

Modeling and Experimental Study on the Traveling Liquidus-Zone Method

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Abstract

We have developed one dimensional TLZ (Traveling Liquidus-Zone) growth model and have revealed the importance of accurate measurements of temperature gradients in the liquidus-zone because sample translation rates for growing homogeneous crystals are directly related to the temperature gradient according to our model. For this purpose, we invented a new method to determine the average temperature gradient in the zone experimentally. In addition, we have measured temperature profiles in dummy samples by using thermocouples and utilized these results for developing numerical analyses of temperature distribution in the sample device. As a result, understanding of the TLZ growth mechanism has been deepened including constitutional supercooling during the crystal growth. Here, experimental results on temperature profile (temperature gradient) measurements and compositional profile analyses based on the TLZ model and measured temperature gradients are summarized together with the TLZ model over view.

1. Introduction

We have invented a new crystal growth method that enables us to grow compositionally homogeneous mixed crystals such as $\text{In}_{1-x}\text{Ga}_x\text{As}$, $\text{Si}_{1-x}\text{Ge}_x$ and so on and named it the traveling liquidus-zone (TLZ) method¹⁾ after the feature of the method. By applying the TLZ method to the growth of $\text{In}_{1-x}\text{Ga}_x\text{As}$, we have obtained homogeneous $\text{In}_{1-x}\text{Ga}_x\text{As}$ crystals with controlled InAs mole fraction in the range $0.2 \leq x$

≤ 0.35 and concentration fluctuation less than 0.02 to a length longer than 20 mm. An example of compositional profile obtained by the TLZ method is shown in Fig. 1.

The principle of the TLZ method is reported elsewhere¹⁻⁴⁾. Therefore, it is briefly summarized here. Figure 2 shows relations among the sample configuration, temperatures and equilibrium phases of the sample in the InAs – GaAs system. The

whole of the sample is heated at a temperature gradient of about 10 to 20°C/cm. A feed with graded or step concentration of InAs is used and part of the feed with low liquidus temperatures (the region of high InAs content) is melted and a narrow liquidus-zone is formed under a temperature gradient of about 10 to 20°C/cm. This liquidus-zone travels spontaneously by the diffusion due to the concentration gradient between the two interfaces (seed-liquidus and liquidus-feed interfaces) and by the segregation at the freezing (seed-liquidus) interface. Diffusion and segregation are driving forces in this growth method.

The spontaneous growth rate V is described as follows²⁻⁴⁾,

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

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. Equation (1) is derived because the solute concentration is almost saturated to the equilibrium concentration when the zone width is narrow at such low temperature gradients as described above. The TLZ (Traveling Liquidus-Zone) method has been named after this character in the growth method. When the sample device is translated in the direction opposite to the spontaneous growth at the same rate of this spontaneous growth rate, the freezing interface is kept at the fixed position, namely the freezing temperature is fixed as shown in Fig. 3 and homogeneous mixed crystals can be grown.

If the zone width is narrow enough, the slope

of the liquidus and the temperature gradient can be considered constant in the whole liquidus zone. Then, the growth rate is fixed constant irrespective of the zone width. This is important because zone width gradually decreases according as crystal growth proceeds due to dilute InAs concentration in the feed. When the growth rate is constant, one can grow homogeneous mixed crystals merely by translating the sample device at the constant translation rate. This is a very easy way to obtain homogeneous crystals. As you can see from the equation (1), the spontaneous growth rate is determined by the temperature gradient, then measurement or evaluation of accurate temperature gradient in the zone is the most important for obtaining homogeneous crystals. Therefore, we made much effort to measure or to evaluate the temperature gradient in the zone this year. Here, we report our experimental activities in determining temperature gradients in the zone and the model evaluation based on the analysis of the relationship between measured temperature gradients and compositional profiles obtained by the TLZ growth. Numerical analyses of temperature distributions in the zone are written elsewhere in this brochure⁵⁾.

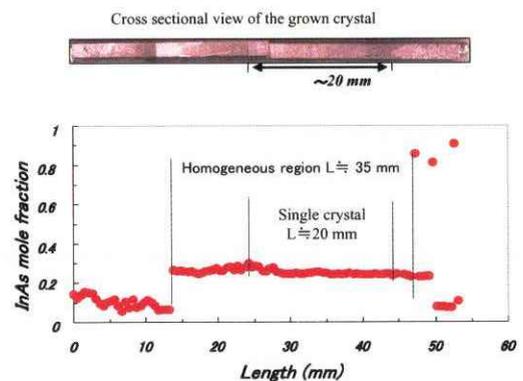


Fig. 1. An example of a compositional profile grown by the TLZ method.

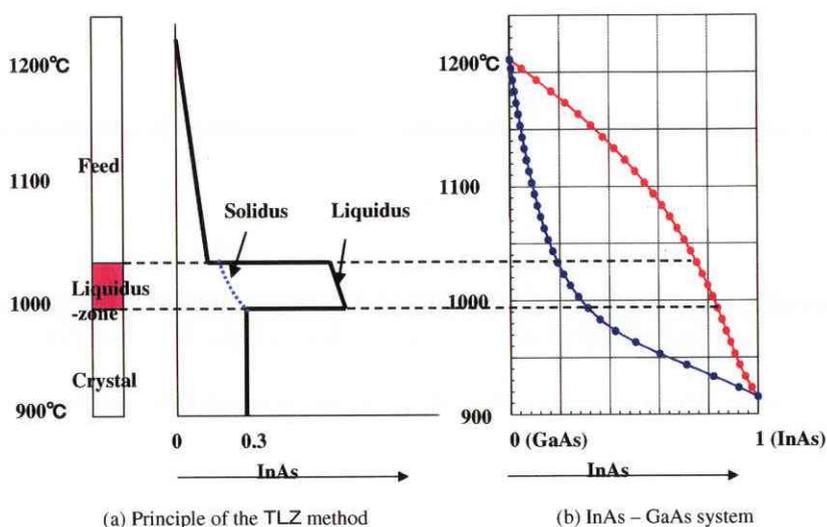


Fig. 2. Principle of the TLZ method.

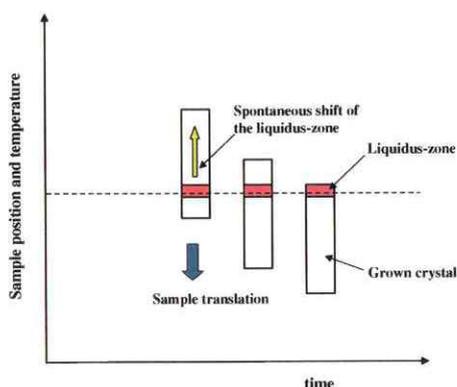


Fig.3. The principle of the maintaining zone at the fixed position.

2. Measurements of temperature gradient in the liquidus-zone

Direct measurement of the temperature distribution in the liquidus-zone is desirable but such measurement is very difficult. If we want to use

thermocouples for temperature measurements, we must find out a way to insert a thermocouple safely into a reactive melt containing arsenic. In addition, we must find out a way to seal thermocouples with $\text{In}_{1-x}\text{Ga}_x\text{As}$ melt having high vapor pressure.

Another way is to measure the liquidus or solidus concentration of the sample because these equilibrium concentrations can be converted into temperatures based on the phase diagram. However, if we measure the liquidus-zone composition of quenched samples, local fluctuation of the composition due to dendrite growth will hinder the measurements by causing scattering of concentration. The solidus composition, on the other hand, can be determined without such problem arisen from dendrite growth. However, solidus composition at the dissolving (liquidus-feed) interface cannot be measured in general due to lack of enough thickness of the layer. This is a problem in utilizing solidus composition.

Finally, we found a good way to determine the

equilibrium composition at the dissolving interface by causing solid and liquid two phase coexisting state⁴⁾, that is, when the solid solution is heated to temperatures higher than the solidus and lower than the liquidus for the given composition, solid and liquid two phases are separated at the quantitative ratio of the distance from the liquidus and the solidus compositions, respectively, and the solidus composition can be determined. Therefore, we prepared a special feed with graded InAs concentration along the axis for this measurement: the InAs mole fraction gradually decreases from 1.0 to 0.05 in the direction from one end to the other end. We set this feed in a furnace together with a seed so that the higher InAs part locates the seed side and heated the whole sample at the same conditions in the TLZ growth, namely, the temperature of the freezing (seed-liquidus) interface was about 1030°C and the temperature of the dissolving (liquidus-feed) interface was about 1050°C. Then, the high InAs content part of the feed was melted to form the liquidus-zone, and the adjacent part to the liquidus-zone got to the composition between the solidus and the liquidus due to the graded InAs concentration in the feed. After 5 hours of soaking, the sample was quenched.

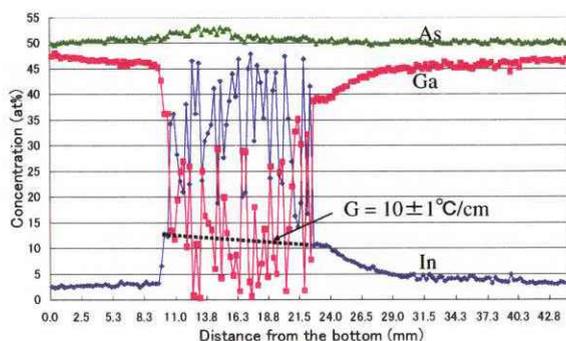


Fig. 4. Temperature profile estimation using two solidus compositions at the freezing interface and at the dissolving interface.

Measured compositional profile for a 2 mm diameter sample is shown in Fig. 4. The reason why the 2 mm diameter sample was used is to suppress convection in the liquidus-zone by reducing the sample diameter. From the figure, we notice that the solid and liquid two phases coexistence region near the dissolving interface was really formed and the InAs mole fractions of the solidus are ranging from 0.212 to 0.206. Temperatures correspond to these compositions are known from the phase diagram and they are between 1048.4 and 1050.7°C. We also notice that InAs mole fractions of the grown crystal are in the range between 0.248 and 0.256. These concentrations corresponds solidus temperatures from 1035.7 to 1037.4°C. The distance between the freezing interface and the dissolving interface is 13.3 mm. Therefore, the average temperature gradient in this zone is measured to be 10 ± 1 °C/cm.

3. Temperature measurements in dummy samples

As stated in the previous section, temperature profile measurements using thermocouples in the real sample are very difficult. Instead, temperature distribution measurements in dummy samples using thermocouples have been performed for the purpose of estimating temperature profile in real samples and obtaining reference data for thermal analysis. The set of materials used for a dummy sample device is mullite and alumina. Alumina has higher thermal conductivity than mullite and was used as a liquidus-zone dummy material. As a solid part dummy material, mullite was selected. This combination gave an approximate ratio of 2 in thermal conductivity. Six thermocouples were set in the sample: three are for axial temperature profile measurements and remaining three are for radial temperature profile measurements. In addition,

more 6 thermocouples were set outside the dummy sample for measuring temperature profiles in a furnace tube. The schematic of the sample device is shown in Fig. 5.

Thermal conductivities of the dummy sample materials are listed in Table 1. Three different heating parameters in a furnace were set and respective temperature profiles in the dummy sample were measured.

Figure 6 shows the relationship between radial temperature gradients and axial temperature gradients in the dummy sample. The radial temperature gradients are approximately proportional to the axial temperature gradients. It should be noted that the

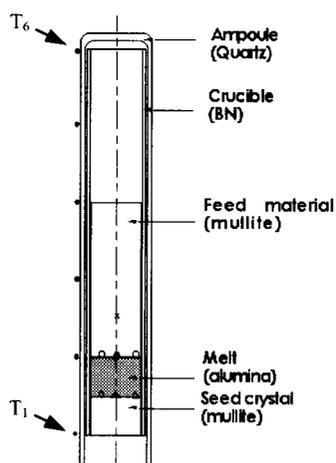


Fig. 5. Schematic of the sample device, T₁ to T₆ denote thermocouple positions.

Table 1 Thermal conductivity of materials used in the dummy sample.

	λ [W/mK]
In _{0.8} Ga _{0.2} As melt	18.9
In _{0.3} Ga _{0.7} As crystal	3.4
BN (Denka N-1)	23.7
Alumina	3.4
Mullite	1.8

temperature is the highest at the center and decreases in the radial direction.

Figure 7 shows the relationship between the outside axial temperature gradients and inside axial temperature gradients. The higher the outside temperature gradient, the higher the inside temperature gradient is. In the figure, open circles show temperature distribution in mullite (feed part in the dummy sample) and solid circles show temperature distribution in alumina (melt part in the dummy sample). The figure shows that the temper-

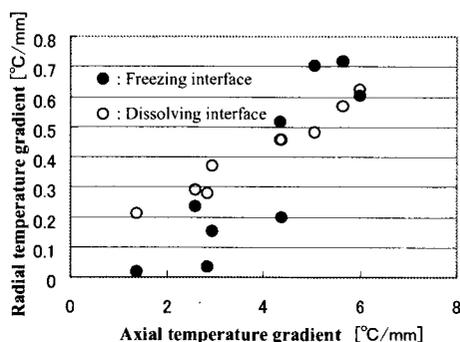


Fig. 6. Relationship between the axial temperature gradient and the radial temperature gradient in a dummy sample device.

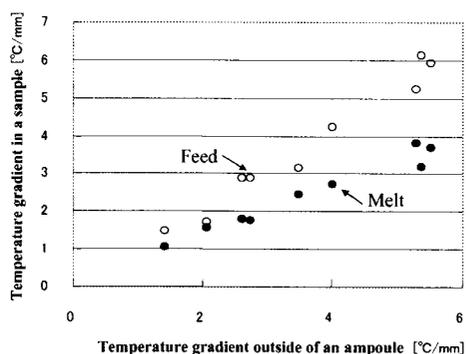


Fig. 7. Relationship between the outside axial temperature gradient and inside axial temperature gradient at two positions corresponding to a melt and a feed in a dummy sample device.

ature gradient in the alumina (melt part) is lower than that in the mullite (feed part). This is because that the thermal conductivity of alumina is higher than that of mullite.

Obtained data are consistent with the environmental thermal condition change and also consistent with the difference in thermal conductivity between the liquid part and the solid part. The data were used as reference data to thermal numerical analysis. Detailed comparison of the obtained data with thermal analysis is described in the latter chapter of this brocher⁵⁾.

3. Compositional profile analyses based on the TLZ model

Supposing that the linear concentration gradient G/m is maintained throughout the liquidus-zone (where G is the temperature gradient in the zone and m is the slope of the liquidus as described bellow), solute concentration in the zone is expressed as a function of distance from the freezing interface z ,

$$C_L(z) = C_{L0} + \frac{kG}{m}z \quad (2),$$

where $1/m = \partial C / \partial T$, $G = \partial T / \partial z$, and k is segregation coefficient. When the sample translation rate is R , the position of the freezing interface after elapsed time t is written as $z = (V + R)t$, while the length of the grown crystal L is Vt . Then the solute concentration at the grown length L is described as,

$$\frac{\partial C_s}{\partial L} = k \frac{\partial C_L}{\partial L} = \frac{kG}{m} \left(1 + \frac{R}{V} \right) \quad (3)$$

It is obvious that if $R = -V$, no concentration change occurs during the solidification. If $R = 0$ the resultant solid composition is written as a function of the growth length L .

$$C_s(L) = C_{s0} + \frac{kG}{m}L \quad (4)$$

This concentration profile is identical to the solidus line. If the sample translation rate is higher than the spontaneous growth rate, the freezing interface shifts towards the lower temperature side and solute concentration of the grown crystal becomes higher and higher as crystal growth proceeds. Supposing that $R = -2V$, the solute concentration obtained based on eq. (3) is written as,

$$C_s(L) = C_{s0} - \frac{kG}{m}L \quad (5)$$

Figure 8 shows the results of the numerical analysis based on our TLZ model as a parameter of the sample translation rate R . In the analysis, temperature gradient in the zone is supposed to be $10^\circ\text{C}/\text{cm}$ and $m = -461$ is used, which is obtained from the InAs - GaAs phase diagram. The diffusion coefficient value of $D = 1.5 \times 10^{-8} \text{ m}^2/\text{s}$ at 1030°C was used. This diffusion coefficient value was obtained in microgravity by using the sounding rocket⁶⁾. Then, the spontaneous growth rate was calculated to be 0.22 mm/h .

Figure 9 shows the InAs concentration profile obtained at the sample translation rate of 0.22 mm/h at a temperature gradient of about $10^\circ\text{C}/\text{cm}$. This figure shows that the grown crystal is very homogeneous with the InAs mole fraction of about

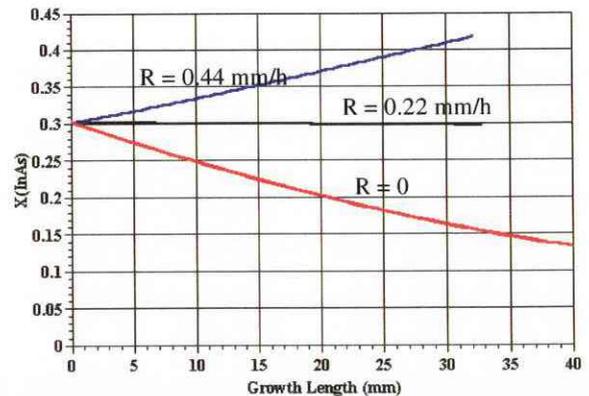


Fig. 8. Results of compositional profile analyses based on the TLZ model.

0.28 to the length of about 30 mm as our growth model predicts. However, InAs mole fraction slightly decreases at a latter part of the grown crystal. This may be caused by the temperature gradient difference due to the decrease of liquidus-zone thickness occurred by the expense of InAs as crystal growth proceeded. The decreasing rate, however, is very small and it can be said that the whole crystal is almost homogeneous.

Figure 10 shows the InAs concentration profile for a crystal grown at $R = 0$. In this case, the sample diameter was 2 mm. As predicted from the numerical analysis, InAs concentration decreased in the growth direction at $R = 0$. Figures 9 and 10 show that our TLZ growth equation well describes the spontaneous growth rate and well predicts compositional profiles of grown crystals.

The TLZ model is derived by assuming the diffusion controlled mass transport state. In general, this condition is not fulfilled on the ground because of the presence of convection but obtained compositional profiles seems to suggest that convective flow velocity is very small in the TLZ method even on the ground. The small convective flow velocity in the liquidus-zone was due to the smallness of the sample diameter as well as the small

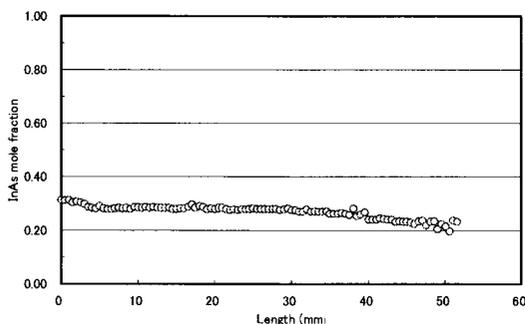


Fig. 9. InAs concentration profile of a TLZ grown crystal along the growth axis; $R = 0.22$

mm/h and sample diameter = 10 mm at the estimated temperature gradient in the zone = $10^{\circ}\text{C}/\text{cm}$.

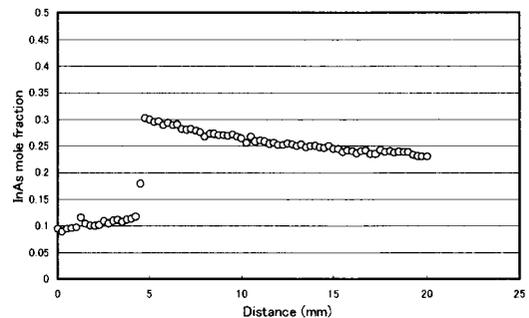


Fig. 10. InAs concentration profile of a TLZ grown crystal at $R = 0$ mm/h. The sample diameter is 2 mm.

zone thickness. In addition, based on the fluid flow analysis, it is shown that two convection vortices in the liquidus-zone are formed and they reduce material transport due to convection in the case of $\text{In}_{1-x}\text{Ga}_x\text{As}$ melt in the top-heated and bottom-cooled configuration.

In conclusion, it can be said that the compositional homogeneity of the TLZ-grown crystals is based on good controllability and stability inherent to the method. Long homogeneous mixed crystals controlled to a desired solute concentration can be grown by merely translating samples at rates calculated from our model equation (1) without any try and errors.

Summary

Our TLZ growth model predicts homogeneous mixed crystal growth conditions when the temperature gradient in the liquidus-zone is known. We therefore made much effort to measure the temperature gradient in the zone and found a method

utilizing two solidus compositions near the freezing interface and the dissolving interface. By using this method, the temperature gradient in the zone was measured to be about 10°C/cm in our experimental conditions and the sample translation rate for obtaining uniform composition was calculated to be 0.22 mm/h. The compositional profile of a crystal grown at a sample translation rate of 0.22 mm/h was very uniform and showed the coincidence with the prediction obtained by our TLZ growth model equation.

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