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Stochastic simulation of nanowire growth in plasma-assisted molecular beam epitaxy

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ABSTRACT

A stochastic model of the growth of an ensemble of nanowires (NW) in a plasma-assisted molecular beam epitaxy is suggested. The model is based on a probabilistic description of surface diffusion, shading, multiple rescattering of atoms, and survival probability. The model is implemented in a form of a direct simulation Monte Carlo algorithm. We present a comprehensive analysis of the kinetics of NW growth from an initial height distribution around tens of nanometers to NW heights up to several thousands nanometers which corresponds to the physical growth time about of 3–4 h. We compare the simulation results with our recently developed phenomenological model and experimental results which show a good agreement. Our main finding concerns a remarkable time evolution of the nanowire height distribution: it turns out that under some conditions, the initially broad NW height distribution converges to a delta-function, which means, that a height equilibration happens independent of the form of the initial NW height distribution. This phenomenon is explained by the multiple rescattering of atoms between the NW surfaces.

1. Introduction

The synthesis of nanowires in a plasma-assisted molecular beam epitaxy has initiated exciting fundamental research and opened a way to innovative electronic devices [1,10,18,2,14,15]. The surface diffusion of adatoms on the substrate and along the NW vertical sidewalls can account for the NW lengthening during the growth phase once NW have been formed [8], but very little is known concerning the nucleation mechanisms leading to the self-induced formation of nanowires [4,7,14].

In [16] we have investigated, both experimentally and theoretically, the axial and radial growth of GaN nanowires upon a variation of the Ga flux during molecular beam epitaxial growth. An increase in the Ga flux promotes radial growth without affecting the axial growth rate. In contrast, a decrease in the Ga flux reduces the axial growth rate without any change in the radius. In [15] we have studied the time evolution of GaN nanowires grown on Si (1 1 1) substrates by plasma-assisted molecular beam epitaxy in the self-induced way, under the temperature of 800 °C. In these experimental study we have observed a NW height equilibration phenomenon where the height distribution was self-preserving in time. To explain this unexpected behavior, we have suggested in [15] a phenomenological stochastic model of NW growth based on a system of stochastic differential equations. This growth model of self-induced GaN nanowires involves the exchange of Ga atoms between nanowires: Ga atoms desorbed from the NW sidewalls readsorb on neighboring nanowires. This process favors the growth of shorter nanowires and gives rise to a narrow nanowire height distribution during the late stages of growth. The model however involves an unknown function $p(h)$ responsible for the scattering of atoms between the neighboring nanowires. This model being phenomenological, could not however explain why the NW height distribution in some growth experiments was not only self-preserving, but even narrowing with time. We mention that other types of nanowire size distribution narrowing are studied in [5,6].

To explain this narrowing height distribution during the NW growth and to validate the phenomenological model [15], we develop in this paper a direct Monte Carlo algorithm which simulates the bottom-up synthesis of a large ensemble of GaN nanowires. The model is based on probabilistic description of the surface diffusion, shadowing, multiple scattering of atoms on the neighboring nanowires, and survival probabilities.

By simulations carried out by this model we have calculated the unknown function $p(h)$ mentioned above, and confirmed the self-preserving behavior of the height-distribution. More interesting,

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we have found a stronger phenomenon: under some conditions, the initially broad height distribution converges to a delta-function, which means, that a height equilibration is narrowing with time independent of the form of the initial NW height distribution.

2. The phenomenological model

The phenomenological stochastic model we suggested in [15] can be shortly described as follows. The flux of adatoms is inclined with respect to the substrate normal, the atoms impinge on both the top and side surfaces of the nanowires. The nanowire is considered as a circular cylinder of radius r. Rotation of the substrate about its axis provides an incidence flux on the side surfaces from all directions.

The ensemble of nanowires is described by a system of stochastic differential equations for the NW height $h(t)$:

$$\frac{dh}{dt} = F\left[f(h) + \frac{2Z_d(h)\tan\theta}{r}\right] + \beta F\frac{Lp(h)}{r^2} \tag{2.1}$$

with the following initial conditions: the positions of the nanowires are randomly and uniformly distributed on the substrate surface. The radii of the nanowires are randomly distributed according to a lognormal probability density. The initial nanowire heights are also lognormally distributed with the relevant mean and variance taken from experiments as described in [15].

In (2.1) $h(t)$ is the NW height at the time instant t, r is the NW radius, F is the impinging flux of atoms taken as 4 nm/min. The function $f(h)$ governs the shadowing of the neighboring nanowire. It is defined as follows: $f(h) = \Theta(h - \eta + l\cot\theta)$ where η is the height of a neighbor nanowire, and l is the distance to this neighbor; θ is the angle between the incoming flux and the nanowire growth direction, $\Theta(x)$ is the Heaviside step function, and the sticking coefficient is taken to be 1. The increase of the nanowire volume $Adh = dt$ due to the direct flux is equal to $FAf(h)$, which gives the first term in (2.1). Here A is the cross-sectional area of the nanowire. Each term in Eq. (2.1) is divided by $A = \pi r^2$.

The second term in (2.1), $Z(h)$ is the height of the side surface region that provides the adatom diffusion to the top facet. The diffusion length is defined by $L = \sqrt{2D\tau}$, where τ is a mean NW life time, and D is a diffusion coefficient.

As long as the sidewall is not shadowed by the neighbors, $Z(h)$ is equal to the diffusion length L on the side surface. When the neighbors partially shadow the sidewall, $Z(h)$ decreases and becomes zero for a total shadowing of the side surface. A compact description of all these cases reads $Z(h) = \min(L; \max(h - \eta + l\cot\theta; 0))$.

The third term of (2.1) describes a collective contribution of the nanowire ensemble to the growth. The atoms desorbed from one nanowire can readsorb on another one. Atoms desorb from a nanowire at a height level z if the nanowire is not shadowed by the neighbors at this level and if its top absorbing part of length L is above this level. We take the density of desorbed atoms at a height z proportional to the total perimeter $p(z)$ of all such nanowires assuming that the distance between the nanowires is small enough and the atoms readsorb at about the same height as they desorb. Thus, $p(z)$ is calculated as the sum of perimeters of all nanowires that satisfy two inequalities, $h - l\cot\theta < z < h - L$. The total perimeter is normalized to the total number of nanowires. The contribution of the reabsorbed atoms to the increase of the nanowire volume is therefore proportional to $FLp(h)$, β in (2.1) is a constant related to the NW cross-section. More details of the evaluation of the function $p(h)$ is given in [15]. It should be noted that the definition of $p(h)$ involves some assumptions about the height profile of the free atoms which are not absorbed on the nanowires and substrate. We calculate this profile without any assumption by the direct Monte Carlo method developed in the next section.

To find the height profile of the function $p(h)$, we have calculated the collision frequency of adatoms with the NW sidewalls for each height layer. The radii and heights of all nanowires in the NW ensemble were fixed as $r = 1$ and $h = 50$ nm, respectively. We use the same notation, θ, for the angle between the incoming flux and the nanowire growth direction. When intersecting a NW side surface at a point $\mathbf{y}$, the adatom is reflected on the NW sidewall according to the Lambert diffusion reflection law in the half-space bounded by the plane tangent to the nanowire at the collision point $\mathbf{y}$. Explicit formulae for this reflection event are given in the next section. The atoms which collide with the substrate and the NW top are absorbed. We divide the height in non-overlapping layers $\Delta_i h,\ i = 1, K$. We calculate the number of atom collisions with the side surfaces of all nanowires in each layer and normalize the result on the number of simulated atoms. This gives an estimation of the mean collision frequency of atoms with a nanowire as a function of height.

In Fig. 1 we present the height profiles of the mean collision frequency with the nanowires for the case when after a collision, the atoms reflect with probability 1, i.e., there is no absorption on the NW sidewall. The curves on Fig. 1(a) shows that at the upper layer of the NW's boundary the collision frequency depends on the angle θ. Indeed, for the angles $\theta < 45^\circ$ the curves have a maximum value, while for larger value of this angle, the frequency first rapidly falls, and then is linearly decreasing when approaching the substrate level. The maximum value at the top of the NW layer appears because after the first collisions, a large portion of atoms leave the volume V in the upper direction. Clearly, this portion strongly depends on the angle θ. The same frequency curves are shown in Fig. 1(b) for different values of the coverage S. It is seen that the maxima are increasing with the increase of S, and the positions of these maxima are shifted to larger heights. With the decrease of the coverage S, the gradient in the collision frequency is decreasing. Note also that for high coverage values, the curves exceed the collision frequency value of 1.0 in the top layer which means, the multiple atom's scattering between the nanowires happens mainly in this top layer.

If the adatoms have a probability to be absorbed on the NW sidewall, which in reality happens indeed, then the drop of the collision frequency with the height decrease is much faster and has an exponential profile, see Fig. 2, where the calculations were carried out for the absorption probability equal to 0.1, and the collision frequency is presented in a log scale.

These direct simulation results support our choice of $p(h)$ made for the model (2.1), and can be used for its further improvements.

In [15] we have found the following remarkable property of the system of Eq. (2.1): with the time increase, the mean solution of this equation, which governs the height distribution in the NW arrays modeled, tends to a self-preserving distribution with two modes: the first, a small heights mode in the region of 100–300 nm, and the second, a large heights mode in the region of top NW heights. The small heights mode after reaching its stable form does not changing anymore with time. The top heights mode preserves its form around its mean height which almost linearly increases with time. Explanation of the behavior of the small heights mode is clear: the small nanowires being in the shadow regions are involved in more and more shadowing as the neighbor nanowires grow. In addition, the number of adatoms reaching the low heights is exponentially decreasing with the height, as the results presented in Fig. 2 show. There is no easy explanation of the behavior of the top heights mode. Indeed, one might thing that the initially variation in the heights of the NW array may only increase with time, since the random contributions to random NW heights can only increase the dispersion of the heights. But this