

Analysis of the Morphology of the Growth Interface as a Function of the Gas Phase Composition during the PVT Growth of Silicon Carbide

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Abstract. The growth conditions of 75 mm SiC crystals in the PVT process is varied by different methods while the temperature field is kept constant. The addition of graphite into the source material leads to the formation of an ordered step flow with step heights of 0.014 μm , while the addition of graphite into the source together with N_2 doping changes the step kinetics on the main facet, leading to very large, bunched steps of 0.17 μm . When elemental Si was added into the source material large macro steps are formed on the whole crystal surface. While the doping induced step bunching is related to the incorporation kinetics, the large steps induced in Si-rich conditions are attributed the reduction of surface energy. With the variation of the inert gas pressure the morphology of the surface is altered, similarly. Under low pressure conditions (0.2 mbar) a fine step structure evolves, while at a high pressure (40mbar) large surface steps are formed on the whole growth interface. Large surface steps are strongly impeded in their lateral motion at defects permeating the growth interface. At these sites the formation of foreign polytypes is facilitated.

Introduction

The technology to grow 4H-SiC single crystals has matured and suppliers continuously improve the crystal quality and increase the diameter. With the transfer to renewable energies and to a decarbonization of the individual traffic, the demand for SiC based power devices rapidly increased. The growth of SiC is limited to crystal-lengths of several 10 mm due to the large temperature gradients and the necessary high temperatures make the process energy intensive. This makes the industrial growth of SiC expensive due to the required manual labor for every growth run and the high energy costs. It is therefore very important to find a process window with a high yield of high-quality crystalline material of the desired polytype.

While in the literature mainly the influence of the doping gas N_2 on the step morphology is discussed [2], we present a simultaneous correlation of nitrogen doping, C/Si-ratio and inert gas pressure which influence the surface morphology of the growing crystal. As SiC occurs in the form of several polytypes, a fine structure of growth steps is advantageous to prevent the nucleation of foreign polytypes [1].

Experimental

Several 75 mm 4H-SiC crystals were grown by the PVT method in the same temperature field while the gas phase composition was varied by different methods (see Table 1). The crystals were grown at a temperature of 2120-2140°C measured at the top of the crucible which corresponds to a temperature of 2350-2370°C at the seed surface as estimated by numerical simulation. Growth is performed on the c-polar face of 75 mm 4H-SiC seeds and powder from the same batch is used for all growth runs.

In a set of experiments, additional 20 wt% of graphite (crystal #1) or silicon (crystal #3) were mixed into the SiC source powder, respectively, without intentional doping. To discriminate the influence of the doping gas N₂ also an experiment with additional graphite and nitrogen doping was conducted (crystal #2). For these experiments an inert gas pressure of 10 mbar is established with Argon. Furthermore, the gas phase composition is varied without additions to the source material, by carrying out crystal growth processes at different inert gas pressures of 0.2 mbar (crystal #4) and 40 mbar (crystal #5) changing the mass transport of the reactive gas species to the growth interface.

Table 1: Growth parameters of the SiC crystals.

| Crystal | #1 | #2 | #3 | #4 | #5 |
|------------------------|----|----------------|----|----------------|----------------|
| Addition to source | C | C | Si | - | - |
| Doping | - | N ₂ | - | N ₂ | N ₂ |
| Growth pressure [mbar] | 10 | 10 | 10 | 0,2 | 40 |

Results and Discussion

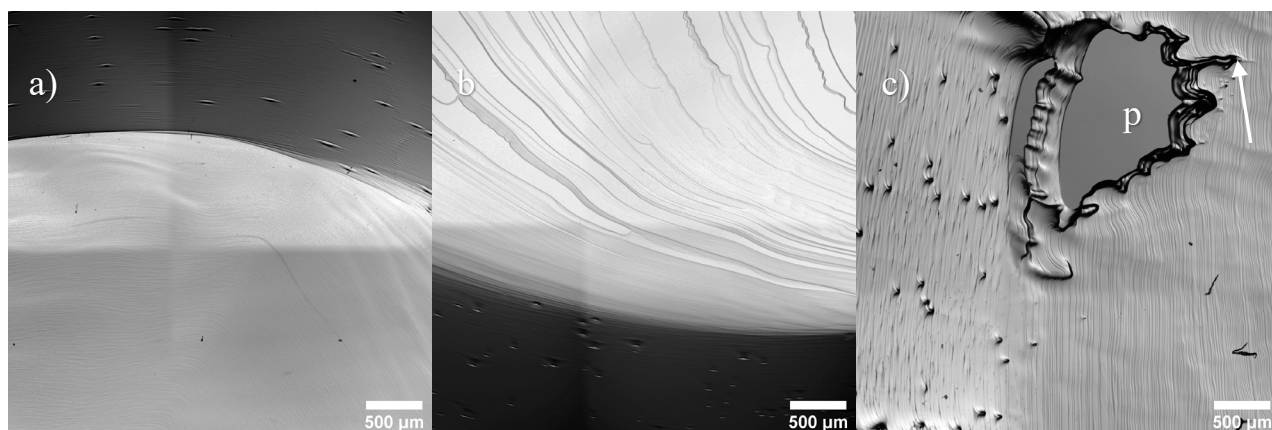


Figure 1: Step structure at the edge of the main facet of a) crystal #1, b) crystal #2 and c) crystal #3. Large surface steps on the surface of crystal #3 pile up at defects. The arrow marks where the formation of the foreign polytype inclusion (p) formed.

Influence of doping. The addition of N₂ into the gas phase changes the step kinetics on the main facet, leading to step bunching as also reported in literature [2]. But in our case, the bunched steps visible in Figure 1 b) are much larger with an average height of 0,17 μm and an average width of 152 μm measured by laser scanning microscopy (LSM). A more detailed inspection of the giant macrosteps on crystal #2 with field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) (Figure 2) reveals that they are build up from closely bundled smaller steps with heights in the range of 10 nm. These bundles of steps are found on the facet of the crystal to be formed dynamically. They can be bunched together very closely giving the impression of a single macrostep but also bundles where the substeps move apart from each other, dissolving the large macrostep are found in Figure 1 b). The undoped crystal in contrast exhibits a very ordered pattern of bunched steps with an average step height of 0.014 μm and width of 5.0 μm determined by LSM. Effects leading to an ordered step structure are the step repulsion [3] as well as the Ehrlich-Schwoebel effect [4]. When N₂ is adsorbed on the crystal surface it is believed to change the incorporation rates of adatoms at the step edges from the upper and lower terrace leading to a density fluctuation of steps [2, 5]. This change in the step kinetics leads to different step patterns on the facet as visible on crystal #1 and #2 in Figure 1 a) and b). The charge carrier concentration of the nominally undoped crystal #1 is determined to be $1.7 \cdot 10^{17} \text{ cm}^{-3}$ while for the N₂ doped crystal #2 it is determined to be $5.9 \cdot 10^{18} \text{ cm}^{-3}$. Both crystals exhibited an overall high polytype stability, but it must be noted that in the case for crystal #1, without nitrogen doping, a singular polytype switch occurred at the end of the growth process. Therefore, the topmost part including the main facet of crystal #1 are of the 6H polytype.

This is important when the fine steps in between the macrosteps are regarded which are of half unit cell size (0.75 nm) for crystal #1. On the large terraces of crystal #2 the very ordered pattern of fine steps visible in Figure 2 a) is of single unit cell step height, validated by AFM. In the convex shaped growth interface besides the main facet both crystals exhibit a very smooth surface.

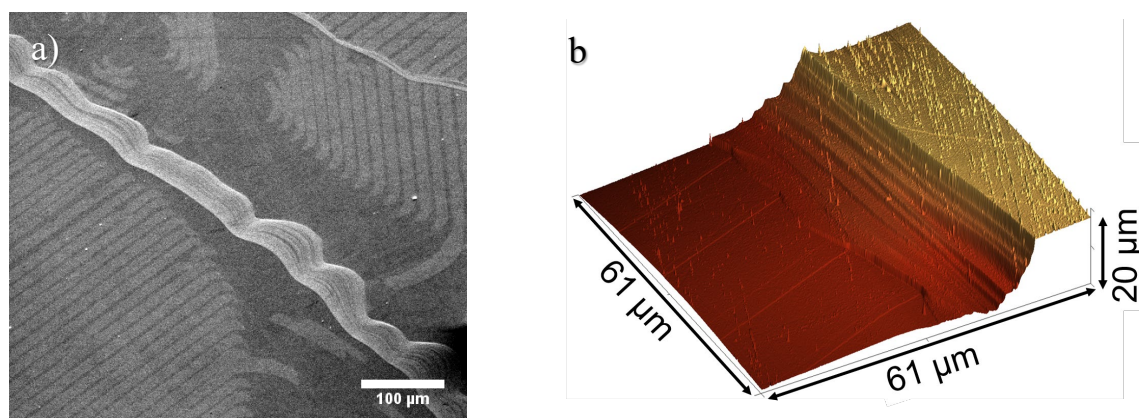


Figure 2: a) FESEM image of the facet of crystal #2. The ordered steps in between the large macro steps are of single unit cell height b) AFM image showing the ordered fine steps on the terrace left and the bundled together macrosteps right.

Influence of C/Si ratio. Although grown nominally undoped, too, the charge carrier concentration of $4.6 \cdot 10^{17} \text{ cm}^{-3}$ for crystal #3 is larger than that of crystal #1, which is attributed to the site competition effect [6]. From in situ CT growth surveillance (not shown here), it is obvious that no molten Si exists during growth of crystal #3. Therefore, a change from SiC-C to SiC-Si equilibrium conditions is not expected. The step structure of crystal #3 grown from a SiC powder source with additional Si compared to crystal #1 grown from a source powder with additional graphite differs not only on the main facet but on the whole crystal surface. With an average height of $0.20 \mu\text{m}$ the steps are bigger and their spacing of $22 \mu\text{m}$ is larger, too. The morphology of the large bunches differs from that of crystal #2 suggesting a different cause of their formation. In AFM measurements the step treads are found to be $(000\bar{1})$ planes where rarely any finer steps are found on top. The step structure seems to be more determined by the reduction of surface energy than by step kinetics, as large low energy $(000\bar{1})$ surfaces are developed between the risers of the macro steps. Low energy surfaces are also found to develop in the solution growth of SiC [7]. The comparison of crystal #1 and #3 shows that the C/Si ratio in the growth cell influences the step morphology on the whole crystal surface. As depicted in Figure 1 c) the surface morphology at the crystal flank besides the main facet is dominated by large surface steps in the case of growth from a Si rich source material. The step flow is disturbed where defects (micropipes in particular) permeate the surface of the crystal. When the steps pile up at a defect, a wide terrace is formed behind it, exposing the basal plane to the growth ambient. Here the 2D nucleation with a different stacking sequence can occur, enabling the formation of a foreign polytype inclusion. This especially takes place in the transition area from the facet to the convex curved part of the growth interface. The asterisk in Figure 1 c) marks where this mechanism led to the formation of a polytype inclusion in crystal #3. When carbon is added into the source material, a very smooth surface is formed at the crystal flank as depicted in Figure 1 a) and b). Defects running along the c-direction seem to hamper the step flow only little. The nucleation of foreign polytypes is reduced.

Influence of inert gas pressure. The temperature at the top (2390°C) of the source leads to the formation of a combined equilibrium pressure of the reactive gas species (Si, SiC_2 , Si_2C) of 23 mbar [9] for the crystals #4 and #5. In the case of crystal #4 this is more than the inert gas pressure of 0.2 mbar allowing the reactive gas species to be transported by a pressure gradient into the gas room. At the large inert gas pressure of 40 mbar for crystal #5, only the transport by the concentration gradient i.e. diffusion of the reactive species through the Ar in the gas room is possible. From the reactive gas species Si has the highest diffusion coefficient while the carbon carrying molecules SiC_2

and Si_2C have lower ones [8], enabling a lower C/Si ratio at the growth interface. This means for crystal #4 the C/Si ratio at the growth interface is larger (more C-rich) than for crystal #5 (more Si-rich) due to the different transport mechanisms. Nevertheless, the difference in the C/Si ratio should be smaller than for crystals #1 and #3. The doping levels of crystals #4 and #5 are comparable with $1.5 \cdot 10^{18} \text{ cm}^{-3}$ and $6.9 \cdot 10^{18} \text{ cm}^{-3}$, respectively.

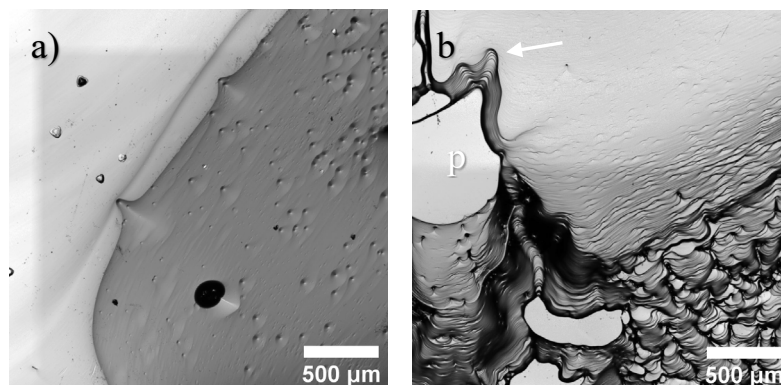


Figure 3: a) smooth surface of crystal #4 b) surface of crystal #5 featuring large steps and a polytype inclusion denoted by p

In Figure 3 differences in the step size on the growth interfaces are visible. For crystal #4 the surface is very smooth with a step height of 0.5 nm on the facet measured by AFM. Crystal #5 is characterized by large steps on the whole crystal surface. The average macro step height on the facet edge is 0.20 μm with an average distance of 4.3 μm measured by LSM. Like in the Si-rich case (crystal #3), the step flow on crystal #5 is strongly disturbed at defects. The large terraces behind a pile up of steps at defects enable the formation of foreign polytype inclusions (Figure 3 b) leading to the formation of diverse foreign polytype inclusions in crystal #5.

Summary

The gas phase composition in front of the growing crystal in the PVT process can be manipulated in several ways. While the doping gas N_2 influences the step kinetics leading to step bunching on the main facet, the C/Si ratio in the gas phase seems to influence the step morphology on the whole crystal surface. A step flow of fine steps seems to be beneficial for the polytype stability and can be induced by additional graphite in the source material as well as by the growth under low pressure conditions without further additions to the source material. Because a foreign polytype inclusion catastrophically deteriorates the crystal quality, growth conditions which promote the formation of fine steps on the growth interface are recommended.

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