



HAL
open science

Nucleation and Growth of 3C-SiC Single Crystals from the Vapor Phase

Didier Chaussende, Jessica Eid, Frédéric Mercier, Roland Madar, Michel Pons

► **To cite this version:**

Didier Chaussende, Jessica Eid, Frédéric Mercier, Roland Madar, Michel Pons. Nucleation and Growth of 3C-SiC Single Crystals from the Vapor Phase. 7th European Conference on Silicon Carbide and Related Materials, Sep 2008, Barcelone, Spain. pp.31-36, 10.4028/www.scientific.net/MSF.615-617.31 . hal-00389062

HAL Id: hal-00389062

<https://hal.science/hal-00389062>

Submitted on 16 Sep 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

Nucleation and Growth of 3C-SiC Single Crystals from the Vapor Phase

D. Chaussende^{1,a}, J. Eid¹, F. Mercier¹, R. Madar¹ and M. Pons²

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

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

^adidier.chaussende@inpg.fr

Keywords: 3C-SiC, nucleation, bulk growth, PVT, sublimation

Abstract. The conditions to succeed in growing 3C-SiC single crystals are first, make available large 3C-SiC seeds and second, develop a suitable growth process. In this paper, we will address those two issues by reviewing the most recent results in the field. Nucleation, growth, structural quality and doping results will be presented. New insights on 3C bulk growth will be discussed with respect to a future development of real bulk 3C-SiC ingots.

Introduction

From the crystal growth point of view, the cubic form of silicon carbide (called 3C-SiC or β -SiC) is a highly challenging scientific issue, mainly because of the discrepancy between the stability range of this polytype and the operating conditions of the available bulk growth processes. It is well established that some criteria have to be fulfilled to grow 3C-SiC. First, a strong deviation from equilibrium is required, together with a low temperature [1]. For too high the temperature and as a consequence of its metastable nature, 3C-SiC undergoes a solid state transition to 6H-SiC [2], which could already occur around 1800°C [3]. Additionally, a high Si/C ratio in the gas phase is suited [4, 5]. Because of those considerations, it is not surprising that during the standard Lely method, the formation of β -SiC is extremely rare [6]. Also, despite some attempts along the last few decades, the seeded sublimation growth method, which is the most common current technique for the growth of 6H- and 4H-SiC ingots, has not demonstrated any bulk 3C-SiC crystals. Apart from those difficulties, the second important problem is the lack of 3C-SiC seeds. Although the Acheson and Lely processes provided a lot of large 6H-SiC seeds for the development of the hexagonal variants, cubic SiC seeds were almost never obtained. The only solution that appeared was the use of different substrates like Si, α -SiC or more exotic compounds. Even if it solved the problem of seeds, it also brought some additional problems coming from the heteroepitaxial nature of the 3C crystals: lattice and thermal expansion mismatches, particular structural defects, mosaicity

To summarize, up to now nobody succeeded in growing real 3C-SiC bulk single crystals. The conditions to succeed are first, make available large 3C-SiC seeds and second, develop a suitable growth process. By addressing those two issues in this paper, we will give new insights on bulk growth of 3C and discuss the possibilities to develop real bulk 3C-SiC ingots.

The CF-PVT process

All the results presented in this paper have been obtained with the Continuous Feed Physical Vapor Transport (CF-PVT) process. It has been described elsewhere [7] and compared to the current SiC growth processes [8]. Briefly, it combines the advantages of both the PVT process for the growth of single crystals and HTCVD process for the in situ formation and continuous feeding of the high purity polycrystalline source. Due to the simultaneous implementation of those two steps and the strong interactions that appear between them, a more flexible control of the supersaturation close to the growing crystal is possible [9] and the thermochemistry of the CF-PVT process can be adjusted

compared to the standard sublimation method [10]. The possibilities offered by this technique most probably contributed to a large extent to the uncommon results obtained on 3C.

Nucleation of the 3C polytype

Spontaneous nucleation. The spontaneous formation of 3C-SiC has been reported in a wide range of temperature, from 1500 to 2000°C, using either a solution [11] or a chemical vapour deposition (CVD) route [12]. This could be explained by the lower nucleation work of the cubic polytype than that of the hexagonal ones [4]. With the CF-PVT process and up to 2100°C, only 3C-SiC crystals have been obtained through spontaneous nucleation on the graphite lid. If the Gibbs free energy of formation of a nucleus together with its critical radius can be monitored with the process parameters, then the nucleation rate/ growth rate ratio can be controlled (Fig.1 and 2). Under optimized conditions, only a few crystals can form.

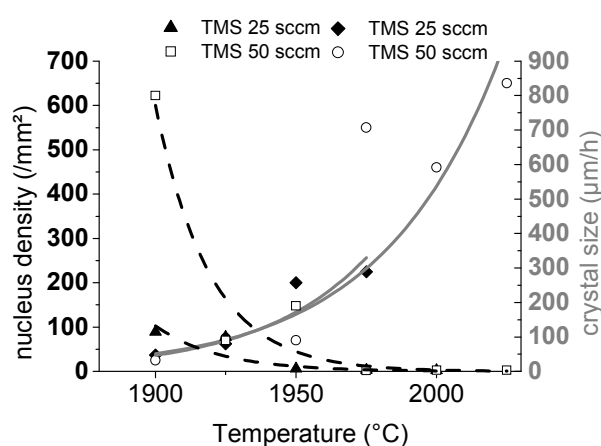
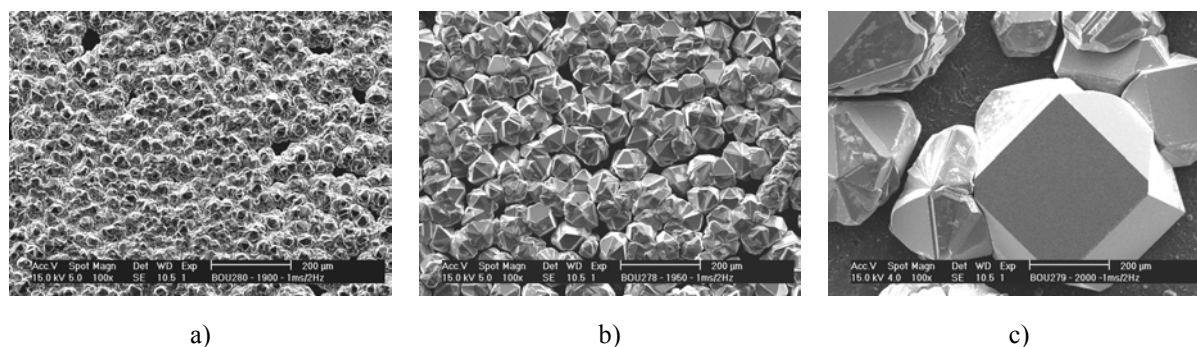


Fig.1: Evolution of nucleus density (left axis, dashed line) and crystal sizes (right axis, solid lines) as a function of growth temperature, for two different TMS flow rates: 25 and 50 sccm.

Fig.2: SEM photographs of spontaneously grown 3C-SiC crystals at a) 1900°C b) 1950°C and c) 2000°C.



a)

b)

c)

Heteroepitaxy. To pass round the lack of 3C-SiC seed, the most realistic way is to grow $\langle 111 \rangle$ oriented β -SiC crystals on (0001) α -SiC nominal substrates. However, in this case twins are usually observed, coming from the two possible orientations of the cubic 3C-SiC axis on the hexagonal 6H-SiC basis. As a consequence this way requires to monitor first the heteropolytypic α - β transition and second the selection of one orientation among the two possible; i.e. elimination of Twin Boundaries (TB).

The α - β transition at high temperature is the typical case of competition between the formation of the thermodynamically stable polytype (3C) and the kinetic replication of the substrate polytype which could be “out-of equilibrium”. The relationships between these two phenomena, which corresponds to a competition between two dimensional (2D) nucleation and “step-flow” growth mode has been extensively studied in the CVD process [13] and in the close space sublimation process [14]. Similar trends are obtained with CF-PVT [15]. Most difficult is the TB elimination. Many authors have pointed out some parameters which strongly affect the TB density, such as seed

polarity, misorientation, C/Si ratio in the gas phase, temperature, seed surface preparation... [See 16 and ref therein]. Apart from the so called “step-free mesas” technique [16], the selection mechanism for the 3C-SiC orientation does not take place during the nucleation step (formation of the 2D nuclei) but after, i.e. during the expansion of those nuclei. The selection is based on a strong interaction between the α -SiC substrate steps and the anisotropic lateral expansion of the β -SiC domains [15]. In other words, the selection requires the simultaneous implementation of two different processes: i) the lateral expansion of the nuclei along the substrate step edges (Fig.3a) and ii) faceting of the 3C domains (Fig.3b). This leads to a fast orientation overlapping by the other (Fig.4). Such observation, probably coming from a similar mechanism, has already been mentioned for the heteroepitaxial growth of 3C-SiC from Vapour-Liquid-Solid mechanism at low temperature [17].

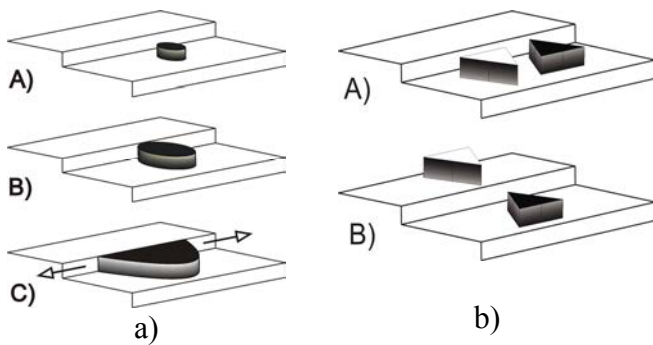


Fig.3: a) effect of the substrate step on the 3C-SiC nucleus lateral expansion along the step edge; b) according to the Wulff construction, faceting of the two twinned 3C-SiC domains leads to different lateral expansion. They could be A) on the same terrace, one variant being blocked by the expansion of the other and B) on different terrace, one variant being overlapped by the other.

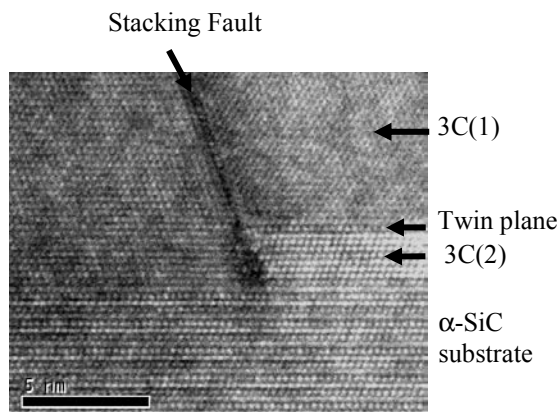


Fig.4: cross sectional HRTEM observation of the α - β interface. A very thin twinned 3C domain suggests that it is overgrown at the early stage of growth.

Growth and characterization of 3C-SiC crystals

Among the different reported results, two must be emphasized. They were obtained at temperature lower than 1800°C by chemical vapor deposition (CVD), either by self nucleation of 3C-SiC crystals on a graphite susceptor [18] or by heteroepitaxy of large area free-standing 3C-SiC wafers on “undulant-Si (001)” substrates [19]. In the first case, crystals of very high structural quality were obtained [20] but the size, about several mm diameter was not compatible with applications. In the second case, up to 6 inches diameter free-standing wafers have been demonstrated but crystals still contain too many structural defects which are intrinsically related to the poor heteroepitaxial SiC/Si system [21]. More recently, we have demonstrated through the CF-PVT technique, that the growth of 3C-SiC was compatible with a high temperature bulk growth process, using significant growth rates. For example, employing the optimized nucleation conditions on α -SiC substrate described above, we have successfully grown a TB free 3C-SiC wafer on ~ 30 mm diameter at 70 $\mu\text{m/h}$ (Fig.5a and [22]). Since this report, with improvements on the growth process and using a VLS seeding step, benefits on the growth rate (140 $\mu\text{m/h}$) and on the structural and optical properties have been achieved [23].

The most interesting results are those obtained through unseeded growth. With a careful monitoring of the nucleus density (see preceding section) and a subsequent growth, perfectly faceted cuboctahedral 3C-SiC single crystals can be grown at 2100°C, with a rate about 200 $\mu\text{m}/\text{h}$ (Fig.5b). The resulting crystals, with an average diameter of 5 mm, developed under close to equilibrium conditions. They all exhibit a high structural quality with defects density in the range 10^4 to 10^5 cm^{-2} . Similarly to the well-known Lely crystals, they are of very high structural quality, with no measurable mosaicity and residual strain. The FWHM of the (111) and (100) X-ray diffraction rocking curves are less than 20 arcsec.

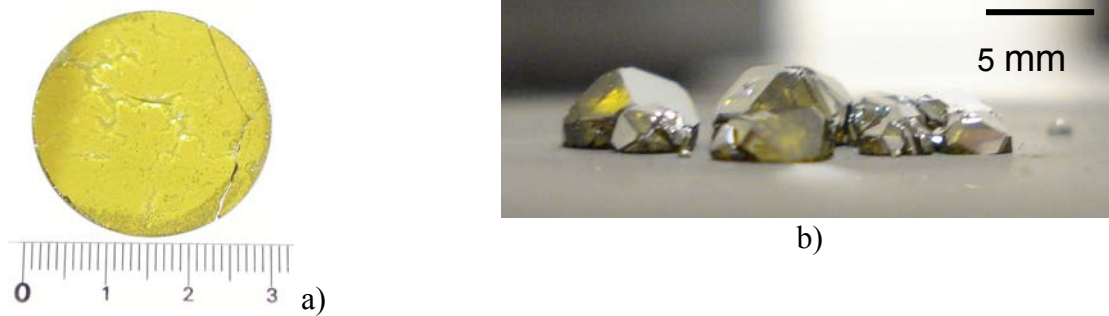


Fig. 5: a) 30 mm diameter β -SiC thick layer free of TB. b) few millimeters size unseeded 3C-SiC crystals exhibiting perfectly faceted shapes

For all the crystals grown on a seed, systematic formation of lamellae is observed, lying along the $\{111\}$ family plans. Those lamellae, which correspond to zones of increasing hexagonality, are related to the solid state 3C-6H transition [24]. Moreover, even with our best material, strong birefringence contrasts are evidenced in planar view (Fig.6a). Self-seeded 3C-SiC crystals exhibit drastically different features (Fig.6b). Lamellae only formed at the boundary between growth sectors but none within the sectors. This total absence of strain is even more marked for the (100) orientation (Fig.7).

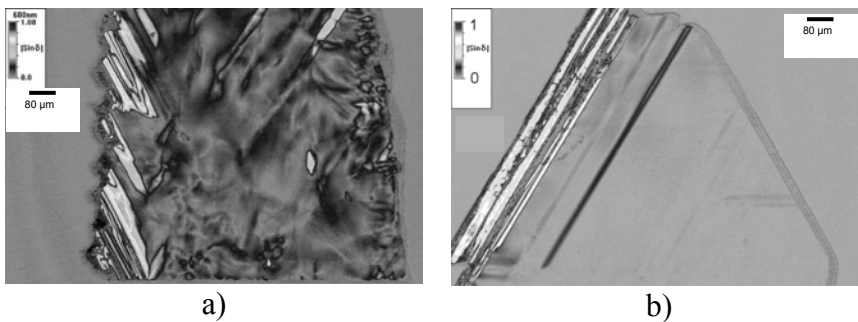


Fig.6: a) planar view of a (111) oriented 3C-SiC thick layer grown on 6H-SiC substrate at 2000°C with a VLS buffer layer. b) Planar view of a (111) oriented self-nucleated 3C-SiC crystal grown at 2100°C. The color scale corresponds to magnitude of birefringence

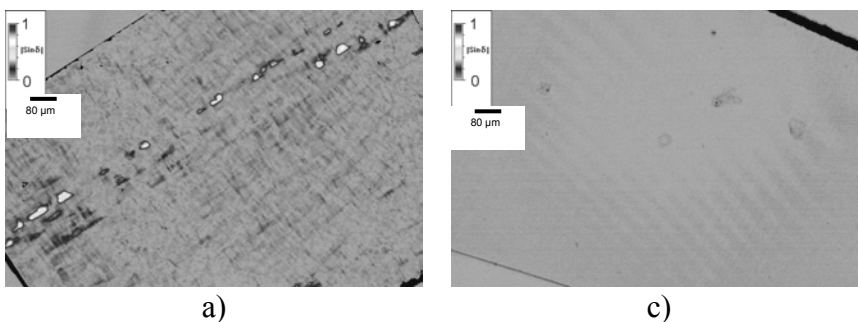


Fig.7: planar view of (100) oriented 3C-SiC crystals: a) free standing wafer from Hoya company (old research grade generation wafer), b) self-nucleated crystal grown at 2100°C. The color scale corresponds to magnitude of birefringence

The problem of stability

From the available literature, the conditions required to stabilize the 3C form are large deviation from equilibrium, low temperature and high Si/C ratio in the gas phase (see references given in the introduction). It is a bit surprising that we came to different conclusions, gathering all the results obtained with the CF-PVT process. The perfectly faceted crystals, together with the few number of nuclei formed, suggest growth conditions close to the thermodynamic equilibrium. We conclude then that a strong deviation from equilibrium is not necessary to stabilize the cubic polytype even at high temperature. The second point is that the CF-PVT process works under a much lower Si/C ratio than the standard sublimation [10]. This peculiarity is probably the reason for the low residual doping level of the crystals, due to the so-called “site competition” mechanism. Si-rich gas phase is thus not necessary for the 3C polytype. Finally, our best unseeded crystals have been obtained at 2100°C. 3C-SiC crystals could probably be grown at higher temperature but 2100°C is the upper limit of the CF-PVT process itself, due to the gaseous precursor used [9]. This shows that the temperature is not the only parameter to consider for the 3C to 6H solid state transition. It is important to note that hexagonal lamellae are only observed in the case of seeded growth and/or at the boundary between growth sectors, i.e. in strained material (see birefringence pictures above) or material containing a lot of extended defects. Said in a different way, depending on the stress state (and possibly the amount of extended defects), the critical temperature for the 6H-3C phase transition can be shifted above 2100°C and probably up to 2600°C if we refer to comments accompanying ref [6]. This solid-state transition is still far from being understood and even the mechanism and the driving force have not been clearly identified. Nevertheless, it can be avoided in the case of strain-free and high quality 3C-SiC crystal growth, and calls in question again the “metastability” of the 3C polytype.

In-situ n-type doping

The low temperature photoluminescence measurements on our unintentionally doped 3C-SiC crystals, presented a nice resolution of near band edge excitonic features (with MBEC resolution up to $m=5$). Such features, corresponding to very high purity and high quality material are very rare (see [23] and references therein). The residual doping level, related to nitrogen incorporation, is typically of 10^{16} cm^{-3} , without any compensation. We have successfully n-type doped our 3C-SiC crystals up to a few 10^{18} cm^{-3} . A sectorial dependence of nitrogen incorporation has been evidenced. It can be attributed to the carbon site density available on a given growing surface. The N incorporation is as follow: (111)-C face > (100) face > (111)-Si face. The incorporation difference is all the more important than the nitrogen flow rate is high in the gas phase [25].

Summary

In this short review, we have tried to address the main difficulties related to the growth of 3C-SiC single crystals. The first problem, which is the availability of seeds, can be solved either by self nucleation or by the use of foreign substrate, the latter being more appropriate for large diameter development. However, it has required deeply studying and understanding the mechanism of twin boundaries elimination. For the second problem, which is the availability of a bulk growth process, we have shown that the peculiar growth conditions existing in the CF-PVT process are able to stabilize the 3C-SiC polytype, at high temperature, at significant growth rate and under close to equilibrium conditions. The resulting material can be free of strain, presents low extended defect density and can be obtained with high intrinsic purity or n-type doped. Even if a lot of works still is required to increase the crystal size, our results pave the way of a future development of real 3C-SiC ingots by a vapor phase route. Apart from this, attention should also be paid to the solution route (not evocated here), which already gives very promising results [26].

Acknowledgements

The authors greatly acknowledge all the collaborators, friends, PhD students who have participated or are still active in the 3C-SiC adventure. Particular thanks are given to the team of Prof. Efstathios Polychroniadis from University of Thessaloniki, the team of Dr. Jean Camassel from Montpellier University, the team of Dr. Alexandre Boulle from Limoges University, the NOVASiC team and of course the team of Dr. Gabriel Ferro from Lyon University. This work was in part supported by the European Commission (Contract Nb. MRTN-CT-2006 -35735), by the French National Research Agency ANR (Contract Nb ANR-05-JCJC-0207-01), the DGA and by NOVASiC.

References

- [1] W. F. Knippenberg: Philips Res. Repts. Vol. 18 (1963), p. 161
- [2] N. W. Jepps, T. F. Page: Progress in Crystal Growth and Characterization Vol. 7 (1983), p. 259
- [3] R. Puesche, M. Hundhausen *et al.*: Journal of Applied Physics Vol. 96 (2004), p. 5569
- [4] Y. M. Tairov, V. F. Tsvetkov: Progress in Crystal Growth and Characterization Vol. 7 (1983), p. 111, and references therein.
- [5] H. N. Jayathirtha, M. G. Spencer *et al.*: Journal of Crystal Growth Vol. 174 (1997), p. 662, and references therein.
- [6] D. R. Hamilton: Silicon Carbide, Proc. Conf. Boston Vol. (1960), p. 43
- [7] D. Chaussende, F. Baillet *et al.*: J. Electrochem. Society Vol. 150 (2003), p. G653
- [8] D. Chaussende, P.J. Wellmann *et al.*: Journal of Physics D Vol.40 (2007), p. 6150
- [9] D. Chaussende, M. Ucar *et al.*: Crystal Growth & Design Vol. 5 (2005), p. 1539
- [10] D. Chaussende, E. Blanquet *et al.*: Chemical Vapor Deposition Vol. 12 (2006), p. 541
- [11] F. A. Halden: Silicon Carbide, Proc. Conf., Boston Vol. (1960), p. 115
- [12] J. T. Kendall: Silicon Carbide, Proc. Conf., Boston Vol. (1960), p. 67
- [13] T. Kimoto, A. Itoh *et al.*: physica status solidi b: Basic Research Vol. 202 (1997), p. 247
- [14] Y. M. Tairov, V. F. Tsvetkov *et al.*: Journal of Crystal Growth Vol. 36 (1976), p. 147
- [15] L. Latu-Romain, D. Chaussende *et al.*: Crystal Growth & Design Vol. 6 (2006), p. 2788
- [16] P. G. Neudeck and J. A. Powell: *Silicon Carbide* (Springer, 2004), p.179
- [17] M. Soueidan, G. Ferro *et al.*: Crystal Growth & Design Vol. 6 (2006), p. 2598
- [18] S. N. Gorin, L. M. Ivanova: physica status solidi b: Basic Research Vol. 202 (1997) p. 221
- [19] H. Nagasawa, K. Yagi *et al.*: *Silicon Carbide* (Springer, 2004), p. 207
- [20] W. M. Vetter, M. Dudley: Journal of Crystal Growth Vol. 260 (2004), p. 201
- [21] E. Polychroniadis, M. Syvajarvi *et al.*: Journal of Crystal Growth Vol. 263 (2004), p. 68
- [22] D. Chaussende, L. Latu-Romain *et al.*: Materials Science Forum Vol. 483-485 (2005), p. 225
- [23] D. Chaussende, F. Mercier *et al.*: Journal of Crystal Growth Vol. 310 (2008), p. 976
- [24] D. Chaussende, F. Mercier *et al.*: Proceedings of the International Conference on Silicon Carbide and Related Materials Oct. 14-19, 2007 Otsu, Japan.
- [25] J. Eid, I. G. Galben *et al.*: this conference.
- [26] F. Mercier, D. Chaussende *et al.*: this conference.