Polytype stability in seeded sublimation growth of 4H–SiC boules

R. Yakimova a,*, M. Syväjärvi a, T. Iakimov b, H. Jacobsson a, R. Råback c, A. Vehanen d, E. Janzén a

aDepartment of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden
bOkmetic AB, Box 255, S-178 24 Ekero, Sweden
cCenter for Scientific Computing, P.O. Box 405, FIN 02101 Espoo, Finland
dOkmetic Ltd., P.O. Box 44, FIN 01301 Vantaa, Finland

Received 5 November 1999; accepted 20 April 2000
Communicated by J.B. Mullin

Abstract

Process conditions for stable single polytype growth of 4H–SiC boules via a seeded sublimation technique have been developed. Reproducible results can be obtained in a narrow temperature interval around 2350°C and on the C-face of 4H–SiC seeds. Evidence is presented that during the initial stage of growth, morphological instabilities may occur resulting in structural defects. A solution is proposed based on the experimental findings, i.e. the first regions of growth ought to be carried out at a low supersaturation (growth rate ~100 μm/h) until a proper growth front has developed.

© 2000 Elsevier Science B.V. All rights reserved.

PACS: 81.10.A; 61.72; 81.10.A; 61.50.K

Keywords: 4H–SiC; Sublimation growth; Morphological instability; Polytype uniformity

1. Introduction

Silicon carbide (SiC) is a material of expectation for high-temperature electronics, high-power switching and high-frequency power generation. While SiC may offer an exclusive combination of physical and electronic properties for many applications, the high processing temperature and chemical stability of this material, as well as the variety of stacking sequences along the c-direction in the close-packed structure of SiC, cause difficulties for growth of high-quality crystals, especially of large single crystals.

Among different crystallographic modifications of SiC, the 4H–SiC polytype is the most interesting one for power device applications. However, due to the low stacking fault energy it is difficult to restrict syntaxy (parasitic polytype formation) during bulk crystal growth and thus to grow a single polytype material. Another well-known problem is the large number of structural defects such as micropipes, mosaicity and dislocations. Moreover,
these problems are interrelated to a large extent; defects easily result in polytype disturbances [1], while polytype inclusions may lead to defect formation [2]. However, little is known about the kinetics and thermodynamics of polytype formation, growth stability, and also the mechanism that produces the periodic sequences. As discussed in Ref. [3], 3C–SiC may be the initial polytype that forms at virtually all growth temperatures and thus acts as a necessary precursor for the phase transformation to other polytypes. Several growth parameters, such as the growth temperature [4,5], supersaturation [3,4], vapor-phase stoichiometry and impurities [3,6], and polarity of seed surface [7] have been discussed to influence the polytype stability.

Seeded sublimation growth has been the most successful method to date for growth of large 4H–SiC boules that can be sliced into wafers. Generally, it is more difficult to grow 4H polytype in comparison with 6H–SiC, considering the size of crystals and the polytype yield. Although significant progress has been made in the polytype control in SiC crystals, research is far from providing a complete understanding of all mechanisms.

This paper describes a study of the growth process at the initial stages of 4H–SiC crystal formation with the aim to develop conditions for stable single polytype growth. The structural quality of the grown material has been investigated using hot KOH etching and high-resolution X-ray diffraction (HRXRD) techniques.

2. Experimental procedure

The growth experiments were performed by the seeded sublimation technique with inductively heated graphite crucible and movable RF-coil. Rigid graphite insulation was used for thermal shielding and the reactor outer walls were air-cooled. The temperature was monitored both at the top and the bottom of the crucible with two-color pyrometers. The growth was performed in the temperature range of 2300–2450°C measured at the bottom of the crucible ($T_b$) and maintained constant during the growth run. Growth took place at a reduced Ar pressure ranging from 5 to 30 mbar depending on the growth temperature. The SiC source powder was purified and sintered before growth to prevent contamination of the seed crystal at the initial stage of the growth process. The purity of the powder was important in order to prevent parasitic nucleation, while pre-heating at about 2000°C served to suppress Si-pressure irruption at the growth temperatures. As seeds, we employed 4H polytype crystals produced via sublimation technique, (0001) well oriented or misoriented to the [1120] direction. Growth was performed on both Si- and C-terminated faces. This variety of seeds was particularly necessary in order to investigate the seed influence on the polytype uniformity and structural quality. When the growth temperature was reached under nearly an atmospheric pressure the growth was initiated by applying a controlled pressure reduction. In order to vary the starting supersaturation we used two different pressure reduction schemes following an exponential decay of 200 s and 15 min, according to the following equation:

$$P = P^* \exp(-t/\tau) + P_0,$$

where $P^* + P_0$ is the initial Ar pressure, $P_0$ is the final pressure, and $\tau$ is the pumping time constant. The supersaturation was changed also by changing the temperature gradient when keeping constant $T_b$. This was achieved by moving the RF-coil.

We examined two groups of samples. First, we studied as-grown surfaces after 6 h of growth, referred to as early stage of growth. This allowed observation of the growth morphology after nucleation had been completed and the crystal habit had been formed. The second group of samples comprised wafers cut from boules and properly processed to permit structural and polytypic uniformity evaluation. The grown material was investigated using an optical microscope with Nomarski interference contrast and crossed polarizers, as well as by HRXRD. Etching in molten KOH at 500°C for different times was also performed. The optical investigations are suitable to observe micropipes and domain boundaries on bare or KOH-etched surfaces, while HRXRD was used to assess domain misorientation and strain in the crystal by recording $\omega$ rocking curves and 20/$\omega$ diffraction curves. X-ray diffraction measurements were utilized to determine the polytype. Computer simulation was
used to better understand temperature and supersaturation distributions near the growth interface.

3. Results and discussion

Morphological stability at early stage of growth is an important characteristic, which was found to affect 4H polytype stability and defect formation. Fig. 1 displays an uneven growth morphology (Fig. 1a) and a regular morphology (Fig. 1b) in case of two different supersaturations over the growing surface when the other process parameters are the same. In the first case, one can observe several misoriented growth centers with an enhanced growth at the edges. After several millimeters of growth the growth front acquired a concave shape, resulting in the formation of domain boundaries, micropipes and dislocations. At some defective areas 15R inclusions were found.

We believe that the observed morphological instability at the growth start (Fig. 1a) is due to a non-uniform supersaturation over the seed surface. As it is known [8,9], in the case of crystal growth from a solution or a vapor, a polyhedral crystal grows in a stable way, retaining its similar shape for low supersaturation. With increasing supersaturation, however, the constituent plane interface becomes unstable due to preferred growth at the edges and corners, and may degenerate into dendritic morphology in extreme cases. This kind of morphological instability is due to the non-uniformity of supersaturation over the interface. The solution of the diffusion equation in the case of growth of a polyhedral crystal yields a non-uniform supersaturation over the growing face, being largest at the corners and smallest at the centers of faces [10]. This non-uniformity of the supersaturation over the surface is also known as Berg effect [8]. Therefore, growth in diffusion-limited sublimation growth is favored at the seed edges. Two consequences may be then expected: (i) many growth centers with different orientations, respectively, domains forming grain boundaries with defects [2] and (ii) non-uniform growth rate leading to non-uniform material properties, e.g. inclusions. The described instabilities are more pronounced in 4H–SiC bulk growth. Growth of 6H–SiC boules does not meet the same problems because this polytype is usually grown at higher temperatures which provide more favorable composition with respect to stoichiometry of the vapor phase, the feeding of the crystal is more efficient at higher temperature and the surface mobility of the species is higher compared to 4H–SiC [3,11]

Several reasons could cause an unstable growth interface: uneven temperature distribution at the growth front due to wrong crucible geometry, improper seed attachment and constitutional supersaturation. The last effect usually takes place if the growth rate is high, which is not in our case. The first two options were excluded by growing on two
adjacent seeds. The result is illustrated in Fig. 2 which shows that the growth took place first on the edges independent of the geometric position of the crystal.

For stable growth at the beginning, the supersaturation needs to be controlled. Fig. 3 depicts calculated temperatures at the axis and inner crucible walls at different coil positions, provided $T_b$ is fixed. The zero position is aligned with the bottom of the crucible cavity and a source height of 20 mm has been used in the simulation. From this and our temperature measurements it was estimated that the temperature gradient can be tuned from 4–5°C/cm to 15–20°C/cm. Large values of the temperature gradient resulted in morphological instabilities (Fig. 1a) due to an increase of the local supersaturation. On the contrary, should conditions for a constitutional supersaturation/supercooling occur, the increase of the temperature gradient would help to avoid it. High-temperature gradient also caused recrystallization within the SiC source powder (Fig. 4), which led to uneven consumption of the source and consequently growth instability. The temperature gradient in the source is sensitive to changes of the coil position as seen in Fig. 3.

To avoid growth instabilities at the initial stage we used a low-temperature gradient (4–5°C/cm) corresponding to a growth rate of approximately 100 μm/h. To select proper growth conditions we have studied growth rate versus temperature, growth rate versus source to seed distance and growth rate versus process pressure dependencies (Figs. 5a, b and c, respectively). The value of the apparent activation energy of the growth process, 126 kcal/mol, derived from the Arrhenius plot of the growth rate, is consistent with the sublimation heat of SiC (148 kcal/mol [12]) and it is within the values commonly obtained in the case when a diffusive mass transport between the source and the seed prevails over free convection. The linear proportionality of the growth rate to the reverse source to seed distance, suggests that the mass supply is diffusion limited considering a broad temperature range (2300–2450°C). With decreasing growth pressure (determined by the inert gas pressure) the...
Fig. 5. (a) Arrhenius plot of growth rate, data are taken at 5 mbar Ar pressure and source to seed distance 5 mm; (b) growth rate versus source to seed (S–S) distance dependence with a linear fit; (c) growth rate versus process pressure p.

growth rate increases and tends to saturate when approaching 1 mbar. The pressure range within which the growth rate varied is characteristic for diffusion-limited species transport. Such behavior is commonly observed for the sublimation boule growth [5] and it is qualitatively consistent with the pressure dependence of the molecular diffusion coefficient [13]. Actually, the growth rate dependence can be fitted with a straight line \( D \sim 1/P \), but the slope is never 1 since the mass transport is not purely diffusive and the effect of the graphite walls cannot be neglected in the case of SiC growth. At very low pressure the growth rate exhibits a saturation behavior. This regime however has not been of our interest for bulk crystal growth.

When growth conditions are properly selected there is only one growth-promoting center (Fig. 1b) from which steps spread out over the whole growing surface in the course of the crystal growth.

Growth results showing conditions for 4H crystal polytype occurrence and stability are summarized in Table 1.

Stable 4H growth with good structural quality is achieved within a narrow temperature range, 2350–2375°C and only on C-face. The pressure of the process gas was 5 mbar but we did not observe an effect of the pressure and pressure reduction rate on the polytype formation. Similarly, the type of source material, neither 6H nor 3C did not affect the polytype. For the results, the applied growth rate is about 100 \( \mu \)m/h at the initial stages of growth and it reaches 0.5 mm/h approximately after 1 mm of growth. The largest diameter of the crystal is 38 mm. The width of the polycrystal ring around the monocrystal area does not exceed 5 mm. A typical 4H–SiC boule is shown in Fig. 6a.

From our results it follows that the occurrence and stability of 4H polytype depend on the
Table 1
4H polytype occurrence at different temperatures and 4H seed orientations

<table>
<thead>
<tr>
<th>Growth temp (°C)</th>
<th>Surface orientation</th>
<th>Surface polarity</th>
<th>Grown crystal polytype</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>2350–2375</td>
<td>On axis</td>
<td>Si-face</td>
<td>6H, 15R inclusions</td>
<td>Spiral growth competition</td>
</tr>
<tr>
<td></td>
<td>Off-axis</td>
<td>C-face</td>
<td>4H (100%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C-face</td>
<td>4H (100%)</td>
<td></td>
</tr>
<tr>
<td>&lt;2350</td>
<td></td>
<td>Si-face</td>
<td>6H, 15R inclusions</td>
<td></td>
</tr>
<tr>
<td>&gt;2375</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Polytype conversion 4H → 6H</td>
</tr>
</tbody>
</table>

Fig. 6. (a) A typical 4H SiC boule grown on the C-face of a 4H–SiC seed, 22 mm in height and 38 mm in diameter; (b) a typical pattern at the growth center on as-grown surface of a 4H–SiC boule, C-face; (c) optical micrograph under crossed polarizers of the as-grown surface of the top wafer cut from a 4H-boule.

The temperature range of 4H stability is different in different studies. Commonly the temperatures are lower than for the growth of 6H–SiC. The upper limit in our experiments is 2375°C above which 4H polytype tends to convert to 6H, while below 2350°C the crystal quality is the limiting factor. The
authors of Ref. [14] suggest that SiC polytypes are kinetically determined metastable phases rather than true thermodynamic phases and therefore a well defined temperature stability range for each polytype cannot be expected. As to the effect of the face polarity of the seed, one can speculate that the lower surface free energy of the C-face facilitates the nucleation of 4H polytype which otherwise is more difficult to form due to the higher formation enthalpy than that of 6H–SiC. Consequently, other polytype inclusions can occur when growing on the Si-face. 4H polytype maintains stable growth in two modes depending on the seed orientation. On on-axis seeds the growth takes place via spiral competition ending with a dominant center in the middle of the crystal. The growth proceeds with the layer–spiral mechanism. On off-axis seeds the growth center is at the seed edge and the lateral step growth is more pronounced in the tilt direction. Both situations allow growth of single polytype material.

Morphologies of as-grown boules prepared on C-terminated faces of 4H–SiC seeds showed patterns (Fig. 6b), which have been previously reported [15]. Typically, C-face exhibits a small pseudo-flat area (mesa) with six ridges emerging in the six equivalent directions <1120>. Often polygonized spirals can be distinguished on the mesa. Microsteps are observed in between the ridges, running along <1100> directions and thus the pattern reflects the six-fold crystal symmetry.

We examined the as-grown surface of the top wafer of a 4H–SiC boule. An optical micrograph taken under crossed polarizers is shown in Fig. 6c. There is strain-associated contrast located at the growth center. A wafer from the region just below the top surface was polished and subjected to structural investigations. Fig. 7 shows images taken in reflection light (Fig. 7a) and crossed polarizers (Fig. 7b) modes from the wafer after KOH etching. It was possible to trace the growth promoting center and observe rows of dislocations along the six symmetrical ridges. Strains are still seen, however no micropipes are visible exactly in the spiral center. The two large hexagonal etch pits outside the spiral center (Fig. 7a) do not appear to be micropipes.

The average micropipe density is about 170/cm² which corresponds to the micropipe density in the seed crystal. It seems that our growth regimes do not provide conditions for creating new micropipes by opening hollow cores of giant screw dislocations. The average density of randomly distributed dislocations is about 15 000/cm², provided the rows are avoided.

The wafer was “mapped” by utilizing ω rocking curves. Fig. 8 gives two representative ω-scans from two areas of the sample, A and B, with a spot size of 2 × 14 mm. The peaks over a large part (A) of the sample (not illustrated) are sharp and symmetric with high intensity and full-width at half-maximum (FWHM) value of 14°. On the area with defects and the growth center (B), corresponding to Fig. 7, the rocking curves show peak broadening, asymmetry and lower intensity. The (2θ/ω)-scan, taken with
Fig. 8. Two representative ω-scans (rocking curves) from area B shown in Fig. 7 and a good-quality area A.

A large spot of 10 × 14 mm, shows a sharp peak with FWHM of 17″ and an intensity of 40 000 counts per second which indicates very little strain.

4. Conclusions

4H polytype SiC crystals have been grown having a single polytype structure at temperatures ranging from 2350 to 2375°C. By controlling morphological stability and the growth front shape, micropipes and mosaicity formation can be reduced. Our grown material had micropipe densities comparable with the seed. For the 4H polytype stability the surface kinetics may play a determining role, most probably related to a higher vapor supersaturation over 4H crystal compared with 6H–SiC. Growth start with a relatively low supersaturation (growth rate ~ 100 μm/h) is considered to be beneficial for the 4H–SiC crystal quality.

Acknowledgements

The SSF Program SiCEP, NUTEK and Okmetic AB are gratefully acknowledged for support.

References