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Seed Surface Preparation for SiC Sublimation Growth

B. Pelissier¹, C. Moulin², E. Pernot¹, M. Anikin¹, P. Grosse², C. Faure²,
B. Ferrand², M. Couchaud², G. Basset² and R. Madar¹

¹LMGP, UMR 5628 INPG/CNRS, BP 46, FR-38402 St. Martin d'Hères Cedex, France

²LETI-CEA Grenoble, 17 rue des Martyrs, FR-38054 Grenoble Cedex 9, France

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Abstract : The seed surface preparation for SiC sublimation growth has been investigated. Two methods have been developed to prepare and improve the seed surface contribution during the growth initiation:

- An in-situ sublimation etching of the seed is performed.
- The seed surface is prepared by ex-situ polishing and chemical and ozone cleaning.

Both methods promote a better lateral growth mechanism, and then promote the preferred step flow growth mechanism. This results in a better crystalline quality of the crystals in terms of mosaïcicity, polytype stability and micropipe density.

I) Introduction

In 1978 the invention of the seeded sublimation growth technique, the so-called "Modified Lely Method", opened the path to the production of large area SiC wafers. However, at present, the material quality still remains an obstacle to a commercial breakthrough of SiC technology. The improvement of the structural properties and an increase of the available size of SiC wafers are key areas of research and development in this field. The seed surface quality has a major influence on the initiation of SiC sublimation growth. A contaminated or damaged surface will lead to defects which propagate into the growing ingot. This results in a high pinhole density and the formation of inclusions. In order to optimize the seed/ingot interface, a number of treatment methods for seed surface preparation have been investigated.

The experimental setup used for the whole study has been previously described [1].

II) The in situ sublimation etching

To remove the damaged and contaminated surface layer, and to initiate lateral growth, Anikin proposed in situ sublimation etching [2]. This technique has been optimised to obtain a calibrated sequence of temperature and pressure as a function of time which improves the reproducibility of the early stages of SiC growth. The etching sequence is as following :

-At the beginning of the growth process, under atmospheric pressure of argon, the temperature is raised to Tise (temperature of in-situ etching) while the temperature gradient is inverted (seed temperature > source temperature).

-Then the pressure is decreased down to Pise (pressure of in-situ etching), while temperature is maintained to Tise. The pressure remains at Pise during Dise (duration time of in-situ etching).

-Finally, the argon pressure is increased to atmospheric level and the temperature gradient is slowly established in accordance to the growth conditions.

According to the model Matsunami et al proposed for CVD growth [3], the average step size on the surface must remain close to the lattice parameter to allow for the step flow growth mechanism. If the steps are too high, the step flow is not homogeneous and structural defects such as inclusions of other polytypes are more likely to be formed. The influence of the parameters Tise, Pise and Dise on the step height have been investigated, on the C-face and Si-face on both 4H and 6H seeds. The experimental samples were pieces of off-axis seeds. On-axis seeds like Lely crystals don't allow to obtain a continuous step structure. The step

structure has been observed by Scanning Electron Microscopy (SEM) and the step height has been measured by Atomic Force Microscopy (AFM).

The steps height on the surface depends exponentially on temperature but also on pressure and etching duration time. In addition, if the Si pressure over the seed is too low, carbonisation of the SiC surface is observed for elevated temperature ($T_{ise} = 2000^{\circ}\text{C}$) and low pressure ($P_{ise} < 50\text{Torr}$).

At high temperature ($T_{ise} = 2000^{\circ}\text{C}$) and for a short duration $D_{ise} = 3\text{min}$, the etching is very efficient and all the surface defects have been removed. The surface is very regular but the steps height RMS value measured by AFM is 757 \AA for $P_{ise} = 50\text{Torr}$ and 306 \AA for $P_{ise} = 150 \text{ Torr}$ (Fig. 1). The etching is too strong to initiate a good step flow mechanism.

As etching efficiency strongly depends on temperature, a lower temperature allows to obtain smaller steps. A compromise between etching depth and step height has been found in a parametric study: At $T_{ise} = 1800^{\circ}\text{C} / P_{ise} = 50 \text{ Torr} / D_{ise} = 10\text{min}$, the step height value is 52 \AA (Fig. 2).

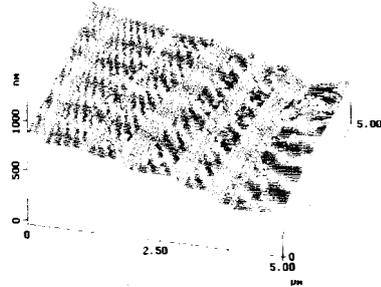


Fig. 1 : AFM image ($5\mu\text{m} \times 5\mu\text{m}$) of a heavily etched 6H Si-face.



Fig. 2 : AFM image ($0.5\mu\text{m} \times 0.5\mu\text{m}$) of a smooth etched 6H Si-face

The influence of the duration D_{ise} has been studied. An Increase of the etching duration T_{ise} results in an increase in step size. At $T_{ise} = 1800^{\circ}\text{C} / P_{ise} = 50 \text{ Torr} / D_{ise} = 1\text{min}$, we observed no significant step structure on the surface. The etching duration is too short to achieve the required removal of material. In opposite, for $D_{ise} = 20\text{min}$, the step height is almost twice as large as for 10min duration.

In all cases we found that the steps are higher on the Si-face than on the C-face. For example, at $T_{ise} = 1850^{\circ}\text{C} / P_{ise} = 150 \text{ Torr}$ and $D_{ise} = 10\text{min}$ the step height is 350 \AA on the Si-face (Fig. 3) and 120 \AA on the C-face (Fig. 4), respectively, for a 6H seed.

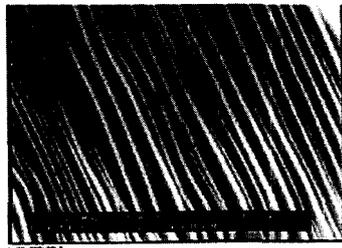


Fig. 3 : SEM image of a 6H Si-face after thermal in-situ etching

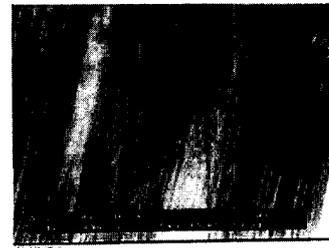


Fig. 4 : SEM image of a 6H C-face after thermal in-situ etching

For 4H substrates, we observed that the minimum temperature necessary to reveal any observable step structure is higher than for 6H. A working point has been found for 4H at $1825^{\circ}\text{C} / 150 \text{ Torr} / 10\text{min}$ with similar consideration like in the 6H study.

III) Ex situ surface preparation process

To prepare and improve the start of growth, two points have been developed. Both of them intend to promote a better lateral growth mechanism. The 4H-SiC seeds under study are 8° off axis. Optical microscopy and micromap (Michelson interference microscope) were used to observe the seed surface.

The seed preparation includes a first step of polishing. The roughness measured by micromap on a 4H-SiC C-face reaches a value of 1 to 2 Å RMS. Possible preferential nucleation due to irregular surface features can be avoided.

A chemical treatment is then performed in order to remove contamination from the seed surface. The first chemical treatment ($H_2O_2+H_2SO_4$) forms a thin oxide layer which is subsequently removed after an acid etch ($HF+HNO_3$). This is followed by an UV ozone cleaning (Jelight model 42-220). The analysis of the seed surface by AES indicate solely silicon, oxygen and carbon. Figures 5a and 5b show the distribution of these elements versus sputter time (directly proportional to depth) after chemical treatment, respectively before and after the ozone cleaning; the characteristic lines of Si-O, Si-C and C-(O,H) bondings have been separated. AES indicates, The contaminated carbon layer is significantly reduced by the ozone cleaning: 40% of C-graphite bonding instead of 60% without ozone cleaning. All the samples contain a silicon oxide layer. Under this layer, a stoichiometric Si/C ratio of 1 is observed. This silicon oxide layer is supposed to act as a protective layer during the initial heat-up and then to desorb from the seed surface at elevated temperature.

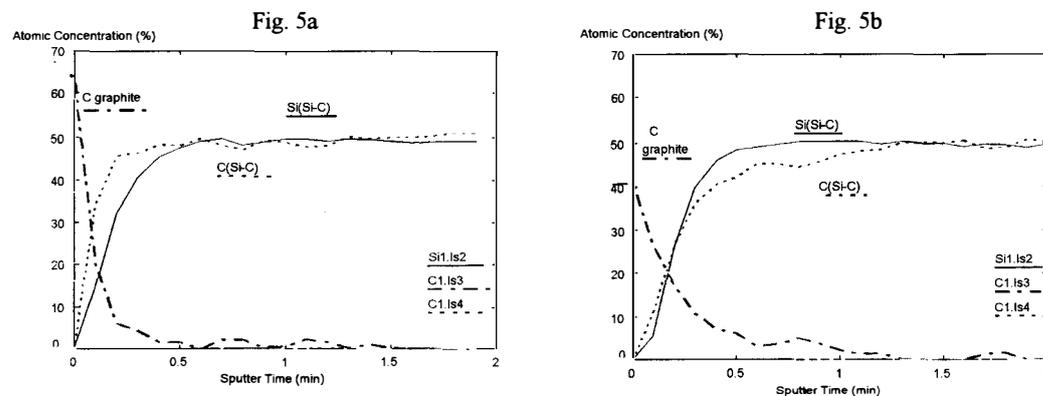


Fig. 5 : Analysis of the seed surface by Auger Electron Spectroscopy after chemical treatment, before ozone cleaning (Fig5a) and after ozone cleaning (Fig5b)

After this ex-situ preparation, great care must be taken during the initial steps of the growth process in terms of the optimization of the pressure and temperature history to avoid the deterioration of the ex-situ prepared surface. Figure 6 shows the seed surface observed by optical microscopy after process interruption during the heat-up. The best surface morphology was achieved at lower temperature value for the increase of the argon pressure, and a higher pressure during the heat-up. If the temperature corresponding to the outgasing is too high, silicon rich species in the vapor can condense on the seed surface. This leads to silicon-like droplets that probably correspond to the dark circle visible in figure 6a. If the pressure is too low during the heat-up, nucleation of undesired polytypes such as 3C inclusions can occur [4]. This can also lead to the premature graphitization of the source powder : the Si/C ratio of the gaseous species is larger than 1 for low temperature [5]. To avoid the sublimation of the source powder at these temperatures, argon is introduced in the growth chamber at a pressure of 600 Torr.

The roughness of the seed surface corresponding to Fig 6b has been determined by micromap measurements after process interruption at 1200°C, 300Torr (during the heat-up). It agreed exactly with the roughness value after polishing ($RMS=2 \text{ \AA}$, $P-V=50 \text{ \AA}$) showing no deterioration of the seed surface.

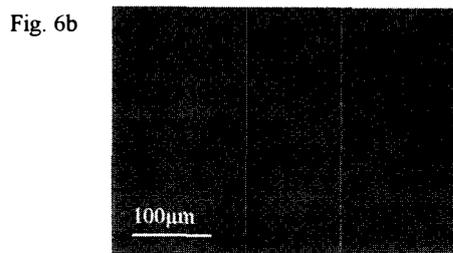
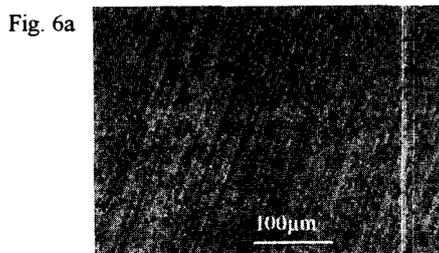


Fig. 6: Optical microscopy observation of the seed surface after heat-up interruption.
 Fig 6a: 1450°C, 50 or 300 Torr and Fig 6b: 1200°C, 300 Torr.

Before the growth process, the SiC powder is heated under vacuum and then sintered inside the PVT reactor at high temperature value and atmospheric argon pressure. This preparation step leads to the formation of more homogeneous steps on the seed surface compared to the results obtained with non-sintered powder (see Figs 7). The process has been interrupted once the growth temperature was achieved and just before decreasing the pressure for crystal growth (interruption at 2050°C, 300Torr). Most likely the source exhibits a more homogeneous sublimation behaviour when it is sintered: sintering leads to more homogeneous grain size and hence, reduces significantly the influence of grain size on evaporation rate.

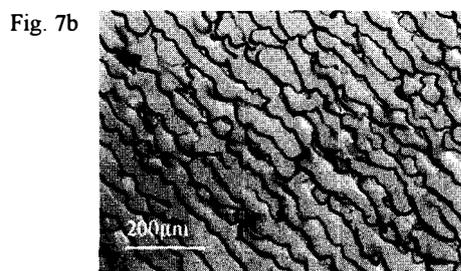
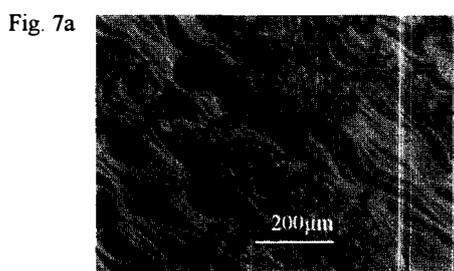


Fig. 7: Optical microscopy observation of the seed surface after process interruption.
 Fig7a: non sintered source powder Fig. 7b: sintered source powder

This seed surface preparation has significantly improved the quality of the boules, especially in terms of a reduction of mosaïcicity: double crystal X-ray diffraction mapping shows misoriented domains with 60 arcsec misorientation. Misorientation was typically 300 arcsec before introducing this method.

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