

# Qualitative Description of the Concentration Gradient Partial Melting Method and Application to $\text{In}_x\text{Ga}_{1-x}\text{As}$

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Solid-liquid reactions, which are expected to occur in concentration gradient partial melting method (CGPM), were examined qualitatively on the basis of the thermodynamics. Using the obtained knowledge, possible processes in CGPM were described qualitatively. In addition, quantitative estimation was carried out to clarify conditions for utilizing CGPM to obtain homogeneous  $\text{In}_x\text{Ga}_{1-x}\text{As}$  crystals with  $x$  value of 0.3.

## Introduction

Much effort has been paid to make compositionally homogeneous semiconductor crystals. However, it is difficult to make the crystal even in microgravity environment<sup>1)-4)</sup>. Recently,  $\text{In}_x\text{Ga}_{1-x}\text{As}$  single crystal was successfully solidified using multi-component zone melting method<sup>5)</sup>, a variation of temperature gradient type zone method<sup>6),7)</sup>, although the reproducibility was not so good.

Concentration gradient partial melting method (CGPM) has been developed to obtain compositionally homogeneous  $\text{In}_x\text{Ga}_{1-x}\text{As}$  mixed crystals<sup>8)</sup>. Homogeneous crystals with high  $x$  value ( $x=0.3$ ) and with the length of more than 30mm were successfully obtained<sup>9)</sup>. However, there is no model, which describes concentration stabilization mechanism of the method, because of its complexity on time dependent stability relationship between solid and liquid.

In this work, we examined solid-liquid reactions of simplified isothermal solid-liquid system, for which various thermodynamic relations were assumed. The obtained knowledge was used to describe the possible reaction, which occurred during the sequences of the CGPM process. Required conditions for

CGPM process were clarified among these examinations.

In addition, quantitative estimation to grow homogeneous  $\text{In}_x\text{Ga}_{1-x}\text{As}$  crystals was made, which included concentration distribution of the feed, optimum growth rate for homogeneous growth, and effect of sample translation rate on the homogeneity.

## Classifications of thermodynamic relationships of solid and liquid

Thermodynamic relationship between solid and liquid are divided into 9 cases for the mixed crystal system. Table 2.1 shows these 9 cases. In this table, 'saturated' means that the composition is equal to either the solidus composition or the liquidus composition at that temperature. 'Undersaturated' means either the solid composition is above the solidus composition, or the liquid composition is above the liquidus composition. 'Supersaturated' means either the solid composition is below the solidus composition, or the liquid composition is below the liquidus composition. For example, saturated liquid means that the liquid has the liquidus composition at the temperature.

Table 2.1 Thermodynamic relationships between solid and liquid

		solid		
		saturated	undersaturated	supersaturated
liquid	saturated	case 1	case 4	case 7
	undersaturated	case 2	case 5	case 8
	supersaturated	case 3	case 6	case 9

Though thermodynamics assumes equilibrium or pseudo-equilibrium conditions, we can estimate the direction of the reaction for the dis-equilibrium system. We examined the direction of the reaction for these 9 cases. For simplicity, the temperature of the system was assumed to be isothermal. Constant liquid composition during reaction was also assumed. The latter assumption is appropriate if the examination is restricted to the direction of the reaction, since the diffusion coefficient of the liquid is much larger than that of the solid.

(1) Reactions with saturated solid

Saturated solid means that the composition of the solid is equal to the solidus composition at that temperature. In this section, we examined reactions to the saturated solid.

Figure 2.1 schematically represents the case 1, in which the saturated solid contacts with the saturated liquid. In these figures, fig.2.1 (a) represents the related compositions, (b) represents free energy curves of the liquid and the solid, (c) represents the initial concentration distribution, and (d) represents the concentration distribution after a long duration. Since the saturated liquid means the liquidus composition at that temperature, compositions of both the solid and liquid coincide with those of solidus and the liquidus. No reaction is expected at the solid-liquid interface since the chemical potentials of the solid at the solid-liquid interface is equal to that of the liquid at the interface, and no concentration gradient exists both in the solid and the liquid.

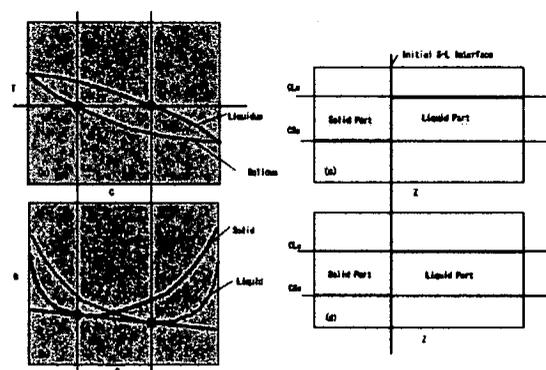


Figure 2.1 Saturated liquid - saturated solid reaction

Next, we consider the case 2, in which saturated solid contacts with undersaturated liquid. Figure 2.2 shows (a) plot of the solid and the liquid on the phase diagram, (b) free energy curves of the liquid and the solid, (c) initial concentration distribution of solid and the liquid, and (d) concentration distribution after a long duration. From fig.2.2 (b), it is clearly shown that the undersaturated liquid is unstable for the stable solid. The only way for the liquid to become stable state is to dissolve the solid, which results in the liquid concentration change toward the saturated state. So, the initial concentration profile of the system (fig.2.2(c)) changes by the simple dissolution of the solid into the liquid (fig.2.2(d)).

As the final part of this section, let us consider the case 3, in which the saturated solid contact with the supersaturated liquid. Figure 2.3 represents the situation. As is shown in fig.2.3(a), the liquid part is in the solid+liquid region. It is clear from fig.2.3(b) that the liquid is unstable even if the liquid does not contact with the solid. The most stable state for this composition is a mixture of the saturated solid and the saturated liquid. This stabilization is attained either the growth of the solid or the spontaneous crystallization of the solid in the liquid. At relatively small supersaturation, saturated solid grows from the initial interface toward the liquid. At relatively large supersaturation, spontaneous nucleation also occurs, and the liquid far from the initial solid-liquid interface becomes a micro-scale solids + liquid mixture.

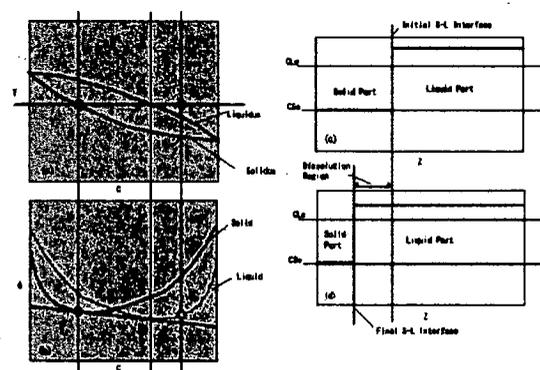


Figure 2.2 Undersaturated liquid - saturated solid reaction

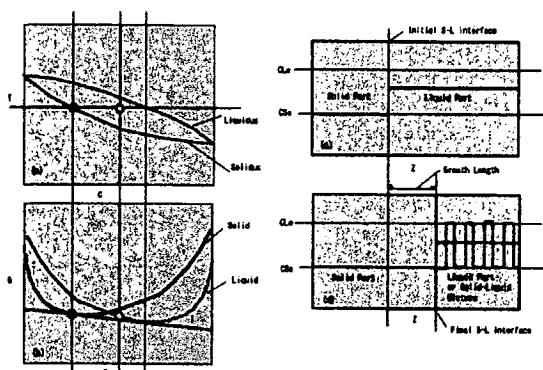


Figure 2.3 Supersaturated liquid – saturated solid reaction

(2) Reactions with undersaturated solid

In this section, we examine solid-liquid reactions with undersaturated solid. As is well known, undersaturated solid is unstable even if the solid does not contact with the liquid. Since the most stable state for the solid is mixture of saturated solid and saturated liquid, phase separation to the liquid + solid from the initially uniform undersaturated solid is expected. Figure 2.4 shows the composition plot (a), free energy plot (b), initial concentration distribution (c) and the concentration distribution after some duration (d) for the case 4. In this case, saturated liquid is contacted with the solid, which means no reaction occurs at the solid – liquid interface.

Figure 2.5 shows the reaction sequences for the case 5. The undersaturated solid becomes the mixture of the saturated solid and the saturated liquid, and the undersaturated liquid has a potential to dissolve saturated solid. So, the initial solid-liquid interface has to move toward the direction of the solid by the dissolution of the

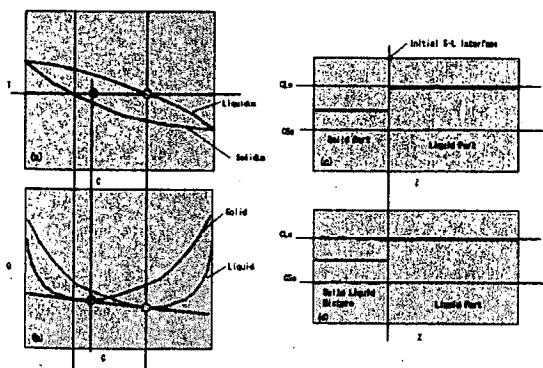


Figure 2.4 Saturated liquid – undersaturated solid reaction

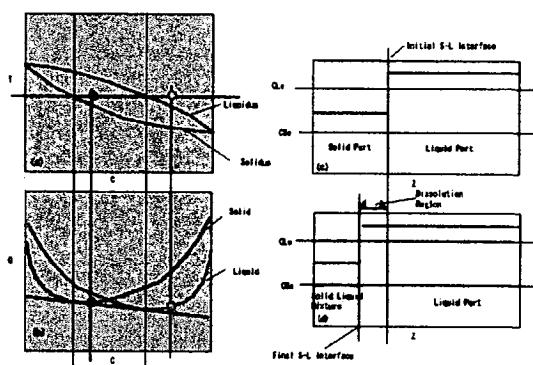


Figure 2.5 Undersaturated liquid – undersaturated solid reaction

saturated solid and by the diffusion of the solute in the liquid. The initial and the resultant concentration distribution by these reactions is shown in fig.2.5(c) and (d), respectively.

Figure 2.6 represents possible reactions for the case 6, the reaction of the undersaturated solid and the supersaturated liquid. In this case, both the undersaturated solid and the supersaturated liquid become mixtures of the saturated solid and the saturated liquid. However, relatively large thermodynamic driving force is necessary for the liquid to become the mixture because of its activation energy for nucleation. So, it is easy for the liquid to reduce its free energy by the growth of saturated solid at the initial solid-liquid interface, where saturated solid particles exist. The resultant concentration distribution is shown in fig.2.6 (d).

(3) Reactions with supersaturated solid

In this section, reactions of supersaturated solid with liquids are examined. First of all, let

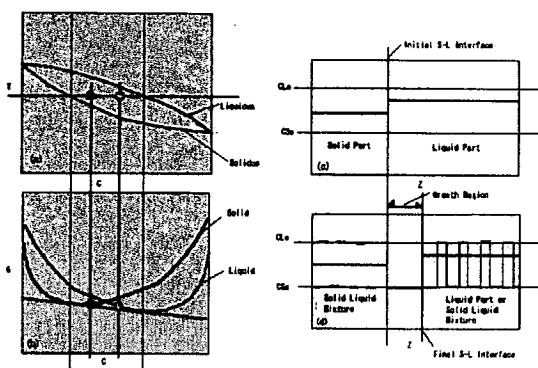


Figure 2.6 Supersaturated liquid – undersaturated solid reaction

us consider the reaction of the supersaturated solid with the saturated liquid. Figure 2.7 shows the results. It is obvious that the supersaturated solid is stable if there is no surrounding liquid. However, if the solid contacts with the saturated liquid, the solid becomes unstable since only the saturated solid can coexist with the saturated liquid. So, the solid at the interface must change its composition to saturated one by rapid reaction with the saturated liquid. After the formation of the reacted surface, the solid and the liquid become stable, without the solute diffusion from the surface toward the inside of the solid (see, fig.2.7 (d)).

Since the diffusion coefficient of the solid is much lower than that of the liquid, the diffusion in the solid is slow enough to create the diffusion boundary layer inside the solid.

Next, let us consider that the supersaturated solid contacts with the undersaturated liquid. From above discussion, the solid composition at the interface should be kept to the saturated solid composition, and this saturated solid dissolves to undersaturated liquid. The resultant reaction sequences are shown in figure 2.8. Namely, the supersaturated solid reacts with the undersaturated liquid, and produces saturated solid. Excess solute is transported toward the inside of the solid by the concentration gradient in the solid. Simultaneously, the dissolution event occurs at the interface, which results in the interface movement and the production of the new reacted layer (saturated solid layer).

The quite different reactions are expected in the case 9, in which the supersaturated solid

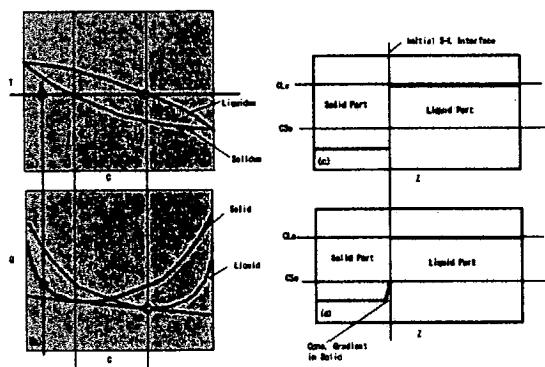


Figure 2.7 Saturated liquid – supersaturated solid reaction

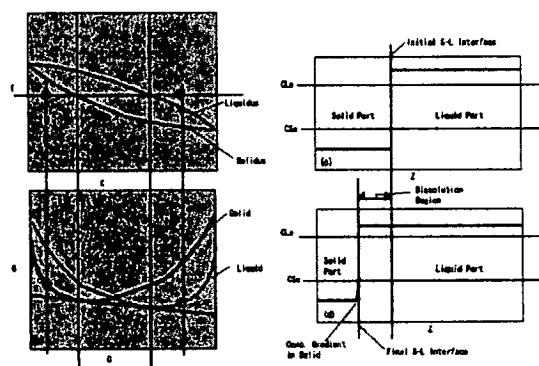


Figure 2.8 Undersaturated liquid – supersaturated solid reaction

contacts with the supersaturated liquid. In this case, the supersaturated solid is unstable to the liquid. However, the supersaturated liquid has an ability to produce the saturated solid spontaneously. So, the growth of the saturated solid occurs at the initial solid-liquid interface. By this growth, the supersaturated solid is isolated to the liquid. Further reaction in the solid is only the mass transport process. On the other hand, the growth can continue as long as the supersaturation in the liquid exists. The results are shown in figure 2.9. It should be noticed that two phase region, which contains the saturated solid and the saturated liquid, may be produced if the supersaturation in the liquid is large enough for nucleation of the saturated solid.

#### (4) Summary of this section

The possible reactions for solid – liquid contact pair were examined. The results were summarized in table 2.2.

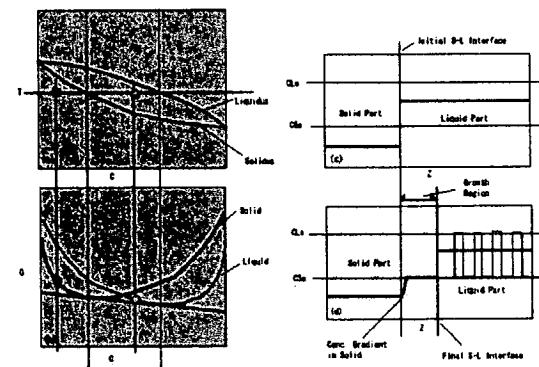


Figure 2.9 Supersaturated liquid – supersaturated solid reaction

Table 2.2 Possible reaction events for solid – liquid pair

Case	State of Solid	State of Liquid	Reaction
1	saturated	saturated	Equilibrium. No reaction occurs.
2	saturated	under-saturated	Solid dissolves into liquid.
3	saturated	super-saturated	Solid with saturated composition grows.
4	under-saturated	saturated	Initial solid part separates to two phase region. Initial S-L interface does not move.
5	under-saturated	under-saturated	Initial solid part separates to two phase region. Liquid part increases by the dissolution of the two phase region.
6	under-saturated	super-saturated	Initial solid part separates to two phase region. Saturated solid grows from initial S-L interface.
7	super-saturated	saturated	Solid reacts with liquid, and produces saturated solid layer at the interface. Concentration gradient is produced in the solid. S-L interface does not move.
8	super-saturated	under-saturated	S-L reaction to form saturated solid and dissolution of the solid simultaneously occurs. Concentration gradient is produced in the solid.
9	super-saturated	super-saturated	Saturated solid grows on the initial S-L interface. Concentration gradient is produced in the solid.

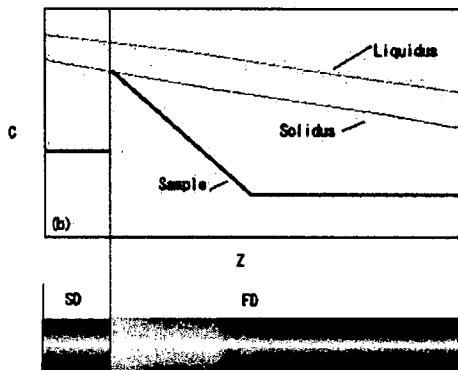
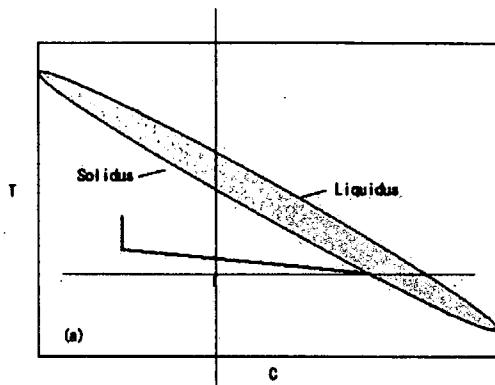
### Description of CGPM sequence

#### (1) Initial stage

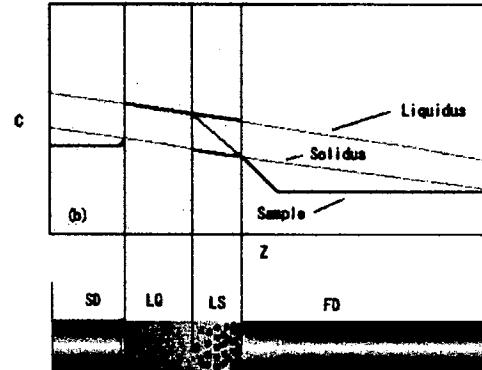
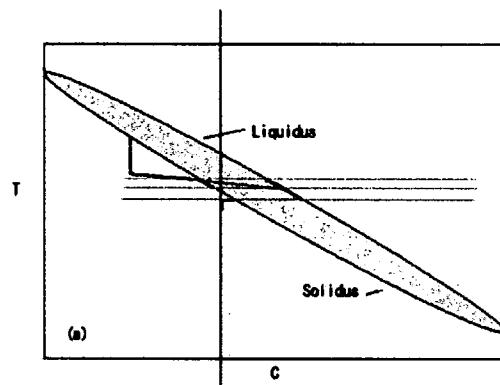
As the increase of the temperature, the highest concentration part in the gradient concentration feed begins to dissolve. In figures 3.1 (a) - (c), concentration - temperature plot (a), concentration - length plot (b), and schematic image of the sample (c) of this stage are represented. In these figures, concentration of the gradient composition sample is above the solidus only at the vicinity of the seed. At this point, the feed begins to separate saturated solid and saturated liquid, and produces two phase zone. The other part of the sample is kept to solid state.

Further increase of the temperature results in the increase of the two phase zone width. Figure 3.2 shows the image of this stage. Both the solid fraction and the solid composition of the two phase zone vary with the position. The compositions of the solid and the liquid are changed with the increase of the temperature, to

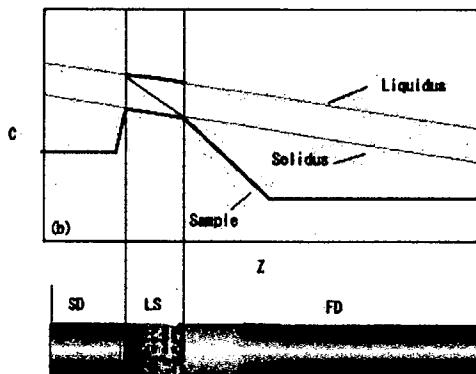
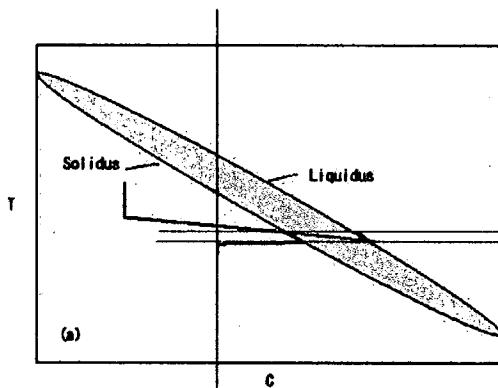
keep the solidus and the liquidus, respectively. Fractions of the solid and the liquid are also changed, but the bulk concentration distribution is almost kept constant, in this two phase region. If the bulk composition exceeds the liquidus, solid disappears and liquid zone is produced. Excess solute, which is defined as the difference between the composition and the liquidus composition, is transferred to the two phase zone, at which the solute reacts with the solid and produces the saturated liquid. Composition of the seed, near the interface, also changes with the increase of the temperature to keep the composition as the solidus composition. This reaction is attained by the interfacial solid - liquid reaction. By these reactions, the composition of the liquid is kept to the liquidus value along the zone. Solute redistribution in the solid also occurs by solid state diffusion, but the rate is low enough to neglect.



(a) (b) **Figure 3.1 Beginning of melting**



(a) (b) **Figure 3.3 End of initial stage**



(a) (b) **Figure 3.2 S+L zone spread**

Finally, characteristic sample configuration is produced at the growth temperature, which is shown in figure 3.3. Seed is dissolved by the excess solute of the liquid, which results to keep both the solid composition and the liquid composition as the saturated ones. Liquid zone is produced in front of the seed because the initial bulk composition of this part is well above the liquidus. The excess solute moves toward the two phase zone, at which the solute reacts with the solid to produce the saturated liquid. The high temperature side of the feed is kept to solid state.

It should be noticed that the concentration gradient in the liquid near the solid - liquid interface induces growth of the crystal. So, the long duration of soaking should be avoided.

## (2) Growth stage

Since the composition of the liquid is fixed to the liquidus composition, concentration gradient in the liquid is also fixed. This means that there is a unique steady state growth rate for which mass flux by the interface movement and the solute removal flux from the interface are balanced.

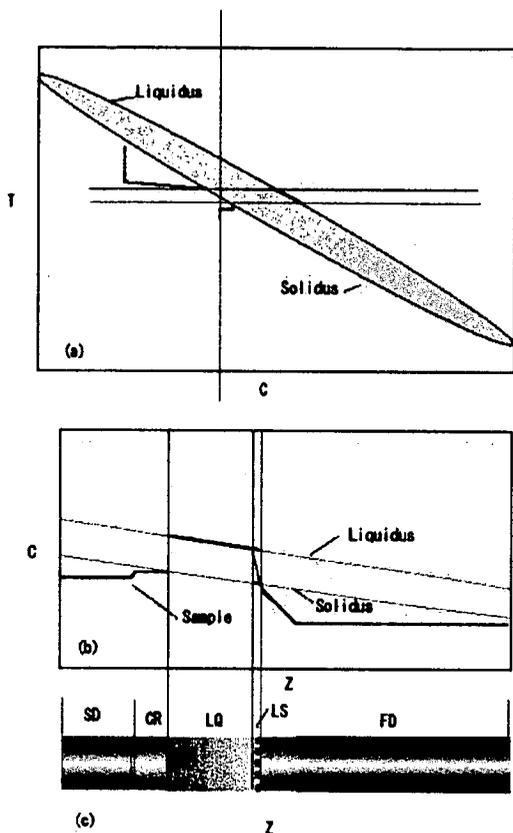


Figure 3.4 Early stage of the homogeneous growth

If we translate the sample downward with equal speed to the steady state growth rate, the position of solid – liquid interface is kept at the desired position at a constant temperature, and the crystal continues to grow with constant composition. Figure 3.4 shows a snap shot of this period. As the growth proceeds, width of the two phase zone decreases due to the dissolution of the solid particles in the zone. The driving force of this dissolution process is excess solute flux, which is transferred from the liquid zone.

After the disappearance of the two phase zone, dissolution reaction between the liquid and the solid feed governs the concentration gradient in the liquid. Figure 3.5 shows the image. Since concentration of the feed surface must be the solidus composition at that temperature, sharp concentration gradient is produced in the feed. The composition of the liquid at the feed – liquid interface is higher than the liquidus composition at the temperature, because undersaturation is necessary for the liquid to dissolve the feed with

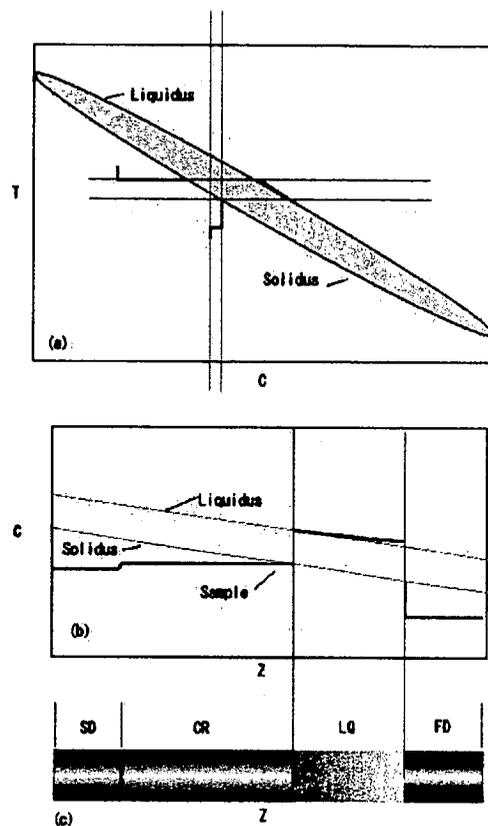


Figure 3.5 Growth without S+L region

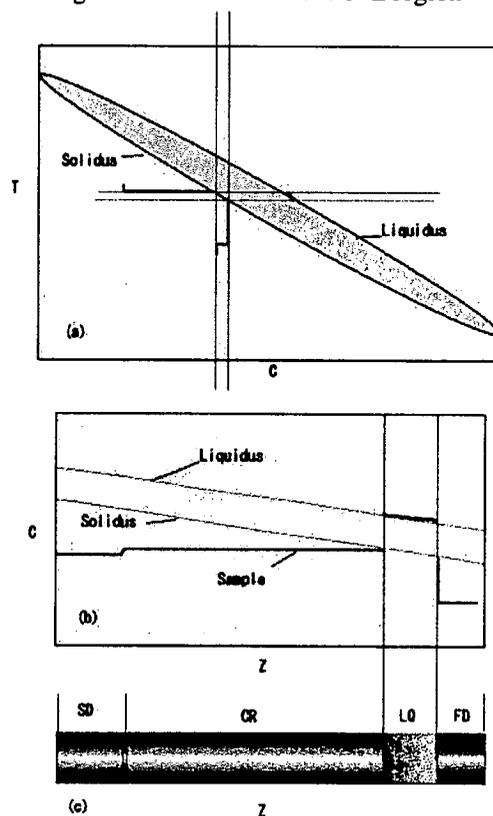


Figure 3.6 Reduction of liquid zone width with the increase of the growth length

finite dissolution rate. However, there is no serious change for the liquid concentration gradient near the crystal- liquid interface, since the degree of undersaturation is not so large.

As the growth proceeds, the width of the liquid zone becomes narrower. Unfortunately, we can not estimate the change of zone width, since no analytical equation exists, which describes the dissolution process. However, it is clear that the zone width must decrease as the growth because of the total mass compensation. Figure 3.6 shows the image.

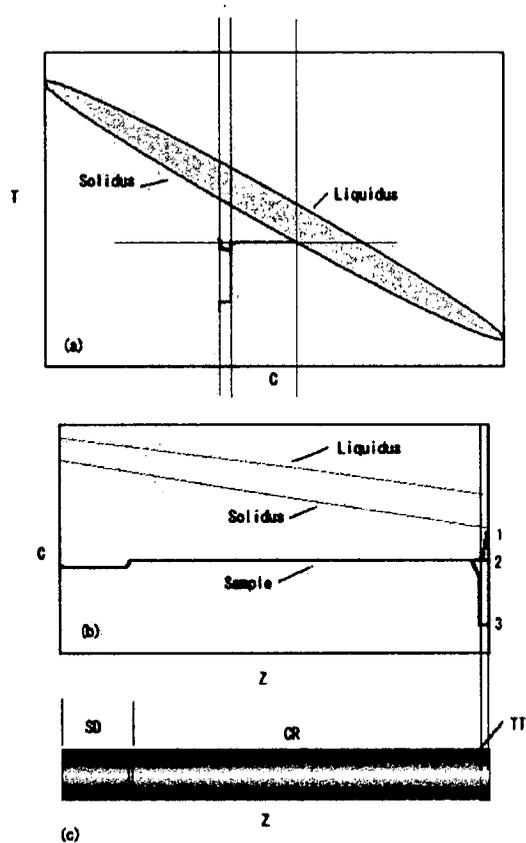


Figure 3.7 Terminal stage of the growth

### (3) Terminal stage

Three different cases are expected in the later stage of solidification. Figure 3.7 shows the image.

If the average concentration of the feed is similar to the concentration of the crystal, the composition of the crystal is kept constant to the end of solidification. This relation is shown as 2 in fig.3.7.

Next case is that the average concentration of the feed is lower than the concentration of the growing crystal, which case is denoted by 3 in fig.3.7. In this case, the liquid zone disappears prior to the zone attach the terminal point of the feed. After the depletion of the zone, there is no dissolution occurs for the rest of the feed.

The final case is that the average concentration of the feed is higher than the concentration of the growing crystal, which case is denoted by 1 in fig.3.7. In this case, the solid part of the feed disappears at relatively early stage. After the disappearance of the solid feed, the concentration governing mechanism at the liquid – feed interface also disappears. As a result, the concentration of the solid increases rapidly, toward the terminal point of the sample. This process is essentially same as the terminal transient of normal freezing type solidification.

### (4) Necessity conditions for CGPM

To utilize the above CGPM, the following conditions have to be satisfied.

#### a. Composition of the growing crystal

Composition of the solid at the growing

interface is the solidus composition at that temperature. It is necessary to control initial position of the solid – liquid interface, to grow the crystal with the desired composition.

#### b. Growth rate

Since both the concentration and the concentration gradient are kept constant in CGPM, a unique growth rate, which keeps both values constant, exists. If the translation rate of the sample is equal to this growth rate, growth of the crystal with constant composition becomes possible. The only way to change the growth rate is to change the temperature gradient of the furnace.

#### c. Sample composition

In CGPM, the two phase region, which exists at early stage of growth, acts as a stabilizer of the liquid composition. But the solid particles beside the crystal – liquid interface may act as the source of poly-crystallization. So, the concentration of

the sample must be above or equal to the liquidus concentration near the seed - liquid interface, it must be below the liquidus concentration at some region, and below the solidus concentration at far from the interface. Average concentration of the feed with gradient solute concentration should be equal to the desired growth concentration.

### Application to the $\text{In}_x\text{Ga}_{1-x}\text{As}$ system

#### (1) Preparation of a gradient concentration feed

It is easy to produce a gradient concentration feed if we use normal freezing method with complete mixing condition. In the normal freezing method with complete mixing, no concentration gradient in the liquid exists and the solid grows with the equilibrium concentration to the liquid. In the case of  $\text{In}_x\text{Ga}_{1-x}\text{As}$ , the concentration of the residual liquid becomes In-rich, due to the increase of the fraction solidified. So, the concentration of the solid also changes with the fraction solidified.

If the distribution coefficient,  $k$ , is constant, the concentration distribution is written as the function of the fraction solidified,  $g$ .

$$X_s(g) = kX_L(g) = kX_{L,0}(1-g)^{k-1} \quad [4.1]$$

Where,  $X_{L,0}$  is the initial liquid concentration<sup>10)</sup>.

In the case of  $\text{In}_x\text{Ga}_{1-x}\text{As}$ , the above equation can not be used since  $k$  varies with the concentration.

There are following three methods to produce gradient concentration feeds with  $x$  values of 0.3.

- 1) To solidify a melt with average  $x$  values of 0.3, and use the full length of the sample.
- 2) To solidify a melt with average  $x$  values lower than 0.3, and cut the sample to use later part of the sample.
- 3) To solidify a melt with average  $x$  values higher than 0.3, and cut the sample to use the initially grown part.

Unfortunately, there is no analytical solution for variable  $K$ . Instead, we carried out numerical calculation.

The amount of the solute,  $\Delta Q$ , which is incorporated into the solid by the change of the small amount of fraction solidified,  $\Delta g$ , is written as follows.

$$\Delta Q = \Delta g k(X_L) X_L \quad [4.2]$$

In addition, the following equation is valid due to the mass conservation law.

$$X_{L,0} = X_L(1-g) + Q \quad [4.3]$$

If  $k$  is constant, the following integration equation can be solved, to form eq[4.1].

$$\int_0^g \frac{k}{(1-x)} dx = \int_0^Q \frac{dy}{(X_{L,0} - y)} \quad [4.4]$$

For the  $\text{In}_x\text{Ga}_{1-x}\text{As}$  system, since  $k$  varies with  $X_L$  or  $X_s$ , eq.[4.2] was directly used to calculate. The calculation flow is shown in figure 4.1.

Figure 4.2 shows the result of the case 1. In this figure, a) is a fraction solidified - concentration plot. b) is a fraction solidified - average concentration plot, the red line indicates the left average concentration, and blue line indicates the right average concentration.

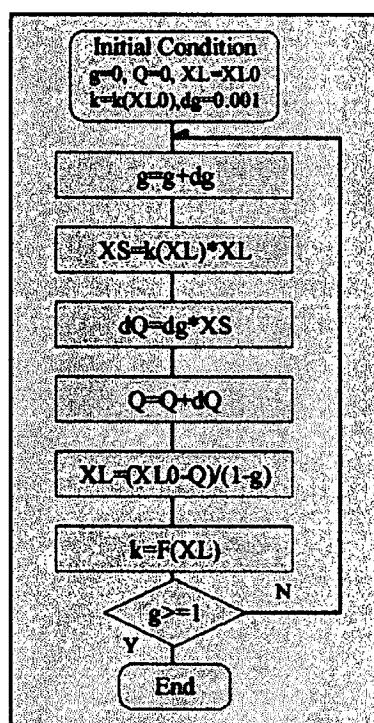


Figure 4.1 Calculation flow of numerical simulation

simulation

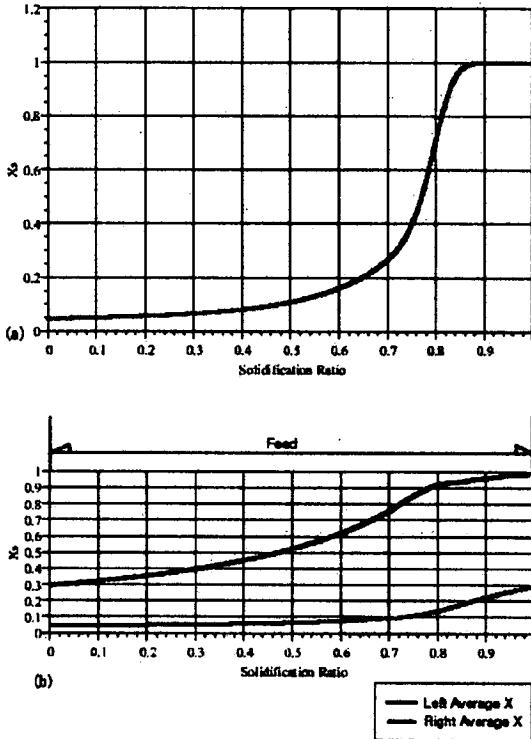


Figure 4.2 Normal freezing pattern for  $X_{ia}=0.3$

It is clear from fig.4.2(b) that the fully solidified sample is necessary to keep the average concentration 0.3.

Figure 4.3 shows the normal freezing pattern (a) and average composition plot (b) for  $x$  values of 0.2. In this figure, it is understood that we can obtain the feed with average  $x$  values of 0.3 by cutting the sample at 0.4 of fraction solidified, and use the right side of the sample.

Figure 4.4 is the normal freezing pattern (a) and average composition plot (b) for  $x$  value of 0.4. In this case, the sample with  $x$  value of 0.3 can be obtained by using the left side of the original sample from 0.85 of solidification ratio.

Experimentally, gradient concentration sample with constant length has to be prepared. To obtain the sample, the length of the original sample must be longer than the length of the feed sample. Figure 4.5 shows the concentration distribution for samples with 50mm in length and with  $x$  value of 0.3, but the average concentration of the original sample is different. From this figure, it was recognized that the increase in the average concentration of the original sample results in the lower concentration gradient.

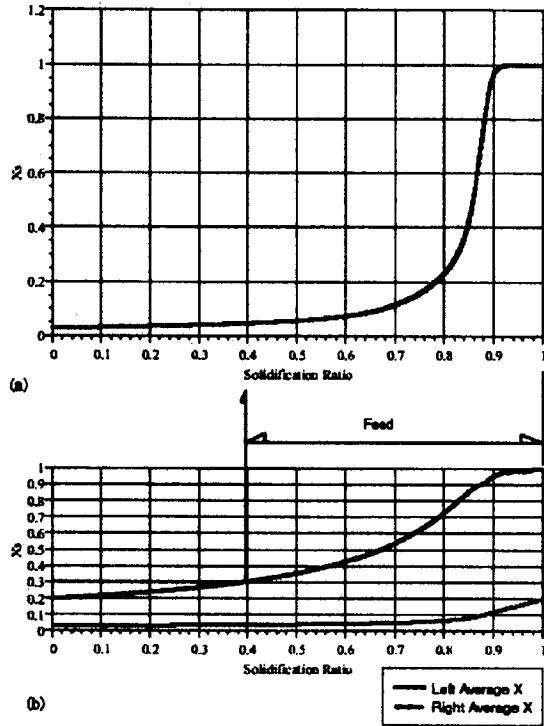


Figure 4.3 Normal freezing pattern for  $X_{ia}=0.2$

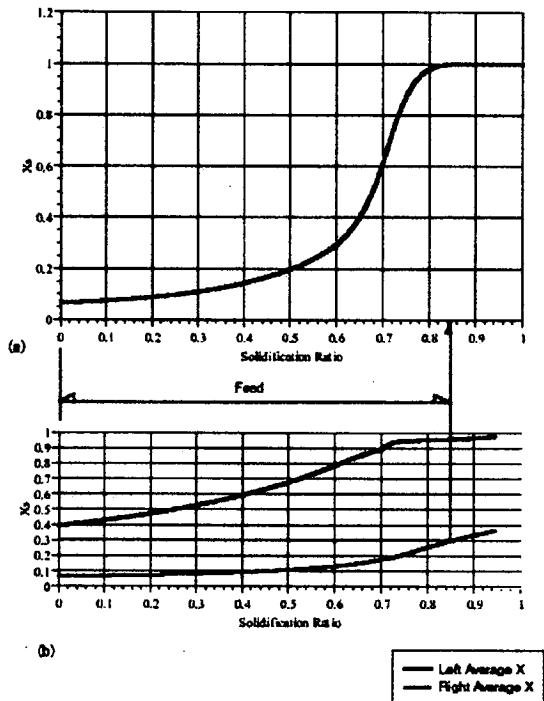


Figure 4.4 Normal freezing pattern for  $X_{ia}=0.4$

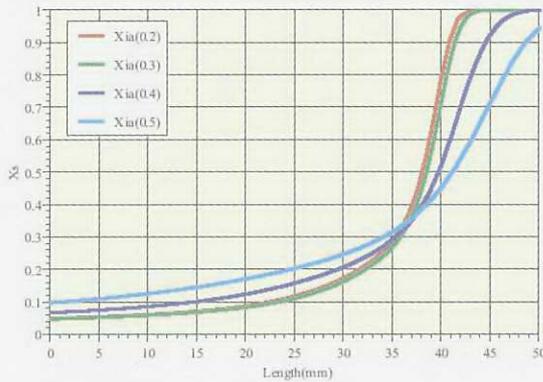


Figure 4.5 Concentration profile of the CGPM feeds with average concentration is 0.3 and 50mm in length, which were made by various  $X_{ia}$ .

(2) Estimation of initial zone character

Next, simple estimation of the zone character was performed. The concentration profile of the gradient concentration sample was superimposed on the length- equilibrium concentration diagram, as was shown in figure 4.6. In this figure, the green line and red line indicate the liquidus and solidus concentration distribution for desired temperature gradient, respectively. The left terminal position of the sample coincides with the position at which the solidus concentration is 0.3. The initial zone width is given by the difference between the left terminal position and the cross point for the sample concentration line and the solidus line. It should be noticed that the surface area of the SA must be smaller than that of SC in fig.4.6(a) to sustain the S+L region in the initially melted region. However, the width of S+L region must be suppressed to sustain liquid region near the seed. To evaluate the degree of the S+L region, average supersaturation is introduced. The term is defined as follows.

$$\sigma_A \equiv \frac{(S_{SB} - S_{SA})}{(S_{SB} + S_{SC})} \times 100(\%)$$

Roughly speaking, if the average supersaturation exceeds 50%, half of the surface area of S+L region, the S+L region contacts with the seed and no liquid region is sustained, at least at the beginning of the growth.

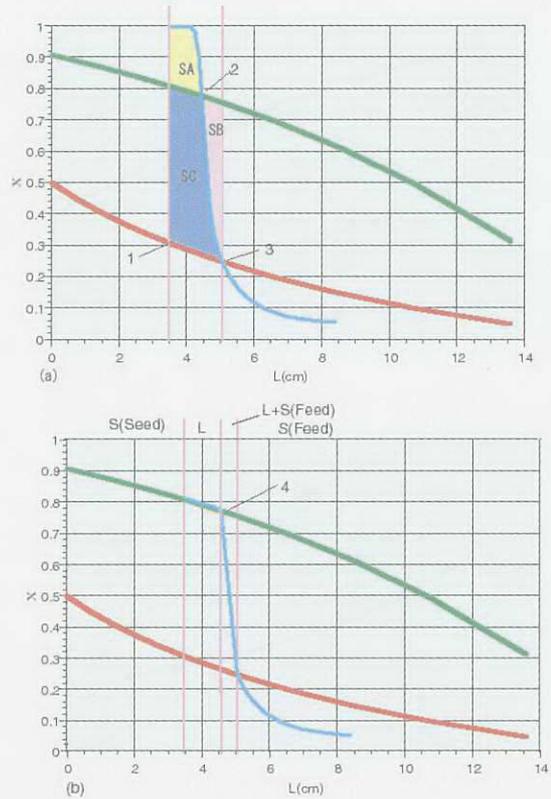


Figure 4.6 Superimposed concentration profile on length - equilibrium concentration plot

Results are shown in figure 4.7 to figure 4.9 and table 4.1. Fig.4.7 shows the superimposed image for the sample which was prepared by the normal freezing of  $X_{ia}=0.3$  composition. In the figure, (a) is for  $G=15K/cm$  and (b) is for  $G=20K/cm$ . It is shown that the initial zone width is larger for  $G=20K/cm$  than for  $G=15K/cm$ . The similar situations are shown in fig. 4.8 and fig. 4.9, which are the images for  $X_{ia}=0.4$  and  $X_{ia}=0.5$ , respectively. Of course, the average composition of these samples are kept to  $X=0.3$ , by cutting off the sample at desired position.

The calculated zone width and the average supersaturation are represented in table 4.1.

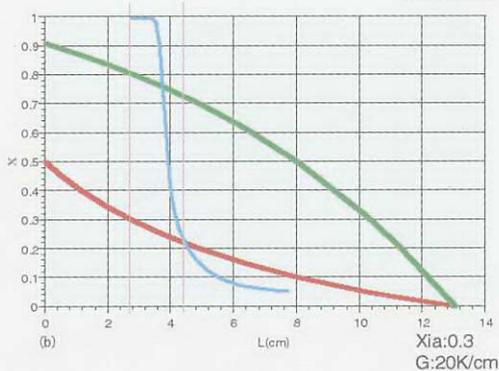
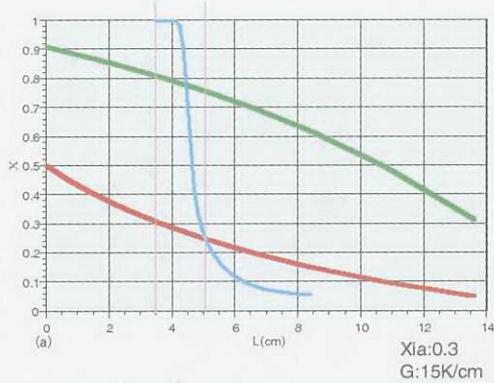


Figure 4.7 Concentration plot for  $X_{ia}=0.3$

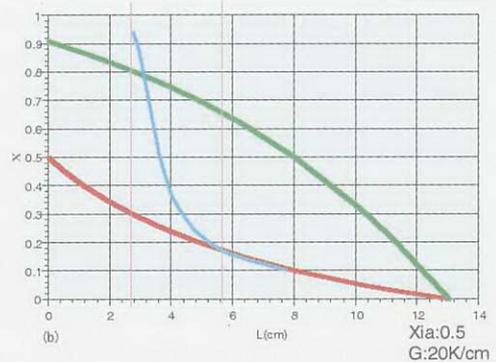
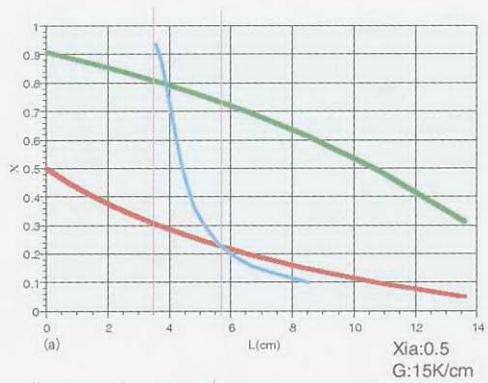


Figure 4.9 Concentration plot for  $X_{ia}=0.5$

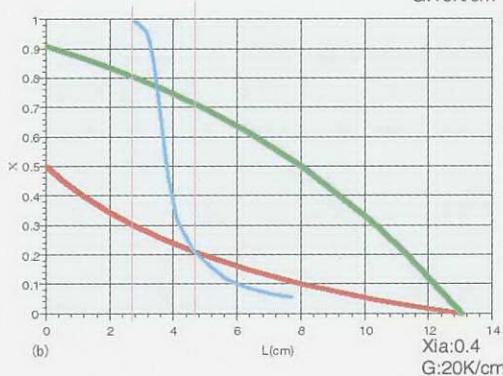
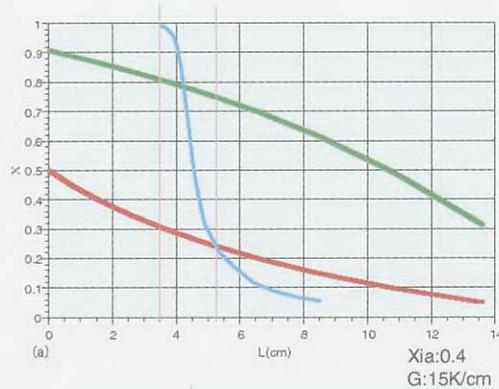


Figure 4.8 Concentration plot for  $X_{ia}=0.4$

From the above estimation, the followings are recognized.

- 1) Initial zone width increases by the increase of the temperature gradient of the experimental system.
- 2) The zone width is also affected by the concentration profile of the sample.
- 3) Since the average supersaturation exceeds 50% for the sample which was prepared by the normal freezing of the  $X_{ia}=0.5$  material, no liquid zone seems to be appeared in the sample.
- 4) In this sample, higher temperature gradient than 20K/cm can not be applicable since the concentration profile of the feed becomes to be higher than the solidus line.

Table 4.1 Estimated zone characters

ID	X <sub>ia</sub>	G(K/cm)	Zone width (mm)	Average super-saturation(%)
1	0.3	15	16.0	3.88
2	0.3	20	16.4	2.63
3	0.4	15	17.0	22.55
4	0.4	20	20.0	28.04
5	0.5	15	26.5	51.51
6	0.5	20	30.0	60.94

### (3) Estimation of growth rate

In CGPM, the concentration gradient in the liquid is governed by the temperature gradient and by the phase diagram. So, if the concentration gradient for steady state growth rate is equal to the governed concentration gradient at the crystal-liquid interface, the growth with constant composition is attained.

The concentration gradient at the interface for steady state growth is given as follows<sup>(11)</sup>.

$$\frac{\partial X_{L,0}}{\partial z} = -\frac{X_{s,0}(1-k)V}{kD}$$

On the other hand, the concentration gradient of CGPM is described as follows.

$$\frac{\partial X_L}{\partial z} = \frac{\partial X_L}{\partial T_{liq}} \frac{\partial T_{liq}}{\partial z} = \frac{\partial X_L}{\partial T_{liq}} G$$

The steady state growth rate for CGPM was calculated for x values of 0.2 to 0.4, and for two different temperature gradients. Figure 4.10 shows the result for which D is assumed to be  $1 \cdot 10^{-8} \text{m}^2/\text{s}^{(12)}$ . In this figure, blue line denotes the rate at G=10K/cm, red line denotes the rate at G=15K/cm, and purple line denotes the rate at G=20K/cm. From this figure, it is noticed that the concentration dependence on the growth rate is relatively small, but the growth rate dependence on the temperature gradient is large.

For example, the growth rate for x value of 0.3 with the temperature gradient of 20K/cm is 0.326mm/h.

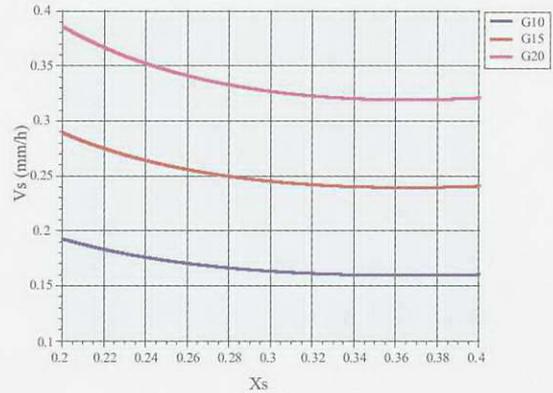


Figure 4.10 Quasi-steady state growth rates for various G and X<sub>s</sub>

### (4) Evaluation of translation rate effect

In the CGPM, the steady state growth rate, V, must be equal to the translation rate of the sample, R. This relation is valid as long as the solid feed exists. However, it is difficult to control the translation rate with the same rate as the growth rate.

The crystal-liquid interface moves due to the difference between the growth rate and the translation rate. This interface movement results in the growth with new concentration, for which the new growth rate is defined. Namely, the new position of the interface after the desired time interval, for temperature fixed coordinate is given as follows,

$$\Delta Z_f = (V_{st}(X_s) - R)\Delta t$$

By this movement, both the temperature of the interface and the solidus composition change as follows,

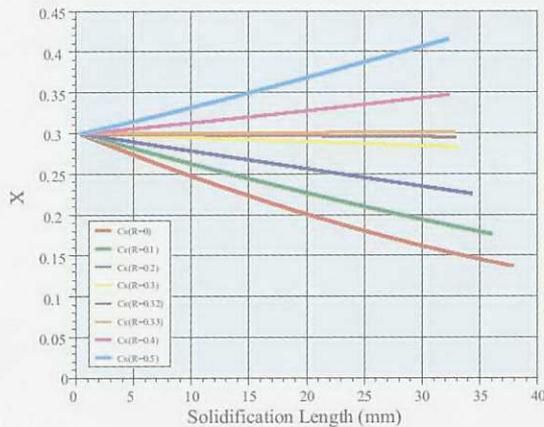


Figure 4.11 Calculated concentration distribution for grown crystals with various pulling rate and start from  $X=0.3$

$$\Delta T = G\Delta Z_f,$$

$$\Delta X_s = \frac{\partial F_s(X_s)}{\partial T} \Delta T$$

Then the steady state growth rate is re-determined for the new  $X_s$ . Figure 4.11 shows the results of the numerical calculation, which evaluates the effect of the rate difference on the concentration change. In this figure, it is recognized that the 20% of rate difference results in the concentration difference of 0.5 after about growth of 30mm. So, it was demonstrated from the figure that there is a translation rate region in which the grown crystal is nearly homogeneous, though the above estimation gives the maximum variation.

### Summary

In the present study, characteristics of CGPM were clarified qualitatively. In addition, quantitative estimation, which includes the concentration profile of feed, initial zone width, the optimum growth rate, and effect of the translation rate, was made for the  $\text{In}_x\text{Ga}_{1-x}\text{As}$  system.

To develop a quantitative model for CGPM, both the mass transport process in two phase region and the dissolution process of supersaturated solid in undersaturated liquid, will be examined quantitatively.

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