Journal of Physics: Conference Series

PAPER • OPEN ACCESS

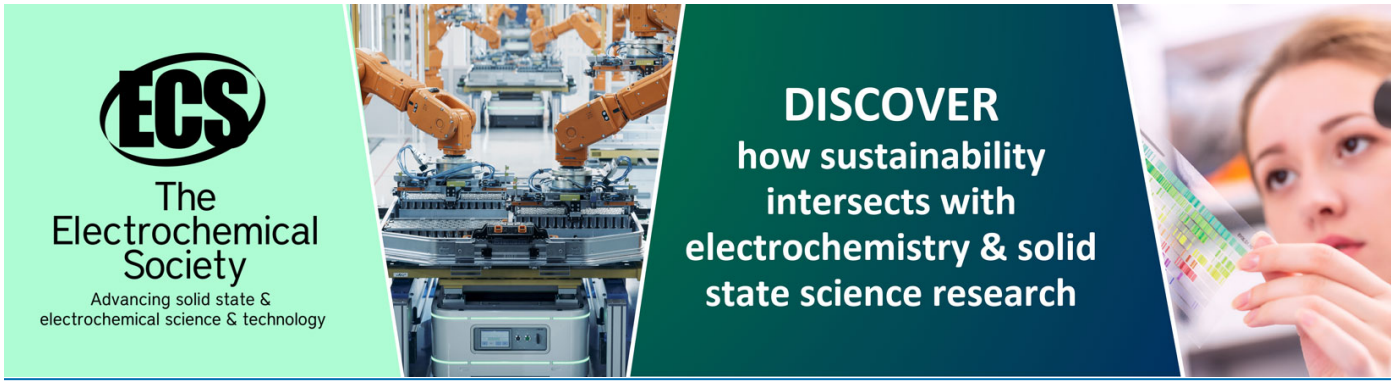
Self-equilibration of the radius distribution in self-catalyzed GaAs nanowires

To cite this article: E D Leshchenko *et al* 2016 *J. Phys.: Conf. Ser.* **741** 012033

View the article online for updates and enhancements.

You may also like

- Mechanism of self-assembled growth of ordered GaAs nanowire arrays by metalorganic vapor phase epitaxy on GaAs vicinal substrates
Premila Mohan, Rajesh Bag, Sunita Singh et al.
- Tailoring the diameter and density of self-catalyzed GaAs nanowires on silicon
Federico Matteini, Vladimir G Dubrovskii, Daniel Rüffer et al.
- Growth map for Ga-assisted growth of GaAs nanowires on Si(111) substrates by molecular beam epitaxy
Faebian Bastiman, Hanno Küpers, Claudio Somaschini et al.



This content was downloaded from IP address 3.15.153.69 on 05/05/2024 at 06:48

Self-equilibration of the radius distribution in self-catalyzed GaAs nanowires

E D Leshchenko[1,2], **M A Turchina**[2], **V G Dubrovskii**[2,3,4]

[1] St. Petersburg State University, Ulianovskaya st. 3, Petrodvorets, 198504 St. Petersburg, Russia
[2] St. Petersburg Academic University, Khlopina 8/3, 194021 St. Petersburg, Russia
[3] Ioffe Physical Technical Institute of the Russian Academy of Sciences, Politekhnicheskaya 26, 194021 St. Petersburg, Russia
[4] ITMO University, Kronverkskiy pr. 49, 197101 St. Petersburg, Russia

Abstract. This work addresses the evolution of radius distribution function in self-catalyzed vapor-liquid-solid growth of GaAs nanowires from Ga droplets. Different growth regimes are analyzed depending on the V/III flux ratio. In particular, we find a very unusual self-equilibration regime in which the radius distribution narrows up to a certain stationary radius regardless of the initial size distribution of Ga droplets. This requires that the arsenic vapor flux is larger than the gallium one and that the V/III influx imbalance is compensated by a diffusion flux of gallium adatoms. Approximate analytical solution is compared to the numerical radius distribution obtained by solving the corresponding Fokker-Planck equation by the implicit difference scheme.

1. Introduction

Theoretical analysis of self-catalyzed growth of III-V semiconductor nanowires (NWs) fabricated via the vapor-liquid-solid (VLS) method attracts great interest. Due to the absence of unwanted gold contamination, the possibility of integration of NW-based photonic devices on Si and pure zincblende crystal structure, such NWs look very promising for applications. The theoretically predicted [1,2] and experimentally confirmed [3] focusing effect whereby the NW radius converges to a certain stationary one in the course of growth is another important feature of Ga-catalyzed GaAs NWs which enables fabrication of size-uniform NW arrays and may play the key role for their optoelectronic applications. As it is known, the atomic flux of group III elements to the droplet consists of the direct atomic flux, proportional to the droplet surface area, and the diffusion from the NW sidewalls, proportional to the droplet base perimeter. Therefore, the regular growth rate of the NW radius in these conditions can be represented as $dr/dt = A + B/r$. Here, r is the dimensionless NW radius at time t, A and B are the kinetic constants. Depending on the V/III flux ratio, the value of A can be either positive or negative. In the former case, the radial growth is infinite, while in the latter case the radius tends to the stationary value $r_s = -B/A$ regardless of the initial condition. However, accounting for the hyperbolic tangent dependence of the diffusion on the NW length [4], the relationship between the NW radius and the growth time becomes more complicated. Radius dependences at different initial radii of individual NWs are presented in Figure 1.

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

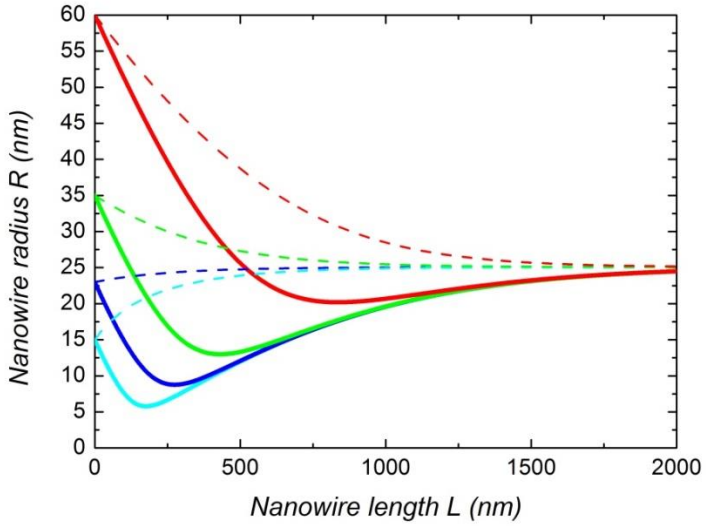


Figure 1. The time-dependent NW radius at different initial radii with (solid curves) and without (dotted curves) accounting for the hyperbolic tangent dependence of the diffusion on the NW length in the self-equilibration regime for $A=-1$ and $B=83.3$.

In the simplified model of Ref. [3] for the radius distribution function, the second derivative in the Fokker-Planck equation was not taken into account. This approximation neglects the role of kinetic fluctuations that should result in the Poissonian broadening of the radius distribution in the infinite growth regime. From an analysis of the radius-time dependence of individual NW, obviously, that in case of self-equilibration growth the radius distribution has to narrow up and tend to the delta function despite the initial droplet size distribution. The purpose of this paper is to describe theoretically the evolution of the NW size distribution.

2. Time evolution of the size spectrum

The After the completion of the nucleation phase, the evolution of the discrete length l or radius r distribution, corresponding to the nuclei growth, is described by the Fokker-Plank type kinetic equation in partial derivatives of the second order [5,6]:

$$\frac{\partial f_s(t)}{\partial t} = -\frac{\partial}{\partial s}\left[(W_s^+ - W_s^-) f_s(t)\right] + \frac{1}{2}\frac{\partial^2}{\partial s^2}\left[(W_s^+ + W_s^-) f_s(t)\right] \quad (1)$$

Here, $s=(r,l)$ is nanowire size, W_s^+ and W_s^- are the attachment and detachment rates. The first derivative describes the drift, whereas the second one describes the pure diffusion effect.

Under steady-state and As limited conditions and neglecting the surface diffusion of group V species, the NW elongation rate equals $W_l^+ - W_l^- = dl/dt = \nu_5$, where ν_5 is the direct atomic flux of group V elements. Then the evolution of the length distribution $f_l(t)$ is given by the Poisson distribution and for large values of l tends to a continuous Gaussian distribution with the dispersion $\sigma^2 = \langle l \rangle$, where $\langle l \rangle = \nu_5 t$ is the mean nanowire length [7]:

$$f(l,\langle l \rangle) \cong \frac{1}{\sqrt{2\pi\langle l \rangle}} \exp\left(-\frac{(l-\langle l \rangle)^2}{2\langle l \rangle}\right) \quad (2)$$

Now consider the case, when $W_r^+ - W_r^- = W_r^+ + W_r^- = dr/dt$. Using the continuum approximation, that is applicable at $r >> 1$, the evolution of the radius distribution $f(r,t)$ writes:

$$\frac{\partial f(r,t)}{\partial t} = -\frac{\partial}{\partial r}\left[\frac{dr}{dt} f(r,t)\right] + \frac{1}{2}\frac{\partial^2}{\partial r^2}\left[\frac{dr}{dt} f(r,t)\right] \tag{3}$$

Since the length-time dependence is linear, the radial growth rate can be expressed through the mean NW length $dr/d\langle l\rangle = a + b/r$ with constants

$$a = \frac{A}{\nu_5} = \frac{\Omega_l}{\Omega_{35} f(\beta)}\left(\frac{\nu_3}{\nu_5} - 1\right); \qquad b = \frac{B}{\nu_5} = \frac{\Omega_l}{\Omega_{35} f(\beta)} \frac{2\sin\alpha_3 \lambda_3}{\pi \chi_3} \frac{\nu_3}{\nu_5}. \tag{4}$$

Here, $\chi_3 = \chi_5 = 1/(\sin^2\beta)$ are the geometrical functions, $\chi_k V_k$ and $\nu_k = \chi_k V_k / h_L$ are the direct atomic fluxes ($k = 3,5$) in units of nm/s and ML/s, respectively, $f(\beta)$ is the geometrical function that reflects the relationship between the droplet volume and the contact angle β, α_3 is the incident angle of the Ga beam, Ω_{35} is the volume of a (III,V) pair in the solid, Ω_l is the group III atomic volume in the liquid state, h_L is the monolayer thickness, λ_3 is the diffusion length of the group III adatoms on the NW sidewalls. It can clearly be seen that the radius self-equilibration effect takes place at $\nu_5 > \nu_3$.

The continuum second order equation (3) has a simple form in terms of the new distribution defined by $g(\rho,t) = (dr/d\rho) f(r,t)$ with the invariant size ρ according to $d\rho/d\langle l\rangle = 1$:

$$\frac{\partial g(\rho,\langle l\rangle)}{\partial\langle l\rangle} = -\frac{\partial g(\rho,\langle l\rangle)}{\partial\rho} + \frac{1}{2}\frac{d\psi(\langle l\rangle)}{d\rho}\frac{\partial^2 g(\rho,\langle l\rangle)}{\partial^2\rho} \tag{5}$$

$$\frac{d\psi(\langle l\rangle)}{d\rho} = \left(\frac{dr(\rho)}{d\langle l\rangle}\right)^{-1} = \frac{1}{(a + b/r)}, \ \psi(\langle l\rangle = 0) = 0 \tag{6}$$

The invariant size is obtained by integration of the differential equation $d\rho/dr = (a + b/r)^{-1}$ with the boundary condition $\rho(r = 0) = 0$:

$$\rho = r/a - b/a^2 \ln(1 + ar/b) \tag{7}$$

The solution for the Green function $g_0(\rho,\langle l\rangle)$ to the equation (5) describing the evolution of the radius distribution from the point source $g(\rho,\langle l\rangle = 0) = \delta(\rho)$, can be approximated as the Gaussian:

$$g_0(\rho,\langle l\rangle) = \frac{1}{\sqrt{2\pi\psi(\langle l\rangle)}} \exp\left(-\frac{(\rho - \langle l\rangle)^2}{2\psi(\langle l\rangle)}\right) \tag{8}$$

Now we introduce the most representative invariant size r_* defined by $dr_*/d\langle l\rangle = 1 + b/r_*$ with $r_*(\langle l\rangle = 0) = 0$, what corresponds to the maximum of the size distribution relating the delta-like initial condition. The value of the most representative invariant size is obtained as the solution to transcendent equation

$$\langle l\rangle = \frac{r_*}{a} - \frac{b}{a^2}\ln\left(1 + \frac{ar_*}{b}\right) \tag{9}$$

The variance can be obtained by integration of the differential equation $d\psi(r_*)/dr_* = (d\psi(r_*)/d\rho)(d\rho/dr_*) = (a + b/r_*)^{-2}$ with the boundary condition $\psi(r_* = 0) = 0$:

$$\psi(r_*) = \frac{r_*}{a^2} + \frac{b}{a^2}\frac{r_*}{ar_* + b} - \frac{2b}{a^3}\ln\left(1 + \frac{ar_*}{b}\right) \tag{10}$$

The convolution of the Green function $g_0(\rho, \langle l \rangle)$ with the initial conditions in the terms of invariant size with the main radius r_0 and the variance ψ_0 gives the general solution to the kinetic equation (3):

$$f(r,t) = \frac{1}{|a + b/r|}\frac{1}{\sqrt{2\pi\Psi(r_*)}}\exp\left(-\frac{y^2(r,r_*)}{2\Psi(r_*)}\right) \tag{11}$$

$$y(r,r_*) = \frac{r - (r_* + r_0)}{a} - \frac{b}{a^2}\ln\left(\frac{ar + b}{(ar_* + b)(ar_0 + b)}\right) \tag{12}$$

$$\Psi(r_*) = \psi_0 + \frac{r_*}{a^2} + \frac{b}{a^2}\frac{r_*}{ar_* + b} - \frac{2b}{a^3}\ln\left(1 + \frac{ar_*}{b}\right) \tag{13}$$

Figure 2 shows the evolution of the radius distribution in the self-equilibration regime in the two cases where the initial mean radius $r_0 << r_s$ and $r_0 >> r_s$, for $a = -0.09$ and $b = 7.5$. As expected, the radius distribution decays at $r_0 >> r_s$ and grows at $r_0 << r_s$. Most importantly, the variance of both distributions gradually decreases so that they acquire a delta-like shape when approaching r_s. For comparison, the numerical solutions of the Fokker-Planck equation by the implicit difference scheme are also shown. The discrepancy between the numerical and analytical solutions is explained by the large step used in numerical calculations and a specific form of the initial condition implied in analytical solution. However, both results match quite well in this case. The analytical scheme does not allow one to consider situations with $r_0 \approx r_s$. The numerical solution of the Fokker-Planck equation by the explicit difference scheme in this case is given in Figure 3. The evolution of the distribution function in the regime of infinite growth is given in Figure 4. It is seen that the distribution spreads up as the NWs grow due to the known effect of Poissonian broadening.

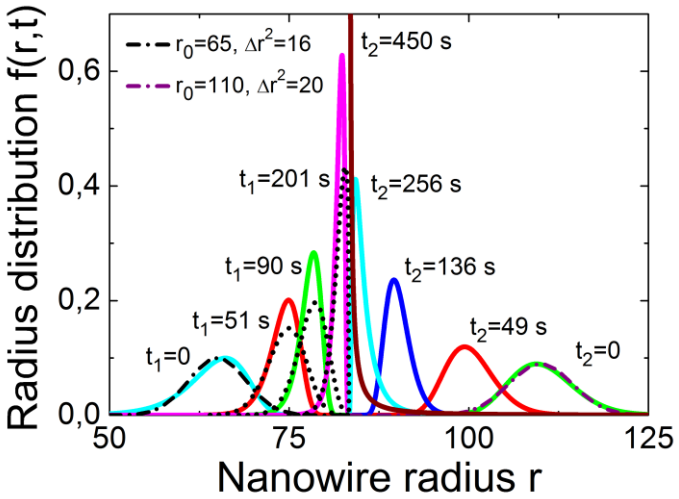


Figure 2. The radius distributions in self-equilibration regime. The solid curves are the analytical solution, the dotted curves are the numerical solution, the dashdotted curves are the initial distributions in Gaussian forms with the expected value r_0 and the variance Δr^2.

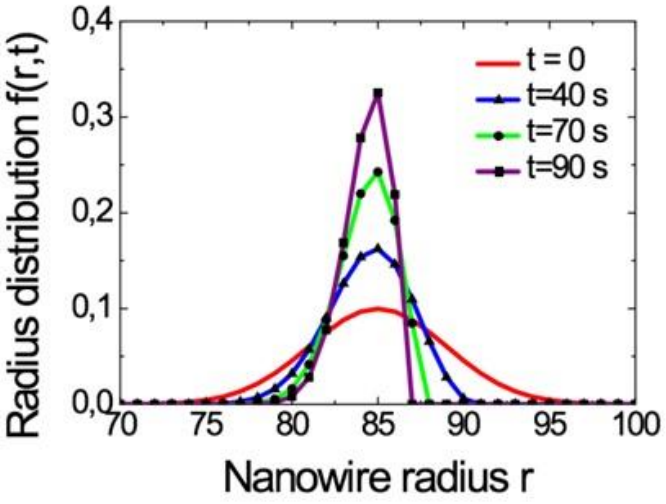


Figure 3. The numerical calculation for the radius distribution for $r_0 = 85$.

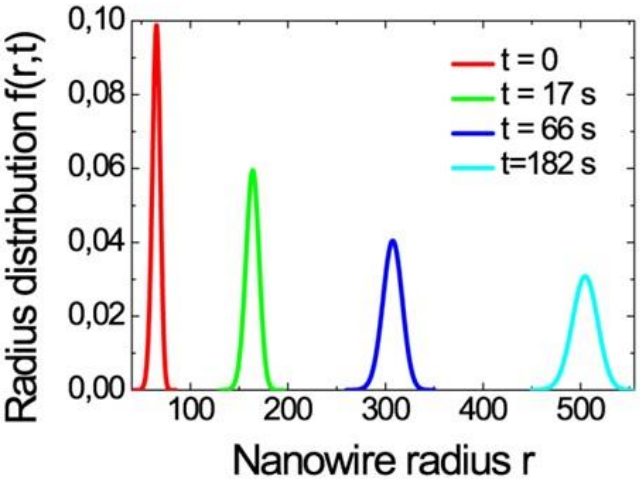


Figure 4. The radius distribution in infinite growth for $r_0 = 65$, $\Delta r^2 = 16$, $a = 0.005$ and $b = 60$.

The Fokker-Planck equation with different kinetic coefficients takes the form

$$\frac{\partial f(r,t)}{\partial t} = -\frac{\partial}{\partial r}\left[\left(a+\frac{b}{r}\right)f(r,t)\right] + \frac{1}{2}\frac{\partial^2}{\partial r^2}\left[\left(c+\frac{b}{r}\right)f(r,t)\right]. \quad (14)$$

Here, constants a and b are the same as in equation (4) and $c = \frac{\Omega_l}{\Omega_{35} f(\beta)}\left(\frac{\nu_3}{\nu_5}+1\right)$.

Analytical solution is the same as in equations (11) and (12) with the variance $\Psi_c(r_*)$

$$\Psi_c(r_*) = \psi_0 + \frac{1}{a^4}\left[acr_* - b(3c-a)\ln\left(1+\frac{ar_*}{b}\right) - b(3c-2a)\left(\frac{1}{1+ar_*/b}-1\right) + \frac{b(c-a)}{2}\left(\frac{1}{(1+ar_*/b)^2}-1\right)\right] \quad (15)$$

The analytical radius distribution and numerical solution are presented in Figure 5. There we can see that under the analytical solution the distribution function does not pass through the stationary radius (what associates with the transition to the invariant size), whereas under the numerical solution it does.

From a physical point of view, due to fluctuations, the distribution function moves to $r > r_s$ region under approaching of the distribution function to the stationary radius, but the function does not have time to return to the stationary value, because of slow growth (which is determined by the first derivative) in $r \approx r_s$ region, and grow further to achieve a stationary form. The form of the distribution function obtained by the numerical method is supported by the experimental data, however, it should be noted that the experimental distribution function is slightly narrower. In the $W_r^+ - W_r^- = W_r^+ + W_r^- = dr/dt$ model both fluctuations and drift speed decrease under approaching of the main radius to the stationary value, what explains the form of the distribution function obtained as a result of the numerical calculations.

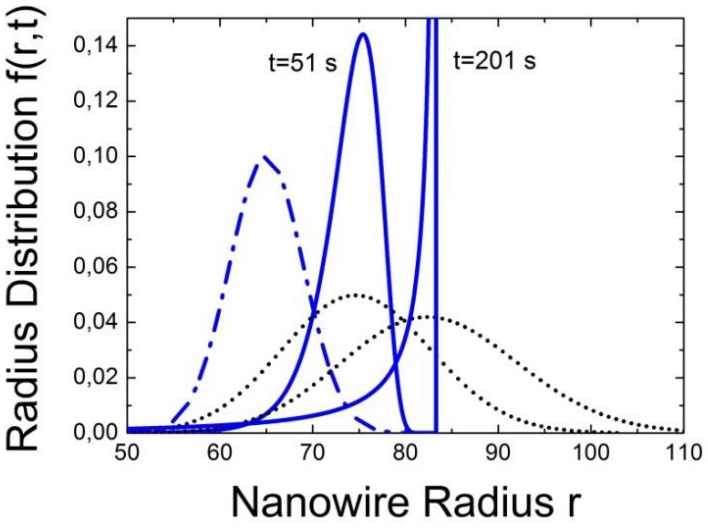


Figure 5. The radius distributions in self-equilibration regime for $a = -0.09$, $b = 7.5$ and $c = 0.116$. The solid curves are the analytical solution, given by equations (11), (12) and (15), the dotted curves are the numerical solution of equation (14), the dashdotted curve is the initial distributions in Gaussian form with $r_0 = 65$ and the variance $\Delta r^2 = 16$.

In conclusion, we demonstrate that the fluctuation-induced broadening of the size distribution can be completely suppressed by appropriate deterministic growth rate that renders the system into the self-equilibration regime. If the absence of radial NW growth, the NW top radius will follow that of the droplet and the NWs will be either tapered or reverse tapered at the beginning to match the stationary radius in the asymptotic stage. Whenever radial growth by a step flow is enabled [8,9], the NWs will have a uniform radius from base to top starting from the time moment at which the droplet reaches the stationary size.

References

[1] Priante G., Ambrosini S., Dubrovskii V. G. *et al*. 2013 *Cryst. Growth Des.* **13** 3976
[2] Tersoff J. 2015 *Nano Lett*. **15** 6609
[3] Dubrovskii V. G., Xu T., Díaz Álvarez A. *et al*. 2015 *Nano Lett.* **15** 5580
[4] Consonni V., Dubrovskii V. G., Trampert A. *et al*. 2012 *Phys. Rev. B* **85** 155313
[5] Dubrovskii V. G. 2009 *J. Chem. Phys*. **131** 164514
[6] Dubrovskii V. G. Nazarenko M. V. 2010 *J. Chem. Phys*. **132** 114507
[7] Dubrovskii V. G. 2013 *Phys. Rev. B* **87** 195426
[8] Dubrovskii V. G., Consonni V.,Geelhaar L. *et al*. 2012 *Appl. Phys. Lett*. **100** 153101
[9] Dubrovskii V. G., Consonni V., Trampert A. *et al*. 2012 Phys. Rev. B **85** 165317