Examensarbete

SiC Homoepitaxial Growth at High Rate by Chloride-based CVD

Yuan-Chih Lin

Examensarbetet utfört i Halvledare Materials grupp vid Linköpings Tekniska Högskola, Campus Valla

2010-06-04

LITH-IFM-A-EX--10/2356--SE
SiC Homoepitaxial Growth at High Rate by Chloride-based CVD

Yuan-Chih Lin

Examensarbetet utfört i Halvledare Materials grupp vid Linköpings Tekniska Högskola, Campus Valla

2010-06-04

Handledare
Stefano Leone

Examinator
Anne Henry
SiC is an attractive material since it has remarkable properties. For several years efforts have been put primarily in electronic applications. High power and high frequency devices can be fabricated on SiC due to its wide band gap, high breakdown field and high thermal conductivity. SiC devices can be used in harsh environment since its operation temperature is significantly high (about 1200 °C). SiC bulk growth has been improved by seeded physical vapour transport (PVT) during last decades. However, the quality and doping concentration of SiC bulk are not good enough to be used as an active layer for devices. SiC epilayer growth by chemical vapour deposition (CVD) was established in the last three decades. Only about 5 μm/h growth rate is achieved by CVD with a standard process. Long deposition time is required to grow ≥100μm thick epilayer for high voltage devices. The main problem in standard CVD is the formation of silicon (Si) droplets due to supersaturation of Si species on the growth surface or in the gas-phase, which is detrimental for devices performance. To solve the problem of Si droplets, chloride-based CVD was introduced. Chlorinated species can dissolve the silicon aggregates through the formation of strong bonds to silicon species compared to Si-Si bonds. Typical chlorinated precursors are hydrogen chloride (HCl) and methyltrichlorosilane (MTS). In this thesis study, HCl was mainly used as chlorinated precursors. Distinct chlorinated species can introduce deep energy levels into the SiC material, which is beneficial for device applications. Deep energy levels can be introduced by adding transition metal such as vanadium (V), chromium (Cr) or tungsten (W). There are some limits which are needed to be overcome for a complete development of SiC. 4H SiC wafers are commercially available on the market, larger diameter would be very useful for the industrial development of SiC. High growth rate and good quality with controlled uniformity are desired for electronic applications. In this thesis, the influences of growth parameters such as C/Si and Cl/Si ratios, comparison between different precursors, growth condition in different areas of reaction chamber and effects of substrate polarity are discussed. Intentional incorporation of tungsten atoms is investigated by deep-level transient spectroscopy measurement and thermodynamic analysis.
Upphovsrätt

Detta dokument hålls tillgängligt på Internet – eller dess framtida ersättare – under 25 år från publiceringsdatum under förutsättning att inga extraordinära omständigheter uppstår.

Tillgång till dokumentet innebär tillstånd för var och en att läsa, ladda ner, skriva ut enstaka kopior för enskilt bruk och att använda det oförändrat för ickekommersiell forskning och för undervisning. Överföring av upphovsrätten vid en senare tidpunkt kan inte upphäva detta tillstånd. All annan användning av dokumentet kräver upphovsmannens medgivande. För att garantera äktheten, säkerheten och tillgängligheten finns lösningar av teknisk och administrativ art.

Upphovsmannens ideella rätt innefattar rätt att bli nämnd som upphovsman i den omfattning som god sed kräver vid användning av dokumentet på ovan beskrivna sätt samt skydd mot att dokumentet ändras eller presenteras i sådan form eller i sådant sammanhang som är kränkande för upphovsmannens litterära eller konstnärliga anseende eller egenart.

För ytterligare information om Linköping University Electronic Press se förlagets hemsida http://www.ep.liu.se/.

Copyright

The publishers will keep this document online on the Internet – or its possible replacement – for a period of 25 years starting from the date of publication barring exceptional circumstances.

The online availability of the document implies permanent permission for anyone to read, to download, or to print out single copies for his/her own use and to use it unchanged for non-commercial research and educational purposes. Subsequent transfers of copyright cannot revoke this permission. All other uses of the document are conditional upon the consent of the copyright owner. The publisher has taken technical and administrative measures to assure authenticity, security and accessibility.

According to intellectual property law the author has the right to be mentioned when his/her work is accessed as described above and to be protected against infringement.

For additional information about Linköping University Electronic Press and its procedures for publication and for assurance of document integrity, please refer to its www home page: http://www.ep.liu.se/.

© Yuan-Chih Lin
Abstract

SiC is an attractive material since it has remarkable properties. For several years efforts have been put primarily in electronic applications. High power and high frequency devices can be fabricated on SiC due to its wide band gap, high breakdown field and high thermal conductivity. SiC devices can be used in harsh environment since its operation temperature is significantly high (about 1200 °C). SiC bulk growth has been improved by seeded physical vapour transport (PVT) during last decades. However, the quality and doping concentration of SiC bulk are not good enough to be used as an active layer for devices. SiC epilayer growth by chemical vapour deposition (CVD) was established in the last three decades. Only about 5 µm/h growth rate is achieved by CVD with a standard process. Long deposition time is required to grow ≥100µm thick epilayer for high voltage devices. The main problem in standard CVD is the formation of silicon (Si) droplets due to supersaturation of Si-species on the growth surface or in the gas-phase, which is detrimental for devices performance. To solve the problem of Si-droplets, chloride-based CVD was introduced. Chlorinated species can dissolve the silicon aggregates through the formation of strong bonds to silicon species compared to Si-Si bonds. Typical chlorinated precursors are hydrogen chloride (HCl) and methyltrichlorosilane (MTS). In this thesis study, HCl was mainly used as chlorinated precursors. Distinct chlorinated precursors result in different chemical reactions which affect the epilayer growth appreciably. The Cl/Si ratio, which is the ratio of the amount of chlorinated precursors to silicon precursors, is a very critical growth parameter for morphology, growth rate and background doping concentration. The C/Si ratio and Si/H2 ratio also affect the epilayer growth appreciably. Besides, growth temperature, growth pressure and temperature ramp up condition are other important growth parameters. In the CVD reaction chamber, the temperature profile and gas species distribution are not uniform along the whole susceptor length, which leads to different thickness of epilayer, morphology and doping concentration at different area of the reaction chamber. The polarity and off-angle of substrates can bring about complete different grown epilayers. Epitaxial defects are mainly replicated from the substrate. Therefore, the quality of substrates is very important as well. Deep energy levels can be introduced by adding transition metal such as vanadium (V), chromium (Cr) or tungsten (W). There are some limits which are needed to be overcome for a complete development of SiC. 4” SiC wafers are commercially available on the market, larger diameter would be very useful for the industrial development of SiC. High growth rate and good quality with controlled uniformity are desired for electronic applications. In this thesis, the influences of growth parameters such as C/Si and Cl/Si ratios, comparison between different precursors, growth condition in different areas of reaction chamber and effects of substrate polarity are discussed. Intentional incorporation of tungsten atoms is investigated by deep-level transient spectroscopy measurement and thermodynamic analysis.
# Table of Contents

1. INTRODUCTION .................................................................................................................. 1

1.1 History ......................................................................................................................... 1

1.2 SiC applications ...................................................................................................... 1

1.3 Future development ................................................................................................. 2

2. SILICON CARBIDE ............................................................................................................. 3

2.1 Introduction ............................................................................................................... 3

2.2 Crystal Structure of SiC .......................................................................................... 3

2.3 Properties of SiC ..................................................................................................... 5

2.4 Bulk crystal growth of SiC ....................................................................................... 6

2.5 Epitaxial growth ...................................................................................................... 7

2.6 Epitaxial defects in SiC .......................................................................................... 10

3. CHEMICAL VAPOR DEPOSITION .................................................................................. 11

3.1 Growth Mechanism ................................................................................................. 11

3.2 Hot-wall CVD reactor ........................................................................................... 13

3.3 Chloride-based CVD ............................................................................................... 15

3.4 Growth Parameters ................................................................................................. 16

3.5 Simulation of Chemical Vapor Deposition ............................................................ 17

4. CHARACTERIZATION TECHNIQUES ........................................................................... 18

4.1 Optical Microscope (OM) ....................................................................................... 18

4.2 KOH Etching ............................................................................................................ 19

4.3 Fourier Transform Infrared Spectroscopy (FTIR) .................................................. 20

4.4 Low Temperature Photoluminescence (LTPL) ....................................................... 21

4.5 Capacitance-Voltage (CV) ...................................................................................... 23

4.6 Deep Level Transient Spectroscopy (DLTS) ............................................................ 24
5. EXPERIMENTAL RESULTS AND DISCUSSION

5.1 Introduction

5.2 Epilayer grown on 4H 8° off-axis SiC substrates

5.2.1 C/Si ratio

5.2.2 Cl/Si ratio

5.2.3 Comparison with MTS process

5.2.4 Growth condition at different areas in reaction chamber

5.2.5 Si-face substrate and C-face substrate

5.3 SiC incorporation with Tungsten

5.3.1 DLTS measurement of W-doped sample

5.3.2 Thermodynamic analysis

6. CONCLUSIONS

7. ACKNOWLEDGEMENT

8. REFERENCE
1. INTRODUCTION

1.1 History

Swedish chemist Jöns Jacob Berzelius found a compound where silicon directly binds to carbon when he was studying silicon. Silicon carbide powder has been used as an abrasive since 1893. Edward Goodrich Acheson used electric batch furnace to fabricate bulk SiC as an abrasive and established the Carborundum Company in 1894. Acheson process was carried out in electric furnace by heating the mixture of carbon and silica (SiO_2) with alumina (Al_2O_3), lime (CaO) and salt (NaCl). The SiC crystal was formed by the synthesis of the mixture. Henri Moissan discovered SiC presence in nature in 1905 when he was investigating Canyon Diablo meteorite in Arizona, USA. Henry Duwoody was the first to use SiC for an electronic application in 1906; this was as a Schottky diode or point-contact detector for radio receivers. Electroluminescence was observed by Henry Joseph Round in 1907 when applying a potential between to contacts positioned on a small crystal of SiC. J. A. Lely produced pure and high quality SiC single crystal by the so-called Lely process or sublimation process in 1955. The Lely process was improved in 1978 via seeded sublimation growth technique by Tarirov and Tsvetkov. Seeded sublimation growth, also called modified Lely process, is till nowadays used to manufacture SiC bulk crystals and it makes possible to fabricate SiC wafers from bulk crystals. Matsunami demonstrated that cubic single crystalline SiC could be grown on silicon substrates in 1981. Nowadays, 4” SiC wafers with high quality are available in the markets and devices made of SiC such as Schottky diodes and MESFETs can be purchased.

1.2 SiC applications

Silicon carbide (SiC) is an innovative material. Its attractive properties make SiC interesting to be investigated in several fields. For instance, SiC has been used in abrasive machining and cutting tools due to its superior hardness. SiC is utilized as components of automobile parts due to its endurance to high temperature and high strength of its composites. In addition to its outstanding material properties in mechanical applications, many efforts have been put in the electronic applications development due to the consideration of SiC advantages: high temperature operation, wide bandwidth and high power operation. Regarding electronic applications, SiC is primarily used in RF devices, power devices and power switches.

In RF applications, large bandwidth of devices and high efficiency are required. SiC devices provide large bandwidth without losing any circuit efficiency. It has been found that the thermal and electrical memory effects can be eliminated easily by SiC devices due to high thermal conductivity and reduced traps in devices, which is an advantage of SiC in RF applications. Alternatively, the linearity of SiC is easily corrected via using digital pre-distortion (DPD) technique[1], which results in higher efficiency operation than devices made of other semiconductor materials. The other commercial application of SiC is the utilization of broadband wireless access called WiMax. WiMax has lower range of wireless internet access and double data rate than the WiFi standard. Device operation shows that 10 W SiC MESFETs can achieve the same linear power as 20 W GaAs MESFETs and SiC MESFETs has 17% higher drain efficiency[1].
The usage of SiC Schottky diodes will primarily affect the computer industries. These devices not only increase the switching frequency but also avoid reverse recovery current during switching. It leads to a size reduction, a weight decrease of devices and systems and an increase of the power density. Besides, SiC Schottky diodes are also important in motor devices. It prevents the losses from switching in diodes and switching turn-on and turn-off in the circuits. High percentage of switching losses has been improved by SiC Schottky and it has been demonstrated by comparing SiC diode to Si diode\textsuperscript{[1]}. Since SiC can be operated at high temperature environment, the design of Si Schottky diodes and SiC power switches is more flexible in cooling system. Therefore, SiC devices can be employed under various harsh environments.

1.3 Future development

High efficiency via using SiC as electronic devices results in the reduction of energy consumption and reduction of carbon dioxide emission. To broaden the usage of SiC in electronic applications, the limitations of SiC growth techniques have to be overcome. SiC homoepitaxial growth by chloride-based CVD has given 10 times higher growth rate than the standard SiC CVD growth without chlorinated precursors. However, the quality of grown SiC epilayers and the cost for the high temperature operation are still a limitation. The high quality of SiC epilayers is strictly required since high density of defects such as basal plane dislocations causes the degradation of power devices. Nowadays up to 4” SiC wafers with low micropipe density are available and their cost is more than 1000$ per wafer. Therefore, growth with high quality operated at lower temperature and shorter deposition time is the direction for the future research in SiC growth.

![Fig 1.1 Distribution of energy consumption all around the world\textsuperscript{[1]}](image)

The energy consumption in Fig 1.1 attributes primarily to the motion category which includes motors for household appliances, for industrial applications and electricity driven transportation. For example, a study\textsuperscript{[2]} shows that the usage of a variable speed motor made of SiC inverters can reduce 40% energy cost by running 10% above of the required power. This control speed motors can be employed in a number of applications. From green technology viewpoint, it reduces greatly not only the energy consumption but also decreases the emission of carbon dioxide. Hence, SiC is an environmental friendly material and it will become widely used in the future.
2. SILICON CARBIDE

2.1 Introduction

Silicon carbide (SiC) has been an attractive material for a couple of decades. Its promising material properties attract the investigation in the semiconductor field. SiC has more than 50 polytypes and each polytype has slightly distinct material properties. Among a number of polytypes, 4H-, 6H- and 3C-SiC are the most common polytypes. SiC has a wide indirect energy band gap. SiC can be used in high power and high frequency devices due to its wide energy band gap, high breakdown field, high thermal conductivity and high operation temperature. The devices based on SiC show great performance with high efficiency and they are friendly to the environment. Nowadays, the SiC substrates are typically prepared by cutting SiC bulk crystal and mechanical chemical polishing. The SiC bulk crystal is fabricated primarily by seeded physical vapor transport (PVT). The quality of grown SiC epilayers is dependent on the quality of SiC substrates to some extent. Furthermore, the polytype of SiC epilayers can be controlled by using off-cut SiC substrates. In the CVD process the step-flow growth mode dominates the growth mechanism since steps created by off-cutting substrates provide the nucleation sites for migrating adatoms. However, some epitaxial defects can be introduced during growth, such as carrot defects, decoration of micropipes, growth pits and some others. The electrical conductivity of SiC epilayers can be controlled by intentional addition of dopants. For example, nitrogen takes the carbon sites in the SiC lattice and gives origin to n-type SiC. Deep energy levels can also be introduced on purpose via transition metals incorporation.

2.2 Crystal Structure of SiC

Silicon carbide is a material with many different stacking sequences, also called polytypes. The polytypism is a phenomenon where crystal structures have one dimensional variation with the same chemical composition. More than 50 different polytypes have been discovered for SiC. However, the most common polytypes structures are 3C, 4H, 6H and 15R. The names of polytypes are given after Ramsdell’s notation. The number in front of the capital letter is the number of stacking layers in the unit cell. The capital letter represents the lattice systems, i.e. C for cubic, H for hexagonal and R for rhombohedral. The cubic structure is also named β-SiC, while the hexagonal are named α-SiC. The close pack of hard spheres shown in Fig 2.1 is utilized to illustrate
the stacking behavior. The SiC crystal structure is constituted by a number of Si-C bilayers. The simplest stacking sequence is ABABAB... (for 2H-SiC) and the crystal structure is usually called wurtzite structure. The stacking sequence ABCABC... (for 3C-SiC) forms the cubic structure called zincblende structure. The units of stacking sequence for 4H- and 6H-SiC are ABCB and ABCACB respectively. The illustration of the crystal structures in the (11 0) plane for 3C-, 4H- and 6H- are shown in the Fig 2.2. The occupancy sites are classified into hexagonal sites and cubic sites. The hexagonal sites labeled \( h \) in Fig 2.2 locate at the zigzag points and the cubic sites labeled \( k \) situate at others than the zigzag points. The number of occupancy sites for 3C-, 4H and 6H is listed in Table 2.1.

The growth of different polytypes significantly depends on their thermodynamic stability, therefore on the temperature and pressure. For example, the 3C-SiC is formed easily at a low temperature (\( \leq 1500 ^\circ C \)), since the growth of 3C-SiC has higher probability to exist when the other polytypes are less stable\(^3\). However, 4H- and 6H-SiC are stable at high temperatures (\( >1500 ^\circ C \))\(^3\).

![Fig 2.2 Arrangement of Si-C pairs in (11 0) plane for 3C-, 4H- and 6H-SiC. The solid circles represent C atoms and the hollow circles represent Si atoms. The h and k stand for the hexagonal sites and cubic sites\(^3\).](image)

<table>
<thead>
<tr>
<th>Polytypes</th>
<th>3C-SiC</th>
<th>4H-SiC</th>
<th>6H-SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic sites</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Hexagonal sites</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 2.1 Number of occupancy sites for 3C-, 4H- and 6H-SiC.
2.3 Properties of SiC

The wide band gap of SiC is formed due to strong binding energy of Si-C bonds which give rise to a large energy difference between bonding and antibonding states. In general, the polytypes of SiC have a wide band gap energy about 2.3-3.4 eV which depends on the crystal structure. The tight bonding of Si-C bonds also leads to high-frequency lattice vibration, i.e. the energy of optical phonons are high. The phonons in SiC crystal give high thermal conductivity and the high saturated electron drift velocity. Furthermore, the electrical conductivity of SiC can be controlled by adding dopants such as nitrogen for n-type and boron for p-typed doped material. Transition metal impurities introduce deep energy levels within energy band gap. The deep-level traps shorten the carrier lifetime and decrease the efficiency of light emission by nonradiative recombination. However, deep-level impurities are sometimes introduced on purpose for high frequency switches. The physical properties of SiC and other semiconductor materials are listed in Table 2.2.

Table 2.2: | a (Å) | E_g (eV) | T (K) | μ (cm²/Vs) | E_B (V/cm) | v_sat (cm/s) | k (W/cm·K) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3C-SiC</td>
<td>4.36</td>
<td>2.23</td>
<td>-</td>
<td>1000</td>
<td>-</td>
<td>2.7 × 10⁷</td>
</tr>
<tr>
<td>4H-SiC</td>
<td>a=3.09, c=10.08</td>
<td>3.26</td>
<td>1230</td>
<td>900</td>
<td>3 × 10⁶</td>
<td>-</td>
</tr>
<tr>
<td>6H-SiC</td>
<td>a=3.09, c=15.12</td>
<td>3.02</td>
<td>1200</td>
<td>450</td>
<td>3 × 10⁶</td>
<td>2 × 10⁷</td>
</tr>
<tr>
<td>Si</td>
<td>5.43</td>
<td>1.11</td>
<td>410</td>
<td>1350</td>
<td>2 × 10⁵</td>
<td>1 × 10⁷</td>
</tr>
<tr>
<td>GaAs</td>
<td>5.65</td>
<td>1.43</td>
<td>570</td>
<td>8000</td>
<td>3 × 10⁵</td>
<td>2 × 10⁷</td>
</tr>
<tr>
<td>GaN</td>
<td>a=3.189, c=5.185</td>
<td>3.39</td>
<td>1250</td>
<td>900</td>
<td>5 × 10⁶</td>
<td>1.5 × 10⁷</td>
</tr>
<tr>
<td>AlN</td>
<td>a=3.112, c=4.982</td>
<td>6.2</td>
<td>2100</td>
<td>1100</td>
<td>1 × 10⁶</td>
<td>1.4 × 10⁷</td>
</tr>
</tbody>
</table>

In conclusion, silicon carbide has remarkable material properties compared to other semiconductor materials. Moreover, distinct crystal structures of SiC result in the difference of material properties such as electric, magnetic, optical and mechanical properties between the different polytypes. Hence SiC can be employed in various semiconductor applications. Further investigation to control the growth of SiC is a fascinating topic.
2.4 Bulk crystal growth of SiC

The bulk growth of SiC can be accomplished by seeded physical vapor transport (PVT) or high temperature chemical vapor deposition (HTCVD). However, the requirement of high operating temperature (above 2000 °C) is needed for bulk quality. Some attempts were investigated to grow bulk crystal of SiC by lower temperature CVD (1500-1800 °C). The concept of HTCVD will be discussed in chapter 3.

![Scheme of PVT system for bulk growth of SiC](image)

**Fig 2.3** Scheme of PVT system for bulk growth of SiC. Three primary regions are defined as crystallization, mass transfer and source regions. The figure is redrawn from the literature [4].

The concept of PVT bulk growth of SiC was based on the Lely process, whereas SiC was grown only on very small seeds (about 10 mm in diameter) and difficulty controls the quality of SiC bulk. The PVT (modified Lely process) was developed without the typical drawbacks of the Lely process[5]. The working principle of PVT is illustrated in Fig 2.3. In the source region a non-stoichiometric powder of SiC (Si, SiC2, Si2C or SiC) is used as source. The powder sublimes into the “mass transfer” region. In the “mass transfer” region, the mass flow is mainly dominated by diffusion and temperature gradient between a lower temperature growth front and the hotter source. In the “crystallization” region, the crystalline SiC Lely platelet is used as seed. The SiC-species are transferred to the seed and begin to nucleate. A study[4] showed the influence of a number of growth parameters on the quality of SiC bulk. For instance, the temperature of sublimation influences the composition of the vapor. The distance between growth front and source affects growth rate significantly, defects generation and polytype stability. The temperature gradient plays an important role in supersaturation condition at the crystallization surface. High growth rate (0.1-1 mm/h) can be achieved but still a high density of dislocations is usually formed inside the crystal due to thermodynamic requirements. Moreover, the formation of high thermal stress in bulk crystal during growth easily causes the generation of defects. Hence, many improvements are needed to reach a high crystal quality for performing electric devices. Further optimum growth conditions still need to be found.
2.5 Epitaxial growth

Epitaxial growth can be classified into heteroepitaxial growth and homoepitaxial growth. Homoepitaxial growth of SiC has been investigated via several growth techniques like sublimation, liquid phase epitaxy (LPE) and CVD for several years on hexagonal substrates. Moreover, homoepitaxial growth of SiC is mainly controlled by step-flow growth and spiral growth. These two growth modes are observed under different conditions which are significantly related to the orientation or off-cut of substrates. The study of off-angle dependence of SiC homoepitaxial growth has been deeply investigated\(^3\). The mechanism of step-flow growth, step-bunching phenomenon and spiral growth are described below.

(a) Step-controlled epitaxy

SiC substrates are usually prepared by cutting α-SiC crystals with a certain tilted angle towards the \(<11\bar{2}0>\) or \(<1\bar{1}00>\) direction. Different polishing processes are appropriately carried prior to epitaxial growth. Steps and kinks are created due to the off-angle cut on the substrate. Once atoms from the gas phase are adsorbed on the substrate, they migrate towards the step edges, owing to low potential energy at kinks. Thus, nucleation process occurs in ordered sequence followed as a flow at steps shown in Fig 2.4. In other words, the lateral growth of step-flow inherits the stacking sequence of substrates.

![Fig 2.4 Step-flow proceeds and migrating atoms nucleate at kinks as same stacking sequence as steps. The polytype shown here is 6H-SiC\(^3\).](image)

![Fig 2.5 Different crystal orientation domains result in the twinned crystalline in this case and different stacking sequence causes polytypes domains. The Figure is redrawn from the literature\(^3\).](image)
Besides the significance of steps, the length of {0001} terrace plays an important role as well. If the length of terrace is too long for migrating species to diffuse to nucleation sites, desorption of atoms from the surface takes place. Moreover, self nucleation at long terrace occurs once the supersaturation is high enough. Distinct polytypes of SiC may nucleate at {0001} terrace and this leads to different domains which can be of different polytypes or crystal orientations, as shown in Fig 2.5. Higher density of steps and shorter length of terrace can be achieved via larger off-angle substrates by which the polytype of the grown epilayer can be controlled easier.

(b) Step-bunching

Step bunching is a kind of macrosteps morphology of the epilayer surface which can be observed under optical microscope as parallel lines of different height and width. To explain the formation of step-bunching, many models of step-bunching have been proposed. The following description is explained in the viewpoint of energy. The 6H-SiC has 3 distinct terraces marked 6H1, 6H2 and 6H3 shown in Fig 2.6. The energy of occupancy at steps in different terraces has been calculated in the study[6]. The migrating atoms are favored in growing in the 6H2 terrace than 6H1 terrace as shown in Fig 2.6(a). The growth rate in 6H2 is higher than it in 6H1 terrace. Thus, the 6H2 terrace overtakes the 6H1 terrace and it forms a step with two bilayers height as shown in Fig 2.6(b). Since the velocity of steps is inversely proportional to the height of steps, the step with two bilayers height has lower growth rate than 6H3. It causes that the 6H3 terrace overtake the 6H1 with two bilayers and three-bilayers height step forms as shown in Fig 2.6(c).

![Fig 2.6(a) the initial stage of formation of step bunching (b) the 6H2 terrace overtakes the 6H1 terrace and two-bilayers height step forms (c) the 6H3 terrace overtakes the 6H1 terrace and three-bilayers height step forms[6]](image)

Other growth conditions may enhance the step-bunching. For example, the C-rich growth condition favorably results in the step-bunching but also higher temperatures. Further investigations for step-bunching have been carried and can be searched in a number of papers.
Fig 2.7 (a) Illustration of screw dislocations as nucleation sites of spiral growth\textsuperscript{[7]} (b) illustration of spiral hillocks by atomic force microscope\textsuperscript{[8]}

The step-flow growth proceeds since the steps provide energetically favorable nucleation sites. The process of spiral growth is similar to the step-flow growth. Spiral growth begins with the help of screw dislocations as nucleation sites shown in Fig 2.7(a). The migrating atoms have a high probability of adsorbing on the growth surface and diffusing to the nucleation sites at screw dislocations. The advancement of spiral growth proceeds when migrating atoms continuously nucleate spirally around the pinned center point. The characteristic of spiral growth is illustrated as hillocks by atomic force microscope as shown in Fig 2.7(b). It has been demonstrated\textsuperscript{[8]} that spiral growth is affected by the C/Si ratio in the shape of spiral hillocks for 6H on-axis SiC by CVD. The variation shape of spiral hillocks is related to the rates of spiral growth and step-flow growth. A high C/Si ratio enhances spiral growth but a low C/Si ratio enhances step-flow growth. The critical radius for nucleus also plays an important role in spiral growth. Furthermore, the growth mode significantly depends on the off-angle of substrates. The investigation\textsuperscript{[9]} showed that the transition from spiral growth mode to step-flow growth mode occurs when substrates are changed from almost perfectly on-axis substrates by 0.06° to unintentional off-axis substrates by 0.33°.

Spiral growth mode is an approach to control polytypes growth of SiC. However, the spiral growth surface is not smooth as for the device fabrication. A series of polishing process is carried out in order to remove the hillocks structure on the surface.
2.6 Epitaxial defects in SiC

Defects control in SiC is one of the most important work to accomplish in order to manufacture devices of excellent performance. The density and size of defects are critical to the quality of epilayers. There are several sorts of defects in the epilayers and most of them are replicated from the substrate. The identification of defects is usually carried out by optical microscopy. The most common defects in epilayers grown on off-orientation substrates are described below.

The one-dimensional defects such as threading edge dislocation (TEDs), threading screw dislocation (TSDs) and basal plane dislocation (BPDs) play an important role in forming macro-defects. These dislocations can be revealed by KOH etching. The basal plane dislocation can be eliminated avoided by growing the epilayer on on-axis substrates. Furthermore, most of BPDs converts into TEDs at the beginning of growth. Beside, the defects usually propagate in the epilayers and appear on their surface. The carrot defects and triangle defects are often observed on off-angle substrates too. They are supposed to originate from the substrate and propagate along step-flow direction. Many investigations for the carrot defects have been done to demonstrate that the origin of carrots is a number of TSDs\textsuperscript{[10]}. The vicinal hillocks are formed by self-consistent nucleation. Micropipes are composed of several TSDs and the formation of micropipes has been proved to release excess strain energy. Other macro-defects are also found on the surface of epilayers such as growth pits, half moon, wavy pits and down-fall defects. The epitaxial defects mentioned above are shown in Fig 2.8. In addition to the defects replicated from the substrates, other defects can occur during the growth like step-bunching and stacking fault (SFs).

![Fig 2.8(a) carrot defects (b) triangle defects (c) vicinal hillocks (d) micropipes (e) growth pits (f) half moon (g) wavy pits (h) down-fall\textsuperscript{[11]}](image)

The defects are influenced with the adjustment of growth parameters. Hence, optimum growth can be achieved once the defects can be eliminated.
3. CHEMICAL VAPOR DEPOSITION

3.1 Growth Mechanism

The biggest difference between chemical vapor deposition (CVD) and physical vapor deposition (PVD) is whether chemical reactions to deposit the migrating species on the substrate occur or not. Chemistry, thermodynamics, kinetics, transportation phenomenon and quantum theory are involved in a CVD system. Every single growth parameter can have a huge impact on the final result. Thus, it is helpful to achieve the optimum growth condition by realizing growth mechanism of CVD system.

![Fig 3.1 Simple scheme for the process of crystal growth by CVD system][12]

A representation of the CVD process is illustrated in Fig 3.1. The gaseous precursors are convectively transported and diffuse to the reaction chamber. Breaking of the precursors bonding occurs mainly in three reactions which are: pyrolysis, reduction and oxidation. Pyrolysis is a process of thermal decomposition and the energy of decomposition depends on the chemical nature of the molecule. Reduction and oxidation depend on the oxidation states of the gas species at the process conditions. Thus, the precursor molecules and their by-products are flowed towards (above, perpendicularly or with an angle) the substrates. They can chemically or physically adsorb onto the surface and diffuse. Two possible events can happen during diffusion on the surface: 1) Desorption of diffused species takes place if the diffusion length is shorter compared to the time needed for the adatoms to encounter a nucleation sites, yet the desorbed molecules still have chance to re-adsorb to substrates; 2) If the diffused species find the nucleation sites, the species bind to it and begin to grow.
Fig 3.2 Nucleation growth modes. 3D island and 2D layer growth mode are called Volmer-Weber and Frank-Van der Merwe respectively. Mixture of 3D and 2D growth modes is named Stranski-Krastanov\cite{13}.

Conventionally, the nucleation can be mainly classified into three growth modes which are island (3D), layer (2D) and mixture modes as shown in Fig 3.2. Island growth mode occurs if the species are more strongly bound to each other than to the substrate. Layer growth mode happens when species prefer to bond to surfaces rather than to themselves. A mixture of growth modes is a combination of island and layer growth modes.
3.2 Hot-wall CVD reactor

The hot-wall CVD reactor mainly consists of vacuum system, gaseous precursors, mass flow controllers with valves and reaction chamber as shown in Fig 3.3, which comprises a quartz tube, quartz liner, susceptor, susceptor plate, insulation and RF-generator. The reactor shown in Fig 3.3 is a horizontal CVD reactor where the gaseous precursors are flowed inside the susceptor horizontally. The substrate wafers placed in the susceptor can be rotated during growth to enhance the uniformity of grown epilayers. Previous investigation showed that thinner grown epilayers were found at downstream area\textsuperscript{[13]}. To compensate the thinner deposition at downstream, tilted susceptor plate is designed as shown in Fig 3.4. The horizontal hot-wall CVD reactor results in great thickness and doping uniformity of the epilayers also thanks to thermal uniformity inside the reaction chamber.

Vacuum is obtained by using a process pump (usually a dry pump) and a turbo pump which is connected with a backing pump (scroll or diaphragm pump) in order to make the turbo pump to operate in high efficiency mode. The vacuum levels are in the range of $10^{-1}$-$10^{-2}$ mbar and $10^{-6}$-$10^{-8}$ mbar for the process pump and turbo pump, respectively. The pressure in the reaction chamber can be controlled by either filling with argon to increase the pressure (gas ballast mode) or evacuating with the pump and the aid of a throttle valve to control the final pressure.
In reaction chamber, the quartz liner is placed inside the quartz tube and aligns the precursor gases into the susceptor inlet more efficiently. The susceptor is made of rigid graphite. The rigid graphite is heated up by electromagnetic coupling with copper coil rf-generator surrounding the quartz tube. The growth temperature is typically in the range 1500~1800°C. To avoid the heat cracking of quartz tube, susceptor is wrapped with low density graphite foam to insulate heat conduction. The temperature just above the susceptor plate is detected by optical pyrometer which is calibrated typically by using Si melting temperature as reference.

A carrier gas in the hot-wall CVD system assists the precursor species to flow uniformly above the surface of substrates. Hydrogen is often selected as the carrier gas. The hydrogen from the high pressure gas bottle has not 100% purity. Bottles contain small amount of impurity gases. The impurity gases may give rise to some extrinsic defects. For example, N₂ incorporates with grown epilayers and it influences the background doping concentration significantly. To prevent the effect of impurity gases, Pd membrane hydrogen purifiers can filter all the other atoms except H atoms. The hydrogen atoms penetrate through the membrane and bind each other to form hydrogen molecule H₂. For normal growth of SiC by hot-wall CVD, the silicon species come from silane (SiH₄) and carbon species originates from light hydrocarbons such as ethylene (C₂H₄) or propane (C₃H₈). The pressure and flow of precursor gases are regulated by electronic pressure controls (EPCs) and mass flow controls (MFCs). However, the variety of usage of precursors is demonstrated in Chloride-based CVD which is discussed in section 3.3.

The SiC substrates are usually prepared by cutting the SiC bulk crystal at a tilted angle from the (0001) plane as shown in Fig 3.5[14]. Then, mechanical and chemical polishing process is carried out to smooth the substrate surface. The SiC substrates are called off-axis substrates. Off-cutting of substrates creates a number of steps on the surface, which provides the nucleation sites for the migrating atoms to grow. As mentioned in section 2.5(a), the steps assist the polytype control which the grown epilayer can replicate the polytype from the substrate. Polytype control by step-flow growth is strongly dependent on off-angle of substrate.

Generally, large off-angle substrates favor step-flow growth. In other words, the polytype control can be easily achieved by large off-angle substrates. In addition to polytype control, the quality of substrates influences the quality of grown epilayers as well. Therefore, substrates also play an important role in hot-wall CVD system.
3.3 Chloride-based CVD

To achieve high growth rate (≥ 100µm/h), Chloride-based CVD has been introduced since 2004\textsuperscript{[15]}. Basically the growth rate can be increased by flowing higher amounts of precursor gases to grow epilayers faster. However, a critical problem occurs because of supersaturation of silicon atoms in the gas phase, which tend to homogeneously aggregate and form Si clusters. The phenomenon of Si droplets coming from the gas phase or aggregating on the substrate, as shown in Fig 3.6, causes horrible morphology and is a fatal factor for device performance. To get rid of Si droplets, three solutions have been proposed: 1) to increase the growth temperature\textsuperscript{[16]}; 2) to decrease the growth pressure\textsuperscript{[17]} and 3) to add species which strongly bind to Si atoms\textsuperscript{[18]}. Growth at higher temperatures causes the evaporation of Si droplets. However, operation at high temperatures cost energy and does not achieve high growth rate efficiently. Decreasing the growth pressure lowers the partial pressure of Si species; therefore supersaturation of Si atoms in the gas phase is suppressed. As a result homogeneous nucleation of Si can be prevented. Nevertheless, decreasing growth pressure also lowers the probability of nucleation of SiC and promotes surface etching by hydrogen and chlorine, i.e. decrease the growth rate. The most suggested solution is the utilization of a halogen atom which can strongly bind Si atoms. The standard enthalpies for Si-Si, Si-F, Si-Cl, Si-Br and Si-I bonds are 2.34, 6.19, 4.15, 3.42 and 2.42 eV respectively\textsuperscript{[14]}. Stronger bonds than Si-Si bonds are recommended to avoid Si aggregation. The atomic radius of halogen atoms is also relevant. Since the bonding with bromine and iodine are not so strong, and the Si-F bonds are too strong, the best partner for Si atoms is definitively chlorine. Chlorine and Si atoms form chlorinated molecules via Si-Cl bonds which avoids the formation of Si droplets.

For standard SiC process by CVD, the most used precursors are silane (SiH\textsubscript{4}) for Si-species and ethylene (C\textsubscript{2}H\textsubscript{4}) or propane (C\textsubscript{3}H\textsubscript{8}) for C-species. For SiC growth by chloride-based CVD, the selection of chlorinated precursors is of high importance. Chlorinated precursors are classified into four categories. First, the standard chloride-based CVD, HCl is used as chloride-based precursors. Second, the hydrogen atoms in SiH\textsubscript{4} are replaced by chlorine atoms. Tetrachlorosilane SiCl\textsubscript{4} (TET) or trichlorosilane SiHCl\textsubscript{3} (TCS) are the most utilized as chlorinated silicon molecules. Third, chlorine atoms replace the hydrogen atoms in hydrocarbon molecules. In this last case chloromethane (CH\textsubscript{3}Cl) is the most used. Forth, a single molecule which contains all the needed atoms: Si, C and Cl, besides than hydrogen. The methyltrichlorosilane SiCl\textsubscript{3}CH\textsubscript{3} (MTS) is most employed for chloride-based homoepitaxial growth of SiC\textsuperscript{[19]}. In conclusion, when selecting a chlorinated precursors, different chlorinated molecules may be used but each of them will result in different chemical reactions with other precursors or their by-products in the gas phase. Alternatively, the choice of chlorinated precursors influences the SiC growth condition. Further investigation is studied through the combined use of different chlorinated precursors.

---

*Fig 3.6 Silicon droplets formed by oversaturation of silicon atoms in gas phases*
3.4 Growth Parameters

Every growth parameter is fundamental in determining the quality of epilayers and growth rate. In general, growth parameters give the similar effects in both cases of on-axis substrates and off-axis substrates, but they must be properly tuned depending on the off-angle and substrate polarity.

a) Growth Pressure

Growth pressure is usually kept fixed to have uniform gas distribution over the susceptor. The equilibrium vapor pressure above the growth surface is significantly related to the growth pressure since partial pressure of all gas species is proportional to the growth pressure. Furthermore, the gas species flow above the growth surface faster when the grow pressure is lower. It decreases the probability of adsorption of gas species onto growth surface. The optimum process pressure has to be found depending on the carrier flow. Proper gas speed is set so that an extended uniform growth area is achieved on the susceptor. Too low speed (high pressure) will result in sudden depletion of the precursors with very high thickness non uniformity. On the other hand too fast gas (low pressure) will cause excessive cooling at the upstream side of the susceptor, inefficient cracking of the precursors, and eventually increased etching of the SiC surface. Pressure affects also the thickness of the stagnant layer existing right above the growing surface. Low pressures facilitate gas diffusion through it. Etching effects are the most dangerous side effects of a too highly reduced process pressure.

b) Growth Temperature

Growth temperature plays an important role in thermodynamics and kinetic of the growth mode. As an example, when growing on 4H on-axis SiC substrates high percentage of 3C-SiC overwhelming 4H-SiC islands and steps were obtained at 1650°C, while 100% of 4H-SiC can be achieved at 1680°C[20]. Higher temperature provide more energy to adatoms diffusion on the surface[9]. Hence, growth temperature has effect on the growth mechanism of SiC epilayers and the polytype stability. In addition to the effect for 4H on-axis SiC, the research for 4°off-axis substrate[21] shows how the growth temperature efficiently controls step-bunching formation. Higher growth temperature results in higher probability of forming step-bunched surfaces. Moreover, it was observed that smooth surface but with many triangle defects could be obtained at 1520 ºC which then changed into less triangle defects but rougher surface at 1550ºC. Besides, higher growth temperature process can have wider range of C/Si before 3C inclusions appear in the epilayers deposited on on-axis substrates[20].

c) Ramp up condition

The in-situ preparation of the surface is usually operated from stabilized temperature to growth temperature. During temperature ramp up, certain gas species are flowed with carrier gas in the reaction chamber with the purpose to prepare suitable condition of the surface. Study[9] focused on on-axis growth found fundamental ramping up by flowing silane with the carrier gas in order to get a smooth surface of substrate. Nevertheless, it negatively affects the off-axis substrate growth due to the formation of Si droplets. Thus,
ramp up with ethylene is suggested to avoid Si droplets phenomenon. Ramp up with HCl may be beneficial, but it is difficult to control it to avoid etching of the substrate surface.

d) Si/H$_2$

The effect of Si/H$_2$ ratio mainly dominates the growth rate without significantly affecting quality of epilayers. The study$^{[20]}$ demonstrates that growth rate increases from 12 $\mu$m/h to 20 $\mu$m/h when the Si/H$_2$ increases from 0.06% to 0.2% for 4H on-axis substrate. In case of off-axis substrates, the growth rate exceeds 100 $\mu$m/h for Si/H$_2$ ratios above 0.5%.

e) C/Si

C/Si ratio primarily influences the polytype stability, morphology and net doping concentration. Since site-competition theory was proposed, the effect of C/Si on net doping concentration is explained well by site-competition theory. It states that a higher C/Si ratio reduces the probability of nitrogen incorporation at C-sites. In other words, n-type doped concentration decreases with higher C/Si ratios. Regarding the polytype stability, higher C/Si ratios give C-rich growth condition which tends to create nucleation sites on the terrace. 3C-SiC has a certain probability of growing at the nucleation sites on the terrace. Furthermore, a high C/Si ratio probably gives rise to the formation of polycrystalline 4H. About morphology, higher C/Si ratios usually result in a rough surface. The criteria of C/Si ratio is strongly related to other growth parameters such as growth temperature and Cl/Si ratio.

f) Cl/Si

Cl/Si ratio is a critical parameter for the homoepitaxial growth of SiC at high rates. It was showed that higher Cl/Si ratio could suppress the formation of 3C-inclusions$^{[20]}$. It also affects the morphology significantly, since smooth surfaces with few defects can be achieved by increasing Cl/Si to an appropriate value. However, no evident influence on the background doping concentration has ever been noted by varying the Cl/Si ratio.

3.5 Simulation of Chemical Vapor Deposition

Chemical vapor deposition involves several coupled physical and chemical reactions. An appropriate simulation assists researchers to quickly realize the situations which can occur in reaction chamber of CVD systems. The simulation software called Ekvicalc is utilized in this thesis. A simulation of a CVD system includes the following physical models and chemical models. Induction heating, mass and heat transport, transport phenomena, chemical equilibrium, chemical kinetics and surface chemistry are the fundamental models utilized in a complicated CVD system. The analysis of simulation mainly focuses on temperature distribution, growth condition and doping concentration of grown layers. The accuracy and validation of simulation results is required to be confirmed by comparing simulation results with experimental data. A number of studies for simulation have been investigated. For instance, a study$^{[22]}$ demonstrates the temperature profile in hot-wall CVD and how to adjust CVD settings for the optimized conditions. The growth predictions of SiC epilayers in CVD were also simulated and reported$^{[23]}$. These investigations demonstrate that the simulations results are valid and convincible. Therefore, the simulation is a powerful tool for CVD systems.
4. CHARACTERIZATION TECHNIQUES

4.1 Optical Microscope (OM)

The optical microscope is utilized to observe the morphology of samples. The morphology is one of the most important features to evaluate the quality of epilayers and the consequent performance of devices. Optical microscope is used to observe surface roughness and structural defects in micrometer size range. To characterize surface roughness in the range of nanometers to micrometers, the atomic force microscope (AFM) is regarded as powerful equipment to analyze the surface for further investigation. The most utilized optical microscope is called Nomarski Differential Interference Contrast (NDIC) mode which can enhance the contrast in unstained, transparent samples. The basic operating principle is described by following the path of the light beam as shown in Fig 4.1[14]. The unpolarized light illuminates toward the mirror and reflects into Nomarski prism. The light beam is separated by a Nomarski prism into two beams which are polarized at 90° and spaced about 1 µm to each other. Then, the two light beams are focused by objective lens before illuminating the samples. When two light beams irradiate the surface, they experience different optical path lengths due to distinct height of surface and refractive index of materials. Thus, a phase difference exists between these two light beams after light beams travel through the surface. Then, both light beams reflect back along the same paths as they irradiate on the sample. The interference occurs while the two light beams combine into a light beam with the help of Nomarski prism prior to eye-inspection. The interference causes the image brighter or darker at different area of samples. Sometimes, inserting a linear polarizer in the path of light beams increases the intensity of certain component of light beam and enhances the contrast of images. The transmission mode can also be utilized in NDIC optical microscope to measure the thickness of epilayers by inspecting the cross-section of epilayers as shown in Fig 4.2.

Fig 4.1 The configuration of NDIC optical microscope is redrawn from literature[14].

Fig 4.2 Cross-section of SiC epilayer with low doping concentration grown on the SiC substrate with heavily doping concentration
4.2 KOH Etching

Several epitaxial defects such as carrots defects, growth pits, wavy pits, micropipes, half moon, in-grown SFs, down falls in SiC epilayers can be observed by optical microscope as shown in Fig 2.8. These defects originate from different dislocations. For example, threading screw dislocations (TSDs) had been suggested as the origin of carrot defects\textsuperscript{10}. Moreover, other dislocations like threading edge dislocations (TEDs) and basal plane dislocations (BPDs) had also been considered as origin of carrots defects\textsuperscript{24}. Observation of these dislocations is of importance since density of dislocations affects the performance of devices significantly. The typical defects on the surface are formed by structure defects beneath the surface which can be revealed by using an etching solvent. The etching solvent dissolves the structural defects with different etching rate along different crystallographic direction. The shape, area and density of etched defects provide the information about the type and concentration of defects. After several experimental investigation, the molten KOH etchant is the most appropriate etchant for SiC\textsuperscript{25}. Threading edge dislocations (TEDs) and threading screw dislocations (TSDs) intersect the surface of epilayers and form hexagonal open up features. Basal plane dislocations (BPDs) emerge on the surface in shell like pits. The appearance of dislocations is illustrated in Fig 4.3.

Fig 4.3 Images taken from the epilayer etched in molten KOH at 500 °C for 5 minutes. TEDs and TSDs appear in small and large hexagonal shape respectively and BPDs appear in shell like pits\textsuperscript{11}. 
4.3 Fourier Transform Infrared Spectroscopy (FTIR)

The non-destructive room temperature FTIR can be employed to measure the thickness of SiC homoepitaxial films. The fundamental concept of FTIR is based on the frequency dependence of the dielectric function, which can differ for epilayer and substrate. The interferometer is utilized to construct interference which originates from the superposition of reflected light from film surface and epilayer-substrate interface as shown in Fig 4.4[26]. For simple calculation, the dot line indicates the neglected multiple reflections in the epilayer. A lightly doped SiC film with refractive index $n_1$ is grown on a highly doped SiC substrate with refractive index $n_2$ and refractive index of air is $n_0$. The lights are composed of reflected light $E_A$ from epilayer surface and reflected light $E_B$ from the interface of epilayer and substrate. The interferogram is recorded by intensity of interfered lights versus position of moving mirror. Evaluation for thickness of epilayer by FTIR system is performed by transforming the interferogram into reflectance spectrum as shown in Fig 4.5[27] and fitting the calculated reflectance spectra with measured reflectance spectra. The calculated reflectance spectra use a model for the frequency dependent dielectric function $\varepsilon(\omega)$ of SiC epilayer and SiC substrate[27]. Difference doping concentration between SiC epilayer and SiC substrate influences the dielectric function appreciably and results in the fringes below reststrahl band in SiC (200-600 cm$^{-1}$) as shown in Fig 4.5. For spectra range where absorption nearly does not occur during beams travelling through the sample, the refractive index is related to the real part of perpendicular component of dielectric function[27] by $n = \sqrt{Re(\varepsilon_L(\omega))}$. Distinct refractive index of epilayer and substrate affects the Fresnel reflection coefficient and transmission coefficient. More different the refractive index between epilayer and substrate is, the higher fringe contrast can be observed. The evaluation of thickness is operated by adjusting the thickness parameter in calculated spectra to fit the measured spectra until interference fringes overlaps with each other. Sometimes the spectra do not match up perfectly due to the rough surface and inhomogeneous doping concentration of epilayer.

Fig 4.5 Reflectance spectrum of 4H-SiC epilayer ($2 \times 10^{15} \ \text{cm}^{-3}$) grown on a 4H-SiC substrate ($3 \times 10^{18} \ \text{cm}^{-3}$). Solid line indicates measured spectrum and dotted line indicates the calculated spectrum[27].
4.4 Low Temperature Photoluminescence (LTPL)

Low temperature photoluminescence (LTPL) is a contactless and non-destructive technique without any special preparation of samples. Characterization is operated at extremely low temperature (2 to 5 K) so that the thermal fluctuation can be avoided. It has been utilized to analyze excitonic energy levels within bandgap of different materials. The types of bonding, energy levels and concentration of impurities can be obtained by LTPL spectrum. Basically the recombination processes occurring in LTPL analysis can be classified into band-to-band transition (B-B), free excitons (FEs), bound excitons (BEs), free-to-bound excitons (F-B) and internal transitions as shown in Fig 4.6[11]. The free excitons are formed by the binding of free electrons and free holes with Coulomb interaction. The binding energy is called exciton binding energy. Free excitons can freely move around in the crystals. The excitons bounded with defects in materials cannot freely travel around and are called bound excitons. The bound excitons (BEs) can be bound at neutral donors (D-BE), neutral acceptors (A-BE) or isoelectronic defects (I-BE).

Fig 4.6 Illustration of different recombination processes[11]

![Fig 4.6 Illustration of different recombination processes](image)

A typical photoluminescence spectrum of 4H-SiC epilayers is illustrated in Fig 4.7. SiC is an indirect bandgap material. Hence, the recombination processes only occur with the help of phonon absorption and emission in order to conserve momentum. Therefore, the inequivalent substitutional lattice sites play important roles when the phonon assisted recombination occurs. Crystals constituted by large unit cells bring about more

![Fig 4.7 LTPL spectrum of 4H-SiC](image)

Fig 4.7 LTPL spectrum of 4H-SiC is measured by 244 nm line of an Ar+ laser at 2K. The thickness is 28 µm and the background doping concentration is $2 \times 10^{14}$ cm$^{-3}$. A typical photoluminescence spectrum of 4H-SiC epilayers is illustrated in Fig 4.7. SiC is an indirect bandgap material. Hence, the recombination processes only occur with the help of phonon absorption and emission in order to conserve momentum. Therefore, the inequivalent substitutional lattice sites play important roles when the phonon assisted recombination occurs. Crystals constituted by large unit cells bring about more
inequivalent substitutional lattice sites. For example, 6H-SiC has two cubic sites and one hexagonal site. 4H-SiC has one cubic site and one hexagonal site. 3C-SiC has only one cubic site. Furthermore, crystals made of large unit cells also lead to more branches in phonon dispersion relations. Theoretically 6H-, 4H- and 3C-SiC have 36, 24 and 6 phonon replicas respectively. The study\cite{28} shows experimentally 22 of 24 phonon replicas in 4H-SiC has been found. The evaluation of doping concentration also can be done in LTPL spectrum. The studies\cite{29-30} show the doping concentration is directly proportional to the ratio of BE zero-phonon lines $R_0$ and $S_0$ in 6H-SiC, $Q_0$ in 4H-SiC to the FE most intensive phonon replica around 77 meV. In conclusion, the non-destructive LTPL technique carries a lot of information of materials and has been commonly used.
4.5 Capacitance-Voltage (CV)

The carrier density in the epilayers can be evaluated by capacitance-voltage (C-V) technique. In the ideal case, the carrier density is regarded as doping density when the material is uniformly doped. The main concept behind the C-V technique relies on the fact that the width of a reverse-biased space-charge region of a semiconductor junction device depends on applied voltage\(^{[31]}\). The contact of Schottky diode or asymmetrical junction is usually employed in C-V measurement. For 4H-SiC, nickel (Ni) deposition is the first candidate for contact of Schottky diode considering the metallic work function of Ni and the energy bandgap. Gold (Au) deposition is considered as the most appropriate material for the contact for 3C- and 6H-SiC. For non-destructive evaluation of doping concentration, a temporary contact is frequently used by a mercury probe\(^{[31]}\). It is a reproducible measurement which can benefit for many measurements on the same sample.

![Fig 4.8 (a) Schottky diode is applied a reverse dc bias V and a superimposed small-amplitude ac bias v. (b) The depletion profile.](image)

The p-type Schottky diode is applied a reverse dc bias V and is superimposed a small-amplitude ac voltage v as shown in the Fig 4.8(a). The reverse dc bias results in depletion region W and the small-amplitude ac voltage causes the depletion region dW. The ac bias depletes small amount dQ\(_m\) of majority carriers (holes) away and leaves negative immobilized charge dQ\(_s\) as shown in Fig 4.8(b). The amount of dQ\(_m\) is the charge increment at metallic contact which is equal to differential amount of charges in semiconductor dQ\(_s\). The small differential capacitance is defined by \(C = \frac{dQ_m}{dv} = -\frac{dQ_s}{dv}\).

According to charge neutrality and assumption that \(N_D^+ = 0\), \(n \approx p = 0\) and all acceptors are ionized, the charges in depletion region can be expressed as \(Q_s \approx -qA\int_0^W N_A dx\), where A is cross-section area of device, \(N_A\) is acceptor concentration. The capacitance can be considered as a parallel plate capacitance (C=\(K_s\epsilon_0A/W\)), where \(K_s\epsilon_0\) is the dielectric constant of material and W is width of depletion region. The differential of depletion width respect to voltage \((dW/dV)\) can be written as \(\frac{dW}{dV} = k_s\epsilon_0A\frac{d(1/C)}{dv}\) which can be substituted in Eq 4.1. It shows that doping concentration shown in Eq 4.2 can be estimated from \(d(1/C^2)/dV\).

\[
C = -\frac{dQ_s}{dv} = qAN_A(W)\frac{dW}{dv} \quad \text{Eq 4.1}
\]

\[
N_A(W) = \frac{2}{qK_s\epsilon_0A^2(1/C^2)/dv} \quad \text{Eq 4.2}
\]
4.6 Deep Level Transient Spectroscopy (DLTS)

To evaluate the concentration and energy level of defects by electrical methods, the deep level transient spectroscopy (DLTS) technique is most recommended mainly due to its accuracy and less time consumption. Deep level defects can be induced by metallic impurities or crystal imperfections such as dislocations, stacking faults, precipitates, vacancies or interstitials. The emission or capture process occurs when optical excitation or electrical excitation changes the electron states from quiescent state to transient state. The emission and capture process are characterized by the emission coefficient (e_n and e_p) and capture coefficient (c_n and c_p) for electrons and holes.

---

**Fig 4.9** (a) the device is applied by a reverse bias –V (b) zero bias at device (c) reverse bias –V is input again. The figure is redrawn from the literature [31].

Deep level transient spectroscopy (DLTS) utilizes thermal activation and emission rate window to identify various deep-level impurities in the material. At the quiescent moment, a reverse bias –V is applied on the n-type substrate with Schottky contact in order to empty completely the electrons from the deep-level centers, as shown in Fig 4.9(a). When the device is input a bias pulse V which compensates the reverse bias to become zero bias in the device at t=0, the deep-level centers near the edge of junction can be entirely occupied with electrons if the width of bias pulse is long enough as shown in Fig 4.9(b). As long as the bias pulse is switched off, the device is at a transient condition and most of electrons at deep-level centers within the depletion region begin to emit to conduction band and be swept out of depletion region rapidly (within a few picoseconds) as shown in Fig 4.9(c). The corresponding response of diode capacitance after the addition of a bias pulse is shown in Fig 4.10(a) [32]. The series of capacitance transient at particular temperature is recorded with various temperatures shown Fig 4.10(a). The selection of the range of emission rate windows is determined by double boxcar, which is illustrated in the Fig 4.10(b) and is determined by the gate settings of t_1 and t_2 [32]. Normalized DLTS signal S(T) is defined in Eq 4.3 and can be expressed as Eq 4.4. Time constant τ_{max} of capacitance transient at maximum of |C(t_1)|−|C(t_2)| is formulated as Eq 4.5. Since the emission coefficient e_n is reciprocally
proportional to the time constant $\tau$, the emission rate window is determined by gate setting of $t_1$ and $t_2$ via Eq 4.5.

$$S(T) = \frac{|C(t_1)| - |C(t_2)|}{\Delta C}$$  \hspace{1cm} Eq 4.3

$$S(T) = \exp(-t_1/\tau) [1 - \exp(-\Delta t/\tau)]$$  \hspace{1cm} Eq 4.4

$$\tau_{\text{max}} = \frac{(t_1 - t_2)}{\ln(t_1/t_2)}$$  \hspace{1cm} Eq 4.5

Since the normalized DLTS signal $S(T)$ is calculated by Eq 4.4-4.5 and $|C(t_1)| - |C(t_2)|$ is obtained from the series measurement of capacitance transient, $\Delta C$ is determined by Eq 4.3. Hence, the concentration of deep-level impurity in the depletion region can be estimated through $N_T = \left(\frac{2\Delta C}{c_0}\right) (N_D - N_A)$.

The simplified approximation of emission coefficient $e_n$ can be derived as Eq 4.6

$$e_n = (N_c \sigma_n v_{th}/g) \exp(-\Delta E/kT)$$  \hspace{1cm} Eq 4.6

The linear dependence of $\ln(e_n)$ with $1/T$ is obviously illustrated in Fig 4.11. Since the adjustable emission rate window has been determined by the double boxcar, trap A and trap B with distinct $\Delta E$ give the system response at different specific temperature. Only when the emission coefficient for trap A or trap B is within the emission rate window, the system response gives the corresponding peaks as shown in Fig 4.11. The deep-level $E_T$ is obtained from the slope of $\ln(e_n)$ versus $1/T$ and the capture cross-section is estimated from the intercept at y-axis of $\ln(e_n)$ versus $1/T$.
5. EXPERIMENTAL RESULTS AND DISCUSSION

5.1 Introduction

The growth experiments were carried out at high temperatures (about 1600 °C) by a hot-wall CVD reactor\cite{33}. Growth temperature and pressure were detected by an optical pyrometer and pressure gauges. The carrier gas was hydrogen purified by Pd membrane purifier. The selected precursors were: silane (SiH$_4$) for Si-species, ethylene (C$_2$H$_4$) for C-species, hydrogen chloride (HCl) as the chlorinated precursor. A small amount of C$_2$H$_4$ was flowed in the reaction chamber during the temperature ramp up to prevent the substrate surface from not only being etched by hydrogen but also to avoid the formation of Si droplets. The pressure and flow of precursor gases were regulated via electronic pressure controls (EPCs) and mass flow controls (MFCs).

![Fig 5.1 System energy versus the arrangement of atoms](image)

The growth temperature for high temperature CVD (HTCVD) was typically in the range 1500-1650 °C. According to thermodynamic calculations, the arrangement of atoms in a solid is required to be well ordered to grow a single crystal, which is a high ordered and symmetric system, i.e. low entropy. The amorphous or polycrystalline state has lower Gibbs free energy than single crystalline. To overcome the energy barrier and transit the system state from the stable to metastable equilibrium as shown in Fig 5.1, high temperature can be employed to provide energy to the system. In kinetics, high temperature supplies energy to adsorbed atoms on the growth surface. It assists adsorbed atoms diffusion to the nucleation sites at steps. Alternatively, high temperature growth facilitates step-flow growth against 2D or 3D growth mode.

In this study all the epilayers were grown on 4H 8°off-axis SiC substrates. The influence of the various growth parameters, a comparison between different precursors systems (MTS- versus standard-process), growth conditions in different parts of the reaction chamber and effects by using distinct polarity substrates will be discussed in section 5.2. Tungsten incorporation in the SiC epilayers will be described in section 5.3.
5.2 Epilayer grown on 4H 8° off-axis SiC substrates

A high growth rate of about 200 µm/h was obtained by chloride-based CVD. However, the morphology, density of defects and net doping concentration have to be monitored accurately. In order to optimize the epilayers quality, the most important growth parameters were investigated. The C/Si ratio is a critical growth parameter for epitaxial layers morphology and net doping concentration, according to the site-competition theory\(^\text{[34]}\). The C/Si was varied from 0.8 to 1.2 with all the other growth parameters fixed and the results are discussed in the following section. The chlorinated precursors react with Si-species precursors and SiCl\(_2\) is formed instead of homogeneous aggregation of Si droplets. In the other word, the variation of Cl/Si ratio gives rise to the change of chemical reactions during the growth. Hence, it influences the net doping concentration as well. The Cl/Si is varied from 1 to 3 and the results are discussed in section 5.2.2. A series of investigations regarding the advantages in employing the chlorinated precursor methyltrichlorosilane (MTS) was already put in evidence\(^\text{[35-36]}\). Therefore it was investigated too and was compared by the use of the HCl-chemistry with the use of HCl+MTS, which is discussed in section 5.2.3. The differences in SiC epilayers grown at different regions of susceptor and the influence of growth on Si-face or C-face substrates are analyzed in the last two sections.

5.2.1 C/Si ratio (0.8 to 1.2)

To analyze the effect of C/Si ratio from 0.8 to 1.2, two series of experiments were done with Cl/Si =1 and Cl/Si=3. All the other growth parameters were fixed: growth temperature T=1560 °C, growth pressure P=200 mbar, carrier gas H\(_2\)=50 l/min and Si/H\(_2\)=0.66 %. Only HCl was flowed as chlorinated precursors. No intentional doping impurity was introduced during growth. During the ramp up from 1200 to 1560 °C, C\(_2\)H\(_4\) was flowed in the reaction chamber.

![Images from optical microscope at variation of C/Si ratio with fixed Cl/Si=1](image)

(a) C/Si=0.8 (b) C/Si=0.9 (c) C/Si=1.0 (d) C/Si=1.2 (all scale bars=100 µm)

Fig 5.2 Images from optical microscope at variation of C/Si ratio with fixed Cl/Si=1 (a) C/Si=0.8 (b) C/Si=0.9 (c) C/Si=1.0 (d)C/Si=1.2 (all scale bars=100 µm)
For Cl/Si=1 and C/Si ratio from 0.8 to 1.2, the optical microscope images are shown in Fig 5.2. From the morphology point of view, the surfaces appeared rough (orange peel) and it became rougher as C/Si was increased, as shown in Fig 5.2(a)-(c). The C/Si ratio did not only have effect on roughness but the formation of monocrystalline stability. Monocrystalline 4H SiC was converted into polycrystalline as C/Si was raised to 1.2, (Fig 5.2(d)). When the concentration of carbon on the surface increased significantly, the 2D growth mode overwhelmed step-flow growth and even 3D island growth mode appeared during crystallization. Once the island and layer growth modes dominated instead of step-flow growth, it may bring about 4H-SiC growth but in a polycrystalline form.

Epitaxial defects usually are replicated from the substrate and were observed in the images shown in Fig 5.2(a)-(c). Nevertheless, the elimination of epitaxial defects seemed to be not related with the variation of the C/Si ratio. Carrot and triangle defects, micropipes, growth pits and downfalls observed in Fig 5.2(a)-(c) are usually related to threading edge dislocation (TEDs), threading screw dislocation (TSDs) or basal plane dislocation (BPDs). These defects have been demonstrated to exist to release system energy[37] but they were found to degrade the electronic device during operation[38]. The excess strain energy is released by the formation of micropipes with radius \( r \) given by \( r = \mu b^2 / 8\pi \gamma \) for 4H SiC. For investigation of related dislocations, the molten KOH etching is employed to remove SiC surface layers with distinct etching rates along different crystallographic direction. The etched epilayer at C/Si=0.8 is examined under optical microscope as shown in Fig 5.3. The KOH etching of micropipes, carrot defects and growth pits reveal the composition of defects. The evidence in Fig 5.3 stated that the carrot defects originated from TSDs and bunch of TEDs, micropipes and growth pits were constituted by numerous TEDs.
For Cl/Si=1 and C/Si ratio from 0.8 to 1.2, the relation with the growth rate is illustrated in Fig 5.4. The growth rate was calculated by converting the length of a carrot or triangle defect into the thickness of epilayer through the equation \( d = l \tan 8^\circ \) where \( d \) is thickness of epilayer, \( l \) is length of carrot defects and 8° is the off angle of the substrate. All the epilayers were grown for 30 minutes. Therefore, the growth rates were on average 175 \( \mu m/h \), 180 \( \mu m/h \), 195 \( \mu m/h \) for C/Si=0.8, 0.9 and 1.0 respectively. The growth rate of the polycrystalline layer grown at C/Si=1.2 could not be evaluated via carrot length.

The LTPL spectrum shown in Fig 5.5 was measured from the sample in Fig 5.2(b) and the spectrum was dominated by the near bandgap emission which indicated very high crystalline quality. A strong free-exciton (I\(_{76}\)) peak and typical nitrogen bound exciton peaks (P\(_0\), Q\(_0\) and phonon replica related peaks P\(_{76}\)) were observed in the spectrum. The D\(_1\) related peak which resulted from intrinsic defects was weakly seen. However, the Ti related peak was not observed. Ti related peak is usually caused by contamination from the uncoated parts of the susceptor’s graphite\[35\. The unintentional net doping concentration was evaluated from the intensity of peaks in LTPL spectral[29]. The doping concentrations are \( 1.4 \times 10^{15} \text{ cm}^{-3} \), \( 2.4 \times 10^{14} \text{ cm}^{-3} \), and \( 3.8 \times 10^{14} \text{ cm}^{-3} \) for C/Si=0.8, 0.9 and 1.0 respectively.
For Cl/Si = 3 and C/Si ratio from 0.9 to 1.2, the morphology is shown in Fig 5.6. The conclusion about the morphology are the same as those discussed above (Cl/Si=1). As a result, the smoother surface could be obtained at lower C/Si ratios. Moreover, there is no evident difference for the epitaxial defects density by varying the C/Si from 0.9 (Fig 5.6(a)) to 1.2 (Fig 5.6(c)). However, the distinguishable phenomenon between Cl/Si=1 and Cl/Si=3 occurs at C/Si=1.2. Even in this C-rich conditions a monocrystalline layer was grown thanks to the higher chlorine input (Cl/Si=3). This result implied that chlorinated precursors can bring more Si-species on the growth surface and thus Si-species can compensate the C-rich condition to avoid the formation of polycrystalline material. The effect of the Cl/Si ratio will be discussed in detail in the next section.

The growth rates were estimated only by carrot length. Further length measurement could be done via FTIR or measuring the cross section of epilayers. The deposition time was always 30 minutes, except for C/Si=1.2 with 15 minutes. The growth rates were in the range of 110 to 130 μm/h. The unintentional net doping concentration was calculated from the peak intensity in LTPL spectrum. The net doping concentration were $2.1 \times 10^{15}$ cm$^{-3}$, and $2.4 \times 10^{14}$ cm$^{-3}$ for C/Si=0.9 and 1.2 respectively. These results are consistent with the site competition theory and within reasonable range of doping concentration.
5.2.2 Cl/Si ratio (1 to 3)

In the study of Cl/Si ratio effect, all the growth parameters were fixed except the Cl/Si ratio which was varied from 1 to 3. The growth conditions were: \( T = 1560 \, ^\circ C, \, P = 200 \, \text{mbar}, \, H_2 = 50 \, \text{l/min}, \, \text{Si/H}_2 = 0.66\% \) and \( \text{C/Si} = 0.9 \). Only HCl was used as chlorine source. No dopant was intentionally supplied during growth. \( \text{C}_2\text{H}_4 = 15.6 \, \text{ml/min} \) was flowed during the temperature ramp up from 1200 to 1560 \( ^\circ C \).

![Fig 5.7 Images of grown epilayers with variation of Cl/Si and fixed C/Si=0.9 (all scale bars=20 \( \mu \text{m} \) )](image)

(a) Cl/Si=1  (b) Cl/Si=2  (c) Cl/Si=3

The morphology of the epilayers was greatly improved by adding more HCl especially from the roughness aspect, as shown in Fig 5.7. The surface appears relatively rough as orange peel at Cl/Si=1, but becomes much smoother when the Cl/Si was increased up to 3 as shown in Fig 5.7(c). Moreover, some epitaxial defects such as growth pits, wavy defects and micropipes are suppressed at high Cl/Si ratios. However, the elimination of carrot or triangle defects did not happen by changing the Cl/Si ratio. Hence, the statement can be inferred that the chlorinated precursors not only assist to get rid of Si droplets but reduce the formation of defects.

![Fig 5.8 Growth rate of epilayer growth with variation of Cl/Si from 1 to 3 and fixed C/Si=0.9](image)
The growth rate trend at a C/Si=0.9 and Cl/Si ratios from 1 to 3 is illustrated in Fig 5.8. Growth rates calculated only by carrot length were 180 µm/h, 136 µm/h and 112 µm/h for Cl/Si=1, 2 and 3 respectively. The decrease of growth rate with increase of Cl/Si by adding more HCl is opposite to the results observed in MTS process[35]. However, similar trend was attained at Cl/Si>3 by MTS process with additional HCl. The speculation which can be made is that the chlorine-containing species from MTS do not etch the growing epilayer as much as HCl etches the growing film.

![Fig 5.9LTPL spectrum of 56 µm thick 4H-SiC epilayer with Cl/Si=3 and C/Si=0.9.](image)

Fig 5.9LTPL spectrum of 56 µm thick 4H-SiC epilayer with Cl/Si=3 and C/Si=0.9. The insert shows the near bandgap emission.

The LTPL spectrum in Fig 5.9 was measured from the sample in Fig 5.7(c). The spectrum also indicated very high crystalline quality since near bandgap emission dominated the spectrum. A weak free-exciton (I₁₇₆) peak, typical nitrogen bound exciton peaks (P₀, Q₀ and phonon replica related peaks P₇₆) and Dᵢ related peak were observed in the spectrum. However, Ti related peak was not observed. In addition to the effect on morphology and growth rate, the Cl/Si ratio affects the net doping concentration. The net doping concentrations were evaluated from the LTPL spectrum. The background net doping concentrations were 2.4 × 10¹⁴ cm⁻³ and 2.1 × 10¹⁵ cm⁻³ for Cl/Si=1 and 3 respectively. The relatively stronger free-exciton peak (I₁₇₆) and weaker nitrogen bound exciton peak Q₀ in Fig 5.5 than I₁₇₆ and Q₀ peaks in Fig 5.9 implied that background doping concentration for growth condition in Fig 5.7(a) was lower than it for growth condition in Fig 5.7(c). From the previous study[39], the chlorinated precursors assist the formation of main Si-species SiCl₂ during growth. In the other word, the effective C/Si is lower than the expected C/Si which is calculated from the input flow of silane and ethylene. Therefore, the addition of HCl has the similar effect as the addition of SiH₄ in perspective of doping concentration. The result here was consistent with site competition theory. The trade-off for morphology, growth rate and net doping concentration from the effect of Cl/Si ratio should be considered deliberately.
5.2.3 Comparison with MTS process

The standard HCl process is compared to the MTS process in morphology, growth rate and net doping concentration. The growth parameters were: T= 1560 °C, P= 200 mbar, H₂= 50 l/min and Cl/Si= 3. The fixed growth parameter Si/H₂ was slightly different for both processes: Si/H₂= 0.66 % for the HCl-process; Si/H₂ = 0.57 % for the MTS-process. No intentional doping impurities were introduced during growth. A flow of 15.6 ml/min of C₂H₄ was introduced during the temperature ramp up 1200 to 1560 °C. The only growth parameter to be tested to compare these processes was the C/Si ratio. The morphology for both processes is shown in Fig 5.10. The morphology difference between HCl-process and MTS-process was not appreciable.

![Comparison images of HCl-process and MTS-process by optical microscope with variation C/Si and fixed Cl/Si=3. Images at upper row are from HCl-process and at lower row are from MTS-process. (a) C/Si=0.9 (b) C/Si=1.0 (c) C/Si=1.2 (all scale bars=100 µm)](image)

About the growth rate, similar trends were found between the two processes, but lower growth rates were obtained for the MTS process (90-120 µm/h) compared to the growth rates for the HCl process (110-130 µm/h). The lower growth rate for MTS process was attributed to the lower Si/H₂=0.57 %. Higher Si/H₂=0.66 % can be reached by using higher MTS molar fraction which results in higher growth rates[13]. The similar trends of growth rate could be explained with the help of simulation which demonstrated that main Si-species SiCl₂ or C-species C₂H₂ for HCl process varies toward the same direction as for MTS process when C/Si changes. However, the study showed that at the same growth condition with variation of C/Si ratio, growth rates for MTS process were higher than growth rates for HCl process[19]. Therefore, growth rates for MTS process were affected significantly by Si/H₂ ratio.
The difference of net doping concentration is clarified in Fig 5.11. The standard HCl process gives rise to much higher (about 30 times) n-type doping concentration ($2.1 \times 10^{15}$ cm$^{-3}$) at C/Si=0.9 than it for MTS process ($6.3 \times 10^{13}$ cm$^{-3}$). According to site-competition theory, the transition from n-type doped epilayer to p-type doped epilayer needs much higher C/Si for HCl process than C/Si=0.9-1 for MTS process. Hence, speculation was made that the MTS process gives more C-rich conditions compared to the HCl process. Thermodynamic analysis by simulation demonstrated that the molar fraction of reactive gases for the HCl process is approximately identical as those for the MTS processes. However, the chemical reactions for nucleation and crystallization may occur in a different way. Distinct chemical reactions may lead to different doping concentrations.

*Fig 5.11 Background doping concentrations for both HCl-process and MTS-process with variation of C/Si ratio from 0.9 to 1.2 and fixed Cl/Si=3*
### 5.2.4 Growth condition at different areas in reaction chamber

Table 5.1 Comparison of grown epilayers between at downstream area and at far downstream area (GR: growth rate, \(N_D-N_A\): background doping concentration)

<table>
<thead>
<tr>
<th>Position</th>
<th>Downstream</th>
<th>Far Downstream</th>
</tr>
</thead>
<tbody>
<tr>
<td>OM images</td>
<td><img src="image1" alt="OM Image" /></td>
<td><img src="image2" alt="OM Image" /></td>
</tr>
<tr>
<td>GR</td>
<td>170-180 (μm/h)</td>
<td>70-80 (μm/h)</td>
</tr>
<tr>
<td>(N_D-N_A)</td>
<td>(1.4 \times 10^{15} \text{ (1/cm}^3))</td>
<td>(1.5 \times 10^{16} \text{ (1/cm}^3))</td>
</tr>
</tbody>
</table>

![Diagram of reaction chamber](image3)

![PL spectrum](image4)
The growth parameters were the same as in Fig 5.2(a). The areas where the 4H 8°-off-axis SiC substrates were placed were defined in the row “susceptor plate” of Table 5.1. The epilayer morphology at downstream area appeared as a rough surface with several defects such as carrots, triangle defects, growth pits and micropipes and so on. However, the morphology of epilayer placed in the far downstream area was in contrast to that at downstream, as shown in Table 5.1. It revealed a smoother surface with less defects at far downstream area than at downstream area. Furthermore, the growth condition at far downstream area resulted in not only lower growth rate but also high background doping concentration than at downstream area. The LTPL spectrum comparison showed a weaker I\text{76.4} and stronger Q\text{0} peaks for the far downstream sample, which implied a higher net doping concentration.

The results at different areas of susceptor suggested that the consumption of carbon at inlet part of the susceptor was more rapid so that less carbon was left available in the far downstream area. Alternatively, more carbon-rich chemistry at downstream area gave rise to higher growth rate and lower n-type background doping concentration. There are probably more Si-species left at far downstream thanks to the higher stability of the SiCl\text{2} specie\textsuperscript{[40]}. Therefore, carbon shortage resulted in lower growth rate and reasonably higher doping concentration (about 10 times).
5.2.5 Si-face substrate and C-face substrate

Table 5.2 Comparison of epilayers grown on Si- and C-face substrates (GR: growth rate, ND-NA: background doping concentration)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Si face</th>
<th>C face</th>
</tr>
</thead>
<tbody>
<tr>
<td>OM images</td>
<td><img src="image1.png" alt="OM images" /></td>
<td><img src="image2.png" alt="OM images" /></td>
</tr>
<tr>
<td>GR</td>
<td>112 (μm/h)</td>
<td>115 (μm/h)</td>
</tr>
<tr>
<td>ND-NA</td>
<td>$2.1 \times 10^{15}$ (1/cm$^3$)</td>
<td>$7.9 \times 10^{15}$ (1/cm$^3$)</td>
</tr>
<tr>
<td>PL spectrum</td>
<td><img src="image3.png" alt="PL spectrum" /></td>
<td><img src="image4.png" alt="PL spectrum" /></td>
</tr>
</tbody>
</table>

The growth parameters were chosen as in Fig 5.6(a). The comparison between the epilayers grown on a Si-face substrate and C-face substrate is shown in Table 5.2. Both epilayers were quite smooth but huge epitaxial defects were observed in the C-face sample. According to the information of C-face substrate from the supplier, the C-face substrates were not chemical mechanical polished which caused worse morphology of grown epilayers. Moreover, C$_2$H$_4$ was flowed in during ramp up from 1200 to 1560 °C, which is not a suitable ramp up condition for C-face substrate. The growth rates for both substrates were evaluated only by carrot length. Growth rates were not affected by distinct polarity of substrates. However, background doping concentration estimated from LTPL spectra was higher for C-face substrates. A previous study[39] stated that higher doping concentration is attributed to the differences in binding probability for incoming nitrogen atoms. An atom at C-sites of C-face can form three bonds to the silicon atoms while it at C-sites of Si-face can bind only one bond to the silicon atom. High background doping concentration was always avoided for fabrication of power device. Therefore, growth on the Si-face substrates is more attractive to be investigated.
5.3 SiC incorporation with Tungsten

5.3.1 DLTS measurement of W-doped sample

Some tests were done in order to incorporate tungsten (W) in SiC epilayers. The samples were grown by chloride-based CVD with the same growth parameters except C/Si and Cl/Si. The growth conditions were the same as described in Fig 5.2(a) for W-doped sample and in Fig 5.6(b) for the reference sample. Metallic flakes of tungsten were cut into tiny pieces which weighed about 200-300 mg. Some tiny W pieces were placed on the upstream part of the susceptor plate and on top of the substrates.

The incorporation of tungsten was investigated via DLTS measurement. Before the measurement, about 420 Å of Nickel Schottky contact was deposited on the epilayer by thermal evaporation, and silver Ohmic contact was glued on the substrate side by silver paint. The diameters of Schottky contacts for reference sample and W-doped sample were 500 mm and 800 mm respectively. The DTLS parameters were set as reverse bias voltage -10 V, pulse +10 V with pulse width 10 ms and the transient time 500 ms between pulses. Lock-in amplifier was utilized to analyze the emission rate of carriers, capture cross section and concentration of defects.

The DLTS spectrum obtained is shown in Fig 5.12. The magnitude of peaks $Z_{1/2}$ or $EH_{6/7}$ in W-doped sample is not comparable to the peaks in reference sample. The evaluations of $Z_{1/2}$ for W-doped sample and reference sample are listed in the Table 5.3.
Table 5.3 lists of $Z_{1/2}$ energy level, capture cross section and concentration for W-doped sample and reference sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>W-doped sample</th>
<th>Reference sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_c-E_{Z_{1/2}}$</td>
<td>0.670 meV</td>
<td>0.692 meV</td>
</tr>
<tr>
<td>Capture cross section</td>
<td>$2 \times 10^{-14}$ cm$^2$</td>
<td>$5 \times 10^{-14}$ cm$^2$</td>
</tr>
<tr>
<td>$Z_{1/2}$ concentration</td>
<td>$3.7 \times 10^{13}$ cm$^{-3}$</td>
<td>$1.0 \times 10^{13}$ cm$^{-3}$</td>
</tr>
</tbody>
</table>

These results can be explained by the difference of C/Si ratio used for epitaxial growth. According to a previous study\cite{41}, higher magnitude of $Z_{1/2}$ or $EH_{6/7}$ is corresponding to lower C/Si ratios, which is consistent with the results in Fig 5.12. Furthermore, the variation of C/Si between 1 and 5 does not significantly influence the magnitude of $Z_{1/2}$ or $EH_{6/7}$\cite{41}. The peaks corresponding to the W related deep-level impurity are resolved obviously in Fig 5.12. From the Arrhenius plot of emission rate, the activation energy and capture cross section can be determined. The concentration of traps can be estimated with the help of capacitance transient $\Delta C$. The evaluation reveals that the activation energy is $E_c-E_{W_1}=$0.177 meV, the capture cross section is $4 \times 10^{-14}$ cm$^2$ and concentration of $W_1$ is $4.6 \times 10^{13}$ cm$^{-3}$ for $W_1$ related impurity. The activation energy is $E_c-E_{W_2}=$1.359 meV, the capture cross section is $4 \times 10^{-14}$ cm$^2$ and concentration of $W_2$ is $5.0 \times 10^{13}$ cm$^{-3}$ for $W_2$ related impurity. The $W_1$ and $W_2$ peaks are suggested to be corresponding to the same defect with different charged states.
5.3.2 Thermodynamic analysis

The simulation for the W-species was carried out in C/Si-, Cl/Si- and temperature-dependence as shown in Fig 5.13. The major solid W-specie was WSi$_2$(s) and the major gaseous W-specie was WCl$_2$(g). The variation of C/Si ratio from 0.8 to 1.2 shown in Fig 5.13(a) influences the amount of C$_2$H$_2$(ethyne) significantly but it does not affect the W-species obviously. For the case of variation of Cl/Si ratio from 1 to 5 as shown in Fig 5.13(b), the primary Si-specie SiCl$_2$(g) and the gaseous W-specie WCl$_2$(g) increases with the flow of chlorinated precursors, but the amount of WSi$_2$(s) remains constant when the Cl/Si ratio changes from 1 to 5. A similar result is obtained by varying temperature from 1773 to 1973 K shown in Fig 5.13(c). The major W-specie WSi$_2$(s) remains constant but the gaseous W-specie WCl$_2$(g) increases evidently. One should be reminded that WSi$_2$(s) is in solid phase but WCl$_2$(g) is in gas phase. Most of interacting species in SiC CVD are in gas phase. However, the results in Fig 5.13 show the most important W-specie for W incorporation is WSi$_2$(s). It confirms the importance of placing W flakes on top of the substrates. Furthermore, Fig 5.13 also shows that high Cl/Si ratio and high temperature give rise to an increased formation of WCl$_2$(g) and it somewhat assists the W incorporation in the epilayers regardless of the amounts of WCl$_2$(g) in the range of $10^{-8}$ molar fraction.
6. CONCLUSIONS

High growth rate (~200 µm/h) of 4H-SiC epilayers deposited on 4H 8° off-axis substrates was achieved by chloride-based CVD. The step-flow growth mode dominated nucleation behavior and led to high quality homoepitaxial layers. High growth temperature (~1560 °C) was required to supply energy to system in order to grow 4H-SiC epilayers with monocrystalline structure. Low pressure (~200 mbar) was kept during growth to flow gases species fast and uniformly above the growth surface. The effects of varying the C/Si ratio from 0.8 to 1.2 were studied with fixed Cl/Si=1 and 3. For both Cl/Si ratios, the roughness of the epilayers surface became smoother at the lowest C/Si of 0.8, but growth rates decreased as well. Moreover, decreasing the carbon supply resulted in an increased background doping concentration due to the decreased occupation of C-sites in the SiC lattice, which gave a higher probability of nitrogen incorporation. The formation of polycrystalline SiC was gained at C/Si=1.2 and Cl/Si=1. It implied that 2D growth and 3D island growth modes overwhelmed step-flow growth due to the C-rich condition. Hence, 4H-SiC formed a polycrystalline film. The effects of varying the Cl/Si ratio from 1 to 3 with a fixed C/Si=0.9 was investigated. Cl/Si played an important role in the epilayers morphology. The roughness and epitaxial defects were improved by the chlorine input. However, increasing the Cl/Si ratio resulted in a reduced growth rate since HCl-etching became more effective. Background doping concentrations were raised by increasing the Cl/Si ratio, since Cl-species assisted the formation of major Si-species SiCl₂. A series of growth by using MTS as precursors was performed. The MTS process was compared to the results obtained by the HCl process. Growth rates for MTS process with Si/H₂=0.57 % were slightly lower than those for HCl process with Si/H₂=0.66 %. It was implied that the Si/H₂ ratio affected growth rates by MTS process significantly and a lower Si/H₂ ratio led to lower growth rates. A p-type background conductivity was measured on 4H-SiC epilayers grown by MTS process at Cl/Si=3 and C/Si higher than 1. Furthermore, results of net doping concentration showed that MTS process had more C-rich condition than HCl process. Distinct epilayer characteristics were found on epilayers grown on substrates placed in different parts of reaction chamber (downstream and far downstream area.), as listed in tables 6.1. Higher growth rates, rougher surfaces with more defects and lower net doping concentration were obtained at downstream area. It implied that the gases distribution of Si-species and C-species were not uniform through the whole reaction chamber. The downstream area was suggested to be C-rich. The effects of substrate polarity were studied by using Si-face and C-face 4H-SiC substrates. Epilayers grown on C-face substrates had higher doping concentration than those grown on Si-face substrates. Worse morphology on C-face substrates may be attributed to the inappropriate preparation of substrates (no chemi-mechanical polishing). Tungsten incorporation on 4H 8° off-axis substrates by HCl process at C/Si=0.8 and Cl/Si=1 was performed and investigated by DLTS technique. DLTS showed that two peaks corresponding to W appeared if the growth was done by placing flakes of W. Thermodynamic analysis suggested that the major W-specie was WSi₂(g) and the Major gaseous W-specie was WCl₂(g). The results of calculations showed that the most important W-specie for W incorporation is WSi₂(s). Furthermore, increased temperature and Cl/Si resulted to a higher WCl₂(g) molar fraction which could assist W incorporation in the epilayers.
7. ACKNOWLEDGEMENT

First of all, I sincerely appreciate Erik Janzén for giving me the chance to do my master diploma work. He arranged an unexpected diploma work for me just a few days after Erik and I had a leisure conversation. The unexpected diploma work gave me the chance to accomplish what I wanted to learn. It also led me to work with members in the group. I really enjoyed the atmosphere in semiconductor material group.

Anne Henry, I would say she is just like my mother. Every time when I got the problems, the first person came into my mind was Anne. She always gave me the solutions and positively encouraged me. She also taught me how to do SiC LTPL measurement and analyze the spectrum. It was tough at beginning to realize everything but she explained every detail patiently. I really appreciate her. Merci!

Stefano Leone, he is a funny guy and is the best supervisor I have ever heard. He taught me not only how to be a researcher but also the life attitude. During my thesis work, he arranged many chances for me to learn other experimental knowledge. The most important thing I have learned from him is to do your best in everything. Besides, He always brought a lot of laughing in our lab. I really enjoy working with him. Grazie!

Sven Andersson, he is a marathon expert and is one of most important technicians in IFM. He always looks joyful when he does everything. I was so glad to do maintenance for Märtha reactor with him. He also treated me nicely and never blamed on me when I broke tools in the lab. Furthermore, we could not get promising results without Sven's help. I'd like to give my great appreciation to him. Tack så mycket!

Franziska Beyer, she has two lovely daughters. I worked with Franziska during Easter holidays. She didn't go for a long vacation but taught me everything for DLTS measurement. In the end of diploma work, she gave me many suggestions how to write the thesis report and she also encourage me a lot. Danke!

Andreas Gällström, he often brought some mysterious metallic pieces to our lab. These mysterious metallic pieces gave us surprising and interesting results. He also taught me how to do FTIR and SiC LTPL measurement. I had learnt a lot from him. Really appreciate for his guide.

Urban Forsberg, I thank him for introducing me to Erik when I was looking for my diploma work. Thanks for his striving to find a diploma work for me.

Eva Wibom, she is a joyful secretary. She arranged an office desk and dealt with some documents work for me when I was about to join the semiconductor material group. Deeply thanks for her help.

My family and Feng-I Tai, I would like to express my greatest appreciation to my parents and sisters. My family has been supporting me since I decided to study in Sweden. My father often shares life experience with me. I always feel pleasant when I talk to my mother and sisters on skype. Feng-I solved the crazy "Microsoft word" and "Endnote" problems for me and always takes care of me. I really love my family.
8. Reference


