Faceted dendrite growth of silicon from undercooled melt of Si–Ni alloy

Kouki Kuniyoshi\textsuperscript{a}, Kengo Ozono\textsuperscript{a}, Minoru Ikeda\textsuperscript{b}, Toshio Suzuki\textsuperscript{b,*}, Seong Gyoon Kim\textsuperscript{c}, Won Tae Kim\textsuperscript{d}

\textsuperscript{a}Department of Materials Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
\textsuperscript{b}Department of Materials Engineering, The University of Tokyo, Tokyo 113-8656, Japan
\textsuperscript{c}Department of Materials Science and Engineering, Kunsan National University, Kunsan, Korea
\textsuperscript{d}Department of Physics, Chonju University, Chonju, Korea

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Abstract

Two-dimensional faceted dendrite growth of silicon from undercooled melt of Si–6 wt%Ni alloy was experimentally investigated, in which molten alloy film from 10 to 20 \textmu m in thickness was undercooled up to 115 K and growing dendrites were observed in situ. Both the in situ observation of dendrite morphology and the EBSP crystallographic analysis for solidified samples showed that both a \langle 211 \rangle twin dendrite and a \langle 100 \rangle twin-free dendrite grew in the range of undercooling from 50 to 115 K. Dendrite growth velocity was also measured for different undercooling conditions. The growth velocity of \langle 211 \rangle dendrites was slightly larger than that of \langle 100 \rangle dendrites. It is concluded that the upper envelope of the data provide the correct dendrite growth velocity and it is compared with that obtained by phase-field simulations. Growth velocity in both follows power relationships to undercooling and the linear kinetic coefficient is estimated to be 0.01 m/s K.

Keywords: Dendritic growth; Semiconductor; Undercooling solidification; Phase field model

1. Introduction

Half a century ago, faceted dendrite growth of germanium was first reported by Billig [1] and its crystallographic aspects were investigated aiming the production of semiconductor ribbons [2,3]. These works revealed that his dendrite had twins along its primary arm and grew in the \langle 211 \rangle direction with (1 1 1) habit faces. Because of the rapid progress of silicon wafer production technology the interest in faceted dendrite growth was subsided for many years until Devaud and Turnbull [4] found a twin-free dendrite in the late 1980s. Thereafter, intensive investigations on faceted dendrite growth of germanium, silicon, and their alloys have been revived for clarifying the transition of growth kinetics. In most experiments germanium or silicon was undercooled using the glass flux technique [4–8] or electromagnetic levitation technique [9–16] and the crystallographic morphology of solidified crystals was examined. The growth velocity of faceted dendrites was also measured for germanium, silicon, and their alloys [8–16]. The results of these works are summarized as follows. The growth of a faceted dendrite changes from that of a twin dendrite with a \langle 211 \rangle or \langle 110 \rangle growth direction to that of a \langle 100 \rangle twin-free dendrite with increasing undercooling. The transition from a twin to a twin-free dendrite is examined by microstructure observation of solidified samples [5–8,10–13], growth velocity measurement [8], and in situ observation of growing interface morphology [13–16], although the twin/twin-free transition is sometimes described as the transition from lateral to continuous growth kinetics in a confusing manner. Battersby et al. [8] measured the growth velocity of germanium and iron-doped germanium dendrites and reported that the undercooling dependency of growth velocity was different for twin and twin-free dendrites. However, the dendrite growth velocity for germanium, silicon, and their alloys was mostly reported to follow a
power relationship with respect to undercooling in spite of the difference in growth kinetics [9–16]. Measured growth velocity was usually analyzed using an analytical dendrite model termed as a BCT [17] or LKT [18] model, although the model assumes interface characteristics that were different from those of faceted one.

In the meantime phase-field approaches to faceted dendrite growth have been recently proposed so as to include highly anisotropic interface energy [19,20] or interface kinetics [21]. Phase-field models have been already applied to many solidification phenomena and show wide potential as introduced in review articles [22–24]. In usual phase-field approaches, the solidification interface energy, $\sigma(\theta)$, is simply assumed to have fourfold symmetric anisotropy as $\sigma(\theta) = \sigma_0(1 + v \cos 4\theta)$, where $v$ is the intensity of anisotropy and $\theta$ is the angle between the direction normal to the interface and the $x$-axis. The equilibrium condition at the interface is given by the Gibbs-Thomson equation. When $v < 1/15$, a smooth and convex non-faceted crystal becomes stable. Conversely when $v > 1/15$, the interface within the missing orientation becomes thermodynamically unstable, the faceted crystal appears to be composed of only interfaces with stable orientations. Therefore, the presence of an edge between faceted interfaces makes the phase-field approach difficult. In order to overcome this difficulty, Eggleston et al. [19] have proposed modification of the governing equation within the missing orientations is changed using that of the interface at the end of the stable orientations and the model successfully reproduces the equilibrium shape and the transient growth toward the equilibrium state of a faceted interface. Debierre et al. [20] have proposed a different type of anisotropic interface energy in their phase-field approach. They performed phase-field simulations of faceted dendrite growth with vanishing interface kinetics. Kasajima and coworkers [25,26] have carried out phase-field simulations of free faceted dendrite growth of silicon using the interface energy model by Eggleston et al. and thin interface limit parameters. Their results are similar to those by Debierre et al. and it indicates that both approaches can be applicable to real systems with faceted crystals such as silicon.

However, there are difficulties in the phase-field simulation of silicon dendrite growth. The capillarity length of silicon is so small that the mesh size should be less than 1 nm so as to obtain correct values of dendrite growth velocity and the calculation area should be at least $10^2 \text{ m}^2$ in the concerned range of undercooling where the twin/twin-free transition is reported to occur. Therefore, three-dimensional simulation of silicon dendrite growth is impracticable and the agreement between two-dimensional phase-field simulations and experimental data is still unsatisfactory [27]. These difficulties would be greatly reduced if data on the two-dimensional faceted dendrite growth of silicon alloys could be provided, because the restrictions on calculation time could be relaxed in simulations of dendrite growth of alloys. Two-dimensional experiments of dendrite growth are generally difficult to perform but the present authors found a way of fabricating a thin film of molten silicon or silicon alloy in a simple manner. Therefore, it becomes possible to compare the results of two-dimensional faceted dendrite growth experiments with phase-field simulations. In the present work two-dimensional faceted silicon dendrites grown from the undercooled melt of silicon–nickel alloy are observed in situ and their morphology and crystallographic features are discussed. Dendrite growth velocity is also measured for different undercooling conditions. Finally, the growth conditions of faceted dendrites are discussed for the comparison of the phase-field simulations.

2. Experimental

The mother alloy of Si–6 wt%Ni alloy was prepared from semiconductor grade silicon and 99.99% nickel. These materials were arc-melted under an argon atmosphere and the solidified alloy was crushed into small pieces. The average nickel content of the alloy was examined by the two following measurements for ten small pieces. One was area analysis using a SEM-EDX, in which nickel content was measured in an area of 300 $\mu\text{m}$ square for each sample. The other is the area fraction measurement of the primary silicon phase using a SEM. As the solidified structure is composed of the primary silicon, and $\text{Si}_2\text{Ni}/\text{SiNi}$ eutectic phases and the solubility of nickel in silicon is sufficiently small, the average nickel content can be evaluated by means of the fraction-weighted sum of nickel content in each phase. The results of both measurements almost perfectly agreed with each other and the nickel content of the alloy was evaluated to be 6 wt% within an error of 1 wt%. This was also confirmed by measuring the liquidus temperature during melting in the experiments.

Fig. 1 shows the experimental setup used in the present work. As shown in the upper part of Fig. 1 the specimen with a mass from 2 to 4 mg was placed between two single-crystal sapphire plates with a (10 $\bar{1}$ 0) surface and 500 $\mu\text{m}$ in thickness. It was melted under a vacuum of about $10^{-5}$ Pa using a resistance furnace with a molybdenum heating wire. Because of good wetting of molten silicon alloy to sapphire, the specimen between the two plates spontaneously spread into a thin film with a thickness in the range from 10 to 20 $\mu\text{m}$. Note that the film thickness was easily controlled by changing the size of the upper sapphire plate and the mass of the specimen. Typical dimensions of the sapphire plates are shown in the lower part of Fig. 1. The specimen was heated up to the superheating temperature of about 30 K and then continuously cooled with a constant cooling rate of 5 or 10 K/min until nucleation started.

Before the series of experiments the output of a thermocouple was calibrated by measuring the melting temperature of silicon and the undercooling in each experimental run was determined as the difference between the liquidus temperature of the alloy and the nucleation temperature.
measured by the thermocouple. The error of measured undercooling was expected to be within 5 K at most, including the variation of nickel content.

As the emissivity of silicon is sufficiently different for the solid and liquid phases, growing crystals can be optically identified through the transparent sapphire upper plate. However, the transparency of the upper sapphire plate was lost because of the evaporation of molybdenum oxide and the number of experimental runs was limited to seven at most. For the observation of dendrite growth, a high-speed video camera attached with a 300 mm telescopic lens was used. Recording was manually triggered after the confirmation of nucleation because the camera had a prerecording function and a sufficiently large memory capacity to record for 10 s. A typical frame rate used for the observation was 250 frames per second. The recorded images were processed to increase their contrast and the locations of growing dendrite tips were measured for each frame. As two or three dendrites independently grew from a nucleation point dendrite growth velocity was measured for each dendrite in an experimental run. After solidification, the primary and secondary arms of the dendrites were clearly identified because of the difference in contrast between the primary silicon and eutectic phases. In addition, the crystallographic orientations of dendrite arms were determined by SEM-EBSP analysis for typical specimens. Note that the alloy was brittle and easily cleaved along the film and no treatment was necessary for the analysis.

3. Results and discussions

3.1. Dendrite growth morphology

Fig. 2 shows the undercooling histogram of 181 experimental runs. Because of the heterogeneous nucleation of silicon on the sapphire surface, the obtained undercooling was expected to fall within a certain narrow range. However, the results show a wide distribution of undercooling from 20 to 115 K, whose mean value and standard deviation are 69.5 and 19.2 K, respectively. This wide distribution is presumably due to the fact that surface roughening during heating produces macro steps on the sapphire surface and they act as nucleation sites with different potentials.

The morphology of growing dendrites is classified into three main types and others on the basis of the angle between the primary arm and secondary arms as shown in Fig. 3. In the figure, the dendrites during growth and their solidified structures are shown in the left and right columns, respectively. The first type is a dendrite with secondary arms inclined at 60° or 120° to the primary stem (Figs. 3(a) and (b)), the second is a dendrite with secondary arms inclined at 90° (Figs. 3(c) and (d)), and the third is a rod-type primary arm without secondary arms. The crystallographic orientations of these dendrites or rods were analyzed using a SEM-EBSP. Table 1 shows a summary of the results, in which the growth plane, defined as the crystallographic orientation perpendicular to the molten alloy film, and the growth directions of the primary and secondary arms are tabulated. These results are the same as those of silicon dendrites reported by Nagashio and Kuribayashi [28,29]. However, a \(110\) dendrite in Table 1 has fourfold symmetry and is different from their \(110\) twin dendrite. For simplicity of description,
the three types of dendrites are denoted as a ⟨211⟩ dendrite, a ⟨100⟩ dendrite, and a ⟨211⟩ rod hereafter. The other dendrites are divided into two groups. The first one is dendrites whose secondary arms are inclined at 35°, 55°, 70°, 80° or one of their supplementary angles to the primary arm. For most of these dendrites, twins along the primary arms are observed. The second group is dendrites whose secondary arms were not clearly observed in their images.

Differences in growth morphology are usually due to differences in growth kinetics. As reported in the literature, ⟨211⟩ and ⟨110⟩ dendrites are twin dendrites whose growth is dominated by lateral growth and a ⟨100⟩ dendrite is a twin-free dendrite with continuous growth kinetics. In the present work, twins are observed only for ⟨211⟩ dendrites with a ⟨110⟩ growth plane, and no twins are observed for ⟨211⟩ dendrites with a ⟨111⟩ growth plane, probably because the twin plane is mostly parallel to the ⟨111⟩ face. Fig. 4 shows a histogram of dendrite types, in which 180 dendrites classified into the main three types are counted. As described above, a few dendrites grew independently from a nucleation point in an experimental run, the total number of observed dendrites is larger than that of runs, and the remaining of 163 dendrites classified into the others group do not appear in Fig. 4. For undercooling smaller than 50 K, crystals grow as a ⟨211⟩ rod, and their frequency decreases with increasing under-
cooling. For undercooling larger than 50 K, \( \langle 211 \rangle \) and \( \langle 100 \rangle \) dendrites become dominant. Nagashio and Kuribayashi [28,29] have reported that the growth of a silicon dendrite changes from that of a \( \langle 110 \rangle \) twin dendrite to that of a \( \langle 100 \rangle \) twin-free dendrite with increasing undercooling and the transition undercooling is about 100 K, but no clear twin/twin-free dendrite transition was observed in the present work. This difference is presumably due to the spatial constraint of the growth plane by the two sapphire plates. As seen in Table 1, the growth planes of dendrites are constrained to be \( \langle 111 \rangle \), \( \langle 110 \rangle \), and \( \langle 100 \rangle \). Once the growth plane has been determined by nucleation, dendrites are forced to grow with that growth plane. In contrast, the optimum growth plane can be selected according to the growth kinetics in levitation experiments. In addition, the observation of solidified B-doped silicon samples shows that a \( \langle 110 \rangle \) twin dendrite grows along the free surface of molten silicon and a \( \langle 100 \rangle \) twin-free dendrite grows toward the inside the specimen [30]. Therefore, the transition of growth morphology corresponding to the change in growth kinetics would be observed only when dendrite growth is fully unconstrained.

### 3.2. Dendrite growth velocity

Fig. 5 shows the relationship between the growth velocity of dendrites and undercooling. In the figure, open triangles, open squares, open circles, and cross symbols show the growth velocity of \( \langle 211 \rangle \) dendrites, \( \langle 100 \rangle \) dendrite, \( \langle 211 \rangle \) rods, and the other dendrites, respectively. The experimental data are widely scattered, and the correct growth velocity of a \( \langle 211 \rangle \) dendrite is estimated from the upper envelope of the data as reported by Suzuki et al. [31], which is shown as a broken line in Fig. 5. The growth velocity follows a power law relationship to undercooling and its power exponent is about 1.5. The scattering of the data is presumably because dendrites with a growth plane inclined to the specimen film grow in a zigzag manner with a smaller velocity. The growth velocity of \( \langle 211 \rangle \) dendrites is slightly higher than that of \( \langle 100 \rangle \) dendrites, but the difference is small at low undercooling and becomes large at high undercooling. Unfortunately, since there is not sufficient the data for \( \langle 100 \rangle \) dendrites at high undercooling, quantitative comparison of the growth velocities of \( \langle 211 \rangle \) and \( \langle 100 \rangle \) dendrites is difficult. However, the results show that there is no direct correlation between growth velocity and growth morphology as reported in the literature [13–16].

Phase-field simulations for the faceted dendrite growth of silicon from the undercooled melt of Si–6 wt%Ni alloy has been carried out under the corresponding experimental conditions. The two-dimensional thin interface limit model [32] has been used and its details are described elsewhere [26,33,34]. In the simulations it is assumed that the system is isothermal and the growth of a dendrite is dominated by solute diffusion. The results calculated with the linear kinetic coefficient of 0.01 m/s K are shown as closed circles and solid line in Fig. 5. The calculated growth velocity follows a similar power relationship to undercooling to experiments but those values are slightly smaller than the upper envelope of the experimental data. In the model the fourfold symmetry of interface energy is assumed and it is the case for a \( \langle 100 \rangle \) dendrite. As described above the growth velocity of a \( \langle 100 \rangle \) dendrite is smaller than that of a \( \langle 211 \rangle \) dendrite and the results are in agreement with experiments. The values of linear kinetic coefficient for \( \langle 100 \rangle \) and \( \langle 111 \rangle \) faces of silicon have been obtained by numerical simulations [35,36] or experiments [37–39], and most of the data for a \( \langle 100 \rangle \) face of silicon are in the range from 0.2 to 0.05 m/s K. The value of linear kinetic coefficient for silicon alloys is not reported but it is supposed to be smaller than that of silicon because the driving force for solute partition at interface would be additionally necessary. Therefore the value of linear kinetic coefficient used in the simulation is acceptable, and the
agreement between simulations and experiment show that the conditions in the simulations have been appropriately assumed.

4. Conclusions

A detailed investigation on a two-dimensional faceted dendrite of silicon from the undercooled melt of silicon–6 wt%nickel alloy was conducted. In the experiments a thin film of molten silicon–nickel alloy was obtained by a simple but new method and it was undercooled from 20 to 115 K. Growth morphology of dendrites was in situ observed and dendrite growth velocity was measured at different undercooling. Crystallographic aspects were also examined by EBPS analysis of solidified samples.

The conclusions obtained in the present work are followings. Both \( \langle 2 \overline{1}1 \rangle \) twin dendrites and \( \langle 100 \rangle \) twin-free dendrites are observed in the same range of the undercooling from 50 to 115 K and that rod-like crystals with \( \langle 2 \overline{1}1 \rangle \) growth direction at small undercooling less than 50 K. Therefore no clear transition from a \( \langle 2 \overline{1}1 \rangle \) twin dendrite to a \( \langle 100 \rangle \) twin-free dendrite is confirmed. It is presumably due to the spatial constraint by sapphire plates. Growth velocity of \( \langle 2 \overline{1}1 \rangle \) dendrites is slightly larger than that of \( \langle 100 \rangle \) dendrites as expected but the difference is not large. However the measured growth velocity data are widely scattered and the quantitative comparison between both is difficult. Growth velocity of \( \langle 2 \overline{1}1 \rangle \) dendrites is estimated from the upper envelope of the data and it follows a power relationship to undercooling with its exponent of about 1.5. Phase-field simulations have been carried out and the results are compared with experimental data. The agreement between both is satisfactory and the value of linear kinetic coefficient is estimated to be 0.01 m/s K.

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