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# Crystallization mechanism control during epitaxy from solution-melt

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Main problems appearing during heteroepitaxy from solution-melts and requirements to time-temperature profiles at the crystallization front have been considered. The substrate cooling possibility by gas feeding to the reactor from outside to provide the crystallization conditions that consecutively combine properties both pulse and quasi-equilibrium conditions growth methods are shown. A model of heat and mass transfer for a priori determination of the cooling gas consumption has been examined experimentally.

Рассмотрены основные проблемы, возникающие при гетероэпитаксии из растворов-расплавов, и требования к температурно-временным профилям на фронте кристаллизации. Показана возможность применения охлаждения подложки при помощи газа, подающегося извне реактора, для получения условий кристаллизации, которые последовательно объединяют в себе свойства как импульсных методов выращивания, так и методов кристаллизации в квазиравновесных условиях. Экспериментально проверена модель тепломассопереноса для априорного определения расхода охлаждающего газа.

Liquid phase heteroepitaxy difficulties appeared due to difference in chemical potentials of solution-melt and substrate and mismatched lattice constants of epitaxial layer and substrate result in distortion of the crystallization front stability. As a result, deviation of epitaxial layer thickness and composition from those necessary to realize planar device structures based on heterojunctions. To prevent the substrate dissolution, the heteroepitaxy from liquid phase that is initially overcooled with respect to equilibrium state is usually used [1]. Strains that usually appear at heteroepitaxy and produce both increasing of the solid phase chemical potential [2] and crystallization front perturbation [3], demand an additional supercooling at the crystallization front and high crystallization rate during initial stages of growth [4]. But taking into account that the controlled growth can be realized only under limited supercooling when the solution melt is not fall to labile region [5], it is not always possible to avoid the problems at the initial heteroepitaxy stages. This decreases the reproducibility of structural parameters and, hence, deteriorates the electrophysical properties of heterojunctions. In this connection, we consider in this work the possibility to provide special conditions at the crystallization front which enable both avoiding traditional heteroepitaxial problems and, at the same time, structural perfection that is typical for liquid phase epitaxy (LPE).

The providing of material structure perfection in LPE conditions under simultaneous blocking of negative phenomena connected with differences in crystal-chemical parameters of substrate and heteroepitaxial layer materials is possible under controlled variation of the layer crystallization mechanism. After a short period of initial growth under high supersaturation and crystallization rate values, which provides formation of planar protective layer by the Frank-van-der-Merve mechanism, a period

of equilibrium crystallization must follow. To provide such conditions at the crystallization front, the pulse cooling with suitable temperature-time profile at the crystallization front (TTPCF) is necessary. Traditional methods of forced cooling cannot provide sharp temperature pulses due to high thermal inertia of the system. The well-known LPE methods providing high crystallization rates (the high-rate and very-high-rate cooling of saturated solution-melt, substrate shooting through the solution-melt, pulse cooling of saturated solution-melt, etc.) do not provide the arbitrary TTPCF control. Besides, at pulse cooling of the substrate-solution-melt system causes the problems mentioned below.

First, the pulse includes not only the temperature dropping front (pulse edge), but also the temperature rising one. This situation is non-trivial for conventional epitaxial layer growth methods. As a result, negative crystallization rates become possible, thus causing the epitaxial layer dissolution and influencing unfavorably the planarity of current layer and next layers. The problem of positive crystallization rates maintaining during the whole epitaxial growth process is very important for providing of epitaxial layer planarity. The problem appears because the temperature at the crystallization front rises after passage of the maximum of supercooling, thus stimulating an increase of the equilibrium solute concentration of in the solution-melt at a rate

$$\frac{\partial C_0(x,t)}{\partial t} = \frac{\partial T(x,t)}{\partial t}m, \tag{1}$$

where $m$ is the liquidus slope. The concentration change in any point due to diffusion is described by the second Fick law

$$\frac{\partial C(x,t)}{\partial t} = D\Delta C(x,t), \tag{2}$$

where $D$ is the diffusion coefficient of surplus solute atoms in the solution-melt.

If the equilibrium solute concentration at the crystallization front changes faster than it is compensated due to diffusion transport, then a negative supersaturation is formed at the epitaxial layer / solution-melt interface. As a result, positive crystallization rate changes to negative one, thus causing a partial dissolution of the epitaxial layer. Absence of dissolution after supercooling maximum passage can be provided only when the change of equilibrium solute concentration at the crystallization front is slower than the diffusion transport:

$$\frac{\partial C(x,t)}{\partial t} - \frac{\partial C_0(x,t)}{\partial t} = D\Delta C(x,t) - m\frac{\partial T(x,t)}{\partial t} > 0. \tag{3}$$

The condition (3) can be realized by providing a suitable TTPCF.

Moreover, during quasi-equilibrium growth at a low crystallization rate requires a prolonged cooling at the crystallization front, that is, a time-unrestricted, continuous heat removal.

From the foregoing facts, the main requirement to heat flow through substrate is that it should be easily controlled, low-inertial and time-unrestricted. In practice, the heat flow is provided by contact of substrate backside with a body colder with respect to it, that is, a heat absorber. The heat absorber should have an unlimited heat capacitance and provide easy time-controlled heat transfer factor from the false substrate backside. Taking into account the typical crystallization process temperature values, those requirements can be satisfied only using a gaseous heat absorber that is fed to the reactor from outside. The reactor outside feeding provides unlimited heat capacitance and heat transfer factor can be changed during the growth by time-controlled gas consumption.

However, to use a gaseous heat absorber, a heat exchanger between substrate and gas in the growth cassette is necessary. For most easy construction heat exchangers open into reactor, the heat absorbing gas should have the same composition as the technological gas inside the reactor.

One of possible heat exchangers constructions is shown in Fig. 1. Substrate 1, that is in contact with saturated solution-melt 2, the equilibrium thereof being provided by contact with substrate support 3, is cooled by gas flow 7, that is fed through a quartz pipe 6 into the heat exchanger, formed by means of quartz plate 5. A graphite plummet 4 fix the false substrate.

For growth realization, it is necessary to know a priori the time dependence of heat absorbing gas consumption to form the required TTPCF, which is also not known completely. But very complicated unsteady heat and mass transfer processes, taking place at pulse epitaxy, make impossible to solve inverse problem of heat and mass transfer: to find TTPCF when the argument is the layer thickness. That is why the required TTPCF is determined by the heat and mass transfer simulation where the starting

parameter is an initial approximation of TTPCF, which is corrected with respect to limitations for the crystallization rates values.

The heat transmission is described by following deferential equation system:

$$\begin{cases} \dfrac{\partial T(x,t)}{\partial t} = \dfrac{\lambda_M}{c_M \rho_M} \dfrac{\partial^2 T(x,t)}{\partial x^2}, \quad x \in (x_1;x_2). \\ \dfrac{\partial T(x,t)}{\partial t} = \dfrac{\lambda_{FS}}{c_{FS} \rho_{FS}} \dfrac{\partial^2 T(x,t)}{\partial x^2}, \quad x \in (x_2;x_3), \\ \dfrac{\partial T(x,t)}{\partial t} = \dfrac{\lambda_G}{c_G \rho_G} \dfrac{\partial^2 T(x,t)}{\partial x^2}, \quad x \in (x_3;x_4). \end{cases} \quad (4)$$

with initial and boundary conditions:

$$\begin{cases} T(x,0) = T_f, \\ T(x_4,t) = T_f, \\ T(x_1,t) = T_{CI}(t), \\ T(x_2 - 0,t) = T(x_2 + 0,t), \\ -\lambda_M \dfrac{\partial T(x_1 - 0,t)}{\partial x} + \lambda_{FS} \dfrac{\partial T(x_1 + 0,t)}{\partial x} - mE_C \dfrac{\partial T(x_1 - 0,t)}{\partial x} = 0, \\ \lambda_{FS} \dfrac{\partial T(x_2 - 0,t)}{\partial x} = \lambda_G \dfrac{\partial T(x_2 + 0,t)}{\partial x} \\ q(x_1,t) + \lambda_M \dfrac{\partial T(x_1 + 0,t)}{\partial x} + J_C E_C \end{cases} \quad (5)$$

Were, $\lambda_M$, $\lambda_{FS}$, $\lambda_G$ are the heat conductivity of solution-melt, substrate support, and plummet, respectively; $c_M$, $c_{FS}$, $c_G$ are the heat capacitance of solution-melt, substrate support, and plummet, respectively; $\rho_M$, $\rho_{FS}$, $\rho_G$ are the densities of solution-melt, substrate support, and plummet, respectively; $j_C$ is the crystallization substance flow; $E_C$ is the crystallization enthalpy, $T_f$ is the furnace temperature; $T_{CF}(t)$ is the temperature at the crystallization front. To determine the crystallizing substance flow, it is necessary to solve the mass transfer problem in solution melt in combination with the heat transmission problem. Diffusion equation of surplus atoms at concentration distribution $N(x,t)$ is

$$\frac{\partial N(x,t)}{\partial t} = D \frac{\partial^2 N(x,t)}{\partial x^2} - m \frac{\partial T(x,t)}{\partial t}, \quad (6)$$
$$x \in (x_1;x_2),$$

with initial and boundary conditions (crystallization rate is assumed to be unlimited):

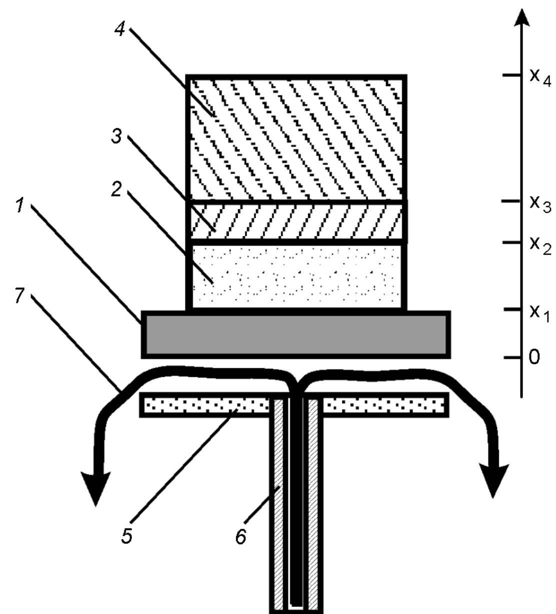


Fig. 1. Schematic construction of heat exchanger for substrate cooling by gas is fed into reactor from outside.

$$\begin{cases} N(x_1,t) = 0, \\ \dfrac{\partial N(x_1,t,)}{\partial t} = \infty, \\ N(x,0) = 0. \end{cases} \quad (7)$$

The heat and mass transfer problem described by equations (4)–(7) can be solved by numerical methods, for example, finite differences method. As a solution, we obtain the expected epitaxial layer thickness and heat flow $q(x_1,t)$. By correcting TTPCF, we find such one which satisfies all the above-considered growth conditions.

The next problem is to find the necessary heat flow through the substrate backside, that is, the heat flow through the heat exchanger. To do this, it is necessary to solve the inverse heat conduction problem. According to Burggraf approach [5], for one-dimensional system with flat geometry,

$$q(0,t) = q(x_1,t) + \sum_{n=1}^{\infty} \frac{x_1^{2n-1}}{(2n-1)!} \frac{1}{\alpha_S^n} \frac{d^n T(x_1,t)}{dt^n} + \sum_{n=1}^{\infty} \frac{x_1^{2n}}{(2n)!} \frac{d^n q(x_1,t)}{dt^n}, \quad (8)$$

where $\alpha_S$ is the substrate thermal diffusivity.

Necessary gas consumption can be found from the heat balance

$$\alpha(G) \cdot (T(0,t) - T_0) = q(0,t), \quad (9)$$

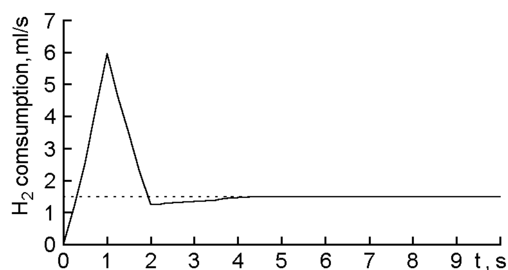


Fig. 2. Calculated dependence of hydrogen consumption on crystallization time. Unsteady region is shown only. Dotted line shows line of equal consumption.

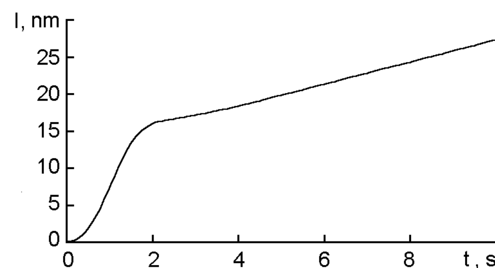


Fig. 3. Calculated dependence of epitaxial layer thickness on crystallization time. Unsteady region is shown only.

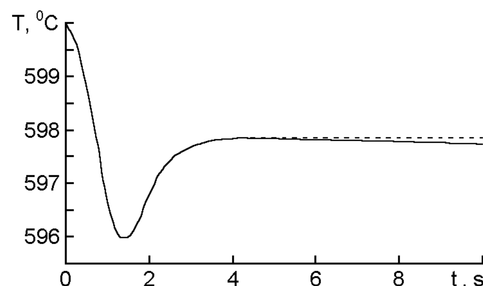


Fig. 4. Calculated dependence of crystallization interface temperature on crystallization time. Unsteady region is shown only. Dotted line shows isotherm.

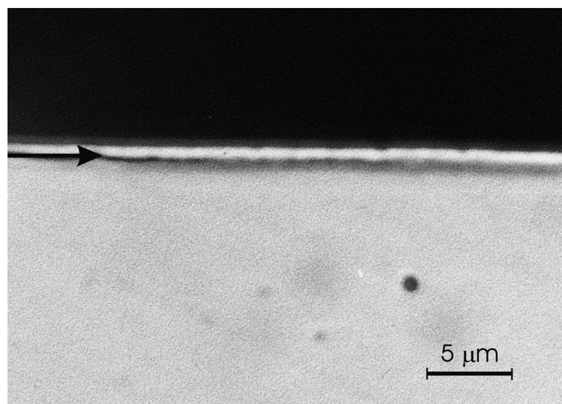


Fig. 5. The cross-section of GaAs/n–GaAs (100) epitaxial structure treated in selective etchant. The arrow marks the position of substrate-epitaxial layer interface.

where $G$ is the gas consumption; $\alpha(G)$, heat transfer factor in the heat exchanger; $T_0$, temperature of gas entering the heat exchanger.

For the proposed heat exchanger, the gas heat transfer factor is determined by Nusselt equation [6]

$$Nu = 1.36 \left(\frac{h}{d}\right)^{0.55} \mathrm{Re}^{0.83}, \quad (10)$$

where $Nu = \frac{\bar{\alpha} d}{2\lambda}$ is the Nusselt number, $\mathrm{Re} = \frac{G}{2\pi\mu h}$ is the Reynolds number; $h$ is the, distance between substrate and quartz plate, $d$ is the effective heat exchanger diameter, $\bar{\alpha}$ is the average heat transfer factor.

The correctness of heat and mass transfer model for the considered method was checked in experiment with p–GaAs epitaxial growth on n–GaAs (100) substrate with carrier concentration $5 \cdot 10^{17}$ cm$^{-3}$. The solution-melt saturation temperature was 600°C. Hydrogen was used as the technological gas and heat absorbing gas. The following requirements to TTPCF were used. To obtain a sharp concentration profile, the initial growth rate had to be high (10–15 nm/s), and following epitaxial layer growth had to be carried out at a low growth rate (1–2 nm/s). Such profile was a model of TTPCF necessary at heteroepitaxy, as has been considered above. The required hydrogen consumption for the accepted TTPCF was calculated. The time dependence of hydrogen consumption adapted for technical realization (piecewise-linear approximated) is shown in Fig. 2 (unsteady region only). The calculated time dependences of the crystallized epitaxial layer thickness and crystallization front temperature (unsteady region only) are shown in Fig. 3 and Fig. 4, respectively.

The growth time was 8 minutes. Then the solution-melt was decanted from the substrate. The cross-section of the sample cleavage was etched in $K_2Cr_2O_7$:$H_2O$: $H_2SO_4$ = 0.3 g:100 ml:1.6 ml mixture. Its photo obtained using a Linnek microinterferometer microscope MII-4 is shown in Fig. 5. The epitaxial layer thickness is estimated to be of 0.7 μm and is in a good agreement with

calculated result (0.75 μm), that confirms the correctness of the heat and mass transfer model.

Thus, the method of substrate cooling by outside gas feeding makes it possible to provide such crystallization conditions that consecutively combine properties of both pulse and quasi-equilibrium growing methods. The heat-mass transfer model developed for a priori determination of heat absorbing gas consumption has been shown to agree well with experiment.

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# Керування механізмом кристалізації при епітаксії з розчину-розплаву

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Розглянуто основні проблеми, що виникають при гетероепітаксії з розчинів-розплавів і вимоги до температурно-часових профілів на фронті кристалізації. Показано можливість застосування охолодження підкладки за допомогою газу, що подається ззовні реактора, для отримання умов кристалізації, які послідовно поєднують в собі властивості як імпульсних методів вирощування так і методів кристалізації в квазірівноважних умовах. Експериментально перевірено модель тепломасопереносу для апріорного визначення витрат газу-охолоджувача.