Investigation of the Growth Kinetics of SiC Crystals during Physical Vapor Transport Growth by the Application of In Situ 3D Computed Tomography Visualization

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Computed tomography using X-rays is applied during the bulk growth of silicon carbide (SiC) to investigate growth kinetics in situ during the physical vapor transport process. In addition to the standard SiC source material, in particular, a pure solid source SiC block is used. It is found that the growth rate is lowered as the sublimation of gaseous species is limited to the top part of the solid source. The morphological changes in the source area during growth differ significantly compared with the process when conventional powder is used. The formation of multiple growth centers on the surface of the seed is monitored in situ with a computed tomography system. In a series of experiments, the influence of the supersaturation on the growth is examined. The in situ computed tomography shows that the curvature of the growth interface is stronger influenced by the thermal field at higher pressures. A high supersaturation leads to the formation of rather smooth surface morphologies, whereas the formation of large steps on the surface is induced at lower supersaturations.

1. Introduction

Power devices based on silicon carbide (SiC) are able to outperform its silicon-based counterparts due to several superior physical properties of the material like the high breakdown field, thermal conductivity, and electron drift velocity. High-defect densities were limiting the device performance, but substrate vendors were able to improve the crystalline quality enabling the material to compete on the power electronics market. The low availability and high price of the substrate material is a problem for the broad application of SiC-based devices. Enabling faster switching, less power dissipation, and smaller packaging compared with silicon-based solutions, SiC devices are promising candidates for the application in electric vehicles. For a broad application in the automotive market high quantities at low price are needed, and therefore, the production of 4H-SiC wafers must increase strongly.

To achieve a high yield of high-quality boules, it is important to identify all parameters that can influence the growth process. The standard growth method used to produce SiC is the physical vapor transport (PVT) method.1 As it was shown by Wellmann et al.2 during the growth of SiC from a powder, morphological changes occur. With this work, we intend to evaluate whether these changes can be suppressed when a solid source block is used as source material and how the growth process is influenced. Furthermore, we investigate how the supersaturation of the gas species in front of the growth interface influences the growth process. In particular, we address the impact of the growth conditions on the surface morphology of the growing SiC crystal.

2. Results and Discussion

2.1. Source Material Variation

2.1.1. Crystal Growth from a Solid Source

When a solid block of polycrystalline material is used as SiC source instead of powder, fundamental changes in the growth process occur. As reported in a previous study, during the crystal growth process from powder, several changes in the source area elapse. The SiC gaseous species sublime at the hottest parts of the powder first, and is leaving behind a skeleton of low-density graphite. Simultaneously, recrystallization takes place at the colder top part of the powder. These processes lead to changes in the thermal properties of the source material. The Si-depleted zone at the crucible bottom exhibits a very low thermal conductivity, whereas the thermal conductivity in the top part increases. During growth, the size of the graphite skeleton increases, whereas the residual source area shrinks.

If a polycrystalline block of SiC is used as source material, the situation changes significantly. The solid block is not permeable for the gaseous species and therefore no gas transport from the bottom to the top of the source material is possible. As shown in Figure 1, the sublimation takes place from the top of the source...
block. Therefore, the distance between source and seed is kept nearly constant throughout the whole growth process in contrast to standard growth from powder. The disassembly of the crucible revealed that on top of the residual source block, a highly porous carbon is left behind after sublimation. Due to its small mass, it is not visible in the in situ computed tomography (CT) images. This material is similar to the graphite skeleton found at the bottom of the crucible when growth is performed from powder. From Laser flash analysis, a rather low thermal conductivity of around 1 W m\(^{-1}\) K\(^{-1}\) is derived in a previous study\(^3\) for this kind of material. As the source block is consumed from its top, it is converted into a porous graphite skeleton, because the gaseous species sublimes incongruently.\(^4\) The low thermal conductivity of the porous graphite leads to a strong drop in temperature. Hence, recrystallization of gaseous species from the hot source takes place, leading to the formation of a needle-like structure of SiC on top of the residual solid source block, visible on top of the residual source block as shown in Figure 1b.

### 2.1.2. Sublimation Kinetics

In Figure 2, the temperature profile at the growth start using a solid source block is compared with an experiment where a conventional powder source is used. The solid source material exhibits a higher thermal conductivity compared with a porous powder, leading to increased temperature at the interface of the source area and gas room. Also, the temperature at the seed surface is increased, although the measured temperature at the crucible top was similar for both experiments. As the diffusive transport conditions are similar in both cases due to an argon background pressure of 20 mbar, respectively, a simplified measure of supersaturation is used to compare the growth conditions. The supersaturation is calculated by

\[
S = \frac{p_s - p_c}{p_c} \quad (1)
\]

where \(p_s\) is the partial pressure of SiC\(_2\) at the top of the source and \(p_c\) at the growth interface. The temperature-dependent values of the partial pressures are calculated using the equations derived by Avrov et al.\(^5\) for a carbon-rich growth environment. Due to the elevated temperatures at the source and also at the seed, a supersaturation of 0.73 is calculated for the growth from the solid source. The supersaturation for the growth from powder results to a value of 0.50. In contrary, the growth rates are 90 and 330 \(\mu\)m h\(^{-1}\) for growth from the solid source and from powder, respectively. The reason for these contradicting findings is attributed to the manner of the sublimation process. While the sublimation from the solid source is restricted from the top surface, the powder source enables sublimation from hotter parts at the bottom of the source area due to its porosity. A recrystallization process at the top area of the powder and the formation of a dense disk was reported by several authors.\(^6\)–\(^9\) Due to the temperature gradient inside the powder, the subliming gaseous species from the hot bottom recrystallize in the colder top part of the powder. One could assume that in the case of a powder source, the sublimation in the hotter areas at the crucible bottom leads to an increased supersaturation at the growth front. But experiments using powder enriched with the \(^{13}\)C Isotope in the bottom part of the source clearly prove that this is not the case.\(^10\) It is shown that the sublimation occurs from the dense disk that forms on top of the powder.\(^11\) Therefore, the difference of the growth rate is attributed to the different surface area where sublimation can take place. The solid source exhibits a flat and, therefore, rather small top surface where the sublimation occurs. In the case of powder the dense disk consists of vertically elongated needles arranged in parallel to each other. This columnar structure implies a much bigger area of surface where sublimation can occur. The bigger free surface area leads to enhanced sublimation, and therefore, increased supersaturation at the growth front. For the solid source, the limited sublimation leads to the small supersaturation resulting in a slow growth rate.

### 2.1.3. Evolution of the Growth Interface

The limited sublimation influences the growth process, in particular, the start phase of growth proceeds differently. Figure 3a

![Figure 1. 2D cut through the CT data depicting the mass distribution in the experiment using a solid source block a) at the growth start and b) after 145 h of growth.](image)
shows the 3D data obtained in situ after a growth time of 12 h. Multiple small growth centers develop next to each other. As the seed is prepared on axis, the gaseous species arrive on the (0001) plane exhibiting a very low density of kink sites for incorporation in the bulk. The solid source block promotes a rather homogeneous radial temperature distribution at the seed surface. In combination with the small supersaturation, this leads to the formation of several growth centers distributed over the seed surface. At low supersaturations on low index planes, the growth via screw dislocations is the dominant growth mechanism.\[11]\] The screw dislocations initiate the growth and slowly expand to “hills” each of them forming their own facet. The hills grow laterally and slowly merge together as observed in Figure 3b,c. Finally, the crystal forms a single facet, but even after a growth time of 60 h, two distinct growth centers are visible in the in situ CT data.

2.2. Pressure Variation

2.2.1. Influence of Pressure on the Growth Interface

To better understand the influence of the supersaturation on the growth kinetics, three growth runs were conducted at different background pressures of the inert gas argon. The pressure in the growth chamber influences the transport of the vapor species from the source area to the crystal. For very low pressures, the mass transport is described by Stefan flow, while inert gas pressures higher than the partial pressures of the reactive species Si, Si$_2$C and SiC$_2$, respectively, will lead to a diffusion-dominated growth process.\[12]\] With increasing pressure, the concentration gradient of the SiC vapor species in the gas room increases. This leads to a smaller supersaturation at the growth front for the higher pressures and a higher supersaturation at the growth front for the low-pressure experiment. The growth rates of the three experiments listed in Table 1 confirm that assumption. A lower background pressure leads to a higher supersaturation,
Table 1. Growth rates of the crystals grown at 0.25, 10, and 40 mbar determined from in situ CT measurements. The length of the grown crystal was measured at several different positions from the seed surface to the growth interface of the crystal.

| Background pressure [mbar] | Mean growth rate [μm h⁻¹] | Deviation [μm h⁻¹] |
|----------------------------|----------------------------|-------------------|
| 0.25                       | 477                        | ±54               |
| 10                         | 114                        | ±18               |
| 40                         | 89                         | ±15               |

and therefore, a higher growth rate. In Figure 4, the difference of the growth front is depicted for the growth with an argon background pressure of 0.25 and 40 mbar. In the very low pressure regime, there are fewer collisions of gaseous species leading to a uniform mass transport from the bottom to the top. In the case of growth at higher background pressures, the mass transport is stronger defined by the thermal field which is shown in Figure 4c. Although, the temperature field is very similar for the two experiments, the growth interface is more convex in case of the pressure controlled growth, as the transport of the vapor species is guided into the center area of the gas room. In other words, the mass transport by diffusion is guided by the temperature gradient which means that the pathways of the gas molecules are perpendicular to the isothermal contours depicted in Figure 4c. Figure 4b shows that in the case of low pressure, the gas transport is less influenced by the temperature field, resulting in a rather flat interface.

Considering the strongly inclined crystal flanks, a rather small (0001) facet evolves with a diameter of 11.5 mm for the growth at 40 mbar, whereas the flat growth interface promotes the formation of a larger facet with a size of 21 mm for the growth at 0.25 mbar.

2.2.2. Influence of Pressure on the Step Morphology on the (0001) Facet

In addition to the influence on the shape of the crystal, morphological changes on the facet become apparent. In Figure 5a, the morphology at the rim of the (0001) facet of a crystal grown at 0.25 mbar is depicted. The surface of the facet is smooth and only steps of small height occur. A distinct transition between the facet and the step flow area at the flank of the crystal is visible. The surface in the facet area is barely disturbed by defects, whereas in the step flow area small depressions are formed. When the supersaturation is decreased larger steps occur as shown in Figure 5b. The transition between facet surface and the bended crystal flank is not very distinct and bunched steps occur. The small terraces appearing as brighter islands behind step edges are probably formed because of too rapid cooling after the growth process. When the growth is stopped by increasing the pressure, a fast drop in temperature can occur as the thermal conductivity of the insulation material is dependent on the inert gas pressure. With the increase of the Ar pressure, the thermal conductivity of the insulation increases and therefore, the temperature in the crucible decreases by 100 °C. In this case, the crystal is cooled down fast while still a lot of SiC gaseous species were close to the growth front. This led to island formation at the surface. For the other experiments, the drop in temperature was prevented by slightly increasing the heating power while increasing the background pressure to stop the mass transport. The cooling rate was the same for all experiments after stopping the growth. In the step flow area at the crystal flanks, larger defects perturb the large macrosteps forming depressions into the surface as depicted in Figure 5b. On the surface of the crystal grown at 40 mbar strong step bunching is visible on the facet and at the crystal flanks (Figure 5c). The step density is large on the facet and defects seem to impede the step flow. The macrosteps are pinned forming v-shaped grooves. At the crystal flanks, the height of the steps is increased and at defects where the step flow is hampered, large incisions into the step occur. Where the step flow is hindered, large terraces can form. On these terraces exhibiting the (0001) plane, nucleation of foreign polytypes occurred during the experiment, resulting in many polytype switches during the growth. The nucleation of foreign polytypes on large terraces is also reported by Liu et al.[13] As a result the top of the crystal consists of the 6H-Polytype as confirmed by Raman measurements. The formation of giant steps on the surface of 6H-SiC is also observed in a previous study.[14] The strong step bunching visible in Figure 5c is, therefore, attributed to the formation of the 6H-Polytype. In addition, the growth conditions led to big surface steps and large terraces in the 4H areas.

In literature, the phenomenon of step bunching at vicinal surfaces is studied extensively for the chemical vapor deposition (CVD) processing of SiC wafers[15] and is also found when growth is performed by sublimation epitaxy.[16] Due to different surface energies for the formation of a new double layer on the surface, the surface tends to form steps of half unit cell height.[17] Steps of this size can be found on top of macrosteps in.

Figure 4. a) 2D Image of the in situ CT data illustrating the growth interface of the crystal grown in diffusion-limited conditions, b) 2D Image of the in situ CT data depicting the growth interface of the crystal grown in very low-pressure conditions, and c) temperature field simulated for the experiments (note: the inert gas of argon of 40 and 0.25 mbar, respectively, has no significant impact the heat transfer inside the crucible). The temperature difference between the isothermal lines is 5 °C.
PVT-grown samples but are of a very different order of magnitude than the steps visible in Figure 5. Also, large-step morphologies can be formed during the CVD process. To reduce the free surface energy during the growth on off-cut SiC wafers, localized faceting occurs on the surface.\[18,19\] The minimization of the surface free energy is believed to be one reason for the formation of the (0001) facet in bulk crystal growth, as its surface free energy is very low.\[20\] However, due to the curved temperature field, the surface of the macroscopic facet is not completely flat but slightly bended\[21\] and in turn, a step morphology is developed. The height and width of these steps may also be influenced by localized faceting. If the crystal grows in conditions close to the thermodynamic equilibrium, i.e., at small supersaturations, the crystal tries to develop small energy surfaces.\[22\] This effect could lead to the formation of macroscopic steps as it is observed here for the growth at high background pressures. When the growth is performed at very low pressures the supersaturation increases and therefore, the step flow velocity is high. The growth process is then shifted from the equilibrium to kinetic-controlled conditions. In this case, the morphology is dependent on the growth velocity of different crystallographic directions.\[23\] Directions with a high kink density grow the fastest.\[24\] Leading sometimes to the development of hexagonal structures on the facet.\[25\] As the kink density is the highest in the <11\overline{2}0> direction, it can grow faster compared with the <1\overline{1}00> direction. Under more kinetically controlled growth conditions, the morphology at the surface seems smoother as shown in Figure 5a.

Dependence of the step structure in the facet plane on the growth temperature has been investigated by Ohtani et al.\[26\] At lower temperatures, bigger steps with large terraces were formed while the step size decreased with increasing temperature. The authors discuss it in terms of nitrogen-induced step bunching as also reported in a previous study.\[27\] But also enhanced nitrogen incorporation due to enhanced adsorption kinetics on the crystal surface at lower temperatures is taken into account. From our findings, it is difficult to assign the origin of the step bunching. Two phenomena are conceivable: either increased nitrogen incorporation into the crystal causes increased step bunching or due to the step bunching large (0001) terraces are exposed to the gas room enabling the carbon substitution by nitrogen and leading to increased dopant incorporation. In the latter case, the increased nitrogen doping at lower temperatures in a previous study\[28\] could also be affected by step bunching due to lower supersaturations. Nevertheless, the nitrogen partial pressure may influence the surface morphologies as shown in Figure 5 because with decreasing background pressure the relative amount of nitrogen in the gas phase decreases. Also, the different shapes of the crystals resulting from the difference in mass transport mentioned in Section 2.2.1 may influence the surface morphology. A crystal comprising surfaces strongly inclined from the basal plane may form higher steps compared with a more flat evolving crystal. As the different step morphologies are also formed on the very flat facet area this effect should play a subordinate role here.

### 3. Conclusions

We have demonstrated that the use of a solid source material is a feasible alternative to a conventional powder source. The morphology of the solid source evolves differently compared with the sublimation behavior of powder. Porous graphite is formed on top of the source as it is consumed. As the sublimation is restricted from the top of the source, the supersaturation and therefore, also the growth rate is decreased compared with a growth run from conventional source material. The very small supersaturation led to the formation of multiple growth centers at the beginning of the experiment as observed live in the experiment by the in situ CT. To evaluate the influence of the
supersaturation on the morphology of the (0001) facet, growth runs at different pressures were conducted. Enhanced step bunching is found for the growth at 40 mbar leading to polytype instabilities. It is concluded that for high pressures, the growth is closer to equilibrium conditions, enhancing localized faceting to achieve minimal free surface energy. This leads to the formation of high step surfaces and wide terraces, facilitating the nucleation of foreign polytypes. For high supersaturations, we find smoother surfaces indicating more kinetically governed growth conditions.

4. Experimental Section

PVT Growth of SiC: 4H-SiC of 75 mm size was grown in a PVT setup using an induction coil to heat the graphite crucible inside the growth chamber. For the experiments evaluating the solid source material, the temperatures measured at the top of the crucible were 2140 °C. The background pressure was set to 20 mbar using Ar mixed with 9% N₂. An undoped polycrystalline boule produced by PVT was used as the solid source block. For the reference growth run, SiC powder produced in our laboratory was used as the source material.

For the experiments with varying growth pressure, the background pressure of Ar mixed with 9% N₂ was set to 0.25, 10, and 40 mbar. All growth experiments were performed using on-axis 4H-SiC seeds with the (0001) plane facing toward the powder.

In Situ CT Measurements: The CT system consists of a digital flat panel X-ray detector (PaxScan 2520 D/CL, Varian Medical Systems) and a 125 kVp DC tungsten anode tube (SB-125-700-P, Source-Ray, Inc) as X-ray source. For each measurement, 400–800 2D projections were taken while the inner setup was rotated incrementally by 360°. The 3D geometry was computed with the Feldkamp Algorithm.

Numerical Modeling: The temperature field was modeled by the finite element method using the commercial software COMSOL Multiphysics.

Optical Microscopy: The microscopy images were acquired with a Polyvar Met microscope from Reichert-Jung using differential interference contrast (DIC).

Raman Measurements: Raman measurements were conducted with a Horiba Jobin LabRam HR Evolution confocal microscope using a grating of 1800 g mm⁻¹ and a laser wavelength of 457 nm.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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