Effects of growth parameters on silicon molten zone formed by infrared convergent-heating floating zone method

Md. Mukter Hossain, Satoshi Watauchi*, Masanori Nagao, Isao Tanaka

Center for Crystal Science and Technology, University of Yamanashi, 7-32 Miyamae,
Kofu, Yamanashi 400-8511, Japan.

*Corresponding author: Satoshi Watauchi Tel:+81-55-220-8656, Fax: +81-55-220-8270,
email: watauchi@yamanashi.ac.jp

Abstract

The effects of rotation rate, filament size, mirror shape, and crystal diameter on the shape of the silicon molten zones prepared using the infrared convergent-heating floating zone method were examined. The crystal rotation rate did not significantly affect the shape of the feed-melt or crystal-melt interfaces, gap between the crystal and feed, zone length, or lamp power required to form the molten zone. More efficient heating was achieved using lamps with smaller filaments and ellipsoidal mirrors with higher eccentricity. The convexity of both the feed and the crystal sides of the molten zone decreased with increasing crystal diameter. However, the required lamp power, gap, and zone length increased with increasing crystal diameter. The stability of the molten zone seemed to reduce with increasing crystal diameter. The minimum melt width divided by the crystal diameter was found to be a good parameter to describe the stability of the molten zone.

Keywords: A1. Heat transfer, A2. Floating zone technique, A2. Growth from melt, B1. Elemental solids, B2. Semiconducting silicon

1. Introduction

The infrared convergent heating floating zone (IR-FZ) method is a promising crucible-free zone melting method for fabricating crystals.¹ This technique has major advantages over the Czochralski (CZ) method, which requires crucibles; crystals can be grown free of contamination from the crucible materials and the segregation of a dopant can be **easier** controlled. The IR-FZ method can also be used for both conducting and non-conducting materials (as long as the materials absorb infrared radiation). On the other hand, the radio frequency heating floating zone (rf-FZ) method is suitable only for conducting materials. For these reasons, the IR-FZ method is widely used for growing crystals from various materials (mainly oxides and semiconductors) for the study of the condensed matter physics.

The effects of the growing conditions on the crystals grown using the IR-FZ method have been examined. For example, it was reported that the shape of the solid-liquid interface² and the crystallinity of the crystal¹ were affected by the rotation rate of the crystal during growth. The range of crystal diameters that can be achieved using this method is very limited, around 4–15 mm.¹⁻⁴

Recently, we have been investigating the effects of modified infrared convergent heating on the interface shape of the molten zone during crystal growth and the diameter of the crystal grown using the IR-FZ.⁵⁻⁹ It was found that the maximum diameter of rutile and silicon crystals can be increased using this method. **The diameter of a rutile crystal grown in the particular tilted ellipsoidal mirror condition was achieved to 19 mm.**⁵ Diameters of around 10–13 mm were reported using the conventional IR-FZ method.² The maximum diameter of a silicon crystal was 45 mm, achieved by a **definite**

combination of mirror tilting and shifting,⁹ which is much larger than the value of 15 mm reported for conventional IR-FZ.³ For both rutile and silicon, further experiments to grow thicker crystals was not possible owing to limitations of the radiation sources of 10 kW. However, the significant improvements in the grown diameters indicate that the IR-FZ method can be used not only for scientific research but also for mass production of single crystals.

These results also suggest that radiation sources with higher power and more effective convergence of the heat supply enable the growth of larger diameter crystals. However, there has been no systematic studies of this reported to date. In this study, we investigated the required lamp output and molten zone length during crystal growth and the effects of the rotation rate, lamp filament size, and eccentricity of the ellipsoidal mirror on the shape of the molten zone, which is closely related with the stability of the molten zone and the successful growth of crystals. We also examined the effects of the crystal diameter on the crystal growth to clarify the challenges of growing thicker crystals.

2. Experimental Procedure

A modified infrared convergent heating image furnace (model FZ-T-10000-H-TY-1, Crystal Systems Corporation) with four ellipsoidal mirrors was used in this study. In the furnace, the ellipsoidal mirror-lamp (M-L) system positions can be moved closer to or further away from the center of the molten zone where the rotation axes of the feed and the crystal cross. A brief description of the positioning of the M-L system was given previously.^{6,8} Using this furnace, we tried to optimize the convergent heating by investigating the rotation rate of the crystal, the filament size of the lamp, and the shape

of the ellipsoidal mirror, and finally observing the effect of these parameters on the size of the resulting crystal. For all experiments, the growth chamber was evacuated up to 3 mPa before the chamber was filled with the high purity argon gas (> 99.9995 %). The flow of high purity Ar was 1 L/min throughout the entire growth experiment. The detailed experimental conditions are summarized in Table I.

To analyze the effect of the rotation on the crystal growth, the rotation rate of the crystal was varied from 15 to 50 rpm. To analyze the effect of the filament size, two different lamps were used, with a maximum power of either 1.5 or 2.5 kW. The size for 1.5 kW filament is about $16 \times 16 \times 6 \text{ mm}^3$ and that for 2.5 kW filament is about $18 \times 20 \times 8 \text{ mm}^3$. Figure 1 shows the photos of the lamps. The differences of the filament sizes are clearly recognized. The arrow shows the vertical direction set in the furnace. Four lamps are set in the furnace in this configuration. Figure 2 shows a schematic illustration of the two kinds of the ellipsoidal mirror sets (type-1 and type-2) used to study the effect of the mirror shape. The major and minor axes and the eccentricity (e) of the type-1 mirrors were 298 mm, 260 mm, and 0.47 respectively, and 210 mm, 166 mm, and 0.67, respectively, for the type-2 mirrors. The distances between the two focal points along the major axis were similar. The type-1 mirrors were supplied with the commercial model of the FZ-T-10000-H furnace. Ideally, the sizes of the lamps and the eccentricities of the mirrors should be changed systematically. But we could not try them due to the experimental limitations.

In this experiment, Si feeds rod with cylindrical shape of 15 mm in diameter and square shape of $20 \times 20 \text{ mm}^2$ were used to elucidate the effects of the mirror shape on the convergent heating efficiency more easily. For crystal growth experiments using the feed of $20 \times 20 \text{ mm}^2$, various positions of the M-L system were used. For the

experiment investigating the effects of the crystal diameter, polycrystalline feed rods with three different dimensions (15mm diameter, $20 \times 20 \text{ mm}^2$ and $25 \times 25 \text{ mm}^2$) were used. These square shape feeds were cut from a large Si ingot. Therefore, the bulk density of the feed is the same with that of the grown crystal. As mentioned in our previous paper⁶, the feed shape does not affect the stability of the molten zone. The cost of the cylindrical grinding process can be saved by using the square shape feeds. Each growth was continued up to about 50 mm in the growth length to achieve the steady diameter.

For all experiments, a minimum lamp power was applied to exclude the lamp power effect on the interface shape as reported previously.⁸ Note here that the minimum lamp power means the lamp power which was required to avoid contact between the feed and the crystal. The shape of the molten zone and the lamp power required to grow the crystal were examined. The interface shape of the molten zone was characterized by the distribution of iron in the quenched molten zone and by analysis of the molten zone during crystal growth because the segregation coefficient of iron into silicon is much smaller than unity ($\sim 8 \times 10^{-6}$). Electron probe microanalysis (EPMA) was used to map the iron distribution.

3. Results and Discussion

3.1 Crystal rotation

The effects of crystal rotation on the shape of the silicon molten zone are discussed here. Figures 3 (a), (b), and (c) show the iron distribution in EPMA mapping images of the cross-section of the quenched molten zone for crystal rotation rates of 15,

30, and 50 rpm, respectively. The diameter of the crystal was 20 mm and it was grown at an M-L system position of +4 mm. The EPMA maps indicate that the minimal gap scenario was realized in all experiments. The shape of the molten zone was similar to those observed previously in our other studies.⁷⁻⁹ To carry out a quantitative investigation of the molten zone, some parameters were defined as shown in the schematic diagram in **Fig. 3 (d)**, where all the measurements are in mm. Here, h/r is the convexity of the solid-liquid interface, where h is the height of the interface and r is the radius of the feed or the grown crystal, the gap is between the feed and crystal interfaces, L is the zone length, and $w_{\min}$ is the minimum melt width.

As an increased rotation rate corresponds to an increased strength of forced convection, it was hypothesized that the convexity would be affected by the crystal rotation rate. However, it was found that the h/r for a 20 mm diameter silicon crystal was independent of the crystal rotation rate, as shown in **Fig. 3 (e)**. As shown in **Fig. 3 (f)**, the required lamp power, L , $w_{\min}$, and the gap between the feed and the grown crystal were almost independent of the crystal rotation rate. These results suggest that the heat flow due to forced convection in the silicon molten zone has no effect on the solid-liquid interface shape. It is possible that thermal conduction is the dominant **heat** flow mechanism rather than convection in silicon melts due to their low Prandtl number.¹⁰⁻¹² However, Marangoni convection caused by the variation of surface tension due to the temperature gradient has been shown to play an important role for silicon melts.¹³

3.2 Filament size

The effects of the filament size on the shape of the solid-liquid interface of the

silicon molten zone are shown in the iron distributed EPMA mapping images in **Fig. 4 (a)**. A narrow gap (less than 1 mm) between the feed and the grown crystal (henceforth referred to as gap) was observed when the molten zone was formed using four lamps with a maximum output of 1.5 kW each. For this growth, the total required lamp power output was 4.6 kW ($=1.15 \text{ kW} \times 4$). This gap value was similar to previously reported results.⁸ On the other hand, a larger gap than 2 mm was observed when using four lamps with a maximum output of 2.5 kW each, although the minimum lamp power was used in these experiments to avoid contact between the feed and crystal regions (i.e., zero gap). As we reported before,⁸ the effects of the lamp power on the interface shape are relatively large. To discuss the effect of the other parameters on the interface shape, the effects of the lamp power should be excluded. Through our experiment, the minimum lamp power condition, in which a gap smaller than 2 mm is found to be suitable from the point of view of the reproducibility of our experiments. The observed larger gap than 2 mm using lamps of 2.5 kW each means that it is difficult to realize the minimum lamp power condition. For this growth, the total required lamp power output was 5.9 kW ($=1.47 \text{ kW} \times 4$). This result was similar to those previously reported⁷. All these results suggest that the intensity of the incident heating radiation at the focus position was decreased due to the larger focal area of the 2.5 kW lamp compared to the 1.5 kW one. The silicon molten zone parameters obtained using the two different lamps are shown in **Figs. 4 (b)** and **(c)**. Changing the lamp from 1.5 kW to 2.5 kW resulted in a decrease in the h/r of around 0.1, meaning only a minor effect on the solid-liquid interface shape from the filament power was observed. On the other hand, the required lamp power, zone length, and gap significantly increased (by 1.3 kW, 1.2 mm, and 1.9 mm, respectively) and $w_{\min}$ slightly decreased (0.6 mm) with increasing filament power,

as shown in **Fig. 4 (c)**. A lamp power around 1 kW **per 4 lamps** higher was required to achieve the same growth properties when lamps of 2.5 kW were used instead of 1.5 kW. These results indicate that more effective heating was achieved using the 1.5 kW lamps rather than the 2.5 kW lamps. This is because the 2.5 kW lamps had larger filaments and hence larger convergent heating areas, **which suggest that the smaller lamps with smaller filament sizes are useful for the more effective heating growth of the other materials although the suitable lamps are dependent on the melting point of the materials.**

3.3 Mirror shape

The effects of mirror shape on the solid-liquid interface of the silicon molten zone were investigated using the type-1 and type-2 mirror systems described earlier. Crystals with two different diameters of 20 mm and 30 mm were grown using cylindrical feeds of 15 mm in diameter and square feeds of $20 \times 20 \text{ mm}^2$.

For the 20 mm diameter crystal growth, the gap between the feed and the crystal was less than 1 mm and the difference in h/r between the two mirror types was ~ 0.1 , as shown in **Fig. 5 (a)**. The zone length (L), $w_{\min}$, gap, and lamp power are shown in **Fig. 5 (b)** as a function of the mirror eccentricity. L decreased $\sim 1.0 \text{ mm}$ and $w_{\min}$ increased $\sim 0.6 \text{ mm}$ when the type-2 mirror ($e \sim 0.67$) was used during growth rather than the type-1 mirror. The lamp power was almost independent of the mirror shape. Therefore, the effect of the mirror on the shape of the solid-liquid interface was negligible for 20 mm diameter crystal growth.

For the growth of a 30 mm crystal, experiments were performed using various

M-L positions. **Figures 5 (c) and (d)** show the behavior of the lamp power and L for both types of mirrors as a function of the M-L system position. The required lamp power during growth for the type-1 mirror ($e = 0.47$) was higher than that for the type-2 mirror ($e = 0.67$) at all positions of the M-L system, as seen in **Fig. 5 (c)**. For example, using type-1 mirrors, the required lamp power at 0 mm (conventional position of mirror-lamp system) was 7.1 kW and that for the type-2 mirrors was 6.3 kW. Note that the type-1 and type-2 ellipsoidal mirrors could converge radiation up to 190° and 250° , respectively, as shown in **Fig. 2**. This suggests that the efficiency of heat convergence of the type-2 mirror should be higher compared to the type-1 mirror and the observed crystal growth behavior for a 30 mm diameter samples was consistent with this. However, no significant effects of the mirror shape were observed for the 20 mm diameter crystal growth. These results suggest that the efficiency of the convergent heating was affected by the size of the grown crystal, **which might be caused by the finite size of the convergent area due to the finite filament size. The size of the molten zone for the 20 mm diameter growth might be smaller than the convergent area and that for the 30 mm diameter growth might be larger. For the more effective heating growth, the smaller lamps and the ellipsoidal mirrors with larger eccentricities are found to be useful.**

As shown in **Fig. 5 (d)**, spiral crystals were grown and the variation of L was larger between the two different mirrors than for larger M-L positions at smaller M-L positions. It was observed that L was almost independent of the M-L system position at the larger positions and cylindrical crystals were observed. The relationship between the behavior of L and the shape of the crystal has already been reported⁷. In the growth experiment using type-2 mirrors, the zone length also decreased. This is partly due to

the lower required lamp power during growth. Therefore, the use of type -2 mirrors can reduce power consumption as well as the zone length during crystal growth.

3.4 Crystal diameter

Figures 6 (a-c) show EPMA mapping images of the iron distribution in cross-sections of quenched molten zones of crystals with diameters of 20, 30, and 40 mm, respectively. These samples were prepared at M-L position of +4 mm using a type-2 mirror. The stability of the molten zone seemed to reduce with increasing crystal diameter. For the 40 mm diameter crystal, ~0.05 g of iron was determined from the EPMA analysis, much lower than the ~0.15 g in the 20 mm diameter crystal because it was very difficult to maintain a stable molten zone. The large amount of iron in the silicon may reduce the viscosity of the melt with increasing temperature.

As seen in the EPMA mapping images (**Fig. 6**), the geometry of the molten zone, including the height of the solid-liquid interfaces of the feed and the crystal with the melt region, the gap, and L are clearly dependent on the crystal diameter. The h/r of the feed side reduced from 0.71 to 0.30 and that of the crystal side from 0.57 to 0.39 with the increase in the growth diameter of 20 to 40 mm, as shown in **Fig. 7 (a)** and **(b)**. Note that the shape of the interface on the feed side was much more dependent on the crystal size compared to that of the crystal side. The behavior of the feed side convexity (h_F/r_F) observed here was similar to that for the growth of a rutile crystal at a no-tilt condition. On the other hand, the crystal side convexity (h_C/r_C) of the rutile crystal increased rather than decreased with increasing growth diameter at a no-tilt condition.

The gap, L , and lamp power increased with increasing crystal diameter, as shown in **Fig. 7 (c)**, where both the gap and L increased by around 4 mm. This means

that the sum of h_C and h_F was almost independent of the crystal diameter. The larger gap observed for larger crystal diameters suggests that the molten zone can be controlled using the lamp power. The feed contacted with the crystal in lower lamp powers. For larger crystal diameters, the volume of the melt was also larger, meaning that longer solidification times are required for larger crystal during the quenching process. Hence, the shape of larger molten zones may be more susceptible to disturbance during processing.

As shown in **Fig. 7 (d)**, the $w_{\min}$ was almost independent of the crystal diameter, but the aspect ratio ($w_{\min}/D$), where D is the crystal diameter, significantly decreased with increasing crystal diameter. As the potential for melt drop was enhanced during the growth of larger crystals, the behavior of $w_{\min}/D$ corresponds to the stability of the molten zone.

Through these experiments, the efficiency of the convergent heating is found to be significantly affected by the filament size of the lamp, the shape and the size of the mirror, and the size of the grown crystal. A simulation considering the size of the filament, geometry of the feed, the grown crystal, the molten zone, and the shape of the mirror would be very useful for precisely elucidating the mechanisms affecting the efficiency of the convergent heating and the melt convection. The solid-liquid interface shapes which observed through these experiments simply represent the distribution of the melting temperature of silicon. The systematic observation of the temperature distribution seems to be useful for more reliable simulation to discuss the effects of the melt dynamics in the molten zone during crystal growth.

Conclusions

Various parameters characterizing the shape of the silicon molten zone (such as convexity, gap, zone length, minimum melt width, and required lamp power) during IR-FZ processing were investigated as a function of the growth parameters. The characteristic parameters of the molten zone were significantly affected by the crystal diameter. A high $w_{\min}/D$ value corresponded to a high stability of the molten zone. The efficiency of the convergent heating was affected by the size of the filament, the shape of the mirror, and the size of the molten zone. We conclude that using a small filament and ellipsoidal mirror with high eccentricity results in efficient convergent heating that allows the growth of larger crystals.

Acknowledgements

This work was partially supported by the Japan Science and Technology Agency (JST), Precursory Research for Embryonic Science and Technology (PRESTO)

Figure Captions

Fig. 1. Photographs of the 1.5 kW and 2.5 kW lamps. The arrow shows the vertical direction set in the furnace.

Fig. 2. Schematic illustration of the geometries of type-1 and type-2 ellipsoidal mirrors.

Fig. 3. Molten zone shape parameters as a function of crystal rotation rates for a 20 mm diameter crystal grown at a mirror-lamp position of +4 mm. EPMA maps of iron distribution for crystal rotation rates of (a) 15, (b) 30, and (c) 50 rpm. (d) Schematic diagram showing the definitions of the characteristic parameters such as convexity (h/r), gap, zone length (L), and minimum melt width ($w_{\min}$), (e) h/r , and (f) gap, L , $w_{\min}$, and required lamp power as a function of crystal rotation rates. The shoulders visible on the left side of melt (Fig. a and c) were appeared due to volume expansion of molten zone when the samples were quenched.

Fig. 4. Summary of the parameters characterizing the shape of the silicon molten zone for a 20 mm diameter crystal grown at a mirror-lamp position of +4 mm. (a) EPMA maps of iron distribution in the molten zone of samples prepared using different heat sources, (b) convexity (h/r) and (c) gap, zone length, minimum melt width, and required lamp power as functions of filament power. The shoulder visible on the left side of melt (Fig. a) was appeared due to volume expansion of molten zone when the sample was quenched.

Fig. 5. Characterizing parameters of the shape of the silicon molten zone for samples grown at a mirror-lamp position of +4 mm. (a) Convexity (h/r), (b) gap, zone length, minimum melt width, and required lamp power for a 20 mm diameter crystal as a function of eccentricity of

the ellipsoidal mirror, (c) lamp power, and (d) zone length for a 30 mm diameter crystal as a function of the position of M-L system. The vertical dash-dot lines indicate the conventional position of M-L position.

Fig. 6. EPMA maps of iron distribution in the molten zone of samples prepared at a mirror-lamp position of +4 mm, showing the feed-melt and crystal-melt interfaces during growth of (a) 20, (b) 30, and (c) 40 mm diameter crystals. The shoulders visible on the left side of melt (Fig. a and b) were appeared due to volume expansion of molten zone when the samples were quenched.

Fig. 7. Parameters of the shape of the silicon molten zone as a function of crystal diameter for samples prepared at a mirror-lamp (M-L) position of +4 mm. (a) Feed side convexity (h_f/r_f), (b) crystal side convexity (h_c/r_c), (c) gap, zone length, and required lamp power, and (d) minimum melt width ($w_{\min}$) and $w_{\min}/D$, as a function of crystal diameter.

References

- (1) Koohpayeh, S. M.; Fort, D.; Abell, J. S. *Prog. Cryst. Growth Charact. Mater.***2008**, *54* (3–4), 121–137.
- (2) Higuchi, M.; Kodaira, K. *Mater. Res. Bull.***1994**, *29* (5), 545–550.
- (3) Eyer, A.; Kolbesen, B. O.; Nitsche, R. *J. Cryst. Growth***1982**, *57* (1), 145–154.
- (4) Kitamura, K.; Kimura, S.; Watanabe, K. *J. Cryst. Growth***1982**, *57* (3), 475–481.
- (5) Watauchi, S.; Abdur Razzaque Sarker, M.; Nagao, M.; Tanaka, I.; Watanabe, T.; Shindo, I. *J. Cryst. Growth***2012**, *360*, 105–110.
- (6) Hossain, M. M.; Watauchi, S.; Nagao, M.; Tanaka, I. *Cryst. Growth Des.***2014**, *14* (10), 5117–5121.
- (7) Hossain, M. M.; Watauchi, S.; Nagao, M.; Tanaka, I. *Cryst. Eng. Comm.* **2015**, *17* (48), 9452–9458.
- (8) Hossain, M. M.; Watauchi, S.; Nagao, M.; Tanaka, I. *Cryst. Eng. Comm.* **2014**, *16* (21), 4619–4623.
- (9) Hossain, M. M.; Watauchi, S.; Nagao, M.; Tanaka, I. *J. Cryst. Growth***2016**, *433*, 24–30.
- (10) Kobayashi, N.; Wilcox, W. R. *J. Cryst. Growth***1982**, *59* (3), 616–624.
- (11) Chang, C. E.; Wilcox, W. R. *Int. J. Heat Mass Transf.***1976**, *19* (4), 355–366.
- (12) Kobayashi, N. *J. Cryst. Growth***1984**, *66* (1), 63–72.
- (13) Sumiji, M.; Nakamura, S.; Hibiya, T. *J. Cryst. Growth***2002**, *235* (1–4), 55–59.

Table 1: Crystal growth conditions

* The underlined parameters were main parameters for each operation.

Operation	Rotation	Filament	Mirror shape	Crystal diameter
Si feed dimension	$\phi = 15 \text{ mm}$	$\phi = 15 \text{ mm}$	$\phi = 15 \text{ mm}, 20 \times 20 \text{ mm}^2$	<u>$\phi = 15 \text{ mm}, 20 \times 20 \text{ mm}^2, 25 \times 25 \text{ mm}^2$</u>
Crystal diameter (mm)	20	20	20, 30	<u>20, 30, 40</u>
Eccentricity of ellipsoidal mirror	0.67 (Type-2)	0.67 (Type-2)	<u>0.47 (Type-1), 0.67 (Type-2)</u>	0.67 (Type-2)
Maximum lamp power (kW)	2.5×4	<u>$1.5 \times 4, 2.5 \times 4$</u>	2.5×4	2.5×4
Shaft rotation (Upper/Lower)(rpm)	6/ <u>15, 30, 50</u>	6/50	6/50	6/15
Mirror-lamp position (mm)	+4	+4	-2, 0, +1, +2, +4	+4
Growth rate (mm/h)	5			
Feeding rate (mm/h)	10			
Iron in molten zone (g)	0.15	0.15	0.15	0.15, 0.05
Growth atmosphere	Ar (> 99.9995%) flow 1 L/min

Fig.1 (Hossain et al.)

Fig. 2 (Hossain et al.)

Fig. 3 (Hossain et al.)

Fig. 4 (Hossain et al.)

Fig. 5 (Hossain et al.)

Fig. 6 (Hossain et al.)

Fig. 7 (Hossain et al.)