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The critical growth velocity for planar-to-faceted interfaces transformation in SiGe crystals

Xinbo Yang,^{1,2,a)} K. Fujiwara,¹ N. V. Abrosimov,³ R. Gotoh,¹ J. Nozawa,¹ H. Koizumi,¹ A. Kwasniewski,³ and S. Uda¹

¹Institute for Materials Research (IMR), Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan

²Research School of Engineering, College of Engineering and Computer Science, The Australian National University, Canberra ACT 0200, Australia

³Leibniz Institute for Crystal Growth (IKZ), Max-Born-St. 2, 12489 Berlin, Germany

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Crystal-melt interface morphological transformation of differently oriented SiGe crystals with different Ge concentrations was observed, and the effect of Ge concentration on critical growth velocity (V_c) for the interface morphological transformation was investigated. A planar-to-faceted morphological transformation for the $\langle 110 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$ interfaces was observed. V_c for planar-to-faceted transformation of the $\langle 110 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$ interfaces decreases nonlinearly with increasing Ge concentration. SiGe faceted interfaces can be attributed to the fact that the perturbation induced in a planar interface was amplified when the constitutional undercooled zone was formed at high growth velocities. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3698336>]

Silicon-germanium crystals ($\text{Si}_{1-x}\text{Ge}_x$, shorted as SiGe), which are promising materials for advanced electronic and optoelectronic devices, have attracted considerable interest recently.^{1–3} At present, however, SiGe crystals are used mainly in the form of Si/SiGe heterostructures and epilayers,^{4–7} because the growth of high-quality SiGe bulk crystals is very difficult owing to the strong segregation of the components during crystal growth, which leads to constitutional undercooling in the melt near the front of crystallization.⁸ Many techniques, such as Czochralski (Cz), horizontal and vertical Bridgman, electron-beam, and float zone methods, have been developed to grow bulk SiGe crystals, and usually a low growth velocity is necessary for stable growth to avoid constitutional undercooling.^{3,9,10} However, the successful growth of SiGe crystals with high performance remains difficult, especially with increasing germanium concentration.

In the growth of crystals from a melt, the properties of crystal-melt interfaces often play a critical role in controlling macro- and micro-structures and defect density. The main difficulty in growing high-quality SiGe crystals is due to the strong segregation of components during the growth,⁸ which depends partly on the shape of the crystal-melt interface during growth. Therefore, controlling the crystal-melt interface morphology during the crystal growth is crucial to obtaining high-quality SiGe crystals. Faceting is a fundamental concern in crystal growth, and the faceted solid-liquid interface of silicon has been frequently investigated.^{11–13} Faceting is also observed during the epitaxial growth of SiGe films,^{14,15} and cellular structure evolution during the growth of $\text{Ge}_{1-x}\text{Si}_x$ single crystals has been investigated by simulations.^{16,17} Recently, we have reported the $\langle 100 \rangle$ crystal-melt interface morphological transformation from a planar to a zigzag facets to a faceted cellular in $\text{Si}_{0.85}\text{Ge}_{0.15}$ crystal and formation mechanism of the cellular structure was clarified.¹⁸ However, the effect of Ge concentration on the crystal-melt interface

morphological transformation in SiGe crystal is still unknown. In this work, a planar-to-faceted transformation of crystal-melt interfaces of differently oriented SiGe crystals with different Ge concentrations was observed using *in situ* observation, and the effect of Ge concentration on critical growth velocity for interface morphological transformation was investigated.

An *in situ* observation system consisting of a furnace and a microscope^{12,13} was used for observing the crystal-melt interfaces of SiGe crystals. High-quality SiGe crystals with different Ge concentrations (1 at. %, 3 at. %, 5 at. %, and 7 at. %) grown by the Cz method in IKZ (Refs. 8 and 9) were used this time, instead of the sample formed by melting Ge and Si wafers.¹⁸ The experimental procedure is shown in Fig. 1. SiGe sheets ($20 \times 10 \times 1 \text{ mm}^3$) with the required orientations were dipped in a buffered hydrofluoric acid (HF) solution for 2 min to remove the oxide layer from the surface before setting them in a quartz crucible. After pumping to a low vacuum, the furnace was filled with high-purity argon gas and then heated. The sample was melted in such a way that an unmelted portion remained, which served as the seed crystal. Then, the furnace was cooled at different rates. Generally, crystal growth began at the initial crystal-melt interface along the side orientation with different growth velocities. Images of the samples during melting and crystallization were monitored and recorded on videotape.

Figure 2 shows the $\langle 110 \rangle$ -oriented crystal-melt interfaces of $\text{Si}_{0.99}\text{Ge}_{0.01}$ (1 at. % Ge) with different growth velocities. After cooling, the crystal growth began at the interface. The interface was planar when the growth velocity was $49 \mu\text{m/s}$ [Fig. 2(a)], and the planar interface was maintained throughout the crystal growth. At lower growth velocities, a planar $\langle 110 \rangle$ interface was always observed. When the interface growth velocity was increased to $55 \mu\text{m/s}$, an interface morphological transformation from planar to zigzag facets was observed [Fig. 2(b)], which can also be observed at higher growth velocities. A similar interface morphological transformation from planar to zigzag facets was also observed in silicon crystals of different orientations.^{12,13} For

^{a)}Author to whom correspondence should be addressed. E-mail: xinbo.yang@anu.edu.au or louis.xbyang@gmail.com. Tel.: +61 (0)2 6197 0112.

FIG. 1. Experimental procedure for *in situ* observation of crystal-melt interfaces of differently oriented SiGe crystals.

the $\langle 110 \rangle$ -oriented silicon interface, this morphology transformation occurred when the interface growth velocity was $124 \mu\text{m/s}$ or higher,¹³ which is more than two times higher than that required for the Si_{0.99}Ge_{0.01} crystal. The result indicates that the interface growth velocity for the planar-to-facets transformation of silicon decreases quickly as the doping of germanium.

Similar experiments were carried out using SiGe crystals with different Ge concentrations. A planar interface was observed in the Si_{0.97}Ge_{0.03} (3 at. % Ge) crystal when the interface growth velocity was $32 \mu\text{m/s}$ or lower, whereas the interface transformed from planar to zigzag facets when the interface growth velocity was slightly increased to $36 \mu\text{m/s}$.

When the Ge concentration in SiGe sample was increased to 5 at. %, the crystal-melt interface was planar when the growth velocity was $21 \mu\text{m/s}$ or lower, and the interface transformation from planar to facets occurred at a growth velocity of $23 \mu\text{m/s}$ or higher. Figure 3(a) shows the melt process of the Si_{0.93}Ge_{0.07} (7 at. % Ge) crystal, in which a blurry layer ($\sim 2 \text{ mm}$ width) was observed in front of the crystal-melt interface. The layer was identified as a polycrystalline wetting layer on the crystal surface,¹⁹ which was not observed for SiGe crystals with lower Ge concentrations as well as in our previous work.¹⁸ We observed that the transformation from planar to facets of the interface occurred when the interface growth velocity was between 12 and $13 \mu\text{m/s}$ [Fig. 3(b)]. Here, we define the critical growth velocity (V_c) for the interface morphological transformation as the average of two experimental values. For example, for the Si_{0.95}Ge_{0.05} sample, V_c is calculated as the average of 21 and $23 \mu\text{m/s}$, i.e., $22 \mu\text{m/s}$. Therefore, the experimental results indicate that V_c for the $\langle 110 \rangle$ -oriented interface morphological transformation from planar to facets decreases with increasing Ge concentration.

The $\langle 112 \rangle$ and $\langle 100 \rangle$ interface morphological transformations in SiGe crystals with different Ge concentrations were also investigated by the same experimental procedure. We observed that the $\langle 112 \rangle$ and $\langle 100 \rangle$ interfaces also exhibited a planar-to-faceted morphological transformation with increasing interface growth velocity. The obtained experimental growth velocities for the $\langle 110 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$ interface morphological transformations of SiGe crystals with different Ge concentrations are summarized in Table I, and the V_c values calculated are shown in brackets. No data of the $\langle 112 \rangle$ -oriented Si_{0.93}Ge_{0.07} (7 at. % Ge) crystal are available because of the short of sample. Figure 4 shows the V_c values of the differently oriented interfaces as functions of Ge concentration in SiGe crystals, and the V_c of pure silicon¹² was shown together. For all the $\langle 110 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$ interfaces, V_c for planar-to-faceted interface transformation decreases nonlinearly with increasing Ge concentration. For a SiGe crystal with a certain Ge concentration, the V_c values show small

FIG. 2. Crystal-melt interface of the Si_{0.99}Ge_{0.01} crystal grown in $\langle 110 \rangle$ orientation at different velocities: (a) $49 \mu\text{m/s}$, planar interface and (b) $55 \mu\text{m/s}$, planar-to-faceted interface.

FIG. 3. Crystal-melt interface of the $\text{Si}_{0.93}\text{Ge}_{0.07}$ crystal in $\langle 110 \rangle$ orientation (a) melt process and (b) interface growth velocity of $13 \mu\text{m/s}$, planar-to-faceted interface.

difference for interfaces of different orientations, which may attribute to the different interfacial energy of different orientations. The results indicate that V_c is mainly determined by the Ge concentration and is weakly dependent of interface orientation.

Fujiwara *et al.* reported that wavy perturbation is induced in a planar crystal-melt interface of silicon, and the perturbation was amplified and resulted in zigzag facets. Faceted interfaces were formed at high growth velocities because the perturbation induced in a planar interface was amplified when the temperature gradient became negative owing to the latent heat of crystallization.¹² The effect of constitutional undercooling was neglected for their work because the sample is high-purity silicon. For SiGe crystals, however, this is not the case. During the SiGe crystals growth, there is a substantial change in the concentration ahead of the interface. Depending on the temperature gradient in the liquid at the crystal-melt interface, there may exist a zone of constitutional undercooling, in which the actual temperature is lower than the local equilibrium solidification temperature. According to the constitutional undercooling theory,^{20,21} this undercooling results in the instability of the planar interface since any perturbation forming on the interface would find itself in undercooled liquid and, therefore, would be amplified and form facets. The constitutional undercooling criterion was developed quantitatively by considering heat and mass flow only at the interface, that is, a planar interface is stable when,²¹

$$\frac{G_L}{V} \geq \frac{m_L C_0 (1 - k)}{D_L}, \quad (1)$$

where G_L is the actual temperature gradient in the liquid at the interface, V is the interface growth velocity, m_L is the slope of the liquidus line in the phase diagram, C_0 is the initial solute concentration in the liquid, D_L is the diffusion coefficient of the solute (Ge in our case), and k is the segregation coefficient. According to Eq. (1), a planar interface becomes unstable as the interface growth velocity increases. For the *in situ* observation of the crystal-melt interface of SiGe crystal, G_L , m_L , D_L , and k can be considered as constants. Therefore, the relationship between V_c and the Ge concentration C_0 can be written as,

$$V_c = \frac{G_L}{K_0} C_0^{-1}, \quad (2)$$

Where $K_0 = \frac{D_L}{m_L(1-k)}$. Equation (2) indicates that V_c decreases with increasing Ge concentration, which is consistent with our experimental results as shown in Fig. 4. We used Eq. (2)

TABLE I. Experimental growth velocities for $\langle 110 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$ interface transformations from planar to facets of SiGe crystals with different Ge concentrations, V_c values are shown in brackets.

Ge (at. %)	$\langle 110 \rangle$ - V_c ($\mu\text{m/s}$)	$\langle 112 \rangle$ - V_c ($\mu\text{m/s}$)	$\langle 100 \rangle$ - V_c ($\mu\text{m/s}$)
0 ^a	107~124 (115.5)	102~129 (115.5)	123~147 (135)
1	49~55 (52)	44~52 (48)	52~64 (58)
3	32~36 (34)	25~29 (27)	27~34 (30.5)
5	21~23 (22)	22~24 (23)	23~27 (25)
7	12~13 (12.5)	—	14~16 (15)

^aExperimental data cited from Ref. 13.

FIG. 4. V_c values for morphological transformation of differently oriented interfaces as functions of Ge concentration in SiGe crystals.

to fit the experimental results, as shown by the brown dash-dotted line in Fig. 4. Equation (2) fits well with the experimental results in a low interface growth velocity region. However, a large fit error was observed for the result of pure silicon. As reported by Tokairin *et al.*,¹² the G_L , which was decided by the thermal undercooling, should be negative for the faceted interface to develop in pure silicon and is not constant. Equation (2) only works well when the initial solute concentrations C_0 is large enough, and the thermal undercooling does not exist.²¹ The fitting results of G_L and K_0 in the high C_0 region (>0.5 at. % Ge) are 85 K/cm and 1.55, respectively. G_L is very close to the measured temperature gradient of the *in situ* observation furnace (~ 80 K/cm). We have reported that the V_c of $\text{Si}_{0.85}\text{Ge}_{0.15}$ crystal was between 1 and $5.8 \mu\text{m/s}$,¹⁸ which agrees well with the fitting value ($\sim 3.2 \mu\text{m/s}$) as shown in Fig. 4. Therefore, we concluded that the faceted interfaces of SiGe crystals were formed at high growth velocities because the perturbation introduced into a planar interface was amplified when the constitutional undercooled zone formed near the interfaces.

In summary, we have investigated the $\langle 110 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$ interface morphological transformation of SiGe crystals with different Ge concentrations. With increasing interface growth velocity, a planar-to-faceted morphological transformation was observed for the $\langle 110 \rangle$, $\langle 112 \rangle$, and $\langle 100 \rangle$ interfaces. V_c for the interface morphological transformation, which was mainly determined by Ge concentration and is almost independent of interface orientation, decreases nonlinearly with increasing Ge concentration. The constitutional undercooling criterion equation fits well with the experimental results, which indicates that the V_c of the SiGe crystals with high Ge concentrations can be predicted using the equation. When the interface growth velocity reaches V_c , a constitutional undercooling zone forms near the interface, and the perturbation induced in a planar interface is amplified, and resulting in the facets.

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