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Influence of Convections on Dopant Segregation in Floating-zone Crystal Growth System

The steady and axisymmetric crystal growth process of floating zone model was studied numerically to concern with the influence of convection and phase change on effective segregation. An iteration method of numerical simulation considering both thermocapillary and buoyancy effects for GaAs crystal growth gave the effective segregation coefficient, which was compared with the space experiment of GaAs on board the Chinese recoverable satellite. The calculated segregation coefficient of a two-dimensional model was found to be smaller than the one suggested by space experiment with the simplified assumption of an one-dimensional model.

1 Introduction

Microgravity environment offers a broad prospect for many studies of science and application. It is attractive to learn what type of materials with better qualities could be produced and how to make it in microgravity environment, which may improve the knowledge of materials processings either on the ground or in space. At present time, the floating-zone method is one of the attractive candidates of crystal growth experiments in space due to its evident advantages [1]. However, the shortcomings of this method have been noted. The non-uniformity of temperature at free surface may introduce thermocapillary convection and oscillation, which is secondary in the materials processings on the ground but is dominant in the space experiment. Thermocapillary convection together with buoyancy convection associated with the floating zone process have been extensively studied in order to promote the microgravity resource.

Recently, an experiment of Si-doped-GaAs (GaAs:Si) single crystal growth was completed by floating-zone technique on board a Chinese recoverable satellite. The dopant impurity striation, dislocation, and segregation in microgravity condition of $10^{-5}\, g_E$ were analyzed [2]. The results of space experiment gave a larger value of segregation coefficient, $k_f = 0.56$ for a sample of 1 cm in diameter in comparison with the value of $k_f = 0.12$ for the same sample under conditions on the ground experiment. This was demonstrated according to the simplified one-dimensional model of solidification process and several basical assumptions as described in [3]. The analyses show that k_f obtained in the space experiment [3] is the effective segretation coefficient. Therefore, how to estimate the theoretical segregation k_0 for a given k_f is a problem which should be analyzed.

Generally, there are, at least, three sorts of effects which should be considered for the process of floating-zone crystal growth, that is, thermocapillary convection, phase change, and segregation. It is known that both thermocapillary effect and phase change have influence on the dopant segregation, and can be described by the results of a two-dimensional model. A lot of papers have been published to discuss these coupling processes [4–11]. In the present paper, the theoretical segregation coefficient k_0 was calculated for the two-dimensional model, in which the coupling effects of various convections and solidification-melting phase change were involved. The results showed the difference between the numerical results and the experimental ones, and the reason was discussed, in particular.

2 Physical Model

According to the analyses in [2], there are basical assumptions in the solidification formula of the one-dimensional model, that is:

(1) The dopant diffusion rate in the solid region is much smaller than the solidification rate, and may be ignored.
(2) The dopant diffusion rate is much greater than the solidification rate, and the dopant distribution is consequently assumed uniform.
(3) The dopant segregation coefficient is constant in the melting region.
(4) The curvature of the solid/liquid interface is neglected, and a plane interface is assumed.

Under these assumptions, the so-called normal solidifying equation of an one-dimensional model may be obtained as

$$C_s = k_f C_0 (1 - f)^{k_f - 1}, \tag{1}$$

where C_0 and C_s are, respectively, the initial dopant concentration and the concentration at the position when the soli-

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dified fraction is f; k_f is the segregation coefficient. Both values of C_0 and C_s can be measured by the van der Paw method as denoted in [2]. It is known from the assumption (2) that, the calculated value k_f should be the effective segregation coefficient.

Firstly, we discuss the one-dimensional model. The BPS equation describing the experimental or effective coefficient k_f in the one-dimensional model may be written as

$$k_f = \frac{k_0}{k_0 + (1 - k_0)\exp(-\delta^* \cdot Pe_s \cdot V_p/D)} \tag{2}$$

with the dimensionless thickness of diffusion layer as

$$\delta^* = -\frac{1}{Pe_s V_p} \ln\left[\frac{k_0(1-k_f)}{k_f(1-k_0)}\right] \tag{3}$$

and

$$k_f = \bar{C}_s/\bar{C}. \tag{4}$$

Concentration $\bar{C}_s$ is the dimensionless average value of the single crystal at the melting interface, and can be measured by the wafer-cutting experimental technique (see, for example, [2]). Concentration $\bar{C}$ is the average value in the melting zone, which is associated with the 'uniform' concentration outside the diffusion layer. Therefore, we have

$$\bar{C} = \iint_{\Omega_m} \xi C(\xi, \zeta)\, d\xi\, d\zeta \cdot \left(\iint_{\Omega_m} \xi\, d\xi\, d\zeta\right)^{-1} \tag{5}$$

and

$$\bar{C}_s = \frac{1}{\xi_0^2}\int_0^{\xi_0} k_0 \xi [C(\xi, \zeta)|_{\zeta = S_1(\xi)}]\, d\xi, \tag{6}$$

where Ω_m is the melting domain.

The main object of the present paper is to analyze the theoretical segregation coefficient of the two-dimensional model. Based on the experimental results given by [2], the segregation coefficient k_f was obtained for GaAs:Si single crystal growth, and the values were $k_f = 0.56$ for the results of space experiment and $k_f = 0.12$ from the laboratory experiment under the same condition on the ground. The steady and axisymmetric model of thermal-solutal convection with phase change convection and moving interfaces for floating-zone crystal growth is shown in fig. 1. The upper rod is the resolidifying single crystal and the lower rod is the feeding crystal, the melt bridge locates in the middle and is heated by a thermal radiation ring. In the case of suitable thermal and operating conditions, a steady process may be accessed for a sufficiently long crystal stick.

The numerical simulation to solve dimensionless governing equations and boundary conditions for the melt bridge and solid regions was suggested in detail [9]. In the present paper, an iterative procedure of the numerical calculation was suggested as follows:

(1) The phase change interfaces and the fields including velocity and temperature were calculated at first as discussed in [9].
(2) The concentration field was decoupled from the flow field for the case $\delta_s = 0$ and was calculated by an assumed value of k_0, and then $\bar{C}$ and $\bar{C}_s$ were calculated from eqs. (5) and (6), respectively.
(3) The segregation coefficient $k_0$was updated if $\bar{C}_s/\bar{C}$ was not equal to the experimental segregation coefficient k_{eff}.
(4) The steps (2) and (3) were repeated until the calculated coefficient k_{eff} was equal to the one given by the experiment.

The numerical tests were successfully completed, and the results were obtained.

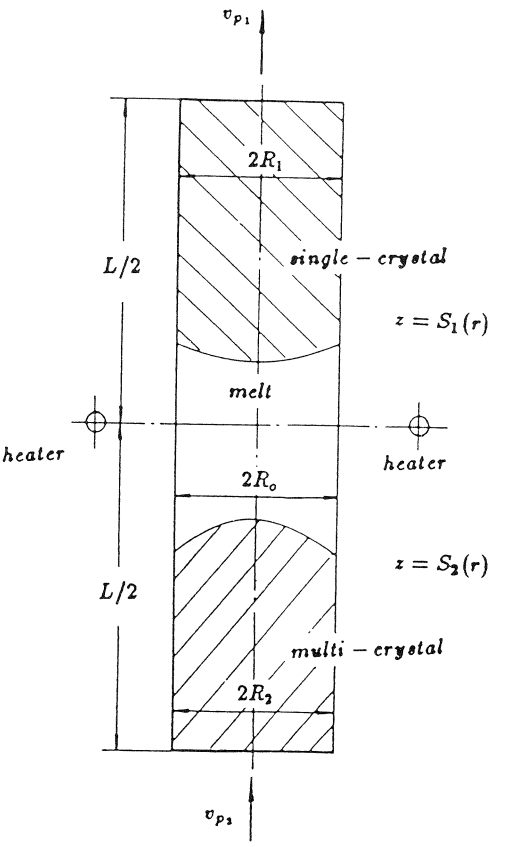

Fig. 1. Schematic diagram of the floating zone system model

3 Numerical Results

A technique of Finite Element Method was developed to solve numerically the problem of crystal growth in floating zone [9]. The quadrilateral iso-parametric elements of all boundaries were densified. The up-wind weight functions were used to overcome the difficulty induced by the strong convection. The phase-change interfaces were updated by the so-called pseudo-transient method. The equations and boundary conditions for the physical model in addition to the numerical method were given elsewhere such as [9, 12], and will not be discussed in detail in the present paper.

The thermophysical properties of GaAs, as listed in [13], were used in the numerical analyses. In consideration of the space experiment of floating zone GaAs crystal growth [22], we adopted the data as follows:

$\varrho = 5.7 \cdot 10^3$ kg/m^3,

$C_p = 4.2 \cdot 10^2$ W/(m · K),

$\varepsilon = 0.55$,

$T_m = 1{,}238$ °C,

$\Delta H = 7.17 \cdot 10^5$ J/kg,

$\nu = 5 \cdot 10^{-7}$ m²/s,

$\sigma'_T = 0.25 \cdot 10^{-3}$ kg/(K · s²),

$\beta = 1.8 \cdot 10^{-5}$/K,

where ϱ and T_m are the density and melting point; C_p, ν, σ, and β are heat capacity, kinetic viscosity, surface tension, and thermal expansion coefficient; ε is the non-dimensional thermal emission, and ΔH the fusion heat of GaAs single crystal. Different Schmidt numbers were adopted for several typical cases in the numerical simulation, where the Schmidt number was defined as $Sc = \nu/D$ and D is the diffusion coefficient.

According to the results of the space experiment [2], two cases of $g = 0$ and $g = 9.8$ m/s² were calculated for the steady and axisymmetric floating-zone crystal growth with the parameters $r_0 = 5 \cdot 10^{-3}$ m, $L = 40 \cdot 10^{-3}$ m, $T_0 = 1{,}338$ °C, $T_\infty = 1{,}070$ °C, $v_p = 0.876 \cdot 10^{-6}$ m/s, where r_0 and L are the diameter of crystal rods and the length of the calculated region including liquid bridge and solid rods, T_0 and T_∞ are, respectively, the highest surface temperature at the plane of the heater and the temperatures at the end planes of both rods, and v_p is the pulling velocity. The numerical simulation results of theoretical segregation coeffcient k_0 and thickness of the non-dimensional diffusion layer δ^* for these cases were listed in tables 1 and 2.

First, we analyze the case of zero-gravity, $g = 0$, associated with a Bond number $Bo = 0$, where the Bond number was defined as $Bo = -\varrho\beta g r_0^2/\sigma'_T$. It can be seen that all theoretical segregation coefficients k_0 have only a little deviation from the assumed value $k_f = 0.56$, which was suggested by the space experiment [13], for 4 values of the Schmidt number. The larger the Schmidt number, the smaller the coefficient k_0, however, the difference between the theoretical segregation coefficients is only $4 \cdot 10^{-3}$ for a Schmidt number change in a range of three orders of magnitude from $5.7 \cdot 10^{-1}$ to $5.7 \cdot 10^2$. The theoretical value k_0 was only small when the effective value k_f of the space experiment was less than $4 \cdot 10^{-3}$. In other words: coefficient k_0 tends to k_{eff}. On the other hand, the thickness of diffusion layer depended sensitively on the Schmidt number as listed in table 2; the larger the Schmidt number, the smaller the thickness of the diffusion layer. The conclusion is reasonable because the smaller Schmidt number associates with larger diffusion effect and then, the diffusion layer becomes thicker.

Table 1. Calculated segregation coefficient k_0 depending on Schmidt number, where $r_0 = 5 \cdot 10^{-3}$ m, and Bond number $Bo = 0$ for $g = 0$ and $Bo = 1.0$ for $g = 9.8$ m/s²

Sc	$5.7 \cdot 10^2$	57	5.7	$5.7 \cdot 10^{-1}$
for $g = 0$ and $k_f = 0.56$	0.5561	0.5580	0.5591	0.5597
for $g = 1\ g_E$ and $k_f = 0.12$	0.1182	0.1192	0.1196	0.1199

Table 2. Calculated thickness of diffusion layer δ^* depending on the Schmidt number. Conditions are the same as in table 1

Sc	$5.7 \cdot 10^2$	57	5.7	$5.7 \cdot 10^{-1}$
for $g = 0$ and $k_f = 0.56$	0.0032	0.0165	0.0742	0.2593
for $g = 1\ g_E$ and $k_f = 0.12$	0.0034	0.0158	0.0720	0.2621

Now, we discuss the case of gravity, $g = 9.8$ m/s², and $Bo = 1$. The concentration field was also calculated for Schmidt numbers, $Sc = 571$, 57.1, 5.71, and 0.571 and fixed effective segregation coefficient $k_{eff} = 0.12$ suggested by the experiment on the ground. A similar conclusion as for the case $g = 0$ could be obtained in this case. It is interesting to note that the non-dimensional thickness of the diffusion layer was quite close for both cases of $g = 0$ and $g = 1\ g_E$, that is, the thickness is sensitive to the Schmidt number but not to the gravity level for the floating zone convection.

Based on the numerical simulation of the present paper, the values of coefficient k_0 were quite close to the value k_{eff} suggested by ground and space experiments, and are not sensitive to the Schmidt number. The explanation of the four times higher difference between the two effective segregation coefficients suggested by the experiments on the ground $k_{eff} = 0.12$ and in space $k_{eff} = 0.56$ was unconvincing. Because the dynamic Bond number is only $Bo = 0.1$ for a typical scale $r_0 = 5$ mm of the GaAs crystal growth by floating-zone method, the thermocapillary convection is dominant even under the condition of ground experiment.

In order to consider the coupling effect involving buoyancy convection, we choose another group of operating parameters, that is, $r_0 = 2.5 \cdot 10^{-2}$ m, $L = 2.0 \cdot 10^{-1}$ m, $T_\infty = 368$ °C, $g = 9.8$ m/s²; other parameters are the same as the previous ones. In this case, $Bo = 25$. The calculated results are shown in table 3. It can be seen from the numerical results that the difference between the segregation coefficient k_f obtained by the experimental method and the calculated theoretical one was still very small. So it may be concluded that the buoyancy driven convection has hardly any influence on the change of the effective segregation coefficient under the conditions assumed here. The reason that caused the great difference between the segregation coefficient measured in the space ($k_f = 0.56$) and the one on the ground ($k_f = 0.12$) will be further investigated.

Table 3. Calculated segregation coeffcient k_0 for Bond number $Bo = 25$ and $r_0 = 2.5$ cm

Sc	$5.7 \cdot 10^2$	57	5.7	$5.7 \cdot 10^{-1}$
for $g = 1\ g_E$ and $k_f = 0.12$	0.1193	0.1198	0.11993	0.11997

4 Discussion

The relationship between the segregation coefficients k_0 and k_{eff} was investigated in the present paper for GaAs crystal growth in the floating zone processing, and the numerical

results of the two-dimensional model were compared with the space experimental results according to the one-dimensional model. The numerical simulation cannot explain why the effective coefficient of the space experiment is 4 times larger than the one of the ground experiment. However, the numerical simulation of the present paper shows that the real situation of the floating zone processing is more complex than the simple assumption of the one-dimensional model. On one hand, the conclusion suggested by analyses of space sample were based on several simplified conditions, whose limitations should be studied further. On the other hand, the theoretical model may be improved to involve more factors. Anyway, the disagreement between theoretical results of the two-dimensional model and the conclusion suggested by the space experiment should be analyzed in the next step.

An up-wind finite element scheme improved from the Galerkin finite element method was applied to overcome the difficulties caused by the convection terms in some case with relative large value of the parameter range. The variables are the linear combinations of node values, and a modified weighting function which may reduce to Galerkin function was introduced in an element (see for details, for example, in [9, 12]). The convergence of the iteration process implies that the calculation is effective. The numerical tests show that the conclusions of the present paper come generally from the physical process, but not from the calculation method, although some secondary effects of the numerical method should be analzyed in the future.

References

1 *Feuerbacher, B., Hamacher, H., Naumann, R. J.:* Materials Sciences in Space. Springer-Verlag, Berlin (1988)
2 *Zhong, X.* et al.*:* Preparation of Si Doped GaAs Single Crystal under Microgravity. German-Chinese Symposium, Bonn (1990)
3 *Pamplin, B. R.:* Crystal Growth. Pergamon, Oxford (1975)
4 *Müller, G.:* in Crystal: Growth, Properties and Application, vol. 12, Springer, Berlin (1988)
5 *Chang, Ch. J., Brown, A.:* J. Crystal Growth, vol. 63, p. 343 (1983)
6 *Wang, Y. H., Kim, Y. J., Kou, S.:* J. Crystal Growth, vol. 911, p. 50 (1988)
7 *Langlois, W. E.:* Ann. Rev. Fluid Mech., vol. 17, p. 191 (1985)
8 *Lan, C. W., Kou, S.:* J. Crystal Growth, vol. 108, p. 351 (1991)
9 *Xiong, B., Hu, W. R.:* J. Crystal Growth, vol. 125, p. 149 (1992)
10 *Chun, Ch. H.:* J. Crystal Growth, vol. 48, p. 600 (1980)
11 *Tang, Z. M., Hu, W. R.:* Microgravity Quarterly, vol. 2, p. 123 (1992)
12 *Xiong, B., Tang, M., Hu, W. R.:* Thermocapillary Convection with Phase Change in the Floating Zone Under Microgravity. Microgravity sci. technol., vol. 6, p. 131 (1993)
13 *Woufers, P., van Schaftingen, J. J., Crochet, M. J., Beyling, F. T.:* International J. Numerical Methods in Fluid, vol. 7, p. 131 (1987)