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Two-dimensional facet crystal growth of silicon from undercooled melt of Si–Ni alloy

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Abstract

The two-dimensional facet crystal growth of silicon from the undercooled melt of silicon–nickel alloys has been investigated using a phase-field model. The phase-field parameters derived at the thin interface limit and the anisotropic interface energy model proposed by Eggleston et al. have been used in the simulation. The calculated dendrite growth velocity depends on the interface width and the correct values are obtained when the interfacial Péclet number is sufficiently small. The growth velocity follows a power law relation to undercooling and the exponents are approximately two for Si–10 wt.% Ni alloy and approximately three for Si–20 wt.% Ni alloy. A dendrite grows maintaining its tip shape and a scaling law between the tip size of a dendrite and the growth velocity is confirmed. The phase-field simulations have been compared with the experimental data on the facet dendrite growth velocity in a thin liquid film of Si–6 wt.% Ni alloy and both are acceptable in agreement.

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

1. Introduction

Phase-field models have already been applied to many solidification phenomena and show a wide potential as introduced in review articles [1–3]. Recently, phase-field approaches to facet crystal growth have been proposed so as to include highly anisotropic interface energy [4,5] or interface kinetics [6]. In usual phase-field approaches, the solid–liquid interface energy $\sigma(\theta)$ is simply assumed to have fourfold symmetric anisotropy as

$$\sigma(\theta) = \sigma_0(1 + \nu \cos 4\theta), \tag{1}$$

where ν is the intensity of anisotropy and θ is the angle between the direction normal to the interface and a fixed axis. The equilibrium condition at the interface is given by the Gibbs–Thomson equation

$$(\sigma(\theta) + \sigma''(\theta))\kappa = f^{\mathrm{L}} - f^{\mathrm{S}}, \tag{2}$$

where κ is the curvature radius of interface, and f^{L} and f^{S} are the free energy densities of the solid and liquid phases, respectively. When $\nu < 1/15$, both sides of the equation are always positive and a smooth and convex non-facet crystal becomes stable. Conversely when $\nu > 1/15$, the left-hand side of the equation becomes negative within so-called missing orientations. As the interface within the missing orientations becomes thermodynamically unstable, the facet crystal appears to be composed of only interfaces with stable orientations. Therefore, the presence of an edge between facet interfaces makes the phase-field approach difficult. To overcome this difficulty, Eggleston et al. [4] have proposed the modification of the interfacial energy within the missing orientations as

$$\sigma(\theta) = \frac{\sigma(\theta_{\mathrm{m}})}{\cos \theta_{\mathrm{m}}} \cos \theta \quad (-\theta_{\mathrm{m}} < \theta < \theta_{\mathrm{m}}), \tag{3}$$

where θ_{m} is the first missing orientation derived from

$$\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\frac{\cos \theta}{\sigma(\theta)}\right) = 0. \tag{4}$$

Namely the interface energy in the governing equation within the missing orientations is changed using that of the interface at the end of the stable orientations and the model

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successfully reproduces the equilibrium shape and the transient growth toward the equilibrium shape of a facet interface. Debierre et al. [5] have proposed a different type of anisotropic interface energy in their phase-field approach as

$$\sigma(\theta) = \sigma_0(1 + \nu(|\sin\theta| + |\cos\theta|)). \tag{5}$$

To avoid discontinuities of the derivatives at the cusps in the interface energy plot, they regularized the interface energy within the orientations near the cusps with sinusoidal functions and performed phase-field simulations of facet dendrite growth with vanishing interface kinetics. Kasajima et al. [7,8] have carried out phase-field simulations of the facet free 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. [5] in spite of the different treatment of unstable interfaces. The similarities between the two approaches are that a facet dendrite is composed of a tip with stable interfaces and a trailing tail with unstable interfaces and that the characteristic size of the tip L_T is related to the growth velocity V with a scaling law of $L_T \propto V^{0.5}$. This indicates that both approaches by Eggleston et al. and by Debierre et al. can be applicable to real systems with facet crystals such as silicon.

However, the direct comparison of simulations with experiments is still difficult. Because of the small capillarity length of silicon, the interface width in the phase-field simulations should be sufficiently small so as to obtain the correct values of dendrite growth velocity, and therefore the range of undercooling in simulations is higher than that in experiments. In addition, the dendrite growth observed in experiments is three-dimensional [9–14], but three-dimensional phase-field simulations are still impractical. These difficulties are markedly reduced when the experimental data on the two-dimensional facet dendrite growth are provided. The experiments for alloy systems are also useful as the reference data for comparison because the solute diffusivity is much smaller than the thermal diffusivity and the computational limitations are relaxed to some extent. Two-dimensional experiments on dendrite growth are generally difficult to perform but the present authors found a way of fabricating a thin film of molten silicon or silicon alloys in a simple manner. Using this technique, Kuniyoshi has measured the growth velocity of dendrites in an undercooled liquid film of Si–6 wt.% Ni alloy [15]. The dendrite growth in a thin liquid film is not strictly two-dimensional, however, this data is comparable with simulations.

In the present study, the two-dimensional phase-field model for the facet crystal growth of a dilute alloy is presented and the dendrite growth of silicon from the undercooled melt of silicon–nickel alloys is simulated using the model. Finally the result of the simulations is compared with the data on the dendrite growth in a thin liquid film and the validity of the model is discussed.

2. Calculations

In the present two-dimensional phase-field model, the interface energy with the fourfold symmetric anisotropy of Eq. (1) is assumed and the anisotropy of interface kinetics is taken into account in association with the anisotropy of interface energy so as to have the same orientation dependence as the interface energy

$$\beta(\theta) = \frac{1}{\mu(\theta)} = \beta_0(1 + \nu_K \cos 4\theta), \tag{6}$$

where $\mu(\theta)$ and ν_K are the angle-dependent linear kinetic coefficient and its anisotropy, respectively. The phase-field ϕ is defined as zero at liquid and unity at solid, and it varies continuously from zero to unity in the interface region. The phase-field equation within stable orientations is given by

$$\begin{aligned}\frac{1}{M}\frac{\partial\phi}{\partial t} &= \varepsilon^2\nabla^2\phi + \varepsilon\varepsilon'\{(\phi_{yy} - \phi_{xx})\sin 2\theta + 2\phi_{xy}\cos 2\theta\} \\ &\quad - \frac{1}{2}(\varepsilon'^2 + \varepsilon\varepsilon'')\{2\phi_{xy}\sin 2\theta - \nabla^2\phi \\ &\quad - (\phi_{yy} - \phi_{xx})\cos 2\theta\} - f_\phi.\end{aligned} \tag{7a}$$

Using the modified interface energy by Eggleston et al., the phase-field equation within missing orientations is given by

$$\frac{1}{M}\frac{\partial\phi}{\partial t} = \left(\frac{\varepsilon(\theta_m)}{\cos\theta_m}\right)^2 \phi_{xx} - f_\phi, \tag{7b}$$

where M, ε, and W are phase-field parameters, and the subscripts under ϕ_1 and f denote the partial derivatives. Here, the orientation with the largest interface energy is taken to be the x-axis and the numerical calculation is carried out for one quadrant. Note that the orientation continuity at the edge is guaranteed by taking the average of edge orientations at adjacent points. The free energy density f, solid fraction $h(\phi)$, and parabolic potential $g(\phi)$ are defined as

$$f = h(\phi)f^S + (1 - h(\phi))f^L + Wg(\phi), \tag{8}$$

$$h(\phi) = \phi^3(3 - 2\phi),$$

and

$$g(\phi) = \phi(1 - \phi).$$

The equation for solute diffusion is obtained using the free energy density,

$$\frac{\partial c}{\partial t} = \nabla\frac{D(\phi)}{f_{cc}}\nabla f_c, \tag{9}$$

where D is the diffusion coefficient. By assuming a dilute solution, the terms on the right-hand side of the equation are simplified as

$$\nabla f_c = \nabla f_{c_L} = \frac{RT}{V_m}\nabla \ln\frac{c_L}{1 - c_L} \tag{10a}$$

$$f_{cc} = \frac{f_{c_Lc_L} f_{c_Sc_S}}{(1 - h(\phi))f_{c_Sc_S} + h(\phi)f_{c_Lc_L}} \tag{10b}$$

$$f_{c_ic_i} = \frac{RT}{V_m}\frac{1}{c_i(1 - c_i)} \quad (i = \mathrm{S, L}), \tag{10c}$$

where c_L and c_S are the solute contents in the solid and liquid phases, R is the gas constant, and V_m is the molar volume. Note