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Bulk Material and Characterization

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Bulk Growth of SiC

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ABSTRACT

The paper reviews the basics of SiC bulk growth by the physical vapor transport (PVT) method and discusses current and possible future concepts to improve crystalline quality. In-situ process visualization using x-rays, numerical modeling and advanced doping techniques will be briefly presented which support growth process optimization. The „pure“ PVT technique will be compared with related developments like the so called Modified-PVT, Continuous-Feeding-PVT, High-Temperature-CVD and Halide-CVD. Special emphasis will be put on dislocation generation and annihilation and concepts to reduce dislocation density during SiC bulk crystal growth. The dislocation study is based on a statistical approach. Rather than following the evolution of a single defect, statistic data which reflect a more global dislocation density evolution are interpreted. In this context a new approach will be presented which relates thermally induced strain during growth and dislocation patterning into networks.

INTRODUCTION

Commercial silicon carbide (SiC) substrates for electronic device applications are generally grown by the so-called PVT (physical vapor transport) growth, also called seeded sublimation technique. The growth process takes place in a quasi-closed graphite crucible system at elevated temperatures above 2000°C. Today 2", 3" and 4" substrates of the two polytypes 4H-SiC and 6H-SiC are commercially available with low defect density. Depending on the application, nitrogen doped n-type and semi-insulating materials are available. In the case of p-type doping only medium conducting material is on the market. 3C-SiC is currently not commercially available in big volume.

VAPOR GROWTH OF BULK SiC CRYSTALS

Fundamental Growth Process

Other than the widely used semiconductor materials silicon and gallium arsenide, silicon carbide single crystals cannot be grown from the melt. SiC decomposes peritectically at approx. 2800°C (figure 1a) into a Si melt with approx. 13% of dissolved C and into pure C which forms graphite clusters. At around 2000°C to 2400°C, however, sublimation of silicon carbide and defined re-crystallization may be carried out. This so called physical vapor transport (PVT) or seeded sublimation technique was first developed by Tairov and Tsvetkov [1] in 1978, who

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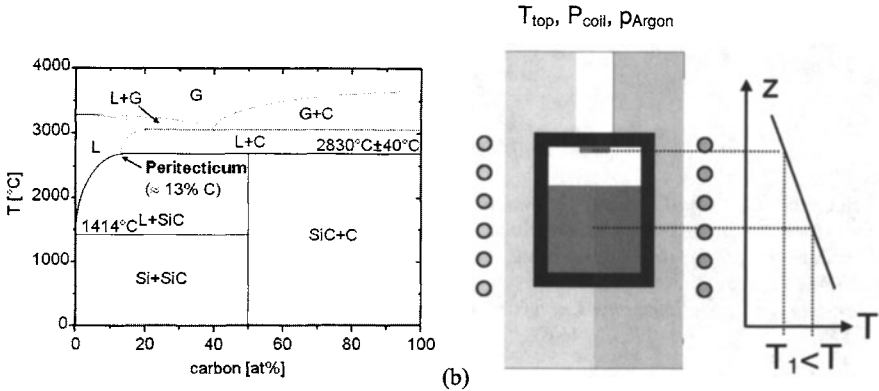
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Figure 1. (a) Phase diagram of SiC. (b) Sketch of physical vapor transport (PVT) growth setup.

modified the self seeded Lely [2] process. The growth cell contains a SiC source material (often SiC powder) and SiC seed which is placed at a slightly colder position (figure 1b). The SiC source material sublimates and re-crystallizes at the colder seed as single crystal.

Although in general the growth process is called to be a physical phenomena, in reality the SiC source material sublimates, mainly forming the molecules Si, Si₂C and SiC₂ which are transported from the hot source zone to the colder SiC crystal growth interface, where they again form a SiC crystal by a chemical reaction. The latter circumstance is one of the reasons, why the C/Si ratio, which is a well known key parameter in classical CVD of SiC using silane and propane (see e.g.) [3], is also of particular interest for SiC bulk crystal growth. Although well established and optimized, the PVT process allows only an indirect control of the sublimation and re-crystallization process. Growth velocity may be controlled by heating power (P_{coil} in figure 1b) and, hence, growth setup temperature (T_{top} in figure 1b) and inert gas pressure (p_{Argon} in figure 1b). Temperature gradient may be set by crucible and isolation material design, as well as inductive heating coil position. The control of parameters like the above mentioned C/Si ratio is only indirectly possible.

Numerical Modeling

To improve and optimize the growth process, numerical modeling of the temperature field as well as SiC sublimation and mass transport has become state-of-the-art [4-7]. Using this tool, especially the radial temperature gradient can be minimized, which is a main source for thermally induced strain and, hence, dislocation generation due to strain relaxation.

X-ray In-Situ Visualization and SiC Mass Transport Labeling

Unlike the well known Czochralski growth process of the semiconductor materials Si and GaAs, the PVT setup offers no optical access to the growth cell interior. For process visualization Wellmann et al. [8] presented a digital x-ray setup that allowed to follow SiC powder evolution

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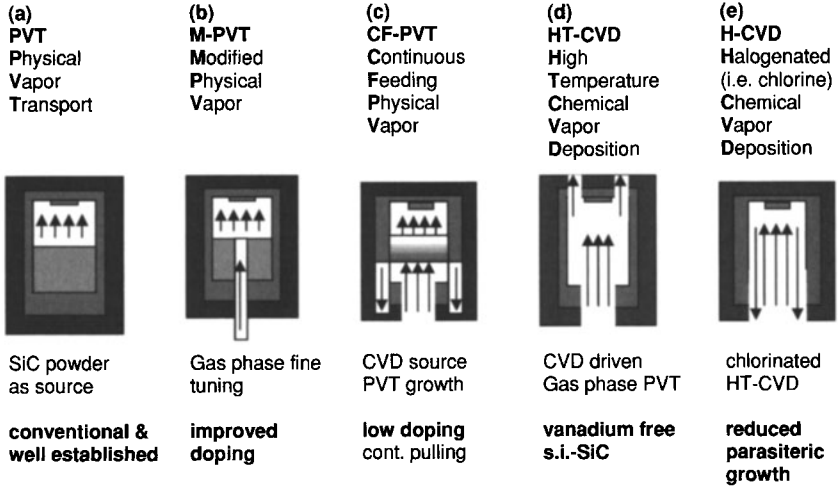


Figure 2. Derivates of the well established PVT process, which allow improvements for selected issues, like improved doping or high purity in the case of M-PVT or HT-CVD, respectively.

(grain re-growth and graphitization) and SiC crystal growth (shape of growth interface, growth velocity) in-situ during growth. Using ¹³C as marker, Hero et al. [9] in addition addressed the SiC-species related mass transport through the growth cell.

Open Issues

Today, growth of 4” SiC single crystalline material has become state-of-the-art (see e.g. [10]). Major emphasis is now put on dislocation density reduction. In the case of the sever micro-pipe defect, reduction to almost zero defect density has been accomplished [10]. Further developments focus on the reduction of threading edge, threading screw and basal plane dislocations.

ADVANCED SiC VAPOR GROWTH APPROACHES

In the following four growth techniques will be addressed – M-PVT (Modified PVT), CF-PVT (Continuous Feeding PVT), HT-CVD (High Temperature CVD) and HCVD (halide CVD using chlorinated gases) – which allow a more flexible control of gas phase composition than classical PVT. These techniques allow overcoming the limitation of PVT. In the latter technique, the deposition chemistry is fixed by temperature and can be mainly guided by the design of the crucible. Consequently, the degrees of freedom are very limited.

M-PVT technique

The idea of the M-PVT (figure 2b) technique is to use an additional gas pipe for fine tuning of the gas phase composition in the growth cell. Major advantage is the improved doping.

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Currently the highest doping levels for p-type SiC using aluminum as acceptor and n-type doping using phosphorus as donor (in situ doped) have been reported [11].

CF-PVT technique

The CF-PVT method (figure 2c) combines classical CVD for formation of solid SiC source, which is used in a subsequent zone of the setup for classical PVT of bulk SiC crystals. The idea is to generate a time invariant SiC source that allows continuous SiC growth, and in principle, pulling of long SiC crystals. The feasibility of such approach has already been shown by Chaussende et al. [12]. To optimize CF-PVT a deeper understanding of feeding gas chemistry as well as SiC mass transport is necessary.

HT-CVD technique

The High Temperature CVD technique (HT-CVD) for bulk SiC growth (figure 2d) was first introduced in 1996 by Kordina et al. [13] and has since then become a mature method [14]. The HT-CVD growth system is based on vertical reactor geometry, where the precursors silane (SiH₄) and ethylene (C₂H₄), diluted in a hydrogen carrier gas, are fed upwards, through a heating zone, to the seed crystal holder. The advantages of this technique are (i) the continuous supply of the source material, (ii) the relatively economical availability of high purity gases, (iii) the direct control of the C/Si ratio and (iv) the principle ability of pulling the growing crystal.

HCVD technique

The Halide CVD technique and its special reactor geometry (figure 2e) were designed with the aim to maximize the source gas efficiency conversion into single crystalline SiC and minimize parasitic deposition. As in all other SiC bulk growth techniques, a vertical crucible design is used. The silicon source gas (e.g. SiCl₄ in Ar carrier gas) and the carbon source gas (e.g. C₃H₈ in Ar:H₂ (1:1) carrier gas) are fed through separate injector tubes into the hot furnace zone (typical gas flux of both species: 1slm) where crystal growth takes place at elevated temperatures (typical T: 2020 °C) [15]. A typical ambient pressure is 200 Torr. The arrangement of separate gas injection allows the precursor gas to be pre-heated to temperatures near growth temperature without cross-reaction and hence parasitic SiC formation and deposition. Due to their thermal stability, the role of the halogenated silicon gas source is to eliminate reactions with the graphite furnace parts prior the crystal growth process in front of the SiC seed surface. The HCVD growth furnace as introduced in [15] is capable of producing crystals with diameters up to 100 mm.

DISLOCATION EVOLUTION DURING BULK SiC CRYSTAL GROWTH

Experimental Details – Growth Process

The study of the influence of the seed temperature (or growth interface temperature) on dislocation evolution during SiC crystal growth was conducted systematically by applying novel approaches to vary the temperature during a single growth run.

Three sets of experiments were conducted: (i) Crystal growth was carried out using standard growth conditions, i.e. constant growth temperature and pressure (crystal A). The temperature was 2300°C. This growth experiment served as a reference to those with continuous

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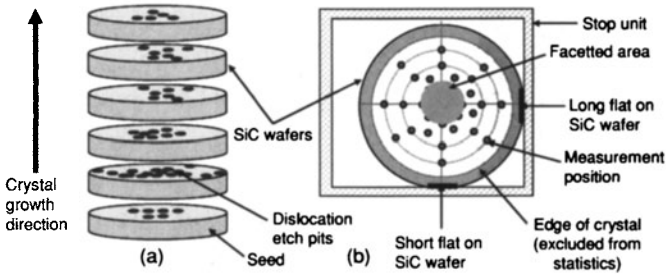
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Figure 3. Statistical approach method for the study of dislocation evolution in SiC single crystals: (a) scheme of etch pit tracking method, (b) positioning of wafer on microscope stage.

temperature change described in points (ii) and (iii) below. (ii) Crystal growth was carried out in such a way that the growth temperature was increased continuously from about 2150°C at the beginning of growth until about 2350°C at the end of growth during a single growth run, while all other conditions remained constant (crystal B). Finally, in a third set of experiments, a reverse temperature mode to that in (ii) was implemented to serve as verification to the latter during dislocation analysis. The growth temperature was decreased continuously from about 2350°C to about 1900°C over the entire growth period (crystal C).

In-situ observation of the growth cell using a digital X-ray imaging technique [8] during the growth process allowed us to follow the crystal growth progress with respect to the growth time and growth temperature making it possible to assign each wafer from the crystals grown with continuous temperature change to the temperature regime in which it was produced with a high accuracy.

Experimental Details – Characterization

Delineation of the dislocations in the wafers was performed by means of defect selective etching in molten KOH. This was achieved in a specially designed and calibrated etching furnace with *in-situ* temperature measurement configuration; the temperature measurements were carried out directly in the KOH melt. Details about the KOH defect etching furnace and optimization of the etching process for dislocation analysis are given in reference [16].

The study of dislocation evolution was carried out by applying a statistical approach. In this method the dislocations are tracked along the length of the crystal from wafer to wafer. The dislocations are counted and their density evaluated in the same crystal or wafer position. In this respect it is not a single dislocation that is tracked but rather the dislocation density obtained statistically is used to interpret dislocation evolution. Each dislocation type is analyzed separately.

Further elaboration of the structural properties of the materials with respect to the applied parameters of crystal growth was performed using high energy X-ray diffraction (HE-XRD) measurements in a triple-axis configuration [3]. The energy of the X-rays was 62.5keV and penetration depths of up to 6cm could be achieved.

Atomic force microscopy (AFM) measurements were carried out on the growth fronts of the as-grown crystals to study their step structure. From the step structure, in relation to crystal growth temperature, we could obtain substantial information about the kinetic processes at the growth front and their relation to dislocation evolution. Figure 3 illustrates this principle.

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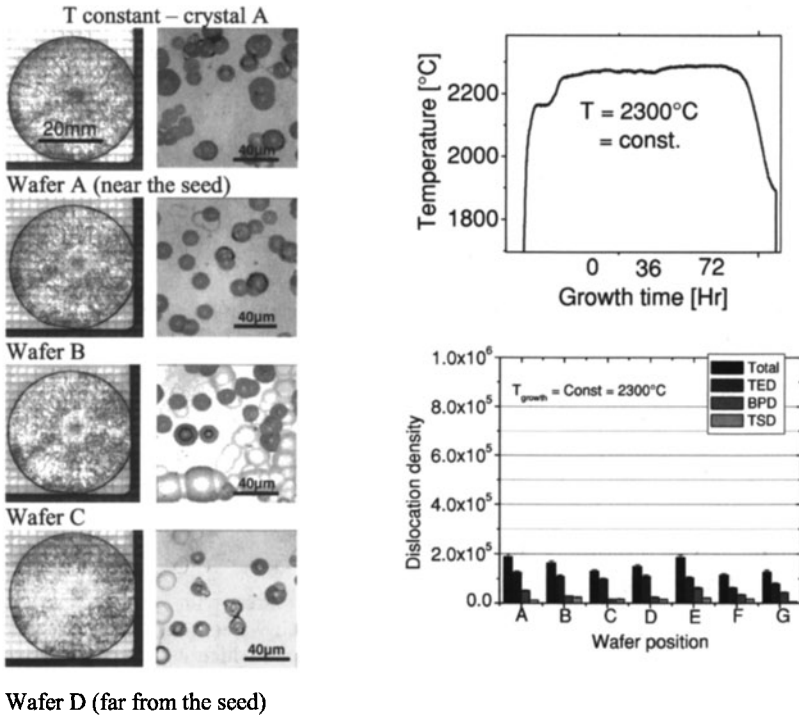
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Figure 4. Dislocation analysis in a crystal (crystal A) grown with a constant temperature.

Results and Discussion - Dislocation Density versus Crystal Growth Temperature

We have observed a distinct relationship between the crystal growth or seed temperature and the overall dislocation density during PVT bulk growth of SiC crystals. On investigating a number of crystals with similar doping levels grown with different temperatures, we have seen a reduction in the dislocation density with increase in the growth temperature. A systematic investigation using crystals grown with continuously changing process temperature confirms these results. In these crystals the run-to-run variations that may occur during growths with different process temperatures in separate runs can be ruled out. By continuously changing the process temperature in a single run, different portions of the crystal are produced at different temperatures such that the effect of high temperature versus low temperature crystal growth can be compared even more accurately by evaluating the overall dislocation density along the crystal growth axis. By comparing the trend in the dislocation density along the crystal growth axis of these crystals with the reference crystal grown at a constant temperature, we were able to establish a solid relationship of the density to growth temperature.

T rises - crystal B

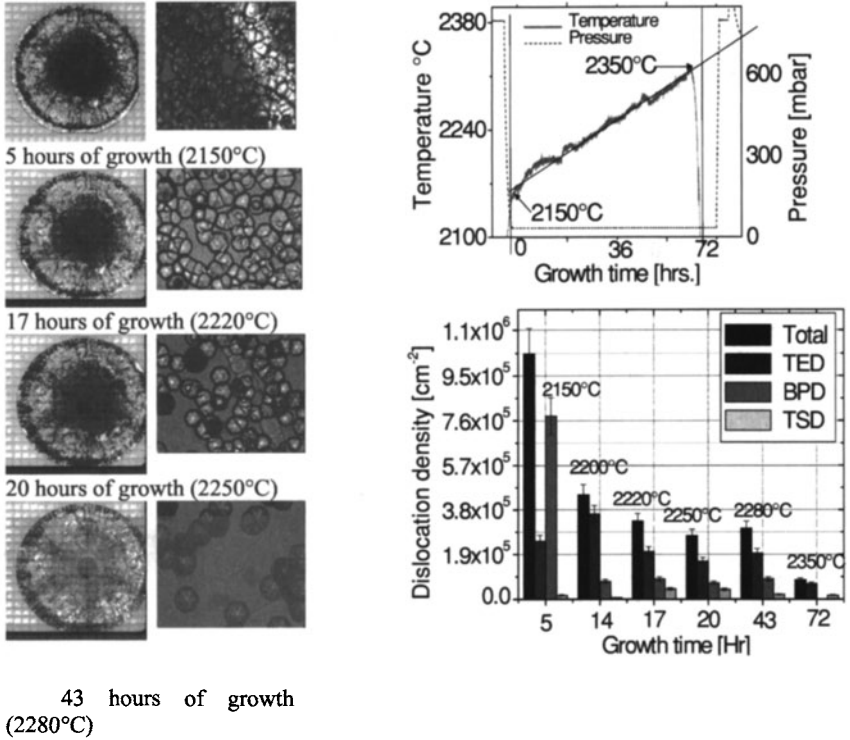


Figure 5. Dislocation analysis in a crystal grown with continuous temperature increase

The results of dislocation analysis in these crystals are shown in figures 4-6. On the left of the figures (first two columns) are KOH etching images, i.e. dislocation mapping over the whole wafer surface at a lower magnification (column 1) and etching images taken at a higher magnification from the center of the wafer (column 2). The darker regions in the mapping images correspond to a high dislocation density. On the right of the images are the applied temperature profiles during the growth processes and dislocation statistics evaluated over the wafer surfaces in several wafer positions.

Crystal A, grown with a constant temperature of 2300°C (figure 4) shows a constant dislocation density of about $2 \times 10^5 \text{ cm}^{-2}$ along the crystal axis. This trend changes conspicuously in crystals grown with a continuous change of the growth temperature during a single growth run. In crystal B, grown with continuous temperature increase (figure 5), the dislocation density decreases dramatically with the growth temperature. It is high at early growth stages (approx. 10^6 cm^{-2}), in low-temperature growth regimes, and then decreases abruptly in high growth

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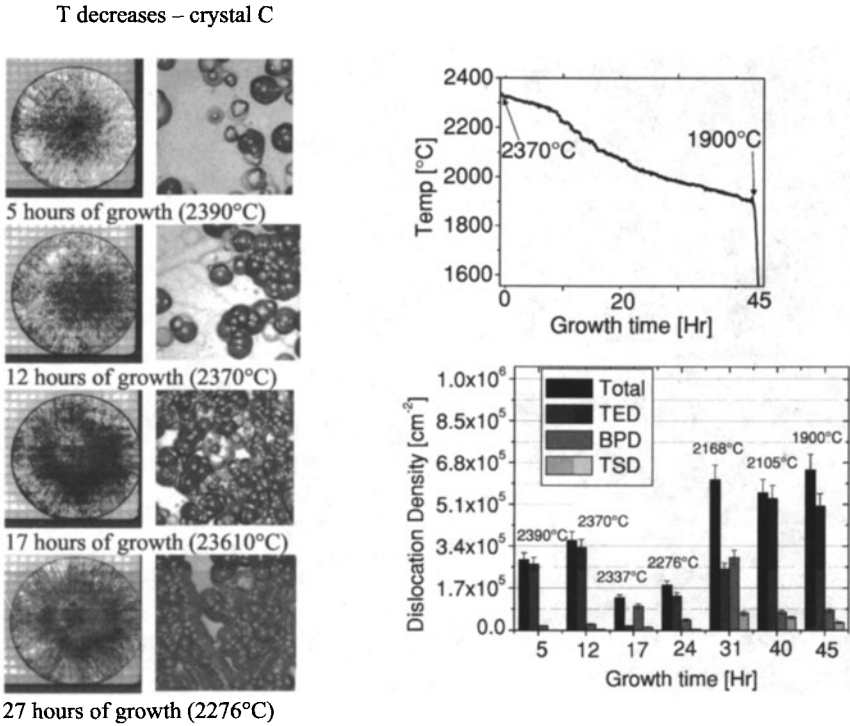
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Figure 6. Dislocation analysis in a crystal grown with continuous temperature decrease.

temperature regimes to a value of about $8 \times 10^4 \text{ cm}^{-2}$. The dislocation density at the initial growth stage is clearly higher than that of the seed used for this growth. KOH etching and optical microscopy revealed the density in the seed to be about $1.2 \times 10^5 \text{ cm}^{-2}$. In the middle of the seed, excluding the edge, it was found to be about $6.8 \times 10^4 \text{ cm}^{-2}$. We attribute the high dislocation density at the initial point of growth to low growth temperature because we did not observe such a high density in, e.g., crystal A in which the temperature was high in the early growth stages. In crystal C, grown with continuous temperature decrease (figure 6), the trend in the dislocation density follows the reverse order to that of crystal B, i.e. low dislocation density ($1\text{--}3 \times 10^5 \text{ cm}^{-2}$) at early growth stages (high growth temperature regime) and high dislocation density (about $6.8 \times 10^5 \text{ cm}^{-2}$) at later stages (low growth temperature regime). Generally, the total dislocation density in the high-temperature growth regimes of crystals B and C, grown by continuously changing the process temperature is comparable to that in crystal A, grown with a constant high temperature.

Evidently, from these results, the dislocation density of PVT-grown SiC crystals is inversely proportional to the temperature of crystal growth. This is a clear indication that high quality crystals can be achieved by high temperature growth.