

# Quantitative Modeling of the Travelling Liquidus-Zone Method

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Travelling Liquidus-Zone (TLZ) Method, which was developed by NASDA, is a powerful method to grow compositionally homogeneous semiconductor mixed crystals. Experimentally, successful results have been obtained in our laboratory. However, there was no quantitative model, which explains the homogeneous growth mechanism or the applicability of the method.

In the present study, one-dimensional quantitative model of the TLZ method has been developed. Some representative results such as a synchronized sample translation rate, maximum growth length, time sequence of the liquidus zone width, and limitation of the TLZ method due to the restriction of the initial zone length, have been calculated using the model. Consequently, quantitative evaluation of TLZ growth conditions became possible.

## 1. Introduction

Compound semiconductor mixed crystals such as  $\text{In}_x\text{Ga}_{1-x}\text{As}$  are one of promising basic materials for opto-electronic devices such as near infrared laser diodes. But it is much difficult to grow compositionally homogeneous mixed crystals since there is large compositional discrepancy between the liquidus and the solidus. Though it is enough for growing the homogenous crystal to fix the interfacial temperature, the operation is not easy because the instantaneous growth rate is functions of both local temperature and solute concentration of the liquid. To overcome the problem, four types of investigations have been performed. The first one is to monitor the interface position and temperature distribution simultaneously. In-situ

observation using X-ray microscopy or infrared microscopy, has been performed by several investigators [1-3]. However the methods are not commonly applicable since they need complicated technology. The second type of growth method is to control the solute concentration near the interface constant by additional operation such as stirring of a melt or solute supply. Continuously feeding LEC method [4, 5] or BGCC method [6] are such cases. These methods have potential to grow homogeneous crystals, in principle. However, the applicability of these methods is limited since these methods have to control many parameters. The third type is to utilize steady state concentration gradient in the directional solidification. Quantitative solute redistribution phenomenon for directional

solidification, was first analyzed by Tiller et al. [7]. They solved the concentration distribution as a function of distance from the freezing interface. If the steady state growth occurs, the solute concentration at the interface becomes to be equal to solid concentration divided by partition coefficient, and the concentration far from the interface becomes to be equal to the solid concentration. So, principally, we can grow a homogeneous crystal if we maintain the steady state growth conditions. However, it is impossible to maintain the steady state condition on the ground since there is convection, which disturbs the steady state concentration distribution. Microgravity environments seemed to be effective to suppress the convection, and a number of experiments were performed. However, perfect diffusion limited concentration profiles in mixed crystals have not been obtained except for the result obtained in EURECA, an unmanned spacecraft mission [8], because of residual gravity or g-jitter on board the space shuttle [9]. In addition, Weber et al. designed the method to reduce the initial transient region and to elongate the homogeneous concentration part by applying ab-initio solutal boundary layer in the feed liquid [10]. Duffar et al. carried out microgravity experiment based on this concept but failed to grow homogeneous crystals due to the pre-growth stage homogenization of the liquid during heating period and due to the effect of the residual gravity [11,12]. From their result, it is shown that the homogeneous solidification is difficult even in space if we apply growth methods, which are based on directional solidification type growth, such as the Bridgman method or the gradient

freezing method.

The fourth method is to utilize zone method. There are some types of zone melting method, but among these methods, temperature gradient type zone melting method, which was first developed by Pfann [13], can be successful to grow semiconductor mixed crystals with homogeneous composition. Suzuki et al. modified the method and proposed multi-component zone melting method, which controls both the temperature decreasing rate and the sample translation rate [14]. Kodama et al. [15] and Nishijima et al. [16] applied multi-component zone melting method, and succeeded in growing  $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}$  homogeneous crystals although the reproducibility was not good. Travelling Liquidus-Zone Method (TLZ Method) has been developed in our research team, and applied to grow homogeneous  $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}$  crystals [17]. Using this method, we have obtained compositionally homogeneous  $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}$  crystals with 40mm in length and 2mm in diameter. The method was found to be superior to the control of the growing solid composition with sufficient reproducibility. Moreover, we have already reported qualitative description to explain the reason why the method can produce homogeneous crystal [18]. However, there was no quantitative model to describe the homogenization mechanism of the TLZ growth, in spite of the early theoretical works by Tiller et al. [7] or Hurle et al. [19, 20] because they focused on the purification mechanism or external force effects.

In this work, we have developed one-dimensional TLZ solidification model to

explain the growth sequences quantitatively, and to clarify the limitations to utilize the method.

## 2. Concept of the TLZ method

The TLZ method is categorized as one of temperature gradient type zone methods (TGZ), which utilize unidirectional temperature gradient. However, the TLZ method focuses on growing compositionally homogeneous mixed crystal by introducing synchronized sample translation. In this section, we describe the concepts of the TLZ method.

Figure 1 indicates the concept of the TLZ method. The important concepts are as follows.

### (1) Interfacial equilibrium

Since the solidification rate of the TLZ method is relatively low, we can assume that the solid-liquid equilibrium is established at the interface.

### (2) Spontaneous concentration gradient

Like TGZ, TLZ method utilizes unidirectional temperature gradient. Since the temperature gradient applied in the TLZ method is relatively low, both the liquidus and the solidus compositions in the liquid zone in fig.1, can be approximated by linear lines with negative inclination. Though both the seed-liquid interface and the feed-liquid interface are assumed to be in equilibrium, the liquid compositions of both ends must be on the liquidus line. Since these two boundaries act as liquid composition stabilizers, the resultant concentration gradient in the liquid zone becomes linear. More detailed discussion for the

stabilization ability is described in Appendix A.

### (3) Negligible diffusion rate in solids

Since diffusion coefficient in solid is much lower than that in liquid, the effect of mass transport in the solid can be negligible. We estimated that the diffusion coefficients of InAs or GaAs in  $\text{In}_x\text{Ga}_{1-x}\text{As}$  solid are less than  $10^{-14}\text{m}^2/\text{s}$  [21-23]. The value is about 5 orders of magnitude less than that in the solution [24]. We also evaluated that concentration boundary layer in solid feed, which represents the concentration change region, is less than  $1\mu\text{m}$  in the growth of the TLZ method. The detailed examination of this effect is described in Appendix B.

So we assumed that the mass transport in the solid is zero, and the solid-liquid equilibrium reaction occurs only at the interface. Using this approximation, we can consider that the solid feed dissolves with its own composition

### (4) Spontaneous growth and dissolution

As described above, a linear concentration gradient is established in the liquid zone. The gradient acts as driving force of solute transport followed by Fick's law. Due to the solute transport, spontaneous growth occurs at the seed interface, and spontaneous dissolution occurs at the feed interface.

### (5) Sample translation with synchronized rate

In the case of compositionally homogeneous growth for concentrated alloys, it is necessary to keep interfacial temperature to the desired solidus temperature. In general, it is difficult to keep the interfacial temperature

constant since the spontaneous growth rate depends on both the temperature gradient and the concentration gradient. However, if the liquidus zone width is relatively narrow, concentration gradient is assumed to be linear and the gradient is governed only by the temperature gradient. We can easily calculate the spontaneous growth rate if we know the concentration gradient near the interface. So, we can grow compositionally homogeneous crystals by translating the sample with the synchronized rate to keep the interfacial temperature constant. This synchronized sample translation is the key point of the TLZ method.

#### (6) Comparison to other method

From the above description, it was found that the TLZ method has the following advantages.

##### 1) Well controllable temperature

A simple temperature gradient type furnace is sufficient to utilize the TLZ growth. Though usual zone method has to apply a steep and symmetric temperature gradient, both the temperature stability and the controllability become wrong. In addition, the TLZ method applies a relatively low temperature gradient, which results in good temperature stability. This relatively low temperature gradient is also useful to reduce thermal stress.

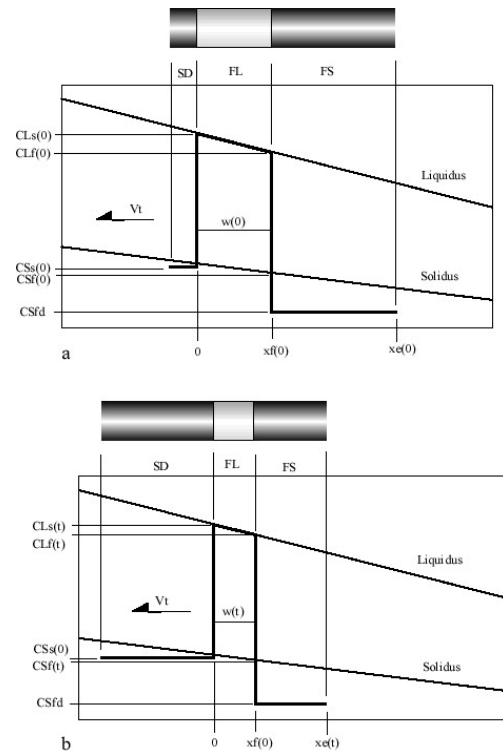
##### 2) Simple control parameter

If the initial seed position and the temperature gradient were determined, the control parameter of the TLZ method is only the sample translation rate, which can easily be calculated by the initial conditions. Other methods such as composition supplementary Bridgman method

have to control many experimental parameters, which results in experimental complexity and lowering reproducibility.

##### 3) Stability to the convection

Since the TLZ method is one of the zone methods with relatively low temperature gradient, natural convection in the liquid is relatively suppressed even on the earth. Since the residual convection is still serious under space station environments in the case of normal freezing, the utilization of the TLZ method is better in microgravity environments.



**Figure 1. Schematic drawing of the TLZ method**

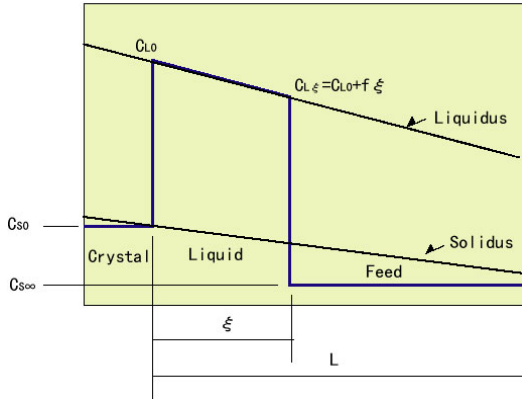
(a) Initial stage of the TLZ growth. SD, FL, FS indicate seed, fluid, feed, respectively. The synchronized sample translation to keep the seed-fluid interface temperature, constant, is applied. (b) After some duration. The zone width

decreases due to the growth of the seed.

### 3. Quantitative modeling of the TLZ method

#### (1) Geometry and assumptions

Simple TLZ geometry is shown in Fig.2. Solidification proceeds from the left side to right side at a spontaneous growth rate. Synchronized sample translation, which means the translation with the same velocity and opposite direction to the spontaneous growth direction, is assumed. Since the interfacial temperature is kept constant, composition of the growing solid is kept constant. The liquid compositions at the seed interface and the feed interface are assumed to be those of the liquidus composition at that temperature. The concentration gradient in the liquid zone is assumed to be constant because of relatively higher diffusion rate of the solute in the liquid.



**Figure 2. Geometrical model of the TLZ method**

#### (2) Synchronized sample translation rate

From the mass balance consideration, the following relation has to be satisfied at the growing interface if the constant concentration

gradient is maintained in the liquid.

$$V(C_{L0} - C_{S0}) = -D \left. \frac{\partial C_L}{\partial Z} \right|_{Z=0} = -Df \quad (1)$$

where, V is the spontaneous growth rate, D is the diffusion coefficient of the solute in the liquid, C<sub>L0</sub> and C<sub>S0</sub> are solute concentrations of the liquid and the solid at the seed interface. f is the liquidus concentration gradient in the liquid zone, and represented as follows.

$$f = \left( \frac{\partial C_{L,eq}}{\partial T} \right) \left( \frac{\partial T}{\partial Z} \right) = \left( \frac{\partial C_{L,eq}}{\partial T} \right) G \quad (2)$$

So, the spontaneous growth rate under the linear concentration gradient is written as follows.

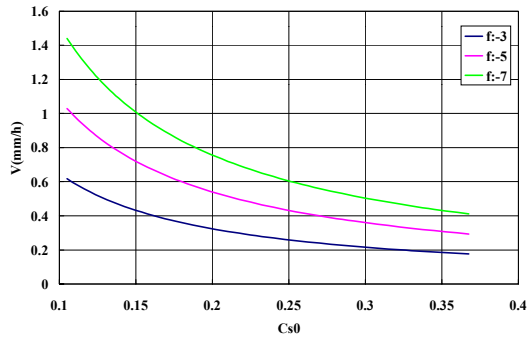
$$V = - \frac{Df}{(C_{L0} - C_{S0})} \quad (3)$$

To keep the interfacial temperature at a constant value, the sample has to be shifted toward the left side of fig.2 with identical rate to the spontaneous growth rate. By this operation, the relative position of the interface is fixed at the desired temperature, which results in the homogeneous growth.

So, the synchronized sample translation rate,  $V_T$  is given as follows

$$V_T = \frac{Df}{(C_{L0} - C_{S0})} \quad (4)$$

Figure 3 shows the synchronized sample translation rate as functions of f and C<sub>S0</sub>.



**Figure 3. Synchronized sample translation rate**

(3) Maximum growth length

Based on mass balance consideration, the amount of the solute in the liquid zone,  $Q_L$ , is represented as follows.

$$Q_L = \frac{(C_{L0} + C_{L\xi})}{2} \xi = \left( C_{L0} + \frac{f\xi}{2} \right) \xi \quad (5)$$

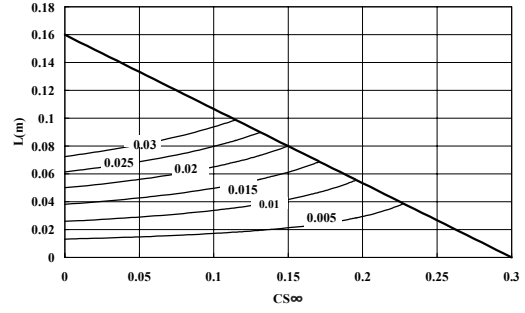
Since the average solute concentration must be identical to the growth composition in the case of maximum length, the following relationship must be satisfied.

$$(L - \xi)C_{S\infty} + \left( C_{L0} + \frac{f\xi}{2} \right) \xi = LC_{S0} \quad (6)$$

As a result, the maximum growth length with constant composition is described as follows.

$$L_{\max} = \frac{\xi \left( C_{L0} - C_{S\infty} + \frac{f\xi}{2} \right)}{(C_{S0} - C_{S\infty})} \quad (7)$$

Figure 4 shows the maximum growth length for the TLZ growth with  $x$  values of 0.3, which is dependent on the temperature gradient, initial zone width, and the feed composition.



**Figure 4. Calculated maximum growth length**

In the figure, numbers labeled on lines denotes the initial zone width,  $\xi$ . Parameter  $f$ ,  $C_{L0}$ ,  $C_{S0}$  were assumed to be  $-5$ ,  $0.8$ ,  $0.3$ , respectively.

(4) Time sequence of the zone width

The solute amount which is removed during time duration  $\Delta t$ ,  $\Delta q_{out}$  and that supplied by the dissolution of the feed  $\Delta q_{in}$  are represented as follows.

$$\Delta q_{out} = C_{S0} V \Delta t \quad (8a)$$

$$\Delta q_{in} = C_{S\infty} R \Delta t \quad (8b)$$

So, the net solute amount change in the zone,  $\Delta Q$ , is represented as follows.

$$\Delta Q = \Delta q_{in} - \Delta q_{out} = (RC_{S\infty} - VC_{S0}) \Delta t \quad (8c)$$

For new amount of the solute in the zone, new zone width is defined as follows.

$$Q + \Delta Q = \left( C_{L0} + \frac{f}{2} \xi \right) \xi + (RC_{S\infty} - VC_{S0}) \Delta t = \left( C_{L0} + \frac{f}{2} (\xi + \Delta \xi) \right) (\xi + \Delta \xi) \quad (9)$$

Since  $\Delta \xi = (R - V) \Delta t$  and  $R = V + \frac{\Delta \xi}{\Delta t}$ ,

the following relationship has to be satisfied.

$$(C_{S\infty} - C_{S0}) V \Delta t = (f\xi + C_{L0} - C_{S\infty}) \Delta \xi \quad (10)$$

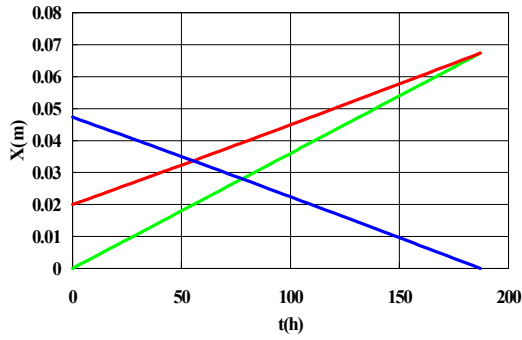
The integral form is written as follows

$$\int_{\xi_0}^{\xi} (f\xi + (C_{L0} - C_{S\infty}))d\xi = \int_0^t (C_{S\infty} - C_{S0})Vdt \quad (11)$$

Integrating the above equation, we can obtain the time-zone width relationship.

$$t = \frac{(C_{L0} - C_{S\infty})(\xi - \xi_0) + \frac{f}{2}(\xi^2 - \xi_0^2)}{V(C_{S\infty} - C_{S0})} \quad (12)$$

Figure 5 shows an example of the zone length change in the TLZ growth.



**Figure 5. Zone width and positions of feed and seed interfaces as a function of time**

Red line, green line, and blue line denote position of the feed-liquid interface, position of the seed- liquid interface, and zone width, respectively.

#### (5) Instantaneous dissolution rate of the feed

The dissolution rate in the TLZ mode is not fixed. However, the following relations have to be satisfied at any period of the growth.

$$\frac{\partial \xi}{\partial t} = R - V \quad (13)$$

The above equation is transformed to the following form, using the equation (10).

$$\frac{\partial t}{\partial \xi} = \frac{(C_{L0} - C_{S\infty}) + f\xi}{V(C_{S\infty} - C_{S0})} \quad (14)$$

So, the dissolution rate is obtained as follows.

$$R = \frac{V(C_{L0} - C_{S0} + f\xi)}{C_{L0} - C_{S\infty} + f\xi} = \frac{V(C_{L\xi} - C_{S0})}{(C_{L\xi} - C_{S\infty})} \quad (15)$$

Namely, the following relationship can be obtained.

$$R(C_{L\xi} - C_{S\infty}) = V(C_{L\xi} - C_{S0}) \quad (16)$$

Mass flux produced at the growing interface,  $J_s$ , and that is spent out at the dissolving interface,  $J_d$ , are represented respectively as follows.

$$J_s = -D \left. \frac{\partial C_L}{\partial Z} \right|_{Z=0} = V(C_{L0} - C_{S0}) \quad (17a)$$

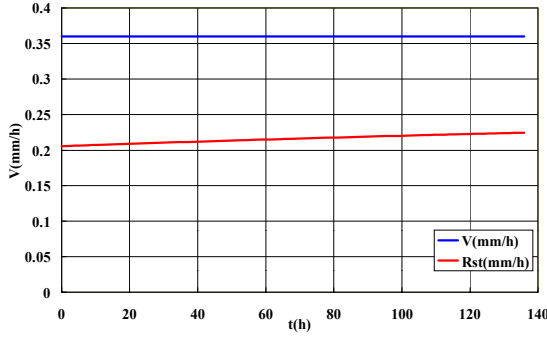
$$J_D = R(C_{L\xi} - C_{S\infty}) < -D \left. \frac{\partial C_L}{\partial Z} \right|_{Z=\xi} \quad (17b)$$

The difference of these flux,  $J$  is written as follows.

$$\Delta J = J_S - J_D = V(C_{L0} - C_{L\xi}) \quad (17c)$$

This difference is identical to the mass flux, which is produced via the advance of the interface.

Figure 6 shows an example of spontaneous dissolution rate change as time increase.



**Figure 6 Spontaneous growth rate and dissolution rate**

#### (6) Maximum initial zone length

In the above section, the maximum growth length is described as functions of temperature gradient and the initial zone width. However, if the zone length becomes longer, approximation of the linear concentration gradient becomes invalid since the diffusion length is represented as follows.

$$x = \sqrt{Dt} \quad (18)$$

So, for wider zone, the mass transport rate is not fast to keep the concentration gradient constant.

In this section, we estimate the maximum zone width with the following assumptions.

- 1) Both the growth rate and the solidified composition are assumed to be constant, which means the pseudo steady state condition is satisfied at least near the growth interface.
  - 2) Liquid composition at the dissolved feed interface is assumed to be the liquidus composition at that temperature.
  - 3) Liquidus composition is described as a function of distance from the growing interface.
- Then, the concentration distribution in the liquid is represented as follows.

$$D \frac{\partial^2 C_L}{\partial Z^2} = -V \frac{\partial C_L}{\partial Z} \quad (19)$$

The solution has to be the following form.

$$\frac{\partial C_L}{\partial Z} = A \exp\left(-\frac{V}{D}Z\right) \quad (20)$$

At the growing interface ( $Z=0$ ), the following has to be satisfied.

$$-D \frac{\partial C_L}{\partial Z} \Big|_0 = V(C_{L0} - C_{S0}) \quad (21)$$

So, the concentration gradient is rewritten as follows.

$$\frac{\partial C_L}{\partial Z} = -\frac{V}{D}(C_{L0} - C_{S0}) \exp\left(-\frac{V}{D}Z\right) \quad (22)$$

Namely,

$$-\frac{D}{V(C_{L0} - C_{S0})} \Delta C_L = \exp\left(-\frac{V}{D}Z\right) \Delta Z \quad (23)$$

Integrating the above equation,

$$\frac{(C_L - C_{L0})}{(C_{L0} - C_{S0})} = \exp\left(-\frac{V}{D}Z\right) + B \quad (24)$$

Since  $C_L = C_{L0}$  at  $z=0$

$$B = -1.$$

Namely,

$$C_L(Z) = (C_{L0} - C_{S0}) \exp\left(-\frac{V}{D}Z\right) + C_{S0} \quad (25)$$

The liquidus composition is represented as follows.

$$C_e = C_{L0} + fZ \quad (26)$$

Since the composition of the liquid at the feed interface has to be on the liquidus line, the following relation is expected.

$$f = \frac{(C_{L0} - C_{S0})}{\xi} \left( \exp\left(-\frac{V}{D}\xi\right) - 1 \right) \quad (27)$$

Exponential term can be expressed by polynomial



form.

$$\exp(x) = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots \quad (28)$$

The following expression is available.

$$\begin{aligned} \exp\left(-\frac{V}{D}\xi\right) &= 1 - \frac{V}{D}\xi + \frac{1}{2!}\left(-\frac{V}{D}\xi\right)^2 \\ &+ \frac{1}{3!}\left(-\frac{V}{D}\xi\right)^3 + \dots \end{aligned} \quad (29)$$

Namely,

$$f = \frac{(C_{L0} - C_{S0})}{\xi} \left( -\frac{V}{D}\xi + \frac{1}{2!}\left(-\frac{V}{D}\xi\right)^2 + \frac{1}{3!}\left(-\frac{V}{D}\xi\right)^3 + \dots \right) \quad (30)$$

This relationship is valid for any  $\xi$ , only if the non-linear term can be neglected. In that case,

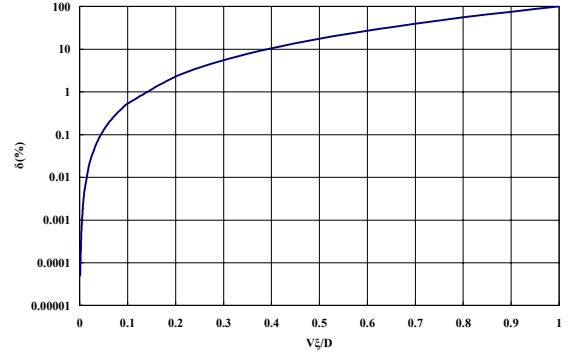
$$f = -\frac{(C_{L0} - C_{S0})V}{D},$$

which means that the concentration gradient due to the spontaneous growth coincides with the liquidus concentration gradient.

Now we evaluate the deviation from the linearity using the following parameter.

$$\delta \equiv \frac{\text{abs}(\exp(-x) - 1 + x)}{\exp(-x)} \times 100 \quad (31)$$

The result is shown in figure 7. If we assume that the restriction of the contribution of higher order term is about 1%, the resultant maximum zone length for the TLZ growth mode becomes a few tens millimeters.



**Figure 7. Relative error increase due to the zone width increase.**

#### 4. Summary

One-dimensional TLZ model has been developed in the present work. Using the model, homogenization mechanism was clarified, and the followings were quantitatively represented.

##### 1) Synchronized sample translation rate

Synchronized sample translation rate, which means the rate with identical velocity to spontaneous growth rate and opposite direction, is given as follows.

$$V_T = \frac{Df}{(C_{L0} - C_{S0})}$$

##### 2) Maximum growth length

Maximum growth length is represented as function of the temperature gradient and the initial zone width.

$$L_{\max} = \frac{\xi \left( C_{L0} - C_{S\infty} + \frac{f\xi}{2} \right)}{(C_{S0} - C_{S\infty})}$$

##### 3) Time evolution of the liquidus zone

The time evolution of zone width was analytically solved. The following relation was obtained.

$$t = \frac{(C_{L0} - C_{S\infty})(\xi - \xi_0) + \frac{f}{2}(\xi^2 - \xi_0^2)}{V(C_{S\infty} - C_{S0})}$$

4) Limitation of the method due to the restriction of the initial zone length

Since the stability of the constant concentration gradient depends on the zone width, there is a limit of initial zone width, which the TLZ mechanism governs. The characteristic length scale depends on  $V/D$ , and about the orders of 20 mm in the case of  $\text{In}_x\text{Ga}_{1-x}\text{As}$ .

The developed model will be useful to predict the appropriate TLZ growth conditions, and to evaluate the experimental results in the sense of mass transport.

<b>Nomenclature</b>
$C_{L0}$ : conc. of liquid at the seed interface
$C_{S0}$ : conc. of solid at the seed interface
$C_{L\xi}$ : conc. of liquid at the feed interface
$C_{S\infty}$ : conc. of the solid feed
$C_L$ : conc. of liquid in the zone
$C_e$ : liquidus concentration
$L$ : sample length
$L_{\max}$ : maximum growth length
$\xi$ : zone width
$Z$ : distance from the growing interface
$x$ : diffusion length
$T$ : temperature
$t$ : time
$f$ : inclination of the liquidus
$D$ : diffusion coefficient in the liquid
$V$ : spontaneous growth rate
$V_T$ : synchronized sample translation rate
$R$ : dissolution rate of feed
$Q_L$ : total amount of solute in the zone
$\Delta q_{out}$ : solute amount removed from the zone during $\Delta t$
$\Delta q_{in}$ : solute amount supplied to the zone during $\Delta t$
$J_S$ : solute flux at the growing interface
$J_D$ : solute flux at the feed interface

## References

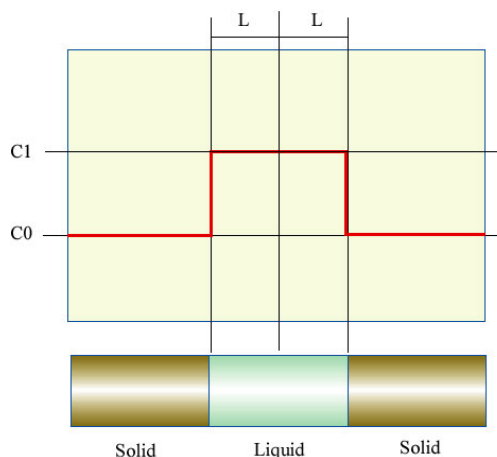
- [1] T. A. Campbell, J. N. Koster, *J. Crystal Growth* 171 (1997) 1-11.
- [2] H. Yin, J. N. Koster, *J. Crystal Growth* 205 (1999) 590-606.
- [3] Y. Azuma, N. Usami, T. Ujihara, G. Sazaki, Y. Murakami, S. Miyashita, K. Fujiwara, K. Nakajima, *J. Crystal Growth* 224 (2001) 204-211.
- [4] T. Kusunoki, C. Takenaka, K. Nakajima, *J. Crystal Growth* 112 (1991) 33.
- [5] K. Nakajima, T. Kusunoki, C. Takenaka, *J. Crystal Growth* 113 (1991) 485.
- [6] P. Huschl, R. Grill, J. Svoboda, P. Hlidek, P. Moravec, J. Franc, E. Belas, *J. Crystal Growth* 138 (1994) 956-963.
- [7] W. A. Tiller, K. A. Jackson, J. W. Rutter, B. Chalmers, *Acta Metall.* 1 (1953) 428-437.
- [8] T. Duffar, M. D. Serrano, C. D. Moore, J. Camassel, S. Contreas, P. Dusserre, A. Rivoallant, B. K. Tanner, *J. Crystal Growth* 192 (1998) 63-72.
- [9] Y. Hiraoka, K. Ikegami, T. Maekawa, S. Matsumoto, S. Yoda, K. Kinoshita, *J. Phys. D* 33 (2000) 1-11.
- [10] W. Weber, T. Duffar, J. J. Favier, *Microgravity Sci. Technol.* 4,3 (1991) 166-171.
- [11] T. Duffar, J. Abadie, in 'Scientific Results of the German Spacelab Mission D-2' (1994) 502-508.
- [12] N. Duhanian, T. Duffar, J. Abadie, C. Marin, E. Dieguez, NASA/CP-1998-206960 (1998) 28-50.
- [13] W. G. Pfann, 'Zone Melting' (1958) New York : J. Wiley & Sons.
- [14] T. Suzuki, K. Nakajima, T. Kusunoki, T. Katoh, *J. Electronic Materials* 25, 3 (1996) 357-361.
- [15] S. Kodama, Y. Furumura, K. Kinoshita, H. Kato, S. Yoda, *J. Crystal Growth* 208 (2000) 165-170.
- [16] Y. Nishijima, K. Nakajima, K. Otsubo, H. Ishikawa, *J. Crystal Growth* 208 (2000) 171-178.
- [17] K. Kinoshita, H. Kato, M. Iwai, T. Tsuru, Y. Muramatsu, S. Yoda, *J. Crystal Growth* 225 (2001) 59-66
- [18] H. Nakamura, H. Kato, K. Kinoshita, S. Yoda, NASDA-TMR-000007E (2000) 15-28.
- [19] D. T. Hurle, J. B. Mullin, E. R. Pike, *Phil. Mag.* 9 (1964) 423-434.
- [20] D. T. Hurle, J. B. Mullin, E. R. Pike, *J. Materials Sci.*, 2 (1967) 46-62.
- [21] J. H. Westbrook ed., 'Intermetallic Compounds' (1967) John Wiley & Sons, Inc.
- [22] D. Kendall, *Appl. Phys. Lett.*, 4, 4 (1964) 67-68.
- [23] H. Kato, M. Yokozawa, R. Kohara, Y. Okabayashi, S. Takayanagi, *Solid State Electron.*, 12 (1969) 137-139.
- [24] K. Kinoshita, H. Kato, S. Matsumoto, S. Yoda, J. Yu, M. Natsuisaka, T. Masaki, N. Koshikawa, Y. Nakamura, T. Nakamura, A. Ogiso, S. Amano, K. Goto, Y. Arai, T. Fukazawa, M. Kaneko, T. Itami, *J. Jpn. Soc. Microgravity Appl.*, 17, 2 (2000) 57-63.

## Quantitative evaluation of concentration stabilizing power of solid sandwich structure

### Introduction

In the temperature gradient zone method, solution is sandwiched by two solid phases. Generally, the interface between the solution and the solid is in equilibrium, which means the solute concentration of the solution is identical to the liquidus concentration at that temperature, and the solid concentration is identical to the solidus concentration. However, it may take some duration for the concentration gradient in the liquid to achieve steady state. The characteristic time to achieve the steady state, can be used as an indicator of stability of the linear concentration gradient to perturbation.

It is difficult to estimate the characteristic time for the actual temperature gradient zone condition, since there are two moving boundaries and the liquid concentrations at the two interfaces are different each other. Instead, we treat simple system, which is shown in figure A1. In the system, the positions of two boundaries are fixed and have the same concentration, which means that no temperature gradient exists in the system. Initial concentration is assumed to be equal to  $C_1$ , and boundary condition is equal to  $C_0$ . After some period, the whole concentration in the liquid becomes  $C_0$ , which means the steady state for this system.



**Figure A1. Schematic drawing of the system**

### Analysis

One dimensional diffusion equation based on Fick's law is applied.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} \quad (\text{a1})$$

Then we apply the following non-dimensional parameters.

$$\text{Concentration: } \bar{C} \equiv \frac{C - C_0}{C_1 - C_0} \quad (\text{a2-1})$$

$$\text{Length: } \xi \equiv \frac{z}{L} \quad (\text{a2-2})$$

$$\text{Time: } \tau \equiv \frac{Dt}{L^2} \quad (\text{a2-3})$$

Using these non-dimensional parameters, the diffusion equation is rewritten as follows.

$$\frac{\partial \bar{C}}{\partial \tau} = \frac{\partial^2 \bar{C}}{\partial \xi^2} \quad (\text{a3})$$

Initial condition and boundary conditions are as

follows.

Initial condition

$$\tau = 0 : \bar{C}(\xi) = 1$$

Boundary conditions:

$$\xi = 0 : \bar{C} = 0$$

$$\xi = 2 : \bar{C} = 0$$

Now we apply variable separation method to solve the above equation, by using the following form.

$$\bar{C}(\xi, \tau) = f(\xi)g(\tau) \quad (\text{a4})$$

Namely

$$\frac{1}{g(\tau)} \frac{dg}{d\tau} = \frac{1}{f(\xi)} \frac{d^2 f}{d\xi^2} \quad (\text{a5})$$

This representation is valid only if the each separated equation has the following values as solutions.

$$\frac{1}{g(\tau)} \frac{dg}{d\tau} = -a^2, \quad \frac{1}{f(\xi)} \frac{d^2 f}{d\xi^2} = -a^2$$

So, the following general solution is obtained.

$$\bar{C}(\xi, \tau) = \exp(-a^2\tau) [B_1 \sin(a\xi) + B_2 \cos(a\xi)] \quad (\text{a6})$$

since,  $g(\tau) = A \exp(-a^2\tau)$ ,

$$f(\xi) = B_1 \sin(a\xi) + B_2 \cos(a\xi)$$

Moreover,  $\bar{C} = 0$  at  $\xi = 0$ .

$$B_2 = 0 \text{ since } 0 = \exp(-a^2\tau) [B_2].$$

In addition, the following relation is obtained

from the fact that  $\bar{C} = 0$  at  $\xi = 2$ .

$$\exp(-a^2\tau) [B \sin(2a)] = 0$$

So,  $a$  must satisfy the following condition.

$$a = \frac{n\pi}{2}$$

The resultant concentration in the liquid is written as follows.

$$\bar{C} = \sum_{n=1}^{\infty} B_n \exp\left(\frac{-n^2\pi^2}{4}\tau\right) \sin\left(\frac{n\pi}{2}\xi\right) \quad (\text{a7})$$

Moreover, the following relation is obtained from

the condition that  $\bar{C} = 1$  at  $\tau = 0$ .

$$1 = \sum_{n=1}^{\infty} B_n \sin\left(\frac{n\pi}{2}\xi\right)$$

Multiplying  $\sin\left(\frac{m\pi}{2}\xi\right)$  for both side of the above equation, and integrating between  $\{\xi : 0, 2\}$ , we can obtain the following relationship.

$$\int_0^2 \sin\left(\frac{m\pi}{2}\xi\right) d\xi = \sum_{n=1}^{\infty} B_n \int_0^2 \sin\left(\frac{m\pi}{2}\xi\right) \sin\left(\frac{n\pi}{2}\xi\right) d\xi \quad (\text{a8})$$

The left side of the equation is rewritten as

$$\frac{2(1 - \cos(m\pi))}{m\pi}$$

The right side of the equation is 0 for  $m \neq n$ , and 1 for  $m = n$ .

$$\text{So, } \frac{2(1 - \cos(m\pi))}{m\pi} = B_m$$

where,  $B_m = \frac{4}{m\pi} : (m = 1, 3, 5, \dots)$

$$B_m = 0 : (m = 2, 4, 6, \dots)$$

The resultant non-dimensional concentration is represented as follows.

$$\begin{aligned} \bar{C} &= \frac{4}{\pi} \left[ \exp\left(-\frac{1}{4}\pi^2\tau\right) \sin\left(\frac{\pi}{2}\xi\right) \right. \\ &\quad \left. + \frac{1}{3} \exp\left(-\frac{9}{4}\pi^2\tau\right) \sin\left(\frac{3\pi}{2}\xi\right) + \dots \right] \\ &= \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{1}{(2n-1)} \exp\left(-\left(\frac{2n-1}{2}\pi\right)^2\tau\right) \\ &\quad \sin\left(\frac{(2n-1)\pi}{2}\xi\right) \end{aligned} \quad (\text{a9})$$

If  $\tau$  is sufficiently large, we can consider only the contribution of first term of the equation. So, the equation is simplified as follows.

$$\bar{C} = \frac{4}{\pi} \exp\left(-\left(\frac{\pi^2}{4}\right)\tau\right) \sin\left(\frac{\pi}{2}\xi\right) \quad (\text{a10})$$

Now we calculate the average concentration in the liquid zone,  $\bar{C}_a$ .

$$\begin{aligned} \bar{C}_a &= \frac{1}{2} \int_0^{24} \frac{4}{\pi} \exp\left(-\left(\frac{\pi^2}{4}\right)\tau\right) \sin\left(\frac{\pi}{2}\xi\right) d\xi \\ &= \frac{2}{\pi} \exp\left(-\left(\frac{\pi^2}{4}\right)\tau\right) \frac{2}{\pi} \left[-\cos\left(\frac{\pi}{2}\xi\right)\right]_0^{24} \\ &= \frac{8}{\pi^2} \exp\left(-\left(\frac{\pi^2}{4}\right)\tau\right) \end{aligned} \quad (\text{a11})$$

Dimensional expression of the above equation is as follows.

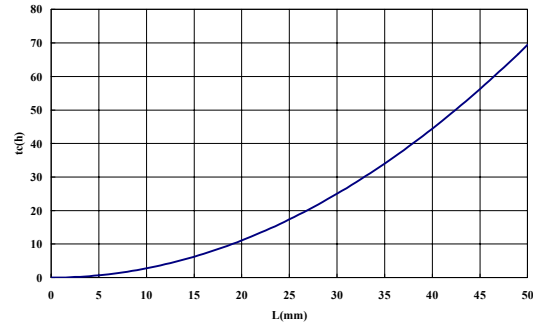
$$\begin{aligned} C_a &= (C_1 - C_0) \frac{8}{\pi^2} \\ &\quad \exp\left(-\left(\frac{\pi^2}{4}\right) \frac{Dt}{L^2}\right) + C_0 \end{aligned} \quad (\text{a12})$$

From the above equation, we can obtain characteristic time,  $t_c$ , which represents the time scale to become steady state after the concentration perturbation.

$$t_c \equiv \frac{L^2}{D} \quad (\text{a13})$$

This time is inversely proportional to the diffusion coefficient of the liquid, and proportional to the square of the zone width.

Figure A2 shows relationship between the characteristic time- and the zone width.



**Figure A2. Relationship between the zone width and the characteristic time**

Nomenclature
$C$ : solute concentration
$C_1$ : initial solute concentration
$C_0$ : boundary solute concentration
$C_a$ : average solute concentration
$\bar{C}$ : scaled solute concentration
$L$ : half width of the system
$Z$ : length
$\xi$ : scaled length
$t$ : time
$t_c$ : characteristic time for homogenization
$\tau$ : scaled time
$D$ :diffusion coefficient

## Evaluation of concentration distribution in the solid feed

### Introduction

In the TLZ method, the feed interface dissolves due to the spontaneous concentration gradient. Since the dissolution rate is sufficiently small, the composition of the liquid and the solid at the solid-liquid interface seems to be identical to those of equilibrium composition. However, it is clear that the solid composition far away from the dissolved interface is sub-solidus composition. Namely, there must be concentration gradient from the interface toward the inside of the solid feed.

In this section, we estimated the order of the concentration gradient in the solid feed.

### Diffusion coefficient in the solid feed

It is important to know the diffusion coefficient to evaluate the mass transport. Unfortunately, there is no inter-diffusion coefficient data for the  $\text{In}_x\text{Ga}_{1-x}\text{As}$  system in the solid. So, we have estimated the value by means of the data for the similar system.

In general, diffusion coefficient in a solid is given in the following Arrhenius form.

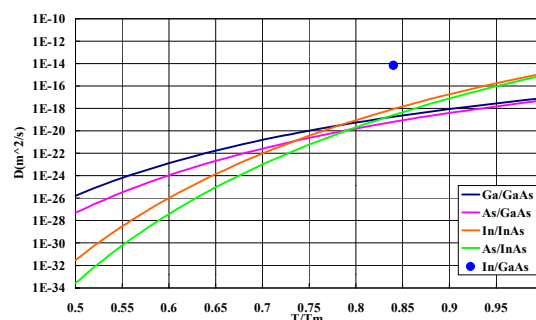
$$D(T) = D_0 \exp\left(-\frac{U}{kT}\right) \quad (\text{b1})$$

Self diffusion coefficient of Ga in a GaAs crystal, and that of In and As in an InAs crystal have been measured and reported in the above form. In addition, tracer diffusion coefficient of In in GaAs was reported though the value was measured only at 1273K. Figure B1 shows the above described values as a function of normalized temperature, which is defined as

follows

$$\bar{T} \equiv \frac{T}{T_M}$$

where,  $T_M$  indicates the liquidus temperature.



**Figure B1. Diffusion coefficients in solids for the InGaAs system**

From this figure, it is found that the diffusion coefficients near the melting temperature are an order of  $10^{-18}\text{m}^2/\text{s}$  for Ga in GaAs and an order of  $10^{-15}\text{m}^2/\text{s}$  for In and As in InAs. So, we estimated the inter diffusion coefficient of InAs-GaAs in solid state as  $10^{-14}\text{m}^2/\text{s}$  near the liquidus temperature.

### Estimation of the concentration boundary layer in the solid

It is possible to calculate concentration gradient in the solid feed by the use of moving coordination system, which moves with the feed interface. For simplicity, it is assumed that the dissolution proceeds with approximately constant velocity. Solid composition at the feed-liquid interface is assumed to be same as the solidus composition at desired temperature.



The basic equation is given as follows.

$$D \frac{\partial^2 C_s}{\partial Z^2} + R \frac{\partial C_s}{\partial Z} = 0 \quad (b2)$$

, where  $R$  is the dissolution rate of a feed.

Boundary conditions are as follows.

$$Z = 0 : C_s = C_{Si}$$

$$Z = \infty : C_s = C_{S\infty}$$

By solving the equation, concentration in the solid feed can be given as follows.

$$C_s(Z) = (C_{Si} - C_{S\infty}) \exp\left(-\frac{R}{D}Z\right) + C_{S\infty} \quad (b3)$$

As a result, concentration gradient at the feed-liquid interface toward the solid feed is given as follows.

$$\left. \frac{\partial C_s}{\partial Z} \right|_{Z=0} = -\frac{R}{D} (C_{Si} - C_{S\infty}) \quad (b4)$$

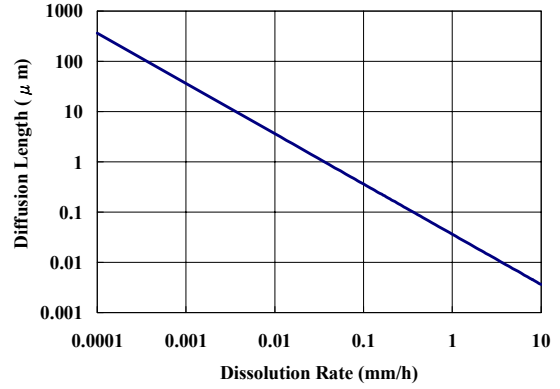
Here, we introduce the boundary layer,  $\delta$ , which is identical to boundary layer in solution growth.

$$C_{Si} + \left. \frac{\partial C_s}{\partial Z} \right|_{Z=0} \delta = C_{S\infty} \quad (b5)$$

Namely,  $\delta = \frac{D}{R}$

It should be noticed that the thickness does not include concentration term. So the thickness is independent of concentration.

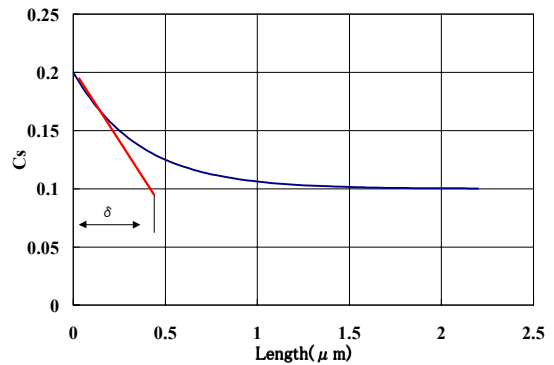
We calculated  $\delta$  value as a function of the dissolution rate, as shown in figure B2. The diffusion coefficient used is  $10^{-14} \text{m}^2/\text{s}$ , which was estimated in the previous section.



**Figure B2. Calculated diffusion length as a function of the dissolution rate**

Figure B3 shows the concentration profile along the feed in the case that interfacial solid concentration is 0.2, bulk concentration is 0.1 and dissolution rate is 0.1mm/h. It is clearly shown that the concentration gradient is steep and the boundary layer thickness is narrow.

From above examination, it was found that the mass transport in the feed is negligible in macroscopic modeling of feed dissolution.



**Figure B3. Calculated diffusion boundary layer width at the dissolving interface**

<b>Nomenclature</b>	
$T$	: temperature
$T_M$	: liquidus temperature
$\bar{T}$	: scaled temperature
$D$	: diffusion coefficient in the feed
$D_0$	: pre-exponential factor of diffusion
$U$	: activation energy for diffusion
$C_{S_i}$	: conc. of solid at the seed interface
$C_{S_\infty}$	: conc. of the feed at infinity
$C_S$	: solute concentration in the feed
$R$	: dissolution rate of feed
$Z$	: distance from the dissolving interface
$\delta$	: diffusion boundary layer width

## Effects of non-uniform solute concentration in a feed on the TLZ growth

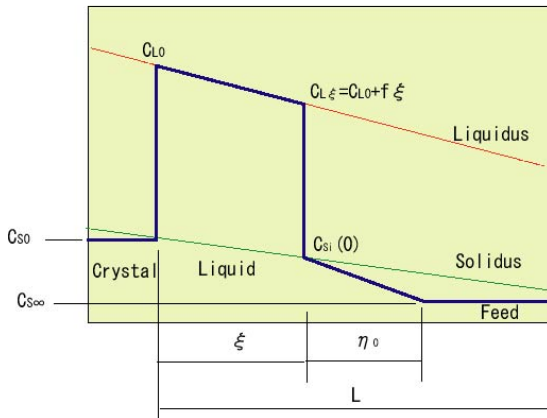
### Introduction

In this appendix, we examine the effect of non-uniform feed on the TLZ growth.

Meaning of the parameters, which are not described in this appendix, are same as those in the text.

### Effect of gradient solute concentration in a feed with sub-solidus composition

Let us consider the TLZ growth with gradient solute concentration in a feed and linear temperature gradient. Figure C1 shows the geometry. In this figure, growth proceeds from the left side to the right side, and the synchronized sample translation from the right to the left is assumed. The composition of the growing solid is assumed to be constant. In addition, linear concentration decrease in the liquid zone, which coincides with the liquidus concentration at that temperature, is assumed.



**Figure C1. System geometry**

Since the constant concentration gradient near the growing interface is assumed, the spontaneous

growth rate is given as

$$V = -\frac{Df}{(C_{L0} - C_{S0})} \quad (c1)$$

where,  $f$  is given as

$$f = \left( \frac{\partial C_{L,eq}}{\partial T} \right) \left( \frac{\partial T}{\partial Z} \right) = \left( \frac{\partial C_{L,eq}}{\partial T} \right) G \quad (c2)$$

The total amount of solute in the liquid zone,  $Q_L$ , is given as follows.

$$Q_L = \frac{(C_{L0} + C_{L\xi})}{2} \xi = \left( C_{L0} + \frac{f\xi}{2} \right) \xi \quad (c3-1)$$

Similarly, both the total amount of the solute in the gradient feed part,  $Q_{S1}$ , and that in the uniform feed part,  $Q_{S2}$  are expressed as follows.

$$Q_{S1} = \frac{C_{Si}(0) + C_{S\infty}}{2} \eta_0 \quad (c3-2)$$

$$Q_{S2} = (L - \xi_0 - \eta_0) C_{S\infty} \quad (c3-3)$$

The average solute concentration of these three parts has to be identical to the growing solid concentration in the case of maximum growth length.

$$Q_L + Q_{S1} + Q_{S2} = LC_{S0} \quad (c4)$$

So, the maximum growth length for this case is written as follows.

$$L = \frac{\xi_0 \left( C_{L0} - C_{S\infty} + \frac{f\xi_0}{2} \right)}{(C_{S0} - C_{S\infty})} \quad (c5)$$

$$+ \frac{(C_{Si}(0) - C_{S\infty})}{2(C_{S0} - C_{S\infty})} \eta_0$$

By comparing the above equation with the equation in the text with constant concentration feed, it is found that the maximum growth length becomes larger with the addition of second term

of the right side of the equation than that of constant feed case.

As the growth proceeds, a feed dissolves. The dissolved length,  $s$ , is given as follows.

$$s = \int_0^t R(t) dt = Vt + \xi - \xi_0 \quad (c6)$$

Solid concentration of feed-liquid interface is expressed as follows.

$$C_{Si}(s) = \frac{(C_{S\infty} - C_{Si}(0))}{\eta_0} s + C_{Si}(0) \quad (c7)$$

Here we represent the amount of the solute, which is removed in the seed by the solidification,  $\Delta q_{out}$ , during time interval,  $\Delta t$ .

$$\Delta q_{out} = C_{S0} V \Delta t \quad (c8-1)$$

Similarly, the amount which is supplied in the zone by the dissolution of the feed,  $\Delta q_{in}$ , during time interval,  $\Delta t$ , is expressed as follows.

$$\Delta q_{in} = C_{Si}(s) R \Delta t \quad (c8-2)$$

The net amount change in the liquid zone,  $\Delta Q$ , is written as follows.

$$\Delta Q = \Delta q_{in} - \Delta q_{out} = (R C_{Si}(s) - V C_{S0}) \Delta t \quad (c8-3)$$

From a mass conservation consideration, the following relationship can be obtained.

$$Q + \Delta Q = \left( C_{L0} + \frac{f}{2} \xi \right) \xi + (R C_{Si}(s) - V C_{S0}) \Delta t = \quad (c9)$$

$$\left( C_{L0} + \frac{f}{2} (\xi + \Delta \xi) \right) (\xi + \Delta \xi)$$

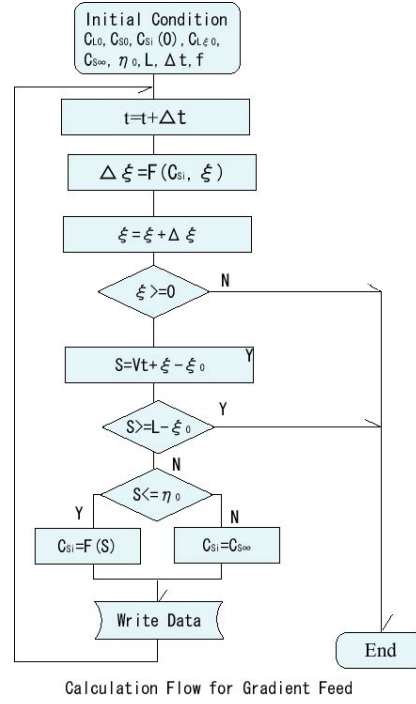
Moreover, since  $\Delta \xi = (R - V) \Delta t$ ,

$$R = V + \frac{\Delta \xi}{\Delta t} \quad (c10)$$

Namely, the resultant relationship is as follows.

$$(C_{Si}(s) - C_{S0}) V \Delta t = (f \xi + C_{L0} - C_{Si}(s)) \Delta \xi \quad (c11)$$

It is impossible to solve the equation analytically, because the solid concentration in the seed is not constant. Instead, numerical calculation has been carried out, using the calculation flow shown in figure C2.



**Figure C2. Calculation flow to calculate time evolution of the zone width**

In addition, the instantaneous dissolution rate can be represented as follows, using the relation,  $\frac{\partial \xi}{\partial t} = R - V$

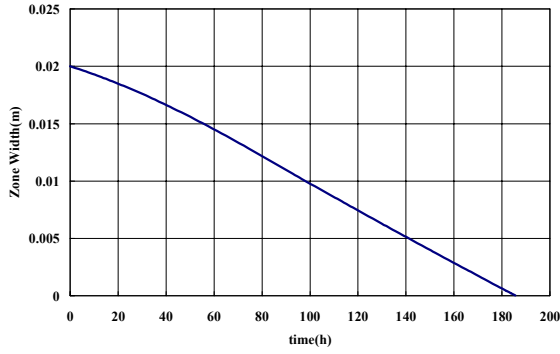
$$R = \frac{V(C_{L0} - C_{S0} + f\xi)}{C_{L0} - C_{Si}(s) + f\xi} = \frac{V(C_{L\xi} - C_{S0})}{(C_{L\xi} - C_{Si}(s))} \quad (c12)$$

Namely, the relationship

$$R(C_{L\xi} - C_{Si}(s)) = V(C_{L\xi} - C_{S0}) \quad (c13)$$

is valid even in the case of concentration gradient exists in a feed.

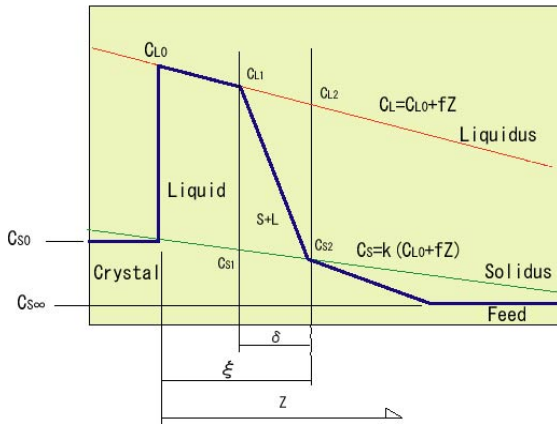
Figure C3 shows time -zone width relationship.



**Figure C3 Time-Zone width relationship for concentration gradient feed**

### Effect of a feed with two phase coexisting region on the TLZ growth

In the TLZ method, solid-liquid mixture region may appear near the dissolving interface if we use a concentration gradient feed. So we evaluate the effect of the two-phase region on the TLZ growth. The geometry to be assumed is shown in figure C4.



**Figure C4 System geometry with two-phase region**

It is clear that the quite identical expression can be used for the growing interface. However,

the treatment of the feed side has to be modified.

Total amount of the solute in two-phase region and solid feed region is described as follows.

$$Q_L = \frac{(C_{L0} + C_{L2})}{2} \xi - \frac{(C_{L2} - C_{S2})}{2} \delta$$

$$= \left( C_{L0} + \frac{f\xi}{2} \right) \xi - \frac{(1-k)}{2} (C_{L0} + f\xi) \delta \quad (c14)$$

Then we have to obtain the amount of the solute,  $\Delta q_{feed}$ , which is removed from the two-phase

region to the solid feed by the temperature change due to the sample translation.

Refers to the coordinate system, which is fixed to the growing interface, the feed moves to a growing interface with a speed of  $-V$ . Due to this movement, a part of two-phase region moves to the solid region since the temperature of the initial two-phase region decreases to the sub-solidus temperature. As a result, new phase boundary between the two phase region and the solid feed region moves to the cross point at which, straight line between  $C_{L1}$  and  $C_{S2}$  cross the solidus line.

Namely, coordinate of the newly defined boundary,  $Z'$  is

$$Z' = \frac{\delta(C_{S0} - C_{S2}) + (\xi - V\Delta t)(C_{S2} - C_{L1})}{(C_{S2} - C_{L1} - kf\delta)} \quad (c15)$$

So, the resultant change of the liquid zone + two-phase zone length is represented as follows.

$$Z' - \xi = \Delta\xi = \frac{-(C_{S2} - C_{L1})V\Delta t}{(C_{S2} - C_{L1} - kf\delta)} \quad (c16)$$

By this change, the following concentration region is removed to the solid feed.

$$\begin{aligned}
C_S(Z') &= C_{S2} + kf\Delta\xi \\
&= C_{S2} - \frac{kf(C_{S2} - C_{L1})V\Delta t}{(C_{S2} - C_{L1} - kf\delta)} \quad (c17)
\end{aligned}$$

The final form of  $\Delta q_{feed}$  is written as follows.

$$\begin{aligned}
\Delta q_{feed} &= -\Delta\xi \frac{(C_{S2} + C_S(Z'))}{2} \\
&\equiv \frac{C_{S2}(C_{S2} - C_{L1})V\Delta t}{(C_{S2} - C_{L1} - kf\delta)} \quad (c18)
\end{aligned}$$

The net change of the solute in the liquid,  $\Delta Q$ , is expressed as follows.

$$\begin{aligned}
\Delta Q &= -\Delta q_{seed} - \Delta q_{feed} = \\
&= -\frac{(C_{S2} - C_{L1})(C_{S0} + C_{S2}) - kf\delta C_{S0}}{(C_{S2} - C_{L1} - kf\delta)} V\Delta t \quad (c19)
\end{aligned}$$

On the other hand, the following equation can be obtained using the mass conservation among the liquid region and two-phase region.

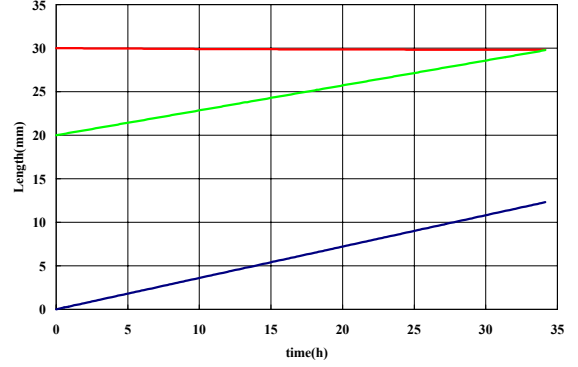
$$\begin{aligned}
\Delta Q &= \Delta\xi \left( C_{L0} + f\xi - \frac{(1-k)}{2} f\delta \right) \\
&= \frac{(1-k)(C_{L0} + f\xi)}{2} \Delta\delta \quad (c20)
\end{aligned}$$

Since these two equations must be identical, the following relationship can be obtained.

$$\frac{\Delta\delta}{\Delta t} = \frac{2V \begin{pmatrix} (C_{S2} - C_{L1}) \\ (C_{S0} + C_{S2} - C_{L2} + \frac{(1-k)}{2} f\delta) \\ -kf\delta C_{S0} \end{pmatrix}}{(1-k)C_{L2}(C_{S2} - C_{L1} - kf\delta)} \quad (c21)$$

This is the basic equation, which represents the time dependence of the length of two-phase zone.

Unfortunately, it is impossible to solve this equation, analytically. So, we carried out numerical calculation. The results are shown in figure C5.



**Figure C5. Time evolution of the seed-liquid interface (blue), liquid-two-phase region interface (green) and two-phase region-solid feed interface (red).**