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## Influence of the kinetics of atomic steps on the growth of multicomponent crystals at elevated supersaturation

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The process of growth of a multicomponent crystal at elevated supersaturations, in cases where the classical approximation of the immobility of atomic steps becomes incorrect, has been studied. Analytical expressions are derived that describe the rate of advancement of an ensemble of steps on a crystalline surface. The crystal growth rate is determined via layer-by-layer and spiral mechanisms. It is shown that the rate can differ significantly from the predictions of the classical theory of crystal growth. The results can be used to optimize the growth processes of both bulk crystals and thick epitaxial films of various multicomponent compounds and, in particular, semiconductor compounds of groups  $A_3B_5$  and  $A_2B_6$ .

**Keywords:** crystal growth theory, atomic steps, growth rate, multicomponent crystals, epitaxy, semiconductors.

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A considerable amount of theoretical work on characterizing various modes of growth of crystals and thin films and surface phenomena ranging from nucleation and spiral growth to different instability types has already been done [1–3]. However, the reported formulae were typically derived for the growth of single-component crystals and, in the general case, are inapplicable to multicomponent systems. That said, many semiconductor materials used in modern epitaxial technology consist of several components (e.g., gallium, indium, and aluminum arsenides, nitrides, and phosphides [4,5] and  $A_2B_6$  compounds). Each component of a crystal or a film has its own individual properties that manifest themselves in epitaxial growth. For example, the coefficients of diffusion of components along the substrate surface, their lifetimes, and several other parameters of components differ substantially. In addition, process engineers have the capacity to adjust the ratio of fluxes of different components to the surface and thus alter significantly the growth rate, the defect density, and the resulting morphology of a growing film [6–8]. Thus, detailed knowledge of the processes of growth in multicomponent systems appears to be crucial and relevant to further progress in semiconductor technology. The classical Burton–Cabrera–Frank (BCF) [13] growth theory has been extended in a series of our earlier studies [9–12] to the process of vapor phase growth of an  $N$ -component crystal in the presence of chemical reactions. Note that the rate of advance of steps is considered negligible (i.e., is considered to have no effect on the distribution of adatoms over the surface) in this theory. At the same time, it has been demonstrated in [14,15] that this assumption is not always valid and the resulting rate of advance of a step at elevated supersaturation (but before the activation of nucleation) may differ substantially

from the one predicted theoretically. Thus, the present study is aimed at analyzing the process of growth of a multicomponent crystal under such conditions when the rate of advance of steps has a significant effect on the distribution of adatoms over the surface and cannot be neglected.

It is assumed in the BCF model for a multicomponent system [9] that a constant partial pressure of each component is maintained above the surface and establishes a uniform flux of atoms of every component to the entire surface area. Adatoms diffuse along terraces and may evaporate or be incorporated into parallel steps located at equal distance  $x_0$ . It is assumed that adatoms interact with each other only upon sequential incorporation into kinks on steps in accordance with reaction



where  $A_i$  is the  $i$ th component,  $v_i$  is its stoichiometric coefficient,  $C$  stands for „crystal,“ and  $N$  is the number of components. Driven by the incorporation of adatoms, a step advances at rate  $v$ . Adatoms do not interact on terraces; they also do not affect the diffusion and deposition of each other. The process is illustrated in Fig. 1, *a*. In order to determine the growth rate, one needs to solve a system of  $N$  differential equations characterizing the distribution of adatoms of each type on a terrace between steps  $n_i(x)$ :

$$\begin{cases} D_1 \frac{\partial^2 n_1(x)}{\partial x^2} + v \frac{\partial n_1(x)}{\partial x} - \frac{n_1(x)}{\tau_1} + J_1 = 0, \\ \dots \\ D_N \frac{\partial^2 n_N(x)}{\partial x^2} + v \frac{\partial n_N(x)}{\partial x} - \frac{n_N(x)}{\tau_N} + J_N = 0, \end{cases} \quad (2)$$

where  $D_i$  is the surface diffusion coefficient,  $\tau_i$  is the desorption time,  $J_i = \frac{P_i}{P_{i0}} \frac{n_i^0}{\tau_i}$  is the flux of atoms from the

gas phase to the surface,  $P_i$  is the partial pressure above the surface,  $P_{i0}$  is the equilibrium pressure, and  $n_i^0$  is the equilibrium concentration of adatoms [9]. The origin of coordinates is at the center of a terrace between steps (Fig. 1, *a*), and axis  $x$  is parallel to the step advancement direction. The following conditions are satisfied for each component: equilibrium concentration  $n_i(x) = n_i^0|_{x=\pm\frac{x_0}{2}}$  is maintained in the immediate vicinity of steps ( $x = \pm\frac{x_0}{2}$ ) due to rapid barrierless incorporation of adatoms [13]. Following substitution  $\varphi_i(x) = \frac{P_i}{P_{i0}} - \frac{n_i(x)}{n_i^0}$  (see [9]), we find

$$\begin{cases} \lambda_1^2 \frac{\partial^2 \varphi_1(x)}{\partial x^2} + v\tau_1 \frac{\partial \varphi_1(x)}{\partial x} - \varphi_1(x) = 0, \\ \dots \\ \lambda_N^2 \frac{\partial^2 \varphi_N(x)}{\partial x^2} + v\tau_N \frac{\partial \varphi_N(x)}{\partial x} - \varphi_N(x) = 0, \end{cases} \quad (3)$$

where  $\lambda_i = \sqrt{D_i\tau_i}$  is the free path length of the  $i$ th component,  $\varphi_i(x) = \sigma_i|_{\pm\frac{x_0}{2}}$ ,  $\sigma_i = \frac{P_i}{P_{i0}} - 1$ .

It is easy to demonstrate that the solution is function

$$\begin{aligned} \varphi_i(x) &= \sigma_i \left( \frac{\text{ch}[\alpha_i x_0] \text{ch}[\beta_i x]}{\text{ch}[\frac{x_0 \beta_i}{2}]} + \frac{\text{sh}[\alpha_i x_0] \text{sh}[\beta_i x]}{\text{sh}[\frac{x_0 \beta_i}{2}]} \right) \\ &\times \exp(-2x\alpha_i), \end{aligned} \quad (4)$$

where  $\alpha_i = \frac{\tau_i v}{4\lambda_i^2}$ ,  $\beta_i = \frac{\sqrt{4\lambda_i^2 + \tau_i^2 v^2}}{2\lambda_i^2}$ .

This is illustrated by the dependences of the concentration of one component on a terrace obtained under different conditions (see Figs. 1, *b* and *c*).

Surface flux  $J_{si}$  of the  $i$ th component to a step from both sides with diffusion and convective contributions taken into account (Stefan condition [14]) is

$$\begin{aligned} J_{si} &= D_i n_i^0 \left( \frac{\partial \varphi_i(x)}{\partial x} \Big|_{x=\frac{x_0}{2}+0} - \frac{\partial \varphi_i(x)}{\partial x} \Big|_{x=\frac{x_0}{2}-0} \right) \\ &+ n_i^0 v = 2D_i n_i^0 \sigma_i \beta_i \left( \frac{\text{ch}[x_0 \beta_i] - \text{ch}[2x_0 \alpha_i]}{\text{sh}[x_0 \beta_i]} \right) + n_i^0 v. \end{aligned}$$

Let us take into account the fact that the fluxes of different components are related to each other and are proportional to stoichiometric coefficients:  $\frac{J_{s1}}{v_1} = \dots = \frac{J_{sN}}{v_N} = J_s$ , where  $J_s$  is the overall flux of „crystal cells“ to a step. Applying the sequence of transformations from [9], we find the following expression for  $J_s$ :

$$J_s = D^{os}(v) \xi^{os} + v n^{os}(v), \quad (5)$$

where

$$D^{os}(v) = \left( \sum_{i=1}^N \frac{v_i^2 \text{sh}[x_0 \beta_i]}{2D_i n_i^0 \beta_i (\text{ch}[x_0 \beta_i] - \text{ch}[2x_0 \alpha_i])} \right)^{-1}$$

— averaged diffusion coefficient,

$$\xi^{os} = \sum_{i=1}^N v_i \sigma_i = \frac{K}{K_{eq}} - 1$$

— multicomponent supersaturation, and

$$n^{os}(v) = D^{os}(v) \sum_{i=1}^N \frac{v_i \text{sh}[x_0 \beta_i]}{2D_i \beta_i (\text{ch}[x_0 \beta_i] - \text{ch}[2x_0 \alpha_i])}$$

— averaged equilibrium concentration.

At the same time, rate of advance of a step  $v$  is itself specified by flux  $J_s$  and density  $n_0$  of crystal cells in a step [13]:

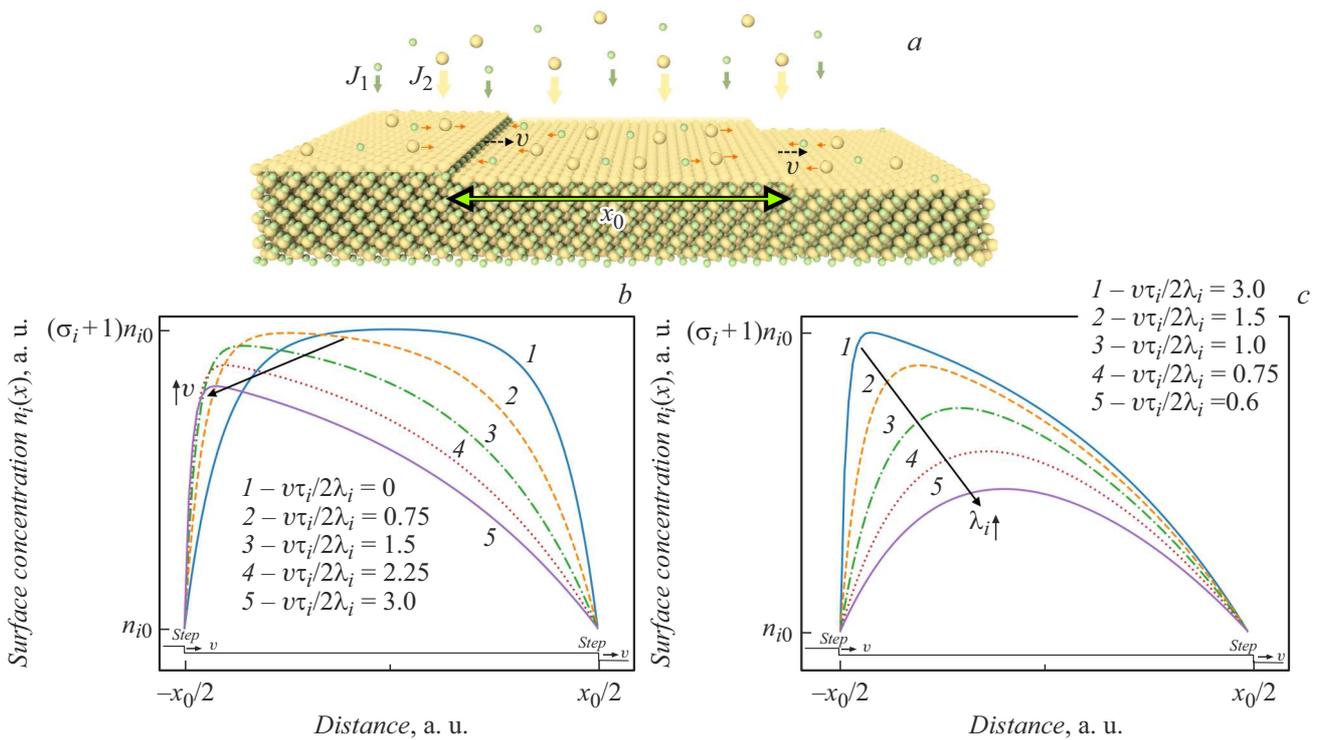
$$v = \frac{J_s}{n_0} = \frac{D^{os}(v) \xi^{os}}{n_0} + \frac{v n^{os}(v)}{n_0}. \quad (6)$$

If  $v$  is known, normal growth rate  $R$  may be expressed [9] as  $R = av/x_0$ , where  $a$  is the lattice parameter. In the case of spiral growth,  $x_0 = 19\rho_c$ , where  $\rho_c$  is the critical nucleus radius. Note that growth rate  $v$  is found both at the right-hand and at the left-hand sides of Eq. (6); i.e., Eq. (6) is a transcendental equation. Therefore, it may be solved numerically if all material constants are known. At the same time, it should be noted that coefficient  $D^{os}(v)$  ceases to depend on  $v$  in the extreme case when the rate of advance of a step is low ( $\frac{\tau_i^2 v^2}{4\lambda_i^2} \ll 1$  or, equivalently,  $\frac{\tau_i v^2}{2D_i} \ll 1$  or  $v \ll \frac{2\lambda_i}{\tau_i}$ ). Under these conditions, it matches the coefficient determined in [9] in the approximation of slow steps:

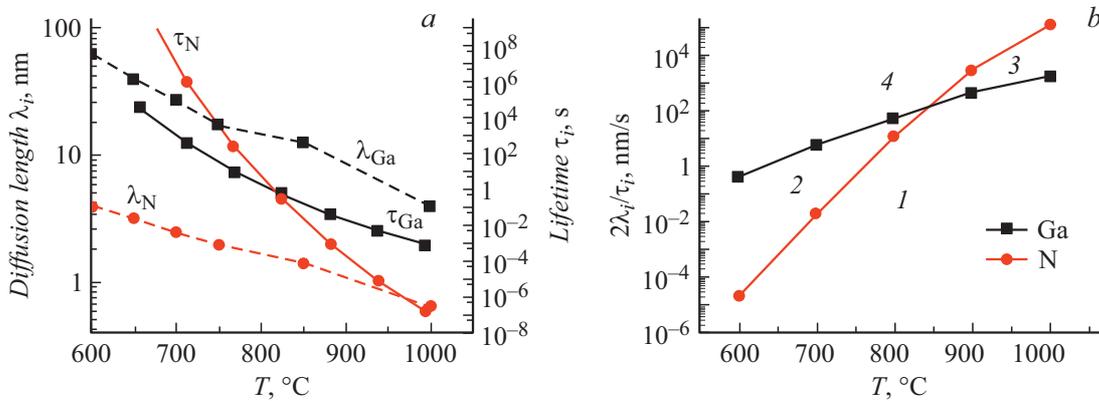
$$\begin{aligned} D^{os}(v) &= \left( \sum_{i=1}^N \frac{v_i^2 \lambda_i \text{sh}[\frac{x_0}{\lambda_i}]}{2D_i n_i^0 (\text{ch}[\frac{x_0}{\lambda_i}] - 1)} \right)^{-1} \\ &\approx 2 \left( \sum_{i=1}^N \frac{v_i^2 \lambda_i}{D_i n_i^0 \text{th}[\frac{x_0}{2\lambda_i}]} \right)^{-1}, \end{aligned}$$

while the coefficient associated with a convective flux vanishes.

Note also that a step may be „slow“ for certain components of a multicomponent system ( $\frac{\tau_i v^2}{2D_i} \ll 1$ ), and „fast“ ( $\frac{\tau_i v^2}{2D_i} \gg 1$ ) for other components, and an erroneous estimate of the dependence of the growth rate on process conditions (or erroneous values of kinetic parameters derived from experimental data) may be obtained if one neglects the convective flux of the latter components. Let us take the molecular-beam epitaxy (MBE) of gallium nitride (GaN) as an example and determine the growth rates at which this phenomenon does become significant. The values of  $\lambda_i$  and  $\tau_i$  for Ga and N adatoms taken from [16,17] are presented in Fig. 2, *a*. Figure 2, *b* shows the temperature dependences of the threshold  $\frac{2\lambda_i}{\tau_i}$  value for both components. When rate of advance  $v$  of steps is below the curve for the corresponding component, it is incorporated into a step in the diffusion mode; when the rate is above the curve, the convective flux needs to be taken into account. Four regions may be distinguished. In region *I*, both Ga and N adatoms are supplied to a step in the diffusion mode and are not „aware“ of the advancement of steps. The theory discussed in [9] is applicable to the



**Figure 1.** Schematic diagram of the discussed problem (a); dependences of the concentration of the  $i$ th component on a terrace between steps at (b) fixed values of free path length  $\lambda_i$  and adatom lifetime  $\tau_i$  and varying rates of advance of a step  $v$  and (c) fixed  $v$  and  $\tau_i$  and varying free path lengths  $\lambda_i$ .



**Figure 2.** a — Dependence of free path length  $\lambda_i$  and lifetime  $\tau_i$  of gallium and nitrogen adatoms on a GaN surface; b quantity  $2\lambda_i/\tau_i$  for Ga and N that specifies the rate of advance of a step at which the contribution of a convective flux becomes significant.

growth process in this case. In regions 2 and 3, one component enters the convective mode (nitrogen in region 2 and gallium in region 3), and the above formulae should be used to characterize growth. In region 4, both components are supplied to a step in the convective mode.

Note that characteristic MBE growth rate  $R$  is on the order of 1 monolayer per second ( $\sim 0.3$  nm/s). At  $x_0 = 100$  nm, steps should advance at rate  $v = 100$  nm/s. Within a wide temperature range, this rate of advance falls into region 4 (see Fig. 2, b) where the convective contribution of both components cannot be neglected. It

should also be noted that MBE conditions are often set so that growth proceeds in the mode of two-dimensional nucleation of islands instead of the BCF mode. It appears that the convective flux of the „slowest“ components should be taken into account even in this mode to obtain a correct estimate of the rate of island growth.

Thus, it was demonstrated that a finite rate of advance of atomic steps often needs to be taken into account to estimate the crystal growth rate correctly. Expressions for this rate of advance were obtained in the approximation of barrierless incorporation of adatoms of different

components into a step and constancy and equality of the rates of advance of all steps (and, consequently, the distances between them). Gallium nitride was used as an example to demonstrate that the advancement of a step in a multicomponent system may exert, depending on the growth conditions, qualitatively different influences on the distribution of components (gallium and nitrogen), their flux to a step, and the resulting growth rate. The presented results may be used to optimize the processes of epitaxial growth of various complex multicomponent compounds from the gas phase (including much-needed  $A_3B_5$  and  $A_2B_6$  compounds).

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### Conflict of interest

The authors declare that they have no conflict of interest.

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