Verification of Homogeneous $In_xGa_{1-x}As$ Crystal Growth by the TLZ (Traveling Liquidus-Zone) Method

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<Abstract>

We have invented the TLZ (Traveling Liquidus-Zone) method as a new crystal growth method, which enables us to grow compositionally homogeneous mixed crystals of $In_xGa_{1-x}As$ (X:0.3). In this study, we examined the relation between sample translation rates and compositions of grown crystals, and verified the TLZ growth model. In addition, we examined the effects of temperature gradient. We tried the growth of a long homogeneous crystal. As a result, we obtained a homogeneous crystal at the sample translation rate in accordance with that calculated from the TLZ growth model. We were not successful in growing homogeneous crystals at other sample translation rates. We also succeeded in a homogeneous crystal growth at another temperature gradient, and a 60mm long homogeneous crystal longer than those crystals obtained so far. We thus verified that the TLZ growth model can be applied to the real crystal growth, and confirmed accuracy of the model prediction.

<Introduction>

Development of the optical communication system for high speed and broad band communication, is being promoted. We need semiconductor lasers which are stable at high temperature for building such system. But present lasers for the 1.3 μ m wave length optical communication system are unstable because confinement of carriers is not sufficient. $In_{0.3}Ga_{0.7}As$ is expected as a substrate material of 1.3 μ m wave length semiconductor laser, because effective carrier confinement is possible if combined with InGaAlAs barrier layer.

But homogeneous $In_xGa_{1-x}As$ crystal growth is very difficult because the gap between the liquidus and the solidus in the InAs-GaAs system is very large, especially the gap is the greatest near the composition of $In_{0.3}Ga_{0.7}As$.

Therefore, we need a method for overcoming such a large discrepancy between the liquidus and the solidus and we have invented the TLZ (Traveling Liquidus-Zone) method as a new crystal growth method. In this study, we examined the relation between sample translation rates and compositions of grown crystals, and compared the results with the prediction of the TLZ growth model. We also tried a long homogeneous crystal growth.

<Principle of the TLZ method>

We explain the TLZ method briefly (Fig.1). A feed with graded or step concentration of InAs is used and inserted in the experimental furnace. A part of the feed with low liquidus temperatures (the region of high InAs content) is melted and a narrow liquidus zone is formed. The solidification is driven by diffusion which occurs by the concentration gradient in the liquidus zone, and the freezing interface shifts upwards of the liquidus zone.

The spontaneous growth rate (V) is given by

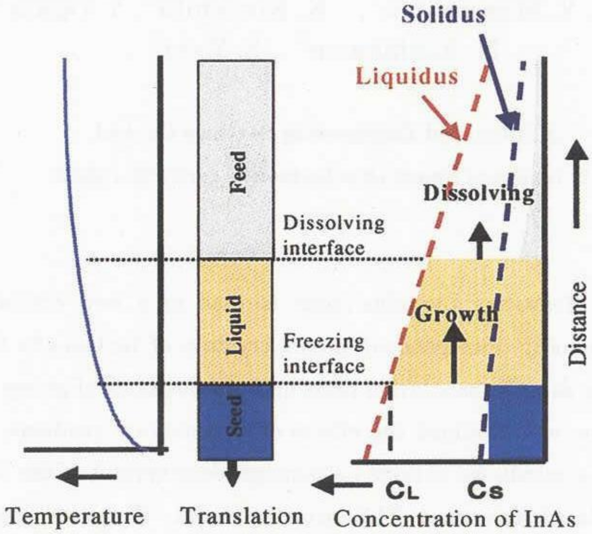

Fig.1. Principle of the TLZ method.

$$V = -D/(C_{LO} - C_{SO}) \times (\partial C_L/\partial T) \times (\partial T/\partial Z) \quad (1),$$

where D is the diffusion coefficient, C_{LO} and C_{SO} are the liquidus and solidus concentration at the freezing interface respectively, $(\partial C_L/\partial T)$ is a reciprocal of the liquidus slope and $(\partial T/\partial Z)$ is a temperature gradient. When the sample device is translated in the direction opposite to the spontaneous growth at the same rate of this spontaneous growth, the freezing interface is kept at the fixed position, and the crystallization temperature is constant. Thus, we can obtain homogeneous crystals.

<Experiments>

(1)Measurement of a temperature gradient in the liquidus -zone

① Measurement of a temperature gradient in the liquidus-zone is indispensable to calculate the spontaneous growth rate from the equation (1). We prepared a sample which has a seed and a feed with graded InAs concentration in a BN crucible. Figure 1 shows relation among the sample configuration, a temperature profile and the InAs concentration of the sample. After inserting the sample into the experimental furnace and keeping for a few hours, we quenched the sample to the atmospheric temperature. The temperature gradient measured at outside of the sample was 20℃/cm

The composition of the sample is analyzed by EPMA. There are the spontaneous growth solid region and the solid and liquid two phase coexistence regions at both ends of the liquidus-zone. We obtained solidus temperatures of these two regions from the compositions of solidus in these regions, finally, calculated the temperature gradient in the liquidus-zone by dividing the temperature difference by the distance between the two.

② We changed the outside temperature gradient from 20℃/cm to 4℃/cm, to investigate the accuracy of the model prediction even though we change a temperature gradient. We measured temperature

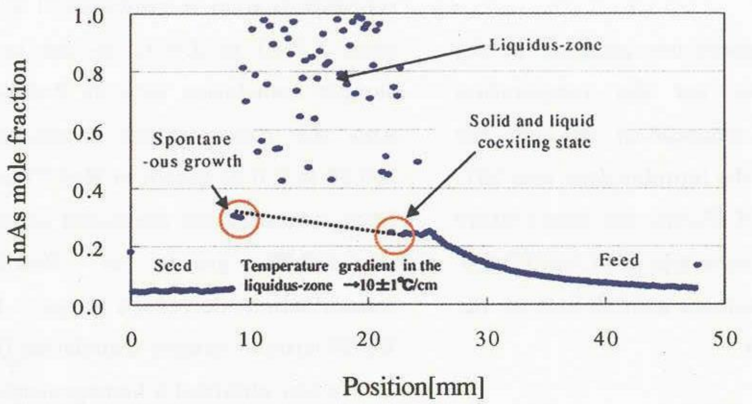

Fig.2. Temperature profile estimation (temperature gradient at outside of an ampoule 20℃/cm).

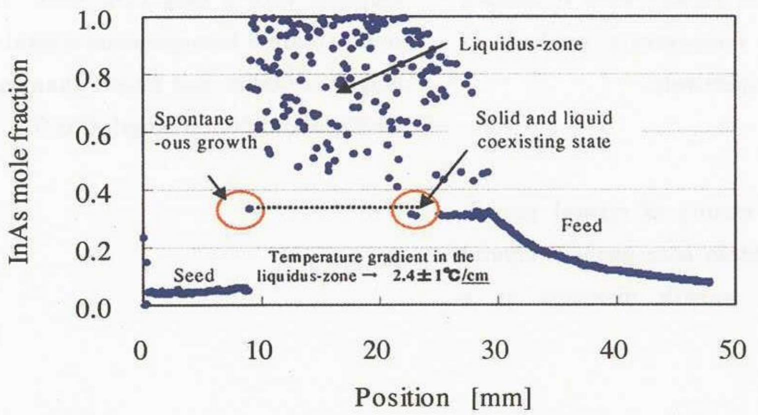

Fig.3. Temperature profile estimation (temperature gradient at outside of an ampoule 4℃/cm).

gradient in the liquidus zone in this case, too.

(2) Crystal growth

① We calculated the spontaneous growth rate by the TLZ model using the result of temperature gradient measurement and the calculated rate was 0.22mm/h for a measured temperature gradient of 10℃/cm. We carried out experiments at several different translation rates including the rate calculated by the model, 0, 0.20, 0.22 (which is calculated by the model), 0.24, 0.27mm. The compositions of all samples were analyzed by EPMA and those results were compared each other to examine the trend.

② We carried out an experiment under lower temperature gradient of 2.4℃/cm. The composition of the sample was analyzed by EPMA, too.

③ We increased the length of the liquidus-zone from 15 to 40mm by increasing the amount of InAs in a feed, to investigate the possibility of lengthening growth distance of a homogeneous crystal.

<Results>

(1)Measurements of temperature gradient in the liquidus–zone, when we set the temperature gradient outside of the ampoule at 20℃/cm, the temperature gradient in the liquidus-zone was 10℃/cm (Fig.2). In the case of 4℃/cm, the temperature gradient in the liquidus-zone was 2.4℃/cm (Fig.3). We calculated the spontaneous growth rate by the model equation as follows.

$$V = -D/(C_{LO} - C_{SO}) \times (\partial C_L/\partial T) \times (\partial T/\partial Z) \quad (1)$$

Here we used $1.5 \times 10^{-8} m^2/s$ as the diffusion coefficient, 0.83 as C_{LO}, 0.3 as C_{SO}, and 1/469 as $(\partial C_L/\partial T)$. The calculated results were 0.22mm/h and 0.05mm/h, for the temperature gradient of 10℃/cm and 2.4℃/cm, respectively.

(2) Crystal growth

① We describe about results of crystal growth experiments. We could obtain homogeneous crystal (X:0.31) (Fig.8) in the growth direction at a translation rate of 0.22mm/h which was calculated by equation (1). But we couldn't obtain homogeneous crystals at other rates. InAs concentration in a grown solid increased slightly from X:0.30 to X:0.31 in the sample grown at sample translation rate at R=0.24 mm/h (Fig.6). And the concentration increased largely from X:0.30 to X:0.33 grown at R=0.27mm/h (Fig.7). The InAs concentration decreased slightly from X:0.30 to X:0.29 grown at R=0.20mm/h. InAs concentration decreased largely from X:0.30 to X:0.23 without sample translation (Fig.4).

② We also obtained a homogeneous crystal (X:0.33) in an experiment of crystal growth under temperature gradient of 2.4℃/cm (Fig.10).

③ We carried out an experiment at 0.22 mm/h (at which we obtained a homogeneous crystal) , using a ampoule with a long InAs feed. As a result, we could obtain a homogeneous crystal (X:0.31), whose length is 60mm and longer than previous crystals having about 20mm length (Fig.9).

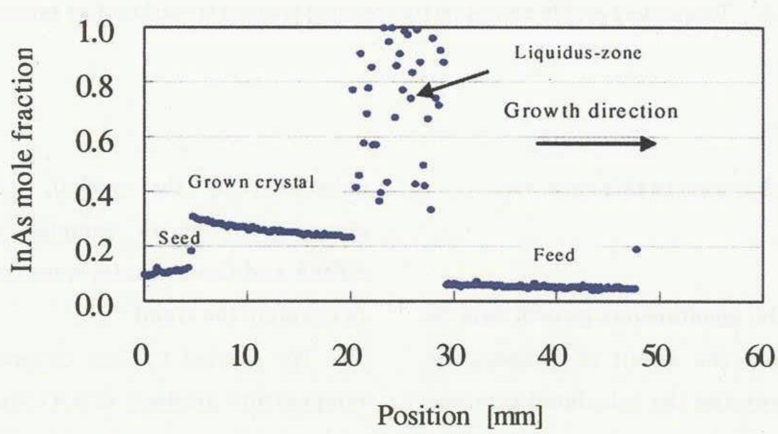

Fig.4. InAs concentration profile of crystal grown at R=0mm/h.

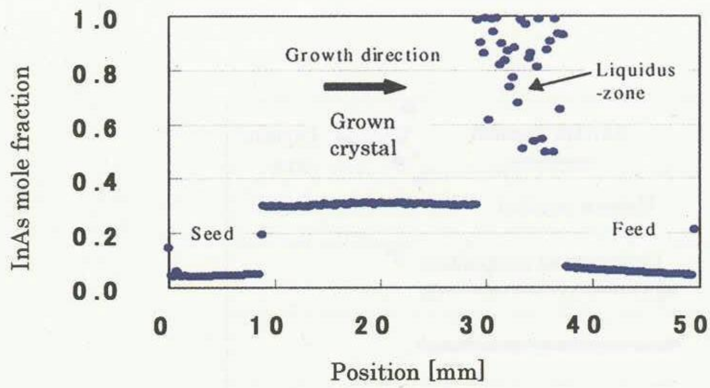

Fig.5. InAs concentration profile of crystal grown at R=0.20mm/h.

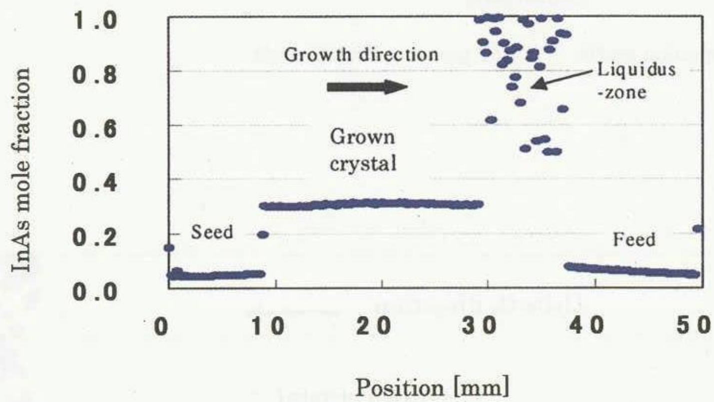

Fig.6. InAs concentration profile of crystal grown at R=0.24mm/h.

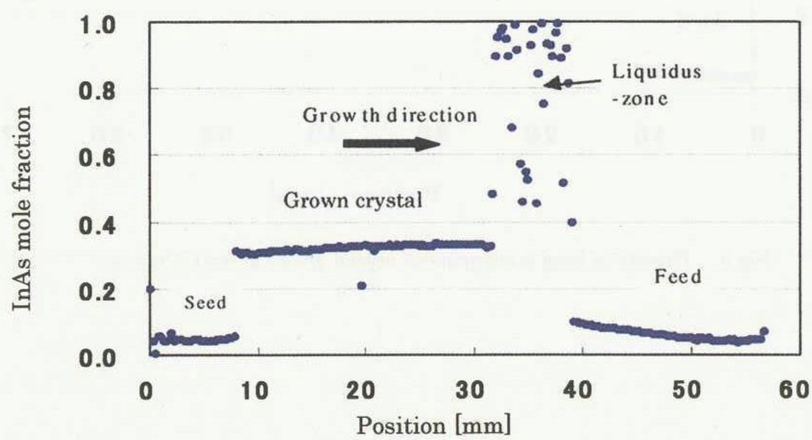

Fig.7. InAs concentration profile of crystal grown at R=0.27mm/h.

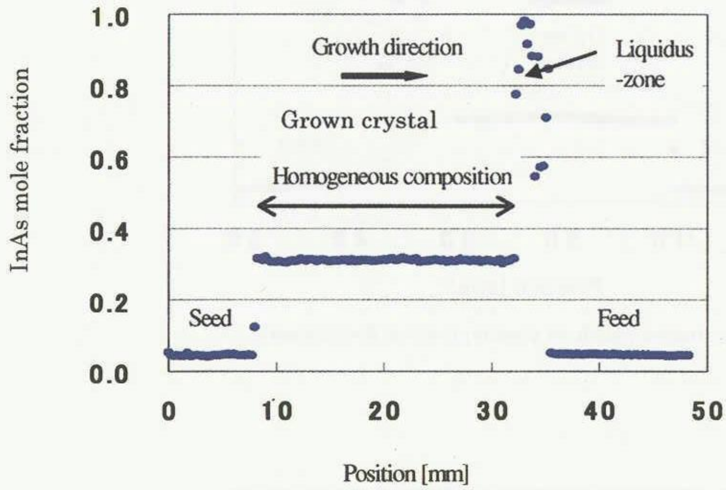

Fig.8. InAs concentration profile of crystal grown at R=0.22mm/h.

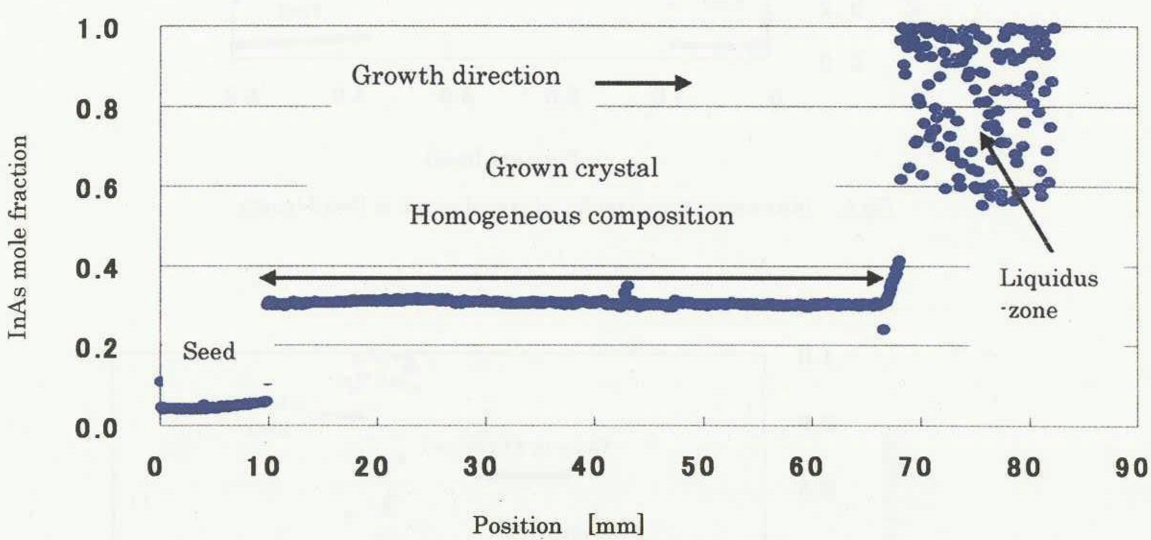

Fig.9. Growth of long homogeneous crystal grown at R=0.22mm/h.

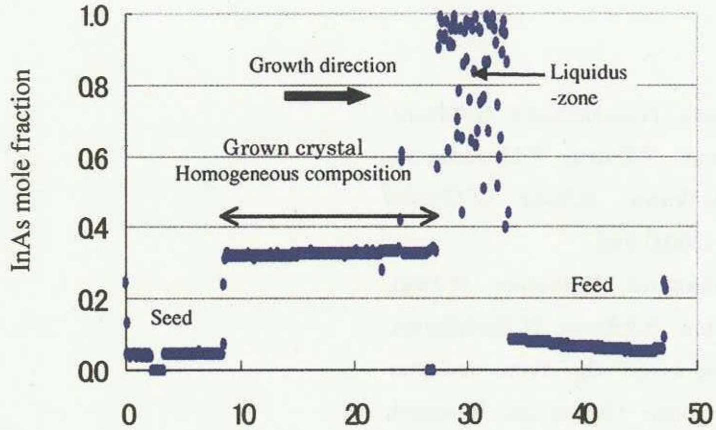

Fig.10. InAs concentration profile of crystal grown at temperature gradient in the liquidus-zone 2.4℃/cm, and R=0.05mm/h.

<Discussion>

We could obtain a homogeneous crystal (X:0.31), as a result of experiment at the translation rate of 0.22mm/h which coincides with a calculated value by the model (Fig.8). While, we couldn't obtain homogeneous crystals at translation rates other than the calculate value by the model. InAs concentration increased largely, at R=0.27mm/h which is faster than the calculated rate (Fig.7). We considered a freezing interface shifted to lower temperature region in this experiment. InAs concentration increased slightly, at R=0.24mm/h which is a little faster than calculated rate (Fig.6). InAs concentration decreased slightly, at R=0.20mm/h which is a little slower than calculated rate (Fig.5). InAs concentration decreased largely, without sample translation (Fig.4). We considered a freezing interface shifted to a higher temperature region in this experiment. We found that we couldn't grow homogeneous crystals at rates other than the rate calculated by the model, even by 0.01mm/h difference. Freezing interface was stable until the sample translation rate of 0.27mm/h and a single crystal was grown. Thus, the precision of the model is proved.

We could also obtain a homogeneous crystal, at a temperature gradient in the liquidus-zone of 2.5℃/cm (Fig.10). This result means that TLZ growth model can be applied in a wide range and we can change parameters in the model.

About a longer homogeneous crystal growth, initially we were concerned that we weren't able to obtain a homogeneous crystal by using a wide liquidus-zone because the temperature gradient in the liquidus-zone would change largely according as crystal growth. But we could obtain a long homogeneous crystal (Fig.9). We confirmed validity of increasing liquidus-zone and possibility of lengthening homogeneous crystals.

<Conclusions>

As results of a series of experiments, we could verify that the model equation of the TLZ method. The success of longer homogeneous crystals will open the door to the device application.

We will further aim at obtaining larger diameter single crystals, in advance to the experiment in μ-gravity to develop the model of the TLZ method.

<References>

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