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# Chloride-based Silicon Carbide CVD

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**Cover:** A failed experiment that rendered in polycrystalline growth on a 4H-SiC 8° off-axis substrate, image taken using optical microscope.

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*and I wonder  
when I sing along with you  
if everything could ever feel this real forever  
if anything could ever be this good again  
the only thing I'll ever ask of you  
you've got to promise not to stop when I say when*

Everlong  
Foo Fighters



# Abstract

Silicon carbide (SiC) is a promising material for high power and high frequency devices due to its wide band gap, high break down field and high thermal conductivity. The most established technique for growth of epitaxial layers of SiC is chemical vapor deposition (CVD) at around 1550 °C using silane, SiH<sub>4</sub>, and light hydrocarbons *e.g.* propane, C<sub>3</sub>H<sub>8</sub>, or ethylene, C<sub>2</sub>H<sub>4</sub>, as precursors heavily diluted in hydrogen. For high-voltage devices made of SiC thick (> 100 μm), low doped epilayers are needed. Normal growth rate in SiC epitaxy is ~ 5 μm/h, rendering long growth times for such SiC device structures. The main problem when trying to achieve higher growth rate by increasing the precursor flows is the formation of aggregates in the gas phase; for SiC CVD these aggregates are mainly silicon droplets and their formation results in saturation of the growth rate since if the gas flow does not manage to transport these droplets out of the growth zone, they will eventually come in contact with the crystal surface and thereby creating very large defects on the epilayer making the epilayer unusable. To overcome this problem, high temperature- as well as low pressure processes have been developed where the droplets are either dissolved by the high temperature or transported out of the susceptor by the higher gas flow. A different approach is to use chloride-based epitaxy that uses the idea that the silicon droplets can be dissolved by presence of species that bind stronger to silicon than silicon itself. An appropriate candidate to use is chlorine since it forms strong bonds to silicon and chlorinated compounds of high purity can be purchased. In this thesis the chloride-based CVD process is studied by using first a single molecule precursor, methyltrichlorosilane (MTS) that contributes with silicon, carbon and chlorine to the process. Growth of SiC epilayers from MTS is explored in Paper 1 where growth rates up to 104 μm/h are reported together with morphology studies, doping dependence of growth rate and the influence of the C/Si- and Cl/Si-ratios on the growth rate and doping. In Paper 2 MTS is used for the growth of 200 μm thick epilayers at a growth rate of 100 μm/h, the epilayers are shown to be of very high crystalline quality and the growth process stable. The growth characteristics of the chloride-based CVD process, is further studied in Paper 3, where the approach to add HCl gas to the standard precursors silane and ethylene is used as well as the MTS approach. A comparison between literature data of growth rates for different approaches is done and it is found that a precursor molecule with direct Si-Cl bonds should be more efficient for the growth process. Also the process stability and growth rate dependence on C/Si- and Cl/Si-ratios are further studied. In Paper 4 the standard growth process for growth on 4° off axis substrates is improved in order to get better morphology of the epilayers. It is also shown that the optimized process conditions can be transferred to a chloride-based process and a high growth rate of 28 μm/h is achieved, using the HCl-approach, while keeping the good morphology. In Paper 5 chloride-based CVD growth on on-axis substrates is explored using both the HCl- and MTS-approaches. The incorporation of dopants in SiC epilayers grown by the chloride-based CVD process is studied in Papers 6 and 7 using the HCl-approach. In Paper 6 the incorporation of the donor atoms nitrogen and phosphorus is studied and in Paper 7 the incorporation of the acceptor atoms boron and aluminum. The incorporation of dopants is found to follow the trends seen in the standard growth process but it is also found that the Cl/Si-ratio can affect the amount of incorporated dopants.



# Sammanfattning

Kiselkarbid (SiC) är ett fascinerande material som samtidigt är mycket enkelt och mycket komplicerat. Det är enkelt eftersom det byggs upp av bara två sorters atomer, kisel och kol. Atomerna bygger upp kristallens struktur genom att bilda Si-C bindningar och man kan beskriva kristallstrukturen som uppbyggd av tetraedrar med en kiselatom (eller kolatom) i mitten och en kolatom (eller kiselatom) i varje hörn på tetradern. Samtidigt är SiC komplicerat eftersom beroende på hur man staplar dessa tetraedrar kan man få olika varianter på kristallstrukturen, så kallade polytyper. Det finns drygt 200 kända polytyper av kiselkarbid, men det är dock bara en handfull av dessa polytyper som är tekniskt intressanta. Kiselkarbid är intressant eftersom det är ett hårt material som inte heller påverkas nämnvärt av kemiskt aggressiva miljöer eller temperaturer upp till 2000 °C; dessutom är SiC en halvledare och tack vare dess tålighet är det ett mycket bra material för elektriska komponenter för högspänningselektronik eller för användning i aggressiva miljöer.

För att kunna tillverka dessa komponenter måste man kunna odla kristaller av kiselkarbid. Det finns i princip två typer av kristalldling; i) odling av bulkkristaller, där stora kristaller odlas för att sedan kan skivas och poleras till kristallskivor (dessa skivor benämns oftast substrat), och ii) odling av epitaxiella skikt, där man odlar ett tunt lager kristall med mycket hög renhet ovanpå ett substrat (ordet epitaxi kommer från grekiskans epi = ovanpå och taxis = i ordning, epitaxiella skikt odlas alltså ovanpå ett substrat och kopierar den kristallina ordningen hos substratet). I det epitaxiella skiktet, eller epilaget som det även kallas, kan man styra den elektriska ledningsförmågan med mycket hög precision genom att blanda in små mängder orenheter i epilaget, man pratar här om att dopa halvledarkristallen. För att odla epilager av SiC använder man CVD, CVD betyder Chemical Vapor Deposition, någon riktigt bra svensk översättning finns inte men det är en teknik för att framställa ett tunt lager av ett material genom kemiska reaktioner med gaser som startmaterial.

I standard CVD-processen för odling av SiC epilager använder man silan ( $\text{SiH}_4$ ) som kiselkälla och lätta kolväten som eten ( $\text{C}_2\text{H}_4$ ) eller propan ( $\text{C}_3\text{H}_8$ ) som kolkälla. Dessa gaser späds kraftigt ut i vätgas och man odlar epilaget vid ungefär 1500-1600 °C. Med denna process kan man odla ca 5 mikrometer (mikrometer = miljondelmeter) epilager på en timme. Men för vissa komponenter behöver man ett epilager som är över 100 mikrometer tjockt, vilket gör tillverkningen av sådana komponenter både tidsödande och kostsam. Ett problem som man måste lösa för att få högre tillväxthastighet i processen är att när man ökar mängden silan, kommer kiseldroppar att bildas i gasfasen och om de kommer i kontakt med substratet blir epilaget förstört. I denna avhandling undersöks ett sätt att lösa problemet med kiseldropparna och därmed kunna tillåta höga tillväxthastigheter för SiC epilager. Idén är att man kan lösa upp kiseldropparna genom att tillsätta något i gasblandningen som binder starkare till kisel än kisel. En mycket bra atom att använda för detta ändamål är klor eftersom klor binder mycket starkt till kisel. Man kallar denna process för klorid-baserad CVD.

Till att börja med använde vi molekylen metyltriklorsilan (MTS), som innehåller både kol, kisel och klor, för klorid-baserad tillväxt av SiC epilager. Genom att använda MTS lyckades vi få tillväxthastigheter mellan 2 och 104 mikrometer i timmen. Vi har även visat att det är möjligt använda MTS för att odla 200 mikrometer tjocka epilager med en tillväxthastighet på 100 mikrometer i timmen utan att den kristallina kvalitén på epilagren försämras. Ett alternativ till att använda MTS är att addera saltsyra (HCl) i gasform till standard processen. För att förstå den klorid-baserade processen bättre, jämfördes de olika alternativen med litteratordata från en process där man istället för vanlig silan hade använt triklorosilan (TCS) för att få en klorid-baserad

process. Det visade sig att MTS- och TCS-processerna krävde mindre kiselhalt i gasfasen för att få en hög tillväxthastighet, med andra ord var de mer effektiva. Vi förklarade detta med att eftersom dessa startmolekyler har tre kisel-kol bindningar är det enkelt att bilda  $\text{SiCl}_2$  molekylen, som har visat sig vara ett viktigt mellansteg i den klorid-baserade processen, eftersom man då bara behöver bryta kemiska bindningar. Om man istället börjar från silan och saltsyra måste kemiska reaktioner ske för att skapa kisel-kol bindningar och därmed  $\text{SiCl}_2$ .

När man odlar kristaller underlättar man tillväxten genom att preparera ytan på substratet med atomära steg. Om man tittar på ytan med atomär förstoring kan säga att ytan liknar en trappa, detta är bra eftersom atomerna som bygger upp epilaget gärna fastnar vid atomära steg eftersom de kan binda in till kristallen både neråt och åt sidan. Vi har optimerat standard processen för att få bättre morfologi, alltså en finare yta, när man odlar på substrat som har mindre andel atomära steg på ytan och visat att denna optimering går att överföra till en klorid-baserad process med hög tillväxthastighet. Vi har även visat att man kan använda den klorid-baserade processen för att odla epilager med hög tillväxthastighet på substrat helt utan atomära steg.

Slutligen har vi studerat doping av kiselkarbid vid höga tillväxthastigheter med den klorid-baserade processen, både n-typ doping (där man dopar med ämnen som har fler valenselektroner än kol och kisel så att man får ett överskott av elektroner i materialet) med kväve och fosfor, och p-typ doping (där man dopar med ämnen som har färre valenselektroner än kol och kisel så att man får ett underskott av elektroner i materialet) med bor och aluminium.

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# Included papers

## Paper 1

Very high growth rate of 4H-SiC epilayers using the chlorinated precursor methyltrichlorosilane (MTS)

H. Pedersen, S. Leone, A. Henry, F. C. Beyer, V. Darakchieva, E. Janzén

*Journal of Crystal Growth* 307 (2007) 334-340

## Paper 2

Very high crystalline quality of thick 4H-SiC epilayers grown from methyltrichlorosilane (MTS)

H. Pedersen, S. Leone, A. Henry, V. Darakchieva, P. Carlsson, A. Gällström, E. Janzén

*physica status solidi – rapid research letters* 2(4) (2008) 188-190

## Paper 3

Growth characteristics of chloride-based SiC epitaxial growth

H. Pedersen, S. Leone, A. Henry, A. Lundskog, E. Janzén

*physica status solidi – rapid research letters* 2(6) (2008) 278-280

## Paper 4

Improved morphology for epitaxial growth on 4° off-axis 4H-SiC substrates

S. Leone, H. Pedersen, A. Henry, O. Kordina, E. Janzén

*submitted for publication*

## Paper 5

Homoepitaxial Growth of 4H-SiC on On-Axis Si-face Substrates Using Chloride-based CVD

S. Leone, H. Pedersen, A. Henry, O. Kordina, E. Janzén

*Materials Science Forum* 600-603 (2009) 107-110

## Paper 6

Donor incorporation in SiC epilayers grown at high growth rate with chloride-based CVD

H. Pedersen, F. C. Beyer, J. Hassan, A. Henry, E. Janzén

*submitted for publication*

## Paper 7

Acceptor incorporation in SiC epilayers grown at high growth rate with chloride-based CVD

H. Pedersen, F. C. Beyer, A. Henry, E. Janzén

*submitted for publication*

## Further publications, not included in the thesis

### Journal papers:

Thick homoepitaxial layers grown on On-axis Si-face 6H and 4H-SiC substrates with HCl addition

S. Leone, H. Pedersen, A. Henry, S. Rao, O. Kordina, E. Janzén  
*in manuscript*

High 2DEG mobility of HEMT structures grown on 100 mm SI 4H-SiC substrates by hot-wall MOCVD

R. R. Ciechonski, A. Lundskog, U. Forsberg, A. Kakanakova-Georgieva, H. Pedersen, E. Janzén  
*in manuscript*

In-situ treatment of GaN epilayers in hot-wall MOCVD

R. R. Ciechonski, A. Kakanakova-Georgieva, H. Pedersen, A. Lundskog, U. Forsberg, E. Janzén  
*in manuscript*

High proton relaxivity for gadolinium oxide nanoparticles

M. Engström, A. Klasson, H. Pedersen, C. Vahlberg, P-O Käll, K. Uvdal  
*Magnetic Resonance Materials in Physics, Biology and Medicine* 19 (2006) 180-186

Towards Biocompatibility of RE<sub>2</sub>O<sub>3</sub> Nanocrystals – Water and Organic Molecules Chemisorbed on Gd<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub> Nanocrystals Studied by Quantum-Chemical Computations

H. Pedersen, L. Ojamäe  
*Nano Letters* 6(9) (2006) 2004-2008

IR and quantum-chemical studies of carboxylic acid and glycine adsorption on rutile TiO<sub>2</sub> nanoparticles

L. Ojamäe, C. Aulin, H. Pedersen, P-O Käll  
*Journal of Colloid and Interface Science* 296 (2006) 71-78

Surface interactions between Y<sub>2</sub>O<sub>3</sub> nanocrystals and organic molecules – an experimental and quantum-chemical study

H. Pedersen, F. Söderlind, R. M. Petoral, K. Uvdal, P-O Käll, L. Ojamäe  
*Surface Science* 592 (2005) 124-140

Synthesis and characterization of Gd<sub>2</sub>O<sub>3</sub> nanocrystals functionalised by organic acids

F. Söderlind, H. Pedersen, R. M. Petoral, P-O Käll, K. Uvdal  
*Journal of Colloid and Interface Science* 288 (2005) 140-148

### Conference papers:

Chloride-based SiC epitaxial growth

H. Pedersen, S. Leone, A. Henry, F. C. Beyer, A. Lundskog, E. Janzén

Oral presentation by H. Pedersen at European Conference on Silicon Carbide and Related Materials 2008

To be published in *Materials Science Forum*

Defects in chloride-based 4H-SiC epitaxy

F. C. Beyer, H. Pedersen, A. Henry, E. Janzén

Oral presentation by F. C. Beyer at European Conference on Silicon Carbide and Related Materials 2008

To be published in *Materials Science Forum*

Growth of thick 4H-SiC epitaxial layers on on-axis Si-face Substrates with HCl-addition

S. Leone, H. Pedersen, A. Henry, S. Rao, O. Kordina, E. Janzén

Poster presentation by S. Leone at European Conference on Silicon Carbide and Related Materials 2008

To be published in *Materials Science Forum*

Growth of 4H-SiC epitaxial layers on 4° off-axis Si-face substrates

A. Henry, S. Leone, H. Pedersen, O. Kordina, E. Janzén

Poster presentation by A. Henry at European Conference on Silicon Carbide and Related Materials 2008

To be published in *Materials Science Forum*

Photo-EPR studies on low-energy electron-irradiated 4H-SiC

P. Carlsson, N. T. Son, H. Pedersen, J. Isoya, N. Morishita, T. Ohshima, H. Itoh, E. Janzén

Poster presentation by P. Carlsson at European Conference on Silicon Carbide and Related Materials 2008

To be published in *Materials Science Forum*

Very high growth rate of 4H-SiC using MTS as chloride-based precursor

H. Pedersen, S. Leone, A. Henry, F. C. Beyer, V. Darakchieva, E. Janzén

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Very high epitaxial growth rate of SiC using MTS as chloride-based precursor

H. Pedersen, S. Leone, A. Henry, V. Darakchieva, E. Janzén

Oral presentation by H. Pedersen at European Conference on Chemical Vapor Deposition 2007

*Surface and Coatings Technology* 201 (2007) 8931-8934

Growth and Photoluminescence Study of Aluminium Doped SiC Epitaxial Layers

H. Pedersen, A. Henry, J. Hassan, J. P. Bergman, E. Janzén

Poster presentation by H. Pedersen at European Conference on Silicon Carbide and Related Materials 2006

*Materials Science Forum* 556-557 (2007) 97-100

Thick Epilayers for Power Devices

A. Henry, J. Hassan, H. Pedersen, F. Beyer, J. P. Bergman, S. Andersson, E. Janzén, P.

Godignon

Invited oral presentation by A. Henry at European Conference on Silicon Carbide and Related Materials 2006

*Materials Science Forum* 556-557 (2007) 47-52

4H-SiC Epitaxial Layers Grown on on-axis Si-face Substrates

J. Hassan, J. P. Bergman, A. Henry, H. Pedersen, P. J. McNally, E. Janzén

Poster presentation by J. Hassan at European Conference on Silicon Carbide and Related Materials 2006

*Materials Science Forum* 556-557 (2007) 53-56

**Licentiate Thesis in Physical Chemistry:**

Experimental and quantum-chemical studies of the surface interactions between organic molecules and nanocrystals of (a)  $\text{RE}_2\text{O}_3$  (RE = Y or Gd); and (b)  $\text{TiO}_2$

Linköping Studies in Science and Technology, Thesis No. 1198

Linköping University 2005

## *Part I:*

An introduction to the field



# Silicon Carbide

*Why even bother?*

Silicon Carbide (SiC) is a fascinating material. In one way it is very simple, there are only two atoms building up the crystal, silicon and carbon, where each atom is  $sp^3$ -hybridised and forms four bonds to four other atoms of the opposite kind. In another way, SiC is quite complicated. The crystal structure gives rise to polymorphism, which means that many polytypes of SiC can be found and today more than 250 polytypes are known [1]. Furthermore silicon carbide is a very hard material, on the hardness scale by Mohs where talc is given 1 and diamond is given 10, SiC has 9.3 [2]. Finally SiC is a semiconductor with a wide band gap of around 3 eV, depending on the polytype.

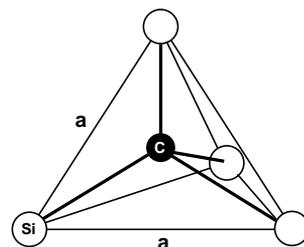
## 1.1 Crystal Structure

The SiC crystal is built up by equal amounts of silicon and carbon atoms. Each atom forms four bonds to four other atoms. The silicon atoms in the crystal are thus surrounded by four carbon atoms in a tetrahedral arrangement and the carbon atoms are surrounded by four silicon atoms in a tetrahedral arrangement as seen in Fig. 1.1. The side of the tetrahedron is equal to the lattice constant  $a$ , which is approximately 3.08 Å [3] and from geometrical considerations the Si-C bond can then be calculated to approximately 1.89 Å. The Si-C bond is considered to be 88 % covalent and 12 % ionic, where Si is considered as more positively charged [3].

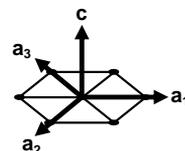
In crystallography the directions and planes in a crystal structure are described by the three Miller indices  $h$ ,  $k$  and  $l$ . But for hexagonal crystals, such as SiC, it is common to use four Miller indices;  $h$ ,  $k$ ,  $i$  and  $l$ , which are related to the four crystal axes in hexagonal crystals  $a_1$ ,  $a_2$ ,  $a_3$  and  $c$ , shown in Fig 1.2. The fourth Miller index is related to the other as  $i = -(h+k)$

therefore the notation  $(h\ k\ .\ l)$  sometimes is seen since  $i$  can be calculated from  $h$  and  $k$ . The SiC crystal can be thought of as being built up by hexagonally close packed layers that are stacked on top of each other along the  $c$ -axis. When one layer of close packed atoms is put on top another, it will not lay exactly on top, but slide with its atoms into the holes between the atoms in the first layer, position B in Fig. 1.3. The third layer can then go directly on top of the first layer (pos A), this will give a ABABAB... stacking which is a totally hexagonally close packed (*hcp*) structure, but the third layer can also go into position C in Fig. 1.3, so that the stacking ABCABC... is obtained which is a face centered cubic (*fcc*) structure.

But for SiC, it might be several hundreds of layer before the stacking repeats itself. This stacking of the atomic layers gives rise to the different polytypes of SiC. The naming of the polytypes follows the scheme proposed by Lewis S. Ramsdell 1947 [4]; the name of the polytype consists of a number and a letter, where the crystal structure (cubic, hexagonal or

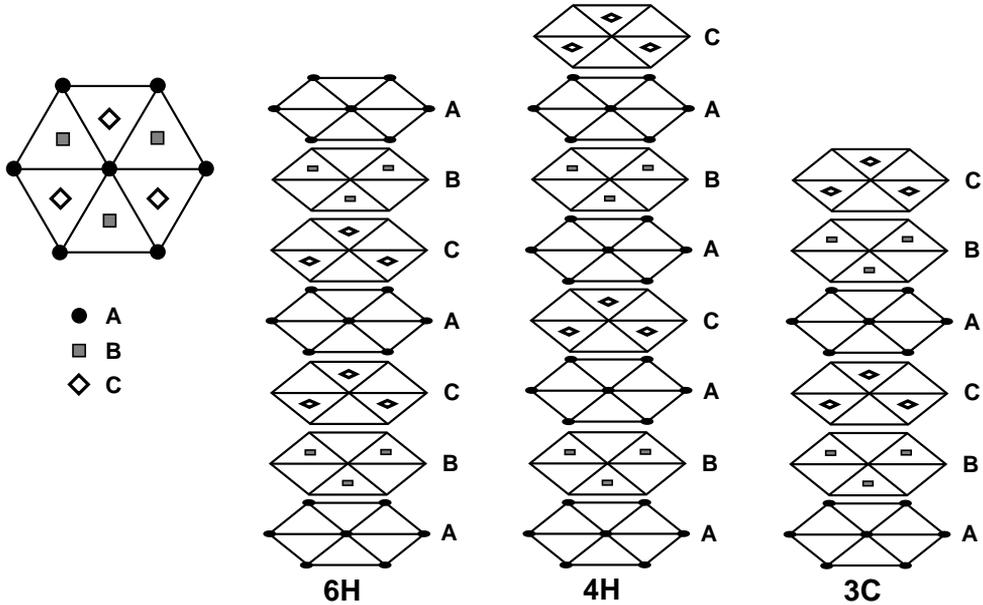


**Figure 1.1:** Tetrahedral arrangement of atoms in SiC



**Figure 1.2:** The four crystal axes in hexagonal crystals

rhombohedral) is indicated by a capital letter (C, H resp. R) and the number is the number of layers in one repeating unit. It is common to refer to the 3C-SiC (ABCABC... stacking) polytype as  $\beta$ -SiC, while the other polytypes are then called  $\alpha$ -SiC. The crystal structure of the 2H-SiC polytype (ABABAB... stacking) is the well known *wurtzite* structure and the structure of the 3C-SiC polytype is the *zincblende* structure.



**Figure 1.3:** Hexagonal close packing and stacking sequences for the three most common SiC polytypes.

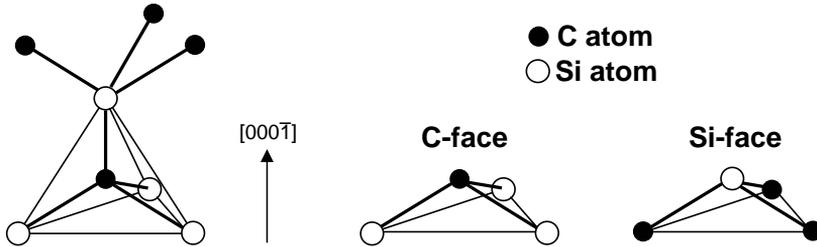
It has been found that the band gap increases more or less linearly with degree of hexagonality in the material [5], and a summary of band gap for different polytypes is given in Table 1.1.

**Table 1.1:** Band gap and percent hexagonality for some SiC polytypes [5, 6]

Polytype	Percent hexagonality	Band gap (eV)
3C	0	2.4
8H	25	2.8
6H	33	3.0
33R	36	3.0
15R	40	3.0
4H	50	3.2
2H	100	3.3

As SiC crystals are sliced into wafers, they are often sliced perpendicular to the c-axis since this is the standard growth direction. This means that the tetrahedrons that build up the crystal get their top chopped off and the Si-C bond is broken. This leads to a situation where one of the new crystal faces is terminated with silicon atoms and the other is terminated with carbon atoms, these faces are usually referred to as Si-face and C-face respectively, shown in Fig. 1.4. These

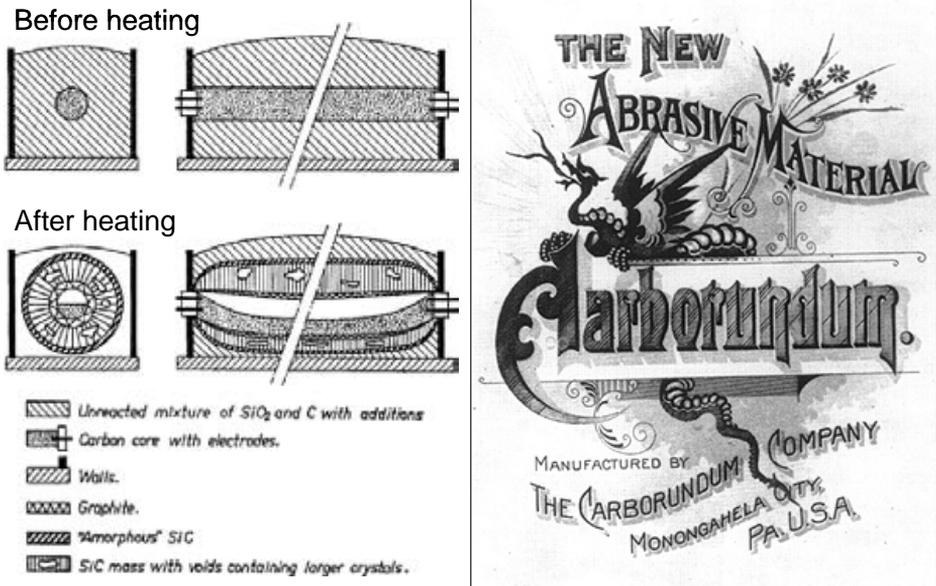
faces have different properties that will affect the amount of incorporated dopants and morphology during epitaxial growth.



**Figure 1.4:** When slicing SiC crystals into wafers, it is done perpendicular to the c-axis and one of the new crystal faces will then be carbon terminated and referred to as C-face, while the other face will be silicon terminated and referred to as Si-face.

## 1.2 History of SiC

The first report on silicon carbide was published 1824 by the Swedish chemist Jöns Jacob Berzelius [7], he discovered a compound where silicon and carbon were directly bonded to each other when he was studying silicon. The first to establish that SiC occurs in nature was Henri Moissan in 1905 when he investigated a meteorite from Cañon Diablo, Arizona, USA [8]. In mineralogy SiC is known as Moissanite. The first person to realize that one could make money out of SiC was Edward G. Acheson who constructed an electrical oven for the synthesis of “carborundum” to be used as abrasive material [9]. Acheson mixed carbon and silica ( $\text{SiO}_2$ ) with additions of alumina ( $\text{Al}_2\text{O}_3$ ), lime ( $\text{CaO}$ ) and salt ( $\text{NaCl}$ ) in the oven and heated until SiC crystals had been formed in the oven. In 1894 Acheson founded “US Carborundum Abrasives Co” and was thereby the first to make money of SiC; the company still exists. In Fig. 1.5 a schematic picture of an Acheson furnace is described together with an advertisement for Carborundum Abrasives.



**Figure 1.5:** Left: A schematic picture of a Acheson furnace for synthesis of carborundum (silicon carbide) [3], right: Advertisement for Acheson’s company U S Carborundum Abrasives Co, the first company to make money of SiC.

When solid-state electronics began to emerge in the 1950's, SiC was one material that attracted interest. But crystals from the Acheson process were not of sufficient quality for such studies. But in 1955 J. A. Lely presented a sublimation process for producing single crystals of high quality [10], this was the boost that the semiconductor SiC needed and in 1958 the first SiC conference was held in Boston. However, the rapidly emerging silicon technology held back the SiC research during the 1960's and 70's and work on SiC was mainly carried out in the former Soviet Union. In 1978 Tariov and Tsvetkov presented the seeded sublimation growth technique to grow SiC bulk crystals [11], which means that now it was possible to make SiC wafers and the SiC research again gained speed. In 1981 Matsunami demonstrated that it is possible to grow cubic single crystalline SiC on silicon substrates [12], this was an important breakthrough since the available SiC substrates at that time was small and of irregular shape. In the 1990's, limitations to the silicon and III-V technologies began to emerge and the interest for SiC started to grow and has been substantial since then. Today it is possible to purchase SiC wafers of very high quality and a diameter of 100 mm as well as Schottky diodes and MESFET made of SiC [13].

### 1.3 SiC as a semiconductor

Silicon Carbide is a semiconductor with a wide indirect band gap. Although initial interest in SiC was directed towards its hardness and applications as abrasive, the very first reports of electroluminescence was reported from experiments with SiC already in 1907 [14]. Some important electrophysical parameters of various semiconductor materials are listed in Table 1.2.

**Table 1.2:** Some electrophysical parameters of some semiconductor materials [15, 16]

Material	$E_g$ (eV)	$T_{operation}$ (K)	$\lambda$ ( $W\ cm^{-1}\ K^{-1}$ )	$E_{critical}$ $10^5$ ( $V\ cm^{-1}$ )
Si	1.1	410	1.5	2.0
GaAs	1.4	570	0.45	2.6
GaP	2.2	800	0.7	4.5
4H-SiC	3.2	1230	5-7	20-30
6H-SiC	3.0	1200	5-7	21
GaN	3.4	1250	1.3	14
AlN	6.2	2100	2	-
Diamond	5.4	2100	22	100

Note:  $E_g$  – band gap,  $T_{operation}$  – maximum operation temperature,  $\lambda$  – thermal conductivity,  $E_{critical}$  – critical breakdown field.

The high critical breakdown field of SiC makes it a material well suited for high voltage devices, the high operation temperature and high thermal conductivity of SiC combined with its hardness and robustness against chemicals make it a material ideal for sensors in harsh environments such as exhausts [17-19].

# Crystal Growth

## *Ordering chaos*

Today's modern semiconductor technology is totally dependent on crystal growth. A crystal is a state of very high order and symmetry, and whether one starts from vapor or liquid, to grow a crystal one needs to order a system of atoms with initially very low order. In other words, the entropy of the system has to be lowered which requires energy, which is why crystal growth is done at high temperatures as seen below. The starting point for every semiconductor component is a crystal growth process. First one needs a big single crystal of high quality that is sliced into wafers that are polished to an atomically well defined surface. The wafers are then the substrates onto which the epilayer, which is an additional layer of single crystal with very precisely controlled doping level, is grown. The crystal then undergoes further processing, e. g. etching, ion implantation and contacting, before the devices are complete.

## 2.1 Bulk Crystal Growth

When growing single crystals of semiconductor materials one is often forced to use gaseous species. There are however exceptions and silicon is perhaps the most well known example of them. Silicon bulk crystals are grown by the Czochralski method [20], named after the polish chemist Jan Czochralski who discovered the method in 1916. The method was initially used for measuring the crystallization rate of metals such as tin, zinc and lead. For crystal growth the method is elegant in its simplicity; the starting (polycrystalline) material is melted and a starting seed is lowered into the melt. As the seed is slowly pulled up material is crystallized onto the seed and a long single crystal is pulled out of the melt.

Silicon carbide bulk crystals can not be grown from melt since the solubility of carbon in molten silicon is too low. There have been attempts to grow SiC from melt by adding a transition metal such as Scandium (Sc) to the melt and thereby making a ternary solution in which carbon can be dissolved to a higher extent [21], but the activity has been focused towards epitaxial growth (see below). Instead bulk SiC crystals are grown by sublimation, where SiC powder is heated in a closed vessel to temperatures in the 2200-2400 °C range. The SiC powder then decomposes to the gaseous species  $\text{SiC}_2$ ,  $\text{Si}_2\text{C}$  and Si that are sublimed onto a SiC substrate mounted on the ceiling of the crucible. The driving force for the process is a temperature gradient between the somewhat warmer SiC source and the substrate [22]. As an alternative to sublimation from powder, a technique for bulk growth from gases called High Temperature Chemical Vapor Deposition (HTCVD) [23] has been developed. This technique takes advantage of the high purity that can be obtained for gases such as silane ( $\text{SiH}_4$ ) and ethylene ( $\text{C}_2\text{H}_4$ ), and a crystal of very high purity can therefore readily be grown; a further advantage is that the source gases can be fed into the reactor during growth, while in sublimation growth the amount of SiC powder is fixed from start and when it is consumed the process must be stopped. Although the process has been developed from chemical vapor deposition, it can be described as gas fed sublimation where small  $\text{Si}_x$  clusters are first formed from  $\text{SiH}_4$ ; these clusters are then allowed to react with

$C_2H_4$ , or fragments of it, to form more stable  $Si_xC_y$  species [24] which are species found also in normal sublimation growth.

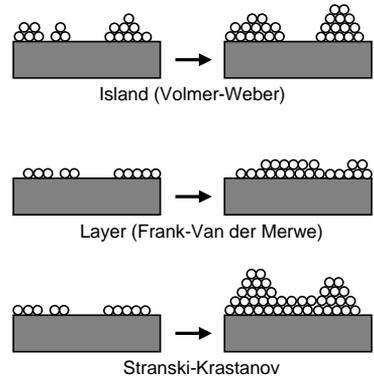
## 2.2 Epitaxial Growth

The word epitaxy comes from the Greek words  $\epsilon\pi\iota$  (epi, placed or resting upon) and  $\tau\alpha\chi\iota\zeta$  (taxis, arrangement) so epitaxial growth is ordered growth on top of something. When making semiconductor devices, the growth of epilayers is a very important step. The device to be produced determines the doping type and doping level and the thickness that are needed for the epilayer. Most devices require multi layers with alternating doping type and/or doping level. Furthermore, the quality of the epilayer determines the performance of the device. If the epilayer has a high density of crystal structural defects, *e.g.* stacking faults and dislocations, the performance of the final device will be affected in a negative way.

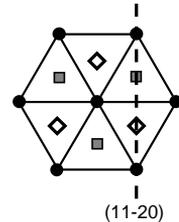
If the epilayer is of the same material as the substrate used, the growth is referred to as homoepitaxial growth, *e.g.* SiC grown on SiC. While if the substrate and epilayer are of two different materials the growth is called heteroepitaxial growth, *e.g.* SiC grown on Si. The reasons for growing heteroepitaxially might be that there are no available substrates of the material to be grown or the available substrates are of high cost and/or low quality. The main problem with heteroepitaxial growth is lattice mismatch. Since it might be impossible to find a substrate material that has the same lattice parameter as the epilayer material, the epilayer will have built in stress.

The initial stage of crystal growth on a surface is ideally classified into three types of growth mode, schematically shown in Fig 2.1. Island growth is growth from small clusters that nucleate on the surface and grow in three dimensions, this growth mode occurs when the atoms in deposit are more strongly bound to each other than to the substrate. This growth mode is common in heteroepitaxial growth. If on the other hand the atoms are more strongly bound to the substrate than to each other, the growth from the initial nucleus will occur only in two dimensions and this will result in a layer growth, which is common in homoepitaxial growth. A combination of the layered and island growth is the Stranski-Krastanov growth mode, here the growth starts by a layered growth that collapses after a few layers and then turns to island growth [25].

In the early days of SiC epitaxy, the SiC substrates available were small and of poor quality which means that homoepitaxial growth needed very high temperatures, around 1800 °C, and a lot of the epitaxial growth activity was directed towards heteroepitaxial growth of 3C-SiC on silicon substrates. One of the most important breakthroughs in SiC technology, and perhaps the most important breakthrough in epitaxial growth of SiC came in the late 1980s when Matsunami and co-workers demonstrated homoepitaxial growth of 6H-SiC on off-axis wafers, and growth temperature could then be lowered with several hundred degrees [26]. The idea is that if the SiC crystal is sliced with a slight off angle to the c-axis, the surface of the wafer will have a lot of atomic steps, and layered growth will then be favored over island growth. The off-angle is mainly towards the [11-20] direction since the (11-20) plane is the plane with the highest atom density, as seen in Fig. 2.2, and an off-cut towards this plane will then have the highest density of atomic steps. A schematic view of off-cut slicing of a SiC bulk crystal is given in Fig. 2.3. Today the standard off-axis angles are 8° for 4H-SiC and 3.5° for 6H-SiC

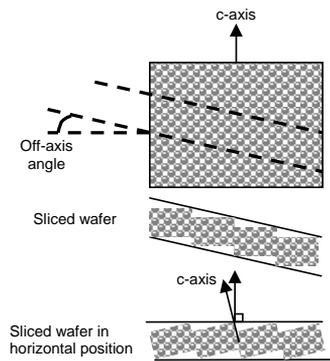


**Figure 2.1:** Schematic view of the three types of growth mode.



**Figure 2.2:** The SiC crystal viewed along the C-axis with the (11-20) plane indicated.

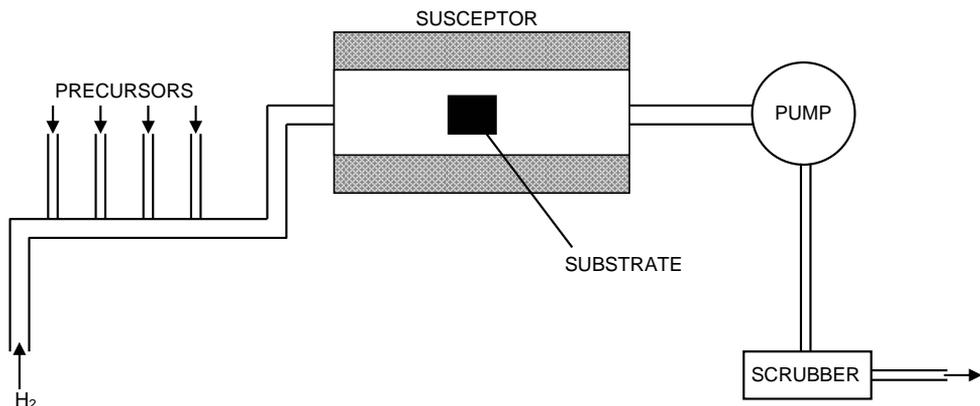
respectively, and off-axis growth has enabled homoepitaxial growth of thick epilayers on large area substrates. There is however a downside to the growth on off-axis substrates; basal-plane dislocations can propagate through the epilayer and thereby affect the performance of a device made from it. In addition a large amount of the SiC bulk crystal that is grown along the c-axis is wasted when cutting the wafers off-axis. A great deal of effort is today directed towards growth on substrates with a lower off-cut, typically  $4^\circ$  for 4H-SiC, and wafers that has zero off-angle *ie* wafers cut on-axis. For growth of 3C-SiC, silicon is still used as substrates although efforts to reduce strain in the epilayers have improved the quality of the grown material [27]. Epitaxial growth of SiC is most often done from gases; there have been reports on sublimation epitaxial growth in order to achieve higher growth rates [28, 29] and also studies to grow SiC epilayers by various types of liquid phase epitaxy (LPE) have been done [21, 30] as well as various types of molecular beam epitaxy (MBE) are used for growth of thin 3C-SiC epilayers on Si-substrates [31, 32].



**Figure 2.3:** Schematic view of off-axis slicing of a SiC bulk crystal resulting in a surface with atomic steps.

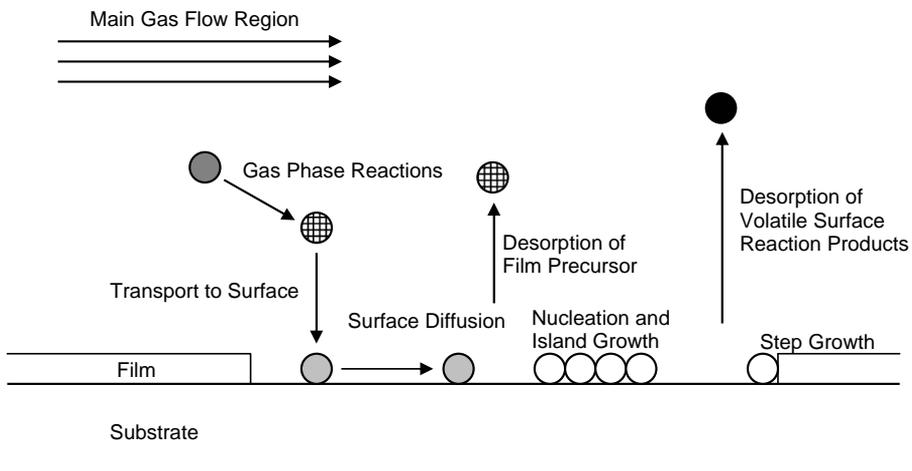
### 2.3 Chemical Vapor Deposition

The most established method for growing epitaxial layers of semiconductors is chemical vapor deposition (CVD). However, CVD is not only used for semiconductor growth, a wide range of coatings and thin films are grown by CVD. In CVD thin films of a solid material, single crystalline, poly crystalline or amorphous, are synthesized from gases by a number of chemical reactions. The chemical reactions are what distinguish CVD from other deposition process commonly used for deposition of thin films such as sputtering and evaporation, which are collected under the name of physical vapor deposition (PVD). The reason why CVD is the most established technique for semiconductor epitaxial growth is that the atoms needed to build up the epilayer are supplied to the process as gases which can be delivered from manufacturers with a very high level of purity which enables the growth of very pure crystals. It is important to keep in mind that the property of a semiconductor crystal is to a high extent modified by foreign atoms and any unwanted atoms in a semiconductor crystal that is to be used for a device might alter the performance of the device.



**Figure 2.4:** Schematic view of a CVD reactor configuration.

A CVD reactor consists, Fig. 2.4, schematically of a gas handling and mixing system where carrier gas, often hydrogen gas or some inert gas such as argon, is mixed with the gases containing the atoms needed to build up the crystal; these gases are named *precursors*. The precursors are either common gases that can easily be purchased in a normal gas bottle, *e.g.* silane ( $\text{SiH}_4$ ), ammonia ( $\text{NH}_3$ ) and carbon dioxide ( $\text{CO}_2$ ), or gaseous species that are formed by chemical reactions, *e.g.* aluminumtrichloride ( $\text{AlCl}_3$ ) that is formed by passing hydrochloric acid (HCl) over aluminum powder. The gas mixture is then led into the *susceptor* where the growth or deposition takes place. The temperature in the susceptor varies over several hundreds of degrees depending on which material is to be deposited. The susceptor geometry can be either horizontal where the substrates are placed on the floor which eliminates sample mounting problems, or the susceptor could have a vertical geometry where the substrates need to be mounted in some way which could induce stress in the material. Another important difference between susceptors is the cold- or the hot wall design. In a cold wall susceptor the substrate is heated from only one side leading to large temperature gradients where the substrate is hot and just a few millimeters above it, the temperature can be much lower. In a hot wall susceptor the susceptor is heated from top, bottom and both sides, leading to a much more uniform heat distribution inside leading to less bowing of the substrate, higher uniformity of growth rate and doping due to more uniform distribution of chemical species in the susceptor and over the substrate and higher cracking efficiency of the precursors. The design of the susceptor can vary substantially depending both on the material to be deposited and the substrate material. Semiconductor materials are grown on flat wafers and multi wafer reactors that are loaded with several wafers are today standard in the semiconductor industry. During the deposition process, gases flow over the substrate and new precursor molecules are continuously reaching the susceptor; this means that the CVD reactor needs a pump to function. Usually a reactor has two pumps, one process pump capable of pumping out the gas that is flowing through the reactor and also a turbo molecular pump that is used to evacuate the reactor prior to growth. It is important to have a low pressure prior to the growth since any residual gas in the susceptor can lead to unwanted side reactions or doped semiconductor crystals. After the pump the gases are passed through a *scrubber* which is a system for removing any toxic molecules from the gas mixture. The scrubber can be *e.g.* a water bath with either high or low pH value, a container with granulates of an adsorbing material or a burner that burns the gases, depending on the particular CVD process.



**Figure 2.5:** Schematics of gas phase reactions and transport processes contributing to film growth by CVD, from [33].

Several processes take place in the susceptor; gas phase reactions, mass transport, adsorption, desorption, surface diffusion, step growth and nucleation are the most important ones. In Fig. 2.5 a schematic picture of the transport and reaction processes occurring during CVD growth is shown.

It can be seen from Fig. 2.5 that CVD is a truly multidisciplinary technique. Besides chemistry one needs knowledge of mass transport, flow dynamics, thermodynamics and crystallography to fully understand the CVD process. And when trying to understand the whole CVD reactor one also needs knowledge on vacuum technology and induction heating.

Typical SiC CVD homoepitaxial growth is done using silane ( $\text{SiH}_4$ ) as silicon precursor and light hydrocarbons *e.g.* ethylene ( $\text{C}_2\text{H}_4$ ) or propane ( $\text{C}_3\text{H}_8$ ) as carbon precursor and hydrogen gas, sometimes mixed with some argon, is used as carrier gas. The growth temperature and pressure is usually between 1500-1650 °C and 100-1000 mbar. The hot wall design [34] is today the dominating susceptor design although the cold wall design is still used. An intermediate design has been developed during the last years called warm wall [35] where the susceptor walls are heated to a less extent than in hot wall, this to even out the temperature gradient but avoiding unwanted polycrystalline SiC deposition on the ceiling and walls, a problem with the hot wall design that can lead to down fall of small SiC particles. The typical growth rate in SiC epitaxy is  $\sim 5 \mu\text{m/h}$ .

When the atom needed for the crystal can not be found as part of a gaseous molecule as is the case for most metals, one can either flow hydrochloric acid over a powder or a melt of the metal to make volatile metal chlorides that can be mixed into the gas mixture or one can use metal organic molecules that are also volatile compounds although liquid at room temperature. When using metal organic molecules as precursors in CVD it is common to refer to the process as MOCVD. Since metal organics are both very toxic and self ignite in air, they are kept in bubblers which are closed containers where the carrier is allowed to bubble through the liquid and then the metal organics are dissolved into the carrier gas and can thereby be delivered to the gas mixture. In the semiconductor industry MOCVD is used extensively to grow III-nitrides and III-V compounds.

Other types of CVD processes commonly found in the literature are laser- and plasma enhanced CVD. In laser enhanced CVD a laser is used either to write patterns on the substrate leading to very local heating enabling patterned growth, referred to as pyrolytic LECVD, or a laser can be used to decompose the precursor molecules in the gas phase which is photolytic LECVD. In plasma enhanced CVD (PECVD), electric discharge is used to decompose molecules in the gas phase to atoms, ions, molecular fragments in various charge states and free radicals. The electric discharge allows this to happen at substantially lower temperatures than thermally activated CVD processes making PECVD a method well suited for growth at low temperature [36].



# Chloride-based Growth

## *Changing chemistry*

The growth of SiC epilayers is, as has been pointed out in the previous chapter, a slow process. A 10 kV blocking device will need an epilayer thicker than 50  $\mu\text{m}$  with a low n-type doping [37], the cost of the long time growth process will be a substantial part of the cost of the final device. The main problem when trying to increase the growth rate by increasing the amount of precursors in the gas mixture, is homogeneous nucleation in the gas phase, *i.e.* silicon droplets will form due to the high silicon concentration in the gas and fall down on the substrate destroying the growing epilayer. There has been three ways to get around this problem; i) increase the growth temperature to dissolve the silicon droplets [38], ii) decrease the pressure in the process to get a lower partial pressure of silicon and a higher gas velocity through the susceptor, this lowers the probability of droplet formation and any formed drops will be transported out of the susceptor faster [39], or iii) add something to the gas mixture that binds stronger to silicon than silicon, and a good candidate here is would be some halogen atom. The standard bond enthalpies for the Si-Si, Si-F, Si-Cl, Si-Br and Si-I bonds are 226, 597, 400, 330, 234  $\text{kJ mol}^{-1}$ , or 2.34, 6.19, 4.15, 3.42, 2.42 eV respectively [40]. The best choice here is chlorine since bromine and iodine are too large atoms and have weak bonds to silicon and fluorine has too strong bond to silicon. Chlorinated compounds are also available in high purity. Addition of chloride to the gas mixture during growth changes the chemistry of the growth process and perhaps the most obvious change is the elimination of the silicon droplets. But the chlorine addition brings more to the growth process since the most important Si-specie will now be  $\text{SiCl}_2$  which has other properties than  $\text{SiH}_2$ , the dominating specie for standard growth conditions.

### 3.1 Growth of Silicon epilayers

The perhaps most mature semiconductor material today is silicon, and although the semiconductor properties of silicon is different from those of silicon carbide, a lot can be learnt from the silicon industry. Chloride-based growth of silicon epilayers was first reported by Theuerer in 1961 [41], where a CVD process with tetrachlorosilane in hydrogen was used to deposit silicon epilayers with a growth rate as high as 300  $\mu\text{m/h}$ . Today the majority of the silicon epilayers is produced by some chloride-based process and it is mainly silane molecules with 2 (dichlorosilane - DCS,  $\text{SiH}_2\text{Cl}_2$ ), 3 (trichlorosilane - TCS,  $\text{SiHCl}_3$ ) or 4 (tetrachlorosilane - TET,  $\text{SiCl}_4$ ) chlorine atoms that are used; TCS and TET are liquids at room temperature while DCS is a gas (boiling point: 8.3  $^\circ\text{C}$ , [42]). Normal silane,  $\text{SiH}_4$ , with addition of HCl is not commonly used in epitaxial growth. Since DCS is a gas at room temperature, it is mostly used for reduced pressure processes. For atmospheric pressure processes, TCS is preferred over TET but for high temperature processes TET is easier to handle and gives less unwanted deposition [43]. The main use for HCl in silicon epitaxial growth is as etching agent. Prior to growth the wafer surface is etched with a small flow of HCl inside the CVD reactor to remove the natural silicon dioxide that is always present on the surface, even after the wet cleaning of the wafer. After growth the reactor is cleaned with a large flow of HCl to remove any deposited silicon in the susceptor and quartz tube, a flow of several tens of liters per minute is used and the etching rate

is about 7  $\mu\text{m}/\text{min}$  [44]. It should be noted that growth of silicon epilayers is done at much lower temperatures ( $\sim 1000\text{-}1200\text{ }^\circ\text{C}$ ) than growth of SiC epilayers ( $\sim 1500\text{-}1800\text{ }^\circ\text{C}$ ). This is due to the fact that the silicon crystal is a much simpler crystal consisting of only *one* sort of atoms, and furthermore the melting point of silicon is 1414  $^\circ\text{C}$  [42] which sets an upper temperature limit. The lower growth temperature and the high growth rate, in the order of a few  $\mu\text{m}/\text{min}$ , have allowed the development of the rapid thermal CVD (RT-CVD), which is done in a cold wall reactor; a single wafer is loaded into the growth zone from a cassette filled with wafers and the growth zone is rapidly heated by lamps. An epilayer is then grown in a few minutes. The rapid heating and cooling, allowed by a very small thermal mass in the reactor, make the total process time for each wafer very short [45].

### 3.2 Growth of Silicon Carbide epilayers

For growth of SiC epilayers by chloride-based growth, addition of chlorine to the gas mixture can be done in four ways; i) add a flow of hydrochloric acid (HCl) gas to the standard precursors, ii) replace the silane with a chlorinated silane molecule ( $\text{SiH}_x\text{Cl}_y$ ), iii) replace the carbon precursor with a chlorinated hydrocarbon molecule ( $\text{CH}_x\text{Cl}_y$ ) or iv) use a molecule that contains both silicon, carbon and chlorine ( $\text{SiC}_x\text{Cl}_y\text{H}_z$ ). Results from all these approaches have been reported for homoepitaxial growth and are shortly reviewed below.

#### HCl

Initially HCl was used together with hydrogen gas for etching the substrate surface prior to growth. Addition of HCl during the etch process increases the etching rate and produces a stepped surface [46-48] which will favor step-flow growth. However in these studies there was no HCl-flow during growth. The use of HCl as a growth additive was initially used as an etching agent *during* growth to etch away 3C inclusions during on-axis growth of 6H-SiC [49] and the target in this study was not high growth rate but polytype stability. The first papers on a chlorinated growth process with a high growth rate were reported during the European Conference on Silicon Carbide and Related Materials 2004 (ECSCRM04) when Crippa *et al* [50] reported 20  $\mu\text{m}/\text{h}$  for a process with HCl added to the standard precursors in a hot-wall CVD reactor and Myers *et al* [51] reported 55  $\mu\text{m}/\text{h}$  for a similar process. The process was then further developed and also results from Schottky diodes made from grown material were reported [52, 53]. A paper reporting a growth rate of 112  $\mu\text{m}/\text{h}$  was published in 2006 [54] and these results were also presented at the European Conference on Silicon Carbide and Related Materials 2006 (ECSCRM06) [55]. The process has also been optimized by optical and electrical characterization of the grown epilayers [56]. Very recently the HCl-approach has also been optimized for growth on 4 $^\circ$  off-axis 4H-SiC substrates where growth of very high quality 38  $\mu\text{m}$  thick epilayers on 3" wafers been grown at 7  $\mu\text{m}/\text{h}$  [57] and an even higher growth rate of 28  $\mu\text{m}/\text{h}$  with high quality morphology has also been demonstrated [58].

#### $\text{SiH}_x\text{Cl}_y$

The approach to use a chlorinated silane molecule instead of normal silane in a high growth rate process was first reported by using tetrachlorosilane ( $\text{SiCl}_4$ ); TET and propane at high temperatures, up to 1850  $^\circ\text{C}$ , in a hot-wall CVD reactor. Growth rates up to 200  $\mu\text{m}/\text{h}$ , high crystalline quality and the growth rate dependence on temperature were reported [59, 60]. The process has been further developed by the studies of the defects in the grown epilayers using X-ray topography [61] and demonstration of thick, heavily p-type doped layers [62].

The use of trichlorosilane ( $\text{SiHCl}_3$ ): TCS as chlorinated silicon precursor was first reported at the International Conference on Silicon Carbide and Related Materials 2005 (ICSCRM05) [63] where  $\text{SiHCl}_3$  and ethylene were used as precursors in a hot-wall CVD reactor at a growth rate of 16  $\mu\text{m}/\text{h}$ . This process has been further developed and growth rate higher than 100  $\mu\text{m}/\text{h}$  has been reported [55] and later also successful growth of 100  $\mu\text{m}$  thick layers grown on 8 $^\circ$  off-axis

substrates and 40  $\mu\text{m}$  thick layers grown on  $4^\circ$  off-axis substrates [64]. The TCS-process has also been used to grow thin device structures with very abrupt junctions [65].

Also chlorosilane ( $\text{SiH}_3\text{Cl}$ ) has been used as chlorinated silicon precursor together with propane in a hot-wall CVD reactor. Initially a growth rate of 20  $\mu\text{m}/\text{h}$  together with device results was reported [66], and the process was then later scaled up to work in a multi-wafer ( $5\times 3''$ ) CVD reactor producing thinner epilayers (20-30  $\mu\text{m}$ ) of very high quality [67].

### $\text{CH}_x\text{Cl}_y$

Use of a chlorinated carbon precursor has been limited to using chloromethane ( $\text{CH}_3\text{Cl}$ ). The first report of growth from  $\text{CH}_3\text{Cl}$  and silane was done in a hot-wall CVD reactor at 1600  $^\circ\text{C}$  giving a growth rate of 7  $\mu\text{m}/\text{h}$  with good morphology [68]. The growth rate was then further increased to 10  $\mu\text{m}/\text{h}$  at 1600  $^\circ\text{C}$  and more than 20  $\mu\text{m}/\text{h}$  for 1700  $^\circ\text{C}$ . Comparisons to the standard process showed at least double growth rate for the  $\text{CH}_3\text{Cl}$  process [69]. The growth activity using  $\text{CH}_3\text{Cl}$  was then shifted towards low temperature; homoepitaxial growth of 4H-SiC at temperatures as low as 1300  $^\circ\text{C}$  and nice morphology and a growth rate of about 2  $\mu\text{m}/\text{h}$  were reported [70, 71]. The process was then further developed, by addition of HCl, and the growth rate could be increased to 7  $\mu\text{m}/\text{h}$  and the morphology improved. Nitrogen and aluminum doping were also studied [72]. The gas phase- and surface chemistry of the low temperature process using  $\text{CH}_3\text{Cl}$ , with and without addition of HCl, have been further studied and a mechanism where  $\text{Si-Si}_x\text{C}_{1-x}$  clusters are formed in the gas phase, similar to what happens in SiC growth by HTCVD, was suggested to explain the trends [73]. A more in depth nitrogen doping study has recently been reported for the low-temperature process with silane and chloromethane without HCl-addition [74]. The advantage of a low temperature process is the possibility to use a mask on the substrate to get selective area growth. This has been realized for the  $\text{CH}_3\text{Cl}$  process by using a  $\text{SiO}_2$  mask on 4H-SiC substrates [75-77].

### $\text{SiC}_x\text{Cl}_y\text{H}_z$

The use of a single molecule approach for homoepitaxial chloride-based growth of SiC was first reported already 1969 [78] where the molecule methyltrichlorosilane – MTS ( $\text{SiCl}_3\text{H}_3$ ) was used to grow 3C-SiC epilayers on 3C-SiC crystals grown from melt. Epitaxial growth was achieved and the authors found a better morphology for epilayers grown using MTS than silane plus propane. The first report of growth of hexagonal SiC grown from MTS was published in 1995 where 6H-SiC was grown in a hot wall CVD reactor [79], however no growth rate was reported. The first report of a high growth rate process using MTS was done by Lu *et al* 2005 [80] where MTS was used to grow 4H- and 6H-SiC epilayers at growth rates up to 90  $\mu\text{m}/\text{h}$  in a cold wall CVD reactor. Further studies of the morphology dependence of the  $\text{H}_2/\text{Ar}$  ratio of the carrier gas and structural defects were published later [81] by the same group. The first report of homoepitaxial growth of 4H-SiC in a hot wall CVD-reactor with growth rates up to 104  $\mu\text{m}/\text{h}$  was published in 2007 [82], background doping behavior and growth rate dependence on C/Si- and Cl/Si-ratios were also reported [83], C/Si- and Cl/Si-ratios were varied by adding silane and/or ethylene. A growth rate of 170  $\mu\text{m}/\text{h}$  has been demonstrated [84] as well as growth of very thick epilayers using MTS [85]. High growth rate processes (up to 20  $\mu\text{m}/\text{h}$ ) for homoepitaxial growth on on-axis substrates, using MTS with or without additional HCl, have also been reported [86].

At the First International Conference on Amorphous and Crystalline Silicon Carbide and Related Materials in Washington DC in 1987 Nishino and Saraie reported the growth of single crystalline 3C-SiC on silicon substrates by using MTS as precursor [87]. Chiu *et al* published the growth of epilayers with highly preferred orientation in a low pressure hot wall CVD reactor [88]. The use of a single molecule precursor was motivated by the possibility to lower the process temperature and in 1995 Kunstmann *et al* reported the use of several *brominated* single molecule SiC precursors as well as MTS. They used a cold-wall CVD reactor and were able to get a higher growth rate for

methyltribromosilane than for MTS but the material was of lower quality, most likely due to lower quality of the starting material [89, 90]. They were also able to eliminate the use of a carbon buffer layer in the growth [91]. The process was further developed and a new temperature profile during the initial stage of the growth led to improved quality of the grown material and decreased interfacial stress; epilayers as thick as 100  $\mu\text{m}$  were demonstrated [92]. Studies of the initial stage of the growth were done by growing very thin layers, 3-1200 nm [93] and also pseudomorphic growth (growth where the epitaxial layer adopts the crystal structure of the substrate rather than its normal crystal structure) of very thin epilayers has been reported [94]. To study the kinetics of the growth *in situ*, growth was done in a thermogravimeter equipped with a hot-wall CVD reactor and the growth rate dependence on temperature and MTS pressure was investigated [95]. In a more recent paper the growth of 3C-SiC on Si using MTS with good morphology and surface adhesion is reported [96].

Growth of 3C-SiC from MTS has also been done on graphite substrates [97-105] which allows higher growth temperatures but the growth is no longer epitaxial. This has been reported already 1967, when 0.5 mm thick yellow transparent crystals were grown [97]. Later even thicker crystals ( $\sim 1.5$  mm) were grown with high crystalline quality [102], and the effect of addition of extra HCl to the process has been studied [104]. Also molybdenum wires have been used as substrates for growth of 3C-SiC using MTS [106].

MTS has also been used as precursor for growth of (small, needle-like) single crystals of 2H-SiC [107] and this process has been used to produce samples for fundamental studies of this rare SiC polytype [108]. A CVD process for growth of polycrystalline 3C-SiC bulk material using MTS as single precursor with growth rates up to 100  $\mu\text{m}/\text{h}$  has been developed [109]. Other use of MTS has been for the application of silicon carbide as a protective coating on metals and ceramics materials which is done by CVD methods [110]. Growth of SiC fibers can also be done from MTS using laser CVD [111].

Since the growth of SiC using MTS has attracted so much interest, several studies aiming to understand fundamental chemical aspects of the process have been conducted. The effect that the HCl formed in the process has on the 3C-SiC surface, has been studied in ultra high vacuum by Auger electron spectroscopy [112] and studies of what happens in the gas phase, both by using theoretical calculations of the decomposition of the MTS molecule [113-117] and by using thermodynamic calculations together with analysis of the process exhaust gas by gas chromatography [118] have been done. All studies agree on one thing; the Si-C bond in the MTS molecule breaks, so there will not be any species having a Si-C bond which will build up the crystal as one might be tempted to think. The key to the higher growth rates and lower growth temperatures lies elsewhere as seen below.

### 3.3 Growth of Silicon Carbide bulk crystals

A chloride-based process for growth of bulk SiC crystals has been developed and was first presented at the International Conference on Silicon Carbide and Related Materials 2003 (ICSCRM03) [119]. The process is like other bulk processes a high temperature process (1900-2150  $^{\circ}\text{C}$ ) and the precursors used are tetrachlorosilane and propane and hydrogen carrier gas. The initial paper reported a maximum observed growth rate of 180  $\mu\text{m}/\text{h}$  and the growth of 6H-SiC crystals with 50 mm diameter and 1 mm thickness having low boron and aluminum background doping and high crystalline quality [119]. The process was further developed and growth rates up to 250  $\mu\text{m}/\text{h}$  and nitrogen and boron concentrations in the  $10^{14}$  atoms  $\text{cm}^{-3}$  range were reported together with dislocation studies [120]. A growth rate of 300  $\mu\text{m}/\text{h}$  together with growth rate dependence of temperature [121] and impurity incorporation studies [122] are later reported, all for the growth of 6H-SiC crystals. Growth of high doped n-type 4H-SiC as well as 6H-SiC crystals with diameter up to 75 mm and thickness of 5 mm was reported [123] together with the findings that methane ( $\text{CH}_4$ ) was a better carbon precursor than propane.

Growth of semi-insulating crystals [124], studies of polytype stability and growth conditions [125] and the useable C/Si-ratio range [126] have been reported.

### **3.4 Simulations of Chloride-based growth**

To gain a deeper understanding of the chemistry in the chloride-based process, simulation is an essential tool. Simulations of chloride-based growth have been done for all the precursor approaches described above: the HCl-approach [127-129], the  $\text{SiH}_x\text{Cl}_y$ -approach [127, 129-132], the  $\text{CH}_x\text{Cl}_y$ -approach [129] and the  $\text{SiC}_x\text{Cl}_y\text{H}_z$  [109] as well as the chloride-based bulk growth process [127, 128, 133, 134]. All studies show the same main result; the chlorinated chemistry in the process changes the most important silicon specie in the growth zone to  $\text{SiCl}_2$ , independently of the starting molecules, for the standard process the main silicon specie is  $\text{SiH}_2$  [135] and this is the explanation of the high growth rate. The  $\text{SiCl}_2$  specie is very stable [136] and it has been found that the most efficient process is achieved when  $\text{SiCl}_2$  is formed easy [137]. The enhanced etching of the SiC surface by HCl formed in the process is also highlighted in the simulation studies.



# Characterization

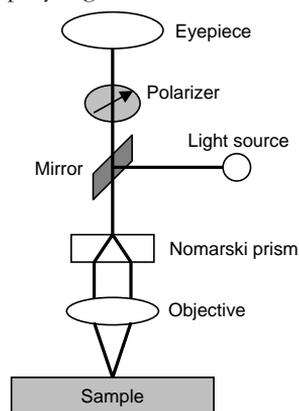
## *A closer look*

After growth of an epilayer there are several techniques to examine the result. The quality of the epilayer is ultimately measured by the performance of the final device, but the processing to make a device is long and not a convenient approach for routine characterization. In order to tune the epitaxial growth process it is common to look at the surface morphology of the epilayer, *i.e.* how smooth is the surface of the epilayer, the thickness of the epilayer and thereby the growth rate of the process and the conductivity type and doping level in the epilayer. Another very important feedback for the crystal grower is the crystalline quality of the grown epilayer.

### 4.1 Optical Microscopy

The morphology is an important factor of the quality of the epilayer; a rough epilayer is hard or impossible to make devices from. The fine tuning of the epitaxial growth process is much directed towards lowering the surface roughness and removing epilayer growth related surface defects. Optical microscopy is a very useful tool for studying the macro roughness and epitaxial growth defects. Micro roughness analysis requires higher resolution and is provided by atomic force microscopy (AFM), see below. The most useful configuration for studying epilayer surfaces is the so called Nomarski Differential Interference Contrast (NDIC) mode. This mode gives high resolution for waviness and in homogeneities of the surface. A schematic view of the optical path for a NDIC microscope is given in Fig. 4.1. The illuminating light is unpolarized and can be regarded as two components of linearly polarized light; it is directed towards the sample by a mirror and hits then a Nomarski prism which separates the two components by about  $1\ \mu\text{m}$  and they then hit the sample. The light then goes back through the objective and the prism where the two components are again merged before reaching the eyes. If there is a path difference between the components, they will interfere with a phase difference and the viewed region will appear darker. A linear polarizer can be inserted in the optical path which can vary the relative intensities of the components increasing the sensitivity of the setup. When maximum sensitivity is achieved, the image produced will appear as if it was illuminated with light at a glancing angle, so structural defects will appear with one side being illuminated and the other side in shadow.

An optical microscope is also a useful tool for studying cross sections of epilayer to directly measure thickness of epilayers. The epilayer is then cleaved into a thin sample and illuminated in transmission mode *i.e.* the light source is placed underneath the sample and the light passes through the sample before it reaches the objective and then the eyes, no polarizer or prism is



**Figure 4.1:** Schematic view of the optical path in a Nomarski Differential Interference Contrast (NDIC) microscope.

used in this application. Difference (if in a few orders of magnitude) in doping level between the substrate and epilayer provides contrast enough to distinguish between the substrate and epilayer.

## 4.2 Thickness measurements

Cutting samples into pieces and measuring epilayer thickness by looking at the cross section view is a time consuming and destructive technique. For a non-destructive thickness measurement, the fact that a crystal's refractive index depends on the carrier concentration can be used. A heavily doped semiconductor crystal has a high concentration of free charge carrier which slightly changes its refractive index compared to an undoped crystal. So if an epilayer with low or moderate doping is grown on a heavily doped substrate or a heavily doped epilayer is grown on a low doped substrate, a small part of incident light can be reflected at the epilayer/substrate interface, Fig. 4.2. The light that is reflected at the interface interfere with the light reflected at the epilayer surface resulting in a spectrum consisting of interference fringes whose spacing depends on the epilayer thickness. Often infrared (IR) light is used in these measurements and the interferogram is generated by a Michelson interferometer; the interferogram is then transformed into a spectrum by Fourier transformation. The measurement technique is then called FTIR reflectance spectroscopy. As one can understand, there are a few limitations to this technique of measuring epilayer thickness; the difference in doping concentration between the epilayer and the surface must be high enough and the surface of the epilayer must not be too rough in order to avoid scattering of the light.

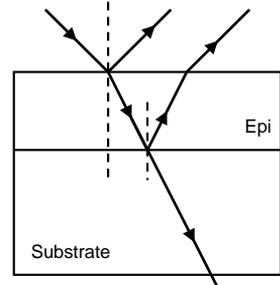


Figure 4.2: Schematics of reflection of light in an epilayer, note that most of the incident light is unaffected by the crystal

## 4.3 Doping measurements

The conductivity type and doping level of the grown epilayer are of high importance since the doping of the crystal affects its electrical properties. The *net doping concentration*, *i.e.* the number of donors minus the numbers of acceptors ( $N_d - N_a$ ) for n-type epilayers or the number of acceptors minus the number of donors ( $N_a - N_d$ ) for p-type layers, can be determined from capacitance-voltage (CV) measurements. To be able to measure on the crystal, electrical contacts are needed. Typically a Schottky contact is placed on the epilayer and an Ohmic contact on the back side of the substrate. The Schottky contacts are formed by evaporating metal (*e.g.* Au or Ni for n-type SiC and a mixture of Ti and Al for p-type SiC) onto the surface, the Ohmic contact is realized by silver paint. The contacts make a simple Schottky diode of the sample. However, the contacts can also both be on the epilayer surface. A faster alternative is to use a mercury-probe, where liquid Hg forms both contacts, typically both are formed on the epilayer surface. During the measurement the diode is reversely biased and the capacitance can then be measured. From this the net doping concentration,  $N$ , can be calculated according to [138]:

$$C = A \sqrt{\frac{\epsilon \cdot \epsilon_0 \cdot N}{2 \left( V - \frac{kT}{e} \right)}}$$

where  $\epsilon_0$  is the permittivity in vacuum,  $\epsilon$  the dielectric constant,  $V$  the reverse bias,  $k$  the Boltzmann constant,  $e$  the elementary charge,  $T$  the temperature in Kelvin and  $A$  is the diode area. If the doping is constant with depth, a plot of  $1/C^2$  versus reverse bias  $V$ , gives a straight line with a slope proportional to the net doping. As pointed out it is the net doping that is given by CV-measurement and not the actual atomic concentrations of dopants. However, it is the net

doping that is important for the electrical properties of the grown crystal and thereby a device made from it. There is always a background doping level in a reactor, rendering concentrations of nitrogen, aluminum and boron, typically in the  $10^{13}$ - $10^{15}$   $\text{cm}^{-3}$  ranges in grown epilayers. These levels are more or less negligible in moderately doped material with an intentional doping in the  $10^{16}$   $\text{cm}^{-3}$  range, but some devices require an intentional doping in the  $10^{14}$   $\text{cm}^{-3}$  range and then a control of the background doping is crucial. When using the mercury-probe, CV measurements can be regarded as a non destructive technique; any residual mercury on the surface can be cleaned away since SiC is such a robust material. CV measurements using mercury-probe can easily be used for routine characterization after growth. When using evaporated contacts on the sample, there is risk for annealing of the contacts making them hard to wash off and the measurements are thereby somewhat destructive and also more time consuming.

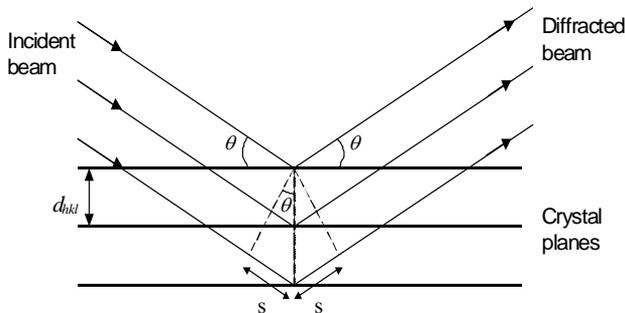
To more precisely study impurities and determine the atomic concentration of dopants (both intentional and unintentional) in an epilayer one can use Secondary Ion Mass Spectrometry (SIMS) where the surface of the epilayer is bombarded with ions, knocking out atoms from the crystal. Some of the ejected atoms are ionized and are then called secondary ions and they can be analyzed with a mass spectrometer. The advantages with SIMS are that atomic concentrations are obtained with depth profiles and one is not limited to analyze only dopants but also other impurities. The drawbacks of SIMS are that it is a destructive technique, the sampling depth is only a few  $\mu\text{m}$  and the detection limits are high for some elements.

#### 4.4 X-ray diffraction (XRD)

The discovery that crystals diffract radiation having about the same wavelength as the spacing between the atomic planes of the crystal was done by W. H. and W. L. Bragg (father and son). In 1913 they determined the crystal structure of NaCl by X-ray diffraction. They also derived the famous mathematical relationship between the wavelength of the X-rays ( $\lambda$ ), the distance between the lattice planes  $hkl$  ( $d_{hkl}$ ), and the angle between the incident X-ray beam and the lattice plane  $hkl$  ( $\theta$ ) known as Bragg's law:

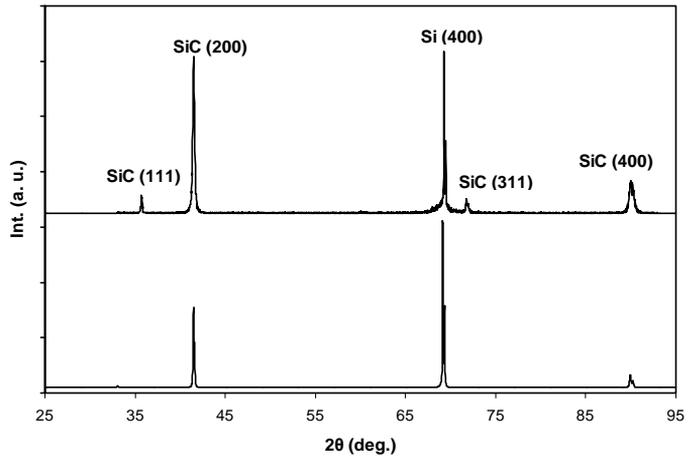
$$2d_{hkl}\sin\theta = n\lambda$$

where  $n$  is an integer  $> 0$  representing the diffraction order. Bragg's law can be derived from Fig. 4.3.



**Figure 4.3:** Diffraction of radiation by the crystal planes  $hkl$ . Constructive interference occurs only when the condition  $2s = n\lambda$  is fulfilled,  $n$  being an integer  $> 0$ .

The simplest form of XRD is the so called  $\theta/2\theta$ -scan, which uses the geometry seen in Fig. 4.3 and the incidence angle of the X-ray beams,  $\theta$ , is varied during measurement meaning that Bragg's law will be fulfilled for various  $\theta$  during measurement depending on the distance between the atomic planes in the crystal. When Bragg's law is fulfilled the incident x-rays will be diffracted and a signal can be detected. The result of the  $\theta/2\theta$ -scan is



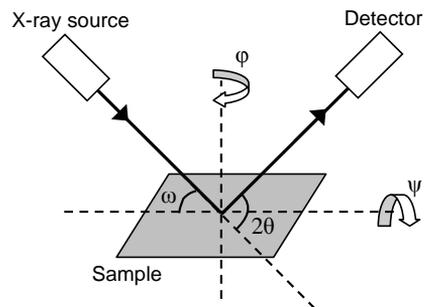
**Figure 4.4:** XRD diffractograms of 3C-SiC grown on Si (100). For an epilayer grown heteroepitaxially only the  $(h00)$  peaks are seen since there is a preferred orientation (bottom), while for polycrystalline growth other peaks can also be seen due to the random orientation of the crystals (top).

a diffraction pattern with peaks for different  $2\theta$ -values as seen in Fig. 4.4. These patterns can then be compared to patterns of known substances and the chemical phase of the sample can be identified.

Another useful application of the  $\theta/2\theta$ -scan is to study orientation of an epilayer. If an epilayer is grown heteroepitaxially it may grow with various preferential orientations, *e.g.* a scan from an epilayer with a [100] preferred orientation will only show the  $(h00)$  peaks (bottom diffractogram in Fig. 4.4) since all crystallites will be oriented with the [100] axis parallel to the surface normal. If the growth process gives a polycrystalline epilayer all diffraction peaks of the material will be visible since crystallites grow with random orientation (top diffractogram in Fig. 4.4).

However to study a homoepitaxially grown epilayer of high quality, high resolution XRD (HRXRD) is needed. In HRXRD, the optics of the diffractometer is more advanced in order to have a very well defined monochromatic X-ray beam and the footprint of the X-rays on the sample is very small, in the order of a few  $\text{mm}^2$ .

Further there are more degrees of freedom for movement of the sample holder as shown in Fig 4.5. A typical HRXRD measurement for studying the crystalline quality of an epilayer is a so called rocking curve or  $\omega$ -scan. In an  $\omega$ -scan the detector is kept fixed at a certain  $2\theta$  value and the sample stage is slightly tilted *i.e.*  $\omega$  is varied and the sample is then moved from a position where it is tilted away from a position where the Bragg condition is fulfilled into the position of the Bragg condition and then out again. The full width at half maximum (FWHM)



**Figure 4.5:** Sample stage used for HRXRD

and the structure of the resulting peak give information on the crystalline quality. The peak will be broadened by a bent lattice and if the epilayer consists of several domains, the latter can also give rise to shoulder on the peak or even multiple peaks. Another useful HRXRD measurement is the  $2\theta/\omega$ -scan, where both the  $\omega$ - and the  $2\theta$ -angles are changed and the detector (*i.e.* the  $2\theta$ -angle) is moved twice as much as the incident beam (*i.e.* the  $\omega$ -angle). Like the  $\omega$ -scan the  $2\theta/\omega$ -scan is done around one peak, the FWHM and shape of the peak give information about

the crystal quality. The peak is here broadened by inhomogeneous strain which affects the interplanar spacing in the crystal.

### 4.5 Atomic Force Microscopy (AFM)

To study the morphology in great detail *i.e.* study the micro roughness of an epilayer a surface topographically sensitive technique such as atomic force microscopy (AFM) is very useful. AFM is one of the techniques that are summarized under the name scanning probe microscopy (SPM), which are all used to study surfaces. The main feature of SPM instruments is that the measurement is done by letting a sharp tip scan over the surface while keeping a very close distance to the surface. Provided that the tip is sharp enough, very high spatial resolution can be obtained and by keeping the tip at a constant distance above the surface while scanning a very fine topographical map of the surface is obtained.

The AFM setup, Fig. 4.6, uses a sharp tip on a cantilever that is brought so close to the surface that Van der Waals forces between the tip and surface starts to affect it. As the tip is scanned over the surface, variations in the surface topography will make the cantilever bend as the tip – sample distance remains constant. The bending of the cantilever is detected by a laser light that is reflected on the cantilever into a photo detector and the amount of motion in the cantilever can then be calculated from the difference in light intensity. Hooke’s law relates the movement,  $x$  to the force needed to generate the motion,  $F$  as:

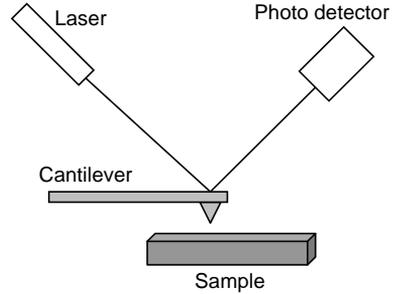


Figure 4.6: Schematic view of the principle of AFM measurement setup.

$$F = -kx$$

The force constant,  $k$ , is a known parameter of the cantilever. The sample height needs to be controlled during the measurement in order to avoid breakage of the cantilever and this control is utilized by a sample holder in a piezoelectric material that can expand or contract by an applied voltage.

AFM measurements can also be done in contact mode where the tip is dragged across the surface, but this technique is associated with problems; there is serious risk for sample damages and the tip might be contaminated with loose material from the surface. The most useful AFM technique for studying epilayer morphology is the *tapping mode*. In tapping mode the cantilever is moving up and down over the surface in an oscillating motion with a frequency of a few hundred kilo hertz, this means that the tip is only in contact with the surface for very short time. The technique has been developed to avoid surface damages during measurement. This is however not a problem when measuring on SiC samples since SiC is so hard, and more likely the tip will be damaged and loose its sharpness.



## Main results

### *What have we learnt?*

In this thesis the chloride-based CVD process for growth of SiC epilayers is studied in order to understand and develop it. The results are reported in seven scientific papers that are published in or submitted to scientific journals. The results are summarized below, for more details see the papers.

A single molecule precursor chloride-based approach was tested by using methyltrichlorosilane (MTS) as precursor; it contributes with silicon, carbon and chlorine to the process. Growth of SiC epilayers using MTS is explored in **Paper 1** where first of all growth rates up to 104  $\mu\text{m}/\text{h}$  without morphology degradation is reported. The growth rate dependence of the silicon molar fraction *i.e.* the input flow of MTS is investigated and it is shown that MTS can be used to grow epilayers with growth rates between 2 and 104  $\mu\text{m}/\text{h}$  with a linear increase of growth rate with increasing silicon molar fraction. The morphology was shown to be unaffected by the growth rate and an average surface roughness of 5.7  $\text{\AA}$  is found on a 49  $\mu\text{m}$  thick epilayer grown at 98  $\mu\text{m}/\text{h}$ , which corresponds to about half a unit cell height in 4H-SiC. The background conductivity is found to switch from n-type to p-type at around 80  $\mu\text{m}/\text{h}$  and the growth rate is found to decrease with decreasing C/Si- and Cl/Si-ratios. The epilayers are found to have very good crystalline quality as demonstrated by HRXRD and low temperature photoluminescence (LTPL).

The motivation behind the chloride-based CVD process is to get higher growth rates which enables the growth of very thick epilayers in a short time and in **Paper 2** MTS is used for the growth of 200  $\mu\text{m}$  thick epilayers grown at 100  $\mu\text{m}/\text{h}$  and thereby demonstrating the stability of the process when using MTS as precursor. The very thick epilayers are shown to be of very high crystalline quality with a very narrow peak in HRXRD and the LTPL spectrum is dominated by the near band gap emission. Further studies using electron paramagnetic resonance (EPR) and Fourier transform infrared (FTIR) spectroscopy reveal that intrinsic defects in the grown epilayer have very low concentrations.

The growth characteristics of the chloride-based CVD process, is further studied in **Paper 3**, where the approach to add HCl gas to the standard precursors silane and ethylene is used as well as the MTS-approach. A comparison between our experimental data and data reported by other groups for different chloride-based approaches is done and it is found that a precursor molecule with direct Si-Cl bonds should be used to get the most efficient process. The high process stability for the MTS-approach is demonstrated by the growth of an epilayer with very thin nitrogen demarcation layers every third minute; the analysis of its cross section view shows a stable growth rate. The growth rate dependence on C/Si- and Cl/Si further studied and it is found with the HCl-approach that the growth rate decreases for lower C/Si-ratios indicating that the growth becomes carbon limited. Extra HCl was added to the MTS-approach and the growth rate was found to decrease for higher Cl/Si-ratios; this trend was explained by enhanced chlorine etching of the growing epilayer.

So far all growth have been done on standard 8° off-axis 4H-SiC substrates, but the SiC industry is more and more turning towards lower off-cuts and in **Paper 4** the standard, non-chlorinated growth process is optimized for growth on 4° off-axis 4H-SiC substrates in order to get better smoother surfaces with less epigrowth-related defects. A low growth temperature and a low C/Si-ratio were found to be the optimum conditions. These optimized process conditions were then transferred to a chloride-based process which allowed the high growth rate to be increased nearly ten times to 28 µm/h, while maintaining good morphology.

The growth on SiC substrates cut perpendicular to the c-axis, so called on-axis, has been shown to be favourable for reducing degradation of devices based on SiC and in **Paper 5** the chloride-based CVD growth on on-axis substrates is explored using both the HCl- and MTS-approaches. The Cl/Si-ratio is found to be very important for reducing cubic SiC inclusions in the epilayer. A growth rate of 8 µm/h was obtained for the HCl-approach while a growth rate of 20 µm/h was demonstrated for the MTS-approach with addition of HCl to get a total Cl/Si of 6. Growth of 20 µm thick epilayers without any cubic SiC inclusions was demonstrated.

The incorporation of dopants in SiC epilayers grown by the chloride-based CVD process is studied in **Papers 6 and 7** using the HCl-approach since this approach gives flexibility when varying the C/Si- and Cl/Si-ratios. In **Paper 6** the n-type doping by incorporation of the donor atoms nitrogen and phosphorus is studied and in **Paper 7** p-type doping by incorporation of the acceptor atoms boron and aluminium is presented. The C/Si-ratio is generally the most important process parameter for controlling the doping in standard, non-chlorinated SiC growth and the incorporation of dopants is found to follow the same trends when using chloride-based process. It is also found that the Cl/Si-ratio is a potentially important process parameter of the chloride-based process for controlling the incorporation of dopant atoms. For n- and p-type doping, using the standard dopants nitrogen for n-type and aluminium for p-type, the doping is found to be stable against minor variations in growth rate, growth temperature and growth pressure.

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*Part II:*

Papers



# My contribution to the papers

## **Paper 1**

I have planned and performed all growth runs and done all characterization except PL and DLTS. I have written the paper.

## **Paper 2**

I have planned and performed all growth runs and the XRD measurements I have written the paper.

## **Paper 3**

I have planned and performed all growth runs and all characterization except SEM. I have written the paper.

## **Paper 4**

I have planned the growth runs with chlorine addition together with the first author. I have performed the growth runs with chlorine-addition and part of the AFM characterization. I have written the paper together with the first author.

## **Paper 5**

I have planned the growth runs together with the first author and I have performed part of the growth runs and characterization. I have discussed the outline of the paper together with the first author.

## **Paper 6**

I have planned and performed all the growth runs and part of the electrical characterization. I have written the paper.

## **Paper 7**

I have planned and performed all the growth runs and part of the electrical characterization. I have written the paper.