Simulation of growth of graded bandgap GaAsP layers at liquid phase electroepitaxy

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The composition control possibility of the $GaAs_{1-x}P_x$ solid solution on $GaAs$ substrate at liquid phase electroepitaxy from the Ga-As-P solution-melt is theoretically considered. It has been established that under steady-state conditions specifying the process parameters such as temperature and/or the thickness of the growth space, it is possible to obtain graded bandgap layers of the $GaAs_{1-x}P_x$ solid solution with P content increasing towards the surface of the layer that possesses the composition gradient from $0.5 \cdot 10^{-4}$ mole fraction/nm to $2.0 \cdot 10^{-3}$ mole fraction/nm. It has been also shown that the composition control of ternary solid solutions at liquid phase electroepitaxy can be realized by use of unsteady electric field.

Теоретически рассмотрена возможность управления составом твердого раствора $GaAs_{1-x}P_x$ на подложке GaAs при жидкофазной электроэпитаксии из раствора-расплава Ga-As-P. Установлено, что в стационарных условиях, задавая такие параметры как температура и/или толщина ростового зазора, можно получить варизонные слои твердого раствора $GaAs_{1-x}P_x$ с увеличением содержания Р к поверхности слоя, который имеет градиент состава от $0.5 \cdot 10^{-4}$ мольн.долей/нм до $2.0 \cdot 10^{-3}$ мольн.долей/нм. Показано, что управление составом тройного твердого раствора в процессе жидкофазной эпитаксии может быть реализовано при использовании нестационарного электрического поля.

Solid solutions of A^3B^5 type with a space-dependent bandgap and thus with built-in electrical fields are used widely in optoelectronics. In particular, to provide effective photovoltaic converters, the graded-bandgap $GaAs_{1-x}P_x$ solid solutions are used with the bandgap width increasing towards the emitter layer surface [1]. Preparation of such structures by epitaxy from the liquid phase allows to improve considerably the operating characteristics due to higher crystal quality of epitaxial layers [2]. The conventional methods of the liquid phase epitaxy (LPE) using forced cooling or isothermal growth from the supersaturated solution-melt do not provide the formation of epitaxial layers with the bandgap width increasing from the substrate/emitter interface towards the emitter layer surface [3].

Usage of the liquid phase electroepitaxy (LPEE) to grow the graded bandgap epitaxial layers provides the following advantages. First, LPEE makes it possible to use isothermal growth conditions, which are more suitable for technological process. Second, the application of electric current allows to decrease considerably the response time of the epitaxial process and to provide the additional control at the epitaxy. In this work, the composition control possibility of a solid solution is theoretically considered taking as an example the $GaAs_{1-x}P_x$ solid solution at the LPEE from the Ga-As-P solution-melt on the GaAs substrate.

Initially, the saturated As solution in the Ga-melt is brought to a contact with the GaAs substrate (referred to as the working substrate) and the GaP substrate (referred to as the source substrate) that is the phosphorus source for the solution-melt. The substrates are situated in parallel to each other at a certain distance.

At the modeling, the following assumptions have been used:

• The growth process is isothermal;

• Mechanical stresses in the system are not taken into account;

• The diffusion mass transfer processes only are present in the solution-melt;

• All the growth and dissolution processes are diffusion limited;

• The transfer processes of the components in the solution-melt are independent;

• Interfaces of solid phases – solution-melt are assumed to be unmovable, hence the Stefan problem does not take place.

According to the assumption of the diffusion limitation of the crystallization process, the concentrations of the components in the solid and liquid phases at the interfaces have to be in equilibrium. For the ternary system of the GaAs$_{1-x}$P$_x$ solid solution, the equations that describe solidus and liquidus lines at the regular solution approach are as follows [4]:

$$x = \left[\frac{4x_{0Ga}^l x_{0P}^l \gamma_{Ga}^l \gamma_P^l}{\gamma_{Ga}^{sl} \gamma_P^{sl}} \cdot \exp\left(\frac{\Delta S_{GaP}^F \left(T_{GaP}^F - T \right)}{RT} \right) \right] \Big/ \gamma_{GaP}^s \tag{1}$$

$$(1-x) = \left[\frac{4x_{0Ga}^l x_{0As}^l \gamma_{Ga}^l \gamma_{As}^l}{\gamma_{Ga}^{sl} \gamma_{As}^{sl}} \cdot \exp\left(\frac{\Delta S_{GaAs}^F \left(T_{GaAs}^F - T \right)}{RT} \right) \right] \Big/ \gamma_{GaAs}^s \tag{2}$$

where $x = x_{GaP}^s$ is the mole fraction of GaP in the GaP$_x$As$_{1-x}$ solid solution; $x_{0Ga}^l, x_{0As}^l, x_{0P}^l$ are the mole fractions of Ga, As, and P, respectively, in the liquid phase that corresponds to the equilibrium with the solid phase at $z = 0$; $\gamma_{Ga}^l, \gamma_{As}^l, \gamma_P^l$, are the activity coefficients of Ga, As, and P, respectively, in the liquid phase; $\gamma_{Ga}^{sl}, \gamma_{As}^{sl}, \gamma_P^{sl}$ are the activity coefficients of Ga, As, and P, respectively, in the liquid phase of stoichiometric composition; $\gamma_{GaAs}^s, \gamma_{GaP}^s$, are the activity coefficients of GaAs and GaP, respectively, in the solid phase; $\Delta S_{GaAs}^F, \Delta S_{GaP}^F$, the specific molar melting entropies of GaAs and GaP, respectively; T_{GaAs}^F, T_{GaP}^F, are the melting temperatures of GaAs and GaP, respectively; T, is the epitaxy temperature; R, is the gas constant.

The activity coefficients can be calculated as follows [4]:

$$\gamma_{Ga}^l = \exp\left[\frac{\alpha_{GaP}^l \left(x_{0P}^l\right)^2 + \alpha_{GaAs}^l \left(x_{0As}^l\right)^2 + \left(\alpha_{GaP}^l + \alpha_{GaAs}^l - \alpha_{AsP}^l\right)x_{0As}^l x_{0P}^l}{RT} \right] \tag{3}$$

$$\gamma_{As}^l = \exp\left[\frac{\alpha_{AsP}^l \left(x_{0P}^l\right)^2 + \alpha_{GaAs}^l \left(x_{0Ga}^l\right)^2 + \left(\alpha_{AsP}^l + \alpha_{GaAs}^l - \alpha_{GaP}^l\right)x_{0Ga}^l x_{0P}^l}{RT} \right] \tag{4}$$

$$\gamma_P^l = \exp\left[\frac{\alpha_{GaP}^l \left(x_{0Ga}^l\right)^2 + \alpha_{AsP}^l \left(x_{0As}^l\right)^2 + \left(\alpha_{GaP}^l + \alpha_{AsP}^l - \alpha_{GaAs}^l\right)x_{0Ga}^l x_{0As}^l}{RT} \right] \tag{5}$$

$$\gamma_{Ga}^{sl} = \gamma_{As}^{sl} = \exp\left(\frac{0.25\alpha_{GaAs}^l}{RT} \right), \quad \gamma_{Ga}^{sl} = \gamma_P^{sl} = \exp\left(\frac{0.25\alpha_{GaP}^l}{RT} \right) \tag{6}$$

$$\gamma_{GaAs}^{s} = \exp\left(\frac{\alpha_{GaAs-GaP}^{s} x^2}{RT}\right), \quad \gamma_{GaP}^{s} = \exp\left(\frac{\alpha_{GaAs-GaP}^{s} \left(1-x\right)^2}{RT}\right),$$ (7)

where $\alpha_{GaAs}^{l}, \alpha_{GaP}^{l}, \alpha_{AsP}^{l}$ are the atomic interaction parameters in the liquid phase for Ga-As, Ga-P, and As-P, respectively; $\alpha_{GaAs-GaP}^{s}$ is the atomic interaction parameter in the solid phase for GaAs-GaP system.

Diffusion processes of the As and P components dissolved in Ga melt are described as follows [5-7]:

$$\frac{\partial x_{As}^{l}\left(z,t\right)}{\partial t} = -\mu_{As} E_z \frac{\partial x_{As}^{l}\left(z,t\right)}{\partial z} + D_{As}^{l} \frac{\partial^2 x_{As}^{l}\left(z,t\right)}{\partial z^2}$$ (8)

$$\frac{\partial x_{P}^{l}\left(z,t\right)}{\partial t} = -\mu_{P} E_z \frac{\partial x_{P}^{l}\left(z,t\right)}{\partial z} + D_{P}^{l} \frac{\partial^2 x_{P}^{l}\left(z,t\right)}{\partial z^2},$$ (9)

where $\mu_{As}, \mu_{P}, D_{As}^{l}, D_{P}^{l}$ are the electrical mobility and diffusivity of As and P ions in the Ga melt, respectively; $x_{Ga}^{l}\left(z,t\right), x_{As}^{l}\left(z,t\right), x_{P}^{l}\left(z,t\right)$, the mole fractions of Ga, As, and P components, respectively, that depend on time t and coordinate z.

The electric field can be found using the formula

$$E_z = J \cdot \rho_{Ga}^{l},$$ (10)

where ρ_{Ga}^{l} is the specific resistance of the solution-melt; J, is the current density.

Due to the diffusion-limited approach of the growth and dissolution processes, the boundary conditions are as follows:

$$x_{P}^{l}\left(0,t\right) = x_{0P}^{l}; \; x_{As}^{l}\left(0,t\right) = x_{0As}^{l},$$ (11)

$$x_{P}^{l}\left(l,t\right) = x_{lP}^{l}; \; x_{As}^{l}\left(l,t\right) = x_{lAs}^{l}$$

where $x_{lGa}^{l}, x_{lAs}^{l}, x_{lP}^{l}$ are the mole fractions of Ga, As, and P, respectively, in the liquid phase, that correspond to the equilibrium with the solid phase at $z = l$.

The initial conditions are:

$$x_{P}^{l}\left(z,0\right) = x_{0P}^{l}; \; x_{As}^{l}\left(z,0\right) = x_{0As}^{l}.$$ (12)

To solve the mass transfer equations (8, 9) with the initial and the boundary conditions (11, 12), the finite difference method was used. The explicit scheme [8] was used to approximate equations (8, 9). Let the discretization of boundary conditions (11) be considered. At the interface $z = 0$ the solid phase composition varies in time due to the crystallization, thus causing an implicit time dependences of x_{0Ga}^{l}, x_{0As}^{l}, and x_{0P}^{l}.

The composition of the layer being crystallized during a time step can be described as

$$x = \frac{1}{\dfrac{x_{As}^{*l} - x_{0As}^{l}}{x_{P}^{*l} - x_{0P}^{l}} + 1},$$ (13)

where x_{As}^{*l}, x_{P}^{*l} are the As and P mole fractions in the liquid phase, respectively, that have been appeared at the current time step due to the mass transfer in the liquid phase at $z = 0$ prior to crystallization. Solving the system of three equations (1, 2, 13) and the normalization requirement $x_{0Ga}^{l} = 1 - \left(x_{0As}^{l} + x_{0P}^{l}\right)$, the equilibrium composition of the liquid and solid phases, i.e.

$x, x_{0Ga}^l, x_{0As}^l, x_{0P}^l$, can be obtained.

The thickness of layer being crystallized per one time step can be found as

$$h^g = \frac{h}{\omega^s} \left[\frac{\left(x^{*l}_{As} - x_{0As}^l\right) + \left(x^{*l}_P - x_{0P}^l\right)}{\left(x_{0Ga}^l \dfrac{M_{Ga}}{\rho_{Ga}} + x_{0As}^l \dfrac{M_{As}}{\rho_{As}} + x_{0P}^l \dfrac{M_P}{\rho_P}\right)} \right], \tag{14}$$

$$\text{where } \omega^s = \frac{8}{N_A \left[x a_{GaP} + (1-x) a_{GaAs}\right]^3} \tag{15}$$

is the mole density [7]; N_A, is the Avogadro constant; a_{GaP}, a_{GaAs}, the lattice constants of GaP and GaAs, respectively; $M_{Ga}, M_{As}, M_P, \rho_{Ga}, \rho_{As}, \rho_P$, are the molar masses and densities of Ga, As, and P, respectively; h, is the spatial step in the finite differences scheme.

Let the digitization of the boundary conditions (11) at the interface GaP substrate /solution-melt ($z = l$) be considered. According to the mass conservation law,

$$\left(x^{**l}_{Ga} + x^{**l}_{As} + x^{**l}_P\right) + \alpha \cdot GaP = x_{lGa}^l + x_{lAs}^l + x_{lP}^l, \tag{16}$$

where $x^{**l}_{Ga}, x^{**l}_{As}, x^{**l}_P$ are the mole fractions of Ga, As, and P, respectively, in the liquid phase, that appeared at current time step due to mass transfer in the liquid phase at $z = l$ prior to dissolution.

The mole fractions of Ga can be found from the normalization requirement:

$$x_{lGa}^l = 1 - \left(x_{lAs}^l + x_{lP}^l\right) \tag{17}$$

$$x^{**l}_{Ga} = 1 - \left(x^{**l}_{As} + x^{**l}_P\right). \tag{18}$$

From equations (16)-(18), we get:

$$\begin{cases} \dfrac{1 - \left(x^{**l}_{As} + x^{**l}_P\right) + \dfrac{1}{2}\alpha}{1 + \alpha} = 1 - \left(x_{lAs}^l + x_{lP}^l\right) \\[4mm] \dfrac{x^{**l}_P + \dfrac{1}{2}\alpha}{1 + \alpha} = x_{lP}^l \end{cases}. \tag{19}$$

Solving the system (19), we get:

$$x_{lP}^l = \frac{0.5\left(2 \cdot x^{**l}_P \cdot x_{lAs}^l + x^{**l}_{As} - x_{lAs}^l\right)}{x^{**l}_{As}}. \tag{20}$$

Solving the system including two phase equilibrium equations (1, 2), normalization requirement (18) and equation (20) at every time step of the calculations gives the equilibrium compositions of the liquid and solid phases at interface of GaP substrate/solution-melt, i.e. $x_{lGa}^l, x_{lAs}^l, x_{lP}^l$.

The simulation was carried out in the temperature range of 600-900°C corresponding to the whole range of GaAs$_{1-x}$P$_x$ solid solutions [10], in the range of substrate spacing (thickness of the growth space) of 0.5-1 mm, and in the range of current densities of 1-9 A/cm². Values of parameters used in calculations are correspond with data [3, 4, 7, 10-12, 13, 14]. From Figs. 1a-1c, it follows that:

• Under steady-state conditions, the current density influences the growth rate of the solid solution layer only and practically does not affect its composition gradient (Fig. 1a);

• Under steady-state conditions, the solid solution composition gradient depends on the growth temperature (Fig. 1b) and on the substrate spacing (Fig. 1c). The growth temperature lowering or the substrate spacing diminution results in increasing composition gradient.
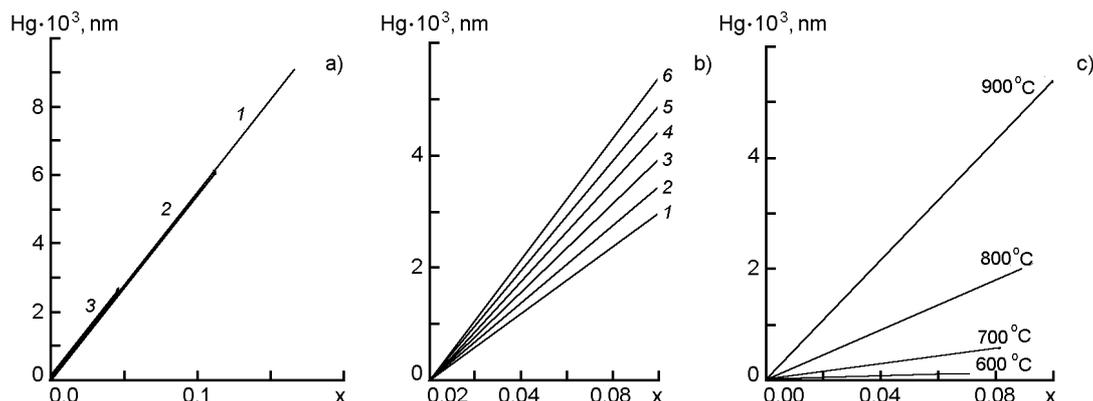
Fig. 1. Dependences of the thickness of the deposited $GaAs_{1-x}P_x$ solid solution layer on its composition: *(a)* at different current densities (curve *1* – 5, *2* – 3, *3* – 1 A/cm²) for the same time of 1 h. (the growth temperature T = 900°C, the growth space thickness l =1 mm); *(b)* at different growth space thickness values (the growth temperature T = 900°C, the current density J =3 A/cm²); *(c)* at different growth temperatures (the growth space thickness l = 1 mm, the current density J =3 A/cm²).

Fig. 2. Dependence of the composition gradient in $GaAs_{1-x}P_x$ solid solution on the growth process parameters: the growth temperature and the growth space thickness. The current density J =3 A/cm². Curves *1* – 600 °C, *2* – 700 °C, *3* – 800 °C, *4* – 900 °C.
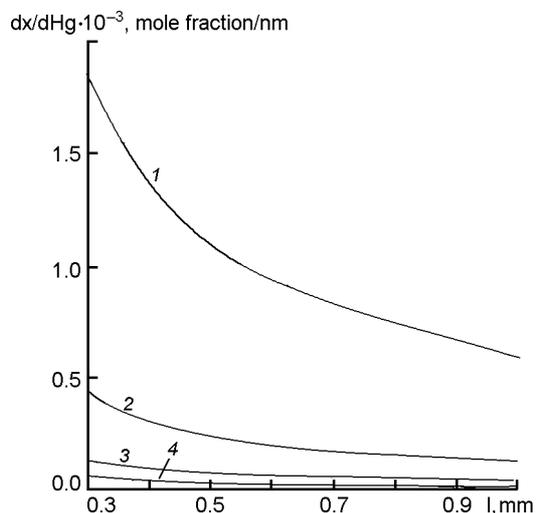
As is seen from Fig. 2, under steady-state conditions changing of such parameters as the temperature of growth and/or the thickness of the growth space makes it possible to control the composition gradient in $GaAs_{1-x}P_x$ solid solution in a wide range from $0.5 \cdot 10^{-4}$ mole fraction/nm to $2.0 \cdot 10^{-3}$ mole fraction/nm.

Let the influence of the current density changes on processes in the system be considered. In Figs. 3a and 3b, the evolutions of P and As atomic concentrations in Ga melt at the current switching off are presented. Prior to the current switching off, considerable difference in concentration profiles of P and As is caused by different directions of electric and diffusion constituents of As and P atomic flows. For P, both electric and diffusion constituents of the atomic flow have the same direction. But for As, the diffusion constituent has the opposite direction. That is why the profile of As concentration distribution depends on the current density to a greater extent than that for P. Changes of the current density result in a considerable redistribution of As concentration in the liquid phase and, as a result, at the crystallization front. This provides shift of equilibrium conditions in the system and moves the figurative work point in the phase diagram. After the current switching off, the As concentration at the crystallization front decreases due to the diffusion. This results in increasing P molar fraction in the solid phase. Thus, it is just changing of the current density value that can be used to control the composition gradient in the solid solution during growth (see Fig. 4.).
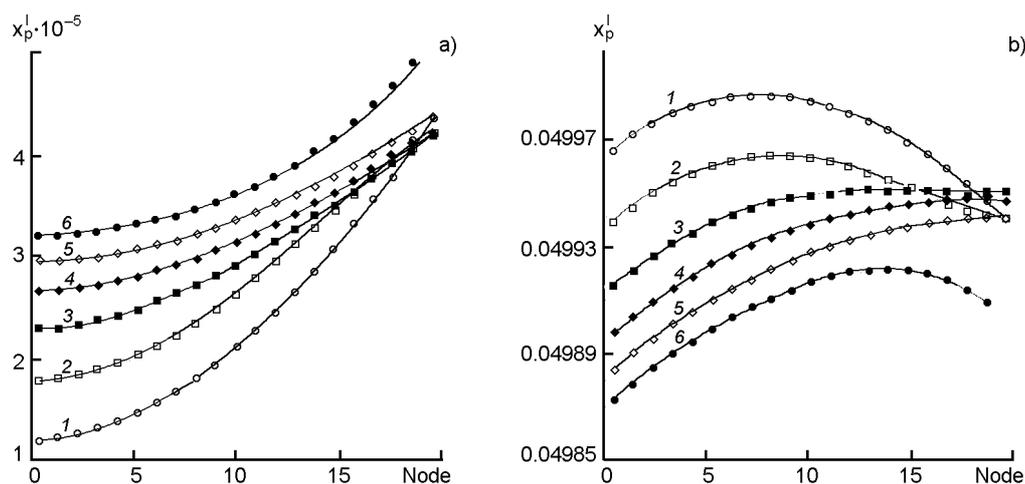
Fig. 3. The node distribution of the P (a) and As (b) mole fractions at different time (curves *1* – 60, *2* – 80, *3* – 100, *4* – 120, *5* – 140, *6* – 160). The growth temperature 900°C, the growth space thickness 1 mm. The current density: till 60 s, 1 A/cm², in the range of 80-140 s, 0 A/cm², and from 140 on, 1 A/cm².
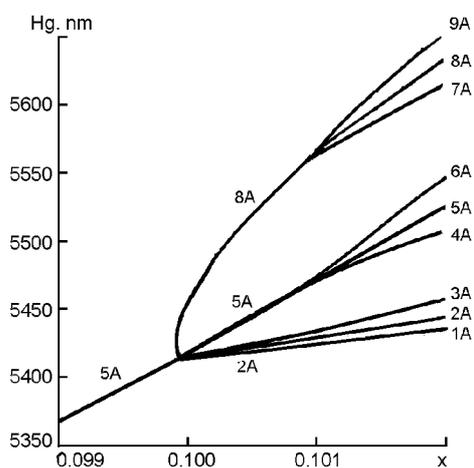

Fig. 4. Dependence of the growing $GaAs_{1-x}P_x$ solid solution layer thickness on its composition at current density intentional changes during the growth and representing unsteady electric field (the growth temperature 900°C, the growth space thickness 1 mm).

To conclude, it has been shown that the use of electroepitaxy from the liquid phase in the isothermal conditions enables in principle to obtain graded bandgap $GaAs_{1-x}P_x$ structures with phosphorus content increasing towards the layer surface. The use of unsteady electric field makes it possible to control effectively the composition of the ternary solid solution.

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Моделювання процесів росту шарів GaAs$_x$P$_{1-x}$ при рідиннофазній електроепітаксії

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Теоретично розглянуто можливість управління складом твердого розчину GaAs$_{1-x}$P$_x$ на підкладці GaAs при рідиннофазній електроепітаксії з розчину-розплаву Ga-As-P. Встановлено, що у стаціонарних умовах, задаючи такі параметри процесу, як температура та/або товщина ростового зазору, можна отримати варизонні шари твердого розчину GaAs$_{1-x}$P$_x$ із збільшенням вмісту P до поверхні шару, що мають градієнт складу від 0.5·10^{-4} мольн.частка/нм до 2.0·10^{-3} мольн.частка/нм. Показано, що керування складом тернарного твердого розчину у процесі рідиннофазної електроепітаксії може бути здійснене при використанні нестаціонарного електричного поля.