# Bulk I

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**Self-Healing Phenomenon of Micropipes in Silicon Carbide**
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**Growth-induced structural defects in SiC PVT boules**

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The size and quality of silicon carbide crystals and wafers have been steadily improving over the last decade. Wafers with three inch diameter are now available commercially and the densities of micropipes, basal plane dislocations, and low angle grain boundaries have decreased by orders of magnitude. Nevertheless, the remaining defects can lead to significant yield loss of electronic devices and/or can severely degrade their performance. This presentation will present a concise summary of the currently observed extended defects in state-of-the-art SiC wafers with special emphasis placed on nucleation mechanisms active during the growth process.

There is an emerging consensus that the basal plane dislocations in SiC boules are due to the excessive thermal gradients imposed on crystal during growth. This effect can be additionally enhanced by the interaction of the growing boule and the graphite crucible. Arising long range thermoelastic stresses can exceed critical resolved shear stress and cause plastic deformation generating dislocations. Experimental evidence of basal plane slip active during growth will be presented and discussed. Threading edge dislocations can have several different origins including grown-in dislocations propagating from the seed wafers, plastic deformation associated with the prismatic slip system, and surface pinning of basal plane dislocations. The least understood is the origin of the elementary screw dislocations. New evidence indicates the connection between the nucleation of two dimensional islands on the (0001) growth surface and the formation of screw dislocations.

High growth temperatures used for the growth of bulk SiC crystals allow for relatively easy dislocation motion. This, in turn, leads to dislocations arranging themselves in characteristic patterns referred to as the domain structure or low angle grain boundaries. Two examples of such patterns (pure prismatic tilt boundaries and mixed prismatic and basal plane tilt boundaries) will be presented and discussed.

# Sublimation grown SiC : growth modes, strains and defects

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In sublimation grown SiC crystals, structural defects may occur because of non-optimised growth initiation and also because of the relaxation of the embedded strain. A good understanding of these phenomena is a prerequisite for obtaining optimum quality crystals.
Firstly, and as commonly observed in epitaxy, the growth mode itself may be responsible for the occurrence of different types of defects. We have carried out a study of the growth front evolution in the early stages. It was found out that the two growth regimes, referred to as the 2-dimensional regime and the step-flow regime may occur simultaneously on different regions of the growth front. These depend upon the local temperature and upon the local surface misorientation. On the one hand, 2-D growth results into the formation of discrete nuclei which, upon coalescence, may give rise to some residual crystal mosaïcity. On the other hand, step flow growth is expected to be favourable in order to reproduce the underlying crystal structure. In this latter case, if the temperature is high enough, step bunching occurs, leaving wide terraces in between "macrosteps" where 2D growth can be favoured again. Figure 1 represents optical and AFM images of the SiC surface as seen at different magnifications.
Secondly, the evolution of the strain and mosaïcity in the crystal was followed by using either X-ray white beam synchrotron topography for assessing the whole crystal or monochromatic X-ray diffraction for assessing the structural quality of successive wafers from the same crystal. X-ray topography reveals that, if growth has been initiated properly, there is no drastic change in the crystal structure as growth proceeds. X-ray diffraction half width in the $\omega$ mode vary from 20 to about 80 arc sec., the higher value corresponding to the wafer taken from the wider part of the crystal from which one expects the higher concentration of thermo-elastic strains. Basal dislocations are commonly observed with a slowly decreasing concentration and c-aligned dislocations thread within the crystal with a density of about $10^4/cm^2$. Interestingly, if measured across a wafer, the threading dislocation density follows a variation which is the exact inverse of the variation of the strain (with a W profile), indicating that these dislocations are introduced in order to release the local strains rather than to compensate for mosaïcity (Cf.Figure 2). When used as a seed, the remaining strain in a wafer may be at the origin of a residual lattice misfit with the overgrown crystal; the misfit strain may be relaxed via the formation of "interfacial" dislocations which were analysed by TEM.

The optimisation of the growth initiation, the assessment of the growth regimes and the understanding of the different processes responsible for the strain and defect formation allowed us to obtain 4H crystals with state of the art structural quality.

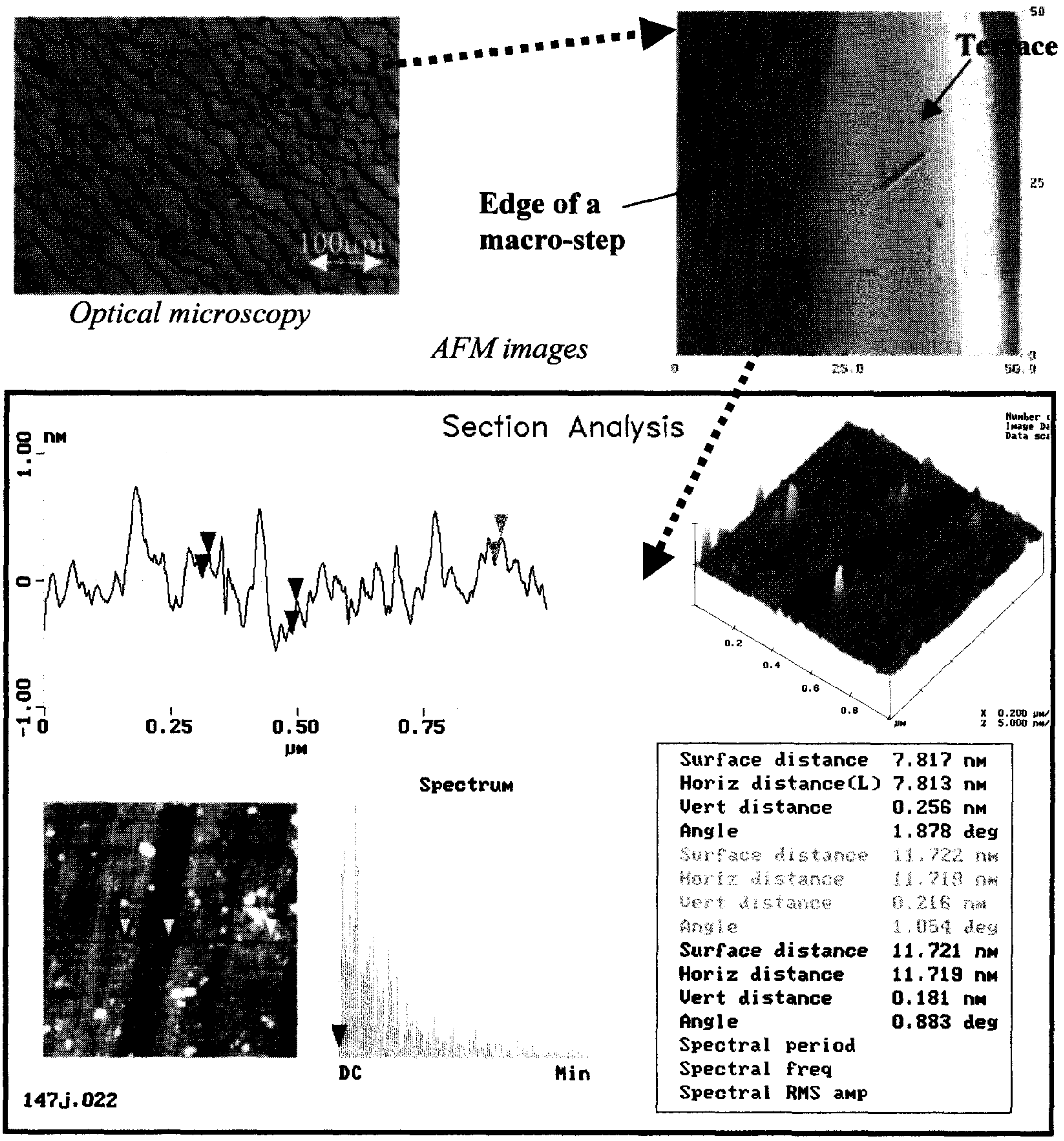


Fig.1. Surface morphology at the initial stages of growth: steps are visible at different scales

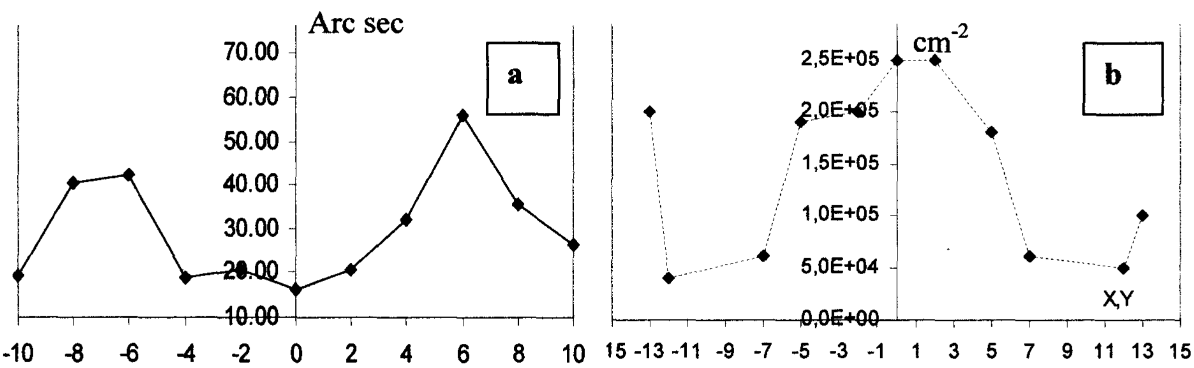


Fig.2. Relationship between the strain distribution (FWHM of the 2θ scan in arc sec, a) and dislocations density (in cm$^{-2}$, b). X –axis : distance from the center of the wafer on a diameter

# On the Preparation of Vanadium-Doped Semi-Insulating SiC Bulk Crystals

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High resistivity, semi-insulating SiC single crystals are gaining more and more importance as substrates for high frequency electronic devices based on both SiC and GaN. Vanadium can act in SiC as a deep level for the electrical compensation of residual impurities. As nitrogen is the predominant impurity in nominally undoped crystals, V doping leads to the activation of the V acceptor level, resulting in a specific resistivity of about $10^{11}$ Ωcm at room temperature. Co-doping of V and a p-type dopant like Al or B is required to activate the almost mid-gap V donor level leading to specific resistivities up to $10^{15}$ Ωcm. In any case, the relatively low solubility limit of V in SiC must not be exceeded. For obtaining bulk crystals of semi-insulating SiC, doping homogeneity is crucial as will be discussed in this paper.

More than 30 bulk 6H-SiC crystals with 35...40 mm in diameter were grown by the modified Lely technique using on-axis seeds. The crystals were doped by boron, vanadium or B/V co-doped by adding solid sources to the SiC starting material. Results from the growth of nominally undoped crystals were taken as a reference. Here, nitrogen was found to be the residual impurity on a very low level, with charge carrier concentration n decreasing exponentially with growth time. Wafers with n as low as $8\times10^{15}$ cm$^{-3}$ were obtained. The dependence of seed polarity on nitrogen incorporation will be addressed. Assuming the residual impurity incorporation is the same for all of our growth experiments, the impact of impurity incorporation on electrical properties during doped SiC growth can be determined.

Tab. 1: Chemical analysis of the B concentration in the sublimation source and in the grown crystals for two experiments, measured both at the beginning and at the end of growth, respectively.

| Boron [ppm wt.] | | SiC powder | SiC crystal |
|---|---|---|---|
| B-doped #1 | Start | 2,7 | 2,0 |
| | End | 5,5 | 2,0 |
| B-doped #2 | Start | 26,7 | 7,3 |
| | End | 5,4 | 4,6 |

The homogeneity of boron incorporation was measured by temperature-dependent Hall effect, absorption mapping and specific resistivity mapping. B incorporation was found to depend on seed polarity (growth on C or Si face). The hole concentration increases with growth time, whereas boron losses during growth lead to a decrease in the boron content of the source material (see Tab. 1). Compensation of boron by nitrogen impurity incorporation can explain this behavior only in the beginning of growth. A mechanism for the increase of hole concentration will be discussed. Also, the influence of dopant incorporation on crystal quality and defect nucleation was investigated with optical microscopy. Lateral homogeneity of a B doped wafer as measured with absorption mapping was as low as $\Delta p/p \approx 15\%$.

V incorporation was found to be related to partial pressure of the V species during growth. Additionally, V is incorporated in higher concentrations when growth on the Si face is

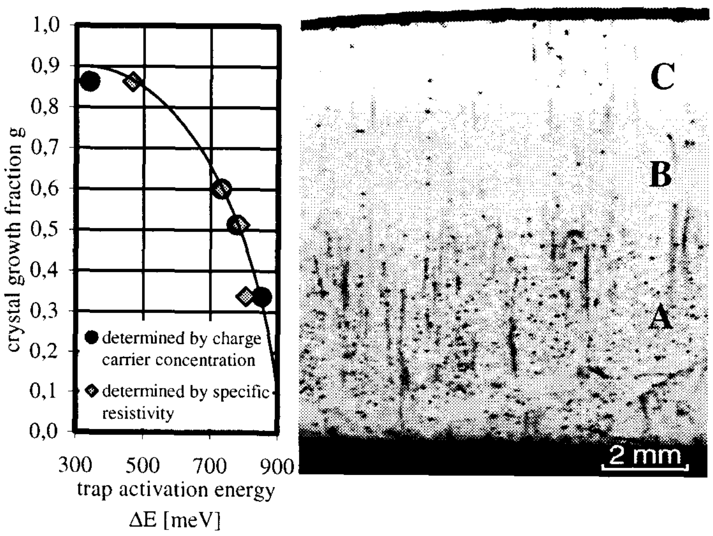


Fig. 1: Cross-sectional cut of a V doped SiC wafer (growth direction is upwards). On the left side, trap activation energies of the respective positions in the crystal are shown. For description of the regions A, B, C see text.

performed. As $p_{VC} > p_{SiC}$ at growth temperature, the V source depletes during growth. The obtained crystals exhibit axial and lateral inhomogeneities (see Fig. 1). When the V solubility limit of $3\ldots5\times10^{17}\,cm^{-3}$ is exceeded, vanadium-rich precipitates form (Fig. 1, A), which were identified by EDX measurements. On the other hand, when the V source depletes, residual nitrogen becomes predominant leading to n-type conducting behavior (Fig. 1, C). By reducing V species evaporation rate, bulk SiC crystals exhibiting precipitate-free, semi-insulating behavior (Fig. 1, B) were obtained.

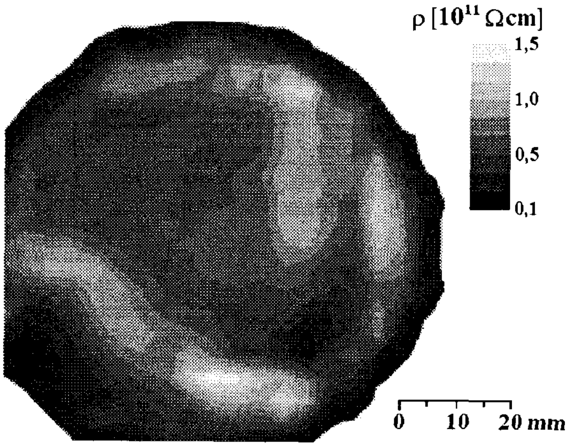


Fig. 2: Specific resistivity mapping on a V doped SiC wafer, obtained by the scanning capacitance method.

Characterisation of doping inhomogeneities and doping-related defects were carried out by optical microscopy and scanning electron microscopy. The electrical properties of V doped SiC crystals were measured by temperature-dependent Hall effect and by the scanning capacitance method. As a result, specific resistivities extrapolated to room temperature are about $2\ldots8\times10^{10}\,\Omega cm$, while resistivity mappings reveal doping imhomogeneities (Fig. 2). The influence of V concentration and compensation ratio on the electrical behavior was analyzed. Optical absorption peak structures in the near infrared, which are attributed to inner shell transitions of $V^{4+}$, and electron spin resonance showing $^{51}V^{3+}$ were used to verify the compensation mechanism in the investigated crystals.

A combination of boron and vanadium doping allows growth of bulk SiC with a specific resistivity of $\rho_{293K} \approx 10^{15}\,\Omega cm$. First results on B/V co-doped SiC crystals show that boron and vanadium incorporation do not interfere with each other. Using the elaborated transfer coefficients for the dopants and their evolution of incorporation during growth time, semi-insulating bulk crystals of B/V co-doped SiC were obtained. Compensation behavior was studied using optical absorption. Specific resistivity mapping as well as temperature-dependent Hall effect measurements were used to determine electrical behavior and doping inhomogeneities.

# Numerical Simulation of Heat and Mass Transfer in SiC Sublimation Growth

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Silicon carbide single crystal has been grown by modified Lely method in a closed carbon crucible. We have reported that grown crystal shape strongly depends on the temperature field, and it is possible to grow high quality crystal by modifying the temperature distribution inside a crucible[1]. We have demonstrated the high quality SiC single crystal growth by using a double-walled crucible[2]. Recently we demonstrated to grow SiC single crystal without poly crystal touching[3], and also proposed to grow high quality SiC single crystal by taking care of initial growth stage[4]. In those methods, the key technology is how to control the heat and mass transfer inside a crucible. In this paper, temperature and concentration field inside a closed carbon crucible was analyzed numerically, and effect to heat and mass transfer on grown crystal quality was discussed with comparing the experiment.

New crucible geometry to grow SiC single crystal separated from poly crystal was proposed.[3] Temperature distribution and mass flux was analyzed numerically. The grown crystal shape has strong relation with temperature distribution and mass flux inside a crucible. It was shown that by controlling them, grown single crystal shape could be controlled. This results shows that it is possible to control the macro crystal quality such as grown crystal shape by modifying the heat and mass transfer.

In-process etching was proposed as a new technique to reduce the defect density of grown crystal.[4] Temperature filed during that process, i.e. etching stage, quasi-equilibrium stage, and growth stage was analyzed. It was pointed out that SiC sublimation growth was composed of source–crystal mass transport and crystal-lid mass transport. Temperature distribution leads to decide which transport process is dominant. It was also shown that by taking care of temperature distribution on the seed surface, defect occurrence could be suppressed and high quality SiC single crystal could be grown. This results shows that it is possible to control the micro crystal quality such as defect density by modifying the heat and mass transfer particularly at the initial growth stage.

In conclusion, heat and mass transfer inside a crucible was analyzed numerically, and its effect on the macro and micro crystal quality was discussed with comparing the experiment.

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# Self-Healing Phenomenon of Micropipes in Silicon Carbide

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Micropipes (MPs) are grown-in hollow tubes penetrating along the growth direction in Silicon Carbide (SiC) crystals. MPs have been also shown to have large Burgars vectors nc: b≥2c for 6H-SiC and b≥3c for 4H-SiC[1] where c is the lattice parameter and n is a positive integer. A unit screw dislocation (SD), namely, remains non-hollow core without the limits of the above magnitude. Therefore, we had believed that MPs would be diminished by decreasing the origins of SDs with large Burgars vectors[2] and reducing the magnitude of Burgars vectors. Recent reports presented the fabrication of SiC wafers with low MP density[3]. Yakimova *et al.* also found that MPs in seed crystal healed in grown layer during the liquid phase epitaxy (LPE)[4]. Note here that the feature of the methods is to reduce the MP density in new grown layers. On the other hand, we found the self-healing phenomenon of MPs in not new grown layers but SiC substrates. The self-healing of MPs was conducted by annealing the substrate with a material over the opening of MPs covered (Fig.1).

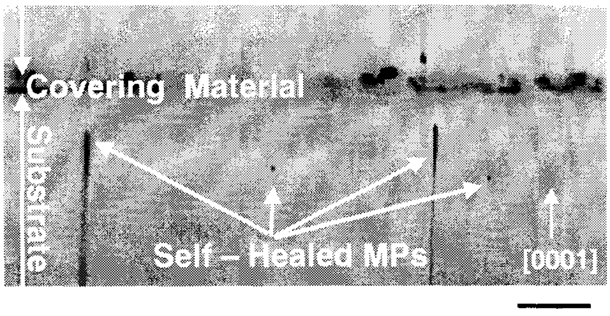


**Fig. 1 Optical micrograph of a vertical sliced 6H-SiC substrate after annealing.**

In this letter the self-healing phenomenon of MPs in SiC substrates has been preliminarily studied by means of the transmission electron microscopy (TEM) analyses and the optical observation, which is presented here for the first time. A TEM study in self-healed region revealed that some part of a hollow tube was transformed into non-hollow core which was composed of dissociated SDs, stacking faults and edge dislocations (Fig.2). There was also some strain in the self-healed region. Considering this experimental observation, one possible mechanism of the self-healing phenomenon of MPs will be discussed.

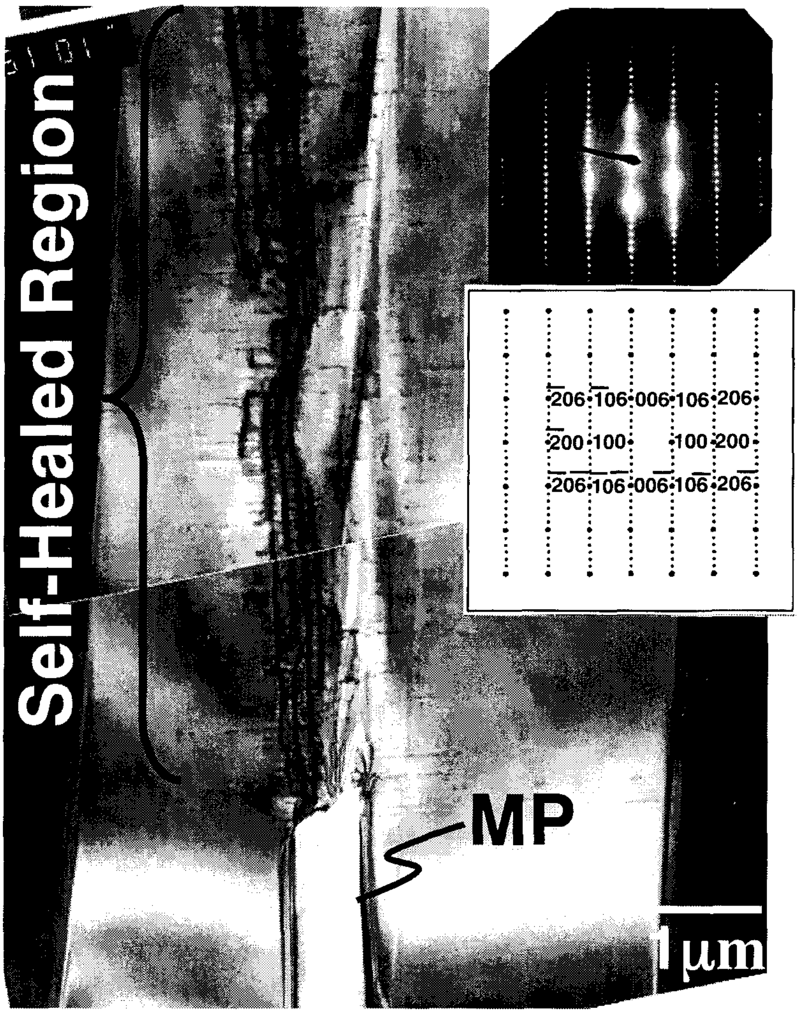


**Fig. 2 Cross-sectional TEM bright-field image and diffraction pattern obtained from the annealed sample. Some part of a hollow tube has been transformed into non-hollow core with strains and mixed defects which consist of screw dislocations, stacking faults and edge dislocations.**

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