Materials Science Forum
ISSN: 1662-9752, Vol. 1062, pp 79-83
doi:10.4028/p-gt22u6

Submitted: 2021-10-18
Revised: 2022-02-15
Accepted: 2022-03-10
Online: 2022-05-31

In Situ Monitoring of Unintentionally Released Nitrogen Gas in the Initial PVT Silicon Carbide Growth Process Using Mass Spectrometry

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Keywords: 4H-SiC, PVT, residual gas analysis, nitrogen adsorption, unintentional background doping

Abstract. Different initial process steps during PVT crystal growth of SiC were monitored with a mass spectrometer. To measure the gas phase composition in the PVT growth machine during these steps the continuously pumped exhaust gas was analyzed by a quadrupole mass spectrometer (PrismaPro QMG 250). In order to reduce unintentionally doping of the crystal by contaminations in the growth setup the focus was on the release of nitrogen during the initial steps of the growth process. During the heat up of the growth setup in vacuum a substantial release of molecular nitrogen was observed at 800 °C. Further, the influence of pump and purge-steps on the amount of nitrogen in the gas phase was examined. After performing a pump and purge step, the intensity of the measurable nitrogen-related signal ($m/z = 28$) was approximately 20 % of the initial value. In-situ monitoring of the gas phase during the initial steps of crystal growth proved to be a versatile tool for the development of a process minimizing unintentionally doping through released nitrogen.

Introduction

Controlled doping is an important issue for bulk growth of silicon carbide. Stable doping density over the whole bulk is desirable for n-type material, for high purity semi-insulating a low doping density is necessary [1, 2]. Therefore, it is important to know the sources of unintentionally background doping. One source of background doping are impurities incorporated in material which are present in the reaction chamber (e.g. powder source, crucible and other carbon part) [3, 4]. These materials could be examined previously and therefore are not the main issue of this study. Another source of background doping are parts in the PVT growth machine with high specific surfaces. A representative of this type is the graphite isolation. Gas species of the ambient air such as nitrogen, could adhere on the surface before installation and could release uncontrolled during crystal growth. Few is known about the release of nitrogen from the growth setup during the initial phases of PVT crystal growth. However, many authors report unintentional background doping with nitrogen [5, 6].

In this work, the evolution of nitrogen release during different initial phases of silicon carbide crystal growth over time is investigated using in-situ mass spectroscopy.

Experimental

Growth machine and setup. The monitoring was conducted during growth processes of 100 mm n-type 4H-SiC crystals in a conventional PVT growth machine with inductive heating. To provide the desired pressure an oil-free, multi-stage roots pump in combination with a control valve is applied to the growth machine. In all the processes the growth setup and the isolation were of the same type and shape. As silicon carbide source nominally undoped material exhibiting a purity of ca. 6N was applied for all growth runs. Temperature measurements above 900 °C were done with quotient pyrometers, below $T = 900$ °C it is an extrapolation and is intended as an illustration (e.g. in figures).

Process steps. The initial phases of crystal growth consist of five steps: (i) pump down to vacuum at room temperature, (ii) holding vacuum during heat up to medium temperature (T < 1500 °C), (iii) T-plateau at medium temperature (T < 1500 °C), (iv) heat up to high temperature (T > 2000 °C) and build-up of an inert gas pressure of p = 800 mbar, (v) gradual reduction of pressure (typically in the range of 5 to 10 mbar) and introducing of nitrogen gas for doping. During this last step the growth of the crystal will begin. Optionally, at the end of process step (iii) it is possible to conduct one (or more) pump and purge-steps. This optional step is divided into two substeps: (iiia) building up an inertgas-pressure of 200 mbar with an argon flow of 100 sccm for 90 minutes, (iiib) stopping the argon flow and pumping down the PVT setup to vacuum pressure again. Between two pump and purge steps an interval of about 120 minutes is necessary to reach a sufficient vacuum in the PVT growth machine.

Residual gas analysis. During all five steps, exhaust is pumped out of the PVT growth machine. A part of the exhaust gas volume can be diverted between the control valve and the roots pump and passed through a high-vacuum pumping station (HiCube 80 Eco, Pfeiffer Vacuum Technology) in a quadrupole mass spectrometer (PrismaPro QMG 250, Pfeiffer Vacuum Technology) for gas analysis. At process step (i), (ii) and (iii) the control valve is fully opened, at step (iv) and (v) the valve is actively controlled to provide the desired pressure. It must be mentioned that the spectra can only be compared if the control valve is in the same position during the measurements. During monitoring of a growth run, a mass spectrum is recorded every ten minutes in the range of m/z = 1 to m/z = 50.

Results and Discussion

Release of nitrogen at initial process steps. In the initial steps of the PVT growth process mainly the process step (ii) and (iii) are of interest, as these steps serve to purify the growth setup. During the heat up in vacuum, there are some abnormalities in the PVT pressure curve observable. In the first part of step (ii) the pressure increases linearly with temperature, followed by a phase of decreasing pressure. After this second part, the pressure increases again and reaches the maximum pressure in step (ii), followed by a phase of slightly decreasing pressure. During this process step, the exhaust gas was continuously analyzed with the mass spectrometer to determine a possible correlation between pressure evolution and nitrogen present in the gas phase.

In Fig. 1 the pressure in the PVT growth machine and the temperature at the top of the crucible over run time of process step (ii) is shown. The figures represent the data of crystal growth run A (top) and B (bottom). For better understanding of the phenomena in the evolving of pressure, the duration of process step (ii) was varied. In growth run A, the length of step (ii) was t = 12 h, in growth run B it was t = 36 h. By examination of the evolution of the molecular nitrogen-related signal (at m/z = 28 in the spectra) with mass spectrometry, it is noticeable, that the curve progression of the nitrogen-related signal shows segments which are in accordance with the pressure curve and others which are not. During two thirds of the run time of process step (ii), the intensity of this signals increases slightly. At the time, which the pressure curve describes the first maxima, the intensity of the nitrogen-related signal still increasing constantly. No connection between the signal and the pressure can be established. The maximum in the curve of the nitrogen-related signal (or in the case of B: the plateau) occur at the same time as the second pressure maximum in the PVT growth machine. Due to the concurrence of these maxima, it seems reasonable to assume that the pressure in the PVT growth machine increases because of the massive release of nitrogen inside the reaction chamber. Maxima of other signals than m/z = 28 could not be seen in the full mass spectra at this time, except the signal at m/z = 12 (not shown). However, it is more than one order of magnitude weaker than the signal at m/z = 28. In both growth runs, the maxima in the nitrogen-related signal were measured at the end of the second third or at the beginning of the last third of the step run time. At this time, both growth setups will be in the same temperature range. So, it seems to be a temperature-dependent release of nitrogen from the growth setup, which reaches the necessary temperature at this point. The part of the growth setup which releases the nitrogen at this time is actually not known. Further examinations are necessary to understand this process.

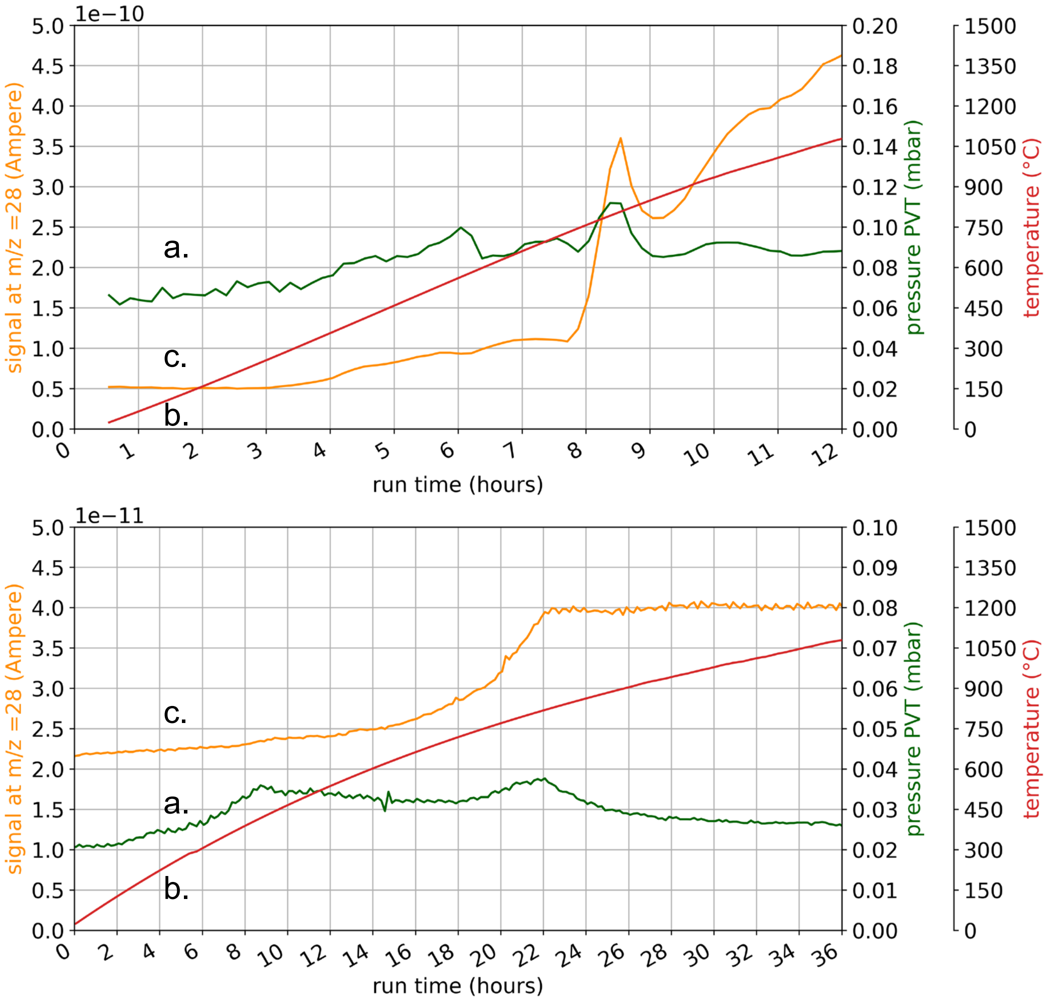

Fig. 1: Pressure (dark green / a.) and temperature (red / b.) in the PVT growth machine during initial step (ii). Additionally, the variation of the mass spectroscopy signal at m/z = 28 during initial step (ii) over time (yellow / c.) is shown. Data from growth run no. A (top) and B (bottom).

Pump and purge steps. To reduce unintentional species from the growth setup it is common to carry out one (or more) pump and purge steps before starting crystal growth.

Analogous to Fig. 1, Fig. 2 shows the pressure in the PVT growth machine, the temperature at the top of the crucible and the measured signal of m/z = 28 during the pump and purge steps at the end of process step (iii). The figure represents the data of crystal growth run B. At the end of process step (iii) the pressure in the PVT growth machine lays constant at $p = 2 \cdot 10^{-2}$ mbar, after the first pump and purge step the pressure reaches a value of $p = 1.75 \cdot 10^{-2}$ mbar. One reason for the significantly lower pressure that can be achieved is the reduction of the present amount of nitrogen. The signal intensity at m/z = 28 was significantly reduced from $3.6 \cdot 10^{-11}$ A at run time t = 73 h to almost $0.8 \cdot 10^{-11}$ A at run time t = 77 h. By pumping and flooding with inert gas again it should be possible to further reduce the amount of nitrogen and the achievable vacuum pressure. Besides the reduction of the amount of molecular nitrogen as a result of the pump and purge steps, a reduction of the signal intensity was also observable at m/z = 2 (molecular hydrogen), m/z = 12 (carbon), m/z = 14 (nitrogen) and others (data not shown). It should be mentioned, that during active argon flow the valve at the exhaust outlet is actively controlled and because of that the signal intensity measured by the mass spectrometer is not comparable to that measured by fully opened valve.

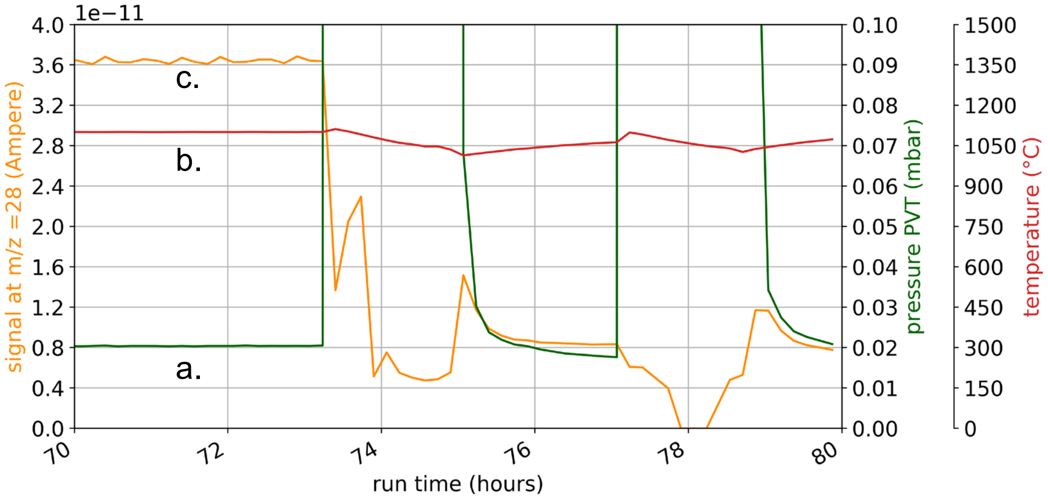

Fig. 2: Pressure (dark green / a.) and temperature (red / b.) in the PVT growth machine during pump and purge steps. Additionally, the variation of the mass spectroscopy signal at m/z = 28 over time (yellow / c.) is shown. Data from growth run no. B.

Summary

The evolution of the amount of nitrogen during the initial steps of silicon carbide crystal growth in a PVT growth machine could be monitored by in-situ mass spectrometry. During heat up in vacuum a sharp rise in the intensity of the nitrogen-related signal was measured in the range of about T = 800 °C. This event could be related to the pressure increase that occurred at the same time in the PVT growth machine. Additionally, the influence of pump and purge steps as part of the initial crystal growth process on the amount of nitrogen in the gas phase was examined. It was shown that the amount of nitrogen could be reduced efficiently with this method.

Using these results further developments of the growth process are possible to minimize the incorporation of unintentionally released nitrogen. Besides this, other species occurring during the process steps could be monitored and examined for further understanding of reaction- and releasing processes.

Acknowledgements

We greatly acknowledge the provision of the experimental setup for gas analysis, consisting of high-vacuum pump station (HiCube 80 Eco) and quadrupole mass spectrometer (PrismaPro QMG 250) by Pfeiffer Vacuum Technology and the financial support by the German Science Foundation (DFG) under contract number WE2107/12-2 and WE2107/15-1.

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