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Kinetics of radial growth of III−V nanowires in vapor phase epitaxy

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A model is proposed for the radial growth of III−V nanowires (NWs) in vapor phase epitaxy on masked substrates, which provides explicitly the NW radius as a function of its length. Analytical solutions are obtained for the NW radius in different stages of growth. A comparison of the model with the data on the growth kinetics of GaAs NWs is presented and a good correlation with the data is demonstrated.

Keywords: III−V nanowires, radial growth, vapor phase epitaxy, modeling.

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The epitaxial growth of nanowires (NWs) of various III−V semiconductor compounds (III−V NWs) on masked substrates with ordered arrays of apertures [1–7] provides an opportunity to synthesize NW ensembles of a uniform size and suppress parasitic growth on the substrate surface. These structures have excellent potential for application in nanophotonics and nanoelectronics [3,8–10], which includes application on silicon and other mismatched substrates. Efficient relaxation of elastic strain on the side surface allows one to grow III−V NWs on silicon substrates without mismatch dislocations and form heterostructures in strongly mismatched material systems [11–14]. For example, the well-known difficulties arising in the synthesis of InAs on silicon (the lattice mismatch parameter is 11.6%) [15] may be overcome in the NW geometry [13]. However, the radius of coherent InAs NWs needs to be fairly small (according to the data from [13], less than 13 nm) in order to suppress dislocations. This illustrates the importance of control over the radius of III−V NWs in their synthesis. The aim of the present study is to construct an analytical model of radial growth of III−V NWs in vapor phase epitaxy (VPE) on masked substrates.

VPE (specifically, metalorganic VPE, MOVPE) of III−V NWs on masked substrates proceeds either via the vapor−liquid−solid (VLS) growth mechanism with a gold catalyst [4,7,13,14,16,17] of via the selective epitaxy (SE) mechanism without a metal catalyst [5,6]. Just as in molecular beam epitaxy (MBE) on unprocessed substrates [18], the overwhelming majority of models of VLS growth of III−V NWs in MOVPE consider the surface diffusion of adatoms of a group III element from the mask surface to the side NW surface to be the key mechanism of material exchange between and a substrate and an NW [4,16,17]. It has been demonstrated in [2] that the key mechanism of molecular exchange in MBE growth of GaP NWs on masked silicon substrates is not the surface diffusion, but the reemission (reflection) of atoms of a group III element from the SiO_x mask surface. This approach has been developed further in relation to MBE growth in [19]. A model of VPE growth of III−V NWs on masked substrates has been proposed in [20].

In order to characterize the radial NW growth in VPE, one needs to consider two diffusion lengths of adatoms on the side NW surface. One of them (λ_3^{inc}) is limited by incorporation into this surface, while the other (λ_3^{des}) is limited by desorption [20]. NWs grow radially only if $\lambda_3^{inc} < \lambda_3^{des}$; in the contrary case, their radius remains constant. The following equations were obtained [20] under the assumption of a constant droplet volume in VLS growth, which holds true in the case of SE, for short cylindrical NWs with radius R and length $\lambda_3^{inc} < L < \lambda_3^{des}$:

$$\frac{d}{dH}(\pi R^2 L) = \left(\chi_d \frac{2\pi R^2}{1+\cos\beta} + \chi_{nw} 2\pi R L\right)\left(2 - \frac{S_{nw}}{cP^2}\right),$$

$$\frac{dL}{dH} = \left(\frac{2\chi_d}{1+\cos\beta} + \frac{2\chi_{nw}\lambda_3^{inc}}{R}\right)\left(2 - \frac{S_{nw}}{cP^2}\right). \quad (1)$$

Here, H is the effective material deposition thickness, χ_d is the efficiency of pyrolysis on the droplet surface or on the upper NW face in SE, χ_{nw} is the efficiency of pyrolysis on the side NW surface, β is the contact angle of a droplet at the NW apex ($\beta = 0$ in SE), cP^2 is the effective surface area per a single NW at an aperture array pitch of P, and S_{nw} is the effective collection area for group III atoms at $L < \lambda_3^{des}$. It is easy to derive a dependence of the NW radius on its length from (1) in the form of a transcendental equation:

$$\frac{2\chi_d}{1+\cos\beta}(R - R_1) + 2\chi_{nw}\lambda_3^{inc}\ln\left(\frac{R}{R_1}\right) = L - \lambda_3^{inc} - \lambda_3^{inc}\ln\left(\frac{L}{\lambda_3^{inc}}\right), \quad (2)$$

where R_1 is the NW radius at $L = \lambda_3^{inc}$. The obtained solution is independent of distance P between NWs.

At $R_1/\lambda_3^{inc} \gg 1$, the solution of (2) is

$$\frac{R}{R_1} = 1 + \frac{1}{A}\left[\frac{L}{\lambda_3^{inc}} - 1 - \ln\left(\frac{L}{\lambda_3^{inc}}\right)\right],$$

$$A = \frac{R_1}{\lambda_3^{inc}} \frac{2\chi_d}{1+\cos\beta} \gg 1. \qquad (3)$$

In the contrary case ($R_1/\lambda_3^{inc} \ll 1$), we find

$$\frac{R}{R_1} = \left(\frac{\lambda_3^{inc}}{L}\right)^{\alpha} \exp\left[\alpha\left(\frac{L}{\lambda_3^{inc}} - 1\right)\right],$$

$$\alpha = 1/(2\chi_{nw}) \geqslant 1/2. \qquad (4)$$

The radius of short NWs increases superlinearly with length at typical parameter values. This is attributable to the fact that NWs grow in volume by collecting group III atoms from the entire NW length, while the length increases only due to the collection of adatoms from the upper NW part with height λ_3^{inc}.

The kinetics of growth of NWs with length $\lambda_3^{des} < L < L_*$ (L_* is the saturation length; on reaching it, an NW array consumes the entire effective flux of group III atoms [2,19,20]) is characterized by equations [20]

$$\frac{d}{dH}(\pi R^2 L) = \left(\chi_d \frac{2\pi R^2}{1+\cos\beta} + \chi_{nw} 2\pi R \lambda_3^{des}\right)\left(2 - \frac{\tilde{S}_{nw}}{cP^2}\right),$$

$$\frac{dL}{dH} = \left(\frac{2\chi_d}{1+\cos\beta} + \frac{2\chi_{nw}\lambda_3^{inc}}{R}\right)\left(2 - \frac{\tilde{S}_{nw}}{cP^2}\right). \qquad (5)$$

Here, $\tilde{S}_{nw}$ is the effective atom collection area at $L > \lambda_3^{des}$. Therefore,

$$\frac{2\chi_d}{1+\cos\beta}(R - R_2) + 2\chi_{nw}\lambda_3^{inc} \ln\left(\frac{R}{R_2}\right) = \left(\lambda_3^{des} - \lambda_3^{inc}\right) \ln\left(\frac{L}{\lambda_3^{des}}\right). \qquad (6)$$

The obtained expression is again independent of distance P between NWs. Quantity R_2 corresponds to the NW radius at $L = \lambda_3^{des}$. Solution (6) may be presented as

$$\frac{L}{\lambda_3^{des}} = \left(\frac{R}{R_2}\right)^{2\chi_{nw}\lambda_3^{inc}/(\lambda_3^{des} - \lambda_3^{inc})} \exp\left[\frac{2\chi_d}{1+\cos\beta} \frac{R - R_2}{\lambda_3^{des} - \lambda_3^{inc}}\right] \qquad (7)$$

or

$$\frac{L}{\lambda_3^{des}} = \bar{r}^{a} \exp\left[b(\bar{r} - 1)\right],$$

$$a = \frac{2\chi_{nw}\lambda_3^{inc}}{\lambda_3^{des} - \lambda_3^{inc}}, \quad b = \frac{2\chi_d}{1+\cos\beta} \frac{R_2}{\lambda_3^{des} - \lambda_3^{inc}} \qquad (8)$$

with dimensionless radius $\bar{r} = R/R_2$. At typical parameter values, the NW radius increases sublinearly with length at this stage, which is attributable to the desorption of material from the side NW surface and the corresponding suppression of radial growth. Note that the length dependence of the NW radius at lengths greater than the critical one (L_*) is also sublinear. In fact, the NW length at the asymptotic growth stage becomes a linear function of time, and the NW radius tends to a constant value specified by distance P between NWs [19]. Therefore, the radius of very tall NWs saturates, and the process of radial growth terminates.

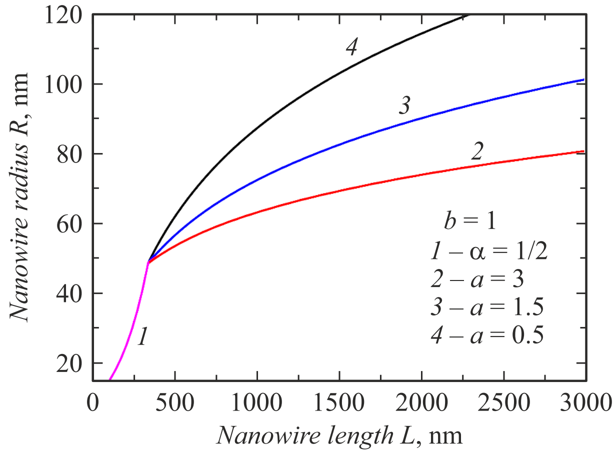

Figure 1. Dependences of the radius of an NW on its length derived from expression (4) and (8) at fixed $R_1 = 15$ nm, $\alpha = 1/2$, $\lambda_3^{inc} = 100$ nm, $\lambda_3^{des} = 335$ nm, $b = 1$, and three values of a.

The obtained results suggest that two fundamentally different regimes of radial growth of cylindrical III–V NWs may be isolated: the regimes of a fast (superlinear) increase in radius as a function of NW length for short NWs with $L < \lambda_3^{des}$ and a slow (sublinear) increase in radius at $L > \lambda_3^{des}$. Figure 1 presents the $R(L)$ dependences obtained in accordance with (4) at $R_1 = 15$ nm, $\alpha = 1/2$, and $\lambda_3^{inc} = 100$ nm and in accordance with (8) at $\lambda_3^{des} = 335$ nm, $b = 1$, and $a = 3$, 1.5, and 0.5. The transition from a superlinear dependence of the radius of an NW on its length to a sublinear dependence occurring at $L = \lambda_3^{des}$ is seen clearly. Note that the radial growth is faster at smaller a values.

GaAs NWs characterized in [6] were grown via the catalyst-free SE mechanism by MOVPE at a temperature of 750°C on processed SiO_2/GaAs substrates with a distance of 600 nm between the centers of apertures (pores) and with different diameters of these apertures (from 125 to 225 nm). The obtained NWs were nearly cylindrical in shape. The length, radius, and volume of NWs were measured at different time points corresponding to the termination of growth after 20, 40, 60, and 80 min of GaAs deposition. Figure 2 presents the experimental dependences of dimensionless NW radius $r = R/R_0$, where R_0 is the pore radius, on the NW length for different pore sizes. All the experimental dependences fit closely the curve derived from expression (4) at $\alpha = 1/2$ and $\lambda_3^{inc} = 710$ nm. The curve $r(L)$ remains applicable within a wide range of pore size variation due to the fact that the initial NW radius R_1 (at the end of the non-stationary growth stage associated with pore filling) is proportional to the pore size. Its is evident that, although the growth temperature is high, a superlinear increase in radius with increasing NW length excludes the possibility of a strong effect of desorption of Ga atoms from the NW surface.

The constructed model allows one to calculate the radius of III–V NWs as a function of length in VPE growth,

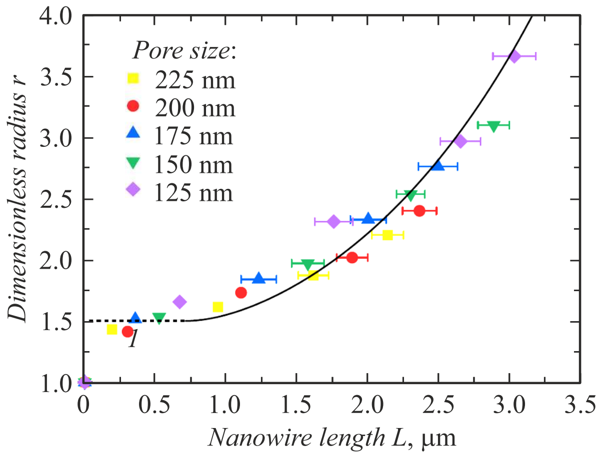

Figure 2. Dependences of the radius of GaAs NWs on their length (expressed in terms of dimensionless radius $r = R/R_0$) from [6] (symbols) and their approximation by formula (4) at $\alpha = 1/2$ and $\lambda_3^{inc} = 710$ nm (solid curve). The dashed curve corresponds to the assumption of $R_1 = 1.5R_0$.

isolate different regimes of radial growth, and determine the diffusion lengths of adatoms of a group II element by comparing the results of calculations with experimental data. Further development of the model should involve the incorporation of more complex NW geometries, which will be done in a separate study.

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Conflict of interest

The authors declare that they have no conflict of interest.

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