Stellingen

Behorend bij het proefschrift:

"Surface Processes in Gas Source Molecular Beam Epitaxy of Si and SiGe Alloys"

Klaus Werner, 20 december 1996

1.

In GSMBE is het niet noodzakelijk het Si substraat voorafgaand aan RHEED intensiteitsoscillatie experimenten bij hoge temperaturen te annealen.

S.M. Mokler et al., J. Crystal Growth 120, 290 (1992)

2.

De technische consequenties van de vergroting van de diameter van siliciumplakken van 200 naar 300 mm zijn schromelijk onderschat. Het is dan ook zeer twijfelachtig of de beoogde kostenreducties gehaald zullen worden.

3.

Toekomstige LPCVD machines voor de epitaxiale groei van Si en SiGe lagen zullen ultra hoog vacuüm compatibel zijn en silaan en germaan als uitgangsmateriaal toepassen.

4.

Het is heden ten dage onmogelijk een productieapparatuur voor de halfgeleiderfabricage op de markt te brengen, zonder patenten van de concurrentie te overtreden.
5.

SiGe zal altijd het materiaal van de toekomst blijven.

6.

Onderwerpen van wetenschappelijk onderzoek worden vaak gegeven door aanwezige dure apperatuur. Alleen al vanuit dit gezichtspunt kan minister Ritzen zijn pogingen tot meer sturing van onderzoek beter achterwege laten.

7.

Een voorspelling over het ontstaan van een bepaald kristalvlak aan het grensvlak tussen masker en kristal kan niet worden gegeven zonder over gedetailleerde kennis van de kinetiek van de groei ter plekke te beschikken.

8.

Het lachende gedoe van de gemiddelde Nederlander bij het zien van een fietser die met valhelm op een gewone (tour)fiets rijdt, geeft blijk van de typisch Nederlandse afkeer om op te vallen, zelfs als de veiligheid er mee gebeat is.

9.

Om het gelijkmatige stuiten van squashballen te bevorderen verdient het aanbeveling alle wanden van de squashcourts uit het zelfde materiaal te vervaardigen.

10.

De populariteit van een boekwerk uit een Nederlandse bibliotheek valt rechtstreeks uit het aantal koffievlekken per pagina af te leiden.
Surface Processes in Gas Source Molecular Beam Epitaxy of Si and SiGe Alloys

PROEFSCHRIFT

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus Prof. ir. K.F. Wakker,
in het openbaar te verdedigen ten overstaan van een commissie,
door het College van Dekanen aangewezen,
op vrijdag 20 december 1996 te 16:00 uur

door

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Meiner gesamten Familie
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Chapter 1
Introduction

1.1 Materials Issues

Today's microelectronics is almost completely based on silicon as a substrate material. Only a few percent of the devices and integrated circuits (IC's) currently sold are made from other materials such as III/V semiconductors. The supremacy of Si is mainly due to the superb insulating qualities of its oxide (SiO₂) together with other materials properties such as mechanical strength and thermal conductivity [Bean90]. The importance of a high-quality insulating layer like the SiO₂ can hardly be overestimated. Its controlled and defect-free fabrication is a key point of current technology, since the functioning of the IC depends crucially on the perfection of the insulating layer. To date, Si technology permits an integration density of about $10^7$ devices cm$^{-2}$ with an enormous complexity and/or functionality on a single chip [Rödde93]. However, besides being amenable to integration also switching speed is an issue, which is one of the weaker points of Si. Due to its band structure, the mobility of electrons and holes is comparatively low and thus the upper ($>10$) giga-hertz frequency domain is dominated by semiconductor material systems like GaAs/AlGaAs or InGaAsP/InP. Furthermore, due to the indirect bandgap of silicon, it does not lend itself naturally for photonic devices such as light emitting diodes (LEDs) and lasers in contrast to most of the III/V materials [Iyer93].

1.1.1 Optimisation of Silicon Technology

Because of the abundance and comparatively low production costs a lot of research is currently devoted towards improvement of the frequency and power characteristic of Si devices and circuits. This is done in order to avoid or at least delay the change to a much more expensive compound semiconductor technology. One obvious possibility to enhance the switching time of transistors is to decrease the length of the path the carriers have to travel on their way through the device. This leads to gate lengths in the sub-micrometer range in MOS (metal-oxide-silicon) devices. For example, state of the art MOS technology employs 0.35 μm minimum feature size and research investigating the fabrication of even smaller structures (< 0.25 μm) is under way [Keers93].

One aspect, which is closely related to the lateral scaling of the device dimensions is the fabrication of extremely sharp and mostly shallow doping profiles. This either calls
for the use of ion-implanters running at very low energy (10 keV range) or for the incorporation of dopant atoms into the Si layers during deposition by an epitaxial growth technique. The latter has the added advantage that a high temperature dopant activation step (annealing), which is mandatory after ion-implantation, is no longer necessary. This avoids the degradation of the shallow doping profiles by out-diffusion. Current deposition techniques such as chemical vapor deposition (CVD) and molecular beam epitaxy (MBE) generally work at temperatures low enough to effectively avoid diffusion related problems.

Thus, by further scaling down and tuning of the devices a significant increase in speed and performance can still be gained for Si. A completely different approach to enhance the overall performance of Si-based circuits utilises SiGe alloys, which makes it possible to exploit the Si/SiGe heterostructure technology.

1.1.2 Silicon-Germanium Alloys

The combination of SiGe alloys with Si can significantly improve the performance of Si-based technology. The first point to consider, and probably the most important one, is that the materials properties of Ge and SiGe alloys make them in principle compatible with Si technology, which gives this approach a considerable advantage over III/Vs. The latter can not simply be monolithically combined with Si as yet, and neither can such a combination be processed in a Si IC production line.

Crystalline Ge is a semiconductor with a bandgap of 0.66 eV at room temperature, compared with 1.12 eV for Si. By alloying Si and Ge, the resulting semiconductor SiGe has a bandgap between that of elemental Si and elemental Ge. Thus, the concept of heterostructures with band offsets in valence and/or conduction band at the heterointerface can be realised in the Si/SiGe system. This idea proved to be very successful for III/V semiconductors such as AlGaAs on GaAs or the quaternary system GaInAsP on InP, since it permits the fabrication of a wealth of new devices exploiting bandgap discontinuities in different ways [Sze90]. Transferring the ideas to the Si/SiGe system, this implies that e.g. optical detectors with high absorption efficiency, tunable to the wavelength range for optical fibre transmission, become possible [Pears86]. Devices featuring extremely high electron and hole mobilities can be realised in modulation doped heterostructures [Kön93, Isma94]. Another example is given by markedly improved bipolar devices, achieving enhanced gain and higher frequency operation - all by the incorporation of a few percent Ge in the very thin (= 40 nm) base layer [Patt90, Gruhl93]. Even electroluminescence has been reported for Si/SiGe structures [Fuka93]. The latter finding is especially remarkable, since the indirect bandgap of Si/SiGe normally does not permit light emission.
1.1.3 Si/SiGe Technology

The added functionality comes at a cost: Ge has a larger (4.18%) lattice constant than Si, which is the cause of some technological problems during material deposition and subsequent processing. Namely, during deposition of SiGe on Si, SiGe first grows pseudomorphically or coherently on Si. That is, the lattice of SiGe is tetragonally distorted in order to fit to the Si substrate lattice (fig. 1.1). This distortion is accompanied by biaxial strain in the layer. At a certain point during deposition, the SiGe lattice can no longer accommodate the incorporated strain and misfit dislocations form which relieve the strain. The thickness at which this happens is called the critical layer thickness and is a strong function of the Ge content (fig. 1.2), and also depends on growth temperature and substrate preparation. However, dislocations are unacceptable in the active region of devices, because they can act as recombination centres or traps and will thus impair device performance. Fortunately, the shrinkage of the bandgap of SiGe alloys with increasing Ge content is enhanced by the incorporated strain. In comparison to bulk SiGe (fig. 1.3) it takes considerably less Ge in a thin strained layer grown on Si(001) to achieve a large valence band offset (e.g. 20% of Ge will result in an offset of ≈ 160 meV). It would take about 46% of Ge to achieve the same band offset in unstrained SiGe material. Also, the bandgap alignment depends on the strain distribution among the constituting layers of the heterostructure. For example, to achieve a bandgap discontinuity in the conduction band to confine electrons in a Si channel (type II-alignment), the Si layer has to be grown tensilely strained on a relaxed SiGe buffer layer. This is done by growing a SiGe layer on a Si substrate with a thickness above the critical layer thickness. The strain is thus relieved and the SiGe layer forms the (pseudo-) substrate that can in turn strain the Si layer [Pears89].

Fig. 1.1: Principal growth modes for lattice mismatched crystalline systems, such as SiGe on Si.
Fig. 1.2: Bandgap for strained and unstrained Si$_{1-x}$Ge$_x$ on Si(001) at 90 K. The strain lifts the degeneracy of the valence and conduction bands in SiGe. The resulting bandgap for the strained SiGe material is shown for the light (3/2±1/2) and heavy hole (3/2±3/2) bands (after [Peo90]).

Yet, most of the deposited SiGe layers are metastable after growth: The layers are strained and no dislocations are formed although the layer thickness is larger than the critical layer thickness predicted by an equilibrium theory [Mat75] (fig. 1.2). The reason is that the formation of misfit dislocations is kinetically hampered by the low growth temperatures [Peop85]. As a consequence, the temperature during the subsequent processing steps for device fabrication must also not exceed the growth temperature in or-

Fig. 1.3: Critical layer thickness for Si$_{1-x}$Ge$_x$ alloys grown on Si(001). Please note the existence of thermodynamically stable and metastable regions.
der to avoid relaxation of the layers [Schäf91]. This fact imposes a severe constraint on the SiGe processing, since it necessitates the development of low temperature fabrication steps.

1.2 Deposition Techniques

As was outlined above, the deposition of Si/SiGe heterostructures has to take place at comparatively low temperatures, say below 750 °C, in order to preserve strain and interface sharpness in the grown layers. This condition automatically rules out all the classical high-temperature deposition systems used by the IC industry. In fact, the technique which has been used first to successfully demonstrate the metastable growth of Si/SiGe is solid source molecular beam epitaxy (SSMBE) [Kasp75]. Although SiGe alloys were grown as early as 1962 [Mill62, Oda62], it took until 1987 before growth temperatures and oxygen incorporation into the films were low enough to guarantee device-quality, strained SiGe films [Gron87].

MBE as well as the old generation of CVD systems have some disadvantages, which may limit their use as growth techniques in production. SSMBE has relatively low throughput and since the source is located inside the UHV chamber, downtime for source replenishment and vacuum reconditioning can be considerable. On the other hand, hot wall CVD reactors are limited in the usable growth temperature range and have problems with the growth of n-type material. Phosphorus as a typical dopant has a high vapour pressure and once used in the reactor produces a large unwanted doping in the subsequent layers (memory effect) [Greve93]. Nevertheless, hot-wall CVD systems are being used to grow state of the art material, and are in principle suitable for batch-based, high-volume processing, at least for wafer sizes up to 150 mm. Larger sizes are handled by single wafer, cold wall reactors [Gran95].

For reasons of cleanliness and process conditions, more and more CVD systems are made of ultra high vacuum (UHV) compatible equipment for reactors and gas manifolds. Also, processing at reduced pressures offers better control over homogeneity and interface sharpness; in addition, it facilitates selective area growth on partially masked substrates [Gould91]. Taking all the developments together, the logical outcome is an MBE system, which is intrinsically UHV-compatible, equipped with gaseous sources to run a CVD-like process. This technique, which appears to offer the best of both worlds (SSMBE and CVD) for the growth of Si and SiGe films, has been coined gas source MBE (GSMBE).
1.2.1 Gas Source MBE versus Solid Source MBE

One of the main advantages of GSMBE compared to SSMBE is the nature of the precursors. The flexibility provided by the use of the gaseous external sources combined with a very reproducible and accurate flux control (see section 2.2) makes GSMBE much easier to use and maintain than SSMBE. Source replenishment in SSMBE necessitates a bake-out period and a tedious recalibration of all flux monitors and dopant fluxes, which takes about two weeks.

In GSMBE, source replenishment boils down to purging the gas lines and connecting a new gas bottle, which takes only a few hours. Similarly, the actual material to be deposited can be changed in the same convenient way. Furthermore, the brute-force evaporation by electron beams in SSMBE causes a considerable amount of defects on the surface due to Si clusters and dust particles emerging from the guns and the chamber environment. This problem is aggravated by the stray and secondary electrons from the guns which can lead to charged particles that are floating through the chamber or can even cause electron stimulated desorption of trace gases, e.g. methane or water from the chamber walls. These species, once arrived at the surface, will also impair epitaxial growth [Kasp84].

Another advantage of GSMBE over SSMBE is the possibility of selective area epitaxy (SAE) [Hira88]. This term denotes the concept that material grows only on the crystal surface with its reactive dangling bonds and not on an 'inert' vitreous mask such as SiO₂ or Si₃N₄. This effect basically results from the difference in reactive sticking coefficients of the molecules on the crystal surface and the mask. In SSMBE, the sticking coefficient of the species equals unity, i.e. the evaporated material always condenses on the substrate (fig. 1.4) and hence SAE is only possible for special conditions (e.g. for growth temperatures above 850°C; see section 7.1.3). Selective area epitaxy can be used to advantage in cases where structures are grown on a masked wafer, which directly produces laterally isolated devices. This obviates the need for an etching step which, since it is typically done by reactive ion etching, may lead to additional damage in the layer due to the creation of defects during interaction with high energy ions [Cheung93]. This point becomes particularly important for the fabrication of submicrometer-sized devices.

1.2.2 GSMBE versus CVD Processes

To understand the more subtle differences between GSMBE and CVD, a CVD silicon growth process will be first considered in the following. The overall reaction during CVD of a material can be divided into 6 different steps (fig. 1.5):
Fig. 1.4: Schematic representation of the SSMBE growth process.

1) transport of the precursor (source material) towards the substrate  
2) adsorption of the precursor at the surface  
3) decomposition and reaction of the precursor and/or precursor fragments at the surface  
4) diffusion of the precursor and/or precursor fragments along the surface  
5) deposition/incorporation of atoms  
6) desorption of reaction products

Please note that each of these steps can be rate-limiting at a given growth temperature and precursor flux. In CVD, the first step is not trivial and a point of considerable concern. Namely, the process pressure is generally such that the mean free path of the molecules ($\lambda_m$ (cm) = $10^{-2}/p$ (mbar) [Leybo86]) is small compared to the reactor dimensions. In hot-wall, multi-wafer systems (e.g. UHV-CVD [Meyer86]), this means that the precursor thermalises on its way to the substrate by interaction with the walls and with other molecules. In principle the same applies to cold wall, single wafer systems where the substrate is the only heated spot in the reactor [Gibbo85]. Yet, in this case the molecules thermalise on their way through the boundary layer towards the substrate by mutual scattering. Hence, gas-phase (homogeneous) reactions occur as opposed to mere surface (heterogeneous) reactions in systems where the process pres-
Fig. 1.5: Schematic representation of a CVD-like growth process (including GSMBE) of silicon using disilane.

sure and the reactor geometry are such that molecular scattering does occur. Generally speaking, gas-phase reactions are undesirable, since they can lead to all sorts of problems during epitaxy such as precipitation on the walls, inhomogeneities and memory effects. Furthermore, they are extremely difficult to model, because their contribution to the growth as compared to surface reactions varies strongly with pressure, linear flow rate, gas-phase composition and reactor design (hot/cold-wall, geometry). Also, gas-phase products can even interfere with the surface reactions, which present additional difficulties to predict the behaviour of the system [Jens84].

Another point, which becomes more and more important at the lower growth temperatures necessary for the SiGe deposition is the fact that the reactivity of the classical CVD precursors such as dichlorosilane (SiH₂Cl₂) becomes very low. Growth rates of micrometers per minute at 1000°C precipitously drop to values as small as few nanometers per hour at 550°C [Jasi87]. Also, at the high growth temperature residual water and oxygen in the reactors do not matter [Meyer86]; at temperatures around 650 °C, however, they heavily contaminate the layers and may even inhibit epitaxy [Greve93]. The contamination problem has also led to the development of load-locked systems. The low growth rate at low temperatures has stimulated the use of different precursors
with higher reactivity such as silane (SiH₄) and disilane (Si₂H₆). Still, for the typical UHV-CVD system using silane, the growth rates are low and memory effects remain, which requires careful planning of the structure to be grown and timely reconditioning of the reactor.

In principle, using disilane growth rates can be high (∼1μm/h) also at low temperatures (∼620°C), but due to its high reactivity, it is not suitable for multi wafer (batch) CVD systems. Here, silicon would deposit only on the outer rim of the closely spaced wafers, hardly in the middle, or even deposit only on the hot walls of the system. Thus, the use of disilane is limited to single wafer systems.

A further difficulty for CVD systems stems from the fact that the growth process can not be followed in situ. Process pressures are such that they preclude the use of UHV analysis tools such as Auger electron spectroscopy or reflection high energy electron diffraction (RHEED), to assess impurity concentrations or the atomic arrangement of the surface, respectively. Moreover, the growth kinetics in CVD is governed by gas-phase as well as surface reactions, both contributing to the growth rate. The exact relation between the two contributions strongly depends on process pressure, linear flow rate, the type of precursor and the actual reactor geometry; a clear separation of the two is usually not possible. In fact, this difficulty is reflected not only in the different values for the activation energy reported e.g. for the growth from silane as a precursor gas, but also in the attempts to model the kinetics in CVD reactors. Not even the adsorption kinetics of silane is properly understood.

The lack of understanding is especially troublesome for the growth of SiGe. Although the material is readily deposited and processed into devices, the knowledge about the processes governing the growth is still quite incomplete. Nearly every reactor has its own calibration curve for the Ge incorporation versus Ge flow and substrate temperature [Greve93], and the limited available data about surface reactions and gas phase effects make it difficult to optimise the process.

In this situation, GSBME can clearly contribute to an improved understanding also of the CVD processes: It combines the cleanliness of an UHV environment with very low process pressures (∼10⁻⁵ mbar), allows employing RHEED for in-situ growth rate calibration and facilitates establishing a thorough description of the growth kinetics, since gas phase reactions do not occur. Nevertheless, the low process pressure dictates the use of a very reactive precursor such as disilane. This in turn limits GSBME to a single wafer technique. Disilane adsorption and reaction kinetics have only been studied for the past few years. Apart from its merits as a growth tool, the features outlined above make GSBME in fact a model system for the investigation of surface reactions for all sorts of deposition processes.
1.3 Aims of this Study

As pointed out in the preceding paragraphs, the GSMBE technology is a combination of an UHV environment taken from MBE with the gaseous precursors and gas handling technology of CVD equipment. The aim of this thesis is to contribute to the clarification and understanding of the fundamental reactions and processes taking place at the growing surface when using this technique. Another objective is to achieve improved control over the growth process and to gain insights in the potentiality and limits of GSMBE for the fabrication of demanding device structures.

1.4 Topics of this Thesis

In view of these goals, our study covers the following topics:

The development of the hardware and its realisation is described in chapter 2. This part comprises the definition of an UHV system with load-lock and growth chamber along with gas manifold and pumping systems and in situ analysis techniques. Special attention is paid to the design and realisation of the gas handling and injection system: It must comply with stringent demands of cleanliness, safety, flow range and homogeneity of the molecular beams.

In order to define a starting point for the investigation of the growth kinetics, the current understanding of the reaction between disilane and the Si(001) surface is reviewed in chapter 3.

RHEED intensity oscillations during the growth of Si from disilane on Si (001) are correlated to surface processes such as growth modi and adatom diffusion in chapter 4. In particular, the activation energy for adatom surface diffusion in the presence of hydrogen is derived and growth anisotropy due to different lateral growth rates of steps in the Si (001) surface is demonstrated. Furthermore, differences in the adatoms surface diffusion between GSMBE- and SSMBE growth are discussed.

Chapter 5 treats the homoepitaxial deposition of Si from disilane on Si(001) in more macroscopic terms. Based on in- and ex situ growth rate measurements a model describing the homoepitaxial kinetics based on Langmuir-Hinshelwood adsorption kinetics is developed. Special attention was paid to the adsorption order of disilane, since this parameter is one of the crucial ingredients for the formulation of a model describing the kinetics. Another section presents a method to independently determine the reactive sticking coefficient for disilane on Si, again an important parameter for the description of the kinetics.

The growth of SiGe alloys and the Si regrowth on Ge layers is dealt with in chapter 6.
A calibration of the Ge contents of the solid depending on the relative Ge concentra-
tion in the flux is given for both cold (77K) and warm (room temperature) growth envi-
ronments. The rate enhancing effect of Ge present at the growing surface is demon-
strated with the help of RHEED intensity oscillations. They permit the analysis of Ge 
surface segregation with atomic resolution during Si growth on a Ge layer. It is shown 
that surface hydrogen acts as a surfactant, which considerably reduces the Ge segrega-
tion and leads to substantially sharper interfaces than achievable with SSMBE for the 
same growth temperatures.

Chapter 7 reports a study on selective area epitaxy (SAE) of Si and SiGe in GSMBE. It 
is shown that absolute selectivity as attainable in silicon CVD with chlorine containing 
precursors cannot be obtained in GSMBE. Work-arounds, critical parameters and pro-
cessing steps are discussed.

Subsequently, the p- and n-type doping of Si and SiGe in GSMBE by phosphine and 
diborane, respectively, is described in chapter 8. Achievable doping concentrations 
and ranges together with doping profiles and effects on the growth rate are dealt with.

Finally, chapter 9 presents two examples of applications of the GSMBE growth tech-
nique developed in this study: A semiconductor point contact device and a double-
barrier resonant tunneling diode (DBRT). These devices basically perform as expected 
from the layered structures of the given design. Furthermore, the electrical and struc-
tural characterisation of these devices permits the identification of weak points of the 
GSMBE growth technique, which need to be addressed for the further optimisation of 
the technology.
Chapter 2

Experimental

This chapter describes the MBE system with its two growth chambers. The computerized RHEED data acquisition system and its most important features are introduced. Last but not least, substrate preparation procedures are outlined.

2.1 The Si/SiGe MBE System

The MBE system was manufactured by Riber, a company specialised in this field. It was designed to process 125 mm sized wafers. Smaller wafers are handled by means of adaptor rings.

The system comprises four UHV-chambers (fig. 2.1): A load-lock, which can store 10 wafers in a cassette, a preparation chamber and two growth chambers: One for SSMBE and one for GSMBE. Wafers have to be transferred one by one from the load-lock, first into the preparation chamber and then into one of the growth chambers.

The heater stages of the substrate holders in the preparation chamber and the two growth chambers are identical and employ pyrolytically coated graphite filaments as heating elements. The filaments form self-supporting meanders, which radiatively heat the substrates from the back to a maximum temperature of about 1100°C. All substrate temperatures are obtained by optical pyrometry, calibrated with the help of temperature standards like InSb or Al placed on test wafers.

In contrast to the substrate holder in the preparation chamber, the ones in the growth chambers can be rotated to compensate for flux inhomogeneities, thereby facilitating the deposition of uniform layers.

2.1.1 The Solid Source MBE Chamber

The solid source system employs proven technology for the growth and doping of Si/SiGe films. Si and Ge are transferred to the gaseous state by means of electron-beam (e-beam) evaporators. n- and p-type doping is performed using Sb and B evaporated from Knudsen-cells. The B-cell is a specially designed high-temperature cell, since the use of elemental boron requires temperatures in the range of 1400 to 1800 °C in order to dope layers to concentrations between $10^{15}$ and $10^{19}$ cm$^{-3}$. Antimony is typically evaporated at cell temperatures of about 410°C. Shutters above the e-beam evaporators
and the Knudsen-cells allow the abrupt interruption of the molecular beams emitted from the sources.

In the case of Sb doping, the incorporation is not as straightforward as it is for B; Sb has a strong tendency to segregate to the surface, since it has a lower surface free energy than Si. This segregation is an activated process, which strongly depends on substrate temperature [Metz84, Jorke88]. One possible way to work around this problem is to grow at low substrate temperatures (approx. 375°C) in order to suppress the segregation. However, at such low temperatures the crystal quality of the films degrades rapidly and only thin layers (< 100 nm) can be grown without introducing too many defects. A second way to overcome segregation of Sb is achieved by 'doping by secon-
dary implantation' (DSI) [Jorke86] or 'potential enhanced doping' (PED) [Kubi85]. Both names denote the same mechanism: A potential (typically a few hundred volts) is applied between the substrate and the e-beam evaporator for Si. The potential accelerates the ionized Si atoms or clusters, which are always present in the flux (~ one percent) [Jorke89]. It is believed that the accelerated ions collide with the Sb atoms at the surface and force them into the subsurface layers (knock on). However, this approach comes at a cost: The accelerated atoms cause damage to the crystal, analogous to damaged produced by ion implantation. The created damage is cured by the intrinsic anneal at the growth temperature during deposition. Nevertheless, it is particularly difficult to achieve a sharp interface between p-type (B) and n-type (Sb) material, since the B will diffuse very rapidly into the n-layer after PED is started, due to locally induced damage. Furthermore, the applied bias will not only attract ionized Si flux atoms to the substrate surface, but also charged dust particles, which are floating around in the UHV chamber [Tats89]. These dust particles, once stuck to the surface, will give rise to growth defects, which can be detrimental for both processing and electrical behaviour of devices. In fact, these defects preclude the use of the grown layers in integrated circuits. It should be mentioned that the severity of the defect creation problem strongly depends on the design of the growth chamber [Jorke89]. Fortunately, in our chamber, PED does not add to the overall amount of visible defects for growth rates that are less than 0.5 μm/h.

Another technological problem is the determination of the flux produced by the e-beam evaporators for Si and Ge. Temperature measurement, which is a convenient and accurate means for the flux determination in case of homogeneously heated Knudsen cells, is not applicable to e-beam evaporation. This is because of the inhomogeneous temperature distribution of the melt in the hearth of the gun. Convection flows in the molten material partly caused by the sweeping electron beam of the gun make it impossible to assess the vapour pressure via the temperature of the melt. Rather, the fluxes are being monitored continuously by a quadrupole mass spectrometer (QMS) [Kasp89] or, as in our chamber, by electron impact emission spectrometry (EIES) [Gogol79]. In the latter approach, an electron beam is directed such as to cross the evaporated flux in a small sensor casing. Flux atoms are excited by the electron impact and decay under emission of a photon. These emitted photons are detected and amplified by a photoelectron multiplier tube. The measured values are used in a feedback-loop to keep the growth rate at a given level.

2.1.2 The Gas Source MBE Chamber

In GSBME external gaseous sources take over the role of internal solid sources in SSMBE. This has marked consequences for the setup of the equipment as will be out-
lined in the following. The GSMBE-vacuum chamber was built by Riber as well, whereas the entire gas-handling and pumping system was designed and attached to the vessel in Delft as part of this project.

### 2.2 Gas Handling Manifold and Injection System

In the course of the project it became clear that the first version of the gas handling system (original setup) was not optimal for all growth conditions (see below). Using the experience gained with the first design, an improved second version (improved setup) was built, which is more flexible and can be used for all process conditions. In the following, both setups are described and the reasons for the change are given.

The layout of the original gas handling system is depicted in fig. 2.2. The gas bottles are located in a safety cabinet with double walls and a stand-alone ventilation system. For the high pressure gases (disilane, germane, phosphine and diborane, \( p_{\text{bottle}} > 2 \) bar) the pressure is reduced in two steps: A first pressure reducer regulates the outlet pressure to less than 2 bars and a second reducer keeps the outgoing line at about 400 hPa. For safety reasons only these low pressure lines leave the cabinet and are fed to the flow regulating valve upstream of the injectors. For low vapour-pressure gases

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**Fig. 2.2:** Schematic representation of the original setup of the gas handling system for GSMBE. 'M' denotes the motor-driven leak-valve, and 'p' marks the capacitance pressure transducers for the flow measurements.
(e.g. digermanc) a single step pressure reduction to less than 400 hPa suffices.

Contrary to CVD-systems, our system does not rely on mass flow controllers (MFCs) to determine the amount of gas flowing into the system. Rather, we use a pressure controlled system, in which the gas flow is measured in terms of the pressure gradient over an injection capillary (fig. 2.3): The pressure at the inlet of the capillary is measured with a capacitance pressure transducer (MKS Baratron type 127AA); at the outlet the pressure is several orders of magnitude less and therefore negligible. The reading of the pressure transducer is thus a measure for the total gradient over the injector and is used in turn to control a stepper motor driven UHV leak valve (MKS 245). This setup has the advantage of having a much larger dynamic range (3 orders of magnitude) and of being much more precise (the error is 0.15% of reading) than a typical MFC with a dynamic range of about 1 order of magnitude and an error of typically 0.5% of full scale [MKS87]. For disilane and germane full scale pressure readings of the baratrons are 10 torr, the dopants are measured with 1 torr types. The injection capillaries are made from either tantalum or stainless steel tubes with a diameter of 3 mm and a length of 260 mm. The capillaries can be heated to prevent condensation of the gases inside the pipes, since the surrounding cryo-shrouds may cool down the injectors considerably. Shutters located directly in front of the injectors permit the interruption of the beams emerging from the tubes and the gas is frozen out on the surrounding cryo-shrouds. This scheme has proven successful for disilane; its efficacy is less for germane and the dopants: the vapour pressure of these gases cannot be neglected at 77K and large memory effects result. This fact precludes the use of LN$_2$-cooled shrouds for the growth of device structures, which usually demand steep het-

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**Fig. 2.3: Sketch of original setup injector with flow control valve and capacitance pressure transducer. Again ‘M’ and ‘p’ denote the motor-driven leak-valve and the capacitance manometer, respectively.**
ero- and doping junction profiles. Therefore, the system setup was revised and the cryo-shrouds have been cooled with water since that time, leading to the improved setup.

When filling the cryo-shrouds with water, the shutters above the injectors lose their efficacy, since the emerging gas is no longer trapped at the shrouds. In order to achieve abrupt changes in the flux composition reaching the substrate surface, a vent/run switching system as known from CVD machines was installed in the improved version of the set up (fig. 2.4). The main feature of such a system is a three-way valve mounted downstream of the control valve and the pressure transducer. One exit of the valve leads towards the vacuum chamber, while the other leads to a position directly upstream of the turbo-molecular pump (vent). Experiments revealed that backstreaming from the vent towards the substrate is negligible.

It is important to balance the conductivity of both the run and the vent channel to avoid pressure surges or drops upon switching of the valve. For this purpose, molecular flow elements were placed in the exits of the three-way valve. The flow elements are small stainless-steel, blank gaskets, in which either 2 or 3 holes were drilled with a diameter of 0.4 mm. The 2-hole version is used for dopants and the 3-hole version for disilane and germane. These flow elements determine the conductivity of the connected piping, and thus ensure a surge-free vent/run switching. Hence, the flows in the new setup are determined by the pressure drop over the flow elements rather than by the pressure dropping over the injection capillary.

Also, the injectors were modified and mounted on a single flange. The tube length towards the substrate was enlarged to 500 mm (the substrate-tube orifice distance

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**Fig. 2.4:** Schematic representation of the improved setup of the gas handling system for GSMBE. 'M' denotes the motor-driven leak-valve, and 'p' marks the capacitance pressure transducers for the flow measurements. Please note the three-way valve that provides the vent/run switching. The remaining part of the gas handling system (gas cabinet, etc.) is the same as in fig. 2.2.
thereby decreased to about 200 mm, see below) and the tube diameter was increased to 6 mm. The main effect of reducing the substrate to tube-orifice distance is an increase in flux density on the substrate for the same mass flow into the system. The pipe diameter was enlarged to ensure that the conductivity of the injector tubes is large. This avoids a significant pressure drop over the injectors, which may otherwise compromise the intended conditions around the flow elements.

2.3 Flux Distribution

For the original injectors, the gas flow through the capillaries at pressures of about 1hPa varies from the viscous ($\lambda_m << d$) flow regime in the beginning, to the molecular flow regime ($\lambda_m >> d$) at the end of the pipe. For the present study, it was important to know the flux distribution at the substrate surface in order to optimise it for uniform deposition of the layers. However, it is impossible to predict the beam profile without knowing the distribution of the flow regimes in the injector. Particularly important is the point within the tube, where the flow enters the molecular regime. This is so, because the shape of the emitted beam strongly depends on the ratio of the remaining tube length over its radius (aspect ratio) [Claus30]. Unfortunately, the transition between the flow regimes depends on the mass flow through the capillary. Thus, also the beam shape and consequently the flux distribution on the substrate depend on the flow. In order to investigate these effects, we studied the mass flow through the capillary employing Monte Carlo simulations [Schei93]. It was found that for our injector geometry and a typical inlet pressures of 1 hPa, the molecular flow regime develops only at the very end of the capillary. As a consequence, the flow pattern in the emerging beam is not determined by the tube geometry [Claus30], but will have a cosine distribution. Also, the gas is transported mainly in the laminar and viscous regime. The total flow ($Q$) through the capillary can in principle be calculated as the product of the pressure gradient over the capillary ($\Delta p$) and the conductivity ($C$). Within the laminar and viscous regimes, $C$ is a linear function of $\Delta p$. Hence, the mass flow through the capillary depends on the square of the pressure gradient over the capillary:

$$Q = C(\Delta p)^*\Delta p \sim \Delta p^2 \equiv p_0^2$$  \hspace{1cm} (2.1).

The experimentally found behaviour of the mass flow indeed follows an almost quadratic dependence (fig. 2.5): The exponent actually amounts to 1.8.

The original-style injectors were mounted on 4 out of 8 ports which were distributed annularly around the bottom of the chamber and pointed upward towards the substrate (figs. 2.1 and 2.6). The distance between the exit of the injector tube and the substrate amounted 444 mm; the tubes were mounted at an angle of about 40° towards the
disilane mass flow (sccm) = \exp(-10.3 + 1.78 \ln(p_{\text{bar}} \text{ (mTorr)}))

Fig. 2.5: Disilane flux vs. inlet pressure ($p_0$) of original setup injector.

substrate normal (fig. 2.6). This value, together with the assumption that the injectors work as cosine emitters allows the calculation of the flux distribution on the substrate [Herm89]. It was found that the flux in the centre of the substrate amounts to $5.5 \times 10^{13}$ molecules cm$^{-2}$ s$^{-1}$ times the injected mass flow (in sccm). The calculated homogeneity of the flux over a 4" wafer is ± 6.5%.

In the case of the warm (= water cooled) chamber environment, the flux onto the wafer surface is determined via the reactor pressure. The injected gases do not freeze-out on the shrouds, leading to a process pressure on the order of $10^{-4}$ hPa. Employing equation 2.2, which connects the pressure with the corresponding flux towards a surface, the flux $\phi$ on the wafer surface can be obtained [Lang13]:

$$\phi = (2\pi m k_b T)^{-1/2} \cdot p_{\text{gas}}$$  \hspace{1cm} (2.2),

with $k_b$, $T$, $m$ and $p_{\text{gas}}$ being the Boltzmann constant, temperature, molar mass and partial pressure of a particular gas, respectively. As an example, fig. 2.7 depicts the disilane mass flow and flux for the improved gas-injection system. The dependence of the mass flow on the cell pressure is now closer to linear. This fact results from the pressure-independent conductivity of the molecular flow elements used.

Disilane, germane, diborane and phosphine (the latter two gases as a 5% mixture with hydrogen) were injected through 4 independent channels. Disilane and germane were supplied by Voltaix Inc. North Branch, New Jersey; the dopants were purchased
Fig. 2.6: Cross section of GSMBE system showing the injector/substrate geometry.


from Scott Specialty Gases.

The mass flow rates were obtained from the product of the effective pumping speed of the turbo molecular pump (1111 l/s ± 3%) and the total pressure in the chamber. The latter was determined for the warm GSMBE system by a spinning rotor friction gauge, which allows high accuracy absolute pressure measurements (± 1%).

2.4 GSMBE Pumping System

In order to be able to follow the crystal growth in situ by RHEED, the process pressure should not be higher than 10⁻⁶ hPa, even at mass flows as high as tens of sccms of disilane. To achieve the necessary enormous pumping speeds (≈ 300,000 l/s for disilane), the system was run with cryoshrouds filled with liquid nitrogen. The shrouds are located along the chamber walls and around the injectors and the manipulator (figs. 2.6,2.8). For the other gases, the pumping efficiency of the shrouds was much less; these species are mainly pumped by a turbo-molecular pump with an effective
Fig. 2.7: Disilane mass flow through the improved setup gas injectors. Note the more linear dependence on cell pressure than for the old-style injectors caused by the characteristics of the molecular flow element.

pumping speed of about 1111 l/s in series with a rotary vane roughing pump. A cryopump with a large pumping speed (1500 l/s) and a high freeze-out capacity for hydrogen (12 bar-l), supported the turbo pump in removing hydrogen, which is the main by-product of the reaction.

Eventually, the cryo-sorbed gases must be removed from the shrouds and pumped out of the system. For this purpose, the liquid nitrogen supply was stopped, the system was allowed to warm up over night and the desorbing gases were pumped out by the turbo molecular pump, the cryo-pump being shut off from the system by a gate valve.

When starting operation, the LN$_2$ supply is switched on automatically and the system is cooled down for a growth run. The base pressure for a cooled-down system, evacuated by the turbo pump was around 10$^{-9}$ hPa due to a large hydrogen background. During stand-by periods, the chamber was pumped by an ion getter pump, which was closed during normal runs. The background pressure at these conditions was about 10$^{-10}$ hPa.

2.5 RHEED Instrumentation

RHEED is an MBE-compatible electron diffraction technique, which may be used to characterise growing crystal surfaces in situ. Together with LEED (low electron energy
diffraction) RHEED might well be the oldest electron diffraction technique, dating back to the discovery of electron diffraction in the 1920's by Davisson and Germer [Davis27]. A RHEED system includes an electron gun (10 keV), producing a small diameter (1mm for our system) electron beam that impinges under a shallow angle (0.2-2°) on the sample surface. The diffracted electron beam is made visible on a fluorescent screen opposite the electron gun (fig. 2.8). Due to the small angle of incidence, the electrons do not penetrate the crystal more than a few monolayers, which renders the diffraction process extremely surface sensitive. This feature makes the technique particularly valuable for the investigation of the growth of crystalline surfaces. Also, because of the geometrical arrangement of gun, substrate and screen in or close to the substrate plane (fig. 2.8), the RHEED-technique lends itself exceptionally well as a tool for in situ analysis in a molecular beam growth environment, where the flux-beams are directed normal to the substrate. LEED, on the other hand, is not compatible with MBE, since it 'views' the surface under normal incidence.

In our apparatus, both growth chambers are equipped with RHEED. The facilities comprise 10 kV electron beam guns mounted on a precision actuator to achieve high accuracy and reproducibility for the setting of the desired angle of incidence. The fluorescent screens for monitoring the diffracted electrons were home made based on a ZnCdS:Ag fluorescent film with a thin (100nm) Al layer on top of the ZnCdS. This method yields screens which are much brighter (by a factor of 10) and have higher

Fig. 2.8: Sketch of the improved GSMBE system with gas manifold, pumping system and RHEED arrangement.
contrast than the ones originally supplied by Riber. The RHEED patterns were monitored by a CCD camera (Philips CCD-module NXA 1011/01) and subsequently digitized and stored by a frame-grabber card (Matrox PIP 512 video digitizer board) with 8 bits resolution in a 80486 processor-based IBM-PC compatible computer. A sophisticated software package for on-line RHEED data acquisition and analysis was written [Maes92a] to define regions of interest in the patterns. In the case of intensity oscillations, the monitored feature was the (00)-streak in all experiments. In particular the region of the (00)-streak, which corresponds to the specular spot, showed the most pronounced intensity variations. The highest achievable sampling frequency is 15 Hz, which is sufficient to conveniently follow growth rates up to 2 ML/s.

Chapter 4, which deals predominantly with the experimental results obtained by RHEED observations of the growing surface, will give a brief introduction to the RHEED technique.

### 2.6 Substrate Preparation

Both 4 and 5" Si wafers were used for the experiments. The substrates were (001) oriented slices of various resistivities and a misorientation between 12' and 1.5'. They were introduced into the MBE-system as received. Prior to transfer into the growth chamber they were degassed at approx. 750°C in the preparation chamber. The native SiO₂ was removed by heating in UHV at approx. 900°C for 10 minutes before starting the actual growth experiments. This procedure was the same for RHEED experiments done with a cold (=LN₂ cooled) system and device runs. The latter were mostly performed with a warm (= water cooled) chamber. For all RHEED experiments and for devices, when permitted by the structure, a 200 nm thick Si buffer layer was grown at about 700 °C. After this preparation procedure, regardless of the actual Si substrate used, the surface reconstruction was always found to be the double domain (2x1)+ (1x2) structure (see section 3.1).

### 2.7 Characterisation

The grown layers were investigated by several structural, optical and electrical characterisation techniques. Si/Ge concentrations were measured by Secondary Ion Mass Spectrometry (SIMS), Rutherford Back Scattering (RBS), X-ray diffraction, X-ray microprobe and by photoluminescence (PL), which was also used for the optical characterisation of the layers. Light (Nomarski) and electron optical microscopy (scanning electron microscopy, SEM), high resolution transmission electron microscopy (HR-TEM) were also used to provide information on the structural and morphological characteris-
tics of the material. In a few cases angle resolved X-ray photoelectron spectroscopy (ARXPS) measurements were performed to assess the near-surface concentration of SiGe layers.

Electrical characterisation was done to obtain the free carrier concentration and mobility in the doped layers. In most cases, Hall-van der Pauw measurements were carried out in addition to simple 4-point resistivity characterisation.
Chapter 3

The Si (001) Surface and its Reaction with Hydrogen and Disilane

Because of its importance from both a scientific and technical point of view, the physics of the Si (001) surface and its reactivity have been subject of a large number of studies. The insights obtained so far are briefly reviewed in this chapter. We first discuss the atomic structure of the bare and hydrogen covered Si (001) surface. Secondly, the current understanding of the adsorption of disilane on a Si(001) surface is outlined.

3.1 The Structure of the Si(001) Surface

The Si(001) surface is probably one of the best known and most often employed surfaces due to its importance in the semiconductor industry. It can readily (and surprisingly cheaply) be produced and be cleaned to an extremely high level, which also makes it an ideal, well-defined substrate for the deposition of different kinds of materials. A bare Si(001) surface on freshly prepared wafers will generally have a (2x1) superstructure (reconstruction). This (2x1) reconstruction is due to the dimerization of adjacent Si atoms in the topmost Si layer along the [110] and [110] directions; this rearrangement is energetically more favourable than leaving 2 dangling bonds per Si surface atom [Robe90] (fig. 3.1). The dimerization was first proposed by Schlier and Farnsworth [Schli59], but its exact form, i.e. whether the dimers are symmetrical or 'buckled' with respect to the bulk has been a matter of long debate [Hoev90]. The discussion was finally settled by direct observation of the surface with scanning tunneling microscopy (STM): Predominantly symmetric dimers were found. Buckling and other more complex atomic arrangements are possible on stepped surfaces [Hamer86].

Adsorbates like hydrogen can have a marked influence on the reconstruction of the Si surface. In order to quantify the amount of hydrogen present on the surface, the absolute hydrogen coverage (θ*) is defined as the ratio of the number of adsorbed hydrogen atoms to the number of silicon atoms in the surface; the latter amounts to 6.8*10^{14} atoms cm^{-2} for Si(001). Since the maximum number of dangling bonds per Si surface atom to which a hydrogen atom can bind is two, θ* will at most have this value. Early work indicated that molecular hydrogen barely reacts with the dangling bonds at the surface [Law59] or not at all [Ilbach74], in stark contrast to atomic hydrogen. However,
Fig. 3.1: Atomic structure of the clean Si(001) surface showing the dimerisation of adjacent Si atoms in the first layer of the crystal. The dimer bond is formed by $\sigma$- and $\pi$-bonding states (after [Hoev90]).

Concerning the adsorption of atomic hydrogen, there has been considerable debate in the literature on the maximum coverage attainable: 1 [Ibach74], 1.33 [Chab84] or close to 2 [Bola90]. Different coverages are accompanied by different types of surface reconstruction. It was found that the dihydride surface ($\theta^* = 2$) with a (1x1)-bulklike reconstruction (fig. 3.2) is stable for substrate temperatures not exceeding room temperature [Bola90,Cheng91]. Interestingly, this kind of surface can be etched (Si atoms be removed as SiH$_4$) by hydrogen atoms [Gates89,Bola90,92], indicating a weakening of the bonds between Si-surface and subsurface atoms at high hydrogen coverages. At somewhat higher substrate temperatures (around 100°C), the saturation coverage decreases to 1.33 and the surface reconstructs into a 3x1 unit cell with alternating rows of monohydride and dihydride species (fig. 3.2) [Chab84, Cheng91, Bola90,92]. On raising the temperature to the range of 300 to 620°C, the saturation coverage equals 1 and the surface exhibits a 2x1 superstructure (fig. 3.2). Here the surface is completely dimerised and only one hydrogen atom is bound to each surface Si atom [Bola90,92, Cheng91, Chab84, Shi93]. For the sake of completeness it should be mentioned that (2x2) and c (4x4) structures have been observed at temperatures above 600°C. However, at these high temperatures the hydrogen coverage is generally low (0.1 to 0.4 ML) [Shi93, Liu92] and hence these reconstructions are not necessarily hydrogen induced. In fact, the c(4x4) superstructure has also been observed in solid source MBE growth
Fig. 3.2: Schematic representation of the main types of hydrogen-induced surface reconstructions on Si(001).

[Sakam79].

Real surfaces always have steps caused by a slight (macroscopic) misorientation of the saw blade during slicing of the crystal ingots with respect to the nominal low index plane. A more thorough description would also include additional step sources like bow, warp and thickness variations of the wafer. This unintentionally yields so-called vicinal surfaces (fig. 3.3) with low index plane terraces separated by steps. The average length \( l \) of a terrace is given by:

\[
l = \frac{h}{\tan \gamma}, \tag{3.1}
\]

with \( h \) being the height of the step and \( \gamma \) the macroscopic angle of misorientation. For surfaces vicinal to Si(001), the steps are monoatomic in height, i.e. \( h \) amounts to \( a_0/4 = 0.1358\) nm. The monoatomic step-height together with the dimerisation and the tetrahedral coordination of the Si atoms leads to a rotation of the dimer rows by 90° for adjacent terraces (fig. 3.3). Hence the steps and related terraces can be differentiated by the direction the dimer rows take with respect to steps: For type-A steps and terraces the dimer rows run parallel to the steps and for type-B the rows run normal to the steps [Chadi87]. This difference in step and terrace type is important, since it gives rise to anisotropic diffusion and incorporation behaviour of the adatoms, as will be discussed later on.

To sum up, Si (001) oriented substrates with small misorientation (< 1° [Auma92]) will generally have monoatomic steps and are reconstructed into a double domain
Fig. 3.3: Schematic representation of a vicinal Si(001) surface, depicting the rotation of the dimerization direction (after Hoese90).

(2x1)-(1x2) surface. This reconstruction does not change between 300 and 620°C regardless of hydrogen coverage.

3.2 Adsorption of Disilane on Si(001)

The first step towards deposition of Si using disilane (H₂Si-SiH₃) in a very low pressure process is its adsorption onto the Si surface. A considerable amount of research has been devoted to this topic in order to understand its mechanisms on Si surfaces of different orientations from a fundamental point of view. First deposition experiments indicated a distinctly higher reactivity of disilane on polycrystalline and (111) oriented substrates compared to that of silane [Buss88, Gates88]. It was found that disilane adsorbs on Si (111) independent of temperature between 50 and 285°C and that the sticking coefficient amounts to about 0.1 [Gates88]. This behaviour was attributed to a molecular precursor state for the disilane on the Si (111) surface. This precursor state can be imagined as the result of the formation of a weak (van der Waals) bond of the molecule with the surface, forming an 'admolecule', which can diffuse along the surface.

From ultraviolet photoemission spectroscopy (UPS) of Si (001) surfaces, which had been exposed to disilane at low temperatures (100 K), irreversible adsorption of disilane in molecular form with unit sticking probability was inferred [Boszo88]. Upon annealing at room temperature, the adsorbed disilane molecule dissociates into two SiH₃ (silyl) groups bonded to a surface Si atom. For reasons given below, this trihydride phase apparently decomposes quickly into SiH₂. At about 250°C the dihydride phase
dissociates into the monohydride phase, which, in turn, decomposes above about 430°C to produce H₂ and a clean Si(001)-(2x1) reconstructed surface.

The evolution of hydrogen, as observed in thermal desorption spectroscopy (TDS) experiments on Si (001) surfaces exposed to disilane, exhibits the same kinetics as that for Si surfaces, which were exposed to and saturated by atomic hydrogen. The similarity in the way hydrogen is bound to the surface, independent of the hydrogen source, was corroborated in electron energy loss spectroscopy (EELS) studies [Suda89,90, Maru82]. Based on the fact that no hydrogen evolving from a possible trihydride phase (SiH₃-Si) could be found, it was concluded that the silyl radical quickly dissociates into SiH₂ (silylene) to form the dihydride surface, even at low temperatures (> 200°C [Lubb91]).

Realising that the desorption of hydrogen is the reaction step that frees surface sites for the adsorption of incoming disilane, a scheme for atomic layer epitaxy (ALE) could be proposed [Suda89]. At low temperatures (approx. 250°C), the stable monohydride phase is desorbed upon irradiation with an ArF excimer laser beam, providing sites for the adsorption of disilane until the surface is saturated again. It was found that the maximum deposition rate per laser pulse was about 0.4 ML; it was concluded that this number also corresponds to the saturation coverage of disilane on Si(001) [Lubb91]. These observations led to the discussion of a model, according to which disilane can either adsorb on the dangling bonds of just one dimer (site D) or on adjacent dimers along one dimer row (site A) (see fig. 3.4 and 3.5a), with adsorption on site D being most probable [Suda90, Lubb91]. In these modelling studies of the adsorption process on the proposed sites, steric hindrance, as corroborated by the experimental findings for the saturation coverage, was included. According to this model, the adsorption process takes place as follows: disilane adsorbs on two dangling bonds on either site D or site A and dissociates instantaneously into two silyl radicals bound to dangling bonds. Above approx. 180°C, the silyl rapidly dissociates into silylene, which forms a double bond to the underlying layer, and a hydrogen atom which ties up another dangling bond on the surface. 'Rapidly' here means that the silyl dissociation reaction is not the rate limiting step for the deposition reaction. The dissociation involves minimal atomic motion and bond breaking (only the dimerization of the adsorption site is lost). The next step in the reaction chain entails the association of two adjacent silylene radicals into a dimer (belonging to the new overlayer) under evolution of hydrogen gas. Thus, the net adsorption reaction 'consumes' four dangling bonds and in turn leaves two Si and four hydrogen atoms bonded to Si at the surface:

\[
\text{Si}_2\text{H}_6 + 4 \rightarrow 2 \text{SiH}_3(s) + 2 \rightarrow 2 \text{SiH}_2(s) + 2\text{H(s)} \rightarrow 2 \text{SiH(s)} + 2\text{H(s)} + \text{H}_2(g)
\]

(3.2),

where the underscore denotes a dangling bond at the surface and s and g stand for surface and gas phase species, respectively. Unless the chemisorbed hydrogen is desorbed
Fig. 3.4: Depiction of disilane adsorption on the Si(001)2x1 surface a) on a single dimer and b) on two adjacent dimers within the same dimer row (after [Suda90]).

from the surface by thermal activation or, as in the ALE experiment, by a laser pulse, no further adsorption and growth from disilane can take place.

The statement that growth cannot proceed on a hydrogen terminated surface was questioned in work done by other groups [Bola91, Kulk90a,b, Gates91]. In an STM investigation of a Si(001) surface that was exposed to disilane at various temperatures, multilayer epitaxial growth was observed at about 420°C [Bola91]. The growth took place on monohydride surfaces and at a rate too high to be explained by the hydrogen desorption speed and the disilane sticking coefficient on monohydride surfaces. This finding would suggest that disilane can also react directly with a surface Si-H group to form surface bound SiH$_3$ and SiH$_4$ gas [Bola91]:

$$\text{Si}_2\text{H}_6 + \text{H}(s) \rightarrow \text{SiH}_4(g) + \text{SiH}_3(s)$$ (3.3)
Fig. 3.5: Disilane adsorption and dissociation in sites A and D. a) depicts SiH₃ radicals after Si-Si bond scission. b) shows the surface after the dissociation of silyl into silylene. (After [Suda90]).

A similar process had already been proposed for the reaction of a Si(111) surface with disilane [Kulk90a,b]. This reaction was invoked again to explain direct-recoil time-of-flight measurements, which determined the hydrogen coverage on disilane exposed Si(001) at various temperatures [Gates91]. Hydrogen coverages between 1 and 1.6 were found below 500°C supposedly produced by reaction 3.3. It should be noted that the incident disilane flux was very large: the equivalent of 294 ML of Si per second. Such a value is not normally used for growth in GSBME. Hence, it might well be that the high
hydrogen coverages reported in this case [Gates91], will not be observed for the usual growth conditions (fluxes on the order of 10ML/s).

3.3 Summary

In conclusion, growth from disilane would seem to proceed via two possible paths: The first one is the direct reaction of disilane with dangling bonds at the surface so that the entire disilane molecule contributes to the deposition. The rate of this process is governed by the limited availability of dangling bonds in the surface. However, the exact number of dangling bond sites necessary for the adsorption of disilane has not been established. The second path requires the association of disilane with a hydrogen atom to form a silyl radical chemisorbed at the surface, accompanied by the evolution of silane (equation 3.3). Obviously, the reaction is affected by the hydrogen coverage of the surface. The question remains, however, to which extent, at a given temperature, hydrogen coverage and disilane flux, the second reaction contributes to Si growth. This question and the determination of the number of dangling bond sites for disilane adsorption is dealt with in chapter 5.
Chapter 4

RHEED Intensity Oscillations and Adatom Kinetics

In our studies we have used the RHEED technique to obtain information on the reactions at the growing surface. This information is particularly contained in the intensity variations of the RHEED patterns. To demonstrate this point, we present in this chapter a brief introduction to the diffraction processes taking place during RHEED. The causes for the development of RHEED intensity oscillations and their relation to the different growth modi are outlined. The dependence of the observation of intensity oscillations on the diffraction conditions are discussed. The bulk of this chapter is concerned with our observations made during growth experiments employing RHEED intensity oscillations. The results obtained for GSMBE are contrasted to those from SSMBE; this approach allows us to draw conclusions about the differences in adatom kinetics in the two techniques.

4.1 RHEED and Intensity Oscillations

Most geometrical aspects of a RHEED diffraction pattern can be interpreted on the basis of a kinematic scattering model [Bauer69]. This implies that conventional concepts such as the reciprocal lattice together with the Ewald construction can be used to infer the overall structure (surface unit cell, reconstructions) of the surface [HøjI73]. However, the electron beam penetrates into the surface and multiple scattering events can not be neglected. In order to correctly describe the apparent width and intensity of diffraction features, a dynamic description of the diffraction processes is inevitable for an in depth analysis [Lars86]. For our study it is sufficient to use the kinematic description for the assignment of diffraction features to surface structures. In the case where the interaction of the electron beam is essentially with a two-dimensional atomic net (idealised crystal surface), the third dimension in real space is missing. Therefore, the surface is represented in the reciprocal space by infinitely long rods, normal to the real surface (fig. 4.1). It should be noted that for a real crystal surface the reciprocal lattice rods have finite thickness due to lattice imperfections and thermal vibrations. Due to the electron beam penetration into the real surface, the reciprocal lattice rods have finite length. Also, the Ewald sphere has finite thickness, for reasons of electron energy spread and beam convergence. The resulting diffraction pattern is a set of streaks rather than spots, which lie on concentric semi-circles around the origin (fig. 4.1).

Not only can RHEED be used to obtain static (structural) information on a given crys-
Fig. 4.1: Generation of a RHEED diffraction pattern from a crystalline surface. $L_n$ denotes the $n_{th}$ Laue zone, $\alpha$ the angle of incidence and $k_0$ the reciprocal wave vector.

tal surface, but the dynamic features of RHEED patterns can be employed to investigate the growth kinetics [Neave83, Sakam86, Aarts86]. It was found that intensity variations of certain diffraction features are related to the growth rate of the crystal. Generally speaking, one period of an intensity oscillation corresponds to the deposition of one atomic monolayer. Obviously, this is a very important fact since this phenomenon makes it possible to use RHEED as an in situ rate monitor, measuring in units of atomic layer distances. However, the one to one relation between intensity oscillations and growth rate is not always valid. Its applicability depends on the actual material being deposited, the orientation of the substrate, the electron beam azimuth and the growth temperature. For example, in the case of GaAs, the oscillations correspond to deposited GaAs molecular layers [Neave83]. For Si on Si(001) one deals with single or double layer oscillations [Sakam85, Aarts86], depending on azimuth and substrate misorientation.

The origin of the intensity oscillations is generally explained by an 'optical' model de-
veloped by Joyce and coworkers [Joyce86]. They assume that the intensity of the specularly reflected beam decreases with the number of diffusively scattering centres on the surface. On real semiconductor surfaces, the steps due to the macroscopic misorientation of the substrate act as such scatterers. Short-wavelength electrons ($\lambda_e \approx 0.012$ nm for 10 keV energy) readily scatter at these steps (height approx. 0.136 nm for monoatomic steps on Si (001)). Figure 4.2 depicts the evolution of the RHEED intensity during the deposition of monolayer fractions of the material. It is assumed that growth starts on an atomically flat surface which corresponds to a maximum in reflected beam intensity. Growth would proceed in a layer by layer fashion via nucleation of islands and their subsequent coalescence into a contiguous layer. Thus, during deposition, islands are formed, the number of which has a maximum when about half a monolayer of material has been deposited (fig. 4.2, $\theta=0.5$). At this point the number of diffusive scatterers (number of atoms in step-sites) is highest and the beam intensity has a minimum. Subsequently, the islands coalesce, and the surface smoothens (fig. 4.2, $\theta=0.75$). After deposition of a monolayer, only few steps remain and the RHEED intensity

**Fig. 4.2:** Development of RHEED intensity oscillations due to a variation of the surface step density by deposition of material. $\theta$ denotes the number of deposited monolayers (after [Joyce86]).

\[ \begin{align*}
\theta &= 0 \\
\theta &= 0.25 \\
\theta &= 0.5 \\
\theta &= 0.75 \\
\theta &= 1.0 \\
\theta &= 1.25 \\
\theta &= 1.5 \\
\theta &= 1.75 \\
\theta &= 2
\end{align*} \]
again has a maximum (fig. 4.2, \( \theta = 1 \) and \( \theta = 2 \)). Yet, because of the remaining islands due to 'premature' nucleation of the following monolayer, the beam intensity does not reach its original value. Hence, with ongoing growth, the RHEED intensity oscillations have smaller amplitude; they are damped. This damping can be complete, i.e. no oscillations are observed after a given time, or the oscillation amplitude will level off at some intermediate value (fig. 4.3) while the growing surface is distributed over several incomplete atomic layers.

At higher growth temperatures, where the island nucleation growth mode changes into the step-flow mode, the one to one correspondence between oscillation and deposited monolayer is no longer valid. Particularly on surfaces with relatively small terrace lengths, a simplistic interpretation of RHEED oscillations can lead to erroneous results.

When the diffusion lengths of the adatoms on the growing surface become high enough (i.e. at elevated substrate temperatures), the adatoms can reach the steps and the growth mode changes from layer-by-layer to step-flow. In the step-flow regime no intensity oscillations occur, since the number of scatterers (terrace steps) does not change during deposition. However, during the transition from layer-by-layer- to step-flow mode, oscillations can still be observed. In this intermediate regime, a considerable number of adatoms can reach terrace steps and does not contribute to island nucle-

\[ 575^\circ C, \phi_{\text{dis}} = 3.2 \text{ ML/s, <100>, 0.3°} \]

**Fig. 4.3:** Typical RHEED oscillation trace from GSMBE. The text box gives the substrate temperature, the disilane flux, the azimuth and the angle of incidence used in this experiment. The flux \( \phi_{\text{dis}} \) is given in units of total supplied silicon atoms by the disilane flow related to the number of Si atoms in the surface. For GSMBE this should not be mistaken for the actual growth rate, which is at least a factor of 10 lower.
ation. Consequently, the oscillation period increases and does no longer correspond to the deposition of precisely one monolayer. The exact value varies between 1.0 and 1.25 ML per period, depending on the growth conditions and the substrate misorientation [Zand91, Shita92]. The larger the misorientation, the smaller are the terraces and the earlier can adatoms reach steps, which may lead to an underestimation of the growth rate. Thus, care must be taken when using RHEED intensity oscillations to monitor the rate close to the step flow regime for growth on vicinal surfaces.

4.2 Diffraction Conditions

The RHEED diffraction conditions are a matter of great subtlety. Depending on the azimuth and the angle of incidence, the phase, damping and frequency of the oscillation may change drastically. In the following, a few of these artefacts, which are also observed in GSMBE, are treated.

In the previous paragraph, an optical model for the explanation of RHEED intensity oscillations was introduced. Because of the small electron wavelengths (for 10 keV electrons approx. 0.012nm), which is about one order of magnitude smaller than the monoatomic step height on the Si(001) surface, the electron beam is diffusely scattered at steps. This leads to intensity oscillations for varying step density, which is in fact the reasoning behind the zeroth-order approach of the optical model. However, from rocking curve analysis, the highly dynamic nature of RHEED is immediately apparent [Joyce86]. On the other hand, the effects of multiple scattering processes do not render the (general) one to one relation of monolayer growth and single oscillation period invalid. Rather, the damping and most prominently the initial phase of the oscillations is affected [Zhang87]. The initial phase is defined as the time it takes from the opening of the shutter to the first oscillation maximum divided by the average oscillation period (as determined from the subsequently recorded, complete oscillations). Furthermore, harmonics in the oscillations can develop due to a superposition of the diffuse background intensity (Kikuchi lines) and the specular beam [Dobs87].

Figure 4.4 shows GSMBE data regarding the change of the angle of incidence for <100> and <110> azimuth. No attempt has been made to correct the angle of incidence for refraction by the crystal surface. Strictly speaking, this effect must be taken into account to determine the effective angle of incidence. However, since structural information comprised in the RHEED pattern has not been used, refraction has been neglected. In fig. 4.4, the amplitude of the oscillations decreases with increasing angle. A plausible explanation argues that the electron beam penetrates deeper into the crystal and thus an increased number of electrons does not take part in the surface diffraction processes. Also, for both azimuths, intensity oscillations practically vanish above 1°. Whereas for the <100> azimuth the intensity oscillations apparently are not affected by
the diffuse background (no harmonics and initial phase changes are observed), the opposite is true for the <110> azimuth. In fact, the straightforward behaviour of the <100> azimuth in GSMBE is quite remarkable. In SSMBE pronounced and irreproducible phase changes depending on the angle of incidence have been observed for both azimuths [Maes92b]. Also, oscillations in SSMBE can still be observed to much larger angles, up to about 2°.

The reasons for these differences are not clear. It may be surmised that hydrogen at the surface together with the more 2-dimensional growth process in GSMBE leads to more reproducible starting conditions (initial oscillation phase) and to higher damping at higher angles.

Another observation made is the following: The first oscillation period for GSMBE in the <100> azimuth is always shorter than the subsequent periods. This effect depends on the incident flux and has not been found in SSMBE. Great care has to be exercised if one is going to correlate growth kinetics with features of the first oscillation period, since the phase generally depends on the angle of incidence. Nevertheless, this initial effect in GSMBE is interpreted in terms of fast adsorption of disilane on a reactive, i.e. hydrogen free Si surface (section 5.3).
In order to avoid diffraction artefacts, the RHEED intensity oscillation experiments done to determine the deposition rate of growing films, are all conducted with an angle of incidence of 0.3\(^\circ\) and an azimuth slightly off the <100> direction (standard conditions). Around this value for the angle of incidence, the largest oscillations amplitudes can be observed. The probable reason for this fact is that the angle of incidence is close to an off-Bragg angle (Bragg minimum), where the diffracted intensity is most sensitive to changes in step density at the surface. The off-azimuth condition is used in order to suppress the superposition of the specularly reflected intensity with the (strong) Kikuchi lines present. To look along the <100> azimuth, finally, ensures an averaged view onto the highly anisotropic Si surface (the terrace steps run along <110> directions). The intensity oscillations were all recorded from the specular spot in the (00) streak.

4.3 RHEED Intensity Oscillation Experiments

One of the striking observations in this work is the ease with which RHEED intensity oscillations can be produced during GSMBE. Figure 4.3 shows a typical oscillation trace that has large oscillation amplitude and low damping. Traces like this are routinely observed after application of the wafer preparation procedure described in section 2.6. The low damping of the oscillation amplitude indicates that the growth mode is practically limited to island nucleation. This is in accordance with surface profiler measurements yielding a one to one correspondence between an oscillation period and the deposition of a monolayer.

Applying the optical model to interpret the trace in fig. 4.3, the surface roughens considerably during growth as is reflected by the precipitous decrease in intensity after the shutter is opened. Similarly, the intensity increases again upon closure of the shutter. It is assumed that during this so called 'recovery' the surface is smoothened on an atomic scale. At temperatures where the kinetic energy of the adatoms is high enough, atoms in the growth front (e.g. at an island, or within a misorientation step) have a certain probability to dissociate from it and diffuse over the surface until they reach another front. This relatively fast, short range reorganisation process results in smooth growth fronts with fewer kinks. A second, slower, long range reorganisation mechanism reestablishes the equilibrium terrace width distribution that was present in the beginning of growth. Nucleated islands dissociate and the formerly island-bound adatoms find themselves a site in a misorientation step. Disintegration proceeds until the islands are completely gone; all the adatoms have found a site on a misorientation step and the equilibrium terrace length has been restored. Both processes are reflected in the intensity increase when growth is stopped [Lewis85]. In general, the recovery proceeds until the original intensity has been restored (fig. 4.5).
Fig. 4.5: The recovery of the GSMBE surface at 535 °C during growth interruptions.

4.3.1 Substrate Temperature induced Effects

Traces like the one in fig. 4.3 were also observed in SSMBE albeit merely at temperatures between 300 and 450°C. Above that range, the oscillations were strongly damped. Also, unlike for experiments in SSMBE, in GSMBE it is not necessary to anneal the substrate at high temperatures between intensity oscillation experiments that are performed at temperatures above 500°C. The surface recovers sufficiently fast (within a few minutes time) for a next experiment. In SSMBE, surfaces have to be annealed at temperatures above 800°C for about 5 minutes to prepare a smooth surface, which permits the observation of oscillations in the next run. In view of the distinct oscillations achievable under almost all circumstances in GSMBE and the inevitable annealing step in SSMBE, one can claim that the surface in GSMBE grows more strongly 2-dimensionally, layer by layer, and needs less restoration than an SSMBE surface. In other words, the distances that have to be travelled for adatoms in SSMBE in order to smoothen the surface are considerably larger than for GSMBE.

In contrast to GSMBE, in SSMBE it was not possible to observe intensity oscillations at temperatures higher than about 590°C. At these temperatures, the diffusion length of the adatoms increases so that misorientation steps can be reached and nucleation on the terraces is suppressed. To achieve distinct oscillations in SSMBE, the lower the substrate temperature the better. For temperatures around 400°C, adatom diffusion is slow and island nucleation prevails. In fact, during growth interruptions at these low
temperatures, the surface structure apparently is 'frozen-in', i.e. no recovery can be observed on the time scale applied, as can be seen in fig. 4.6.

The investigation of the transition between the island nucleation and the step flow growth mode allows the determination of the average diffusion length. At the transition temperature, the adatom diffusion length $\lambda$ is of the order of the average terrace size $l$ at the surface. This fact has often been used to determine the diffusion coefficients of adatoms [Kajik92 and references therein]. In our study, the wafers used for these RHEED experiments had a misorientation angle $\gamma$ of $0.35\pm0.15^\circ$, which yields an average terrace length $l$ between 16 and 39 nm. The data of fig. 4.7 demonstrate the transition from island nucleation to step flow growth for SSMBE at a given flux with increasing deposition temperature. The transition temperature is slightly higher than 575°C, since oscillations are still discernible at this temperature. Due to the nature of the transition between island nucleation and step-flow growth mode, the determination of an exact transition temperature is not possible.

The diffusion length $\lambda$ for the two dimensional case is linked to the diffusion coefficient $D$ by:

$$\lambda^2 = 4D\tau$$  \hspace{1cm} (4.1),

with $\tau$ being the 'lifetime' of the adatom. This lifetime is usually regarded as the period of time the atom can move freely on the surface before it gets incorporated into the crystal at a step edge or forms a nucleus whenever it encounters another adatom.

---

![Graph](image)

**Fig. 4.6:** The 'freeze-in' of adatom mobility in SSMBE at 400°C substrate temperature as observed during growth interruption.
\[ \phi_{\text{dis}} \approx 0.05 \text{ ML/s, } <100>, 0.5^\circ \]

575°C

530°C

490°C

440°C

Intensity (a.u.)

Time (s)

Fig. 4.7: The transition between island nucleation and step flow growth mode with increasing temperature in SSMBE. The traces have been offset for clarity.

A crude approximation for \( \tau \) is given by the mean time elapsed between the successive arrival of atoms at a specific site:

\[ \tau = \frac{N_{\text{Si}}}{\phi_{\text{Si}}} \quad (4.2), \]

where \( N_{\text{Si}} \) is the number of Si atoms per cm\(^2\) and \( \phi_{\text{Si}} \) is the incident Si flux in units of atoms per cm\(^2\) per second.

Hence, at the transition temperature, the majority of adatoms reaches a step within the time \( \tau \), before they meet another adatom and form a nucleus. Using eq. 4.1, with \( \lambda \) obtained from the terrace length for the misorientation \( \gamma \) of the substrates used (\( \gamma = 0.35 \pm 0.15^\circ \)) and \( t \) from eq. 4.2, it is found that the diffusion coefficient has a value between \( 3.2 \times 10^{-14} \) (\( \gamma = 0.5^\circ \)) and \( 1.9 \times 10^{-13} \text{ cm}^2/\text{s} \) (\( \gamma = 0.2^\circ \)) at 590°C. These values are similar to those inferred from RHEED intensity oscillation experiments reported in the literature \( (1.2 \times 10^{-14} \text{ cm}^2/\text{s} \ (\gamma = 0.5^\circ)) \) [Hoev89]. However, the diffusion coefficient seems much too low when compared to data (approx. \( 10^{-12} \text{ cm}^2/\text{s} \)) obtained from an STM study [Mo91]. This discrepancy might be mainly due to the use of completely different analysis techniques for the determination of the diffusion coefficient. Yet, in our case the choice of \( \tau \) (equ. 4.2), is known to underestimate the adatom lifetimes [Kajik92] so
that overestimated values for the diffusion coefficients are obtained. A better approach would take into account that an adatom typically samples a certain surface area during its lifetime as a consequence of its movement over the surface, or would consider the effect of a non-unity sticking coefficient for an adatom reaching a step site [Kajik92]. In view of the limited available data from SSMBE, improved modelling was not attempted.

4.3.2 Flux induced Effects

From the above it is clear that the transition temperature also depends on the magnitude of the impinging flux. The higher the flux, the higher the chance for nucleation before the adatoms can reach a step and the higher the temperatures at which intensity oscillations can still be observed. The set of oscillation traces from GSMBE experiments, shown in fig. 4.8, illustrates the above statement. This experiment was performed at a temperature of 650°C. In this case, the transition takes place for a flux of about 5 ML/s. At lower temperatures, the transition occurs at correspondingly smaller fluxes (see fig. 4.9).

It would be interesting to perform the same sort of experiment in the SSMBE system.

![Graph showing RHEED oscillations with increasing flux](image)

*Fig. 4.8: The development of RHEED oscillations with increasing flux in GSMBE.*
Fig. 4.9: The transition between island nucleation and step flow growth mode in GSMBE as triggered by the incident flux for different temperatures. Also given is the surface coverage with hydrogen at the transition points.

Unfortunately, fluxes on the order of a few monolayers per second in SSMBE render the chamber environment very noisy due to stray electrons and gun instabilities so that RHEED intensity oscillation experiments become practically impossible. However, at lower growth rates and somewhat lower substrate temperatures, a flux-induced growth mode transition was indeed found, albeit not as distinct as in GSMBE. Fact is that RHEED intensity oscillations in SSMBE above 590°C cannot be restored with a flux of up to 3 ML/s. Note that in SSMBE this flux value also corresponds to the growth rate. In GSMBE, on the other hand, 5 ML/s of disilane flux do provoke intensity oscillations, but the growth rate is only on the order of 0.6 ML/s. Thus, the number of Si adatoms at the growing surface can be considerably lower in GSMBE than for SSMBE. Yet, oscillations can be observed for the former and not for the latter for nominally identical experimental conditions. This important difference is explained by the effect that the surface hydrogen coverage has on the mobility of the Si adatoms. Most likely, the surface hydrogen [Lin92] and possibly also the disilane molecules in the precursor state, both reduce the diffusivity of the adatoms in such a way that intensity oscillations are observable in GSMBE with considerably fewer Si adatoms present than are necessary in SSMBE. The hydrogen coverage at the transition points is also shown in fig. 4.9. Apparently, already a small amount of hydrogen and maybe also disilane at the surface is sufficient to seriously hamper the diffusion of adatoms. The incident disilane flux together with the substrate temperature determine the total amount of hydrogen present at the surface and hence the adatom mobility in the growing GSMBE surface.

Using eq. 4.1, the flux data from fig. 4.9 and the growth rates at the transition points, the diffusion coefficient for different growth temperatures may be calculated. This is
carried out employing incident fluxes and actual growth rates for the calculation of τ. From the Arrhenius plot of these data (fig. 4.10), an activation energy of 3.1 eV is deduced for the former case and 2.4 eV for the latter. Also given in the figure is the diffusion coefficient for SSMBE growth. The calculation using the incident flux in GSBME leads to diffusion coefficients (uppermost curve in fig. 4.10), which are an order of magnitude larger than those obtained using growth rate data (two lower curves in fig. 4.10). Also, the activation energy for diffusion is considerably larger in GSBME (3.1 and 2.4 eV) than in SSMBE: Values between 0.67 and 1.57 eV [Mo91, Sakam89, Ichio78, Kas72, Farr74] have been reported for SSMBE. (In fig. 4.10, 1 eV was used in the calculation). Upon comparison of the GSBME curves the question arises, which way to calculate the diffusion constant is the 'correct' one. Most likely, the truth lies somewhere in between: The use of the incident flux in the computation overestimates the diffusivity of the adatoms because not all of the incoming flux will adsorb at the surface nor will all the disilane molecules go through the precursor state. The calculation employing the growth rate, on the other hand, does not take into account other adsorbed species like disilane in the precursor state, hydrogen or silyl and silylene. Hence, it is believed that the diffusivity of adatoms and admolecules in GSBME is higher than that of adatoms in SSMBE at least in the investigated temperature range. It might be speculated that the monohydride-dimer and other higher hydride species are weaker bound to the underlying layer than Si atoms without hydrogen attached.

**substrate temperature (°C)**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Diffusion Coefficient (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>630</td>
<td>6 x 10⁻¹²</td>
</tr>
<tr>
<td>605</td>
<td>3 x 10⁻¹³</td>
</tr>
<tr>
<td>580</td>
<td>1 x 10⁻¹⁴</td>
</tr>
<tr>
<td>555</td>
<td>2 x 10⁻¹⁵</td>
</tr>
</tbody>
</table>

**diffusion coefficient for GSBME calculated via:**
- ●: incident Si flux; $E_a = 3.1 \pm 0.1$
- ○: growth rate; $E_a = 2.4$ eV $\pm 0.1$

**diffusion coefficient for SSMBE; $E_a = 1$ eV**

![Arrhenius plot of the diffusion coefficient in SSMBE and in GSBME determined at the transition to step flow growth mode. The solid lines for GSBME data are fits to data points; the grey line for SSMBE is calculated using the measured value at 590°C and a typical value for the activation energy taken from the literature.](image)

Fig. 4.10: Arrhenius plot of the diffusion coefficient in SSMBE and in GSBME determined at the transition to step flow growth mode. The solid lines for GSBME data are fits to data points; the grey line for SSMBE is calculated using the measured value at 590°C and a typical value for the activation energy taken from the literature.
Hence, adatoms and admolecules in GSBME can travel larger distances so that the surface remains smoother on a larger scale than for SSMBE for all growth modes. This also explains the observation that GSBME surfaces do not need special annealing treatments prior to oscillation experiments in contrast to those surfaces generated in SSMBE.

The difference in activation energies of the diffusion coefficients in GSBME (2.4 and 3.1 eV) and SSMBE (1 eV) may again be attributed to the presence of hydrogen on the GSBME surface. The activation energy of 2.4 eV for the GSBME curve derived using growth rate data certainly reflects the activation energy (2 eV) for hydrogen desorption as growth rate limiting step (see section 5.2). Reasons for the even larger activation energy for the GSBME curve inferred from flux data cannot currently be given.

4.3.3 Growth Anisotropy on Si(001)

For some of the substrates used, intensity oscillations with a double period are found in the <110> azimuth at an angle of incidence of 0.3° (fig. 4.11). Comparing fig. 4.11 with the traces of fig. 4.4b taken at an angle of incidence of 0.9 and 1.0°, one might argue that the former is also merely a diffraction artefact. However, this is not the case. Close inspection reveals that the former trace clearly shows a distinct change of oscillation structure from single layer to double layer oscillations. In contrast, the traces from fig. 4.4b do not change their overall structure; only the oscillation amplitude decreases, which eventually leaves one out of two oscillation maxima discernible, resembling

![Graph showing intensity oscillations](image)

**Fig. 4.11: Transition from single to double period oscillations indicating growth anisotropy on the Si(001) surface observed in the <110> azimuth.**
double layer oscillations. Furthermore, double layer oscillations in the <110> azimuth have been reported in both SSMBE and GMBE [Sakam86, Hiroi92, Mok92b]. However, it is known that the phenomenon does not always show up [Aarts86]. Also in our case, the double period oscillations are not observed on all substrates used. They are most reproducible on 0.35 ± 0.15° misoriented Si(001) wafers, which indicates that the substrate misorientation is an important parameter.

It is generally believed that this kind of oscillation trace is related to anisotropic growth on the Si(001) surface. Adatoms can diffuse faster in the direction of the dimer rows than normal to the rows and can bind easier at B-type steps (dimer rows normal to step edge) than at A-type steps (dimer rows parallel to step edge) [Hoefv89, Mo92]. During growth, the B-steps grow faster than the A-steps; the edges catch up with each other and eventually form biatomic steps with the dimer rows normal to the edge (D_b-step) on a single domain surface [Hoefv89]. The single-domain surface thus produced would reveal double-period oscillations. During annealing, the surface would redevelop the double domain structure.

Although this explanation appears quite plausible, and certainly constitutes an important element of a complete model to describe the behaviour of a growing Si(001) surface, not all arguments can be accepted in view of the RHEED results: The bonding anisotropy of adatoms at step edges, together with the anisotropic diffusion may explain the STM observation of double layer growth. However, for the observation of RHEED intensity oscillations island nucleation and coalescence conditions must prevail and it is very hard to imagine that islands nucleate directly in double layers. One could envisage quasi double layer growth at terrace steps, when a B-type terrace catches up very quickly with a growing A-type terrace, but this growth mode would preclude the observation of RHEED intensity oscillations. Hence, the above mentioned explanation for double-period oscillations in MBE growth cannot be considered definite as yet.

4.4 Conclusions

RHEED intensity oscillations have proved to be a very valuable tool for the investigation of surface processes, also in our studies. We may conclude that the adatom kinetics of SSMBE and GMBE are very similar: In both cases the same basic features in RHEED intensity oscillations are observed. However, the presence of hydrogen and/or disilane at the GMBE surface modifies the adatom kinetics: The diffusivity is higher than in SSMBE and more strongly activated. This is evident in the considerably relaxed conditions necessary to observe RHEED oscillations in GMBE. These insights on GMBE growth provide the basis for the detailed investigation of the growth process, which is dealt with in the next chapters.
Chapter 5

Homoepitaxial Deposition of Si on Si(001) from Disilane

The results of the study described in the previous chapter on the interaction of disilane with the silicon surface constitute a firm basis for modelling the growth kinetics of the homoepitaxial deposition. In the present chapter, a model is presented, based on Langmuir adsorption kinetics, that accurately predicts the observed rate dependence on flux and growth temperature. The necessary growth rate data to formulate the model is provided by RHEED intensity oscillation measurements. The RHEED technique also allows us to determine the sticking coefficient of disilane on Si(001), which is an essential quantity for describing the growth rate in this system.

5.1 Dependence of Growth Rate on Disilane Flux and Substrate Temperature

Growth rates determined by RHEED intensity oscillations under standard conditions (section 4.2) for different disilane fluxes and substrate temperatures are shown in figure 5.1. The most prominent feature is the strong dependence of the rate on the growth temperature: The same flux yields a growth rate of $3 \times 10^{-3}$ ML/s at 468°C compared to 0.5 ML/s at 644°C, a difference of more than two orders of magnitude. Furthermore, the rate increases strongly with flux for small fluxes, but tends to saturate for higher fluxes. The strong rate increase at smaller fluxes ($< 1$ ML/s) is not completely observable with RHEED intensity oscillations at the two highest temperatures, since at those deposition parameters the growth is still in the step-flow regime (see section 4.1).

5.2 Modeling of Reaction Kinetics

5.2.1 Langmuir Adsorption Isotherms

The observed behaviour (fig. 5.1) of the growth rate with increasing flux at a given temperature closely resembles that of Langmuir adsorption isotherms [Lang18]. In the course of his work on surface adsorption, Langmuir developed a theory that describes the adsorption of gases on solids for almost all conceivable conditions (mono- and diatomic gases, solids with different kinds of adsorption sites, etc.). His ideas categori-
Fig. 5.1: Growth rate of Si from disilane on Si(001) versus flux for 4 different growth temperatures. The curves through the markers are fits to the data (see text).

cally broke with the accepted notion of molecules or atoms being reflected from surfaces in cases where hardly any adsorption or reaction was found. Instead, his theory assumes that all molecules or atoms do initially adsorb on the surface of the solid and that low coverages are due to quick re-evaporation of the species. In the following, the deposition of Si on Si(001) from disilane will be treated in terms of adsorption and desorption processes similar to Langmuir's theory.

5.2.2 Rate Equation

The model for disilane adsorption and growth (see section 3.2) assumes that the growth rate is determined by the availability of adsorption sites for disilane. The number of adsorption sites, however, is determined by the surface hydrogen coverage and the desorption rate of hydrogen.

As has been pointed out, the overall deposition reaction (eq. 3.2) can be divided into three steps:

\[
\begin{align*}
\text{Si}_2\text{H}_6 + 2_\text{H}_2 & \rightarrow 2 \text{SiH}_3(\text{s}) \quad (5.1), \\
2 \text{SiH}_3(\text{s}) + 2_\text{H}_2 & \rightarrow 2 \text{SiH}_2(\text{s}) + 2 \text{H}(\text{s}) \quad (5.2), \\
2 \text{SiH}_2(\text{s}) + 2\text{H}(\text{s}) & \rightarrow 2 \text{SiH}(\text{s}) + 2\text{H}(\text{s}) + \text{H}_2(\text{g}) \quad (5.3).
\end{align*}
\]
The underscore again denotes a dangling bond at the surface and s and g denote surface and gas phase species, respectively. Equation 5.1 describes the adsorption reaction, 5.2 the dissociation of silyl and 5.3 the dissociation of silylene. It is assumed that the Si atoms from the disilane, once bonded to the surface, do not desorb.

Whether or not the disilane actually adsorbs and dissociates is determined by the availability of surface sites and the reactive sticking coefficient $\alpha_{\text{dis}}$ of disilane on Si (001). The reactive sticking coefficient is defined as the ratio between the adsorbed and reacting (dissociating) molecules on a hydrogen-free surface and the total number of incoming disilane molecules. The reactive sticking coefficient should be compared with the reaction efficiency $\varepsilon$: The latter is simply defined as the ratio of the growth rate over the total incoming flux. $\alpha_{\text{dis}}$ and $\varepsilon$ are equal in situations, in which the growth rate is supply limited, like for the lowest fluxes in fig. 5.1. Under these conditions, both parameters are close to 0.1.

The concentration of surface sites available for adsorption equals the concentration of dangling bonds, $\theta_{\text{db}}$. One can define an effective hydrogen coverage $\theta_{\text{h}}$ which determines the number of dangling bonds via:

$$\theta_{\text{h}} = 1 - \theta_{\text{db}} = \theta_{\text{mh}} + \theta_{\text{hh}}$$

(5.4),

with $\theta_{\text{mh}}$ being the monohydride surface coverage and $\theta_{\text{hh}}$ the coverage with higher (di- and tri-) hydrides. The effective hydrogen coverage should not be confused with the previously mentioned absolute hydrogen coverage $\theta^*$, which is simply the total number of hydrogen atoms present at the surface divided by the number of surface Si atoms. $\theta^*$ can be larger than unity for low temperatures and high fluxes (fig. 5.2), since at these conditions also a number of silyl and silylene radicals is apparently present at the surface. $\theta^*$ is therefore not the proper quantity to describe the number of dangling bonds.

For a further interpretation of the adsorption data in the Langmuir picture, one needs to know the number of sites required for the molecule to adsorb on the surface. Equation 5.1 indicates that two adjacent dangling bond sites suffice for mere adsorption, but four dangling bonds are consumed in the total reaction. Assuming a stochastic distribution of dangling bonds, the chance for finding two and four adjacent dangling bonds is $(\theta_{\text{db}})^2$ and $(\theta_{\text{db}})^4$, respectively. With the further assumption mentioned above that Si atoms, once bonded to the surface, do not desorb, the growth rate can be written as:

$$r = 2 \cdot \alpha_{\text{dis}} \cdot \phi_{\text{dis}} \cdot (\theta_{\text{db}})^n = 2 \cdot \alpha_{\text{dis}} \cdot \phi_{\text{dis}} \cdot (1 - \theta_{\text{h}})^n$$

(5.5),

$n$ being either 1,2 or 4, depending on the actual order of the adsorption-reaction. $\phi_{\text{dis}}$
Fig. 5.2: Absolute surface hydrogen coverage $\theta$ depending on disilane flux and substrate temperature on Si(001) (after Gates92). The solid lines are guides to the eye.

denotes the disilane flux and the factor of two accounts for the fact that two Si atoms per disilane molecule contribute to the growth rate.

As stated in section 3.2, the source for the adsorbed hydrogen on the Si (001) surface (atomic hydrogen or disilane) does not affect the properties of the hydrides formed [Boszo88, Uram89]. The hydrogen desorption processes for the hydrides formed from disilane adsorption are the same as those for the hydrides formed by the adsorption of atomic hydrogen. For the discussion below, it is important to note that all studies on hydrogen desorption from Si(001) agree on the fact that the desorption process follows a first-order rate law [Sinn89, Wise91, Evel92]. This finding has been tentatively ascribed to preferential occupation of both dimer atoms with hydrogen so that the latter atoms can desorb as H$_2$ in a concerted fashion [Wise91, Evel92]. Although the investigations all agree on the first-order rate law, they differ in the values for the activation energy of hydrogen desorption: Values between 2.0 and 2.9 eV have been reported, also depending on the technique used to study desorption (laser-induced thermal desorption, temperature programmed desorption [Sinn89, Wise91, Liehr90]).

Based on the foregoing, we can now formulate the steady state equation governing the growth from disilane: Equation 5.5 describes the adsorption of disilane on 1,2 or 4 dangling bonds. In total, 4 dangling bonds are consumed during the reaction of a disilane molecule with the Si(001) surface. Thus, for steady state conditions ($\theta^*$ or $\theta_h$ does not change), 4 dangling bonds have to be created in a first order desorption process per reacting disilane molecule:
\[ \alpha_{\text{dis}} \cdot \phi_{\text{dis}} \cdot (1 - \theta_h)^n = 4 \cdot v \cdot \theta_h \] (5.6),

with \( v \) being the hydrogen (atom) desorption rate in ML/s; this quantity is a strong function of temperature. The exponent \( n \) again denotes the number of dangling bonds necessary for the adsorption of a disilane molecule.

### 5.2.3 Fitting Procedure

To learn more about the actual number of dangling bonds necessary for the adsorption of disilane, eqn. 5.5 was fitted to data sets like those of fig. 5.1 (growth rate versus flux) using different values for \( n \) (1, 2 or 4). Both the effective hydrogen coverage \( \theta_h \) and the desorption rate \( v \) are unknown and have to be obtained from the fit. For this purpose, equation 5.6 is solved for \( \theta_h \), which yields a linear, quadratic or 4th order relation with \( \theta_h, \alpha_{\text{dis}}, \phi_{\text{dis}} \) and \( v \) as variables. The relation was then put into rate equation 5.5 and fitted to the data. It should be noted that the reactive sticking coefficient was assumed to be 0.1 and no temperature dependence of the adsorption was taken into account [Liu92, and section 5.3].

Fits were done to 10 sets of experimental data. The data was taken at temperatures ranging from 464 up to 644°C. For greater clarity, a few of these fits, together with the data and the calculated effective hydrogen coverage, are plotted on a linear scale (figs. 5.3-6).

Visual inspection shows that the best fits are obtained for second and fourth order adsorption. Taking the sum of all \( \chi \)-square parameters of the fits, the fits for 4th order adsorption yield the smallest value, which means that the adsorption of disilane most likely requires 4 adjacent dangling bond sites. Yet, the margin to the second order fits is quite small. On the other hand, the chi-square values for the first order fits are dis-

**Figs. 5.3:** Fit employing different adsorption orders to a data sets of growth rate versus applied flux at 468°C. Also given is the effective hydrogen coverage (right hand axis).
Figs. 5.4-5.6: Fits employing different adsorption orders to data sets of growth rate versus applied flux taken at temperatures of 539, 580 and 644 °C. Also given is the effective hydrogen coverage (right hand axis).
tinctly larger. We can therefore exclude the first order adsorption path.

The fits at 468°C do not allow any conclusion as to which adsorption process is governing the kinetics: The scatter in the experimental data is too large. At this temperature, the growth rate is very low. Typically only a few oscillations can be recorded, affecting the accuracy with which the rate can be determined. Moreover, the temperature during the long runs (typically several hours) is not perfectly stable, which causes additional scatter in the data.

The fits to the growth rate versus flux data at a given temperature (fig. 5.1 and similar data) allow the derivation of the hydrogen desorption speed $v$ as a function of substrate temperature $T$ (fig. 5.7). This in turn also yields $\theta_h$ as a function of $\phi_{\text{dis}}$ and $T$. Next, $\theta_h$ was calculated for the data in figs. 5.3-6 and plotted in the same figures (right hand axes). This allows comparison to the absolute hydrogen coverage $\theta^*$ as determined by direct recoil measurements [Gates92]. For this purpose the data of fig. 5.2 is shown again, now including $\theta_h$ from the fits to second and fourth order adsorption (fig. 5.8). $\theta_h$ from the second order fits follows $\theta^*$ up to about 0.7, whereas the fourth order fits deviate somewhat earlier at a coverage of about 0.6. Hence, in contrast to the rate vs. flux fits for fig. 5.3-6, the comparison of $\theta^*$ with the calculated $\theta_h$, appears to favour the second order adsorption model.

From fig. 5.8 it is clear that only for higher coverages ($>0.6$) do higher hydrides contribute considerably to the absolute coverage. Simultaneously, also the applicability of the developed model (eq. 5.6) becomes more and more questionable, since the dangling bonds are only produced by desorption from the monohydradine phase and not from the higher hydride phase. Particularly at lower growth temperatures (e.g. fig. 5.3), the calculated $\theta_h$ rises above the critical value of 0.6. Yet, also the fits at low growth temperatures yield good agreement with experimental data (see below) so that

Fig. 5.7: Hydrogen desorption speed at various temperatures and for first and second order adsorption kinetics. The activation energies are also given.
the influence of higher hydrides in first approximation can be neglected over the investigated range of temperatures and fluxes.

It should be noted that the agreement between the predicted $\theta_h$ and the measured $\theta^*$ for lower coverages is remarkably good, particularly so for the data for a flux of 294 ML/s. This flux is much larger than any flux used in GSMBE for the investigations that have led to the modeling described above.

### 5.2.4 Activation Energy for Hydrogen Desorption Limited Growth

From the above discussion, it follows directly that also the growth rate $r$ can be calculated for arbitrary values of flux and growth temperature. Fig. 5.9 shows an Arrhenius plot of the dependence of the growth rate on the inverse of the substrate temperature for deposition at various fluxes. Both experimental data and calculated rates based on the fits to the data in fig. 5.1 and 5.7 are given. The obviously close agreement over more than four orders of magnitude is certainly remarkable. It should be mentioned that the experimental data that were used for the modelling (rate vs. flux curves) and the results presented in fig. 5.9 (rate vs. inverse temperature) were obtained in different experiments. The experimental results in fig. 5.9 depict a strongly temperature acti-
vated, kinetic branch at lower temperatures (below approx. 500°C). In this region, the growth rate depends almost completely on temperature and hardly on flux (analogous to the saturation behaviour in fig. 5.1). This is the region, in which hydrogen desorption is probably limiting the rate. It is only at higher temperatures for smaller fluxes that the rate increase does not follow the kinetic branch any longer and levels off. Here, the growth becomes mass transport (flux) limited. Since the RHEED intensity oscillations vanish for these conditions, the transport limited region can not be probed entirely by the oscillations.

The transition region between hydrogen desorption limited and transport limited growth moves to higher temperatures with increasing flux. This is due to the increase in hydrogen coverage with rising flux at a given growth temperature. Using the calculated effective hydrogen coverage given in fig. 5.8, it may be concluded that the transition for hydrogen desorption to transport limited growth occurs at a \( \theta_h \) of about 0.3.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure5.9}
\caption{Arrhenius plot for growth of silicon from disilane in GSMBE.}
\end{figure}
The fits based on the rate versus flux data yield an activation energy for the hydrogen desorption rate between 2.1 and 2.4 eV, depending on the adsorption order considered (fig. 5.7). These values should be compared with the activation energy of the growth rate in the low temperatures regime (400-500°C) (fig. 5.9). The latter amounts to about 2.0±0.1 eV, which agrees rather well with the activation energies for hydrogen desorption. Indeed, the value found for the activation energy for the growth rate in the kinetic branch (2.0 eV, fig. 5.9) and those for hydrogen desorption (2.1-2.4 eV, fig. 5.7) lie close to those reported for the activation energy for hydrogen desorption in the literature [Sinn89 (1.9 eV), Liehr90b (2.0 eV)] and are also compatible with values from other groups investigating GSMBE Si growth from disilane at low process pressures [Mok92a (1.7 eV)]. Obviously, the assumption that hydrogen desorption constitutes the rate limiting step is well supported by our data.

5.2.5 Additional Reaction Mechanism of Disilane with Si(001):H?

The excellent agreement between calculated and measured rates over the entire investigated temperature range casts some doubt on the assumption of an additional reaction mechanism of disilane with a hydrogen terminated Si surface [Kulk90b, Gates91, Bola91]. Namely, these studies propose a reaction mechanism of disilane directly with hydrogen atoms at the surface in order to explain some low temperature (around 400°C) multilayer growth results (see eq. 3.3, section 3.2). This mechanism is thought to exist in addition to the reaction of disilane with the bare Si surface (eq. 3.2). Our data do not support this idea at all. We have shown, that also the low temperature growth can be readily described in terms of a reaction of disilane with bare Si only. It should be noted, that the idea of an additional reaction mechanism was first developed in a study dealing with a Si(111) surface [Kulk90b], where the structure as well as the hydrogen desorption mechanism is markedly different from that of Si(001) [Koehl88]. This idea was then invoked again during a study performed on the Si(001) surface [Gates92]. This study reported the observation of absolute hydrogen coverages larger than one (fig. 5.8) upon high incident fluxes (2.9 and 294 ML/s) at low growth temperatures. Obviously, the authors felt the need to explain ongoing growth despite the fact that the surface is completely covered with hydrogen. However, as we have described before, growth can still take place by adsorption of disilane to dangling bonds in the surface; it is only that higher hydrides are also present at the surface giving rise to an absolute hydrogen coverage exceeding unity.

The other work claiming an additional reaction mechanism [Bola91] is an STM study conducted on Si(001). Here, higher growth rates at low temperatures were found than expected. The disagreement may be due to the lack of statistics and resolution in time for this kind of (quasi-static) investigation.
It may be concluded from our data that the Langmuir adsorption isotherm-scheme obviously also holds for the low temperature region (> 400°C). Thus, one does not need to resort to an additional reaction path to explain the low temperature growth results (at least for low fluxes). Also at the low temperatures the formation of dangling bonds is governed by the hydrogen desorption rate.

5.3 Determination of the Reactive Sticking Coefficient

For the fits to the previously discussed results, the reactive sticking coefficient was assumed to be 0.1, without any dependence on the substrate temperature. However, it is not at all clear why the adsorption process would not be thermally activated. In order to verify this assumption, the reactive sticking coefficient has to be measured at various temperatures and fluxes. One way to obtain its value is the determination of the reaction efficiency \( \varepsilon \) at small fluxes. At these conditions, the hydrogen coverage has a minimum value so that all incoming molecules can adsorb, and \( \varepsilon \) equals \( \alpha_{\text{dis}} \) (see section 5.2). In the following, a dynamic method is described to determine the reactive sticking coefficient of disilane upon adsorption to a hydrogen-free surface making use of the response of the RHEED intensity signal.

5.3.1 The \( \tau_i \) Approach

This approach is based on the observation that the first oscillation period in GSMBE is always shorter than those of the remaining oscillation trace. Particularly the first half of the initial oscillation shows a steep decrease in intensity towards the first minimum within a time \( \tau_i \) (fig. 5.10). Recalling the optical model for the explanation of RHEED

![Fig. 5.10: RHEED oscillation trace showing the decrease in intensity after the beginning of growth. \( \tau_i \) and \( \tau_r \) denote the times for the first half monolayer and a steady state growth period, respectively.](image-url)
intensity oscillations (see section 4.1), this decrease is interpreted in terms of the rapid growth of half a monolayer of Si from disilane on an initially hydrogen free surface.

In contrast to the steady state of the forgoing section, here a non-equilibrium situation needs to be considered: During the adsorption of disilane on the initially hydrogen-free surface, hydrogen coverage builds up and blocks additional adsorption sites. During the first half of a monolayer, the hydrogen coverage develops towards its equilibrium value. Consequently, the growth rate varies with time until the steady state concentration has been reached somewhat later.

Further analysis requires the determination of the time dependent effective coverage $\theta_h(t)$ by solving equation 5.7 for different values of the adsorption order $n$:

$$\frac{d\theta_h(t)}{dt} = \alpha_{\text{dis}} \phi_{\text{dis}} \left( 1 - \theta_h(t) \right)^n - 4v \theta_h(t)$$  \hspace{1cm} (5.7).

Using the solution for $\theta_h$, we obtain the growth rate as a function of $t$ (see eq. 5.5):

$$r(t) = 2 \alpha_{\text{dis}} \phi_{\text{dis}} \left( 1 - \theta_h(t) \right)^n$$  \hspace{1cm} (5.8).

After integrating the rate up to a thickness of 0.5 ML, we should solve the resulting equation for the time $\tau_i$ required to deposit half a monolayer. Unfortunately, the latter step is only possible for $n=1$, i.e. the case we are least interested in. Nevertheless, the analysis was pursued for this case, since it was shown in the previous section that also the fits for first order adsorption are not distinctly off and, most importantly, the information of a possible temperature dependence of $\alpha_{\text{dis}}$ is not affected by the chosen adsorption order. It follows for $n=1$:

$$\tau_i = \frac{W(\alpha_{\text{dis}} \phi_{\text{dis}}/4v - 3 \alpha_{\text{dis}} \phi_{\text{dis}}^2/16v \alpha_{\text{dis}} \phi_{\text{dis}}^2 - 3 \alpha_{\text{dis}} \phi_{\text{dis}} / 16v + 1/2)}{4v + \alpha_{\text{dis}} \phi_{\text{dis}} - 3 \alpha_{\text{dis}} \phi_{\text{dis}}^2/16v \alpha_{\text{dis}} \phi_{\text{dis}}^2}$$  \hspace{1cm} (5.9),

$W$ being Lambert's $W$-function [Corel93]. In section 5.3.3, the experimental findings for $\tau_i$ are fitted to this formula, using $\alpha_{\text{dis}}$ and $v$ as parameters.

5.3.2 Diffraction Artefacts

As was already mentioned in chapter 4.1.1, RHEED diffraction conditions have a major impact on the observed oscillation features. Particularly the first intensity oscillation may be affected by variations in diffraction parameters [Joyce88]. For example, depending on diffraction conditions already the assignment that the first minimum
corresponds to 0.5 ML may be incorrect. In order to establish the magnitude of the possible error, experiments were carried out to check for diffraction effects on the initial phase of the intensity oscillations. The angle of incidence was varied between 0.3 and 0.8°. No change in initial decay time nor in the overall shape of the oscillations was observed in the [100] azimuth (see also fig. 4.4a). Furthermore, if the findings of the GSBME experiments were due to diffraction artefacts, SSMBE growth should give the same results. For this reason, experiments were performed in the SSMBE chamber, where the same wafers and similar diffraction conditions (angle of incidence around 0.5° and [100] azimuth) were used. It turns out that the ratio \( \tau_i/\tau_r \) (\( \tau_r \) is the steady state growth period, see fig. 5.10) is indeed sensitive to the angle of incidence. A slight variation, e.g. from 0.4 to 0.5°, changes \( \tau_i/\tau_r \) by as much as 30%. However, as long as the diffraction conditions are not changed, \( \tau_i/\tau_r \) remains constant over the entire range of deposition parameters investigated: growth temperatures from 300 to 500°C and growth rates from 0.07 to 1.0 ML/s. These findings are in marked contrast to those of the GSBME experiments, where \( \tau_i/\tau_r \) varies strongly with incident flux. Thus, in view of the different adsorption kinetics governing the growth in SSMBE and GSBME, it is concluded that the RHEED-related experimental conditions in GSBME did not affect \( \tau_i/\tau_r \) and accordingly, diffraction related phase effects have not been considered in the analysis of the data.

5.3.3 Results and Discussion

Experimental data on the dependence of \( \tau_i \) on the incident disilane flux at various substrate temperatures are given in fig. 5.11. The curves for the different temperatures are very similar. Thus, \( \tau_i \) appears not to be affected by the temperature (a point, which

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**Fig. 5.11:** Dependence of \( \tau_i \) on incident disilane flux and substrate temperature. The connecting lines are a guide to the eye.

- 464°C
- 520°C
- 539°C
- 566°C
- 580°C
has already been used in chapter 5.2), but is strongly dependant on the disilane flux.

In order to deduce the sticking coefficients from the data, the curves were fitted to equation 5.9 with the sticking coefficient and the hydrogen desorption rate as parameters. Fig. 5.12 shows the results of the fitting procedure. $\tau_i$ is plotted against the inverse flux, which has the advantage that the fits to the data appear roughly as straight lines. The legend of the graph gives the calculated values for $\alpha_{\text{dis}}$. Obviously, the model describes the initial non-equilibrium region fairly well. The fitted values for the sticking coefficient vary between 0.04 and 0.08. This range may be partly explained from the experimental error inherent in the data. Particularly for the low fluxes, the exact location of the first minimum is difficult to establish, because of the small slope around the minimum of the RHEED intensity trace. Another systematic error results from the use of the first order adsorption model, whereas those for second or fourth order are certainly more appropriate.

Interestingly, it appears from the analysis that the hydrogen desorption rate $\nu$ hardly affects $\tau_i$. This is quite surprising, since we know from the analysis for the steady state growth (section 5.1) that $\nu$ varies by more than a factor of 10 over the temperature range investigated.

As stated above, a clear dependence of $\alpha_{\text{dis}}$ on substrate temperature could not be found. Thus, either the adsorption of disilane on Si(001) is a non-activated process, or the activation energy is small and not discernible within the experimental error. Our results are therefore compatible with findings from other studies which use only a weak temperature dependence of the sticking coefficient [Gates92, Mok92a]. The value of $\alpha_{\text{dis}}$ implies that, within the investigated temperature range, about 10% of the in-

---

**Fig. 5.12:** The measured values of $\tau_i$ together with their fits versus the inverse of the disilane flux. The legend gives the sticking coefficients deduced from the fit.
coming disilane chemisorbs on the Si (001) surface as long as dangling bonds are available.

5.4 Conclusions

Our analysis shows that the steady state growth process in GSBME on a Si surface can be understood in terms of Langmuir-Hinshelwood adsorption kinetics for the disilane molecules on a surface partly covered with hydrogen. At higher fluxes and lower substrate temperatures the increase of the growth rate with increasing temperature is activated by about 2 eV, which is very similar to the activation energy for hydrogen desorption. This leads to the conclusion that growth is hydrogen desorption limited for these growth parameters. At low fluxes and/or high growth temperatures, the growth rate is basically transport (flux) limited.

For the modeling of steady state growth, it was assumed that the reactive sticking coefficient for disilane on Si is temperature independent, and has a value of about 0.1. This assumption could be verified with the so-called $\tau_1$ approach, which considers the adsorption of disilane on a hydrogen-free surface in a non-equilibrium situation.

In the next chapter we will show that this picture of the homoepitaxial deposition of Si from disilane is drastically modified by the addition of Ge from germane for the heteroepitaxial growth of SiGe alloys.
Chapter 6

Heteroepitaxial Growth of Si/SiGe in GSMBE

As discussed in chapter 1, the introduction of Ge into the Si technology permits the fabrication of devices and circuits with distinctly improved characteristics. However, the growth of these $\text{Si}_{1-x}\text{Ge}_x$ structures is complicated by some effects brought about by the presence of Ge. The larger lattice constant of $\text{Si}_{1-x}\text{Ge}_x$ as compared to that of Si, the associated strain energy and the smaller surface free energy of Ge considerably affects the epitaxial growth of these layers on Si substrates.

This chapter is concerned with the heteroepitaxial deposition of $\text{Si}_{1-x}\text{Ge}_x$ layers in GSMBE. We discuss the roughening of strained SiGe layers caused by the Stransky-Krastanov growth mode, the segregation of Ge at the growing surface, the possibility of reducing the segregation by hydrogen at the surface and the enhancement of the growth rate by the addition of Ge.

However, we first show how to arrive at a certain Ge content in the SiGe alloy by varying the flow ratio of disilane and germane for cold and warm shrouds. The GSMBE results are compared to those for CVD systems using dichlorosilane (DCS) and silane; the role of the reactivities of the different source materials is discussed.

6.1 Calibration of the Ge Mole Fraction

In principle, various analytical techniques can be used to determine the Ge content in SiGe layers, such as high resolution X-ray diffraction, photoluminescence (PL) and Rutherford back scattering (RBS). The latter two methods have been used extensively throughout this study. A typical calibration structure for use in PL-measurements contains an undoped, strained SiGe layer with a thickness of about 10 nm, sandwiched between two undoped Si layers. The SiGe layer should not be thinner than 10 nm. Otherwise, the quantum confinement in the narrow well would shift the recombination energies to higher levels due to subband formation, which would suggest less Ge in the well than is actually present. The energy value of the no-phonon SiGe peak is used in combination with data from the literature [Robb92] to determine the Ge content of the well. Fig. 6.1 depicts the PL-spectrum obtained from a sample with a $\text{Si}_{0.9}\text{Ge}_{0.1}$ well. Similar structures, albeit with thicker SiGe layers ($\geq 50$ nm) were used for the RBS analysis.

Fig. 6.2 gives the calibration results for both the LN$_2$- and the water cooled system in
Fig. 6.1: Low-temperature photoluminescence spectrum of a Si_{0.9}Ge_{0.1} layer grown by GSMBE. The arrow denotes the position of the no-phonon assisted, excitonic recombination (X_{SiGe}^{NP}) used for the calibration. The peak labeled X_{Si}^{TO} is the substrate related, momentum-conserving transverse optical (TO) phonon replica for recombination of free excitons. Similarly, X_{SiGe}^{TO} denotes the TO phonon replica of the no-phonon peak of the alloy.

terms of the Ge mole fraction in the solid obtained for different values of the relative Ge content in the flux, \(x_{\text{flow}}\):

\[
x_{\text{flow}} = \frac{\phi_{\text{ge}}}{(2\phi_{\text{dis}} + \phi_{\text{ge}})}
\]

with \(\phi_{\text{ge}}\) and \(\phi_{\text{dis}}\) being the germane and disilane flux, respectively. The factor of 2 in front of the disilane flux accounts for the fact that per disilane molecule 2 Si atoms are contributed.

The Ge concentration \(x\) in the solid is determined by the ratio of the growth rates of the two species:

\[
x_{\text{Ge}} = \frac{x_{\text{Si}} r_{\text{Ge}}}{x_{\text{Si}} r_{\text{Si}}} = \frac{\alpha_{\text{Ge}} \phi_{\text{ge}} (1 - \theta)^n}{2 \alpha_{\text{dis}} \phi_{\text{dis}} (1 - \theta)^4 + \alpha_{\text{ge}} \phi_{\text{ge}} (1 - \theta)^n}
\]

Unfortunately, the adsorption order \(n\) for germane in eq. 6.2 is unknown. Choosing that of a somewhat similar species, silane, does not help much, since for silane different values for \(n\) (1, 2 and 4) have been reported [Comf89, Gates91b, Hiro91]. Taking \(n=4\), eq. 6.2 simplifies to:

\[
x_{\text{Ge}} = \frac{x_{\text{flow}}}{K(1 - x_{\text{flow}}) + x_{\text{flow}}}
\]
Fig. 6.2: Calibration of $x_{Ge}$ in the solid against the Ge to total flow ratio in the flux. The solid lines are fits to the data points (see text).

with $K = \alpha_{dis}/\alpha_{ge}$. The data for growth in the warm and in the cold system in fig. 6.2 were fitted to equation 6.3 (solid lines in fig. 6.2) and yield values for $K$ of $4.6 \pm 0.1$ and $0.89 \pm 0.03$, respectively. In the literature, the relation between $x$ and the flux composition is often given by:

$$\frac{x_{Ge}}{1-x_{Ge}} = m \frac{\phi_{ge}}{2\phi_{dis}}$$  (6.4),

which is equivalent to our description, when putting $m = 1/K$. Reported values for $K$ for LN$_2$ cooled growth systems lie around 1 [Yamad91, Li92], those for warm systems approach 6 [Yasu93]. Generally speaking, the small value of $K$ for the cold system is due to the rather efficient freeze-out of disilane on the cryo shrouds compared to the less effective removal of germane: the vapor pressure of germane is 2 orders of magnitude larger than that of disilane at a given temperature [crc63]. Hence, the effective Ge flux is considerably higher than that calculated via the geometric flux distribution (section 2.2) and is determined by the partial pressure of this species in the growth chamber. This view is supported by the fact that growth runs in our system without cryo-pump led to significantly higher Ge concentrations in the layers than with cryo-pump. The cryo-pump was generally used in our studies using the cold system. With cryo-pump, the pumping speed for germane is higher than with turbo-pump and cooled
shrouds alone; this reduces the partial pressure of germane in the system. Also, in reference [Li92], the authors claim to be able to change the factor K by varying the shroud temperature: the lower the temperature of the shrouds, the higher the pumping speed for disilane and the higher the Ge concentration in the layer. However, adjusting the temperature of the cryo-shrouds by tuning the liquid nitrogen flow is not a reproducible process and should therefore be abandoned. The factors K given for cold systems strongly depend on the pumping facilities of the respective growth system and can not be related to adsorption characteristics of the gases without knowing the exact flux values. Nevertheless, from fig. 6.2 it is clear that within experimental error, the adsorption of disilane and germane does not depend on temperature: the Ge content stays the same for the same flux ratio. The same result was found for growth in the warm system, although this finding can only be substantiated over the small temperature range of 40° around 600°C. This view is supported by similar reports in the literature for GSBME [Yasu93] and also LPCVD using silane as silicon precursor shows the same behaviour [Raca90]. In contrast to this finding, CVD systems employing DCS as Si precursor show a pronounced temperature dependence of the Ge incorporation for the same DCS and germane gas flows [Boer91]. This makes the control of the SiGe alloy composition and thickness more difficult, since it is essential that the SiGe alloy is grown at low temperatures in order to maintain steep composition profiles and to retain incorporated strain. At these temperatures, the thermal activation of the homogeneous decomposition of DCS plays a strong role, which leads to the temperature dependence of the Ge content in the alloy. Hence, the use of hydride based silicon precursors at the low temperatures necessary for the SiGe growth is clearly advantageous in terms of achievable growth rate and compositional control.

The reliable data for the flux values in our warm GSBME system permit the calculation of the reactive sticking coefficient of germane, $\alpha_{\text{ge}}$. It amounts to 1/4.6 times that of disilane, which yields a value of 0.02 in our case. This value is similar to the one reported by [Yasu93]: 0.017, and is comparable to those which can be inferred from results from LPCVD using silane and germane. In the latter case, the value of K equals 0.3, which means that $\alpha_{\text{ge}}$ is about 3 times as large as the reactive sticking coefficient for silane, $\alpha_{\text{si}}$. The latter is on the order of 3·10^{-3} [Greve93 and references therein], which yields an $\alpha_{\text{ge}}$ of 0.01. Hence, like the adsorption of disilane (see sec. 5.3), the adsorption of germane is not an activated process, at least within the temperature range investigated here.

6.2 Stransky-Krastanov Roughening of SiGe Layers in GSBME

Device applications usually require smooth, 2-dimensional (2D) layers. However,
during the growth on Si(001), SiGe tends to grow in a 3 dimensional (3D) mode [Koide91]. Usually, in the absence of any strain in the layer, the growth mode is determined by the free energies for the substrate/layer, layer/vacuum and substrate/vacuum interfaces. Depending on these interfacial energies, the layer either wets the substrate (Frank-van der Merve growth mode (FvdM)) or it does not (Vollmer-Weber growth mode). Considering only surface free energies, the growth of Ge on Si is predicted to be FvdM due to the lower surface free energy of Ge compared to that of Si. However, the accumulation of strain energy in the pseudomorphic SiGe layers is expected to produce 3D growth (islanding) after reaching some layer thickness (Stransky-Krastanov growth mode (SK)). The actual onset of roughening (the 2D-3D transition) is governed by surface kinetics and is as such strongly dependent on substrate temperature, Ge concentration, growth rate, magnitude of the incident fluxes and thickness of the SiGe layer. Furthermore, the roughening transition can be strongly influenced by surfactants, which modify the balance of the interfacial free energies [Copel89, Osto93]. It should be noted that strain relaxation via Stransky-Krastanov growth competes with the relaxation induced by the formation of misfit dislocations. If SK growth can be suppressed, dislocations will eventually be formed and will relieve the strain. Hence, to determine the process window for the growth of smooth (2D), strained SiGe layers one needs to bear in mind the action of both strain relaxation mechanisms.

The experiments on surface roughening were all carried out in the LN2-cooled GSBME system to permit the use of RHEED for in-situ surface analysis. In this particular case [Storm95], four RHEED patterns could be distinguished and related to the final surface roughness by ex-situ SEM investigations: a) the (2x1)+(1x2) reconstructed, flat 2D Si(001) surface; b) (8x2)+(2x8) reconstructed, Ge containing, flat (2D) surfaces; c) the (8x2)+(2x8) reconstructed, Ge containing, rough (3D) surfaces with [118] facets and d) 3D surfaces with both [113] and [118] facets [Oshi90]. The SiGe layers were grown at various temperatures for two hours on Si buffer layers at a rate of about 1 nm/min.

A chart of the surface structure as a function of Ge concentration and temperature is shown in fig. 6.3. Clearly, for fixed Ge concentrations a transition from 2D to 3D growth occurs for increasing temperatures. Also, at a constant substrate temperature, increasing Ge concentrations yield a smooth-to-rough growth mode transition. If one compares the GSBME results with those from SSMBE [Bean84] (dashed curve in fig. 6.3), it is clear that the roughening transition in GSBME occurs much earlier, i.e. at lower temperatures and/or germanium concentrations. We assume that this difference is mainly caused by the large variation in growth rates: 1 nm/min in GSBME versus 30 nm/min in SSMBE. Adatom surface diffusion is impeded at high growth rates; hence also roughening, i.e. facet formation, which requires material transport over the surface is suppressed. Another reason for the different 2D/3D transition regions could be
the presence of hydrogen at the surface in the case of GSMBE: hydrogen reduces the surface free energy of the growing film, which makes islanding (increase in surface area) more 'affordable'. Thus, surface hydrogen favours roughening at an earlier stage when there is less accumulated strain in the layers. On the other hand, it also reduces adatom diffusivity (see section 4.3.2) and in this way counteracts the increased driving force for islanding.

It should be noted that the 'roughening' is not random but quite orderly. This is implicit in the observation of faceted surfaces which form during growth. In fact, a high degree of ordering can be achieved in these 'rough', islanded layers. The SEM photographs of fig. 6.4 show two examples of SiGe layers grown well above the 2D-3D transition. In fig. 6.4a the layer was grown at 750°C with nominally 11% Ge; the layer in figure 6.4b was grown at 725°C and 48% Ge content. The sausage-shaped structures in fig. 6.4a are aligned along <100> directions in the surface and are bounded by (111) and (113) facets. The same surfaces are found in fig. 6.4b, which was verified by cross-sectional TEM inspection (fig. 6.5). Although the Ge content in the dots is as high as 48% (extrapolated calibration), and the dots are as high as 40 nm, only one dislocation
Fig. 6.4: Scanning electron micrographs of two SiGe layers which were grown at:

a) 750°C with 11% Ge content and

b) at 725°C with 48% Ge content. The images measure 10.9 and 4.8 μm across, respectively. Both pictures also show a small part of the oxide mask for SAE.

Fig. 6.5: Cross-sectional transmission electron micrograph of the sample from fig. 6.4b. The islands are bounded by the same [111] and [113] facets as larger structures, which are grown selectively on oxide-patterned wafers (chapter 7). The island measures 0.19 μm in diameter and is 40 nm high. The arrow marks a dislocation line.
line is visible (arrow in fig. 6.5). Other, comparable dots did not show dislocations at all. This Ge concentration in a 2D layer would lead to the formation of misfit dislocations already after some 10 nm layer thickness, particularly at the high growth temperature. Hence, the islanding indeed efficiently relaxes the strain in the dots, although some strain still remains, as can be deduced from the strain-induced interference fringes in the substrate beneath the dots.

It will be clear that this islanding tendency of the SiGe system can be utilised for the manufacture of quantum dot based devices [Apetz95]. However, more research is needed to predict the number density and sizes of the islands as a function of the growth parameters and Ge content [Cull94].

6.3 Growth Rate Enhancement and Segregation of Ge

It is known from the literature that during growth of Si on SiGe layers, part of the Ge segregates to the surface of the Si layer being deposited. This effect reduces the achievable interface sharpness at these so called normal interfaces [Zalm89, Naka91]. We studied this effect for the GSMBE growth process with the help of RHEED intensity oscillations. It will be shown that the smear out can be monitored by the variation of the growth rate, as manifested by the change in the period of the intensity oscillations. SIMS and ARXPS were used as additional analytical techniques. First, Ge was deposited on the Si surface; this was followed by the growth of Si from Si₂H₆. The Ge films were deposited either in the SSMBE chamber or by GSMBE the day before the Si regrowth. Between these two growth steps, in GSMBE the cryoshrouds were warmed up over night so that the adsorbed germane could be pumped out and none remained during the Si regrowth. This was done to rule out the smear out of the Ge profile by the germane memory effect. The deposition of the Ge film was also monitored by RHEED oscillations whenever possible (i.e. for substrate temperatures ≤ 430°C). Generally, the (8x2) reconstruction pattern featuring 1/8-order streaks was observed, indicating smooth 2D growth and a Ge thickness of about one monolayer [Koid91]. For slightly thicker layers (in excess of 2 to 3 monolayers Ge), <811> streaks were also found, which indicates roughening of the growing surface by (811) faceted islands [Koid91] (see previous section). However, these streaks quickly vanished during the deposition of Si on the Ge-layers.

As was pointed out in chapter 3, in GSMBE the growth process of Si from Si₂H₆ is assumed to start with the adsorption of the molecule at dangling bonds on the surface. Immediate dissociation of the hydride molecule into two silyl radicals and subsequent split-off of the hydrogen atoms provide the Si atoms for the actual film growth. Four out of the six hydrogen atoms are also bonded to the Si surface and, unless thermally
desorbed, saturate dangling bonds and block the surface against further disilane adsorption.

The situation is modified when the Si is grown on top of a Ge layer: Figure 6.6 depicts a typical RHEED intensity oscillation trace for the growth of the silicon top layer. One observes a distinctly higher growth rate of silicon for the first few monolayers and a gradual decrease to the homoepitaxial value. From this plot, two conclusions are evident: The presence of Ge at the growing surface leads to a considerable enhancement of the silicon growth from disilane. The rate enhancement is not confined to the first layer only: the germanium continues to segregate towards the growth front, sustaining the rate enhancement until the Ge is completely incorporated into the growing layer. These observations will be dealt with in detail in the next sections.

6.3.1 Rate Enhancement and the Activation Energy for Hydrogen Desorption from Ge(001)

The increase of the growth rate in the presence of Ge is well known in the CVD of SiGe, where it can amount to a factor of 25 for silicon deposited from silane [Greve93 and references therein]. It could be shown, that hydrogen desorption (in this case the study was actually performed with deuterium) is much easier from Ge than it is from Si in a temperature programmed desorption (TPD) experiment [Ning92]. Furthermore, the activation energy for hydrogen desorption from Ge (001) and (111) surfaces is only 1.5 eV [Surn84] compared to 2.0 eV for Si (001) (section 5.2.4). Most likely the low activation energy for the hydrogen desorption from Ge and the easier desorption in TPD experiments also lead to an increased absolute desorption rate. Hence, at the same flux and (low) growth temperature the hydrogen coverage of a Ge containing surface is

![Graph](image)

*Fig. 6.6: RHEED intensity oscillation trace of silicon deposited on 2 ML of Ge at 500°C.*
lower than that of pure Si, which leads to larger growth rates on Ge through the availability of more dangling bonds. It appears that the same rate-enhancing mechanism applies to GSMBE growth of Si from disilane, since also in this case at low temperatures the desorption of surface hydrogen has been identified as the rate limiting step (section 5.2).

Si regrowth experiments on Ge in GSMBE were carried out at different temperatures and fluxes and were monitored by RHEED intensity oscillations (using LN$_2$ cooled shrouds). The observed growth rate for a given oscillation is plotted in fig. 6.7 against the number of the oscillation for temperatures of 500 and 540°C. The incident Si flux was varied between 0.6 and 8.3 ML/s. Clearly, the rate enhancing effect of Ge at the surface depends on substrate temperature and incident disilane flux. The lower the in-

![Graph showing growth rate vs. oscillation period for different fluxes at 500°C and 540°C.]

**Fig. 6.7:** Growth rate of silicon from disilane on Ge(001) versus number of oscillation period at two different temperatures (LN$_2$ cooled shrouds).
coming flux, and the higher the substrate temperature, the smaller the enhancement of the rate by the Ge adatoms will be since the growth rate then is supply limited. The enhancement is most pronounced for the higher fluxes at lower temperatures. Figure 6.8, which shows the rate enhancement for a constant Si flux of 1.3 ML/s at different growth temperatures, illustrates the above statement. Above 550°C, the temperature for which the growth at this flux is no longer desorption limited, the Ge at the surface indeed does not have an enhancing effect any more. It should be noted that the temperature of 550°C as a limit for the rate enhancing effect is only valid for this particular case at the given disilane flux. In the warm growth chamber, the disilane fluxes are much higher (of the order of 30 ML/s) so that the rate enhancement extends to much higher temperatures. For example, a growth rate enhancement by a factor of 20 was found at 580°C for a Si₀.₇Ge₀.₃ layer grown with a flux of 22 and 41 ML/s for Si and Ge, respectively.

Returning once again to fig. 6.7 and the flux dependence of the periods of the first oscillations, it may be noticed that for silicon fluxes of 6.4 ML/s and higher the rate does not increase significantly any more: the growth rate is limited by the hydrogen desorption from the pure Ge surface at these two temperatures. This observation allows the determination of the activation energy for hydrogen desorption from Ge: We find an activation energy of 1.2 eV, which is not too different from the reported value of 1.5 eV [Surn84]. The difference between the two values is most likely caused by the assumption of strictly desorption limited growth at 540°C, which is probably not quite correct.

6.3.2 Surface Segregation of Germanium

The second conclusion drawn from fig. 6.6 is related to the segregation of Ge to the growing surface: The rate enhancement does not stop upon completion of the first

Fig. 6.8: Growth rate enhancement (= heteroepitaxial rate/homoepitaxial rate at a given temperature) of silicon from disilane on Ge(001) of the first oscillation period versus substrate temperature. (LN₂ cooled shrouds).

\[ \phi_{\text{dis}} = 1.3 \text{ ML/s} \]
monolayer grown on the Ge surface, which would be expected, if the Ge were completely covered up at this point. Instead, judging from the exponential decay of the growth rate at different temperatures at constant flux (fig. 6.9), a roughly constant fraction of the Ge obviously floats at the growing surface. The segregating Ge will sustain the rate enhancement for several monolayers until the concentration of Ge at the surface is too small for a rate enhancement observable by RHEED intensity oscillations. It should be noted that the rate enhancement at a given temperature and disilane flux does not depend on the thickness of the Ge layer. This means that only the topmost Ge monolayer takes part in the segregation process, which was also found in similar SSMBE experiments [Fuji91]. The data in fig. 6.9 clearly show that the number of deposited Si monolayers necessary to reach the homoepitaxial growth rate is significantly smaller at lower temperatures. Hence, the segregation is suppressed at lower temperatures. It is also reduced at higher fluxes, as demonstrated in fig. 6.7, in which the higher fluxes lead to steeper slopes of the curves.

In order to assess the correlation between the relative rate enhancement and the Ge distribution, ARXPS experiments were performed ex situ after completion of growth on the structures deposited at 500 and 540°C in the experiments of fig. 6.9. The results are depicted in fig. 6.10, which shows the Ge(3d)/Si(2p) and the Ge(2p3)/Si(2p) photoelectron intensity ratios, corrected for the analyser transmission. The native oxide layer had been removed by sputtering prior to the ARXPS measurements, so that the Ge concentration at the very surface could not be assessed. In our case, the Ge(3d) electrons have a calculated inelastic mean free path $\lambda$ of about 3 nm, whereas that for the Ge(2p3) electrons amounts to only 1 nm [Tanu91]. In ARXPS, the sampling depth is roughly given by $\lambda \sin \Theta$, in which $\Theta$ is the take-off angle (angle between surface plane

![Fig. 6.9: Growth rate of silicon from disilane on Ge(001) versus number of oscillation period (LN$_2$ cooled shrouds).](image-url)
and detector) of the photoelectrons. Therefore, the signal from the Ge(2p3) electrons at small take-off angles, found on the left hand side of fig. 6.10, is dominated by the surface, whereas the Ge(3d) signal at the right hand side is dominated by the deeper layers. It should be noted that the signal is in fact a Laplace-transformation of the depth distribution of Ge. In principle, if a qualitative model for the Ge distribution exists, the depth distribution can be determined quantitatively from such ARXPS measurements [Alkem93]. However, even without a quantitative analysis of the data of fig. 6.10, the decrease of the Ge content towards the surface for the sample grown at the lower temperature (500°C) is clear. For the sample grown at 540°C the Ge signal and thus also the concentration is roughly constant over the entire Si toplayer. This is in agreement with the small slope of the corresponding RHEED oscillation curve in fig. 6.9. Hence, the Ge concentration at the surface is directly related to the observed growth rate enhancement. Nevertheless, we observe that the subsurface Ge signal (Ge (2p3) electrons, grazing incidence) does not vanish in either case. This suggests that at the very surface the Ge concentration during growth was not zero. Yet, the growth rate on both samples had reached the homoepitaxial value (fig. 6.9). Apparently, the catalytic effect of Ge on the rate requires a minimum amount of this element at the surface, but it is not possible to give an exact value due to the qualitative nature of the ARXPS results.

In SSMBE, surface segregation of Ge is well known [Eberl87,Zalm89,Fuka91] and has been studied extensively. The segregation may be described using a two-state exchange model [Harris84], schematically depicted in fig. 6.11. It only considers the segregation of the subsurface layer and neglects interdiffusion of Ge and Si via other routes as well as the effects of surface steps or lattice strain [Fuka91]. In this model, subsurface Ge atoms may jump to the surface state surmounting the kinetic barrier $E_a$.
Fig. 6.11: Schematic representation of the two-state-exchange model, describing the surface segregation of Ge on a Si substrate. $E_a$ denotes the kinetic barrier, $E_b$ is the heat of segregation and $E_d$ is the energy required for Ge desorption from the surface.

(1.63±0.1eV [Fuka91]) and return from the surface into the subsurface state by jumping over the barrier given by the sum of $E_a$ and the heat of segregation, $E_b$ (0.28±0.1eV [Fuka91]). Desorption of Ge from the surface can be neglected, since the desorption energy $E_d$ for Ge from Si is much larger than $E_a + E_b$ in the epitaxial growth temperature range [Naka91].

The segregation in SSMBE is considerably more pronounced than in GSMBE. To achieve the same interface sharpness, GSMBE growth has to take place at very low temperatures. The sharper interfaces in GSMBE, which were also found in SiGe CVD growth [Boer91] and other studies [Gates92, Grütz93] may be attributed to the surfactant action of hydrogen. It is interesting to note that hydrogen as a surfactant is presently even used in SSMBE to improve interface sharpness [Ohta94]. So far, low temperature growth [Eberl87], high growth rates and also other surfactants such as As and Sb were used [Zalm89, Copel89] in SSMBE to improve the interfaces. The latter surfactants, however, also dope the layers, which can not always be tolerated in view of device applications.

An intuitive explanation of the surfactant action of hydrogen in GSMBE or CVD is the blocking of surface sites by the hydrogen atoms, so that Ge can not move up from the sub-surface layer. From the point of view of the two-state-exchange model, it could either be an increase of the kinetic barrier $E_a$, or a decrease of the thermodynamic driving force, the heat of segregation $E_b$. It was found that $E_b$ is reduced to about 0.13eV at 520°C [Ohti93]. Still, this value strongly depends on the applied flux, which together with the substrate temperature ultimately determines the hydrogen coverage. Most likely, the value for the heat of segregation is considerably lower in atmospheric pressure CVD systems, where hydrogen is used as the carrier gas during epitaxy and interacts with the growing surface. Here, extremely sharp transitions have been achieved [Boer91, Grütz93]. In GSMBE, the hydrogen is supplied by the dissociation of disilane only. For this reason, SiGe/Si interfaces should be grown at large incident disilane fluxes to achieve maximum hydrogen coverage. In this case, the surfactant action of
hydrogen is supported by the higher growth rate of the growing overlayer: The Ge is buried by the rapidly growing layer and does not have occasion to move up to the surface layer.

6.4 Conclusions

Our study shows that up to a concentration in the solid of at least 30% the mole fraction of Ge incorporated in the growing SiGe film is proportional to that in the flux. Like that for disilane, the sticking coefficient of germane appears to be independent of the growth temperature. Both cold and warm system environments yield the same results in this respect.

Roughening of SiGe layers grown by GSBME occurs earlier (already for thinner layers, and for less Ge) than in SSMBE.

Similar to CVD, in GSBME Ge at the surface raises the growth rate, provided the incident fluxes are larger than the hydrogen desorption rate from the growing surface. The latter point is important for understanding the different values reported for the growth rate enhancement in CVD. Hydrogen in GSBME and CVD also acts as surfactant in the reduction of surface segregation of Ge. The more hydrogen present, the higher the growth rate of the overlayer and the sharper the heterointerface obtained in the process.
Chapter 7

Selective Area Epitaxy (SAE)

Localised epitaxial growth on partially masked semiconductor surfaces has great potential for device-insulation in integrated circuits [Ishi86]. It avoids post-growth mesa etching or localised oxidation steps. With SAE, the insulating layer is applied first and acts as a mask during the subsequent growth of the device structure. Ideally, no material at all should deposit on the mask. In the III/V technology, metal organic MBE (MOMBE), a technique, which is very similar in nature to GSMBE, was found to offer optimal conditions for SAE [Hein86]. Using CVD-SiO₂ as a masking material, the deposition reaction in the covered areas may be completely suppressed.

Unfortunately, in the case of GSMBE of Si and SiGe, the masking action only holds for a limited deposition time so that selectivity is lost after the so-called incubation or nucleation time (τᵣ). Furthermore, facets form at the edges of the grown layers, which in some uses is undesirable for further processing. A typical example of these effects is shown in fig. 7.1: A faceted crystal results from selective growth out of a small seeding hole in the masking oxide. The picture demonstrates important aspects of SAE: The localised epitaxial deposition of material with epitaxial lateral overgrowth on the mask (the seeding hole is smaller than the size of the facetted crystal suggests), the development of crystal facets other than (001), and last but not least the loss of selectivity as evident from the already coalescing polycrystalline grains on the oxide mask.

In the following, the current understanding of SAE and the factors leading to the breakdown of SAE are discussed. Subsequently, results obtained for selective area

Fig. 7.1: SEM micrograph showing a faceted Si crystal that has been grown selectively from a hole of about 2 μm diameter. The crystal extends laterally over the oxide mask and is surrounded by polycrystalline grains on the oxide, which already start to coalesce. About 65% of the oxide surface is covered with polycrystalline grains. In this case, {113} and {101} facets have been formed. The image measures 4 μm across [Heeu94].
growth of Si and SiGe by means of GSMBE and the development of facets are presented.

7.1 Fundamentals of Selective Area Epitaxy

To date, the underlying mechanisms that determine the nucleation time $\tau_n$ are not well understood. Some general trends have been noted, but a thorough theory has not been developed. The conceptual difficulties responsible for this lack of understanding will be outlined below.

7.1.1 Nucleation on the Mask

At a certain time ($\tau_n$) after starting the deposition process, selective area growth breaks down due to the formation of stable nuclei on the mask. This means that the adatoms on the mask coalesce into clusters of a few atoms, which continue to grow and eventually form a closed polycrystalline layer. The nuclei must be stable to increase in size, which means that the number of atoms per nucleus is larger than a critical amount ($n_c$). From a technological point of view, $\tau_n$ should be large enough to avoid nucleation on the mask before the desired layer thickness in the seed windows is reached. In an atomistic model, the parameters that govern the nucleation process are the adatom density, the adatom surface lifetime, the diffusivity of the adatoms, and the number of atoms necessary to form a stable nucleus. The fundamental difficulty lies in the determination of these parameters. In fact, none of these are known nor can they be inferred from the available data. This problem may be circumvented by choosing a macroscopic criterion, namely the supersaturation, $\sigma$, of the system, to predict nucleation. For a species $j$ (atoms or molecules) at a given surface the supersaturation is defined as:

$$\sigma_j = \ln(\phi_{ji}/\phi_{j0})$$ (7.1),

with $\phi_{ji}$ being the incident flux and $\phi_{j0}$ the desorbing flux (in the steady state) of the reactive species $j$. Depending on the relative magnitudes of the fluxes and referencing the supersaturation to the situation at the window one has:

$\sigma = 0$: no growth,
$\sigma < \sigma_{crit}$: selective growth (no stable nuclei are formed on the mask),
$\sigma > \sigma_{crit}$: loss of selectivity (stable nuclei are formed on the mask).

Even though the definition of supersaturation and its application are rather simple
and straightforward, it is difficult to find values for this quantity in the literature. Some data is available for the SiCl$_2$H$_2$/Cl$_2$/H$_2$ system from which a limit of 6 may be derived for $\sigma_{\text{crit}}$ at T=600°C, or of 2.2 for $\sigma_{\text{crit}}$ at 850°C [Vesc94]. Supersaturation exceeding these values entails breakdown of selectivity. It should be noted that this data is based on calculations assuming thermodynamic equilibrium and that only the situation above the Si seed windows is considered; thus, they can only give an indication for the actual situation in a CVD reactor [Comf89]. The question arises, whether the situation above the mask that leads to nucleation on the mask can be determined from data calculated for the gas phase above crystalline Si. As a matter of fact, the so called loading effect directly manifests the different conditions above the mask and the seed windows. It basically denotes a variation in composition or thickness of the grown layers in the seed windows depending on the mask- to window area ratio. It is ascribed to a variation in gas phase composition above the mask relative to the crystal surface and/or to abundant material on the mask which diffuses towards the window to be incorporated at the outer edges of the seed window [Vesc94, Sedg93]. Depending on the width of the mask around the window, this contribution from the mask may vary. Loading effects have not been observed in GSBME at all. Again, the processes and composition of the gas phase above the mask, which determine the adatom concentration on the mask, are difficult to assess. In this situation, $\sigma$ above the seed windows is used as a qualitative measure for the adatom concentration. However, quantification is only possible with detailed knowledge of the reactive sticking coefficients for the species on the mask, which is not available as yet.

One of the conclusions which can be drawn from the above is that in order to simultaneously achieve large deposition thicknesses and perfect selectivity, the adatom density on the mask must be kept as low as possible. This is the opposite of what should hold in the seed windows to achieve high growth rates and clearly presents a dilemma. Apart from the obvious parameters like substrate temperature and flux of source molecules there is ample evidence for the effect of several additional factors on the selectivity, such as the nature of the masking material, the cleanliness of the process and the substrate, and most importantly, the types of precursors used and the related chemistry. These parameters all affect $\tau_n$ in one way or another, as will be discussed in the following.

7.1.2 Masking Material and Cleanliness

To avoid nucleation, the masking material should not contain reactive sites for the adsorption and decomposition of precursor molecules. Thus, the surface of the mask
should be chemically inert. Materials which fulfill these requirements and are frequently used in conjunction with Si are SiO₂ and Si₃N₄. Masks made from the latter material were reported to be inferior. On Si₃N₄ the value of τₙ for the growth of Si from disilane was found to be considerably smaller than on SiO₂ [Tats92]. This finding also holds for silicon CVD using silane with or without HCl and dichlorosilane (DCS) [Claas80a,b]. These results indicate a higher reactivity of the nitride in comparison to the oxide masks, regardless of the precursors used.

In the present study, only thermally grown SiO₂ was used as a masking material. At the early stages of the investigation, the masks were not specially cleaned after resist removal. However, for most of the work, an RCA cleaning process [Kern90], slightly modified by the addition of an intermediate HF dip to remove the oxide in the seed windows, was selected. Samples cleaned with fuming HNO₃, used in nominally identical growth runs, showed a lower selectivity (τₙ was 10% smaller) than samples subjected to the standard cleaning process. These results emphasise the importance of proper mask cleaning.

Together with the in situ thermal treatment in the growth chamber (see section 2.6) this extensive cleaning procedure had to be followed, since it is essential to have not only the seed windows as clean as possible, but also to remove all residual impurities from the mask. Impurities will act as nucleation centers for incoming molecules. Direct evidence for the presence of initial adsorption sites stems from the observation that the RHEED electron beam used prior to growth to briefly check the proper removal of the native oxide in the seed windows, leaves a trace on the mask, which can be seen by the naked eye. Inspection of the trace by electron microscopy reveals a considerably smaller density of nuclei than for unirradiated areas (fig. 7.2). It is believed that the RHEED beam removes or at least passivates the initial adsorption sites on the oxide so that the formation of nuclei in this area is suppressed or postponed.

Despite all cleaning efforts, a few nuclei are always observed on the mask. Hence, when comparing different growth parameters and mask materials one must ascertain reproducibly clean starting conditions so that the results (e.g. for τₙ) are not obscured by preferential nucleation at impurities on the mask. This is particularly true for growth processes like GSBME that do not use chlorine-containing species, which can remove the impurities and adatom (see following sections).

One of the ideas pursued to provide ultimately clean oxide masks for selective growth in GSBME was to first etch a few nanometers of the oxide away by a high temperature silicon deposition step in SSMBE (10 nm at 950°C at a rate of 2.4 nm/min) to remove the 'dirty' surface of the oxide via the evaporation of SiO. The wafer was then moved into the GSBME chamber through the UHV transfer system and the Si layer was deposited. Contrary to expectation it was found that the selectivity is completely
lost on the oxide subjected to high temperature growth in SSMBE: a closed and smooth polycrystalline silicon film was obtained on the mask. Apparently, the remaining oxide surface was very reactive. This may be due to unsaturated bonding in the oxide produced during the reduction of the SiO$_2$ in the SSMBE chamber. These sites apparently may act as efficient adsorption and decomposition centres for disilane and for the subsequent formation of polysilicon grains. The polycrystalline films on this oxide are continuous, which is not encountered in the standard selectivity experiments (untreated oxide) for all but the thickest layers. The layers can not be removed by etching in buffered HF. This 'lift-off' process normally etches the underlying SiO$_2$ away and thereby also removes the poly-Si on top. The etching step is usually done to assess the thickness of the epitaxial layers in the seed windows.

In conclusion, the oxide pretreatment in SSMBE does not provide a way to circumvent the mask contamination/reactivity problem. Rather, ex situ cleaning steps such as the RCA procedure are necessary to provide sufficiently clean Si and oxide surfaces, which allow proper epitaxial and selective growth.

7.1.3 Selectivity Enhancing Reactions - SiO$_2$ Reduction

SiO$_2$ masks enable a direct, selectivity promoting mechanism. That is, for substrate
temperatures above approx. 800°C, the SiO₂ is reduced to volatile SiO upon reaction with deposited Si atoms:

\[ \text{Si} + \text{SiO}_2 \rightarrow 2 \text{SiO (g)} \]  \hspace{1cm} (7.2).

Hence, in addition to the removal of the top layer of the oxide, as discussed in section 7.1.2, the oxide reduction reaction (7.2) can also be employed to remove Si nuclei from the oxide surface. In the case of nucleation of Si on the mask at not too high a rate, this reaction effectively etches the SiO₂ and simultaneously removes the nuclei [Yone82]. It is believed that this mechanism also improves τ_n and thus the maximum thickness of the epitaxial films which can be grown in GSMBE at high temperatures without breakdown of the selectivity ([Aket91, Merc89]).

Reaction 7.2 can even be used to obtain selective epitaxial growth in SSMBE: By growing at high temperatures (approx. 900°C) and at low growth rates (approx. 2 nm/min) the reaction is fast enough to prevent the formation of poly-grains on the mask. However, the mask is consumed by the incoming flux and only epitaxial films of limited thickness can be grown. Also, the mask roughens considerably by the etching reaction (fig. 7.3), which explains in part the increased reactivity of the oxide and the resulting deposition from disilane (see previous section).

The ratio of SiO₂ thickness removed to the Si thickness nominally deposited was determined experimentally and amounts to approx. 1.4 ± 0.15. About the same value (1.3) was found by Yonehara and coworkers for the etching of fused quartz by Si, also in SSMBE [Yone82]. However, the theoretical value, based on a density of 2.64 g/cm³ for SiO₂, is 1.9. This discrepancy is as yet not understood. One might guess that the desorption of Si adatoms without reaction at the high growth temperatures causes the observed lower value. Still, this is not the case, since the incoming flux is 4 orders of

**Fig. 7.3:** Electron micrograph depicting the roughened oxide mask together with a Si layer in a window after extended etching in SSMBE. At this particular position on the wafer also Si spheres are visible on the oxide. The Si spheres were formed, since the temperature at this location was apparently not high enough to permit the complete reaction to SiO of all Si arriving at the mask.
magnitude larger than the desorbing flux. Hence, this problem remains unresolved for the time being.

7.1.4 Selectivity Enhancing Reactions - the Chlorine Containing Systems

As mentioned before, the values reported for $\sigma_c$ in silicon CVD are surprisingly large: on the order of 6 at 600°C [Vesc94]. The reason for the fact that the growth is still selective for these values for the supersaturation, lies in the presence of chlorine, which gives rise to an etching reaction:

$$\text{Si} + 2\text{HCl} \rightarrow \text{SiCl}_2(\text{g}) + \text{H}_2(\text{g})$$

(7.3)

This reduces the adatom density on the mask and enlarges the incubation time. The extent to which selectivity can be enhanced depends on the Cl/H ratio in the reactor. The higher the ratio the better the selectivity, but also the lower the growth rate in the seed windows. The chlorine either stems directly from the precursors (chlorosilanes) or is injected separately in the form of HCl or Cl$_2$ when using silane as the Si-precursor.

In GSMBE, addition of Cl$_2$ to Si$_2$H$_6$ is also effective to improve selectivity ($\tau_n$). However, this improvement goes at the expense of the growth rate [Tas92] so that the overall gain in obtainable selectively grown layer thickness is small.

7.1.5 Selectivity Enhancing Reactions - Addition of Germane

During studies of the growth of SiGe from gaseous precursors it was observed that the selectivity improves considerably with the addition of germane as a precursor for Ge. The improvement does not depend on the additional presence of chlorine containing precursors: it works equally well with disilane in GSMBE [Hira90b] and with dichlorosilane [Zhong90] and silane [Raca91] in CVD. For the deposition of Ge by itself, perfect selectivity was obtained [Dumi70, Otz90]. The reaction enhancing selectivity would be the formation of volatile GeO on the SiO$_2$ mask [Zhong90]:

$$\text{Ge} + \text{SiO}_2 \rightarrow \text{GeO}_2 + \text{Si}$$

(7.4),

$$\text{Ge} + \text{GeO}_2 \rightarrow 2 \text{ GeO (g)}$$

(7.5).

According to these authors, this scheme is operative in a temperature range from 500 to 800°C. However, this idea appears quite unlikely, especially at low temperatures. In the first place, reaction (7.4) produces additional silicon on the mask. SiGe growth ex-
Fig. 7.4: Electron micrograph depicting the etching of the oxide mask by Ge species for SAE of a SiGe layer at 775°C. The image measures 1.7 µm across.

Experiments performed in the present study show evidence of a etching reaction above about 700°C: The mask is clearly etched by atoms from clusters (fig. 7.4), a fact, which was not observed for Si growth by itself even at temperatures as high as 825°C. Another problem related to the proposed mechanism is the absence of any reaction step promoting the removal of Si, which is also present on the mask material.

7.1.6 Selectivity Enhancing Reactions - Hydrogen Adsorption on the Mask

An increase in the incubation time with increasing partial pressure of hydrogen for temperatures lower than 900°C in the SiH₄-HCl-H₂ and SiH₄-H₂ systems has been observed for SAE in CVD [Claas80a,Yew89]. The growth experiments were performed at atmospheric and at very low pressure (0.1 Pa). The finding was attributed to a blocking of adsorption sites for silane on the oxide mask by adsorbed hydrogen. Although the interaction of hydrogen with an SiO₂ surface is weak [Shellb77], this mechanism could play a role in CVD processes. However, its importance in GSMBE is negligible in view of the much lower hydrogen background pressure. On the other hand, atomic hydrogen is present on the mask as a dissociation product of adsorbed disilane. Atomic hydrogen may be more reactive than H₂ towards the mask, analogous to its behaviour on Si (001) surfaces. It is known that strong O-H bonds may form on SiO₂ surfaces at moderate temperatures. These bonds may in turn passivate the oxide mask against further adsorption and dissociation of disilane.
7.2 Nucleation on the Oxide Mask in GSMBE

Suppression of nucleation on the mask appears to be a difficult problem in GSMBE of Si and SiGe. The growth of binary III/V semiconductors, like GaAs, in MOMBE, using triethylgallium (TEG) and thermally cracked arsine (AsH₃), offers a clear advantage in this respect: The metal Ga is only released for deposition upon interaction of arsenic with TEG at the GaAs substrate. The sticking coefficient for arsenic on an SiO₂ mask at 600°C is extremely low, so that practically no Ga or GaAs is formed on the mask. In this manner perfect selectivity is achievable [Hein94]. The different nucleation behaviour of Si and SiGe in GSMBE will be the topic of the present chapter.

7.2.1 Detection of Nucleation

The experimental determination of the value of $\tau_n$ turns out to be quite difficult. Ideally, one would like to employ a technique that is capable of detecting the onset of nucleation in situ. Unfortunately, because of the small number density and size of the grains that start to form after $\tau_n$, such an analytical technique does not exist. Ex situ analysis by scanning electron microscopy (SEM) readily permits the determination of size and density of the nuclei, albeit after the deposition. RHEED as in situ surface analysis technique has a detection limit of about 15% of coverage of the oxide by polycrystalline grains. This means that after termination of the deposition upon observation of Debye-Scherrer rings, inspection by SEM reveals the mentioned coverage. About the same sensitivity (15%) can be achieved by optical inspection either by the naked eye or by interference contrast microscopy. Hence, for the investigation of nucleation a fundamental experimental problem exists: How to detect the very onset of nucleation - if possible in situ?

The variety of inspection tools together with different sensitivity and resolution explains to some extent the variation in reported values for the thickness ($t_{sc}$), to which material can be deposited in the oxide windows without loss of selectivity for nominally similar deposition systems. In view of the detection limit of the inspection tools used most often in this study (RHEED, optical microscopy) the transition between selective and non-selective growth is set at 15% of areal coverage ($c_p$) of the mask by polycrystalline grains (fig. 7.5).

Moreover, the polycrystalline grains can be easily removed by a 'lift-off' process. That is, the oxide is etched away (either completely or for a few nanometers only) using hydrofluoric acid, simultaneously removing the silicon grains on top. In most cases, the oxide was removed completely in order to facilitate the thickness measurement of the deposited layer with a profiler. The etching procedure is successful for all but the
thickest non-selectively grown layers. In those cases the poly-layers are continuous and the oxide underneath is not attacked by the acid.

7.2.2 Development of Stable Nuclei on the Mask

From growth on masked substrates in SSMBE, one knows that the growth rate is the same for material deposited on the mask and in the seed windows. This means that the Si adatom lifetime is close to infinity and that desorption is negligible. We assume that roughly the same conditions for adatoms hold in GSMBE. Hence, once an adatom is produced on the mask by dissociation of adsorbed disilane, it will not desorb at temperatures low enough to avoid the oxide reduction reaction (7.2). The dissociation of disilane on the mask and the formation of adatoms thus also entails the formation of nuclei. The loss of selectivity in GSMBE is perceived as follows:

The mask can be considered inert with the exception of a few reactive sites. The exact nature of the reactive sites which are initially present is unknown. Probably, cleaning residues, impurity atoms or irregularities in the oxide network (e.g. dangling bonds) can establish such sites. When deposition begins, adsorption and dissociation of disilane that leads to the production of SiH_{n}, ad-molecules with 0≤n≤3 on the mask can only take place at these reactive sites. It is believed that the ad-molecules can dissociate in much the same way as for the decomposition on a crystalline surface and eventually become Si adatoms. It may be that the intermediate dissociation products desorb more readily from the mask surface than from the Si crystal surface, but no evidence for either assumption was found. Once adatoms are formed, they will also act as adsorption
centres for incoming disilane due to the availability of dangling bonds.

The following step is the diffusion of the adatoms over the mask surface. Assuming that a single atom already forms a critical nucleus [Claas80a], adatoms that encounter another adatom or nucleus on the mask will form a new (2-atom) cluster or will be incorporated into the existing nucleus. From the almost perfectly spherical shape of the polycrystalline grains (fig. 7.6) a large interface energy between Si and SiO₂ can be inferred. Correspondingly, the adsorption energy is small. This again supports the notion that disilane hardly (if at all) reacts with the mask itself, and that the selectivity is lost due to adsorption on particular, reactive sites.

In order to get an impression of the order of magnitude of the reactive sticking coefficient for the adsorption of disilane on the initial reactive sites on the mask, growth runs with low \( c_p \) (\( c_p = 1\% \)) were evaluated. The number density and size distribution of the poly-grains (like those of fig. 7.6) was used to estimate the total number of Si atoms on the mask. This number is then related to the total silicon dose from disilane:

\[
\alpha_{\text{rm}} = \frac{R_{\text{Si}}}{t_{\text{g}}} * \phi_{\text{dis}} \tag{7.6}
\]

with \( \alpha_{\text{rm}} \) the reactive sticking coefficient, \( \phi_{\text{dis}} \) the disilane flux on the oxide mask, \( t_{\text{g}} \) the growth time and \( R_{\text{Si}} \) the total number of deposited Si atoms. At 650°C, the value for \( \alpha_{\text{rm}} \) is approximately \( 4*10^{-3} \). This value should be regarded as an upper limit for the adsorption on the mask, since it also includes contributions from the adsorption of disilane on Si adatoms. The probability for adsorption on nuclei is much higher (see below). \( \alpha_{\text{rm}} \) is about two orders of magnitude smaller than the coefficient for adsorption in the seed window \( \alpha_{\text{dis}} \), which is not too large a difference. The sticking coefficient in

**Fig. 7.6:** SEM micrograph depicting nuclei on the oxide mask for a \( c_p \) of about 40%. Note that apart from the large coalescing grains also small (\( a = 50 \text{ nm} \)) nuclei are present. The image measures 1200 nm across.
turn can be used to determine the number density of initially present reactive adsorption sites. If one assumes very efficient adsorption centres (sticking coefficient on the sites = 1), the reactive sticking coefficient directly gives the ratio between the number of reactive to the total number of surface sites.

With rising coverage, the overall sticking coefficient for mask plus poly-grains increases to about 0.1 for closed polycrystalline films. This is the same value as was determined for the adsorption on monocrystalline Si(001), indicating that the average number of reactive sites is roughly the same for poly- and monocrystalline surfaces.

Once the adsorption on the mask has produced enough adatoms to outnumber the initial adsorption sites, the increase in adatom density is mainly governed by the availability of these adatoms for adsorption. It is expected that, similar to the adsorption on the crystalline Si(001) surface, adatoms with hydrogen still attached are blocked for further adsorption of disilane. Additional growth at these adatoms is determined by the hydrogen desorption rate, completely analogous to the growth on Si (001) as discussed in section 5.2.

7.3 Dependence of Selectivity on Growth Parameters

Using our practical definition for selective growth (c_p ≤ 15%), data for different growth conditions are given in figure 7.7, with respect to the criterion selective/non-selective growth in the cold GSMBE system. These data were obtained from a large number of GSMBE Si and SiGe growth runs on patterned Si substrates. The thickness of the deposited layer per run is plotted against the growth temperature. Since this way of plotting permits the direct determination of the achievable selectively deposited layer thicknesses, it was preferred to a critical reactant volume plot against temperature. The critical volume can only be linked to layer thicknesses via a detailed knowledge of the actual process (precursor, temperature, pressure) and therefore does not allow a straightforward comparison of growth techniques.

The shaded area in the figure roughly indicates the transition between selective and non-selective regions using a c_p of 15%. Generally speaking, for GSMBE t_{sc}, the thickness reached for t_n lies between 300 and 400 nm with the exception of growth temperatures above 750°C, where selectivity can last up to about 600 nm. Samples grown at temperatures below 550°C all exhibited selective growth but very little material was deposited because of the low growth rates. One could therefore argue that the selectivity is simply due to the fact that hardly any material is deposited. On the other hand, selectivity at these low temperatures is also maintained for long growth runs (4 h) and large fluxes (> 14 ML/s). This stands in contrast to the situation at higher temperatures (about 600°C), at which selectivity is already lost for moderate flows (5ML/s) after
about 120 min of deposition. Hence, enhanced selectivity is observed at low and high temperatures, which suggests that two different mechanisms govern the selectivity in the investigated temperature range. The mechanism operative at the low temperature could not be identified. It may be speculated that the adsorption probability on the active sites on the mask decreases stronger with decreasing temperature than the growth rate of Si in the windows. The selectivity improvement in the high temperature region is most likely due to the effectiveness of the oxide reduction reaction (7.2).

Another important process parameter is the applied flux since it gives the amount of material which impinges on the mask: One expects decreased selectivity at high fluxes. Minor flux variations ($\phi_{\text{dis}}$ between 1 and 5 ML/s) at a given temperature did not result in significant changes of $t_{\text{sc}}$. However, switching to the warm growth environment with much higher fluxes ($\phi_{\text{dis}}$ of the order of 30 ML/s) shows a much earlier break-
down of selectivity.

The effect of the addition of germane for the deposition of SiGe, which is known to considerably improve overall selectivity, cannot be readily found back in the graph. Yet, direct comparison among growth runs, which were nominally identical apart from the addition of a small amount of germane, reveal a clear improvement of selectivity. For example, fig. 7.8 shows the surface of the oxide masks on samples used for Si and SiGe deposition at 650°C. Clearly, the selectivity is completely lost in case of the pure Si layer; a continuous, about 300 nm thick polycrystalline layer has formed on the oxide next to an 800nm thick Si layer grown in the window. In contrast, a $c_p$ of only 15% is found for the growth of a 400 nm thick SiGe layer. The total number of adatoms on the mask next to the SiGe layer is considerably smaller than in the case of Si deposition. Hence, it seems as though the Ge adatoms or ad-molecules can readily desorb from the SiO$_2$ surface and that these species are even capable of taking Si adatoms or ad-molecules with them. Although this definitely supports the observation of the selectivity improvement for the growth of SiGe layers, the question remains, whether equations 7.4 and 7.5 correctly describe the reactions taking place on the mask.

One of the problems in this study of selective area growth was the large scatter in the data as depicted in fig. 7.7. It is believed that this poor reproducibility is not due to the experimental conditions in the vacuum chamber: For growth on maskless substrates the growth was found to be very reproducible. Therefore, the non-reproducibility is at-

---

**Fig. 7.8:** Electron micrographs depicting the surfaces of Si/SiO$_2$ - (left) and a SiGe/SiO$_2$ layers(right) both grown at 650°C. Except for the addition of a small amount of Ge the growth parameters were the same. The images measure 12 and 4.8 μm across, respectively.
tributed to the variation in mask quality depending on the cleaning procedure and the storage time of the masked substrates after preparation.

7.4 Facets

The growth within seed windows inevitably requires the formation of an interface between the crystalline Si and the surrounding amorphous mask. In the case considered here, the interfacial energy between the oxide and the Si is so high that direct growth on the oxide is energetically unfavourable, causing the growing Si crystal to avoid the contact with the mask. As a result, additional crystal planes develop, which generally grow at a lower rate than the (001) plane itself. These slower growing planes will therefore eventually even eliminate the (001) facet (see figure 7.1) and determine the appearance of the crystal in the window. From the point of view of IC-processing facet formation may be undesirable. However, it can also be used to advantage. For example, heterostructures in pyramids of the type depicted in fig. 7.1 can behave as quantum dots (zero dimensional systems) or may be utilised to obtain field emitters.

7.4.1. Facet Formation

Two ingredients are necessary to form a stable facet: The nucleation of a certain crystal plane and the stability of the nucleated plane at the applied growth conditions. The latter condition requires a lower growth rate than that on competing crystal planes, since only the slowest growing plane(s) will eventually survive. A low growth rate can be the consequence of a comparatively small number of reactive surface sites (adsorption sites) and/or different surface diffusivity, which would facilitate the loss of adatoms to other crystal faces. The number of reactive sites generally corresponds to the number of available (dangling) bonds in the surface, which also determines the surface free energy (\(E_s\)). Thus, low index planes with a low \(E_s\) are the planes which are most likely stable. For crystalline silicon, the order of decreasing stability is:

\[(111) > (113) > (001) \tag{7.7}\]

which corresponds to the order of increasing growth rate

\[r_{111} < r_{113} < r_{001} \tag{7.8}\] [Brek74].

This simple consideration has been used to explain the observed facets [Aoya94, Garde91]. However, there is strong evidence that the facet formation is modified by the kinetics at the Si/SiO\(_2\) boundary: To a large extent, the development of a facet depends on the nucleation of the respective crystal plane. It was found that facet formation depends on the alignment of the oxide mask boundaries with respect to the substrate crystal orientation [Ishi85, Drow88, Gould91]. Facetting is also affected by the shape of the oxide surface at the bottom of the seed window [Gould91]. These results
are explained by atomistic models assuming steric hindrance at the interface between mask and deposited layer [Drow88, Gould91]. One research group [Ishi85] attributes the facetting to local loading effects leading to non-uniform rates at the beginning of the growth process, but also observes the orientation dependence (no facets appear along [100] oriented masks). Clearly, although loading effects may lead to rate deviations, the orientation dependence can not be explained by this argument.

Another modification of the simple thermodynamic picture for the growth rate stems from geometry: in order for the \{111\} plane to show up at all, its growth rate must be lower than a critical value related to the rate for the \{113\} facet. A similar argument holds for the \{113\} facet with respect to the \{001\} surface. Figure 7.9 depicts the situation for oxide sidewalls normal to the \{001\} substrate oriented along \{110\}. Geometric considerations for the mentioned crystal planes yield the following maximum growth rates for the \{113\} and \{111\} facets with respect to the rate for the \{001\} surface in order that \{113\} and \{111\} facets show up in addition to the \{001\} surface:

\[
r_{001} : r_{113} : r_{111} = 1 : 0.9 : 0.58
\]

(7.9).

The observation of both \{113\} and \{111\} facets thus indicates that the rates for these fac-

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig7.9.png}
\caption{The development of facets at an oxide wall oriented along \{110\}. It is assumed that the facets all grow with their respective growth rate \(r_{\text{facet}}\). Hence, within the time \(t_{1}-t_{0} = t'\) they grow \(r_{\text{facet}} \times t'\) length units. From the figure it is clear that for example the growth rate of the \{111\} facet must be smaller than \(b/t'\) in order to have this facet developing in competition with the \{113\} surface. A similar criterion holds for the \{113\} facet in relation to the \{001\} surface.}
\end{figure}
ets are lower than the maximum given in the above equation.

The derivation of the exact growth rates from the measured facet widths is somewhat more involved. One method uses lateral overgrowth of material on the mask assuming that the overall facet shape does not change during overgrowth [Drow88, Maes95]. The situation is depicted in fig. 7.10, which shows the development of a pyramid, extending laterally over the mask, from a hole in the oxide. In order to determine the growth rate of the facet, the seeding window diameter and the lateral extension of the pyramid over the mask need to be known. Particularly the window diameter is often difficult to assess. For holes in wet chemically etched masks, the upper window diameter is different from the bottom diameter, and during annealing of the substrates in the growth system the diameter of the holes changes due to the oxide reduction reaction.

Another method to derive the growth rates of the various facets does not necessitate overgrowth, but only takes the length of the \{111\}- and \{113\} facets and the layer thickness as input (see fig 7.11). Assuming vertical oxide side walls, the rates can be derived from geometrical considerations:

\[
r_{113} = r_{001} \cos \alpha_{113} - (L_{113} \cos \alpha_{113} + L_{111} \cos \alpha_{111}) \sin \alpha_{113} \quad (7.10)
\]

\[
r_{111} = \cos \alpha_{111} (r_{001} - L_{111} \sin \alpha_{111} - L_{113} \sin \alpha_{113}) \quad (7.11)
\]

The weakness of this method is the assumption of a vertical oxide wall at the window edge. In reality this can only be achieved by anisotropic reactive ion etching of the oxide mask. However, from wet (isotropically) chemically etched masks, the edge is more or less rounded (fig. 7.12). Under these circumstances, equations 7.10 and 7.11 are not exactly valid and can only be used as approximations. Also the condition for the maximum permissible growth rate for a particular facet to show up is relaxed. The growth rate for the \{111\} facet can even be larger than that for the \{113\} face and the former would still develop, at least in the early stages of the window-filling process. Another important consequence of the rounded, wet etched oxide mask is the forced lateral overgrowth onto the oxide. Drowley and coworkers [Drow88] claim that \{111\}

---

**Fig. 7.10:** Development of a pyramid, laterally overgrowing the oxide from a hole in the mask. The solid lines indicate the shape of the pyramid at different stages during growth.
facets nucleate only during lateral overgrowth. They do not observe this facet inside reactively ion etched holes with vertical oxide walls; it is observed directly after overgrowth on the mask starts. This view is supported by the formation of (111) facets during growth inside windows, which were wet chemically etched [Aoya94] (fig. 7.12).

The control of facet nucleation is further affected by the oxide undercut, which develops during the oxide removal (cleaning) step prior to growth (see section 2.6). A small portion of the masking oxide at the interface with the substrate at the edge of the seed

Fig. 7.12:
Facet development at a wet chemically etched oxide wall. In comparison to a vertical oxide wall, the condition for the maximum growth rate is somewhat relaxed.
window is removed (fig. 7.13). A crystal deposited in the seed hole inevitably grows around the rounded corner of the oxide at the edge of the window. The growth along this barrier, which, from the point of view of the growing crystal, continuously changes its inclination can be easily imagined to be defect-prone. It is known that this difficult geometry can cause severe problems in terms of facet and/or defect nucleation [Gould91]. Most often, twinning is observed originating at the oxide 'nose' at the undercut [Drow88, Maes95].

7.4.2. Facets in GSMBE

After the more general considerations about facet formation outlined in the previous section, we now turn to the details of facetting in GSMBE. Basically, Si-GSMBE follows the trends observed in Si-CVD systems in this respect. Most prominently, the \{113\}, \{111\} and \{117\} facets are formed in masks aligned along the [110] directions (fig. 7.14). The oxide undercutting, mentioned in the preceding section, is also observed. Figure 7.15 depicts the resulting ear of a crystal, which has grown around the nose, together with the \{113\} facet (the masking oxide has been removed). Yet, in contrast to CVD, which can produce a wealth of facets by changes in the process conditions, particularly at higher pressures [Gould91], in GSMBE only the above mentioned facets plus the \{101\} facet along the \langle 100 \rangle directions (fig. 7.1) were observed, with the \{113\} facet being predominant.

In the beginning of growth, along the \langle 110 \rangle directions in the seed windows only the \{113\} facet develops. Somewhat later, also the \{111\} facets appear, most likely formed at or near the 'nose' of the undercut profile. At a later stage, upon extended lateral overgrowth on the mask surface, the \{111\} planes almost vanish and the \{113\} facets be-

Fig. 7.13:
Schematic drawing of the oxide undercut developed during the oxide removal step.
Fig. 7.14: Cross sectional SEM image of the Si-layer/oxide wall interface with facets. Clearly discernible are the \{111\} and \{113\} facets. The third facet, which makes an angle of about 10° with the (001) surface, is probably a \{117\} facet.

come the predominant feature, often accompanied by \{110\} facets in the \langle100\rangle directions.

However, the symmetry and appearance of the facets in GSMBE do not reproduce very well (fig. 7.16). Most likely this is due to the ill-defined wet chemically etched oxide mask/seed window interface used in the experiments. The asymmetry of the facet formation is caused by the nucleation process, which may or may not produce a particular plane depending on the microscopic structure of the interface between the oxide and the growing layer. Interestingly, the \{113\} facets have a much more regular appearance in the case of heavily boron doped layers (fig. 7.17). Obviously, the nucleation and the growth rates favour the formation of the \{113\} facet. This may be caused either by a modification of the adsorption behaviour of disilane on the surface (see also section 8.1.1 for the changes in growth rate under heavy doping) or by an enhanced diffusion of adatoms off the facet.

Using the overgrowth method to determine the growth rates of the \{111\} and \{113\}

Fig. 7.15: Side view of the protrusions that develop in the deposited Si film around the 'nose' of SiO₂ during deposition. The oxide mask was removed for clarity.
facets, the following values are found in GSMBE:

\[
\begin{align*}
r_{001} : r_{113} & = 1 : 0.25 \pm 0.05 \quad \text{[Maes95b]} \\
r_{001} : r_{113} : r_{111} & = 1 : 0.4 : 0.3 \quad \text{[Heuv94]}
\end{align*}
\] (7.12).

Values reported for CVD are:

\[
\begin{align*}
r_{001} : r_{113} : r_{111} & = 1 : 0.6 : 0.35 \quad \text{[Drow88]}
\end{align*}
\] (7.14).

The method employing direct measurement of the facet lengths yields for our samples:

\[
\begin{align*}
r_{001} : r_{113} : r_{111} & = 1 : 0.5 (\pm 0.06) : 0.2 (\pm 0.05)
\end{align*}
\] (7.15).
The variations are considerable and the differences with literature values are partly due to different process conditions (GSMBE/CVD). The differences between the GSMBE data are mostly due to the poorly defined oxide walls causing poorly defined hole geometries and varying facet shapes.

To study the dependence of facet formation on the alignment of the seed windows with respect to the crystal orientation, a special 'star' mask was used. Layout and alignment are depicted in fig 7.18a. The beams of the star make an angle of 15° with each other and are confined to a 2 by 2 cm square. 6 stars with a line width of 0.5, 1, 2, 5, 10 and 20 μm were transferred to the oxide mask. The resulting pattern on the substrate is depicted in figure 7.18b for a 10 μm star. Since no correction was applied to compensate for the overexposure of the central area, it developed into a larger opening. Also, the beams of the star are somewhat wider than the projected width, due to overetching of the mask oxide.

Figure 7.19 shows a top view of part of a 20μm star with the surrounding oxide removed. Clearly visible are the facets formed along all the beams independent of orientation. Apart from the faceting along the [110] directions, which was discussed above, the development of crystal faces along the [100] and other directions is particularly interesting. For the [100] direction, other workers using CVD or GSMBE, have observed normal side walls, i.e. {100} facets, or the appearance of a {101} surface upon lateral overgrowth [Gould91, Drow88, Hiroi92b]. In contrast to these findings, our GSMBE

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Fig. 7.18a left: Asterisk shaped test pattern. 6 of these structures with 2 cm side length and line widths of 0.5, 1, 2, 5, 10 and 20 μm, were exposed onto the oxide mask of a single wafer.

7.18b right: The actual pattern on the substrate after resist removal. The overexposed central region is enlarged. The image on the right measures 2mm across.
study shows the formation of alternating \{113\} and \{101\} facets as sidewalls of the [100] beam of the star (fig. 7.20). It is remarkable to observe this arrangement of facets in our case with wet chemically defined oxide windows, whereas in another GSMBE experiment only straight side walls developed [Hiroi92b]. In the latter case the windows were defined by reactive ion etching; this again emphasises the important role of the shape of the oxide walls in the nucleation of particular crystalline surfaces.

Similar alternating structures develop along the other oblique directions \(<1+\sqrt{2}, 1, 0>\) and in the areas, where the beams merge into the central area of the star. \{113\},\{111\} and also \{101\} facets are involved in the formation of the side walls (fig 7.20) along the beams.

A dependence of the facet formation on the size of the patterns could not be found. The exception to this statement is the formation of the (001) facet (substrate plane): It
generally does not develop for small windows, but the details depend on the deposited layer thickness and the formation of competing facets (see fig. 7.11+12).

7.5 Conclusions

Our study shows that in GSMBE perfect selectivity cannot be realised using hydride precursors on partly oxide-masked substrates. Due to the initial presence of reactive sites, adatom formation on the mask appears to be unavoidable. Removal of adatoms only functions at high temperatures, which makes this approach unattractive. In this respect the behaviour of silicon and SiGe must be contrasted with the MOMBE of III/V semiconductors from group III metalorganic precursors and group V hydrides, where perfect SAE is easily obtained.

To reach maximal attainable selectivity in GSMBE of Si, clean masks, low fluxes and as high a growth temperature as feasible should be used. For the growth of SiGe layers, selectivity is somewhat more easily attained than for pure Si films. The mechanism of this effect is as yet unclear. Passivation of the mask by exposure to hydrogen, as practiced in the CVD at atmospheric pressure, is not possible in GSMBE. Perfect selectivity at low temperatures can only be achieved using chlorine or chlorine compounds as participants in the reaction.

As an alternative approach to attain SAE device structures a lift-off process may be used with masks and deposited films of comparable thickness.

Facetting in GSMBE appears to be dominated by the nucleation of \{113\} facets along the generally ill-defined interface between mask and deposited film. Also the thickness of the mask plays a role in these effects, so that the formation of \{111\} and \{101\} facets may be suppressed by choosing thicker masking oxides. It appears that windows attained by reactive ion etching produce more reproducible facet formation than wet chemically etched windows.
Chapter 8

Doping of Si and SiGe in GSMBE

One of the requirements of the growth of semiconductor films for device applications is the possibility to control the doping concentration and its distribution within a layered structure. Also GSMBE must meet this demand. In the following, doping of Si and SiGe layers with diborane and phosphine and its effect on growth rate and surface morphology will be discussed. Doping experiments were carried out both in the cold-wall (LN$_2$ cooled shrouds) and warm-wall (water-cooled shrouds) environment. The results for the doping of Si were mostly obtained from runs with LN$_2$-cooled shrouds, whereas the doping of SiGe was mainly studied with water-cooled shrouds. The latter approach was necessary to achieve steep gradients for the dopants and Ge, since the cold-wall environment gives rise to profound memory effects.

The cold-wall doping experiments were all performed on specially prepared substrates [Heue94], having Hall-crosses for electrical measurements and structures to determine the growth rate, patterned into the SiO$_2$ layer. This way, the possibility for selective area growth (chapter 7) of the process was exploited, and post-growth etching was not necessary. For low doping concentrations, Al contacts were evaporated and annealed at 400°C. Highly doped layers could be measured directly. For p-type doping, n-type wafers were used and vice versa, in order to avoid parallel conduction through the substrate.

8.1 p-type Doping with Diborane

Growth experiments were carried out with different diborane fluxes at a typical growth temperature of 650°C and a silicon flux of 4.8 ML/s. The data, depicted in figure 8.1, shows that carrier concentrations between $2 \cdot 10^{17}$ and $2 \cdot 10^{19}$ cm$^{-3}$ were obtained for the investigated flux, ranging from $5 \cdot 10^{-5}$ to $2 \cdot 10^{-3}$ ML/s. The incorporation of boron with increasing flux shows a power law dependence: $N_B \sim \phi_B^{1.5}$. The same behaviour was also found for growth in a low pressure CVD system using silane and diborane [Kirch91]. The carrier concentration, determined from the Hall-measurements and the incorporated boron concentration, obtained from SIMS analysis, agree within experimental error, which is indicative of complete electrical activation of the dopant.

Comparison of the hole mobility, determined by Hall-measurements, with literature values at a given concentration of acceptors (fig. 8.2) shows that our values are at least
as large. This fact again indicates the high level of substitutional incorporation of the boron dopant.

### 8.1.1 Dependence of Doping Efficiency and Growth Rate on Diborane Flux

To assess the effectiveness of diborane as a dopant gas, we determined the boron doping efficiency $\varepsilon_{bd}$ for this hydride. This efficiency is defined as the quotient of the atom ratio of boron and silicon in the layer and the ratio of the boron and silicon flux. In Fig. 8.3 $\varepsilon_{bd}$ is plotted for different fluxes. It turns out that the doping efficiency of
Fig. 8.3: Doping efficiency of diborane in GSmBE of Si from disilane.

Boron in GSmBE increases with increasing boron flux. Also, the values for the efficiency are very high (of the order of unity). This is in contradiction to values reported in the literature, which are on the order of $10^{-4}$ [Yu86]. This discrepancy may be only partly explained by errors in the flux calibration of the very low fluxes in our case. Furthermore, the experiments in [Yu86] employ dosing of the Si surface by diborane without growth, which is not exactly the same as doping during growth of Si. However, the discrepancy stands as yet unresolved.

High diborane fluxes cause a reduction of the growth rate of silicon in GSmBE (fig. 8.4). For doping levels up to $10^{18}$ cm$^{-3}$ the growth rate is identical to the rate for un-
doped Si deposition. It is only above this level that the rate is significantly reduced. The actual mechanism is not clear, but obviously with an increase in boron coverage the surface becomes less reactive to disilane, and/or the desorption of hydrogen is inhibited by the presence of boron at the surface. In CVD, a similar reduction of the growth rate with increasing diborane mass flow has been found [Meyer87]. Most likely, the decrease in reactivity is not due to the hydrogen from the diborane molecules. First of all, the number of hydrogen atoms thus delivered to the Si surface is much smaller than that supplied by disilane. Secondly, the decrease in growth rate was also found in a study using disilane and HBO\(_2\) evaporated from a Knudsen cell [Hira90]. However, in that particular study, a decrease in growth rate was found only for doping levels above \(10^{20}\) cm\(^{-3}\). It appears possible that here the oxygen atoms from the HBO\(_2\) molecule might play a prominent role in the reduction of the growth rate.

### 8.1.2 Surface Morphology of Boron Doped Films

The surface of the boron doped layers grown at temperatures around 650°C is quite rough. Inspection by optical and electron microscopy reveals that the surface is covered with rectangularly shaped, indented areas (figs. 8.5 and 8.6). These areas have about the same lateral size and are also of roughly equal depth; the sides are aligned along the <100> directions, i.e. 45° off the dimer row directions on the surface. In a number of cases residues of unknown nature were observed in these rectangles (fig. 8.6). This could be precipitated boron, since boron was found to produce precipitates on the Si(001) surface [Armi77]. It has also been reported that heavy boron doping can

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**Fig. 8.5:** SEM micrograph of rectangular defects in a boron doped layer. The layer was grown selectively. The mask has been removed (some residue can be seen). The defect-edges are aligned along <100> directions.
lead to surface segregation of boron [Parry92]. Such layers might cause the surface to become passivated for further growth. This hypothesis is supported by the fact that the number density of the rectangles increases with increasing doping concentration, but a quantitative relationship was not established. However, p-type doping during growth at more elevated temperatures (approx. 800°C) does not produce rectangular defects at all and the layers are smooth. Also, the growth rate reduction observed at a given doping level at lower temperatures does not show up at these more elevated temperatures. Hence, the formation of rectangular defects at lower growth temperatures is probably a kinetic effect that can be avoided by growing at higher temperatures. As a matter of fact, the rectangular defects are absent in case of boron doping in the water-cooled system. Here, the incident disilane flux is generally considerably higher, which leads to a higher hydrogen coverage of the growing surface. It may be speculated that the higher hydrogen coverage prevents the formation of precipitates at lower growth temperatures (approx. 600°C).

8.2 n-type Doping with Phosphine

N-type doping with phosphine was investigated in a manner similar to that for boron doping. Fig 8.7 depicts the free carrier concentration versus the dopant flux for growth temperatures of 650 and 700°C. For the investigated flux ranging from $5 \times 10^{-5}$ up to $1.5 \times 10^{-3}$ ML/s, doping concentrations from $6 \times 10^{17}$ up to $1.3 \times 10^{19}$ cm$^{-3}$ were achieved. The doping experiments were carried out at two different temperatures, which precludes further analysis of the data as one consistent set. Hence, in this case the determination from these data of the relationship between flux and incorporation of phosphorus is not meaningful.

The Hall mobility of the electrons at different free carrier concentrations is given in figure 8.8 together with values from the literature. Again the mobility compares favourably with reported values.
8.2.1 Dependence of Doping Efficiency and Growth Rate on Phosphine Flux

Analogous to the boron doping case, the phosphorus doping efficiency $\varepsilon_{pd}$ is defined as the quotient of the ratio of the phosphorus and silicon atoms in the grown layer and the ratio of phosphine- and silicon fluxes. The plot of the incident phosphorus flux in fig. 8.9 shows that $\varepsilon_{pd}$ decreases with increasing flux to one third of the value obtained for the lowest flux. It has the same magnitude as the boron doping efficiency. However, unlike $\varepsilon_{bd}$, $\varepsilon_{pd}$ decreases with dopant flux, which indicates a different incor-
Fig. 8.9: Doping efficiency of phosphine in GSMBE of silicon from disilane. The solid line is a guide to the eye.

Dissociation mechanism. From other investigations it is known that phosphine has a sticking coefficient of the order of unity on Si (001) [Yu86]. Phosphine readily dissociates at typical growth temperatures (600°C) and the remaining phosphorus completely blocks the Si surface against adsorption of incoming molecules. This causes the growth rate to decrease markedly at higher doping levels (fig. 8.10) [Hira89]. At a flux of about 2x10⁻⁴ ML/s, the rate drops to values as low as approx. 0.4 nm/min, requiring long growth runs for highly doped material. Interestingly, a reduction of the rate is not observed in atmospheric pressure CVD growth of similar layers [Sedg93], which again points to the surface reaction limited growth process in GSMBE.

Fig. 8.10: Growth rate of n-type silicon versus phosphorus flux at fixed disilane flux. The solid line is a guide to the eye.
Another problem, which is shared by the usual n-type dopants for Si (P, As, Sb) is their strong tendency towards segregation on the growing surface. This point is demonstrated in the SIMS depth profiles of P in Si layers (figs. 8.11 and 8.12), which were grown using water-cooling of the GSMBE system to avoid memory effects. Fig. 8.11 depicts the depth profile of a Si layer, doped with only a thin (δ-) layer of phosphorus (the supply of disilane was stopped during the injection of phosphine). The resulting P

Fig. 8.11: SIMS depth profile of a phosphorus δ-doped Si layer. The measurement was done with a 6 keV O₂⁺ beam at 60 nA current. The dashed line indicates the dosing of the Si surface with phosphine during growth interruption to produce a δ-doped layer.

Fig. 8.12: SIMS depth profile of a phosphorus doped Si layer. The measurement was done with a 6 keV O₂⁺ beam at 60 nA current. The dashed bars give the intended doping profile. The arrow indicates the second largest phosphine flux value (see text).
profile (viewed in growth direction) is that of a peak with a long tail towards the surface. In this manner, doping profiles can be completely smeared-out as is demonstrated in fig. 8.12, which depicts SIMS data for a different P-doped Si layer. A SiGe layer has been used as a marker for the detection of the layer-substrate interface. Clearly, the intended doping profile (dashed bars) was completely lost during growth. The segregating phosphorus even accumulates to such an extent that the maximum of the incorporated concentration is reached for the second largest phosphine flux value (arrow in fig. 8.12), due to the contribution of earlier, segregated P-doping.

8.3 p-type Doping of SiGe with Diborane

Boron doping of SiGe using diborane is as convenient as doping of elemental Si. In both cases the achievable doping concentrations are the same. As an illustration, fig. 8.13 shows a SIMS depth profile of a structure with alternatingly doped (to different concentrations) and undoped Si and SiGe layers. Both materials allow steep boron gradients and high concentrations without any detectable segregation and with only small changes of the growth rate, when using the water-cooled GSMBE system to minimise memory effects. The only difference is that in adjacent Si and SiGe layers the boron concentration is slightly lower in the latter, although the diborane flux was kept the same (arrows in fig. 8.13). The reason for this lies partly in the different growth rates of

![Image of SIMS depth profile](image)

Fig. 8.13: SIMS depth profile of boron and germanium in Si (60 nA, 6 keV O₂⁺ beam). The boron concentration in the SiGe layers is slightly lower than in the Si layers (same B-flux) as a consequence of different growth rates. The minor B and Ge peaks at about 650 and 370 nm are due to interface contamination at the substrate/layer transition and an overnight growth interruption, respectively.
the layers: the growth rate for SiGe is higher than that of Si by a factor of 2.5 (see chapter 6). If one assumes that the doping efficiency of diborane for SiGe is the same as for Si, the dopant concentration in the SiGe layer should be lower than that in Si by a factor equal to the ratio of the growth rates. Yet, the doping concentration ratio of Si to SiGe is considerably smaller than the growth rate ratio. This implies that in this case, the doping efficiency of diborane in SiGe is higher by a factor of about 2.

8.4 n-type Doping of SiGe with Phosphine

Phosphorus doping of SiGe using phosphine is much easier than it is for elemental Si. Particularly, steep doping gradients can be achieved and the reduction in growth rate is considerably smaller. Concentrations in excess of $10^{19}$ cm$^{-3}$ with complete activation and much steeper profiles than those for Si can be readily obtained. Fig. 8.14 depicts the SIMS depth profile of a P-doped Si/SiGe layer. The doping was only applied to the SiGe layers. The complete incorporation of the dopant is attributed to the competition between P and Ge: both elements prefer surface sites. Ge obviously dominates the segregation process (see chapter 6), forcing P into the bulk of the layer. The effect of phosphorus in reducing the growth rate is much weaker for SiGe than for elemental Si: The 4 SiGe layers in fig. 8.14 were all grown for the same time. The thickness (and therefore the growth rate) of all SiGe layers is reduced, but significantly only for the last two SiGe layers (viewed in growth direction), which were doped to a phosphorus concentration in excess of $2\times10^{19}$cm$^{-3}$. Similar to the boron doping of SiGe, the doping efficiency of phosphine is considerably higher in SiGe than it is in Si. This

![Fig. 8.14: SIMS depth profiles of P in SiGe layers (80 nA, 6 keV O$_2^+$ beam). The dopant-junctions in SiGe are much sharper than for plain Si.](image-url)
can be inferred from the fact, that the region around 400 nm (fig. 8.14) was doped with the same phosphine flux as the adjacent SiGe layer. Yet, the phosphorus concentration in the Si layer is about a factor of 10 smaller than that in SiGe. Hence, taking the growth rate variation into account, the doping efficiency of phosphine in SiGe is larger by a factor of about 20 compared to that in Si.

8.5 Conclusions

For p-type doping, boron from diborane is an almost ideal dopant source in GSMBE: With suitable gas-handling, boron can be incorporated over a range of 5 orders of magnitude to levels up to $10^{20}$ cm$^{-3}$ with complete activation and very steep concentration gradients in Si and SiGe. The use of a water-cooled system is recommended, since boron precipitates on the surface, which give rise to defects, are avoided, whereas the reduction of the growth rate at doping levels above $2 \times 10^{18}$ cm$^{-3}$ is much smaller than in the LN$_2$-cooled system.

n-type doping from phosphine is more problematic: Growth rates are severely reduced for both cooling methods and strong surface segregation precludes the growth of steep doping profiles in Si. Phosphorus behaves much better in SiGe, where the growth rate reduction is less severe than in Si; much sharper doping transitions with distinctly higher efficiency can be realised in SiGe.
Chapter 9

GSMBE Growth of Device Structures

The data presented in the foregoing chapters demonstrate the insights in the deposition mechanisms of Si and SiGe films gained in this study. It was shown that the GSMBE technique allows satisfactory control in the deposition of individual layers, particularly in the case of SiGe. Remains the question of its suitability for the growth of small device structures. Using two examples: 1) silicon point contacts [Maes96], and 2) double barrier resonant tunneling diodes (DBRT's) [Storm96], we will briefly discuss in the present chapter the potential of GSMBE in the Si technology.

9.1 Silicon point contacts

Point contacts are short constrictions with dimensions of a few tens of nm separating two large 3D contact areas. Traditionally, metallic point contacts were made by mechanical methods, for example by pressing a sharp needle on a flat metallic counterpart. Using such point contacts, a wealth of information has been obtained on fundamental transport properties of metals at low temperatures [Point92]. However, comparable data on point contacts made from semiconducting materials like Si is hardly available [Lehr90]. The reasons lie in irreproducibilities and instabilities of the mechanical construction of such semiconductor point contacts. Specifically, the oxide layer and the charge buildup at the surface of the point contact have a pronounced influence on the electrical characteristics. This problematic situation strongly improved with the availability of nanofabrication methods, which allow the reproducible preparation of stable point contact geometries.

The Si point contact structure, used in the present study, were realised using SAE of B-doped Si into small holes (85 - 5000 nm) in a thin (~ 35 nm) oxide mask on a p-type Si (001) substrate. The oxide mask acts as an insulator between two 3D contacts and of course also as a mask for the SAE. The Si deposited inside the window constitutes the actual point contact. Figure 9.1 shows this structure after lateral overgrowth on the mask. The overgrown area is used as the second electrode and has to be much larger than the area of the constriction itself in order to obtain the point contact geometry. The diameter of the overgrown area in fig 9.1 is about 5 times larger than the hole, which has a diameter of approx. 100 nm. To further enlarge the upper electrode, 1 μm of B-doped Si was grown on top of the structure of fig. 9.1 in the SSMBE system, after
Fig. 9.1: SEM-micrograph of a point contact crystal formed by SAE of B-doped Si in a 100 nm hole. The crystal formed measures $500 \times 500$ nm$^2$.

The growth of the first layer in GSMBE was completed. The transfer to SSMBE took place in vacuum (see fig. 2.1). The regrowth yields a vertically enlarged crystal surrounded by polycrystalline material. Further processing finally produces the device depicted schematically in fig. 9.2 with current and voltage contacts for 4-point measurements. Proper cleaning of the hole prior to SAE is essential for the successful fabrication of this structure. The transmission electron micrograph of fig. 9.3 shows an almost defect free interface between substrate and layer; absence of contamination is a condition for perfect epitaxy. Yet, twinning defects are introduced at the mask/layer interface due to steric hindrance of the adatoms upon incorporation in the layer [Drow88].

Electrical measurements at room temperature show the linear dependence of the resistance of the point contacts on the reciprocal diameter, as expected from a Maxwel-

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Fig. 9.2: Schematic representation of a completed point contact device.
Cross-sectional transmission electron micrograph of a point contact. Note the twinned areas on top of the oxide mask. The dark spots at the interface are caused by strain contrast due to contaminants.

lian resistor [Maes95] (fig. 9.4). With decreasing temperature, the resistance increases and below 40 K changes from linear to non-linear behaviour at higher fields. This behaviour of the resistance below 40 K is interpreted in terms of Mott variable range hopping, which is field activated above a critical voltage. Interestingly, the field dependence of the characteristics of the Si point contact differs considerably from the

Fig. 9.4: Room temperature resistance values (R) of the p-type point contacts plotted against the inverse diameter (1/d).
dependencies found in bulk samples. This behaviour can be understood assuming a spherical region of non-ohmic hopping transport inside the point contact [Maes96].

9.2 Si/SiGe Double Barrier Resonant Tunneling Diodes

The double barrier resonant tunneling (DBRT) diode derives its name from the fact that the quantum mechanical phenomenon of resonant tunneling governs the electrical transport of carriers through such a device. It constitutes an example of exploiting the possibilities of bandgap engineering in the SiGe material system. A DBRT-diode basically functions as follows [Chang74]: The device consists of potential barriers defining a well (fig. 9.5), with states according to the particle in the box problem. A particle with energy smaller than the barrier height only has a significant chance to tunnel through the structure, if its energy coincides, in good approximation, with one of the subband energies in the well. In this case, the particle wavefunction interferes constructively with itself inside the well (it resonates) and the transmission probability has a maximum. Hence, one expects peaks in the I/V characteristic for voltages over the device, which correspond to subband energy positions. Between those peaks, the current drops off, which gives rise to negative differential resistance. Typical applications of DBRT-diodes are therefore found in oscillator circuits.

The alignment of the bandgaps in Si/SiGe heterostructures is such that the difference in bandgap manifests itself almost completely in the valence band (see section 1.1.2). A DBRT device in the Si/SiGe technology therefore uses holes as carriers in the valence

![Graphs showing potential landscape and transmission spectrum](image)

Fig. 9.5: Schematic view of the potential landscape for a double barrier structure (left) and the corresponding transmission spectrum (right). A subband energy level in the well is indicated in the left hand side figure.
band with thin Si layers as barriers and SiGe layers as contacts and well (fig. 9.6). The overall thickness of the Si$_{0.2}$Ge$_{0.8}$ layers was kept below the critical limit (see section 1.1.2), also with respect to 3D growth (see section 6.2). To further lower the risk of roughening, the SiGe contact layers were graded, reducing the overall strain in the layers, while keeping the barrier height as large as possible. The diodes were grown using oxide-masked substrates to exploit SAE. However, in the warm growth environment, selectivity is lost quickly due to the much higher fluxes in comparison to the cold system. Hence, the polycrystalline material on the mask had to be removed by etching after growth. Fig. 9.7 depicts a TEM micrograph of the active region of the DBRT layer structure, revealing that the structure was indeed obtained. Some unintended constrictions in the DBRT structure were also observed (at distances of a few hundred nanometers), which are attributed to imperfect cleaning. Obviously, cleaning of the windows in the mask requires further attention. Fig. 9.8 schematically shows a completed device. It should be noted that the active layers of the DBRT structure follow the facet formation characteristics at the oxide/layer interfaces as discussed in section 7.4. Unfortunately, for the proper functioning of the device, these facets constitute thinner layers and thus give rise to enhanced parallel conduction along the circumference of the device. This conduction tends to dominate the electrical characteristics of

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**Fig. 9.6: Schematic representation of the SiGe hetero-structure grown for the DBRT-diodes.**

- **growth direction**
- **x=0**
- **200 nm cap**
- **x=0.20**
- **25 nm contact**
- **x=0.20**
- **5 nm barrier**
- **4 nm well**
- **5 nm barrier**
- **x=0**
- **30 nm buffer**
- **Si**
- **Si$_{1-x}$Ge$_x$**
- **substrate**
the diodes. Only for the largest area diodes (which exhibit the largest ratio of surface area to circumference) could negative differential resistance be found in I/V measurements at low temperatures (fig. 9.9). Nevertheless, the voltages measured for the resonant tunneling peaks agree well with the values calculated for this particular structure. It may be concluded that the layer structure as such has been grown successfully and that it would perform as intended, were it not for the parasitic conduction along the circumference of the window. Most likely, the parallel conduction could be suppressed by using a dry etching process for separation and isolation of the devices. This approach is used as a standard procedure on similar layers grown by SSMBE, leading to excellent DBRT-device performance [Lukey95].

9.3 GSMBE as a Tool for Device Fabrication

At this point, we believe it is appropriate to put the GSMBE technology into perspective with competing growth techniques like SSMBE and CVD with respect to its device fabrication capabilities. GSMBE shares with SSMBE the ultra clean apparatus, the excellent control of the fluxes and the in situ monitoring facilities. All this adds up to a crystal growth technique that is well furnished for the growth of prototype device
structures and/or the investigation of new materials. Compared to SSMBE, GSMBE is more flexible as regards the choice of precursor material, even though the nature of some of the precursors may bring about difficulties during the decomposition/desorption steps. Also, the possibility of SAE is an advantage for GSMBE. On the other hand, both MBE based techniques do not lend themselves naturally for large volume production. The general design of the apparatus is not optimised for production purposes and uptime of UHV systems particularly with internal sources is still a problematic issue. The relatively low growth rates are less of a problem, since the growth temperatures for SiGe and subsequently grown Si films need to be low anyway and for these circumstances, the growth rates are roughly the same for all techniques here considered.

CVD systems can be easily tailored for mass volume production, but they lack the high degree of control of the MBE systems. CVD usually employs chlorine based Si precursors, which work best at elevated temperatures (> 700°C), but make the growth of SiGe alloys quite difficult to control. Namely, at these low temperatures the decomposition of DCS is strongly activated, which results in Si growth rate variations for minute temperature changes and hence varying Ge content. UHVCVD using silane and germane circumvents this problem, but only permits low growth rates, and also offers less selectivity than the chlorine containing growth chemistries can attain.

Summarising, one could say that all delicate, and/or novel SiGe structures are best grown by MBE. When layers become thicker, or high volume production is intended, single wafer (AP)CVD machines using dichlorosilane or silane and germane are best suited. Simultaneously, if selective area growth needs to be employed, chlorine containing growth chemistries ought to be used. Batch reactors like the UHVCVD type of reactors will eventually vanish, since the diameter of the industrially used Si wafers
becomes so large (200 mm today with 300 mm diameter at the horizon) that single wafer reactors must be used for uniformity reasons and throughput.

9.4 Conclusions

The two device structures grown by GSMBE are good examples to demonstrate the strong points of the technology. The point contacts have been grown using SAE. This technique offers the possibility of in situ monitoring for the loss of selectivity. The DBRT structures require a high degree of control over growth parameters (particularly the GeH$_4$ fluxes). Here again the RHEED system could be used to monitor the flatness of the growing surface of SiGe layers deposited under conditions close to those for the roughening transition. Also for DBRT devices, the layers were grown using SAE, but in this case the inherent facet formation along the rim of the windows impaired the electrical characteristics at least for small devices. Hence, when employing SAE in GSMBE, one first needs to assess whether facet formation affects the functioning of the intended structures.
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Summary

Surface Processes in Gas Source Molecular Beam Epitaxy of Si and SiGe Alloys

The goal of this study is to provide insight into the mechanisms of a low temperature crystal growth process for Si and SiGe alloys on Si (001) substrates using disilane and germane as principal precursors. This improved understanding of the process should lead to better control of its technical application in the preparation of devices with nanometer dimensions. Most effort is spend on the investigation of surface processes during deposition. Using an ultrahigh vacuum chamber as reactor, deposition is performed at well defined and ultra clean conditions. The technique is coined Gas Source Molecular Beam Epitaxy (GSMBE) and has to be contrasted with SSMBE (solid source MBE), which uses elemental source materials.

Mass flows into the GSMBE reactor are controlled by high precision UHV leak valves. Further downstream, injection capillaries form molecular beams of the injected precursor molecules. In the course of this study, a vent/run gas manifold was added, which provides superior flux switching behaviour and improved interface sharpness and doping transients in a water-cooled reactor. Use of a water-cooled reactor implies operation at room temperature rather than at low (liquid nitrogen) temperatures.

Since the growth was performed at very low pressures, the in situ monitoring of the growing surface by RHEED is possible. The RHEED analysis technique plays a dominant role in the investigation of the surface processes during growth of the Si and SiGe layers: It is used for the measurement of growth rates and as a monitor for surface reconstructions.

It is shown that the surface mobility of Si adatoms in GSMBE is higher and stronger activated than in the case of SSMBE. This behaviour is attributed to the presence of hydrogen at the growing surface in GSMBE. The hydrogen stems from the pyrolysis of the hydride precursors on the Si substrate. Most likely, for growth with high fluxes of incoming disilane or germane and/or at low temperatures, the desorption of hydrogen from the surface constitutes the growth rate limiting step. This is inferred from the fact that the activation energy for the growth rate is the same as that for hydrogen desorption (about 2 eV).

The growth kinetics can be modelled in terms of Langmuir-Hinshelwood adsorption. The product of the hydrogen desorption rate and the effective hydrogen coverage of the surface determines the generation rate of dangling bonds, which are required for the adsorption of disilane. The question regarding the adsorption order of disilane can
not be answered unambiguously: Both fits for second and fourth order adsorption agree equally well with the experimental data. The model allows the numerical evaluation of growth rates over more than 4 orders of magnitude for temperatures between 400 and 650°C and a range of fluxes. Introduction of a direct reaction of disilane with hydrogen at the surface as postulated by other workers is not required to fit growth rate results at low temperatures.

To perform the numerical fitting procedure, a value for the reactive sticking coefficient of disilane of 0.1 is assumed, independent of temperature. This assumption is verified using the $\tau_i$ approach, which is a non-equilibrium method employing the RHEED intensity decay upon adsorption of disilane on a hydrogen-free surface. Within the investigated temperature range (488 up to 580°C) no temperature dependence of the sticking coefficient could be found. It is concluded that disilane adsorbs in a non-activated manner, presumably via a precursor state.

The addition of germane to the growth system in order to deposit SiGe alloys, modifies the growth kinetics. The presence of Ge markedly increases the hydrogen desorption rate so that the growth rate rises considerably at low temperatures as compared to the homoepitaxial rate. The Ge content in the solid is a linear function of the germane flux to total flux ratio. From the proportionality constant, a reactive sticking coefficient of 0.03 for germane is deduced. It is found that SiGe layers develop rough surfaces more easily in GSMBE than in SSMBE. This tendency maybe explained by the generally lower growth rates in GSMBE and by the presence of hydrogen at the surface, which reduces the surface energy and makes roughening more affordable from an energetics point of view. It should be noted that the rough surfaces actually have a regular crystalline structure and are usually bounded by [113] and [111] facets.

A further effect, which can be observed directly by RHEED intensity oscillations is the smearing of the SiGe/Si heterointerface due to Ge segregation to the surface. It could be shown that the segregation of Ge is suppressed by the presence of hydrogen, so that a larger hydrogen coverage of the surface results in a sharper heterointerface. For this reason, these interfaces can be grown much sharper in GSMBE than in SSMBE.

Selective area epitaxy in GSMBE using Si wafers, which are partially masked by SiO$_2$, is only possible in a relatively small process window. Perfect selectivity at moderate growth temperatures cannot be achieved due to the absence of a reaction step, that efficiently removes adatoms from the mask. Low fluxes, as high a growth temperature as tolerable and the addition of germa ne improve the selectivity in GSMBE. At high temperatures, in excess of 700° C for SiGe alloys and above 850°C for Si, adatom removal from the mask is promoted by oxide reduction reactions. Between 300 and 400 nm layer thickness can be deposited at usual growth temperatures (500-600°C) in the seed windows before the material deposited on the mask covers more than 15% of
the mask area. It should be noted that the nucleated polycrystalline Si and SiGe on the mask can be readily removed by an HF dip that etches the underlying oxide and hence takes away the crystals on the mask. When thick oxide masks (approx. 1 μm) are used, this lift-off process is possible even when the nucleated material completely covers the mask.

Due to the interaction between the growing crystal and the oxide mask defining the seed window, crystal facets are formed. In our experiments, where the seed windows are defined by wet chemical etching of the mask, (111) and most prominently (113) facets are observed. These facets form independent of the orientation of the oxide windows on the substrate. The dimensions of the individual facets are found to vary significantly. This is attributed to the ill-defined geometry of the mask window at the substrate/mask interface. The annealing step prior to growth rounds off the sharp, wet chemically created oxide mask edge. The crystal has to grow around this mask edge, which results in the nucleation of various facets and also of twinning defects at this mask/layer interface.

Doping in GSBME requires a water cooled chamber in order to avoid memory effects that prevent the realisation of steep doping gradients. p-type doping with diborane can be readily achieved over a wide range of concentrations. With the baratron setup used in our study, boron concentrations ranging from $10^{17}$ up to $2 \times 10^{19}$ cm$^{-3}$ can be achieved for both Si and SiGe layers. A larger flow range will also increase the range for the concentration in the solid. Segregation of boron is not observed. The doping efficiency of diborane for SiGe layers is about 2 times as large as that for Si. Phosphorus from a phosphine source is used as n-type dopant. It segregates strongly to the Si surface and markedly reduces the growth rate. A concentration range between $6 \times 10^{17}$ and $2 \times 10^{19}$ cm$^{-3}$ is obtained with our injection system. Phosphorus incorporates much more readily into SiGe than in Si layers. The attainable doping profiles are much sharper than in Si and also the growth rate reduction is less severe.

To check the usefulness of GSBME for technological applications, two different types of electronic devices were fabricated in the course of this study. The first one is a semiconductor point contact, which is basically a small volume of semiconducting material between two large electrodes; it is grown using selective area epitaxy and lateral overgrowth of p-doped Si in GSBME. Our growth technique permits perfect epitaxial regrowth in the small seeding holes. The point contacts show the expected electrical behaviour: A linear dependance of the resistance across the contact on the inverse hole diameter. For this device, selective area growth, facetting and lateral overgrowth function as expected and lead to the desired result.

A second device structure deposited by GSBME is a double barrier resonant tunneling diode. The required tight control of the doping profiles and the Ge concentration is perfectly realised. Also in this case it is attempted to achieve device isolation by selec-
tive area growth. However, the facetting along the seed window edges gives rise to leakage currents that dominate the electrical characteristics of the diodes. Only for the largest area diode, negative differential resistance can be found. It is expected that the use of standard reactive ion etching techniques for the definition of the diodes will lead to devices with the intended characteristics.

Our device results thus demonstrate that a judicious use of modern methods for patterning and film deposition is required for the fabrication of devices with nanometer dimensions. The level of control of film thickness, composition and doping obtainable with GSMBE, provides an important contribution to realise this goal.
Samenvatting

Oppervlakte processen in Gas Bron Moleculaire Bundel Epitaxie van Si en SiGe Legeringen

Het doel van dit onderzoek is nader inzicht te krijgen in de mechanismen van een lage temperatuur kristalgroei proces voor Si en SiGe legeringen. Hierbij wordt gebruik gemaakt van disilaan en germanium als primaire uitgangsstoffen. Het verbeterde inzicht van het proces zou moeten leiden tot een betere controle tijdens het prepareren van electronische devices met nanometer afmetingen. De studie gaat vooral over de oppervlakte processen tijdens het deponeren. Gebruikmakend van een ultra hoog vacuüm (UHV) kamer wordt de depositie onder goed gedefinierde en ultra schone omstandigheden uitgevoerd. Deze techniek wordt gas bron moleculaire bundel epitaxi (GSMBE) genoemd. Dit in tegenstelling tot SSMBE (vaste stof bron MBE), die gebruik maakt van elementaire uitgangsmaterialen.

De massa fluxen naar de GSMBE reactor worden geregeld door hoge precisie UHV lek-kleppen. Verderop in de richting van de gasstraling zorgen injectie capillairen voor het aanmaken van moleculaire bundels van de aangevoerde moleculen. Tijdens deze studie werd een vent/run gas systeem geïnstalleerd, welke superieure flux om- schakeling en scherpe laag overgangen en doteerstof profielen mogelijk maakt in een water gekoelde reactor. Het gebruik van een water gekoelde reactor houdt in dat de reactor op kamer temperatuur gehouden wordt in tegenstelling tot eveneens mogelijke afkoeling tot vloeibaar stikstof temperatuur.

Omdat de groei bij hele lage drukken plaatsvindt, is het mogelijk tijdens het proces met behulp van RHEED naar het groeiende oppervlak te kijken. De RHEED analyse techniek speelt een zeer belangrijke rol in het onderzoek naar de oppervlakte processen gedurende de groei van Si en SiGe lagen: Zij wordt gebruikt voor de bepaling van de groei snelheden en als monitor voor oppervlakte reconstructies.

Het wordt aangetoond dat de oppervlakte bewegelijkheid van Si adatomen in GSMBE hoger is en sterker is geactiveerd dan in het geval van SSMBE. Dit gegeven wordt toege- schreven aan waterstof wat tijdens GSMBE groei op het oppervlak aanwezig is. De waterstof is afkomstig uit de pyrolyse van de hydride moleculen aan het Si substraat. Tijdens de groei met hoge disilaan of germanium fluxen en/of lage temperaturen is zeer waarschijnlijk de waterstof desorptie van het oppervlak de groeisnelheids bepalende reactiestap. Dit werd afgeleid uit het feit dat zowel de groei-snelheid als ook de waterstof desorptie de zelfde activeringsenergie hebben (ongeveer 2 eV).
De groei kinetiek kan worden beschreven in termen van Langmuir-Hinshelwood adsorptie. Het product van de waterstof desorptiesnelheid en de effectieve waterstof be- dekking van het oppervlak bepaalt de aanmaak snelheid van vrije bindingen. Het laat- ste is noodzakelijk voor de adsorptie van disilaaan. De vraag naar de orde van de adsorptie van disilaaan kan niet eenduidig worden beantwoord. Fits voor tweede en vierde orde adsorptie komen even goed met experimentele gegevens overeen. Het model kan worden gebruikt voor de numerische bepaling van de groeisnelheid over meer dan vier ordes van grote voor temperatures tussen 400° en 650°C. Het blijkt niet nodig een directe reactie van disilaaan met waterstof aan het oppervlak aan te nemen wat soms in de literatuur aangevoerd wordt, om de groeisnelheid ook bij lage tempera- turen te kunnen vitten.

Voor de numerische fit werd een waarde van 0.1 voor de reactieve hechtings coeffi- cient van disilaaan verondersteld, onafhankelijk van de temperatuur. Deze veronder- stelling werd geverifieerd met behulp van de \( \tau_1 \) techniek. Deze methode werkt in een niet-evenwichts situatie en maakt gebruik van de RHEED intensiteits afname tijdens de adsorptie van disilaaan op een waterstof vrij oppervlak. Over het temperatuur bereik (488 tot 580°C) kan geen temperatuur afhankelijkheid van de hechtings coefficient worden vastgesteld. De conclusie is dat disilaaan op een niet geactiveerde manier ad- sorbeerde en dat waarschijnlijk middels een 'precursor' toestand.

Het toevoegen van germanium voor de groei van SiGe legeringen verandert de groei kinetiek. De aanwezigheid van Ge verhoogt de waterstof desorptiesnelheid, zo dat de groeisnelheid bij lage temperaturen toeneemt in vergelijking met de homoeptaxiele waarde. De Ge concentratie in de vaste stof is een lineaire functie van de verhouding van de Ge flux tot de totale flux. Via de proportionaliteits constante vindt men een re- activie hechtingscoefficient voor germanium van 0.03. Verder wordt opgemerkt, dat SiGe lagen in GSMBE eerder ruw groeien dan in SSMBE. Dit feit kan misschien worden ver- klaard door de lagere groeisnelheden in GSMBE en door de aanwezigheid van waterstof aan het oppervlak. Het laatste vermindert de oppervlakte energie wat de ver- ruwing vanuit energetisch oogpunt makkelijker maakt. Het moet worden opgemerkt, dat de ruwe oppervlakken nog steeds een reguliere, monokristallijn structuur hebben, die door \{113\} en \{111\} facetten begrenst worden.

Een ander effect wat met behulp van RHEED intensiteits oscillaties direct zichtbaar wordt, is de uitsmering van het SiGe/Si heterointerface. Deze uitsmering wordt ver- oorzaakt door de segregatie van Ge aan het groeiende oppervlak. Het kon worden aangetoond, dat de Ge segregatie door de aanwezigheid van waterstof onderdrukt wordt, en dan wel op een manier dat meer waterstof aan het oppervlak in scherpere heterointerfaces resulteert. Daarom kunnen deze overgangen met GSMBE veel scherper gegroeid worden dan met SSMBE.

Selectieve epitaxie in GSMBE op Si plakken die gedeeltelijk gemaskeerd zijn met een
SiO₂ laag, is alleen mogelijk binnen een relatief klein proces venster. Perfecte selectiviteit onder normale omstandigheden is niet mogelijk wegens het ontbreken van een reactie stap die adatomen op een efficiënte manier van het masker kan verwijderen. Lage fluxen, groeitemperatures zo hoog mogelijk en het toevoegen van germaan verbeteren de selectiviteit in GSMBE. Bij hoge temperaturen (meer dan 700 °C voor SiGe en meer dan 850°C voor Si) kunnen adatomen van het masker worden verwijderd dooroxide reductie reacties. Tussen 300 en 400 nm laagdikte kan worden gedeponeert onder de normale groeimstandigheden (500-600°C) in de maskervensters, voordat het materiaal wat op het masker is gedeponeerd meer dan 15% van het maskeroppervlak bedekt. Polykristallijn Si en SiGe op het masker kan later eenvoudig met behulp van HF weggehaald worden. Het zuur etst het onderliggende oxide weg en verwijdert op die manier ook de polykristallijne laag erop. Als dikke oxide maskers gebruikt worden (circa 1μm), kan bovengenoemd lift-off proces ook toegepast worden, als het poly-materiaal het masker volledig bedekt.


Om fatoorlijk te kunnen doteren moet de GSMBE reactor met waterkoeling bedreven worden. Anders (bij vloeibaar stikstof koeling) ontstaan geheugen effecten die de realisatie van scherpe doteerstof overgangen voorkomen. p-type dotering met diboraan kan makkelijk worden bereikt over een breed concentratie bereik. De flux regeling met een baratron zoals gebruikt in dit onderzoek maakt het mogelijk boor concentraties tussen 1·10¹⁷ en 2·10¹⁹ cm⁻³ in Si en SiGe lagen te verkrijgen. Een groter instelbaar fluxbereik zal ook het concentratie bereik in de vaste stof vergroten. Segregatie van boor werd niet gezien. De doping efficiëntie van diboraan voor SiGe is ongeveer een factor 2 groter dan voor Si. Fosfor afkomstig van fosfine wordt gebruikt voor het doteren van n-type materiaal. Fosfor segregeeert sterk in het Si oppervlak en reduceert behoorlijk de groeisnelheid. Met ons injectie systeem kan een doteerstof inbouw tussen 6·10¹⁷ en 2·10¹⁹ cm⁻³ gehaald worden. Fosfor wordt veel makkelijker in SiGe dan in Si ingebouwd. Ook zijn voor SiGe de bereikbare doteerstof profielen duidelijk scherper en is de teruggang van de groeisnelheid met toenemend fosfine flux minder ernstig.

Twee verschillende electronische schakelelementen werden tijdens dit onderzoek ge-
fabriceerd om de GSMBE technologie voor applicaties te testen. Het eerste element is een halfgeleidend punt-contact. In wezen is dit een klein volume halfgeleidend materiaal tussen twee zeer veel grotere electroden. Het werd vervaardigd met behulp van selectieve epitaxie en lateraal overgroei van p-gedoteerd Si in GSMBE. De techniek maakt perfect epitaxiale hergroei in de kleine gaten mogelijk. De punt contacten tonen het verwacht elektrisch gedrag: De afhankelijkheid van de weerstand over het kleine contact volume is lineair in de reciproke gat diameter. Voor dit type device leiden selectieve epitaxie, facettering en lateraal overgroei tot de verwachte resultaten.

Het tweede device bevat een met GSMBE gegroeide dubbele barriere resonante tunnel diode. De benodigde uitstekende controle over de doteerstof profielen en de Ge concentratie kon perfect worden gerealiseerd. Ook in dit geval werd gepoogd de devices met behulp van selectieve epitaxie van elkaar te isoleren. Helaas geeft de facettering langs de randen van de groeivensters aanleiding tot lekstromen die de elektrische karakteristiek van de dioden domineren. Daarom kon alleen voor de grootste diode negatief differentieel weerstand worden gevonden. De verwachting is dat het gebruik van standaard reactief ionen ets technieken voor het defineren van de diodes tot betere devices zal leiden.

Onze device resultaten tonen aan dat een doordachte keus van moderne methoden voor het patroneren en deponeren voor de fabrikage van devices met nanometer afmetingen nodig is, om de beoogde resultaten te realiseren. De mate van controle over film dikte, compositie en dotering die met GSMBE behaald kan worden, levert een belangrijke bijdrage voor dit doel.
Publications

This thesis is based on the following publications:


K. Werner, S. Butzke, S. Radelaar and P. Balk, J. Crystal Growth 136, 322 (1994) "Determination of the sticking coefficient of disilane on Si(001) using the first reflection high energy electron diffraction oscillation period".


Earlier publications and those on related subjects:


E. van der Drift, T. Zijlstra, R. Cheung, K. Werner and S. Radelaar, Micoelectronics Engineering 23, 343 (1994), "Reactive ion etching mechanism study on Si/GeXSi1-x".


194, 1225 (1994) "Weak localisation and correlation effects in a 2-dimensional hole gas in Si/Si$_{1-x}$Ge$_x$ Heterostructures".


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J. van Wingerden, E.C. van Halen, K. Werner, P.M.I.O. Scholte and F. Tuinstra, Surface Science 352, 641 (1996) "Origin of rippled structures formed during growth of Si on Si(001) with MBE".

Postscriptum

This thesis is the result of several years of research spent at the Delft Institute of Microelectronics and Submicron Technology within the group of Prof. Radelaar. Originally planned as a six months intermezzo, the involvement in the definition and the negotiations for a new MBE system soon called for a prolongation of my contract. This "prolongation" finally added up to almost nine years, which I thoroughly enjoyed in an atmosphere of freedom and trust. I am very thankful to both, Prof. Radelaar and Prof. Balk for creating this (almost) ideal environment.

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