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Diffusion-induced growth of nanowires: Generalized boundary conditions and self-consistent kinetic equation

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ABSTRACT

In this work, we present a theoretical analysis of the diffusion-induced growth of “vapor–liquid–solid” nanowires, based on the stationary equations with generalized boundary conditions. We discuss why and how the earlier results are modified when the adatom chemical potential is discontinuous at the nanowire base. Several simplified models for the adatom diffusion flux are discussed, yielding the $1/R^p$ radius dependence of the length, with p ranging from 0.5 to 2. The self-consistent approach is used to couple the diffusion transport with the kinetics of 2D nucleation under the droplet. This leads to a new growth equation that contains only two dimensional parameters and the power exponents p and q, where $q=1$ or 2 depends on the nucleus position. We show that this equation describes the size-dependent depression of the growth rate of narrow nanowires much better than the Gibbs–Thomson correction in several important cases. Overall, our equation fits very well the experimental data on the length–radius correlations of III–V and group IV nanowires obtained by different epitaxy techniques.

1. Introduction

The so-called “vapor–liquid–solid” (VLS) growth mechanism, proposed by Wagner and Ellis in 1964 [1], is now widely used for bottom-up fabrication of semiconductor nanowires with well-controlled properties for different applications [2–5]. In the early days of “nanowhisker” technology, the VLS growth was usually performed from chemical precursors that required high surface temperatures for their decomposition [1,6]. In this case, a liquid droplet at the wire top acts as a chemical catalyst which facilitates chemical reactions at the vapor–liquid surface, while the pyrolysis at the solid surfaces is almost completely suppressed. Consequently, the diffusion-induced contributions to the wire growth rate are negligible. Without surface diffusion and the Gibbs–Thomson enhancement of desorption from small droplets [6,7], the sole rate-limiting step for nanowire growth is the thermally activated metal-catalyzed dissociative adsorption directly on the catalyst droplet and the vertical growth rate is radius-independent [8]. When the Gibbs–Thomson effect is included, the nanowire elongation rate becomes zero for a certain minimum droplet size below which the entire VLS growth ceases [6,7,9], as in the Givargizov–Chernov model [10].

In modern metal organic chemical vapor deposition (MOCVD), however, pyrolysis takes place also at the solid surfaces (the substrate surface and the nanowire sidewall facets) producing surface adatoms which can subsequently diffuse to the nanowire top and contribute to its elongation [11]. In molecular beam epitaxy (MBE) and related techniques [12–14], the VLS nanowire growth cannot be understood without surface diffusion. Rather than a chemical catalyst, the droplet acts as a material collector whose low chemical potential directs the adatom diffusion fluxes to the top. This explains why nanowires are higher than the surface layer which always grows between them. Due to paramount importance of the diffusion-induced nanowire growth, several models have been proposed [11–17] based on the earlier works [6,18–20]. These models are capable of describing several major effects. In particular, a purely diffusion growth yields the diffusionlike decreasing radius dependence of the growth rate in the form $1/R^p$, where the exponent p depends on the growth conditions. More advanced models account for surface diffusion and the Gibbs–Thomson effect simultaneously, leading to the experimentally observed non-monotonous length–radius correlation with a maximum [21–23]. Size-dependent diffusion-induced VLS growth of III–V and group IV nanowires continues to attract much interest in connection with non-linear effects in nanowire growth and crystal structure [23], growth kinetics and nucleation statistics in individual nanowire [24], narrowing the length distribution of nanowires [25], and the radius dependence of the

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growth rate under different conditions [26]. Furthermore, diffusion growth models originally developed for VLS semiconductor nanowires are now widely used in studies of other highly anisotropic objects such as self-induced GaN nanowires [27] and carbon nanostructures [28,29].

Functional form as well as kinetic coefficients of the diffusion-induced nanowire growth rate largely depends on the boundary conditions. To find the diffusion flux to the top, one needs to solve two second order equations for the adatom concentrations on the substrate surface and the nanowire sidewalls, which requires four boundary conditions [19,22,23,30]. In this work, we present a new analytical solution for the diffusion-induced nanowire growth rate with the generalized boundary conditions that describe correctly the potential relief at the nanowire–substrate and the nanowire–droplet boundaries. Our solution contains the previous results [15–27] as particular cases. We then develop a self-consistent approach where the diffusion transport is equalized to the nucleation-mediated sink at the liquid–solid interface. Finally, a simplified growth equation is derived, which contains only two fitting parameters and allows one to explain very well most experimental data on the radius-dependent nanowire growth rates in different VLS techniques [14,15,21,22,31–35].

2. Generalized boundary conditions

The diffusion-induced growth rate at a time-independent nanowire radius R should generally be obtained from the equation

$$\left(\frac{dL}{dt}\right)_{diff} = -\frac{2\Omega_S}{R} D_f \frac{dn_f}{dz}\bigg|_{z=L} \tag{1}$$

Here, the right hand side gives the appropriately normalized diffusion flux of adatoms through the circular triple phase line at the nanowire top (at vertical coordinate $z=L$), with L as the nanowire length, Ω_S as the elementary volume in the solid, D_f as the diffusion coefficient and n_f as the z-dependent adatom concentration on the sidewall facets, labeled "f". We consider the diffusion flux of only one element, which is the case for group IV nanowires and is also a good approximation for III–V nanowires such as GaAs, because arsenic does not diffuse along the sidewalls [36]. We also assume that the growth rate of GaAs nanowires is Ga-limited, i.e., each Ga adatom diffusing to the top subsequently finds its As pair and incorporates to the solid. This requires an excessive As influx, the property which usually holds for the Au-catalyzed VLS growth [4] but not for the Ga-catalyzed case [36].

In order to calculate the diffusion flux, we should consider two steady state diffusion equations for the substrate (n_s) and sidewall (n_f) adatoms [22,23]:

$$D_s \Delta n_s + I\cos\alpha - \frac{n_s}{\tau_s} = 0; \tag{2}$$

$$D_f \frac{d^2 n_f}{dz^2} + \omega I \sin\alpha - \frac{n_f}{\tau_f} = 0. \tag{3}$$

The first terms here describe the diffusion, the second stand for the adsorption from the flux I directed at an angle α to the substrate normal, and the third give the adatom sinks. The Δ is the two-dimensional Laplace operator in the substrate plane (r), D_s is the adatom diffusion coefficient on the substrate surface, and τ_s, τ_f are the effective lifetimes on the substrate and sidewall surfaces, respectively. These lifetimes are limited by either desorption from the corresponding planes or incorporation to surface steps. The coefficient ω in Eq. (3) equals 1 in MOCVD and $1/\pi$ in MBE. The angle α does not enter the diffusion equations in the case of vapor deposition. Instead, the temperature-dependent pyrolysis efficiencies χ_f and χ_s can be introduced into the adsorption terms to account for different precursor decomposition probabilities at different surfaces [23].

General solutions to Eqs. (2) and (3) are given by

$$n_s(r) = I\tau_s\cos\alpha + c_1 I_0(r/\lambda_s) + c_2 K_0(r/\lambda_s); \tag{4}$$

$$n_f(z) = \omega I\tau_f\sin\alpha + a_1\cosh(z/\lambda_f) + a_2\sinh(z/\lambda_f). \tag{5}$$

Here, $\lambda_s = \sqrt{D_s\tau_s}$ is the effective diffusion length of adatoms on the substrate surface and $\lambda_f = \sqrt{D_f\tau_f}$ is that on the sidewalls. The functions $I_m(\xi)$ and $K_m(\xi)$ here and below denote the modified Bessel functions of the order m in standard notations, the I increasing and K decreasing at $\xi\to\infty$. The physics of the growth process is now determined by the four boundary conditions that are required for finding the four coefficients c_1, c_2, a_1 and a_2.

For a single nanowire, the first boundary condition for the substrate adatoms writes down as $n_s(r\to\infty) = I\tau_s\cos\alpha$, meaning simply that the adatom concentration is constant far away from the nanowire. This yields $c_1 = 0$ to eliminate the increasing Bessel function I_0. For an array of nanowires with the average spacing $2R_W \sim 1/\sqrt{N_W}$, where N_W is the surface density of the wires, this condition is changed to [30]

$$\frac{dn_s}{dr}\bigg|_{r=R_W} = 0, \tag{6}$$

implying zero diffusion flux at equal distance between the wires. Dubrovskii et al. [22,23,30] proposed using the conditions of continuity of adatom chemical potential and flux at the nanowire base ($r=R$), given by

$$\sigma_s n_s(R) = \sigma_f n_f(0); \tag{7}$$

$$D_s \frac{dn_s}{dr}\bigg|_{r=R} = -D_f \frac{dn_f}{dz}\bigg|_{z=0}. \tag{8}$$

The second boundary condition given by Eq. (7) follows from the expression $\mu = k_B T\ln(\sigma n) + \text{const}$ for the chemical potential of both adatom subsystems "s" and "f" in an ideal adsorbate, with σ_s and σ_f being the elementary areas on the substrate and sidewall surfaces, respectively. The third condition is simply the continuity equation at the nanowire foot.

Johansson et al. [16] put zero boundary condition at the nanowire top: $n_f(L) = 0$, which was also used by us [14,15,30] and some other authors (see, e.g., the recent paper by Lu et al. [26]) as the fourth boundary condition. With this condition, the diffusion flux is always directed to the top where the adatom concentration is zero. Dubrovskii et al. [22,23,25] then changed the condition at the wire top to the continuity of chemical potentials at the triple phase line

$$k_B T\ln[\sigma_f n_f(L)] = \mu_l^\infty + \frac{2\gamma_{LV}\Omega_L\sin\beta}{R}, \tag{9}$$

where μ_l^∞ is the chemical potential of an infinitely large liquid phase. This regards for the Gibbs–Thomson effect of elevation of chemical potential due to the curvature of the droplet surface. It has been shown that such a condition has rich implications for describing non-linear growth effects such as negative growth [23] and narrowing the length distribution of nanowires [25]. Eq. (9) can be re-arranged in the equivalent form

$$n_f(L) = \frac{\theta_l}{\sigma_f} = \frac{\theta_l^\infty}{\sigma_f}\exp\left(\frac{R_{GT}}{R}\right) \equiv \tilde{n}_f \tag{10}$$

by using the liquid activity $\theta_l = \exp(\mu_l^\infty/k_B T + R_{GT}/R)$, with T as the surface temperature, k_B as the Boltzmann constant, $R_{GT} = (2\Omega_L\gamma_{LV}\sin\beta)/(k_B T)$ as the characteristic Gibbs–Thomson radius, Ω_L as the elementary volume in the liquid phase, γ_{LV} as the droplet surface energy and β as the contact angle of the droplet at the nanowire top. Now, $\tilde{n}_f$ has a sense of quasi-equilibrium