

Cubic Silicon Carbide Sublimation Growth using 1.2 deg off-axis substrates

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Abstract

Cubic Silicon Carbide (3C-SiC) was grown on 1.2 degree off-axis 6H- substrates by the sublimation epitaxy technique. Various growth parameters were investigated for optimization of high quality 3C-SiC, including growth temperature, gas ambient, substrate geometry, growth time and backside graphite plates. A growth temperature of 1950°C at 0.5 mbar nitrogen pressure was found to be favorable for the 3C growth on the low off-axis substrates. With longer growth time the quality of the film increased and bulk-like 3C-SiC could even be made possible. The surface morphology of the 3C-films was characterized as well as the quality or crystallinity of the samples. Aluminum (Al) was studied as a p-type dopant, and the influence Al concentration on 3C stabilization was also studied.

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1 Introduction

Modern electronics and IC (Integrated circuits) are everywhere in this modern world, and these are based on semiconductor devices. Semiconducting materials are a crucial part of this growing industry, and from the previous centuries Si has become the dominating material for the electronics. As the device design technology needs to be carried on to the next level, faster device concepts are required. This means that higher carrier mobility should be available but Si is more and more unable to meet this demand. The silicon carbide has more than 200 polytypes, some of which can be facilitated in different applications and provide better performances concerning electrical devices. The advantages include wider bandgap, higher electron mobility, higher thermal conductivity and higher electric field breakdown strength, and these properties make it possible that Silicon Carbide becomes an up-and-coming substitute. However, SiC is not only rarely existing in nature, but also hard to achieve in production of high-quality single crystal wafers as can be achieved in silicon. The difficulties in growth control have made it challenging for SiC mass production and lead to a delay in replacement of other industrial semiconductor materials.

Several SiC growth techniques are considered very promising. The most common method, Chemical Vapor Deposition (CVD), synthesizes high quality layers on SiC wafers. The technique supplies smooth epilayers which are almost free of defects and well controlled in polytype stability from substrate to epilayers. Such CVD-grown 6H- and 4H-SiC epitaxial layers are nowadays commercially available. The growth rate of 5-10 $\mu\text{m}/\text{hr}$, however, is not suitable for large scale production considered both from timely and economical perspective.

As an alternative developed from the successful modified Lely process, the Fast Sublimation Growth Process (FSGP) has a high growth rate up to 1 mm/hr , showing great potential of making thick epilayers. Most interestingly, both homoepitaxy and heteroepitaxy can be performed through the sublimation epitaxial growth. Growth parameters such as temperatures, gas ambient, and substrates could influence the growth mechanisms and thus determine polytypes and quality of the film. Since there are no available single crystalline 3C seeds existing, which has the result that there are no 3C substrates available from boule growth, heteroepitaxy on 6H wafers is applied for 3C-SiC growth. In this thesis, the conditions to optimize high quality 3C with large domains were studied on low off-axis 6H-SiC.

The 6H- together with 3C-SiC grown on 6H-SiC substrates has been previously investigated [1]. However, the growth of 3C in the temperature range above 1900°C and thick layers with bulk properties was not studied. More knowledge of growth parameters that lead to bulk like 3C-SiC needs to be established in order to obtain optimization of growth parameters for n-type 3C-SiC, which is also the attempt of this thesis work. In order to explore the quality of the material, p-type material by Al doping was produced.

Growth was carried out mainly at 1950°C with different ambient pressure, different ramp up rate and spacer geometry. The experiments were followed by Optical Microscope (OM) and Scanning Electron Microscope (SEM) characterizations. The quality of the 3C films was measured by High Resolution X-ray Diffraction (HRXRD), and Photoluminescence (PL) was later explored for the N and Al-doped 3C-SiC series.

2 SiC

Another name of silicon carbide is moissanite, but this mineral is very rare on earth so synthesis is a must. Silicon carbide was first used as an abrasive material and as jewelry for its superior hardness and transparency close to that of diamond. In addition, SiC has a high chemical inertness and radiation resistivity. The most recent interests in SiC are related to the semiconductor applications. The SiC prevails over Silicon in both physical properties and electrical applications, and becomes more and more promising as the fabrication maturity of the material increases.

2.1 Structure

The chemical unit of SiC is two bonded IV-group elements, Silicon and Carbon. The sp³ bond between these two atoms has a short length of 1.89 Å and the high bonding energy around 4.53 eV makes this compound hard and chemically stable. The basic structure of SiC is a shape of tetrahedron, where a C atom sits on tetrahedral site and surrounded by four Si atoms locating at the corners, as shown in Fig.1.

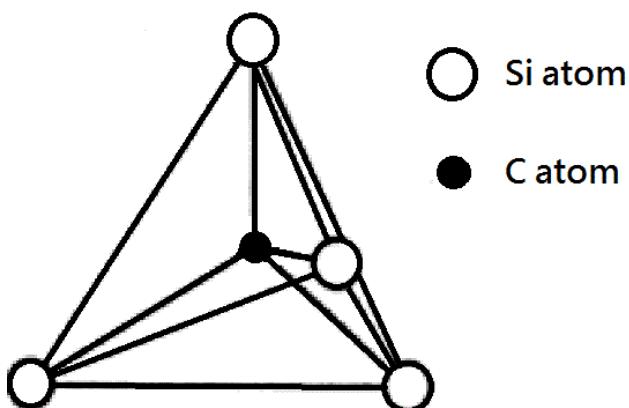


Fig.1 A tetrahedron showing the fundamental structure of Silicon Carbide

If we consider the closest Si and C close-packed layers into a bilayer structure element, there are 3 different positions referring to c-axis to place the second bilayer which we call A, B, and C, the top view is illustrated in Fig.2. The various stacking sequences of the bilayers provide this simple compound the ability to form over 200 different polytypes.

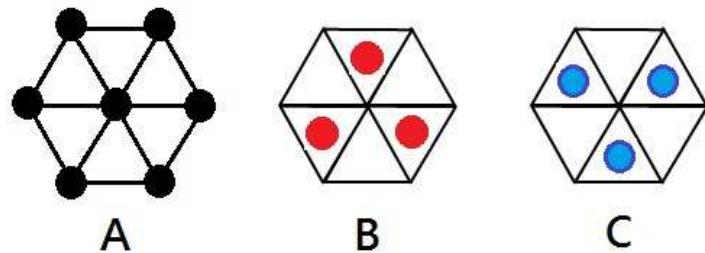


Fig.2 Three stacking positions for a close-packed SiC structure

2.2 Polytypes

On top of the very first bilayer, called A, the second bilayer could be positioned on either position B or C. The third bilayer could choose to occupy one of the two positions other than the second and so on. Different constitution of stacking creates unique polytypes classified into hexagonal (H), cubic (C) and rhombohedral (R) Bravais lattice structures. The most common polytypes of SiC are 4H, 6H and 3C, as shown in Fig.3 [2]. The 4H-SiC has the stacking sequence of ABCB... while 6H is formed by an ABCACB... sequence. The only cubic structure of SiC (3C) repeats the order of ABCABC... Each polytypes has similar properties such as bond lengths and thermal conductivity, while some are slightly different from the others (like bandgap).

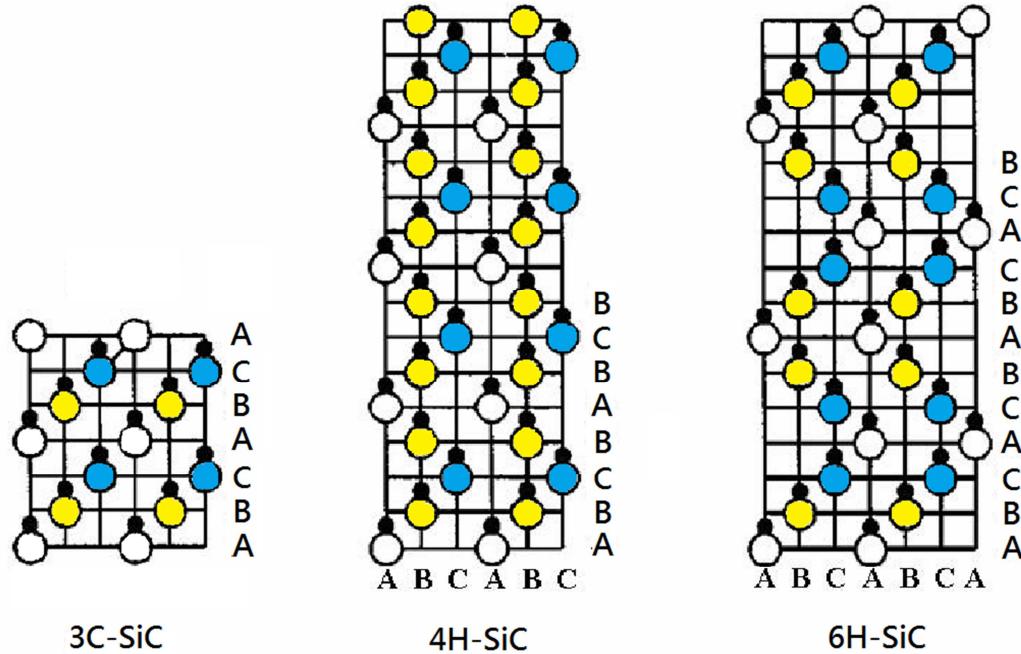


Fig.3 Three common polytypes of SiC—3C, 4H and 6H

2.3 Electrical Properties

Some of the physical properties of SiC have been mentioned while electrical properties have more to do with this project. Unlike Silicon, the wide bandgap (up to 3.23 electron volts for 4H polytype) of SiC has the electronic transition energy falling in the visible light region thus enables optoelectronic interests. Moreover, its large bandgap together with high thermal conductivity makes high-temperature and large voltage-switching devices possible. The high breakdown electric field makes SiC suitable for high-voltage and high-power devices [3].

The world's very first light emitting diode (LED) was made out of SiC in 1907. Although Gallium Nitride was later found more efficient because of its direct bandgap, nitrogen and boron doped 6H-SiC has a renewed interest as LED material as a replacement of phosphor converter. The 3C-SiC, on the other hand, is the only cubic polytype and hence have isotropic physical properties. It may be utilized in MOSFET structures and is very interesting as solar cell material if doped with boron [4]. It can be active as High Electron Mobility Transistor (HEMT) when combined with other polytypes to create a two dimensional electron gas; the splendid biocompatibility makes 3C-SiC appealing for biomedical devices [5]. Only very recent research, Graphene grown on 3C-SiC was proved to have the highest uniformity of the monolayers compared with the 6H-SiC and 4H-SiC [6].

3 Growth techniques

In this section several most commonly applied SiC growth techniques are described. Each growth method has its strong points and drawbacks simultaneously. For different purposes we could choose suitable processes from below.

3.1 Chemical Vapor Deposition (CVD)

There is a wide variety of CVD processes for epitaxial growth which are differentiated by the type of initial chemical reactions. The basic principle of the CVD family is that the precursor gases are brought into the chamber, decompose through chemical reactions and deposited on the substrate as a new compound. An advantage is that gases are very pure so that the layers can have a high purity. The growth typically needs to apply a hydrogen pre-etching procedure to remove surface damages from the substrate polishing. The high purity together with the high quality and smoothness of the epilayers grown is the superiority of CVD, but the growth rate is low and could be an issue in commercial production.

3.2 Physical Vapor Transport (PVT)

This bulk growth method is also known as the modified Lely method. This technique utilizes sublimation of a SiC powder source for growth and enlargement of the size of a single crystal seed. The PVT growth for bulk SiC growth is the most established method. There are two main drawbacks in comparison to the quality obtained in epitaxial growth. One of them is that the long source-to-substrate distance (5-30 mm) brings disturbance to the transportation of the vapor species sublimed. This introduces defects. The other is the difficulty to control the vapor ratio of Si and C, which usually results in growth instability and graphitization, and contribute to defects and point dislocations.

3.3 Fast Sublimation Growth Process (FSGP)

Sublimation Epitaxy was applied in this thesis. This unique growth process is also called sublimation sandwich method; it was developed in 1979 [7] and commercialized in 2010. The advantages of Sublimation Epitaxy are the fast growth rate and no complicated substrate preparation needed as in other epitaxy. A short source-to-substrate distance (typically less than 5 mm) is an important feature since it combines the high growth rate of the PVT method and a high structural quality of the material. The short distance also allows the FSGP to operate at relatively low growth temperature than other sublimation growth techniques. This is in particular interesting since 3C-SiC can form at the applied growth temperatures. Since it is limited by the distance from the source material to the substrate, SiC boules cannot be grown but bulk-like thick films with high quality are possible.

4 Growth of 3C-SiC

The 3C-SiC is a meta-stable polytype. It rarely forms at high temperatures like in PVT. In our case, we show that 3C-SiC films with thickness up to 1.1 mm can also be grown by this setup.

Besides practical applications, the growth mechanisms of 3C-SiC had also received intensive interests in the research area since this is a key issue and there still remains many issues to understand the growth of 3C-SiC. These include polytype stability of Silicon Carbide, growth conditions and the resulting transition behavior.

4.1 Growth mechanisms

The processes to develop a material (particularly a from an epitaxial to bulk crystal in this thesis) are governed by fundamental growth mechanisms which have to be

understood. From thermodynamics point of view, all islands and films are formed in a way that the crystal gains have the lowest total energy. This is the reason why adatoms usually migrate to positions with kinks, steps or dislocations after arriving at the substrate surface.

Growth mechanisms are determined to a large extent by growth parameters and the conditions of the substrate surface. By different growth mechanisms, even the same vapor species could form different films having different polytypes, and the quality can differ between films. In this thesis we study growth on 6H-SiC substrates. The 2D-nucleation and step flow growth are two main growth mechanisms for 3C heteroepitaxy, while spiral growth mode is more typical for 6H-SiC.

4.1.1 2D-nucleation

After the sublimation starts, vapor species from the source are transported to the 6H-SiC substrate and adsorbed by the surface. The illustration is as Fig.4. Desorption could occur for these adatoms but the overall effect is that there are more atoms on the surface of the arriving atoms than which have desorbed. The atoms diffuse to the thermodynamically favored spots and this enables the growth. In case of stepped surfaces and when the terrace width (surface of the steps) of a step is large, like when using on-axis or low off-axis substrates for example, the incoming adatoms might not have enough energy to migrate to the substrate steps to form homoepitaxial growth. Instead they start gathering as a cluster in the middle of the terraces. These initial clusters could either dissolve later or become two-dimensional nuclei if the diameter exceeds the critical size [8]. In this thesis, 6H-SiC substrates with 1.2 degree off-axis are used. Since 3C-SiC islands have lower nuclei formation energy, 2D-nucleation exists as 3C-SiC growth rather than homoepitaxial growth of 6H-SiC.

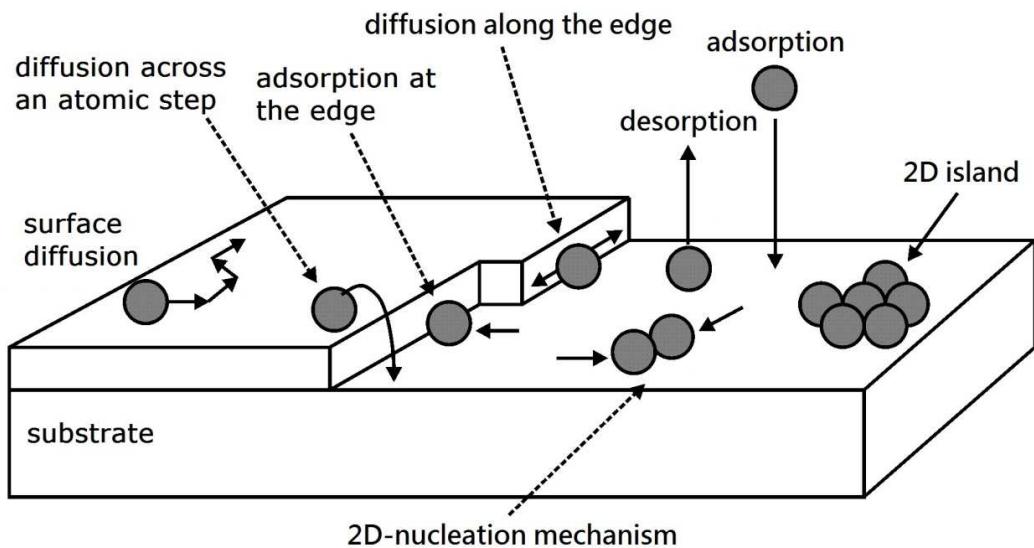


Fig.4 The process of all mechanisms occurring once adatoms reach the surface

4.1.2 Step flow growth

When adatoms arrive at the surface of the substrate and are able to migrate to energetically favored kink sites of the steps, and hence the steps can expand in the down-step direction, it's called step flow growth mechanism. This typically occurs on substrates having an off-orientation of the surface from a low index surface. When the substrates have a small off-orientation there will be a competition between 2D growth and step flow growth. In case of growth parameters that favor growth of 3C-SiC, after the 2D-nucleation, 3C-SiC grows faster than 6H and overgrows the 6H steps. When the whole surface is covered by a 3C film, the later coming adatoms thicken the film by the step flow growth mechanism as well.

4.1.3 Spiral growth

Spiral growth mode on 6H-SiC substrates usually appears in on-axis growth, especially at high temperature, and results in 6H homoepitaxy. A spiral is initiated from a screw dislocation which already exists in the substrate with a spiral shape of a step. Atoms from the sublimation of the source arrive and easily diffuse to the kink site of the step. When more and more adatoms come, this step starts growing outwards while the spiral center stays pinned by screw dislocation.

An advantage of spiral growth is that no new steps or islands are needed to be created like in the 2D-nucleation growth mode. At low supersaturation the spiral growth mechanism restrains 2D-nucleation and the 6H-SiC polytype of the substrate is maintained. However, at high supersaturation the incoming adatoms are too many

and they easily nucleate on random positions and continue the growth by other polytypes than the one of the substrate.

The typical growth procedure for 3C-SiC in this thesis would be: 2D nucleation occurs on the large terrace width formed by step-bunching or at the edge of the low off-axis 6H-SiC substrate, and these nuclei expand laterally in the down-step direction. In the end the 3C-SiC overgrows the whole 6H-SiC substrate area and is dominant.

4.2 Defects

The imperfections occurring in periodic crystals are named defects. In SiC, the most common defects are dislocations, stacking faults, twin boundaries and double positioning boundaries and polytype inclusions. Defects in crystals interfere with the order of atoms, affect the quality of growth and as a result degrade electrical properties of the material. Introduction of these defects are as below.

4.2.1 Dislocations

Dislocations are the most often seen defects in all kinds of materials. They are one-dimensional defects making irregularity in crystalline structures. Dislocations are characterized by two major properties, dislocation line and Burger's vector. The dislocation line is the direction which the mismatch spreads through the lattice. The difference between the grown crystal loop and a perfect crystal loop is called a Burger's vector, shown in Fig.5 [9]. It can be seen in Fig.5 and 6 that dislocations are classified into two categories: edge dislocation and screw dislocation. When a dislocation is perpendicular to its Burger's vector, an extra layer appears and this is named an edge dislocation. On the other hand, the dislocation direction is parallel to the Burger's vector in screw dislocations. The spiral growth mechanism utilizes screw dislocation as built-in steps, as mentioned above.

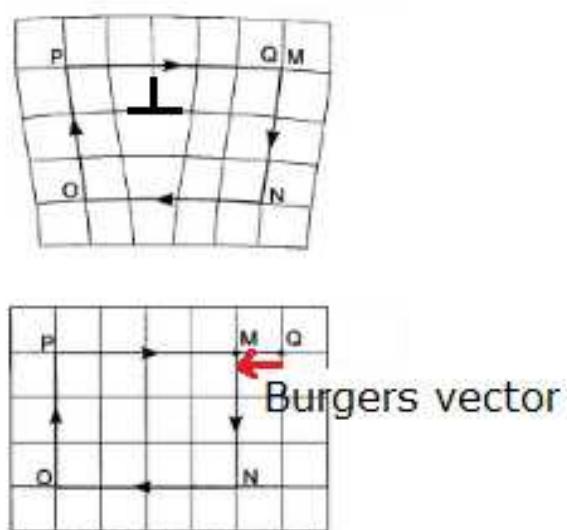


Fig.5 The comparison with a perfect crystal; the extra path needed in order to close the loop is the Burger's vector.

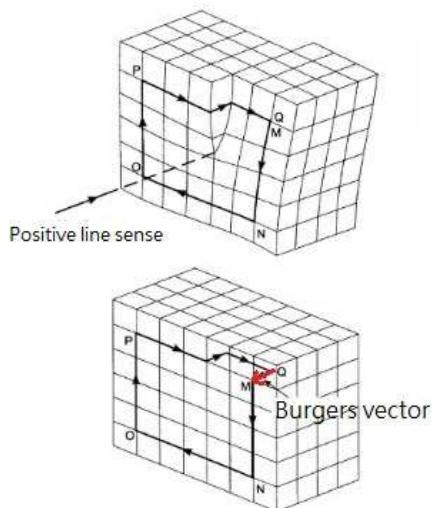


Fig.6 The crystal with screw dislocation and a perfect crystal

During growth, dislocations arise from inner stress caused by mismatch of the grown layer and the substrate. The remaining dislocations in crystals can have serious influences on both physical and electrical properties of the materials, for instance the dislocations cause scattering of carriers and hence decrease the electron mobility.

4.2.2 Stacking Faults

When the stacking sequence of the crystal is disturbed at some point, for example from hexagonal (ABACA) to face-centered cubic (ABCABC), the planar defect is called a stacking fault. Stacking faults could be either intrinsic or extrinsic, that is by either

an absent layer or adding several extra planes into a stacking order.

Stacking faults are most commonly seen in closed-packed crystals since there is no necessity to break the bonds, and therefore low formation energy is required.

4.2.3 Twin Boundaries and Double Positioning Boundaries

Before discussing Double Positioning Boundaries (DPB), a schematic picture, Fig.7 could be used as a simple illustration of terraces of 6H-SiC substrates. Assume that the steps obtained by an off-axis cut have a step height of a single atom, and the neighboring terrace surfaces have different layer position to each other.

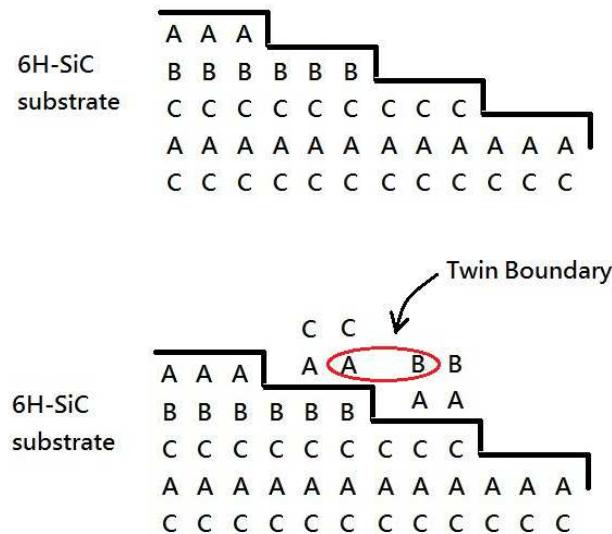


Fig.7 The original off-axis steps and the formation of twin boundaries

When 3C-SiC nucleates on the terraces of a 6H substrate, it could deposit in two stacking sequences, ABCABC... or ACBACB. As shown in Fig.7, a twin boundary appears when the different stacking sequences between steps cause opposite orientations from one and another, just as the mirror reflection.

Double positioning boundaries, on the other hand, describe the situation when two 3C-SiC nuclei nucleate on the very same terrace, but follow different stacking sequences. The illustration is given in Fig.8. Both nuclei extend until they collide. Domains with different orientations can't coalesce so the boundary still remains as the film grows. Since 6H is 6-fold symmetric crystal while 3C is 3-fold, there is 50% of possibility for each layer position to form 2D-nucleation, and the neighboring domains across DPB have 60 degrees of misorientation which emerge as triangular defects on the surface. The DPBs are the main obstacles for enlargement of domain sizes.

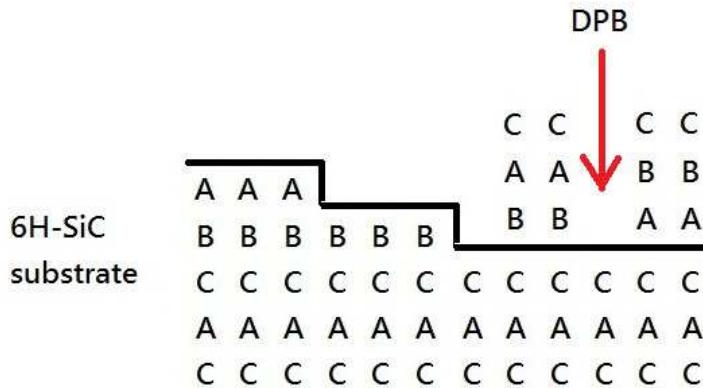


Fig.8 Illustration showing the formation of DPBs

4.2.4 Inclusions

Inclusions are referred to as unwanted polytypes in the films during growth. The source of inclusions could be crystalline particles from the source, or graphite from the graphite growth container. The general view of polytype inclusions is 3C-SiC inclusions in 6H-SiC or 4H-SiC homoepitaxial films. In the heteroepitaxial growth of 3C-SiC on 6H-SiC substrates such inclusions are substrate polytype (6H-SiC) inclusions in the 3C-SiC film.

4.3 Parameters of 3C-SiC growth

Growth mechanisms are highly determined by the combination of various factors in the growth environment. With moderately selected growth conditions, qualities could be controlled, doping can be modified and polytypes can be chosen. The dominant parameters are introduced in the following sections.

4.3.1 Temperature

The temperature is one of the key conditions controlling the growth. The growth temperature has a strong influence on the polytypes of grown layers, as summarized in Fig.9 [10], and it has a great impact on the microstructures.

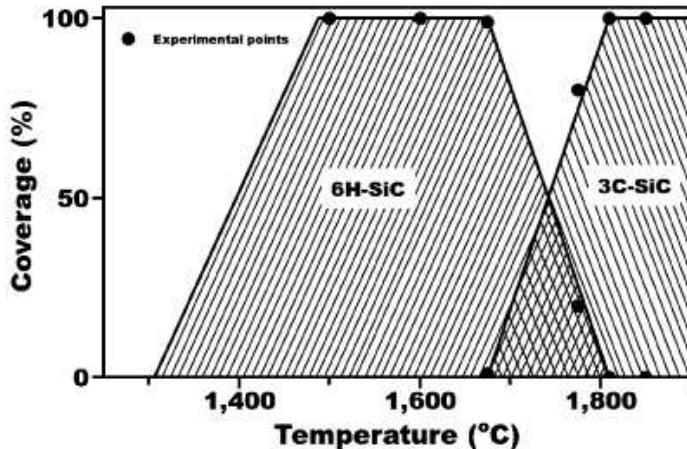


Fig.9 Coverage of the substrate by different polytypes of SiC at different temperatures.

The destined temperature is the crucial parameter to control the sublimation rate of the source. Combined with the speed of heating up the system, called ramp up rate, the supersaturation as well as Si/C ratio in vapor phase could be affected, and consequently decide the nucleation mechanisms, surface morphology and the growth rate of the film. The temperature is the initial trigger of all changes in growth.

4.3.2 Ambient Condition and Supersaturation

An introduced gas ambient could influence the growth in three ways: the pressure in the chamber, the supersaturation of the sublimed species in the crucible, and the doping of the epilayers.

First of all, the sublimed vapor species from the source are transported under the background pressure before reaching the substrate. The higher pressure applied during growth, the harder it is for SiC to sublime and transport. This is closely related to the second issue, the supersaturation. Saturation is a fixed quantity for fix conditions, but supersaturation could occur when the system does not have sufficient time to reach equilibrium. High ramp-up rate and low pressure both end up in high supersaturation. A high supersaturation indicates that much vapor species are sublimed and the whole bunch of atoms that are reaching the substrate will favor new nucleation centers to form. When the supersaturation is high enough, clusters on the surface get a driving force to extend and once exceeding the critical size, these clusters become real, stable nuclei. Consequently, the supersaturation is also the key point to determine the governance of 2D-nucleation or spiral growth mode, and thus decide whether 3C- or 6H-polytype will be dominant.

Specific types of gases may get introduced in epilayers and be present as doping species. Inert gases such as argon only act as a stable ambient pressure, while nitrogen also substitutes for a certain amount of carbon in the SiC layers, and this brings us to the next parameter—Silicon/ Carbon ratio.

4.3.3 Si/C ratio

Vapor composition is a crucial condition in the growth of silicon carbide because it strongly affects the polytype of grown layers. Being a chemical compound SiC should have a 1:1 composition in the source. However, interaction with the graphite components at high temperature can change the ending Si/C ratio close to the growing film and by that influence the quality or doping. When heated up, SiC starts to sublime in several forms: Si, Si₂C and SiC₂..., some are Si-rich phases and the others C-rich. In this thesis, all materials having direct contact with the source and substrate-- including the crucible, spacer and the backside graphite plate-- are made of graphite. At elevated temperature, participation of these additional carbon atoms in growth is hard to avoid, they interact with the SiC vapor and ultimately enhance a C-rich composition.

Besides the external effect, silicon also sublimes faster than carbon, so in the end of the growth a thin layer of carbon is often left on the source, and this is the basic principle to synthesize graphene [11]. In growth of SiC, however, the formation of this extra carbon layer, called graphitization, is unwanted since it highly reduces the growth rate in sublimation epitaxy. In order to control the Si to C ratio, a Tantalum foil is used. This foil functions as a C-getter to minimize graphitization as well as enhance the Si portion to favor 3C-SiC polytype [12].

4.3.4 Substrate

The substrate surface is of great significance since it is where the growth begins. The most important consideration would be the material of the substrates. Before SiC wafers are commercialized, silicon substrates were used for SiC growth. However, the resulting films suffer from tremendous defects because the lattice misfit and the difference in thermal expansion between these two materials.

The quality of the substrate is also influential. Except dislocations which have been discussed above, there is a special feature of the substrates in our investigation named off-orientation or off-axis. Cutting a perfect crystal along an off-axis direction leads to micro-steps on the surface. The 6H-SiC utilize step-flow growth mechanism

on off-axis substrates, while 3C-SiC is usually formed by 2D-nucleation on the terraces. The degree of off-orientation fixes both terrace width and step height which are the two main characteristics of the surface of epilayers.

In previous work [13], 3C-bulk growth utilizing both on-axis and low off-axis (0.8, 1.0 and 1.2 degree) 6H-SiC substrates were investigated. When considering moderate terrace width as well as steps allowing 3C islands to extend, 1.2 degree off-oriented substrate gave the largest domains and hence the best 3C quality among all off orientations. Consequently, 1.2 degree substrates were used for this thesis.

4.3.5 Growth time/ Layer Thickness

Thickness, which relates to growth time, could also show an influence on both terrace width and step behavior, and hence change nucleation mechanisms. Thickness or growth time could also be an important factor to modify the surface morphology of the film. After a long growth time, dominant grains prevail in the competition between growth mechanisms and domain enlargement could be seen.

5 Experimental Details

In this chapter, the equipment setup as well as process is introduced, followed by the description of sample series with selected growth conditions.

5.1 Equipment construction

The experimental configuration is described in this section. Specific elements used during growth are also explained.

5.1.1 Geometrical arrangement

The sublimation epitaxy was performed under selected ambient pressure in a furnace where a vertical quartz tube type of reactor was utilized. A cylindrical graphite growth crucible consisting of a bottom piece and a lid was mounted inside the thermally insulating graphite foam. The full configuration is shown in Fig.10 (a) and the positioning of source and substrate, as well as a spacer and metal foil, inside the crucible is shown in Fig.10 (b) . Inside the crucible a polycrystalline SiC source (as ceramic silicon carbide grown by CVD) and a 6H-SiC substrate were separated 1 mm from each other by a graphite spacer. The temperature is hotter at the source and colder at the substrate. A Ta-foil was placed at the bottom of the assembly as a carbon getter, since at elevated temperature graphitization of the source and the substrate can easily change the vapor composition of SiC. For the second and the

third series a graphite plate was placed on top of the configuration to minimize backside sublimation of the substrate which is colder than the source but hotter than the upper part of the lid. The graphite crucible was heated using an inductive coil around the quartz tube using a RF generator operating at approximately 40 kHz. The top and bottom flanges of the reactor created a closed space of the quartz tube and the flanges were water cooled.

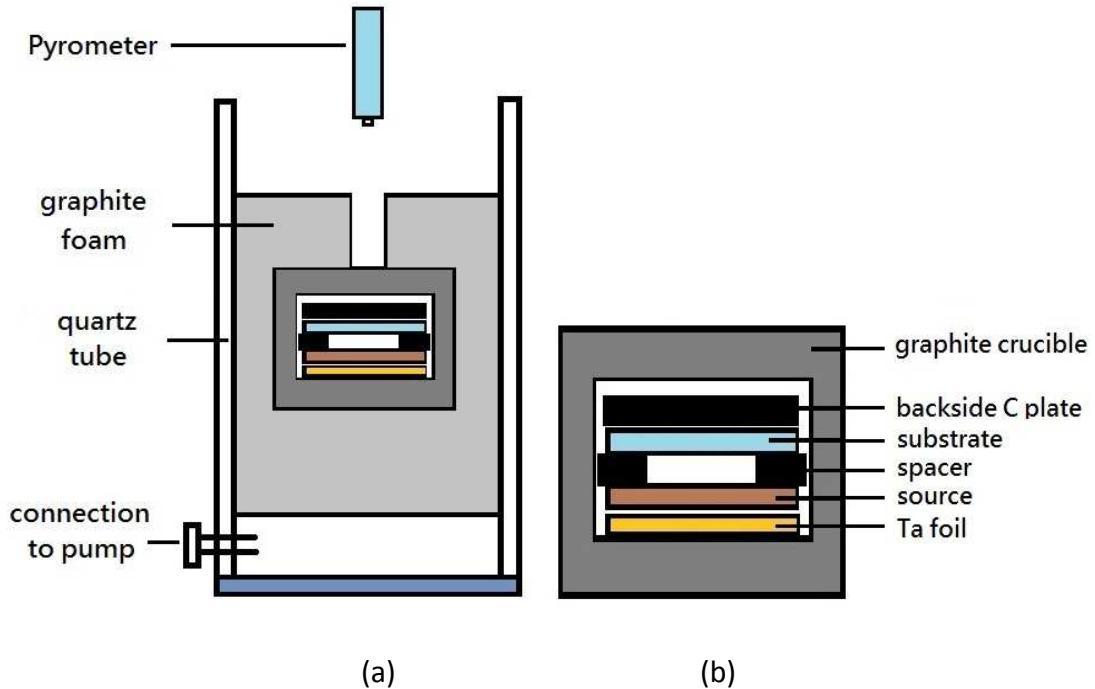


Fig.10 schematic illustration of the experimental constructions (a) the complete setup (b) the arranges inside the crucible

5.1.2 Substrate

In this thesis all samples have thick SiC layers grown on research grade 6H-SiC substrates with surface off-orientation of 1.2 degrees from the basal (0001) plane in the $\langle 11\bar{2}0 \rangle$ direction. All substrates were of $10 \times 10 \text{ mm}^2$ size with only one exception (ELS 301, quarter substrate) and the sublimation growth took place on the Si-face of the substrates.

5.1.3 Ta foil

Graphitization in growth decreases the growth rate by suppressing the sublimation rate of the source. Usually metallic materials which tend to interact with carbon, called a “carbon-getter,” could be applied to absorb excess carbon atoms and control the Si/C ratio in the system.

In this work, a Tantalum foil is placed at the bottom of the crucible, right below the

source in order to balance the Si/C ratio of vapor composition and avoid graphitization. At an elevated temperature TaC is formed on the surface of the Ta sheet. The 3C-SiC is the polytype which is favored by a high Si/C ratio while lower amount of silicon to carbon proportion stabilizes 6H. By selecting the “freshness” of the Ta foil, meaning a not previously used foil, or only 1-2 times used, could also influence 3C-SiC, or when the foil is extensively used it decreases the Si/C ratio and lowers the 3C-SiC formation probability and 6H-SiC homoepitaxy could also be obtained.

5.1.4 Backside Graphite Plate

In the second and the third series a backside graphite plate was introduced. The aim was to investigate the growth of 3C at 1950°C to have thick layers with bulk properties. A graphite plate was placed on top of the substrate in order to increase the growth time and at the same time prevent the substrate from vanishing by the backside sublimation. Such sublimation otherwise caused the layer to drop when the substrate was completely sublimed.

5.2 Growth procedure

A brief description of two parts of experimental procedure for growth is as below.

5.2.1 Growth

The crucible with the whole stacking as described in 5.1.1 was put inside the cylindrical carbon foam and placed in the chamber. The system was pumped overnight at room temperature using a turbo-molecular pump in order to reach vacuum condition ($<10^{-5}$ mbar).

Growth took place either in static vacuum or in nitrogen. Before heated to growth, the pump was turned off if static vacuum was applied. In the cases when nitrogen ambient was required, the chamber was filled with 1000 mbar of nitrogen and pumped down again to the initial pressure, and then the heating started and increased until the growth temperature was reached. A color pyrometer was fixed above the chamber window. The heat losses by radiation from the heated crucible causes a wavelength shift with changed temperature and by this relation the temperature can be determined. By applying a higher temperature at the source, the sublimation occurred and the material was deposited on the cooler SiC substrate. After keeping the system at the growth temperature for a set growth time, the generator was turned off.

5.2.2 Re-sublimation

During growth, SiC was deposited not only on the substrate, but also on the spacer and the lid of the crucible. In order to use the same setup in all the growth runs, after each growth re-sublimation must be operated to get rid of unwanted deposition on these areas.

For re-sublimation, the lid of the crucible was placed at the bottom, followed by a dummy cleaning graphite plate, the spacer to be cleaned, and a dummy graphite piece on top. During heating, previous deposition on the lid and spacer are re-sublimed onto the cleaning C plate and the dummy piece, respectively. After re-sublimation the clean crucible could be used for the next growth.

5.3 Sample description with selected conditions

All the samples were done separately in three series, ELS298-306, ELS317-326, and ELS355-362. To make it clear, forms are made to indicate the difference of growth conditions.

Table.1. Growth conditions of the first series (ELS298-306), in this series there was no graphite plate at backside of substrate.

Sample name	ELS298	ELS299	ELS300	ELS301	ELS302	ELS303	ELS304	ELS305	ELS306
Growth temperature (C)	2000	1900	1950	1950	1950	1950	1950	1950	2000
N2 RT (mbar)	0.5	0.5	0.5	0.5	0.5	0.5	5	5	0.5
Temperature ramp up (K/min)	20	20	20	20	10	30	20	20	20
Growth time (min)	30	30	30	30	30	30	30	90	15
Growth rate ($\mu\text{m}/\text{hr}$)	Fell	410	860	790	720	640	256	220	1300
Layer thickness (μm)	Fell	205	430	395	360	320	128	330	325
p.s.				quarter					
XRD (arcsec)			120, 181	52-62					

From ELS298 to 300, temperature modification to optimize 3C polytype was made, and 1950°C was selected as the growth temperature throughout the first and second series.

For ELS 301 a quarter substrate was used in order to see if the geometry of substrate only could cause any difference in the growth. Since no graphite plate was used, the area of sublimation was different. The amount of sublimed species will therefore also differ. The species are distributed in the inner cavity of the crucible, and therefore could affect the 3C-SiC formation by the Si/C ratio. Afterwards, ELS302 and 303

together with ELS300 were made to investigate if the temperature ramp up rate would influence the growth using 0.5 mbar nitrogen pressure at the start of the growth.

The samples ELS304 and 305 show the study of growth under high nitrogen pressure (5 mbar). The sample ELS304 has the same growth time (30 min) as the previous samples in this series using 0.5 mbar. However, with such high pressure the growth rate decreased abruptly, so ELS 305 was grown for 90 min in order to achieve the same thickness as previous series and compare layers at similar layer thicknesses.

Table.2. Growth conditions of the second series (ELS317-326)

Sample name	ELS317	ELS318	ELS319	ELS320	ELS321	ELS322	ELS323	ELS324	ELS325	ELS326
Growth temperature (C)	1950	1950	1950	1950	1950	1950	1950	1950	1950	1950
N2 RT (mbar)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Temperature ramp up (K/min)	20	20	20	10	20	30	20	20	20	20
Growth time (min)	30	60	120	30	30	30	30	30	60	60
Growth rate ($\mu\text{m}/\text{hr}$)	610	580	540	660	610	688	660	520	630	590
Layer thickness (μm)	305	580	1080	330	305	344	330	260	630	590
p.s.			2 sources							
Backside C plate	yes	yes	Yes	yes	Yes	yes	German	recessed	yes	yes
XRD (arcsec)	60-220	40-59, 81-99	54-77, 81-101						60-104	

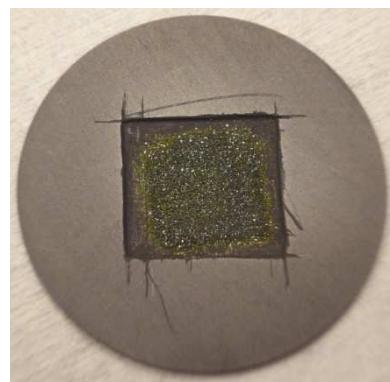


Fig.11 The recessed graphite plate used in ELS324

In the second series (ELS317-326), a backside graphite plate was utilized on top of the substrate. This is the only geometrical difference between this series and the previous one.

For ELS317 to 319 different duration of growth was investigated. In case that a single source would be run out of during 120 min of growth, 2 pieces of source was loaded for ELS319 to make a millimeter thick layer.

The temperature ramp up was studied again in ELS320-322.

For ELS323 and 324 other types of backside graphite plates were used. In ELS323 a C plate from a different supplier but with the same shape replaced the original one. For ELS324 the original plate was used, though it was recessed as a cover, resembling the shape of a hat, as shown in Fig.11. These two samples were aimed to explore the influence of various backside graphite plates.

Table.3. Growth conditions of the third series (ELS355-362)

Sample name	ELS355	ELS356	ELS357	ELS358	ELS359	ELS360	ELS361	ELS362
Growth temperature (C)	1930	1920	1920	1920	1920	1920	1920	1920
N2 RT (mbar)	static	static	static	static	static	0.5	0.5	0.5
Temperature ramp up (K/min)	20	20	20	20	20	20	20	20
Growth time (min)	60	60	60	60	60	60	60	60
Growth rate ($\mu\text{m}/\text{hr}$)	695	630	580	625	625	6H-220, 3C-280	480	504
Layer thickness (μm)	695	630	580	625	625	6H-220, 3C-280	480	504
p.s.	ref	ref	static Al	static#1	static#2	N2 Al	N2#1	N2#2
XRD (arcsec)							82-295	

In the series ELS355-362, the foam was slightly different from the previous two series. If different thermally insulating graphite foam was used, heat distribution would change and thus modification of growth temperature should be made. After two reference runs in static vacuum, ELS355 and 356, a temperature of 1920°C was set in the rest of the series since it gives similar growth rate as the second series (ELS 317-326).

This third series was in particular to study growth of Al-doped 3C-SiC using either an Al doped substrate on backside as a first run, or using the Al contaminated graphite setup to grow doped material. Before the series started, the entire sublimation system including the graphite foam and the crucible cell were contaminated with certain amount of Al utilizing the stacking sequence shown in Fig.12 (a) For the first sample after the two reference runs, an Al-doped SiC with approximately 10^{18} cm^{-3}

concentration was put on top of a 1.2 degree off-oriented 6H-SiC substrate, and while sublimation of the source occurring as the ordinary growth process, the Al-doped SiC also sublimated into the gas ambient and diffused into the 3C-film (ELS357). For the following 2 samples, ELS358 and 359, Al-doped SiC was removed and the configuration had the standard stacking as Fig.12 (b). Static vacuum was applied from ELS357 to 359.

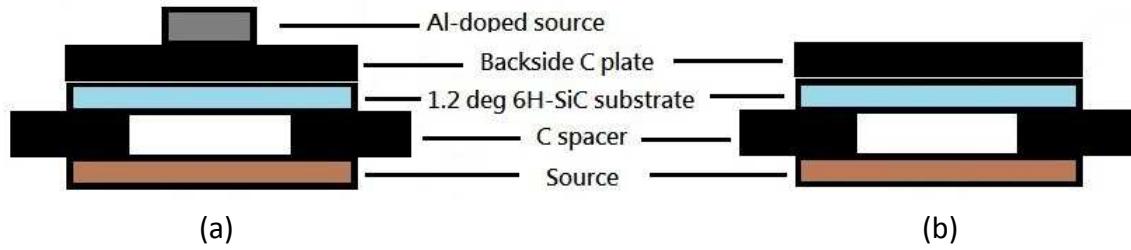


Fig.12 The stacking order of the Al-doped series inside the crucible (a) with Al source
(b) without Al source

From ELS360 to 362, the same sequence as ELS 357-359 was repeated, i.e. first with Al-doped source on top and the later two samples without. The only difference was that this time 0.5 mbar nitrogen pressure was introduced.

6 Characterization techniques

All samples were characterized by Sony Kaiser RAI optical microscope. Scanning electron microscope Phenom from FEI, high resolution X-ray diffraction and room temperature photoluminescence were done on selected samples with most promising features.

6.1 Optical Microscopy (OM)

Optical Microscopy with Nomarski differential interference contrast (NDIC) was utilized for surface morphology characterization. The 50X, 200X, 400X and 1000X of magnification could be used. There are two modes available. Through the reflection mode all defects and other features on the surface could be studied in detail. The transmission mode of the microscope mainly helps identifying the polytype, yellow for cubic while light green to transparent white is characteristic for 6H.

6.2 High resolution X-ray Diffraction (HRXRD)

The X-ray diffraction is a technique that reveals crystal structures and chemical compositions. By observing the scattering of the X-ray beam incident onto crystal

planes, one can get the fundamental information about the sample after analyzing the angles and intensities of the diffracted X-ray beam.

In this study, HRXRD was used to determine the quality of 3C films. High intensity and low FWHM (Full Width at Half Maximum) means high crystallinity or low mosaicity. In this thesis a spot size of $1 \times 1 \text{ mm}^2$ of X-ray beam and footprint of $1 \times 3 \text{ mm}^2$ were used in all XRD measurements. With $1 \times 1 \text{ mm}^2$ spot size the actual sample area being characterized is $1 \times 3 \text{ mm}^2$ which is a quite large area and therefore able to reflect the general quality. The omega angle (rocking scan) was measured using the (111) Bragg reflection. Nowadays the commercialized 6H-SiC wafers have FWHM values around 50 arcsec. The 3C-SiC in research field has shown much higher values so far, typically 200-400 arcsec. In this work, some 3C-SiC samples reached FWHM results similar to the commercial 6H and 4H-SiC, which is very inspiring.

6.3 Scanning Electron Microscope (SEM)

The surface topography could be scanned and reproduced by the electron beams in Scanning Electron Microscope. Focused electrons scan over the samples and in the meanwhile the reflected or inelastic scattered electrons are detected. By analyzing the intensities of the signals, surface topography with high resolution is obtained. In this thesis a Tabletop SEM, PHENOM, from FEI was applied.

6.4 Room Temperature Photoluminescence (RTPL)

Residual doping level was obtained by means of Room Temperature Photoluminescence. After optical excitation, a radiative emission results from recombination in the samples from donors and acceptors acting as dopants. The emission is collected by a monochromator and then goes through a detector. Spectrums are shown on computer, and the dopants can be identified by comparing with known peak positions and characteristics.

7 Results & Discussion

In this thesis the overall aim is to increase the 3C-SiC coverage as well as increase the 3C-domain enlargement.

To make it clear and easier to follow, this result and discussion part will follow the same order as the parameters listed in section 4.3. First, the choice of an optimum growth temperature is described. Then the influence of ambient gas pressure, which is affecting the resulting supersaturation and nitrogen doping will be presented with

comparison of different samples. The discussion about temperature ramp up rate will also be included since it also contributes to the changes of supersaturation, and in particular at the initial stage of 3C-SiC formation. Thereafter the possible relation between geometry of substrates and Si/C ratio will be stated. Demonstration of a series with different growth time for increasing layer thickness followed by a display about backside graphite plates will be made afterwards. Finally, a separate section concerning aluminum (Al) doping concentration will be addressed.

7.1 Growth temperature

As stated in section 4.3.1, 3C-SiC was found to be stabilized by applying higher temperature compared with 6H-SiC homoepitaxial growth. In ELS298 and 299, growth temperatures of 2000°C and 1900°C grown for 30 min were applied at a nitrogen ambient pressure of 0.5 mbar introduced at room temperature. The growth rate at 1900°C was 410 µm/h. However, ELS298 experienced a too high sublimation rate of the source and the source thickness was insufficient for a growth time of 30 min. The result was that the source was finished before the growth was finished, and a sublimation of the substrate backside made the substrate to be sublimed away. The same temperature of 2000°C but a shorter growth time of 15 min of growth was applied with ELS306, but the growth rate was still very high. As a result the surface morphology was too rough, see Fig.13 (c). On the other hand the results indicate a transition temperature for 6H and 3C stability. In Fig.13 (a) we can see that 6H polytype was still dominant in the lower temperature growth at 1900°C while a shorter growth time of 15 minutes at 2000°C shows a higher formation percentage of 3C-SiC. This shows that a high growth rate (high supersaturation) is needed to form 3C-SiC, and the layer thickness is not the dominating effect. In order to have sufficient formation of 3C-SiC and at high growth rate (ELS300), a growth temperature of 1950°C was applied. This seems to be a suitable growth temperature, with a corresponding growth rate of about 0.7-0.8 mm/hr, for 3C polytype. This growth temperature was applied throughout the following first and second series.

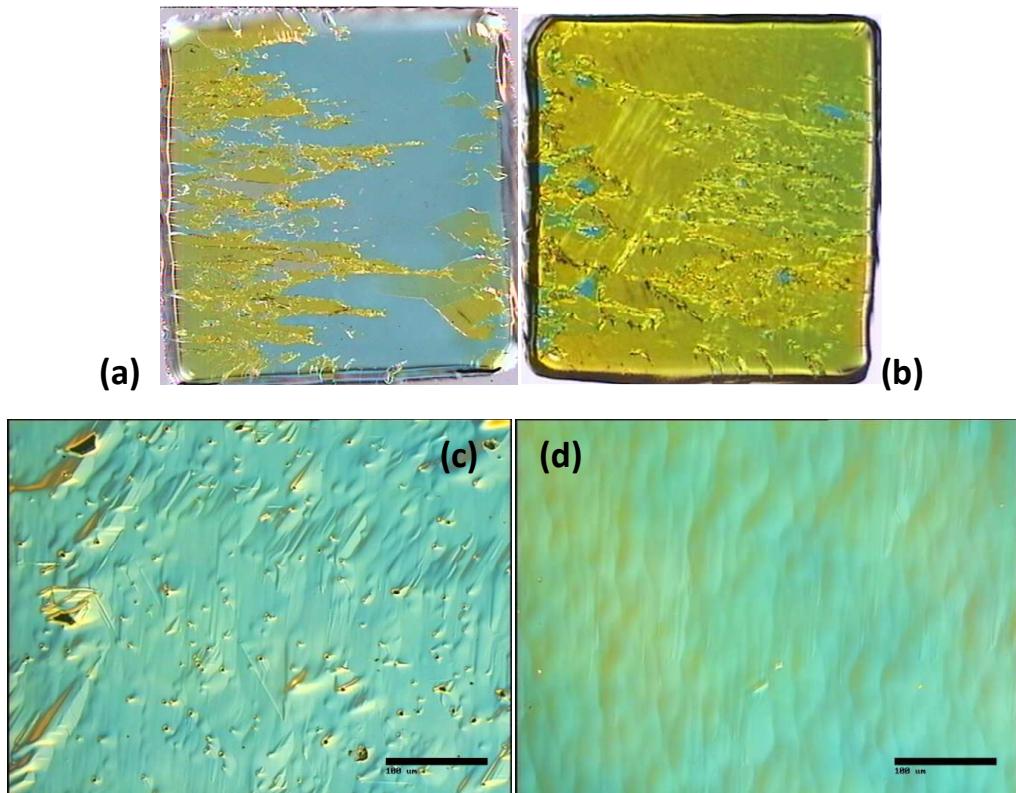


Fig.13 The top two pictures show the overview of (a) ELS299, 1900°C and (b) ELS300, 1950°C. (c) and (d) show the comparison of surface morphology between 2000°C and 1950°C growth temperature under same magnification.

7.2 Ambient Gas Condition

An ambient gas that is introduced could change three parameters: supersaturation at the growing surface, growth pressure and dopants in the films. Except the gases introduced, the temperature ramp up rate is a major way to control the supersaturation, in particular at the initial stage of growth, which will be discussed below.

7.2.1 Growth pressure

In the previous section the stability of 3C-SiC with growth temperature was studied with a nitrogen ambient pressure of 0.5 mbar at room temperature. The influence of a higher ambient pressure of 5 mbar was investigated in ELS304 and 305. The higher pressure showed a lower growth rate, as seen in Table.1.

The pressure also resolves an influence on the dominant polytype. This is shown by comparing ELS300 with ELS304, illustrated in Fig.14. In ELS304, growth at nitrogen pressure 5 mbar, the 3C-coverage dropped to a 4% in comparison to ELS300 (0.5mbar N₂) which had a coverage of 97%. The difference in growth rate (256 and 860 μm/h,

respectively) is responsible for this phenomenon. At a growth pressure of 0.5 mbar the growth is determined by the sublimation of the source, while at a growth pressure of 5 mbar the species need to diffuse through the nitrogen vapor. This growth determining step is moved from kinetically limited by the sublimation of the source to the diffusion in nitrogen when increasing the growth pressure from 0.5 mbar to 5 mbar. As a result, the supersaturation is decreased in 5 mbar growth and conditions are less favorable to form 3C-SiC by 2D nucleation. The result also indicates that homoepitaxial growth can be achieved when using a higher ambient pressure. A decrease of temperature would decrease the growth rate, and the remaining 3C-SiC inclusions may be avoided.

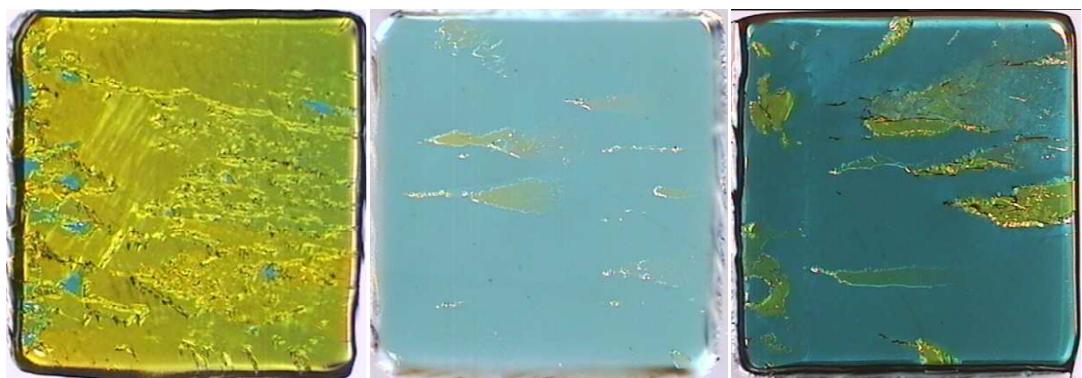


Fig.14 Overview pictures of ELS300, ELS304 and ELS305 from left to right

Most interestingly, it seems that there is nucleation of 3C-SiC at the edge and this may extend in the down step direction. In Fig.15 stitched Optical Microscope pictures of ELS300 and 304 with 50X of magnification are shown. At 5 mbar there is no formation of 3C-SiC at the edge of the substrate. As a result there is no clear domain behavior and extension from the edge. In ELS300 grown at 0.5 mbar there is a formation of 3C-SiC at the edge, as seen by the flat region on the left side. The domain extends along the off-axis direction and continues several millimeters. In this way the polytype of the 3C-SiC, which is formed at the edge, is continued along the step flow direction. It shows that domains may be extended by formation using 2D nucleation and a subsequent step flow mechanism.

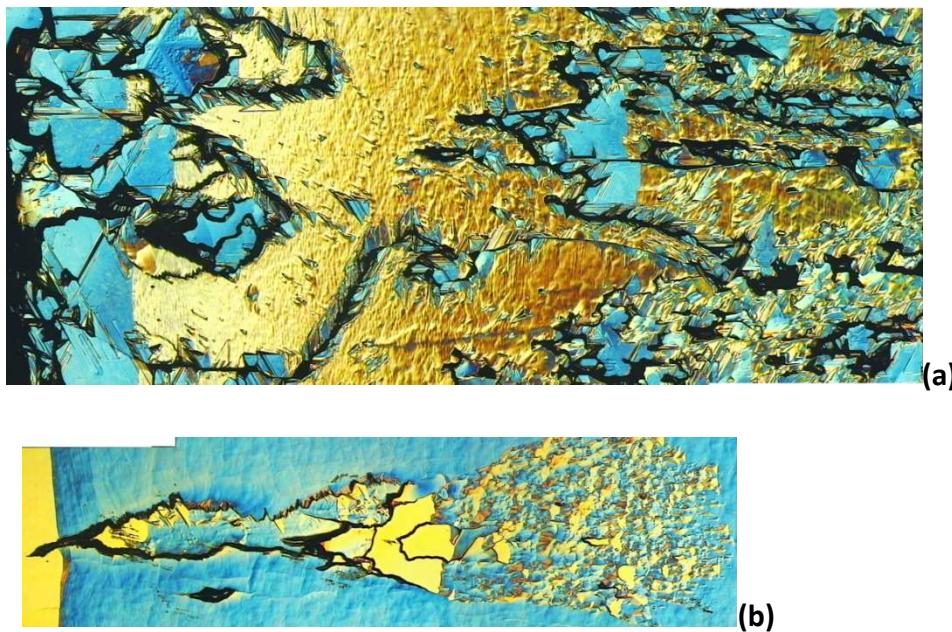


Fig.15 Down step direction from left to right, showing domain enlargement along the off-axis direction. (a) ELS300 and (b) ELS304

7.2.2 Samples grown in 5 mbar Nitrogen (ELS304-305)

The result above indicates that several growth mechanisms may be involved. In this section we describe some defect observation which may be used to indicate the growth mechanisms.

Table.4 shows information about samples grown in 5 mbar Nitrogen. Domain enlargement was also seen in ELS304 and 305. The average growth rate decreased with longer growth duration.

Table.4. Samples grown under 5 mbar Nitrogen

Sample	ELS304	ELS305
Growth time [min]	30	90
Growth rate [$\mu\text{m}/\text{h}$]	256	220
Layer thickness [μm]	128	330
3 C [%]	4	25

The layer thickness shows only a minor influence on the formation of 3C-SiC in 5 mbar nitrogen. The sample ELS305 has roughly a similar order of thickness as ELS300

but the polytype coverage is only 25%. This indicates that the 6H-SiC growth mechanism is dominating. The surface morphology of the 6H-SiC was very smooth and regular 6H steps were observed under 1000X magnification, as shown in Fig.16 (c). The 3C-SiC domains were found as larger domains, and not distributed as a large number of small domains. The 3C domains were almost free from typical 3C defects such as triangular feature and domain positioning boundaries under 400X magnification. Some new and interesting features were also observed in unstable 3C domains. The features resemble spirals but were concentric with no clear spiral feature typical of SiC spiral growth which would be replications of the substrate polytype. The presence of these circular defects indicated the instability of growth, competitions between growth mechanisms causing some disturbances on the 3C polytype growth. Fig.16 (a) shows an overview of ELS305 under 50X magnification, and the corresponding location of features (b)(c)(d). A SEM picture of the spiral-like defect with clear concentric steps is shown in Fig.17.

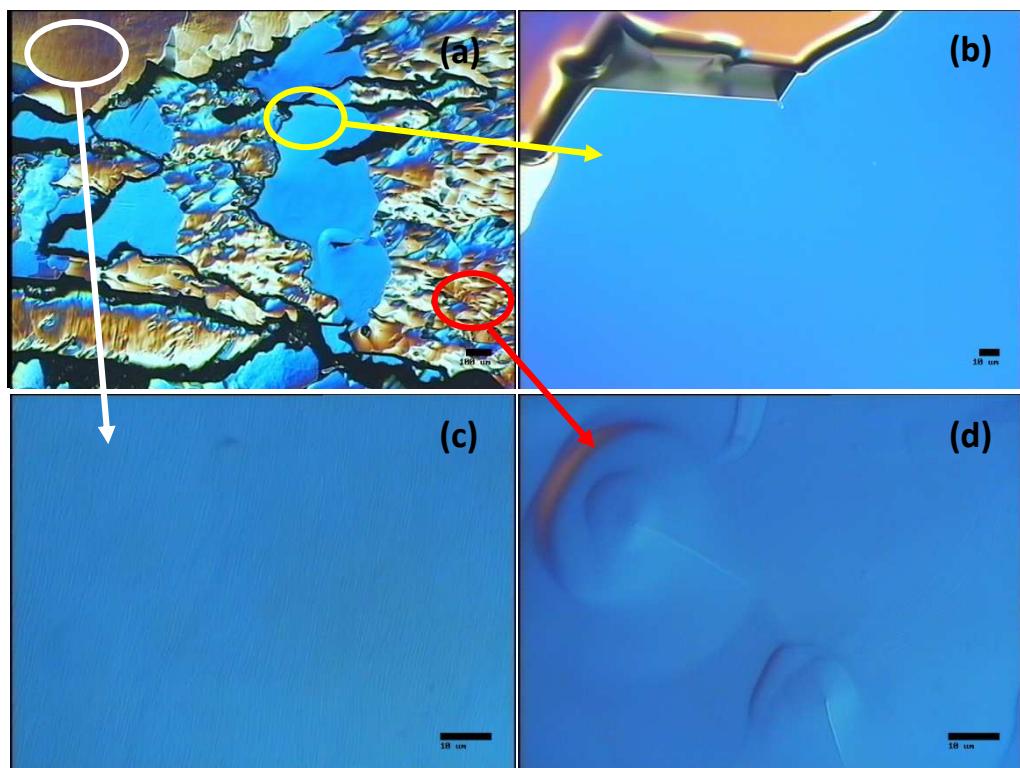


Fig.16 (a) OM pictures of ELS305 at 50X magnification, the circles correspond to the locations of (b) smooth and defect-free 3C domains, (c) 6H grains where steps could be observed, and (d) spiral-like defects seen at 1000X magnification

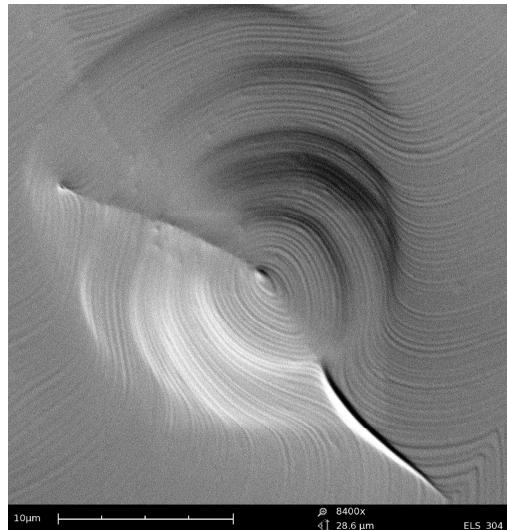


Fig.17 SEM image of the concentric spiral-like defects

Despite the fact that ELS305 shows large 3C domains without pronounced defects, they are very thin if examined in the transmission mode of the optical microscope, shown in Fig.18. This indicates that these 3C-SiC domains are not formed at the beginning of growth, but at a later growth stage. A reason could be that there are large terraces on which 3C-SiC appears by 2D nucleation. The 6H-SiC growth is given by step flow growth, and terraces increase with increasing layer thickness. As seen in the sample ELS304, a smaller layer thickness gives less 3C-SiC. For any domain enlargement one can believe that the grain boundary is too large to overcome. It seems that at a high pressure, the supersaturation is too low that 3C-SiC could not nucleate fast enough in the initial stage. Then they could not expand either and the 3C-coverage was too low even when growing to a 340 µm of thickness. Thus it is realistic that growth under 5 mbar nitrogen is in the diffusion limited region while 0.5 mbar is near the transition region from kinetically limited (e.g. dominating when using dynamic vacuum) to diffusion limited. Since growth in dynamic vacuum shows a high percentage of 3C-SiC but with many small domains, the stability of 3C-SiC should be optimized at this transition region around 0.5 mbar.

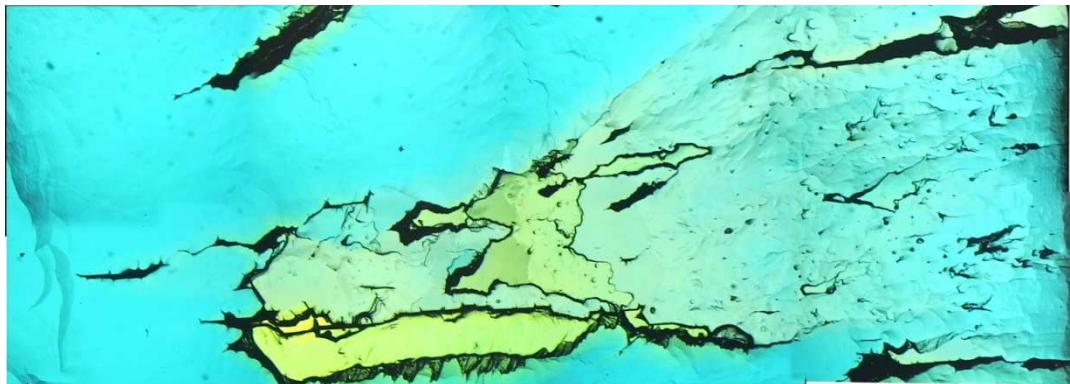


Fig.18 Stitched OM pictures of ELS305 at 50X magnification under transmission mode

7.2.3 Temperature Ramp Up Rate and Supersaturation

In previous work [14] it was observed that the ramp up rate influences the formation of 3C-SiC using on-axis substrates. At a fast ramp up the coverage of 3C-SiC is increased while the size of the 3C-SiC domains is larger when using a slow ramp up rate. In our case of low off-axis substrates the ramp up rate does not seem to influence to a similar extent. In this thesis two ramp-up series were made but no clear tendency was observed. Fig.19 shows the growth rate versus 10, 20 and 30K/min of ramping. There is a slight variation of growth rate between the samples, but no clear tendency. The reason could be that the thermal heating is influenced by the contact with the tantalum foil, and shows an effect at such extremely high epitaxial growth rates. In comparison of the samples, there is no clear tendency with ramp up on the coverage of 3C-SiC. Possibly the higher 3C coverage in the sample with 20 K/min is related to the higher growth rate than the ramp up rate to the growth temperature.

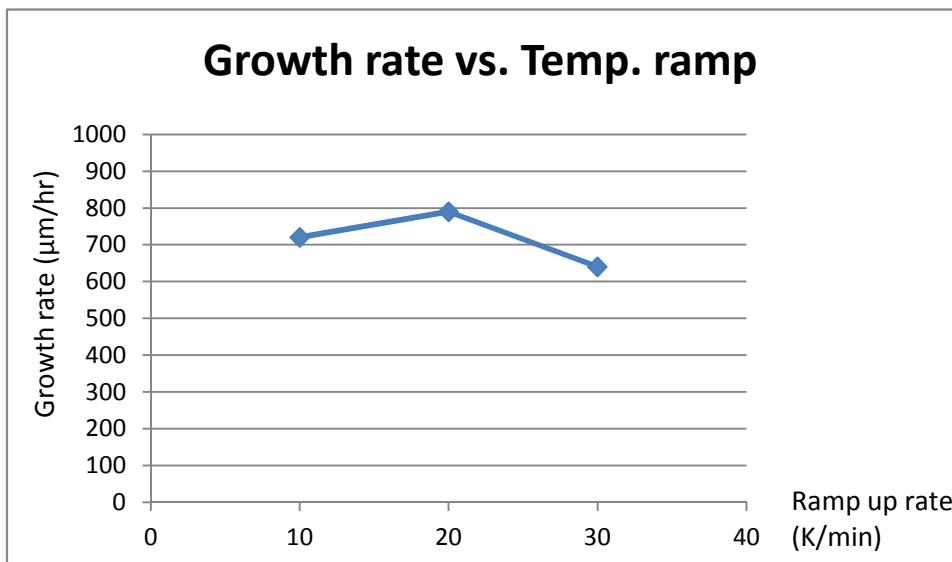


Fig.19 Growth rate plotted versus temperature ramp up rate



Fig.20 Samples with 10, 20 and 30 K/min of temp ramp up rate (from left to right)

Theoretically, a fast temperature ramp up leads to massive but small 3C domains due to a high supersaturation. In Fig.20, however, there's no clear domain size relation in this series using low off-axis substrates. A possible reason could be that at such high growth temperature as 1950°C, the growth rate is high and there is a competition between growth mechanisms, like 2D nucleation, spiral growth, and step-controlled epitaxy. The 3C-coverage in both 10 K/min and 30 K/min ramp samples are low, 60% and 68% respectively in comparison to the 20 K/min ramp up. More detailed studies of initial stage are needed to understand the influence of competing growth mechanisms on the formation of 3C-SiC.

7.3 Geometry of substrates

In order to optimize 3C-SiC, we also studied using different shapes of substrates. In our configuration there is sublimation from the backside of the substrate. This can be pronounced when no graphite plate is used, like in the series ELS299-306. Instead of the 10x10 mm substrate used in all the other samples, in ELS301 a quarter piece of a 2 inch substrate was used in the experiment. The idea was to enhance the concentration of vapor species in the crucible, and possibly the Si/C ratio, by higher amount of sublimed SiC from this larger substrate during growth. Table.5 shows some information of ELS300 and 301. In comparison, the growth rates are very similar and variations are within the general variations at such extreme epitaxial growth rates. In case of 3C-SiC formation, the coverage is slightly higher in the larger substrate. However, the coverage is similar and still could be due to the growth mechanisms acting on the low off-axis substrate. Another indication would be by the quality of the materials. The XRD rocking curves show a slightly better quality in the larger size sample. These results indicate that the backside sublimation could influence the vapor composition in the geometry when there is no graphite plate. Due to the low number of quarters of 2 inch substrates, complementary experiments

were not possible to make.

Table.5. Information of samples with different substrates

Sample	ELS300	ELS301
Substrate	standard	quarter
Growth time [min]	30	30
Growth rate [$\mu\text{m}/\text{h}$]	860	790
Layer thickness [μm]	430	395
3C coverage [%]	97	99
XRD FWHM (arcsec)	120-181	52-62

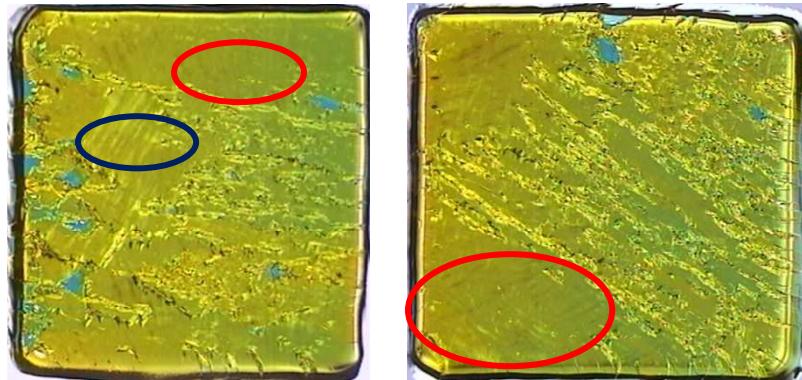


Fig.21 Overview pictures. The left one is ELS300 and the right one is ELS301 (Quarter substrate). The $[1120]$ direction for ELS301 is from top left to bottom right. The highlighted regions were measured by HRXRD.

In other 10x10 mm substrates the pieces were cut parallel to the off-axis direction. In this quarter substrate experiment (ELS301) , however, the spacer was unintentionally placed in another way compared with 10x10 mm substrates, as shown in Fig.22, and thus the $[11\bar{2}0]$ direction became align with the diagonal of the square film. This difference makes the up-step part of the sample ELS301 had only a corner but not a long edge like in 10x10 mm pieces.

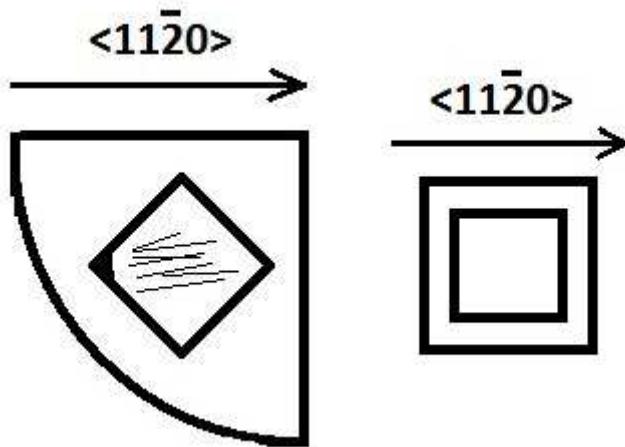


Fig.22 Illustration of different growth directions of quarter and standard samples

In table.5 the XRD results of ELS301 show a good quality, while ELS300 has FWHM values twice or even three times of ELS301. The position of the spacer enables ELS301 to have a large domain in the corner, but whether the position helps achieving the extra-high quality or if Si/C ratio also contributed is unknown. Experiments with the spacer placed in the normal position on a quartered substrate would be interesting to study.

Since 3C- and 6H-SiC are always competing during growth, in ELS300 and 301 sometimes the 6H islands may be thicker and overgrow the 3C, and sometimes vice versa. One thing worth noting is that in both samples, spirals could only be observed on the 6H islands overgrowing the 3C. When 6H were overgrown by 3C, no spirals could be found even with 24000X magnification in SEM. The case with spirals is explained first. In section 4.1.3 it was mentioned that since no new steps are needed, at low supersaturation the spiral growth usually suppress 2D-nucleation. Therefore, for those 6H islands utilizing spiral growth they can extend more easily than nearby 3C and hence these 6H dominate. However, the supersaturation and evolution of the increased layer thickness caused formation of 3C during subsequent growth, possibly from terraces of steps, and the incoming adatoms formed 3C 2D-nuclei directly on terraces. As a result the original 6H spirals could not expand over the whole sample but were still present.

On the other hand, for those 6H islands without spirals, they followed step flow growth mechanism and in the end 3C nucleation overgrew the 6H. Once again, there seems to be an influence of the growth mechanisms on the formation. Initial growth stage study would clarify the parameters of growth mechanisms and thereby stability

of 6H vs 3C growth.

7.4 Growth time / layer thickness

The layer thicknesses have to be several hundreds of micrometer to achieve free standing material. In this section cubic silicon carbide films have been grown with increasing growth time under same parameters (1950°C, 0.5 mbar nitrogen ambient, and ramp up rate of 20 K/min) with 30, 60, and 120 minutes of durations. Table.6 shows different growth time and their resulting growth rate as well as XRD results for ELS317, 318 and 319.

Table.6. Information of samples with different growth time

Sample	ELS317	ELS318	ELS319
Back side C plate	yes	yes	yes
Growth time [min]	30	60	120
Growth rate [$\mu\text{m}/\text{h}$]	610	580	540
Layer thickness [μm]	305	580	810
3 C [%]	98	100	100
XRD (arcsec)	60-220	40-59, 81-99	54-77, 81-101

The growth seems to be directed in the off-axis direction. The growth in the up-step edge of the sample starts with an on-axis region. In this region 2D-nucleation starts, then new nucleation sites are formed and try to expand. If other nuclei appear on top of these large and flat domains, there could be disturbances of the original domains as shown in Fig.23. This phenomenon usually happens in down-step direction in off-axis homoepitaxial part and similar disturbance is an issue in 3C thick epitaxial growth.

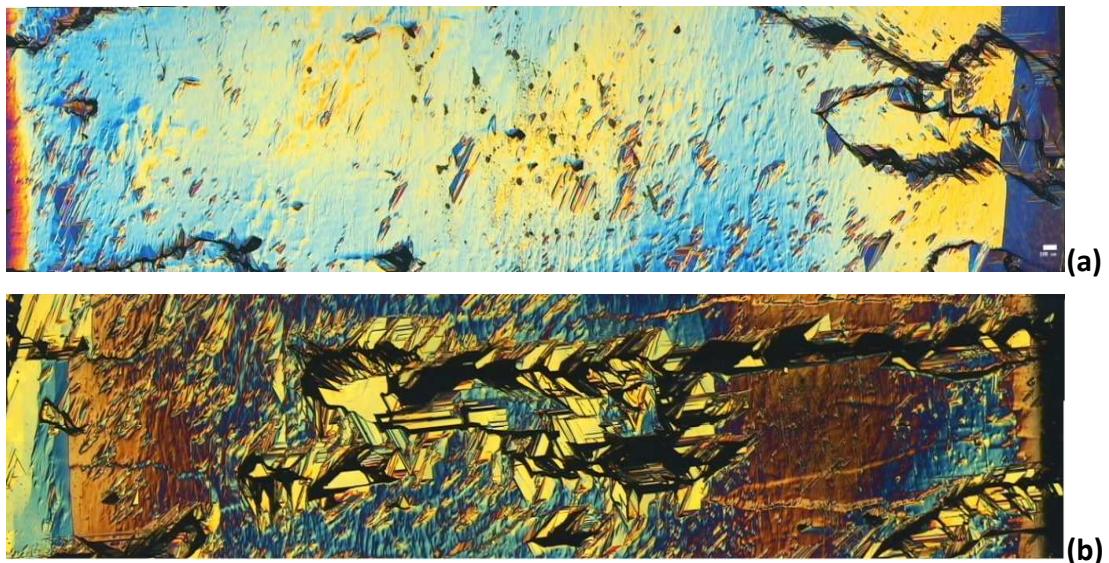


Fig.23 Two 50X OM pictures showing (a) domains extending throughout the whole sample, and (b) disturbance of new nuclei. Both pictures have length of the entire sample, which is 10 mm.



Fig.24 Showing samples with increasing layer thickness and domain evolution.

On most of the 3C sublimation samples new domains nucleated in the step flow region, i.e. in the center of the sample and not at the edge. This is the result of 2D nucleation on the large terrace. In order to approach larger domains or even single crystal growth, grains that nucleate at the edge of the film and extend all over the sample in the down-step direction would be more favorable. This mechanism is not straight forward to control due to the growth mechanisms that influence, and change with layer thickness. One can see that there are instabilities in both of the stitched OM pictures taken from one sample. In the upper case the domains extend fairly smoothly without major disturbances, and only the grooves between the domains appear. At other regions, the domain enlargement in the down-step direction has been disturbed and rough areas appear.

In Fig.24 the domain enlargement effect can clearly be observed by comparing ELS319 with 317. After 30 min of growth, different domains are still competing with each other, but in comparison with 120 minutes growth there are dominant grains that prevail in the competition. The remaining domains distribute quite homogenously throughout the entire sample, i.e. there are fewer new nucleation centers to interrupt the expansion of domains in the down-step direction.

There is a clear drop in XRD FWHM from ELS317 to ELS319 as seen in Table.6. The 30 min sample shows a large variation in values measured at different locations on the sample. The FWHM values and variation drops in the 60 min sample. All the FWHM values are lower than 100 arcsec. The variation and number are similar in the 120 min sample. We can interpret the observation in this way: different domains are still competing after 30 min of growth. After 60 min all the dominating domains have taken over and other domains have been overgrown. From 60 min to 120 min the change was not as pronounced since the dominant domains were already fixed and only grew thicker.

The growth rate versus growth time relation is plotted in Fig.25. The reduction in growth rate for longer growth time is attributed to the increasing graphitization of the sources with growth time. The sources are shown in Fig.26. Since the sublimation of the source is the growth determining step, the decrease in growth rate with growth time can be understood.

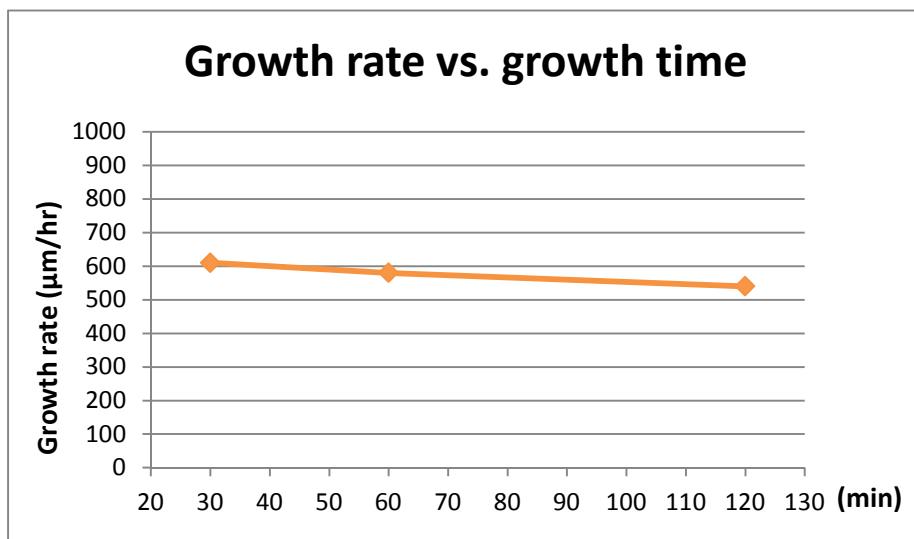


Fig.25 Average growth rate plotted versus growth time



Fig.26 Images of source graphitization of ELS317, ELS318 and ELS319 from left to right. The squares in the middle are the sublimed areas which correspond to the shape of the grown film. The graphitization appears as an increasing black area in the sublimation part of the source.

Most interestingly ELS319 has 1.08 mm of thickness, which reflects growth of bulk-like SiC by the sublimation growth method. The samples ELS317, 318 and 319 also presented the best XRD results of all three series.

7.5 Backside graphite plate

7.5.1 Temperature Ramp Up investigation with Backside Graphite Plate

The influences of introducing a graphite plate at the backside of the substrate and how the shapes of plates affect the growth will be discussed in this part. The samples ELS320, 317, and 322 are grown with backside graphite plates using different temperature ramp up rates of 10, 20, and 30 K/min, respectively. The samples are shown in Fig.27. The sample can be compared with ELS302, 300 and 303 which have been grown without a graphite plate (described in section 7.2.2). Table.7 shows the information about samples with graphite plates.

Table.7. Information about investigation of temperature ramp up rate

Sample	ELS320	ELS317	ELS322
Back side graphite plate	yes	yes	yes
Ramp rate [K/min]	10	20	30
Growth time [min]	30	30	30
Growth rate [$\mu\text{m}/\text{h}$]	660	610	688
Layer thickness [μm]	330	305	344
3 C [%]	99	98	99

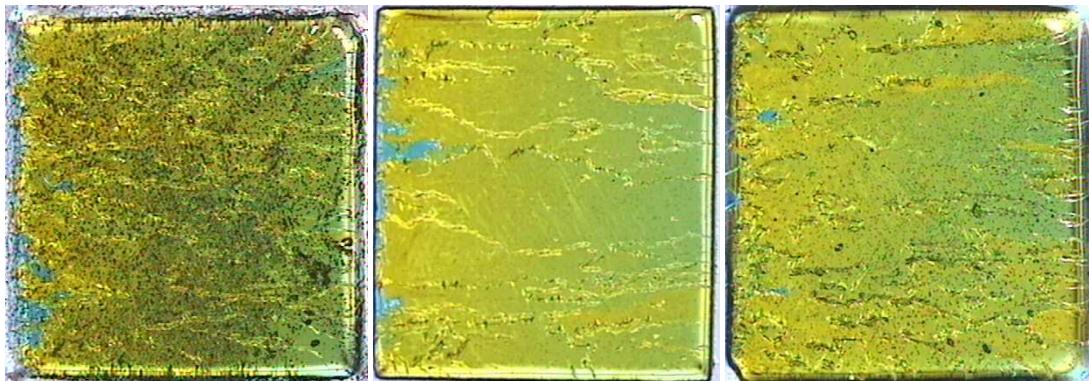


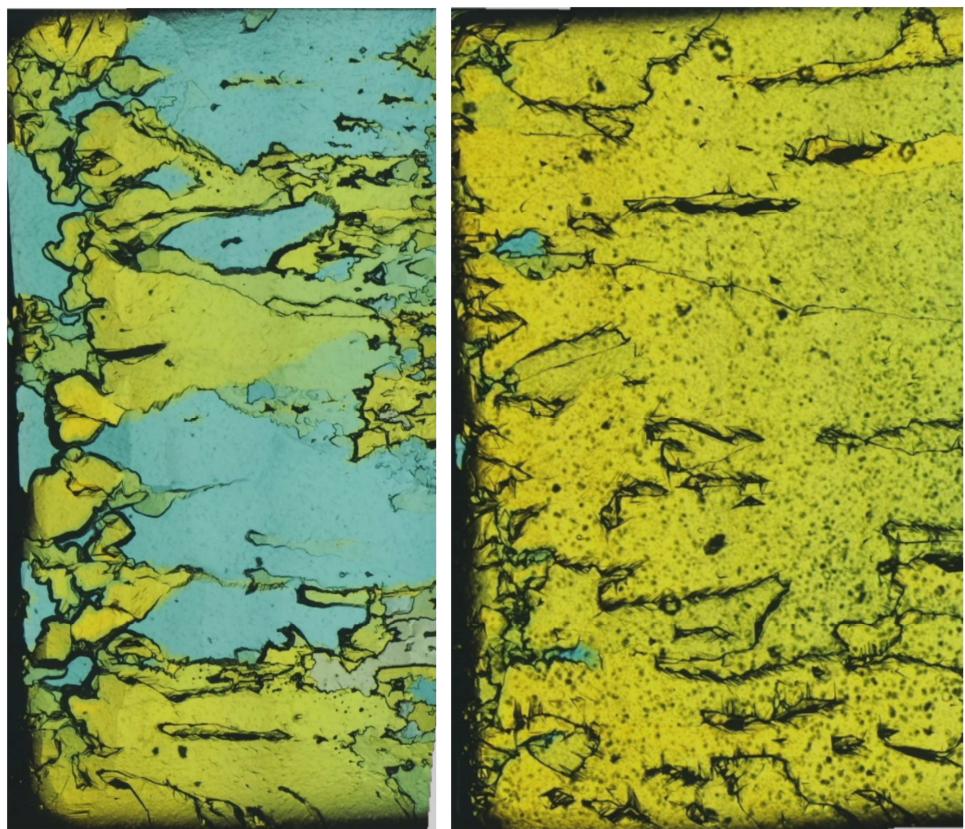
Fig.27 Overview OM pictures of ELS320, ELS317, and ELS322 from left to right

In case of on-axis growth, there is an influence of ramp up rate and larger domains are observed using a slower temperature ramp up to the growth temperature. However, in the case of low off-axis substrates there is no obvious influence of the ramp up rate when using a graphite plate at the backside. This is similar to the observation without graphite plate. On the other hand, the 3C-SiC coverage is high in all cases using a graphite plate at the backside of the substrate but there is no pronounced behavior of domains.

Table.8 and Fig.28 below clearly show the difference of applying backside graphite plate or not when using the same temperature ramp up rate. The first and the most obvious difference is the polytype distribution. In the sample ELS303 grown without a graphite plate the 3C coverage is only 60% while ELS322 grown with a graphite plate has almost 100% of 3C. The second would be the domain enlargement effect. Both pictures (a) and (b) include the entire edge of the sample. In ELS303 there were massive 3C nucleated at the edge but not able to extend or merge, while ELS322 could show two to three large, dominating domains.

Table.8. Comparison between grown with and without backside graphite plate

Sample	ELS303	ELS322
Back side C plate	no	yes
Growth time [min]	30	30
Growth rate [$\mu\text{m}/\text{h}$]	640	688
Layer thickness [μm]	320	344
3 C [%]	60	99



(a)

(b)

Fig.28 Stitched 50X OM pictures showing difference between two 30K/min ramping samples, (a) without (b) with backside graphite plate

Fig.29 shows the growth rate versus temperatures ramp up rate. The curves look opposite for using and without backside graphite plates. Besides the backside sublimation, this graphite plate could remove the heat slightly faster from the substrate, and consequently changed the thermal gradient inside the crucible.

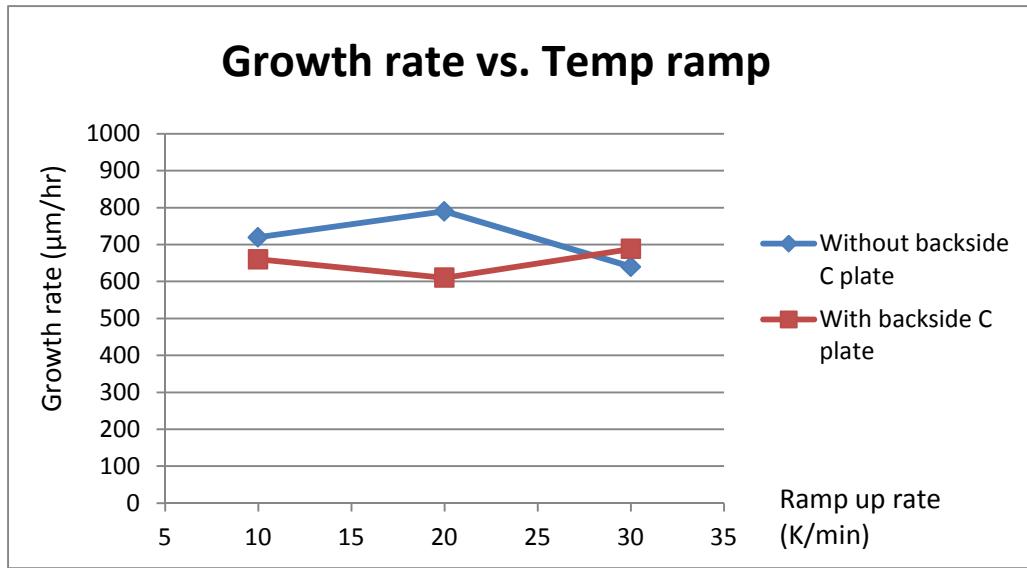


Fig.29 Growth rate changes with different temperature ramping, the red curve with square marker shows samples using backside graphite plate.

7.5.2 Different graphite plates

In the second set (ELS317 to 326), all samples were grown using backside graphite plates, and we found that these samples had higher 3C-coverage than in samples grown without a backside graphite plate. In this section we compare these and an intermediate situation with a recess on the backside plate. This creates a small cavity between the substrate backside and the backside plate but there is not direct contact.

Table.9 includes comparison of ELS300 (without graphite plate), ELS317 (with a normal graphite plate), and ELS324 (with a recessed plate). The OM pictures below also show the overview of these three samples.

Table.9. Comparison between different backside plate conditions

Sample	ELS300	ELS317	ELS324
Back side graphite plate		yes	recessed
Growth time [min]	30	30	30
Growth rate [μm/h]	860	610	520
Layer thickness [μm]	430	305	260
3 C [%]	97	98	91

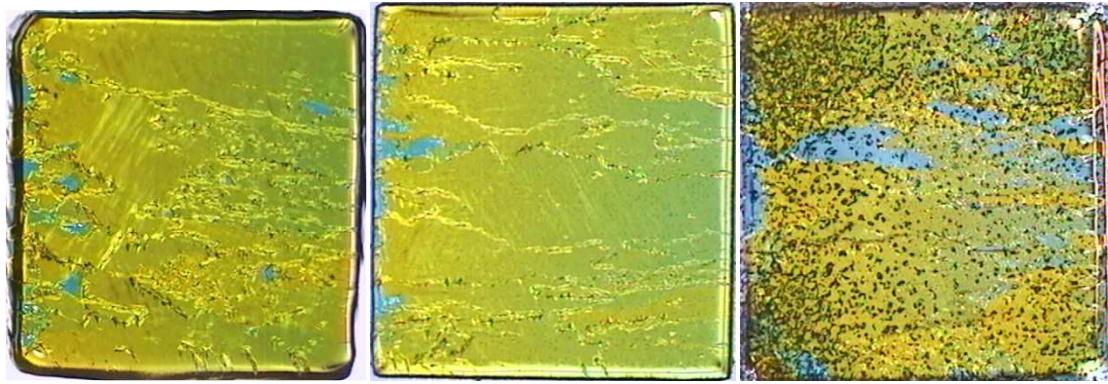


Fig.30 Overview OM pictures for ELS300, ELS317, and ELS324 from left to right

The samples ELS300 looks slightly more yellowish than ELS317, this was due to the difference in growth rate and resulting thickness being about 100 μm more. However, almost all the domains nucleating at the edge of ELS317 could extend to the end of the sample so the final surface morphology was very smooth, while a tremendous amount of tiny nuclei interrupted this domain enlargement effect in ELS300. This could be due to a higher temperature at the surface of the ELS317. Since the growth rate seems slightly lower, the temperature gradient is smaller and the surface has a higher temperature in case of graphite plate. As a consequence the surface kinetics is enhanced. A higher temperature gradient in samples without graphite plate could also cause more nucleation in the step-flow region in the middle of the sample, and these could disturb the extension of domains from the edge.

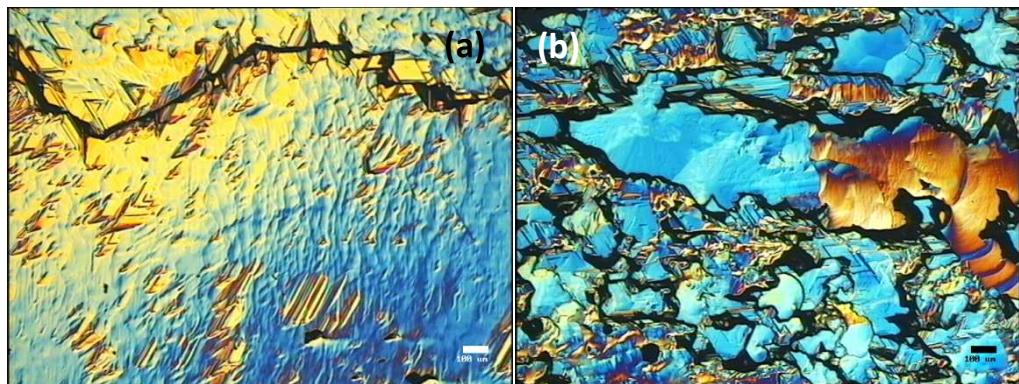


Fig.31 Morphology of (a) ELS317 and (b) With recessed plate (ELS324)

If we compare ELS317 with ELS324, the influence of the shape of the graphite plates, or more precisely the influence of the contact between the substrate and the plate, can be seen. In Fig.31 (b) we can see that with the recessed plate, not only polytype coverage was changed, but also there is a large difference in the size of domains. Since the recessed plate does not have direct contact with the substrate but with the spacer, and graphite is known to have a good heat conducting property, we assume

that this hollow space between the substrate and the recessed plate act as a thermos mug. Such effect would decrease the temperature gradient, and this is in agreement with the lower growth rate. In this sample the backside sublimation of the substrate was even more severe than without a plate. The temperature gradient was slightly changed into a way that the nucleation instability was enhanced, as shown by the non-uniform growth. If the substrate is hotter and the temperature gradient between the source and substrate is smaller, the supersaturation is decreased and hence 3C is more difficult to form. The complete mechanisms are not clear, and more experiments have to be done to confirm the reasoning. The following graph shows the growth rate drop when using backside the graphite plates.

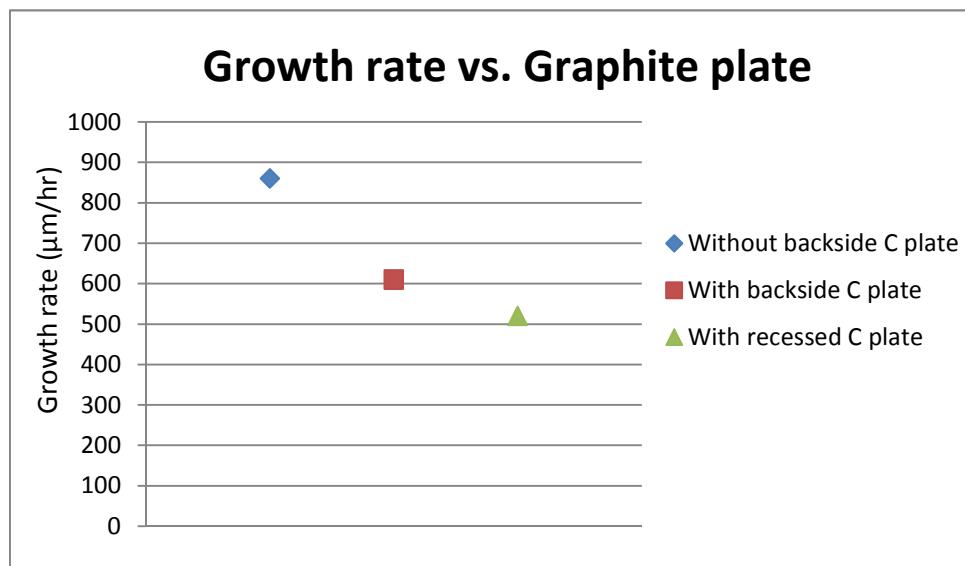


Fig.32 Growth rate of various graphite plate conditions

7.6 Al-doped SiC

In this section the third series (ELS355-362) with Al doping will be discussed. Two reference runs were done in static vacuum in the beginning of the series to adjust the growth temperature for new thermally insulating graphite foam. The temperature 1920°C was set in the rest of the series since it gives similar growth rate of around $600 \mu\text{m}/\text{hr}$ as the second series (ELS 317-326). The plan was to grow three 3C samples (ELS357-359) in static vacuum, the first one with Al-doped SiC source on top of the backside graphite plate. For the following two samples this Al-doped source was removed from the setup so we could study Al concentration decrease since there will be Al in the graphite set from the first run, but the Al will be outgassed with each subsequent run. Afterwards another three samples (ELS360-362) were grown in the same order but this time in 0.5 mbar nitrogen.

First we compare the reference run (ELS356) to the other samples grown in static vacuum. Table.10 shows that the growth rates of these samples grown in static vacuum are very similar, and also close to the average of the undoped runs ELS317-326. The morphology is similar too. The OM pictures with 50X magnification are shown in Fig.33.

Table.10. Information of reference (ELS356) and Al-doped series in static vacuum

Sample	ELS356	ELS357	ELS358	ELS359
ps	reference	Al-doped source	#1 after	#2 after
Growth pressure	Static vacuum	Static vacuum	Static vacuum	Static vacuum
Growth time [min]	60	60	60	60
Growth rate [$\mu\text{m}/\text{h}$]	630	580	625	625
Layer thickness [μm]	630	580	625	625
3 C [%]				

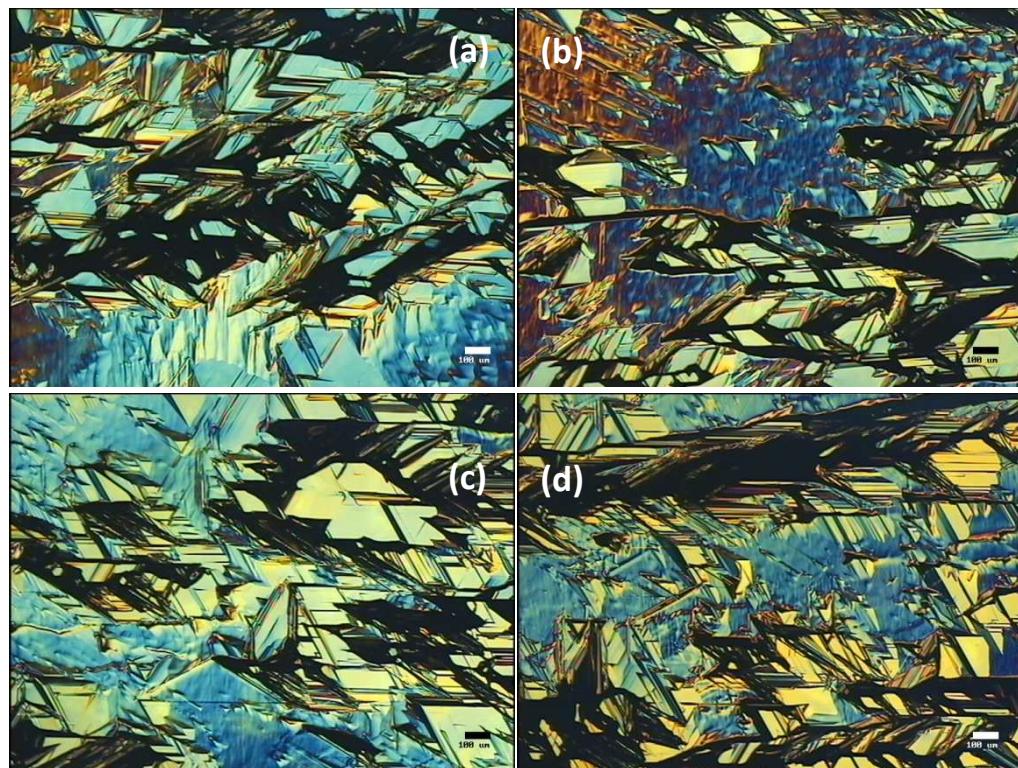


Fig.33 OM images with 50X magnification of (a) reference, ELS356,(b) with Al-doped source, ELS357, (c) without Al source, ELS358, and (d) ELS359

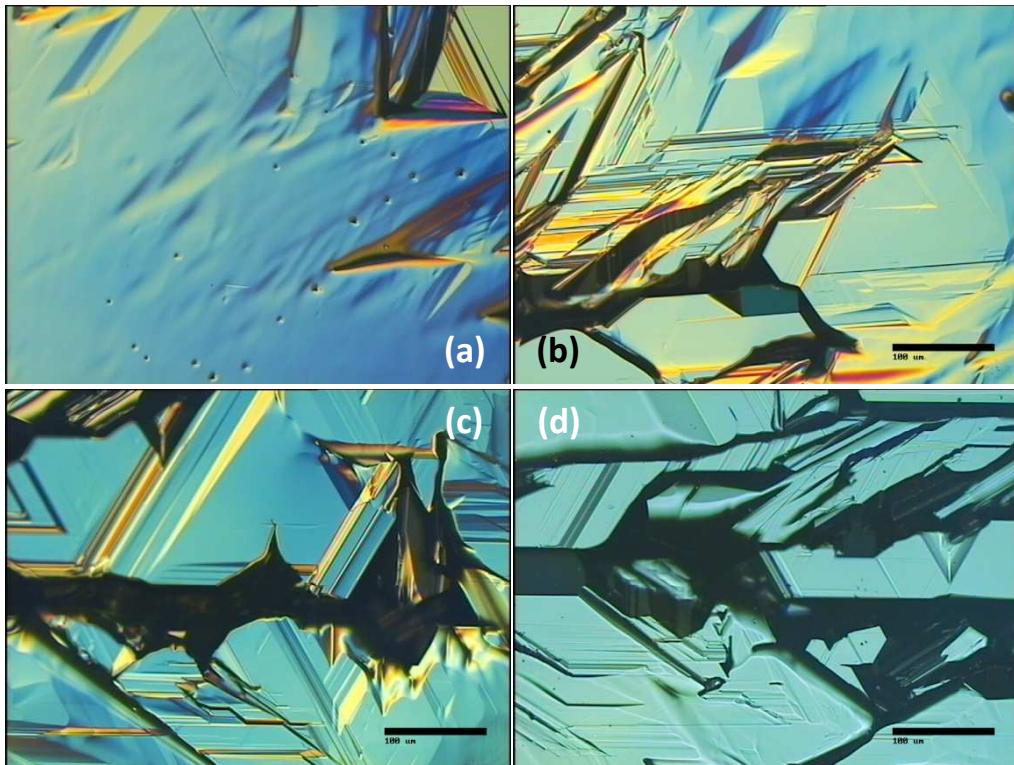


Fig.34 OM images with 200X magnification of (a) reference, ELS356,(b) with Al-doped source, ELS357, (c) without Al source, ELS358, and (d) ELS359

There is a difference in comparison to the growth in static vacuum when it comes to Al doping under nitrogen ambient. Table.11 lists comparison between ELS357 and 360, both with Al-doped source on top but with different growth ambient. Overview images are also shown below. It was previously found that Al stabilizes polytypes with a high hexagonality (6H, 4H) [15], and from ELS360 to 362 we also found this trend. Together with nitrogen, the high Al-doping enhanced the 6H-coverage to 40% in ELS360, and this 6H area was very bluish which indicates an Al doping. The ELS361 and 362, however, were back to 100% 3C-coverage again. When comparing samples grown with Al doped substrate on the top, there is much more 6H-SiC in the sample grown in nitrogen ambient. The reason could be that the growth rate is higher in the static vacuum grown sample. A higher growth rate generally results in a lower doping. Thus there would be less Al in the static vacuum grown sample and less stabilization of the hexagonal 6H-SiC. In addition, the higher growth rate favors formation of 3C-SiC.

The growth rate was also suppressed by the use of Al doping in the N₂ ambient, as seen in Fig.36 In the expected decrease of Al concentration from ELS360 to 362, the growth rate increased substantially while in static vacuum there was no change of

growth rate.

Table.11. Information of static vacuum (ELS357) and Al-doped series (ELS360-362)

Sample	ELS357	ELS360	ELS361	ELS362
Al-doped source	yes	yes	no	no
Growth pressure	Static vacuum	0.5 mbar N2	0.5 mbar N2	0.5 mbar N2
Growth time [min]	60	60	60	60
Growth rate [$\mu\text{m}/\text{h}$]	580	6H-220 3C-280	480	504
Layer thickness [μm]	580	6H-220 3C-280	480	504
3 C [%]			100	100
XRD (arcsec)				83-89

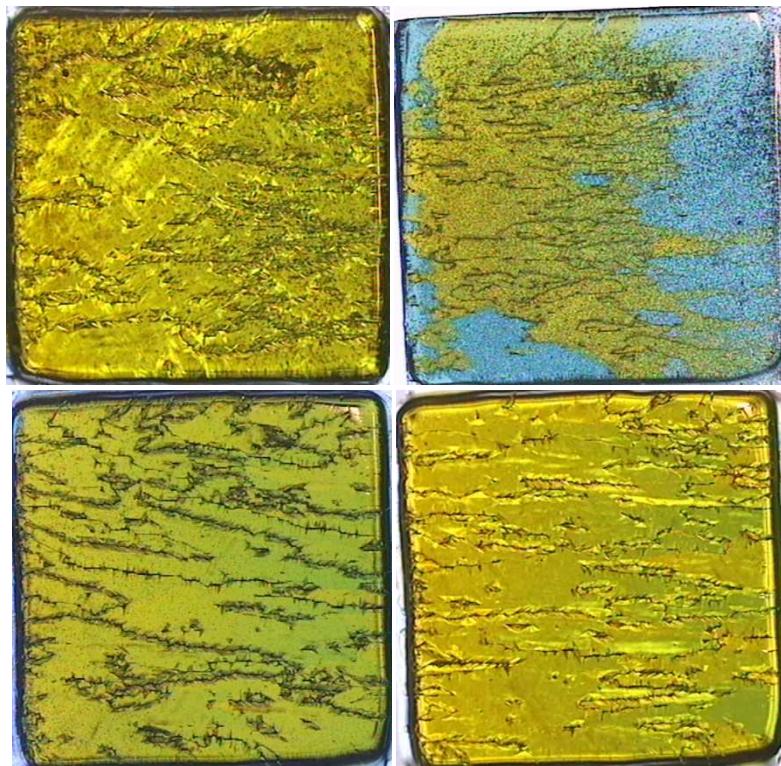


Fig.35 Overview pictures of (a) ELS357, (b) ELS360, (c) ELS361, and (d) ELS362

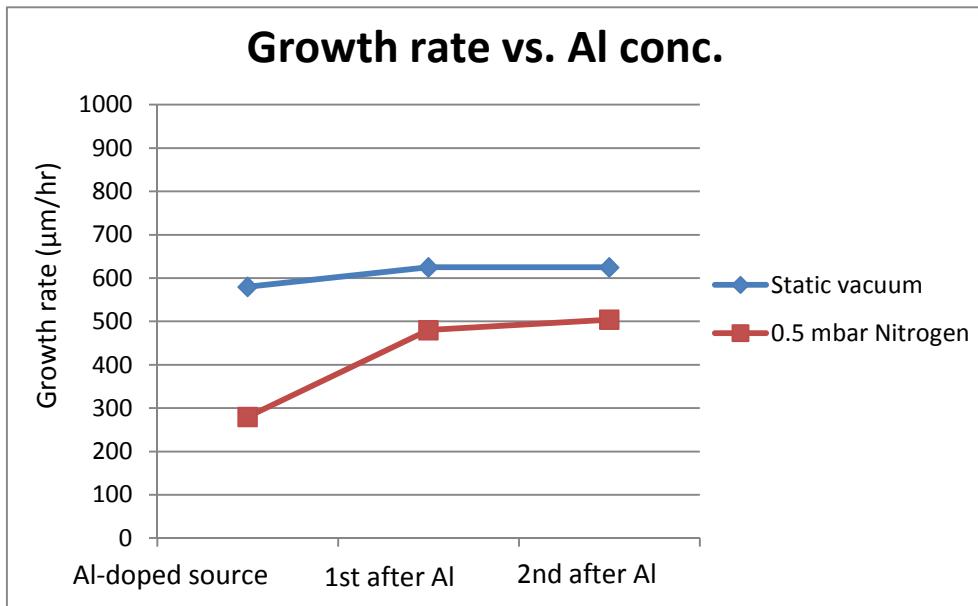


Fig.36 Growth rate changes with Al concentration in static vacuum and 0.5 mbar Nitrogen

The growth rate is probably related to a graphitization of the source for the first run, with the Al doped substrate, and the graphitization decreases with less Al.

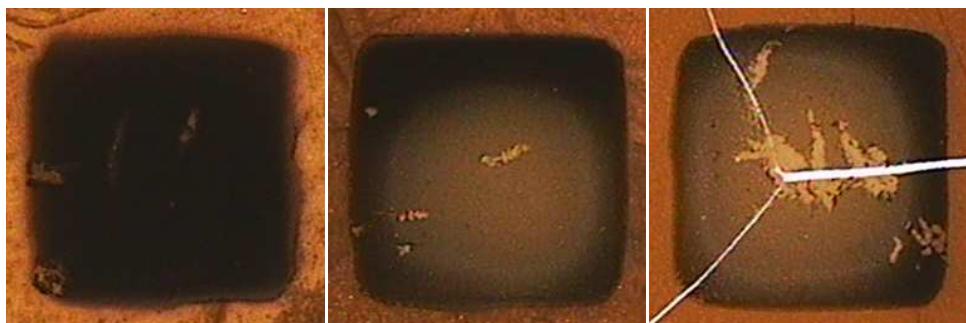


Fig.37 Sources used in samples ELS360 to ELS362 (from left to right).

The film thicknesses seem more non uniform with Al doped samples. Fig.38 shows film thickness non-uniformity of various samples. By measuring thickness of 10 random points on each sample, standard deviation divided by average thickness was calculated and called non-uniformity. The samples ELS320 to 322 are the ramp up series investigation. From ELS355 to 362 are a complete series, and we could see that with reference runs in the Al doped crucible (from a previous use of the foam for Al doped 6H) the non-uniformity of thickness is already higher than the previous three without any Al doping. Also, in both static vacuum and nitrogen ambient the non-uniformity dropped with decrease of Al concentration.

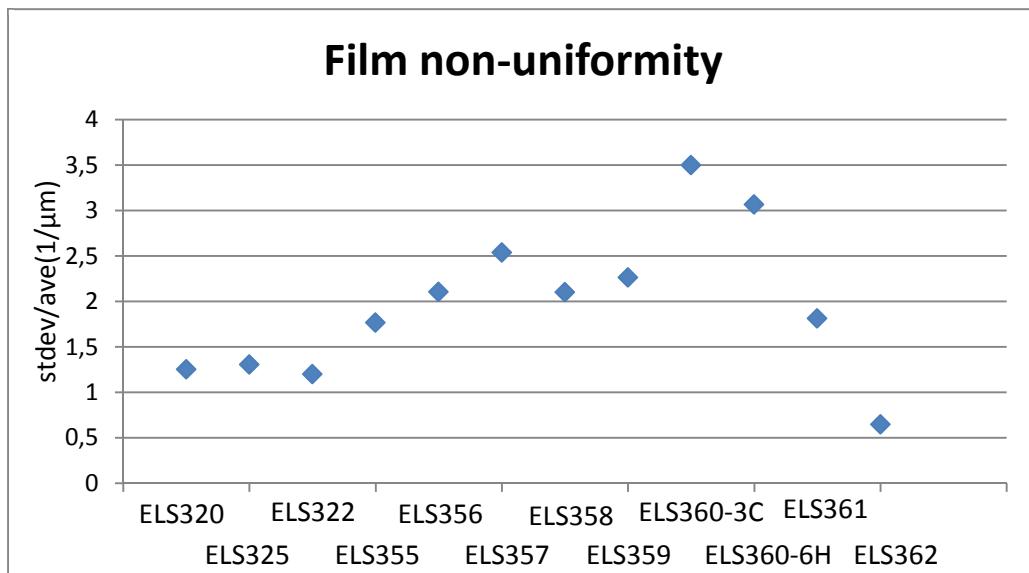


Fig.38 Film thickness non-uniformity

A nitrogen doping causes an increasing green color of 6H-SiC. The Al incorporation may be observed in 6H-SiC as an increasing bluish color. In 3C-SiC the color changes are more difficult to see. The doping of samples can be observed in photoluminescence. Fig.39 shows RTPL spectra of the purely N-doped (ELS300 and 301) and N-Al-doped (ELS357) 3C-SiC. The N-doped samples only showed the near-band-edge emission (NBE). In the Al-doped sample, however, the N-bound peak almost disappeared and N-Al donor acceptor pair (DAP) emission dominates.

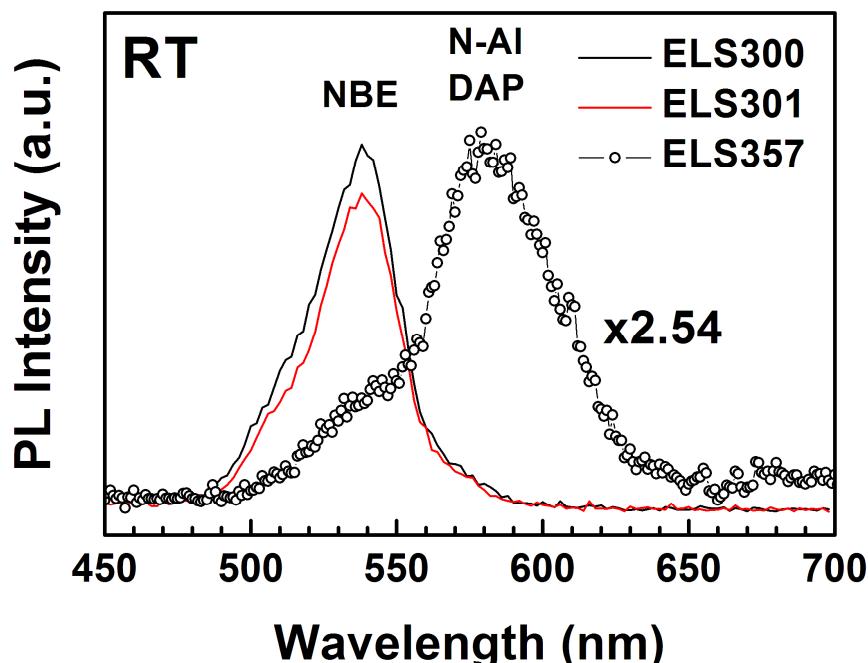


Fig.39 Room temperature Photoluminescence for ELS300, 301 and 357

Conclusion

In this thesis various conditions to optimize cubic silicon carbide by means of sublimation epitaxy using 1.2 degree off-axis 6H-substrates were investigated. For undoped series, 1950°C was found to be an optimum growth temperature with a corresponding growth rate of 600-800 µm/hr. There is an influence of ambient gas pressure on the supersaturation and the pressure consequently affects the growth rate and polytype coverage. When increasing the pressure from 0.5 to 5 mbar, the growth determining step is moved from kinetically limited to the diffusion in nitrogen. At 0.5 mbar the 3C nuclei were able to form on the edge and extend in the down-step direction while 5 mbar of nitrogen stabilized the 6H polytype.

The temperature ramp up rate also contributes to the changes of supersaturation, and the contact of Ta-foil could bring to difference in growth rate and hence different 3C coverage. But with low off-axis substrates no clear tendency could be found. This reflects that the competition of growth mechanisms is a complex relation.

The geometry of substrates and Si/C ratio affect the 3C films showed that a larger substrate results in better XRD results and higher 3C coverage, but if the influence is given by the Si/C ratio or the position of the film remains a question. The observation that 6H islands which overgrow 3C had clear spiral morphologies while the 3C that overgrow the 6H did not have clear spiral features, again show the differences in growth mechanisms.

In 3C layers with increasing thickness the 3C domains usually forms in the step flow regions and compete with each other, but after some time the dominant domains prevail over the others and distribute homogeneously. The samples with 30 min of growth have larger FWHM while samples grown for 60 and 120 min have FWHM lower than 100 arcsec, comparable with commercial 6H and 4H wafers. The growth rate decreased slightly with longer growth duration because of higher graphitization of the source.

Backside graphite plates also make a pronounced difference. The graphite plates could change the thermal gradient, so with a normal backside graphite plate not only 3C coverage but also domain enlargement are enhanced. However, a recessed plate shrinks the thermal gradient between the source and the substrate, consequently reduces supersaturation so both 3C coverage and domain sizes are suppressed.

In static vacuum, the growth rate as well as morphology is very similar from sample to sample in undoped runs or 0.5 mbar nitrogen ambient. In Al doping using 0.5 mbar nitrogen ambient, however, only the highest Al-doped sample shows bluish 6H inclusions. The growth rate is lower with higher Al concentration in the sample and a higher non-uniformity was observed. In RTPL measurements the Al together with N appear as DAP emission while only NBE was seen for samples without Al doping.

Finally, most interestingly the sample ELS319, grown for 120 min has 1.08 mm of thickness with a low FWHM, which reflects growth of high quality, bulk-like SiC by the sublimation growth method. This could be a way to develop a bulk growth method for 3C-SiC based on the findings presented in this thesis.

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