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CVD Growth of Silicon Carbide for High Frequency Applications

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Till mina föräldrar

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Abstract

Silicon Carbide (SiC) is an important wide band gap semiconductor with outstanding electronic properties. With figures of merit far better than silicon, SiC is believed to replace and outcompete silicon in many applications using high frequencies, high voltage and high temperatures.

With the introduction of seeded sublimation technique, a realisation of substrates with large diameter and high quality became possible. Recent progress in the bulk growth using high temperature chemical vapour deposition (HTCVD) has shown excellent results with high purity substrates with semi insulating (SI) properties. The availability of high quality SI substrates allows the fabrication of microwave devices with low rf losses such as the Metal Schottky Field Effect Transistor (MESFET). With the introduction of the hot-wall CVD technique, thick low doped n-type epitaxial layers have been grown for high power devices (> 4 kV) such as the PiN diode.

The main contribution of the present work relates to the investigation of growth of MESFET structures. The goal has been to demonstrate the ability to grow MESFET structures using the hot-wall CVD technique. The challenge with abrupt interfaces and controlled doping has been investigated. A comprehensive investigation has been made on how nitrogen and aluminum dopant atoms incorporate into the SiC lattice using the hot-wall CVD technique. Fundamental research of MESFET structures has been combined with growth of device structures for both Swedish and European groups as well as industries. The research has been focused towards the understanding of dopant incorporation, characterization of doped

epitaxial layers, the growth of device structures, the modelling of temperature distribution in a hot-wall susceptor and the development of growth systems for future up scaling.

The thesis in divided into seven papers.

In paper 1 we present how the nitrogen dopant is incorporated into the SiC lattice. The influence of several different growth parameters on the nitrogen incorporation is presented. Equilibrium thermodynamical calculations have been performed to give a further insight into the incorporation mechanism. The investigation shows that the N_2 molecule itself does not contribute directly to the nitrogen incorporation, however, molecules like the HCN and HNC are more likely.

In paper 2 the incorporation of the aluminum dopant into the SiC lattice is investigated in a similar way as the nitrogen incorporation in paper 1. The results show that the aluminum incorporation in SiC is mainly controlled by the carbon coverage on the SiC surface. The investigation shows that it is difficult to obtain high aluminum doping on carbon face whereas the silicon face is sensitive to changes of the growth parameters. High growth rate resulted in a diffusion controlled incorporation.

In Paper 3 we present the results from the growth of MESFET structures as well as characterization of the structures and final device properties. Knowledge taken from paper 1 and 2 was used to improve the abruptness of the grown structures.

Paper 4 presents the results obtained by low temperature photoluminescence (LTPL) on separately grown 4H-SiC epitaxial layers. Doping calibration curves for nitrogen in the doping range from $1 \cdot 10^{14}$ to $2 \cdot 10^{19}$ cm⁻³ are presented. A discussion concerning the Mott transition is also presented.

Paper 5 presents the results of the use of simulation to investigate the heating of a hot-wall CVD reactor. New susceptor and coil design are tested. The simulation has been verified with experimental heating tests which show excellent agreement. The new design has a temperature variation of less than 0.5 % over more than 70% of the total susceptor length in addition to a decreased power input of 15 %.

In the final two papers, paper 6 and 7, we present work of growth of AlN on SiC. Thin films were grown and characterized with different techniques concerning crystal quality and thickness. The use of infrared reflectance and the features of the AlN reststrahl reflectance band allowed us to determine the thickness of AlN films as thin as 250 Å.

PREFACE

This thesis is divided into two sections. The first one gives a general overview of this work, giving the background and motivation of the research conducted. The aim has been to develop and investigate epitaxial growth of SiC MESFET devices. The second section lists the papers published or submitted.

This thesis was carried out at the Materials Science Division at Linköpings University during the period 1997-2001.

I wish you a pleasant and interesting time reading this thesis.

Urban

Linköping, 7th of August 2001

PAPERS INCLUDED IN THE THESIS

- Nitrogen doping of Silicon Carbide: Effect of Process Parameters
 U. Forsberg, Ö. Danielsson, A. Henry, M.K. Linnarsson and E. Janzén. Submitted to Journal of Crystal Growth June 2001
- Aluminum doping of Silicon Carbide: Effect of Process Parameters
 U. Forsberg, Ö. Danielsson, A. Henry, M.K. Linnarsson and E. Janzén. Submitted to Journal of Crystal Growth August 2001
- Growth and characterisation 4H-SiC MESFET structures grown by Hot-Wall CVD
 U. Forsberg, A. Henry, N. Rorsman, J. Eriksson, M.K. Linnarsson, Ö. Danielsson, L. Storasta and E. Janzén, Submitted to Journal of Applied Physics August 2001
- Determination of nitrogen doping concentration in doped 4H-SiC epilayers by low temperature photoluminescence
 U. Forsberg, A. Henry, M.K. Linnarsson and E. Janzén, Submitted to Applied Physics Letter, June 2001
- 5. Investigation of the temperature profile in a hot-wall SiC chemical vapour deposition reactor
 Ö. Danielsson, U. Forsberg, A. Henry and E. Janzén.
 Submitted to Journal of Crystal Growth, April 2001
- 6. Growth of high quality AlN Epitaxial Films by Hot-Wall Chemical Vapour Deposition
 U. Forsberg, J. Birch, M. F. MacMillan, P. O. Å. Persson and E. Janzén, Materials Science Forum 264-268 (1998) 1133-1136
- 7. Infrared Reflectance of Extremely Thin AlN Epi Films Deposited on SiC Substrates
 M.F. MacMillan, U. Forsberg, P.O.Å. Persson, L. Hultman and E. Janzén, Materials Science Forum 264-268 (1998) 649-652

$M_{\rm Y}$ contribution to the papers

- PAPER 1 I have redesigned the growth system for the need of intentional nitrogen doping. I have planned and performed all the growth runs. I have analysed all the results. The thermodynamical part has been performed together with the second author. I have written the manuscript.
- PAPER 2 I have re-designed the growth system for the need of intentional aluminum doping. I have planned and performed all the growth runs. I have analysed all the results. The thermodynamical part has been performed by the second author. I have written the manuscript.
- PAPER 3 I have planned and optimised the growth system for the growth of MESFET structures. I have planned and performed all the growth runs. I have initiated the characterisation part. I have written the manuscript except the parts on electrical measurements and device results.
- PAPER 4 I have planned and performed all the growth runs. I have written the first draft of the manuscript.
- PAPER 5 I have taken an active part in the planning of the experiments. I have educated the first author to perform all the experiments of his own. I have taken an active part in the discussion of the experiments. I have discussed the outline with the first author.
- PAPER 6 I have planned and performed all the growth runs. I have initiated the characterisation and analysed the results together with the other authors. I have written the manuscript.
- PAPER 7 I have planned and performed all the growth runs. I have been involved in the characterisation part.

$P_{\ensuremath{\text{APERS}}\xspace}$ related to but not included in the thesis

High-Voltage (>2.5 kV) 4H-SiC Schottky Rectifiers Processed on Hot-Wall CVD and High-Temperature CVD Layers
T. Kimoto, Q. Wahab, A. Ellison, U. Forsberg, M. Tuominen, A. Henry and E. Janzén, Materials Science Forum, 264-268 (1998) 921-924

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O.P.A. Lindquist, H. Arwin, U. Forsberg, P. Bergman and K. Järrendahl Materials Science Forum, **338-342** (2000) 575-578

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Aluminum Doping of Epitaxial Silicon Carbide grown by Hot-Wall CVD, Effect of Process Parameters

U. Forsberg, Ö. Danielsson, A. Henry, M.K. Linnarsson and E. Janzén, accepted for oral presentation at ICSCRM2001 in October, Japan

Incorporation of Hydrogen (¹H and ²H) in 4H-SiC during Epitaxial Growth M.K. Linnarson, U. Forsberg, M.S. Janson, E. Janzén and B.G. Svensson, accepted for ICSCRM2001 in October, Japan

Influence of the trenching effect on the characteristics of buried-gate SiC junction field-effect transistors

S.-M. Koo, S.-K. Lee, C.-M. Zetterling, M. Österling, U. Forsberg and E. Janzén, accepted for ICSCRM2001 in October, Japan

Investigation of thermal properties in fabricated 4H-SiC high power bipolar transistors

E. Danielsson, C.-M. Zetterling, M. Österling, U. Forsberg and E. Janzén, accepted for ICSCRM2001 in October, Japan

Characterization of bulk and epitaxial SiC material using photoluminescence spectroscopy

A. Henry, A. Ellison, U. Forsberg and E. Janzén, accepted for ICSCRM2001 in October, Japan

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AN INTRODUCTION TO SILICON CARBIDE

OR WHY SO MUCH FUZZ ABOUT SIC?

The electronic boom

The electronic "boom" that the world has experienced during the last 50 years is almost only due to one specific material, silicon (Si). The invention of the first silicon based bipolar junction transistor was made in 1948 by Shockley, Bardeen and Brattain [1] at Bell Telephone Laboratories, USA. Still, silicon is, and will continue to be, the most dominant semiconductor material for many years to come. The rapid expansion of telecommunication in the post-war era has lead to products like personal computers (PC), routers (back bone in the internet), mobile phones, TV and radios. Still, other semiconductor materials like indium phosphine (InP) and gallium arsenide (GaAs) are competing with silicon within other applications like high frequency and optoelectronic devices. However, the drawback with the current semiconductor materials is that they are not well suited to handle large current densities and high voltages. This crucial limitation has open for new materials and these materials are usually named wide band gap materials, Silicon Carbide (SiC) is one of them.

It is somewhat honourable to say that SiC was first discovered here in Sweden in 1824 by the Swedish scientist Jöns Jacob Berzelius (1779-1848) while he was trying to synthesize diamonds. As we all know, he was not successful in his attempts. However, SiC was also synthesized to be used as coating material on cutting tools and grinding (sand papers) where the hardness could be significantly improved. Another name of SiC is "Moissanite" or "Carborundum". The research in SiC has advanced tremendously during the last ten years. Large diameter substrates are available as well as extremely low-doped, semi-insulating (SI) substrates [2,3]. The concentration of the "main" defect, the micropipe, has been reduced to less than 1 cm⁻². This material research development in combination with the technological development of large scale production machines are currently enabling a commercialisation of SiC based devices.

Although SiC is a relatively new material with outstanding physical properties the devices that should be manufactured have to be reliable and have lower energy losses than current silicon based devices. For high-voltage DC current transmission systems, motor drives and traction, the installation and operational cost should be much lower to be able to compete with silicon. If SiC does not fulfil this, SiC-based power devices may not be a reality.

M ATERIAL PROPERTIES AND APPLICATIONS

To understand the advantage with SiC it is necessary to extract the important physical properties and to compare them with other relevant (or competing) semiconductors, see Table 1. The materials can be divided into two groups. The first group contains Si and GaAs, which is characterized by its small bandgap. The second group contains the other materials and are known as wide band gap materials.

	Si	GaAs	С	2H-GaN	4H-SiC	6H-SiC	3C-SiC
Band gap energy $E_g (eV)$	1.11	1.43	5.45	3.4	3.26	3.02	2.23
Lattice Constant (Å)	5.43	5.65	3.56	a=3.189 c=5.185	a=3.08 c=10.083	a=3.08 c=15.117	4.36
Electron mobility μ (cm ² V ⁻¹ s ⁻¹)	1350	8000	2200	1000	900	450	1000
Breakdown electric field $E_B (\cdot 10^6 \text{ Vcm}^{-1})$	0.2	0.3	10	4	3	3	
Saturated electron drift velocity v_{sat} ($\cdot 10^7 \text{ cms}^{-1}$)	1	2	2.7	1.5	2.7	2	2.7
Thermal conductivity $\alpha_{therm} (Wcm^{-1}K^{-1})$	1.5	0.5	20	1.3	5		
Johnson figure of merit (JFM) (VGHz) ²	1	1.5	>2000	400	400		

Table 1 Physical properties of the three most common SiC polytypes compared to Si, GaAs, gallium nitride (GaN) and diamond (C). The JFM value is normalized to Si.

SIC- THE POWER SEMICONDUCTOR MATERIAL FOR THE FUTURE

Diodes, thyristors, transistors and insulated gate bipolar transistors (IGBTs) are key components among the power electronic devices. Theses devices should be capable of blocking high voltage in the off-state, conducting large currents in the onstate and being switched from one state to the other with a minimum of energy losses.

For a pn-diode the minimum thickness W of the junction, assuming a triangular electric field distribution, is given by:

$$W > \frac{2U_b}{E_{\max}}$$

where U_b is the blocking voltage and E_{max} is the critical electrical breakdown field. SiC has about ten times higher electrical break down field strength than Si and for a given voltage the required thickness of a SiC device will therefore be only one tenth of the

thickness required for a Si-based device. SiC enables higher operation temperature, up to 500 °C, whereas Si is limited to around 125 °C. This enables SiC devices to operate at high power levels and still dissipate the large amounts of excess heat generated.

Mesfet

The metal semiconductor field effect transistor (MESFET) is a device for high frequency applications (RF and microwave, 0.01-100 GHz). GaAs MESFETs have been widely used. The MESFET device is similar to a junction FET (JFET) but instead of using a p-n junction to deplete the channel, a Schottky barrier is used. The MESFET structure comprises of a p-type buffer, a n-type channel and a n^{++} -type contact layer, see Figure 1. The structure is usually grown on a semi insulating (SI) substrate, which has a high resistivity (~ $10^{10} \Omega$ cm). The source and the drain ohmic contacts are placed on top of the highly doped contact layer whereas the Schottky gate contact is placed on the medium doped (typically 1.10¹⁷cm⁻³) channel layer. The majority carriers flow in the channel from the source to the drain and the current flow is controlled by the Schottky gate voltage. By modulating the gate voltage the depletion of the channel layer can changed. The use of SI substrate will eliminate the propagation of the signal through the substrate and the p-type buffer layer can be omitted if the substrate has good enough properties. In Figure 2 a processed quarter wafer is shown. The MESFET structure has been grown within the work of this thesis and the structure has been processed at Chalmers University, Gothenburg.



Fig. 1 A schematic picture of a MESFET structure comprising of a ptype buffer layer (~ 0.5-5 μ m, ~0.5-5 $\cdot 10^{17}$ cm⁻³), a n-type channel layer (~ 0.2-0.7 μ m, ~1 $\cdot 10^{17}$ cm⁻³), n-type cap layer (~ 0.15 μ m, >3 $\cdot 10^{19}$ cm⁻³).



Fig. 2 A processed quarter wafer (θ =35 mm) [4].

For high frequency applications (RF and microwave, 0.01-100 GHz) the maximum operating frequency is given by:

$$f \propto \frac{v_s}{L}$$

where v_s is the saturated electron drift velocity and L is the gatedrain width [5]. The physical properties of SiC enable higher operating frequencies than Si. Diamond is also a promising material for high frequency devices but there are still problems with large, mono-crystalline device quality substrates as well as doping techniques for obtaining donors and acceptors with low activation energies [6].

It is sometimes convenient to present figures of merit that is only related to material parameters and for high frequency the Johnson's figure of merit [7], JFM, is often used:

 $JFM = \text{constant} \cdot (E_c v_s)^2 \ge PRf^2$

where P is the power delivered by the transistor, R is the load impedance, f is the frequency of operation, E_c is the breakdown electric field and v_s is the saturation velocity for carrier. The value of the dimensionless constant is independent of the material considered. The JFM for SiC is several hundred times higher than for Si or GaAs.

The SiC substrates are also extensively used as substrates for epitaxial growth of GaN, since it does not exist any bulk growth technique of GaN. Today, blue and ultra violet light emitting diodes have been fabricated from GaN on SiC. Due to the chemical and mechanical stability of SiC it is also a promising material in harsh environments like high temperature gas sensors [8] (close to the exhaust of an engine) and in high radiation areas (in space). Finally, being almost as hard as diamond, SiC has acquired attention as gemstones in jewellery, which may be of help for many men around the word.

GENERAL PROPERTIES OF SILICON CARBIDE

Silicon Carbide is a IV-IV compound semiconductor consisting of silicon and carbon atoms. The building block is easiest visualized by a tetrahedron, consisting of one carbon atom bonded to four silicon atoms, or vice versa, see Figure 3. The Si-C bond is 88% covalent and 12% ionic, Si being positively charged. The silicon atom on the top has a larger distance to the carbon atom compared to the three silicon atoms placed at the bottom, when viewed from the side. When the SiC crystal is cut orthogonal to the [0001] direction it is most likely that this bond will be broken. The result will be two crystals with different faces, one denoted the Si-face and one denoted the C-face. The electronic structure of these faces is very different which will influence both the epitaxial growth, the surface morphology and the incorporation of dopants.



Fig. 3 The tetrahedron building block consisting of four silicon and one carbon atoms. The length of the Si-C bond is 1.89 Å, the distance between two neighbouring silicon or carbon atoms, a, is 3.08 Å and the interlayer distance, b, is 2.52 Å.

The bonding of the Si-C is very short (1.89 Å) and very strong (4.5 eV) which makes SiC a very hard material. SiC is the most prominent of a family of close-packed materials that exhibit a

one-dimensional polymorphism called polytypism. The SiC polytypes are differentiated by the stacking sequence of the tetrahedrally bonded Si-C bilayer. The closed packed structure of the hexagonal crystal is usually described by the Miller-Bravais indices (h,k,i,l) which are referred to the four axes (a_1 , a_2 , a_3 , c), see Figure 4.



Fig. 4 Direction indices in the basal plane (a_1, a_2, a_3) is $\{1/3[2\overline{1}\overline{1}0], 1/3[\overline{1}2\overline{1}0], 1/3[\overline{1}\overline{1}20]\}$ and corresponding important planes used to visualize the crystal structure and polytype.

The first three indices are related by the equation:

h + k = -i

and equivalent planes are obtained by interchanging the position and sign of the these three indices. The c-axis is perpendicular to the basal plane created by the a-axis. The most common polytypes are the hexagonal (H), the cubic (C) and the rhombohedral (R) crystal structures. Let us consider a closed packed system in the (0001) plane, see Figure 5. The first layer is denoted A. The second layer can be built in two different way, rotated 60° to each other. The two different layers are denoted B and C. By combining the stacking sequence in different ways

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different polytypes can be obtained. For example, 3C has the stacking sequence ABCABC..., 4H ABACABAC... and 6H ABCACBABCACB... where the number stands for the periodicity and the capital letter stands for the crystal symmetry.



Fig. 5 Closed-packed system in the (0001) plane. The three different stacking sequences are denoted A, B and C. The right figure shows the stacking sequence for 4H-SiC.

The different polytypes have different physical properties. The band gaps differ widely among the polytypes ranging from 2.3 eV for 3C-SiC to around 3.3. eV for 2H-SiC. The periodicity of the stacking sequence for the hexagonal polytypes will produce a zigzag pattern when viewed along the $[11\overline{2}0]$ direction, see Figure 6. SiC is believed to crystallise itself in more than 200 polytypes with the most common polytypes being the 3C, 4H, 6H and 15R.



Fig. 6 Arrangement of the Si (open circles) and C (closed circles) atoms in the $(11\overline{2}0)$ plane for 3C- and 4H-SiC polytype. The corresponding stacking configuration for 4H-SiC as obtained in a transmission electron microscope. The black circles represent the silicon atom [9].

SILICON CARBIDE CRYSTAL GROWTH TECHNIQUES

WHY CRYSTAL GROWTH ?

In the last century the growth of single crystals has received enormous importance for both academic research and for mass production of electronic devices. The range of fields involved for crystals in general is huge. Almost all electronics today are built around a crystal, and the most common is silicon. It is very easy to buy an electronic component, which can be even done on the internet. What most people do not realize is that there have been several hundred process steps just to manufacture one single electronic device. Among the first steps in this long chain is the growth of the crystal.

EARLIER WORK OF GROWTH OF SINGLE CRYSTAL SIC

THE ACHESON PROCESS

The first production of SiC started with the Acheson process already in 1892, see Figure 7.



Fig. 7 Schematic picture of a Acheson furnace before (top) and after heating (bottom) [10].

A mixture of silica, carbon, sawdust and common salt (e.g. 50% SiO₂, 40% C, 7% sawdust and 3% common salt (NaCl)) is heated by an electric furnace to a temperature around 2000 °C. Inside the mixture small platelets will start to crystallize, typically some millimetres in size. The quality of these platelets is usually quite bad and the process enables no control of the polytype. Still, some small samples can be found that can be used for seeds for growth of larger SiC crystals. The main idea is however not to produce seeds but rather to produce large volume of raw material for grinding and for coating on cutting tools.

THE LELY METHOD

The Lely method was introduced in 1955 allowed the fabrication of micropipe free platelets of up to 1 cm^2 , see Figure 8. The high crystal quality allows them to be used as seeds for growth of larger crystals. The purity of the grown material depends on the purity of the source material but the platelets are usually highly doped with nitrogen up to 10^{19} cm^{-3} . The Lely furnace is shown in Figure 8.



Fig. 8 Schematic picture of a Lely furnace [10].

The growth is performed in a graphite crucible filled with porous SiC. Upon heating to around 2500 °C the SiC will sublime and SiC platlets will be grown on the inner wall.

BULK GROWTH TECHNIQUES USED TODAY

There are mainly two different crystal growth techniques used today to grow large area wafers, the seeded sublimation technique and the recent developed High Temperature Chemical Vapour Deposition (HTCVD) technique.

THE SEEDED SUBLIMATION TECHNIQUE

Most groups and companies around the world is using the seeded sublimation technique, also known as the modified Lely method introduced in 1978 by Tairov and Tsvetkov [11]. The growth is performed in a graphite crucible, see Figure 9.



Fig. 9 A Schematic picture of a seeded sublimation growth cell.

The SiC seed crystal is placed at the lid above the SiC power source material. When the crucible is heated to around 2200-2500 °C the SiC powder will start to sublime. The seed crystal

will be maintained at a lower temperature compared to the SiC powder and thereby allowing mass transport of silicon and carbon species to be deposited at the seed crystal. Typical growth rates are usually between 0.5-2 μ m/h. Boules with large diameter (>75 mm) and a couple of centimetres in length are possible to produce.

THE HTCVD TECHNIQUE

The HTCVD technique is a development of the well established CVD technique for growth of epitaxial layers of SiC. Instead of using SiC as a source material, as in the seeded sublimation technique, high purity gases are used. Silane is used as a silicon precursor, ethylene as a carbon precursor and helium as carrier gas. Typical growth temperature is around 2200-2300 °C and a typical growth rate is 0.8 mm/h. The advantage with the HTCVD technique is the use of high purity gases that enables the growth of very low doped crystals. Residual nitrogen concentration is in the low 10^{15} cm⁻³. High purity Semi Insulating (SI) substrates with a resistivity of higher than 10^{10} Ω cm have also been reported [12]. The HTCVD technique is illustrated in Figure 10.



Gas Inlet

Fig. 10 Schematic view of the HTCVD system [13].

The gases are introduced from the bottom of the susceptor and are heated as they travel upwards. The seed crystal is placed at the top of the susceptor and the growth of the crystal is towards the gas inlet.

EPITAXIAL GROWTH

There are mainly three different techniques used to grow epitaxial layers of SiC. Liquid phase epitaxy (LPE), sublimation epitaxy and chemical vapour deposition (CVD). The first two techniques are characterised by their high growth temperature (1700-2000 °C) and high growth rate (from 15 μ m/h to more than 2 mm/h). Although these two techniques have shown promising results concerning the high growth rate and relative low residual doping they are not as well suited for growth of device structures as the CVD technique. The high temperature used releases unwanted impurities (like boron, titanium and aluminum) from the graphite which might be difficult to remove. The ability to perform intentional doping for growth of device structures may also be difficult.

The only technique used today for production of device quality epitaxial layers is the CVD technique. The CVD technique is sometimes called vapour-phase epitaxy (VPE) and the name used is more related to which school you have been raised at. If the precursors contain metal-organic compounds the process is usually called metal-organic CVD (MOCVD). There have been several different reactor configurations used for epitaxial growth, see Figure 11.



Fig. 11 Typical CVD reactor configurations: (a) horizontal (cold wall) reactor; (b) vertical reactor; (c) barrel reactor; (d) pancake reactor; (e) multi-wafer-in-tube reactor [14].

The most commonly used CVD reactor is the cold-wall CVD reactor. The susceptor has a relatively simple design where the substrate is supplied heat only from the bottom. The substrate "sees" a cold environment on the sides and above itself. The cold-wall reactor is characterized by the large temperature gradient from the substrate to the upper part of the quartz tube.

The development of SiC CVD reactors are towards rotation of the substrates which is probably necessary to obtain the high doping and thickness uniformity needed for certain devices. The precursors used for growth of SiC is usually silane (SiH₄) and propane (C_3H_8) whereas hydrogen is used as carrier gas. Nitrogen (N_2) and trimethylaluminum (TMA) are used as dopants to obtain n- and p-type, respectively. The CVD process used in this thesis is a horizontal hot-wall CVD, see Figure 12.



Fig. 12 Principle of the horizontal CVD process used for SiC.

The SiC coated graphite susceptor is inductively heated by Joule effect caused by an AC current in the radio frequency (RF) coil. Insulation is placed between the quartz tube and the susceptor to prevent melting of the quartz. Typical growth parameters are 100-1000 mbar, 1500-1600 °C and a growth rate of around 1-10 μ m/h. CVD growth from the vapour is usually divided into three fundamental processes:

- 1 Gas phase reactions
- 2 Mass transport
- 3 Surface kinetics

Epitaxial growth is a highly controlled phase transition from vapour to solid. Thermodynamics determines the driving force and thereby the maximum growth rate for the growth process. Thermodynamics also describes the reactions in the source gases that will form the reactive species that will participate in the growth of the SiC crystal. It also involves homogeneous vapour phase reactions where solid particles can be formed in the gas phase. All these processes are denoted gas phase reactions in Figure 13.



Fig. 13 Schematic representation of some of the gas phase and surface processes during CVD growth.

Mass transport involves important steps like hydrodynamics, diffusion of species in the gas phase and from the gas phase down to the crystal surface. The last process, surface kinetics, involves nucleation and growth of crystal, adsorption and desorption of reactants, surface diffusion, 2 and 3 dimensional growth and reactions at steps. The crystal growth is also connected to the crystal surface. For SiC, with its polarity dependence, the growth parameters are different for the different faces. This is clearly seen on the morphology of the grown epitaxial layers but also on the very different behaviour of dopant incorporation on the different faces [15].

Although the main CVD process can be divided into several "small" processes the overall process, as well as high thickness and doping uniformity, is also closely connected to the susceptor

design. The susceptor can be designed and heated in different ways. For example, by changing the coil design (number of turns, diameter and shape of the coil) the coupling between the RF coil and the susceptor can be altered significantly. Heat losses, due to radiation, at the inlet and outlet of the susceptor can be reduced with proper susceptor design, insulation and RF coil.

The temperature profile of the susceptor will determine the concentrations of different silicon and carbon containing species as the gas is flushing through the susceptor [16]. The temperature in the susceptor is usually determined by placing small pieces of silicon on the floor of the susceptor. Since silicon melts at around 1412 °C in a hydrogen atmosphere it is possible to determine the temperature along the susceptor by using a pyrometer. Until now the design of the susceptor and coil has been on a more or less trial and error basis, although with some "clever" ideas, feed back from previous growth runs and from visual determination of the deposition on the susceptor walls. This feed back has allowed us to develop new improved susceptors and coils. A more efficient way to proceed is to use simulation in the development of both susceptors and coils.

Simulation is a powerful tool to investigate various physical phenomena in the CVD process. These investigations can help us to design the susceptor and coil to obtain an optimum temperature distribution, see paper 5 in this thesis. The temperature distribution of the susceptor used in this thesis is presented in Figure 14.



Fig. 14 The temperature distribution inside the susceptor used in this thesis. The temperature profile can be improved significantly by applying a different coil design in combination with insulation at the inlet and outlet, paper 5 in this thesis [17].

A correctly simulated temperature distribution is the first step of the understanding of the SiC CVD process. The next step is to develop a tool for the chemistry and a prediction of the growth rate dependence along the susceptor. Although there are so many parameters that need to be taken into account to predict for example the growth rate, a picture of a correct temperature distribution is very valuable. The problems with up scaling of CVD reactors for larger wafer capacity can be reduced with simulation and the cost for new susceptors can be minimized by first simulate the temperature distribution. An improved susceptor design (with larger area of homogeneous temperature) usually demands lower power input which also make it more cost efficient.

DOPING OF EPITAXIAL SILICON CARBIDE

Impurities in SiC

A perfect SiC crystal does not contain anything else except carbon and silicon atoms. To grow a completely undoped SiC crystal is not possible. Impurities from precursors and the growth system itself will always contribute with impurities. Common impurities in SiC are nitrogen, aluminum, boron and titanium. One cubic centimetre of SiC contains roughly 10^{22} atoms, 50 % silicon and 50% carbon. Although we have access to highly sophisticated and sensitive characterization techniques, we are only able to detect impurities with a concentration larger than 10^{11} - 10^{12} cm⁻³. It is probably not too wrong to say that one cubic centimetre of SiC contains from most of the elements in the periodic table.

An undoped SiC crystal is an insulator and of no use (although interesting in a characterization point of view) for electronic applications. By adding a controlled amount of impurities, called doping, the electrical characteristics of the crystal can be favourably altered. There are mainly three different methods of doping, diffusion, ion implantation and epitaxial doping. Diffusion has been successfully used in the silicon semiconductor industry but in SiC is not possible due to the very low diffusion coefficient of impurities [18]. Ion implantation is mainly used for obtaining desired doping in certain areas on the wafer. Unfortunately, ion implantation also creates lattice damages that are difficult to remove [19]. The third doping technique, epitaxial doping, is performed during the growth of the epitaxial layer. By adding impurities to the precursor gas flow, a very controlled doping of the epitaxial layers is obtained.

A dopant atom can be incorporated into the SiC lattice via several different mechanisms. For example, a dopant can substitute a host atom in the SiC lattice and the dopant atom is then called substitutional. It can also be incorporated into the lattice but not at a substitutional site, the dopant is then called interstitial. The third possibility is that it forms a complex together with an intrinsic crystal defect, such as a vacancy. In SiC there are mainly two important dopant atoms, aluminum and nitrogen, and they are believed to substitute the silicon and the carbon lattice site, respectively. Intentional nitrogen and aluminum doping will be discussed further with the assumption that all dopant atoms are substitutional.

The nitrogen and aluminum incorporations in SiC have been investigated by several groups [20,21] and the incorporation of dopants is influenced by several different process parameters. One of the most common process parameter is the C/Si ratio, which relates the propane to the silane input flows. Changes of the C/Si ration will influence both the nitrogen and the aluminum incorporations. A common model used is the sitecompetition theory [22] which states that nitrogen and aluminum dopants compete with carbon and silicon, respectively, for a specific lattice site. For example, as the C/Si ratio is increased, i.e. by increasing only the propane flow, the increased carbon will outcompete the nitrogen atoms and consequently, the nitrogen incorporation is reduced on the Si-face.

NITROGEN DOPING

The most common n-type dopant in SiC is nitrogen, which is available in high purity. The nitrogen molecule itself is very stable with a dissociation energy close to 9.8 eV [23]. At a growth temperature of 1600 °C only 10⁻⁷ of all the N₂ molecules have dissociated into atomic nitrogen, see paper one in this thesis. This indicates that there are other nitrogen containing molecules that contribute to the nitrogen doping.

We have shown in paper 1 in this thesis that the main nitrogen containing species that contribute to the doping are the HCN and the HNC molecules. The adsorption of these molecules to the SiC surface can be performed by either the carbon or the nitrogen atom. The Si-face and the C-face will attract and bond the HCN and HNC molecule differently [24] resulting in different amount of bonded HCN and HNC molecules on the Si-face compared to the C-face. The surface analysis of how these nitrogen containing molecules bond and dissociate is very complex and out of the scope for this thesis.

In Figure 15 a schematic picture is presented of the SiC surface during silicon and carbon rich growth conditions, respectively.



Fig. 15 Schematic picture of the Si-face surface during silicon rich (left) and carbon rich (right) growth conditions. Open and closed circles denote Si and C atoms, respectively. The gray circles represent the HCN and the HNC molecules. The figure is not in scale.

> The Si-face surface is believed to be mainly silicon terminated at silicon rich growth condition. As the C/Si ratio is increased

the surface becomes more carbon terminated. The increased carbon coverage will result in less available sites for the HCN and the HNC molecule to bond to and as a result the nitrogen incorporation on Si-face is reduced with increased C/Si ratio. The C-face is believed to be carbon terminated at low (silicon rich growth conditions) as well as at high (carbon rich growth conditions) C/Si ratio [20]. From the HCN and the HNC molecules point of view, the C-face surface looks more or less the same, consequently, the nitrogen incorporation on C-face is constant for different C/Si ratio.

The nitrogen incorporation is strongly connected to the chosen C/Si ratio. The C/Si ratio is, as mentioned above, determined from the propane and silane flows. It would be more convenient to know the *effective* C/Si ratio, i.e. the C/Si ratio close to the SiC surface. As different process parameters are changed, for example the total pressure or the growth rate, the *effective* C/Si ratio is changed although the C/Si ratio is kept constant, and as a result the nitrogen incorporation is changed.

Aluminum doping

To obtain p-type SiC material a dopant atom, like aluminum, from the group III element should be added. Aluminum is obtained from usually the metal organic compound trimethylaluminum (TMA). The TMA molecules $[(Al(CH_3)_3)_2]$ is in our case a "gigantic" molecule which contains both aluminum and carbon. When the TMA molecule is entering the growth chamber it will start to decompose and the decomposition is believed to start already at a temperature of 100 °C. The decomposition of TMA has been extensively studied [25] and the most common aluminum containing species Al. AlH, AlH_2 , AlH₃ and AlCH₃. Equilibrium are thermodynamical calculations yields the same results, with the AlH_2 , Al and $AlCH_3$ species with the highest concentration, during typical CVD growth conditions, see paper 2 in this thesis.

The relative large amount of atomic aluminum enables a slightly different incorporation model compared to that of nitrogen incorporation. As mentioned before, the aluminum atom is believed to substitute the silicon atom in the SiC lattice. On the Si-face the aluminum atom may bond to the underlying surface to three carbon atoms. As the growth conditions become more carbon rich a larger fraction of the Si-surface will be terminated with carbon atoms, see Figure 16.

The increased carbon termination will supply more suitable and stable lattice sites for the aluminum atoms to bond to. It seems like these sites are more suitable for the aluminum atom than for the silicon atom, although they are competing for the same site. The growth is performed on off-axis substrates (8 ° for 4H- and 3.5° for 6H-SiC) and the growth process is referred to as step-flow growth [26], i.e. the Si-C nucleation occurs at the steps. The aluminum atoms that are present on the surface will bond to surface where they will "sit" and wait until the growing step is buring them into the crystal.



Silicon terminated surface

Carbon terminated surface

Fig.16 Schematic picture of the Si-face surface during silicon rich (left) and carbon rich (right) growth conditions. Open and closed circles denote Si and C atoms, respectively. The gray circles represent aluminum atoms. The figure is not in scale.

As mentioned during previous section of the nitrogen doping, the C-face is believed to terminated with carbon atoms, even during silicon rich growth conditions. The increased carbon coverage does not influence the surface structure in such a way that it makes it more favourable for the aluminum atom to bond to it, resulting in a constant doping incorporation as the C/Si ratio is varied. Calculations of the adsorption energy of the Al atom on the C-face have shown that the Al atom bonds more than two times stronger on the Si-face compared to the C-face [27].

The *creation* of available lattice sites is according to this model related to the carbon coverage, or indirectly to the C/Si ratio. Changes in process parameters usually lead to changes in the C/Si ratio close to the SiC surface, although the propane and silane input flows are constant, i.e. constant C/Si ratio. Very high growth rate will saturate the aluminum incorporation. The incorporation-limiting step is now diffusion of aluminum species in the gas phase, i.e. all aluminum species on the surface are now incorporated.

CHARACTERIZATION OF SILICON CARBIDE

Low temperature thotoluminescence

Low temperature photoluminescence (LTPL) spectroscopy is an optical characterisation technique that has been extensively used to characterize epitaxial layers. A frequency doubled argon-ion laser is used as an excitation source to excite an electron from the valence band into the conduction band leaving a hole in the valence band. The laser has a wavelength of 244 nm which is equivalent to an energy of 5.08 eV. The band gap of the most common polytype of SiC is less than 3.3 eV which means that we excite the electrons and holes far into the bands. The charged carriers in the conduction band will rapidly relax via phonon emission down to the band minima where several different radiative recombination paths are available, as shown in Figure 17.





One common recombination path in SiC is the creation and annihilation of an exciton. An exciton is an electron-hole pair bound together by Coulomb attraction. In semiconductors where the bonds are mainly covalent, this exciton is referred to as Wannier-Mott type [28,29]. The exciton is free to move in the lattice and is therefore called a free exciton (FE), often denoted I in a LTPL spectrum. The radiative relaxation of the FE can occur in several different ways, involving both photons and phonons. As the FE is moving through the lattice, it can be captured by impurities (like nitrogen and aluminum) or various defects and form a localized bound exciton (BE). Studies of these excitons reveal information of the material. This work has been focused towards BE at impurities and I will therefore only discuss relaxation processes related to impurities.

Impurities, such as nitrogen, can capture a moving FE. The binding energy of such as captured FE is related to which site in the lattice the nitrogen atom is occupying. The number of inequivalent sites depends on the polytype. In 4H-SiC the nitrogen atom can occupy two inequivalent sites in the lattice, denoted **h** for hexagonal and **k** for cubic. 6H-SiC has three inequivalent sites denoted **h**, \mathbf{k}_1 and \mathbf{k}_2 . In 4H-SiC these two sites will produce two shallow energy levels below the conduction band, see Figure 18, whereas the 6H-SiC will produce three energy levels. 3C-SiC which has a cubic crystal structure has only one possible lattice sites and consequently the nitrogen atom will only produce one energy level below the conduction band.



Fig. 18 The nitrogen donor energy levels in 3C-, 4H- and 6H-SiC. CB and VB denote the conduction and valence band, respectively.

A donor bound exciton is denoted a D-BE and in 6H-SiC the three equivalent sites for nitrogen will give rise to three non phonon lines in the PL spectra denoted P_0 , R_0 and S_0 . In 4H.-SiC they are denoted P_0 and Q_0 for the hexagonal and cubic site respectively. The band structure of all SiC polytypes is indirect which means that both energy and crystal momentum ($\hbar k$) need to be released during the recombination. The phonon replicas involved in these transitions are for 4H-SiC denoted P_{hv} and Q_{hv} , as such as the P_{76} line.

Now when we have the basic theory clear let us investigate how the bandgap in the SiC crystal is changing as the nitrogen concentration increases. For low doped material the shallow donor energy levels are discrete. As the doping is increased the distance between the donor atoms decreases and a point will be reached when donor electrons will begin to interact with each other. When this occurs the single discrete donor energy will split into a band of energies, see Figure 19. At very high doping the band of donor energy states widens and they start to overlap with each other and with the conduction band, the semiconductor is now degenerated, or metallic.



Fig. 19 Schematic picture of the changes in donor energy for 4H-SiC as the doping increases. E_g denotes the bandgap and E_m the reduced bandgap when the semiconductor is degenerated. CB and VB denotes the conduction and valence band respectively.

The transition where the SiC crystal is changing from a semiconductor to a metallic state is called the Mott transition, named after Sir Nevill Mott, Nobel price winner 1977. Calculations have shown that the critical nitrogen doping concentration for this transition to occur is $5.6 \cdot 10^{18}$ and $2.6 \cdot 10^{19}$ cm⁻³ for 4H- and 6H-SiC respectively [30]. It is not clear whether this transition is a discreet transition or not and if all donor levels (two for 4H-SiC) makes the transition individually or together. As the nitrogen concentration is increased even further bandgap narrowing will occur.

The PL spectra are also changing when the concentration of nitrogen is increased. For very pure material the PL spectra will be dominated by FE related lines but as the nitrogen concentration is increased the FE lines decrease in intensity and luminescence from D-BE and related lines starts to dominate the spectra. When the doping is increased to above 10¹⁸ cm⁻³ the PL

spectrum is changed into a broad band. We have shown (paper 4 in this thesis) that it is possible to relate the energy position of this peak to the nitrogen concentration in the epitaxial layer.



Fig. 20 LTPL spectra of a) low doped p-type $(\sim 10^{14} \text{ cm}^{-3})$ b) a low doped n-type $(\sim 10^{14} \text{ cm}^{-3})$ c) a medium doped n-type $(\sim 10^{17} \text{ cm}^{-3})$ and d) a highly doped $(\sim 10^{19} \text{ cm}^{-3})$ epilayer.

Typical LTPL spectra in the near bandgap emission of the 4H-SiC polytype are shown in Fig. 20. For low doped p-type Al-Be exciton can be observed (Fig. 20.a) together with strong FE lines. In the low doped n-type material the FE line all dominate the spectrum (Fig. 20.b) however the nitrogen BE lines are distinguished weakly. For medium doped n-type material ($\sim 10^{17}$ cm-3, Fig. 20.c) only the NBE are observed. In Fig. 20.d a highly doped, as for a cap layer in a MESFET structure, shown a broad band which is related to nitrogen and can be used for calibration, see paper 4 in this thesis.

SECONDARY ION MASS SPECTROMETRY

The Secondary ion mass spectrometry (SIMS) technique has gained wide spread acceptance as a tool for studying surfaces due to its high sensitivity and its ability to give information on the chemical composition of the surface. SIMS is an analytic technique where the surface is bombarded with ions, knocking atoms from their normal lattice positions that are then ejected from the surface [31]. The ejected atoms can be either electrical charged, they are then called secondary ions, or neutral. The scattered ions are then analysed by a mass spectrometer, in this thesis a Cameca IMS 4f microanalyser has been used.

The SIMS data can be recorded as mass spectra, depth profiles or ion images. The depth profiling is obtain by continuously analysing while sputtering. Depth profiling is very useful when characterising MESFET structures where the abruptness and the thickness are clearly visualized. In this thesis, SIMS has primarily been used to determine the aluminum and the nitrogen atomic concentrations in grown epitaxial layers. The detection limit for the nitrogen and the aluminum concentration is $1-5 \cdot 10^{16}$ and $1 \cdot 10^{14}$ cm⁻³, respectively, and the abruptness can be determined within 10 Å/decade. The resolution of the SIMS measurement is dependent on the surface morphology. A rough surface will result in an inaccurate SIMS profile. In Figure 21 a SIMS depth profile of the aluminum incorporation on the Si-face 4H-SiC presented. The growth was started with a high growth rate, 5.5 μ m/h, and was then reduced to 2 μ m/h in five steps. The growth of the structure was started and terminated with an undoped layer.

As the growth rate is reduced from 5.5 to 4.0 μ m/h the aluminum incorporation is unchanged. This is seen as a flat line at a depth of 1.6-3.2 μ m. Two small steps are seen at a depth of 2.2 and 2.85 μ m which are due to the changes in the precursor flows as the growth rate is decreased. The last two steps, at depth of 0.5-1.6 μ m, show a significantly decrease in the aluminum incorporation. The aluminum incorporation and its

dependence of the growth rate is explained in paper two in this thesis.



Fig. 21 A SIMS depth profile of a aluminum doped epitaxial layer. The structure has been grown by varying the growth rate while maintaining the TMA flow constant.

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