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

The influence of convection in a melt on the compositional homogeneity of the TLZ-grown $In_{0.3}Ga_{0.7}As$ crystals has been investigated by growing crystals with various dimensions on the ground. Excellent compositional homogeneity such as 0.3 plus or minus 0.01 in InAs mole fraction for a distance of 25 mm was obtained when the melt diameter was limited to 2 mm and convective flow in the melt was suppressed. On the other hand, when the crystal diameter was increased to 10 mm, both axial and radial compositional homogeneity was deteriorated due to convection in the melt. Comparing with the numerical simulation, convective flow velocity less than 1.4 mm/h may be sufficient for growing homogeneous crystals and it is not so difficult to suppress convective flow velocity below 1.4 mm/h for 10 mm diameter crystals in microgravity. Therefore, larger homogeneous $In_{0.3}Ga_{0.7}As$ crystals are expected to be grown by the TLZ method on board the International Space Station.

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. Here we report results of the terrestrial TLZ growth experiments on $In_{0.3}Ga_{0.7}As$.

PRINCIPLE OF THE TLZ METHOD

Figure 1 explains the principle of 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. Relations among temperatures, zone position, concentration profile in a sample device and the equilibrium phase diagram of the InAs-GaAs system are depicted in the figure. 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. 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

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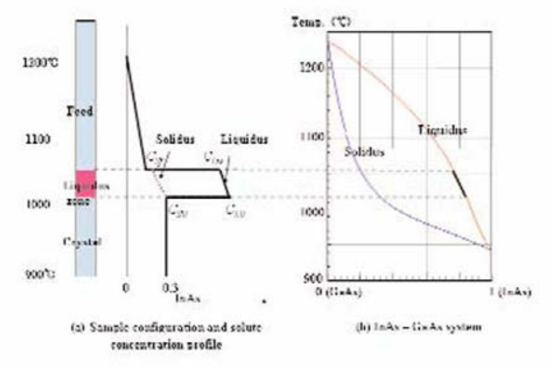
relative to a furnace and the freezing temperature is kept constant. Then, the constant concentration of a growing crystal is achieved. Based on our one-dimensional model [3, 4], the spontaneous interface shift V is calculated as

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

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. $\partial C/\partial T$ and $\partial T/\partial z$ 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°C/cm plus or minas 1°C/cm for the present heating conditions and V is calculated to be 0.22 mm/h for $\partial C/\partial T$ = 10°C/cm.



(a) Sample configuration and solute concentration profile

(b) InAs – GaAs system

Fig. 1. Principle of the TLZ method.

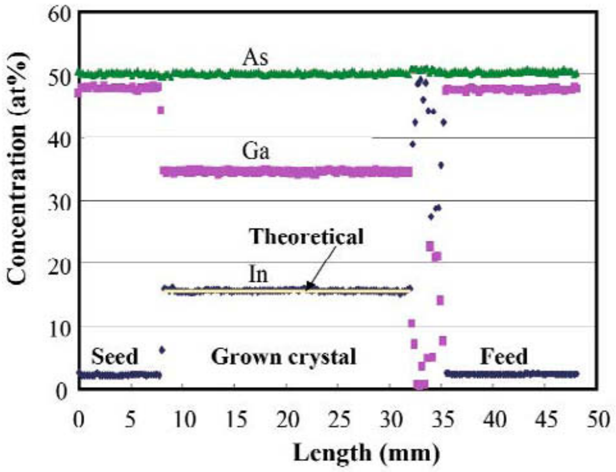


Fig. 2. Concentration profiles along the growth axis of a 2 mm diameter crystal.

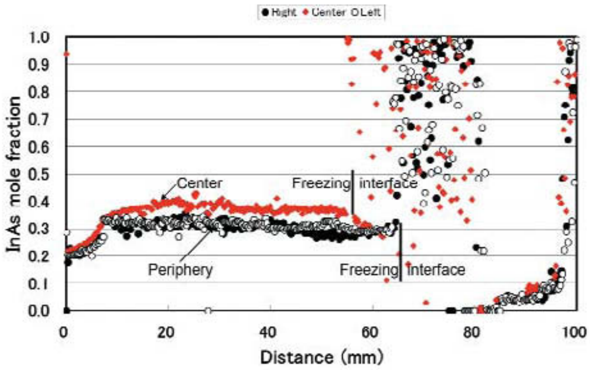


Fig. 3. InAs concentration profiles for a 10 mm diameter crystal.

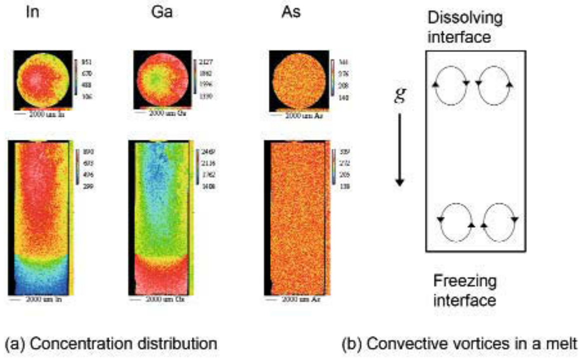
RESULTS AND DISCUSSION

(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 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°C/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



(a) Concentration distribution

(b) Convective vortices in a melt

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

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 homogeneity is worse than that of the 2 mm diameter crystal, especially in the radial direction: InAs concentration is highest at the center. The concentration inhomogeneity is more clearly shown in Fig. 4(a), in which cross sectional InAs 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.

(3) Plate-like crystal growth

Substrates for devices require large area but compositional homogeneity was deteriorated by convection in larger diameter crystals as described above. Therefore, plate-like crystals with 2 mm in thickness by 10 mm in width 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. 5. 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.

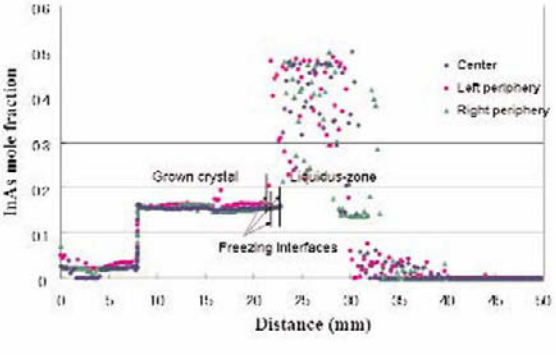


Fig. 5. InAs concentration profiles for a plate crystal with 10 mm width and 2 mm thickness.

EXPECTATION FOR SPACE EXPERIMENTS

A series of TLZ-growth experiments on the ground showed that suppression of convection in a melt is crucially important for growing compositionally homogeneous mixed crystals by the TLZ method. The most convenient way for suppression of convection on the ground is limitation of a melt size, but this is not relevant for obtaining large area substrates for devices. Suppression of convection in microgravity is promising for obtaining large diameter homogeneous crystals by the TLZ method.

CONCLUSIONS

It is concluded that 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 below 1.4 mm/h.

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