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1. Objectives

Final objectives of our semiconductor research team are to elucidate compositionally homogeneous single crystal growth conditions of $In_{0.3}Ga_{0.7}As$ and to establish a method for growing homogeneous mixed crystals.

We have been studying growth of homogeneous mixed crystals of $In_{0.3}Ga_{0.7}As$. Control of solute concentration and temperature at the freezing interface is a key for obtaining homogeneous mixed crystals. For this purpose, we have invented a new crystal growth method [1]. In this method, solute concentration and concentration gradient at the freezing interface are stably maintained by utilizing a molten zone saturated by a solute. This method originates from a temperature gradient zone melting method that was first proposed by Pfann [2], and was theoretically analyzed by Hurle *et al.* [3, 4] and Tiller [5, 6]. We revised the method for growing long homogeneous crystals by introducing active sample translation mechanism. When the sample translation rate matches the spontaneous zone traveling rate, solute concentration and temperature at the freezing interface are kept constant and long homogeneous mixed crystals can be grown. We, therefore, named the new method the traveling liquidus-zone (abbreviated as TLZ) method.

Formation process of a liquidus-zone and its relation to solidus are schematically shown in Fig. 1. In the case of $In_{0.3}Ga_{0.7}As$ crystal growth by the TLZ method, a feed with graded In/Ga ratios is used. When the feed is heated at a relatively low temperature gradient, part of the feed with low liquidus temperature is melted and a narrow melt zone is formed. At the solid/liquid interfaces, InAs saturated liquidus is formed by the reaction between the solid and the liquid. Since the solubility depends on temperature, concentration gradient of InAs is set in the zone by the imposed temperature gradient.

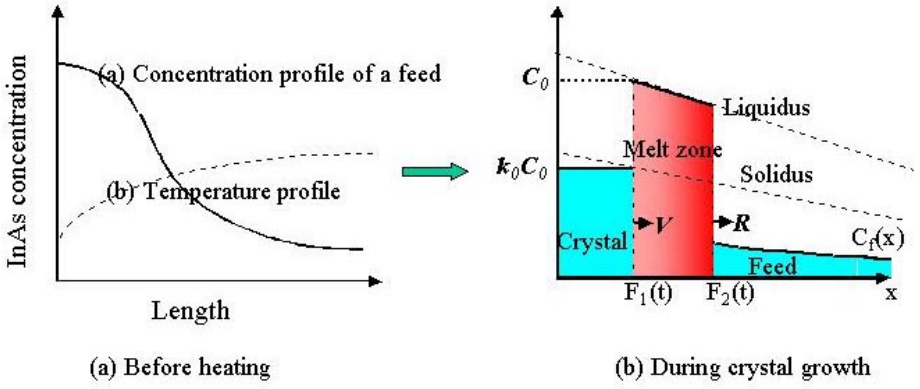

Figure 1. Schematic drawings showing TLZ method principle. Temperature and concentration profiles before heating (a) and compositional profiles of a grown crystal, of a zone and of a n unmelted feed are shown (b). *V* is the growth rate and *R* is the feed dissolving rate.

This causes diffusion of InAs towards the low concentration side. At the freezing interface, crystal growth proceeds due to the decrease in InAs concentration by diffusion. While, InAs concentration increases at the opposite side of the zone and part of the feed is dissolved. In the crystal growth process, InAs is piled up at the freezing interface due to segregation and the piled-up InAs is transported by diffusion towards the dissolving interface. Thus, the zone spontaneously and successively travels along the liquidus towards the hot end of the feed. Long homogeneous crystals can be grown when the sample is translated according as the zone traveling rate.

The merit of this method is that solute transport rate is controlled by the temperature gradient at the freezing interface and that the compositional homogeneity is not so much affected by convection. Detailed explanation will be described in section 3, Hypothesis. In reality, compositional homogeneity of terrestrially grown crystals is excellent: a 20 mm long homogeneous $In_{0.25}Ga_{0.75}As$ single crystal with a 2 mm diameter was grown at a sample translation rate of 0.25 mm/h under a 20°C/cm temperature gradient. This was the first success in the world for this mixed semiconductor crystal grown with high InAs concentration. Therefore, the TLZ method is the most useful method for homogenous mixed crystal growth. However, numerical analysis based on one-dimensional model shows that the growth rate should be 0.4 mm/h for a temperature gradient of 20°C/cm. Such discrepancy may arise from the decrease in concentration gradient at the freezing interface due to convective mixing. On the ground, three-dimensional convection occurs in a melt. If we can make a three-dimensional model, we can compare experimental results with the model. However, three-dimensional theoretical model is very difficult to establish. In microgravity, one-dimensional axially symmetrical growth conditions are realized in the absence of convective flow. Results obtained in microgravity experiments are directly compared with our one dimensional TLZ model to prove the validity of our model.

Moreover, study on the effect of constitutional supercooling in the liquidus-zone is indispensable for developing the TLZ method as well as the temperature gradient zone melting method [2 - 6]. We think that the reason why the single crystal growth became difficult with increasing crystal diameter is due to constitutional supercooling and a study on the allowable limit of constitutional supercooling is necessary. This study should also be done in the absence of convection to obtain precise data.

2. Specific Aims

Specific aim of the proposal is to make sure the model of the TLZ method.

Following two points should be confirmed for verifying our TLZ growth model quantitatively. As described in the section of hypothesis, to verify relations expressed by equations 3 and 6 makes our TLZ growth model complete.

1) Relation between growth rate and temperature gradient

The TLZ growth is possible by the establishment of the concentration gradient in the zone under the imposed temperature gradient. Mass transport by diffusion occurs under such concentration gradient and the zone travels spontaneously towards the hot end of the feed. Then, the zone traveling rate is proportional to the temperature gradient. Homogeneous crystals can be grown by the successive translation of the

sample in accordance with this zone traveling rate (Fig. 2). In addition, according to our model, growth rate should be uniquely determined irrespective of the zone width. We want to verify the relation between the growth rate and the temperature gradient, and the relation between growth rate and the zone width by growth experiments in microgravity.

2) Critical zone width for maintaining TLZ growth

Since a relatively wide zone (such as the zone width of 20 mm) is required for growing long homogeneous crystals, we investigate the critical zone width for maintaining the TLZ growth. If the zone width is wider than the limit, say 40 mm or so, as shown in Fig. 3, solute concentration profile in the zone deviates from the ideal linear profile and homogeneous crystal growth becomes difficult. We investigate the maximum allowable zone width for obtaining homogeneous crystals not only by changing the zone width but also by imposing pulsed translation change during the steady-state growth. Recovery process from the disturbed state gives information on the tolerability of the TLZ growth. Such a study is possible only in the absence of convective disturbance.

3. Hypothesis

1) TLZ growth model

The liquidus-zone traveling rate is numerically derived on the assumptions that the thermodynamic equilibrium is maintained at the solid/liquid interfaces because of immediate reaction between the two, and diffusion in the solid is negligible compared with that in the liquid.

At the freezing interface, the following relation holds at a constant interface traveling rate V if we assume the steady-state growth,

$$V(C_{L0} - C_{S0}) = VC_{L0}(1 - k_0) = -D \cdot \left(\frac{\partial C_L}{\partial z} \right)_{z=0} \qquad \text{(eq. 1)}$$

where D is the diffusion coefficient, C_{L0} and C_{S0} are respectively the liquidus and solidus concentrations at freezing interface, and k_0 is equilibrium segregation coefficient. The growth direction is along Z-axis and z = 0 is set at the freezing interface. The spontaneous growth rate means that the freezing interface shifts spontaneously by the diffusion process towards the hot end of the feed under the imposed concentration gradient. The concentration gradient ($\partial C_L / \partial z$) is given by,

$$\left(\frac{\partial C_L}{\partial z} \right)_{z=0} = \left(\frac{\partial C_L}{\partial T} \right) \left(\frac{\partial T}{\partial z} \right)_{z=0} \qquad \text{(eq. 2)}$$

Then, the growth rate is given by,

$$V = -\frac{D}{(C_{L0} - C_{S0})} \left(\frac{\partial C_L}{\partial T} \right) \left(\frac{\partial T}{\partial z} \right)_{z=0} \qquad \text{(eq. 3)}$$

Equation 3 shows that the spontaneous growth rate is proportional to the diffusion

coefficient and temperature gradient in the zone, and is reciprocally proportional to the slope of the liquidus. This relation is the basic relation which holds for the steady-state growth. In addition, it should be noted that growth rate is determined irrespective of the zone width if equation 3 holds. We will verify these points by growth experiments in microgravity.

In the TLZ growth method, the sample is translated in such a way as to maintain constant temperature, constant solute concentration, and constant concentration gradient at the freezing interface. If the sample translation rate U matches the spontaneous zone traveling rate, long compositionally homogeneous crystals are grown. If U is higher than the spontaneous zone traveling rate, solute concentration of grown crystals increases according as crystal growth proceeds. On the other hand, if U is smaller than the spontaneous zone traveling rate, solute concentration decreases as the crystal growth proceeds. The relation between the sample translation rate U and the concentration profile is analyzed in the case of $In_{0.3}Ga_{0.7}As$ and is depicted in Fig. 2 for a temperature gradient of 20°C/cm.

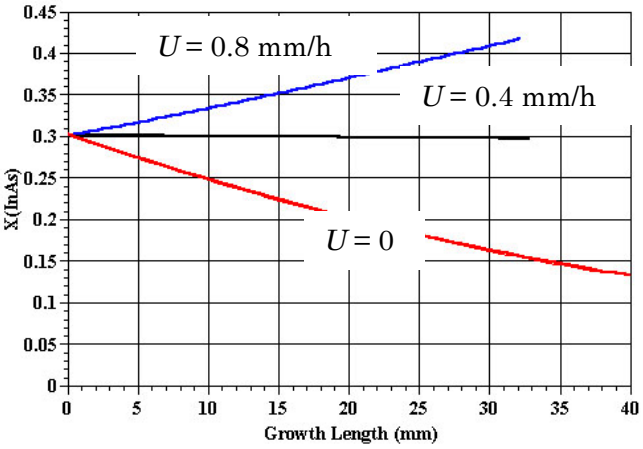

Figure 2. Relation between the sample translation rate (U) and InAs concentration profile in crystals grown at a temperature gradient of 20°C/cm.

2) Critical zone width for maintaining TLZ growth

If convection in the zone is suppressed, the piled-up solute at the freezing interface is transported by diffusion towards the dissolving interface. The solute concentration profile in the zone at a distance z from the freezing interface in the quasi-steady-state growth is expressed by [7],

$$C_L(z) = (C_{L0} - C_{S0})\exp\left(-\frac{V}{D}z\right) + C_{S0} \qquad \text{(eq. 4)}$$

The liquidus concentration C_e in the zone is given by eq. 5 if we assume that it is expressed by the linear combination with the distance z, $C_e = C_{L0} + fz$, where f is a variable depending on the zone width ξ, and by considering the boundary condition that the solute concentration coincides with the liquidus concentration at the dissolving interface,

$$C_e(z) = C_{L0} + \frac{(C_{L0} - C_{S0})}{\xi}\left(\exp\left(-\frac{V}{D}\xi\right) - 1\right)z \qquad \text{(eq. 5)}$$

If we obtain the difference Δc between the actual concentration and the liquidus concentration, it is expressed as,

$$\Delta c = C_L(z) - C_e(z) = \frac{(C_{L0} - C_{S0})}{\xi}\left(\xi\left(\exp\left(-\frac{V}{D}z\right) - 1\right) - z\left(\exp\left(-\frac{V}{D}\xi\right) - 1\right)\right) \qquad \text{(eq. 6)}$$

This difference gives a degree of deviation from the ideal state in the TLZ process and also gives a degree of constitutional supercooling in the TLZ process. This equation yields the difference in the steady-state. In the actual crystal growth, the process is not steady-state and the difference in the non steady-state should be calculated. Results of the numerical analysis are shown in Fig. 3. Constitutional supercooling is very small when the zone width is narrow. Constitutional supercooling increases as the zone width increases. If we compare the critical degree of constitutional supercooling estimated in the directional solidification experiment [8], which is about 10 %, the maximum allowable zone width seems to be about 35 mm. Therefore, we choose two zone widths: one is well below this critical value, e.g. 20 mm, and the other exceeds this critical value, e.g. 40 mm. Therefore, we investigate our estimation on the critical zone width agrees with the actual TLZ growth experiments at constant sample traveling rate in microgravity.

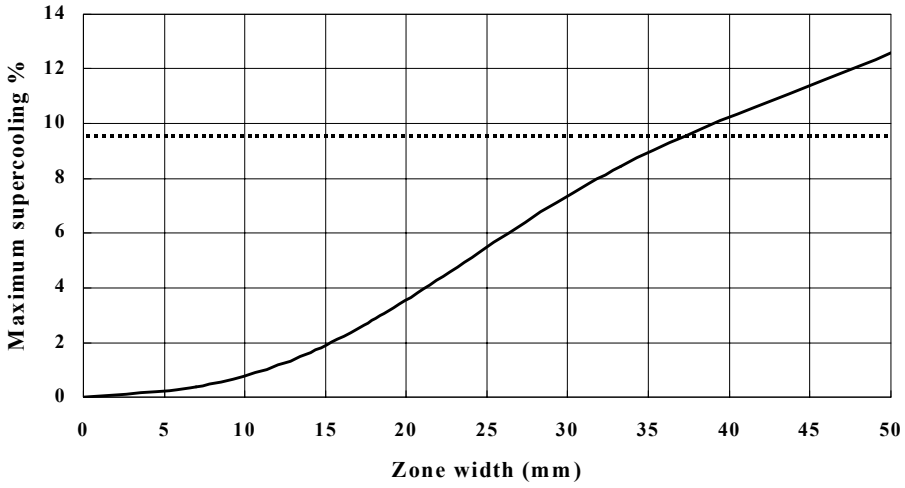

Figure 3. Relation between zone width and degree of constitutional supercooling. The dotted line is the estimated maximum allowable degree of supercooling based on the constitutional supercooling experiments during the directional solidification.

We also investigate the maximum allowable limit of zone width for the TLZ growth by imposing pulsed sample translation rate change. This is because more sensitive measurements can be performed if we give disturbances to the zone. We observe recovering process after giving abrupt change of sample translation rate for a while such as 1 h. If the zone is saturated by a solute, no big changes in the

concentration of a grown crystal are observed. If the zone is too wide as 40 mm, substantial changes in the concentration occur. In addition, crystals become poly crystalline because constitutional supercooling occurs in this case.

4. **Background**

1) Invention of the TLZ method

$In_{0.3}Ga_{0.7}As$ is a promising material as substrates for fabricating laser diodes with wavelength of 1.3μm. However, the growth of homogeneous crystals is very difficult because convection in the melt combined with segregation at solidification causes compositional variation in the grown crystal. Especially near the composition $In_{0.3}Ga_{0.7}As$, separation of the liquidus and solidus is greatest as shown in the phase diagram (Fig. 4) [9], and homogeneous crystal growth is most difficult. Various crystal growth methods such as the double crucible method [10] and the traveling heater method [11] have been applied to grow homogeneous single crystals of $In_{1-x}Ga_xAs$, but these methods resulted in insufficient control of homogeneity. We thought that the stable transport of the solute is the basis of homogeneous crystal growth and therefore came up with a new crystal growth method named the TLZ method [1].

A schematic drawing of the TLZ method is shown in Fig. 5 in comparison with the traveling heater method. Concentration and temperature profiles along the growth axis and the zone position are shown in the figure. The growth configuration is similar to the vertical Bridgman method. However, part of a feed is melted and a narrow liquidus-zone is formed. This is different from the Bridgman method in which all of the feed is melted. Formation of a narrow melt zone is similar to the traveling heater method. However, heating a feed at low temperature gradient is different from the traveling heater method in which steep temperature gradient is imposed. In addition, melt composition is not saturated in the traveling heater method.

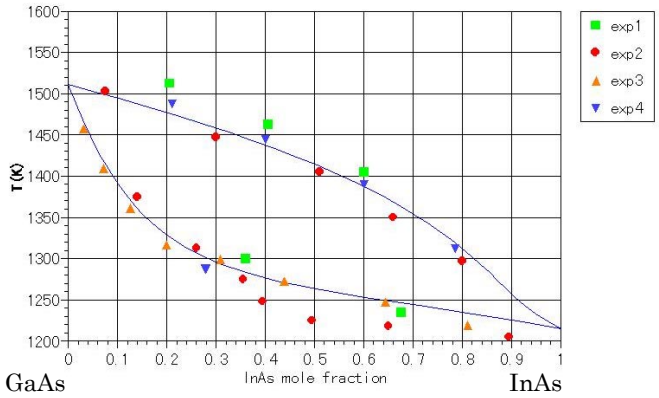

Figure 4. Pseudobinary phase diagram of the GaAs–InAs system [9].

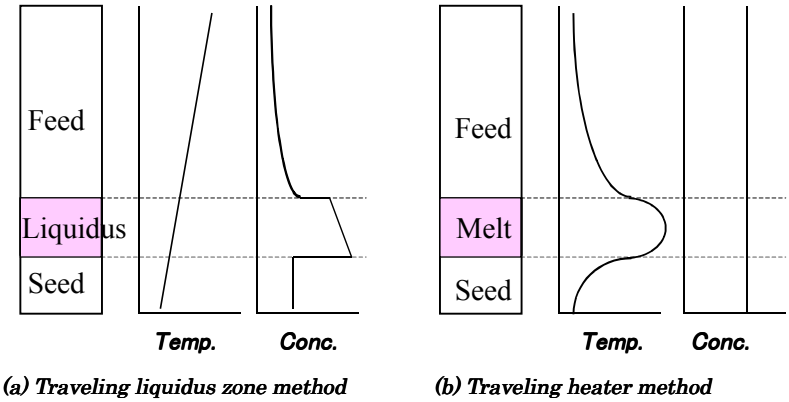

Figure 5. Comparison of the traveling liquidus-zone method (a) and the traveling heater method (b)

2) Preliminary experiments on the ground

Figure 6 is an example of the compositional profile of a TLZ-grown crystal. Crystal diameter is 2.0 mm and the cross sectional view of the crystal along the growth axis is shown together with the compositional profile. Homogeneous $In_xGa_{1-x}As$ crystal with InAs mole fraction x = 0.25 $\pm$0.02 extends to a distance longer than 35 mm and a single crystalline grain longer than 20 mm is observed. In this experiment, temperature at the position of the seed and feed butted part was set at 1050^{o}C, and the ampoule was lowered at a rate of 0.25 mm/h after 1 h soaking. Temperature gradient in the furnace was about 20^{o}C/cm.

As we succeeded in growing small diameter homogeneous single crystals of $In_xGa_{1-x}As$ with x = 0.2 to 0.33, we tried to grow large crystals with diameter ranging from 5 to 20 mm. Single crystal growth got difficult with increasing crystal diameter: no single crystals region was obtained for diameters larger than 14.5 mm. However, compositional homogeneity of the crystal with d = 14.5 mm was excellent and InAs mole fraction x = 0.27$\pm$0.02 was achieved in the whole region of the grown crystal.

Such results show that the TLZ method is useful for obtaining compositionally homogeneous $In_{0.3}Ga_{0.7}As$ crystals even when convection in the melt exists; In large diameter crystals with $d \geqq 10$ mm, convective flow velocity higher than 10 mm/s is numerically derived [12]. The reason why homogeneous crystals are grown in the presence of convection is that transport rate at the freezing interface is controlled by the temperature gradient at the interface. On the other hand, local supercooling due to difference between the actual and equilibrium composition in the liquidus-zone induced by the convection may cause polycrystallization.

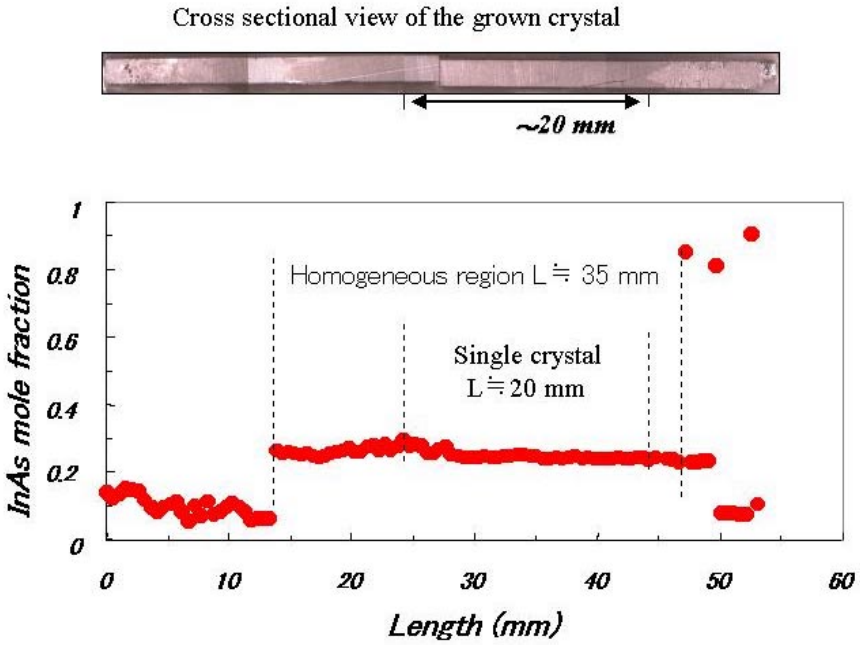

Figure 6. Cross sectional view of a grown crystal and InAs mole fraction along the growth axis (d = 2 mm), showing homogeneous crystal growth with x = 0.25.

3) Polycrystallization by constitutional supercooling

Terrestrial experiments showed that single crystal growth got difficult with increasing crystal diameter in the TLZ method. Since increase in crystal diameter enhances convection, we think that convection in the liquidus-zone relates poly crystallization via supercooling.

We observed that constitutional supercooling due to rapid crystal growth (growth rate: 2 mm/h at temperature gradient of 43°C/cm) produced nuclei ahead of the interface as shown in Fig. 7 [8]. Many investigators have reported on Mullins-Sekerka type morphological instability, that is, cellular growth by the constitutional supercooling [7, 13, 14]. However, we observed different type of instability caused by constitutional supercooling. Polycrystallization ahead of the freezing interface was observed [8, 15]. We consider that polycrystallization occurred by heterogeneous nucleation around foreign particles such as impurity. Similar poly crystallization has been reported in the Al-Mg system [16]. Supposing that such poly crystallization is dominant when the supercooling increases beyond the allowable limit, we have to avoid the supercooling for growing single crystals and the knowledge on the maximum allowable limit of supercooling is indispensable.

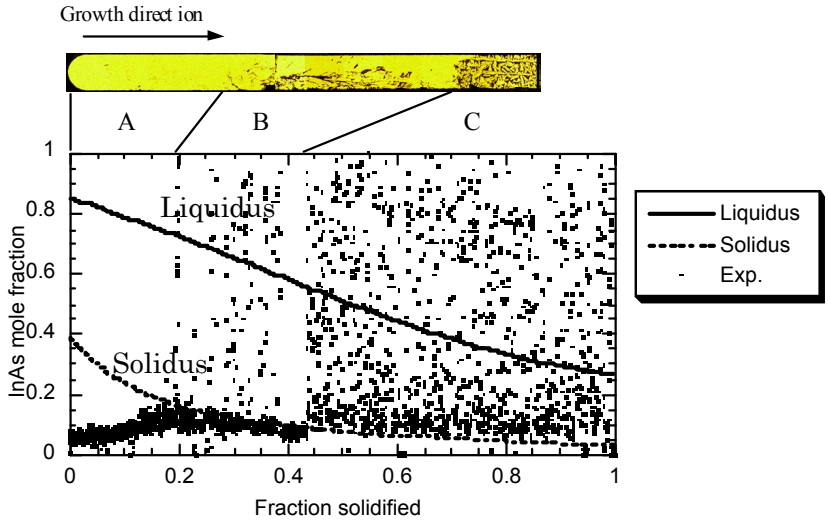

Figure 7. Compositional profile and cross sectional view of a sample in which constitutionally supercooled region is observed. The region denoted by B is a constitutionally supercooled region. Region A is normally solidified region and C is a melt before quenching.

5. Necessity of Long Duration Microgravity Conditions

Convection in the liquidus-zone induces concentration difference along radial direction and enhances mass transport between the seed and feed interface. In order to verify our growth model with the TLZ method, we need growth experiments in diffusion-controlled conditions. Crystal growth in such ideal conditions allows us the direct comparison between the experimental results and our growth model. We calculated convective flow, temperature and concentration field numerically in order to check whether microgravity conditions are beneficial to our purpose. The calculation method has been developed by one of the co-investigators of our team [12]. Thermophysical properties used in the simulation are listed in Table 1. Interdiffusion coefficients between InAs and GaAs have been measured for improving precision of the simulation [17]. Residual acceleration of 10^{-6} G is imposed perpendicular to the growth axis in microgravity. This direction of the residual acceleration is the severest direction in which the greatest convection occurs. On the other hand, 1 G is imposed parallel to the growth axis as terrestrial conditions and this direction is the most stable direction in which convective flow velocity is minimized. Maximum convective flow velocity in the 20 mm diameter melt is 4.5 μm/s in the worst case in microgravity which is about 4 orders of magnitude smaller than that of 2 mm diameter melt in the best case on the ground. We analysed the Sherwood number, *Sh*, in order to estimate the effect of convection on the mass transport. *Sh* is the nondimensional number showing the relative degree of the mass transport against diffusion. When *Sh* is equal to1, mass transport is dominated by diffusion. Figure 8 shows the average Sherwood number near the freezing interface in the liquidus-zone. The mass transport on the ground is enhanced twenty times larger by convection comparing with that due to pure diffusion. Even if we make experiments using a 2 mm diameter melt, *Sh* is 8.2. In

microgravity, *Sh* is almost 1 for a 20 mm diameter melt. Therefore, microgravity is beneficial for attaining the diffusion-controlled conditions and this allows us to check the TLZ growth model.

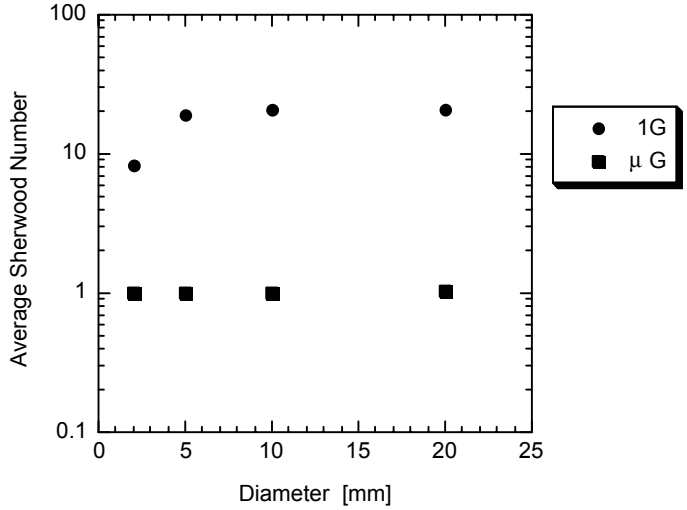

Figure 8. Comparison of average Sherwood number between 1G and 1μG conditions as a function of melt diameter (zone width = 20 mm). Growth configuration is different between terrestrial experiments and space experiments and the most stable fluid flow conditions under 1G are compared with the most unstable fluid flow conditions under microgravity.

Table 1 Physical properties used in the simulation.

Kinematic viscosity	ν_L	$[m^2s^{-1}]$	1.5×10^{-7}
Density	ρ_0	$[kgm_{-3}]$	5.9×10^{3}
Thwemal conductivity of melt	λ_L	$[Wm^{-1}K^{-1}]$	3.0
Thermal conductivity of crystal	λ_S	$[Wm^{-1}K^{-1}]$	1.2
Thwemal conductivity of container	λ_C	$[Wm^{-1}K^{-1}]$	3.0
Temperature coefficient of volume expansion	β	$[K^{-1}]$	9.34×10^{-5}
Concentration coefficient of volume expansion	γ	[−]	1.89×10^{-1}
Thermal diffusivity of melt	κ_L	$[m^2s^{-1}]$	1.1×10^{-5}
Thermal diffusivity of crystal	κ_S	$[m^2s^{-1}]$	3.0×10^{-6}
Thermal diffusivity of container	κ_C	$[m^2s^{-1}]$	1.6×10^{-7}
Interdiffusion coefficient in melt	D_L	$[m^2s^{-1}]$	2.0×10^{-8}
Interdiffusion coefficient in crystal	D_S	$[m^2s^{-1}]$	1.0×10^{-11}
Latent heat	L_{SL}	$[Jkg^{-1}]$	5.0×10^{5}

Application of a magnetic field is one of among several methods for suppressing convective flow in a melt. We calculated the effect of the magnetic field and the result showed that the convective flow velocity is reduced from 20 mm/s to about 5 mm/s by applying a 10 T magnetic field in the case of a $In_xGa_{1-x}As$ melt. However, such a reduction is insufficient for obtaining diffusion-controlled conditions.

We also investigated the effect of *g*-jitters on the crystal growth process by altering gravity sinusoidally with time. The combinations of amplitude and frequency were

(10^{-6}G, 0.01 Hz), (10^{-5}G, 0.1 Hz), (10^{-4}G, 1.0 Hz) and (10^{-3}G, 10 Hz), respectively. The time variations of the concentration of In at the interface is shown in Figure 9 where the amplitude and frequency of *g*-jitter are 10^{-4}G and 1.0 Hz, respectively. In the international space station, such amplitude at frequency of 1.0 Hz is the allowable highest one and is severe for fluid motion. As a result, the concentration does not fluctuate with time at all. The situation was the same for the other combinations of the amplitude and frequency. In other words, the effect of *g*-jitters on the crystal growth process is not so serious. However, since the directions and amplitudes of the actual *g*-jitters change randomly, we need further investigation. The situation was the same for the investigations based on three-dimensional simulations.

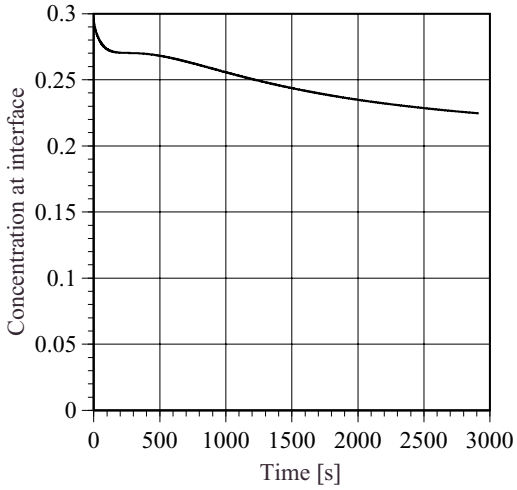

Figure 9. Time variations of concentration of InAs at the melt side of the interface. The amplitude and frequency are 10^{-4}G and 1.0 Hz, respectively.

Long duration microgravity is required for crystal growth because the appropriate growth rate is in the range between 0.2 and 0.5 mm/h. For example, 200 h are needed to grow a 50 mm long crystal when the growth rate is 0.25 mm/h.

6. Experimental Design and Methods

Research objectives are achieved by the interactive work among space experiments, terrestrial experiments, and fluid flow analysis. We will measure temperature distributions in the liquidus-zone more accurately. The data are used for growth rate analysis and for fluid flow. We will further develop a simulation method of crystal growth of $In_xGa_{1-x}As$ by the TLZ method so that the phase change between solid and liquid is treated more exactly. The methods for revealing polycrystallization mechanism are further developed and we collect data on the mechanism using terrestrially grown crystals in advance to space experiments.

6.1 Space Experiments

1) Preparation of a feed

The feed used in this method has indium concentration gradient (the In

concentration is high at the seed side and gradually decreases towards the end of the feed). This concentration gradient is useful to form a narrow liquidus-zone at low temperature gradient. The feed was prepared by the directional solidification of a melt with nominal composition of $In_{0.3}Ga_{0.7}As$ solidified at sample translation rates between 0.5 and 1.0 mm/h at temperature gradients between 20 and 40°C/cm [15]. The In/Ga compositional profile along the axis was similar to those obtained by the normal freezing of the melt. We prepare several kinds of feed with different compositional profile by controlling nominal composition of the starting materials and by controlling the whole length of the ingot.

The prepared ingot was inversely inserted into a crucible so that the first part to freeze part becomes the end of the feed. When the feed with such In concentration gradient is heated at a low temperature gradient, only part of the feed with high In content where its liquidus temperature is lower than the rest is melted. Since the compositional profile of a feed is important for obtaining homogeneous crystals and for seeding, we developed a nondestructive method for measuring compositional profile by using Raman scattering [18, 19].

2) Preparation of a seed

Multi-component zone melting method [20] is applied to prepare seed crystals. Diameter of a seed should be equal to that of the feed for homogeneous crystal growth because mass balance is important for growing homogeneous crystals by the TLZ method. Therefore, conical part used in many crystal growth methods should be avoided. We are going to grow crystals with 20 mm diameter in microgravity. However, growth of such large diameter homogeneous single crystals is very difficult on the ground. We have developed the multi-component zone melting method using a GaAs seed. Now we are successful in growing 5 mm long homogeneous single crystals with 15 mm diameter [20]. We will further develop the method and we will prepare seeds with 5 mm homogeneous single crystal part with composition of $In_{0.3}Ga_{0.7}As$ and diameter of 20 mm by the flight experiment. Seed orientation is <111>.

3) Cartridge design

i) Configuration

By integrating the required wall thickness of the cartridge into the suitable cartridge configuration, we designed the flight cartridge as shown in Fig.10. This cartridge satisfies the safety requirements to be described later and is suitable for single crystal growth in microgravity. The cartridge is made from tantalum or WC-103 alloy (standard material of one of niobium alloys). A quartz ampoule is installed in the cartridge. Inside the ampoule, a crucible and a heat sink are sealed in vacuum at about 1×10^{-4} Pa. A seed spliced with a feed is put into a crucible together with a plunger. The plunger is powered by a carbon spring for eliminating free melt surface areas when the feed is melted. This is done for avoiding Marangoni convection. Diameter of both seed and feed is 20 mm and the total length is 100 mm.

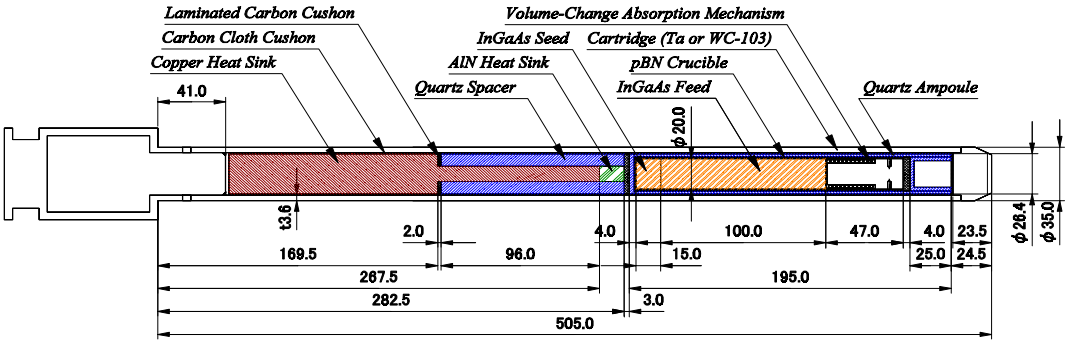

Figure 10. Cross sectional view of a cartridge (dimensions in mm).

ii) Interface curvature control

Flat solid-liquid interface is important for single crystal growth as well as homogeneous crystal growth. To obtain the convex shape, it is required to control heat flow. We use a heat sink adjacent to the quartz ampoule. We have developed a numerical code based on the boundary fitted coordinate method to investigate a cartridge configuration being suitable for the convex shape. The code can solve simultaneously the governing equations of energy transport, mass transport, stream function and vorticity transport in a cylindrical coordinates. The shape is determined by balancing heat and mass fluxes across the interface and by considering a phase diagram. Finally we obtained a suitable configuration. Figure 11 shows a typical result of the interface shape in the TLZ method under 10^{-4} G. The shape is convex and the degree of the convexity is about 0.4 mm. This convexity is enough to prevent polycrystallization caused by nucleation near a crucible wall. In addition, we consider that the curvature of the interface should be small in the TLZ method. The convexity agrees with this requirement.

iii) Safety design

An $In_{1-x}Ga_xAs$ sample must be confined in a triplex container. The gradient heating furnace (GHF) and its standard cartridge are originally designed to work as a container. We have to design a cartridge so that the confinement is proved. Arsenic vapor pressure is high above the melting temperature in the InAs-GaAs system. In addition, arsenic is a toxic material and the maximum allowable concentration for spacecrafts is very low. Total weight of arsenic for one sample is about 50 g and this exceeds the maximum allowable limit. Therefore, great care should be paid so that arsenic is confined in the cartridge. In order to investigate wall thickness of the cartridge, we estimated the vapor pressure and measured consumption by both $In_{1-x}Ga_xAs$ vapor and melt in the cases of Ta and WC-103. We obtained the required thickness to prevent destruction caused by elastic expansion and creep rupture and added the consumption to the thickness. Finally obtained thickness is 3.3 mm at 1500 °C both in the case of Ta and in the case of WC-103.

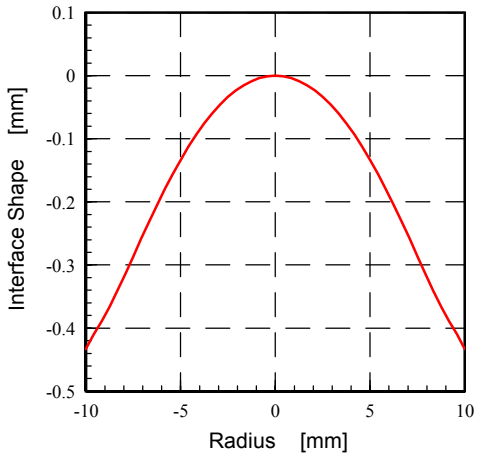

Figure 11. Typical example of interface shape (calculated).

4) Crystal growth

i) Growth procedures

A seed crystal is fusion spliced with a feed by heating the butted position at 1000 °C for 1 h in a sealed quartz ampoule. It is then inserted into a crucible together with a plunger and both of them are sealed in a quartz ampoule at about 1×10^{-4} Pa. They are put into a cartridge and are heated to about 1000～1100 °C so that the temperature gradient in the crucible becomes 20 °C /cm by using the GHF with a 100 °C /h heating rate. The temperature of the spliced part between the seed and the feed is set at 1025 °C so that the grown crystal composition is $In_{0.3}Ga_{0.7}As$. After 1 h soaking, the cartridge is translated and a crystal is grown. Translation speeds are changed for three of the samples as described in the section of growth parameters.

ii) Growth parameters

We will grow four crystals at four different growth conditions. Temperature gradient in the furnace is fixed at the value between 10 and 20 °C/cm. The most appropriate temperature gradient for growing single crystals will be determined by further terrestrial experiments. Growth rate and zone width are changed. Growth rates are controlled by the cartridge translation rate. Zone width is controlled by the solute concentration profile in feeds. Growth conditions are as follows: (1) zone width = 20 mm and constant sample translation rate 0.4 mm/h, (2) zone width = 40 mm and constant sample translation rate 0.4 mm/h, (3) zone width = 10 mm and sample translation rate is varied from 0.4 mm/h to 4 mm/h for 1 h after a 100 h growth, (4) zone width = 40 mm and sample translation rate is varied from 0.4 mm/h to 4 mm/h for 1 h after a 100 h growth.

iii) Estimation of required crew time for the operation of this experiment

Since the GHF furnace has automatic sample exchange device, no crew time is needed for sample exchange. The growth conditions are memorized in the memory of the GHF furnace in advance, the only required operations for crews are to choose correct program for each experiment and to put on the start button and an interval

inspection of the safety of the cartridge. The required crew time for each experiment is estimated to be less than 20 min, and such short duration may not give much trouble to crews in the space station.

6.2 Terrestrial Experiments

1) Determination of appropriate temperature gradient for single crystal growth

As described in the section of hypothesis, temperature gradient controls mass transport rate in the liquidus zone. Therefore, temperature gradient is the most important parameter in the TLZ crystal growth method. We will determine the most appropriate value carefully. For this purpose, we make more experiments by changing temperature gradient.

2) Measurements of temperature distributions

For obtaining data on boundary conditions upon simulation, we will measure axial and radial temperature distributions in the sample as well as in the furnace accurately.

3) Analysis of polycrystallization mechanism

The methods for revealing polycrystallization mechanism are further developed and we collect data on the mechanism using terrestrially grown crystals prior to space experiments. The position at which polycrystallization occurs is detected and the relation between polycrystallization and degree of supercooling is investigated in combination with various characterization methods and results of fluid flow analyses.

6.3 Simulation

We will further develop a simulation method of crystal growth of $In_xGa_{1-x}As$ by the TLZ method so that the phase change between solid and liquid is treated more exactly. We analyze fluid flow for various growth conditions in microgravity as well as on the ground. Convective flow velocity, temperature and concentration profiles, and distribution of degree of supercooling in a liquidus-zone are calculated for each experiment performed on the ground and in space. These parameters are used for the evaluation of grown crystals and for investigating mechanism of homogeneous crystal growth by the TLZ method as well as for investigating mechanism of polycrystallization.

7. Data Analysis

1) Characterization method

i) Composition

We have developed nondestructive optical techniques to characterize both polycrystalline feeds for the TLZ method as well as crystals grown in space. In mixed crystals such as $In_{1-x}Ga_xAs$, both electronic band structure and phonon structure are modified by the compositional ratio of x. Therefore, we can evaluate the composition by measuring electronic band gaps or phonon energies with their calibrated compositional-dependences. By using a micro-Raman scattering (MR) technique, we have successfully measured two-mode phonons; that is, TO-like and LO-like phonons in polycrystalline $In_{1-x}Ga_xAs$ feed and evaluated the composition from their Raman peaks

in a good accuracy by calibrating with precise chemical analysis made separately in the whole range of x [18, 19]. The MR technique is very powerful for us, because we can evaluate the composition of as-grinded samples with rough surfaces and therefore we have a strong possibility that we will be able to characterize crystals to be grown in space without any surface treatment. Crystal orientation and crystallinity can also be characterized from Raman selection rule and Raman line shape.

After nondestructive measurements, crystals are cut and used for compositional analyses as well as optical microscopic observation. Radial and axial distributions of In, Ga and As are measured by using electron probe microanalysis (EPMA) for evaluating crystal homogeneity. Quantitative analyses are performed by using GaAs and InAs as standard samples. The probe beam size is about 10 μm and the accuracy is within ± 0.01 in mole fraction of InAs and GaAs. In addition, we use a scanning photoluminescence (SPL) technique to make two-dimensional mapping of composition in crystals grown in space as well as in seed crystals grown on the ground. Although SPL needs optical flat surface, it is already established and widely used to characterize III-V compound materials [21]. By measuring photoluminescence spectra due to band-to-band transition, we can easily evaluate the composition with well-known composition dependence of fundamental energy gap.

ii) Crystallinity

After nondestructive measurement of compositional profile by using Raman scattering, grown crystals are cut parallel to the growth axis by using a wire saw. Surface are polished flat and chemically etched for the microscopic observation of dislocation density and twin boundary (if exists). KOH etchant is used for revealing etch pits.

In order to characterize crystallinity, we use IR transmittance and birefringence measurements with a scanning infrared polariscope (SIRP), which we have developed to characterize residual strains in III-V compound materials [21, 22]. IR transmittance measurement gives us special information on homogeneity of crystals while birefringence measurement gives us residual strain distribution in crystals. It was successfully used to characterize GaAs crystals [23].

iii) Electrical properties

Carrier concentration, mobility, and type of conduction are measured by Van der Pauw method. Relation between electrical properties and growth conditions is analyzed.

2) Aims for data analyses

i) Compositional profile vs. sample translation rate change

Compositional profile is one of the most important measures for our TLZ growth model. As shown in Fig. 2, compositional profile is dependent on the sample translation rate. If the equation 3 holds, sample translation rate for producing homogeneous composition should be uniquely determined irrespective of the zone width. By the four experiments under the different zone width, above assumptions are checked by analyzing compositional profiles. Compositional variation induced by

pulsed sample translation rate change will give further insights into the allowable limit of liquidus-zone width.

ii) Crystallinity vs. growth rate and liquidus-zone width

As shown in equation 6, degree of supercooling is dependent on growth rate and zone width. We can obtain information on maximum allowable limit of supercooling by the inspection of single crystallinity. If polycrystallization is detected, supercooling has exceeded allowable level.

iii) Electrical properties vs. growth rate

Electrical properties depend on point defects in crystals. We are afraid that constitutional supercooling increases point defects in crystals and deteriorates electrical properties. Such assumption will be checked by measuring electrical properties of crystals grown at various growth rates and by comparing space grown crystals with terrestrially grown crystals.

8. Expected Results and Potential to the Future

1) Deep understanding on the mechanism of the TLZ method will establish modeling of the TLZ growth method.
2) Single crystals with homogeneous $In_{0.3}Ga_{0.7}As$ composition and theoretically predicted length will be grown in microgravity and the space-grown crystals serve as benchmark crystals for the terrestrial growth. Methods and techniques for suppressing convection below the tolerable limit in the terrestrial growth will be developed for obtaining benchmark quality crystals.

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