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# Top Seeded Solution Growth of 3C-SiC single crystals

F. Mercier<sup>1, a</sup>, D. Chaussende<sup>1, b</sup>, J-M. Dedulle<sup>1, c</sup>, M. Pons<sup>2, d</sup> and R. Madar<sup>1, e</sup>

<sup>1</sup>Laboratoire des Matériaux et du Génie Physique, Grenoble INP – CNRS, 3 parvis Louis Néel, BP257, 38016 Grenoble, France

<sup>2</sup> Science et Ingénierie des Matériaux et Procédés, Grenoble INP – CNRS - UJF, BP 75, 38402 Saint Martin d'Hères, France

<sup>a</sup>Frederic.Mercier@inpg.fr, <sup>b</sup>Didier.Chaussende@inpg.fr, <sup>c</sup>Dedulle@ltpcm.inpg.fr, <sup>d</sup>Michel.Pons@ltpcm.inpg.fr, <sup>e</sup>Roland.Madar@inpg.fr.

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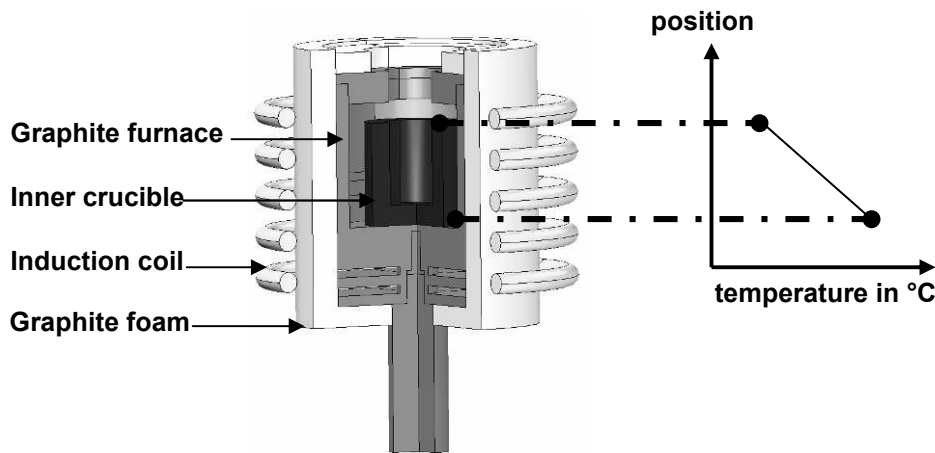
**Abstract.** The main problem for the development of 3C-SiC electronics is the lack of an adapted bulk growth process. The seeded sublimation method is not very adapted for the 3C polytype because of the solid-state transition from cubic to hexagonal that occurs at high temperature (above 1800°C). In this paper, we propose a new experimental set-up for the development of a solution route for the growth of high quality 3C-SiC crystals. By a coupled approach involving experiments and global process modeling, we have addressed the problems of dissolution and crystallization, elimination of parasitic nucleation and stabilization of the growth front. With an appropriate control of the different convection mechanisms, a stable growth front is demonstrated, with a growth rate of a few tens of  $\mu\text{m/h}$  at 1650°C. Further improvements and potentialities of this approach are discussed.

## Introduction

Despite some attempts in the 1960's by Bartlett [1] and Ellis [2] in a carbon saturated silicon melt, and more recently by Ujihara [3] and Eid [4], the solution route has always retained less attention than sublimation. Indeed, silicon has such a small solubility for carbon at reasonable temperatures that the method never seemed very practical, mainly because of low growth rate, unstable system with evaporation of solvent and reaction with the crucible. However, with respect to sublimation, the classical process for the growth of hexagonal ingots, solution growth presents some interesting assets which make it highly interesting to reconsider. Particularly, solution growth approach leads to high structural quality crystals with reduction of dislocation density and healing of micropipes [5]. To develop a solution growth process, the first points to address are i) the control of dissolution and crystallization areas, ii) the elimination of parasitic nucleation and iii) the obtaining of a significant growth rate with a stable growth front. For this, we have used a coupled approach, involving global modeling of the process, experimentation and characterizations.

## Experiments and numerical modeling

A modified Czochralski crystal pulling-machine is used for this work. The crucible set-up (see Fig.1) consists of one large graphite crucible insulated with graphite felt (called graphite furnace). It contains a smaller graphite crucible that acts as a container for liquid silicon and as the carbon source. The graphite furnace is heated by electromagnetic induction. Its geometry and its location with respect to the coil are fixed. The inner crucible is heated by radiation from the furnace. To study the different effects, both the design and the location of this inner crucible have been changed. The solvent is high purity silicon (9N) melted in a high density graphite crucible. Growth runs are performed in purified argon atmosphere, at low overpressure. Two types of experiments have been conducted. The first set consists of spontaneous nucleation. The aim was to visualize the dissolution and crystallization areas with respect to the temperature distribution. In the second set, single



crystalline seeds were mounted on a graphite holder and dipped in the solution in order to demonstrate the epitaxial growth of SiC.

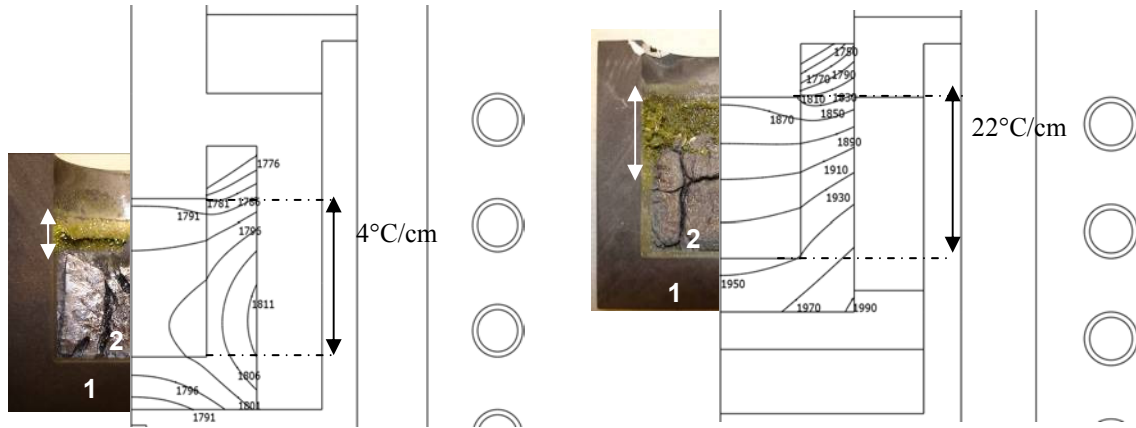
**Fig. 1:** Schematic view of the 3C-SiC solution growth setup with inner crucible

(black) which acts as liquid container, large graphite crucible called furnace and heated by induction (gray) and graphite foam (white)

The whole temperature distribution in the reactor and the fluid dynamics inside the liquid are computed under steady state with the COMSOL Multiphysics 3.4 ® software in a 2D-axisymmetric geometry. Heat transfer simulations include induction heating, conductive and radiative phenomena. Surface to surface radiation in the different graphite cavities have been taken into account, together with surface to ambient radiation, for instance at the surface of the liquid. Convection with ambient gas is neglected. Thermal physical properties used are temperature dependent. A complete induction heating modeling and optimization has already been reported in a previous work [6]. The different convective phenomena considered are buoyancy, stirring, electromagnetic and thermal Marangoni. Both solutal Marangoni and solutal buoyancy convections are not considered in this work because the carbon concentration in liquid silicon is very low, below 1% under the used conditions. It is thus reasonable to assume that the variation of liquid surface tension and the liquid density with carbon concentration is negligible. To make the simulations more readable, we only displayed the fluid part of the crucible.

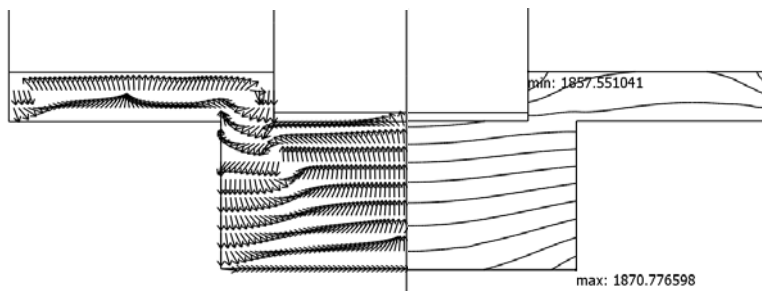
## Results and discussion

**Unseeded growth.** Computed temperature distribution together with a slice of the crucible are presented in Figure 2, for two different positions of the inner crucible. With the small axial thermal gradient (Fig.2 left), the crystallization only occurs at the liquid surface, starting from the crucible wall. For higher vertical thermal gradient (Fig.2 right), SiC crystallization also propagates inside the liquid and the total SiC amount is larger. As can be expected from the curvature of the liquidus line in the Si-C phase diagram, an increase of the temperature gradient leads to an increase of the carbon concentration gradient. Consequently, the supersaturation required for SiC crystallization is high enough on a wider area. In both configurations and for temperatures from 1500°C to 1800°C, silicon carbide appears as small, transparent, yellow needle-like crystallites with typical dimensions of 3 mm long and 0.4 mm in diameter. XRD patterns only indicate 3C-SiC. However, this spontaneous crystallization has to be avoided in the case of seeded growth. Indeed, if this parasitic crystallization develops to a too large extent, long-time growth runs cannot be implemented because of damageable effects such as modification of flow patterns, rotation of crystal altered, single crystal surrounded by polycrystal leading to mechanical stress. A compromise must thus be found between a small thermal gradient that permits transport of carbon in a precise part of the crucible and a high thermal gradient which leads to high yield of crystallization.



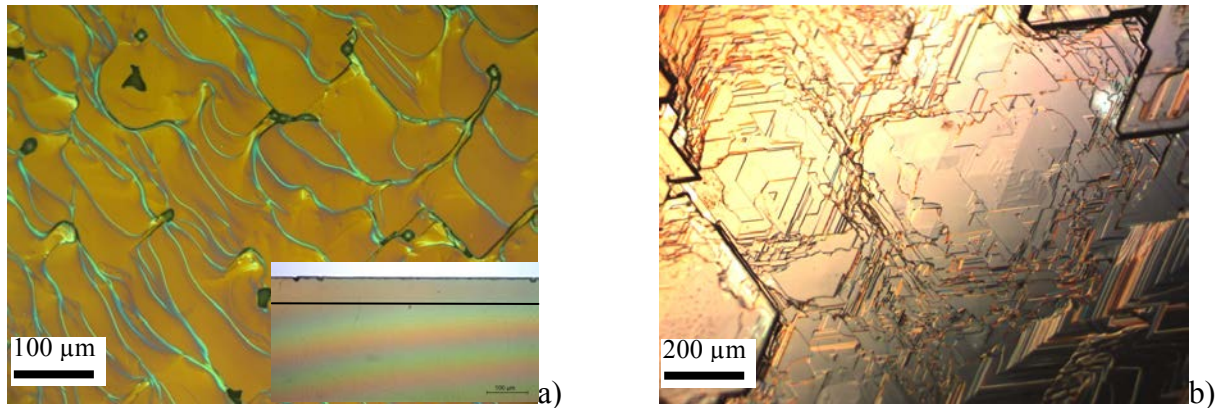
**Fig. 2:** Simulation and experiment in two different thermal gradient environments. White arrow symbolizes area of crystallization inside the graphite container (1). Silicon is partially leached by HF/HNO<sub>3</sub> solution (2). Left: low thermal gradient configuration, isotherms separated by 5K. Right: high thermal gradient configuration, isotherms separated by 20K.

**Seeded growth.** 3C-SiC(100) seeds from Hoya Corp or (0001) oriented 6H-SiC seeds have been used. They were stuck on a graphite holder and dipped 2 millimeters below the surface once the thermal equilibrium of the liquid is reached. Different crucible designs have been investigated in order to weight the contributions of each fluid dynamics phenomenon in the liquid. As a rule, we have found that both Marangoni and electromagnetic convections are damaging to get a stable growth front and to avoid parasitic crystallization. Those two effects are known to promote unsteady behaviours [7]. To limit those effects, we proposed the crucible design presented in Figure 3. In this geometry, convection loops resulting from Marangoni forces and electromagnetics forces are mainly located in the top lateral part of the liquid. Consequently, they show a very limited effect on mass transfer close to the seed surface. Below the seed, mainly rotation of crystal is responsible of the convection. The fluid velocity in this area is 5 to 20 times smaller than velocity in the lateral part of the fluid. The thermal gradient inside this cavity is less than 10°C/cm. This crucible configuration is very close to the convection free cell proposed by Tiller [8]. However, in his case, parasitic crystallisation inside the liquid is very hard to avoid because of baffles present below the seed.



**Fig. 3:** Velocity vectors (left) and isotherms (right) inside liquid separated by 1K for a crucible design adapted to long time experiments.

By using the crucible of Figure 3, two selected results of seeded growth at 1650°C are presented in Figure 4. Size of the seed is 1\*1cm<sup>2</sup>. In the first case, a low thermal gradient close to the 3C-SiC seed is applied. The growth front is stable with a two dimensional growth mode. Few inclusions are detected and growth rate is 10 μm/h, homogeneous over all the crystal. In the second case, the thermal gradient close to a 6H-SiC on axis seed surface has been increased. The resulting growth rate is 45 μm/h. Even if some polytype transitions have been evidenced, the process is perfectly stable over 20 hours. There is no reason that it could be maintained for even longer times.



**Fig.4:** NDIC images of seeded 3C-SiC crystal growth at 1650°C in Si melt. a) 3C-SiC (001) seed, surface of crystal after 6 h growth run. Embedded: cross section, interface has been underlined for a better visualisation. b) 6H-SiC (0001) seed, surface of the crystal after 20 h growth run.

## Conclusion

We have presented a new experimental set-up for the development of a solution route for the growth of high quality 3C-SiC crystals. By a coupled approach involving experiments and global process modeling, we have successfully addressed the following issues: i) control of the dissolution and crystallization areas, ii) elimination of parasitic nucleation, iii) stabilization of the growth front over long time without any polycrystal occurrence. First experiments with the aim of improving the growth rate have shown that bulk compatible growth rates (a few tens of  $\mu\text{m/h}$ ) at a seed temperature about 1650°C can be easily reached. Further works are under progress to increase the growth rate, keeping a stable growth front. This solution growth process could be an alternative to sublimation, particularly for the growth of “low temperature polytype” like 3C-SiC.

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