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Effects of microgravity environment on growth related properties of semiconductor alloys (InGaAs)−Growth of homogeneous crystals−

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Contents

Preface

The homogeneous compound semiconductor crystal growth team was established in 1997 in the Space Utilization Research Program (SURP) in NASDA for performing team research in collaboration with researchers outside NASDA to perform systematic research for demonstrating the potential of microgravity utilization by producing benchmark results and promote microgravity utilization in future. After NASDA was combined with the National Aerospace Laboratory of Japan (NAL) and the Institute of Space Astronautical Science (ISAS), and was merged into the Japan Aerospace Exploration Agency (JAXA) on Oct. 1, 2003, the research was carried out in the ISS Science Project office in JAXA.

For growing compositionally homogeneous alloy crystals, mass balance between segregation and transportation at the growth interface is required, that is, just the same amount of rejected solute by segregation should be transported away from the interface. However, direct control of the transport rate is impossible and this uncontrollability makes compositionally homogeneous crystal growth extremely difficult.

The most popular method for growing homogeneous crystals that has been used so far is the growth in the diffusion limited steady state, but the solute transport rate in this method is determined indirectly through the solute concentration profile that depends on inter-diffusion rate between the solute and the solvent, and the rate also depends on the crystal growth rate. Besides, convection in a melt makes the establishment of the steady-state concentration impossible by the mixing of the melt. Therefore, many microgravity experiments were performed in order to suppress convection in a fluid. However, very little satisfactory results have been obtained. The reason may be due to insufficient considerations to the effects of residual acceleration and g-jitter on the melt behavior, which could have prevented the purely diffusion-controlled mass and heat transport during crystal growth. An example is $Pb_{1-x}Sn_xTe$ crystal growth experiment in the FMPT mission. The compositional profile was not uniform and suggested partial mixing of a melt during crystal growth. This result agreed well with the computer simulation on fluid flow in the melt; residual acceleration on the order of 10^{-4}g causes convective flow whose velocity exceeds PbTe-SnTe inter-diffusion rate.

Objectives of this research are, therefore, to invent a new method for growing compositionally homogeneous alloy crystals that can control the mass transport rate at the growth interface directly and can avoid the effects of residual acceleration and g-jitter on the crystal growth from a melt and to apply the new method to the growth of alloy crystals such as $In_{0.3}Ga_{0.7}As$ and to verify the feasibility of the new method. $In_{0.3}Ga_{0.7}As$ is promising as a substrate for laser diodes for 1.3 mm wavelength but its large homogeneous single crystals have never been obtained on the ground.

Based on the study of the graded solute concentration method for compensating the effects of residual acceleration and introduction of the partial melting method, we have invented a novel crystal growth method named "the Traveling Liquidus-Zone Method (abbreviated as the TLZ method)". In the TLZ method, we have succeeded in controlling the solute transport rate directly for the first time in the history of alloy crystal growth by the sophisticated utilization of the liquidus in the equilibrium phase diagram. Namely, by utilizing the fact that saturated concentration of the

solute is uniquely determined only by the temperature, then the concentration gradient in the saturated liquidus-zone is controlled by the temperature gradient. As a result, we have succeeded in growing long homogeneous $In_{0.3}Ga_{0.7}As$ crystals.

We developed a one-dimensional model for the TLZ growth and proposed microgravity experiments in 2001 in order to verify our TLZ growth model by the crystal growth in the convection suppressed conditions. The proposed theme to the 1st International Announcement of Opportunity (IAO) for microgravity science research "Growth of Homogeneous $In_{0.3}Ga_{0.7}As$ Single Crystals in Microgravity" has been selected as one of candidates for the ISS experiments by the microgravity science committee of Japan after international peer review in Jan. 2002. In the 2003 fiscal year, although organization reform was done, we have further developed the TLZ method experimentally and theoretically and have applied the method to the growth of $Si_{0.5}Ge_{0.5}$ crystals. We were successful to obtain funds from NEDO (New Energy and Industrial Technology Development Organization) for fabricating substrates for laser diode used in the optical communication system and started growth of plate like $In_{0.3}Ga_{0.7}As$ crystals. Plate crystals can be grown in convection suppressed conditions during crystal growth in a melt because convection in a melt sandwiched by two crucible surfaces located closely is difficult to occur even on the ground and surface areas for substrate use can be obtained.

In this paper, we report results of our activities in the 2003 fiscal year.

Semiconductor Team

Brief Summary of Results

(1) Growth of Homogeneous $Si_{0.5}Ge_{0.5}$ Single Crystals by the Traveling Liquidus Zone Method

As an application of the traveling liquidus-zone (TLZ) method, we tried to grow $Si_{0.5}Ge_{0.5}$ homogeneous crystals since the Si-Ge system has similar feature as the InAs-GaAs system : liquidus and solidus are widely apart each other and homogeneous bulk crystal growth is extremely difficult on the ground. We grew 2 mm diameter crystals as is the case of $In_{0.3}Ga_{0.7}As$ because convection in a melt is suppressed in 2 mm diameter melt even on the ground in the InAs-GaAs system. In the TLZ method, diffusion coefficients play an important role for establishing compositional homogeneity because mass is transported only by diffusion when convective mixing is prohibited. However there is no accurate data concerning the diffusion coefficients of the Si-Ge system. Therefore, we first used the simulated diffusion coefficient of $D = 1.7\times10^{-4}cm^2/s$ obtained by the first principle and calculated the sample translation rate using the one-dimensional TLZ model that we have modeled out, then we adjusted the sample translation rate based on compositional profiles of grown crystals. As a result, a homogeneous $Si_{0.5}Ge_{0.5}$ bulk single crystal was grown (Fig. 1). Germanium concentration of the grown crystal was in the range of 0.50 ± 0.016. Detailed results are described in the section of detailed results in this period.

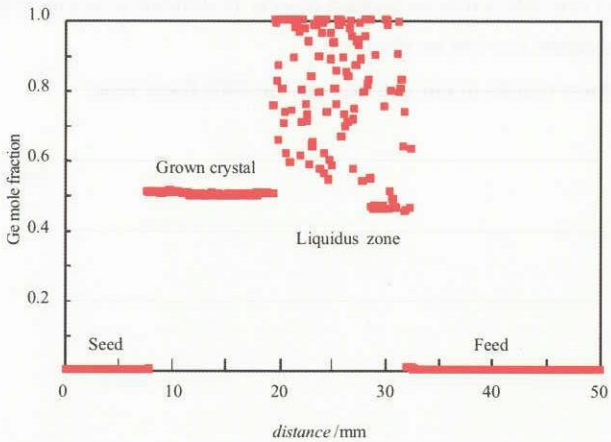


Fig. 1 Ge concentration profile grown by the TLZ method at appropriate sample translation rate.

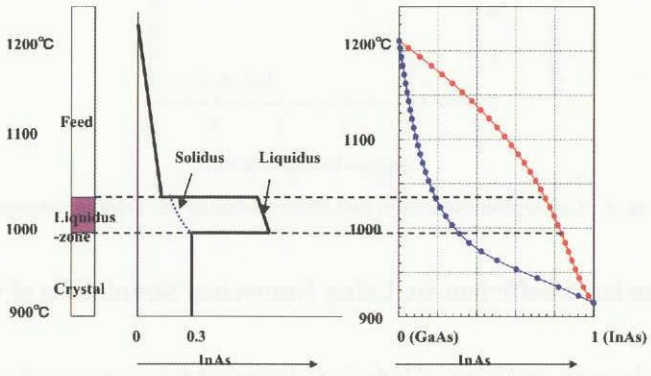
(2) $In_{0.3}Ga_{0.7}As$ Plate Crystals Grown by the Traveling Liquidus-Zone (TLZ) Method

As another application of the TLZ method, we tried to grow plate crystals of $In_{0.3}Ga_{0.7}As$. As previously shown, when the convection in a melt is suppressed in the TLZ method, the extreme compositional homogeneity is possible. However, the suppression of convection requires small melt diameter and it has already been shown that the maximum crystal diameter for obtaining compositional homogeneity on the ground is about 2 mm. This result is experimentally obtained but numerical analysis of convective flow velocity as a function of crystal diameter also shows the similar results. However, such small diameter crystals cannot be used for device application. Then, we tried plate crystal growth for obtaining large surface area since the limitation of the thickness in plate crystal is useful for suppressing convection in a melt. $In_{0.3}Ga_{0.7}As$ plate crystals with 10 mm width and 2 mm thickness showed good compositional homogeneity as expected when a sample device was translated according to the model equation as,

$$V = -\frac{D}{C_{L0} - C_{S0}}\left(\frac{\partial C}{\partial T}\right)\left(\frac{\partial T}{\partial z}\right)_{z=0} \qquad \text{(eq. 1)},$$

where D is InAs-GaAs interdiffusion coefficient, C_{L0} and C_{S0} are solute concentrations in a liquid and in a solid at the freezing interface, respectively. "C/"T is reciprocal of the slope of the liquidus and "T/"z is temperature gradient.

The grown crystals were poly crystals. Single crystallization of plate crystals is required for device fabrication and we analyzed factors causing poly crystallization and we concluded that the greatest problem is lack of good $In_{0.3}Ga_{0.7}As$ seeds.



(a) Principle of the TLZ method (b) InAs_GaAs system

Fig. 2 Principle of the TLZ method.

(3) Numerical Investigation on Two-dimensionality in the Traveling Liquid.3us-Zone Method

The raveling liquidus-zone (TLZ) method is one of the most sophisticated growth techniques to obtain a homogeneous crystal of a ternary compound semiconductor such as $In_{1-x}Ga_xAs$ crystals as described above. However, growth of large diameter homogeneous single crystals gets difficult : the maximum diameter is limited to about 2 mm on the ground. One of great factor of polycrystallization is convection in a melt because convection increases as the melt diameter increases. Another factor is two-dimensional heat distribution in large diameter crystals. Therefore, we numerically investigated the effect of two-dimensionality in the TLZ growth. First, we introduced a two-dimensional TLZ model and defined the two-dimensionality. Then, we calculated the two-dimensionality as a function of sample diameter and as a function of gravity level. The calculated two-dimensionality is shown in Fig. 3. In the case of the sample diameter of 2 mm, the two-dimensionality is about 4% at its maximum on the ground. This is small enough and does not hinder to grow a homogeneous crystal. On the other hand, in both the 5 mm and the 10 mm cases, the two-dimensionality is about 16% and 33% at the maximum, respectively. Compositional homogeneity is deteriorated at such high two-dimensionality and causes polycrystallization. Therefore, we have to find out a good way to reduce the two-dimensionality in larger diameter crystalas. The simulation also showed that one way to avoid high two-dimensionality is the use of a seed with high thermal conductivity and microgravity is not useful to reduce two-dimensionality.

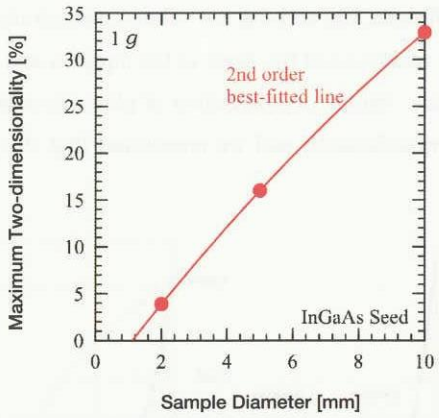


Fig. 3 Calculated maximum two-dimensionality vs. sample diameter.

(4) Estimation of Diffusion Coefficient by Using Numerical Simulation of the Traveling Liquidus-Zone Method

We estimated an interdiffusion coefficient of InAs-GaAs by comparing a numerically obtained InAs concentration profile with the experimentally obtained one because the concentration profile is determined by diffusion rate in the TLZ method if convection in a melt is suppressed. In the diffusion coefficient estimation, it is also required that the phase diagram of the InAs-GaAs system and temperature profile in a melt are known. In a two-dimensional numerical simulation, the energy transport equation, the mass transport equation, the energy balance equation and the mass balance equation are simultaneously solved. We apply this simulation to a sample with 2 mm in diameter. In the 2 mm sample, it has been already clarified that the convection effects on mass and thermal transports are negligibly small. Therefore, 2 mm sample is suitable for both the experimental estimation of the diffusion coefficient and the calculation time reduction. We calculated concentration profiles for several diffusion coefficients. Among them, the diffusion coefficient of 1.1×10^{-4}cm^2/s gives best fitted results including the growth length as shown in Fig. 4. Therefore, the diffusion coefficient of $In_{0.83}Ga_{0.17}As$ melt is estimated to be 1.1×10^{-4}cm^2/s at 1293 K.

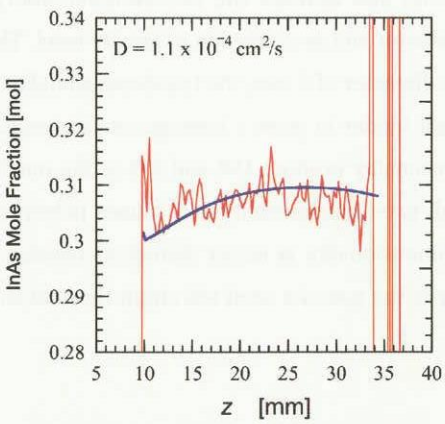


Fig. 4 Comparison of a simulated concentration profile (blue solid line) with an experimentally obtained one (red solid line) in the case of D = 1.1×10^{-4}cm^2/s.

Detailed Results of This Period

Growth of Homogeneous $Si_{0.5}Ge_{0.5}$ Single Crystals by the Traveling Liquidus-Zone Method

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Abstract

We have challenged the $Si_{0.5}Ge_{0.5}$ bulk crystals growth. Si-Ge homogeneous single crystals are difficult to grow so far. In the present research, we have applied the Traveling Liquidus-Zone method (TLZ method) which was invented in our group as a new crystal growth method to the growth of Si-Ge. The diameter of grown crystal was 2mm and the length was 15mm. Crystals were well seeded and had the orientation of silicon seeds in spite of the large lattice mismatch. The compositional variation of the crystals was very small and the composition was in the mole fraction range of 0.5 ± 0.016 in germanium. The lattice constant determined by the X-ray powder diffraction was 55.38nm.

1. Introduction

A large number of studies on SiGe have been done energetically because SiGe thin film[1-4] is expected higher speed[5-7], lower noise[8] and lower electric power consumption compared with the existing device of Si series.

However, few investigations on the bulk crystal growth of SiGe have been done because the growth of homogeneous crystals was very difficult by the existing techniques[9, 10].

In this study, we tried to grow homogeneous $Si_{0.5}Ge_{0.5}$ crystals by the TLZ method, and evaluated the quality of grown crystals.

2. Traveling Liquidus-Zone method

We explain here the TLZ method briefly by using our previous experimental results in the InGaAs system.

InAs and GaAs bulk crystals, which are sealed in vacuum in a qualtz ampoule, are set in an electrical furnace having a temperature gradient so as to form the liquidus-zone between GaAs seed and feed as shown in Fig. 1.

By the interdiffusion in the liquidus-zone, spontaneous growth takes place at the interface between the seed crystal and liquidus-zone. According to our one-dimensional model, this spontaneous growth rate V is described by the following equation[11, 12] provided that diffusion-limited mass transport is realized in the liquidus-zone.

$$V = -\frac{D}{C_{L0} - C_{S0}} \left(\frac{\partial C}{\partial T}\right)\left(\frac{\partial T}{\partial z}\right)_{z=0} \qquad (1)$$

where D is InAs-GaAs interdiffusion coefficient, C_{L0} and C_{S0} are solute concentrations in a liquid and in a solid at the freezing interface, respectively. $\partial C/\partial T$ is reciprocal of the slope of the liquidus and $\partial T/\partial z$ is temperature gradient.

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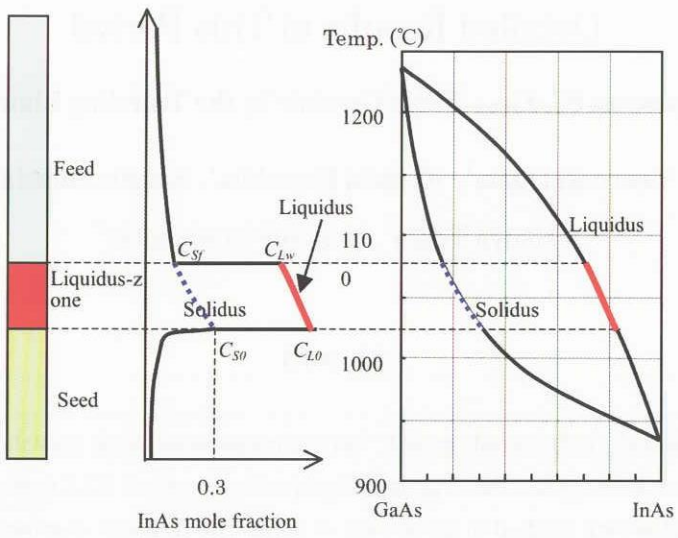

Fig. 1 The relationship among the sample configuration, solute concentration profile in the TLZ method and the phase diagram of the InAs-GaAs system.

In the spontaneous growth, the interface shifts gradually to the hotter side. As a result, the concentration of InAs at the interface is decreased.

In the TLZ method, the sample device is translated toward the colder side in harmonizing with the spontaneous

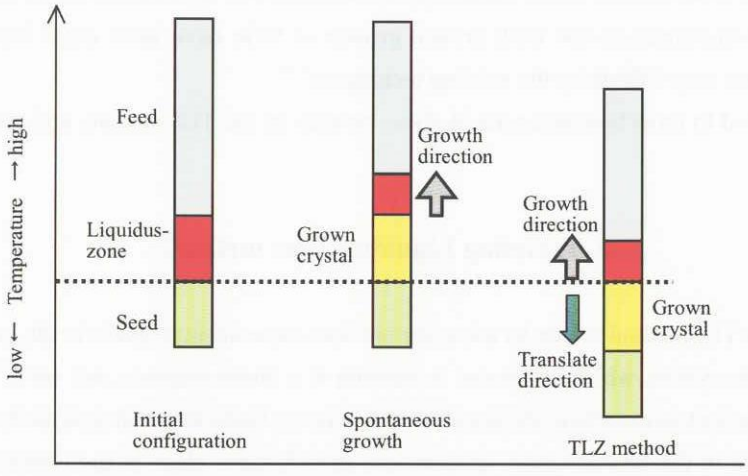

Fig. 2 Principle of realizing homogeneous concentration by the TLZ method.

growth rate, resulting in homogeneous concentration[13] (Fig. 2).

3. Procedure for growing homogenious $Si_{0.5}Ge_{0.5}$ crystals

The Si-Ge phase diagram is reported[14]. Therefore, we can determine C_{L0}, C_{S0} and $\partial C/\partial T$ easily from the diagram (Fig. 3). The respective value is 0.83 for C_{L0}, 0.50 for C_{S0} and 1.48×10^{-3}/ K for $\partial C/\partial T$. Concerning $\partial T/\partial Z$, 10℃/cm which was used for the growth of InGaAs is applied because the growth of $Si_{0.5}Ge_{0.5}$ is carried out under

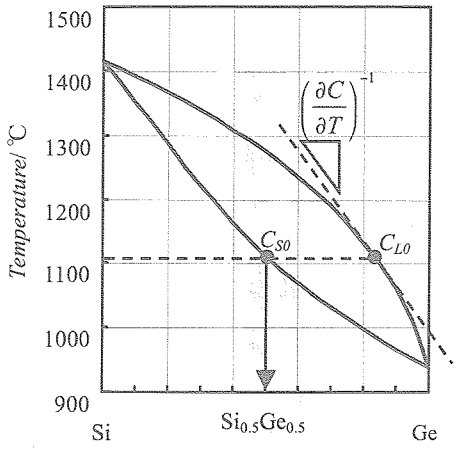

Fig. 3 Phase diagram of the SiGe system[14].

the same furnace conditions as those for the InGaAs growth.

However, it is difficult to determine a precise V from the one-dimensional model under the conditions in which the interdiffusion coefficient is unknown. Then we tried to determine the V for homogeneous composition by the following steps :

1) With using the calculated interdiffusion coefficient $D=1.7\times10^{-4}$cm^2/s by the first principle[15], $V=0.27$mm/h was lead as a first approximation. Then the crystal growth test was carried out. For grown crystal, compositional variation is mesured by an electron probe micro-analyzer (EPMA).

   Still the value of interdiffusion coefficient in this case was the average of several values of Si and Ge calculated at around the melting point.

2) If germanium composition is decreased as the crystal growth proceeds, it means that sample translation rate is too slow. Then the sample translation is set faster in the following growth experiment. Conversely, if the germanium composition is increased, sample translation rate is set slower than the previous experiment.

   Such regulations in translation rate are repeated until homogeneous composition is achieved, and the most proper rate is determined.

4. Experiments

① Growth of SiGe crystal

The setup of growth configuration is schematically given in Figure 4. As shown in the figure, a silicon seed of 2mm in diameter and 10mm in length, a germanium rod of 2mm in diameter and 20mm in length and a silicon feed of 2mm in diameter and 50 mm in length are loaded in a BN crucible sequentially, and are sealed in vacuum in a qualtz ampoule. The reason for using such slender seed and feed is to reduce the influence of thermal convection in a melt. On the outside of the ampoule, six thermocouples were placed at fixed intervals. One of them was placed at the position of the interface between the silicon seed and the germanium rod. The temperature of the interface was kept at 1098℃ in order to obtain homogeneous composition of $Si_{0.5}Ge_{0.5}$. The sample translation was done in accordance with the procedures described in the section 3.

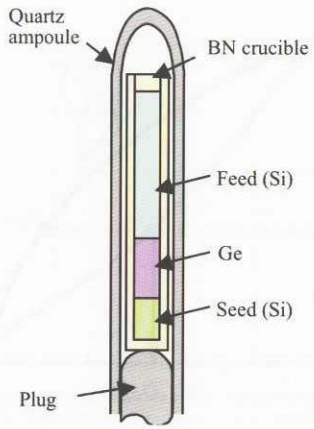

Fig. 4 Schematic diagram of a sample device.

② **Analysis of composition**

After growth experiment, grown crystals were polished on the buff with diamond partticles of about 3 μm, and subsequently mirror polished with alumina particles of about 1 μm. Compositional analyses were carried out by EPMA at 100 μm intervals along the axis of growth direction.

③ **Characterization of grown crystals**

Crystallinity especially poly crystallized or monocrystallized structure, together with seeded state in the vicinity of the interface between the seed and the grown crystal were examined by the back reflection Laue camera. For grown crystals, their lattice parameters were also examined by the X-ray powder diffraction method.

5. Results and Discussion

① **Composition of grown SiGe crystals**

EPMA analyses made clear that germanium concentration decreased slightly with growth in the crystal grown at the sample translation rate of 0.27mm/h based on the first principle. On the contrary, the concentration increased gradually in the crystal obtained at 0.39mm/h. These results mean that the rate is slower in the former case and it is faster in the latter as compared with an appropriate rate. After fine regulations on the rate, it was found that an expected homogeneous crystal could be obtained at 0.29mm/h.

Figure 5 shows details of the experimental results mentioned above. The vertical axis corresponds to the variation of germanium concentration from the initial one in the growth direction. Germanium concentration of the crystal grown at 0.29mm/h is in the range of 0.50 ± 0.016 (Fig. 6). Therefore, the variation of composition is very small through the entire grown crystal.

Considering the proximity of this experimental result, that the proper translation rate was 0.29mm/h, to the calculated rate 0.27mm/h, the interdiffusion coefficient based on the first principle is approximately equal to its true value.

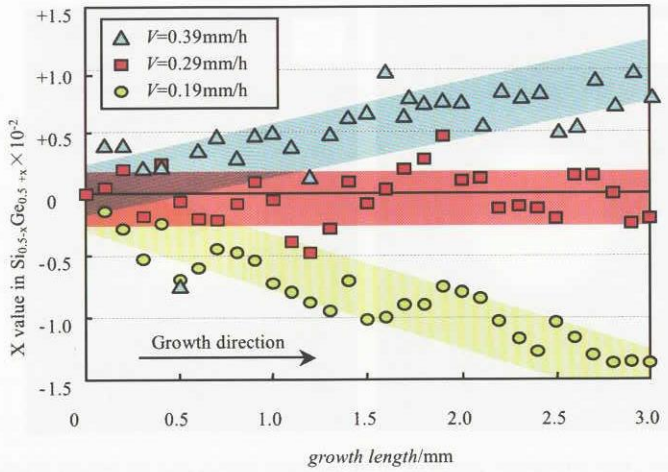

Fig. 5 Compositional profiles of SiGe crystals grown at various sample translating rates.

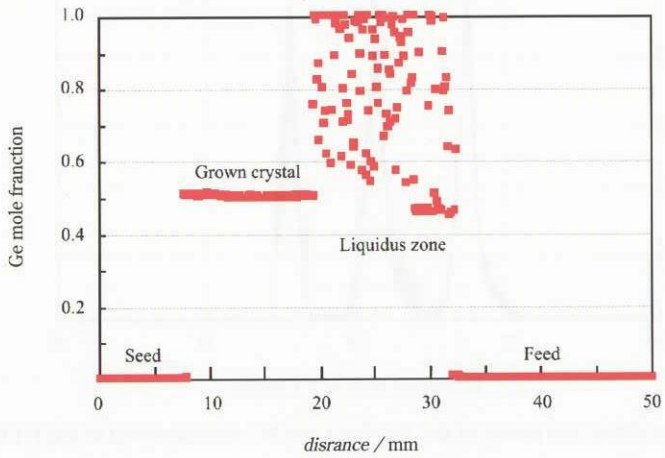

Fig. 6 Ge concentration profile in SiGe crystal grown by the TLZ method at the optimal sample translation rate.

② Crystallinity of grown SiGe crystals

The back reflection Laue patterns obtained in the seed and grown crystal regions are shown in Fig. 7. It becomes clear, from the figure, that these patterns are similar each other and excellent seeding is achieved in spite of the large compositional difference between the seed and the grown crystal. The reason why Laue spots of the grown crystal are unclear compared with those of seed is explained by relative inferiority of crystalline state. These results considerably differ from those of the InGaAs system, in which only poly crystals were grown from a GaAs seed. Further investigations on the seeding of the SiGe system will be needed in order to overcome difficulties in the seeding of the InGaAs system. Figure 8 shows diffraction peaks of Ge, $Si_{0.5}Ge_{0.5}$ and Si corresponding to the (111) reflection. The lattice constant of $Si_{0.5}Ge_{0.5}$ is 55.38nm, which agreed with the value determined by the Vegard's law, which is known as an experimental law for various alloys.

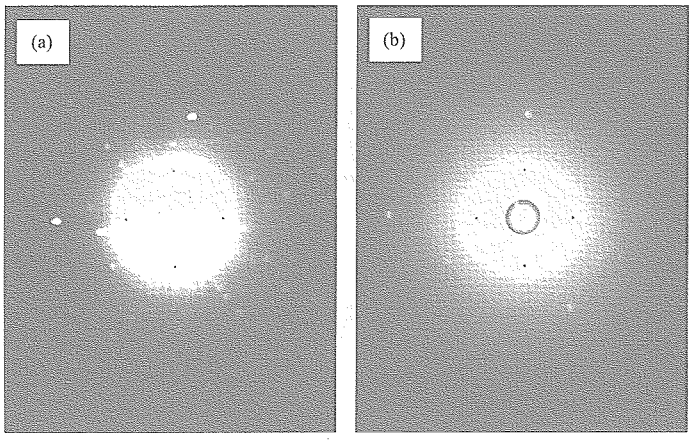

Fig.7 X-ray back Laue diffraction patterns of (a) Si-seed region and (b) grown crystal region.

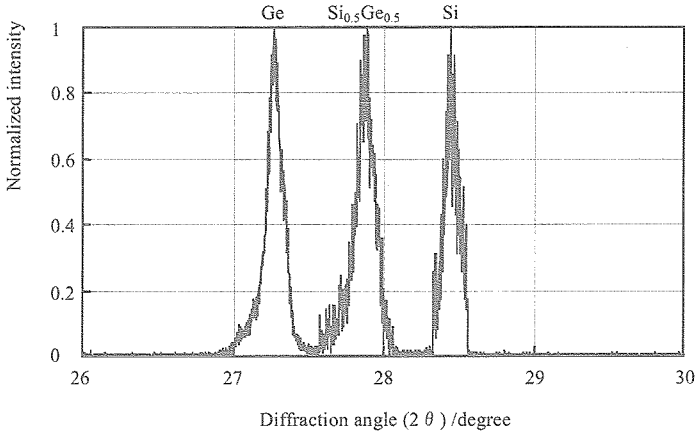

Fig. 8 X-ray powder diffraction peaks of Ge, $Si_{0.5}Ge_{0.5}$ and Si corresponding to the (111) reflection.

6. Conclusion

Growth of homogeneous $Si_{0.5}Ge_{0.5}$ single crystals by the TLZ method was tried and the following results were obtained.

1) Homogeneous $Si_{0.5}Ge_{0.5}$ bulk crystals of 2mm in diameter and 15mm in length were grown.
2) The compositional variation of the grown crystals was very small and ranged in 0.5 ± 0.016 in germanium mole fraction.
3) From diffraction patterns of back Laue camera, $Si_{0.5}Ge_{0.5}$ grown crystals took over the orientation of the Si seed crystal in spite of the large lattice mismatch.
4) From the results of X-ray powder diffraction, lattice constant of the $Si_{0.5}Ge_{0.5}$ grown crystal was 55.38nm.
5) Experimental results showed that the TLZ method was likely to be applicable to the Si-Ge system.

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$In_{0.3}Ga_{0.7}As$ Plate Crystals Grown by the Traveling Liquidus-Zone (TLZ) Method

Kyoichi Kinoshita[1)*], Yasuyuki Ogata[1)], Satoshi Adachi[1)], Naokiyo Koshikawa[2)], Tetsuya Tsuru[3)], Hiroaki Miyata[3)], Yuji Muramatsu[3)] and Shinichi Yoda[3)]

Abstract

The TLZ method is a new crystal growth method which we have invented for the growth of homogeneous mixed crystals. The influence of convection in a melt on the compositional homogeneity of TLZ-grown $In_xGa_{1-x}As$ crystals was investigated by the growth of various diameter crystals on the ground. The results have shown that excellent compositional homogeneity is realized even on the ground if the crystal diameter is less than 2 mm and convection in a melt is suppressed. However, such small diameter crystals cannot be used for device application. Then, we tried plate crystal growth for obtaining large surface area since the limitation of the thickness of plate crystal is useful for suppressing convection in a melt. $In_{0.3}Ga_{0.7}As$ plate crystals with 10 mm width and 2 mm thickness showed good compositional homogeneity as expected but the grown crystals were poly crystals. Single crystallization of plate crystals is required for device fabrication and we made effort for growing plate-like $In_{0.3}Ga_{0.7}As$ single crystals. Here, we report those results obtained in our study in the fiscal year of 2003.

Introduction

One of the popular methods for growing homogeneous mixed crystals is the directional solidification method in the diffusion limited regime and many investigators have tried this method in microgravity because convection in a melt is suppressed. However, very little successful results have been obtained.

Microgravity conditions less than 10^{-6} G are pointed out for growing homogeneous mixed crystals by the directional solidification method [1], but maintaining such microgravity conditions are very difficult due to various g-jitter in the space craft. Therefore, we have invented a new crystal growth method which requires less severe microgravity conditions for growing homogeneous mixed crystals and we named the new method the traveling liquidus-zone (TLZ) method [2-4].

We are now preparing for growth experiments of $In_{0.3}Ga_{0.7}As$ by the TLZ method aboard the International Space Station (ISS) in order to verify the superiority of the TLZ method and to verify our one-dimensional TLZ growth model for predicting homogeneous growth conditions. For maximization of the results of space experiments, we have studied TLZ growth conditions in detail on the ground and have revealed that excellent compositional homogeneity is obtained when convection in a melt is suppressed even on the ground.

One of the most effective methods for suppressing convection in a melt is to reduce the melt dimension. However, small diameter crystals cannot be used for device fabrication. Instead, plate crystals have an advantage of large area and dimension in the thickness is limited. If high quality plate crystals are grown, they can be used as

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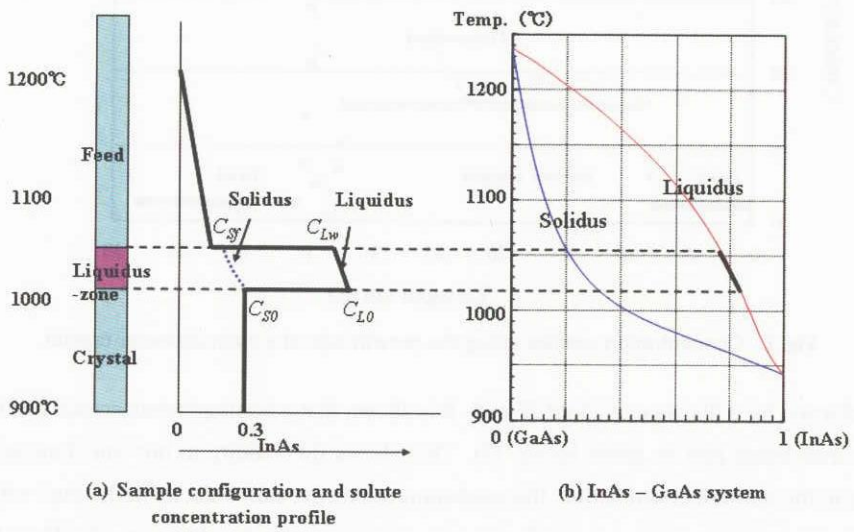
substrates for semiconductor laser diodes and the development of $In_{0.3}Ga_{0.7}As$ crystals will be accelerated. For this purpose, we tried plate crystal growth of $In_{0.3}Ga_{0.7}As$ on the ground. Here we report results of those trials performed for growing high quality $In_{0.3}Ga_{0.7}As$ single crystals including plate-like crystals in the fiscal year of 2003.

PRINCIPLE OF THE TLZ METHOD

Here, we briefly explain the principle of the TLZ method. Figure 1 explains sample configuration, solute (InAs) distribution in the sample, and its relation to the InAs-GaAs phase diagram in the TLZ method. The feature of the method is the formation of a saturated solution zone (liquidus-zone) under the temperature gradient. Such zone is formed by heating a feed having step or graded InAs concentration with excess InAs concentration in the seed side. The unique point of the TLZ method is the spontaneous growth without sample cooling : the freezing interface travels spontaneously towards the lower InAs concentration side (higher temperature side) due to interdiffusion between InAs and GaAs in the zone. At the freezing interface, InAs is supplied by segregation on solidification. Therefore, spontaneous growth continues under the imposed temperature gradient. The driving force in the TLZ method is thus interdiffusion and segregation.



(a) Sample configuration and solute concentration profile

(b) InAs – GaAs system

Fig. 1 Principle of the TLZ method.

When the sample device is translated in the opposite direction to the interface shift at the same rate of freezing, the interface is fixed at the same position relative to a furnace and the freezing temperature is kept constant. Then, the constant concentration of a growing crystal is achieved. Based on our one-dimensional model [3, 4], the spontaneous interface shift V is calculated as

$$V = -\frac{D}{C_{L0} - C_{S0}}\left(\frac{\partial C}{\partial T}\right)\left(\frac{\partial T}{\partial z}\right) \quad (1),$$

where D is the interdiffusion coefficient between InAs and GaAs, C_{L0} and C_{S0} are InAs concentration in a liquid and in a solid at the freezing interface, respectively. "$C/"T$ and "$T/"z$ are reciprocal of the slope of the liquidus and the temperature gradient at the freezing interface respectively and z is the distance measured from the freezing interface. The eq. (1) shows the importance of accurate temperature gradient measurements and we measured by knowing both

solidus compositions at the freezing interface and at the dissolving interface [4]. The obtained average temperature gradient in a melt is 10℃/cm plus or minas 1℃/cm for the present heating conditions and V is calculated to be 0.22 mm/h for "C/" T = 10℃/cm.

RESULTS AND DISCUSSION

(1) Crystal growth by using capillary tubes

Figure 2 shows the compositional profile along the growth axis for a terrestrially grown crystal at the sample translation rate of 0.22 mm/h using a 2 mm bore capillary tube.

Convection in a melt was suppressed by confining a melt in a capillary tube. Note that excellent compositional

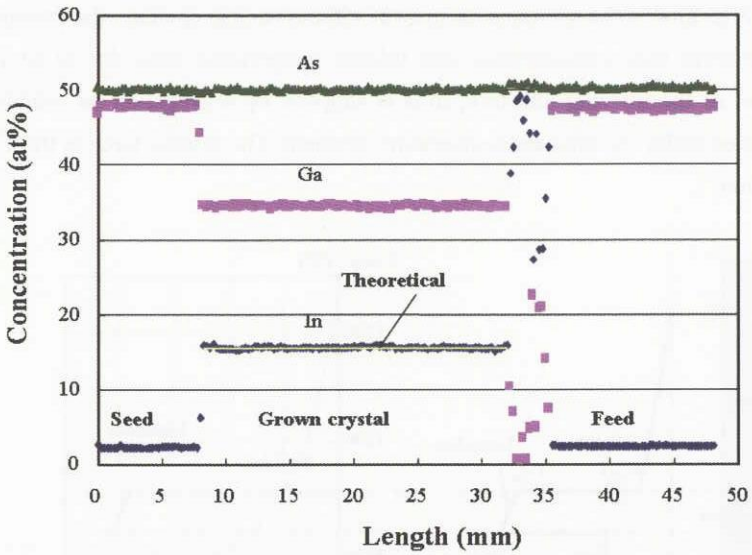


Fig. 2 Concentration profiles along the growth axis of a 2mm diameter crystal.

homogeneity is achieved for a distance of about 25 mm. It is shown that a homogeneous crystal has been grown at the predicted sample translation rate as given by eq. (1). This shows the validity of our one-dimensional TLZ growth model. According to the numerical simulation, the maximum convective flow velocity in the melt with dimensions of 2 mm in diameter by 15 mm in length is 1.4 mm/h at a temperature gradient of 10℃/cm [5]. Therefore, if convective flow velocity is suppressed below 1.4 mm/h, such excellent compositional homogeneity is obtained at just the start of the crystal growth and to the end of the growth by simply translating the sample device at the constant rate as predicted by eq. (1).

(2) Larger-diameter crystal growth

Since our TLZ growth model predicts precisely the sample translation rate for growing homogeneous crystals when convection in a melt is suppressed, larger-diameter crystals were grown in order to elucidate convection effect in a melt. Crystals of 5 or 10 mm in diameter were grown at the same conditions as those for 2 mm diameter crystals except for the crystal diameter. InAs axial concentration profiles along a center and along two surfaces of a 10 mm diameter crystal are shown in Fig. 3. Right and left peripheries in the figure are rotated by 180° in the cylindrical crystal. Compositional homoge-neity is worse than that of the 2 mm diameter crystal, especially in the radial direction : InAs concentration is highest at the center.

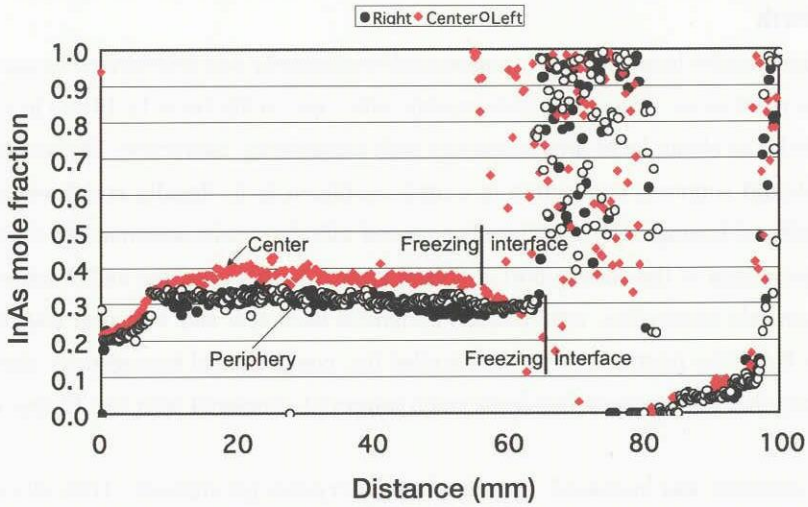


Fig. 3 InAs concentration profiles for a 10 mm diameter crystal.

The concentration inhomogeneity is more clearly shown in Fig. 4(a), in which cross sectional concentration distributions in both the axial and radial directions are depicted for In, Ga and As, respectively. Such concentration distribution is well understood when convection in the melt is considered. According to the numerical simulation [5], convective vortices occur at two interfaces due to thermo-solutal density difference as shown in Fig. 4(b). The InAs rich melt is transported to the center by the convective flow at the growth interface and InAs concentration at the center becomes higher than the periphery. Once the InAs rich part is formed, the InAs concentration becomes richer due to delay of freezing and accumulation of segregated InAs because InAs melting temperature is lower than that of GaAs. In the experiment, the sample was quenched and InAs concentration scattered part in Fig. 3 is the melt part during the crystal growth. Figure 3 also shows the freezing interface position as marked by bars and about 10 mm interfacial position difference is observed between the center and the periphery. Convection in the melt should be suppressed in order to obtain homogeneous mixed crystals by the TLZ method. According to the numerical simulation, the maximum convective flow velocity was calculated to be 3600 mm/h in the 10 mm diameter melt, about 2500 times as high as that in the 2 mm diameter melt.

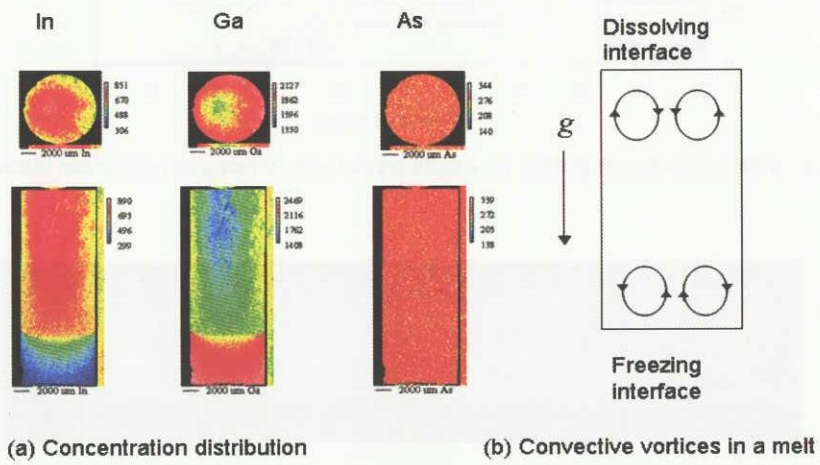


Fig. 4 In, Ga and As concentration mapping (a) and schematic drawing of convective vortices near the freezing and dissolving interfaces (b).

(3) Plate crystal growth

Substrates for devices require large area but compositional homogeneity was deteriorated by convection in larger diameter crystals as described above. Therefore, plate-crystals with 2 mm in thickness by 10 mm in width as shown in Fig. 5 were grown in order to obtain large area substrates with suppressing convection. Decreasing thickness of a rectangular crucible should suppress convection in a melt contained in it. Results are shown in Fig. 6. Much improvement in compositional homogeneity is achieved compared with the results shown in Fig. 3. Freezing interface was observed due to quenching of the sample during crystal growth in this case, too and the interface position is marked by a bar for each axis (center line, right and left peripheral lines near side surfaces) and the tie line shows that the interface is not flat. If the interface shape is controlled flat, compositional homogeneity should be improved more. However, it is true that homogeneity has been much improved compared with the 10 mm diameter crystal shown in Fig. 3.

When the crystal diameter was increased, growth of single crystals got difficult. Difficulty in single crystal growth was not exceptional for plate crystals because width has large dimension. Figure 7 is a polished surface photograph of the crystal of which InAs concentration profiles are shown in Fig. 6.

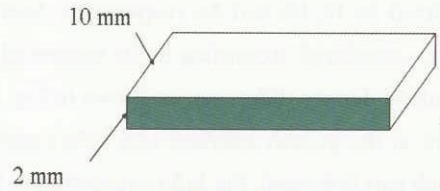


Fig. 5 Dimensions of plate crystals for substrate use.

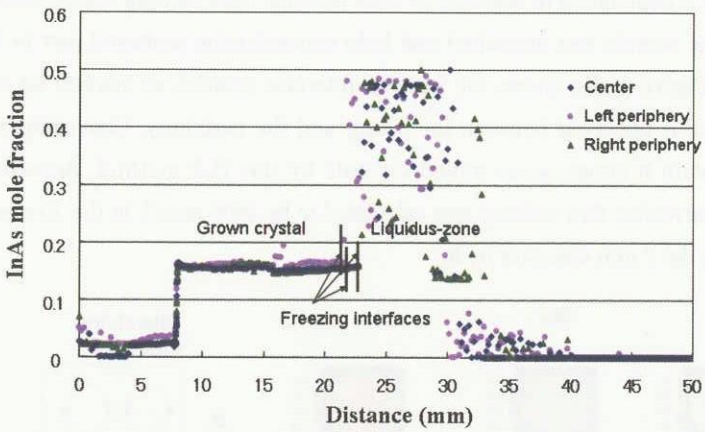


Fig. 6 InAs concentration profiles for a plate crystal with 10 mm width and 2 mm thickness.

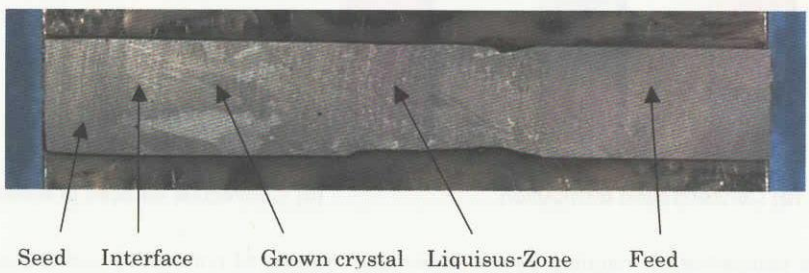


Fig. 7 Polished surface of a plate crystal of which InAs distribution is shown in Fig. 6.

Poly-crystallization occurred at the interface between a seed and a grown crystal, which meant that the seeding was not successful. There are many factors causing poly-crystallization. They are, lattice mismatch between a seed and a grown crystal, grain growth from crucible wall, thermal stress especially in the radial direction, constitutional supercooling during the growth, impurity or other materials included in a melt, concave curvature of the solid-liquid interface, leakage of a melt into a gap between a seed and a crucible wall, and so on. For growing single crystals, these factors should be eliminated. The most difficult problem may be lack of a good seed having $In_{0.3}Ga_{0.7}As$ composition. When we use GaAs as a seed, lattice mismatch between GaAs and $In_{0.3}Ga_{0.7}As$ is inevitable.

Another big problem is leakage of a melt into a gap between a seed and crucible wall and/or into a gap between a feed and crucible wall. If leakage occurs, single crystal growth and control of composition of a growing crystal get difficult due to the irregularity at the solid and liquid interface. In Fig. 8, an example of leakage of a melt into a gap in the feed side is schematically shown. Powder of boron nitride on a seed and on a feed was effective for avoiding leakage of a melt because wettability of boron nitride to GaAs or InAs is bad. Figure 9 shows grown crystal surfaces with and without boron nitride powder around a seed and a feed. Note that irregularity at the solid-liquid interface is improved by the use of boron nitride powder. Inhomogeneous heat flow causing the solid liquid interface curvature concave is another factor for poly-crystallization. This problem is analyzed elsewhere in this annual report in detail [6].

For $In_{0.3}Ga_{0.7}As$ substrate fabrication, we can say that control of the composition is settled and the remaining problem is single crystallization of grown crystals.

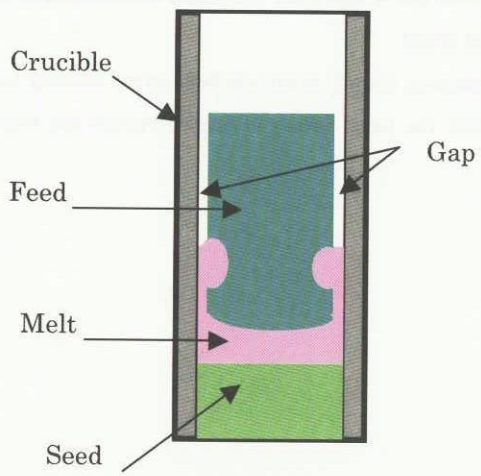


Fig. 8 Leakage of a melt into a gap between a feed and a crucible wall.

Fig. 9 As grown crystal surfaces without and with boron nitride powder around a seed and a feed: (a) without powder and (b) with powder.

CONCLUSIONS

Mixed crystal growth by the TLZ method is one of the most promising themes of microgravity utilization due to the superiority of the TLZ method and due to the necessity of suppression of convection in a melt. Excellent compositional homogeneity with InAs mole fraction of 0.3 plus or minus 0.01 for a distance of longer than 20 mm was obtained when convective flow velocity was suppressed in capillary tubes. For earlier development of $In_{0.3}Ga_{0.7}As$ crystals as substrates of laser diodes, plate crystals which have benefits of large surface area and small dimension in thickness were grown on the ground. Good compositional homogeneity was achieved by the suppression of

convection due to limited thickness but poly-crystallization could not be avoided. Since high quality $In_{0.3}Ga_{0.7}As$ seed crystals cannot be obtained, lattice mismatch between a seed and a grown crystal is a big problem. Utilization of (110) preferred orientation for single crystal growth [7] may be one of potential methods for growing single crystals of $In_{0.3}Ga_{0.7}As$ composition.

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Numerical Investigation on Two-dimensionality in the Traveling Liquidus-zone Method

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Abstract

In order to investigate the two-dimensionality in the traveling liquidus-zone (TLZ) method, the two-dimensional TLZ model is introduced. Basing on the two-dimensional model, the two-dimensionality is defined. From the numerical results in various sample diameters, the two-dimensionality is obtained. In the case of the sample diameter of 2 mm, the two-dimensionality is negligibly small on the ground. However, in the case of 10 mm, the two-dimensionality is large even though under no gravity condition if an InGaAs seed is used.

Introduction

The traveling liquidus-zone (TLZ) method[1, 2] is one of the most advancing growth techniques to obtain a homogeneous crystal of a ternary compound semiconductor such as InGaAs crystals. The feature of the TLZ method is to determine the proper sample translation rate easily for homogeneous crystal growth. In order to determine the translation rate, the one-dimensional theoretical model[3] has been introduced. This model predicts the growth rate precisely. Thus single crystals of 2 mm in diameter and of more than 20 mm in length have been successfully obtained with good reproducibility on the ground. However, it becomes difficult to grow a homogeneous crystal with a larger diameter than 2 mm on the ground. In order to understand the reason for the difficulty, we introduce a two-dimensional TLZ model. By considering the two-dimensional model, definition of two-dimensionality is discussed. To calculate the two-dimensionality, two-dimensional numerical simulations in various sample diameters are carried out. From the numerical results, the two-dimensionality is estimated and is discussed.

Two-dimensional TLZ model

In order to investigate two-dimensionality, a two-dimensional TLZ model is introduced. The generalized expression of solution growth can be described as

$$(C_L - C_S)\, u \cdot \hat{n} = -D \left.\frac{\partial C_L}{\partial n}\right|_{z=int}, \tag{1}$$

where n is a normal direction to an interface, u a vector of growth rate and $\hat{n}$ a unit vector being perpendicular to the interface. Here, we assume that the z-coordinate is a function of the r-coordinate and time t, that is,

$$z = f(r, t). \tag{2}$$

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By using Eq. (2), the unit vector $\hat{n}$ can be described as

$$\hat{n} = \frac{1}{\sqrt{1+\left(\frac{\partial f}{\partial r}\right)^2}}\left(-\frac{\partial f}{\partial r}, 1\right). \tag{3}$$

By substituting Eq. (3) to Eq. (1), the following equation

$$(C_L - C_S)\frac{\partial f}{\partial t} = -D\left(\frac{\partial C_L}{\partial z} - \frac{\partial C_L}{\partial r}\frac{\partial f}{\partial r}\right) \tag{4}$$

is obtained. Here,

$$\left.\frac{\partial C_L}{\partial z}\right|_{z=int} = \left.\frac{\partial C_L}{\partial T}\right|_{z=int}\left.\frac{\partial T}{\partial z}\right|_{z=int} \quad \text{, and} \tag{5}$$

$$\left.\frac{\partial C_L}{\partial r}\right|_{z=int} = \left.\frac{\partial C_L}{\partial T}\right|_{z=int}\left.\frac{\partial T}{\partial r}\right|_{z=int} \tag{6}$$

are assumed. These are the same assumption as the one-dimensional TLZ model[3], that is, the concentration in the liquid is a function of only the temperature. Thus, the equation of

$$(C_L - C_S)\frac{\partial f}{\partial t} = -D\frac{\partial C_L}{\partial T}\left(\frac{\partial T}{\partial z} - \frac{\partial T}{\partial r}\frac{\partial f}{\partial r}\right)_L \tag{7}$$

is obtained. This is the two-dimensional TLZ model. On the other hand, the one-dimensional TLZ model[3] is described as

$$(C_L - C_S)R = -D\frac{\partial C_L}{\partial T}\left.\frac{\partial T}{\partial z}\right|_L, \tag{8}$$

where R is a growth rate. By comparing Eq. (7) with Eq. (8), it is found that the term of $-\frac{\partial T}{\partial r}\frac{\partial f}{\partial r}$ changes the growth rate estimated from the one-dimensional model. This means that the following expression is used as the definition of the two-dimensionality δ;

$$\delta = \left.-\frac{\partial T}{\partial r}\frac{\partial f}{\partial r}\right/\frac{\partial T}{\partial z}. \tag{9}$$

Two-dimensional Numerical Simulation

In order to calculate Eq. (9), temperature gradients along r- and z-directions and an interface shape are required. To obtain these parameters, two-dimensional numerical simulations are carried out. In the simulation, the energy transport equation, the mass transport equation, the stream function equation, the vorticity transport equation, the energy balance equation and the mass balance equation are simultaneously solved. We use the boundary fitted

coordinate (BFC) method[4-11], which is a kind of finite difference method, in order to solve these equations. The BFC method solves the governing equations that are transformed from the physical space to the computational space. The transformed governing equations are described as Eqs. (10) − (16).

$$\rho C_p\left\{\frac{\partial T}{\partial t}-\frac{1}{J}(z_\eta T_\xi - z_\xi T_\eta)\frac{\partial r}{\partial t}-\frac{1}{J}(-r_\eta T_\xi + r_\xi T_\eta)\frac{\partial z}{\partial t}\right\}-\rho C_p\frac{1}{r}\frac{1}{J}(\psi_\xi T_\eta-\psi_\eta T_\xi), \tag{10}$$
$$=k\frac{1}{J^2}(\alpha T_{\xi\xi}-2\beta T_{\xi\eta}+\gamma T_{\eta\eta})+k\frac{1}{r}\frac{1}{J}(z_\eta T_\xi - z_\xi T_\eta)$$

$$\frac{\partial C_L}{\partial t}-\frac{1}{J}(z_\eta C_{L\xi}-z_\xi C_{L\eta})\frac{\partial r}{\partial t}-\frac{1}{J}(-r_\eta C_{L\xi}+r_\xi C_{L\eta})\frac{\partial z}{\partial t}-\frac{1}{r}\frac{1}{J}(\psi_\xi C_{L\eta}-\psi_\eta C_{L\xi}), \tag{11}$$
$$=D_L\frac{1}{J^2}(\alpha C_{L\xi\xi}-2\beta C_{L\xi\eta}+\gamma C_{L\eta\eta})+D_L\frac{1}{r}\frac{1}{J}(z_\eta C_{L\xi}-z_\xi C_{L\eta})$$

$$\frac{\partial C_S}{\partial t}-\frac{1}{J}(z_\eta C_{S\xi}-z_\xi C_{S\eta})\frac{\partial r}{\partial t}-\frac{1}{J}(-r_\eta C_{S\xi}+r_\xi C_{S\eta})\frac{\partial z}{\partial t}, \tag{12}$$
$$=D_S\frac{1}{J^2}(\alpha C_{S\xi\xi}-2\beta C_{S\xi\eta}+\gamma C_{S\eta\eta})+D_S\frac{1}{r}\frac{1}{J}(z_\eta C_{S\xi}-z_\xi C_{S\eta})$$

$$-rJ^2\omega$$
$$=\alpha\psi_{\xi\xi}-2\beta\psi_{\xi\eta}+\gamma\psi_{\eta\eta}, \tag{13}$$
$$-\frac{J}{r}(z_\eta\psi_\xi - z_\xi\psi_\eta)$$

$$\frac{\partial\omega}{\partial t}-\frac{1}{J}(z_\eta\omega_\xi - z_\xi\omega_\eta)\frac{\partial r}{\partial t}-\frac{1}{J}(r_\eta\omega_\xi - r_\xi\omega_\eta)\frac{\partial z}{\partial t}+\frac{1}{r}\frac{1}{J^2}(-r_\eta\psi_\xi+r_\xi\psi_\eta)\cdot(z_\eta\omega_\xi - z_\xi\omega_\eta)$$
$$-\frac{1}{r}\frac{1}{J^2}(z_\eta\psi_\xi - z_\xi\psi_\eta)\cdot(-r_\eta\omega_\xi+r_\xi\omega_\eta)-\frac{1}{r^2}\frac{1}{J}\omega(-r_\eta\psi_\xi+r_\xi\psi_\eta)$$
$$=\nu\frac{1}{J^2}(\alpha\omega_{\xi\xi}-2\beta\omega_{\xi\eta}+\gamma\omega_{\eta\eta})+\nu\frac{1}{r}\frac{1}{J}(z_\eta\omega_\xi - z_\xi\omega_\eta)-\nu\frac{1}{r^2}\omega$$
$$+\frac{1}{J}Bg(z_\eta T_\xi - z_\xi T_\eta)+\frac{1}{J}Gg(z_\eta C_\xi - z_\xi C_\eta), \tag{14}$$

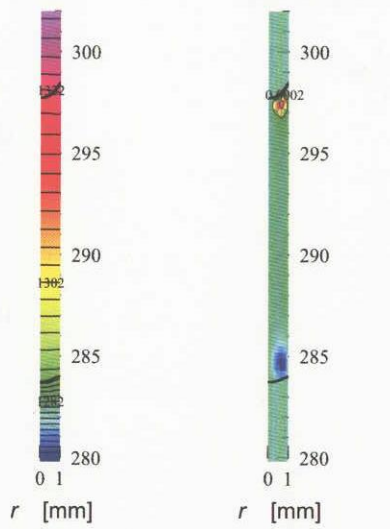
$$L_{SL}\rho\frac{\partial f}{\partial t}$$
$$=-k_L\frac{1}{r_\xi}\frac{1}{J_L}(-\beta T_\xi+\gamma T_\eta)_L, \tag{15}$$
$$+k_S\frac{1}{r_\xi}\frac{1}{J_S}(-\beta T_\xi+\gamma T_\eta)_S$$

$$(C_L-C_S)\frac{\partial f}{\partial t},$$
$$=-D_L\frac{1}{r_\xi}\frac{1}{J_L}(-\beta C_{L\xi}+\gamma C_{L\eta})_L \tag{16}$$

where $\alpha = r_\eta^2 + z_\eta^2$, $\beta = r_\xi r_\eta + z_\xi z_\eta$, $\gamma = r_\xi^2 + z_\xi^2$, $J = r_\xi z_\eta - r_\eta z_\xi$, ξ and η are the computational coordinates corresponding to r and z in the physical space, ψ the stream function, ω vorticity, T temperature, ρ density, C_p specific heat, κ thermal conductivity, ν kinetic viscosity, L_{SL} latent heat, B thermal volume expansion coefficient, G the buoyancy coefficient by the specific gravity difference, g gravity, t time, C the concentration, D the diffusion coefficient. Subscripts of L and S indicate the liquid side and the solid side, respectively.

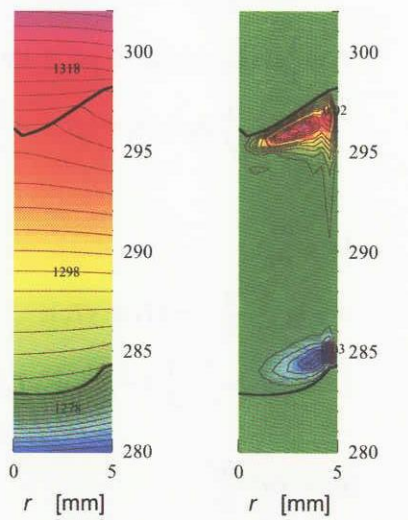
Results and Discussion

The typical results of the numerical simulation in the case of the sample diameter of 2 mm and 10 mm are shown in Fig. 1 and 2, respectively. The gravity condition is 1 g. The thermal convection in the 2 mm case is weaker than that in the 10 mm case due to both the small diameter and the radially small variation of the temperature. For example, the convection effect on the mass transport is negligibly small in the 2 mm case[12] due to the weak convection. In addition, the two-dimensionality may be also negligibly small in the 2 mm case. By using the numerical results, the two-dimensionality is calculated and is shown in Fig. 3 as a function of the radius. In this figure, the two-dimensionality in the 2 mm, 5 mm and 10 mm cases are plotted as the red line, the blue line and the green line, respectively. As shown in Fig. 3, the two-dimensionality in the 2 mm case is only about 4 % at the maximum. This result indicates that the radial difference of the growth rate in the 2 mm case is within ± 0.01 mm/hr since the growth rate is about 0.216 mm/hr in the ground-based crystal growth experiments. The difference of ± 0.01 mm/hr is usually negligibly small from the viewpoint of the experimental technique. However, the two-dimensionality increases with the sample diameter, that is, about 16 % in the 5 mm case and about 33 % in the 10 mm case at the maximum. These values are not negligible and this should be one of the reasons that a homogeneous crystal growth with a large diameter is difficult on the ground. The two-dimensionality increases as the radial position increases as a macroscopic tendency. This tendency indicates that the InAs mole fraction in the solid decreases as the crystal grows near the outer radius if the InAs fraction is almost constant on the axis. This is qualitatively consistent with the experimentally obtained InAs mole fraction in the 10 mm case as shown in Fig. 4. Although the data scattering in Fig. 4 may be caused by grain boundaries, the mole fraction variation can be clearly observed.



(a) Temperature (b) Stream Function

Fig. 1 Typical results in 2 mm case



(a) Temperature (b) Stream Function

Fig. 2 Typical results in 10 mm case

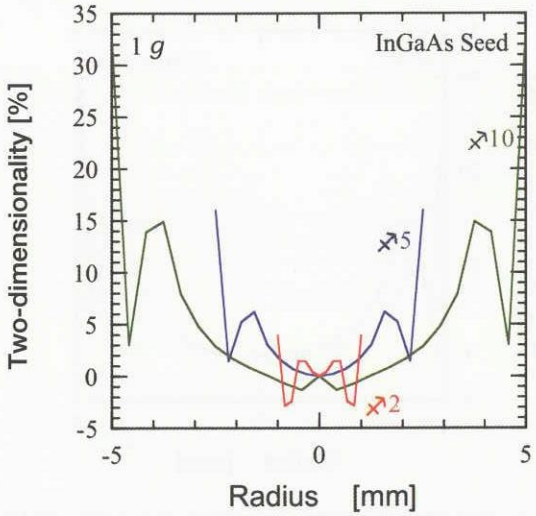


Fig. 3 Radial variation of two-dimensionality

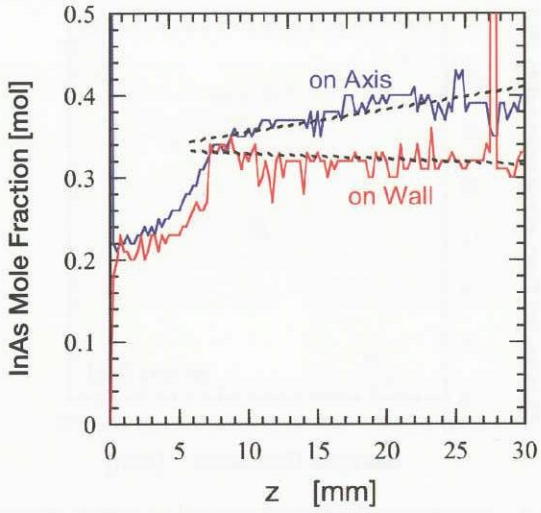


Fig. 4 Experimentally obtained InAs mole fraction along growth direction

As shown in Fig. 3, the two-dimensionality once decreases near the crucible wall then is maximized on the wall. This means that the lattice mismatch is maximized near the wall. This may enhance polycrystallization. The combination of this lattice mismatch with the constitutional supercooling on the wall may be the reason that single crystal growth is difficult on the ground. This issue should be investigated more deeply in future. By plotting the maximum two-dimensionality, the dependency of the two-dimensionality on the sample diameter is obtained and is shown in Fig. 5. By fitting the second order curve, the sample diameter, at which the two-dimensionality is zero, is estimated and is slightly larger than 1 mm. This estimation indicates that the two-dimensionality becomes almost perfectly negligible if the sample diameter is 1 mm.

The thermal convection may enhance the two-dimensionality. Therefore, the two-dimensionality variation against the gravity condition is investigated. Figure 6 is the comparison between the two-dimensionality under 1 g condition and that under no gravity condition. The red line and the blue one represent the two-dimensionality under 0 g and that under 1 g. This figure shows that the two-dimensionality under 0 g is smaller than that under 1 g. However, the two-dimensionality under 0 g is about 26 %, while the two-dimensionality under 1 g is about 33 %. This is not small enough to obtain a homogeneous crystal. This result indicates that the contribution of the convection to the two-dimensionality is not so large. Another possibility of the large two-dimensionality is the thermal conductivity difference between the seed crystal and the crucible. Namely, the heat is mainly transferred to the wall at the interface rather than to the seed crystal. If this speculation is true, the two-dimensionality should decrease by using another seed, of which the thermal conductivity is higher than that of the InGaAs crystal, for example, a GaAs seed. The thermal conductivity of the GaAs is about 16.0 W/K·m, while that of the $In_{0.3}Ga_{0.7}As$ is about 3.0 W/K·m. The effect of the GaAs seed on the two-dimensionality is investigated. The result is shown in Fig. 7. This figure clearly shows that the two-dimensionality in the GaAs seed case is drastically small as compared with that in the InGaAs seed case. It is summarized that the GaAs seed is much appropriate for the homogeneous crystal growth with a large diameter from the viewpoint of the two-dimensionality. However, the lattice mismatch at the initial interface may prevent single crystal growth. So this issue should also need further investigation in future.

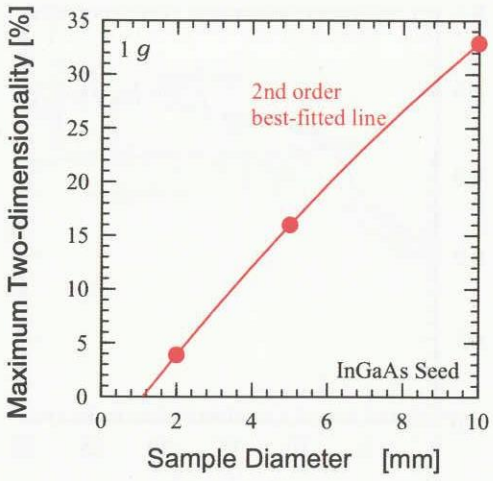


Fig. 5 Two-dimensionality dependency on sample diameter

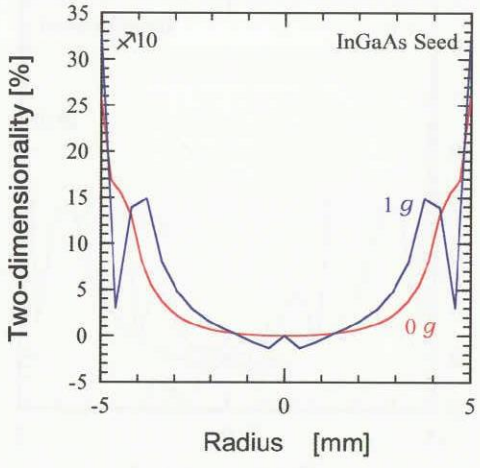


Fig. 6 Two-dimensionality comparison in 1 g case and in 0 g case

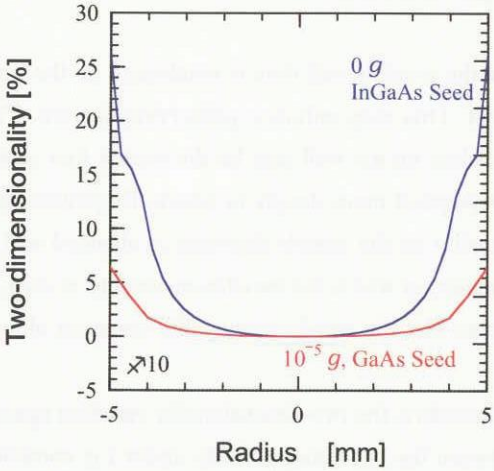


Fig. 7 Two-dimensionality variation in InGaAs seed case and in GaAs seed case

Conclusions

By introducing a new two-dimensional TLZ model, the two-dimensionality is defined from the viewpoint of the interface shape. To calculate the two-dimensionality, two-dimensional numerical simulations are carried out. By using the numerical results, the two-dimensionality is calculated in various sample diameters. In the case of the sample diameter of 2 mm, the two-dimensionality is about 4 % at maximum on the ground. This is small enough to grow a homogeneous crystal. On the other hand, in both the 5 mm and the 10 mm cases, the two-dimensionality is about 16 % and 33 % at the maximum, respectively. These values are not negligible and this may be one of the reasons why homogeneous crystal growth with a large diameter is difficult on the ground. Because the thermal convection becomes strong as the sample diameter increases, the increases of the two-dimensionality in the 5 mm and the 10 mm cases may be caused by the convection. Therefore the two-dimensionality under the 0 g condition is investigated. From the comparison of the two-dimensionality in 1 g with that in 0 g, the decrease of the two-dimensionality is not enough though it decreases under the 0 g condition. This suggests that the large two-dimensionality is caused

another mechanism rather than the convection. To investigate this speculation, the two-dimensionality in the GaAs seed case is calculated. From the result, it is found that the two-dimensionality is drastically reduced. Therefore, the GaAs seed is much appropriate for homogeneous crystal growth. However, the lattice mismatch at the initial interface may cause polycrystallization. This issue will be investigated in future.

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Estimation of Diffusion Coefficient by Using Numerical Simulation of the Traveling Liquidus-zone Method

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Abstract

In order to estimate a diffusion coefficient, an InAs mole fraction profile, which is obtained by numerical simulation, is compared with a profile, which is experimentally obtained. The simulation result agrees well with the experimentally obtained profile. The diffusion coefficient is estimated to be about $1.1\times10^{-4}cm^2/s$ by comparing the numerically obtained growth length with the experimentally obtained one.

Introduction

The traveling liquidus-zone (TLZ) method[1, 2] can easily grow a homogeneous crystal of a ternary compound semiconductor such as InGaAs crystals. To grow a homogeneous crystal by the TLZ method, it is required to translate a sample by an appropriate translation rate. The translation rate is determined to be the same rate as a growth rate. The growth rate is estimated by using the one-dimensional TLZ model[3]. By using the TLZ method, single crystals of 2 mm in diameter and of more than 20 mm in length have been successfully obtained with good reproducibility on the ground[1, 2]. However, the one-dimensional TLZ model requires a diffusion coefficient. Therefore, to measure the diffusion coefficient, a microgravity experiment[4] was carried out by using a sounding rocket. From the experimental results, the coefficient and its temperature dependency was successfully obtained. However, it is often difficult to carry out the microgravity experiment to measure the diffusion coefficient. Therefore the diffusion coefficient is estimated by comparing a result from numerical simulation with an experimental result.

Two-dimensional Numerical Simulation

In this study, a numerically obtained InAs mole fraction profile is compared with an experimentally obtained profile. In order to obtain the profile, a two-dimensional numerical simulation is carried out. In the simulation, the energy transport equation, the mass transport equation, the energy balance equation and the mass balance equation are simultaneously solved. We apply this simulation to a sample with 2 mm in diameter. In the 2 mm sample, it has been already clarified that the convection effects on mass and thermal transports are negligibly small. Therefore, 2 mm sample is suitable for both the experimental estimation of the diffusion coefficient and the calculation time reduction. Thus we neglect the vorticity transport equation, the stream function equation and the terms related to the convection from the governing equations to shorten the calculation time. We use the boundary fitted coordinate

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(BFC) method[5-12], which is a kind of finite difference method, in order to solve these equations. The BFC method solves the governing equations that are transformed from the physical space to the computational space. The transformed governing equations are described as Eqs. (1) — (5).

$$\rho C_p \left\{ \frac{\partial T}{\partial t} - \frac{1}{J}(z_\eta T_\xi - z_\xi T_\eta)\frac{\partial r}{\partial t} - \frac{1}{J}(-r_\eta T_\xi + r_\xi T_\eta)\frac{\partial z}{\partial t} \right\} , \\ = k\frac{1}{J^2}(\alpha T_{\xi\xi} - 2\beta T_{\xi\eta} + \gamma T_{\eta\eta}) + k\frac{1}{r}\frac{1}{J}(z_\eta T_\xi - z_\xi T_\eta) \tag{1}$$

$$\frac{\partial C_L}{\partial t} - \frac{1}{J}(z_\eta C_{L\xi} - z_\xi C_{L\eta})\frac{\partial r}{\partial t} - \frac{1}{J}(-r_\eta C_{L\xi} + r_\xi C_{L\eta})\frac{\partial z}{\partial t} , \\ = D_L\frac{1}{J^2}(\alpha C_{L\xi\xi} - 2\beta C_{L\xi\eta} + \gamma C_{L\eta\eta}) + D_L\frac{1}{r}\frac{1}{J}(z_\eta C_{L\xi} - z_\xi C_{L\eta}) \tag{2}$$

$$\frac{\partial C_S}{\partial t} - \frac{1}{J}(z_\eta C_{S\xi} - z_\xi C_{S\eta})\frac{\partial r}{\partial t} - \frac{1}{J}(-r_\eta C_{S\xi} + r_\xi C_{S\eta})\frac{\partial z}{\partial t} , \\ = D_S\frac{1}{J^2}(\alpha C_{S\xi\xi} - 2\beta C_{S\xi\eta} + \gamma C_{S\eta\eta}) + D_S\frac{1}{r}\frac{1}{J}(z_\eta C_{S\xi} - z_\xi C_{S\eta}) \tag{3}$$

$$L_{SL}\rho\frac{\partial f}{\partial t} \\ = -k_L\frac{1}{r_\xi}\frac{1}{J_L}(-\beta T_\xi + \gamma T_\eta)_L , \\ + k_S\frac{1}{r_\xi}\frac{1}{J_S}(-\beta T_\xi + \gamma T_\eta)_S \tag{4}$$

$$(C_L - C_S)\frac{\partial f}{\partial t} , \\ = -D_L\frac{1}{r_\xi}\frac{1}{J_L}(-\beta C_{L\xi} + \gamma C_{L\eta})_L \tag{5}$$

where, $\alpha = r_\eta^2 + z_\eta^2$, $\beta = r_\xi r_\eta + z_\xi z_\eta$, $\gamma = r_\xi^2 + z_\xi^2$, $J = r_\xi z_\eta - r_\eta z_\xi$, ξ and η are the computational coordinates corresponding to r and z in the physical space, ψ the stream function, ω vorticity, T temperature, ρ density, C_p specific heat, κ thermal conductivity, ν kinetic viscosity, L_{SL} latent heat, B thermal volume expansion coefficient, G the buoyancy coefficient by the specific gravity difference, g gravity, t time, C the concentration, D the diffusion coefficient. Subscripts of L and S indicate the liquid side and the solid side, respectively.

Results and Discussion

The generated grid and the initial configuration in this simulation are shown in Fig. 1 (a). The generated grid at the end of the growth is also shown in Fig. 1 (b). Although interface shapes are initially given as a flat shape, the shapes vary as the time evolves. This shape variation can be understood by comparing the initial grid with the final

grid. As the temperature boundary condition, the temperature profile, which is shown in Fig. 2, is given on the crucible surface. The temperature profile moves towards the right side in Fig. 2 as the time evolves by the rate of 0.216 mm/hr, which is the experimentally optimized sample translation rate to grow a homogeneous $In_{0.3}Ga_{0.7}As$ crystal. Under these conditions, the numerical results are obtained. The typical result in the case of the diffusion coefficient of $1.2\times10^{-4}cm^2/s$ is shown in Fig. 3. In this figure, the red line and the blue one represent the InAs mole fraction measured by the electron probe micro-analyzer (EPMA) and the numerical result. As shown in Fig. 3, although the numerically obtained profile agrees well with the experimentally obtained one, the growth length obtained by the simulation is slightly longer then the experimental one. Therefore, another simulation in the case of the diffusion coefficient of $1.1\times10^{-4}cm^2/s$ is carried out. The comparison between the simulation and the experiment is shown in Fig. 4. This figure also shows that the InAs mole fraction profile and the growth length obtained from the simulation agree well with those from the experiment. Therefore, the diffusion coefficient of $In_{0.83}Ga_{0.17}As$ melt, which is the equilibrium composition to the solidus composition of $In_{0.3}Ga_{0.7}As$, is estimated to be $1.1\times10^{-4}cm^2/s$. In this simulation, the temperature at the growth interface is about 1293 K.

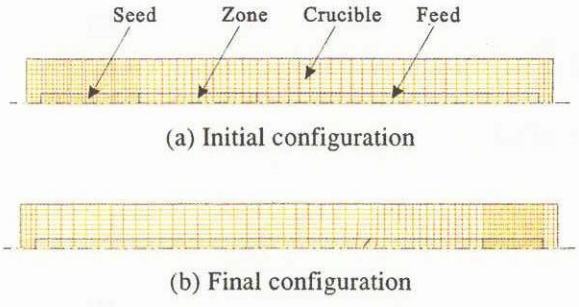

Fig. 1 Generated grids and configurations

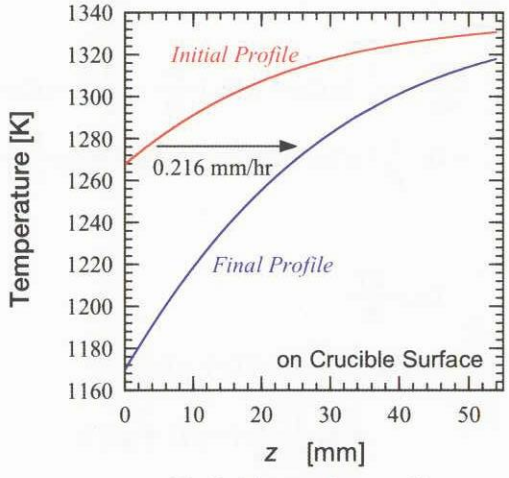

Fig. 2 Temperature profile

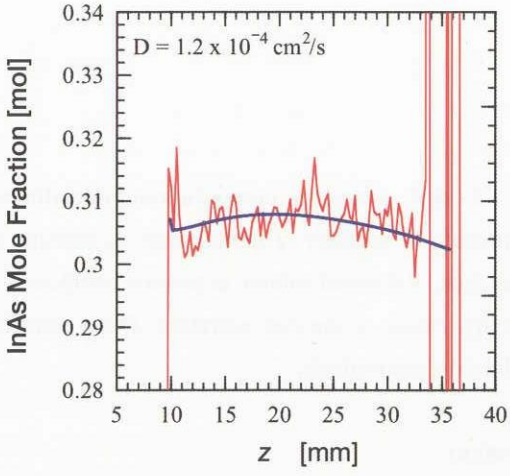

Fig. 3 Comparison between numerical and experimental results ($D = 1.2\times10^{-4}cm^2/s$)

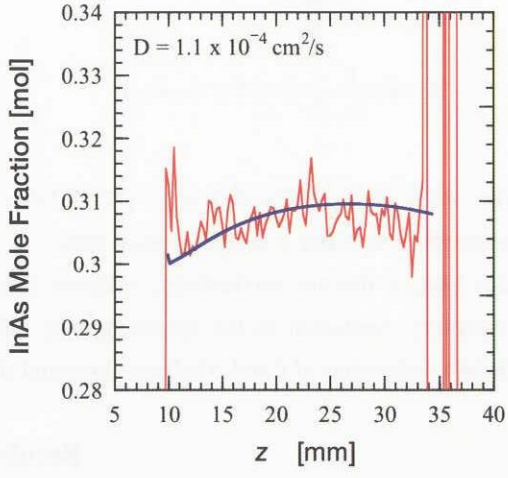

Fig. 4 Comparison between numerical and experimental results ($D = 1.1\times10^{-4}cm^2/s$)

In order to investigate the reliability of the estimation of the diffusion coefficient, the experimental results of the diffusion coefficient measurement by using the sounding rocket[4] is referred. The experimental results are shown in

Fig. 5. The natural logarithms of the measured coefficients are plotted in this figure. In Fig. 5, the minimum coefficient at each temperature is represented by a red closed circle. The middle one is represented by a blue closed circle. One scattered data is represented by a green closed square. The lower black line passes through the red circles and the upper one is the best-fitted linear line by using the blue circles. At 1293 K, the lower black line indicates that the diffusion coefficient is about $1.1\times10^{-4}cm^2/s$ and the upper black one indicates that the diffusion coefficient is about $1.4\times10^{-4}cm^2/s$. Therefore, the true diffusion coefficient may exist between $1.1\times10^{-4}cm^2/s$ and $1.4\times10^{-4}cm^2/s$. This is consistent with the estimation from the simulation. It is summarized that the estimation of the diffusion coefficient by the simulation is reliable enough.

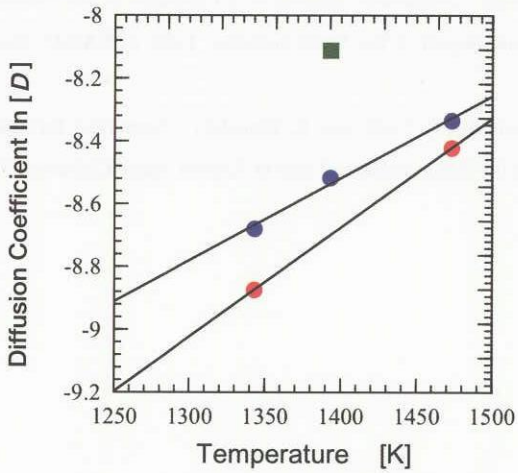

Fig. 5 Experimental result of diffusion coefficient measurement by using sounding rocket [4)]

Conclusions

In order to estimate a diffusion coefficient, numerical simulation is carried out. The InAs mole fraction profile obtained from the simulation is compared with that from the experiment. It is found that the numerically obtained profile agrees well with the experimentally obtained profile. In the case of the diffusion coefficient of $1.1\times10^{-4}cm^2/s$, the growth length also agrees well with the experimental result. Therefore, the diffusion coefficient of $In_{0.83}Ga_{0.17}As$ melt is estimated to be $1.1\times10^{-4}cm^2/s$ at 1293 K. To investigate the reliability of this estimation, the measurement results of the diffusion coefficient by using a sounding rocket is referred. From the experimental results, the diffusion coefficient is $1.1\times10^{-4}cm^2/s$ to $1.4\times10^{-4}cm^2/s$. This is consistent with the estimation by the simulation.

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Appendix

Publications of the Semiconductor Crystal Growth Team (2003. 4−2004. 3)

Papers

(1) H. Nakamura, Y. Hanaue, H. Kato, K. Kinoshita and S. Yoda, "A one-dimensional model to predict the growth conditions of $In_xGa_{1-x}As$ alloy crystals grown by the traveling liquidus-zone method", *J. Crystal Growth*, 258 (2003), pp. 49-57.

Presentations (International)

(1) K Kinoshita, Y. Ogata, S. Adachi, N. Koshikawa, S. Yoda, H. Miyata and Y. Muramatsu, "A new crystal growth method for growing homogeneous mixed crystals of $In_{0.3}Ga_{0.7}As$: the traveling liquidus-zone (TLZ) method", 10th International Space Conference of Pacific-basin Societies, Tokyo, Japan December 10-12, C7-09, 2003.

Presentations (Domestic)

(1) K. Kinoshita, Y. Ogata, N. Koshikawa, S. Adachi, S. Yoda, M. Iwai, T. Tsura and Y. Muramatsu, "Constitutional supercooling in the crystal growth of $In_xGa_{1-x}As$", the 33rd National Congress on Crystal Growth, 730aD4 (2003).

(2) T. Tsuru, H. Miyata, M. Iwai, Y. Muramatsu, K. Kinoshita, Y. Ogata, S. Adachi, N. Koshikawa, and S. Yoda, "Evaluation of homogeneous $In_xGa_{1-x}As$ crystal growth model by the TLZ (Traveling Liquidus-Zone) method", the 64th Annual Meeting of the Japan Society of Applied Physics, 30a-P1-32 (2003).

(3) H. Miyata, T. Tsuru, M. Iwai, S. Y. Muramatsu, K. Kinoshita, Y. Ogata, S. Adachi, N. Koshikawa, S. Yoda, "Homogeneous SiGe crystal growth by the TLZ (Traveling Liquidus-Zone) method", The 19th Annual Meeting of the Japan Society of Microgravity Application, JASMAC-19, B217 (2003).

(4) K. Kinoshita, Y. Ogata, S. Adachi, N. Koshikawa, T. Tsura, H. Miyata and Y. Muramatsu, "Growth conditions for homogeneous $In_{0.3}Ga_{0.7}As$ single crystals by the TLZ method", The 20th Space Utilization Symposium, (2004).

(5) S. Adachi, Y. Ogata, S. Matsumoto, K. Kinoshita, and S. Yoda, "Numerical Investigation on Two-dimensionality in a Flight Cartridge for the Traveling Liquidus-Zone Method," The 20th Space Utilization Symposium, (2004).

(6) K. Kinoshita, "Homogeneous alloy crystal growth by utilizing microgravity conditions", The 38th Meeting of 161 Committee "Techniques and Sciences in Crystal Growth" in the Japan Promotion of Science (2004).

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