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２次元流動を考慮した液相成長のシミュレーション

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液相成長（ＬＰＥ）の実験において、成長初期の組成変動が観測された。その原因は、成長開始前に、溶液全体を、基板のない場所から、基板まで移動させるときに発生する溶液の流れと考えられている。モデル化した移流項を追加した Diffusion limited model を使用して、ＩｎＧａＰ結晶成長を対象にした１次元モデルで、この現象がシミュレーションされた。溶液の速度分布は Stokes's first problem で近似された。溶液の流れがない場合よりも大きいＩｎ組成をもつ固相が成長することが示された。この論文では、溶液の流れに２次元モデルを採用する。成長界面以外は、溶質の輸送にも２次元モデルを採用する。結果は、１次元モデルと同様なものが得られた。さらに、組成変動には、複雑な構造が現れた。

Simulation of Liquid Phase Epitaxy considering two dimensional flow

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Compositional variation in initial growth was observed in experiments of Liquid Phase Epitaxy (LPE). It is thought that the cause is the flow of the melt which is generated by the movement of the whole melt from the place where there isn't substrate to substrate before growth. The phenomenon was simulated with one dimensional model in InGaP growth with diffusion limited model to which simplified convection term is added. The velocity of melt flow was approximated to Stokes's first problem. It was shown that the solid of larger In composition than In composition in the case of no flow of melt grew. In this paper, two dimensional model of melt flow is adopted. In transport of solute, two dimensional model is also adopted except for the growth interface. Similar result to one dimensional was obtained. Moreover, complicated structure exists in compositional variation.

1. Introduction

In LPE, the growth condition at the interface is approximated to equilibrium between the solid phase and the liquid phase.

The part far from the interface is supersaturated during the growth. Therefore in more precise simulation, transport phenomena of materials are considered in addition to equilibrium at the interface. Diffusion limited model for the transport phenomenon was used for the simulation of LPE.

Last year, the method to solve diffusion limited model for compositional variation was proposed[1)].

On the other hand, before crystal growth starts, melt is moved from the place where there isn't substrate to substrate. The process generates flow in the melt. It needs to add convection term to diffusion limited model to describe compositional varia-

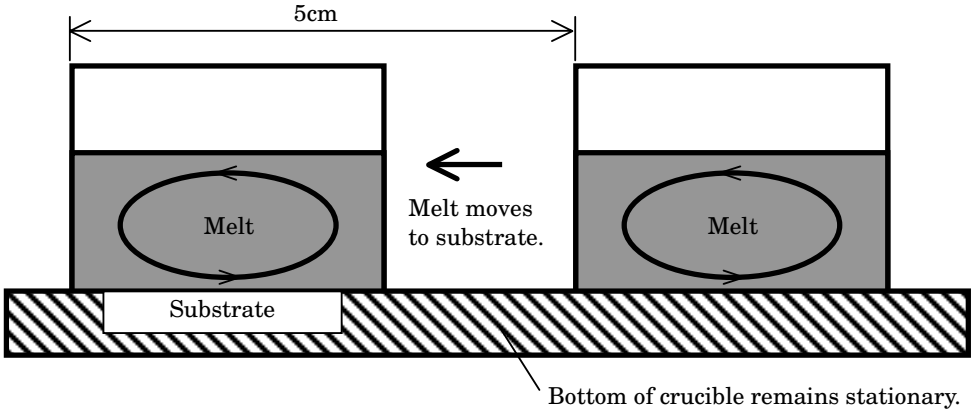

Fig.1 Movement of melt just before crystal grows

tion. It was shown by calculation that the convection affects compositional variation.[2] The calculation model of flow was one dimensional model.

In this paper, melt flow is two dimensional model. The diffusion equations are two dimension.

2. Calculation model

2.1 Experiment to analyze and thermodynamic model

In this paper, the experiment of LPE in reference 3) is analyzed. Crystal grown on substrate is InGaP.

The melt consists of In, P and Ga. Solvent is In.

Melt and solid phase at the interface were treated as equilibrium state. Thermodynamic model at the interface is same as reference 3). The phenomenon within 1 second after growth start is treated. Therefore temperature is approximated to constant during the growth. It was adopted that growth temperature is 782 degrees in the reference 3).

2.2 Flow of melt

In LPE process, melt is supersaturated where there isn't substrate. Then melt is moved to substrate to grow crystal on the substrate. Because the bottom which the melt touches remains stationary, the movement generates flow in the melt (**Fig.1**). In calculation model, it is represented as follows.

(a) Initially, melt is stationary.

(b) Next, the bottom of the melt moves at a speed of U_0 for time t_0= (the distance of the movement 5 cm) /U_0 and sides of melt remain stationary.

(c) The velocity of the bottom is set to 0.

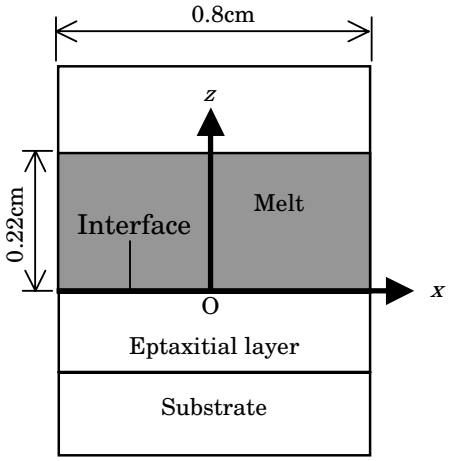

Fig.2 Coordinate system

The coordinate system is shown in **Fig.2**. The melt size of x direction is 0.8 cm and that of z direction is 0.22 cm. Origin of coordinate is located at the mid point of the interface.

2.3 Review of one dimensional model[2]

Velocity of melt flow is approximated to the analytic solution of Stokes's first problem. x component of velocity u is given as follows.

$$u = U_0 \left\{ \operatorname{erfc}\left(\frac{z}{2\sqrt{\nu(t_0+t)}}\right) - \operatorname{erfc}\left(\frac{z}{2\sqrt{\nu t}}\right)\right\}, \quad (1)$$

where ν is the kinematic viscosity of the melt and

is 1.7E-3 cm^2/s[4),5)]. Diffusion equation was added to simplified convection term.

$$\frac{\partial X_i^l(x=0,z,t)}{\partial t} = -u\frac{2}{L}((X_i^l(0,\infty,t) - (X_i^l(0,z,t)) + D_i\frac{\partial^2 X_i^l(0,z,t)}{\partial z^2}, \quad (2)$$

$$\frac{\frac{1}{2}(1-a)r - X_{Ga}^l(0,0,t)}{\frac{1}{2}r - X_P^l(0,0,t)} = \frac{D_{Ga}\frac{\partial X_{Ga}^l(0,z,t)}{\partial z}\Big|_{z=0}}{D_P\frac{\partial X_P^l(0,z,t)}{\partial z}\Big|_{z=0}}, \quad (3)$$

where L is the size of melt in the x direction. a is composition of solid $In_aGa_{1-a}P$. $X_i^l(x,z,t)$ is the mole fraction of component i in the melt at position x,z and growth time t. Component i represents Ga and P. D_i is the diffusion coefficient of component i. $D_{Ga}/D_P = 0.56$. The value was used in reference 3) to fit simulation to experimental results. D_P = 1.6E-4 cm^2/s so that calculated growth thickness is fit to experimental results. Equations (2) were solved by finite difference method explicitly. Mesh size in the direction of z is 6.6E-5 cm to detect compositional variation of solid at t=0.01s. Time interval Δt is set so that equation (2) is solved stably.

2.4 Calculation of two dimensional flow

Basic equations are the conservation of mass and Navier-Stokes equations.

$$\frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} = 0, \quad (4)$$

$$\frac{\partial u}{\partial t} = -u\frac{\partial u}{\partial x} - w\frac{\partial u}{\partial z} - \frac{1}{\rho}\frac{\partial p}{\partial x} + \nu\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial z^2}\right), \quad (5)$$

$$\frac{\partial w}{\partial t} = -u\frac{\partial w}{\partial x} - w\frac{\partial w}{\partial z} - \frac{1}{\rho}\frac{\partial p}{\partial z} + \nu\left(\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial z^2}\right), \quad (6)$$

where ρ is density and p is pressure. These equations were solved numerically with SIMPLE[6)]. Mesh size in the direction of x is 2.9E-3 cm. Mesh size in the direction of z= 1.4E-3 cm. Time interval Δt is set so that courant number is less than 0.5.

2.4.1 Transport of solute in the melt

The basic equation is as follows.

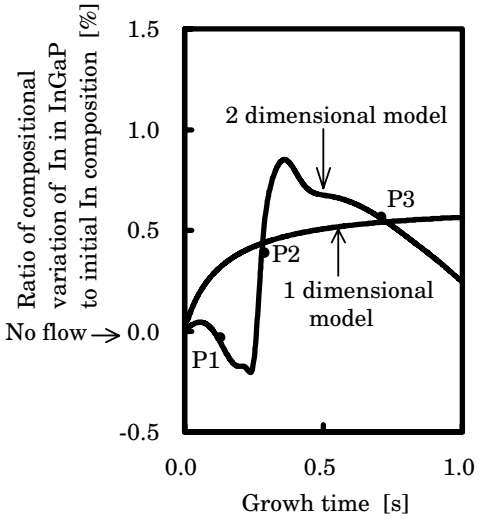

Fig.3 Compositional variation of In in InGaP

$$\frac{\partial X_i^l(x,z,t)}{\partial t} = -u\frac{\partial X_i^l(x,z,t)}{\partial x} - w\frac{\partial X_i^l(x,z,t)}{\partial z} + D_i\frac{\partial^2 X_i^l(x,z,t)}{\partial x^2} + D_i\frac{\partial^2 X_i^l(x,z,t)}{\partial z^2}, \quad (7)$$

The boundary condition is equation (3). And the solutions are substituted to $X_i^l(x, z=0, t)$ and In composition of $In_aGa_{1-a}P$ a on all over the interface. Equations (7) were solved by finite difference method using u and w solved from equations (4),(5) and (6) explicitly. Mesh size in the direction of x is same as that to calculate the flow of the melt. Mesh size in the direction of z is same as above one dimensional model. Time interval Δt is set so that equation (7) is solved stably . Mesh size in the direction of z and Δt are much smaller than those used to solve the flow. Therefore u and w were interpolated by the cubic spline for z direction and linearly for time.

3. Results and discussion

In the experiment[3)], the solid InGaP of large In composition grew for the period within 5 seconds from growth start. It is thought that the convection of the flow in the melt was strong for the period. After the period, the solid InGaP of small In composition grew for the period when it is thought that

the convection of the flow in the melt was weak.

In one dimensional calculation[2] it was shown that the solid InGaP of larger In composition than In composition in the case of no flow of the melt grew initially. In two dimensional calculation, similar result was obtained. Moreover, complicated structure, for example such as smaller In composition than In composition in the case of no flow of the melt grew when growth time was between 0.105 seconds and 0.259 seconds, exists. **Fig.3** shows the results ,where 0 of vertical axis corresponds to In composition in the case of no flow of the melt.

The complicated structure is caused by the flow of the melt. When the flow transports concentrated solution, boundary layers are filled with solutes[2]. When the flow transports dilute solution, opposite phenomenon occurs. Diffusion coefficient of P is larger than diffusion coefficient of Ga. Therefore the boundary layer of P is affected more strongly than that of Ga because that of P is longer than that of Ga.

The composition is decreased at point P1 when growth time is 0.12 seconds. A vorticity is generated near the mid point of the growth interface. The fluid around the vorticity flows form the growth interface where solution is dilute and upward near the mid point of the growth interface. Because the flow transports dilute solution, decrease of P is larger than that of Ga. Intuitively, it causes that the incorporation of P to solid more decreases than that of Ga. In solid InGaP, total mole number of In and Ga is same as the mole number of P. Therefore the incorporation of In more decreases than that of Ga.

In Fig.3, composition of In in InGaP is increased at point P2 growth time 0.278 seconds. The flow transports concentrated solution to the mid point of the growth interface. The increase of In in InGaP is understood by similar consideration.

In Fig.3, composition of In in InGaP is decreased at point P3 growth time 0.7 seconds. The melt flows upward at the mid point of the growth interface. The flow decreases In composition in solid InGaP for the same reason.

4. Conclusions

Compositional variation of solid InGaP is calculated with two dimensional model of the melt flow and the transport of solutes except for boundary condition at the growth interface in LPE. The solid InGaP of larger In composition than In composition in the case of no flow of the melt grew initially. This point is consistent with experiment and one dimensional model. In two dimensional model, In composition is greater than that in the case of no flow at almost growth time, but decreases when the flow transports dilute solution. This phenomenon is understood by considering the influence of the flow on the mole fraction near the boundary layer.

Acknowledgments

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