CONCENTRATION PROFILE SURFACES AND CONTOUR STUDIES OF GaP BY LIQUID PHASE EPITAXY

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ABSTRACT

The concentration profile surfaces of Phosphorus (P) atoms in Ga-melt in front of the growing GaP crystal under normal conditions of liquid phase epitaxy has been constructed three-dimensionally using the two-dimensional numerical simulation technique. The concentration contours of P atoms inside the solution at different experimental conditions have been constructed along the distance perpendicular to the substrate. The growth rate and the thickness of the grown layer of GaP have been estimated along the distance perpendicular to the substrate for different cooling rates, time and temperatures of growth using the concentration gradient existing at the interface. The temperature contours in the melt have also been constructed by solving an appropriate two-dimensional heat equation for different cooling rates and growth temperatures. Our simulated values have been compared with the experimentally reported values.

INTRODUCTION

Liquid Phase Epitaxy (LPE) is an important crystal growth process for both practical and fundamental point of views[1]. The LPE growth of Gallium phosphide (GaP) is one of the most important semiconductor materials used for optoelectronics[2,3] and high temperature devices[4] . The major interest of GaP has been centered on its use of red- and green-emitting electroluminescent diodes[5] . These devices are fabricated in such a way that one or more types of GaP layers are grown on a substrate. The LPE growth is the only suitable method for growing a desired layer thickness on the substrate than the other methods (VPE, OMVPE, MBE etc.). Normally, LPE growth takes place on a substrate placed in a graphite boat along with a supersaturated solution or fluxed melt. Super-saturation is usually maintained by gradually lowering the temperature during the growth, as in the LPE “tipping”, “sliding” and “sandwich cell” techniques[6, 7]. The use of relatively low temperature in LPE, gives crystals closer to stoichiometric composition with less dislocation and electrically and optically active point defects. The concentration of growth units is reduced gradually at the growing interface by reducing the temperature

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of the substrate, rises to concentration gradient at the interface which provides a driving mechanism for bulk transport in the liquid phase.

It has been also recognized that transport limited phenomena have a profound influence on the device-quality of the grown crystal layers. Several numerical simulation studies have been devoted to the modeling of bulk transport in order to predict concentration profiles, dimensionless concentration, growth rate and thickness, but most of the authors[8,9,10] have solved the one-dimensional mass transport differential equation numerically with appropriate boundary conditions at the interface.

This paper presents a numerical simulation of two-dimensional concentration profiles, concentration-contours, temperature-contours and growth rate for different temperatures and cooling rates during the liquid phase epitaxial growth of GaP. Two-dimensional mass-transport limited and heat-transport limited differential equations have been solved by the Laplacian[11] based on a centered difference method with an appropriate initial boundary conditions.

The numerical simulation has been carried out under the following assumptions and boundary conditions to find out the concentration profile surfaces and concentration contours, i) diffusion is the only cause of transportation of P atoms towards the growing interface; ii) the liquid and the solid are in equilibrium at the interface and iii) the diffusion coefficient and the gradient of the liquidus curve are constant during growth.

MATHEMATICAL MODEL

Solute diffusion equation

In the fast growth kinetic process, the two dimensional Cartesian coordinate system for the solute transport-limited (diffusion) equation in front of the growing crystal interface for liquid phase epitaxy (LPE) can be expressed as

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2}\right) \tag{1}$$

where C(x, y, t) is the concentration of Phosphorus (P) atoms inside the Gallium Phosphide (GaP) solution at the given instant, D is the diffusion coefficient of phosphorus (P) atoms in Gallium Phosphide (GaP) melt along the x-axis and y-axis. The value of diffusion[12] coefficient 2.12×10^{-5} cm^2/sec has been used in our numerical simulation procedure. The above equation is solved under the appropriate boundary conditions corresponding to the configuration of LPE growth of GaP.

Configuration of the LPE crystal growth for GaP

The LPE growth cell processes in our model system is shown in Fig.1 which consists of a horizontal substrate of 5mm length in a graphite boat along the yz-plane and the x-axis is perpendicular to the substrate. At the initial temperature of 1118K[12], the saturated GaP solution has been taken above the substrate. For the construction of concentration

profile surfaces of Phosphorus (P) atoms during the growth process we have considered a solution thickness of 5mm in front of the substrate along the x-axis and the length of the

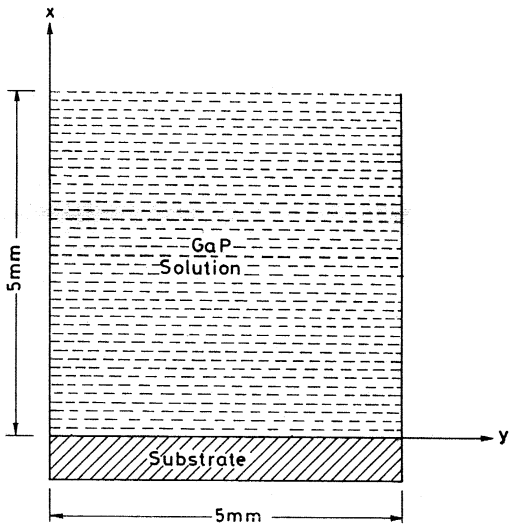

Fig.1. Liquid phase epitaxial growth cell configuration for GaP system.

substrate is 5mm along the y-axis. The solution is divided into 25×25 equally spaced meshes of width ε along the x-axis and y-axis. The mesh numbers along x-axis and y-axis can be written as a matrix form and the corresponding concentration will be written as C(x, y, t) = C (i , j, n; i = 1 to 25 and j = 1 to 25), where $t = n\tau$, $x = i\varepsilon$ and $y = j\varepsilon$. Growth proceeds by gradually lowering the temperature of the substrate at the given cooling rate of α to maintain the super saturation. The gradual depletion of solute in the solution will occur and this generates concentration gradients in the solution at the immediate vicinity of a growing liquid-solid interface. The two-dimensional diffusion equation has been solved by the forward difference in time and the formula for Laplacian[11, 13] based on a centered difference in both x and y axes is

$$C(i, j, n+1) = C(i, j, n) + \{D\tau/\varepsilon^2\} \times \{C(i-1, j, n) + C(i+1, j, n) + C(i, j-1, n) + C(i, j+1, n) - 4C(i, j, n)\} \quad (2)$$

where the factor $D\tau/\varepsilon^2$ is called the modulus $|M|$. It is necessary to select $|M|$ in such a way as to make $|M| \leq 1/4$ for stability condition[11] and we have used the value of τ= 4sec. The initial concentration of P along the substrate direction at the interface is denoted as C (0, j, 0) where j = 1 to 25. The concentrations of the other solutes at different meshes are found in matrix form by using the above equation (2).

Heat Diffusion Equation

The two-dimensional heat diffusion equation in liquid for the liquid phase epitaxy (LPE) can be written as [11]

$$\frac{\partial T}{\partial t} = K\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2}\right) \quad (3)$$

where T is the temperature of the solution and K is the thermal diffusivity along the x-axis and y-axis. The temperature at the interface can be found out[14] by the following equation

$$T(0 , j , n) = T_E - \alpha t \quad (4)$$

when $1 \le j \le 25$, T_E is the equilibrium temperature of the GaP melt at t=0, α is the cooling rate and t is the cooling time. The temperatures for the other i values (i.e., $1 \le i \le 25$) are found from the solution of equation (3).

BOUNDARY CONDITIONS

Initial condition

i) When t=0, $C(i, j, 0) = C_E$

where C_E is the equilibrium concentration (initial concentration) of Phosphorus (P) atoms at the initial temperature (1118K) of the solution. An equation for the equilibrium concentration has been developed by using the data reported in the literature[15] as

$$C_E = 4.58 \times 10^{22} \exp(8.705 - 1.58 \times 10^4 / T) \quad (5)$$

where T is the substrate temperature in Kelvin at any given instant of time. This equation is a fairly good representation of the Ga-P liquidus line on the Ga-rich side for the temperature range 1000 K to 1150 K.

ii) When t > 0, the concentration of the Phosphorus (P) atoms at the interface along the y-axis (substrate direction) in the melt is the equilibrium concentration C_E and the other concentration of Phosphorus atoms at different meshes can be found by using the equation (2).

Boundary conditions at the first and last segments are

when $t \ge 0$, $\partial C/\partial y \big|_{y=0} = 0$, $\partial C/\partial y \big|_{y=26} = 0$ and $\partial C/\partial x \big|_{x=25} = 0$

Computational boundary conditions

a) When time t=0, the temperature (T) is equal to the equilibrium temperature i.e. T_E=1118K, then $C_E = C(i , j , n)$ for $0 \le i \le 25$ and $1 \le j \le 25$.
b) When time $t \ge 1$, then $C_E = C(i , j , n)$ for $1 \le j \le 25$ and $i = 0$.
c) When time $t \ge 0$, then $C_E = C(i , j , n)$ for 1) j=1 and $1 \le i \le 25$; 2) j=25 and $1 \le i \le 25$; 3) i=25 and $2 \le j \le 24$.
d) When time $t \ge 1$, then the concentration in the other meshes are given by the equation (2) for $1 \le i \le 24$ and $2 \le j \le 24$.

Calculation of Growth Rate and Thickness of GaP

The growth rate of GaP LPE layer has been calculated by the rate at which P atoms diffuse towards the interface only along the x-axis (perpendicular to the substrate). An equation for the growth rate, R (j), can be obtained at the growing interface in terms of a

segmented solution[10,16] at the end of each time step in the computation of the equation(2) as well as updated equilibrium concentration equation (5).

$$R(j) = \frac{D(C(1,j,n) - C(0,j,n))}{\varepsilon(C_S - C(0,j,n))} \tag{6}$$

when $1 \le j \le 25$; C(0, j, n), C(1 , j, n) and C_S are the concentrations of Phosphorus (P) atoms at the interface (perpendicular to the substrate), first layer and in the solid GaP respectively. The thickness of the grown crystal at any given time is obtained by the summation of the growth rate.

$$G(j) = \sum_n R(j)\tau = \sum_n \frac{D\tau}{\varepsilon} \frac{(C(1,j,n) - C(0,j,n))}{(C_S - C(0,j,n))} \tag{7}$$

RESULTS AND DISCUSSION

The concentration profile surfaces of Phosphorus (P) atoms in GaP solution in front of the liquid-solid interface perpendicular to the substrate for different growth temperatures (1118K, 1078K and 998K) at a given cooling rate of 1K/min. are shown in Fig.2. As growth proceeds, the solute concentrations at the vicinity of the interface is decreased in the direction perpendicular to the substrate (i.e. along the x-axis) due to the

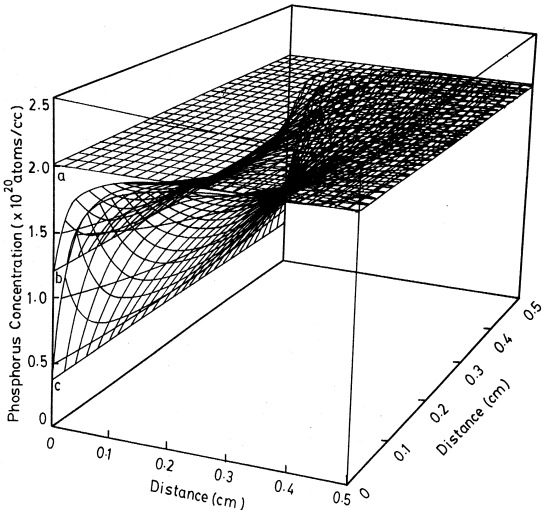

Fig. 2. Concentration profile surfaces of Phosphorus (P) atoms in front of the liquid-solid interface for the cooling rate of 1 K/min and for the different growth temperatures : a)1118K, b) 1078K and c) 998K.

adsorption and crystallization of Phosphorus(P) atoms. Fig. 3 presents the simulated concentration contours of Phosphorus (P) atoms inside the GaP solution in front of the interface for a cooling rate of 1K/min. and at the given growth temperature of 1078K. The nature of the concentration contours is convex type inside the solution with respect to the substrate, which means that at the boundary wall of the solution (i.e. at the edges of the substrate) the concentration of the Phosphorus atoms is more than that at the middle region of the substrate. Due to the more concentration of Phosphorus atoms at the boundary wall of the solution, the thickness of the grown GaP layer at the edges of the

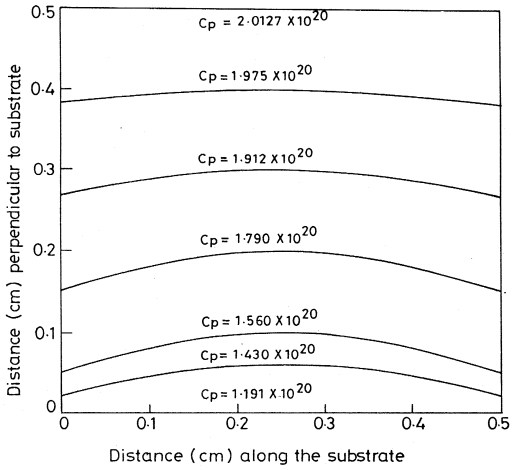

Fig. 3. Simulated concentration contours of Phosphorus (P) atoms in the GaP melt for the given cooling rate of 1 K/min with a growth temperature of 1078 K.

substrate is more compared with the middle region of the substrate. Thickness of the grown film as a function of the distance along the substrate for a fixed growth time of 30min with the different cooling rates (0.25K/min, 0.5K/min and 1K/min) has been shown in Fig. 4. It is seen that the growth is higher for higher cooling rates compared to

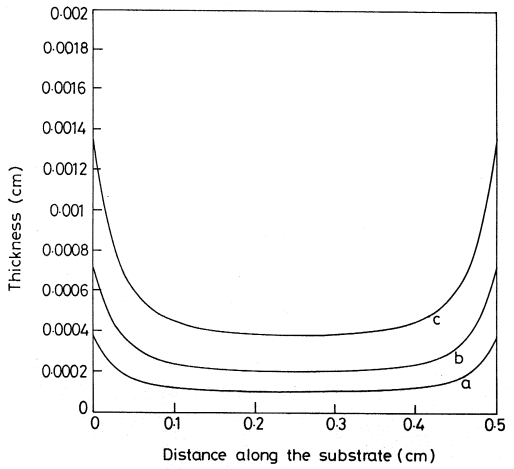

Fig. 4. Thickness of the grown GaP film on the substrate for different cooling rates : a) 0.25K/min, b) 0.5K/min and 1K/min with a fixed time duration of 30min from the equilibrium temperature T_E =1118K.

the lower cooling rates for a fixed duration of growth. The temperature contours have been constructed along the substrate and perpendicular to the substrate directions in front of the interface for a given growth temperature of 1078K, when the substrate is cooled with a cooling rate of 1K/min. from the initial temperature of 1118K. The nature of the contours are also convex type near the interface, which means that at the boundary wall of the solution (i.e. at the edges of the substrate) the temperature is more than that at the middle region of the substrate and the contours are shown in Fig.5. Fig.6 compares

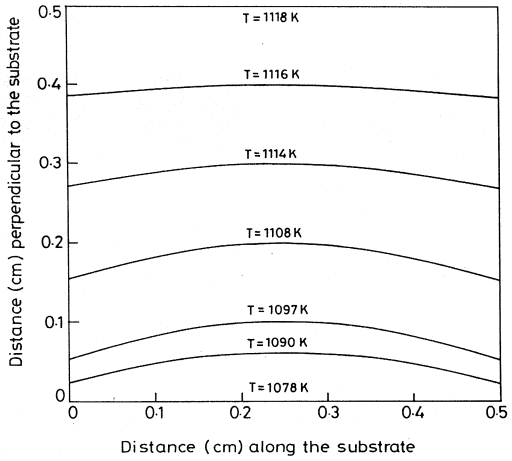

Fig. 5. Temperature contours in the GaP melt near the interface for the given cooling rate of 1 K/min and a growth temperature of 1078 K.

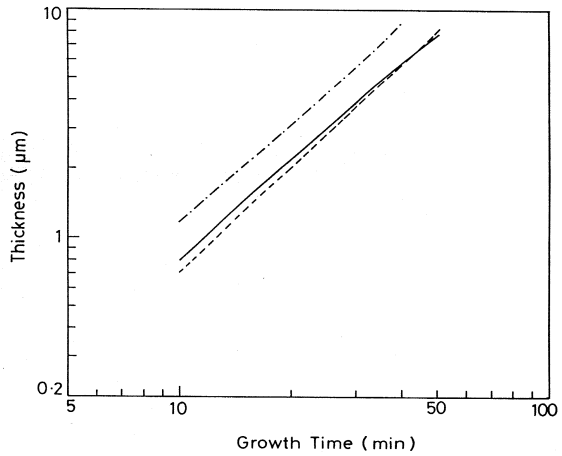

Fig.6. Comparison between our theoretical findings and experimentally reported values (for T_E=1118K and cooling rate of 1K/min). (- - - -) calculated values with a model equation for equilibrium cooling[12] , (- · - - -) experimentally reported values[12] and (——) the present work.

our theoretical calculation on the average thickness of the grown GaP with reported experimental values for the same growth parameters such as time and temperature and the same is compared with the theoretical model of equation for equilibrium cooling process[12] , when the cooling rate is 1K/min. and at the equilibrium temperature T_E=1118K. It was observed that our theoretical findings have shown good agreements with the reported theoretical values calculated from the model equation for equilibrium cooling process, but do not exactly match with experimentally reported values. A possible reason may be either there was no initial super-saturation or precipitation may

not have been initiated due to the lack of concentration differences between the solution and the interface for the experimental growth process.

CONCLUSION

Two-dimensional thermal and diffusive mass transport equations have been solved by the Laplacian based on a centered difference method. A computer simulation technique has been used to construct the concentration profile surfaces and contours of Phosphorus (P) atoms in front of the growing crystal interface along the distance perpendicular to the substrate. The concentration profile surfaces of the Phosphorus (P) atoms are bent near the interface with growth temperature. It is seen that the bend is more for lower growth temperature. It is also observed that the concentration contours near the interface is convex type, which means that the concentration of the Phosphorus atoms is more at the boundary wall of the solution than that of the middle region of the substrate with respect to the distance perpendicular the substrate. The temperature contours in the melt is also followed by the concentration contours in a similar pattern. The average thickness of the Gallium Phosphide (GaP) has been plotted with experimentally reported values for the same growth parameters such as time and cooling rate and the same was compared to the reported values. Our simulated values on average thickness of Gallium Phosphide shows good agreement with the reported values[(12)] .

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