Segregation Mechanism in $Si_{1-x}Ge_x$ Single Crystal Fiber Growth by Micro-pulling Down Method

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1. Introduction

We have been developing a micro-pulling-down (μ-PD) technique (Fig. 1) to grow a single crystal fiber with good compositional homogeneity [1-3]. In this paper we show that the solute diffusion boundary volume is differentiated into the molten zone (zone I) next to the interface and the capillary zone (zone II) leading to the bulk melt (Fig. 1) and the steady state solution is obtained for each zone. The solute mass balance at the zone boundary between zone I and II is essential to the steady-state growth and the instant breakage of the mass balance represents the onset of the intermediate transient. Moreover, we obtained the equilibrium partition coefficient, k_0 and the diffusion constant, D, for Ge in $Si_{1-x}Ge_x$ melt ($x = 0.05$) for the growth by μ-PD method, which were compared with those obtained based on Czochralski method.

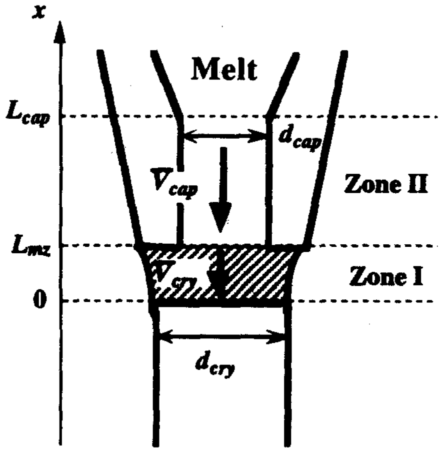

Fig. 1 Solute accumulation volume consisting of two zones

2. Analytical and Experimental

2.1 Steady State Analysis

It is possible at high growth rate that the solute enriches to be C_0/k_0 at the interface leading k to be unity since the size of the liquid volume which is kept from convection can be large. It is assumed that zone I and II are not significantly affected by melt convection and the solute flux is considered one-dimensionally and then described basically in terms of the gradient of the solute

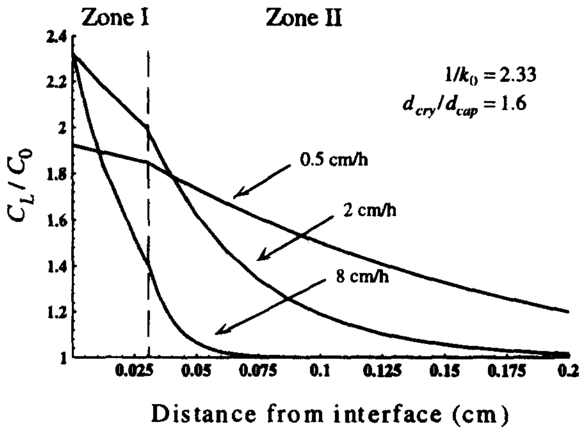

Fig. 2 Calculated curves of steady-state Ge distribution in zone I and II with various growth rates

concentration and the growth velocity. The steady-state solutions for these two zones are obtained and Fig. 2 shows the Ge distribution during steady-state growth for different growth rates. It should be noted that the Ge concentration at the interface is not saturated when the growth velocity is small. Fig. 3 shows the Ge distribution for the variable ratios of diameters between crystal and capillary channels. Large ratio leads to a drastic change of distribution due to the poor solute communication at the zone boundary.

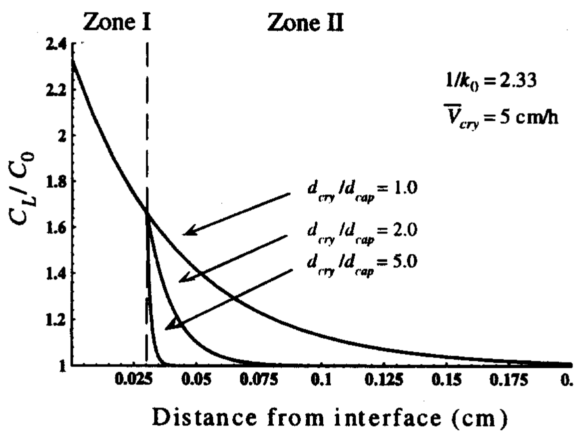

Fig. 3 Calculated curves of steady-state Ge distribution in zone I and II with various diameter ratios between crystal and capillary channel

2.2 Initial Transient Analysis

We may be allowed to use Smith et al's equation (no mixing model) [4] for the analysis of the initial transient growth since the deflection point at the zone boundary is much less discernible when d_{cry}/d_{cap} is close to unity or V_{cry} becomes large enough to lead k to be unity; i.e., zone I + zone II is treated as a one zone. In such a case, we concern the Ge flux in the vicinity of the interface and primarily along the axis of the symmetry rather than all over the zone. Fig. 4 represents the Ge distribution in the initial transient to steady state. By fitting data with Smith et al's equation via a nonlinear programming, we obtained k_0 to be 0.43 and D_{Ge} to be 5.6×10^{-5} cm^2 s^{-1}. The value of D_{Ge} is an order of magnitude smaller than those of various dopants in Si melt which were previously reported. This was due to the little radial flow effect on solute partitioning in μ-PD method.

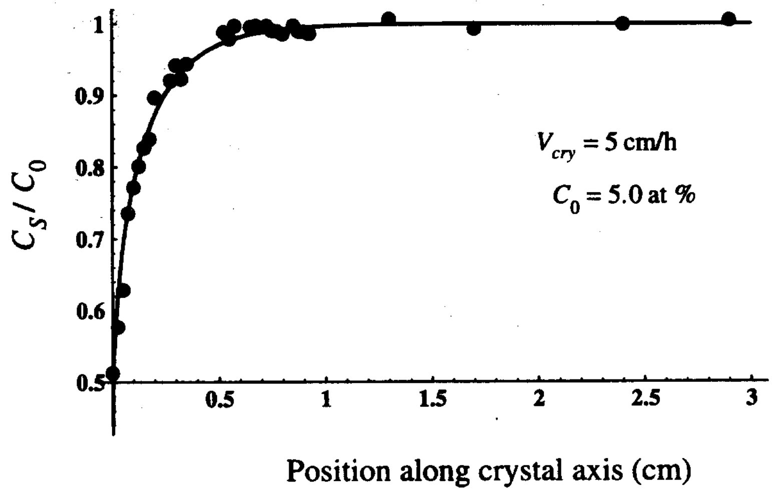

Fig. 4 Ge distribution in the initial transient to steady state

2.3 Intermediate Transient

An abrupt change of growth velocity during steady-state growth from V_{cry} to V'_{cry} ($V_{cry} < V'_{cry}$) yields a transient rise in the concentration in the liquid in the vicinity of the interface and the consequent concentration rise in the solid (Fig. 5). Then the system will be back to the same steady state after a while as the one before the velocity changes. Since the abrupt change of the growth velocity was not satisfactory in experiments, the concentration rise due to the sudden increase of the growth velocity from V_{cry} to V'_{cry} was much lower than expected by the calculation. This was demonstrated in Fig. 6 for the growth velocity change of V_{cry} = 3 cm/h to V'_{cry} = 6 cm/h. The intermediate transient is explained in terms of the solute accumulation diversity in the vicinity of the interface due to the sudden change of the growth conditions.

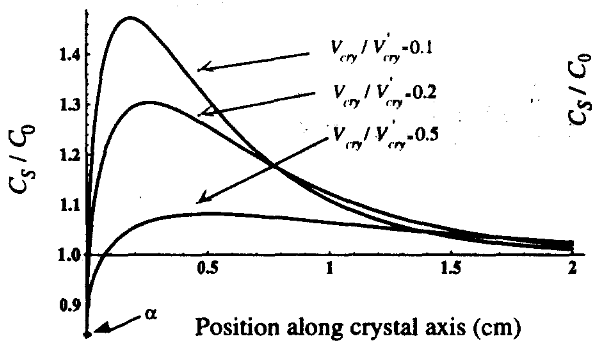

Fig. 5 Illustration of calculated intermediate transient for various growth rate changes

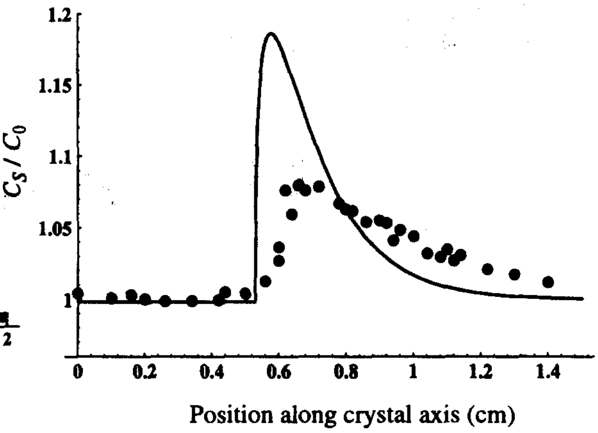

Fig. 6 Intermediate transient rise of Ge concentration due to the sudden change of growth velocity

3. Discussion

The influence of the melt convection in the molten zone on partitioning due to Marangoni flow and the central down flow from the capillary should be discussed to justify analysis taken above. Experiments tell that there was well-developed solute accumulation layer with gradient near the interface which is not much influenced by the convection when V_{cry} is large and $1.0 < d_{cry} / d_{cap} < 2.8$, giving k_{eff}^{Ge} unity. For those cases, we could use the no mixing model for the analysis without large errors.

References

[1] D. H. Yoon, I. Yonenaga, T. Fukuda and N. Ohnishi, *J. Crystal Growth* **142** (1994) 339.

[2] D. H. Yoon, P. Rudolph and T. Fukuda, *J. Crystal Growth* **144** (1994) 207.

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[4] V. G. Smith, W. A. Tiller and J. W. Rutter, *Can. J. Phys.* **33** (1955) 723.

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Background

μ -PD method

-Very little defects

-Easy to control melt convection

-Easy to control shape, size and compositional homogeneity

Semiconductor

Si

SiGe

Oxide

LN

KLN

KLTN

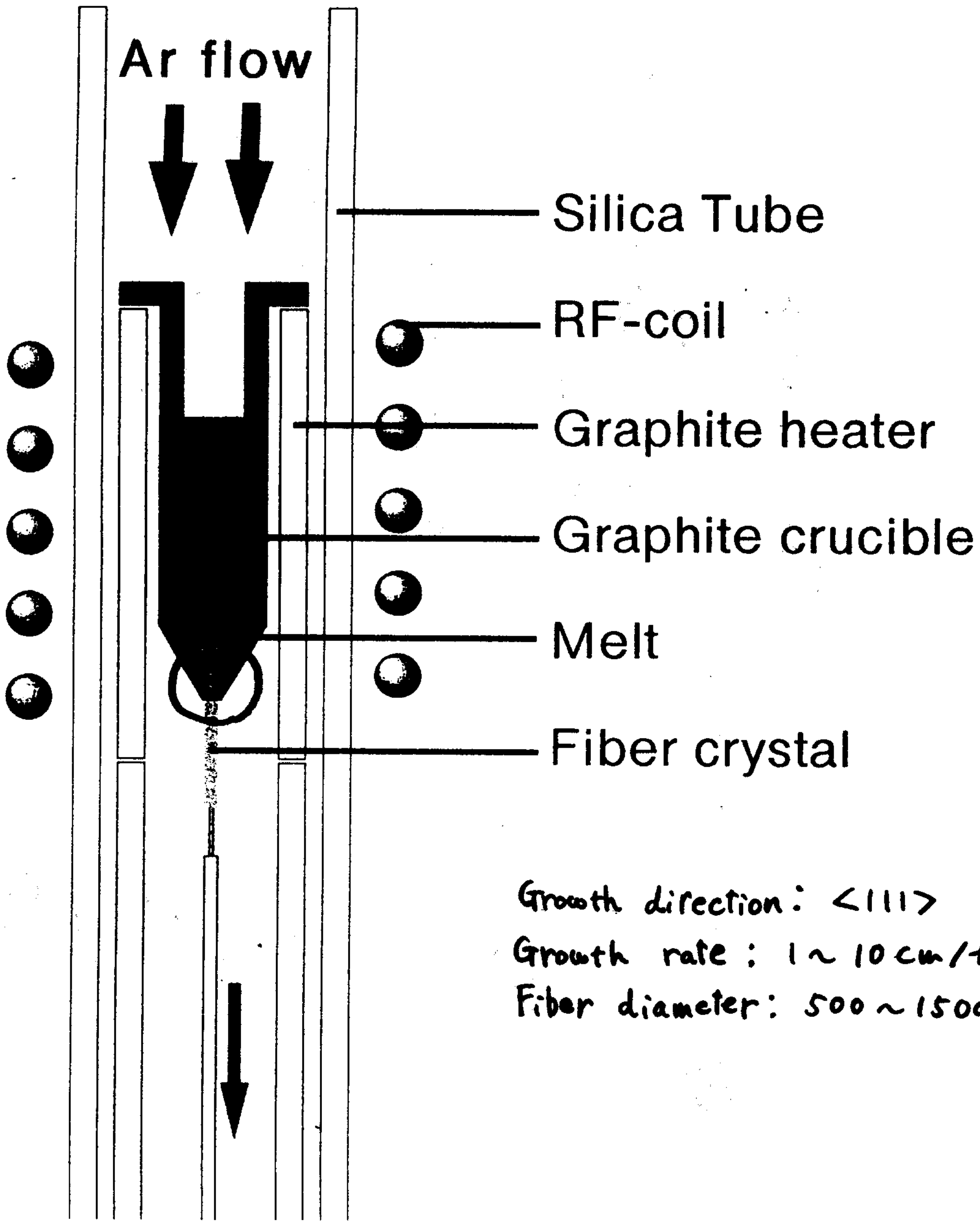
This study

Analysis of growth mechanism by μ -PD method

-Solute distribution

-Effect of melt convection

-Composition control



Growth direction: <111>
Growth rate: 1 ~ 10 cm/h
Fiber diameter: 500 ~ 1500 μm

Apparatus for $Si_{1-x}Ge_x$ fiber crystal growth by micro-pulling down method

Steady-state analysis

Differential Equation

<zone I > $D_{Ge}\dfrac{\partial^2 C^1}{\partial x^2}+\overline{V}_{cry}\dfrac{\partial C^1}{\partial x}=0$

<zone II > $D_{Ge}\dfrac{\partial^2 C^2}{\partial x^2}+\overline{V}_{cap}\dfrac{\partial C^2}{\partial x}=0$

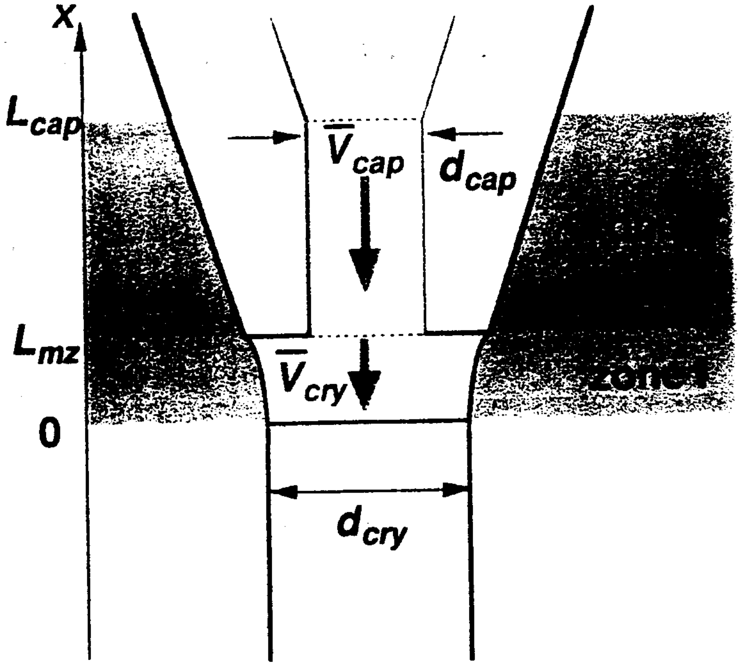
Boundary Conditions

<zone I > $\overline{V}_{cry}(1-k_0)C^1_{(0)}+D_{Ge}\left(\dfrac{\partial C^1}{\partial x}\right)_{x=0}=0$

$C^1_{(Lmz)}=C_L$

<zone II > $C^2_{(Lmz)}=C_L$

$C^2_{(Lcap)}=C_0$

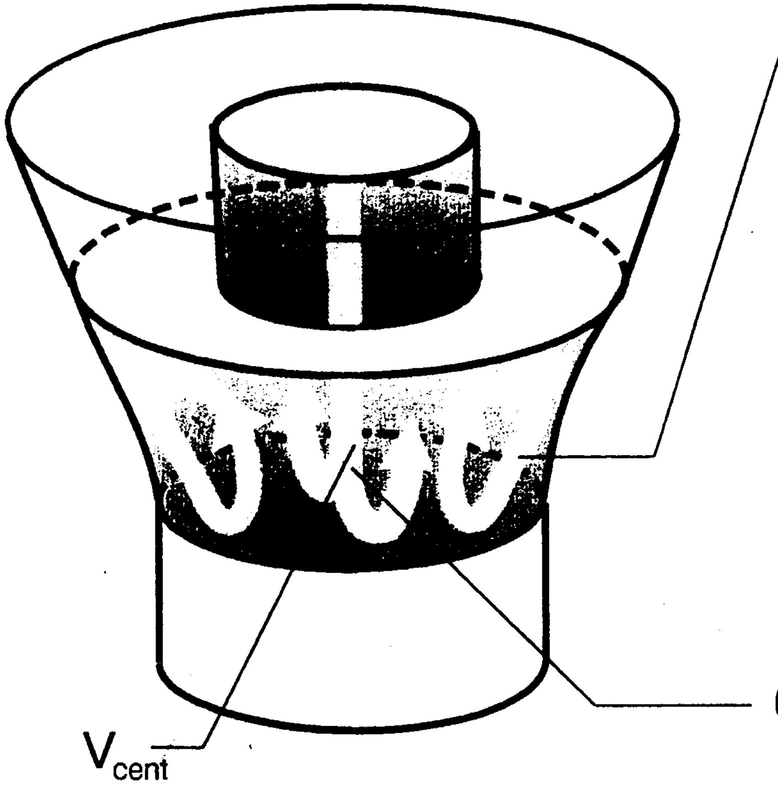


Mass conservation at zone boundary

($J_1S_1=J_2S_2$ at $x=L_{mz}$)

$$\pi d_{cry}^2\left(D_{Ge}\frac{\partial C^1}{\partial x}+\overline{V}_{cry}C^1\right)=\pi d_{cap}^2\left(D_{Ge}\frac{\partial C^2}{\partial x}+\overline{V}_{cap}C^2\right)$$

Melt convections in the molten zone



① Marangoni flow

Marangoni number: $Ma = -\left(\frac{\partial\gamma}{\partial T}\right)\left(\frac{\Delta Th}{\bar{\eta} D_T}\right)$

here $D_T = k / \rho c_p$

$\left(\frac{\partial\gamma}{\partial T}\right)$: Surface tension gradient with temperature

h : Molten zone length

ΔT : Temperature difference

$\bar{\eta}$: Viscosity

k : Thermal conductivity

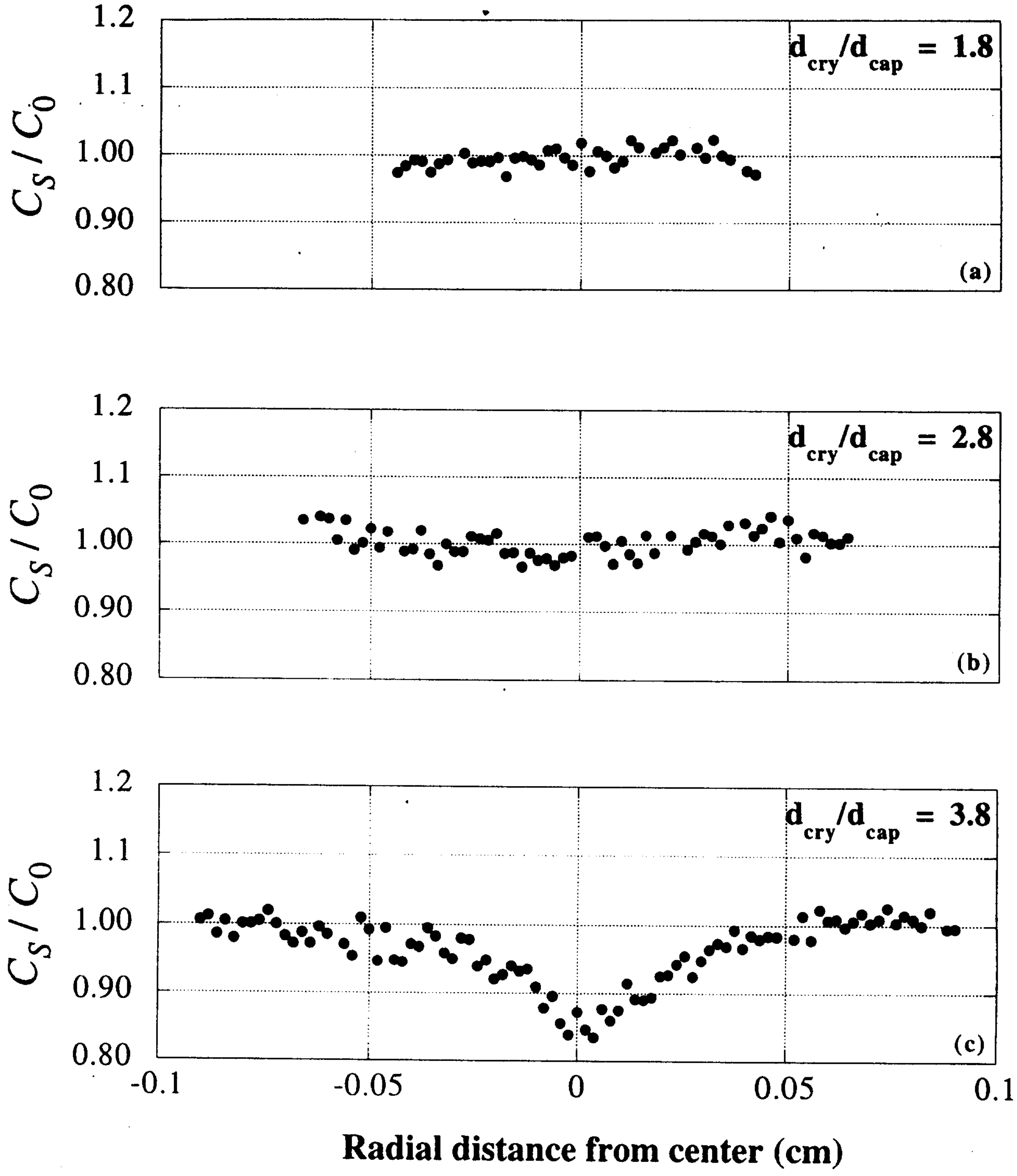
ρ : Density

D_T : Thermal diffsivity

c_p : Specific heat

② Central down flow

$$V_{cent} = 2V_{cry}\left(\frac{d_{cry}}{d_{cap}}\right)^2$$



Radial distribution of Ge in the steady-state growth

d_{cap} = 500 μm, L_{mz} = 300 μm and V_{cry} = 6.0 cm/h

Influence of melt flow on segregation

① Marangoni flow

Marangoni number: $Ma \approx 70$ ⟶ Small

Bérnard flow

Rayleigh number: $Ra \approx 0.1$ ⟶ Small

② Central down flow

Large V_{cry} and/or large d_{cry}/d_{cap}

⟶ Large V_{cap}

⟶ Strong central down flow > Marangoni flow

⟶ Significant effect on the solute diffusion boundary layer

◎ Otherwise (small V_{cry}, $1.0 < d_{cry}/d_{cap} < 3.0$),
No effect of melt flows on
solute partitioning

One dimensional solute analysis using no mixing model is well acceptable

Steady-state solutions for zone I and zoneII

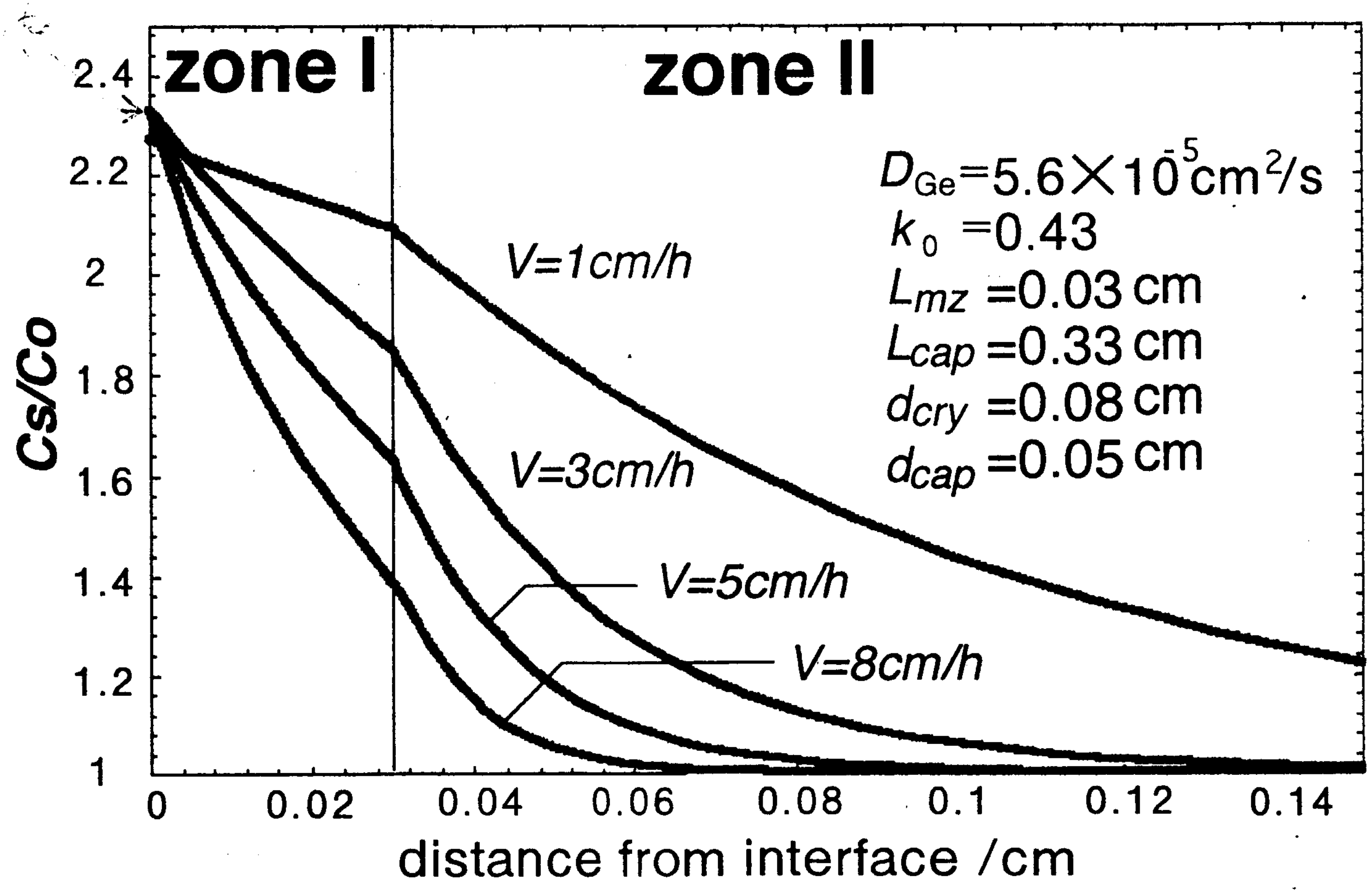
$$C_x^1 = C_L \frac{(k_0 - 1)\exp\left(-x\overline{V}_{cry} / D_{Ge}\right) - k_0}{(k_0 - 1)\exp\left(-L_{mz}\overline{V}_{cry} / D_{Ge}\right) - k_0}$$

$$C_x^2 = C_L + (C_L - C_0)\frac{\exp\left[(L_{cap} - x)\overline{V}_{cap} / D_{Ge}\right]\left(-1 + \exp\left[(x - L_{mz})\overline{V}_{cap} / D_{Ge}\right]\right)}{1 - \exp\left[(L_{cap} - L_{mz})\overline{V}_{cap} / D_{Ge}\right]}$$

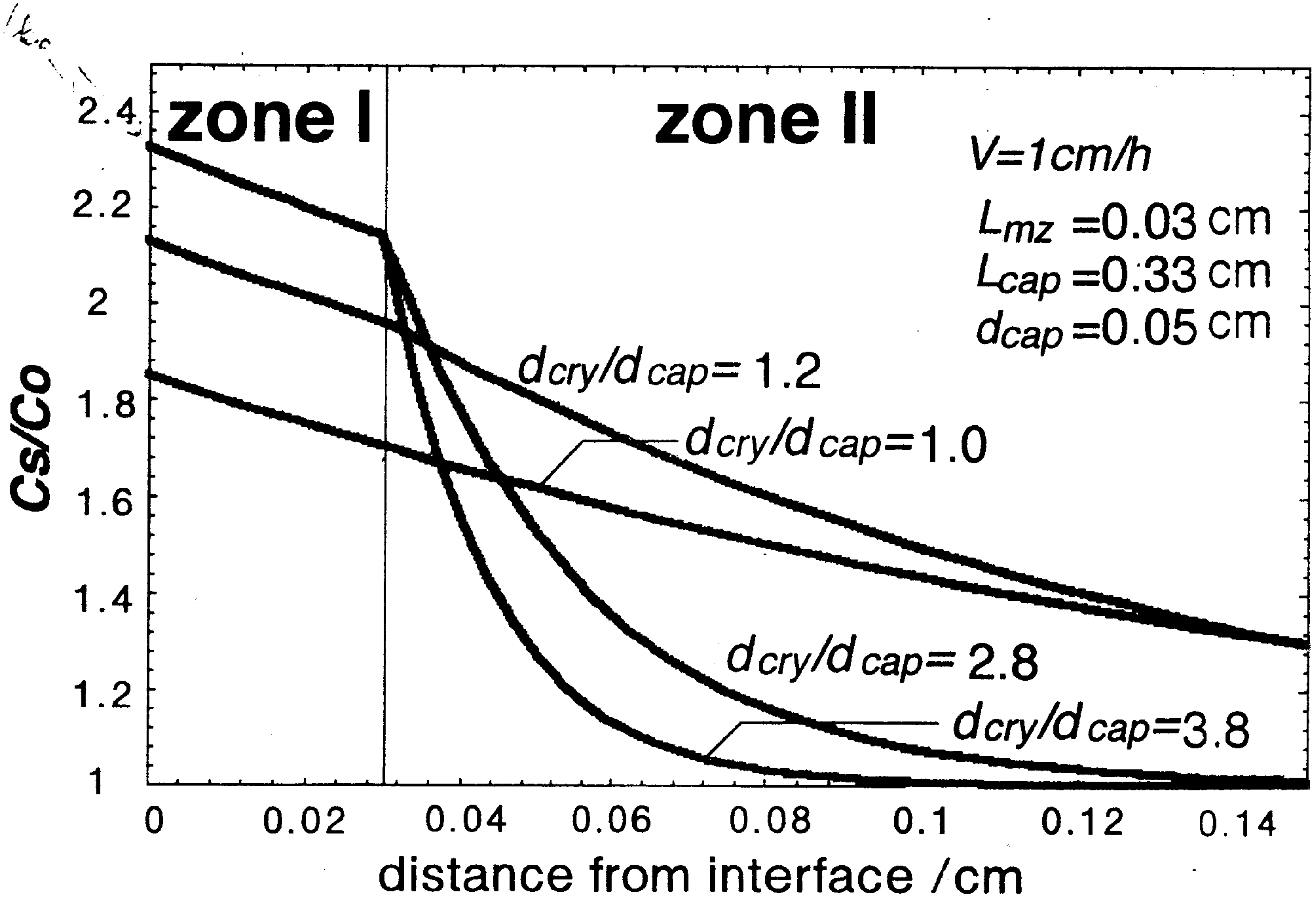
where $C_L = A / B$

$$A = C_0 \overline{V}_{cap} \exp\left(L_{cap}\overline{V}_{cap} / D_{Ge}\right)\left(1 - k_0 + k_0 \exp\left(L_{mz}\overline{V}_{cry} / D_{Ge}\right)\right)$$

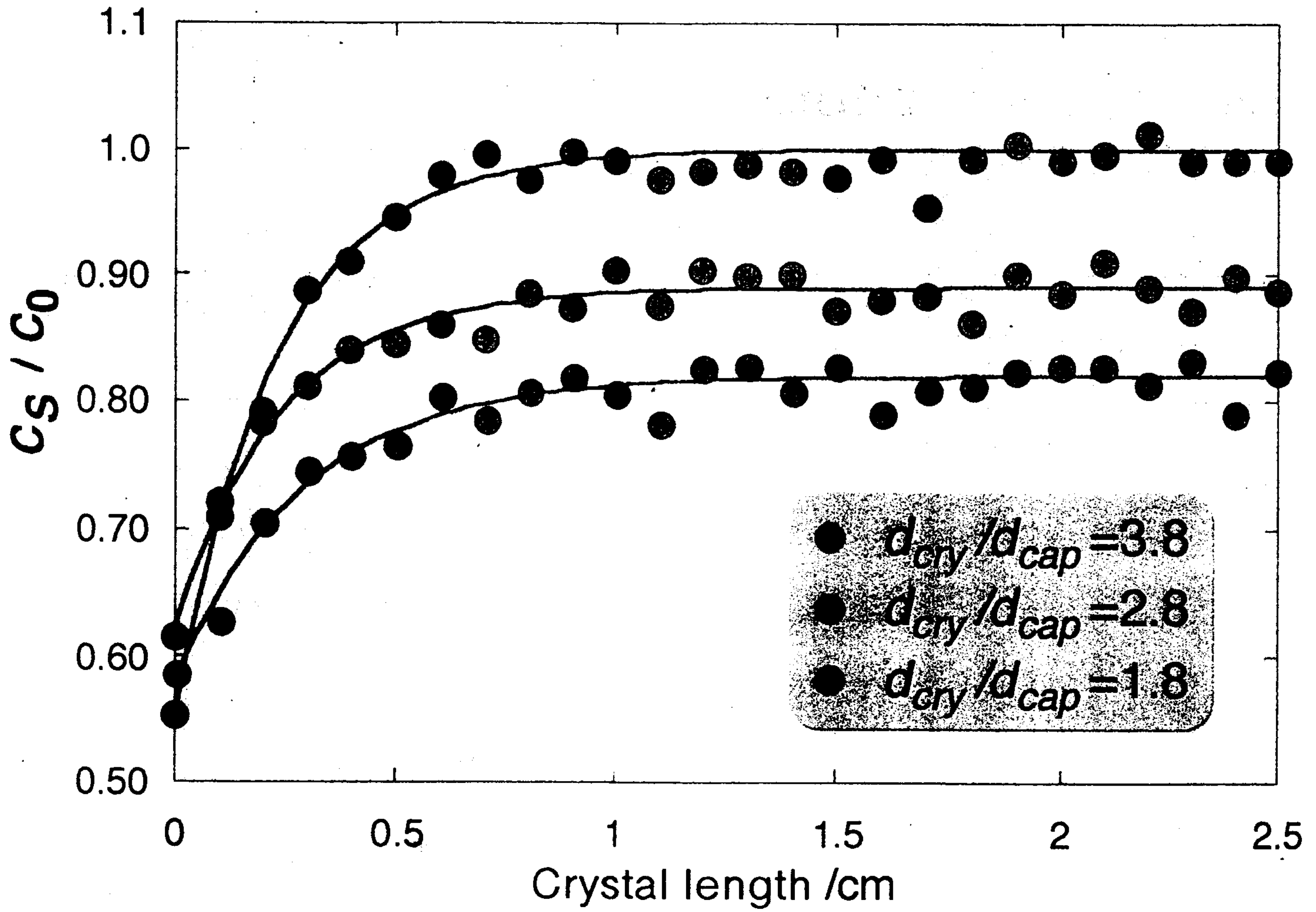
$$\begin{aligned} B = {} & \overline{V}_{cap} \exp\left(L_{mz}\overline{V}_{cap} / D_{Ge}\right)(1 - k_0) \\ & + k_0 \exp\left[\left(\overline{V}_{cap} + \overline{V}_{cry}\right)L_{mz} / D_{Ge}\right]\left(\overline{V}_{cap} - \left(\frac{d_{cry}}{d_{cap}}\right)^2 \overline{V}_{cry}\right) \\ & + k_0 \overline{V}_{cry}\left(\frac{d_{cry}}{d_{cap}}\right)^2 \exp\left[\left(L_{cap}\overline{V}_{cap} + L_{mz}\overline{V}_{cry}\right) / D_{Ge}\right] \end{aligned}$$



Calculated curves of steady-state distribution of Ge in zone I and zone II with various growth rates



Calculated curves of steady-state distribution of Ge in zone I and zone II with various d_{cry}/d_{cap} for costant V_{cry} (=1cm/h)



Ge distributions in the initial-transient to steady-state region with various d_{cry}/d_{cap} (d_{cap} =500μm, V=1cm/h)

Analysis of initial transient region

Apply Smith et al's equation to the analysis of initial transient region

$$\frac{C_S}{C_0}=\frac{1}{2}\left\{1+\mathrm{erf}\left(\frac{\sqrt{(V_{cry}/D_{Ge})x}}{2}\right)+(2k_0-1)\exp\left[-k_0(1-k_0)(V_{cry}/D_{Ge})x\right]\mathrm{erfc}\left[\frac{(2k_0-1)}{2}\sqrt{(V_{cry}/D_{Ge})x}\right]\right\}$$

Co=5at% , V_{cry}=5cm/h

↓

Nonlinear fitting

Equilibrium partition coefficient, $k_0=0.43$

Diffusion coeffcient, $D_{Ge}=5.6\times10^{-5}\,cm^2/s$

D_{Ge} (present work) ≈ 0.1 D_{Ge}(previous work)

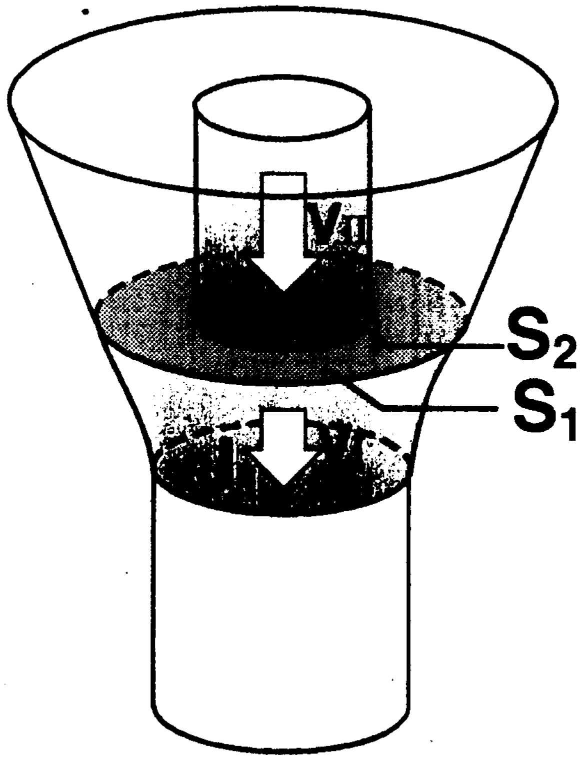
↓

Effect of radial flow component is very little

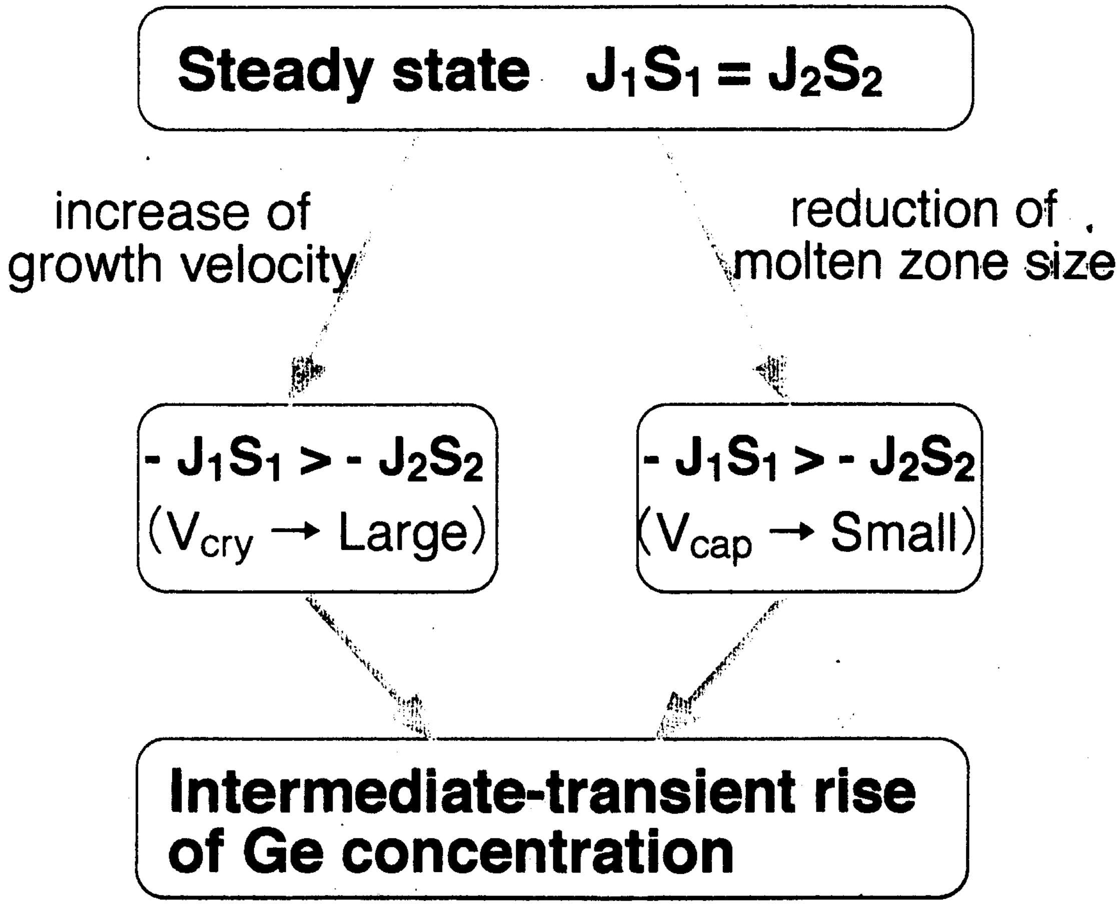
↓

One dimentional analysis is acceptable

Intermediate-transient rise of Ge concentration due to the sudden change of growth conditions



$$J = -D\frac{\partial C}{\partial x} - VC$$



Steady state $\mathbf{J_1S_1 = J_2S_2}$

increase of growth velocity

reduction of molten zone size

$- J_1S_1 > - J_2S_2$
(V_{cry} → Large)

$- J_1S_1 > - J_2S_2$
(V_{cap} → Small)

Intermediate-transient rise of Ge concentration

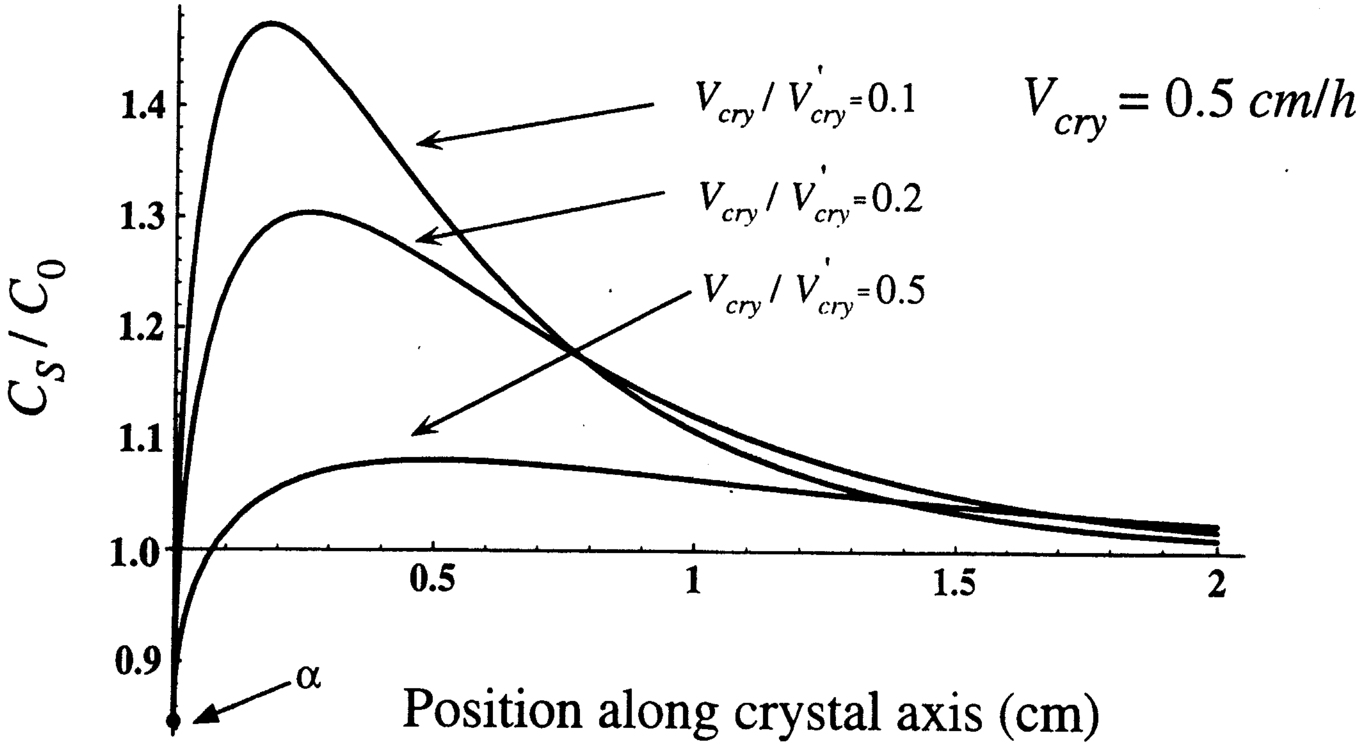
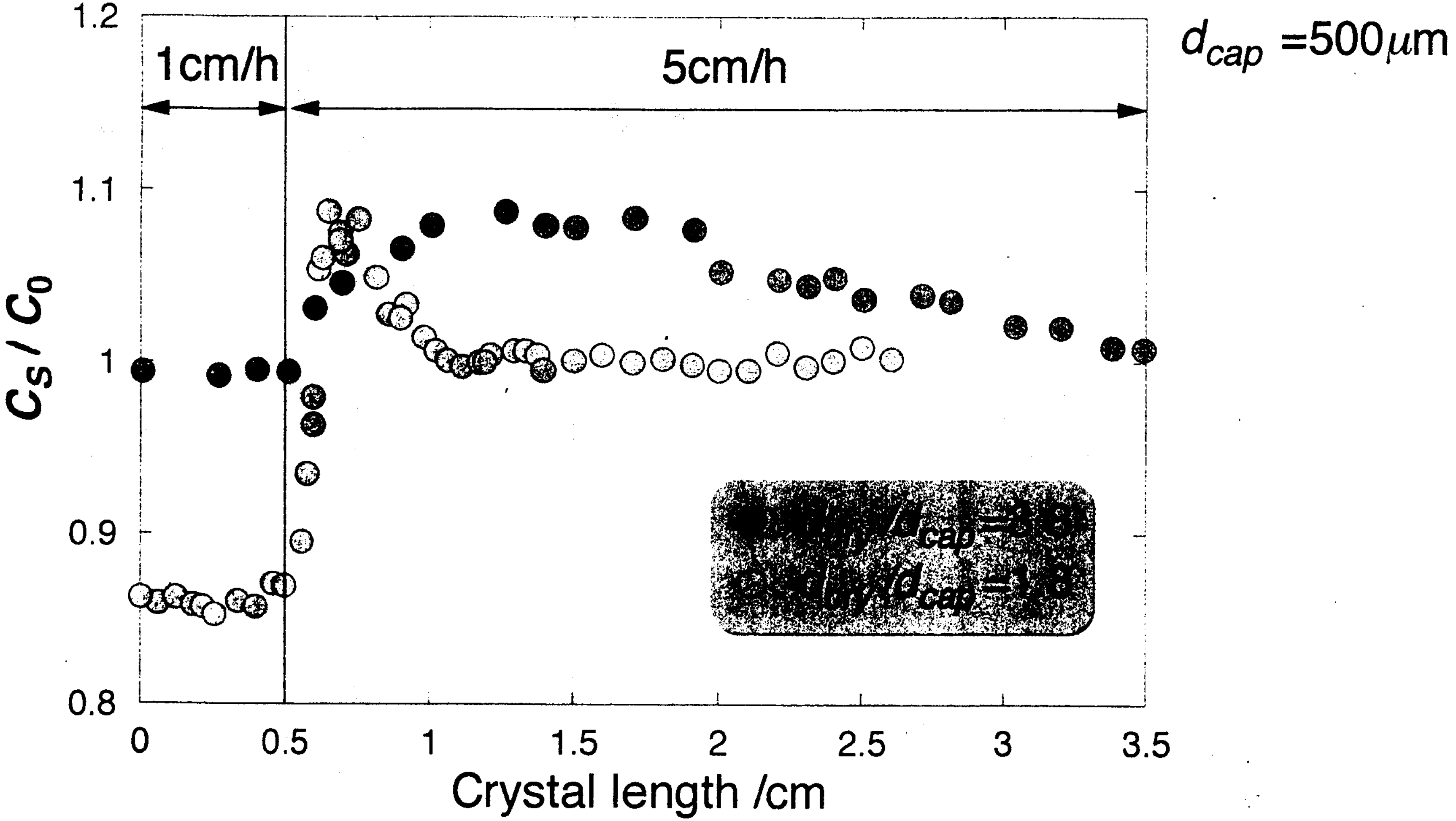
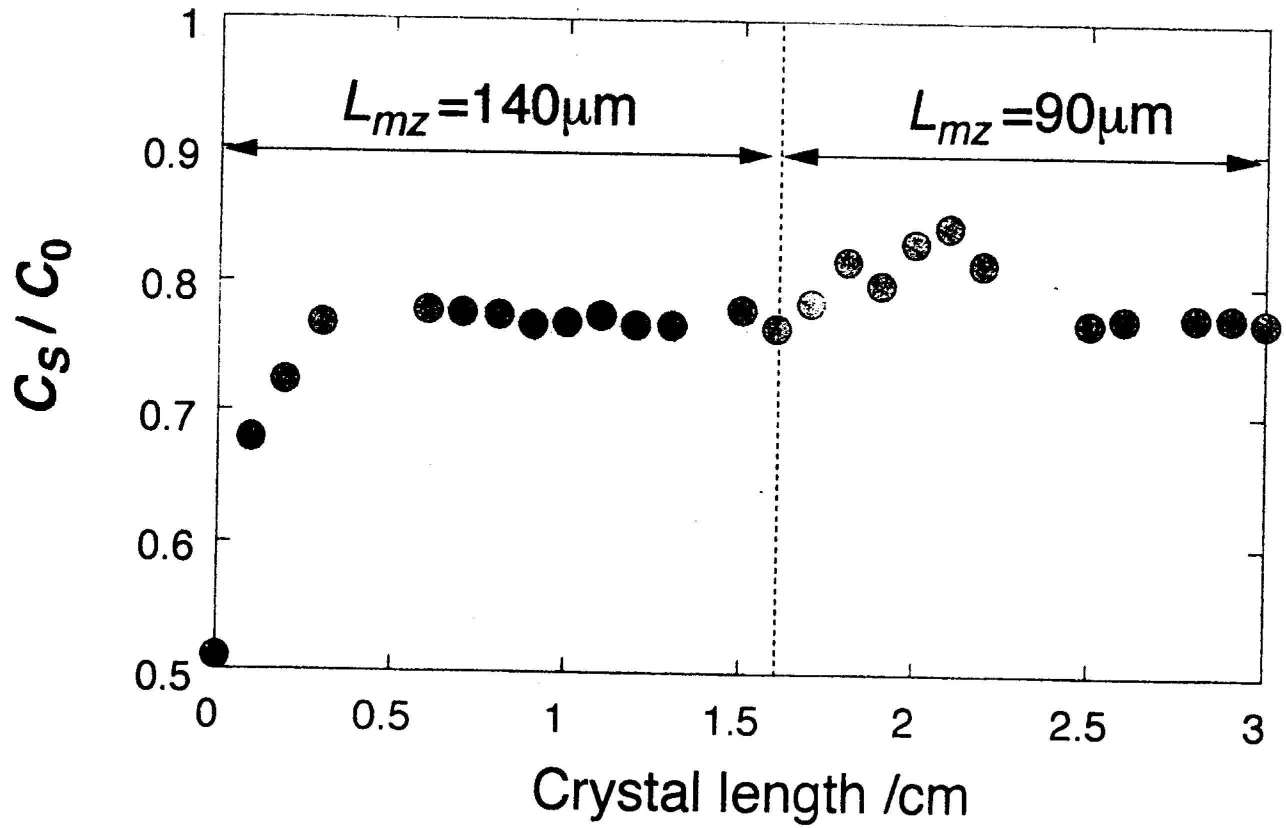


Illustration of calculated intermediate transient

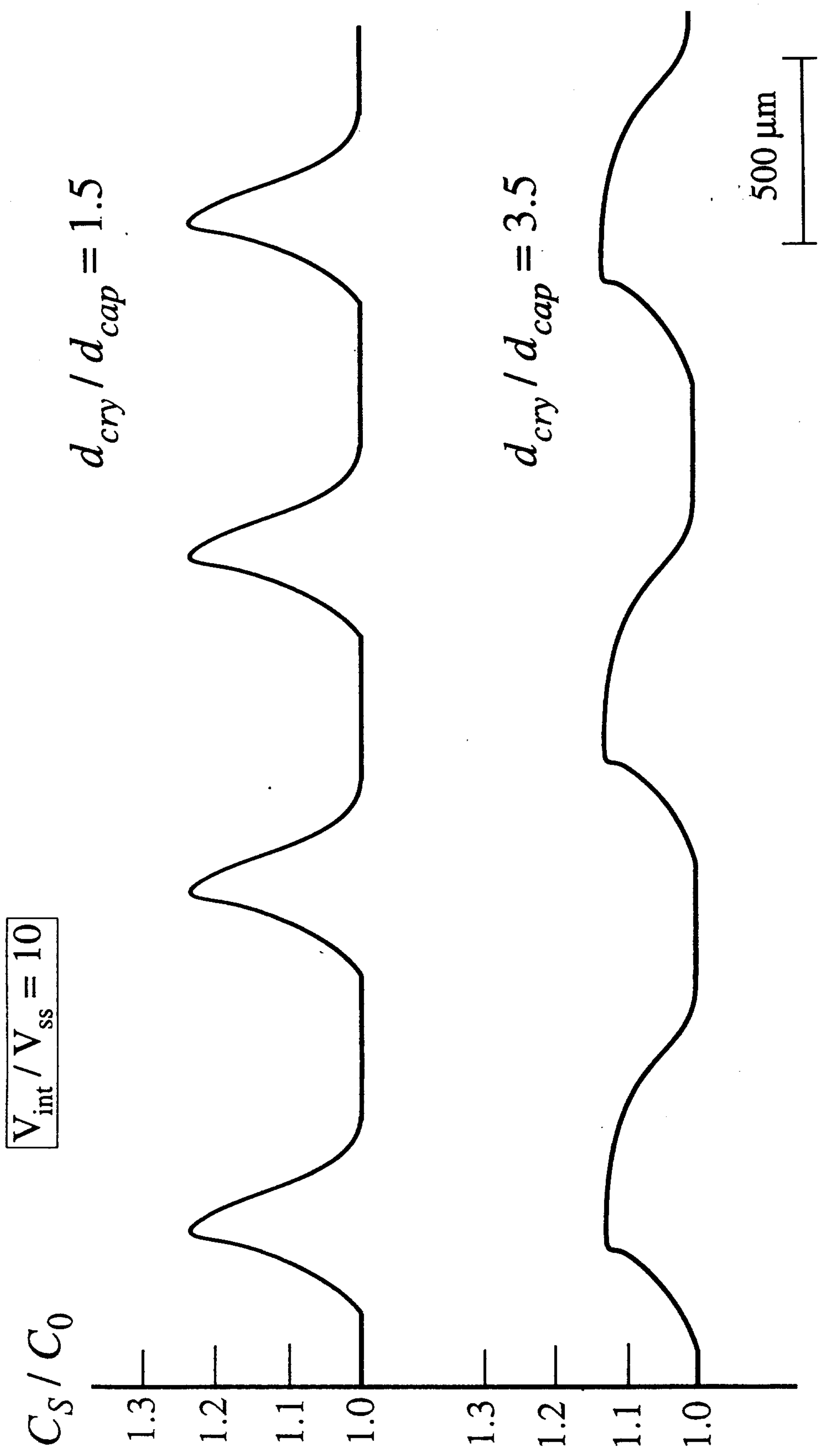


Intermediate-transient rise of Ge concentration due to the sudden change of pulling rate



Intermediate-transient rise of Ge concentration due to the sudden change of molten zone size

Periodic variation of solute in solid



Summary

(1) The solute distribution mechanism was analyzed for the $Si_{0.95}Ge_{0.05}$ single crystal fiber by μ-PD method.

(2) The steady-state solutions were obtained for the molten zone and the capillary zone.

(3) The effect of the convection in the molten zone on partitioning was not significant for many cases.

(4) Intermediate transient rise of Ge was shown by the sudden change of the growth velocity or molten zone height.

(5) Periodic compositional modulation can be designed by using the intermediate transient.