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Model of step propagation and step bunching at the sidewalls of nanowires

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ABSTRACT

Radial growth of vertically aligned nanowires involves formation and propagation of monoatomic steps at atomically smooth nanowire sidewalls. Here we study the step dynamics with a step flow model taking into account the presence of a strong sink for adatoms at top of the nanowire and adatom exchange between the nanowire sidewall and surrounding substrate surface. Analytical expressions for velocities of steps propagating from the nanowire base to the nanowire top are obtained. It is shown that the step approaching the nanowire top will slow down if the top nanowire facet is a stronger sink for adatoms than the sidewall step. This might trigger bunching of the steps at the sidewall resulting in development of the pencil-like shape of nanowires such as observed in, e.g., the Au-assisted MBE growth of InAs.

1. Introduction

In recent years vertically aligned semiconductor nanowires have attracted great attention due to prospects of their use in microelectronics, optoelectronics, photovoltaics, nanosensing etc. [1–4]. Specific properties of nanowires are related to their highly anisotropic shape, which may vary a lot depending on the deposition conditions [4–6]. Moreover, even at the given deposition conditions the nanowire shape may change in course of the growth [7–10].

In general the nanowire shape is determined by the interplay of the lateral and axial growth of nanowires [7,11]. In that respect it is essential that the nanowire sidewalls remain atomically smooth while the nanowire is growing laterally. This indicates that the lateral growth of nanowires occurs in the layer-by-layer or step-flow fashion involving nucleation of new steps at the sidewall facets and their propagation along the facets. Monoatomic steps at the sidewalls of nanowires were directly visualized by transmission electron microscopy [12–14] and scanning tunneling microscopy [15,16].

Bearing in mind the step-flow mechanism of the radial growth of nanowires it is tempting to relate the experimentally observed transformations of the nanowire shape with a kinetic instability of the steps propagating along the sidewall facets. For instance, it is known that on vicinal surfaces the kinetic step bunching may lead to the surface faceting [17]. Similarly, the step bunching may be responsible for the formation of new facets at the nanowire sidewalls such as the {10–11} facets of pencil-like InAs nanowires grown by the Au-assisted MBE [9]. The transition from cylindrical to pencil-like shape of InAs nanowires was explained in earlier theoretical works [9,10] by the onset of the radial nanowire growth by nucleation and propagation of steps at some critical length of the nanowire. However dynamics of the steps at the sidewall was not considered explicitly within the models developed in [9,10]. Therefore it remains unclear why the appearance of the steps leads to the specific nanowire shape observed in the experiment.

Intuitively, one would expect that the step velocity should be considerably higher than the axial growth rate of the nanowire, because the advance of the step by one atomic position requires formation of an atomic row along the step edge whereas the increase of the nanowire length by the same distance requires deposition of a whole atomic layer on the nanowire top facet. Therefore, one would expect the steps moving in the direction of the nanowire top to catch up and join the nanowire top facet leading to the thickening of the nanowire including its upper part near the catalyst droplet. However, in the aforementioned experiments on the InAs nanowires growth [9] the nanowire radius at the top did not change with time. In [18] the formation of tapered InP nanowires with non-tapered sections at the top was observed. These observations clearly indicates that for some reasons the steps slow down in the upper part of the nanowire instead of catching up the nanowire top facet.

In the present work we model the axial and radial growth of nanowires treating explicitly dynamics of the steps nucleating sequentially at the nanowire base. This allows us to go beyond the

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earlier material conservation models [9,10] and reproduce different scenarios of the nanowire growth: thickening of nanowires while preserving their cylindrical shape and gradual transformation of the nanowire shape due to bunching of the steps at the nanowire sidewalls. We show that the step bunching might be conditioned by the slowing down of the leading step approaching the nanowire top due to the transfer of atoms from the step to the nanowire top with the later being a stronger sink for adatoms than the step itself. Results of numerical simulations of the step dynamics and of the corresponding evolution of the nanowire shape are in good agreement with the experimental observations of the shape transformations of the InAs nanowires [9].

2. Model

Let us consider a cylindrical nanowire with k steps of the monoatomic height nucleated at the nanowire base and propagating from the base to the nanowire top (Fig. 1). The axisymmetric configuration of the steps shown in Fig. 1 is similar to that considered in the earlier model of filamentary crystal growth by Schwoebel [19] and resembles the “wedding cake” step configuration widely used to model growth and dissolution of mounds (see e.g. [20–23]). However, in contrast to the model of mounds, the steps in our model propagate towards the nanowire top without growing in the lateral direction.

Considering the axial growth of the nanowire it is generally believed that under the catalyst droplet the top nanowire facet grows layer-by-layer by nucleation and spreading of two-dimensional (2D) islands [3,11,24–26]. The energy per unit length of a step in contact with a liquid phase is typically much smaller as compared to the energy of a step in contact with a gas phase. Moreover, the curvature of the step on the nanowire top may be negative if the 2D island nucleates as a circular step at the triple phase line [27] (this nucleus position favors formation of the wurtzite structure of III–V semiconductor nanowires [28]). This means that due to the Gibbs–Thomson effect the nanowire top facet should be a stronger sink for the sidewall adatoms than the sidewall step. This is again in contrast with the case of mounds where the Gibbs–Thomson effect generates the downhill flux of atoms from the upper (more curved) steps to the lower (less curved) steps [21–23] leading to shrinkage of the topmost terraces and, as a consequence, to gradual flattening of the mounds at the absence of the deposition flux.

Concentration of adatoms on the substrate surface, n_s, and on the terraces between the steps on the sidewall, n_i, obey the steady-state diffusion equations [11,29]

$$\frac{D_s}{r}\frac{d}{dr}\left(r\frac{dn_s}{dr}\right)+J\cos\alpha-\frac{n_s}{\tau_s}=0, \tag{1}$$

$$D_f\frac{d^2n_i}{dz^2}+J\omega\sin\alpha-\frac{n_i}{\tau_f}=0, \tag{2}$$

where D_s and D_f are the surface diffusion coefficients on the substrate surface and on the sidewall, respectively, τ_s and τ_f are the respective life times of adatoms before desorption, J is the deposition flux, and α is the angle between the deposition flux direction and the nanowire axis (it is assumed that the nanowires grow normal to the surface). The coefficient ω is equal to $1/\pi$ in the case of molecular beam epitaxy considered in the present work. Index i in Eq. (2) enumerates the sidewall steps as sketched in Fig. 1.

General solutions of Eq. (1) and (2) read

$$\begin{aligned} n_s(r)&=J\tau_s\cos\alpha+C_1I_0(r/\lambda_s)+C_2K_0(r/\lambda_s),\\ n_i(z)&=J\tau_f\omega\sin\alpha+A_i\cosh(z/\lambda_f)+B_i\sinh(z/\lambda_f), \end{aligned} \tag{3}$$

where $\lambda_s=(D_s\tau_s)^{1/2}$ and $\lambda_f=(D_f\tau_f)^{1/2}$ are the diffusion lengths of adatoms on the substrate surface and on the nanowire sidewall, respectively, $I_0(r/\lambda_s)$ and $K_0(r/\lambda_s)$ are the modified Bessel functions. The integration constants C_1, C_2, A_i and B_i are to be determined from the appropriate boundary conditions.

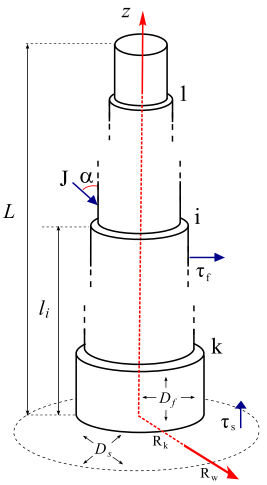

Fig. 1. Schematic view of a nanowire with steps at the sidewall.

Following [11,29] as the first boundary condition we request that the diffusion flux on the substrate surface vanishes at certain distance R_W from the center of the nanowire base

$$\left.\frac{dn_s}{dr}\right|_{r=R_W}=0. \tag{4}$$

In the present paper we consider R_W as a model parameter having a meaning of an effective radius of the feeding area around the given nanowire.

Boundary conditions at the nanowire base follow from the conditions of balance of the diffusion fluxes and the resulting fluxes of adatoms crossing the boundary between the nanowire sidewall and substrate surface [30,31]

$$\begin{aligned} D_s\left.\frac{dn_s}{dr}\right|_{r=R_k}&=k_{sf}n_s(R_k)-k_{fs}n_{k+1}(0),\\ D_f\left.\frac{dn_f}{dz}\right|_{z=0}&=k_{fs}n_{k+1}(0)-k_{sf}n_s(R_k). \end{aligned} \tag{5}$$

Here k_{sf} and k_{fs} are the rate constants of the transitions from the substrate surface to the sidewall surface and vice versa, and R_k is the radius of the nanowire base: $R_k=R+kh$, where R is the radius of the nanowire top, and h is the height of the monoatomic step at the nanowire sidewall.

The balance equations for the diffusion fluxes and the resulting fluxes of adatoms incorporating into the steps from the upper (-) and lower (+) terraces give us $2k$ boundary conditions of the form

$$\begin{aligned} -D_f\left.\frac{dn_{i+1}}{dz}\right|_{z=l_i}&=\beta_-[n_{i+1}(l_i)-\tilde{n}_i],\\ D_f\left.\frac{dn_i}{dz}\right|_{z=l_i}&=\beta_+[n_i(l_i)-\tilde{n}_i], \end{aligned} \tag{6}$$

where l_i is the distance from the nanowire base to the i-th step ($i=1\ldots k$), β_- and β_+ are the kinetic coefficients of the step [32], and $\tilde{n}_i$ is the adatom concentration in equilibrium with the i-th step.

The last boundary condition represents the balance equation for the diffusion flux and the resulting flux of adatoms to the nanowire top [30,31]

$$-D_f\left.\frac{dn_1}{dz}\right|_{z=L}=k_{ft}n_1(L)-k_{tf}C_{top}=k_{ft}[n_1(L)-\tilde{n}_t], \tag{7}$$

where L is the nanowire length, k_{ft} and k_{tf} are the rate constants of the transitions of adatoms from the sidewall facet to the nanowire