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## Limiting factors for the growth rate of epitaxial III–V compound semiconductors

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Received January 25, 2023

Revised February 21, 2023

Accepted February 21, 2023

Limiting factors for the growth rate of epitaxial III–V compound semiconductors are investigated. A model based on the two connected diffusion equations for the group III and V adatoms applies for planar layers and different nanostructures including III–V nanowires. An expression for the step growth rate is obtained and a physical parameter is revealed which determines an element which actually limits the growth process.

**Keywords:** III–V compound semiconductors, surface diffusion of adatoms, desorption, step growth rate.

DOI: 10.21883/TPL.2023.04.55886.19512

It is common knowledge [1–5] that the growth rate in the process of epitaxy of planar layers and various types of nanostructures of III–V semiconductor compounds (for brevity, they are referred to as III–V nanostructures) may be limited by the kinetics of either group III elements or group V elements. Different limiting growth factors have also been examined in the general case of formation of crystal steps in multicomponent systems with chemical reactions [6]. The presence of surface diffusion of group III adatoms under conditions of enrichment in group V is normally assumed in simulations of growth processes [1,2]. The number of group V adatoms on the surface is then considered to be sufficient to crystallize with group III adatoms supplied to the boundaries of a growing step. Owing to high volatility of As, P, and N, the surface concentration of group V adatoms is assumed to be the result of a certain balance between the processes of their supply from the gas phase and desorption.

In the case of III–V nanowires (NWs) [7–16], Au-catalyzed vertical vapor–liquid–solid (VLS) growth [7,9,11,14] and catalyst-free growth by selective area epitaxy [8,13,14] are commonly assumed to be governed by the kinetics of group III atoms, and only the process of self-catalyzed VLS growth with a Ga droplet at the NW tip is thought to be controlled by adsorption and desorption of group V atoms on the droplet surface [12,16]. However, it is clear that the diffusion length of group V adatoms on the surface cannot be zero, since it would then be impossible for these adatoms to desorb in As<sub>2</sub>, P<sub>2</sub>, or N<sub>2</sub> dimers. The diffusion of P atoms along the side surface of a GaP NW over distances up to 400 nm has recently been examined in [17]. It is also a distinct possibility that the radial growth of NWs [8,11,13,14] (regardless of the presence of a catalyst and its type) is controlled by the flux of a group V element. The aim of the present study is to construct a simple model for the rate of growth of III–V layers via surface diffusion of both elements and determine

the conditions under which this growth is indeed controlled by the diffusion of group III adatoms.

The considered geometry of a step bunch with distance  $P$  between steps on a planar surface or a side NW surface is shown in Fig. 1. Steady-state diffusion equations for the concentrations of group III adatoms ( $n_3$ ) and group V adatoms ( $n_5$ ) are written in their common form [18–20]:

$$\begin{aligned} D_3 \frac{d^2 n_3}{dx^2} + I_3 - \frac{n_3}{\tau_3} &= 0, \\ D_5 \frac{d^2 n_5}{dx^2} + I_5 - \frac{n_5}{\tau_5} &= 0. \end{aligned} \quad (1)$$

Here,  $I_k$  are the atomic fluxes of elements  $k = 3$  and  $5$  to the surface,  $D_k$  are the surface diffusion coefficients, and  $\tau_k$  are the characteristic adatom desorption times. It is assumed in Eq. (1) for  $n_5$  that group V atoms are desorbed in singles, which is possible only if they combine with other atoms (e.g., hydrogen) in gas-phase epitaxy [5,10]. In the case of molecular-beam epitaxy, a group V element is always desorbed in dimers (As<sub>2</sub>, P<sub>2</sub>, or N<sub>2</sub>) [2,7,16]. The corresponding diffusion equation then takes the form

$$D_5 \frac{d^2 n_5}{dx^2} + I_5 - 2D_5 n_5^2 = 0. \quad (2)$$

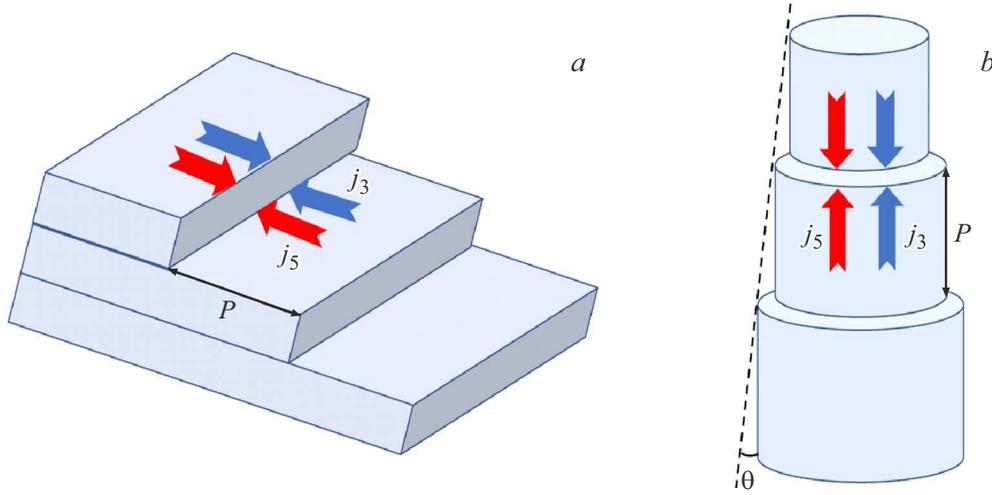
Assuming that the spatial nonuniformity of group V adatoms is low, one may linearize expression (2) with respect to average concentration  $n_5^0 = \sqrt{I_5/2D_5}$ :

$$D_5 \frac{d^2 n_5}{dx^2} + 2I_5 - \sqrt{8I_5 D_5} n_5 = 0. \quad (3)$$

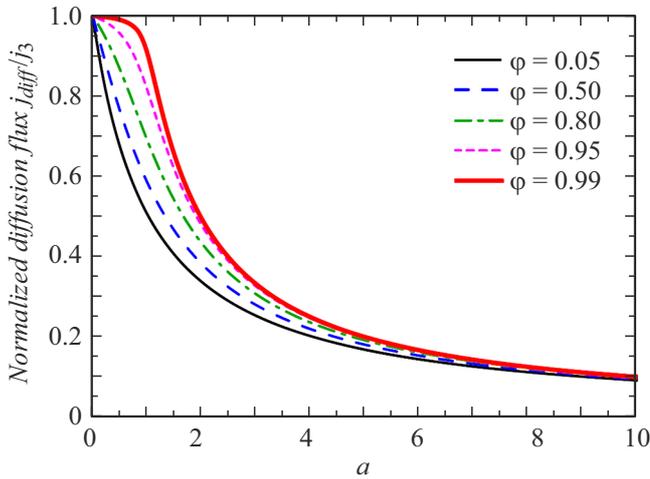
With substitutions

$$I'_5 = 2I_5, \quad \tau'_5 = 1/\sqrt{8I_5 D_5}, \quad \lambda'_5 = [D_5/8I_5]^{1/4}, \quad (4)$$

this equation assumes form (1); therefore, diffusion equations in form (1) symmetric with respect to element  $3 \leftrightarrow 5$  change are used below.



**Figure 1.** Illustration of epitaxial growth of III–V compounds due to the motion of a step bunch on a planar substrate (a) and the side surface of a vertical NW (b).



**Figure 2.** Dependences of diffusion flux  $j_{diff}$  normalized to  $j_3$  on parameter  $a = j_3/j_5$  at different degrees of supersaturation  $\varphi$ , which are indicated in the figure.

It follows from symmetry considerations that diffusion fluxes should turn to zero at  $x = P/2$ . The first two boundary conditions for (1) are thus obtained:

$$\left(\frac{dn_3}{dx}\right)_{x=P/2} = \left(\frac{dn_5}{dx}\right)_{x=P/2} = 0. \quad (5)$$

For a III–V compound to have a stoichiometric composition, diffusion fluxes at the step boundary need to be equal:

$$j_{diff} = 2D_3 \left(\frac{dn_3}{dx}\right)_{x=0} = 2D_5 \left(\frac{dn_5}{dx}\right)_{x=0}. \quad (6)$$

Diffusion flux  $j_{diff}$  is the one that specifies the step growth rate. The chemical potential of a pair of III–V adatoms at the step boundary should also be equal to the equilibrium chemical potential of a pair of III–V adatoms in equilibrium

with a step:

$$n_3(x=0)n_5(x=0) = n_3^{eq}n_5^{eq}. \quad (7)$$

The solution of the problem for a diffusion flux with these boundary conditions takes the form

$$j_{diff} = 2\lambda_3 \tanh\left(\frac{P}{2\lambda_3}\right) I_3 \varphi F, \quad (8)$$

$$F = \frac{1+a}{2a\varphi} \left(1 - \sqrt{1 - \frac{4a\varphi}{(1+a)^2}}\right),$$

where  $\lambda_3 = \sqrt{D_3\tau_3}$  and  $\lambda_5 = \sqrt{D_5\tau_5}$  are the diffusion lengths of group III and V adatoms. Thus, the growth rate is controlled by two parameters:  $\varphi$  and  $a$ , which are given by

$$\varphi = 1 - \frac{n_3^{eq}n_5^{eq}}{I_3\tau_3 I_5\tau_5}, \quad a = \frac{\lambda_3 \tanh(P/2\lambda_3) I_3}{\lambda_5 \tanh(P/2\lambda_5) I_5}. \quad (9)$$

Quantity  $\varphi$  is proportional to the degree of supersaturation of a system of adatoms with concentrations  $I_3\tau_3$  and  $I_5\tau_5$  away from a step with respect to a stoichiometric III–V crystal and is the driving force behind growth. Parameter  $a$  specifies which of the elements controls the growth process. The physical meaning of  $a = \lambda_3 I_3 / \lambda_5 I_5$  is particularly apparent at  $P \rightarrow \infty$ : this is the ratio of numbers of group III and V adatoms collected over distances equal to diffusion lengths  $\lambda_3$  and  $\lambda_5$ , respectively. Function  $F \rightarrow 1$  at  $a \rightarrow 0$ , and the step growth rate is specified by the classical expression  $j_{diff}(a \rightarrow 0) = 2\lambda_3 \tanh\left(\frac{P}{2\lambda_3}\right) I_3 \varphi$  [20] for a group III element. The process of growth is governed by group III adatoms under these conditions, and a group V element affects only the degree of supersaturation ( $\varphi$ ) via a coordinate-independent concentration of group V adatoms ( $I_5\tau_5$ ) in the denominator of (9) [1,2,7–11]. Function  $F \rightarrow 1/a$  at  $a \rightarrow \infty$ , and the growth rate is specified by the same expression  $j_{diff}(a \rightarrow \infty) = 2\lambda_5 \tanh\left(\frac{P}{2\lambda_5}\right) I_5 \varphi$  [20],

although this time it corresponds to a group V element. The process of growth is governed by group V adatoms under these conditions.

Thus, parameter  $a$  is given by  $a = j_3/j_5$ , where  $j_3 = j_{diff}(a \rightarrow 0)$  and  $j_5 = j_{diff}(a \rightarrow \infty)$  — are the diffusion fluxes of group III and V adatoms, respectively. The first expression in (8) then assumes a form symmetric with respect to element  $3 \leftrightarrow 5$  change:

$$j_{diff} = \frac{j_3 + j_5}{2\varphi} \left( 1 - \sqrt{1 - \frac{4\varphi}{(1 + j_3/j_5)(1 + j_5/j_3)}} \right). \quad (10)$$

Figure 2 illustrates the variation of the ratio between diffusion flux  $j_{diff}$  to a step and diffusion flux  $j_3$  of group III adatoms with increasing  $a$ . It is evident that the step growth rate is controlled by a group III element at low  $a$  and by a group V element at high  $a$ . Note also that the solution becomes asymmetric if group V atoms are desorbed in dimers. At  $P \rightarrow \infty$ , the control parameters of the growth process take the form

$$\varphi = 1 - \frac{n_3^{eq} n_5^{eq}}{I_3 \tau_3 \sqrt{I_5} / 2D_5}, \quad a = \frac{\lambda_3 I_3}{(2D_5)^{1/4} I_5^{3/4}}. \quad (11)$$

The obtained solutions for the diffusion flux may be useful in modeling of various growth processes, including the radial growth of III–V NWs and, possibly, their vertical growth under the conditions of surface diffusion of group V adatoms [17]. These results may be generalized to the case of growth of ternary III–V compounds and modeling of their composition as a function of the composition of the gas phase.

## Funding

This study was supported by a research grant from the St. Petersburg State University (ID 93020138).

## Conflict of interest

The author declares that he has no conflict of interest.

## References

- [1] T.F. Kuech, Prog. Cryst. Growth Charact. Mater., **62**, 352 (2016). DOI: 10.1016/j.perysgrow.2016.04.019
- [2] J.R. Arthur, Surf. Sci., **500**, 189 (2002). DOI: 10.1016/S0039-6028(01)01525-4
- [3] P. Kratzer, E. Penev, M. Scheffler, Appl. Phys. A, **75**, 79 (2002). DOI: 10.1007/s003390101057
- [4] Y. Kangawa, T. Akiyama, T. Ito, K. Shiraishi, T. Nakayama, Materials, **6**, 3309 (2013). DOI: 10.3390/ma6083309
- [5] S.Yu. Karpov, J. Cryst. Growth, **248**, 1 (2003). DOI: 10.1016/S0022-0248(02)01838-9
- [6] A.V. Redkov, S.A. Kukushkin, Cryst. Growth Des., **20**, 2590 (2020). DOI: 10.1021/acs.cgd.9b01721
- [7] V.G. Dubrovskii, G.E. Cirilin, I.P. Soshnikov, A.A. Tonkikh, N.V. Sibirev, Yu.B. Samsonenko, V.M. Ustinov, Phys. Rev. B, **71**, 205325 (2005). DOI: 10.1103/PhysRevB.71.205325
- [8] S. Hertenberger, D. Rudolph, M. Bichler, J.J. Finley, G. Abstreiter, G.J. Koblmüller, Appl. Phys., **108**, 114316 (2010). DOI: 10.1063/1.3525610
- [9] G.E. Cirilin, V.G. Dubrovskii, N.V. Sibirev, I.P. Soshnikov, Y.B. Samsonenko, A.A. Tonkikh, V.M. Ustinov, Semiconductors, **39**, 557 (2005). DOI: 10.1134/1.1923565
- [10] L.E. Froberg, W. Seifert, J. Johansson, Phys. Rev. B, **76**, 153401 (2007). DOI: 10.1103/PhysRevB.76.153401
- [11] M.C. Plante, R.R. LaPierre, J. Appl. Phys., **105**, 114304 (2009). DOI: 10.1063/1.3131676
- [12] F. Oehler, A. Cattoni, A. Scaccabarozzi, J. Patriarche, F. Glas, J.C. Harmand, Nano Lett., **18**, 701 (2018). DOI: 10.1021/acs.nanolett.7b03695
- [13] V.G. Dubrovskii, ACS Omega, **4**, 8400 (2019). DOI: 10.1021/acsomega.9b00525
- [14] V.G. Dubrovskii, Nanomaterials, **12**, 253 (2022). DOI: 10.3390/nano12020253
- [15] M.R. Ramdani, J.C. Harmand, F. Glas, G. Patriarche, L. Travers, Cryst. Growth Des., **13**, 91 (2013). DOI: 10.1021/cg301167g
- [16] F. Glas, M.R. Ramdani, G. Patriarche, J.C. Harmand, Phys. Rev. B, **88**, 195304 (2013). DOI: 10.1103/PhysRevB.88.195304
- [17] A. Pishchagin, F. Glas, G. Patriarche, A. Cattoni, J.C. Harmand, F. Oehler, Cryst. Growth Des., **21**, 4647 (2021). DOI: 10.1021/acs.cgd.1c00504
- [18] S.A. Kukushkin, A.V. Osipov, Prog. Surf. Sci., **51**, 1 (1996). DOI: 10.1016/0079-6816(96)82931-5
- [19] V.G. Dubrovskii, Yu.Yu. Hervieu, J. Cryst. Growth, **401**, 431 (2014). DOI: 10.1016/j.jcrysgro.2014.01.015
- [20] W.K. Burton, N. Cabrera, F.C. Frank, Phil. Trans. R. Soc. London, **243**, 299 (1951). DOI: 10.1098/rsta.1951.0006