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Modeling the growth of tapered nanowires on reflecting substrates

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The formation of tapered self–catalyzed nanowires grown on reflecting substrates is studied theoretically. Within the model, the nanowire radius may be obtained as a function of length. The model describes the morphology of tapered nanowires. We study the influence of different growth parameters, including the III/V flux ratio and pitch, on the nanowire morphology.

Keywords: III–V nanowires, morphology, self–focusing effect, modeling

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Among nanostructures of different shapes and dimensionalities, nanowires (NWs) are ones of the most promising due to their unique properties. High crystal quality, ability to grow free of dislocation-free NWs on mismatched substrates [1], controllability of the composition [2], morphology [3] and crystal structure [4] of NWs enable their numerous various applications in optoelectronics [5], photonics [6] and medicine [7]. The most common methods for the NW growth are molecular beam epitaxy [8] and vapor phase epitaxy [9] by the vapor–liquid–crystal mechanism [10]. In this case, NWs are synthesized on surfaces activated by catalyst droplets as a result of depositing a semiconductor material. Rejection of using external catalysts (e.g. gold [11]) and transition to the self–catalyzed growth procedure [12] make it possible to ensure high purity of the synthesized NWs.

Most of optoelectronic applications need synthesizing an ensemble of uniformly–sized small–radius NWs. Sub-Poissonian narrowing of length distributions was considered in [13]. Formation of NWs uniform in radius is possible in the case of self–catalyzed growth due to the radius self–focusing effect [14] consisting in that radii of all NWs tend to the stationary value independently of the initial distribution. However, in works [14,15] the re-emission flux has been either considered within the effective flux or ignored. In all the cases, the influence of the NW dimensions on the reemission flux was not considered. Radial growth of cylindrical NWs on reflecting substrates was studied theoretically in [16]. However, of especial interest is the growth of tapered NWs [17] in the absence of radial growth which makes possible formation of thin radius–uniform NWs. Therefore, we devoted this work to studying the morphology of tapered NWs grown on reflecting substrates without any radial growth.

From the material balance considerations, equations describing variations in the numbers of group V (N_5) and III (N_3) atoms in a droplet have the following form:

$$\frac{dN_5}{dt} = \frac{\chi_5 v_5}{\cos\alpha_5}\frac{\pi R^2}{\Omega^{35}} - \frac{\pi R^2}{\Omega^{35}}\frac{dL}{dt}, \tag{1}$$

$$\frac{dN_3}{dt} = \left(S + \left(1 - \frac{S}{cP^2}\right)S'\right)\frac{v_3}{\Omega^{35}} - \frac{\pi R^2}{\Omega^{35}}\frac{dL}{dt}, \quad \frac{S}{cP^2} \leqslant 1, \tag{2}$$

$$\frac{dN_3}{dt} = cP^2\frac{v_3}{\Omega^{35}} - \frac{\pi R^2}{\Omega^{35}}\frac{dL}{dt}, \quad \frac{S}{cP^2} > 1, \tag{3}$$

where

$$S = 2RL\tan\alpha_3 + \frac{\chi_3}{\cos\alpha_3}\pi R^2,$$

$$S' = 2RL\tan\alpha_3 + \frac{\chi_3'}{\cos\alpha_3}\pi R^2, \quad L \leqslant \lambda_3, \tag{4}$$

$$S = 2R\lambda_3\tan\alpha_3 + \frac{\chi_3}{\cos\alpha_3}\pi R^2,$$

$$S' = 2R\lambda_3\tan\alpha_3 + \frac{\chi_3'}{\cos\alpha_3}\pi R^2, \quad L > \lambda_3. \tag{5}$$

Here dL/dt is the rate of NW vertical growth, L is the NW length, R is the NW radius, $\chi_5 = \chi_3 = 1/\sin^2\beta$ where β is the constant contact angle, v_5 and v_3 are the fluxes of group V and III atoms, respectively, Ω^{35} is the III–V pair volume in solid, P is the inter–NW distance (pitch), c is the coefficient describing mutual arrangement of NWs, α_3 and α_5 are the incident angles of the group III and V atoms, λ_3 is the diffusion length of the group III atoms. Term $(1 - S/cP^2)S'$ describes the reemission flux that must be taken into account when NWs are grown on reflecting substrates. Thus, term $S' = 0$ corresponds to the case when NWs are grown on adsorbing substrates. Equation (3) describes variations in the number of group III atoms in the droplet under the condition of complete shadowing. Subdivision into two modes (equations (4) and (5)) allows accounting for the fact that diffusion collection for short NWs ($L \leqslant \lambda_3$) is performed from the entire NW length,

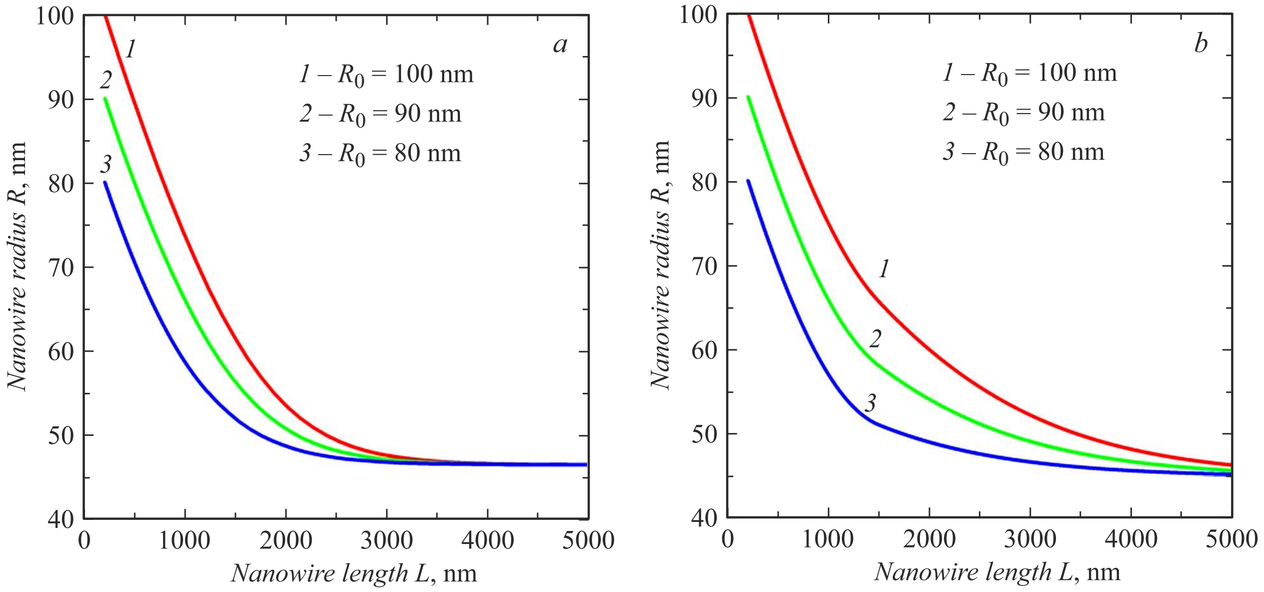

Figure 1. Self–catalyzed NW radius versus length at different initial radii for the reflecting (a) and adsorbing (b) substrates.

while diffusion collection for long NWs proceeds only from the NW upper part λ_3 in length.

Assuming that the growth mode is stationary ($dN_5/dt=0$), obtain the linear growth rate:

$$\frac{dL}{dt}=\frac{\chi_5 v_5}{\cos\alpha_5}. \tag{6}$$

Analysis of the droplet geometry shows that $N_3=(\pi R^3/3)f(\beta)/\Omega^l$, where

$$f(\beta)=(1-\cos\beta)(2+\cos\beta)/[(1+\cos\beta)\sin\beta].$$

Then we can easily derive from (2) and (6) the following relation:

$$\varepsilon\frac{dR}{dL}=\frac{\cos\alpha_5}{\chi_5}\frac{v_3}{v_5}\left(\frac{S}{\pi R^2}+\left(1-\frac{S}{cP^2}\right)\frac{S'}{\pi R^2}\right)-1,$$

$$S/(cP^2)\leqslant 1. \tag{7}$$

Here $\varepsilon=f(\beta)\Omega^{35}/\Omega^l$. The equation which links the NW radius R_* and length L_* corresponding to the moment of the complete shadowing onset may be obtained based on equation $S/(cP^2)=1$:

$$2R_*L_*\tan\alpha_3+\frac{\chi_3}{\cos\alpha_3}\pi R_*^2=cP^2. \tag{8}$$

For the case of growing under the complete shadowing, one obtains

$$\varepsilon\frac{dR}{dL}=\frac{R_s^2}{R^2}-1, \qquad S/(cP^2)>1. \tag{9}$$

Here $R_s^2=cP^2v_3\cos\alpha_5/(\pi\chi_5 v_5)$, where R_s is the stationary radius. The equation (9) solution may be represented as follows:

$$L-L_*=\varepsilon\left(\frac{R_s}{2}\ln\left|\frac{R_s+R}{R_s-R}\right|-\frac{R_s}{2}\ln\left|\frac{R_s+R_*}{R_s-R_*}\right|-\left(R-R_*\right)\right). \tag{10}$$

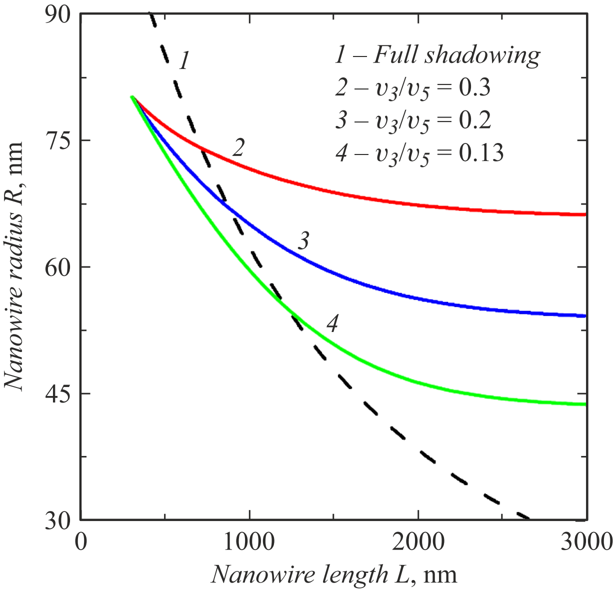

Figure 2. Self–catalyzed NW radius versus length at different III/V flux ratios (solid lines). The dashed line calculated via equation (8) separates the complete–shadowing region.

Let us begin the analysis with comparing morphologies of self–catalyzed NWs grown on the adsorbing (end without the shadowing effect) and reflecting substrates. Curves describing the NW growth on the reflecting substrate were calculated using (7) and (10). Fig. 1 presents the dependences of NW radius on length at different initial radii. Hereinafter assume that $\alpha_5=\alpha_3=32^\circ$, $\beta=135^\circ$, $\Omega^{35}/\Omega^l=2$, $\chi_3'=0.5$, $c=\sqrt{3}/2$. Notice that the case of $\Omega^{35}/\Omega^l=2$ is rather common (for instance, it is valid for the GaAs and GaP NWs). The initial NW length was

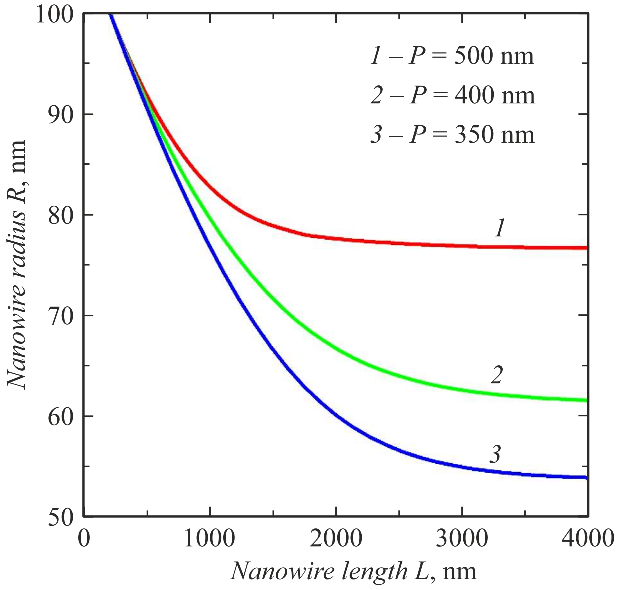

Figure 3. Self–catalyzed NW radius versus length at different pitch values.

$L_0 = 200$ nm, while $v_3/v_5 = 0.15$ and $P = 350$ nm. One can see that in both cases the NW radius tends to stationary value $R_s \approx 46$ nm. However, in the case of the reflecting substrate the stationary value of the radius gets reached faster, which is explained by accounting for the shadowing effect.

Now consider the influence of the III/V flux ratio on the NW morphology (Fig. 2). In calculation, we assumed that $L_0 = 300$ nm, $R_0 = 80$ nm and $P = 350$ nm. Equation (8) clearly demonstrates that the flux ratio has no effect on the complete–shadowing region but affects the stationary radius. Reduction of the flux ratio from $v_3/v_5 = 0.3$ to 0.13 leads to the stationary radius reduction from $R_s \approx 65$ to ≈ 43 nm.

Lastly, Fig. 3 illustrates the pitch influence on the NW morphology. Parameters were selected as follows: $v_3/v_5 = 0.2$, $L_0 = 200$ nm and $R_0 = 100$ nm. The distance between NWs affects both the region of complete shadowing (a decrease in pitch results in that the complete shadowing occurs at shorter NWs) and stationary radius. For instance, the pitch decrease from $P = 500$ to 350 nm leads to the stationary radius decrease from $R_s \approx 77$ to ≈ 54 nm, which may be explained by a decrease in area from which NW collects the material and, actually, in the number of group III atoms arriving due to reflection from the substrate.

The constructed model describes the morphology of tapered self–catalyzed NWs growing on reflecting substrates. The NW radius has been shown to tend to the stationary value that decreases with decreasing pitch and III/V flux ratio. It has been also shown that, contrary to the previous model, here the rate of declining to the stationary radius value is higher because of the flux overestimation due to ignoring the shadowing effect. The model may be applied to describe the NW morphology of any binary system. The obtained results may be used to optimize growth parameters of NWs with the preset morphology.

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Conflict of interests

The authors declare that they have no conflict of interests.

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