Theoretical analysis of the length distributions of Ga-catalyzed GaAs nanowires

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Abstract. In this work, we analyze the length distributions of self-catalyzed GaAs nanowires grown on in-situ processed SiOx/Si(111) substrates. We propose the model that accounts for (i) gradual emerging of Ga droplets and nanowires, (ii) fluctuation-induced broadening of the length distributions, and (iii) the effect of nucleation antibunching in individual nanowires on the length distribution shapes. Both theoretical and experimental results show the broadest length distributions on unprocessed substrate, narrowing in samples with processed oxide surface and sub-Poissonian length distribution in samples with an optimized substrate preparation.

Introduction
Gold-free self-catalyzed growth of III-V nanowires (NWs) by the vapor-liquid-solid (VLS) mechanism [1-3] is proven effective for monolithic integration of III-V materials with silicon electronic platform, opening new perspectives in the design of novel optoelectronic devices. Certain applications require a high level of size uniformity within the array of NWs in terms of their length and diameters [4]. It has recently been shown that the diameter homogeneity of self-catalyzed III-V NWs can be accessed in the so-called “self-focusing” growth regime [3,5]. Despite the fact that narrow NW length distributions (LDs) are more difficult to achieve, markedly sub-Poissonian LDs of self-catalyzed GaAs NWs were reported in Ref. [6]. However, this paper considers the statistics of NW lengths only in one specific growth protocol. In this work, we study theoretically and experimentally the LDs within the ensembles self-catalyzed GaAs NWs grown by different procedures yielding different NW densities, based on the experimental data of Ref. [7].

Description of experiments
During the sample preparation [7], in situ surface modification procedure (SMP) of native SiOx/Si(111) substrates was used for some samples that precedes the GaAs NW growth and decouples the Ga/SiOx interaction from the subsequent Ga-assisted NW nucleation. The SMP consisted of the following three steps: (1) thermal annealing of the substrate, (2) Ga deposition and droplet formation, and (3) second thermal annealing of the substrate for complete evaporation of the Ga droplets. The subsequent growth of GaAs NWs was performed at a substrate temperature $T$ of 615 °C, with the Ga flux fixed at 0.16 ML/s (as given by the equivalent growth rate on planar GaAs(001) substrate) and the V/III ratio of 11. The substrate was first exposed to the As$_4$ flux and the NW growth was initiated 10 min later by opening the Ga shutter. After 15 min of growth, the As$_4$ and Ga beams were interrupted simultaneously and the
substrate temperature was ramped down to 300 °C at a rate of 50 °C/min. We compare the distributions over the NW lengths measured for three samples prepared differently with or without SMP.

Model
In the growth process of Ref. [7], no Ga droplet pre-deposition is employed and hence the droplets always emerge concomitantly with NWs. The formation of new droplets enables the NW nucleation at the time-dependent rate $J(t)$. Within the model for the kinetics of Ga adatoms on SiO$_2$/Si(111) developed in Ref. [2], the nucleation rate of NWs emerging from the newly formed droplets is given by

$$J(t) = J_0 g^2 \left( \frac{t}{\Delta t} \right)^{3/2}.$$  \hspace{1cm} (1)

Here, $J_0$ is a constant, $g(\gamma) = e^{-\gamma} \int_0^{V(t)} dx e^{x^2} x^{-1/3}$ and $\Delta t$ is the characteristic nucleation time of NWs catalyzed by the randomly emerging Ga droplets. Without the effect of kinetic fluctuations [8], the NW LD can be obtained in the form [2]

$$f(L, L_{\text{max}}) = A g^2 \left( \frac{L_{\text{max}} - L}{\Delta L} \right)^{3/2}.$$  \hspace{1cm} (2)

with $A$ as the normalization constant and $L_{\text{max}}$ as the maximum NW length in the ensemble after a given growth time. The width of this LD is controlled by the parameter $\Delta L = V \Delta t$ which includes the length-independent instantaneous growth rate of NWs $V$ (limited by the As flux [1-3,5-7,9-11]).

Equation (2) does not account for kinetic broadening of the LD described by the second derivative in the continuum Fokker-Planck equation [8]. According to the general growth theory [8,11,12], more precise LD is obtained by convoluting the NW nucleation rate with Green’s function that describes time evolution of the LD starting from the delta-like peak at $t = 0$. According to Refs. [10,11], Green’s function in the case of length-independent axial growth rate of NWs is given by

$$F(s, t) = \frac{1 + e \rho(s)}{\sqrt{2\pi D(t)}} \exp \left[ \frac{-(\rho(s) - z(t))^2}{2D(t)} \right].$$  \hspace{1cm} (3)

Here, $s$ is NW length measured in the numbers of monolayers (MLs) ($s = L/h$, where $L$ is the NW length in nm and $h = 0.326$ nm is the height of the GaAs ML in the growth direction), $\rho(s) = (e^{s \varepsilon} - 1)/\varepsilon$ is the invariant size, $z(t) = (e^{V(t)} - 1)/\varepsilon$ is the most representative invariant size [8] and $D(t) = z(t) + e \varepsilon^2(t)/2$ is the variance of the LD. The $\varepsilon$ parameter determines the strength of nucleation antibunching caused by the instantaneous depletion of the droplet with its As in each ML growth cycle [10-14]. As shown in Ref. [13], the probability to nucleate new ML decreases by the factor $\exp(-\varepsilon^2)$ immediately after the formation of preceding ML. This effect leads to a sub-Poissonian Green’s function, while Poisson distribution corresponds to the VLS growth without antibunching (at $\varepsilon = 0$) [14]. The resulting LD is now obtained numerically from

$$f(s, t) = B \int_0^t dt \ F(s, \tau) J(t - \tau).$$  \hspace{1cm} (4)

with $F(s, \tau)$ given by Eq. (3), $J(t)$ defined in Eq. (1) and $B$ as the normalization constant. In this way, we are able to account for three effects: (i) random nucleation of Ga droplets and subsequently NWs, (ii) fluctuation-induced broadening of the LDs and (iii) possible effect of nucleation antibunching in individual NWs on the LD shapes. The maximum NW length $L_{\text{max}}$ and the growth rate $V$ in Eqs. (2) and (4) can be measured directly. Therefore, the shape and width of the NW LD in our model is controlled by the two parameters, the characteristic nucleation time $\Delta t$ and the antibunching parameter $\varepsilon$ which enters the $\rho(s)$, $z(t)$ and $D(t)$ values in Green’s function given by Eq. (3). Clearly, the $\Delta t$ is responsible for random nucleation of NWs from Ga droplets with the universal nucleation rate given by
Eq. (2), while the $\epsilon$ describes the narrowing effect induced by nucleation antibunching with respect to the Poissonian case with $\epsilon = 0$.

**Results and discussion**

We now compare the experimental NW LDs for samples 1, 2 and 3 and their fits by our model expressions. For sample 1, which was obtained without SMP (as in the case of self-catalyzed GaAs NWs described in Ref. [2]), we observe very broad and asymmetric LD shown in Fig. 1 (a), similarly to Ref. [2]. The deterministic curve given by Eq. (2) yields the fit which is almost identical to that obtained from Eq. (4) that includes kinetic fluctuations. The characteristic nucleation time equals 35 s. The NW nucleation step is quite long, leading to a long left tail of the LD. We can thus conclude that the main source of the LD width in the regime of simultaneous Ga and As deposition is the initial incubation time required to form the Ga droplets in the oxide holes [1], while the follow-up fluctuation-induced Poissonian broadening is almost negligible. This is confirmed by the fact that the observed LD features a pronounced asymmetry toward the long left tail corresponding to the NWs that have emerged later, without any noticeable transition to the symmetric Poissonian shape. Standard deviation of this LD, $\sigma = \sqrt{D}$ (both $\sigma$ and $D$ are given for the dimensionless LDs, i.e., measured in MLs and squared MLs, respectively) equals 1376 MLs, which is 16 times larger than the Poissonian standard deviation $\sigma_p = \sqrt{\langle s \rangle} = 88$ MLs for the measured mean length of 7789 MLs.

![Figure 1](attachment:image.png)

**Figure 1.** Measured LDs for samples 1 (a), 2 (b) and 3 (c) (histograms), fitted by Eqs. (2) and (4) in (a) and (b) and Eq. (4) in (c). The inserts in (b) and (c) show the zoomed views of the central parts of the histograms in comparison with the fits by Eqs. (2) and (4) and Poisson distribution for the same mean length (solid magenta lines). Standard deviations of the LDs are 1376 MLs in (a), 784 MLs in (b) and 60 MLs in (c). The LD shown in (c) is 1.6 times narrower than Poisson LD, whose standard deviation equals 98 MLs.

All three steps of the SMP were performed during the substrate preparation of sample 2. In this case, we observe more narrow LD shown in Fig. 1 (b), whose standard deviation $\sigma = 428$ MLs is more than two times smaller than in sample 1 for a similar mean length. However, this standard deviation remains
much larger than the Poissonian value of 89 MLs for $\langle s \rangle = 7956$ MLs. The deterministic LD given by Eq. (2) yields a much narrower LD than observed experimentally. Therefore, in this case the width of the resulting LD should be due to a combined effect of the NW nucleation randomness and kinetic fluctuations, best fitted by Eq. (4) with $\Delta t=1.3$ s. The extracted value of the antibunching parameter $\varepsilon$ stays within the interval of the fitting error, showing the effective absence of nucleation antibunching in this case.

Surprisingly narrow sub-Poissonian LD was obtained in sample 3 after the optimization of the SMP. Figure 3 (c) clearly demonstrates that this LD is noticeably narrower than Poissonian, with $\sigma = 60$ MLs against $\sigma_p = 98$ MLs for the mean length $\langle s \rangle = 9612$ MLs. The model fit gives a very short nucleation time $\Delta t$ on the order of 0.01 s, showing that all droplets emerge simultaneously after the optimized SMP and almost instantaneously give rise to NWs. The LD shape is almost symmetric for such a short nucleation delay. The best fit for Green’s function gives the value of $\varepsilon$ around 0.0002, corresponding to a weak nucleation antibunching. It leads, however, to saturation of standard deviation of Green’s function at the value of $1/\sqrt{2\varepsilon} \approx 50$ MLs with respect to infinitely increasing width in the Poissonian case [15].

Table 1. Statistical parameters of different NW LDs

| Sample                        | Growth temperature $T$ (°C) | Mean length $\langle s \rangle$ (MLs) | Standard deviation $\sigma$ (MLs) |
|-------------------------------|-----------------------------|--------------------------------------|-----------------------------------|
| Sample 1, this work           | 615                         | 7789                                 | 1376                              |
| Sample 2, this work           | 615                         | 7956                                 | 428                               |
| Sample 3, this work           | 615                         | 9612                                 | 60                                |
| Sample 1 of Ref. [2]           | 604                         | 13365                                | 1006                              |
| Sample 2 of Ref. [2]           | 624                         | 10172                                | 2196                              |
| Sample 3 of Ref. [2]           | 643                         | 7733                                 | 2248                              |

Table 1 summarizes the statistical parameters of our NW LDs along with the corresponding data for the three samples of Ref. [2] that were grown at different temperatures by simultaneously depositing Ga and As after the annealing step, as in our sample 1. Figure 2 shows that standard deviations for self-catalyzed GaAs NWs grown without SMP follow the clear trend to narrow up at lower temperatures due to a shorter nucleation time [2]. However, all these LDs are very broad and asymmetric, with a typical shape shown in Fig. 1 (a) and well described by Eq. (2). Their $\sigma/\sqrt{\langle s \rangle}$ ratios, showing the dimensionless LD widths with respect to Poisson distribution, are on the order of ten or even more. Introducing the complete SMP of SiOx/Si(111) substrates before depositing GaAs improves the length homogeneity within the NW ensembles. The narrowing effect is rather small for sample 2 but large for sample 3, where the resulting LD is narrower than Poissonian.

In Ref. [6], markedly sub-Poissonian LDs were systematically obtained within a range of the growth times for Ga-catalyzed GaAs NWs grown on SiOx/Si(111) substrates via a lithography-free procedure. Sub-Poissonian LDs reported in Ref. [6] were attributed to a combination of relatively fast nucleation of NWs and nucleation antibunching. Additionally, the collective effect of shadowing of the arsenic flux by neighboring NWs in the directional MBE deposition technique was shown to broaden the LDs of long enough NWs. Here, we only report the LDs corresponding to a fixed moment of time (15 min). Their time evolution will be considered elsewhere. However, we strongly believe that sub-Poissonian narrowing described here for sample 3 has the same origin as in Ref. [6]. As regards the differences in SMP for samples 2 and 3 that lead to the striking improvement in the length homogeneity, the full picture requires a detailed study of the initial nucleation step from differently prepared Ga droplets. At the moment, we note that (i) the resulting droplet/NW density in sample 3 is 30 times smaller than in sample 2 and (ii) the mean NW length in sample 3 is 1.3 times larger than in sample 2. The nucleation of Ga droplets on unpatterned SiOx/Si(111) substrates is a complex process that includes the Ga precipitation into the thermally annealed oxide openings [2]. Lower surface density of available holes makes it easier
to collect the Ga adatoms in the absence of competition for the gallium diffusion flux, which could be the first explanation of the faster nucleation in sample 3 than in sample 2. Longer NWs in sample 3 under very similar deposition conditions should be due to a smaller shadowing in the lower density array, which improves the length homogeneity according to Ref. [6]. Finally, the NWs of sample 3 are slightly thinner, and nucleation antibunching is known to be stronger for smaller diameter NWs [11,13,14].

![Figure 2](image-url)

**Figure 2.** Standard deviations of the GaAs NW lengths of this work and Ref. [1], normalized to the Poissonian value $\sqrt{\langle s \rangle}$. Dashed line corresponds to Poisson distribution with $\sigma/\sqrt{\langle s \rangle} = 1$.

In conclusion, we have developed a model that quantitatively explains the differences in the shapes and widths of the LDs of self-catalyzed GaAs NWs grown on SiO$_x$/Si(111) without pre-deposition of Ga and using different substrate preparation procedures. One of the samples shows sub-Poissonian narrowing of the LD. Therefore, the optimized SMP may be further used for obtaining highly-uniform ensembles of GaAs NWs and probably extended to other III-V NWs.

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