Phase-field modeling for facet dendrite growth of silicon

Hisashi Kasajima\textsuperscript{a}, Etsuko Nagano\textsuperscript{a,1}, Toshio Suzuki\textsuperscript{b,*,} Seong Gymoon Kim\textsuperscript{c}, Won Tae Kim\textsuperscript{d}

\textsuperscript{a}Graduate School, \textit{The University of Tokyo}, Tokyo, Japan
\textsuperscript{b}Department of Materials Engineering, \textit{The University of Tokyo}, Tokyo, Japan
\textsuperscript{c}Department of Materials Science and Engineering, Kunsan National University, Kunsan, South Korea
\textsuperscript{d}Department of Physics, Chongju University, Chongju, South Korea

Received 3 September 2003; revised 12 September 2003; accepted 12 September 2003

Abstract

Dendrite growth of silicon from its undercooled melt was investigated by using the phase-field model for a faceted crystal with anisotropic interfacial energy. The phase-field parameters at the thin interface limit were derived and used in the simulation. The accuracy of the model was estimated from the calculated equilibrium interface shape. The errors in anisotropy and Gibbs-Thomson coefficient were within 1\% and 10\%, respectively. The growth of a silicon crystal from its undercooled melt has been analyzed and it is shown that the shape of growing crystal changes from square-like to dendritic with increase of undercooling. In a facet dendrite growth the tip grows keeping its shape and the shape is the same regardless of undercooling or growth velocity. It is also shown that there exists the scaling law between the characteristic length of the tip and growth velocity similar to that of a non-facet dendrite.

Keywords: Phase-field model; Anisotropic interface energy; Facet dendrite

1. Introduction

Recently many attentions have been paid to the dendrite growth of semiconductor materials from their undercooled melts, so as to obtain useful information on their crystal growth mechanism. Experiments have been carried out mainly for silicon and germanium and it is shown that the periphery surfaces of a dendrite are all (111) faces and the crystal growth behavior is classified into three categories: lateral growth, continuous growth and rapid growth at high undercooling [1–4]. Change in growth mechanism has been confirmed by in situ observation of growing interface morphology and the growth velocity at the ranges of lateral and continuous growth is reported to be approximately proportional to the square of the degree of undercooling [3,4]. Though the growth velocity and the transition velocity from lateral to continuous growth have been examined using a conventional dendrite growth theory for non-faceted crystals [4], its physical meaning is still unclear.

Phase-field modeling is one of the possible tools to analyze the facet crystal growth, which is powerful in describing the growing interface morphology, and a large number of examples show its wide applicability to the problems [5–8]. In addition it is shown that the thin interface limit phase-field model gives a quantitative prediction [9–11]. However, the model for the facet crystal growth should be modified so as to include highly anisotropic interfacial energy as proposed by Egglestone et al. [12]. Namely the interface of a facet crystal within a range of so-called missing orientations becomes unstable and the interface energy in the governing equation for missing orientations should be changed to that at the edge of the stable orientation. Their model successfully reproduced the equilibrium shape and the growth of a facet crystal. In the present work, the dendrite growth of silicon from its undercooled melt is investigated using a phase-field model with thin interface limit parameters. The morphology of a growing dendrite and its change with increase of undercooling are examined and discussed in comparison with the experiment.
2. Calculation

2.1. Governing equations and phase-field parameters

In two-dimensional phase-field modeling, interface energy with four-fold symmetric anisotropy, \( \sigma \), is assumed.

\[
\sigma(\theta) = \sigma_0(1 + \nu \cos 4(\theta - \pi/4))
\]

where \( \nu \) is the intensity of anisotropy and \( \theta \) is the angle between the direction normal to the interface and the \( x \)-axis. Here the orientation with the largest interface energy is rotated by \( 4\pi/2 \) from the \( x \)-axis and the numerical calculation is carried out at a quadrant. The angle dependent curvature of radius, \( R(\theta) \), can be found from the Gibbs–Thomson equation.

\[
(\sigma(\theta) + \sigma'^{2}(\theta))/R(\theta) = f^{L} - f^{S}
\]

where \( f^{L} \) and \( f^{S} \) are the free energy density of solid and liquid phases, respectively. Since the right hand side of the equation is positive in an isothermal system with a solid particle in the undercooled liquid, a convex non-facet crystal shape becomes stable when \( \nu \leq 1/15 \). Conversely when \( \nu > 1/15 \), the left hand side of the equation becomes negative within the missing orientations. Then a facet crystal comes to be composed of the interface with stable orientations. The missing orientations correspond to the range with concaved shape in the Wulff’s 1/\( \sigma \) plot. In order to get rid of the missing orientations, the anisotropic interfacial energy is modified as [12],

\[
\sigma(\theta) = \frac{\sigma(\theta_m + \pi/4)}{\cos \theta_m} \cdot \cos(\theta - \pi/4)
\]

\( (-\theta_m < \theta - \pi/4 < \theta_m) \)

where \( \theta_m \) is the first missing orientation and is derived by

\[
\frac{d}{d\theta} \left( \frac{\cos \theta}{\sigma(\theta)} \right) = 0.
\]

The anisotropy of interface kinetic should be taken account in association with anisotropic interfacial energy, but isotropic linear kinetic is assumed for simplicity [10].

A phase-field model for crystal growth is based on the Ginzburg–Landau free energy functional. The phase field is defined as 0 at liquid and 1 at solid, and it varies continuously from 0 to 1 at the interface region. The phase-field equations with four-fold interface energy anisotropy within stable orientations are given by,

\[
\frac{\partial \phi}{\partial t} = M \left[ \varepsilon^2 \nabla^2 \phi + \varepsilon \epsilon' \left( \sin 2\theta(\phi_{xy} - \phi_{xx}) + 2 \cos 2\theta \phi_{xy} \right) \right]
\]

\[
- \frac{1}{2} (\varepsilon'' + \varepsilon') \left( 2 \sin 2\theta \phi_{xy} - \nabla^2 \phi - \cos 2\theta(\phi_{xy} - \phi_{xx}) \right) - f_{\phi}
\]

and within missing orientations

\[
\frac{\partial \phi}{\partial t} = M \left[ \varepsilon(\theta_m + \pi/4) \left( \frac{\phi_{xx} + \phi_{xy} + \phi_{yy}}{2} \right) - J_{\phi} \right]
\]

where \( M, \varepsilon \) and \( \phi_{\phi} \) are phase-field parameters defined below, and the subscripts under \( \phi \) and \( f \) denote the partial derivatives. Note that it guarantees the orientation continuity to take the average of edge orientations at the adjacent points. The angle of interface normal, \( \theta \), free energy density, \( f \), solid fraction, \( h(\phi) \), and a parabolic potential \( g(\phi) \) are defined by

\[
\tan \theta = \phi_x/\phi_y
\]

\[
f = h(\phi)f^{S} + (1 - h(\phi))f^{L} + W_{g}(\phi)
\]

\[
h(\phi) = \phi(3 - 2\phi)
\]

\[
g(\phi) = \phi(1 - \phi).
\]

The equation for thermal diffusion is given by

\[
\frac{\partial \phi}{\partial t} = D_{\phi} \nabla^2 \phi + h(\phi) \frac{\Delta H}{C_p} \frac{\partial \phi}{\partial t}
\]

where \( D \) is thermal diffusivity, \( \Delta H \) is latent heat per unit volume, and \( C_p \) is specific heat per unit volume.

The phase-field parameters \( \varepsilon \) and \( W \) are related to interface energy, \( \sigma \), and the interface width, \( 2\lambda \), respectively and \( M \) is related to linear kinetic coefficient, \( \mu \).

\[
2\lambda = \frac{4\sigma}{W}
\]

\[
\varepsilon = \frac{4\sqrt{2}}{\pi} \frac{\sigma}{\sqrt{W}}
\]

\[
M^{-1} = \frac{\varepsilon^2 \Delta H}{\sigma \mu T_m} \left[ \frac{1}{\mu} + \frac{\Delta H}{D_{\phi} C_p} \int_{-\infty}^{+\infty} h(1 - \phi) \frac{dx}{\sqrt{\phi(1 - \phi)}} \right]
\]

where \( T_m \) is melting temperature. The parameters are derived at the thin interface limit as shown in the Appendix A.

2.2. Numerical calculation

For the numerical calculation Eqs. (1a), (1b) and (2) were discretized on uniform grids using an explicit finite difference scheme. In order to reduce the calculation time, calculation area was divided into small, middle and large size mesh areas as shown in Fig. 1. The time changes of phase-field and thermal field near the interface were calculated in the small size mesh area and thermal field...
away from the interface were calculated in the middle or larger size mesh areas, whose mesh sizes were four or 16 times of small mesh size, respectively. During the calculation the small size mesh area was rearranged according to the interface movement so as to pursue the interface. The total calculation area was 3008 £ 3008 in small size mesh of $2 \times 10^{-9}$ m. An initial solid of 40 £ 40 meshes was put at the corner of the calculation area. The interface thickness was set to be 1 £ $10^{-9}$ m (5 meshes) and the physical properties of silicon used in the calculation are shown in Table 1.

### Table 1

| Properties                  | Symbol | Unit           | Value          | Ref. |
|-----------------------------|--------|----------------|----------------|------|
| Specific heat per volume    | $C_p$  | J/m$^3$K       | $2.14 \times 10^6$ | [13] |
| Thermal diffusivity         | $D$    | m$^2$/s        | $2.80 \times 10^{-8}$ | [13] |
| Melting temperature         | $T_m$  | K              | 1685           | [13] |
| Latent heat of fusion       | $\Delta H$ | J/m$^3$ | $4.15 \times 10^9$ | [13] |
| Interface energy            | $\sigma$ | J/m$^2$      | 0.438          | [14] |
| Anisotropy                  | $\gamma$ | –            | 0.15           | [13] |
| Linear kinetic coefficient  | $\mu$  | m/Ks           | 0.4, 0.13, 0.04 | –    |

3. Results and discussions

Before the simulation of a dendrite growth the calculation accuracy by the model has been examined by comparing the calculated crystal shapes with the analytical equilibrium crystal shapes. The shape anisotropy evaluated from the ratio of the maximum to minimum radius and the curvature radius at the position with the minimum interface energy are compared with analytical ones for different values of mesh sizes. The relative errors in anisotropy and curvature radius are within 1 and 10%, respectively. These values are similar to those for non-facet crystal and the model is confirmed to be good enough to describe the growth of a facet crystal.

Fig. 2 shows the time change in the dendrite shape at the undercooling of 300 K. As seen in the figure the interface near the tip is stiff so that the tip region keeps its shape during the growth. The interface behind the tip, however, becomes unstable to form secondary arms at the sides. The interface morphology is dependent on the degree of undercooling or growth rate as shown in Fig. 3. In the figure the contour lines of interface are drawn every certain time steps as guides to the eye to demonstrate the change in interface shapes. For each calculation the ratio of radius in the $\pi/4$ direction, $r_{\pi/4}$, to that in the $x$-direction, $r_x$, is evaluated every 10,000 time step. The solid shape changes once from an initial square shape to a round shape and then approaches to an equilibrium shape. Therefore the ratio, $r_{\pi/4}/r_x$, increases from 1 to about 1.2 of an equilibrium shape as interface proceeds. At small undercooling the ratio gradually approaches to the equilibrium

Fig. 3. Change in the interface morphology with undercooling ($\nu = 0.15$, $\mu = 0.4$ m/sK, $\Delta T = 300$ K).

(a) $\Delta T = 50$ K

(b) $\Delta T = 80$ K

(c) $\Delta T = 100$ K

(d) $\Delta T = 150$ K.
value without exceeding it, and thus the interface keeps its square-like shape without forming a leading tip. With increase of undercooling the ratio increases rapidly and exceed the equilibrium value and the leading tip proceeds to form a dendritic shape. Therefore there exists a transition from the square-like to dendritic morphology as seen in the experiment and the transition undercooling is about 60 K. The transition is always observed when \( \nu \) is larger than 0.14 though the transition undercooling does not depend on \( \nu \).

It is reported the growing crystal morphology changes from a plate-like crystal to dendritic one at the undercooling of about 100 K and the change is explained by the transition of growth mechanism from lateral to continuous growth \[3\]. The present result, however, shows that the apparent change of growing interface morphology occurs without any change in interface kinetics. Though the present two-dimensional results are not directly comparable with the experiment, the transition of growing interface morphology presumably relates to the instability of growing facet interface and not to the change in kinetics.

To obtain the steady state growth of a dendrite it is known that the growth distance of the dendrite should be several times larger than its diffusion length. The growth distance in the present work was at most three times of diffusion length and the steady state condition was not satisfied because of the computational time limitation. Therefore the obtained growth velocity is slightly larger than the steady state one but the dendrite tip shape is the steady state one. In facet dendrite growth the edge of the tip region does not proceed continuously but conciliatorily as schematically shown in Fig. 4, in which the edge and the tip region are schematically defined. It is due to that the growth direction at the edge is given as the average values of adjacent points in the model and the adjacent interface grows preferably to the edge. During the growth the shape of the tip region is kept to be the same and its size changes with growth velocity. In order to examine the shape and size of the tip region, the curvature radius is evaluated at different points from the edge to the end of tip region, where the interface normal angle to the growth direction becomes \( \pi/4 \). The curvature radius is normalized by the value at the end of the tip region because it is difficult to evaluate it at the edge. Fig. 5 show the change in normalized curvature radius with angle of interface normal. In the figure the symbols are the results calculated for different values of undercooling and kinetic coefficient, and the solid line curve shows an equilibrium shape. The shape of the tip region is different from the equilibrium one but the same for all.

For a non-facet dendrite there exists a scaling law, \( r^2V = \text{const} \), between tip radius, \( r \), and growth velocity, \( V \), and the similar relationship is obtained for a facet dendrite growth. Since the curvature radius at the edge is not uniquely determined the length of tip region, \( L \), is selected as a characteristic length as defined in Fig. 4. In the Fig. 6 the values of \( 1/L^2 \) are plotted against growth velocity. The data are on a line and there exists the relationship of \( L^2(V - V_0) = \text{const} \) even for a facet dendrite. The offset value of growth velocity, \( V_0 \), presumably corresponds the limit of the square-like crystal growth described above. It is difficult to examine it but it would be clarified in the work in the near future.

Fig. 4. Schematic drawing of the tip region in a facet dendrite for denoting the edge and the characteristic length, \( L \).

Fig. 5. Normalized curvature radius vs. angle of interface normal. The symbols are the calculation results and the curve corresponds to an equilibrium shape.

Fig. 6. Relationship between characteristic length of tip region and growth velocity. The solid line is a guide to the eye and demonstrate that the dependence of \( V \) of \( 1/L^2 \) is linear.
4. Conclusions

The thin interface limit phase-field model has been successfully applied to the growth of a facet crystal by modifying the governing equation so as to include the highly anisotropic interface energy. The equilibrium shape of a crystal has been reproduced with good accuracy by the model. The errors of shape anisotropy and Gibbs–Thomson effect are within 1 and 10%, respectively. The growth of a silicon crystal from its undercooled melt has been analyzed using the model and it is shown that the shape of growing crystal changes from square-like to dendritic ones with increase of undercooling. The tip shape of a dendrite is the same regardless of undercooling or growth velocity and the characteristic length of the tip region is scaled to growth velocity as in a non-facet dendrite.

Acknowledgements

This work is partially supported by the Grant-in-Aid for Scientific Research (A) (No. 14205106) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Appendix A

Phase-field parameters at thin interface limit

Under the boundary condition of $\phi(-\infty) = 1$ and $\phi(+\infty) = 0$, a one-dimensional stationary solution for phase-field $\phi(x)$ is obtained by solving the following equation.

$$\varepsilon^2 \left( \frac{d\phi}{dx} \right)^2 = W_\gamma(\phi)$$  \hspace{1cm} (A1)

Integrating after differentiating and multiplying $d\phi/dx$ on both side of the equation yields

$$\phi(x) = \frac{1}{2} \left( 1 - \sin \frac{\sqrt{2W}}{\varepsilon} x \right)$$  \hspace{1cm} (A2)

Interface energy and interface thickness are given by

$$\sigma = \varepsilon^2 \int_{-\infty}^{+\infty} \left( \frac{d\phi}{dx} \right)^2 dx = \frac{\pi}{8} \varepsilon \sqrt{2W}$$  \hspace{1cm} (A3)

$$2\lambda = -\int_{0}^{1} \left( \frac{dx}{d\phi} \right) d\phi = \pi \frac{\varepsilon}{\sqrt{2W}}$$  \hspace{1cm} (A4)

We write the thermal equation in one-dimensional steady state

$$\frac{dT}{dx} = \frac{D}{V} \frac{d^2 T}{dx^2} - \frac{2}{Vc_p} \frac{dH}{H(\phi)} \frac{d\phi}{dx}$$  \hspace{1cm} (A5)

where $V$ is interface velocity. At the thin interface limit, $D/V \gg 2\lambda$, the left hand side of the equation can be neglected and one obtains

$$\frac{D}{V} \frac{d^2 T}{dx^2} - \frac{\Delta H}{c_p} H'(\phi) \frac{d\phi}{dx} = 0$$  \hspace{1cm} (A6)

By integrating twice,

$$T(x) = T^* + Ax - \frac{\Delta H}{c_p} \frac{V_n}{D} \int_x^{\infty} h(\phi) dx$$  \hspace{1cm} (A7)

where $T^*$ is the temperature at the interface and $A$ is an integration constant. Then we call the phase-field equation

$$-\frac{V}{M} \frac{d\phi}{dx} = \varepsilon^2 \frac{d^2 \phi}{dx^2} - \frac{\Delta H}{T_m} \frac{V_n}{D} (T - T_m) - W_g'(\phi)$$  \hspace{1cm} (A8)

Integrating the equation after multiplying $d\phi/dx$ and inserting $T(x)$ yields

$$-\frac{V}{M} \frac{\sigma}{\varepsilon^2} = -\frac{\Delta H}{T_m} \frac{V_n}{D} \left[ \int_x^{\infty} h(\phi) dx - T_m \int_x^{\infty} \frac{d\phi}{dx} dx \right]$$  \hspace{1cm} (A9)

By comparing Eq. (A9) with the relationship $T^* = T_m - V/\mu$, one can obtain the phase-field mobility, $M$, of Eq. (3c).

References

[1] C.F. Lau, H.W. Kui, Acta Metall. Mater. 42 (1994) 3811–3816.
[2] D. Li, K. Eckler, D.M. Herlach, Acta Metall. Mater. 44 (1996) 2437–2443.
[3] T. Aoyama, K. Kuribayashi, Acta Mater. 48 (2000) 3739–3744.
[4] T. Aoyama, K. Kuribayashi, Mater. Sci. Engng. A 304 (2001) 231–234.
[5] M. Ode, T. Suzuki, S.G. Kim, W.T. Kim, Sci. Tech. Adv. Mater. 1 (2000) 43–49.
[6] W.J. Boettinger, S.R. Coriell, A.L. Greer, A. Karma, W. Kurz, M. Rappaz, R. Trivedi, Acta Mater. 48 (2000) 43–70.
[7] L.Q. Chen, Ann. Rev. Mater. Res. 32 (2002) 113–140.
[8] M. Ode, S.G. Kim, T. Suzuki, ISIJ Int. 41 (2001) 1076–1082.
[9] A. Karma, W.J. Rappel, Phys. Rev. E 57 (1998) 4323–4349.
[10] J. Bragard, A. Karma, Y.H. Lee, M. Plapp, Int. Sci. 10 (2002) 91–103.
[11] S.G. Kim, W.T. Kim, T. Suzuki, Phys. Rev. E 69 (1999) 7186–7197.
[12] J.J. Eggleston, G.B. McFadden, P.W. Voorhees, Physica D 150 (2001) 91–103.
[13] W.T. Kim, S.G. Kim, J.S. Lee, T. Suzuki, Metall. Mater. Trans. A 30 (1999) 807–813.