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Fluorinated SiC CVD

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Front cover: SiC sample grown using SiF₄ and CH₄ as precursors. The sample was grown in the in the early exploration of the process window under the influence of technical issues. The growth is highly localized to an area of approximately 2 mm × 7 mm shaped as a banana.

Back cover: SiC sample grown using SiF₄ and CH₄ as precursors when pushing the limits of the process window. The appearing ghost clearly indicates the dangers using fluorinated chemistry.

About the images: These images were taken by using an optical microscope equipped with a Nomarski prism and afterwards image manipulated to enhance the contrast of surface features. The colors are therefore not true colors. The samples are transparent and slightly greenish.

During the course of the research underlying this thesis, Pontus Stenberg was enrolled in Agora Materiae, a multidisciplinary doctoral program at Linköping University, Sweden.

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"The Guide is definitive.
Reality is frequently inaccurate."

– Douglas Adams,
The Hitchhiker's Guide to the Galaxy

ABSTRACT

For the emerging semiconductor material silicon carbide (SiC) used in high power devices, chemical vapor deposition (CVD) is the most prominent method to create the electrically active SiC epitaxial layers in the device. The process of growing such epitaxial layers is to use a hydrocarbon and silane diluted in hydrogen flow through a hot chamber where chemical reactions take place in such a manner that Si and C finally deposit epitaxial SiC. The addition of chlorine (Cl) to the process has been thoroughly investigated due to its ability to reduce homogeneous nucleation in the gas phase attributed to the stronger Si-Cl bond compared to the Si-Si bond. In this thesis the fluorinated chemistry has been investigated, since the Si-F bond is even stronger than the Si-Cl bond and the fluorinated chemistry for SiC CVD has remained poorly understood.

Using SiF_4 as Si precursor in growth experiments combined with thermal equilibrium calculations of gas phase composition and quantum chemical computations of the surface chemistry first the silicon chemistry in the CVD process has been probed. It is shown that while growth rates on the order of $35 \mu\text{m/h}$ can be achieved with a fluorinated chemistry, the deposition chemistry is very sensitive to the mass flows of the precursors and not as robust as the chlorinated CVD chemistry which routinely yields $100 \mu\text{m/h}$ over wide conditions. By using the position for the onset of epitaxial growth along the gas flow direction as a new measurable, together with modeling, it is concluded that SiF is the main Si growth species with SiHF as a minor Si species contributing to growth.

The carbon chemistry in a fluorinated SiC CVD process has been probed by a similar approach. Here it is found that the slow kinetics of the

SiF_4 molecule needs to be matched by a carbon precursor with comparable slow kinetics. It is shown that methane is a suitable carbon precursor in combination with SiF_4 .

Before a fluorinated CVD chemistry can be adopted in device processing, the effect of fluorine on the dopant incorporation must be understood since dopant incorporation is of paramount importance in semiconductor manufacturing. Dopant incorporation studies for n-type doping with N using N_2 and p-type doping with Al using TMAI in fluorinated CVD of homoepitaxial SiC are presented. It is found to be possible to control the doping in SiC epitaxial layers when using a fluorinated CVD chemistry for both n- and p-type material using the C/Si ratio as in standard SiC CVD. However, large area doping uniformity seems to be a challenge for a fluorinated CVD chemistry, most likely due to the very strong Si-F and Al-F bonds. Furthermore, it is found that no additional optically or electrically active defects are created due to the use of fluorine in the CVD process.

Finally, the fluorinated chemistry is compared to the chlorinated and brominated chemistries for SiC CVD and an overall model for halogen addition to SiC CVD is presented.

POPULÄRVETENSKAPLIG SAMMANFATTNING

Elektronik har en viktig betydelse för människan idag. Elektronik hjälper oss att styra spänningar och strömmar. När dessa spänningar och strömmar är stora är dagens främsta material för elektronik, kisel, inte det bäst lämpade. Ett material som för detta ändamål har bättre egenskaper är kiselkarbid (SiC). Detta eftersom att SiC kan transportera stora strömmar genom en liten tvärsnittsytta utan att bli för varmt och klarar av höga spänningar över ett kort avstånd utan att kortsluta. Den idag uteslutande mest använda metoden för att tillverka de skikt av SiC som är de elektriskt aktiva är chemical vapor deposition (CVD).

CVD bygger på att gaser flödar genom en kammare där gaserna reagerar, och bildar nya molekyler och radikaler, varav vissa binder till det prov som är placerat i kammaren där det är avsett att skiktet ska tillverkas. Gaserna som flödar genom kammaren innehåller bland annat så kallade källmolekyler, som i fallet när SiC ska tillverkas innehåller kisel (Si) och kol (C). I källgaserna är Si och C bundet till andra grundämnen, vanligast väte eller klor. Det är ändå bara Si och C som fastnar i SiC-skiktet. Men väte och klor spelar en stor roll för hur Si och C beter sig – vilka Si-C-H-Cl-molekyler eller -radikaler som finns i gasfasen och slutligen binder till ytan.

Vad händer om klor byts ut mot fluor? Klor (Cl) och fluor (F) ligger i samma grupp i periodiska systemet (halogenerna) och kan därför antas reagera på liknande sätt. Dock binder F starkare än Cl till Si. Denna avhandling syftar till att ingående besvara denna ställda fråga. Det görs genom att kombinera experimentella resultat med resultat från olika sorters simuleringar.

VIII

Vad som framkommit i arbetet är att SiF, som förekommer i rätt liten utsträckning, är den huvudsakliga radikalen som får Si ner på ytan. F, som binder starkt till Si, verkar i hög grad även binda till ytan på så sätt att C har svårt att binda till ytan och därmed fortsätta tillväxten av SiC. Att Si och F binder starkt får som konsekvens att det är svårt att bryta bindningar som frigör Si för att odla skiktet. Detta måste källmolekylen som innehåller C anpassas för genom att väljas på ett sådant sätt att även C frigörs långsamt till skiktet. Förekomsten av F i systemet försvårar därmed tillväxten, men i övrigt följer F-kemin de mönster med inkorporering av dopämnen och defekter som gäller för andra kemierna.

PAPERS INCLUDED IN THE THESIS

1. **P. Stenberg**, P. Sukkaew, I. Farkas, O. Kordina, E. Janzén, L. Ojamäe, Ö. Danielsson, H. Pedersen, "*Silicon Chemistry in Fluorinated Chemical Vapor Deposition of Silicon Carbide*", accepted; J. Phys. Chem. C, 2017, DOI: 10.1021/acs.jpcc.6b10849
2. **P. Stenberg**, Ö. Danielsson, E. Erdtman, L. Ojamäe, E. Janzén, H. Pedersen, "*Matching precursor kinetics to afford a more robust CVD chemistry: a case study of the C chemistry for silicon carbide using SiF₄ as Si precursor*", submitted
3. **P. Stenberg**, H. Pedersen, E. Janzén, "*Incorporation of dopants in epitaxial SiC layers grown with fluorinated CVD chemistry*", submitted
4. **P. Stenberg**, I. D. Booker, I. G. Ivanov, R. Karhu, E. Janzén, "*Defects in silicon carbide grown by fluorinated chemical vapor deposition chemistry*", in manuscript
5. P. Sukkaew, **P. Stenberg**, O. Kordina, E. Janzén, H. Pedersen, L. Ojamäe, Ö. Danielsson, "*Opening the black box of silicon carbide chemical vapor deposition*", submitted

MY CONTRIBUTION TO THE PAPERS

1. I have planed the experimental work and done the main part of experiments as well as been actively involved the discussions regarding the simulations that were done in the study. I have interpreted the results and together with the co-authors written the manuscript.
2. I have planed and done all the experimental work as well as actively discussed the simulations within the study. I have interpreted the results and together with the co-authors written the manuscript.
3. I have planned the done all the experimental work. I have interpreted the results and together with the co-authors written the manuscript.
4. I have planned the study and grown the epitaxial layers that were characterized. Together with the co-authors I have interpreted the results and with them written the manuscript.
5. I have contributed with experimental experience (especially from the fluorinated chemistry), been involved in the scientific discussions and participated in the writing of the manuscript.

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CHAPTER 1

INTRODUCTION

Silicon Carbide (SiC) is a semiconductor material at the same time being a hard material. Because of its hardness one application of SiC is as an abrasive. Here, however, the focus is on SiC as a semiconductor. It is often compared to Silicon (Si), which probably is *the* semiconductor today.

1.1 Silicon carbide as a semiconductor

Silicon Carbide (SiC) is a semiconductor with properties suitable for electrical power devices. [1] Power devices are devices running at high voltages and/or currents. One of these suitable properties is the wide band gap (3.26 eV compared to 1.1 eV for Si). This gives the material a high electric break down field, i.e. how much voltage that can be applied over a certain material thickness. The electrically active layer in a SiC device can, thanks to this, be as thin as roughly 1/10 of the equivalent Si device. [2] It also allows a SiC device to run at higher temperatures since fewer electrons will be thermally excited into the conduction band reducing leak currents. Another property that makes it attractive for high power devices is the high saturation electron drift velocity. [3] This allows more current per area in the device, which can reduce the areal size of the device. Yet another property that SiC possesses is a high thermal conductivity [4] which makes it even more attractive as a power device since more generated heat from power losses can faster be conducted away from the electrical active area.

What is SiC not suitable for? SiC does not have as good properties as

gallium nitride (GaN) for LED and high frequency applications. That is because SiC has an indirect band gap. The high production costs makes it not competitive to Si devices for normal electronic applications.

To summarize SiC is good for electronic device applications involving high currents (e.g. bipolar transistors), high voltages (e.g. rectifying diodes), high temperatures and low frequencies.

1.2 Electronic devices

There are several different kinds of electronic devices. One of them is the transistor. The transistor is a component with which it is possible to control electric currents or voltages. It was invented in 1947 by John Bardeen, Walter Brattain and William Shockley. At that time it was made out of germanium (Ge), but in 1954 the first silicon (Si) transistor was produced.

The electronic devices consist of differently doped layers with electrical contacts. In some cases there are also an insulating layer in between the contact and the doped layer. A diode consists of two layers, i.e. PN, and a transistor consists of three differently doped layers, i.e. NPN or PNP, where N is a layer doped with donors and P with acceptors. By applying a voltage over the first two layers, or a current to the middle layer, the voltage or current at the third layer can be controlled.

To be able to have the desired electric properties of the devices the amount of dopants in the different layers has to be correct as well as the thickness of the layer. One way of implanting these dopants is during the growth of the layer itself. That is why dopant incorporation during growth is important to control.

Dopants can be considered as defects in the crystal to alter its electrical properties. These defects are wanted. There are also non-wanted defects. These can be other elements or misplacements in the crystal, which can severely alter the electrical properties. Non-wanted defects originating from the SiC substrate has for long made SiC devices a challenge. [5]

To avoid other elements and dust, the electronic device manufacturing takes place in cleanrooms.

1.3 Silicon carbide for electronic devices

For the design of the electrical device, the correct material thickness and amounts of the desired defects are wanted. In order to do so a method with

high degree of control over the process is needed. The supreme method which has become standard for SiC based devices is chemical vapor deposition (CVD) [6] described in more detail in chapter 3.2. Here, gases containing silicon and carbon are heated to react with a SiC surface in such a way that new SiC layers are formed in a controlled fashion on top of the previous, building a SiC epitaxial layer.

1.4 Fluorinated SiC CVD

To understand the process of building up a SiC epitaxial layer, a fundamental understanding of what is happening in a CVD system is needed. Different chemistries, i.e. what gases are used, in the CVD system produces widely different results. Adding chlorine to the SiC process has been shown to enhance growth. [7, 8] Chlorine (Cl) is a halogen, and other halogens like fluorine (F) [9, 10] and bromine (Br) [11] can also be added to the process with different effects.

This work has mainly been focusing on the fundamental understanding of the F chemistry — what gas species are formed, what gas species are depositing on the surface and how F chemistry compares to other chemistries.

CHAPTER 2

SILICON CARBIDE

Silicon carbide is a crystal built up of silicon and carbon with every second atom being a silicon (Si) atom and every second atom being a carbon (C) atom. Every Si atom binds to four C atoms and every C atom binds to four Si atoms. This can, however, be done in several different ways, as will be described in chapter 2.2. Before that, some properties of the two elements Si and C will be pointed out.

2.1 Silicon and carbon

Both Si and C are group 14 elements – they have 4 valence electrons. The angle between two bonds become 109.5° . C is the smallest group 14 element with atomic number 6, and below it in the periodic table is Si with atomic number 14. C might be familiar from organic chemistry, but C bonded together by sp^3 -bonds also exists in crystal form known as diamond – which is a semiconductor. Diamond has even a larger band gap than SiC. Si, which also takes the same crystal structure as diamond (the diamond structure) has a smaller band gap than SiC.

Table 2.1: Some properties of the chemical bonds related to C and Si

	<i>C-C (C)</i>	<i>C-Si (SiC)</i>	<i>Si-Si (Si)</i>
Bond strength (<i>kJ/mol</i>) [12]	618	447	310
Bond length ($\text{\AA}$) [13]	1.53	1.87	2.33
Band gap (<i>eV</i>) [14, 15]	5.5	2.3-3.3	1.1

Figure 2.1: The two possible configurations for a Si and a C atom to bind to each other. Si is represented by the larger sphere on top, C is represented by the smaller sphere below and the chemical bonds represented by the sticks. a) Hexagonal configuration. The bonds are pointing in the same direction. b) Cubic configuration. The bonds are pointing in the opposite direction.

2.2 Building the SiC crystal

SiC possesses a property called "polytypism". That is how the Si and C atoms are stacked before the order is repeated. There are two ways of stacking a Si and a C atom together shown in Figure 2.1 – either the bonds point in the same direction, which is referred to as the hexagonal configuration (h), or they can point as much away from each other as possible, which is the cubic configuration (k).

From this way of describing bonds it might be possible to imagine that since the bonds are closer to each other in the hexagonal configuration, the electronic repulsion is stronger here than in the cubic configuration, where they are farther from each other. This can be used to get an estimate of the band gap in different polytypes of SiC – higher degree of hexagonal configuration gives a higher band gap, while higher degree of the cubic configuration gives a lower band gap, seen as the spread in Table 2.1.

However, this way of describing the stacking will make the surface termination a bit unintuitive, because when referring to the SiC crystal's different faces, the face refers to the atom with one bond out (i.e. normal to the surface) and the other atom is known as its termination. What is shown in Figure 2.1 is a Si terminated C-face, assuming the top surface in the

Figure 2.2: The cubic configuration rotated. Upwards the non-terminated Si-face and downwards the non-terminated C-face.

Figure 2.3: Again, the two possible configurations for a Si and a C atom to bind to each other. a) Hexagonal configuration. b) Cubic configuration. The lower Si atom is rotated to have the same configurations as in Figure 2.1.

horizontal plane. By instead only using the cubic configuration block, the surface, and its termination can be more easily recognised.

In Figure 2.2, a surface at the top of the Si atom can be imagined if the Si-C unit is repeated. This would build up the cubic polytype of SiC. If now two Si-C units are joined together, and of which the lower Si atom is rotated to have the same configurations as in Figure 2.1 with the C atom above – the hexagonal configuration. This is shown in Figure 2.3a. This unit repeated would build up the hexagonal polytype – the 100% hexagonal polytype. The cubic SiC polytype with 2 Si-C units is shown in Figure 2.3b.

There can be arbitrary combinations of hexagonal (h) and cubic (k) units. A common polytype today though is the "hk" polytype (the sequence hk repeated), used to compare SiC to Si in chapter 1.1, shown in Figure 2.4.

Figure 2.4: The 50% hexagonal polytype. Every second unit is hexagonal and every second unit is cubic.

Every second layer of Si-C units is hexagonal, and the polytype is therefore 50% hexagonal. Its bandgap is in between the purely hexagonal and the cubic polytype.

So far the view of the Si-C units has been from the side, viewing the so called *c*-direction which then goes vertical (from the C-face to the Si-face). Now taking a top view, facing towards the *c*-direction, one bilayer of SiC (Si-face) would look like Figure 2.5a, with one bond from the Si facing up, and one bond from the carbon facing down (thereby not seen from a top view). This view can resemble how adatoms in growth experience the surface/crystal as they are placed on top the previous layer. The next layer can have two different orientations. Either it is a similar layer, which would position the next Si atoms above the void of the hexagon as in Figure 2.5b (AB), or above the carbon atoms of the previous layer (AC). From here the AB and AC may look similar. Eventually, just stacking ABs on top of each other would create an equivalent stacking as ACs on top of each other – just rotated 120° . These positions were only taken as starting definitions for

Figure 2.5: Stepwise stacking of bilayer. Here the formation of the ABC stacking with a) one bilayer in A position, b) two bilayers in the AB positions, c) three bilayers in the ABC positions.

how next layers relate to each other. From the AB stacking the next bilayer can be positioned such that the Si atoms again will be in the voids of the previous layer which is above the carbon atoms of the first layer, referring to the C position thereby becoming an ABC-stacking (Figure (2.5c), or such that the Si atoms are above the previous layer's carbon atoms, which were above the first layer's Si atoms corresponding to the A position, thereby having an ABA stacking. The ABC stacking corresponded to always put the next layer's Si atoms in the void of the previous layer's hexagon. The next stacking in the same way would then be above equal to the A position and the ABC would repeat. If the next layer from the ABA stacking would be at the B position there would be an ABAB stacking, or just AB stacking repeated.

It can here be noted that this letter nomenclature corresponds to adding or subtracting 1 in a modulus 3 fashion. $1+1 = 2$, $2+1 = 3$, $3+1 = 4 \rightarrow 1$, $1-1 = 0 \rightarrow 3$.

Here, a continuation in letters (e.g. ABC and CBA) corresponds to a cubic unit (k), while a swap back (e.g. ABA and BAB) corresponds to a hexagonal unit (h). C to A is a continuation. The previously mentioned hk stacking (hkhkhk...) is equal to kh (permuted one step) could then be written as ABCB, which would then repeat (ABC is a continuation (cubic) and BCB is a swap back (hexagonal)). Except for the stacking ABC, this notation tells how many bilayers there are in the unit cell of the polytype. AB has 2, ABCB has 4, while ABC has 1 because it is a Si-C unit repeated.

Although the notation of using h and k, called the Jagodzinski notation [16], is useful when predicting the band gap, and using the position of the atoms relative to each other denoted A, B and C can predict the size of the unit cell, probably the most common notation is the so called Ramsdell notation. [17] It does not say whether the hexagonality is 100% or 50%

or what the exact stacking sequence is, but states how many Si-C layer there before the letter sequence is repeated together with if the polytype is cubic (C), hexagonal (H) or rhombohedral (R). The ABC stacking, which is cubic is in Ramsdell's notation denoted 3C, while AB and ABCB are hexagonal denoted 2H and 4H respectively. The rhombohedral structure appears when the stacking sequence has incremented one cycle, i.e. a subset of the sequence increment one letter. 15R is such a polytype. The order is ABCACBCABACABCB. The subset of increment is every 5 layers i.e. ABCACBCABACABCB. It can be written in the Jagodzinski notation as (kkhkh)₃. By this way of looking at a rhombohedral sequence, Ramsdell also points out that 3C, written as ABC can be thought of as a rhombohedral structure. [17]

In this work the 4H polytype, or the hk polytype, was used in growth. These sites can be recognized for instance when characterizing doped layers using photoluminescence (chapter 7.4), since a dopant atom will be positioned at a different energy level compared to the conduction band depending on if it is incorporated at a cubic or hexagonal site.

2.3 The surface

Previously the two faces Si-face and C-face were mentioned. The Si-face was in the direction where one bond from the (each) Si atom pointed out from the crystal, and at the other end of the crystal the C-face was found, where one bond from each C atom pointed out.

The difference in growing on the Si-face or the C-face appear when the different monolayers grow. When growing on the Si face, one bond per Si atom points for the C atoms to attach to. The C atoms then bond with one bond to the Si layer, then having three bonds each pointing out for the Si atoms to attach to. When growing on the C face, one bond per C atom points for the Si atoms to attach to. The Si atoms then bond with one bond to the C layer, then having three bonds each pointing out for the C atoms to attach to.

Previously it was mentioned that dopants take different sites. The so called "site competition theory" [18] suggests that nitrogen (N) atoms take C sites, while aluminium (Al) atoms take Si sites. Growing on the C-face, where Si will have 3 bonds out for the C layer, N will be more likely to adsorb than growing on the Si-face. Growing on the Si-face will therefore create a lower background doping N.

An adatom coming down on the surface can migrate on the surface before it either leaves the surface or find a position where it is stabilized. To

enhance growth a surface where adatoms are stabilized are preferred. Such a position can be where multiple bonds bind to the adatom. Such a surface can be created by polishing the surface so that it becomes slightly tilted compared to the *c*-direction. The tilt is referred to as the off-cut angle, where 0° corresponds to no tilt, i.e. the surface has the *c*-direction as its normal. In this work, substrates (i.e. the crystal that the epitaxial layer has been grown on) have had an off-cut angle of 4° . The tilt is in the $11\bar{2}0$ -direction, which is the direction where most bonds get exposed.

CHAPTER 3

GROWTH METHODS

In this chapter two significantly different approaches to grow silicon carbide will be given. Physical vapor transport, which for SiC is used to grow boules that will be sliced into wafers, and chemical vapor deposition, mainly used to grow the active layers in devices.

3.1 Physical vapor transport

Physical vapor transport (PVT) makes use of the flux originating from the temperature difference of two surfaces. A hotter surface evaporates more than a cold surface, and therefore a flux of gas species from hotter to the colder appear.

The basics for SiC PVT is a volume in which SiC powder (small crystals) have been put, above which (with a small gap) a seed SiC crystal has been placed, and over the gap a temperature gradient has been applied at high temperatures. This is referred to as seeded sublimation growth. This technique was improved by Tairov and Tsvetkov [19] and later lead to the first commercial SiC wafer from Cree Research Inc.

3.2 Chemical vapor deposition

The chemical vapor deposition (CVD) incorporates growth techniques that have in common that the precursors enter the growth cell in gaseous form and start gas phase reactions and/or surface reactions to grow the material. The machine in which the CVD is done is often referred to as a reactor.

The reactions in the reactor can then be enhanced in different ways – e.g. enhanced by heat, as in thermal enhanced CVD or enhanced by energy as in laser or plasma enhanced CVD.

Here, however, the thermal CVD has been of interest. There are different flavours of thermal enhanced CVD. Some of them are briefly described below.

3.2.1 Cold wall reactors

By having a CVD reactor where only the substrate and its holder are heated, the gases are predominantly heated above this surface, forming growth species and react with the surface resulting in growth. The reactor walls are cold since they will only be passively heated, e.g. by the radiation from the substrate and the substrate holder, giving the reactor type its name – cold wall reactor.

The large thermal gradients that appear above the substrate can drastically change the gas phase composition at heights as small as 0.1 mm. [6] This can result in more directed deposition of the precursors, creating less parasitic deposition, but it has a risk of creating high thermal gradients in the substrate due to that irradiation mainly cools the surfaces.

3.2.2 Hot filament reactors

Instead of having a hot substrate and cold gas as in the cold wall reactors, a reactor can be constructed by heating gases just before the substrate by letting them pass through a hot filament (or hot wires). This creates the growth species at the hot filament which can then hit a significantly colder substrate. One benefit with this method is that substrates not withstanding a high temperature can be used in the growth. For example, this has been done using $\text{SiF}_4 + \text{CH}_4$ to grow polycrystalline 3C-SiC on Si substrates. [20]

3.2.3 Hot wall reactors

The hot wall reactor got its name from that it, compared to the cold wall reactor also has hot walls around the substrate. By this, irradiation heats the substrate reducing thermal gradients. For a SiC process this also require less power since less power is lost to radiation. [21] The hot walls also heat the gas mixture creating growth species already prior to the substrate. The hot wall reactor will be described further and in more detail in chapter 4, where a more complete description of a CVD system will be given as well. For

a SiC process, temperatures in the range 1500 °C and 1700 °C are usually used. Compared to the cold wall reactor, the hot wall reactor can operate in a larger process window. [6]

3.2.4 Horizontal or vertical gas flow

There are many flavors of CVD reactors. One more dimension of this is if the gas flow is horizontal or vertical. For vertical, the gas flow can be directed upwards or downward. This affects the gas flow dynamics, where the downward direction has shown to yield higher growth rate and better dopant uniformity. [22]

CHAPTER 4

THE HORIZONTAL HOT WALL CVD REACTOR

So far, a couple of different concepts for the so called hot zone have been presented. The hot zone will be discussed in detail in chapter 4.2 focusing on the horizontal hot wall CVD system in this work. But a CVD reactor is much more than just the hot zone. Therefore chapter 4.1 will give a brief overview of what more there is in a CVD system.

4.1 A CVD reactor

A CVD system is a complicated system with many different components. To more easily get an overview of a CVD system it can be divided into a couple of subsystems, briefly described below, each with a specific task.

- A *gas system* providing the correct amount of gases to the right gas line at the right time, e.g. precursors to the growth cell when growth starts. This is done by valves, regulators, mass flow controllers (MFCs) and electric pressure controllers (EPCs).
- A *vacuum system* taking care of the gases either they go via the growth cell or not. The vacuum is provided by vacuum pumps. To increase conductivity of the gas, especially at low pressure, the vacuum system is generally built using wide tubing. The vacuum system is not necessarily a subsystem – the functionality can be incorporated in the gas system, removing the fuzzy line where the gas system stops and the vacuum system takes over. One important feature here is the scrubber, which can be a so called burner or can

be a scrubber using an adsorbent which adsorb the hazardous process gases.

- The *growth cell* is where the hot zone is, which is where the growth takes place. The growth cell encapsulates the hot zone as well as reduces turbulence in the gas flows prior to entering the hot zone.
- The *heating system* provides the hot zone with the heat for the chemical reactions. Here it is done by an electric coil creating a magnetic field in the hot zone, resulting in a circulating electric current in the hot zone, which turns into heat.
- There can also be a *control system* controlling the other subsystems, both automatic and by the operator, as well as managing interlocks reducing the risk for the operator to give detrimental commands to the reactor (e.g. let gases go in to the wrong gas line at the wrong time). There can also be automatic shut down of the CVD system if an accident occurs.
- Depending on reactor design there can also be a *cooling system* to keep certain parts cool, e.g. a quartz tube, electric coil or flanges with O-rings, which cannot withstand the high temperatures created during process.

The subsystems together form the CVD system and provides what is necessarily to grow SiC in the hot zone.

4.2 The hot zone

It is in the hot zone where the flowing gas gets heated. When the gas heats up, chemical reactions begin forming growth species. If the growth species hit the surface it can be adsorbed by surface reactions.

Figure 4.1 shows a drawing of the hot zone. The hot zone consists of mainly two things; a susceptor and an insulation. Depending on design, the power from an external magnetic field is either suscepted by the susceptor or, as in the design used in this work, an extra part surrounding the susceptor which absorbs the power, turning it into heat, which then transfer the heat to the susceptor by radiation as well as thermal contact. The insulation pieces surrounding the susceptor reduces the amount of heat leaving the susceptor.

As process temperatures are high the supreme material for the design of susceptor, heating ring and insulation is graphite. This graphite has though other elements incorporated (where boron (B) is the main issue today) and is not pure enough to be used directly where the SiC sample is exposed to the graphite. This mainly concerns the susceptor, which is therefore a SiC

Figure 4.1: Three-quarter section view of the hot zone for the horizontal hot wall reactor used in this work. The susceptor consists of a bottom part (A_1) where the substrates are placed, a top part (A_2) and a susceptor inlet (A_3). It is inside here the process gases flow (in this figure from left to right). To heat the susceptor, a heating ring (B) is transferring the magnetic field, provided by the electric coil (E), into heat. The susceptor and the heating ring are surrounded by rigid graphite insulation (C_1 , C_2 , C_3) as well as a thermal break (A_4) upstream of the susceptor inlet. The parts labeled A, B and C forms the hot zone. The hot zone is encapsulated in a quartz tube (D_1). To further enhance the gas flow into the hot zone, a quartz gas liner (D_2) is mounted. On the exhaust side an inner quartz tube (D_3) is placed to increase protecting for the outer quartz tube from deposition and heat, as well as reducing turbulence in the susceptor due to the fast change in gas cross section.

coated as delivered. For the insulation, a rigid graphite is used.

The heating of the hot zone in this set-up is using an electric coil, which generates a magnetic field inside the hot zone. This results in a force on the electrons in the graphite. Since the graphite makes a complete circuit (i.e. the graphite ring), the electrons can create a circular current in the graphite ring. Due to the resistance in the material, heat is created.

The rigid graphite, used as insulation, has its fibres mainly perpendicular to the direction of which isolation is desired. Therefore, different fibre directions are used depending on where the isolation piece is situated. For the insulation outside the heating ring, the fibres should be perpendicular to the radial direction, while in the front and the rear, the fibres should preferable be in a radial plane. The insulation keeps the quartz tube surrounding the hot zone from melting, as SiC process temperatures are well above what the quartz should be exposed to not to break.

The susceptor should preferable have low temperature gradients in the susceptor while operating at process temperatures. The process gases entering the susceptor via the susceptor inlet are cold and get heated up along their path through the susceptor. This results in a larger cooling effect from the gas at the susceptor inlet than at the rear. To compensate for this, the susceptor inlet is tapered to reduce cooling caused by radiation. The angle on the tapering susceptor inlet must though be small to avoid turbulence in the gas. A turbulent gas flow will locally let more gas species pass which can result in uneven deposition rates.

Prior to the susceptor inlet is a thermal break to stop heat by conduction in a solid material by a poor material contact to the thermal break. The thermal break is further connected to a quartz gas liner. It is inside this liner which the process gases travel before entering the susceptor. While travelling through the liner, the desired laminar flow is stabilized after exiting the narrow gas pipes in the gas system.

Outside of the quartz gas liner, but still inside the quartz pipe, is another gas flow which is supposed to go through the insulation of rigid graphite. This gas flow consists of argon (Ar) gas, while the process gases mainly consist of hydrogen (H_2) gas. Ar has lower thermal conductivity than H_2 . By suppressing H_2 from passing the insulation, ideally exchanging it to Ar, the insulation properties of rigid graphite are further improved. Since connections between the parts are not gas tight, but rather loose, H_2 still slips trough the insulation.

The gas flow of process gases going trough the susceptor creating SiC, will also create and carry particles downstream of the hot zone depositing

Figure 4.2: Half section view of the hot zone for the horizontal hot wall reactor used in this work, exposing the pyrometer hole drilled from the back in the susceptor.

on all surfaces, e.g. quartz and pipes. To avoid this happening on the quartz pipe, an inner quartz pipe is placed at the rear inside the quartz pipe. This quartz pipe can be taken out on run-to-run basis to get cleaned. The smaller radius on this inner quartz pipe compared to encapsulating quartz pipe also reduces turbulence to develop already inside the susceptor, due to the abrupt change in cross section for the gas flow.

To measure the process temperature a tool called pyrometer is used. The pyrometer measures the intensity of light at one or two certain frequencies for converting intensity to temperature. All objects emit electromagnetic radiation, where the intensity as a function of frequency depends on the temperature and emissivity of the object (according to Planck's law). A two color pyrometer measures the ratio between the intensity, from which the temperature can be derived, thereby not having to take the emissivity into account. A one color pyrometer on the other hand uses the absolute intensity of the radiation, taking the emissivity into account, to derive the temperature. The pyrometer used in this work was a one color pyrometer with a spot size of 4 mm.

The susceptor bottom is designed with a 6 mm hole drilled into it, about 10 cm deep, called the pyrometer hole (Fig. 4.2). The pyrometer is directed such that it collects the light emitting from pyrometer hole. In such a cavity

as this, the light can be reflected multiple times inside the hole before it hits the pyrometer. Doing so the emissivity approaches 1, thereby reducing the error from the emissivity. At process temperature an emissivity error of 0.02 corresponds to an error of 10 °C. The temperature in the pyrometer hole can be expected to be somewhat higher than at the susceptor surface due to the temperature gradient caused by the cooling gas on the inside and the heating ring on the outside. Furthermore, the sample does not have perfect contact with the susceptor, why it is even cooler.

CHAPTER 5

EFFECT OF RELATED PROCESS PARAMETERS

In chapter 3.2 it was discussed how different ways of initiating chemical reactions gave the type of CVD its name, e.g. hot wall CVD. Temperature – as in thermal CVD – gives the molecules the vibrational energy to break a bond, but it also gives the molecules, or atoms velocity to overcome the activation energy to form a new bond. A suitable temperature therefore depends on what it should be used for. If there are strong bonds that should be broken, a high temperature is preferred, but risk that less weaker bonds form because they will break faster. For adsorbed gas species on a surface, a tuned temperature can break and form bonds in such a manner that the gas species become mobile on the surface, promoting epitaxial growth rather than polycrystalline growth. A too high temperature on the other hand will break the bonds, making the surface species desorb from the surface.

There are several parameters effecting the growth and doing so in different, or multiple, ways. Here the parameters are divided into "physical" and "chemical" parameters, although there is no straight line in what should be considered as physical and chemical. However, a typical SiC process will first be discussed to be followed by a discussion on how the process parameters effect it.

5.1 A SiC CVD process

A typical SiC process in a hot wall CVD reactor consists of a so called carrier gas, which is hydrogen gas (H_2), in which so called precursors are

diluted. Precursors are the gases containing the elements that are supposed to adsorb on the surface during growth, e.g. Si, C and sometimes dopant atoms.

When the carrier gas together with the precursors enter the hot zone – first the susceptor inlet and later the susceptor itself – they begin to heat up from the hot walls. It is only these mentioned surfaces that heat the gas. The gas is therefore warmest closest to the surface. When the gas heats up, chemical reactions start to take place. Some of the newly formed gas species can, by chemical reactions, adsorb on the surface. If they do so without desorbing from the surface, they will contribute to the crystal growth. Most of the gas species will though pass through the hot zone without adsorbing on the surface.

Typical Si precursors are $\text{SiX}_x\text{H}_{4-x}$ where $x = 0 - 4$ and X is a halogen – preferable Cl but was in this work exchanged for F where also x was equal to 4, i.e. the Si precursor was SiF_4 . As C precursor, typically a light hydrocarbon is used – C_3H_8 , C_2H_4 or even CH_4 . The precursors are normally diluted to less than 1 % in H_2 . Typically, this is given as the fraction of Si in H_2 , e.g. $\text{Si}/\text{H}_2 = 0.25$ %, while the amount of C is then related to the amount of Si in a Si/C ratio, which is normally in the order of 1. The temperatures for a SiC process is normally around 1500 - 1800 °C at a process pressure in the order of 100 mbar ($\approx 1/10$ of atmospheric pressure). [7]

The amount of hydrogen is such that the average gas velocity becomes in the order of 10^1 m/s when pressure is taken into account.

5.2 Physics related process parameters

Pressure is a parameter that has several effects. If the pressure is reduced the mean free distance between particles increase, thereby the time between collisions, thereby reducing the reaction rate. The lower pressure also decreases the partial pressure of species thereby reducing the impingement rate of growth species on the surface, decreasing the growth rate. A higher pressure increases the thermal conductivity of the gas which affects thermal gradients in the hot zone and can also give rise to a higher quartz tube temperature, limiting the process window or put higher demands on reactor design. It also affects the gas velocity – a lower pressure increases the gas velocity, which in turn has other effects.

The pressure together with gas flow (m^3/s) in a certain cross section (m^2) gives rise to an average gas velocity (m/s). But due to sheer friction in the gas, a gas velocity that is low enough to be laminar results in a so

called boundary layer where the velocity is even lower than the average gas velocity, which is reduced for a higher gas velocity. How the gas velocity boundary layer thickness changes over a flat surface, e.g. a susceptor, is described in equation 5.1 below

$$\delta \sim \sqrt{\frac{\mu x}{\rho U_{\infty}}} \quad (5.1)$$

where δ is the boundary layer thickness, μ the viscosity of the gas, x the distance along a surface, ρ the density and U_{∞} the bulk gas velocity. [23]

The gas velocity and the pressure influences the cold finger, i.e. the temperature gradient in the gas and thereby the gas species concentration along the susceptor. Temperature gradients in the susceptor along the gas flow direction are small compared to the gradients normal to the susceptor surface, and therefore there are large species concentration gradients in these directions.

The substrate itself also effects the growth. The orientation of the crystal, with either Si or C face results in either one bond per surface site for the C growth species and three bonds for the Si growth species or three bonds per surface site for the C growth species and one for Si growth species. More bonds generally enhance adsorption. Either the Si growth species get this benefit, or the C species do.

The off-cut angle of the substrate changes the atomic step concentration. Due to a higher concentration of chemical bonds at the steps there is a higher possibility for adatoms to stick at the step than on a terrace, where the adatom's bond can more easily break (depending on the temperature) and leave the surface. The discovery of using off-cut samples helped to reduce the growth temperature as well as improve the quality of the grown material. [24]

5.3 Chemistry related process parameters

One of the probably most obvious parameters that effects the growth is the amount of precursors put in, i.e. how much Si and C are put in. Previously the gas flow was mentioned. The gas flow consists of a carrier gas and the precursors. The choice of precursors are of great importance for the adsorption of Si and C on the surface. Different precursors form growth species at different rates. This changes the gas phase composition and the impingement of growth species on the surface. At the same time the growth species have different likeliness to adsorb.

Depending on how much of Si and C is diluted in the carrier gas, the growth rate can be limited by either the amount of Si or the amount of C, i.e. if the growth rate varies if the amount of one of them is varied. This is known as Si-limited or C-limited growth. When doping the epitaxial layers, the incorporation efficiency of different dopants differs depending on how much available Si and C there are. This is further described for the fluorinated chemistry in Paper 3.

The amount of halogens play an important role in the gas phase as well as on the surface. In the gas phase the halogens help to reduce homogeneous nucleation of Si, also known as silicon droplets, which appears if a too high concentration of Si precursor is used. Silicon droplets on the surface makes the epitaxial layer not usable for devices. A halogenated chemistry therefore allows for higher concentration of precursors, thereby increasing the growth rate.

On the surface, however, the halogens can terminate the SiC surface thereby reducing the growth rate. For the case of F this is a prominent effect, described in Paper 2.

CHAPTER 6

MODELLING

Many conclusions drawn in this work was done by comparing findings from experiments with results from modelling. Although modelling was not a part of this thesis work, this chapter briefly describes three of the modelling methods used in papers (1, 2, 5) (Three, Sir!) included in this thesis.

In the hot zone there are both gas phase reactions as well as surface reactions taking place. These reactions and the gas phase composition can be modelled by different methods, described briefly below.

6.1 Density functional theory

Density function theory (DFT) is a method in quantum chemistry to calculate the energy of a many-body system, like a molecule. The name origins from that the method uses the electron density of the system to calculate the energy using different functionals. For example, two functionals that have been used in calculating the Gibbs free energy of reaction related to chemical reactions in F SiC CVD are B3LYP [25, 26] and M06 [27].

When the Gibbs free energy of reaction has been calculated from DFT, the result can be used in other modelling, for instance thermodynamic equilibrium and kinetic simulations of the gas phase. It is also possible to achieve the activation energy of a reaction by calculating the Gibbs free energy for the transition state. Since the DFT calculations are often used for further modelling, it is of great importance that these are correct. [28]

6.2 Thermal equilibrium

In Paper 1, 2 and 5, thermodynamic equilibrium modelling has been used to estimate the fraction of different species in the gas phase as well as fractions of different surface terminations. Thermodynamic equilibrium is achieved when the Gibbs free energy of the system is minimized. By knowing the entropy (H) and enthalpy (S) for the allowed species in the system, the concentrations of them in thermodynamic equilibrium is achieved when the Gibbs free energy ($\Delta G = \Delta H - T\Delta S$) for the whole system is minimized.

From thermodynamic equilibrium modelling it is not possible to retain what chemical reactions are taking place, only the end result products (and their concentrations).

6.3 Kinetics

Kinetics takes time into account. While thermal equilibrium can be considered as kinetics after infinite time, kinetics can show how concentrations of gas species evolve with time, which is not possible using equilibrium modelling.

The equations governing the rate at which the concentrations change are called rate equations. The rate equation is a differential equation relating the change of one species to the concentrations of other species. It is first when this differential equation is integrated that the time dependence for the concentration of a species is revealed.

A chemical reaction, with both forward and backward reactions may be written as

In this case the rate r_f at which A and B forms C and D is

$$r_f = k_f \cdot [A]^a [B]^b \quad (6.2)$$

where $[X]$ being the concentration of X and k_f being the rate constant for the forward reaction expressed as

$$k_f = k_{AB} \cdot T^n \cdot e^{-E_a/RT} \quad (6.3)$$

where k_{AB} being a reaction constant, T the temperature, n the order of the temperature dependence, E_a the activation energy of the reaction and R the ideal gas constant. Both k_{AB} and n can be calculated using DFT, but can as well be determined experimentally.

If there is a forward reaction there is also a backward reaction forming A and B from C and D. This reaction occurs at the rate

$$r_b = k_b \cdot [C]^c [D]^d \quad (6.4)$$

where (6.4) is constructed in a similar manner as (6.2) and (6.3). The net rate r at which A and B forms C and D is then

$$r = r_f - r_b \quad (6.5)$$

which can, by definition, also be expressed in terms of how the concentrations change with respect to time as

$$r = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt} \quad (6.6)$$

It is when $r = 0$ equilibrium is reached since then the forward and backward reactions cancel.

$$\begin{aligned} r = 0 &\Leftrightarrow r_f = r_b \Leftrightarrow \\ &\Leftrightarrow k_f \cdot [A]^a [B]^b = k_b \cdot [C]^c [D]^d \Leftrightarrow \\ &\Leftrightarrow \frac{k_b}{k_f} = \frac{[A]^a [B]^b}{[C]^c [D]^d} \end{aligned} \quad (6.7)$$

CHAPTER 7

CHARACTERIZATION

The characterization techniques related to this work are described below; optical microscopy, scanning electron microscopy, capacitance-voltage measurements and photoluminescence.

7.1 Optical Microscopy

For this work the most used characterization tool has been the optical microscope (sometimes abbreviated OM). It has been used to get a magnified image of a large area of sample from which surface morphology be determined. It can be used to measure distances on the surface in the range of micrometers and upwards, which could be used for rough estimates of thickness from triangular surface defects. The surface morphology around the onset of epitaxial growth (Paper 1) could be studied by the optical microscope.

The optical microscope uses optical lenses to enlarge objects. The object, which here has been the surface of a grown sample, can be studied in large magnification such that features in the μm range can be seen. The set-up used in this work was a differential interference contrast optical microscope using Normarski prisms. That is used to enhance height contrast in studied objects by letting polarized light passing through double refracting prisms. Doing so light polarized in different directions will exit the first Normarski prism slightly shifted, giving rise to slightly shifted light rays. That will create two slightly shifted images after finally reflect on the object, depending on polarization. The now slightly shifted

images will, when superimposed, give rise to constructive or destructive interference due to phase shift from where the light has travelled different long paths for the different images. The front cover of this thesis shows an example of this. Due to the change in height there will be constructive or destructive interference of different wave length, resulting in the color shift around the feature.

7.2 Scanning Electron Microscopy

A scanning electron microscope (SEM) uses electrons instead of light to illuminate the sample. By focusing the electron beam, accelerated to a few kV, on to a small spot of the sample and measure the intensity of e.g. backscattered (used in this work) or secondary electrons, an image is built up, pixel by pixel, as the electron beam is scanning the sample. Different intensities are achieved depending on features and composition of the material.

Different doping intensities will give rise to different conduction of electrons in the material. Higher conductivity will reduce the amount of backscattered electrons thereby resulting in a lower intensity. SiC substrates are normally high doped while unintentionally doped grown epitaxial are low doped. This gives a contrast difference between the substrate and the epitaxial layer and the thickness of the epitaxial layer can be measured.

There are a few problems associated with measuring thickness of SiC epitaxial layers using SEM. First, the sample has to be cut in half in order to get a cross section of the sample. By then irradiating the sample with accelerated electrons creates defects in sample such that other characterization methods should be done prior to SEM. Also, while scanning, charge is built up in the material due to the bad electrical conductivity of SiC, such that the intensity of backscattered electrons is lower from an area previously scanned. This imprint allows never to zoom out or move the scanning area a fraction of the image, or otherwise is a darker imprint of the image. An example of this is shown in Figure 7.1.

7.3 Capacitance-Voltage measurements

One way to estimate doping concentration in a sample is by calculating it from capacitance-voltage (CV) measurements. The method does not measure the dopant concentration (i.e. the concentration of N and

Figure 7.1: An example of a SiC cross section taken with SEM. Features due to a not clean cut are visible as well as imprints of previous zoomed in scans. Although a clear difference between the substrate and the epitaxial layer is seen.

concentration of Al), but the net dopant concentration, which when measuring the net donor concentration is the difference in electrically active donors and electrically active acceptors. The capacitance-voltage meter measures how much the capacitance changes when different voltages are applied over the epitaxial layer. From this, the net dopant concentration can be calculated.

7.4 Photoluminescence

Photoluminescence (PL) is a characterization method where the carriers are excited and the radiative recombination of the carriers is studied. This excitation is usually done with photon energies above the band gap of the semiconductor (E_g), normally by a laser. Above-band-gap excitation creates excitons, which is electron-hole pairs bound by their Coulomb interaction that is free to move in the crystal. The excitons may recombine

as free excitons, or be captured at defects and impurities present in the crystal (bound excitons) and recombine there. In the latter case, the exciton energy is decreased by an amount equal to the binding energy of the exciton to the crystal imperfection, which is specific to the defect binding the exciton. In this way it is possible to study what defects and/or impurities are present inside the material, e.g. dopants and intrinsic defects.

The detection part of a photoluminescence setup usually consists of a monochromator containing a diffraction grating and a photosensitive detector (e.g. a photomultiplier or a CCD camera). The luminescence from the sample is collected with optical lenses directed to the grating, where the different wavelengths will diffract differently and produce a spectral image on the CCD. In a direct band gap semiconductor, the energy from the recombination of a free exciton is

$$E = \hbar\omega = E_g - E_{FE} \quad (7.1)$$

where E_{FE} is the Coulomb energy binding the free exciton. However, in indirect semiconductors like SiC, the momentum conservation prohibits direct recombination of the free exciton and leads to the appearance of the so-called phonon replicas in the spectrum. This is because a part of the exciton recombination energy is spent on the creation of momentum conserving phonon. Therefore, equation 7.1 becomes

$$E = \hbar\omega = E_g - E_{FE} - E_{phonon}, \quad (7.2)$$

where E_{phonon} is the energy of the phonon conserving the momentum. The free exciton can move in the lattice and bind to a dopant atom or a defect from where a bound exciton is created. If the bound exciton recombines, the recombination energy becomes

$$E = \hbar\omega = E_g - E_{FE} - E_{BE}, \quad (7.3)$$

where E_{BE} is the energy of binding of the exciton to the defect. This energy is defect-specific. This can then tell which impurities or defects are present in the material. Often the intensity of the PL lines is proportional to the defect concentration, and in some cases it is possible to determine, for instance, the nitrogen concentration in SiC by comparing the intensities of the free-exciton and nitrogen-bound exciton lines. [29]

To avoid broadening of the peaks due to that phonons are generated from heat in the material thereby broadening the needed energy of the phonon, measurements are usually performed at liquid helium temperatures $\sim 2\text{K}$. This is called low temperature photoluminescence (LTPL).

CHAPTER 8

FUTURE WORK

In this chapter I take the opportunity to briefly give you my thoughts on the fluoride based chemistry and what I would have thought would have been interesting to investigate further in this area. Personally I do not see that the fluoride chemistry will be able to compete with neither the chloride based chemistry nor the standard chemistry, if there is not a special reason for it, which goes beyond chemistry, e.g. isotopes. In my opinion the fluoride based chemistry has too many drawbacks – narrow process window, low and uneven deposition rates and dopant inclusions, as well as unpleasant exhaust gases, as demonstrated in Paper 1, 2 and 3.

The fluoride based chemistry has – as I see it – a role in the fundamental understanding of halogenated chemistries. Therefore, I see comparisons with the chlorinated and brominated chemistries as the most important future work in this area, as well as their comparison to the standard chemistry, a work which is now started (Paper 5). For further understanding of the fluoride based chemistry, growth using other precursors is my suggestion. In this work the F has been added via the Si precursor SiF_4 . It can also be added via the carbon precursor or by the addition of HF. The latter one gives a good possibility to compare it to standard and the halogenated chemistries since $\text{SiH}_4 + \text{HX}$, $\text{X} = \{\text{Cl}, \text{Br}\}$ are already investigated, as well as it gives a better opportunity to investigate the F/Si than was done in Paper 2.

I also suggest that the surface chemistry is further investigated. To our current knowledge, a fluorinated chemistry causes fluorine terminated surface, but the mechanism behind creating the termination is still unclear.

From a modelling point of view, further investigation of the kinetics, as well as using the results in a CFD model can give more insights to the understanding of the fluoride based chemistry.

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SUMMARY OF THE INCLUDED PAPERS

In **Paper 1** we investigate the Si chemistry in F SiC CVD by using SiF_4 as the Si precursor and source of F. We find that the epitaxial growth is possible only if the effective C/Si is low enough. By creating a system which upstream has a too high effective C/Si ratio, which decreases along the susceptor, we could probe where the effective C/Si is low enough for epitaxial growth. This position – which we named "the onset of epitaxial growth" – is used as a measurable to compare experiments to gas phase simulations using thermodynamic equilibrium. Doing such we were able to identify two Si species which could be growth species in the fluorinated chemistry. Then, using quantum chemical computations for surface reactions, we were able to conclude that SiF is the main growth species with SiHF as minor growth species.

In **Paper 2** we continue to use the onset of epitaxial growth to identify the C growth species in F SiC CVD using SiF_4 . Here, we use three different C precursors and compare their positions for the onset of epitaxial growth. We also use kinetic gas phase modelling to compare the three different C precursors. We find that what C growth species are created (C_2H_2 and CH_3), and their concentration over time, is highly dependent on the choice of C precursor. We also show that the C precursor CH_4 is a good choice of C precursor together with SiF_4 . From the kinetic simulations we also discover that atomic Si could temporarily be a Si growth species. As the C growth species are to attach to a Si monolayer, we here also investigate surface terminations on the Si face in a fluorinated environment by thermodynamic equilibrium. We find that the surface become highly F terminated. To investigate the role of F further we reduce

the F/Si ratio by substituting SiF_4 to SiH_4 to different extent and conclude that the increase in growth rate when the amount of F is reduced could be attributed to the reduced amount of F in the system.

To investigate if F SiC CVD could be adopted for devices, we study dopant incorporation in **Paper 3** in the F chemistry. For the doping, we show that the dopants behave like we are used to, although the presence of F influences the incorporation. We find large area doping homogeneity difficult – both for n-type using N_2 and p-type using TMAI – most likely due to the higher amount of released F, discussed in Paper 2.

Despite the difficulties in doping uniformity, **Paper 4** investigates if there are defects related to the F chemistry that makes the F chemistry inapplicable for growth of the active layer in devices. From photoluminescence and deep level transient spectroscopy no F-related defects were found.

Paper 5 puts the fluorinated chemistry in to a bigger context by comparing it to the other halogenated chemistries as well as the standard chemistry. Here it is shown that thermodynamic equilibrium calculations of the gas phase is good tool for investigating the gas phase composition by comparing them to the gas phase composition derived by kinetic. Here it is shown that the growth species in the other chemistries are similar to those in F system, namely C_2H_2 , CH_3 , Si, SiH_x , SiX and SiHX , where $\text{X} = \{\text{Cl}, \text{Br (and F)}\}$.

Papers

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