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Nucleation and growth of polycrystalline SiC

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Abstract. The nucleation and bulk growth of polycrystalline SiC in a 2 inch PVT setup using isostatic and pyrolytic graphite as substrates was studied. Textured nucleation occurs under near-thermal equilibrium conditions at the initial growth stage with hexagonal platelet shaped crystallites of 4H, 6H and 15R polytypes. It is found that pyrolytic graphite results in enhanced texturing of the nucleating gas species. Reducing the pressure leads to growth of the crystallites until a closed polycrystalline SiC layer containing voids with a rough surface is developed. Bulk growth was conducted at 35 mbar Ar pressure at 2250°C in diffusion limited mass transport regime generating a convex shaped growth form of the solid-gas interface leading to lateral expansion of virtually [001] oriented crystallites. Growth at 2350°C led to the stabilization of 6H polytypic grains. The micropipe density in the bulk strongly depends on the substrate used.

1. Introduction

Fluorescent silicon carbide (f-SiC) is a promising candidate in the field of optoelectronics for the fabrication of a novel monolithic all-semiconductor white LED structure [1]. Such devices require thick layers (> 100µm) of high crystalline quality and proper doping. The fast sublimation growth process (FSGP), a sublimation epitaxial technique, is proven to fulfil these requirements for growing f-SiC [2] when adequately doped solid state source materials are applied. In the case of fluorescent SiC, the research is very new and donor-acceptor co-doped sources are necessary. As no such materials exist we have previously reported on polycrystalline nitrogen and boron doped bulk SiC crystals grown using the physical vapour transport (PVT) technique [3]. It was also stated elsewhere that such source material is beneficial regarding minimization of graphitisation in the source and achievable layer quality at high growth rates [4].

In this work we investigate the growth of SiC crystallites on isostatically pressed highly purified and hereon deposited pyrolytic graphite substrates at the initial stages of growth of polycrystalline bulk SiC source material, i.e. when diffusion limited mass transport is activated due to the decrease of the environmental argon system pressure. The shape of the crystals, their orientation and density distribution in radial direction of the substrate is treated using optical and electron microscopy (SEM) as well as x-ray powder diffraction (XRD) as analytical methods. The results are in agreement with the temperature field distribution inside the growth chamber derived from numerical calculations using the Virtual Reactor® code. Moreover, results from polycrystalline bulk growth experiments on the before mentioned substrates at higher temperature are presented and the influence on polytype stabilization and structural quality is discussed. Additionally, the modification of texture during bulk growth is explained in terms of growth kinetics.
2. Experimental

Polycrystalline SiC boules were grown by the physical vapour transport (PVT) technique [5] in an inductively heated 2 inch setup. The complete process consists of the following steps: (I) evacuation of the reactor and heating with moderate power, (II) filling to 800 mbar with Ar and heating until the set temperature is reached, (III) pumping down to growth pressure and growth and (IV) refilling with Ar to 800 mbar and reduction of the heating power. Two kinds of substrates were used: (a) isostatically pressed highly purified graphite (referred to as isostatic graphite) and (b) isostatic graphite with a pyrolytic graphite coating (referred to as pyrolytic graphite). In Table 1 the characteristics of the two substrate materials are summarized. The main difference is that the pyrolytic graphite has no open porosity and is [001] textured [6] whereas the isostatic graphite is isotropic regarding its grain orientation. Isostatic graphite substrates were used as-machined resulting in relatively high surface roughness RMS values. Due to the pyrolytic coating the surface roughness is slightly reduced.

<table>
<thead>
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<th>Table 1. Characteristics of the seeds used in this work</th>
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<td>Surface roughness (µm)</td>
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<td>Isostatic graphite</td>
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<td>Pyrolytic graphite</td>
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In order to investigate the nucleation process and layer formation three interruption experiments were carried out (referred to as sample A, B and C) during the first part of process step (III) which is displayed in Figure 1. Sample A was ended up at 800 mbar after temperature reached convergence at 2185°C. Sample B was interrupted 90 min after pumping down was initialized at 266 mbar and 2195°C. Sample C was terminated 180 min after sample A when 35 mbar (growth pressure) was reached and the corresponding temperature was 2233°C. Note that pressure reduction follows an exponential decay and results in reduced thermal conductivity of the insulation which causes the temperature increase. Samples A and C were nucleated on isostatic graphite, sample B on pyrolytic graphite. Bulk growth experiments were conducted at 35 mbar Ar atmosphere with various doping concentrations for 50h growth time and are described in more detail elsewhere [3].

Figure 1. Excerpt of the growth process at the initial stage of nucleation showing the exponential decay of the pressure (solid line, left scale) and corresponding temperature (dash-dotted line, right scale). Interruption experiments A, B and C are denoted at the left side. Thin lines are drawn to guide the eyes.

Numerical modelling using the software package Virtual Reactor© was applied to determine and optimize the temperature field and distribution in the growth cell. The initial nuclei and grown layers were investigated using optical and scanning electron microscopy, micro-Raman spectroscopy as well as XRD in Bragg-Brentano geometry. Polycrystalline boules were cross-sectional sliced and polished with diamond suspension to surface roughness RMS values below 3 nm.
3. Results and Discussion

3.1. Nucleation of SiC on graphite

Sample A was aborted after the set temperature (2180°C) was reached at 800mbar. At this pressure regime in conjunction with the distance of 30 mm between the SiC powder source material and the graphite substrate, mass transport is expected to be low [7]. Moreover, the system is in near-equilibrium conditions due to slow heating afore and the dwell period of 1h after the last heating step in which no significant temperature increase is measured by the optical pyrometer on top of the crucible. This assumption is confirmed by numerical simulation (Fig. 2 bottom) where the axial temperature gradient is calculated to be as low as 20 K/cm at the symmetry axis of the setup, i.e. the left border of the plot. Herein the temperature difference between isolines is 1 K. The calculated mass transport is displayed by small arrows where thick ones indicate increased transport compared to thin ones, corresponding to region I, III and II, respectively. Note that those regions are centro-symmetric circles when viewed normal to substrate surface which can be seen in the middle of Fig. 2 where a corresponding section of a photograph of the graphite substrate with nucleated crystals is shown. It is obvious that in region I and III the density of crystals is higher and the crystal size is increased compared to region II. Thus experiment and numerical modelling are consistent with each other.

![Figure 2](image)

**Figure 2.** Numerical simulation of the temperature distribution near the graphite seed (bottom) for process parameters of sample A, respective section of a photograph (middle) and SEM images of the marked areas (top left and right). Temperature difference between isolines is 1K.

The reason for increased growth of crystals in region I and III is the lower temperature of the substrate and the increased axial temperature gradient, respectively, both resulting in higher local
supersaturation compared to region II. Generally, when the supersaturation increases the nucleation frequency increases while the crystal size is supposed to decrease. The reason for the observed larger crystals in region I and III is that the initial nucleation occurred before sample A was aborted between Si-rich gaseous species and the graphite. Thus the herein displayed crystallites result from grain selection and growth due to kinetics. Nevertheless, nucleation started earlier in the two regions mentioned before resulting in an increased growth time. A more detailed view into region I and II (Fig. 2 top) exhibits SiC crystals of hexagonal platelet shape, known as the close to the equilibrium shape of the 4H, 6H and the rhombohedral 15R polytype, deduced from spontaneous nucleation in Lely growth experiments. Such crystals reveal large {001} faces as well as inclined {h0l} pyramidal and {100} prismatic planes. As can be seen the majority of crystals show inclination between the <001> direction and the normal to the surface (Fig. 3 top left). Moreover, growth occurs dominantly along the <110> directions on the {001} faces resulting in the formation of the above mentioned pyramidal and prismatic planes and the platelet nature of the crystals. Note that no crystals were found showing the kinetic form of the cubic polytype which was also confirmed by micro-Raman measurements. That is because the process conditions are not favourable for the growth of β-SiC that is known to appear at lower temperatures and high temperature gradients resulting in high supersaturations.

**Figure 3.** XRD patterns of samples A, B and C (bottom), relevant reflexes are edited. SEM pictures of the samples (middle) and corresponding outtakes (top).
In order to investigate the further growth of the crystals and to determine when a closed poly-SiC layer is formed on the graphite substrate experiments B and C were carried out and XRD powder diffraction was measured (Fig. 3 bottom) where diffraction peaks were identified using powder diffraction files PDF 00-029-1131 for 6H, PDF 00-022-1317 for 4H and PDF 01-072-4530 for 15R. From the XRD and Raman measurements it is derived that the crystals are a mixture of the 4H, 6H and 15R polytype, which can also be seen from the cross-sectional cut of a bulk crystal in Fig. 4. When taking into account relative diffraction intensities from homo-polytypic SiC powders with statistically distributed crystals one can conclude that texture is present at all samples, nevertheless it is hardly possible to distinguish to which amount each polytype incurs into the total intensity of the individual diffraction peaks since multiple reflexes may overlap. Despite this, the (102), (202) planes of 6H and the (015), (1,1,15) planes of 15R do incline approximately 62°, 75° and 71°, 73° with the {001} face, respectively, and such crystals can be seen on the corresponding SEM images (see arrows in Fig. 3 top left). Sample B was grown on pyrolytic graphite and the XRD pattern shows one distinct reflex at 2-Theta 35.7° accounting for growth on (102) and the basal plane of 6H, since lattice spacings are nearly equal. Moreover, the reflex also accounts for (105) of 15R as well as <001> oriented 4H. Nevertheless, micro-Raman measurements revealed that the majority of crystallites are of 6H polytype. Thus growth on pyrolytic graphite results in enhanced texturing but not solely on the {001} faces (Fig. 3 middle column). Regarding the coverage of the graphite substrate surface it can be mentioned that a closed layer containing voids is present at the process conditions of sample II. Such voids never completely disappear during on-going growth and are the reason for the formation of micropipes penetrating the bulk crystal as described to some more extent in the following section.

3.2. Bulk growth of polycrystalline SiC

Bulk crystals were grown at 35 mbar Ar pressure for 50h growth time at temperatures of 2250°C or 2350°C on isostatic and pyrolytic graphite substrates. Since at this pressure diffusion limited mass transport is present, growth forms of the crystals are observed displaying the curvature of the temperature field inside the crucible (Fig. 4). Contrary to the close to the equilibrium shapes of the crystallites during the initial growth stages resulting in a rough surface, the latter begins to smoothen with shapes that are convex. Note that mass transport in Fig. 2 is calculated for the initial growth stages at 800 mbar and depicts only the region close to the graphite gas interface therefor most of the mass flow vectors are aligned normal to the substrate surface. The resulting growth form (calculation not shown here) develops during growth in which grain selection and coarsening commences. It was shown elsewhere that grains with low inclination angles between the [001] direction and the normal to the surface laterally overgrow heavily inclined grains resulting in less variation of the off-axis orientation of the individual grains during growth, i.e. texturing towards [001] is observed [3,8]. This lateral overgrowth can lead to the formation of voids in areas where heavily inclined platelets enclose empty space that is not filled before being overgrown. Thus a micro-cavity is formed in which a temperature gradient is present leading to sublimation within the bulk material and the formation of micropipes propagating along the growth direction.

Figure 4. Polycrystal grown on isostatic graphite at 2250°C (left) and on pyrolytic graphite at 2350°C (right). Note that the narrowing at the side on the right-hand side crystal is due to removed graphitized areas.
It was found that the adoption of pyrolytic graphite strongly reduces the micropipe formation which is attributed to the fact that the initially grown crystallites are highly textured and thereby the probability of empty space formation between individual platelets is reduced. Bulk growth at 2350°C led to the stabilization of the 6H polytype for most of the grains (Fig. 4 right) which is known to be the high-temperature stable modification of SiC during bulk growth. Compared to growth at 2250°C, where grains in the millimetre range are obtained, grains up to 20 mm in length were established depicting the fact that the grain size as well as the polytype is a function of the growth temperature.

4. Conclusion
We have grown polycrystalline SiC bulk crystals on either isostatic or pyrolytic graphite substrates at 2250°C and 2350°C in a 2 inch PVT growth setup at 35mbar Ar pressure. Growth of initial crystallites of SiC was investigated at 800 mbar, 266 mbar and when reaching 35 mbar. It was found that under near-thermal equilibrium conditions at 800 mbar crystals exhibit forms close to the equilibrium shape. Their radial density distribution and size is a function of the temperature field and the corresponding temperature gradients inside the growth cell. When employing pyrolytic graphite as substrate increased texturing towards the [001] direction is observed. When mass transport is initiated the crystals emerge and form a dense polycrystalline layer with a rough surface and included voids being the reason for micropipe formation in the bulk, which can be significantly suppressed by using pyrolytic graphite. Due to the formation of growth forms the surface smoothens and lateral overgrowth takes place leading to grain selection and coarsening. Bulk growth at 2350°C led to the preferential formation of 6H polytypic grains.

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