One and Two Dimensional Analyses of Growth Conditions of $In_xGa_{1-x}As$

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We developed a calculation method of one-dimensional crystal growth of InAs-GaAs binary semiconductors and investigated the effect of the cooling rate and the temperature gradient on the crystal growth process. We found that crystals of uniform composition can be grown by the one-directional growth method with a nonuniform concentration gradient in the solution if the growth rate is 3 ~ 5 mm/h. Furthermore, we investigated the occurrence of constitutional supercooling and found that the degree of supercooling can be reduced if the temperature gradient is higher than 30 K/cm. We also developed a calculation method of two-dimensional crystal growth of InAs-GaAs binary semiconductors and investigated the effect of residual gravity and the inclination of ampoule on the crystal growth process. We found that convection is induced even under 10^{-6} g conditions and that the crystal-solution interface is deformed by the convection. Convection is reduced and diffusion conditions can be almost realised if the growth direction is opposite to gravity. Convection becomes quite strong when the growth direction is perpendicular to gravity.

1. Introduction

One of the factors which determine the quality of grown crystal is convective instabilities induced in melt or solution during the crystal growth process. Growing a multi-component semiconductor crystal which has a uniform composition is very difficult from both fluid dynamical and thermodynamical point of view [1-5]. Therefore, microgravity experiments of crystal growth have been intensively carried out in recent years in order to reduce buoyancy convection and grow high quality crystals [6,7]. We organised a research project of numerical analysis of $In_{0.3}Ga_{0.7}As$ crystal growth in the International Space Station which will start operation in 2004. When InGaAs is grown, InAs is ejected into the solution at the solution-crystal interface (see the phase diagram shown in Figure 1) and therefore the concentration of InAs becomes higher near the interface in the solution. The concentration profile of InAs in the growing InGaAs crystal is determined depending on convection which is induced by temperature and InAs concentration gradients, residual gravity, g-jitters, the diffusion speed of InAs and so on. In this report, the solution growth process of InGaAs is analysed numerically and the validity of a new technique for growing an InGaAs crystal of a uniform composition is examined. In section 2, a numerical model of InAs-GaAs binary crystal growth, in which convection is not taken into account, is developed and the optimal conditions for the production of uniform InGaAs crystals are discussed. In section 3, the crystal growth process of InAs-GaAs under microgravity conditions, in which convection is taken into account, is analysed and the effects of the Rayleigh number based on the heater power and

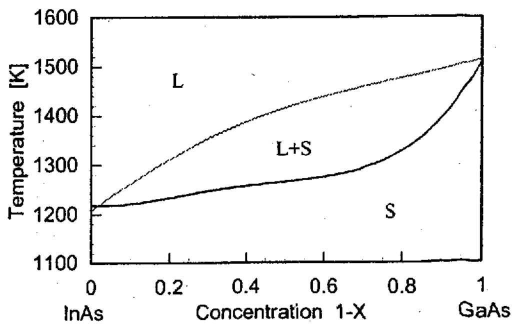


Figure 1 Phase diagram of $In_xGa_{1-x}As$

residual gravity and the angle between the directions of crystal growth and residual gravity on the convective instability and are investigated. In the final section, we summarise the results obtained through the above analyses.

2. One-dimensional analysis of crystal growth of InGaAs

Our project proposed a new method of growing a binary semiconductor crystal which has a uniform composition. In this section, we develop a calculation method of InAs-GaAs binary crystal growth and investigate the validity of the method numerically. The effect of the cooling rate and the temperature gradient on the generation of constitutional supercooling and the compositional uniformity of the grown crystal is made clear.

2.1 Numerical model

The calculation model is shown in Figure 2. The left wall is heated and the right wall is cooled. The solution faces the crystal at the interface. The effect of convection is not taken into account. The coordinate x, time t and temperature T are nondimensionalised using the length between the heated and cooled walls L, the thermal diffusivity of the solution κ_L and the temperature difference between the heated and cooled walls $\Delta T \equiv T_h - T_c$.

$$X \equiv \frac{x}{L}, \quad \tau \equiv \frac{t}{L^2/\kappa_L}, \quad \theta \equiv \frac{T - T_c}{T_h - T_c} \qquad (1)$$

The governing equations are summarised below.

Solution

Heat conduction equation;

$$\frac{\partial \theta_L}{\partial \tau} = \frac{\partial^2 \theta_L}{\partial X^2} \qquad (2)$$

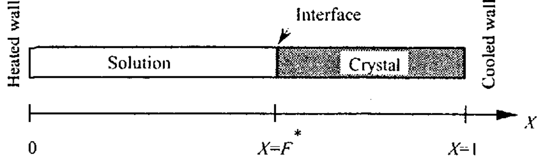


Figure 2 One-dimensional analytical model of crystal growth of InGaAs

Diffusion equation;

$$\frac{\partial C_L}{\partial \tau} = R\frac{\partial^2 C_L}{\partial X^2} \qquad (3)$$

where R is the ratio of the diffusion coefficient of InAs in the solution to the thermal diffusivity of the solution.

Crystal

Heat conduction equation;

$$\frac{\partial \theta_S}{\partial \tau} = K\frac{\partial^2 \theta_S}{\partial X^2} \qquad (4)$$

Diffusion equation;

$$\frac{\partial C_S}{\partial \tau} = B\frac{\partial^2 C_S}{\partial X^2} \qquad (5)$$

where K is the ratio of the thermal diffusivity of the crystal to that of the solution and B is the ratio of the diffusion coefficient of the crystal to the thermal diffusivity of the solution.

Solution-crystal interface

Thermal energy balance equation;

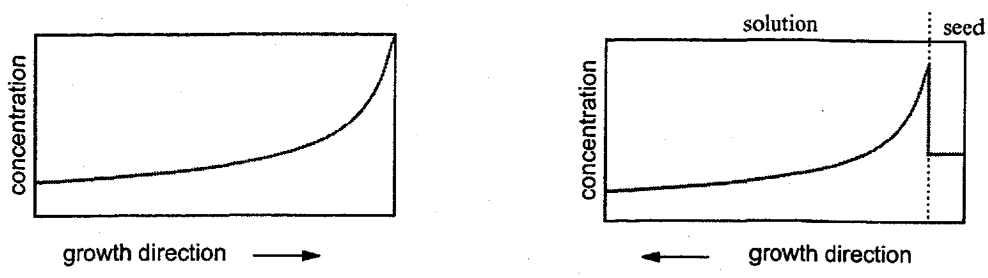
$$\frac{\partial F}{\partial \tau} = Sf\left(-G\frac{\partial \theta_S}{\partial X} + \frac{\partial \theta_L}{\partial X}\right) \qquad (6)$$

Mass balance equation;

$$\left(C_L - C_S\right)\frac{\partial F}{\partial \tau} = R\left(-E\frac{\partial C_S}{\partial X} + \frac{\partial C_L}{\partial X}\right) \qquad (7)$$

where F is the nondimensional position of the solution-crystal interface and Sf is the Stefan number. G is the ratio of the thermal conductivity of the crystal to that of the solution and E is the ratio of the diffusion coefficient of InAs in the crystal to that in the solution.

Although temperature is continuous at the interface, concentration is discontinuous as the liquidus and solidus curves are separate (see Figure 1). The concentrations at the interface are related to the temperature via the liquidus and solidus curves and therefore eqs.(6) and (7) are connected to each other. We approximated the liquidus and solidus curves by polynomial functions of 5th order. The boundary conditions are;



(a) (b)

Figure 3. A new technique for the production of uniform InGaAs crystals
(a) InGaAs is grown under 1g conditions. The concentration of InAs is not uniform.
(b) The earth grown InGaAs is heated to become a solution. The initial concentration distribution is maintained in microgravity. Crystal growth starts in the opposite direction.

$$X = 0; \quad \theta_L = 1 - \alpha\tau, \; \frac{\partial C_L}{\partial X} = 0,$$
$$X = 1; \quad \theta_S = -\alpha\tau, \; \frac{\partial C_S}{\partial X} = 0 \qquad (8)$$

where α is the speed of the drop in temperature at the heated and cooled walls. The governing equations were transformed introducing new coordinates defined below.

Solution

$$\xi \equiv \frac{X}{F(\tau)} \qquad (9)$$

Crystal

$$\eta \equiv \frac{X - F(\tau)}{1 - F(\tau)} \qquad (10)$$

Thanks to this coordinate transformation, this moving boundary problem of crystal growth can be solved efficiently. The transformed governing equations were solved by the finite difference method. The time and spatial derivatives were approximated by the first-order explicit formula and the second-order central formula, respectively.

2.2 A new technique for the production of semiconductors of uniform compositions and discussion

If the initial concentration of InAs has a positive gradient in the solution towards the growing crystal, a crystal of a uniform composition may grow. We call this technique 'One-directional growth method with a Nonuniform Concentration Gradient in the solution' which is abbreviated to the 'NCG method'. The initial concentration distribution does not remain on earth because of strong buoyancy convection. However, it can be maintained in microgravity. We investigated the dependence of the relaxation time of concentration on the microgravity level [8]. The relaxation time is over 1000 s if the residual gravity is 10^{-4} g and the temperature gradient is 100 K/cm. This new crystal growth technique is described in Figure 3 and summarised in the following; (1) We grow InGaAs under 1g conditions. In this case, the concentration distribution of InAs in the grown crystal is not uniform (Figure 3 (a)). (2) The grown crystal is heated to become a solution in microgravity. As we mentioned, the initial concentration distribution in the solution is maintained under microgravity conditions. We start growing a crystal in the opposite direction (Figure 3 (b)).

The concentration distribution of InAs in InGaAs grown by the NGC method is shown in Figure 4 where the initial temperature gradient is 150 K/cm. The concentration does not drop in the early stages of the crystal growth. Note that the concentration drops in the early stages when the initial concentration in the solution is uniform. If the cooling rate is 0.01, which corresponds to a growth rate of 3.6 mm/h, a crystal of uniform concentration

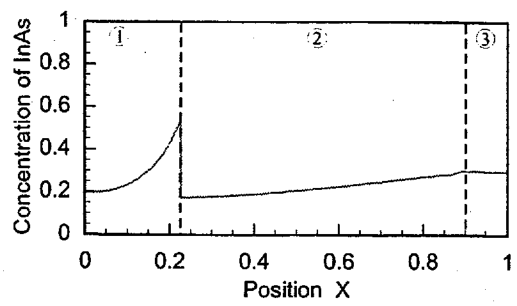


Figure 4 Spatial distribution of the concentration of InAs

The initial concentration has a positive gradient towards the crystal.

1: Solution 2: Grown crystal 3: Seed

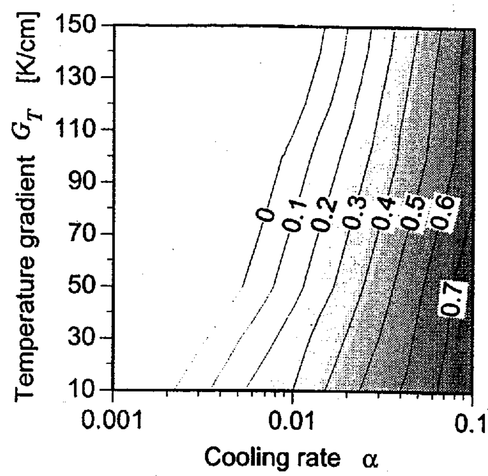


Figure 6 Dependence of the maximum value of the degree of supercooling on the initial temperature gradient and the cooling rate

grows. However, one serious problem arises, that is, the generation of constitutional supercooling. As the initial concentration is already high near the interface, constitutional supercooling tends to occur. We defined the degree of constitutional supercooling as below.

$$S \equiv \frac{c - c_{sat}}{c_{sat}} \tag{11}$$

where c_{sat} is the saturation concentration of InAs in the solution corresponding to the local temperature. The area where S is positive is supercooled. The time variation of the spatial distribution of constitutional supercooling is shown in Figure 5. As we mentioned, the solution is already supercooled near the interface in the early stages. However, the degree of supercooling is reduced by setting a high initial temperature gradient. The dependence of the maximum value of S on the initial temperature gradient and the cooling rate is shown in Figure 6. As both the temperature gradient and the cooling rate become higher, constitutional supercooling is reduced.

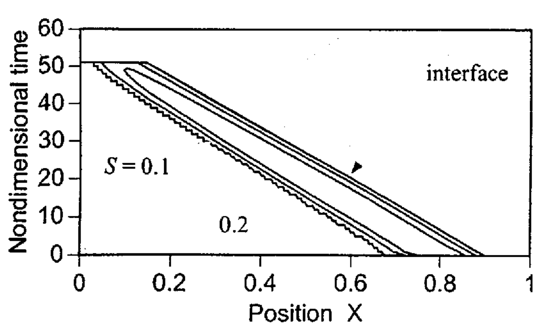


Figure 5 Time variation of constitutional supercooling in the solution

($\alpha = 0.01$, $G_T = 50$ K/cm)

3. Two-dimensional analysis of crystal growth of InGaAs

We investigated the crystal growth process of InAs-GaAs under microgravity conditions and checked the effects of the Rayleigh number based on the heater power and residual gravity and the angle between the directions of crystal growth and residual gravity on the convective instability and the crystal growth process.

3.1 Numerical modelling and calculation method

An outline of our numerical model of InAs-GaAs crystal growth is shown in Figure 7. The calculation area is divided into two regions, that is, single crystal and solution. The solution and the solid are placed in a two-dimensional container. The heat flux at the outer surface of the container is given externally as shown in Figure 7.

The governing equations for the solution are (1) the continuity equation, (2) the momentum equations where the buoyancy forces based on both the

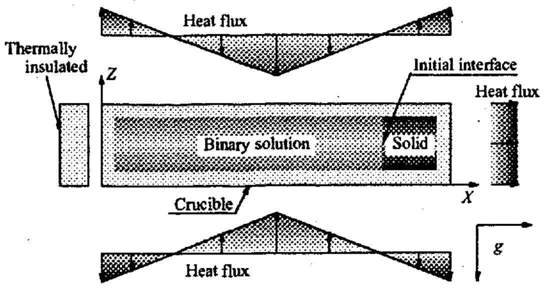


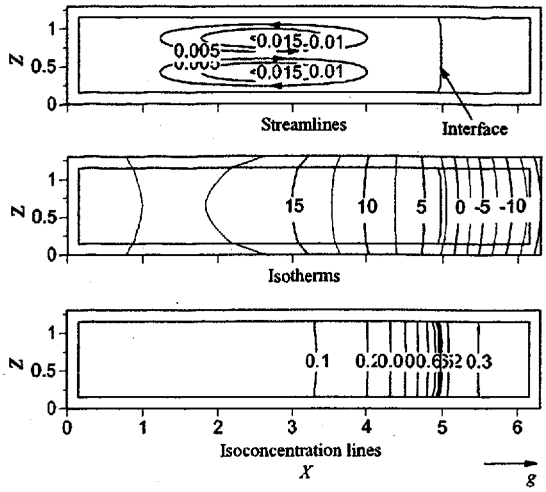
Figure 7 Two-dimensional analytical model of crystal growth of InGaAs

temperature and concentration differences are included, (3) the energy equation and (4) the transport equation of concentration. Heat conduction and concentration diffusion equations are necessary for the solid. The temperature and concentration at the interface, the shape of the interface and the crystal growth rate are determined by the heat and mass balance equations at the interface and the liquidus and solidus curves of the InAs-GaAs phase diagram (see Figure 1). As the shape of the interface changes with time, we solved the crystal growth problem transforming the governing equations by the boundary fit method (see eqs.(9) and (10)). The transformed equations were solved by the finite difference method.

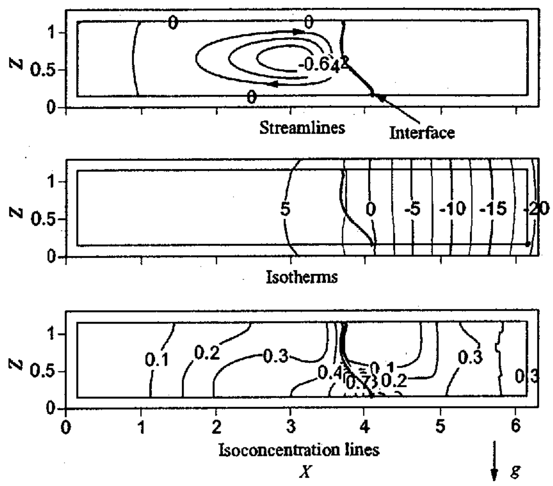
3.2 Result and discussion

The streamlines, isotherms, isoconcentration lines and the interfacial shape are shown in Figure 8. When crystal grows in the horizontal direction, the concentration field and the shape of the solid-solution interface are seriously deformed even when the Rayleigh number is as small as 8. When crystal grows in the antigravitational direction, convection is very weak and, as a result, the deformation of the concentration field and the interfacial shape is not large.

The time variation of the concentration at the centre is shown in Figure 9 where the Rayleigh numbers are different, that is, the heater power is doubled in the case of Figure 9(b) compared with Figure 9(a). The concentration profile is completely different depending on the heater power.



(a) The angle between the crystal growth direction and residual gravity , φ, is 0°



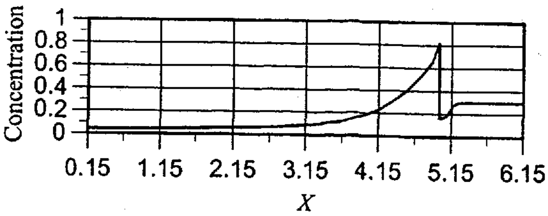
(b) $\varphi = 90°$

Figure 8 Streamlines, isotherms, isoconcentration lines, and interfacial shapes
$Ra^T = 8$, $Ra^C = -3000$, $Pr = 0.06$, $Sc = 10$,
$Sf = 0.68$, $\tau = 5.0$, $q_0 = 1.0 \times 10^4$ [W/m^2]

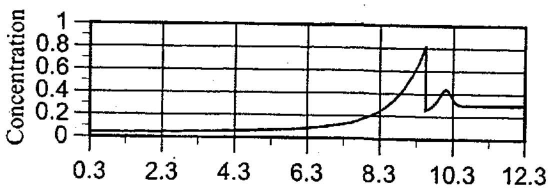
4. Summary

We carried out numerical analyses of crystal growth of InAs-GaAs binary semiconductors and the following results have been obtained;

(1) One-dimensional analysis of InGaAs: We developed a calculation method of one-dimensional InAs-GaAs binary crystal growth and checked the effect of the cooling rate and the temperature gradient on the generation of constitutional supercooling and



(a) $Ra^T = 8$



(b) $Ra^T = 16$

Figure 9 Distribution of concentration

the compositional uniformity of the grown crystal. It has been found that a crystal of a uniform composition can be grown by setting a positive concentration gradient of InAs in the direction of the growing crystal in the solution initially. The dependence of the degree of constitutional supercooling on the initial temperature gradient and the cooling rate was made clear.

(2) <u>Two-dimensional analysis of InGaAs</u>: We developed a calculation method of two-dimensional InAs-GaAs binary crystal growth and checked the effects of the Rayleigh numbers based on the heater power and residual gravity and the angle between the directions of crystal growth and residual gravity on the convective instability and the crystal growth process. We found that the concentration field and the shape of the crystal-solution interface are deformed even in microgravity and that crystal should be grown in the antigravitational direction so that convection is reduced and uniform crystals may be grown.

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