

## The effect of rotation on the macro-steps formation during 4H-SiC solution growth

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**Abstract** New insights about macro-step formation has been investigated. The phenomena of surface instability caused by the interaction between step flow and fluid flow was describe in mechanical way. The rotation of the seed crystal in a clockwise direction was applied with a speed varied from 30 to 200 rpm during the TSSG process on the Si- and C-faces 4H-SiC. The macro-steps were formed along the two specific directions at different locations on the crystal for each, i.e., [10-10] or [01-10] directions or both. From the results, it is suggested that the macro-steps were generated from the micro-steps by interaction between step flow and fluid flow during the rotation of seed crystal. Furthermore, The fluid flow could be effective to control the micro- and/or macro-step behavior during solution growth.

**Key words** SiC, Solution growth, Surface instability, Macro-steps, Fluid dynamics

### 1. Introduction

The development of the top seeded solution growth process is of special interest to SiC bulk crystal growth because it is seen as a suitable method for obtaining high quality crystal with low defect density [1-3]. However, the stability of the growth front over long growth time is one of the key issue as it can give rise to polytype and solvent inclusions.

For example, on the vicinal surface, such as the standard 4H-SiC  $4^\circ$  off-oriented towards  $\langle 11-20 \rangle$  direction, usually exhibit huge step bunching. Macroscopically, the step bunching is viewed as a rearrangement of the surface to a hill and valley structures which lowers the total interfacial energy [4]. At a nanoscopic scale, the step bunching phenomenon also indicates that an additional energy barrier exists at the step edge, reducing the diffusion of adatoms toward the down-step [5]. During SiC solution growth, macro-step formation has already been observed and showed different consequences. On the one hand, the generation and movement of macro-steps contribute to improve the crystal quality as under specific conditions, a defect conversion mechanism can occur. If the macro-steps propagate in the basal plane from the center toward the edge of the crystal, the dislocation lines can be bent and pushed outside the crystal

while the growth front moves [6,7]. On the other hand, the macro-steps can dramatically decrease the crystalline quality, as they can be at the origin of solvent inclusions, polytype inclusions and for the worse case a total and definitive transition from single to polycrystal. The combination of phenomena affecting the surface stability is extremely complex and is the subject of many investigations in the crystal growth community. In order to obtain the high crystalline quality, it is necessary to understand and control such surface instabilities for both formation and evolution of the macro-steps.

Recently, Zhu et al. suggested that large macro-steps could be observed if the fluid flow and the step flow had the same direction (parallel flow condition) while they can be suppressed under antiparallel flow condition [8]. They observed this trend locally and the question arising is the following: what would be the interaction between a vicinal surface and the fluid flow during rotation of the crystal? This is of the first importance for the further development of the process, especially for further upscaling. Thus, in this paper, we will show that the rotation of crystal introduces an intrinsic source of inhomogeneity when coupled to off-axis crystal orientation. In addition, new insights about the macro-step generation is discussed. All the consideration about the step-bunching behavior in TSSG process will be explain with the mechanical behavior without complex thermodynamics, such as the temperature related physical phenomena, in order to easily understand the step generation

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mechanism in TSSG process.

## 2. Experimental Procedure

A standard top seeded solution growth (TSSG) experiments have been implemented in an induction heating Czochralski furnace. High purity silicon (99.999 %) was used as solvent and placed in a graphite crucible having 50 mm in inner diameter. Experiments were carried out in a 1700°C temperature range and a high purity Ar (99.999 %) pressure of 1.05 bar. Both Si- and C-face 4H-SiC crystal 4° off-oriented towards  $\langle 11\text{-}20 \rangle$  direction were used as seed crystals with a diameter of 15 mm. We applied a clockwise rotation to the seed crystal and the rotation speed was varied from 30 to 200 rpm. The growth duration was 1~5 hrs. The melt was held at growth temperature a few tens of minutes before growth, i.e., before dipping the seed crystal.

Residual solvent on the as-grown surface was removed by acid etching in HF and HNO<sub>3</sub> mixture solution by 1 : 1 ratio. Polytype of as-grown crystals was investigated by Raman scattering spectroscopy. The wavelength of the incident laser was 532 nm. The morphology of as-grown surface has been observed using Nomarski differential interference contrast (NDIC) microscopy and scanning electron microscopy (SEM). The height of micro/macro-steps were investigated by atomic force microscopy (AFM) measurements.

## 3. Results and Discussion

For clarity purpose, we will classify hereafter the steps observed in three different categories. The first category consists of nanometer scale step height, typically of a few SiC bilayers and will be referred to “nano-steps”. The second category, the steps are bunched with a height of 100 nm typically and will be called “micro-steps”. The last category, typical of liquid phase growth of SiC are much higher and can reach the micrometer scale in height. They are the so-called “macrosteps” and are due to the bunching of microsteps.

Figure 1 shows NDIC microscopy images taken from the as-grown crystal surface at different areas. Depending on the location, micro-steps were observed with three different types of elongated black lines, defined here as “macro-step”. The micro-step bunching occurred systematically along the off-cut orientation of the crystal. Therefore, the micro-step trains propagate in the  $[11\text{-}20]$

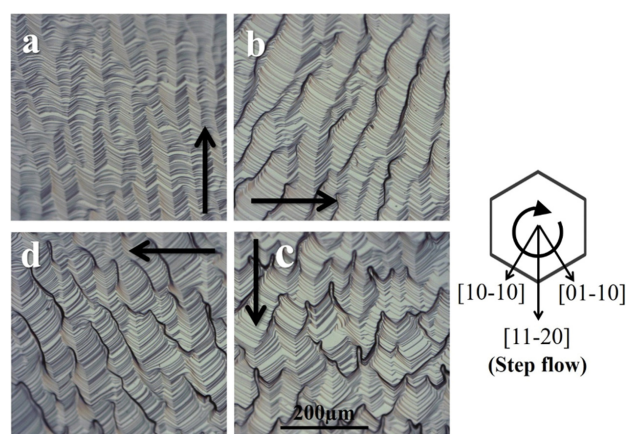


Fig. 1. NDIC microscopy images of an as-grown surface, from a sample grown at 1700°C and applying a rotation rate of 30 rpm. The pictures come from different locations of the sample. a) typical micro-steps formed in solution growth. The elongated black lines in b) to d) are the so-called “macro-step”.

direction decorating the whole surface after growth as the Fig. 1(a). The micro-step height was up to 100 nm. While the macro-steps were observed in the other areas of the crystal with specific directions (Fig. 1(b-d)). The angle between two macro-steps was 60°. Thus, these macro-steps located in the  $[01\text{-}10]$  and  $[10\text{-}10]$  directions, respectively. The average terrace width between macro-steps in the Fig. 1(d) was 5.1 μm and the Fig. 1(b) was 5.9 μm. The Fig. 1(c) shows the zigzag shaped of macro-steps along the  $[11\text{-}20]$  direction which the step flow direction. In this case, the height of micro-step was maximum ~330 nm, the height of macro-steps were varied from a few hundred nm to a few μm. We considered that All of the macro-steps were generated after micro-steps formation and by the micro-steps distortion.

Also, Fig. 2. shows the comparison of the as-grown crystal morphologies under the different rotation speed of seed crystals with the Si- and C-faces. We employed Si-face and rotated at below 100 rpm and 200 rpm (Fig. 2(a~b)). The results are clear that the similar tendency of the macro-steps formation were observed, and the surface instabilities have been increased with increasing the rotation speed of seed crystal. As shown in the Fig. 2(b), when the speed of rotation increases, the density of macro-steps increased. On the other hand, we employed C-face seed crystal and rotated up to 100 rpm (Fig. 2(c)). We obtained similar tendency of macro-step formation, but the shape of macro-step was not clear because the C-face has a lower surface energy compared to Si-face. Hence, we considered that the balance of the boundary layer near the crystal/liquid interface was destroyed by strong rotational effect of fluid.

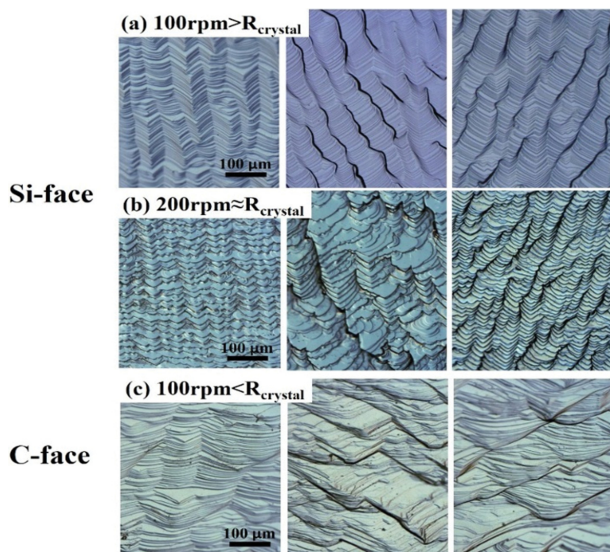


Fig. 2. NDIC images of morphological instabilities of macro-steps on the C and Si-faces of as-grown surface with different seed rotation speed, (a) below 100 rpm, (b) over 100 rpm, and (c) around 200 rpm, respectively.

#### 4. Macro-step Growth Mechanism

The bunch of step is a kind of surface equilibrium state when the surface energy is minimized during the growth process [9]. Formation of step bunching in SiC growth is as follows: I) “atomic-steps”, II) “micro-steps” and III) “macro-steps”, which are  $\mu\text{m}$  (or a few hundreds of nm) scale height steps. The latter comes from the bunching of micro-steps during the crystal growth, consists of a large number of superimposed micro-steps and usually has the height of over nano-scale.

According to Zhu et al., the macro-step formation is deeply linked to the fluid flow, i.e., if the fluid flow has the same direction with step flow (parallel), accumulated macro-steps and wide terraces can be observed. But, if these directions are not same (antiparallel), it becomes a strong stabilizing factor. Considering the reaction near the growth surface, the macro-step in the Fig. 1(b) was formed in the parallel and Fig. 1(d) was formed in the antiparallel. This is in fact not correctly described the observed morphologies. Under the parallel, the micro-step bunching can be exacerbated to the step flow direction by the carbon concentration distribution near the step-edge in the fluid flow direction. On the other hand, under the antiparallel condition, carbon concentration distribution changes asymmetric with the fluid movement to the opposite direction, hence, it will be controlled the formation of macro-step [8].

The schematic of the Fig. 3 shows the development of

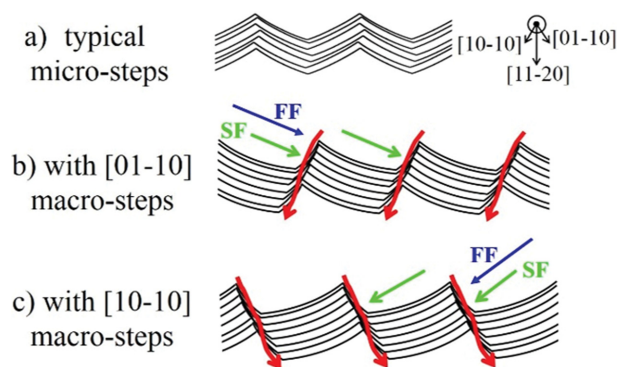


Fig. 3. The schematic of macro-steps development (depicted by the red lines) and the direction of step flows (SF; green arrows) and fluid flows (FF; blue arrows), respectively.

macro-steps with the direction of step flow and fluid flow, respectively. Figure 3(a) can be adapted to Fig. 1(a), which is the case of without macro-step formation during growth, because the fluid flows almost opposite direction of the step flow in this area and it has effect to suppress the step bunching phenomenon. Figure 3(b) shows the case of Fig. 1(b) area, and Fig. 3(c) shows the case of Fig. 1(d). Generally, the growth mechanism of misorientated SiC crystal follows step growth motion and formation of multiple-height steps roughness, if carbon concentration is higher at the edge of the steps. And the SiC crystal growth rate in the  $\{1-100\}$  planes are larger than other planes. Hence, during the growth, the possibility of the surface morphology could be zigzag shape with  $[10-10]$  and  $[01-10]$  directions, instead of a straight shape of step trains.

In addition to the step flow, if the fluid also moved in the same direction with step motion direction, we could obtain a strong effect of step propagation to generate the macro-step as the Fig. 1(c). Therefore, we consider that if the fluid at the growth interface having a specific directional characteristic by the rotation of the seed crystal, it can give a stronger synergy to the step propagation. In order to understand the generation mechanism of two different steps (micro and macro), the scenario of macro-step formed from micro-steps are presented in Fig. 4. These optical microscopy images were taken at four different locations on the same as-grown crystal surface. From them, we can suggest four steps of macro-step formation in the  $[01-10]$  direction, which can be generalized to the other directions as well:

- i) If the fluid flow moves in the same direction with the step flow, small steps are subject to bunching in the  $[01-10]$  direction.
- ii) The formed the micro-step, though of small height,

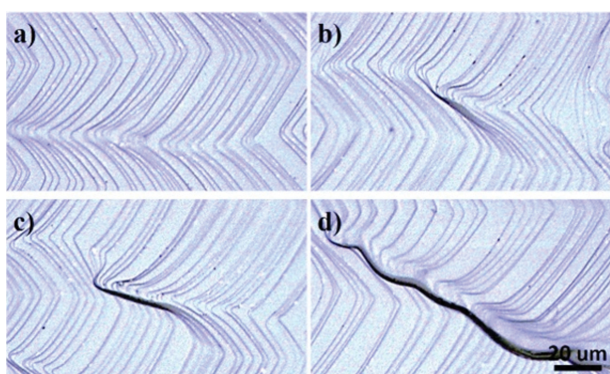


Fig. 4. NDIC images of macrostep formation under the condition of parallel direction between step and fluid flows, which were observed from the middle of crystal (a) toward the edge of crystal (d).

forms a small protuberance that will affect locally the fluid flow pattern (see Fig. 4(b)).

iii) Due to a higher supersaturation at the protuberance tip, the top of the micro-step will develop (see Fig. 4(c)).

iv) These processes can only extend for forming the big and long macro-steps (see Fig. 4(d)).

After the macro-step formation, the top of the macro-step can move faster than the bottom of the macro-step creating a hole with solvent trapping. In this latter case, the growth front can be considered as destabilized. Thanks to the evolution of the fluid velocity along the seed surface, especially due to the azimuthal and radial components, there is a kind of macro-step size and density gradient along the radius, for a given azimuth.

## 5. Summary

The macro-step generation mechanism have been studied and the interaction between fluid flow and step flow have been investigated. The seed crystal rotation technique has been carried out various from below 100 rpm to over 200 rpm to understand of the surface instability. The macro-steps over the micro-steps are provoked by the interaction between the direction of the rotation of the crystal (i.e., direction of the fluid) and the micro-step propagation direction. High rotation rate of seed crystal can increase the growth rate, however, there

exists a critical rotation speed above which the interaction between the step flow on the crystal surface and the fluid flow pattern can interact to create surface instabilities, which in turn can give rise to solvent inclusion. This can be qualitatively described by considering first the step flow direction (after “hexagonalization” of the original train of parallel steps and second the fluid flow direction which must be split into two azimuthal and radial components.

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## References

- [ 1 ] D.H. Hofmann, “Prospects of the use of liquid phase techniques for the growth of bulk silicon carbide crystals”, *Mater. Sci. Eng.* B61-62 (1999) 29.
- [ 2 ] K. Kamei, “Crystallinity evaluation of 4H-SiC single crystal grown by solution growth technique using Si-Ti-C solution”, *Mater. Sci. Forum* 717-720 (2012) 45.
- [ 3 ] K. Kusunoki, “Top-seeded solution growth of three-inch-diameter 4H-SiC using convection control technique”, *J. Cryst. Growth* 395 (2014) 68.
- [ 4 ] T. Kimoto, “Step bunching in chemical vapor deposition of 6H- and 4H-SiC on vicinal SiC(0001) faces”, *Appl. Phys. Lett.* 66 (1995) 3645.
- [ 5 ] R.L. Schwoebel, “Step motion on crystal surfaces”, *J. Appl. Phys.* 37 (1966) 3682.
- [ 6 ] Y. Yamamoto, “Stable growth of 4H-SiC single polytype by controlling the surface morphology using a temperature gradient in solution growth”, *Mater. Sci. Forum* 717-720 (2012) 53.
- [ 7 ] T. Ujihara, “Conversion mechanism of threading screw dislocation during SiC solution growth”, *Mater. Sci. Forum* 717-720 (2012) 351.
- [ 8 ] C. Zhu, “Influence of solution flow on step bunching in solution growth of SiC crystals”, *Cryst. Growth Des.* 13 (2013) 3691.
- [ 9 ] T. Kimoto, “Step bunching mechanism in chemical vapor deposition of 6H- and 4H-SiC{0001}”, *J. Appl. Phys.* 81 (1997) 3494.