Master Thesis

Epitaxial and bulk growth of cubic silicon carbide on off-oriented 4H-silicon carbide substrates

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Epitaxial and bulk growth of cubic silicon carbide on off-oriented 4H-silicon carbide substrates

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The growth of bulk cubic silicon carbide has for a long time seemed to be something for the future. However, in this thesis the initial steps towards bulk cubic silicon carbide have been taken. The achievement of producing bulk cubic silicon carbide will have a great impact in various fields of science and industry such as for example the fields of semiconductor technology within electronic- and opto-electronic devices and bio-medical applications. The process that has been used to grow the bulk cubic silicon carbide is a modification of the seeded sublimation growth, and the seeds have been grown by sublimation epitaxy. Selected samples have been characterized with a variety of different methods. The surface morphology of the samples has been examined using optical microscope, atomic force microscope and scanning electron microscope. The crystal structure has been investigated by the methods X-ray diffraction and transmission electron microscopy. The electrical resistance of the grown seeds was evaluated by four probe measurements. High crystal quality seeds have been grown with semiconductor properties and bulk silicon carbide was demonstrated using the seeds.
Abstract

The growth of bulk cubic silicon carbide has for a long time seemed to be something for the future. However, in this thesis the initial steps towards bulk cubic silicon carbide have been taken. The achievement of producing bulk cubic silicon carbide will have a great impact in various fields of science and industry such as for example the fields of semiconductor technology within electronic- and opto-electronic devices and bio-medical applications. The process that has been used to grow the bulk cubic silicon carbide is a modification of the seeded sublimation growth, and the seeds have been grown by sublimation epitaxy. Selected samples have been characterized with a variety of different methods. The surface morphology of the samples has been examined using optical microscope, atomic force microscope and scanning electron microscope. The crystal structure has been investigated by the methods X-ray diffraction and transmission electron microscopy. The electrical resistance of the grown seeds was evaluated by four probe measurements. High crystal quality seeds have been grown with semiconductor properties and bulk silicon carbide was demonstrated using the seeds.

Sammanfattning

Materialtillväxt av kubisk kiselkarbid i bulkform har sedan länge ansetts vara en sak för framtiden. I detta examensarbete har de första stegen mot bulk-tillväxt tagits. När man lyckas tillverka kubiskt kiselkarbid i bulkform kommer det att påverka flera områden inom både forskning och industri såsom till exempel inom halvledarteknik såsomlektronikapparater och applikationer för biomedicin. Metoden som har använts för att växa kubiskt kiselkarbid är en modifierad version av "seeded sublimation growth" och för att tillverka "seeds" har sublimationsepitaxi använts. Proverna har karaktäriserats med ett flertal metoder. Ytstrukturen har undersöks med hjälp av optiskt mikroskop, atomkraftmikroskop (AFM) och svepeelektronmikroskop (SEM). Kristallstrukturen har granskats med röntgen diffraction (XRD) och transmissionselektromikroskop (TEM). Den elektriska resistansen har mätts med "four probe mätningar". Hög kvalitativt startmaterial genom så kallade "seeds" har producerats och från dessa 'seeds' har också bulk prover producerats.
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/Olof Norén
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Chapter 1

Introduction

Silicon carbide (SiC) is a group IV-IV semiconductor compound. Both silicon
and carbon have four valence electrons each, together they form a crystal bond
with covalent bonds. These covalent bonds are strong chemical bonds and due to
these strong bonds SiC is a formidable stable material. It is a chemically stable
compound that also remains stable at harsh conditions such as high temperature
and high level of electromagnetic radiation.

Silicon carbide is a wide band gap semiconductor with band gaps ranging from
2.4 eV to 3.2 eV [1]. Silicon carbide has a range of band gaps because it has
a great variety of crystal structures, called polytypes, i.e. it can be structured
in over two hundred different ways [2]. The three most common polytypes are
the hexagonal 4H, 6H and the cubic 3C. The 4H and 6H polytypes have reached
the point where substrates of industrial quality are available for purchase. The
cubic polytype has not yet reached this stage. When the mentioned polytypes of
SiC crystallize they form the hexagonal structure called wurtzite or in the case
of the cubic structure, the structure called zinc blende is formed. Due to the
cubic structure of cubic silicon carbide (3C-SiC) it is an isotropic material, i.e. it
has the same properties in all crystallographic directions in the crystal. This is
advantageous in comparison with the hexagonal polytypes which has anisotropic
properties and therefore different material properties in different crystallographic
orientations.

Polytype stability is for 3C-SiC obtained using the method of sublimation
epitaxy in the temperature interval between 1800°C-2000°C [1 3] in vacuum at
about $10^{-5}$ mbar. Using other methods one can achieve polytype stability of
3C-SiC at lower temperatures.

Cubic silicon carbide is due to its wide band gap (2.4 eV), high carrier satu-
ration velocity ($2.5 \text{ cm/s}$) [4], a long carrier lifetime ($8.2 \mu\text{s}$) [5], high breakdown
field($4 \text{ MVcm}^{-1}$) [6], good thermal and chemical stability a very good candidate
material for the next generation of electrical devices. Already in 1986 there were
MOSFETs produced experimentally according to Y. Kondo et.al. [7]. But due
to quality related problems no further investigation was performed at the time.
However, more recent articles shows promising characteristics and compares dif-
ferent types of transistors [8 9]. Not only can electrical devices be produced from
the 3C-SiC substrates but also for example optoelectronic components as solar
cells [10] [11]. Already in 1907 SiC (called Carborundum at the time) was found to emit light when a current was led through the material [12] [13]. One idea for solar cell containing 3C-SiC is proposed by H. Heidarzadeh, et.al. [14] in a so called tandem solar cell. Another suggestion that has been investigated is as proposed by G. Beaucarne, et.al. [10] with an so called impurity photovoltaic solar cell (IPV-solar cell) structure. According to S. Saddow [15] 3C-SiC can also be used in the field of bio-medicine since the human body does not find the material invasive, it does not react with 3C-SiC, so it is a suitable material for medical implants. Cubic silicon carbide also shows some promising properties as a cathode material and therefore another possible application for 3C-SiC is to be used as photo cathode in a water splitting process where hydrogen is produced [16] [17]. Today cubic silicon carbide is topic for extensive research activity [1] [5] [8] [12] [14] [18]. Yet the growth of bulk 3C-SiC and substrates of the cubic polytype have not yet been achieved with a desirable crystal quality. Substrates of high quality and consistency can be found commercially of the polytypes 4H-SiC and 6H-SiC from several companies [19] [20]. Substrates are the key to the fabrication of any semiconductor device. As mentioned by D. Chaussende, et.al. [21] the need for good quality seeds is crucial in order to be able to produce wafers for production of substrates. These seeds need to be of good crystal quality and also of a size that is sufficiently large to make production economically viable. When being able to produce seeds one can later use these seeds for bulk growth. The first concern of this thesis work is to produce 3C-SiC seeds on 4° off-axis 4H substrates using a growth method called sublimation epitaxy. Once able to produce seeds the production of bulk 3C-SiC samples using seeded sublimation epitaxy can commence. The steps towards production of bulk 3C-SiC samples are the main goal for this master thesis work. Structural- and electronic characterization of these samples will be performed to provide information of the samples.
Chapter 2

Silicon carbide

Some more important information about silicon carbide will be given in this chapter such as historical background, crystal structure, polytypes and properties.

2.1 Historical background

The history of SiC starts with its discovery in 1824. The SiC was discovered by the Swedish chemist Jöns Jacob Berzelius, originally from the city of Linköping in Sweden [22]. In 1892, Eugene G. Acheson invented the first method to produce SiC through an electrochemical process [23]. In 1955 Jan A. Lely created his famous method for producing high quality single crystalline SiC, the method was given the name the Lely process [24]. In 1978 Russian scientists named Tairov and Tsvetkov improved the Lely process by adding some modifications to the method, mainly to use a seed for crystal enlargement. These modifications led to larger sized SiC crystals and higher crystal quality, this method was given the name the modified Lely method or more generally, the growth concept is denoted Physical Vapor Transport (PVT) [25].

2.2 Crystal structure

The crystal structure of SiC is a tetrahedral structure with the smaller carbon atom in the center surrounded by the larger silicon atoms as shown in Figure. The inter atomic distances are $a_{Si-C} = 1.89 \ \text{Å}$, $b_{Si-Si} = 3.08 \ \text{Å}$ and $c_{inter-plane} = 2.51 \ \text{Å}$. In this denotation, $c$ is the height of the tetrahedron, i.e. the same as the distance between the atomic layers. The binding energy between the silicon and carbon atom is $E_B = 4.53 \text{eV}$. 
Silicon carbide is a unique material composition since it is composed by two group IV elements and that it can form in a tremendous amount of different structures that are called polytypes. Polytypes will be addressed in more detail in section 2.3. The atoms in this tetrahedral configuration are strongly bound to one another and also the inter atomic distances are short. This gives a stable material that withstands several chemical and irradiative environments.

2.3 Polytypes

A polytype of a material is when the stacking order of the atomic planes are not only the common hexagonal close packed (hcp) and face centered cubic (fcc). This has been described by M. Grundmann [26].

The properties of silicon carbide are very depending on how the atomic planes are arranged when the material is formed. There are so many different stacking sequences of SiC that it has more than 200 polytypes [2]. In this thesis the three most common polytypes will be described. These polytypes are the hexagonal 4H and 6H, and the cubic 3C. They have got their names from the order of the stacking of their atomic layers, this can be seen in Figures. 2 and 3. The 4H and 6H have the hexagonal close pack (hcp), structure which is also called wurtzite. The cubic polytype 3C-SiC has the close packed cubic structure zinc blende. The different lattice positions that the atoms take in the lattice decides which structure will form. Growth conditions such as temperature, supersaturation and growth rate determine which structure that will dominate the lattice.
Figure 2: The stacking order of the A, B and C layer in a SiC lattice and also the lattice plane [11-20] is shown.

Figure 3: Three common SiC polytypes, 3C(Cubic), 4H(Hexagonal) and 6H(Hexagonal).
2.4 Properties

Some properties that make 3C-SiC such an interesting material to study and to potentially produce devices from are shown in Table. \[1\] In addition, its biocompatibility, radiation resistance and chemical stability makes it a very interesting material with promising future prospects.

If comparing 3C-SiC with the other semiconductors that are included in Table. \[1\] we can see that 3C-SiC shows some different properties. The properties that makes 3C-SiC stand out among the other materials is the high working temperature in combination with high breakdown electric field, a high carrier saturation drift velocity and a wide band gap. This makes 3C-SiC highly desirable for fabrication of some devices in particular, especially for high power applications MOSFETs \[1\] that are to be used in environments where other semiconductors cannot operate or has severe difficulties to perform \[8\].

<table>
<thead>
<tr>
<th>Material</th>
<th>Si</th>
<th>GaAs</th>
<th>GaN</th>
<th>AlN</th>
<th>Diamond</th>
<th>3C-SiC</th>
<th>4H-SiC</th>
<th>6H-SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Constant (Å)</td>
<td>5.43</td>
<td>5.6</td>
<td>a=3.189</td>
<td>a=3.11</td>
<td>c=5.185</td>
<td>3.56</td>
<td>4.34</td>
<td>a=3.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c=5.185</td>
<td>c=4.98</td>
<td></td>
<td></td>
<td></td>
<td>c=10.08</td>
</tr>
<tr>
<td>Bandgap energy (eV)</td>
<td>1.1</td>
<td>1.4</td>
<td>3.4</td>
<td>6.1</td>
<td>5.45</td>
<td>2.4</td>
<td>3.2</td>
<td>3.0</td>
</tr>
<tr>
<td>Carrier saturation drift velocity (10^7 cm/s)</td>
<td>1.0</td>
<td>2.0</td>
<td>2.5</td>
<td>1.8</td>
<td>2.7</td>
<td>2.5</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Carrier mobility (cm^2/Vs)</td>
<td>1350</td>
<td>8500</td>
<td>2000</td>
<td>1100</td>
<td>1900</td>
<td>1000</td>
<td>a=720</td>
<td>a=370</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c=650</td>
<td>c=50</td>
</tr>
<tr>
<td>Breakdown electric field (10^6 V/cm)</td>
<td>0.3</td>
<td>0.4</td>
<td>5.0</td>
<td>11.7</td>
<td>5.6</td>
<td>4.0</td>
<td>2.0</td>
<td>2.4</td>
</tr>
<tr>
<td>Thermal conductivity (W/cm K)</td>
<td>1.5</td>
<td>0.5</td>
<td>1.4</td>
<td>2.5</td>
<td>20.0</td>
<td>3.2</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Dielectric Constant</td>
<td>11.8</td>
<td>12.8</td>
<td>8.7</td>
<td>5.5</td>
<td>9.75</td>
<td>10.0</td>
<td>9.7</td>
<td></td>
</tr>
<tr>
<td>Maximum operating Temperature</td>
<td>300°C</td>
<td>460°C</td>
<td>1100°C</td>
<td>1240°C</td>
<td>1240°C</td>
<td>1240°C</td>
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</tr>
</tbody>
</table>

Table 1: In this table one can see that semiconductors have varying properties and values for several of these properties. \[4\] [5] [6] [27]

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1Metal Oxide Semiconductor Field Effect Transistors (MOSFETs).
Chapter 3

Growth methods

There are different ways to produce SiC. The most common ways to produce SiC is to use chemical vapor deposition (CVD) or physical vapor transport (PVT). The PVT is used to grow bulk silicon carbide substrates of hexagonal polytypes of SiC. In this master’s thesis work the processes of choice is sublimation epitaxy and seeded sublimation growth to produce the cubic polytype 3C-SiC.

3.1 Chemical Vapor Deposition

One common technique to produce epitaxial layers of 3C-SiC is chemical vapor deposition. The process of CVD can be thoroughly controlled by the control of gas flow and temperature. When using this process technique, different precursors (gases) are let into the chamber were the substrate is placed. The atoms from the precursors are then adsorbed on the substrate surface and react to form the desired product, in this case 3C-SiC. Using this method the process is controlled by the change of the temperature in the chamber, or in some cases the temperature of the substrate itself, temperatures used during CVD are normally around 1100-1600$^\circ$C [28]. Also the flow rate of the precursors can be controlled. Through controlling the growth environment the thickness and quality can be controlled precisely. However, the CVD method is only for epitaxial films due to its low temperature and therefore low growth rate.

3.2 Physical Vapor Transport

The Physical Vapor Transport uses the growth by sublimation of a source that is transported by the temperature gradient in the chamber. The distance between the source and the seed is normally about 20 mm or more. This growth method normally uses a growth temperature that is too high for controlled initial 3C-SiC growth, the temperature is higher than 2000$^\circ$C. This high temperature is not suitable for the initial growth stages and does not provide a stable environment for the growth of 3C-SiC. However, one can continue growth if one has a 3C-SiC seed and this way grow a bulk of the material. This is because the polytype is more prone to stay the same when using a seed for growth. So this method needs to be combined with another method or be modified to be able to make good bulk samples, e.g. as [21] uses the vapor liquid solid (VLS) method to make the seed. The PVT method is since many years used to create bulk of 4H-SiC and 6H-SiC.
3.3  Sublimation Epitaxy
In this thesis work the process of choice is the sublimation epitaxy (SE) method. This growth process is a modified PVT method that has been developed for the growth of 3C-SiC seeds. With this method it is possible to grow thick single crystalline layers of 3C-SiC on 4°off-axis cut 4H-SiC substrates. The SE method uses the setup seen in Figure. 14. The distance between substrate and source is 1 mm and the temperature gradient that transports the vapor species is about 18° C/mm. Since various parts inside the crucible and the crucible itself are made out of graphite, it creates a carbon rich environment. Due to that 3C-SiC prefers a Si/C ratio\textsuperscript{2} that is higher than one, a Tantalum-foil (Ta-foil) is used as carbon getter to achieve a more favorable environment for 3C-SiC growth.

3.4  Seeded Sublimation Growth
This method uses a very similar setup as the one used for sublimation epitaxy. The system used for growth is the same in both processes, Figure. 14 but the difference in the Seeded sublimation growth (SSG) is that now a 3C-SiC seed is used as substrate and the source that are being utilized is a SiC powder, Figure. 15. The powder has been sintered\textsuperscript{3} before growth. The distance between the powder and the seed can be from 5-20 mm and the growth temperature is about 2000° C. Since the source used in this method is a sintered powder, it is necessary to either apply an argon atmosphere or a static vacuum to maintain the favorable conditions for 3C-SiC growth. Both atmospheric conditions have been implemented to investigate which one is more suitable for the intended growth of 3C-SiC.

\textsuperscript{2}Si/C ratio is the ratio of silicon and carbon gas species in the gas ambient in the chamber. This is influenced by the growth temperature and also varies through time since the source is being depleted. This due to that silicon has a lower evaporation temperature and evaporates more rapidly than the carbon-rich species.

\textsuperscript{3}Sintering is a process when you produce a solid from a powder without melting the material, this is done by applying heat in a pressurized atmosphere to make a solid
Chapter 4

Growth Mechanisms

The growth mechanisms that will determine polytype, defect density and kind of defects are in fact depending on several growth parameters. Some of these growth mechanisms are: spiral growth, step-flow growth and two dimensional growth (2D-growth). These growth mechanisms depend on the growth temperature, the pressure in the chamber, the Si/C ratio and supersaturation of the gas species. The vicinal surface of the 4H-SiC substrates, the off-axis cut, affects how the 3C-SiC forms on top of the substrate. This surface orientation favors the growth mode of step flow growth instead of the two dimensional growth. These two are the most important for 3C-SiC growth and they will be described in this section together with spiral growth mode that is more commonly occurring for the hexagonal polytypes.

4.1 Spiral growth

Spiral growth is known to exist for the hexagonal polytypes and occurs at a lower supersaturation than the other growth mode, see Figure. As the name suggests spiral growth creates spirals when the material is growing thicker. This is due to the formation of screw dislocations that grows larger and larger when the crystal thickness increases. These spirals form differently depending on if growth is performed on carbon face SiC or on silicon face of SiC. The name of the faces indicates with what element the crystal is terminated. On the silicon face one can clearly see actual spirals that have formed on the surface. However, on the carbon face the supposed spirals look like pyramids with a hexagonal base.

A vicinal surface is a surface which surface normal deviates slightly from a major crystallographic axis. In this case the 4H-SiC substrate has a 4° angles from the [0001] plane towards the <11-20> direction.
4.2 Step Flow Growth

The step flow growth is when the Si and C species nucleate only at the steps on the substrate surface. It is known from earlier performed growth by [29] that the 3C-SiC nucleates with high density of nucleation sites on on-axis substrates. However this leads to high density of stacking faults (SF) and double positioning boundaries (DPB). A vicinal surface is used as substrate when producing seeds in order to try to decrease the density of defects in the produced samples. This has been proven to work by [30].

The step flow growth occurs because of that the diffusion rate is sufficient for the Si and C species to diffuse and adsorb at the most energetically favorable nucleation sites, i.e. in this case the surface steps. When the growth continues the 3C-SiC polytype continuously grows in this step flow direction [29, 30].

4.3 Two Dimensional Growth

The two dimensional growth is when the atoms adsorb and diffuse in such a way that a layer by layer deposition of atoms is obtained with a very smooth surface as a result. This growth mode requires well-tuned supersaturation and Si/C ratio in combination with a well-defined surface temperature on the substrate to promote sufficient diffusion on the surface. However, to create defect free layers all coalescence of grains need to occur without the creation of defects.
Chapter 5

Defects

In this chapter some of the most common defects are explained regarding their appearances.

5.1 Dislocations

Dislocations are defects that originate from dislocated atomic planes in the lattice structure. These defects are one-dimensional that cause irregularities in the lattice. To be able to characterize different kinds of dislocations, two properties of the dislocation have been named and defined: the dislocation line and the Burger’s vector. The dislocation line is the line defect that spreads in the lattice. The Burger’s vector is the difference between the as grown loop and the perfect crystal loop, as shown in Figure. From these properties one defines two different dislocation defects, edge dislocation and screw dislocation. An edge dislocation is defined as when the Burger’s vector is perpendicular to its dislocation line, due to the introduction of an extra layer in the crystal. However, when the dislocation line of the lattice is parallel to its Burger’s vector the defects are called a screw dislocation.

![Figure 5: An illustration of the Burger’s vector and the different dislocation. In the figures a) and c) the as grown crystal can be imagined by its dislocations. In a) we see the edge dislocation and in c) the screw dislocation can be seen. In the parts b) and d) of the figure the respective Burger’s vector is shown in the perfect crystals.](image)
5.2 Stacking Faults

Stacking faults are defects that arise when the order of stacking of the different layers of the SiC crystal is perturbed. As explained by M. Grundmann [26], stacking faults exist in different variety. There are the intrinsic and the extrinsic stacking faults. The intrinsic stacking faults are defined in such a way that when an atomic plane from the ordinary stacking order \([ABC][ABC][ABC]\) is missing and instead forms \([ABC][AC][ABC]\). The extrinsic stacking fault is when an extra atomic plane has been inserted in the lattice and the final stacking order is as \([ABC][ABAC][ABC]\). Stacking faults are defects that are common in all SiC polytypes that are being produced today. The energy needed to form stacking faults is less when growing 3C-SiC comparing to other polytypes and this makes the stacking fault more common in 3C-SiC. The stacking faults shows up in the crystal as triangular defects on the surface of the layer and are typical defects found in 3C-SiC. These defects can easily be seen by optical microscopy and one can use the stacking faults as a strong indication of 3C-SiC. However, these stacking faults are not solely a defect in 3C-SiC and exists in the commercial 4H-SiC and 6H-SiC as well.

5.3 Double Positioning Boundaries

Double positioning boundaries occur when two grains of SiC intend to coalesce, however, if their stacking sequences do not coincide they will not merge and a boundary will form in between the two grains. If the two grains intend to coalesce on the surface of the sample and their stacking order do not match, a Double Positioning Boundary (DPB) will form, as seen in Figure 6. These defects will show up in the optical microscope as different thick lines depending on the elemental growth of 3C-SiC. As seen in Figure 7 the cubic area will be growing slightly to the right or to the left depending on the stacking of the atomic layers. At the location where the domains grow together, a thin line will be visible. At the location where the domains grow away from one another, a thicker line will be seen since the space in between these domains will be full of randomly stacked cubic areas and possibly also other polytypes.

5.4 Inclusions

Inclusions are when other elements or polytypes than the desired ones are included into the crystal structure of the produced sample. These inclusions can originate from any source of foreign materials that come in contact with the substrate before or during growth. For example, origins could be graphite from the crucible or the graphite foam, excess silicon from the source due to unfavorable growth conditions, other SiC polytypes also due to non-favorable growth conditions. Biological residues can contaminate and metal can originate from other parts of the equipment.
5.4 Inclusions

Figure 6: The stacking errors are creating double positioning boundaries at the interface with the 4H-SiC substrate.

Figure 7: Double positioning boundaries at grain level.
Chapter 6

Characterization techniques

In this chapter a theoretical background is given to the characterization techniques used in this thesis work.

6.1 Structural characterization

The structural characterization methods used in this thesis are optical microscopy, atomic force microscopy, scanning electron microscope, x-ray diffraction and transmission electron microscope.

6.1.1 Optical microscope

The optical microscope used is a Nikon CFW 10xM 8 The optical images were captured by an "Infinity 1" camera. The microscope works in both transmission and reflection mode. The transmission mode gives the possibility to examine the bulk structure of the samples. This is of great interest since in the visualization and analysis of the bulk of the material is the main purpose in this thesis. In the reflection mode one can get a good image of the samples surface features. This is also interesting since some defects are commonly not bulk specific but continues up to the surface.

Figure 8: A schematic drawing of an optical microscope. [31]
6.1.2 Atomic Force Microscope

The atomic force microscope (AFM) is a tool that is excellent for surface structure studies. The AFM used is an Veeco Enviroscope\textsuperscript{TM} AFM and the schematic setup can be seen in Figure.\textsuperscript{9} An AFM is conveniently used for studying surface structures since no vacuum is needed for high quality images. The resolution in the off plane direction can be as good as a few nanometer. The setup seen in Figure.\textsuperscript{9} consists of various important parts. The cantilever should be a material that can bend without breaking and at the end of the cantilever there is a tiny tip, preferably one atom wide at the very tip. The thickness of the tip decides the resolution of the instrument. Since the image that appears is not the real image but a convolution of the tip interacting with the surface, the tip should be tiny to give as small artifacts as possible. The laser beam that reflects of the cantilever is being measured by photodiodes. The basic working principle of an AFM is that the Van der Waals force which is being measured between the tip and the sample surface. This force makes the tip to deflect from the surface and this change in position can be measured by the photodiodes as the change in laser beam position.

There are three imaging modes which are possible with the device provided: Contact mode, tapping mode and non-contact mode. In contact mode the tip is as the name suggests in contact with the surface at all time. This provides high resolution images but also a higher risk of damaging both the tip and the sample surface. In tapping mode the tip is oscillated at its resonance frequency and is not in constant contact with the sample. Since the interaction force between the sample and the tip alters this frequency at which the cantilever is oscillating the tip, one can measure the change in surface topology. This provides the high resolution images with less risk of damaging the tip or the surface of the sample. In non-contact mode the tip is oscillated at a frequency even higher than the resonance frequency and this keeping the tip at all times above the surface. It is measuring the interaction force as a change in frequency. This non-contact mode gives not as high resolution as the other two modes but ensures that tip and the sample are intact after the measurement.

The most used mode of operation when using the AFM is the tapping mode, this the mode of operation used in this work, since it provides higher resolution and a decreased risk of damaging the sample or the tip. The AFM provides advantages compared to other microscopic tools. The AFM provides a three dimensional
image of the surface while other methods only provides two dimensional images. The size of the scanned area is limited using the AFM, about 100 $\mu$m x 100 $\mu$m. The AFM is a reliable choice for producing atomic resolution images without extensive sample preparation.

### 6.1.3 Scanning Electron Microscope

The scanning electron microscope (SEM) is a versatile tool since it gives the opportunity to focus both at low magnification and at very high high magnification. The SEM used is a Zeiss of the model 'GEMINI'. It works by emitting electrons from a filament and these electrons are collimated in such a way that one focused beam of electrons scan the sample surface. The tool is shown in Figure. 10. When the electron beam hits the surface the electrons interact with the sample atoms and scatter in such a way that some of the electrons are directly back scattered from the sample. These electrons that are being scattered from the sample are detected by a detector and this is then being reproduced as an image. The SEM does require vacuum to function. This is because the electrons need a long enough mean free path to be able to reach the sample and not scatter with molecules in the medium before the sample. The sample then needs to be vacuum compatible. The sample also needs to be conductive in order to not build up a charge during the scanning procedure with the electron beam. However, when the sample is mounted and a vacuum is created in the chamber, the images are rapidly produced and visible on the screen for the user.

![Figure 10: A schematic drawing of the SEM setup.](image)
6.1.4 X-Ray Diffraction

The X-Ray Diffraction (XRD) measurements are one of the most used methods for determining the crystalline quality of materials. The equipment used is a so called 'Philips X’PERT*. The source was Cu-K\(\alpha\) radiation with the wavelength of 1.54 Å. The spot size used is of 1*1 mm\(^2\) with an X-ray beam that has a footprint of 1*3 mm\(^2\), so this gives a total area of 1*3 mm\(^2\) that is being characterized. Since this area is fairly big, the complete sample is circular with a diameter of 7 mm, it can be seen as the general quality of the sample. Using this X-Ray Diffraction method the crystal structure of the samples can be revealed. The technique uses X-ray beams that irradiate a sample at different incident angles and depending on how the atomic planes are oriented and structured in the sample the data can be collected and interpreted to determine the samples crystal structure and quality. The data that one can gather is the Full Width at Half Maximum (FWHM) and the peak intensity. Using this data it is possible to examine the crystal quality of the sample using the FWHM and peak intensity values. The smaller the FWHM, the peaks are more narrow and sharp, and the higher intensity for the same peaks gives an indication of a good crystal structure of high quality. When a sample has many defects, this alters the crystal structure and makes the x-rays scatter in the sample. This gives the x-rays other angles of exit compared to the x-rays that are interacting with a perfect crystal and this creates the broader peaks that indicates lower crystal quality. The intensity of the peaks can also be decreased by this same scattering. Both the commercial 6H-SiC and 4H-SiC wafers have a value of FWHM < 30 arcsec [19]. From Figure. 11 one can derive the Bragg law and it looks as seen in Equation. 1.

\[2dsin(\theta) = n\lambda\]  \hspace{1cm} (1)

The Bragg law

Figure 11: X-rays incident on atomic planes gives us the Bragg condition. [34]
6.1.5 Transmission Electron microscope

The Transmission electron microscope (TEM) is a tool that has the working principle of a usual optical microscope with a few important alterations. Photons are replaced by electrons, instead of a light bulb an electron gun is used and the lenses are not made of glass but are purely electromagnetic lenses. This gives the TEM a resolution that can be increased to about 1 Å under good conditions [35]. Good conditions mean that the electrons travel through vacuum to increase their mean free path, that the electron beam is well collimated and that the lenses and apertures are functioning correctly. The schematics of a TEM can be seen in Figure 12. The TEMs primary use is to give high resolution images at atomic resolution.

![Figure 12: The schematic of a TEM.](35)
6.2 Electrical characterization

The method used for electrical characterization of the samples is the four probe measurement.

6.2.1 Four probe measurement

This method consists of a fairly simple setup where you use four different probes to inject electrical current, charge carriers, and to measure the voltage drop that these carriers experience in the material. The machine used for these measurements is a '4D Automatic Four Point Probe Meter Model 280C'(4D-280C). The four probes are located as seen in Figure. 13 where the two outer probes provide (and collect) the current and the inner two probes measure the voltage difference over that distance. By using this setup one can achieve extremely exact values for the materials resistance. The values for the resistivity that can be expected have an accuracy of +/- one Ω.

Figure 13: A schematic drawing of the four probe measurement setup.
Chapter 7

Experimental Details

In this chapter the experimental setups and experimental execution are explained.

7.1 Growth

Two different experimental growth methods will be used during the course of this thesis work. The growth methods that are used in this thesis work are the Sublimation Epitaxy (SE) and the Seeded Sublimation growth (SSG). This SSG process uses a SiC powder source and this is the first time in the research group that this is attempted for growth of bulk 3C-SiC. The growth methods use a similar layout as the one seen in Figure. 14. The complete system is heated by a Radio Frequency (RF) generator that can accurately achieve and maintain the desired temperature. The difference in the methods is how the materials are ordered inside the graphite crucible. This can be seen when comparing crucible from Figure. 14 with the crucible in Figure. 15. Before growth the different parts have to be accommodated in the graphite crucible. Firstly to grow seeds that will be used for seeded sublimation growth, the setups looks as in Figure. 14. Inside the crucible there is a tantalum foil, a polycrystalline SiC source, a spacer, the substrate and a graphite plate. The tantalum foil is used in this setup as a carbon getter to achieve a more 3C-SiC favorable Si/C ratio during growth [27, 36]. The substrates that are used in this thesis work are of the polytype 4H-SiC and they have an off-axis cut of 4°. The substrate is separated from the source by a spacer. A graphite plate is added on top to diminish backside sublimation of the substrate. Secondly, to grow the bulk, the setup looks as in Figure. 15. Here we have a SiC powder source, a spacer, the substrate and a graphite plate on top. The setup is different because of the reason that a more long lasting source is necessary to allow bulk growth. No tantalum foil was used in these runs since the powder on the bottom of the crucible would prevent the tantalum foil from being effective if the foil was to be placed under the powder source.

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5 The off-axis cut is in this case the angle from the [0001] plane towards the <11-20> direction.
Experimental Details

Figure 14: A schematic overview of the growth chamber with the crucible enlarged to the right with the distinct parts seen in cross section.

Figure 15: A cross sectional overview of the crucible used for bulk growth.

The graphite crucible is placed inside a graphite foam which is acting as thermal isolation, and this is then inserted into the chamber. The system (Figure 14) is pumped out to achieve a vacuum. The desired vacuum is a pressure of about $10^{-5}$ mbar. When the desired vacuum has been achieved, the heating process of the chamber commences. The heating of the chamber is divided in various steps that are important for the final quality of the sample. The ramp up of the temperature is kept at about 20 K/min. When reaching the desired temperature, 1885°C, the process is considered to have reached the growth stage. Here the temperature is maintained for the desired amount of time (1h) that is required to have a controlled growth start. A second ramp up of the temperature is implemented after the first growth stage to have higher growth rate after initial nucleation. After this second ramp up, another growth stage is maintained for one hour at 1910°C to achieve a thicker film. When increasing the temperature, the growth rate is increased since there are more vapor species available for adsorption on the substrate surface. The growth rate is about 350-400 $\mu$m/hr at the chosen temperature of 1910°C. The system is let to cool down after the deposition process is complete. When the system has reached a low enough temperature, the graphite crucible can be removed from the chamber. After this the crucible is opened and the sample can be retrieved and further examine the results of the deposition. For graphical
When the sample has been removed from the crucible, the crucible is put back with a dummy piece and the system is re-sublimed to get rid of excess carbon and silicon-carbide residues that have been accumulated during the growth of the sample. These residues end up on the dummy piece and the crucible can be used again for the next sublimation process.

### 7.1.1 Pre-growth procedures

There are some important pre-growth procedures to have in mind. The tantalum foil that is being used in the experiments has been pre-treated, annealed briefly at growth temperature. This is to provide a better Si/C ratio during growth and also to prevent any bending of the foil during growth. The foil can bend if it is not annealed in the pre-annealing, the bending now instead occurs before growth and the foil is more stable during subsequent growth step. One foil is only used for one growth run since its carbon getter ability is decreased after usage. The powder source has also been pre-treated before growth to make the source more stable. The powder is being sintered at about 2000°C in Argon ambient before using the powder for growth. This is carried out since any initial sublimation can cause silicon droplets. The spacers have to be cleaned in the same manner as the crucible and this is carried out before the next use of the spacer.
7.2 Seed production

The production of seeds is a crucial part of the work towards larger single crystalline 3C-SiC crystals. A seed is used to produce larger 3C-SiC crystals and since the higher quality of the seed that can be obtained, the easier it will be to maintain this high crystal quality when producing crystals. A process has during this work been fine tuned to produce a single domain in seeds at an as high growth rate as possible to minimize growth time. One temperature step was initially used and this makes the process slow since a lower temperature is needed during the initial face of growth. The process was then altered to include two temperature steps to increase the growth rate. The process was developed to consist of two temperature steps at which growth occurs. At the first step the first nucleation of 3C-SiC occurs on the vicinal 4H-SiC surface. Later when the initial nucleation has been established, the temperature is ramped up once more to achieve a higher growth rate. This is possible since the already nucleated 3C-SiC will expand in the step flow direction and in the end overgrow the 4H substrate. All the pure 3C-SiC seeds were grown under vacuum conditions ($10^{-5}$ mbar) and at the same temperatures, nucleation temperature 1885 °C and 1910 °C for higher growth rate. The seeds that were deliberately doped with boron were grown at 1850 °C for about 2-5 hours to investigate how good quality and how thick layers that could be grown.

The seeds that were produced can be seen in section 8.
7.3 Bulk 3C-SiC

The possibility to grow bulk 3C-SiC was investigated by using a powder source and different distance to the powder. A cross section of the crucible with powder can be seen in Figure. 17. During the bulk growth process a higher pressure, 700 mbar of argon and a higher temperature is needed. The higher pressure is needed to control the vapor species in such a way that the Si-rich species do not become dominant on the seeds surface. The argon that is used during growth creates a more favorable Si/C ratio for 3C-SiC growth. This by inhibiting too high sublimation rate of the powder this way making the silicon and carbon gas species more equally sublimed. The argon atmosphere also lowers the supersaturation so that there is less parasitic nucleation at the initial growth stage. Too high Si/C ratio could lead to the formation of silicon droplets and this exhibits the 3C-SiC crystal growth. The higher temperature is needed to increase the growth rate and this favors the 3C-SiC crystal growth.

Figure 17: A cross section of the crucible with powder.

---

6 Longer distance gives the opportunity to grow thicker material since it allows the material to grow further before merging with the source.
Chapter 8

Results and discussion

In this chapter the results that have been obtained during this thesis work are presented and discussed. The chapter is divided into two major parts that is 3C-SiC seed fabrication and 3C-SiC bulk fabrication. The seeds that were produced during this thesis work have been of two different types: undoped and doped. The first is the ordinary 3C-SiC seeds and the second type of seeds that were produced are boron doped seeds.

8.1 3C-SiC seeding layers

The seeds that were produced without doping are of good quality and with a smooth surface structure. On the other hand, the seeds that were produced using a doped source is not of that high quality. The undoped sources are ceramic SiC which is commercially available while the doped sources are made in the lab and still under development. The good structural quality have been confirmed by several techniques such as Optical microscope, TEM and XRD and the surface structure by AFM and SEM. The electrical resistivity of the produced seeds has also been measured by four probe measurements.

8.1.1 Optical Microscope

All samples have been observed using the the optical microscope to examine the quality as a first evaluation. This gives a good idea about the seeds that have been produced. The quality is changing from sample to sample, this can be observed directly by the optical microscope. This due to circumstances and parameters that we cannot control yet since the growth process is being developed. However, what have been observed is that it is possible to control the nucleation rate and therefore the amount of nucleation sites. When there are fewer nucleation sites it is more likely that domains of the same stacking order will form and have the possibility to merge later. In any case, the 3C-SiC polytype always appear and variations in surface topography occur due to various nucleation sites. Such may be expected due to the high growth rate.
Results and discussion

(a) A seed that shows many defects and was grown using one step process at 1910°C.
(b) A seed that shows many defects and was grown using one step process at 1875°C.

(c) A seed that shows few defects and a pronounced terrace that was grown using two step process at 1885°C and 1910°C.
(d) A seed that shows a clearly pronounced terrace with few defects that was grown using two step process at 1885°C and 1910°C.

Figure 18: Optical microscope images of seeds produced during this thesis and the development of the quality of the produced seeds. The scale used is 100 µm.

One observation that can be made by looking at these optical microscope images is that the quality of the seeds has been improved by using the two step process for making seeds. Finally, the produced 3C-SiC layers are completely free from other polytypes and have a relatively low defect density when compared with the samples grown using single step process. The fact that there is a pronounced terrace that keeps expanding during growth is also good since the best quality is normally found within this terrace area.
8.1 3C-SiC seeding layers

8.1.2 Four probe measurements

The electrical resistivity of the seeds was measured and can be seen in Table. 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Material</th>
<th>Sheet resistivity</th>
<th>Layer thickness</th>
<th>Bulk resistivity</th>
<th>Face of sample</th>
<th>Tool</th>
<th>Sample type</th>
</tr>
</thead>
<tbody>
<tr>
<td>#5</td>
<td>3C-SiC</td>
<td>41.5 kΩ</td>
<td>700 μm</td>
<td>2.9 kΩcm</td>
<td>Si</td>
<td>4D-280C</td>
<td>Seed</td>
</tr>
<tr>
<td>#7</td>
<td>3C-SiC</td>
<td>1.5 Ω</td>
<td>825 μm</td>
<td>127 Ωcm</td>
<td>Si</td>
<td>4D-280C</td>
<td>Seed</td>
</tr>
<tr>
<td>#11</td>
<td>3C-SiC</td>
<td>300 Ω</td>
<td>800 μm</td>
<td>24 Ωcm</td>
<td>Si</td>
<td>4D-280C</td>
<td>Seed</td>
</tr>
</tbody>
</table>

Table 2: The sheet resistivity of the sample have been measured and the bulk resistivity calculated using Equation. 2. The sheet resistivity is the mean value of several measured values\(^7\), to give a more accurate value. The samples that are not represented in this table could not be measured due to the morphology of the samples. The tool used is a "4D Automatic Four Point Probe Meter Model 280C" (4D-280C).\(^8\)

The reasons that we have very few values from the measured samples are probable to be because of the quality of the samples so that the current was scattered and could not be retrieved by the instrument. Another possibility or contributing factor is that the samples are doped by boron-atoms and nitrogen-atoms in such a way that compensation occurs and due to this effect no current could be measured. These contaminating species come from the parts of the setup that cannot be replaced and have been contaminated in earlier growth series. These measurements are the first ones in these materials. The electrical characterization and the material quality need to be developed further. Additionally, the background compensation could be applied to prepare high resistivity material. The values give an indication what is the case today. The values that was measured shows that we have a range from 24-2900 Ωcm. The large variation in this result is likely to originate from the different defect densities that can be found in the different samples. However, when measuring the same sample various times the values differed by only a small amount. The measured values are interesting since the good quality hexagonal wafers that are available in industry have values in the range of 20-40 mΩcm. The samples that have been produced in this master thesis may not be within these quality standards. However, when the method have been further developed the true value may be even lower than the ones measured here. This is intriguing for future development of 3C-SiC devices.

\[
\Omega_{Bulk} = \frac{\Omega_{Sheet} \times Thickness_{Layer}}{10^4} \tag{2}
\]

\(^7\)These values are the values given by the apparatus and formulas are given from supervisor to be able to calculate the bulk resistivity.

\(^8\)\(\Omega_{Bulk}\) have the unit of Ω cm and hence the need to divide with 10\(^4\) to achieve the correct unit.
8.1.3 TEM

The TEM gives a great insight in the structure of 3C-SiC at atomic level. Here in Figures. 19a and 19b [37], we can see the well ordered structure of the samples that have been produced. The atomic resolution shows that a perfect atomic arrangement can be obtained. Even though TEM is a local measurement, the observation of atomic perfection is an promising indication. In any case, XRD was used to assess the crystal quality over large area.

(a) The structural quality of the produced 3C-SiC seeds are shown using TEM micrographs. 

(b) Higher magnification image of the crystal structure of the produced seed.

Figure 19: TEM images of high quality seed. Courtesy to Patricia Almeida Carvalho and Sintef for the images.
8.1.4 XRD

Since the TEM results given showed nice quality and crystal structure of the as grown crystals, we decided to make XRD measurements on some selected samples and this way confirm the crystal quality from the TEM. To make sure what angles to scan, the angles were calculated in beforehand using Equation. [3] These values are close to the ones measured by R. Hristu et. al. [38].

\[ 2\Theta = 2 \arcsin \frac{n\lambda \sqrt{h^2 + k^2 + l^2}}{2a} \] (3)

Where for the \{111\} plane we have:
\[ n = 1, \ \lambda = 1.54 \ \text{Å}, \ h = k = l = 1 \text{ and } a_{3C} = 4.34 \ \text{Å} \text{ gives} \]

\[ 2\Theta = 2 \arcsin \frac{1.54\sqrt{1^2 + 1^2 + 1^2}}{2 \times 4.34} = 2 \arcsin \frac{1.54\sqrt{3}}{8.68} = 35.794^\circ \] (4)

The scans that were made were omega scans and the result can be seen in Figures. 20a, 20c, 20b and 20d. The values of achieved FWHM can be seen in Table. 3. It would be possible to improve the accuracy of the measurements by including more data points and spending more time with the diffractometers for making the XRD measurements. The main focus for this thesis work has been to develop the growth and therefore not so much time could be spent on the XRD measurements. The quality of the produced seeds can also be improved if the growth process can be more stable by introducing a more stable system for growth. However, since these tests are simply initial tests and the process is under development one should consider these values as a milestone. This is how far the process has come in producing good quality samples and through continuing improving the methods used better quality will be achieved in the future. In comparison, the FWHM of 3C-SiC grown on silicon typically shows a value of 400 or more.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Seed 4</th>
<th>Seed 6</th>
<th>Bulk growth 6 (BG6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FWHM [°]</td>
<td>0.07</td>
<td>0.03</td>
<td>NaN</td>
</tr>
<tr>
<td>FWHM [arcsec]</td>
<td>252</td>
<td>108</td>
<td>NaN</td>
</tr>
</tbody>
</table>

Table 3: The full width at half maximum values obtained for \{1 1 1\} plane in the two seed samples.
Figure 20: The XRD measurements that were performed were omega scans of three samples.

The shift in omega for the different samples is believed to be a consequence of that the substrates that are used does not have exactly the same off-axis angle or that the backside of the substrates have been sublimed to different extent. If the off-axis angle is the reason for this it could also be affecting the growth of 3C-SiC since the off-axis angle affects the growth mode. However, the most likely reason for this is that the backside of the sample has been sublimed at a slightly different angle for each sample. The bulk sample that was measured does show a double peak and this since there are various orientations present in the crystal. This makes it possible to say that the bulk crystal quality is not yet as good as the quality of the seeds.
8.1.5 AFM

Two selected seeds were examined with a Veeco EnviroScope\textsuperscript{TM} AFM using the tapping mode. The examined samples are seeds number 4 and number 6. Seed number 4 is the smoother one with one single domain but still on sample number 6 that consisted of more double positioning boundaries it was fairly easy to find an area that was smooth and suitable for the AFM tool. The images retrieved from this can be seen in Figures.\textsuperscript{21} and \textsuperscript{22}. The steps on the surface were also measured and the result can be seen in table\textsuperscript{4}.

The AFM table is showing the heights and widths of the surface steps from two seeds. The average height and width are also displayed along with maximum and minimum values.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1</td>
<td>0.954</td>
<td>39.217</td>
<td>Step 1</td>
<td>1.005</td>
<td>42.416</td>
</tr>
<tr>
<td>Step 2</td>
<td>1.309</td>
<td>43.139</td>
<td>Step 2</td>
<td>1.068</td>
<td>58.322</td>
</tr>
<tr>
<td>Step 3</td>
<td>1.697</td>
<td>54.904</td>
<td>Step 3</td>
<td>0.936</td>
<td>53.020</td>
</tr>
<tr>
<td>Step 4</td>
<td>1.202</td>
<td>43.139</td>
<td>Step 4</td>
<td>1.386</td>
<td>47.718</td>
</tr>
<tr>
<td>Step 5</td>
<td>1.166</td>
<td>43.139</td>
<td>Step 5</td>
<td>1.270</td>
<td>53.020</td>
</tr>
<tr>
<td>Step 6</td>
<td>1.415</td>
<td>43.139</td>
<td>Step 6</td>
<td>0.723</td>
<td>37.114</td>
</tr>
<tr>
<td>Step 7</td>
<td>1.732</td>
<td>54.904</td>
<td>Step 7</td>
<td>1.187</td>
<td>53.020</td>
</tr>
<tr>
<td>Step 8</td>
<td>1.484</td>
<td>50.982</td>
<td>Step 8</td>
<td>1.260</td>
<td>53.020</td>
</tr>
<tr>
<td>Step 9</td>
<td>1.414</td>
<td>47.060</td>
<td>Step 9</td>
<td>1.463</td>
<td>58.322</td>
</tr>
<tr>
<td>Step 10</td>
<td>1.873</td>
<td>58.824</td>
<td>Step 10</td>
<td>1.336</td>
<td>58.322</td>
</tr>
<tr>
<td>Average</td>
<td>1.425</td>
<td>47.845</td>
<td>Average</td>
<td>1.163</td>
<td>51.429</td>
</tr>
<tr>
<td>Max. value</td>
<td>1.873</td>
<td>58.824</td>
<td>Max. value</td>
<td>1.463</td>
<td>58.322</td>
</tr>
<tr>
<td>Min. value</td>
<td>0.954</td>
<td>39.217</td>
<td>Min. value</td>
<td>0.723</td>
<td>37.114</td>
</tr>
</tbody>
</table>

Table 4: Ten peaks from each seed was measured, both the height and width.

The AFM gives us an insight in how the surface structure looks like and since we can see the surface steps when scanning a smaller area. This tells us that the surface is fairly smooth since the steps are in the range of 1-2 nm in height. This is comparable to homo-epitaxial layers of 4H-SiC and 6H-SiC.
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(a) 25x25 µm
(b) 5x5 µm
(c) 2x2 µm
(d) 1x1 µm

Figure 21: AFM images of seed 4.
Figure 22: AFM images of seed 6.
8.1.6 SEM

One seed was examined by SEM and the results can be seen in Figure. 23.

(a) Several extended defects on the surface of the sample.

(b) Double positioning boundary extending across the surface.

(c) Steps can be seen with the SEM.

(d) Steps can be seen in high resolution with SEM.

Figure 23: SEM images of seed 4.

Some surface defects are also found extending over the surface and one DPB extends over the whole sample. One can clearly see that the surface steps are present in this seed. The steps that were seen in the AFM could also be seen with the SEM. This confirms the steps that were observed in the AFM.
8.1.7 Boron doped 3C-SiC on seeding layers

The doped seeds that were produced were a series of boron doped samples which were produced with different doping level. The main result from this growth series was that the quality of the sample drastically deteriorates from the initial seed to the grown boron doped seed. The process that was used to produce these samples was the epitaxial sublimation process. The difference from earlier growth was that a 3C-SiC seed was used and the source to feed the growth was doped with boron. The undoped source is as mentioned commercially available ceramic SiC and the doped source have been produced in the lab. The different growth runs had different sources in the sense that the source had been doped with different amounts of boron, see Figure. 24.

![Figure 24: The three boron doped samples that were produced.](image)

(a) Sample that has been doped using a source with a boron concentration of $10^{18} \text{cm}^{-3}$.

(b) Sample that has been doped using a source with a boron concentration of $10^{19} \text{cm}^{-3}$.

(c) Sample that has been doped using a source with a boron concentration of $10^{20} \text{cm}^{-3}$.

One can notice in Figure. 24 that the quality deteriorates with higher doping level. So introducing boron into the 3C-SiC alters the crystalline stability in the lattice and more defects occur. The sample in 24a was doped with a source with $10^{18} \text{cm}^{-3}$ atoms of boron. Comparing the image 24a with the higher doped 24b and 24c it is clear that the structure of the crystal is less ordered and the crystal quality is deteriorated.
8.2 Bulk 3C-SiC

In this section the growth configuration for bulk growth was used to fabricate the samples. After initial testing with the crucible filled with adequate amount of powder as seen in Figure. 15 it was noted that the growth rate was about 50 µm/hr at 1975 °C and 5 mbar (Argon atmosphere). The quality of the grown layer can be seen in Figure. 25a and was grown on a seed in the initial test. It somewhat followed the quality of the seed and therefore it was decided to increase temperature even further (2000 °C) to achieve a higher growth rate. This resulted in higher growth rate but still the quality of the 3C-SiC crystal was not, by optical observation, as good as desired, Figure. 25b.

![Grown for two hours.](image1)

![Grown for ten hours.](image2)

Figure 25: Both samples were produced at the same growth conditions but the sample in 25b was grown for a longer time than the sample in 25a.

The next step was to grow the crystals in static vacuum. The expectations for growth in static vacuum were that the growth rate would be higher than the growth in argon. Due to this the temperature was decreased to 1950 °C. This gave crystals of somewhat better quality, as evaluated through optical microscopy characterization. Two samples were produced using this static vacuum approach. The samples turned out with different thickness but similar quality 26a and 26b. Still we could not replicate the achieved quality from the seeds in the larger crystals.

A possible reason is that the powder source creates a silicon rich environment, due to that the silicon rich species sublime at a higher rate than the carbon rich species. This then leads to the formation of Si-droplets early in the growth process. Experiments to test this theory were carried out. First the appearance of silicon droplets early in the growth process was tested. When no significant change in result could be seen, a smaller amount of powder in a smaller crucible was used for further testing. Growth for 30 minutes was performed on seeds which were not good enough for 3C-SiC growth, but it was useful to obtain information about the appearance of the silicon droplets which were the main goal. In the first test

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*The chamber was sealed from the pump, when a temperature of 1200 °C was achieved, and the pressure was allowed to build up in the chamber from the gas species which were sublimed during growth.*
it was found that Si-droplets indeed form at the early stages of growth, this was performed with the crucible assembly from earlier growth runs. The sample looked like in Figure. 27a. The second test also resulted in a Si rich growth and Si-droplets formed. A final test was made and this sample can be seen in Figure 27b. As a subsequent step a pressurized ambient to prevent the appearance of Si-droplets was tested. A pressurized argon ambient (700 mbar) during the temperature ramp-up and cooling down was applied, with only the powder source and the seed in the crucible. This seems to have worked to suppress the occurrence of Si-droplets as seen in Figures. 27c and 27d. The silicon droplets can be seen as black round spots in the optical microscope.

In the first test, the formation of silicon droplets in the initial stage of growth was investigated. As seen in Figure. 27a one can see that silicon droplets are present. In the second test a smaller amount of powder in a smaller crucible was tried and this resulted in some decrease in the amount of silicon droplets, Figure. 27b. Introduction of argon gas into the chamber during ramp up was executed in the third test, Figure. 27c. In the third test, when 700 mbar of argon was introduced, we could see some decrease of the amount of silicon droplets. In the fourth test argon was introduced during the temperature ramp-up and during the cooling process after growth. The silicon droplets were eliminated, as seen in Figure. 27d. This is due to that when introducing argon in such a large amount, 700-800 mbar, the sublimation process is inhibited. During the temperature ramp-up and the cool-down process the temperature reaches a point where the Si/C ratio is too high and a Si-rich atmosphere is present. It is possible to let the sublimed gas species reach the seed only when the conditions are favorable. This can be done through the introduction of argon and this way avoids sublimation and growth at lower temperatures.
(a) The first test. With earlier growth conditions. Growth time was 30 minutes.

(b) The second test. With smaller crucible and less powder. Growth time was 30 minutes.

(c) The third test. Small crucible and introduction of argon during ramp-up. Growth time was 30 minutes.

(d) The fourth test. Small crucible and introduction of argon during ramp-up and cool down. Growth time was 30 minutes.

Figure 27: As seen in this graphics the amount of silicon droplets, black round spots, have been drastically decreased during the process and in Figure 27d in which there is a very low density of silicon droplets.
8.2.1 SEM

Three bulk samples were selected to be examined by SEM. What we saw in the optical microscope could be confirmed, that there were a lot of different grains with different crystal orientations. However, each individual grain seems to have a smooth surface and on some grains even surface steps was observed. The different samples can be seen in the Figures.

(a) A large number of grains with different shapes and orientations can be observed on the surface.

(b) Steps can be seen also on the bulk sample surface with the SEM.

(c) Triangular defects that are characteristic for the cubic polytype can be observed.

(d) A closer look at the edge of the sample where one can see that the grains are stacked on top of one another and do not continue from the substrate to the surface.

Figure 28: SEM images of "Bulk Growth 4".
Results and discussion

(a) Surface steps on the surface of a grain in sample Bulk Growth 6.

(b) Steps on another grain, also on the sample Bulk Growth 6.

(c) Measuring the angle between defects in sample Bulk Growth 6, result is almost 60°.

(d) Measuring the angle between defects in sample Bulk Growth 8, the result is 60°.

Figure 29: SEM images of 'Bulk Growth 6' and 'Bulk Growth 8'. For more SEM images see Appendix A.

The general results from this initial bulk growth are crystals with a lot of grains with different orientation. However, one can observe that the majority of the grains are 3C-SiC and this is important since other polytypes would complicate the growth of 3C-SiC even more. This can be observed as many grains have the shape of triangles with angles of 60°. This is a characteristic feature for cubic silicon carbide defects. It is very encouraging for further studies that the 3C-SiC polytype could be maintained at such thickness.
Chapter 9

Conclusions

In this thesis both the sublimation epitaxy and the seeded sublimation growth of 3C-SiC have been studied and discussed.

Production of 3C-SiC seeds have been demonstrated and single crystal seeds have been produced. The growth using two temperature steps for growth was more successful than only using one temperature step. Seeds of good crystal quality have been produced and confirmed by several characterization techniques such as TEM and XRD. The surface of the produced seeds have been characterized by AFM showing some small steps on the surface originating from the vicinal surface of the 4H-SiC substrate. The boron doped seeds which were produced had lower crystal quality compared to the unintentionally doped 3C-SiC seeds. The higher doping concentration of boron introduced more defects in the crystal. The produced bulk 3C-SiC did not reach the same crystal quality as the 3C-SiC seeds that were produced. However, the bulk 3C-SiC that was produced after some alterations in the growth process had a better crystal quality than the first bulk sample. The main reason is the appearance of silicon droplets early on in the growth process deteriorated the quality of the first grown crystals. This was solved by introducing argon (700-800 mbar) during the temperature ramp-up and also during cooling down after growth.

The electrical resistance of the seeds has been measured and the values that were measured gave some interesting results. The measured electrical resistance of the seeds are in the range of 24-2900 $\Omega$cm. This compared to 4H-SiC wafers, that have values from 15-28 m$\Omega$cm gives that the 3C-SiC that have been produced during this thesis nearly comes within the range for these commercial wafers. This will be very interesting to see in the future how low resistance that can be achieved for the 3C-SiC polytype. There are some main limiting factors that need to be studied further to achieve higher quality material. The purity of the 3C-SiC needs to be higher without contamination and unintentional doping. Crystal quality of the can also be improved by improving the growth method. When being able to adjust the process in such a way that these main limiting factors are not causing defects during growth some highly interesting material will be seen.
Chapter 10

Future work

In the future more investigation is needed to understand how the growth process should be adjusted in order to produce high quality bulk cubic silicon carbide samples. Several things should be investigated and optimized for the bulk process to be as effective as the seed production: the influence of the amount of powder, time for annealing of the powder, the distance between the powder and the seed, what is the optimum temperature, the optimum pressure and the optimum growth rate. The influence of using different gases during pressurization could also be interesting. To produce doped samples for devices one also needs to investigate what doping concentrations that are suitable and what elements to dope the cubic silicon carbide with. As a final suggestion for future work it would be interesting to see if cutting or polishing the seed at an off-axis angle similar to the 4H substrate could improve the bulk growth and promote the step flow growth even further.
Bibliography


Appendix A

Table 5: The seed and bulk samples produced and their thicknesses. The bulk thickness is the combined thickness of the seed and the layer grown using the seeded sublimation growth method.
Figure 30: SEM images of 'Bulk Growth 8'.
Figure 31: SEM images of "Bulk Growth 4".
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