Modeling of semiconductor nanowire selective-area MOCVD growth

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Abstract. A numerical approach to the determination of gas kinetics in the case of non-planar nanostructure growth via the selective-area metal-organic chemical vapor deposition is developed. The direct simulation Monte-Carlo method is utilized to model the rarefied gas flow of precursor particles nearby the substrate. The computation is performed for the GaAs nanowire growth via the selective-area metal-organic chemical vapor deposition. The model allows the quantitative description of the decrease of nanowire length with the increase of distance between nanowires (the so-called synergetic effect). The optimal pitch of the mask that corresponds to the maximal nanowire length is found for typical growth conditions. In particular, our calculation shows that the optimal pitch increases with the increase of the nanowire diameter.

1. Introduction
During the last decade, much interest has been focused on the selective-area metal–organic chemical vapor deposition (SA-MOCVD) growth of semiconductor III-V nanowires (NW) [1-3]. This method facilitates the formation of highly uniform NW array and has high productivity compared to molecular-beam epitaxy technics. As a result of the intensive studies, the growth conditions of III-V NW have been found. Also, the following facts regarding the impact of the mask size and pitch on the NW morphology have been estimated: (i) at the mask edges, the NW growth rate is usually several times higher than that in the middle part of the mask [3, 4]; (ii) the NW growth rate decreases with the increase of the mask window size [1, 5]; (iii) the increase of the mask pitch p leads to the increase [6] or decrease [1] of the NW length. The first dependence is explained by the additional gas-phase and surface fluxes of species from the area without the mask windows to the NW array [3, 4]. The second dependence is explained within the models [4, 5] from which it follows that the NW growth rate is inversely proportional to the NW diameter or squared diameter. The models also claim that the NW length is proportional to the area per one NW, i.e. squared pitch, at any value of p. Consequently, the third dependence can not be completely described by these models. The dependence of the NW length on the pitch can be explained quantitatively within the model [7] constructed for the catalytic MOCVD growth of NW. The key assumption of the model is that two material fluxes should be considered: the initial precursor flux coming to the substrate and reflected flux produced by the precursor decomposition on the surface of catalyst droplet seated at the NW top facet. At large values of p, the decrease of the NW length is associated with the decrease of the reflected flux from the neighboring NW (the so-called synergetic effect).
In this paper, a quantitative model of SA-MOCVD NW growth is developed. The model enables the description of the non-monotonic dependence of the NW length on pitch. At large distances from the substrate, the precursor flux in the gas-phase is found by solving the diffusion equation assuming that the macroscopic velocity of gas flow in the boundary layer equals to zero (the boundary layer model [8]). Nearby the substrate, the Knudsen number for the precursor molecules can be large $Kn \approx 1$. In this case, the rarefied gas fluxes are determined by the direct simulation Monte-Carlo method [9]. The computation is performed for the GaAs NW growth on GaAs(111)B substrate coated by SiO$_2$ mask [1]. Within the model, the optimal pitch of NW growth is found to minimize the NW growth time.

2. Model
Consider a semiconductor substrate coated by a dielectric mask as shown in figure 1. The hexagonal-shaped mask windows of the size $d_0$ form the rectangular lattice of the pitch $p$. For simplicity, we consider a region of the substrate located far from the mask edges to neglect their influence. For all NWs within this region, the growth conditions are identical. Then, we divide the mask area into equal hexagons and construct regular prisms with the height $H$. It is sufficient to consider one of the equivalent prisms due to the translational symmetry of the system. Orient the $z$ axis perpendicular to the substrate in the direction from the lower base of the prism to the upper base. The height $H$ equals to the thickness of the boundary layer in which the material transport over the distances much larger than the diffusion length $\lambda$ in the gas-phase can be described by the diffusion equation. The ratio of the diffusion coefficient of the precursor to the boundary layer height characterizes the material transport to the substrate. Following the work [10], the value of $H$ is estimated by using the equation $H = (1/0.89)(D s_s/s_y/V)^{1/3}$, where $D$ is the diffusion coefficient of precursor, $s_s$, $s_y$ are the height and length of the reactor chamber, respectively, $V$ is the velocity of the gas flow.

The group V precursor pressure is much higher than the group III precursor pressure [1], therefore, the crystal growth is limited by the group III flux. Following the work [7], we consider the initial flux of group III precursor coming to the substrate and reflected flux of group III produced by collisions of precursor molecules with the NW facets or mask openings. In the experiment [1], the GaAs NWs were
synthesized at the growth temperature of 750 °C using trimethylgallium (TMGa) as a group III precursor. It is known that at such a temperature and the pressure of the carrier gas (H2 in our case) of 0.1 atm, TMGa molecules partially decompose in the gas-phase [8]. In the general case, the decomposition of TMGa molecules proceeds through a series of reactions that is often unknown [8]. For the sake of concreteness, the flux of monomethylgallium (MMGa) is considered as the initial flux in the further discussion [11]. As a result of single or multiple collisions with the GaAs crystals, MMGa molecules decompose producing gallium atoms that recoil back into gas phase. We neglect the possibility of the Ga atom to incorporate into a growing crystal without re-evaporation. Also, we suppose that MMGa decomposition on the mask is negligible [11]. To consider the surface diffusion of Ga atoms, the diffusion length on NW side facets and mask are introduced, $\lambda_i$ and $\lambda_s$, respectively [12]. Their values determine the collection areas of the growth material (figure 1). In the model, the surface diffusion lengths of MMGa molecules are put to be zero. Estimates made for the standard GaAs NW growth conditions [1] show that the gas-phase diffusion lengths $\lambda$ for the MMGa molecules and Ga atoms equal approximately 0.4 μm and 0.9 μm, respectively. The values of $\lambda$ are of the same order of magnitude as the sizes of system ($L$, $d_0$, $p$, where $L$ is the NW length) or larger. Therefore, the material transport is governed by diffusion only in the bounded region $h < z < H$, where $h >> \lambda$ (figure 1). In the region $0 < z < h$, the direct simulation Monte-Carlo method is used for the determination of the rarefied gas fluxes.

For the MMGa flux, the stationary diffusion equation

$$D \Delta C = 0,$$

where $D$ and $C$ are the diffusion coefficient and concentration of MMGa molecules, respectively, is solved with the boundary conditions

$$C(H) = C_0 \quad \text{and} \quad j(h) = -k C(h),$$

where $j$ is the MMGa flux density, $k$ is the effective reaction rate constant of the surface $z = h$. The solution of equation (1) is obtained in the form of $C = A z + B$, where $A$, $B$ are constant, neglecting the concentration dependence on $x$ and $y$. Then, the solution for the flux density $j$ is

$$j(h) = -\frac{k C_0}{1 + \frac{k (H - h)}{D}}.$$  \hspace{1cm} (3)

Following the work [11], the effective reaction rate constant $k$ can be expressed in terms of the effective sticking coefficient $\alpha$

$$k = \frac{\alpha / 4}{1 - \alpha / 2} v.$$  \hspace{1cm} (4)

Here $v = (8k_B T / \pi m)^{1/2}$ is the mean velocity of the MMGa molecules, $k_B$ is the Boltzmann constant, $T$ is the growth temperature, $m$ is the MMGa molecule mass. The coefficient $\alpha$ equals to $N_d / N$, where $N_d$ is the number of MMGa molecules decomposed on the GaAs crystals per second, $N$ is the total number of MMGa molecules crossed the surface $z = h$ in the direction to the substrate per second. Introduce the sticking coefficient $\alpha'$ that equals $N_0 / N_d$, where $N_0$ is the number of Ga atoms stuck to the GaAs crystals per second. The total Ga flux feeding the NW growth can be found by the formula $J = |j(h)| \alpha' S$ (in $s^{-1}$), where $S = 3^{3/2} p^2 / 6$ is the area of substrate per one NW, or

$$J = \frac{3^{3/2} \alpha' v C_0 p^2}{24(1 - \alpha / 2)\left[1 + \frac{\alpha (H - h)}{4(1 - \alpha / 2) D}\right]}.$$  \hspace{1cm} (5)

Note, we neglect the term to the total flux $J$ from the Ga atoms reflected from the region $h < z < H$. Strictly speaking, the diffusion equation for the Ga atoms should be solved with the boundary
conditions similar to (2) in the region $h' < z < H'$, where $h'$ and $H'$ are the boundary layer heights for Ga atoms. Expand (5) in powers of $\alpha$ (our calculations show that $\alpha$ can be treated as a small parameter, $\alpha < 0.5$) and, for a simple analysis, retain only the first term

$$J \approx (3^{3/2} / 24) v C_0 \alpha_{tot} p^2.$$  

Here $\alpha_{tot} = \alpha \alpha'$ is the total sticking coefficient, that equals $N_s / N$. In the general case, this coefficient depends on the geometry of the system, sticking coefficients and diffusion lengths of MMGa and Ga on the GaAs crystals and mask surfaces.

To find the NW length at the growth time $t$, we integrate the material balance equation

$$\frac{dL}{dt} = \frac{\Omega}{S} J$$  

with the initial condition $L(t_0) = 0$, where $dL/dt$ is the NW growth rate, $\Omega$ is the volume of the GaAs pair in solid, $S = 3^{3/2} / 6 d^2$ is the area of the top NW facet, $d \approx d_0$ [1] is the NW diameter, $t_0$ is the time between the switching on the material sources and complete filling of the mask openings (the so-called incubation time). By substitution (6) into (7), the following formula for the NW growth rate is obtained

$$\frac{dL}{dt} \approx \Omega v C_0 \alpha_{tot} p^2 / 4d^2.$$  

As the total flux, the incubation time is a function of the geometry of the system and material constants. If the reverse gallium flux to the substrate is neglected, the incubation time equals to infinity. This work is focused on the NW growth stage, therefore, a model scheme is used to account for the incubation time. For this purpose, the following initial condition is used $L(0) = L_0$, where $L_0$ is the effective NW length such that the NW growth rate equals to the mask filling rate during the incubation time. This length can be estimated by means of equating the area of the mask opening $3^{3/2} / 6 d_0^2$ to the area of the NW side facets $\pi d_0$, $L_0 \approx d_0 / 4$.

### 3. Results and discussion

Consider the case when the sticking coefficients of MMGa on the NW side facets, mask openings and mask surface [11] are negligibly small. Introduce the sticking coefficients of Ga on the top NW facets, side NW facets and mask, $\alpha_t$, $\alpha_s$ and $\alpha$, respectively (figure 1). Also, we take into consideration the Ga diffusion length on the NW side facets and mask, $\lambda_t$ and $\lambda$, respectively. The total sticking coefficient $\alpha_{tot}$ and, consequently, the NW growth rate are determined by the Ga atoms sticking to the part of the NW side facets of length $\lambda$ after single or multiple collisions with the NW side facets, mask surface or facets of the prism of height $H$. Note, that the reflection of species from the NW facets and mask surface is assumed to be diffuse, but the reflection from the facets of the system is specular. If $L \leq \lambda$ then the total sticking coefficient $\alpha_{tot}$ has a term of the diffusion flux from the substrate region of the radius $\lambda + d / 2$. For the determination of the dependence of $\alpha_{tot}$ on the parameters of the system in the first approximation, we neglect the collisions between species in the region $0 < z < h$ considering the free molecular flows. Thus, the coefficient $\alpha_{tot}$ is a function of the following parameters of the model: $p$, $d$, $L$, $\alpha_t$, $\alpha_s$, $\lambda_t$, $\lambda$. The parameters $p$ and $d$ are determined by the mask shape. The NW length $L$ is found during modelling. The material constant $\alpha_t$, $\alpha_s$, $\lambda_t$ and $\lambda$, strongly depend on the surface reconstructions that are often unknown. For the particular experiment, it is easy to estimate only the orders of these constants. Therefore, the parameters $\alpha_t$, $\alpha_s$, $\lambda_t$ and $\lambda$ should be treated as fitting parameters of the model.

The results of the calculation of $\alpha_{tot}$ by the direct simulation Monte-Carlo method are shown in figure 2. The dependences of $\alpha_{tot}$ on the NW length have two linear regions: with a high slope at
Figure 2. The dependence of the total sticking coefficient $\alpha_{\text{tot}}$ on the NW length $L$ at $d = 80 \text{ nm}, \lambda_f = 0.3 \mu\text{m}, p = 0.6 \mu\text{m}$ (a), NW diameter $d$ at $L = 3 \mu\text{m}, \lambda_f = 0.3 \mu\text{m}, p = 0.6 \mu\text{m}$ (b), sticking coefficient $\alpha_t$ at $d = 80 \text{ nm}, L = 3 \mu\text{m}, p = 0.6 \mu\text{m}$ (c) and pitch $p$ at $L = 3 \mu\text{m}, d = 80 \text{ nm}, \lambda_s = 0.5 \mu\text{m}$ (d) (shown by the white dots). The dependences of the total flux on the pitch at $L = 3 \mu\text{m}, d = 80 \text{ nm}, \alpha_f = 0.3, \lambda_s = 0.5 \mu\text{m}, C_0 = 0.646 \mu\text{m}^3$ are shown by the gray dots (d). The diffusion length on the mask $\lambda_s$ equals to 0 in the computation.

$L < 2.5\lambda_f$ and low slope at $L > 2.5\lambda_f$. The dependences of $\alpha_{\text{tot}}$ on the NW radius and sticking coefficient $\alpha_t$ are close to linear. The dependences of $\alpha_{\text{tot}}$ on the pitch have a maximum. At small values of $p$, $\alpha_{\text{tot}}$ increases as $1 - d^2 / p^2$, because the MMGa molecules adsorbed on the top NW facets recoil and escape the system. If a MMGa molecule enter the space between the NWs it sticks to the NW side facets with a high probability after several collisions. At large values of $p$, the decrease of $\alpha_{\text{tot}}$ is caused by the decrease of the probability that the MMGa molecules adsorb on the NW side facets and, consequently, decompose and, at the same time, by the probability that the Ga atoms escape the system increases. Here, it is necessary to emphasize the importance of the introduction of the reflected flux for the explanation of the experimental data. When we only consider the initial flux, the MMGa molecules decompose on the NW side facets as a result of single collisions and produce the Ga atoms that instantly incorporate with the probability $\alpha_t$. In such a case, the coefficient $\alpha_{\text{tot}}$ decreases slower than $1 / p^2$. Then, the total flux $J \sim \alpha_{\text{tot}} p^3$ is the increasing function at the large $p$ (figure 2, d). Let us assume that, as a result of single collisions, the MMGa molecules decompose
producing the Ga atoms, but the direct incorporation is negligible. Then, the coefficient $\alpha_{tot}$ is approximately a constant at large $p$ (figure 2, d). Note, if $\alpha_i < 0.1$ the dependence $J(p)$ is a weak decreasing function in the range of $p$ about 0.5 - 0.9 $\mu$m and this function becomes a constant in the range of $p$ larger than 1 $\mu$m. In this case, the calculations are not in quantitatively agreement with the experiment [1]. To obtain a satisfactory agreement with the data [1], we should assume that, after two collisions with the NW side facets, the MMGa molecules decompose producing the Ga atoms. Also, we neglect the direct incorporation of Ga atoms. Then, the coefficient $\alpha_{tot}$ decreases faster than $1/p^2$ and the total flux is the decreasing function at large $p$ (figure 2, d). This result can be interpreted as follows. The probability of decomposition of the MMGa molecule is small during the first collision. When a MMGa molecule collides with the GaAs crystals, the molecule becomes activated and, after the second collision, decomposes with a high probability.

It should be also noted that the NW growth rate $dL/dt$ decreases with an increase of $d$, because $\alpha_{tot}$ increases linearly with an increase of $d$ and $dL/dt \sim \alpha_{tot}/d^2$. We compare the results of modeling with the experimental data. The dependence of the NW length on the mask pitch is shown in figure 3. The parameters used in the computation are: $\alpha_i = 0.18$ (at the AsH$_3$ pressure $1 \times 10^{-3}$ atm), $\alpha_i = 0.32$ (at the AsH$_3$ pressure $5 \times 10^{-4}$ atm), $\alpha_i = 0.45$ (at the AsH$_3$ pressure $2.5 \times 10^{-4}$ atm), $\lambda_i = 0.3 \mu$m, $\lambda_i = 0$, $C_0 = 0.646 \mu$m$^{-3}$, $t = 1200$ s, $T = 750^\circ C$, $d = 80$ nm. At the large values of the mask pitch, the model predicts the decrease of the NW length that is in agreement with the experiment [1]. Thus, the synergetic effect can be described by the consideration of the gas fluxes with neglecting the surface diffusion on the substrate, i.e. at $\lambda_i = 0$. In the model, the decrease of the NW length with the increase of the AsH$_3$ pressure (figure 3) is described by the decrease of the sticking coefficient on the NW side facets $\alpha_i$. In figure 3, it is seen that there is a maximum of the NW length at $p_0 \approx 0.4-0.5 \mu$m. This maximum was not observed in the work [1], because the measurements were not performed at the small values of the mask pitch. By growing NWs at $p_0 \approx 0.4-0.5 \mu$m, it is possible to minimize the growth time. Therefore, the value of pitch $p = p_0$ can be called the optimal pitch for the particular growth condition. The figure 4 shows the optimal pitch dependence on the NW diameter.
The optimal pitch increases with the increase of $d$. The best-fit analysis shows that this dependence is close to a parabolic dependence. Note that the dependence of $p_0$ on the NW length (not shown) is increasing at $L < 0.3-0.5 \, \mu m$ and very weak at $L > 0.5 \, \mu m$ for $\lambda_i = 0.3 \, \mu m$.

In summary, the model of the SA-MOCVD growth of III-V NWs was developed. The model allows the quantitative description of the decreasing dependence of the NW length on the mask pitch. The role of the reflected flux of precursor in elucidating of this dependence was shown. The results of simulation are in agreement with the experimental data on the GaAs NW growth. The dependence of the optimal pitch that corresponds to the maximal NW length was found as a function of the diameter and length of NW.

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