Homogeneous SiGe crystal growth in microgravity by the travelling liquidus-zone method

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Abstract. Homogeneous SiGe crystal growth experiments will be performed on board the ISS “Kibo” using a gradient heating furnace (GHF). A new crystal growth method invented for growing homogeneous mixed crystals named "travelling liquidus-zone (TLZ) method" is evaluated by the growth of Si0.5Ge0.5 crystals in space. We have already succeeded in growing homogeneous 2mm diameter Si0.5Ge0.5 crystals on the ground but large diameter homogeneous crystals are difficult to be grown due to convection in a melt. In microgravity, larger diameter crystals can be grown with suppressing convection. Radial concentration profiles as well as axial profiles in microgravity grown crystals will be measured and will be compared with our two-dimensional TLZ growth model equation and compositional variation is analyzed. Results are beneficial for growing large diameter mixed crystals by the TLZ method on the ground. Here, we report on the principle of the TLZ method for homogeneous crystal growth, results of preparatory experiments on the ground and plan for microgravity experiments.

1. Introduction
Growth of homogeneous mixed bulk crystals has been investigated by many researchers and variety of zone melting methods have been invented [1-4]. Among them, the travelling liquidus-zone (TLZ) method is the most promising method for growing homogeneous mixed bulk crystals [4-6]. Validity of the method has been proved by the growth of InGaAs platy crystals and 2mm diameter SiGe crystals on the ground by confining melts in thin layers or capillary tubes for suppressing convection [4-11]. However, large diameter cylindrical crystals are difficult to be grown on the ground due to convection in melts. We plan crystal growth experiments by the TLZ method in microgravity for proving usefulness of the TLZ method by the growth of larger diameter crystals; 10mm diameter Si0.5Ge0.5 cylindrical crystals will be grown and radial compositional homogeneity as well as axial one will be evaluated. In evaluation, measured compositional profiles will be compared with our two-dimensional TLZ growth model equation and conditions for growing large diameter homogeneous mixed crystals will be established.
Here, we report on the principle of the TLZ method for homogeneous crystal growth, results of preparatory experiments on the ground and plan for microgravity experiments.

2. TLZ method

The TLZ method is a kind of zone melting method but is different from conventional zone melting method in forming a liquidus-zone in which solute is almost saturated. Such liquidus-zone is possible when temperature gradient is low, zone width is narrow and low melting temperature material is rich in the zone. Sample configuration, concentration profile in the sample and its relation to the phase diagram is shown in Figure 1 in the case of Si$_{0.5}$Ge$_{0.5}$ crystal growth.

![Figure 1. Principle of the TLZ method, (a) sample configuration, (b) Ge concentration profile in the sample and (c) Si-Ge phase diagram.](image)

Ge concentration profile as shown in Figure 1 is obtained by heating a sample in which Ge is sandwiched by a Si seed and a Si feed at around 1100°C and at a temperature gradient of about 10°C/cm. At the freezing interface, a melt coexists with a grown crystal and therefore Si concentration is saturated. At the dissolving interface, the melt coexists with a solid feed and Si concentration is saturated, too. If temperature gradient is low and melt zone width is narrow, Si concentration in the melt is almost saturated in the whole as shown in Figure 1. Then, we named such a solute saturated melt zone as a liquidus-zone.

Crystal growth occurs spontaneously due to inter diffusion of Si and Ge because Ge and Si concentration difference is formed in the liquidus-zone. When Ge is transported away from the freezing interface, Si becomes richer than its equilibrium concentration at the corresponding temperature and crystal growth proceeds. At the crystal growth, Ge is segregated and the segregated Ge is transported to the dissolving interface (opposite side of the freezing interface). At the dissolving interface, Ge concentration increases due to transported Ge and its concentration exceeds equilibrium concentration and excess Ge dissolves a solid Si feed and the dissolving interface becomes equilibrium again. By the continuation of this process, crystal growth proceeds spontaneously.

We estimated crystal growth rate as described in the references [6, 9, 11]. The obtained equation is as follows.

\[ -R = \frac{D}{(C_{L0} - C_{SO})} \left( \frac{\partial C_L}{\partial T} \right)_{Z=0} = \frac{D}{(C_{L0} - C_{SO})} \left( \frac{\partial C_L}{\partial T} \right) \left( \frac{\partial T}{\partial Z} \right)_{Z=0} \]  

(1)

Here, \( R \) is freezing rate, \( C_{L0} \) and \( C_{SO} \) are liquidus and solidus concentrations at the freezing interface, \( D \) is interdiffusion coefficient between solute and solvent. Since solute is saturated, \( (\partial C_L / \partial T)_{Z=0} \) is expressed by the reciprocal of the slope of the liquidus line \( (\partial C_L / \partial T) \) multiplied by temperature.
gradient ($\partial T / \partial Z$). Very important point in equation (1) is that freezing rate $R$ is controlled by temperature gradient. Then it is very easy to translate a sample device synchronizingly in the opposite direction to the freezing rate and to keep freezing interface temperature constant. Relation between $R$ and $(\partial T / \partial Z)$ in equation (1) was confirmed by measuring temperature gradient in a melt and growth rate $R$, and by comparing the measured growth rate with the calculated one [6].

3. Experimental procedures

A Ge zone forming material was sandwiched by a Si seed and a Si feed and was inserted into a boron nitride crucible. The crucible was vacuum sealed by a quartz ampoule. This sample device was heated in a temperature gradient furnace. Sample configuration and its relation to temperature profile in the furnace is shown in Figure 2. Growth experiments were performed on the ground using a laboratory furnace or a ground model furnace. According to equation (1), temperature gradient of 7°C/cm in a melt gives growth rate of 0.1 mm/h for the composition Si$_{0.5}$Ge$_{0.5}$. Therefore, temperature gradients between 7 and 14°C/cm were selected for Si$_{0.5}$Ge$_{0.5}$ growth experiments. Crystals with 2mm diameter and 10mm diameter were grown for elucidating effects of convection in melts. In 2mm diameter crystals, convection in melts is suppressed due to small bores of crucibles while convection in melts will occur in 10mm diameter crystal growth on the ground.

![Figure 2. Sample configuration and its relation to a temperature profile.](image)

Grown crystals were cut parallel to the growth axis and were mirror polished. Concentration profiles were measured by an EPMA (electron probe micro-analyzer) and crystallinity was evaluated by EBSP (electron back scattering pattern) and by XRD (X-ray diffraction).

4. Results and discussion

4.1. Confirmation of the TLZ growth model

Since the TLZ growth requires diffusion-controlled mass transport, principle of the TLZ method is studied by the growth of 2mm diameter crystals with suppressing convection in melts [6, 9]. Figure 3 shows an example of axial concentration profiles for a TLZ-grown 2mm diameter crystal. A 13mm long compositionally uniform Si$_{0.49}$Ge$_{0.51}$ crystal was obtained. In the figure, Ge concentration profile of a Bridgman-grown crystal is depicted for comparison. No homogeneous part is observed in a Bridgman-grown crystal. Superiority of the TLZ method in compositionally uniform mixed crystal growth is clear. In the growth, measured temperature gradient was 8°C and sample translation rate was 0.11mm/h. This result agrees well with equation (1) if we use Si-Ge inter diffusion rate $9.5 \times 10^{-8}$ m$^2$/s which is estimated by Adachi et al. [9].

4.2. Large diameter crystal growth

Since we succeeded in growing compositionally uniform small diameter Si$_{0.5}$Ge$_{0.5}$ crystals by the TLZ method, we tried 10mm diameter crystal growth. It was shown that radial compositional inhomogeneity increased as crystal growth proceeded. Figure 4 shows a result of two dimensional Ge
concentration analysis. Freezing interface can clearly be seen because Ge concentration in the crystal is different from that in the liquidus zone. It can be said that the freezing interface is concave towards the liquidus zone. Seed/crystal interface (the initial freezing interface) is almost flat but radius of curvature of the freezing interface is about 20mm at the growth length of about 10mm. Therefore, the interface curvature degrades radial compositional uniformity. Figure 5 shows radial Ge concentration profile near the freezing interface which is about 10mm away from the initial interface. About 1 at% higher at the center of the crystal compared to the peripheral region.

Figure 3. Axial compositional profiles of a TLZ-grown 2mm diameter crystal along with Ge concentration profile of a Bridgman-grown crystal.

![Figure 3](image)

Figure 4. Two-dimensional Ge concentration map.

Figure 5. Radial Ge concentration near the growth interface.

4.3 Two-dimensional model
As described above, when crystal diameter is increased, radial composition degrades and two-dimensionality should be considered. We therefore proposed a two-dimensional TLZ growth model [12]. In the model, radial temperature gradient term is added to the equation (1), and we obtain equation (2).

\[
\frac{\partial f}{\partial t} = -\frac{D}{(C_L - C_S)} \left( \frac{\partial T}{\partial Z} - \frac{\partial T}{\partial r} \frac{\partial f}{\partial r} \right) \left. \right|_{z=0}
\]  

(2)

Where, the z coordinate of the freezing interface is defined by equation (3). \( \frac{\partial f}{\partial t} \) in equation (2) expresses interface translation rate and coincides with \( R \) in equation (1). It should be noted that equation (2) coincides with equation (1) if the second term in the parenthesis of right side of equation (2) is zero.

\[
z = f(r, t)
\]  

(3)

We want to compare freezing interface position of large diameter Si\(_{0.5}\)Ge\(_{0.5}\) crystals with our two dimensional growth model but interface shapes are not always reproductive for terrestrially grown crystals. A variety of interface shape were observed. In Figure 6 two examples of interface shapes are shown. Regular interface shape as shown in figure 4 is very rare and irregular interface shapes as
shown in figure 6 are often observed. Origin of such irregularity may be caused by convection in a melt because density difference between Si and Ge is considerable; density of Si in a liquid phase is about 2.5 whereas density of Ge is about 5.6 at 990°C. Thus, two-dimensional growth model equation cannot be applied to terrestrially grown crystals. One aim of our space experiments is to obtain interface curvature dependence on growth rate (on temperature gradient) and on growth length without convection in a melt and compare interface curvature with our two-dimensional model. If we succeed in quantitative evaluation of equation (2), we can calculate effect of radial temperature gradient on radial compositional profile and we can estimate critical radial temperature gradient for establishing compositional uniformity in the radial direction. Such estimation will be useful for growing large homogeneous crystals by the TLZ method.

4.4 Preparatory experiments on the ground
Since heater length of the GHF is shorter than the usual laboratory furnace, maintaining a constant temperature gradient is difficult. Therefore, growth conditions which were obtained using laboratory furnace cannot be directly applied to a flight model of the GHF. We investigated growth conditions for a flight model of the GHF using a ground model of the GHF. At first, temperature profiles were measured using a dummy sample which is composed of solid Si as a seed, solid boron nitride as a zone and solid Si as a feed. By the translation of heater zones, temperature profiles were changed. Therefore, we changed heating conditions so that the temperature profile is not varied by the translation of heater zone. In the second step, we grew SiGe crystals by the TLZ method. In the first run, initial composition and temperature gradient were deviated from the expected values as shown in Figure 7. However, adjustment of heating conditions are easy because composition reflects interface temperature and growth rate reflects temperature gradient in the TLZ method. After several experiments, we obtained appropriate growth conditions for the flight model furnace. Figure 8 shows one example of adjusted compositional profiles obtained on the ground. It is shown that Si and Ge concentrations are 50 ± 1 at% in a grown crystal for the length of more than 15mm.

Figure 6. Two examples of interface curvature of terrestrially TLZ-grown crystals.

Figure 7. Si and Ge concentration profiles in the first run crystal.

Figure 8. Si and Ge concentration profiles in a crystal after several times adjustment of growth conditions.
5. Plan for microgravity experiments
We are planning to obtain reproducible interface curvatures in the absence of convective flow in a melt and we will compare two dimensional TLZ growth model equation with experimentally obtained interface curvatures. Data obtained by microgravity experiments are used to obtain large sized homogeneous Si$_{1-x}$Ge$_x$ crystals which are useful as substrates of high speed CMOS devices. The GHF furnace for crystal growth experiments has already been on board the ISS “Kibo” and is being checked on its feasibility. After checking out, growth experiments will be performed.

6. Summary
A new crystal growth method named the TLZ method has been invented for growing homogeneous mixed crystals. Axial compositional homogeneity has been evaluated by the growth of small diameter crystals on the ground because convection in a melt is suppressed. However, evaluation of radial compositional homogeneity in large diameter crystals is not so easy because convection causes local compositional inhomogeneity on the ground. Therefore, microgravity experiments are planned for controlling radial compositional inhomogeneity and for evaluating a two dimensional TLZ growth model. Some results of preparatory experiments on the ground and plan for space experiments are described.

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