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Asymptotic stage of self-catalyzed growth of III-V nanowires by molecular beam epitaxy

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A new analytic theory is developed for asymptotic stage of self-catalyzed growth of III−V nanowires (NWs) by molecular beam epitaxy (MBE), where NWs collect all group III atoms deposited from vapor. The shadowing NW length is derived which corresponds for the full shadowing of the substrate surface in MBE. The NW length and radius are derived depending on the effective deposition thickness and MBE growth parameters. It is shown that the NW length increases, and their length decreases with decreasing the array pitch and increasing the V/III flux ratio.

Keywords: II-V nanowires, shadowing effect, length, radius, surface density, modeling

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III−V nanowires (NWs) are promising objects for the design of optoelectronic heterostructures integrated with a silicon platform [1]. Owing to the efficient release of elastic stresses on lateral surfaces, III−V NWs may be grown on mismatched silicon substrates without the formation of mismatch dislocations [2,3]. For example, the well-known difficulties in obtaining coherent InAs on Si (the lattice mismatch is 11.6%) [4] may be overcome in the geometry of NWs with a diameter below the critical one (25 nm) [3]. III−V NWs are grown either in accordance with the vapor–liquid–solid (VLS) method with the use of Au catalysts [5] or catalyst metals of group III (Ga, In) (in the latter case, the VLS growth is called self-catalyzed [6]) or by selective epitaxy [7]. The majority of NWs growth models (see their review in [8]) are applicable to isolated NWs and leave out collective effects, including the shadowing effect (the blocking of fluxes directed at the substrate and the lateral NW surfaces in molecular-beam epitaxy (MBE) [9]).

The flux of group III atoms (Ga) reaching the substrate surface between NWs induces either the growth of a parasitic layer [10,11] or reflection from the surface of the oxide mask [12]. The radial expansion of NWs plays a critical part in the growth kinetics of NWs [11] (especially self-catalyzed NWs [13]). Data on MBE growth of self-catalyzed GaP NWs in ordered arrays of apertures on SiO_x/Si(111) surfaces were analyzed theoretically in [13] with the reflected Ga flux, radial growth, and the effect of substrate shadowing taken into account. It was demonstrated that the flux of Ga to NWs tends to the maximum value equal to the direct flux to a surface area corresponding to one NW. The aim of the present study is to formulate a theory of MBE NW growth at this stage.

We consider fluxes of elements of groups III (index 3) and V (index 5) directed at the same angle to the normal to the surface: $\alpha_3 = \alpha_5 = \alpha$. The following is derived for Ga atoms from the material balance condition:

$$v_3 \cos\alpha = N \frac{d}{dt}(\pi R^2 L) + N \frac{dV_{drop}}{dt} + v_r. \tag{1}$$

Here, $v_3 \cos\alpha$ is the deposition rate of Ga (equivalent two-dimensional growth rate) from flux v_3 [nm/s], N is the area density of cylindrical NWs of the same radius R and length L, V_{drop} is the volume of the droplet at the top of an NW in VLS growth, and v_r is the flux of Ga reaching the substrate. In the case of growth in a regular square array with pitch P, we have $N = 1/P^2$. The thickness of Ga deposition in time t is $H = v_3 \cos\alpha \cdot t$. In what follows, the droplet volume is assumed to be constant: $dV_{drop}/dt = 0$. This requires that a certain ratio between contact angle β of the droplet and radius R in the cylindrical geometry be maintained [14].

The start of the asymptotic stage corresponds to vanishing of the flux of Ga to the surface ($v_r = 0$). According to (1), NWs then consume the deposited material entirely. This occurs at certain values of H_*, R_*, L_*, and contact angle β_* of the droplet. If the NW volume directly prior to the start of the asymptotic stage increased due to direct transfer of Ga to the droplet and the lateral NW surface [8], we derive the shadowing length from relation

$$\frac{d}{dt}(\pi R^2 L) = (\pi R^2 \chi + 2RL \sin\alpha) v_3 = \frac{v_3 \cos\alpha}{N} \tag{2}$$

at $R = R_*$, $L = L_*$ and $\chi = \chi_*$ in the form

$$L_* = \frac{\text{cotan}\alpha}{2NR_*} - \frac{\pi R_* \chi_*}{2\sin\alpha}. \tag{3}$$

In the above expressions, $\chi = \chi_3 = \chi_5$ is the geometric function of angles α and β that defines the area normal to

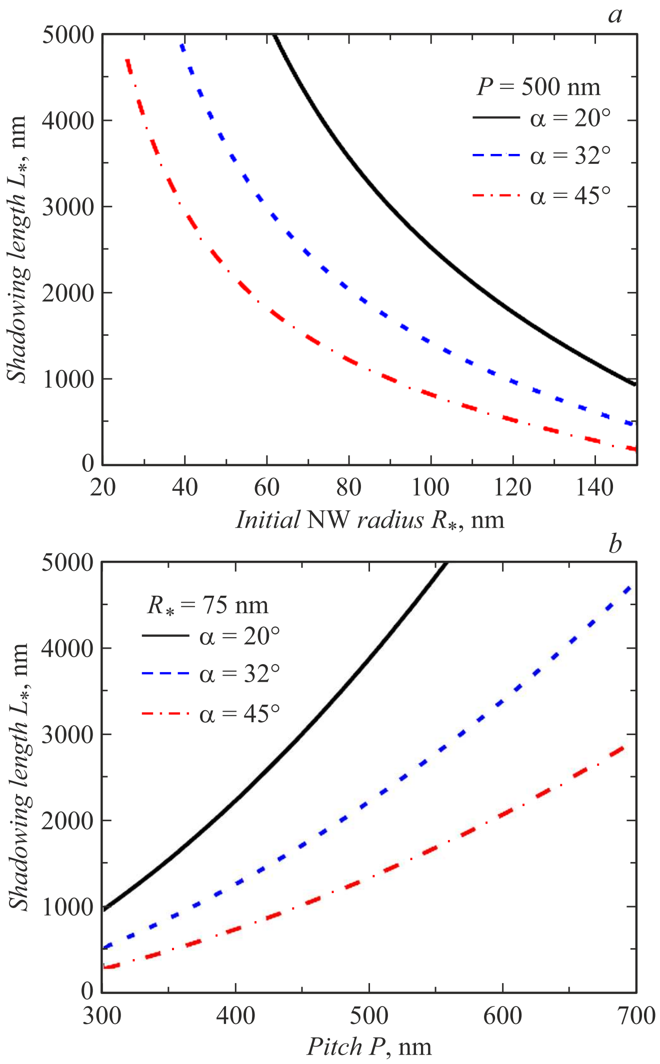

Figure 1. Dependences of the shadowing length corresponding to the complete blocking of the substrate surface in MBE on the NW radius at the start of the asymptotic stage at fixed $P = 500$ nm and three different α values (a) and on the distance between NWs at fixed $R_* = 75$ nm and the same α values (b).

the directed flux intercepted by the droplet in MBE [15]. According to the data from Fig. 1, length L_* increases with distance P between NWs and decreases as R_* grows. Naturally, the asymptotic stage commences earlier at larger angles of incidence of the flux α. The asymptotic stage actually starts at the very first moments of growth in dense arrays of wide NWs (at NW length $\cong 300$ nm for $R_* = 75$ nm, $P = 300$ nm, and $\alpha = 45°$).

Rewriting (1) at $v_r = 0$ in terms of H in the form $d(R^2L)/dH = 1/(\pi N)$ and integrating with the corresponding initial condition, we obtain

$$R = \left(\frac{h}{\pi NL}\right)^{1/2}, \quad h = H - H_* + \pi N R_*^2 L_*. \tag{4}$$

The NW elongation law is characterized by the following well-known expression [8,10,11]:

$$\frac{dL}{dh} = \frac{\chi}{\cos\alpha} + \frac{2\xi_3\lambda_{inc}\tan\alpha}{\pi R}, \tag{5}$$

which implies that the NW length increases due to direct transfer of material to the droplet and diffusion of fraction ξ_3 of Ga atoms from length λ_{inc}. This length is limited in the present case by the incorporation into steps and radial NW growth. The remaining material is spent on radial growth. Inserting expression (4) for R into (5), we find the Chini equation that was examined in [16]. Relation $dL/dt = \chi v_5$ is often fulfilled in self-catalyzed growth. This implies that the NW elongation rate is proportional to the atomic flux of group V element (As) to the droplet [17,18]. Rewriting this expression in the form

$$\frac{dL}{dh} = \frac{\chi}{\cos\alpha}\frac{v_5}{v_3} \tag{6}$$

and equating it to (5), we obtain

$$\chi = \frac{1}{v_5/v_3 - 1}\frac{2\xi_3\lambda_{inc}\sin\alpha}{\pi R}. \tag{7}$$

Thus, in order to keep the Ga droplet volume constant, one needs to reduce χ (and, consequently, contact angle β) when NW radius R increases.

Applying (7) to (5), we obtain the law of elongation of a self-catalyzed NW

$$\frac{dL}{dh} = c\left(\frac{L}{h}\right)^{1/2}, \quad c = \frac{1}{1 - v_3/v_5}\frac{2\xi_3\lambda_{inc}\tan\alpha}{\pi}(\pi N)^{1/2}. \tag{8}$$

Its solution takes the form

$$L = \left[\sqrt{L_*} + c(\sqrt{h} - \sqrt{h_*})\right]^2, \quad h_* = \pi N R_*^2 L_*. \tag{9}$$

The asymptotics at $h \gg h_*$

$$L \to c^2 h, \quad R \to R_c = \frac{1}{(\pi N)^{1/2} c} \tag{10}$$

demonstrate that the NW length at large growth times is proportional to the deposited Ga thickness and increases with coefficient c. The NW radius tends to stationary value R_c, which decreases as c grows. Since the value of $R_N = 1/(\pi N)^{1/2}$ corresponds to the merger of NWs into a solid film, NWs may remain isolated at large growth times only at $c > 1$.

Naturally, radial growth of NWs may occur only at $R_* < R_c$. If this is not the case, the NW radius does not vary with time, and the NW length is characterized by the usual expression

$$L = L_* + \frac{\chi_*}{\cos\alpha}\frac{v_5}{v_3}(H - H_*). \tag{11}$$

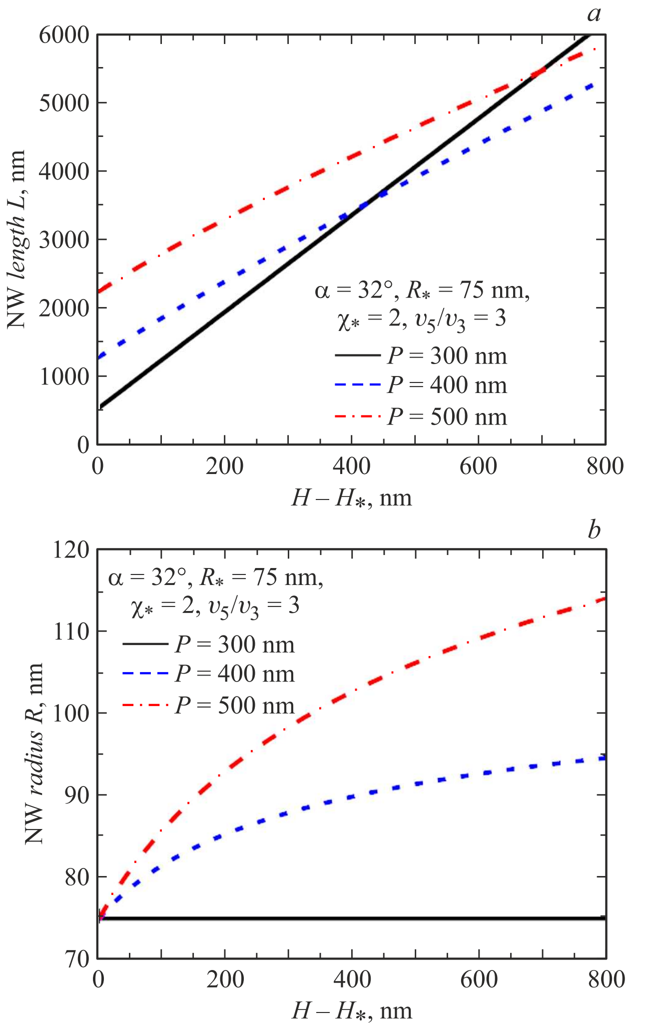

Figure 2. Dependences of the length (a) and the radius (b) of NWs on Ga deposition thickness $H - H_*$ from the start of the asymptotic stage obtained with parameter values indicated in the figure and in Table 1, three different P values, and a fixed ratio of V/III atomic fluxes ($v_5/v_3 = 3$). At the minimum $P = 300$ nm, the asymptotic stage starts at a shorter length, but NWs grow strictly upward and become longer than the other NWs at the late stage of growth. When the distance between NWs increases, radial growth becomes more pronounced, and the dependence of the NW length on $H - H_*$ (or growth time) is weaker than linear.

Table 1. Calculation parameters for the curves in Fig. 2

P, nm	L_*, nm	c	R_c, nm	χ_c
300	516	2.66	64	2
400	1263	1.995	113	1.327
500	2224	1.596	177	0.847

Several important relations also follow from (7), (8), and (10):

$$c = \pi^{1/2}\chi_* \frac{v_5}{v_3}\frac{R_*}{P}, \quad \chi = \chi_* \frac{R_*}{R}, \quad R_c = \frac{v_3}{v_5}\frac{1}{\pi\chi_*}\frac{P^2}{R_*}. \qquad (12)$$

They demonstrate directly that the NW length increases (while the NW radius decreases) if the ratio of fluxes V/III v_5/v_3 grows and distance P between the NWs becomes shorter.

Formulae (4) and (9) for the radius and the length of self-catalyzed NWs and relations (12) at the asymptotic growth stage are the key results of the present study. They are illustrated by Figs. 2 and 3. Fig. 2 presents the dependences of the length and the radius of NWs on deposited Ga thickness $H - H_*$ at fixed v_5/v_3 and different values of P, while Fig. 3 shows the same dependences at

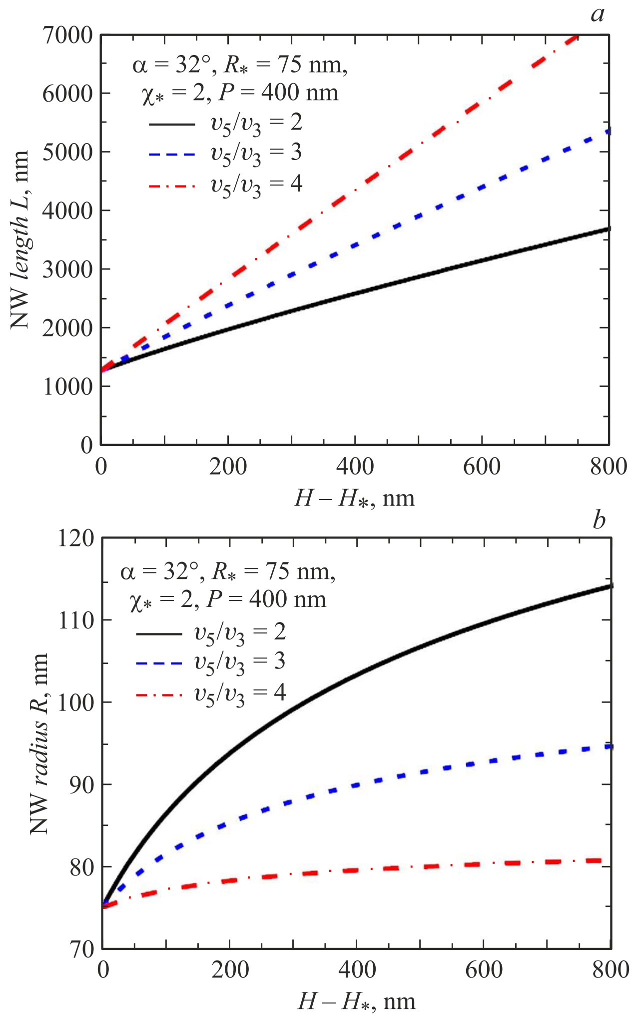

Figure 3. Dependences of the length (a) and the radius (b) of NWs on Ga deposition thickness at fixed $P = 400$ nm and three different ratios of atomic fluxes V/III. The other parameters are listed in Table 2. When the V/III flux ratio increases, axial growth intensifies, while radial growth becomes less pronounced.

Table 2. Calculation parameters for the curves in Fig. 3

v_5/v_3	c	R_c, nm	χ_c
2	1.33	170	0.882
3	1.995	113	1.327
4	2.66	85	1.765

fixed P and different v_5/v_3 values. The curves in Fig. 2 were obtained at $\alpha = 32^\circ$, $\chi_* = 2\,(\beta_* = 135^\circ)$, $R_* = 75\,\text{nm}$, and $v_5/v_3 = 3$. The other calculation parameters are listed in Table 1. The curves in Fig. 3 were obtained at $\alpha = 32^\circ$, $\chi_* = 2$, $R_* = 75\,\text{nm}$, and $P = 400\,\text{nm}$. The other calculation parameters are listed in Table 2. Note that the obtained asymptotic χ_c values correspond in both cases to a reduction in the contact angle of the droplet, which goes from 135° to approximately 90°. According to [19], this should induce changes in the crystalline phase of GaAs NWs (from the cubic phase to the hexagonal one and vice versa).

We note in conclusion that the formulated model allows for simple analytical solutions for the length and the radius of self-catalyzed NWs at the asymptotic stage of MBE growth with the collective shadowing effect taken into account. The obtained results demonstrate that the NW morphology may be adjusted by altering the ratio of V/III fluxes and the distance between NWs.

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Conflict of interest

The authors declare that they have no conflict of interest.

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