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# Experimental Investigation of 4H-SiC Bulk Crystal Growth

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**Abstract :** 4H-SiC single crystal ingots up to 1 inch in diameter have been grown by the Modified Lely Method. A growth sequence is proposed. The polytype study by Raman spectroscopy has shown that, in our configuration, 4H ingots could be reproducibly obtained on the (000 $\bar{1}$ )C face of a 4H-SiC seed. The ingot contamination by transition metals (Ti, V) is discussed in the light of low temperature photoluminescence.

## Introduction

Owing to its intrinsic physical characteristics, 4H-SiC is currently considered as the most attractive silicon carbide polytype for the fabrication of power and high frequency electronic devices. However, despite a constant progress in crystal growth, the development of industrial applications has been severely limited by the insufficient quality and small size of the commercially available substrates. A deeper understanding of growth rate and quality limiting processes by fundamental research is strongly needed.

Basically, there are three main experimental approaches, which have been reported for the growth of 4H-SiC by the modified Lely method [1]:

- growth in the presence of an excess of carbon in the vapor phase,
- growth on the (000 $\bar{1}$ )C face of a SiC substrate,
- growth in the presence of selected impurities like Sn in the vapor phase [2].

The first method is related to the thermodynamic aspect of the growth process (modification of the Si/C ratio in the gas phase) while the last two ones are mainly connected with the nucleation and surface diffusion effects. Up to now, these different approaches have been used together in most reported papers and it is difficult to determine the respective role of each parameter. Following our previous work on 6H-SiC [3,4], in order to get a better understanding of their individual role, we have undertaken a systematic study of their influence. In this paper we will report the results obtained so far during the study of the influence of substrate nature and polarity.

## Experimental procedure

Our sublimation system is quite similar to the one already described by Yu.M. Tairov [5]. A high purity silicon carbide powder contained in a graphite crucible is heated by a R.F. inductive system. The monocrystalline (0001) oriented SiC seed is set on the graphite lid. Using both water cooled concentric quartz tube and graphite felt, the temperature of the crucible can reach 2400°C. A secondary vacuum of 10<sup>-6</sup> torr is performed before the growth in order to provide a clean environment for the growth process. We have previously shown [3,4] that temperature-gradient-controlled SiC growth of 6H-SiC reduces the pinhole density. In this work, we have found that the in situ etching acts differently for 6H-SiC and 4H-SiC seeds. While the surface of Lely 6H-SiC platelets is smooth after sublimation etching, the 4H-SiC seed surfaces partially carbonize. These different behaviors led us to choose a pressure-controlled crystal growth process consisting of three steps :

- initial heating and pumping. At this stage, the graphite crucible remains open up to 1450°C allowing outgasing of the whole reactor ;
- at 1400°C the argon pressure is set to 400 torr in order to avoid growth at low temperature ;
- finally, reaching the growth temperature, the argon pressure is slowly reduced to the final value. Depending on this value the growth rate can vary from 1 to 2 mm.h<sup>-1</sup>.

This growth sequence has been successfully applied for the growth of 6H-SiC ingots before trying to obtain the 4H-SiC polytype. Although it has been reported that the growth of 4H-SiC may occur on the carbon face of Lely 6H-SiC seeds [6], we have found that, in our crucible geometry and growth conditions, we always had growth of 6H-SiC on the C-face of 6H-SiC substrates. Accordingly, all seed were 4H-SiC crystals provided by Yu.M. Tairov [1]. The seeds were polished and etched by molten KOH in order to determine the substrate polarity before the experiment. The influence of the polarity of the 4H-SiC seeds has been studied. Since we report results collected on 4 typical samples, the corresponding growth parameters are listed in Table 1:

Table 1: Growth parameters of the samples.

	Seed polytype	Growth surface	Powder treatment	T seed* (°C)	T source* (°C)	Growth rate (mm.h <sup>-1</sup> )
Sample A	4H-SiC	C face	None	2375	2100	2.1
Sample B	4H-SiC	C face	acid+annealing	2250	2000	1.5
Sample C	4H-SiC	Si face	acid+annealing	2400	2100	2.2
Sample D	4H-SiC	Si face	acid+annealing	2380	2080	1.8

\*The so called seed and source temperatures are obtained by pyrometer measurement respectively on top and back of the crucible. They do not correspond to the real temperature.

## Results and discussion

Polytypic conversion is a constant problem in SiC growth. In order to investigate the polytype of the samples and its homogeneity, Raman spectroscopy has been performed. We have used a micro-Raman spectrometer from Dilor equipped with a CCD camera. The spatial resolution of the laser spot (1 µm) allows a careful investigation of the homogeneity. Two different back-scattering geometries have been used: either propagating along the c axis (this was done for all samples) or perpendicular to the c axis (only for sample D). We have found the following results:

i) for all samples grown on the C-face of the 4H seed, within the 2200°C-2400°C temperature range, we obtained a reproducible spectrum typical of 4H-SiC with no evidence of other polytypic inclusion. This is shown by the observation of the doublet E<sub>2</sub> lines (196 cm<sup>-1</sup>, 203 cm<sup>-1</sup>), the A<sub>1</sub> line (611 cm<sup>-1</sup>) and the E<sub>2</sub> line (775 cm<sup>-1</sup>) respectively arising from the folding of the planar acoustic, axial acoustic and planar optic branches of the large zone [7] ;

ii) on the opposite, ingots grown on the Si-face of the 4H seed gave either evidence of 6H inclusions in the periphery (sample C) or, even, pure 6H conversion (sample D). Those results clearly establish that, in the case of our experimental setup, the polarity of the seed is a drastic parameter for the 4H polytype control.

iii) finally, to investigate the polytypic conversion occurring during the growth, we have investigated a slice cut of sample D parallel to c. Results are shown in Fig.1. Clearly, focusing at successive distances from the seed (a) up to the ingot surface (d) we found that the first 200 µm thick region above the seed corresponds to pure 4H polytype. Notice that, in this configuration, the 4H frequencies are E<sub>1</sub> mode at 265 cm<sup>-1</sup>, A<sub>1</sub> mode at 611 cm<sup>-1</sup> and A<sub>1</sub> mode at 839 cm<sup>-1</sup>. On the top of the sample we find a typical 6H spectrum (d). At the interface between the two polytypes we find a mixing of the 4H and 6H spectra (c) revealing its flatness (within the apparatus resolution). The experimental parameters are similar for sample C and D (Table1). In both cases we have used the C-face of 4H-SiC seeds and similar temperatures. The main difference arising from the seed quality, we confirm, that polytypic conversion is extremely sensitive to defect concentration in the seed. For sample D, the polytype could only be maintained during the early stage of growth (for about 10 min.). After, an increase of the nucleation rate and/or defects density have led to the loss of control. For sample C, nothing similar appeared and inclusion free 4H-SiC could be grown in the ingot center.

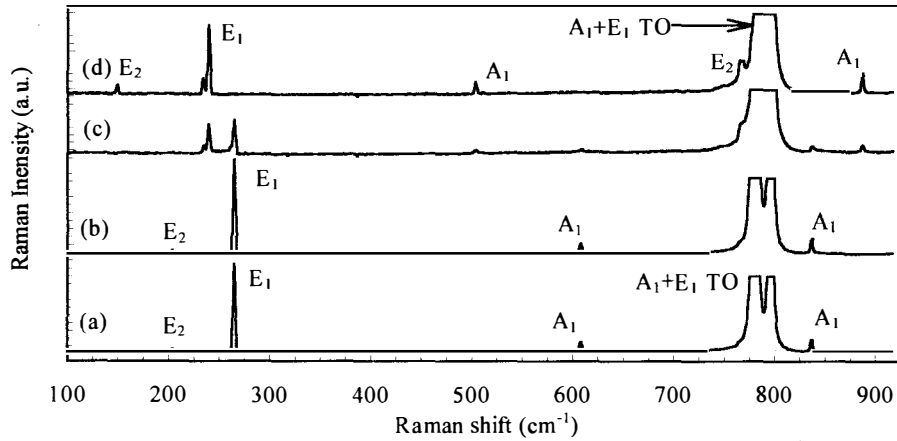
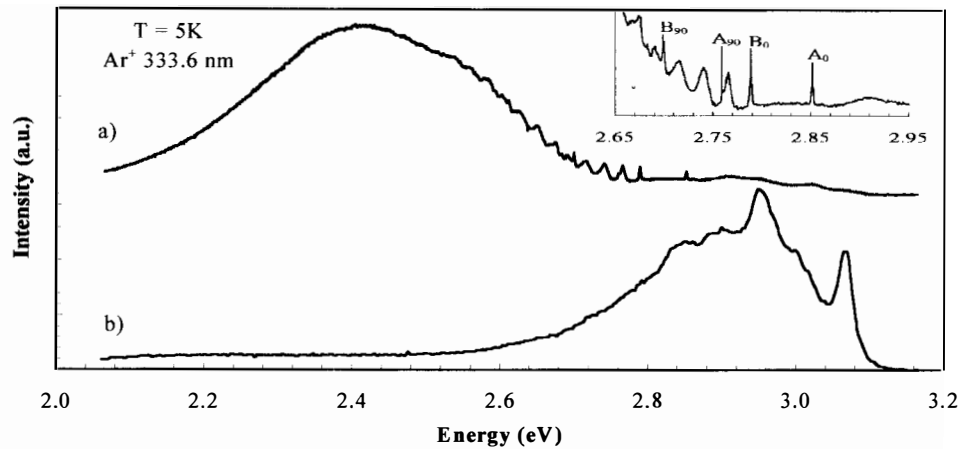


Figure 1 : Raman spectra of sample D collected a) on the seed, b) 100  $\mu\text{m}$  above the seed, c) 200  $\mu\text{m}$  above the seed at the 4H/6H interface and d) in the converted 6H polytype.

The mosaic structure of the crystal has been investigated by measuring the rocking curve. While the apparatus resolution is  $0.2^\circ$ , we found global FWHM  $\sim 1^\circ$  for all samples. Actually, the line analysis reveals, that there are at least four grains with different orientations. This result is not surprising if we consider the intrinsic mosaicity of seeds and should be easily improved by using home-made seeds. Concerning the defect density, as for the mosaicity, we do not expect better results for the grown ingots than for the starting seed. This is indeed what is found for samples B, C and D where the average micropipe density (MPD) is about  $200 \text{ cm}^{-2}$ . For the best sample (B) a  $5 \text{ mm}^2$  zone with  $\text{MPD} < 10 \text{ cm}^{-2}$  could be found while, on the opposite for sample A, a  $\text{MPD} > 10^3 \text{ cm}^{-2}$  was found. This is clear evidence of the drastic importance of improving the powder purity. To summarize, from these structural results, we can see, that the main defects observed in our crystals arise from the seed and the powder. As a consequence we expect drastic improvements when better quality (Lely or home-made) seeds will be available. In addition to these structural defects, the modified Lely grown ingots generally contain electrically and/or optically active impurities resulting from contamination by the powder and/or the crucible.

In order to determine the nature of the impurities present in our crystals, low temperature photoluminescence has been used. Two spectral ranges have been studied: a NBE (Near Band Edge) UV-visible one ( $3800 \text{ \AA} - 6500 \text{ \AA}$ ) and an infrared one ( $12000 \text{ \AA} - 15000 \text{ \AA}$ ), where vanadium related transitions occur. In the visible range two different spectra are obtained for samples A and B (Fig.2). In the case of sample B (Fig.2b), we find the classical (N) donor-(Al) acceptor pair (DAP) spectrum of 4H-SiC [8]. It correlates with the absence of exciton bound to N lines and indicates a rather high compensation level. This is because, even if the powder is purified, an important amount of Al is still present in the starting material. In the case of sample A (unpurified powder) the situation is quite different (Fig.2a). Although a very weak DAP (N-Al) band is still visible, a broad band centered around  $2.4 \text{ eV}$  dominates the spectrum. A blowup of the well resolved lines, at the high energy side of this band, is shown in the upper right corner of Fig.2. The  $A_0$  and  $B_0$  lines and their TO replicas related to Ti are clearly visible [9]. Considering the amount of Ti in our powder ( $2.5 \text{ ppm}$ ), this result is not surprising. It has to be noticed that the broad band between  $2.3 \text{ eV}$  and  $2.8 \text{ eV}$  has already been observed by several authors in the same time as the sharp Ti lines [10, 11]. However, up to now, no explanation has been given. On the high energy side of this band, we observe well resolved lines which become closer and closer with the energy decreasing. This is typical of a DAP spectrum. However the observed band does not correspond to DAP lines reported in the literature (i.e. N-Al, N-Ga, N-B). As this broad band appears jointly with the Ti related lines, one possibility is that it could be due to a Ti related deep level. In 6H-SiC the affinity of N for Ti to

form a  $\text{Ti}_\text{Si}-\text{N}_\text{C}$  complex which acts as a deep donor ( $E_c-0.6\text{eV}$ ) has been reported [11]. These Ti-N pairs has also been observed in 4H-SiC but their electrical activity is still unknown [11]. We then suggest, that this complex could be a deep donor (like in 6H-SiC). In this case, the observed broad band could be (Ti-N) donor to (Al) acceptor pair spectrum with a typical donor binding energy of 0.7 eV. Additional experiments varying the amount of Ti are necessary to confirm this assumption.



**Figure 2 :** Low temperature photoluminescence spectra for sample A (a) and B (b). The  $A_0$ ,  $B_0$ ,  $A_{90}$ ,  $B_{90}$  Ti related lines are shown in the blowup of the 2.65 eV- 2.95 eV region of spectrum (b).

In the infrared range the same spectra are obtained for sample A and sample B. They exhibit the characteristic emission of the vanadium  $\text{V}^{4+}$ . The crystal polytype is confirmed by the observation of the two sets of zero phonon lines assigned to substitutional vanadium occupying the cubic and the hexagonal site in 4H-SiC.

## Conclusion

We have grown 4H-SiC ingots by the Modified Lely Method. For the as described reactor geometry and processing conditions, the 4H polytype is stable, in a wide temperature (2200-2400°C) and pressure (10-20 torr) range if the  $(000\bar{1})\text{C}$  face of a 4H seed is used. The pinhole density (200  $\text{cm}^{-2}$ ) presently found in our ingots will be reduced by the optimization of the in-situ etching process of the 4H-SiC seed.

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