

Investigation of the Nucleation Process During the Initial Stage of PVT Growth of 4H-SiC

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Abstract. Due to high growth temperatures during the physical vapor transport (PVT) it is still almost impossible to gain proper insight into the actual growth conditions. Therefore, computer tomography (CT) is used as an in-situ monitoring during the crystal growth process. With the help of this technique, it is possible to observe the nucleation centers during the initial stage of growth (CT after 0 h) of a 4H-SiC single crystal. These growth islands are likely formed before the actual growth conditions are reached. Raman investigations of the area around a growth island located directly on the interface between seed and grown crystal is used to support this assumption. In addition, optical analysis after KOH etching were made to reveal the defects around the growth island. The island exhibits a inhomogeneous doping concentration in comparison to the surrounding grown crystal.

Introduction

Silicon carbide (SiC) is a superior semiconductor for high power electronics. In recent years, the physical vapor transport (PVT) method to grow bulk SiC single crystals has been established (for a review see [1]). Due to the high temperatures during the growth process it is still almost impossible to gain proper insight into the actual growth conditions. However, with the help of computer tomography (CT) it is feasible to establish an in-situ monitoring of the grown crystal during the growth process. The growth cell is radiographed with X-rays, while the crucible is rotated which results in a 3D-radiogram. In this way, it is possible to observe the crystal during growth and to draw conclusions about the existing growth rate or growth conditions. The detailed setup is described in [2, 3]. During the growth process several CTs are made.

In this work a n-type doped 75 mm 4H single crystal is grown with an 4°-off-cut angle to the {11 $\bar{2}$ 0}-plane. The CT-radiogram at the initial stage of growth (0 h), where the growth pressure was just reached, reveals some growth islands. These islands are likely formed before the actual growth conditions are reached. Especially a growth island, which lays exactly on the interface between seed and grown crystal is of interest. To support this assumption, Raman measurements (maps and line scans) were carried out in the area around this growth island on a wafer directly above the seed. In addition, this wafer was also etched with molten KOH to reveal defect structures and analyzed under an optical microscope.

Experimental

A n-type doped 75 mm 4H single crystal is grown with an 4°-off-cut angle to the {11 $\bar{2}$ 0}-plane through the physical vapor transport at approximately 2100°C, measured on the crucible lid. The growth cell is equipped with computer tomography (CT). The detailed setup is described in [2, 3]. During the growth, CTs are made at different stages of growth. The grown crystal was sliced in wafer with an

off-cut, like it is shown in Figure 1. The wafers were scanned with an Epson Perfection V800 Photo with an optical resolution of 2400 dpi, to get an overview about the whole wafer. Raman measurements were carried out with a Horiba LabRAM HR Evolution confocal Raman microscope. The wavelength of the used diode-pumped solid-state laser was 532 nm. The magnification of the microscope was set to 50 x and the grating to 1800 gr/mm. Maps around a growth island located directly on the interface between seed and grown crystal in the area of the FTO (776.6 cm^{-1} - 777.1 cm^{-1}) and the LOPC (960 cm^{-1} - 1035 cm^{-1}) were taken. Moreover, line-scans above this area were made. The doping concentration was calculated from the peak shift of the LOPC after an approximation of Nakashima et al. [4]. The relative stress was also estimated from the peak shift of the FTO after an approximation of Sugiyama et al. [5]. Afterwards the wafers were etched with molten KOH to reveal defect structures and analyzed under an optical microscope (Axio M1m Image from Carl Zeiss).

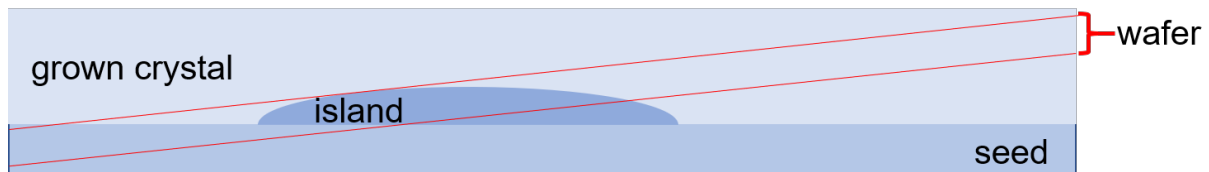


Figure 1 Schematic drawing of the orientation of the wafer prepared out of the grown 4H-SiC single crystal. The wafer were prepared with an off-cut.

Results and Discussion

The CT-radiogram at the initial stage of growth (0 h), when the growth pressure was just reached, is shown in Fig. 2a). The radiogram reveals several growth islands, which show a dark contrast in comparison to the surrounding material of the seed surface. An optical scan of the wafer above the seed (Fig. 2b) shows a varying defect distribution between the growth islands and the surrounding material. Especially a nucleus, which lays exactly on the interface between seed and the first layer, presents a pronounced difference. Fig. 2b) shows the interface between seed on the left side and the grown crystal on right side, which is indicated with the dotted line. The red square indicates the area around the growth island. The interface between seed and first layer can be observed in these images due to slight off-cut angle of the wafer to the growth direction.

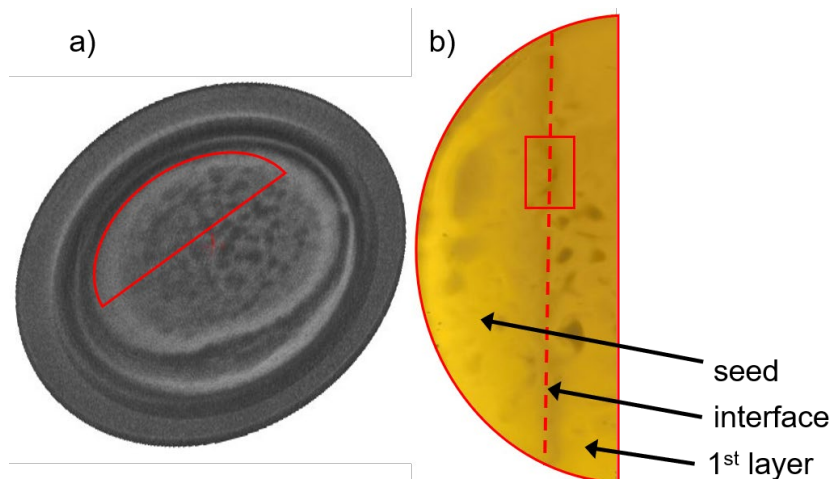


Figure 2 Overview of the measurement area. a) shows the CT-radiogram of the seed crystal during the initialization of growth (0 h CT). The red semicircle represents the area around the seed, which is discussed in this paper. b) is an optical image of the same area as portrayed in a). The interface between seed and first layer of growth is indicated by a dashed line. The area around the growth island which is located exactly on this interface is indicated by a rectangle.

The KOH etched interface is illustrated in Fig. 3a) and b), where the red rectangle in Fig. 3a) indicates the region around the island as well. The interface shows a cluster of different dislocations, which are aligned along the interface. In contrast, an almost dislocation free area lies directly on the region, where the growth island is supposed to be. This observation indicates, that a distinct amount of stress is introduced on the direct interface between seed and grown crystal. Some authors [6, 7] suggest that this stress arises from an abrupt increase of dopant concentration during the initial stage of growth in comparison to the seed.

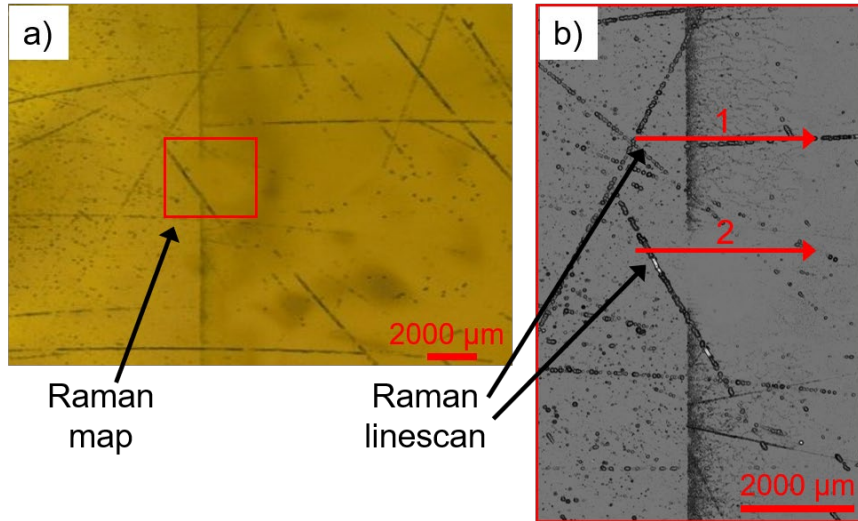


Figure 3 Optical Images of the etched area around the growth island. a) shows the optical image of the etched area around the growth island. The rectangle indicates the area for the Raman maps. b) shows the same area within the rectangle with higher magnification. The red arrows (1 and 2) indicate the positions of the line scans. Line scan 1 is located directly over the interface between seed and grown crystal. Line scan 2 is measured from seed over the growth island to the grown crystal.

To further characterize the growth island, Raman maps and line scans are taken. The FTO and LOPC-peaks are investigated. The maps are shown in Fig. 4 a) and b), respectively. The edge of the map is cropped due to a shift during the Raman measurement and for the FTO the background shift was subtracted. Due to the fact that Raman bands shift with stress, because the atomic distances are changed under stress, the FTO-peak position can be utilized to evaluate the stress in a crystal in a relative manner [8]. Compressive stress leads to a peak shift to a higher frequency and a tensile stress to a lower frequency [5, 9]. The FTO-peak position of stress free 4H-SiC single crystals lies around 777 cm^{-1} [5, 6]. Since the longitudinal optical (LO) mode interacts with free carriers (plasmon), which form the LO phonon-plasmon coupled (LOPC) mode, the LOPC mode changes sensitively with the free carrier density [8, 10]. The LOPC-peak shifts to higher frequency with increasing carrier density. Thus, the LOPC-peak position can be used to calculate the carrier concentration in SiC [4, 8]. On the one hand, the map of the FTO-peak position (Fig. 4a) reveals a similar peak shift of growth island, seed and grown crystal. On the other hand, the direct interface between seed and grown crystal shows a distinctive deviation to the surrounding material. The LOPC-peak position indicates a different carrier concentration between seed and grown crystal in the order of approx. $6 \cdot 10^{18}\text{ cm}^{-3}$ (Fig. 4b). The difference in carrier concentration between seed and growth island is only in a range of approximately $3 \cdot 10^{18}\text{ cm}^{-3}$ and is thus only half as large. The interface between seed and grown crystal shows the highest peak shift and thus indicates the most pronounced difference of the carrier concentration and therefore an abrupt transition. However, the seed has the lowest carrier concentration.

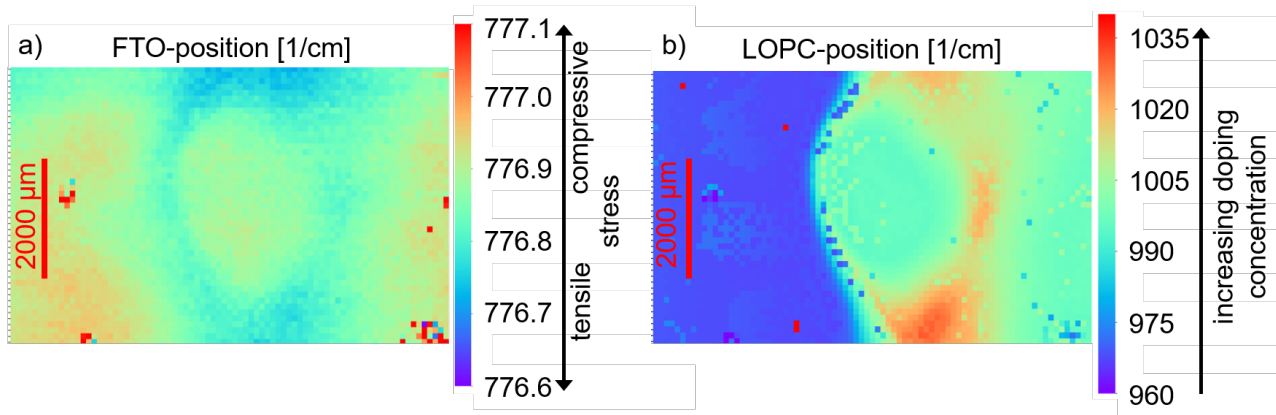


Figure 4 Comparison of FTO- and LOPC-positions in the area around the growth island. a) shows the map of the FTO-peak. The left side of the image represents the seed. b) is the map of the LOPC-peak whereof the distribution of the doping density can be estimated. The edge of the map is cropped due to a shift during the Raman measurement and for the FTO the background shift was subtracted. The FTO-peak position (a) indicates a tensed region at the boundary of the growth island and a more tensed region at the direct interface between seed and grown crystal (blue color). The LOPC-peak position indicates more pronounced increase (red color) of the doping concentration at the direct interface in comparison to the growth island.

Besides the Raman maps two line scans are carried out. The diagrams of the LOPC-peak position are illustrated in Figure 5. The dashed line indicates the interface between seed and grown crystal. The first line scan (line scan 1) reaches from the seed over the interface to the grown crystal (Fig. 5a). In contrast the second line scan (line scan 2) is measured over the growth island on the interface (Fig. 5b). Line scan 1 shows an abrupt transition from seed (left side) to grown crystal (right side), where a pronounced increase of the doping concentration can be observed. In contrast the growth island shows a smoother transition to the seed and grown crystal. Nakashima et al. [4] determine a simple relationship between the carrier concentration and the LOPC mode frequency relative to the bare LO phonon frequency in pure 4H-SiC. This relationship is used to calculate the carrier concentration of both line scans. The only value, which is needed for the calculation besides the LOPC-peak position of the Raman measurement, is the frequency of the LO phonons ω_L of undoped 4H-SiC. For the setup used, ω_L was determined to be 963.46 cm^{-1} based on Hall measurements by Steiner et al. [6]. Similar values were also reported in literature [4, 8]. In both line scans the seed has the lowest carrier concentration of $8.2 \cdot 10^{17} \text{ cm}^{-3}$. In line scan 1 the area on the interface and the grown crystal have a carrier concentration of $6.9 \cdot 10^{18} \text{ cm}^{-3}$ and $4.4 \cdot 10^{18} \text{ cm}^{-3}$, respectively. In line scan 2 the growth island has a carrier concentration of $4.0 \cdot 10^{18} \text{ cm}^{-3}$ and the grown crystal of $5.0 \cdot 10^{18} \text{ cm}^{-3}$. The high peak in the second line scan at the x-position of approximately 0.2 mm leads to a calculated value of $6.4 \cdot 10^{18} \text{ cm}^{-3}$. The pronounced increase in doping concentration at the interface can be explained by an unintentional increase of nitrogen in the gas phase. This increase likely comes from residual nitrogen present in isolation material and growth ambient, which will experience desorption during the initial pressure decrease [6].

The growth island reveals a lower doping concentration in comparison to the interface between seed. Thus, it can be expected, that the growth islands (= local redistribution of SiC species on the seed surface) are grown before the actual crystal growth or seeding nucleation (= transport of new SiC-related species from the SiC powder source materials to the seed) starts. Throughout further crystal growth, the growth islands will coalesce and introduce additional stress within the crystal [6, 7, 11]. Therefore, the formation of these growth islands should be prevented. Since the growth islands are observable in the CT-radiogram at 0h of growth, the in-situ computer tomography can be used to identify an insufficient seeding during the initial stage of growth.

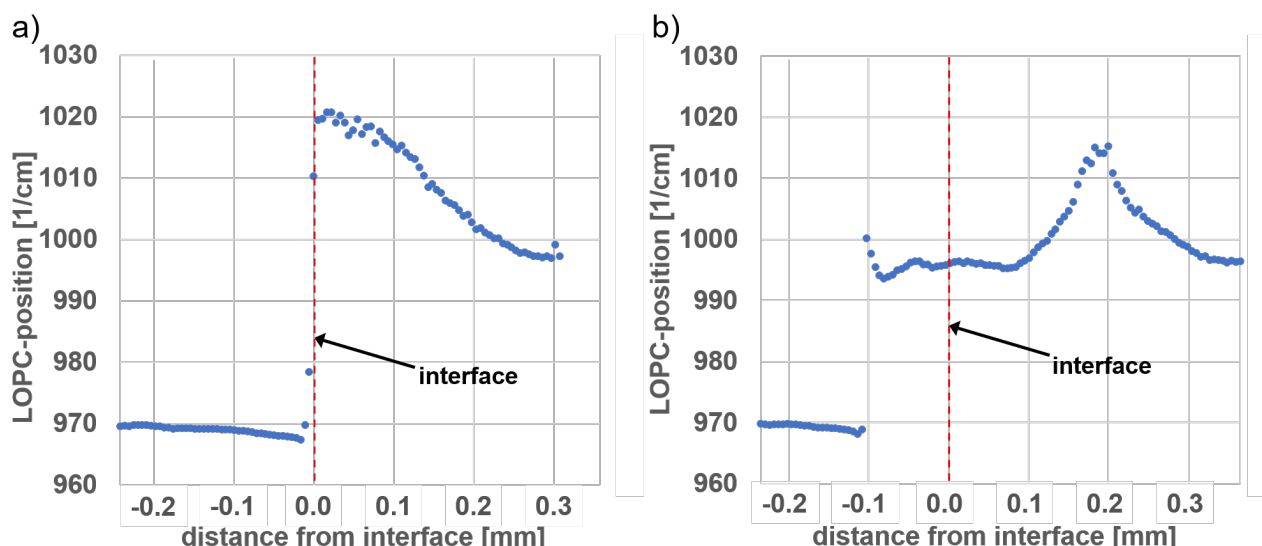


Figure 5 Diagrams of the peak position of the LOPC of the both line scans (1 and 2) in the area of the growth island. The interface between seed and grown crystal is represented by the dashed line. a) shows the peak position of line scan 1 from the direct interface between seed and grown crystal. b) shows the peak position of line scan 2, which goes from the seed over the growth island to the grown crystal. The peak shift of a) (line scan 1) exhibits a more drastic increase at the interface than the peak shift of b), where the growth island reveals a smoother transition.

Summary

In this paper it was shown, that the in-situ visualization via computer tomography can be used to observe the nucleation process during the seeded sublimation growth of SiC. Nucleation centers on the seed are visible and indicate an improper initial stage of growth. The doping concentration of a growth island, which lies directly on the interface between seed and grown crystal, was calculated from the LOPC-peak position. The growth island exhibits a lower doping concentration. This indicates that these nucleation centers were grown before the growth conditions are reached. In the current case is obvious that it is mandatory to match the doping levels of the seed and the grown SiC boule by fine tuning the doing gas fluxes in the initial stage of PVT growth.

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