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In Situ **Monitoring of the Ambient Gas Phase during PVT Growth of Nominally Undoped High Resistivity SiC Boules**

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Abstract. The aim of this study is to show the applicability of continuous residual gas analysis for growth monitoring of undoped SiC with physical vapor transport (PVT). For this purpose, two crystals were grown, one without doping and one with continuous nitrogen doping. During the processes continuous residual gas analysis were conducted and evaluated with emphasis on the temporal variations of the nitrogen content. The charge carrier concentration of the final crystals was determined by optical methods (spectrally resolved absorption measurement with UV-VIS and Raman spectroscopy) and the results were compared with the residual gas analysis during growth. A correlation was found between the measured nitrogen-related signal and the charge carrier concentration in the samples.

Introduction

Over the last decades, PVT-grown Silicon Carbide bulk material has become increasingly popular as a substrate for manufacturing of different electronic devices. Mainly in the area of GaN-based light-emitting diodes (LEDs) and for fabrication of high power SiC devices (e.g., SiC MOSFETs) substrates from the PVT-process are established [1]. In both, nitrogen doped material (n-type) with different impurity concentrations (below 10^{17} cm^{-3} for LED substrates [1] and highly doped for power devices) is used.

In the last years, components have been developed and applications found for which semi-insulating (SI) or undoped SiC substrates are required. High-frequency power devices based on the structure GaN-on-SiC (e.g., High Electron Mobility Transistors, HEMTs) are an example for this development [1]. These transistors are used as RF power amplifiers e.g., in 5G base station application [2], [3]. Similar to LED substrates, the near lattice-match to GaN and the high thermal conductivity are key properties [2]. Furthermore, for fabrication of HEMT structures high-resistivity substrates are necessary to avoid electrical coupling between the active area and the substrate. Those substrates could be produced via compensating of residual impurities or selective reducing of impurities during PVT growth [1], [4]. The majority of the currently available SI-SiC is based on the compensating mechanism of deep-level dopants (mainly vanadium), although other compensation mechanism are being investigated [5]. Another option for producing of SI-SiC is to minimize the impurity concentration in the material, so-called high-purity semi-insulating (HPSI) SiC. Therefore, it is essential to reduce the impurity concentration in the PVT reactor previously to the process. All materials and components used (powder, graphite parts, insulation, etc.) should be as pure as possible, and special pre-growth process steps can be performed to clean the equipment [8]. Among other things, SiC is used in research projects in the field of quantum spintronics [6], [7]. Although there has been a longer research presence in this area, there is comparatively little information on manufacturing approaches and strategies of HPSI substrates.

By producing SiC via the PVT-process, the single crystalline bulk crystal is built up with material present in the gas phase. During the growth mainly C- and Si-rich species are present in the gas room, which are formed by sublimation of the source powder. Other elements acting as dopants in the final crystal are also present in the gas room e.g., nitrogen due to active doping or as background impurity. Therefore, in-situ monitoring of the gas phase composition during growth can provide information on which and how many potential impurities can be incorporated into the crystal at any given time.

The aim of this work is to show that continuous monitoring of the gas phase during growth is a versatile tool to ensure conditions for production of undoped material. For this purpose, SiC-crystals are grown in a 100 mm PVT reactor with and without active nitrogen doping. During the crystal growth processes, the ambient gas from the reaction chamber are continually monitored with a mass spectrometer.

Experimental

Crystal Samples and Growth Processes. Two 100 mm 4H-SiC crystals were grown for this study, crystal A and crystal B (top right of Fig. 1 and Fig. 2). The processes were carried out under comparable growth conditions in terms of growth setup, isolation design and growth conditions. In both nitrogen-doped 4° off-axis seeds were used. To ensure constant conditions during growth, the pressure was actively controlled via an exhaust gas control valve while argon gas was introduced into the reactor. During the growth of crystal B, in addition to argon nitrogen was introduced continually into the reaction chamber as dopant gas (5% of argon flow). This crystal is used as a reference to obtain comparative values of high doping as well. Crystal A was produced without introducing dopant gas or adding dopants into the powder. Additionally, pump & purge steps were carried out to reduce the nitrogen amount in the reaction chamber before growth. A previous publication addressed the effectiveness of this method in reducing nitrogen [8].

For the optical determination of the charge carrier concentration, wafers were prepared from the crystals and polished on both sides until final polishing with 1/4 µm grain size.

Gas Analysis with mass spectrometer. For the in-situ monitoring, a fraction of the exhausted gas from the reaction chamber was conducted through a high-vacuum pump station (HiCube 80 Eco, Pfeiffer Vacuum) and in a quadrupole mass spectrometer (PrismaPro QMG 250, Pfeiffer Vacuum). With the setup, a wide range mass spectroscopy is possible during process steps with medium to low pressure (< 100 mbar). This allows continuous monitoring from m/z = 1 to m/z = 70 during heat-up in vacuum and during crystal growth and is typically performed every ten minutes. The analysis of gas phase monitoring during heat-up in vacuum can be found elsewhere [8].

Determination of Doping Levels. The charge carrier concentration in the wafers were determined based on spectrally resolved absorption measurements and Raman measurements. The former were carried out at room temperature with an UV-VIS-NIR spectrometer (Perkin Elmer Lambda 19) in the range of λ = 800 nm to 350 nm. Sensitive to the doping concentration in 4H-SiC is the absorption band at λ = 464 nm (n-type / nitrogen-related) [9-11], for p-type doping there are no characteristic peaks observable. After [9] the charge carrier concentration n of nitrogen can be using the following formula:

$$\propto_{BBGA} = (2.4 \pm 1.3)\ cm^{-1} + (3.6 \pm 0.1) \times 10^{-17}\ cm^{2} \times n \qquad (1)$$

For this purpose, the absorption coefficient $\propto$ is plotted against the energy of the incident light. At the energy where below-bandgap-absorption (BBGA) occurs, the height of the peak minus the background level was determined. This value is used to calculate the charge carrier concentration after formula (1).

The determination of the charge carrier concentration using Raman microscopy are based on the shift of the LOPC peak at a wavenumber of around 965 cm^{-1}. The description of the setup and the measurement parameter can be found elsewhere [12]. After [13] the charge carrier concentration can be calculated with the following formula:

$$n = 1.25 \times 10^{17}\ cm^{-2} \times (\omega_{LOPC} - \omega_0) \qquad (2)$$

In the formula the value ω_0 represents the carrier concentration in pure 4H-SiC. According to [12], this value was set to $\omega_0 = 963.46\ cm^{-1}$.

Results and Discussion

A picture of the nominally undoped crystal A is shown in Fig. 1 (top right), the corresponding diagram with data regarding the growth process (temperature, pressure) and the variation of the nitrogen-related signal (at m/z = 28) measured by the mass spectrometer is shown in Fig. 1. Equivalently, the data for crystal B (nitrogen-doped) are shown in Fig 2, a picture of the grown crystal can be found in the top right of the figure. Note that the nitrogen-related signal in Fig. 2 is an order of magnitude higher than in Fig. 1. At the beginning of growth of crystal A a signal intensity over $4.5*10^{-12}$ A was measured, during process the value describes an undulating course with a steadily decreasing tendency. At the end of the growth a value of under $2.5*10^{-12}$ A was measured, the growth duration was t = 161 h. The decrease in signal intensity over process duration was to be expected, as this indicates a steadily decreasing amount of nitrogen in the gas phase. When the PVT machine was loaded only a limited amount of nitrogen is introduced in the chamber via the components, which released it steadily during the process. The reservoir degrades over time. As a cause for the wavy course of the measured signal, a repetitive process in the reactor chamber can rather be excluded. It is suspected that this is a measurement artifact due to changes in external factors affecting the measurement unit (e.g., temperature fluctuations in the laboratory). The time interval between two peaks is constant at t = 24 h. In this context, it should be mentioned that the signal at this intensity is rather in the lower measuring range.

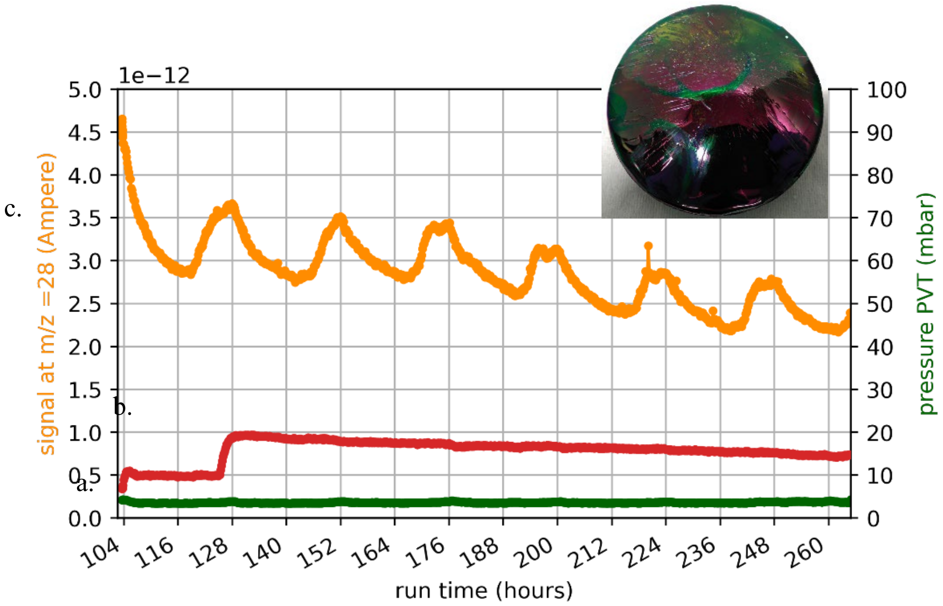

Fig. 1. Data from growth run of crystal A. Pressure (dark green / a.) and temperature (red / b.) in the PVT growth machine during crystal growth. The latter is for illustration, the temperature during growth was in the range of 2000 °C (± 100 °C). Additionally, the variation of the mass spectroscopy signal at m/z = 28 during the process over time (yellow / c.) is shown. The picture in the upper right represents the corresponding crystal.

The signal intensity during the growth of crystal B is approximately constant under $6*10^{-11}$ A with a slight increasing tendency. A constant signal intensity was to be expected, since the nitrogen gas flow was hold constant during growth. In contrast to the monitoring during growth of crystal A, no signal fluctuation with constant period could be observed.

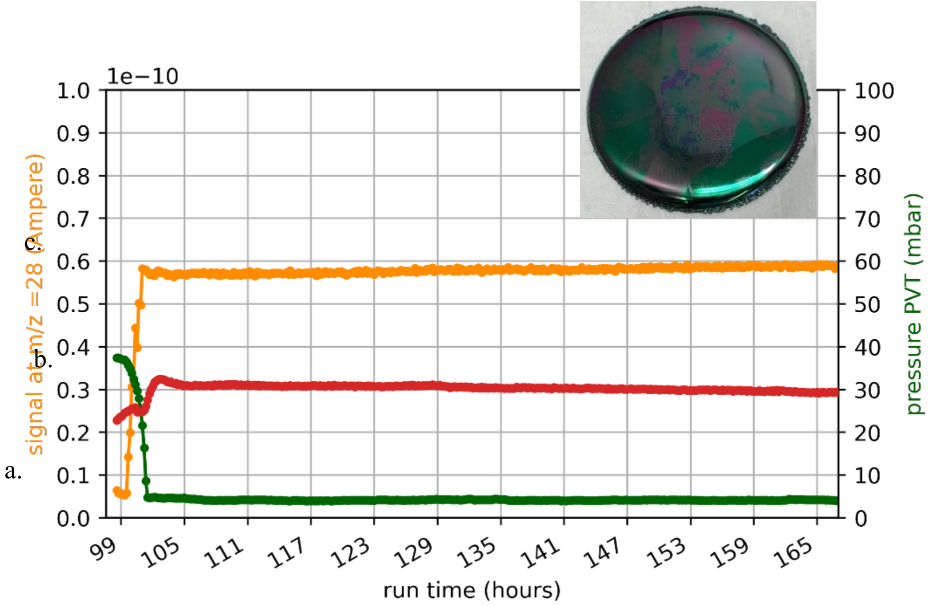

Fig. 2. Data from growth run of crystal B. Pressure (dark green / a.) and temperature (red / b.) in the PVT growth machine during crystal growth. The latter is for illustration, the temperature during growth was in the range of 2000 °C (± 100 °C). Additionally, the variation of the mass spectroscopy signal at m/z = 28 during the process over time (yellow / c.) is shown. The picture in the upper right represents the corresponding crystal.

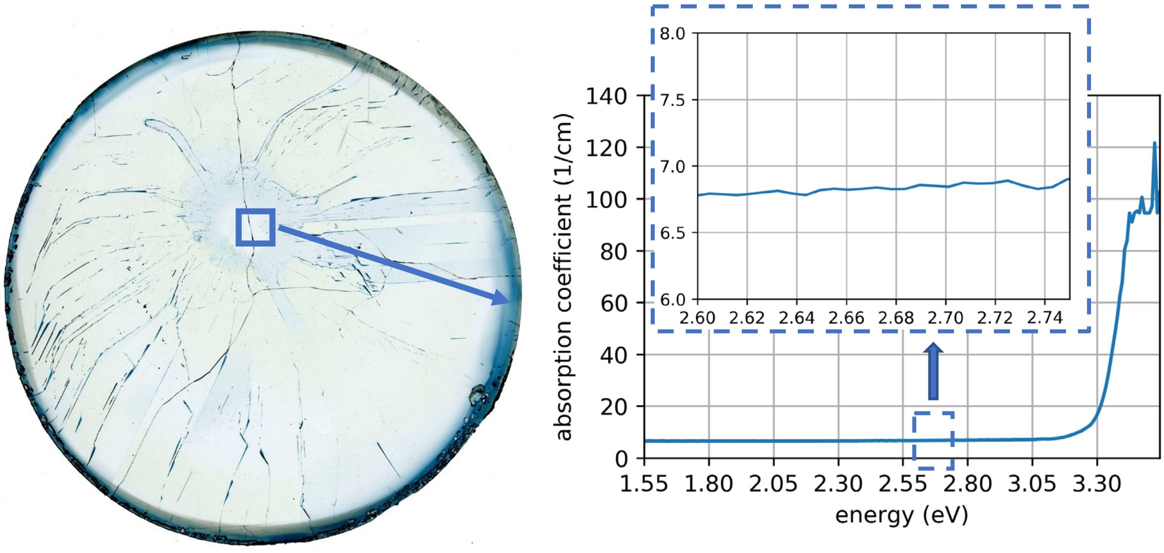

Fig. 3. Polished wafer from crystal A (left) with marked point of absorption measurement and Raman spectroscopy. In the diagram on the right side the calculated absorption coefficient over the energy at the measurement point is shown.

In Fig. 3 and Fig. 4 on the left side wafers from the grown crystals are shown. On both wafers spectrally resolved absorption measurements were carried out, the resulting absorption coefficient over the energy of the incident light are shown in the diagrams of the right side of the figures. In the diagram corresponding to the wafer from crystal B it can be seen very clearly the high below-bandgap-absorption around λ = 464 nm (E = 2.67 eV, dashed frame in the diagram) due to the high concentration of nitrogen in the material. In contrast, the wafer from crystal A shows no high absorption in the interesting range. It is assumed that the doping concentration of nitrogen is so low that no characteristic peak is formed at λ = 464 nm. The authors who have introduced this method have shown its experimental applicability in the range of $3*10^{17}$ to $3*10^{18}$ cm^{-3} [9], [11]. Others [10] applied this relationship down to a carrier concentration of $1.2*10^{17}$ cm^{-3}. Due to the measurement and the data available in the literature, it is assumed that the charge carrier concentration in the range of $1.2*10^{17}$ to $3*10^{17}$ cm^{-3} or lower.

Raman measurements at the marked area of the investigated wafer from crystal A support this thesis. The peak position of the LOPC mode is in the range of ω_{LOPC} = 964.23 to 964.99 cm^{-1}. After equation (2) this indicates a carrier concentration of n = $9.39*10^{16}$ to $1.89*10^{17}$ cm^{-3}. However, similar to the absorption measurement, this method is used at the edge or outside its experimentally confirmed range.

In order to determine the charge carrier concentration in the investigated wafer, further measurement methods are necessary. In addition, a chemical analysis of the material is also interesting in this context.

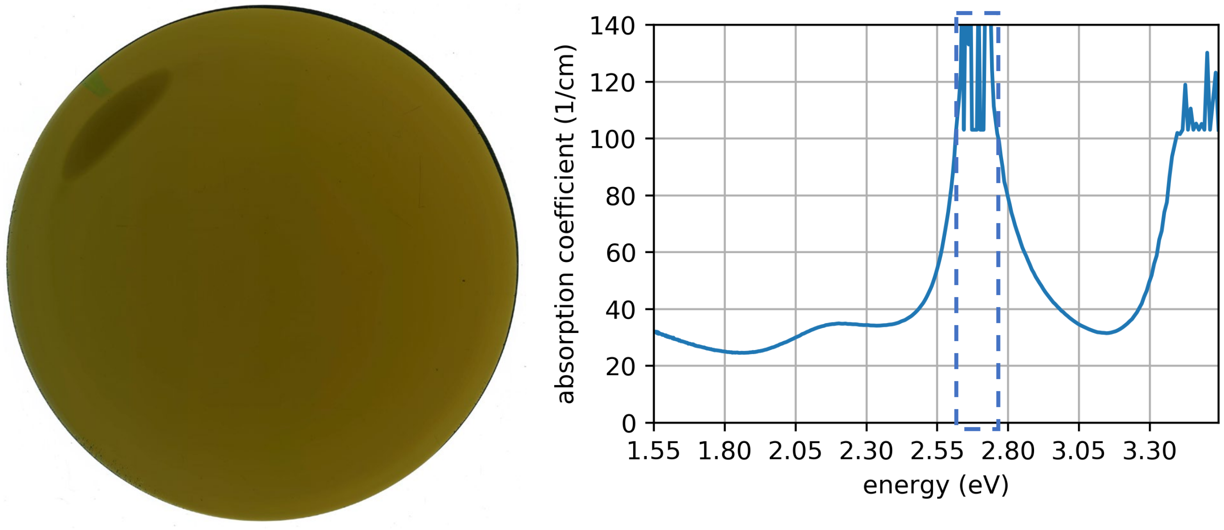

Fig. 4. Polished wafer from crystal B (left). In the diagram on the right side the calculated absorption coefficient over the energy is shown.

Summary

In this study it was shown that residual gas analysis with a mass spectrometer during PVT can be applied to monitor the growth of nominally undoped SiC. Two crystals (undoped: crystal A / nitrogen doped: crystal B) were grown for this study, residual gas analysis were performed during the processes. The variation over time of the nitrogen related signal intensity (at m/z = 28) was evaluated and compared to the results of the optical determinations of the charge carrier concentration. The intensity of the nitrogen related signal was one order of magnitude lower during the growth of crystal A than that of crystal B. In the first case the signal described a decreasing intensity over the process duration, which corresponds to a declining nitrogen amount in the gas phase. During growth of crystal B, the signal remained approximately constant. The charge carrier concentration in crystal A could not be determined conclusively because the methods used are not designed for this low carrier concentrations. Based on the stated validity limits, it is presumed that the concentration is in the lower 10^{17} cm^{-1} range or below. In summary, the intensity of the nitrogen related signal in the gas phase shows a correlation with the charge carrier concentration in the final crystal.

It would be very interesting to establish a quantitative relationship between the measured signal intensity and charge carrier concentration in the final crystal. However, further investigations are required to obtain this.

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