Morphological Transition in Crystallization of Si from Undercooled Melt

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Abstract. Using CO$_2$ laser equipped electro-magnetic levitator, we carried out the crystallization of Si at undercoolings from 0 K to 200 K. From the point of the interface morphologies, the relationship between growth velocities and undercoolings was classified into two regions, I and II, respectively. In region I where the undercooling is approximately less than 100 K, needle-like thin plate crystals whose interface consists of faceted plane were observed. In region II, the morphology of growing crystals changed to massive dendrites. Although the interface morphologies look quite different between region I and II, the growth velocities are expressed by two dimensional (2D) nucleation-controlled growth model, and at undercoolings larger than 150 K, the growth velocities asymptotically close to the analysis of the mono-parametric linear kinetics growth model. In this stage, the kinetic coefficient of 0.1 m/sK is equivalent to that derived by the diffusion-controlled growth model. This result means that with increase of undercooling, the rate-determining factor changes from 2D nucleation on the faceted interface to random incorporation of atoms on the rough interface.

1. Introduction
The rapid increase in the demand for a polycrystalline Si solar cell has caused a shortage in Si raw materials. This has brought a great deal of attention to a drop-tube process for manufacturing spherical crystals with a diameter of approximately 1mm. The first trial of drop-tube processing for spherical crystallization of Si was performed by McKee in 1982 [1]. In drop-tube process, raw materials of Si are melted in a crucible and then ejected into a drop-tube to be spherically crystallized during free fall. Although this process is very simple, the quality of as-dropped samples was much less than that of single crystals grown by conventional crystal growth techniques such as Czochralski (CZ) and Bridgeman methods. In order to improve the quality of as-dropped samples, remelting and regrowing treatment has to be introduced as the post drop-tube process. The cost-up associated with this extra process incurs the disadvantage of spherical crystals for use to solar cell. In fact, although many venture companies in Japan intend to produce the single-crystalline sphere without any extra processes [2-5], the method hasn’t been established.

In order to elucidate the crystallization behavior of Si droplets during free fall, Aoyama and Kuribayashi [6] (referred to hereafter as AK) carried out containerless crystallization of Si using a CO$_2$ laser equipped electro-magnetic levitator (EML). They revealed that at low undercooling less than 100 K (region I) plate-like facet crystals grow and at undercooling larger than 100 K (region II) the morphology of the crystal-melt interfaces changes to a dendritic microstructure. Nagashio and Kuribayashi [7] (referred to hereafter as NK) suggested that the plate-like facet crystals are to be grown by the preferential incorporation of atoms into the re-entrant corners formed at the edge of two
parallel twin planes (Twin-related Lateral Growth: TrLG), while the dendritic crystals are grown by random incorporation of atoms on the non-faceted rough interface (Twin-free Continuous Growth: TfCG).

In crystal growth of Si, the concept of TrLG was first proposed as one of morphologies of facet dendrites more than half a century ago [8, 9]. However the related experiments carried out recently on containerless solidification into the undercooled melt have been analysed based on the simple dendrite growth model incorporating kinetic undercooling [10, 11]. It is well known that the dendrite growth model proposed by Lipton, Kurz and Trivedi (hereafter referred to as LKT) [12] is principally based on the assumption that the crystal-melt interface is rough so that atoms can be incorporated at any sites of the interface. However, in the case of Si, plate-like crystals formed at low undercoolings suggest that the crystal growth is controlled by either the screw dislocation-assisted spiral growth or the two-dimensional (2D) nucleation [13].

Until now, however, a lack of precise data for growth velocities at low undercoolings has prevented the mechanism of the crystal growth of spherical Si to be clarified. Hence, in the present investigation, the growth velocities particularly at relatively low undercooling are measured and the mechanism of spherical crystallization of Si is discussed.

2. Experimental

Figure 1 shows a schematic illustration of the used electro-magnetic levitator (EML). Undoped 5N Si spheres with a diameter of 8 mm were melted by a CO$_2$ laser were levitated in a 5N Ar gas atmosphere. The sample, after heating to approximately 1800 K, was cooled to predetermined temperatures by blowing of 5N He gas. Nucleation was triggered by touching the side of levitated sample with a molybdenum needle.

![Figure 1. Schematic illustration of the electro-magnetic levitation (EML) furnace. In order to apply EML to semiconductive material, a CO$_2$ laser serves as a pre-heater.](image)

Figure 2 shows the typical temperature vs. time profile measured with a pyrometer with operating wavelength: 900 nm and 1,550 nm. After recalescence, the temperature oscillates in a definite range. In semiconducting Si, since the emissivity $\varepsilon$ of the solid phase is much larger than that of the liquid phase, this temperature oscillation can be attributed to the fluctuation of the location of the measuring point from liquid to solid phase in the levitated sample. The undercooling was determined by adjusting $\varepsilon$ so that the temperature just after the recalescence represents the equilibrium melting temperature of Si. The growth velocities of samples were measured using a colour High-Speed Video (HSV) with a maximum sampling rate of 640,000 frames/s.
3. Results

The selected HSV images taken during recalescence are shown in Fig. 3, where $\Delta T$ is the undercoolings. The dark and bright area respectively show the undercooled melt and the solidified region. The release

Figure 2. Typical profile of temperature vs. time measured with a pyrometer. The temperature of the samples was determined by adjusting the emissivity so that the temperature just after the recalescence is the equilibrium melting temperature of Si.

Figure 3. HSV images of samples taken during recalescence. Dark and bright area respectively show the undercooled melt and the solidified region. (a) HSV images taken at low undercooling, $\Delta T = 37$ K, showing anisotropic line-shaped crystal that forms a circumferential ring on the surface of the sample. (b) HSV images taken at medium undercooling, $\Delta T = 110$ K, showing a faceted dendrite. (c) Mixed-mode of faceted dendrites and line-shaped crystals. The solidification front initially advances massively, and subsequently line-shaped crystal protrudes from the faceted dendrite showing a mixed-mode of both morphologies. The velocity of line-shaped crystal is much higher than that of faceted dendrites.
of latent heat as well as the difference of emissivities between the solid and the liquid phases enhances the brightness of the solidified region.

In this figure, (a) is typical HSV images taken successively at low undercooling, \( \Delta T = 37 \) K, showing anisotropic line-shaped crystal that forms a circumference ring on the surface of the sample. Note that this ring is discontinuous, suggesting that the line-shaped crystal is not a “line” crystal located on a surface but a plate-like crystal that penetrates the sample. Faceted dendrites with a similar shape appear when the undercooling becomes higher than 100 K. At medium undercooling, however, not only a faceted dendrite but also a mixed mode of faceted dendrites and line-shaped crystals are observed. The solidification front initially advances massively, and subsequently line-shaped crystals protrude from faceted dendrites showing a mixed mode of both morphologies. The velocity of the line-shaped crystal is much higher than that of faceted dendrites.

According to the LKT model, the bulk undercooling \( \Delta T \) for pure material is given by

\[
\Delta T = \Delta T_t + \Delta T_r + \Delta T_k,
\]

where \( \Delta T_t \) is the thermal undercooling given by

\[
\Delta T_t = \frac{\Delta H_f}{C_p} \left( 1 - \frac{1}{2} \right) \text{exp} \left( \frac{P_f}{P_i} \right) \text{d}P_i,
\]

for the case in which the shape of the growth front can be approximated as an elliptical paraboloid. In this equation, \( \Delta H_f \) is the enthalpy of fusion, \( C_p \) is the specific heat of the melt at constant pressure, and \( \text{exp} \left( \frac{P_f}{P_i} \right) \) is the Ivantsov function given by

\[
\text{exp} \left( \frac{P_f}{P_i} \right) = \frac{P_i \text{exp} \left( \frac{P_f}{P_i} \right)}{P_i} 
\]

where \( P_i = VR/2a_0 \) denotes the thermal Peclet number, \( V \) the growth velocity, \( R \) the radius of the growth front, and \( a_0 \) the thermal diffusivity.

In Eq. 1, \( \Delta T_r \), the curvature undercooling due to the Gibbs-Thomson effect, is expressed by

\[
\Delta T_r = \frac{2\Gamma}{R},
\]

where \( \Gamma = \gamma \Delta S_t \) is the Gibbs-Thomson coefficient.

The kinetic undercooling \( \Delta T_k \) is related to growth velocity depending on the interfacial kinetics. If the interface is assumed to be rough, \( \Delta T_k \) is expressed by

\[
\Delta T_k = \frac{V}{\mu}
\]

where \( \mu \) is the kinetic coefficient. According to the marginal stability analysis [14], the radius of the growth front that is assumed to be equal to the wavelength of a critical perturbation of a planar interface \( \lambda \) is derived as

\[
R = \frac{\Gamma/\sigma^*}{P_i \frac{\Delta H_f}{C_p} \left[ \frac{1}{1 + \left( \sigma^* P_i \right)^{1/2}} \right]^{1/2}}
\]

where \( \sigma^* \) a stability constant, was approximately derived to be 0.025 using the marginal stability criterion.

The growth velocities of samples measured as a function of undercoolings are plotted in Fig. 4, where squares and triangles correspond to those of the plate-like crystal and the faceted dendrite, respectively [15]. In this figure, the growth velocities denoted by \( T_r \) were those of the samples where the nucleations were triggered by touching with molybdenum needles, and the others are of the
samples where the nucleation occurred spontaneously. In this figure, the solid and dotted lines correspond to the cases where the kinetic coefficient, \( \mu \), is assumed to be 0.1 m/sK and 0.02 m/sK, respectively. The physical parameters used in the calculation are listed in Table 1.

![Figure 4. Growth velocities as a function of undercoolings. Squares and triangles correspond to those of the plate-like crystal and the faceted dendrite, respectively. Solid and dotted lines, which are calculated using the LKT model with linear kinetics, correspond to the cases that the kinetic coefficient \( \mu \) is assumed to be 0.1 m/sK and 0.02 m/sK, respectively. Data denoted by Tr correspond to those where the nucleations were triggered with molybdenum needles, and the others are where the nucleation occurred spontaneously.](image)

### Table 1. Physical properties used in the calculation

| Parameter                      | \( T_m \) | \( \Delta S_f \) | \( \Delta H_f \) | \( \gamma \) | \( a_l \) | \( C_p \) | \( \Gamma \) |
|-------------------------------|-----------|------------------|------------------|-------------|----------|---------|----------|
| Melting temperature           | 1687      | 29.99            | 5.06\times10^4   | 0.438       | 2.35\times10^{-3} | 25.6    | 9.61\times10^{11} |
| Entropy of fusion             |           |                  |                  |             |          |         |          |
| Heat of fusion                |           |                  |                  |             |          |         |          |
| Surface energy                |           |                  |                  |             |          |         |          |
| Thermal diffusivity           |           |                  |                  |             |          |         |          |
| Specific constant             |           |                  |                  |             |          |         |          |
| Gibbs Thomson coefficient     |           |                  |                  |             |          |         |          |

### 4. Discussions

In Fig. 4, \( V \) vs. \( \Delta T \) for plate-like crystals can be fitted by \( \mu = 0.02 \) m/sK at relatively low undercoolings – less than 100 K. However, at medium and high undercoolings larger than 100 K, \( V \) vs. \( \Delta T \) can be fitted by \( \mu = 0.1 \) m/sK. Although this result seems to show that the kinetic coefficient is enlarged with increasing undercoolings, it is to be unable to express \( V \) vs. \( \Delta T \) with a mono-parametric \( \mu \), suggesting a change in the mechanism of the interface kinetics.
With regard to other interface kinetics, two types of mechanisms have been put forward [13]. The first one is quadratic kinetics given by

$$V = \phi (\Delta T_K)^2,$$  \tag{7}

where $\phi$ is the kinetic coefficient for quadratic kinetics. The second one is exponential kinetics given by

$$V = \beta \exp \left( -\frac{E}{k_B \Delta T_K} \right),$$  \tag{8}

where $\beta$ and $E$ are the kinetic coefficient for the exponential kinetics and the energy barrier for forming a critical nucleus, respectively. These two models describe screw-dislocation assisted spiral growth and 2D nucleation controlled growth, respectively. It has been well-known that at relatively low undercooling the quadratic kinetic or 2D nucleation model controls the crystal growth, whereas at relatively high undercooling linear kinetics is the rate determining factor. AK previously reported that the relationship between growth velocities and undercoolings in Si can be well expressed by LKT model with the mono-parametric interface linear kinetics [6]. As mentioned previously, the interface linear kinetics, which describes the random attachment of thermally activated atoms onto the interface, is well applied to the metallic materials having a rough interface. However, for $\{111\}$ in Si that is an atomically smooth interface, atoms are incorporated to preferential sites of interface such as a kink and/or a step. If the plate-like crystal which is observed at region I was grown with the twin-plane re-entrant corner mechanism, the crystal growth kinetics may be controlled not by interface attachment linear kinetics but by either the screw dislocation assisted spiral growth mechanism or the 2D nucleation model. In the case of a diamond lattice, however, the lattice distortion at the core of the screw dislocation with Burgers vector along $<110>$ direction is too large for the covalent bonds to be formed there [16]. This implies that the rate-determining process at the growth of the plate-like crystal is not the interface attachment kinetics but the 2D nucleation model.

![Figure 5](image)

Figure 5. (a) Schematic illustration of the tip of a faceted dendrite: In FCC and DC lattices, if we can assume a non-isothermal interface, the level of the undercooling is highest at the tip where the interface attachment kinetics controls the growth velocity. The undercooling decreases along the slope that continues away from the tip. (b) Arrows indicate heat flow: Compared with the case of isothermal interface where the heat flows perpendicularly from interface to melt, the faster growth velocity can be expected.

On the faceted dendrite, Maurer et al. [17], using NH$_3$Br as a sample for crystal growth, reported that faceted dendrite shape strongly depends on the growth velocity. Namely, facet planes become visible at the trail of the tip forming a faceted dendrite at decreased growth velocities, while at large velocities the shape of the crystal appears unfaceted. For this shape, they determined a parabola which fits the interface over distances appreciable compared to its own tip radius of curvature, and then obtained the relationship between the length of facet area, $\lambda$, and the growth velocity, $V$, as

$$\lambda \propto V^{-0.5}.$$  \tag{9}
Furthermore they evaluated the product between a square of tip radius, $\rho^2$, and $V$, and observed that at high growth velocity the value of $\rho^2V$ is large and at low growth velocity small. This result implies that the stability constant $\sigma^*$ of facet interface is larger than that of dendrite. In fact, Dougherty and Gollub [18] experimentally obtained the stability constant of NH$_3$Br as 0.081±0.02, despite that the dependency on the growth velocity is small than expected.

On the other hand, for faceted dendrite Tiller provides us with a highly suggestive hint in his literature. Based on the hierarchic model of terrace-ledge-kink (TLK), he proposed a novel idea to solve the conflict which is inherent in understanding faceted dendrite [19]. Figure 5 shows the concept of his idea. That is, if we can assume the non-isothermal interface, the level of the undercooling is highest at the tip where the interface attachment kinetics controls the growth velocity. The undercooling decreases toward the sloping region that continues away from the tip. At the sloping region, instead of linear kinetics, spiral growth or 2D nucleation controls the growth velocity, forming a facet plane (Fig. 5(a)). In this case the direction of heat flow is denoted with arrows as shown in Fig. 5(b). Compared with the case of isothermal interface growth where the heat flows perpendicularly from interface to melt, a faster growth velocity can be expected. According to this hypothesis, the plausible geometrical configuration of the dendrite which meets the conditions is a fourfold <100> dendrite, because there is maximum number of heat sink ({111} planes) adjacent to the tip. His suggestion implies that even in facet dendrite rate-controlling process is not interface attachment kinetics but 2D nucleation on {111} slope area.

![Figure 6](image_url)  
Figure 6. Growth velocities as a function of undercoolings. Two orange and blue lines are calculated using LKT model with an exponential kinetics. Parameters $\beta$ and $E/k_B$ are optimized to $7.0 \times 10^5$ and $3.5 \times 10^2$ K, respectively. The stability constant $\sigma^*$ is set to 0.05 for plate-like crystal, including the mix-mode case, and 0.025 for faceted dendrites in region II. Each of these two lines qualitatively agrees with the respective relations between growth velocities and undercoolings.

On the basis of this idea, instead of applying linear kinetics we incorporated the exponential kinetics given by Eq. 8 into the LKT model to fit the experimental data. Figure 6 shows the results for these two cases of $\sigma^*$, where $\beta$ and $E/k_B$ are optimized to $7.0 \times 10^5$ and $3.5 \times 10^2$ K, respectively. Each of these two lines qualitatively agrees with the observed relationship between growth velocities and undercoolings. Note that we must relax our interpretation of the LKT model when applied to crystallization of faceted material, particularly in respect to use of the Ivantsov function. Here, the
narrow area around the tip must be approximated by a paraboloid of revolution even for a faceted material.

As clearly shown in this figure, the exponential kinetics provides a fit to the experimental data. However, at relatively high undercoolings typically \( \Delta T > 150 \text{ K} \), the behaviour is better asymptotically by the linear interface kinetics - the coefficient of which is that of Wilson-Frenkel model [20, 21]. At high undercoolings, dendrite breakdown due to the Gibbs-Thomson effect causes poly-crystallization of the droplet, where fragmented dendrite can change the rate-controlling process from 2D nucleation to interface attachment kinetics, due to the formation of seed crystals. Hence, it can be summarized that the crystal growth at relatively low and medium undercoolings is controlled by the 2D nucleation not only in twin-related \(<110>\) facet dendrite but also in twin-free \(<100>\) case, and at relatively high undercooling by diffusion-controlled linear kinetics.

5. Conclusion
The recent approach to containerless crystallization of semiconductive material was presented including the historical background for production of spherical Si for solar cell. Although the pioneer work on the crystallization into the undercooled melt was carried out more than half a century ago, the related containerless experiments are now analysed in terms of modified dendrite growth models. The plate-like crystals formed at low and medium undercoolings suggest that the growth mechanism is not the simple heat-rejection-controlled model but the interface kinetic-controlled model. In this paper, precise observation of microstructure allows identification of the growth mechanism is the twin-plane reentrant corner mechanism; the rate-controlling process is the 2D nucleation not only in plate-like crystal but also in faceted dendrite.

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