Contribution of droplet volume fluctuation to dispersion of nanowire length

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Abstract. In this work we study features of vapor-solid-liquid mechanism of nanowire growth. We consider variation of droplet volume during the growth caused by droplet depletion and refilling. Here we take into account the changes in material transport due to volume variation, which was neglected previously. We also discuss the impact of this effect on nanowire length distributions.

1. Introduction

Size uniformity of III-V nanowires (NWs) is predominant for many applications in optics and optoelectronics [1-3]. For vapor-solid-liquid (VLS) growth mechanism the homogeneity of final structures is primarily determined by features of nucleation process at the liquid-solid interface [3-6].

Commonly assumed approach to VLS mechanism implies layer-by-layer growth of nanowire when 2D island on top facet nucleates and then instantaneously spreads to form a new monolayer [3,6-12]. Most of theoretical models for VLS growth consider steady-state regime where monolayers nucleate randomly and independently from each other which results in Poissonian form for length distributions [9,10]. Meanwhile, there are few recent theories that take into account certain anti-correlation between the successive nucleation events and results in sub-Poissonian distributions of nanowire lengths [11, 12].

However, these models describe oscillations of concentrations in the droplet but neglect the change of radius and volume which, in general, has an impact on the material transport to the droplet. In this work we consider the volume variation due to droplet depletion and refilling after formation of each new monolayer. We study the role of variation of adatoms flux to the top of nanowire and discuss its impact on variance and distribution of nanowire lengths. Here we are not discussing the effect of gradual droplet inflation or deflation which were observed in case of self-catalyzed growth [13, 14], so we assume that volume around constant mean value $\langle V \rangle_t = \text{const}$. Also we do not consider the growth kinetics of ensembles of nanowires or effects of diffusion induced growth which can lead to much greater broadening of distributions than the effects considered in the current work [15].
2. Model
In our model we consider direct impingement as the only mechanism of adatoms transport to the droplet. Hence, the material balance implies for variation:

\[ \Delta V(t) = J \alpha V^{2/3} \Delta t - \pi R_{NW}^2 h \Delta L(t), \]  \tag{2}

where \( J \) is influx rate, \( R_{NW} \) is nanowire radius, \( \Delta t \) is the duration of a time step. The geometric factor \( \alpha \) depends on droplet contact angle [3]. For following numerical calculations we introduce dimensionless volume \( v = V/\pi R_{NW}^2 h \) to Eq. (2)

\[ \Delta v(t) = B v^{2/3} - \Delta L(t), \]  \tag{3}

with the coefficient \( B = \frac{\alpha J \Delta t}{\pi h R_{NW}^2} \). The first term in the right hand side of Eq. (3) corresponds to material influx to the droplet. Further we discuss the effect of its replacement by constant \( B \langle v \rangle^{2/3} \).

We model the layer-by-layer growth of nanowire and consider elongation \( \Delta L \) at each time step as a random variable dependent on droplet volume \( v(t) : \)

\[ \Delta L = \begin{cases} 
1 & \text{with probability } p(v) \\
0 & \text{with probability } 1 - p(v) 
\end{cases} \]  \tag{4}

Common approach assumes a very steep exponential dependence of the nucleation probability on the nucleation barrier through the Zeldovich nucleation rate [3,8-12]. Due to this very steep dependence we consider the nucleation barrier to be linear with the number of atoms in the droplet. Since the droplet volume proportional to the number of atoms inside we obtain exponential dependence for \( p(v) : \)

\[ p(v) = A_{exp} e^{\Gamma v(t)}, \]  \tag{5}

where \( A_{exp} \) and \( \Gamma \) are constants. We also consider linear dependence of nucleation probability on the volume of the droplet:

\[ p(v) = A_l v(t). \]  \tag{6}

Next, we apply the condition of constant mean volume \( \langle v \rangle = const \) to Eq. (3) and use Eqs. (5) or (6) to obtain \( A_l = \frac{2B \langle v^{2/3} \rangle}{\langle v \rangle} \) for linear dependence or \( A_{exp} = \frac{2B \langle v^{2/3} \rangle}{\langle exp(\Gamma v) \rangle} \) for exponential dependence of nucleation probability on droplet volume.

3. Results and discussion
For certain number of time steps \( t_{max} \) we repeat 400 times the calculation of nanowire length \( L = L(t_{max}) \) and evaluate the mean length \( \langle L \rangle \) and variance \( \sigma^2 \). For \( \langle v \rangle = 100 \) we perform two series of simulations with variable and constant material impingement to the droplet to investigate the impact on length homogeneity. In case of constant impingement we substitute the volume by its mean value in the first term in the right hand side of Eq. (3). We obtain much broader distribution with slightly smaller mean length in case of variable adatoms impingement as shown in Figure 1(a). We simulate the growth at different times changing \( t_{max} \) and study change of variance with \( \langle L \rangle \). We observe saturation of variance in case of constant material influx and almost linear increase for variable rate.
Meanwhile, both cases demonstrate similar dependences in the initial stage. Figure 1(b) summarizes simulation results for $\Gamma = 0.02$ and 0.04.

![Figure 1](image1.png)

**Figure 1.** (a) Histograms of nanowire lengths and (b) Variance dependence on mean length at constant and variable material impingement to the droplet. The inset shows the dependences at short lengths.

We repeat the same procedure at different $t_{max}$ for both dependences of nucleation probability (Eq. (5) and (6)) and observe linear increase of NW length variance with $\langle L \rangle$ in both cases. Figure 2(a) shows that calculated $\sigma^2(\langle L \rangle)$ linear dependences are less steep than Poissonian broadening with $\sigma^2\langle L \rangle$.

![Figure 2](image2.png)

**Figure 2.** (a) Variance dependence on mean nanowire length measured in number of monolayers; (b) Variance $\sigma^2$ to mean length $\langle L \rangle$ ratio variation with $\Gamma$.

In case of exponential law of nucleation probability the linear slope $\sigma^2/\langle L \rangle$ increases with decrease of parameter $\Gamma$ and approaches the slope of linear law when $\Gamma$ is around 0.01.

In conclusion we compare our results with the results of the previous studies with constant material influx to the droplet. Modeling of nucleation process during VLS nanowire growth in references [11, 12] demonstrates saturation of the NW length variance with time in accord with or results for constant impingement to the droplet. Moreover, our model shows that variance increase infinitely and linearly
with time or mean length when we take into account the fluctuation volume and its impact on material transport.

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