Length distributions of Au-catalyzed III-V nanowires in different regimes of the diffusion-induced growth

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Abstract. We present a model for kinetic broadening effects on the length distributions of Au-catalyzed III-V nanowires obtained in the growth regime with adatom diffusion from the substrate and the nanowire sidewalls to the top. We observe three different regimes for the length distribution evolution with time. For short growth times, the length distribution is sub-Poissonian, converting to broader than Poissonian with increasing the mean length above a certain threshold value. After the diffusion flux from the nanowire sidewalls has stabilized, the length distribution variance increases linearly with the mean length, as in the Poissonian process.

1. Introduction

Semiconductor nanowires (NWs) and in particular III-V NWs are considered promising for fundamental nanoscience as well as building blocks of the next generation electronic and optoelectronic devices. NWs allow for almost unlimited bottom-up bandgap engineering and can be grown on dissimilar substrates without dislocations [1,2]. For example, it is very difficult to grow defect-free InAs Stranski-Krastanow islands on silicon substrates (lattice mismatch 11.6%) [3], while high quality epitaxial InAs NWs can easily be grown on Si(111) if their diameter is smaller than the critical dimension for plastic relaxation (~ 25 nm) [4]. However, size (length and diameter) uniformity within the NW ensembles remains an issue for various electronic and photonic applications [5-7]. NWs obtained by Au-catalyzed vapor-liquid-solid (VLS) growth technique were previously thought, and sometimes without grounds, to have high degree of the length uniformity [8,9]. Broadening of the length distributions (LDs) induced by kinetic fluctuations are expected to be Poissonian [10,11] in the case of length-independent axial growth rates. Recent studies of III-V NW length statistics show that slow NW nucleation from the catalyst droplets resting on the substrate surface and surface diffusion of group III adatoms from the NW sidewalls lead to a considerable broadening of the LDs [12,13]. So far, the NW LDs were analysed for systems with negligible adatom diffusion from the substrate. However, in some VLS systems this transport mechanism dominates in the initial growth stage [14-17]. Consequently, in this work we investigate the effect of different kinetic pathways of surface diffusion on the NW LDs.
2. Model

We consider diffusion-induced growth of Au-catalysed III-V NWs limited by transport of group III atoms, deposited from vapor with the influx $I$ onto the droplet surface. We use the rate equations (REs) approach to describe the LDs over the ensemble of NWs \[11,12\]

\[
\frac{d n_0}{d t} = -K_0 n_0, \tag{1}
\]

\[
\frac{d n_s}{d t} = K_{s-1} n_{s-1} - K_s n_s, \tag{2}
\]

where $n_s$ is the surface density of NWs having the length of $s = L/h$ monolayers, with $L$ as the NW length and $h$ as the height of a monolayer.

According to the model of Ref. \[17\], the diffusion-induced axial growth rate of NWs at a time-independent radius $R$ depend on the NW length $L$ and the diffusion lengths of surface ($\lambda_s$) and sidewall ($\lambda_f$) group III adatoms:

\[
\left(\frac{dL}{dt}\right)_{\text{diff}} = V \frac{BU(L/\lambda_f) + C}{U(L/\lambda_f)}. \tag{3}
\]

Here, $V \equiv \Omega_s \cos \alpha$ is the normalized influx from vapour, with $\Omega_s$ as the elementary volume in the solid phase, $\alpha$ is the beam angle with respect to the substrate normal (we write all the equations using the language of molecular beam epitaxy). The radius-dependent coefficients $B$ and $C$ describe the diffusion fluxes originating from the NW sidewalls and the substrate, respectively, which are determined by the adatom activities in the liquid droplet ($\theta_l$), on the NW sidewalls ($\theta_f$) and on the substrate ($\theta_s$) according to \[17\]

\[
B = \frac{2\lambda_f \tan \alpha}{2\pi R} \left( 1 - \frac{\theta_l}{\theta_f} \right), \tag{4}
\]

\[
C = \frac{2\lambda_f}{R} \left( 1 - \frac{\theta_l}{\theta_s} \right). \tag{5}
\]

For a dilute ensemble of NWs, the $F$ function is given by $F = K_i(R/\lambda_s)/K_0(R/\lambda_s)$, where $K_i$ are the modified Bessel function of second kind of the order $I$ \[17\].

When the diffusion lengths and the NW radius are much larger than the lattice constant, the function $U$ is reduced to \[17\]

\[
U(L/\lambda_f) = \sinh \left( \frac{L}{\lambda_f} \right) + b \frac{\lambda_f}{\lambda_s} F \left( \cosh \left( \frac{L}{\lambda_f} \right) - 1 \right), \tag{6}
\]

with $U' \left( \frac{L}{\lambda_f} \right) = dU/d \left( \frac{L}{\lambda_f} \right)$ in Eq. (3). In Au-catalysed VLS process, NWs emerge from pre-existing gold droplets, which initially have the surface density $n_{tot}$. During growth, the sum of the surface densities of differently sized NWs and the remaining surface droplets stays constant, yielding the conservation of zero moment of the LD: $n_{tot} = \sum_{s>0} n_s = \text{const}$. Using Eq. (3) and neglecting the direct impingement term with respect to diffusion, we can rewrite the REs given by Eqs. (1) and (2) in terms of the normalized LD $f_s = n_s/n_{tot}$ and the dimensionless time $\tau = \frac{V}{h} t$.
\[
\frac{df_0}{d\tau} = -v_0 f_0, \tag{7}
\]

\[
\frac{df_s}{d\tau} = v_{s-1} f_{s-1} - v_s f_s, \tag{8}
\]

with

\[
v_s = \frac{ds}{d\tau} = \frac{B U(x) + C}{u'(\frac{x}{\Lambda_f})}. \tag{9}
\]

Here, \(\Lambda_s = \frac{\lambda_s}{h}\) and \(\Lambda_f = \frac{\lambda_f}{h}\) are the diffusion lengths measured in numbers of monolayers, \(C = \frac{2 \Lambda_s F}{r} \left(1 - \frac{\theta_1}{\theta_s}\right)\), and \(F = K_1(r/\Lambda_s)/K_0(r/\Lambda_s)\), with \(r = R/h\) as the dimensionless NW radius.

**Figure 1.** Three regimes of the axial growth rate versus the NW length: decrease of \(v_s\) due to diminishing diffusion flux from the substrate (I), its increase in the intermediate range where group III atoms are collected from the entire NW length (II), and stabilization after a certain length when the group III atoms are collected only from the topmost section of a NW (III).

### 3. Results and discussion

We can now numerically solve the REs given by Eqs. (7) to (9). We observe different growth regimes corresponding to different dependences of the \(v_s\) on the NW length. Figure 1 shows the growth rate versus length obtained from Eq. (9) at \(r = 40, \Lambda_s = 150, \Lambda_f = 310, B = 15.5, C = 5\). The \(v_s\) first decreases due to diminishing diffusion flux from the substrate, then increases at intermediate lengths as long as the material is collected from the entire NW length [11] and finally saturates to a constant for long NW that collects the material only from its topmost section with a length on the order of \(\Lambda_f\). Such a behavior has been observed experimentally and described theoretically [17]. In regime (I) with decreasing \(v_s\), numerical solution of the REs gives rather uniform LDs which appear narrower than Poissonian as shown in Figure 2 (a). When the NW length exceeds the threshold value \(s_{\text{min}}\) corresponding to the minimum of the growth rate, increasing \(v_s\) (regime II) leads to rapid spreading of the LDs which become broader than Poissonian as shown in Figure 2 (b). This process is similar to the diffusion-induced broadening described in Ref. [11]. For longer NWs whose length exceeds the sidewall diffusion length, the growth rate stabilizes to a constant, which corresponds to regime III.
Figure 2. NW LDs obtained by numerical integration of Eqs. (7) and (8) with the growth rates given by Eq. (9) (thick lines) in regimes I (a) and II (b), compared to the Poissonian LDs (thin lines).

Analytical solution for the LDs obtained in Ref. [11] predicts that the LD variance scales as the mean length $\langle s \rangle$ in the case of $s$-independent growth rate and is proportional to $\langle s \rangle^2$ in case of $s$-linear growth rate. This property is confirmed by Figure 3 showing the variance versus the mean length, which becomes linear for NWs much longer than the diffusion length $\Lambda_f$. The variance increases faster than linear in the intermediate growth stage corresponding to regime II with an increasing growth rate. In contrast to the results of Ref. [11], a sharp change from superlinear to linear regime just above $\Lambda_f$ is replaced by a smooth transition between them. This difference is related to a more precise expression for the growth rate used here compared to the one in Ref. [11].

Figure 3. Variance of the NW LD versus the mean length obtained from Eqs. (7) to (9) (thick lines), compared to the linear Poissonian variance (thin lines). The inset shows the same dependence for short NWs. Dashed line shows the diffusion length of adatoms on the NW sidewalls $\Lambda_f$.

Quite interestingly, ensembles of short NWs feature sub-Poissonian variance that has not been reported so far, even in modelling. This is explained by the fact that a very limited number of works consider growth rates that decrease with the NW length. In real systems, this initial narrowness may be
hidden by the nucleation randomness for the NW themselves [12], disregarded in this study. In our modelling, the LDs narrower than Poissonian can only be observed in regime I and strongly depend on the NW radius, assumed identical for all NWs in the ensemble. Figure 4 shows the variations of $v_s$ and the LD shapes with the NW radius $r$. For large radius $r = 100$, the growth rate shows very slow length dependence that corresponds to almost Poissonian LD. For smaller radii, the length dependence of the growth rate becomes steeper and this effect narrows the LD.

Figure 4. Growth rate dependences on the NW length (a) and the corresponding LDs (b) for different NW radii $r$.

In conclusion, we have developed a model for the LDs of Au-catalyzed NWs growing by surface diffusion from the substrate surface and the NW sidewalls. Non-linear length dependence of the axial NW growth rate yields an interesting time evolution of the LDs whose nucleation rate is fast. At the beginning, the growth rate decreases with length and the LDs of sufficiently short NWs is sub-Poissonian. After the substrate diffusion flux is disabled, the axial growth rate increases with length and the LD rapidly spreads. Finally, after the diffusion flux from the NW sidewalls has stabilized, the LD variance becomes linear in the mean length, as in the Poissonian growth. These predictions are better for highly desired length uniformity than the earlier results of Ref. [11]. Overall, this study identifies major factors influencing the LD shapes in different stages of the diffusion-induced growth of NWs.

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