Experimental study of $In_xGa_{1-x}As$ homogeneous single crystal growth by the traveling liquidus-zone (TLZ) method.

Yasuhiro Hanaue†, Masayuki Iwai††, Tetsuya Tsuru††, Yuji Muramatsu††
and Kyoichi Kinoshita†

† National Space Development Agency of Japan, 2-1-1 Sengen, Tsukuba, Ibaraki 305-8505, Japan,
†† Advanced Engineering Service Co. Ltd., 1-6-1, Takezono, Tsukuba, Ibaraki 305-0032, Japan

Newly invented "traveling liquidus-zone" (TLZ) method was applied to grow $In_{0.3}Ga_{0.7}As$ single crystals. Homogeneous growth conditions were confirmed experimentally though controlling temperature gradient in the liquidus-zone and accrate measurements of it should be further developed. The validity of using heat sink to improve the heat flow for realizing flat or slightly convex growth interface was also confirmed.

1. Introduction

Bulk mixed semiconductor single crystals, such as $In_xGa_{1-x}As$, are promising materials for substrates of laser diodes. However difficulty of the crystal growth prevent the industrial use of them.

Homogeneous crystal growth should be realized if the temperature and solute concentration in the melt at the growth interface is kept constant. Usually the mixed crystal system shows segregation, so the solute concentration in a melt near the growth interface should have an appropriate gradient depending on growth rate and diffusion coefficient for the homogeneous crystal growth.

We invented the traveling liquidus-zone method which made possible to keep concentration gradient of the solute at the growth interface in proportional to temperature gradient, and compositionally homogeneous crystals are grown if the suitable translation rate of a sample in accordance with the zone traveling rate is given[1)].

In this paper we report the experimental details and results of homogeneous single crystal growth of $In_xGa_{1-x}As$ by the TLZ method.

2. Apparatus and experimental procedures

Experimental setup is schematically shown in Fig. 1. A seed crystal and an $In_xGa_{1-x}As$ feed material with gradient InAs concentration were set into a sintered BN crucible and were sealed in a quartz ampoule at 10^{-4} Pa.

A 4-zone gradient heating furnace with sample translation mechanism (MATELS Inc MAT-50VGA) was used for crystal growth. Temperatures of ampoule surface were measured by 6 sheath thermocouples. Feed materials were prepared by the directional solidification of an $In_{0.3}Ga_{0.7}As$ melt[2)].

Compositional profiles of samples were analyzed by an electron probe micro-analyzer (EPMA: CAMECA SX100) on the polished surfaces.

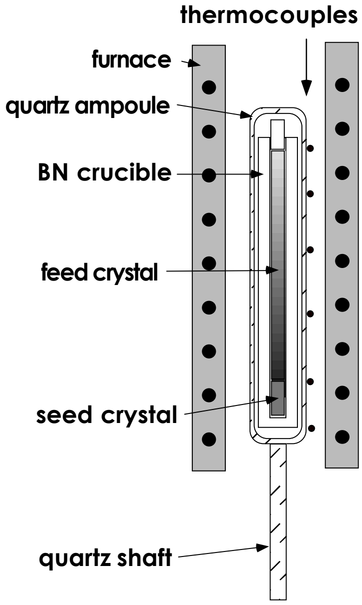


Fig. 1. Experimental setup of the TLZ method

3. Results and discussion

3.1 Compositional homogeneity

The sample translation rate was fixed to 0.22mm/h for all TLZ experiments. A moderate value of 7 deg/cm as a temperature gradient for homogeneous growth conditions is calculated at this translation rate1). Since the thermal conductivity of melt is about three times larger than that of crystals in InGaAs, "effective" temperature gradient should be lower than the "measured" temperature gradient of the ampoule surface. So the furnace should be set at steeper temperature gradients. At first, we tried to make use of the maximum temperature gradient of the furnace around freezing temperature. In these cases, the ampoule surface temperature gradient was about 30 deg/cm, and the axial compositional profiles of TLZ grown crystals were shown in Fig. 2. It is obvious that good compositional homogeneity was obtained for 5mm diameter samples but slight increase in InAs concentration was observed for a 10 mm diameter sample. This difference should be caused by the difference in effective temperature gradient originated by the radial temperature gradient. Such a radial temperature gradient should induce not only the compositional inhomogeneity but also the instability of the growth interface shape and result in poly-crystallization.

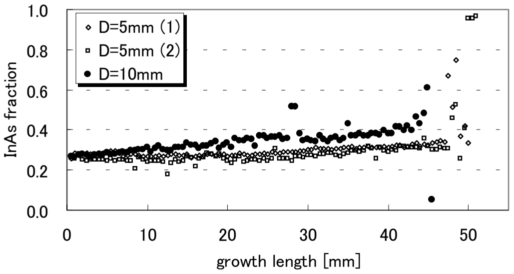


Fig. 2. Compositional profiles of TLZ grown crystals

Then, we tried to suppress the radial temperature gradient. In order to suppress the radial temperature gradient, the thermal flow should be controlled by setting temperatures of a furnace, ampoule and crucible design etc. A powerful method to control the thermal flow using a copper heat sink nearby the seed crystal was proposed by our research members 3).

Experimental setup of this method is schematically shown in Fig. 3. To avoid the reaction of As vapor dissociated from InGaAs sample with the copper heat sink, the quartz ampoule was separately sealed after evacuated. The quartz ampoule was carefully shape-controlled to obtain good thermal contact with the copper heat sink.

Compositional profiles of the grown crystals were shown in Fig. 4. Though the temperature gradient of the ampoule surface was not significantly affected by this modification of experimental setup, compositional profiles indicated the significant increase of the effective temperature gradient.

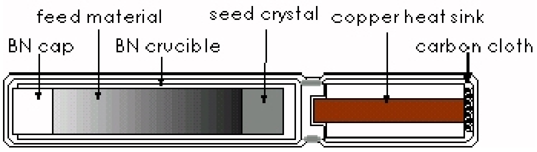


Fig. 3. Schematic drawing of the ampoule with a heat sink for the TLZ growth

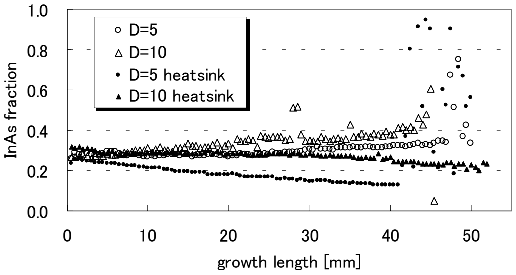
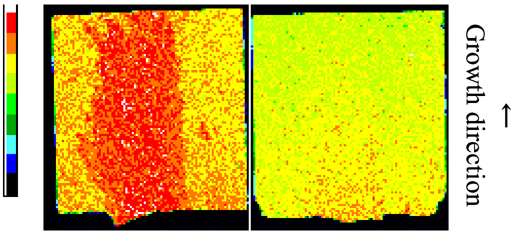


Fig. 4. Effect of a heat sink on compositional profiles of TLZ grown crystals

The radial temperature gradient also induces the radial compositional gradient as shown in Fig. 5(a), and this radial compositional inhomogeneity was also improved by using a heat sink (Fig. 5(b)).

These results confirmed the role of the heat sink, and proved qualitative relations between temperature gradients and growth rates. However, we should more accurately evaluate the effective temperature gradient, and further investigate the effect of convection on growth rate. In addition, there still remains difficulty of detail design of a heat sink. We are planning more experiments and numerical simulations to solve these issues. The microgravity experiments should make clear the effect of convection.



(a) (b)

Fig. 5. Indium concentration map of TLZ grown crystals (a)without heat sink, (b) with heat sink

3.2 Investigation of a seeding method

Seeding method is one of most technical part of crystal growth experiments. Small size crystals or needle like nuclei materials were often used for seed materials, so we tried in some experiments to use small size $In_xGa_{1-x}As$ single crystals and GaAs chips for a nucleus material. Small size $In_xGa_{1-x}As$ single crystals with x value of 0.1 - 0.3 were produced by the TLZ growth of 1.5 mm diameter experiments[4].

Figure 6 shows the seed part of the TLZ grown crystals. A 5mm diameter feed and a 1.5 mm diameter seed with a BN sheath were used in these experiments. In both cases, after back melt of the seed, a 1.5 mm diameter single grain over the seed crystal was grown, and poly-crystallization occurred at spreading points.

These results revealed a serious problem of changing growth diameter in the TLZ method. Since the characteristic compositional profile of liquidus-zone is realized based on homogeneous transportation by diffusion, change of the growth diameter spoils the transportation balance. Then it resulted in the compositional change and the poly-crystallization which should be caused by constitutional supercooling.

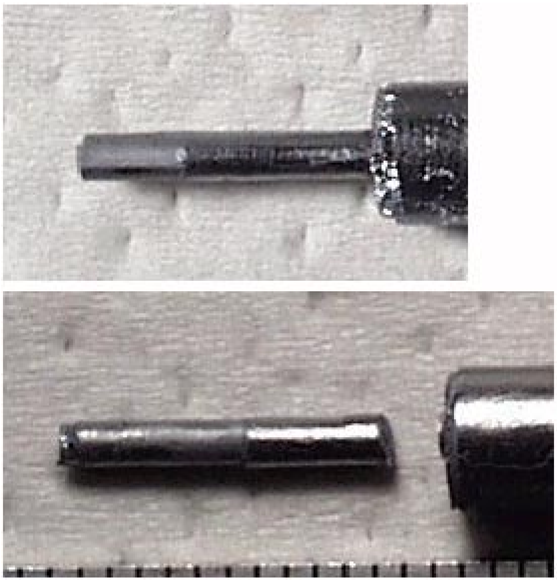
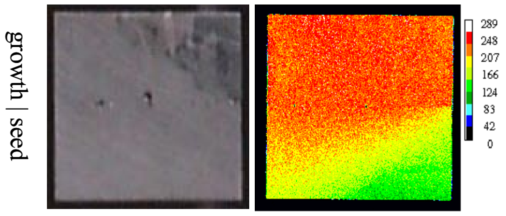


Fig. 6. Photos of seeding part of TLZ grown crystals.

In addition, at the initial stage of the TLZ growth, under-saturated melt zone should be formed in the relation between the feed concentration profile and the temperature profile. Then the under-saturated melt reacts with a seed and solid part of a feed to produce saturated melt (so called liquidus- zone) 1). If the cross section area of the seed crystal is smaller than the feed material, reaction with the initial melt and the seed crystal should advance into the seed crystal influenced by not only temperature but also mass transportation by diffusion. This results in the difficulty of controlling back melting length.

The initial solid-liquid interface position is a very important parameter in the TLZ method because it determines the growth composition.

Therefore, a seed crystal with the same size to a growth crystal diameter should be needed in the TLZ method. Figure 7 shows an example of successful seeding using the same size seed with diameter of 10 mm.



(a) (b)

Fig. 7 (a) Photo of polished surface and (b) In concentration map of the seeding part of a TLZ grown crystal.

3.3 Poly-crystallization in the TLZ growth

It was experimentally revealed that difficulties in growing single crystals by the TLZ method increased with the increase in growth diameter. Accompanying the increase in crystal diameter, radial temperature gradient and effects of convection should increase. So we proposed some hypotheses of poly-crystallization mechanisms concerning with the radial temperature gradient and convection.

- instability of growth interface by convection and radial temperature gradient
- transportation of solid particles by convection from solid-liquid coexistence region between the liquidus-zone and the feed crystal.
- local supercooling in the liquidus-zone by convection

Some of experimental results indicated instability of growth interface in the TLZ method. Figure 8 shows the latter half of a TLZ grown crystal (poly-crystallized). Both of the growth interface and feed interface were crooked and the liquidus-zone was broken. Thermodynamic examinations indicated that there are no driving forces to keep flat interface in the TLZ method because the liquidus-zone is ideally saturated in the whole regions5).

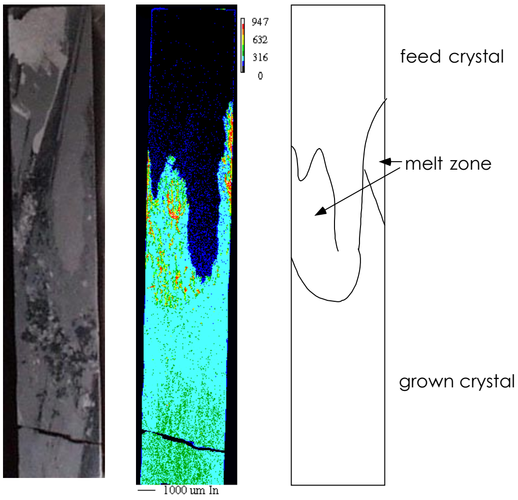


Fig. 8 Polished surface, In concentration map and schematic drawing of a quenched specimen grown by the TLZ method.

Though the densities of solid particles are lower than liquids in $In_xGa_{1-x}As$ system, it is suggested by the numerical simulations that few 10 micrometer particles should be transported by convection under 1G conditions[6].

It is obvious that the convective flow toward growth interface should induce the local supercooling in the TLZ method because the thermal diffusivity is superior to the mass diffusivity.

In the $In_xGa_{1-x}As$ system, if we set the growth direction vertical, the only driving force of convection is the radial temperature gradient. Then, we should take care of the experimental setup to suppress the radial temperature gradient. It is effective not only to keep compositional homogeneity but also to avoid poly-crystallization.

4. Summary

The TLZ method was applied to grow compositionally homogeneous $In_{0.3}Ga_{0.7}As$ single crystals.

Compositionally homogeneous growth was successful by the TLZ method for 5 mm diameter samples while some of experimental problems with increasing crystal diameter in the TLZ method were revealed. Seeding conditions and control of heat flow by using a heat sink were experimentally examined.

We conclude that the precise control of temperature gradient is necessary for the TLZ method.

References

1. H. Nakamura H. Kato, K. Kinoshita and S. Yoda, "Qualitative description of the concentration gradient partial melting method and application to $In_xGa_{1-x}As$", NASDA-TMR-000007E (2000), 15.

2. M. Tatsumi, H. Kato and K. Kinoshita, "Preparation of InGaAs starting materials having the gradient InAs concentration", NASDA -TMR -000007E (2000), 55.

3. S. Adachi, K. Kawachi, M. Kaneko, H. Kato, S. Yoda and K. Kinoshita, "Reliability investigation on numerical analysis by comparison with experimental result", NASDA-TMR-000007E (2000), 65.

4. K. Kinoshita, H. Kato, M. Iwai, T. Tsuru, Y. Muramatsu, S. Yoda, "Homogeneous $In_{0.3}Ga_{0.7}As$ crystal growth by the traveling liquidus zone method", J. Cryst. Growth, 225, (2001) 59.

5. H. Nakamura and K. Kinoshita, (must be written).

6. T. Maekawa, S. Matsumoto et al., to be published.