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Instability of crystal/melt interface in Si-rich SiGe

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An investigation was carried out into the instability of the crystal/melt interface in Si-rich SiGe, and the effects of the Ge concentration and growth velocity on the periodicity of zigzag facets at the interface were determined. It was found that the periodicity at the onset of instability became shorter with the increasing growth velocity and Ge concentration. *Published by AIP Publishing.*
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I. INTRODUCTION

Binary and pseudobinary semiconductor materials with a completely miscible-type phase diagram, such as Si-Ge, GaAs-GaP, and AlN-GaN, are promising for use as epitaxial substrates for electronic devices owing to their tunable bandgaps and lattice constants, provided that an appropriate composition is selected.¹⁻⁴ Large single crystals of SiGe alloys with various compositions have been grown by the Czochralski method.⁵⁻⁸ However, it is well known that obtaining high-quality single crystals is difficult because the formation of a cellular structure and polycrystallization occur readily during crystal growth from the melt.⁹⁻¹² The tendency for morphological transformation of the crystal/melt interface from planar to cellular or to zigzag facets is known as interface instability.¹³⁻¹⁷ Miller and coworkers performed a detailed study of cellular growth of Ge-rich $\text{Ge}_x\text{Si}_{1-x}$ single crystals by simulation using a phase-field method.^{10,11} They found that the diffusion coefficient for Si in the Ge-rich melt and the temperature gradient at the interface are critical parameters for the evolution of cellular structures. We previously carried out *in situ* observations of the formation of a cellular crystal/melt interface in Si-rich SiGe¹² and determined the critical growth velocity for the morphological transformation of the interface from planar to zigzag facets.¹⁸ It was found that the critical growth velocity decreased with the increasing Ge concentration. We also investigated zigzag faceting of pure Si and found that the periodicity of the facets decreased with the increasing growth velocity.^{19,20} However, similar studies have not been conducted for SiGe alloys.

Therefore, in the present study, we investigated the instability of the crystal/melt interface in Si-rich SiGe, focusing on the periodicity of the zigzag facets at the interface at the onset of instability.

II. EXPERIMENTAL

An *in situ* observation system²¹ consisting of a furnace and a digital microscope was used. Si and Ge wafers were cut into small pieces, which were dipped into acetone for ultrasonic cleaning. After rinsing with ultrapure water, the wafer pieces were dipped into an aqueous hydrogen fluoride solution

(HF+H₂O) to remove the surface oxide layer. They were then rinsed again with ultrapure water, dried with nitrogen gas, and placed in a silica crucible. The size of the silica crucible was 10 mm × 20 mm × 10 mmH, and inside of the crucible was filled with the pieces of Si and Ge wafers. The furnace was evacuated by a rotary pump and then filled with G1 grade Ar gas. The sample in the furnace was heated under flowing Ar gas until the Si and Ge pieces were completely melted. We kept the melt at 1723 K. During the melting process, the surface of the melt shook intensely, and therefore, we thought Si and Ge were sufficiently mixing. The crystallization was promoted from one side by controlling the furnace temperature. For each sample, the effect of the growth velocity on the transformation of the crystal/melt interface from planar to zigzag facets was investigated. During the crystal growth process, a video camera was used to determine both the growth velocity and the periodicity of the zigzag facets. The method for measuring the growth velocity is shown in Fig. 1. Then, the Ge concentration at the observed area in all samples was measured by SEM-EDX (Energy Dispersive X-ray spectroscopy). From the EDX analysis, it was found that we could observe the interface instability at a Ge concentration of 0.65, 2.00, 5.20, 5.90, or 11.6 at. %.

III. RESULTS AND DISCUSSION

Figure 2 shows typical crystal growth behavior from a Si-rich SiGe melt. The Ge content at the observed area was 0.65 at. %. When the growth velocity was low, the interface was planar (left image and Fig. 1) and then took on a zigzag shape owing to the interface instability when the growth velocity increased (center image). The size and periodicity of the zigzag facets gradually increased during growth as neighboring peaks merged (right image). Therefore, it was necessary to measure the periodicity of the zigzag facets immediately after the onset of instability to determine the relationship between the growth velocity and the periodicity.

Figure 3 shows the crystal/melt interface just after the onset of instability for different growth velocities for a sample with a Ge content of 0.65 at. %. It can be seen that the periodicity of the zigzag facets decreases with the increasing growth velocity, as in the case of pure Si.^{19,20}

Figure 4 shows the crystal/melt interface at the onset of instability for samples with different Ge contents at a growth velocity of around 20 $\mu\text{m/s}$. The period of the zigzag facets

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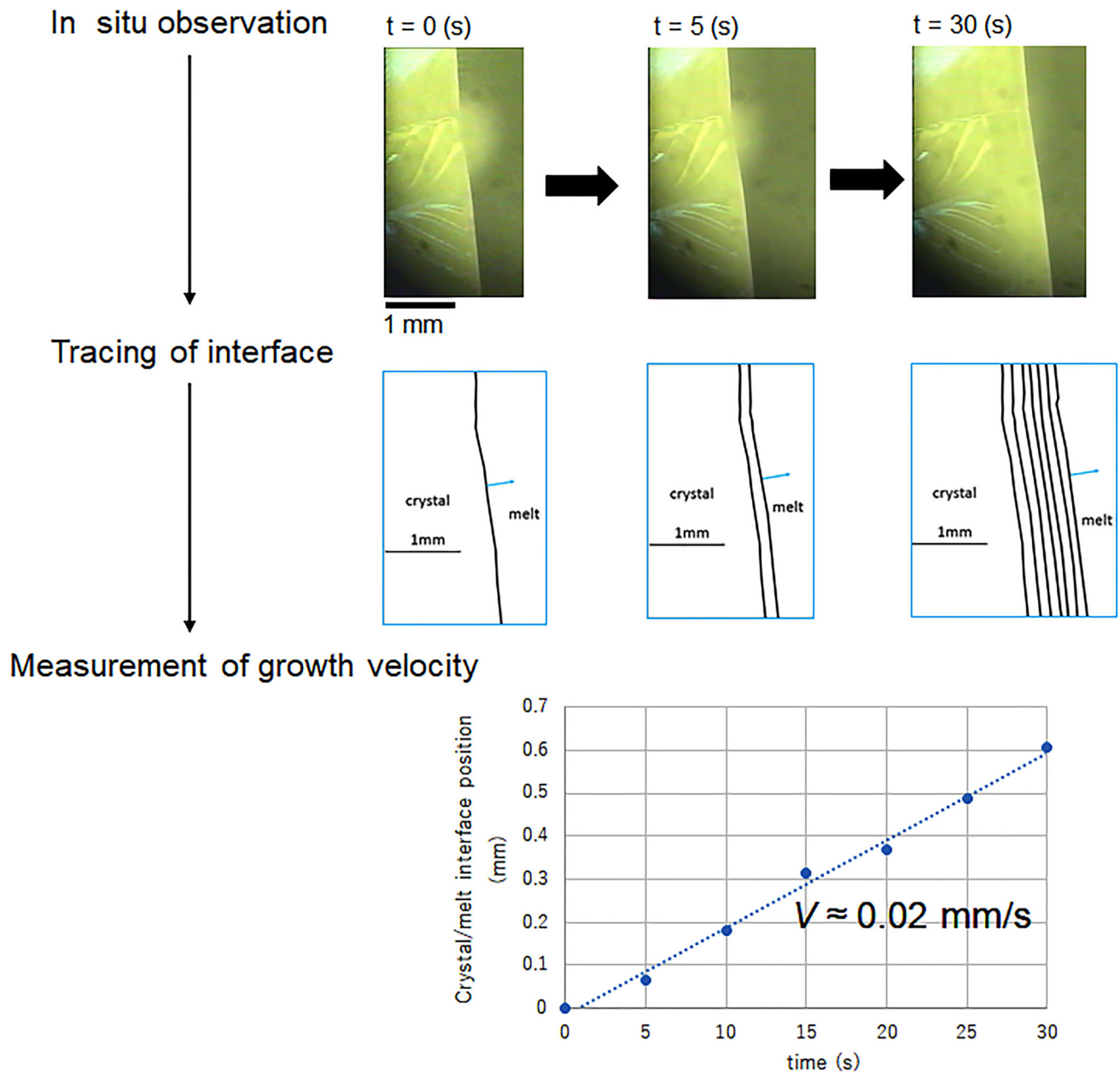


FIG. 1. Method for measuring the crystal growth velocity by *in situ* observations.

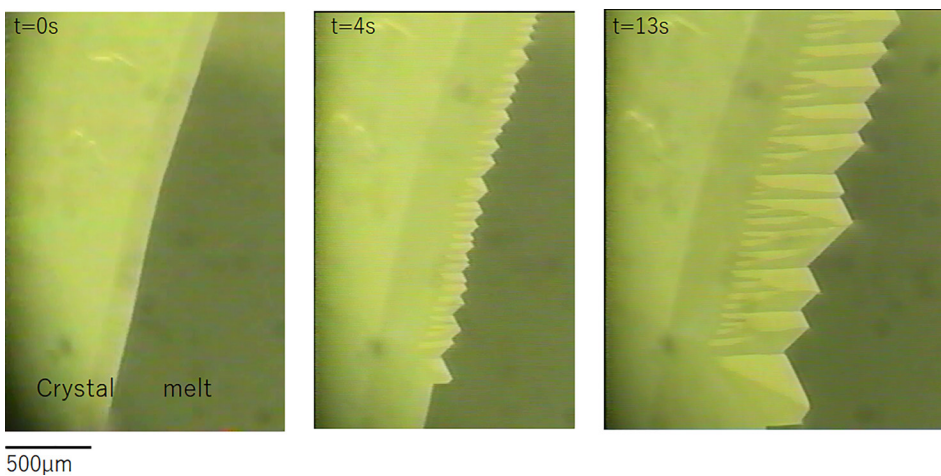


FIG. 2. Morphology of the crystal/melt interface for SiGe (Ge = 0.65 at. %).

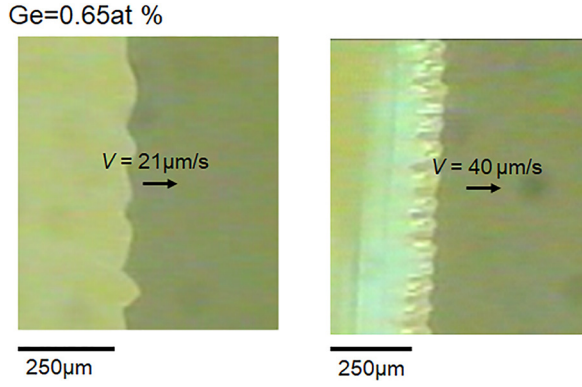


FIG. 3. Morphology of the crystal/melt interface for SiGe (Ge = 0.65 at. %) at different growth velocities.

tends to decrease with the increasing Ge concentration. We performed similar experiments with different growth velocities for each Ge concentration, and the periodicity at the onset of instability was measured (see Table I). We also measured the periodicity for pure Si and included the results in Table I for comparison. These experiments revealed that the period of the zigzag facets tended to decrease with the increasing growth velocity and Ge concentration.

Here, we compare our experimental data with theoretical calculations. Figure 5 illustrates the wavy (sinusoidal) interface at an instability, the theory behind which was presented by Mullins and Sekerka.¹³⁻¹⁷ It is well known that wavy interfaces are formed at the onset of instability in non-faceted materials such as metallic alloys. We previously showed that this also occurs in the case of Si (faceted material).¹⁹ Therefore, here, the model in Fig. 5 is also applied for SiGe. However, some of the physical properties of SiGe needed for the calculations, such as thermal conductivity, thermal capacity, and interfacial energy, were difficult for us to obtain, and thus, we used the values of Si instead of those of SiGe. Therefore, the following arguments have only the qualitative meaning for the explanation of the tendency of our experimental results.

Based on Fig. 5, the periodicity of zigzag facets (λ) is expressed as^{13-17,22}

$$\lambda = 2\pi \left(\frac{\Gamma}{C \left(\frac{\Delta T_0 V}{D} \right) - G_i} \right)^{\frac{1}{2}}, \quad (1)$$

where Γ , the Gibbs-Thomson coefficient, is given by $\Gamma = \sigma/\Delta s_f$ ($\Delta s_f = \Delta h_f/T_m$, σ is the solid/liquid interfacial energy, Δs_f is the entropy of fusion per unit volume, Δh_f is the latent heat of fusion per unit volume, and T_m is the melting temperature), ΔT_0 is the difference between the liquidus and solidus temperatures for a given Ge content in the phase diagram, V is the growth velocity, D is the diffusion coefficient for Ge in the SiGe melt, G_i is the temperature gradient at the interface, and C is a constant satisfying $0 < C < 1$. In the calculations, the Δh_f and σ values for Si (4.122 J/mm³ and $\sigma = 0.45 \times 10^{-6}$ J/mm, respectively) were used instead of the values for SiGe as an approximation. T_m and ΔT_0 were obtained from the Si-Ge phase diagram, and C was selected to give the best fit. The diffusion coefficient was $D = 6.5 \times 10^{-5}$ cm²/s.²³ We next needed to determine the value of G_i for the calculations. Equation (1) was established for a constant temperature gradient, and G_i was treated as a mean value between the temperature gradients of the crystal (G_c) and liquid (G_l), as $\bar{G} = (G_c k_c + G_l k_l)/(k_c + k_l)$, where k_c and k_l are the thermal conductivities of the crystal and liquid, respectively.^{13-17,22} The thermal field around the crystal/melt interface would be changed by changing the growth velocity because the amount of the latent heat increases with the increase in the growth velocity. Therefore, we calculated the temperature gradient in the melt and crystal at the crystal/melt interface as a function of the growth velocity as follows. In our experimental setup, the temperature in the melt and crystal, $T_{l,c}$, along the growth direction (x), was obtained via¹⁹

$$T_{l,c} = A_{l,c} \exp \left(\frac{-x}{l_{l,c}} \right) + Gx + \frac{\rho_{l,c} C_{p,l,c} G V l_q l_{SiGe}}{2k_q} + T_i,$$

$$l_l = \frac{2}{\rho_l C_{p,l} V / k_l + \sqrt{(\rho_l C_{p,l} V / k_l)^2 + 8k_q / k_l l_q l_{SiGe}}},$$

$$l_c = \frac{2}{\rho_c C_{p,c} V / k_c - \sqrt{(\rho_c C_{p,c} V / k_c)^2 + 8k_q / k_c l_q l_{SiGe}}},$$

where $\rho_l C_{p,l}$, $\rho_c C_{p,c}$, k_l , k_c , k_q , l_q , l_{SiGe} , and V are the heat capacity of the melt and crystal, the thermal conductivity of

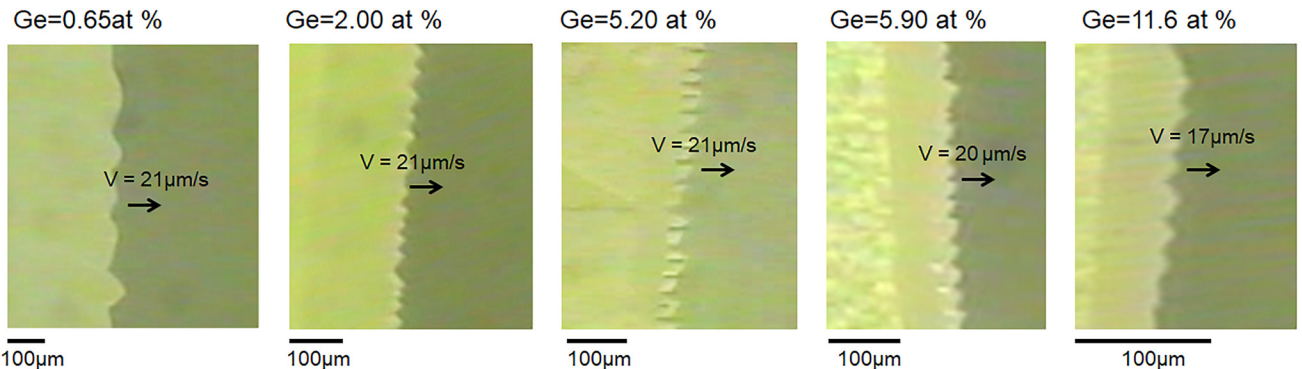


FIG. 4. Crystal/melt interfaces at the onset of interface instability for comparable growth velocities ($V \approx 20 \mu\text{m/s}$) in SiGe with different Ge concentrations.

TABLE I. Growth velocities and periods of zigzag facets during interface instability.

Ge concentration in the melt, C (at. %)	Growth velocity, V ($\mu\text{m/s}$)	Period of zigzag facets, λ (μm)
0 (pure-Si)	122	263
	126	210
	131	131
	151	105
0.65	21	105
	31	79
	40	48
	49	53
2	18	56
	19	53
	21	47
	24	42
5.2	2	157
	4	132
	10	53
	21	37
5.9	7	63
	10	50
	20	32
	25	26
11.6	7	47
	10	33
	14	28
	17	26

the melt and crystal, the thermal conductivity of the silica crucible, the crucible wall thickness, the sample thickness, and the growth velocity, respectively. We used the physical properties of Si for $\rho_l C p_l$, $\rho_c C p_c$, k_l , and k_c as $\rho_l C p_l = 2.53 \times 10^{-3} \text{ J/mm}^3 \text{ K}$, $\rho_c C p_c = 2.29 \times 10^{-3} \text{ J/mm}^3 \text{ K}$, $k_l = 5.4 \times 10^{-2} \text{ W/mm K}$, and $k_c = 2.2 \times 10^{-2} \text{ W/mm K}$.²⁴ k_q was also reported as $k_q = 4.3 \times 10^{-3} \text{ W/mm K}$.²⁴ G is the temperature gradient in the furnace, which was measured as $G = 9 \text{ K/mm}$ in our experiment, and T_i is the temperature at the crystal/melt interface. l_q and l_{SiGe} were based on our experiments as $l_q = 1.0 \text{ mm}$ and $l_{\text{SiGe}} = 10 \text{ mm}$. The constant A was determined by the boundary conditions, i.e., energy conservation and temperature continuity at the crystal/melt interface. The temperature gradient in the melt and crystal at the crystal/melt interface ($G_{i, l, c}$) is given by

$$G_{i, l, c} \equiv \left. \frac{\partial T_{l, c}}{\partial x} \right|_{x=0} = -\frac{A_{l, c}}{l_{l, c}} + G.$$

The relationship between G_i and V , obtained by the above equation, was found to be approximately linear: $G_{il} \approx -59V + 7$ and $G_{ic} \approx 63V + 8$. Therefore, the mean temperature gradient $\bar{G} = (G_c k_c + G_l k_l)/(k_c + k_l) \approx -23.7V + 7.3$. We can then determine the relationship between the periodicity (λ) and the growth velocity (V) at the onset of instability of the crystal/melt interface by using Eq. (1).

Figure 6 shows the relationship between λ and V obtained by the present experiments and by theoretical calculations. In the fitting using Eq. (1), the C constant was used as $C = 0.35$ for pure Si, $C = 0.3$ for SiGe (Ge = 0.65 at. %), $C = 0.1$ for SiGe (Ge = 2.00, 5.20, and 5.90 at. %), and $C = 0.08$ for SiGe (Ge = 11.6 at. %). Now, we consider the meaning of the C constant. According to the Mullins-Sekerka model of Fig. 5, the periodicity λ is expressed as $\lambda = \varepsilon \sin(2\pi/\omega)$. The difference in the undercooling between the top and bottom parts of the perturbation is written as $(\Delta T_t - \Delta T_d)/2\varepsilon = -(4\sigma T_m \pi^2)/(\Delta H \lambda^2) - G_{il}$. The value of $(\Delta T_t - \Delta T_d)/2\varepsilon$ will be close to the value of the temperature gradient in the melt at the crystal/melt interface $-G_{il}$ ($G_{il} < 0$), when the value of λ becomes larger. The smallest value of λ_0 exists at $(\Delta T_t - \Delta T_d)/2\varepsilon = 0$. This means that various periodicities larger than λ_0 can appear at the interface instability. However, in reality, we could observe a certain periodicity at a certain growth velocity and a certain Ge concentration in our experiments, i.e., the observed periodicity λ could be determined by the C constant, as the relation of $(\Delta T_t - \Delta T_d)/2\varepsilon = -CG_{il}$, where $0 < C < 1$. From Eq. (1), it is found that smaller periodicity could be observed when the C constant has a smaller value. For the fitting in Fig. 6, the C constant was smaller when the observed periodicity became shorter with an increase in the Ge concentration. Although it cannot be said that the value of the C constant used for the fitting was appropriate because we did not use the physical properties of SiGe for the calculations, it can be seen that the tendency of the instability for SiGe is well represented by the model in Fig. 5. The periodicity of the zigzag facets at the crystal/melt interface decreases with the increasing growth velocity. It was also found that the addition of a small amount of Ge (e.g., 0.65%) promotes interface instability even at a low growth velocity. This explains why single-crystal SiGe is hard to grow by the Czochralski method or the Bridgman method because instability, which results in cellular structures, occurs readily in SiGe, as directly observed in the present study.

IV. SUMMARY

Instability-related phenomena at the crystal/melt interface of Si-rich SiGe with various Ge contents were directly observed. The relationship between the growth velocity and the periodicity of the zigzag facets at the onset of instability was investigated both experimentally and theoretically.

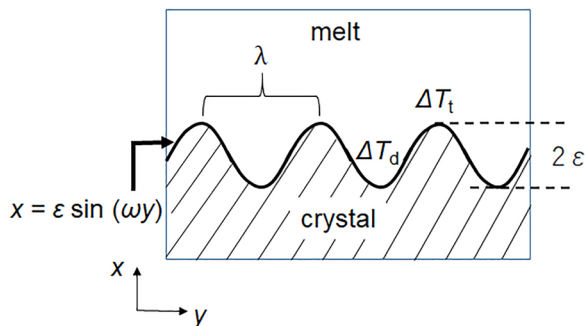


FIG. 5. Schematic of the crystal/melt interface at the onset of instability.

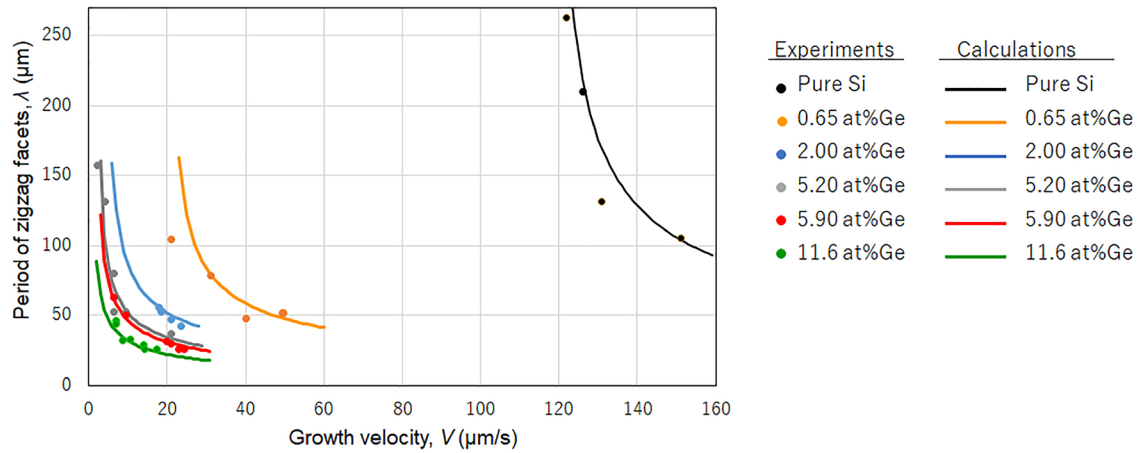


FIG. 6. Relationship between the growth velocity and the periodicity of zigzag facets in SiGe with different Ge concentrations.

Instability was induced by the addition of a small amount of Ge, and a zigzag faceted interface was formed at a low growth velocity. The periodicity of the zigzag facets decreased with the increasing growth velocity for a fixed Ge concentration, and this fits to the model of Mullins and Sekerka.

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