overhang. Figure 1 shows the typical growth behavior at these conditions when CCl₄ is added to the process gases. Fig. 1(a) shows growth around a 5.5-μm-high mesa formed along the [110] direction. It is obvious that no nucleation occurs at the nitride mask, which is in accordance with the experiments using chlorine containing compounds where large areas were masked. This figure also shows that the growth rate is about the same at the mesa walls as at the (001) substrate plane, but there is no growth at the phosphorous-rich [111]B planes until the [111]B and (001) growth meet, then growth is mainly propagating at the (001) plane and planes near [112] directions. The result is a nearly planar regrowth of the mesa, not limited by the mesa height or shape, and the overall behavior is similar to that obtained with HVPE. In Fig. 1(b) growth under the same conditions around a mesa formed along the [110] direction is shown. Again, nucleation occurs at the mesa walls and it seems to orient toward the exact [110] plane despite the mesa slope. There is no growth on the [111]B planes (face down), while the growth at the indium-rich [111]A planes (face up) results in overgrowth. The grooves originating from the mesa base are probably due to gas-phase depletion of reactants. The figure shows a representative example but growth geometry differs a lot from mesa to mesa and is possibly due to the density of atomic steps at the mesa walls and hence to the exact mesa shape. For example, the grooves are sometimes filled, but the growth rate at the [111]A planes is always high.

Figure 2 shows the normal growth behavior for mesas oriented along both the [110] and [110] directions when the reactor pressure is increased to 600 mbar, while the nominal V/III ratio is kept constant. However, raising the pressure is equal to raising the effective V/III ratio at the substrate surface and at the same time increasing the residence time of reactants, while the gas-phase diffusion is dimin-
isled. There is only minor growth at the mesa walls and from the mesa base growth is propagating at planes near the (114) plane just until the mesa top is reached, where planarization with the (001) plane occurs. However, sometimes nucleation does not occur on the walls of mesas oriented along the [110] direction when growth is performed at these conditions, and growth is then restricted by {111}A planes originating from the mesa base. It seems that growth on the mesa walls is very sensitive to the slope of the mesa and is probably due to stochastic nucleation at lattice step sites.

When the V/III ratio is raised to 900 at a reactor pressure of 600 mbar, the growth proceeds as shown in Fig. 3. Around mesas oriented in the [110] direction [Fig. 3(a)] growth behaves as at a V/III ratio of 200 and a pressure of 100 mbar [compare Fig. 1(a)], while around mesas in the [110] direction [Fig. 3(b)] growth is like that occurring at a V/III ratio of 200 and a pressure of 600 mbar (compare Fig. 2). However, at some mesas the small white edges at the nitride edge has grown up at the [111]A planes and given rise to overgrowth.

From the experiments, it is obvious that selective and planar regrowth around mesas oriented in the [110] direction is not critical when CCl₄ is added to the process gases, while problems might occur at growth around [110] oriented mesas. This seems mainly due to the fact that CCl₄ hinders growth at the phosphorous-faced {111}B planes but not at the indium-faced {111}A planes. Growth at these latter planes and at the {110} mesa walls seems to be reduced at higher total reactor pressure, while raising the phosphine flow rate to some extent again increases the growth rate at these planes. CCl₄ is believed to react with indium, forming volatile InCl₄ molecules, which could explain the reluctance to grow at the phosphorous-faced

![Image](https://example.com/image1.png)

**FIG. 1**. Regrowth around a 5.5-µm-high mesa at 625 °C, 100 mbar, and a V/III ratio of 200. (a) mesa oriented along the [110] direction, (b) mesa oriented along the [110] direction.

![Image](https://example.com/image2.png)

**FIG. 2**. Regrowth around a 5.5-µm-high mesa at 625 °C, 600 mbar, and a V/III ratio of 200. This growth behavior is equal for mesas in both the [110] and the [110] direction.

![Image](https://example.com/image3.png)

**FIG. 3**. Regrowth around a 5.5-µm-high mesa at 625 °C, 600 mbar, and a V/III ratio of 900. (a) mesa oriented along the [110] direction, (b) mesa oriented along the [110] direction.
planes, where next layer to grow is an indium layer with only one bond to the underlying phosphorous atoms. The increase in growth rate at the indium-faced $\{111\}$A planes at raised $V/III$ ratio at high reactor pressure might be due to reduced indium desorption from the efficiently phosphorous-covered indium-faced surface. The reduction in growth rate on planar substrates with an increasing CCl$_4$ flow at a $V/III$ ratio of 200 and a reactor pressure of 100 mbar is shown in Fig. 4. The extrapolation to zero growth gives a CCl$_4$/TMI ratio of about 1:4 (i.e., a Cl:In ratio of 1:1), which indicates that nearly all CCl$_4$ does react with indium.

The usefulness of CCl$_4$ for regrowth is strongly dependent on the material quality obtained while adding CCl$_4$ during epitaxy. The background doping level, measured with electrochemical C-P' etch profiling, did not increase above our normal level of $3 \times 10^{15}$ cm$^{-3}$, which confirms previous reports. Neither did addition of CCl$_4$ influence the doping level of intentionally Si-doped $n$-type material. Iron-doped layers, used for current blocking in e.g. laser diodes, were also grown. The Fe level was determined with secondary ion mass spectroscopy (SIMS) using oxygen as primary beam and positive ion detection. The result showed that CCl$_4$ did not influence the doping level. Since neither background doping nor iron doping were changed by adding CCl$_4$, the semi-insulating properties were expected to be maintained. This was confirmed by measuring the resistivity: $1 \times 10^{10}$ $\Omega$ cm was obtained and this compares favorably to values measured on samples grown without CCl$_4$. However, the surface morphology, as observed by Nomarski interference microscopy, is slightly deteriorated if large CCl$_4$/TMI ratios are used.

In conclusion, we have obtained planar and selective MOVPE regrowth of InP at standard growth temperatures around high and narrow reactive ion etched stripe mesas in InP substrates by adding CCl$_4$. Mesas oriented along the [110] direction are preferable to those oriented along the [110] direction, although growth morphology around the latter is improved at high reactor pressure. In addition, we have shown that CCl$_4$ does not influence doping levels and hence that this method could be used for regrowth of InP in a wide range of integrated optoelectronic applications.

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Influence of MOVPE growth conditions and CCl$_4$ addition on InP crystal shapes

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Growth of InP with metalorganic vapour phase epitaxy (MOVPE) around reactive ion etched stripe mesas has been studied. The mesas were oriented along the [110] and [110] directions. Marker layers of different doping were introduced in order to follow growth with respect to time. The growth parameters were varied in order to investigate the influence of reactor pressure, V/III ratio, substrate temperature and addition of CCl$_4$ on the overall growth behaviour. The final crystal shape could, in general, be well described in Wulff diagrams. The results are discussed with respect to diffusion, chemical reactions and surface kinetic aspects. The significant improvement of regrowth properties observed when CCl$_4$ was added is most probably due to CI adsorption to group V sites, acting as an inhibitor for P adsorption and hence restricting growth on (111) planes. With CCl$_4$ present, the reactor pressure and V/III ratio could be used to further control growth on the (111)$_A$ and (110) planes. Due to the asymmetry between (110) and (111) planes, the growth habit was found to be sensitive to the slope of the mesa walls. However, the effect of this sensitivity was diminished when adding CI.

1. Introduction

Metalorganic vapour phase epitaxy (MOVPE) is the leading technique for growth of high quality III–V optoelectronic materials for device applications. Detailed control of growth on masked and non-planar substrates is becoming increasingly important when device performance and integration rise the need for more complicated three dimensional structures and processes involving several steps of etching and epitaxial growth. Especially demanding are high performance lasers which may require as many as five steps of epitaxy [1], where embedding of the laser mesa with semi-insulating material has been a morphological challenge [2–5]. Although, some promising results have been obtained [6–8] but there still remain problems to be solved. Another field where growth on patterned substrates has proven to be useful is fabrication of nanostructures, which has taken advantage of the variation of growth rate with crystallographic orientation [9–11]. The GaAs/AlGaAs material system has been extensively examined with respect to orientation dependent growth [12–16]. The possibility to grow and stain etch structures consisting of alternating GaAs and AlGaAs in order to follow the development of growth with time has in some cases facilitated these studies. Asai made some simple experiments growing GaAs around circular mesas and developed a model for the growth habit based on the atomic arrangement at lattice planes and kink sites [17]. Later the relative growth rates on the fundamental lattice planes of GaAs at ordinary MOVPE growth conditions have been published [18]. Some growth habit studies have also been made for InP/InGaAs [19–22]. It is claimed that InGaAs to a greater extent than InP is reluctant to grow on the (111) lattice planes. This makes studies where InGaAs marker planes have been inserted in order to temporally resolve the growth process less reliable for determination.
of the growth behavior of InP. Some growth studies of purely InP on etched and/or masked substrates have been made [2–5,23,24], but only one adopts the use of marker layers (ref. [5]) where doping changes have been used to achieve contrast.

Growth on patterned substrates with masked areas requires mask selectivity. Experimental evidence indicates that high growth temperatures, low growth rate and low reactor pressure decreases the nucleation probability on the mask [25,26]. In recent years chlorine containing compounds have been successfully used to inhibit these depositions, even at atmospheric pressure [27–29]. Addition of chlorine during growth also seems to influence the relative growth rates between lattice planes and especially to reduce growth on (111) planes [11,27,30].

In general, models which describe the growth behavior are lacking. A rough estimation of growth shapes can be done using the modified Wulff construction, which is the solution to the equations determining the crystal shape if the growth rates on the planes forming the steady state shape are known and constant all over the structure [18]. Hence the construction agrees with the crystal shape when growth is limited by surface kinetics but disagrees when, e.g., surface migration is significant or when the supply of reactants is inhomogeneous. This provides a sensitive tool to distinguish between different effects contributing to the growth behavior.

Most papers in this field focus on only one or a few growth parameters and the results are most probably dependent on reactor configuration and substrate pattern. Still, there is a lack of reports on simultaneous influence of several fundamental parameters examined in a reproducible environment. We have investigated the growth habit of InP around high, nearly rectangular stripe mesas, with respect to changes in V/III ratio, reactor pressure, substrate temperature and addition of Cl. The salient features of the regrowth are described by Wulff constructions, but to determine the detailed crystal shapes other effects, such as reaction kinetics and diffusion, have to be taken into account. Probable mechanisms that could explain the observed growth habits are discussed.

2. Experimental procedure

Approximately 4 μm high and 1 μm wide stripe mesas were formed along the [110] and [110] directions (within ±1°) on (001) ± 0.5° oriented S-doped InP substrates with reactive ion etching (RIE). A SiN₄ mask deposited by plasma enhanced chemical vapor deposition was used both for RIE and the subsequent epitaxy. RIE was performed at 15 mTorr and 150 W with CH₄ and H₂ as active gases, in some cases together with Ar. It was found that mesas etched without Ar were slightly underetched, showing a reentrant profile with a "neck" about 1 μm below the top (fig. 1a), while the walls of the mesas etched with addition of Ar were sloping outwards (fig. 1b) with an angle α between the substrate plane and the mesa wall of about 95° to 100°, increasing with increasing Ar molar fraction. No mask overhang was formed in either case. Despite the fact that the form of the mesa was found to influence the detailed growth morphology, it did not considerably change the relative growth rates between crystallographic orientations and hence did not influence the conclusions of this investigation. After RIE the remaining polymers were removed in an oxygen plasma. Prior to growth the samples were rinsed in semiclean, H₂SO₄ and water and baked in the MOVPE reactor at 250°C for 40 min in PH₃/H₂ atmosphere; this treatment did not change the mesa

![Fig. 1. Mesa shape after RIE without (a) and with (b) addition of Ar.](image-url)
shape. Growth was performed in a horizontal MOVPE reactor, described in detail elsewhere [31]. PH₃ and trimethylindium (TMI) were used as growth precursors, while silane and ferrocene were used for n-type Si doping and semi-insulating Fe doping, respectively. In some experiments, CCl₄ was added with a CCl₄/TMI ratio of about 0.1 in order to provide chlorine to the growth surface. Epitaxial structures consisting of alternating n-doped and semi-insulating layers, each of a few hundred nanometers in thickness, were grown at a growth rate of 1–2 μm/h. The samples were cleaved perpendicular to the mesa, stain etched in 1 g K₃Fe(CN)₆: 4 g KOH: 16 g H₂O under illumination and examined in a scanning electron microscope (SEM).

3. Results

A summary of growth rates on different lattice planes for varied growth conditions is given in table 1. Some representative samples are further presented in SEM micrographs, polar growth rate diagrams and Wulff plots. Squares in the polar diagrams depict measured relative growth rates on the basic lattice planes. When making the Wulff constructions, the growth on other planes has been assumed not to contribute to the final crystal shape, in accordance with the interpolation proposed by Shaw [32], which is indicated with dots in the polar diagrams. The starting point around which growth is to be predicted (preferably a discontinuity on the crystal surface, e.g., a mask edge or an etched corner) is placed in the origin of the polar growth rate diagram and growth rate vectors are drawn to the periphery. The final crystal shape is defined by the envelope of normals to these vectors. Growth performed on a convex contour is determined by the slowest growing planes and growth on a concave contour by the fastest growing planes. Detailed guidelines for the use of Wulff constructions are given in refs. [18] and [32]. In order to clarify the construction method, growth rate vectors in the figures are indicated with broken lines, their normals with thin lines and crystal contours with thick lines. Since a mesa oriented along the [110] direction on a (001) surface is equivalent to a mesa oriented along the [110], the [110], the [110] and the [110] direction on a (001)

<table>
<thead>
<tr>
<th>Sample</th>
<th>V/III ratio</th>
<th>Depositor temperature (°C)</th>
<th>Reactor pressure (mbar)</th>
<th>[CCl₄]/[TMI]</th>
<th>Normalized relative growth rate at plane (001)</th>
<th>Relative growth rate at plane (001)</th>
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<tr>
<td>A</td>
<td>100</td>
<td>625</td>
<td>100</td>
<td>-</td>
<td>1.0 0.7 0.7 1.0 0.7 0.7 0.7 0.7 0.3 0.3 0.3 0.3</td>
<td>0.7 0.7 0.7 0.7 0.7 0.7 0.7 0.7 0.7 0.7 0.7 0.7</td>
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<tr>
<td>B (fig. 2)</td>
<td>200</td>
<td>625</td>
<td>100</td>
<td>-</td>
<td>1.0 0.65 1.0 0.7 0.7 0.7 0.7 0.7 0.3 0.3 0.3 0.3</td>
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Fig. 2. Growth behaviour of sample B: (a) mesa oriented along the [110] direction; (b) mesa oriented along the [1\bar{1}0] direction; (c) polar growth rate diagram; (d) Wulff plot for mesa oriented along the [110] direction; (e) Wulff plot for mesa oriented along the [1\bar{1}0] direction; (f) formation of an extended (111)B plane on a mesa oriented along the [110] direction.
Fig. 3. Growth behaviour of sample D: (a) mesa oriented along the [110] direction; (b) mesa oriented along the [110] direction; (c) polar growth rate diagram; (d) Wulff plot for mesa oriented along the [110] direction; (e) Wulff plot for mesa oriented along the [110] direction.
surface, the polar diagrams can be used for both mesa directions.

Growth rate data have been collected from several mesas and are in some cases from a couple of growth runs under reproduced conditions. The uncertainties in relative growth rates are about 10%. The growth rate on the (001) plane is measured at the substrate between the mesas used for growth rate normalization. The growth rate on the [110] mesa walls is often lower at mesas oriented along the [110] direction than at mesas oriented along the [110] direction and an average of the two growth rates has been depicted (cf. section 4.3).

3.1. Growth without CCl₄

Fig. 2 shows the crystal shape of sample B grown at our normal conditions, i.e. a reactor pressure of 100 mbar, a susceptor temperature of 625°C and a V/III ratio of 200. Figs. 2a and 2b show SEM micrographs of growth around mesas oriented along the [110] and [110] directions, respectively. A slight decrease in growth rate is observed from (001) to (111)A, (110) and (111)B, as depicted in the polar diagram (fig. 2c). The Wulff plots of growth around the mesas in the [110] and [110] direction are shown in figs. 2d and 2e, respectively. Important to notice are the details in growth behaviour not included in the Wulff plots. At the base of the [110] oriented mesa, growth seems to creep up and form a rounded profile which never aligns with the exact [110] mesa walls. At the [110] oriented mesa, growth does indeed occur on the exact [110] planes and does not follow the curvature of the mesa, and a sharp line separates the (001) and [110] growth regions. For both mesa shallow grooves are formed where the (110) and (001) planes meet. In the Wulff plots it is indicated that there should be two peaks restricted by (111) and (001) planes at the top of the mesa. At the [110] oriented mesa, the two peaks have grown together after about six periods of alternating Si- and Fe-doped InP, while at the other mesa, both peaks are maintained and a bright delineating line is seen at their intersection. The absence of

the (001) planarization on top of the peaks indicates that the ratio between the growth rate on the (001) and (111) planes is underestimated.

Fig. 2f shows a common defect occurring at mesas oriented along the [110] direction. A very thin and 10–50 μm long plane has grown along the [112] direction during a few periods after which the thickness increases uniformly (in this case to about 2 μm). As the plane acts as a "shadow mask" [33], the growth rate on the substrate below the plane is reduced. Experiments with a non-rotating susceptor with mesas aligned parallel and perpendicular to the gas flow direction showed that growth asymmetries are not associated with the gas flow direction, but rather with the crystallographic orientation of the mesa walls.

At the susceptor temperature of 625°C and reactor pressure of 100 mbar, the V/III ratio was lowered to 100 (sample A) and raised to 900 (sample C). The growth habit did not change from normal to low V/III ratio, but the high V/III ratio resulted in a halved growth rate on the (001) plane and a decreased relative growth rate on the (111)B planes.

Fig. 3 shows the growth behavior at a susceptor temperature of 625°C and a V/III ratio of 200 but with the reactor pressure increased to 600 mbar (sample D). For the mesa oriented along the [110] direction (fig. 3a), growth at the mesa top starts on the (111)B and (001) planes but after about five to six periods, the growth rate on the (001) plane increases and the (111)B surface tilts towards [110]. In the Wulff plot for this case (fig. 3d) two alternative shapes of the overgrowth are proposed, where the one restricted by the (001) plane at a low level is the correctly constructed. However, the (001) growth rate at the mesa top in fig. 3a is nearly double that at the substrate and hence it should not restrict the crystal shape. For the mesa oriented along the [110] direction (figs. 3b and 3e), slow growing planes near (114)A makes the overgrowth heart-shaped. From the Wulff plot it is assumed that these planes also should be visible at the mesa base, but instead growth in this region is determined by depletion of reactants resulting in formation of deep grooves.
Fig. 4. Growth behaviour of sample E: (a) mesa oriented along the [110] direction; (b) mesa oriented along the [1\overline{1}0] direction; (c) polar growth rate diagram; (d) Wulff plot for mesa oriented along the [1\overline{1}0] direction; (e) Wulff plot for mesa oriented along the [110] direction.
Fig. 5. Growth behaviour of sample G: (a) mesa oriented along the [110] direction; (b) mesa oriented along the [1\bar{1}0] direction; (c) polar growth rate diagram; (d) Wulff plot for mesa oriented along the [110] direction; (e) Wulff plot for mesa oriented along the [1\bar{1}0] direction.
Fig. 6. Growth behaviour of sample I: (a) mesa oriented along the [110] direction; (b) mesa oriented along the [110] direction; (c) polar growth rate diagram; (d) Wulff plot for mesa oriented along the [110] direction; (e) Wulff plot for mesa oriented along the [110] direction.
When the susceptor temperature is raised to 680°C at a reactor pressure of 100 mbar and a V/III ratio of 200 (sample E and fig. 4), the growth rate is considerably reduced on the (110) and (111)A planes but maintained on the (001) and (111)B planes. The difference in growth rate on the walls of mesas oriented along the [110] (fig. 4a) and [110] (fig. 4b) is obvious. For the former mesa, growth is creeping up the wall where some deposition does occur but there is no restriction to exact lattice planes. However, an alignment with planes close to (111)B proceeds during the last periods when the grooves, where growth on the substrate and mesa walls meet, are filled. In this figure and in the corresponding Wulff plot (fig. 4d) it is also seen how mask overgrowth starts from the nucleations near the nitride. The Wulff plot suggests a rectangular overgrowth (the inner thick lines) but again relative growth on the (001) plane is underestimated and the overgrowth is restricted primarily by (110) and (111) planes. Due to the Wulff plot in fig. 4d some nucleation should occur on the mesa walls and mouse ears appear at the nitride. This growth was also seen, but the most common growth behavior is shown in fig. 4b. Here both the mesa walls and the (111)A planes are non-growing and the shape of the crystal is the same that should be the case at a convex contour (the (111)A stop planes are indicated by a thin line in the Wulff plot).

3.2. Growth with CCl₄ added

The result obtained with CCl₄ added at 100 mbar reactor pressure, 625°C susceptor temperature and a V/III ratio of 200 is shown in fig. 5 (sample G). The remarkable change in growth with Cl support is that the (111)B planes are completely reluctant to growth (cf. sample B). This will considerably change the growth behavior around mesas along the [110] direction (fig. 5a). Growth on the mesa walls is restricted by the (111)B planes and when they meet the growing (001) plane, growth will proceed on the (112)B planes, until the mesa top is reached. At this point growth will planarize with the (001) plane and no growth will occur over the nitride mask due to the non-growing (111)B planes. The Wulff construction for this case has to be done in three steps, following the growth, as indicated in fig. 5d. At the left side are shown the first two steps, with the intersection between the (111)B and (001) planes indicated with an arrow at 1 and the point where the (112)B plane reaches the mesa top with an arrow at 2. At the right side, the final construction step is shown. For the mesa oriented along the [110] direction (figs. 5b and 5e) the growth behavior is not considerably changed by CCl₄ addition.

When the V/III ratio is increased from 100 to 200 and 900 (samples F, G and H respectively) at a constant susceptor temperature of 625°C and a reactor pressure of 100, the relative growth rates decrease for the (111)A and (112)B planes. The increase in overall growth rate at the highest V/III ratios is, to some extent, due to a lower [CCl₄]/[TMII] ratio, but the significant decrease as observed for sample C does not occur.

A reactor pressure of 600 mbar at a susceptor temperature of 625°C and a V/III ratio of 200 gives the growth behaviour shown in fig. 6 (sample I). Still there is no growth on the (111)B planes and the relative growth rates on the (111)A and [110] planes are reduced, while growth on high index planes is pronounced. These planes are near [114] but slightly bowed and hence not possible to exactly specify. The growth rate on the mesa walls is higher for mesas oriented along the [110] direction (fig. 6a) than for mesas along the [110] direction (fig. 6b), but in both cases growth on the high-index planes originates from the mesa base and proceeds until the top of the mesa is reached, where planarization with the (001) plane occurs. The reluctance to grow on the (111)B planes guarantees that no overgrowth will occur at mesas oriented along the [110] direction, as seen from the micrograph and the Wulff plot in fig. 6d. This is in contrast to the plot in fig. 6e, representing growth around a mesa in the perpendicular direction, where two different crystal shapes are indicated. The one to the left is made directly from the data in the polar diagram (fig. 6c), assuming a low growth rate on the mesa walls; nucleation above the nitride is hence predicted. This growth habit has also been observed.
The construction to the left is made with the assumption that no growth occurs on the (110) mesa walls but otherwise in accordance with the polar diagram, and this comes close to the crystal shape in Fig. 6b.

For sample J, the V/III ratio was raised to 900 at the reactor pressure of 600 mbar and a susceptor temperature of 625°C. The result is presented in Fig. 7. Compared to sample I, the relative growth rates are increased on the mesa walls and (111)A planes, but decreased on the higher-index planes. This reveals a growth behaviour similar to that obtained at 100 mbar reactor pressure for the mesa along the [110] direction (sample G). Again the variation in growth habit is large for mesas along the [110] direction. Fig. 7b shows one example but there have also been mesas with no growth on the walls and hence no overgrowth [30]. However, the planes near (115)A always appear. Furthermore, the overall growth rate is halved, in accordance with sample C, grown at high V/III ratio without CCl₄, but contrary to sample H grown at high V/III ratio and low pressure.

Finally, growth was performed at a susceptor temperature of 680°C, with reactor pressure and V/III ratios varied. At a V/III ratio of 200 and a pressure of 100 mbar (sample K) growth on the (111)B planes occurs, despite addition of CCl₄. Growth rate on the mesa walls is low and there is no growth at all on the (111)A planes. The overall crystal shape is quite similar to that obtained at the same growth conditions but with no CCl₄ added (sample E), but there is no deposition in the vicinity of the nitride mask for any of the mesa orientations. For sample L the reactor pressure is raised to 600 mbar and for sample M the V/III ratio is increased to 900 at this pressure. The growth behaviour for these samples is similar and close to that at low temperature and low pressure. However, the relative growth rate is increased on the (110) and (111)A planes and decreased on the (112)B planes. The overall growth rate does not seem to be influenced by the pressure or V/III ratio at this high temperature.

4. Discussion

4.1. Effects of diffusion limitations

In Figs. 2–4, the (111) growth rate at the mesa top is overestimated compared to the (001) growth rate. This is most significant for sample D, grown at high reactor pressure (Fig. 3), where also the planes which are near (111) change direction due to enhanced nucleation near the top of the crystal formation. This is most probably due to a higher reactant concentration gradient near the mesa top than over the planar substrate (Fig. 8) and the fact that the growth rate is limited by the amount of reactants diffusing to the growing surface. This effect has been observed for growth in channels.
[14] and successfully modelled [34]. The grooves where the growth on the mesa walls and substrate planes meet cannot be included in the Wulff plot because stop planes in concave geometries can only be perpendicular to vectors originating from the innermost point in the concavity and directed out from the crystal surface. These grooves are hence most probably due to variation in the concentration gradient. An anomaly related to this effect is illustrated in fig. 4b, where the non-growing {111}A planes originating from the mesa base behave as if this point was convex. The low concentration of reactants at the mesa base when growth starts might establish the convex geometry which is conserved during growth by the low nucleation probability on the mesa walls and {111}A planes. However, in some cases (e.g. figs. 2f and 3b), the growth rate is reduced by hindered supply of reactants due to a shading crystal formation. The growth shape is then close to what is expected from shadow masks [33].

A defect caused by surface migration is shown in fig. 2f. The enhanced growth in the [11\overline{2}] direction seems to be initiated by diffusion of reactants to an edge, where nucleation occurs. The edge ceases to grow when it has become thick enough to be regarded as a stop plane. Hence the length of this plane (10–50 \mu m) is determined by the surface diffusion length and the adsorption/desorption ratio. The observation that these defects always extend along the {111}B planes suggests that the reaction probability on these planes is low. This is in accordance with reports on growth of As-containing compounds which state that the {111}B plane is a non-growing plane with high surface mobility [14,20]. This growth habit could be explained by the fact that the {111}B plane, due to the overpressure of group V material, forms a planar group V surface which provides only one bond to each group III atom. Despite this, an appreciable growth rate is observed on InP {111}B planes, indicating a low desorption probability due to relatively strong bonds between In and P. At higher reactor pressure the ability to form atomically planar {111} surfaces decreases (fig. 3), which indicates a lower surface mobility.

High temperature is believed to enhance both surface migration [14] and desorption. As seen in fig. 4, a large variation in growth rate on the lattice planes is observed. In some regions near the mesa the marker planes are disappearing, which indicates a disordered three dimensional nucleation and growth. This, and the reluctance to grow on the {111}A planes and {110} mesa walls, is likely to be due to the enhanced P evaporation from the surface.

4.2. Effects of Cl species

For the samples grown with addition of CCl₄ the Wulff plots are in general in good agreement with the crystal shapes (figs. 5 and 6), especially when the non-growing {111}B planes are exposed. This indicates that the growth is limited by surface kinetics rather than diffusion and surface migration. From thermodynamical considerations CCl₄ in PH₃ will form HCl and the elements at ordinary growth temperatures [35]. As shown in refs. [30] and [35], introducing CCl₄ at moderate V/III ratios results in a reduction of growth rate on the (001) plane in a stoichiometric relation of roughly 1:1 between In and Cl, indicating that volatile InCl is formed, which does not contribute to the growth. If this reaction was solely homogeneous, the growth rate should decrease compared to normal MOVPE, but no other difference in growth behaviour should occur. This is in contrast to observations; hence Cl must be adsorbed at the surface, possibly bound to In atoms as in vapor phase epitaxy based on Cl precursors (VPE) [36].
The reluctance to grow on the (111)B planes could either be due to Cl strongly bound to P sites hindering In adsorption or to long diffusion lengths of Cl and In species on the smooth P-covered surface, providing large probability for InCl formation. Growth on the (112)B planes is supported by the occurrence of step sites where In atoms could be tightly bound. When the Cl/In ratio is raised, the growth rate on the (001) plane decreases, while the relative growth rate on the (112)B plane increases. This is in accordance with VPE results where the relative growth rate on high-index planes is even higher and no growth occurs on the (111)B planes [37,38]. The growth habit on the (111)A planes is not much changed by the addition of CCl₄. At this plane there are three indium bonds to the underlying phosphorus layer, which results in a low reaction probability with Cl. The P excess provides a new surface for indium nucleation. When the V/III ratio is raised the relative growth rate on the (111)A and (112)B planes decreases. This might be due to an increase of relative growth rate on the (001) and (110) planes and could be explained from the Langmuir–Hinshelwood model [39] as a competition between Cl and P about the group V lattice sites. Cl is acting as an inhibitor with low desorption probability and hence high surface occupation in relation to the gas phase concentration. P has a high desorption probability but is supplied in large excess. Providing more P will lower the relative Cl surface occupation and the growth rate will increase. The (111)A and (112)B planes are not so sensitive to changes in P/Cl ratio and their growth rates are less affected.

At raised reactor pressure with CCl₄ added, nucleation is driven to occur on high-index planes while growth on the (111)A and (110) planes is considerably reduced. This indicates an increased Cl adsorption to the surface, which is consistent with low surface mobility and desorption. The high-index planes have a high density of nucleation sites which provides three bonds for the In atom to the surface. These sites are preferential for growth when the probability of InCl formation increases. When the V/III ratio is raised growth again occurs on the (111)A and (110) planes. This is in accordance with the assumption.

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**Fig. 9.** Configuration of surface bonds on mesa walls for: (a) a mesa oriented along the [110] direction; (b) a mesa oriented along the [110] direction.
of a competition between Cl and P for the group V nucleation sites. The high PH₃ concentration will diminish the Cl surface adsorption and hence the crystal shape will approach the low pressure appearance.

At increased temperature and low effective V/III ratio, growth occurs also on the (111)B plane despite addition of CCl₄, while no deposition occurs on the mask. Growth on the (111)B planes is inhibited at raised effective V/III ratio. This indicates that a reasonably high P pressure at the crystal surface prevents high surface mobility of In species and hence a disordered nucleation.

The reduced (001) growth rate observed at high V/III ratio (sample C) might be due to substantial parasitic gas phase reactions [40]. Since the growth rate is not altered by a total pressure change (sample D), one can exclude the possibility that solely increased surface coverage of P should give this result. This growth rate reduction is not seen when CCl₄ is added under same growth conditions (sample H), while it does occur at high V/III ratio combined with high reactor pressure (sample J). Tentatively we suggest that Cl might heterogeneously catalyse adduct decomposition and thereby increase the In incorporation.

4.3. Effects of bonding configuration

Common for all growth conditions is a higher growth rate on the mesa walls and more rounded growth surfaces in the vicinity of mesas oriented along the [110] than along the [1$\bar{1}$0] direction. In the latter case growth tends to align with the exact (110) planes and sometimes a non-growing (111) plane originates from the mesa base. While growth rates on different planes change with growth conditions these effects are unaffected and hence not due to diffusion or chemical composition of the gas but rather to the configuration of the lattice itself. Growth at (110) step sites is extensively discussed for GaAs in ref. [17]. In figs. 9a and 9b are shown the atomic configurations of walls of mesas oriented along the [110] and [1$\bar{1}$0] directions, respectively. Growth rate is limited by surface adsorption of In atoms (shaded in the figures) and to them P atoms are bound at sufficient P excess (i.e. at high V/III ratios and moderate temperatures). Indium is attached to the (001) plane with two bonds which are perpendicular to the [110] but parallel to the [1$\bar{1}$0] direction. This will preserve steps and support growth perpendicular to [110] oriented mesas. This is significant at high substrate temperature when steps are rapidly filled at the mesa base and (111)B planes are formed. At mesas oriented along the [110] direction the preferential growth direction is parallel to and up the mesa and steps at the mesa walls are eliminated. P bound to In atoms on the surface with only one bond are directed away from the steps at the mesa walls which makes this surface very sensitive to P depletion at raised temperatures. The asymmetry between the (110) and (1$\bar{1}$0) planes makes the regrowth properties sensitive to slopes of mesa walls and exact mesa orientation. The fact that unwanted embedding of the nitride mask due to deposition on (111) planes most often originates from growth on the mesa walls further enhance the importance to control this growth. Hence optimisation of the mesa shape has been of great importance, especially when no Cl is added during growth [2–4].

5. Conclusions

In summary we have presented an extensive study of the growth behaviour of InP around masked stripe mesas. We have determined the relative and absolute growth rate variations for the important lattice planes as a function of growth parameters. The Wulff constructions were found to be a valuable tool to describe the final crystal shape. Influences of diffusion limitations, chlorine surface reactions and surface bonding arrangements have been discussed for specific cases. We believe that the data and qualitative explanations presented here provides a good basis for continued work on selective regrowth on patterned surfaces in general and would thus be important for future work in the direction of integrated optoelectronics.
Acknowledgements

Dan Haga is gratefully acknowledged for mesa fabrication and S. Lourdudoss for fruitful discussions.

References

MOVPE REGROWTH OF SEMI-INSULATING InP AROUND REACTIVE ION ETCHED LASER MESAS

Indexing terms: Semiconductor devices and materials, Semiconductor lasers, Laser

Semi-insulating iron doped InP was grown with MOVPE around reactive ion etched laser mesas without using any wet etchant to optimise the mesa shape or to form a mask overhang. To achieve good planarity and selectivity, growth was performed at high temperature and low pressure. The resulting 3dB modulation bandwidth of the buried heterostructure laser was 7.9 GHz at 10.5 mW.

Introduction: InP/InGaAsP buried heterostructure (BH) lasers are key devices for optical communication at high frequencies. To meet the increasing demand for high performance BH lasers it is important to develop a laser fabrication process with high reliability and reproducibility. Metal organic vapour phase epitaxy (MOVPE) has proved to be a technology which can offer uniform growth over 2 inch wafers and high crystal quality both for the active laser structure and for regrowth of the surrounding current blocking layer. 1,2 Formation of the laser mesa and the subsequent regrowth have been shown to be important and nontrivial steps in fabrication of these devices. Reactive ion etching (RIE) provides a non-selective etch for formation of mesas with high accuracy in width and height, contrary to the usually used wet etchants,3 but there are considerable problems in growth of planar and selective epitaxial layers with MOVPE around RIE etched mesas due to the undefined lattice planes at the mesa walls. These problems largely disappear when regrowth is performed using wet etched mesas with a smooth mesa profile4 or a mask overhang which will suppress vertical growth at the mesa edge. 5,6 Optimised mesa profiles can also be obtained using a combined process including a dry etch step followed by wet etch prior to regrowth7 but for accurate process control the wet etch step has to be avoided.

We report on successful planar and selective MOVPE regrowth of semi-insulating Fe-doped InP around RIE etched laser mesas where no wet etch step was used.

Regrowth and semi-insulating properties: The desired result after regrowth is a planar structure with no deposition on the nitride mask which covers the laser mesa. To obtain this the growth parameters have to be chosen so that surface migration of the reactants relative to the growth rate is enhanced. This is believed to be the case at high susceptor temperature, low reactor pressure and low growth rate. Our experiments (which will be presented in detail elsewhere) show that no significant improvement can be obtained by only changing the growth rate and pressure, but growth temperatures increased to 680°C as opposed to the normal 625°C give the required planarity and selectivity. Wafer cleaning also seems to be important for the selectivity.

Iron doped InP grown on planar substrates was of high resistivity (about 5 x 10^8 Ωcm) and the iron content measured with secondary ion mass spectroscopy (SIMS) was about 1 x 10^18 cm^-3, which is well above the solubility limit of iron in InP. This may result in formation of some iron phosphide precipitates, but will not necessarily lead to poor overall crystal quality.8

Device fabrication: The laser structure (Fig. 1) is grown in the (001) direction on a 5-doped InP substrate using low pressure MOVPE. The active region is lattice matched to InP and consists of five 6 nm wide InGaAs quantum wells (MQW) between 8 nm thick barriers of InGaAsP (λ = 1.3 µm). The quantum wells are surrounded by a symmetrical graded index separate confinement layer (GRINSCH) with the band gap graded from InGaAsP (λ = 1.01 µm) to InGaAsP (λ = 1.3 µm) in 12 equal 0.73 nm wide steps.

2 µm wide and 2.5 µm high mesa stripes were formed by reactive ion etching along the (110) direction using CH3 and H2 as active gases and Si3N4 as mask. Prior to regrowth the structure was cleaned in organic solvents, semiconductor and H2SO4 and also baked in the MOVPE reactor for 40 minutes in PH3 atmosphere. The regrowth was performed at 100 mbar and 680°C using trimethylindium, phosphine and ferrocene as precursors at a growth rate of 1.5 µm/h. 6 µm wide contact stripes were made on the laser stripes after regrowth.

Device performance: The devices had a lasing wavelength of 1.46 µm and measurements at 20°C on 300 µm long lasers at

![Fig. 2 Modulation response for different optical output power](image)

(i) 2 mW
(ii) 10.5 mW
(iii) 7.5 mW

CW operation gave a threshold current of 30 mA, an output power of 20 mW per facet and a quantum efficiency of 20% per facet. Small signal frequency response measured at various output power levels is shown in Fig. 2. A 3 dB bandwidth of 7.9 GHz was obtained at 10.5 mW optical power. The frequency response curves indicate that the bandwidth is not limited by parasitic capacitances.

![Fig. 1 Laser structure](image)

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Conclusion: We have for the first time demonstrated regrowth with MOVPE of semi-insulating iron doped InP around reactive ion etched mesa without using any wet etchant to modify the mesa shape or to form a mask overhang. The device performance was regular and the high frequency response was not limited by parasitic capacitances. This regrowth technique will provide exact and reproducible control of the mesa width and hence the width of the active region, also in large scale production of optoelectronic components.

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References