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Criterion for the growth selectivity of III-V and III-N nanowires on masked substrates

© *V.G. Dubrovskii*[1], *E.D. Leshchenko*[2]

[1] St. Petersburg State University, St. Petersburg, Russia
[2] Submicron Heterostructures for Microelectronics, Research & Engineering Center, RAS, Saint-Petersburg, Russia
E-mail: dubrovskii@mail.ioffe.ru

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A model is developed for the initial stage of nucleation of III−V nanowires including nitrides (III−V NWs) and other nanostructures grown by selective area epitaxy on masked substrates with regular arrays of pinholes. A criterion for the growth selectivity is obtained, which ensures nucleation of III−V NWs within the pinholes but not on a mask surface. The temperature, group III and V fluxes, pinhole radius and pitch dependences of the selective growth zones are analyzed

Keywords: III−V nanowires, selective area epitaxy, masked substrate, nucleation.

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One-dimensional geometry and a small area of contact of different materials provide an opportunity to grow III−V and III-N nanowires (NWs) on silicon substrates without the emergence of mismatch dislocations and form heterostructures in strongly mismatched material systems [1–3]. The growth of III−V and III-N NWs by selective area epitaxy (SAE) on masked substrates with regular arrays of pinholes [4–11] allows one to synthesize NW ensembles uniform in size with exactly determined positioning of NWs and distances between them. The SAE technique is also used to synthesize nanomembranes [12,13] and nanoislands [14] of various geometry. These structures hold much promise for application in nanophotonics and nanoelectronics with an option for integration into silicon electronic technology. The selectivity of SAE of NWs without growth catalyst droplets in arrays of pinholes in a SiO_x mask on a Si(111) substrate [4–11] is ensured by (1) nucleation of NWs within pinholes on the Si surface; (2) lack of nucleation of parasitic structures on the oxide mask surface. The aim of the present study, which is a continuation of [9–11], consists in determining the criterion for growth selectivity of III−V and III-N NWs and other types of nanostructures in the process of SAE on masked substrates with arrays of pinholes.

Let us write the system of steady-state kinetic equations for surface concentrations of group III adatoms within pinholes (n_3) and on the mask surface ($\bar{n}_3$) in the following way:

$$\pi R^2\left[I_3-\frac{n_3}{\tau_3}-D_3\left(n_3n_5-n_3^{eq}n_5^{eq}\right)\right]=2\pi R\left(k^-n_3-k^+\bar{n}_3\right), \tag{1}$$

$$\left(S-\pi R^2\right)\left[I_3-\frac{\bar{n}_3}{\bar{\tau}_3}-\bar{D}_3\left(\bar{n}_3\bar{n}_5-\bar{n}_3^{eq}\bar{n}_5^{eq}\right)\right] = -2\pi R\left(k^-n_3-k^+\bar{n}_3\right). \tag{2}$$

The growth process is assumed to be limited by the kinetics of group III atoms with their surface diffusion taken into account [15]. The left-hand part of (1) is the number of group III atoms supplied to a pinhole with radius R from gas atomic flux $I_3[\mathrm{nm}^{-2}\cdot\mathrm{s}^{-1}]$ minus desorption (with characteristic lifetime τ_3 on the substrate surface) and nucleation due to dimerization of group III and V (with surface concentration n_5) atoms as a result of diffusion of group III adatoms with diffusion coefficient D_3. Quantity $n_3^{eq}n_5^{eq}$ is the temperature-dependent activity of a III−V pair; nucleation is feasible only at $n_3n_5 > n_3^{eq}n_5^{eq}$. The right-hand part of (1) is the diffusion flux through a pinhole boundary with length $2\pi R$. Here, k^+ and k^- are the rate constants of transitions of adatoms from the mask surface to a pinhole and in the opposite direction and $\bar{n}_3$ is the concentration of adatoms on the mask surface [16–19]. The adatom density distribution is assumed to be spatially uniform both within a pinhole and on the mask surface [20] (to introduce non-uniformity, one needs to solve the corresponding steady-state diffusion equations for n_3 and $\bar{n}_3$ [18,19]). Equation (2) is similar in meaning to (1), but is formulated for fraction $S-\pi R^2$ of the mask surface per a single pinhole. Here, $S = cP^2$ is the surface area per a single pinhole, P is the distance between pinhole centers, and c is the shape constant (e.g., $c = 1$ for a square lattice of pinholes with side P). Quantities $\bar{\tau}_3$, $\bar{D}_3$, and $\bar{n}_3^{eq}\bar{n}_5^{eq}$ are the desorption time, the diffusion coefficient of group III adatoms, and the equilibrium activity of a III−V pair on the mask surface, respectively.

Concentrations n_5 and $\bar{n}_5$ of group V adatoms found in (1) and (2) may be determined in a first approximation using the following relations: $I_5 = 2D_5n_5^2 = 2\bar{D}_5\bar{n}_5^2$. These relations imply that the atomic flux of a group V element is balanced by desorption of dimers As_2, P_2, or N_2 that occurs when two adatoms meet due to surface diffusion with diffusion coefficient D_5 within a pinhole and $\bar{D}_5$ on the mask surface [9]. Thus, we find $n_5 = \sqrt{I_5/2D_5}$ and $\bar{n}_5 = \sqrt{I_5/2\bar{D}_5}$; i.e., surface concentrations of group V adatoms are independent of the concentrations of group III adatoms. The solutions of (1) and (2) then take the form

$$n_3 = A\tau\left[1+\left(\frac{S}{\pi R^2}-1\right)\frac{F-\varepsilon}{1+F}\frac{\tilde{A}}{A}\right], \quad \bar{n}_3 = \bar{A}\bar{\tau}\frac{1+\varepsilon}{1+F}. \quad (3)$$

Functions F and ε are defined as

$$F = \frac{2\pi R(k^+\bar{\tau} - k^-\tau)}{S - \pi R^2 + 2Sk^-\tau/R},$$

$$\varepsilon = \frac{2\pi Rk^-\tau}{S - \pi R^2 + 2Sk^-\tau/R}\left(\frac{\bar{A}}{A} - 1\right) \quad (4)$$

with coefficients

$$A = I_3 + D_3 n_3^{eq} n_5^{eq}, \quad \bar{A} = I_3 + \bar{D}_3 \bar{n}_3^{eq} \bar{n}_5^{eq},$$

$$\frac{1}{\tau} = \frac{1}{\tau_3} + D_3 n_5, \quad \frac{1}{\bar{\tau}} = \frac{1}{\bar{\tau}_3} + \bar{D}_3 \bar{n}_5. \quad (5)$$

The obtained solutions allow one to analyze the kinetics of nucleation and growth of NWs under SAE at various stages. We limit ourselves to the initial NW nucleation stage, where $A = \bar{A} = I_3$, $\varepsilon = 0$, $\tau = \tau_3$, and $\bar{\tau} = \bar{\tau}_3$ may be assumed. Expressions (3) and (4) are simplified in this case:

$$n_3 = \frac{I_3\tau_3}{1+F}\left(1 + \frac{S}{\pi R^2}F\right),$$

$$\bar{n}_3 = \frac{I_3\bar{\tau}_3}{1+F}, \quad F = \frac{2\pi R(k^+\bar{\tau}_3 - k^-\tau_3)}{S - \pi R^2 + 2Sk^-\tau_3/R}. \quad (6)$$

Naturally, NW nucleation within mask pinholes is feasible only when the activity of a pair of III–V adatoms is above the equilibrium one. The inverse inequality ensures the lack of nucleation of parasitic structures on the mask surface. Thus, the criterion for NW growth selectivity may be written as

$$n_3 n_5 > n_3^{eq} n_5^{eq}, \quad \bar{n}_3 \bar{n}_5 < \bar{n}_3^{eq} \bar{n}_5^{eq}. \quad (7)$$

With (6) taken into account, these conditions are equivalent to the following system of inequalities for the flux of group III atoms:

$$\sqrt{\frac{2D_5}{I_5}}\frac{n_3^{eq}n_5^{eq}}{\tau_3}\frac{1+F}{1+(S/\pi R^2)F} < I_3 < \sqrt{\frac{2\bar{D}_5}{I_5}}\frac{\bar{n}_3\bar{n}_5}{\bar{\tau}_3}(1+F). \quad (8)$$

Using Arrhenius-type temperature dependences of diffusion coefficients, desorption times, and equilibrium activities, one may present criterion (7) in the following form:

$$\frac{Ce^{-E/k_\mathrm{B}T}}{I_5^{1/2}}\frac{1+F}{1+(S/\pi R^2)F} < I_3 < \frac{\bar{C}e^{-\bar{E}/k_\mathrm{B}T}}{I_5^{1/2}}(1+F). \quad (9)$$

Here, constants C and $\bar{C}$, which are independent of temperature T, fluxes, and the geometry of a pinhole array, aggregate the pre-exponential factors of Arrhenius-type temperature dependences of different quantities. The activation energies in (9) are determined as $E = \Lambda + E_5^{diff}/2 + E_3^{des}$ and $\bar{E} = \bar{\Lambda} + \bar{E}_5^{diff}/2 + \bar{E}_3^{des}$. Quantities Λ, E_5^{diff}, and E_3^{des} are the latent heat of dimerization and the activation barriers of surface diffusion of group V adatoms and desorption of group III adatoms on the substrate surface, respectively. Quantities $\bar{\Lambda}$, $\bar{E}_5^{diff}$, and $\bar{E}_3^{des}$ pertain to the mask surface.

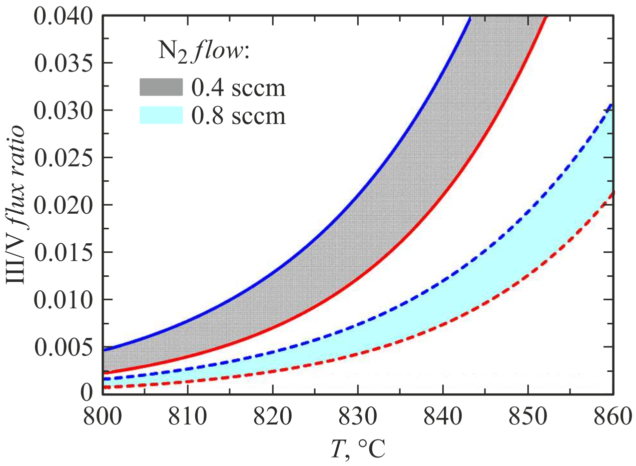

Figure 1. Regions of SAE of GaN NWs on the SiO_x/Si(111) surface for a fixed geometry of a pinhole array ($P = 1600$ nm, $R = 225$ nm) on the temperature–III/V flux ratio plane at two N_2 flow rates (0.4 and 0.8 sccm). The curves were plotted in accordance with Eq. (9) at $C/I_5^{3/2} = 1.2 \cdot 10^{24}$ and $\bar{C}/I_5^{3/2} = 3.6 \cdot 10^{21}$ for a flow rate of 0.4 sccm; $E/k_\mathrm{B}T = 66\,000$ K and $\bar{E}/k_\mathrm{B}T = 59\,000$ K. The region of the optimum III/V flux ratio, which corresponds to the criterion for growth selectivity, expands with temperature and contracts with increasing N_2 flow rate. The SAE region at an N_2 flow rate of 0.4 sccm characterizes the experimental data from [9].

The criterion for growth selectivity in form (9) is the key result of the present study. Analyzing it, we arrive at the following conclusions. As was already noted in [9–11], the flux of a group III element in the process of SAE should be sufficiently high to ensure NW nucleation within pinholes and sufficiently low to suppress parasitic nucleation on the mask surface. The flux of a group III element (or III/V flux ratio I_3/I_5) needed to achieve growth selectivity increases with temperature [9]. Higher fluxes of a group V element yield lower optimum values of I_3. These properties are illustrated by Fig. 1, which corresponds to the experimental data on SAE of GaN NWs on Si(111) substrates with a SiO_x mask by molecular beam epitaxy at an N_2 flow rate of 0.4 sccm, $S = P^2$, $P = 1600$ nm, and $R = 225$ nm [9].

According to (6), F is proportional to $k^+\bar{\tau}_3 - k^-\tau_3$. It assumes a positive value if $k^+\bar{\tau}_3 > k^-\tau_3$ (i.e., the diffusion flux of group III adatoms is directed from the mask surface to pinholes) and is negative in the contrary case (as in [18,19]). This translates into radically different patterns of behavior of the SAE region under variation of the radius

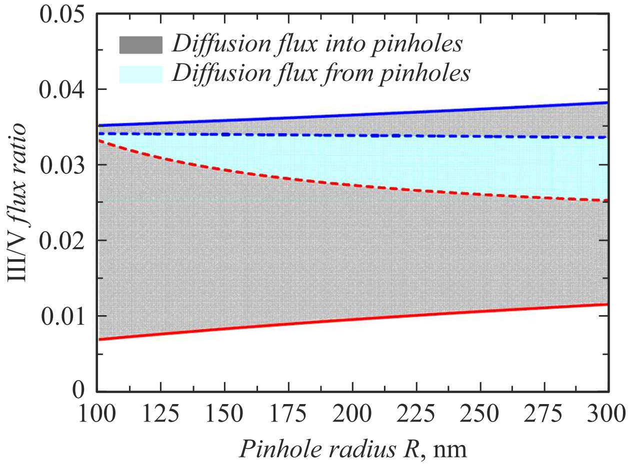

Figure 2. Optimum III/V flux ratios corresponding to the criterion of SAE of GaN NWs on a SiO$_x$/Si(111) surface as functions of the radius of pinholes in SiO$_x$. Calculations were performed in accordance with (9) for the same parameters as those used in Fig. 1. The N_2 flow rate was 0.4 sccm, $P = 1600$ nm, $k^-\tau_3$ was fixed at 30 nm, and $k^+\overline{\tau}_3$ was set to either 200 nm (the diffusion flux of group III adatoms is directed from the mask surface to pinholes) or 1 nm (the diffusion flux is directed from pinholes to the mask surface). The SAE region contracts considerably in the latter case.

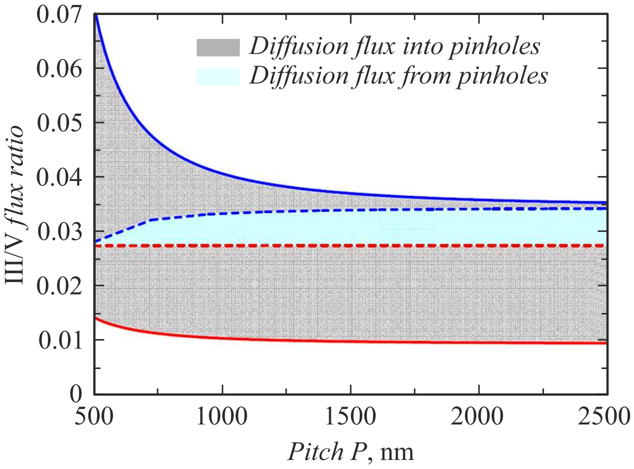

Figure 3. Optimum III/V flux ratios as functions of the distance between pinhole centers. Calculations were performed in accordance with (9) for $R = 200$ nm and the same parameters as those used in Fig. 2. The SAE region contracts considerably when the diffusion flux of group III adatoms is directed from pinholes to the mask surface.

of pinholes and the distance between them. Specifically, the maximum III/V flux ratio value increases with R and with decreasing P if $k^+\overline{\tau}_3 > k^-\tau_3$. If $k^+\overline{\tau}_3 < k^-\tau_3$, the pattern is reversed. Figures 2 and 3 illustrate the behavior of regions of SAE of GaN NWs as functions of R and P at different directions of the diffusion flux. It is evident that SAE regions contract considerably when the diffusion flux of group III adatoms is directed from pinholes to the mask surface.

Thus, the constructed model provides an explanation for the dependence of SAE regions on temperature, fluxes, and the pinhole array geometry. The obtained results should be of use in selecting the optimum SAE growth regimes for III–V NWs and other nanostructures in various technological applications.

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Conflict of interest

The authors declare that they have no conflict of interest.

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