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

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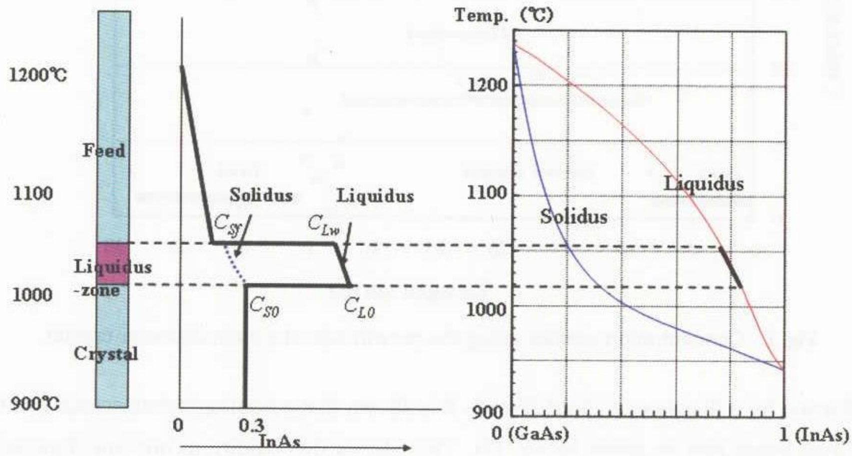
substrates for semiconductor laser diodes and the development of $In_{0.3}Ga_{0.7}As$ crystals will be accelerated. For this purpose, we tried plate crystal growth of $In_{0.3}Ga_{0.7}As$ on the ground. Here we report results of those trials performed for growing high quality $In_{0.3}Ga_{0.7}As$ single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

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

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

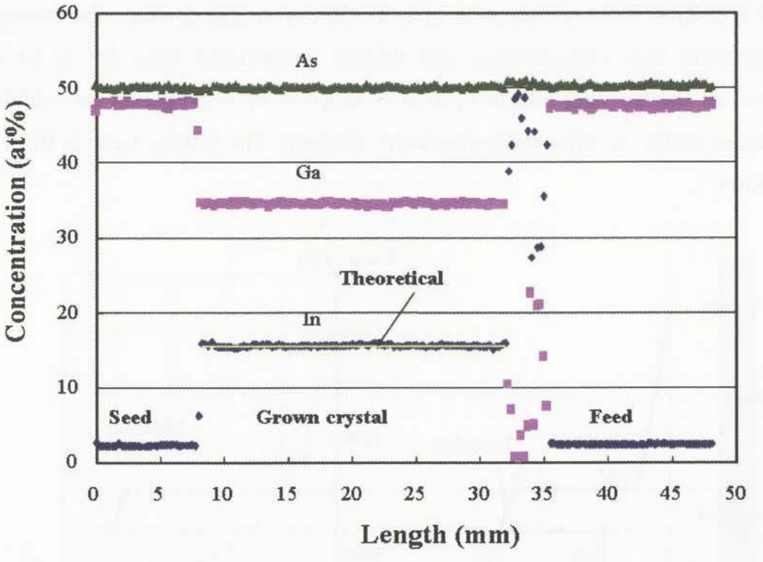


Fig. 2 Concentration profiles along the growth axis of a 2mm diameter crystal.

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.

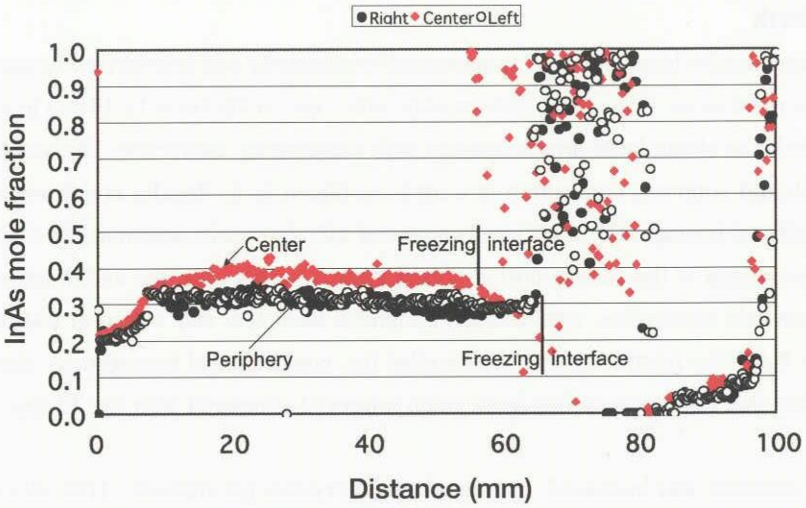


Fig. 3 InAs concentration profiles for a 10 mm diameter crystal.

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.

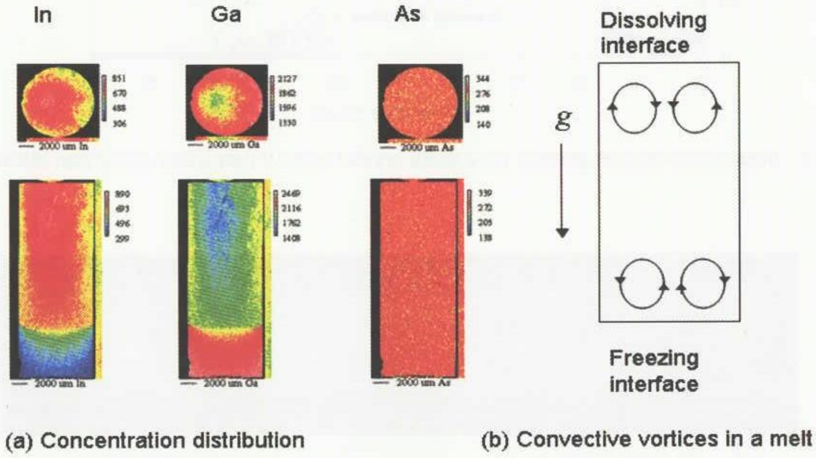


Fig. 4 In, Ga and As concentration mapping (a) and schematic drawing of convective vortices near the freezing and dissolving interfaces (b).

(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.

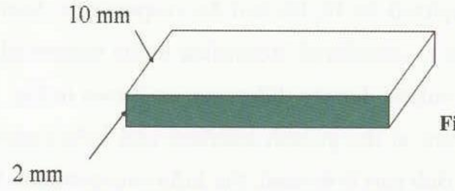


Fig. 5 Dimensions of plate crystals for substrate use.

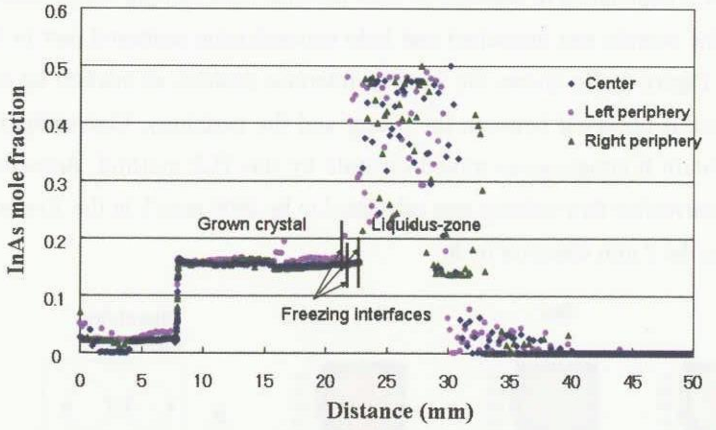


Fig. 6 InAs concentration profiles for a plate crystal with 10 mm width and 2 mm thickness.

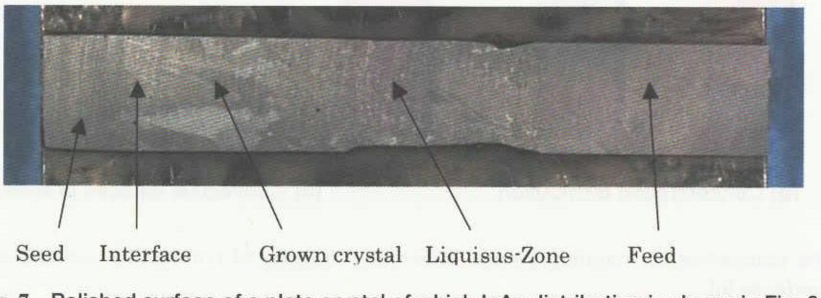


Fig. 7 Polished surface of a plate crystal of which InAs distribution is shown in Fig. 6.

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.

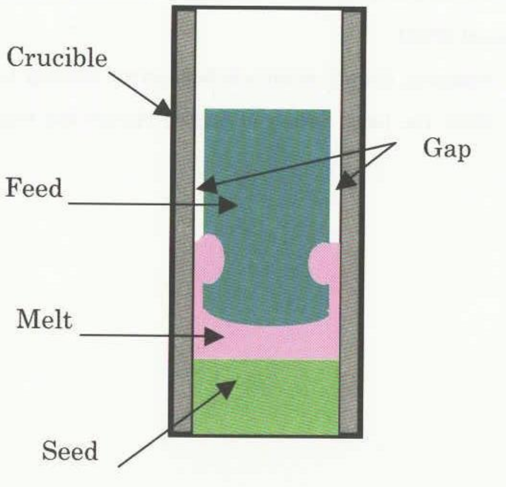


Fig. 8 Leakage of a melt into a gap between a feed and a crucible wall.

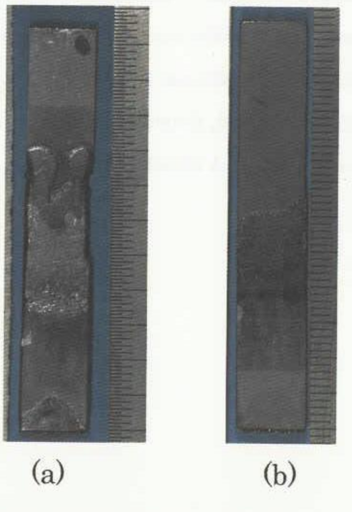


Fig. 9 As grown crystal surfaces without and with boron nitride powder around a seed and a feed: (a) without powder and (b) with powder.

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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