

# Ga-assisted catalyst-free growth mechanism of GaAs nanowires by molecular beam epitaxy

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The mechanisms of Ga-assisted GaAs nanowires grown by molecular beam epitaxy are addressed. The axial and radial growth rates as a function of the Ga rate and As pressure indicate that on the opposite of what is observed in thin film epitaxy, the growth rate of the nanowires is arsenic limited. As a consequence, the axial growth rate of the wires can be controlled by the  $\text{As}_4$  pressure. Additionally, due to the small  $\text{As}_4$  pressure leading to nanowire growth, the deposition on the facets is very slow, leading to a much lower radial growth rate. Finally, we present a model that is able to accurately describe the presented observations and predicts a maximum length of nontapered nanowires of 40  $\mu\text{m}$ .

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## I. INTRODUCTION

Semiconductor nanowires are of interest for use as building blocks of future nanoscale devices and circuits. Equally important, nanoscale objects often exhibit new properties that can be exploited into new device concepts such as thermoelectric applications and/or solar cells.<sup>1,2</sup> As a consequence, fundamental and applied research on nanowires has dramatically increased in the last few years. One issue of crucial importance is to avoid the use of gold as nucleation and growth seed of the nanowires, as gold is a fast-diffusing metal that significantly harms the properties of semiconductors. To date, this has been achieved by the use of alternative metals such as aluminum and titanium or by simply avoiding the use of a catalyst.<sup>3–6</sup> These alternative methods involve new deposition techniques, which mean that the growth mechanisms necessarily differ from the standard Au-assisted vapor-liquid-solid/vapor-solid-solid (VLS/VSS) growth. As shown in the past, the full understanding of the growth mechanisms is essential for optical and electronic applications of nanowires.<sup>7,8</sup> Only by fully characterizing the microscopic processes it is possible to obtain the materials and their properties in a reliable and reproducible way.

Recently, catalyst-free growth has been achieved both with metal organic chemical vapor deposition and molecular beam epitaxy (MBE) techniques.<sup>9–12</sup> This type of growth has always been linked to the existence of a full or patterned  $\text{SiO}_2$  surface, whose role is to provide nucleation sites on the surface imperfections. In a recent work, we presented a detailed study on the nucleation stage of the nanowires and on the role of the  $\text{SiO}_2$  in the growth of GaAs nanowires.<sup>6</sup> In this paper, we present an extended study on the growth mechanisms, and it is structured as follows. After introducing the experimental frame in Sec. II, we show the growth results in Sec. III. The physical mechanisms are discussed in Sec. IV where a model is presented. The paper is concluded in Sec. V.

## II. EXPERIMENT

GaAs nanowires were grown in a high purity Gen-II MBE system. Two-inch GaAs wafers sputtered with a 10–20 nm thick silicon dioxide film were used as substrates. In order to

ensure a contamination-free surface, the substrates were dipped for 2 s in a buffered HF (10% HF) aqueous solution (1HF:2H<sub>2</sub>O), nitrogen blow dried, and transferred immediately after into the load lock of the growth chamber. After the HF dip, the thickness of the remaining oxide was more than 6 nm in all cases. In order to desorb any remnant adsorbed molecules of the surface, the wafers were heated to 650 °C for 30 min prior to growth. The synthesis was carried out at a temperature of 630 °C, arsenic ( $\text{As}_4$ ) partial pressure between  $3.5 \times 10^{-7}$  and  $2.3 \times 10^{-6}$  mbar, a Ga rate from 0.12 to 0.82 Å/s, and under rotation of 4 rpm. As a difference to standard VLS nanowire growth, no external metal catalyst was used for the nucleation and growth of the nanowires.

## III. RESULTS

GaAs nanowires were obtained under different growth conditions by changing the  $\text{As}_4$  pressure between  $3.5 \times 10^{-7}$  and  $2.3 \times 10^{-6}$  mbar and the Ga rate from 0.12 to 0.82 Å/s. The temperature was kept constant at 630 °C. A typical example of a nanowire formed under such conditions is shown in Fig. 1. In this case, the growth was realized on a (111)*B* GaAs wafer. The nanowires perpendicularly grow to the surface, following the (111)*B* direction of the underlying substrate. The orientation relation between the substrate and

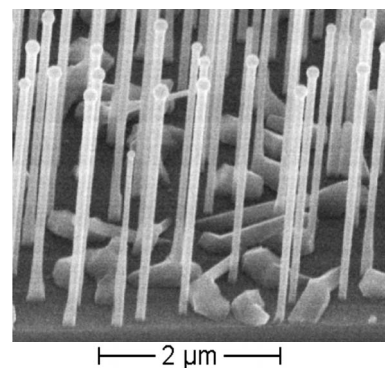


FIG. 1. Scanning electron micrograph of MBE grown GaAs nanowires on a (111)*B* GaAs substrate sputtered with a 10 nm  $\text{SiO}_2$  layer.

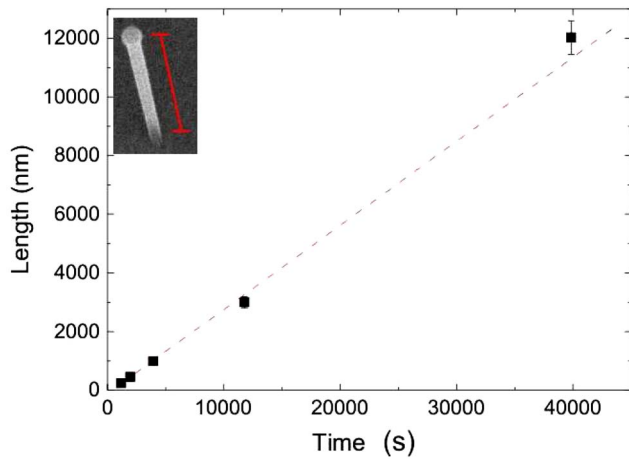


FIG. 2. (Color online) Time dependence of the length of the nanowires grown with a 0.25 Å/s Ga rate, As<sub>4</sub> pressure, and 630 °C.

nanowires is observed only when an oxide thickness smaller than 30 nm is used. We have found that the interaction of the reactive gallium with the SiO<sub>2</sub> pinholes induces the formation of nanocraters, a key prerequisite for the nucleation of the nanowires.<sup>13</sup> For thicker oxides, nanowire growth still occurs, although their orientation with respect to the substrate is random. More details on the nucleation and orientation mechanism can be found in previous publications.<sup>6</sup> At the top of the nanowires, a spherical cup is observed. This is similar to standard VLS/VSS grown nanowires,<sup>13</sup> with the difference that the typical Au droplet has now been substituted by a Ga rich droplet.

In order to get a more complete understanding of the growth mechanisms of the GaAs nanowires, the morphology of the nanowires was studied as a function of time for the range of conditions where nanowire growth occurred. In

Fig. 2, the length as a function of time during the nanowire growth is presented. It is important to note that the different points in the graph correspond to different growth runs realized under identical conditions. In this specific case, a partial pressure of  $7 \times 10^{-7}$  mbar As<sub>4</sub> and Ga rate of 0.25 Å/s were used. Clearly, the length linearly increases with time and no saturation in the growth rate is observed for growth runs up to 11 h. The growth rate can be deduced from the slope of the linear fit. In this case, we obtain a growth rate of 2.8 Å/s, which is more than a factor 11 of the nominal Ga rate. The existence of an offset in the beginning of the growth should also be noted. This is related to the existence of a nucleation time, as reported earlier.<sup>14</sup> The growth rate of nanowires was also measured for other growth conditions. First, we report on the effect of the Ga rate. As shown in Fig. 3(a), the growth rate of the nanowires does not significantly change when the Ga rates are varied from 0.12 to 0.82 Å/s. This result indicates that under these conditions, the growth of the nanowires is not limited by the amount of Ga adatoms arriving at the surface, as it is usually the case in epitaxial growth of GaAs thin films. We also investigated the morphology of the nanowires as a function of the Ga rate. Indeed, as shown in the inset of Fig. 3(b), wires grown under high Ga rate conditions exhibit an inverse tapered geometry. The diameter tends to increase as a function of time because of the large arrival rate of Ga adatoms that tend to enrich the Ga droplet at a higher rate. These results clearly indicate the role of Ga in the nanowire growth as a liquid reservoir for the GaAs deposition, as a result of the reaction with the incoming As<sub>4</sub> molecules.

The effect of the As<sub>4</sub> partial pressure was also investigated. The growth rate as a function of the As<sub>4</sub> pressure is plotted in Fig. 4. Between  $3.5 \times 10^{-7}$  and  $8.0 \times 10^{-7}$  mbar, the growth rate of the nanowires  $\Gamma_{NW}$  is proportional to the pressure of arsenic adatoms  $P_{As_4}$ . These results clearly indicate that arsenic is driving the growth. By fitting the data of Fig. 4, the growth rate can be expressed as follows:

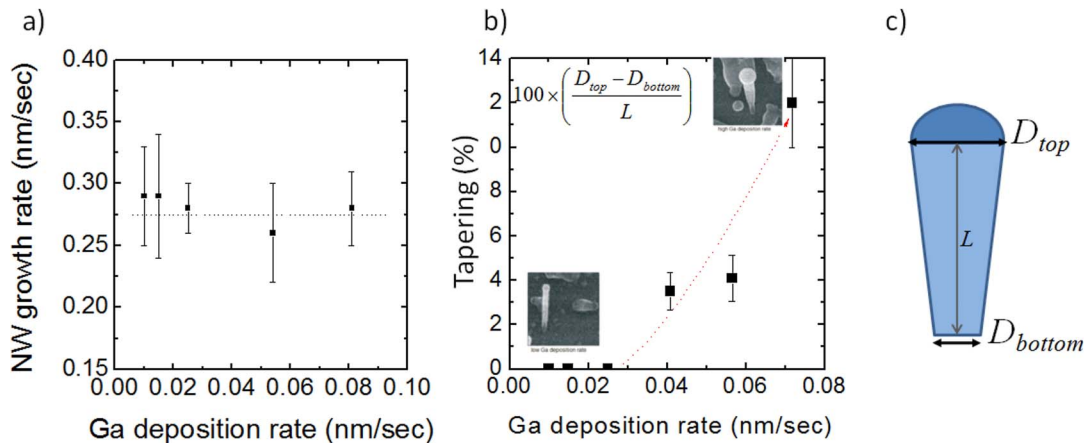


FIG. 3. (Color online) Effect of the Ga deposition rate: (a) growth rate of the nanowires as a function of the Ga deposition rate and (b) tapering of the GaAs nanowires as a function of the Ga rate, defined as the percentage increase of the diameter between the top and the bottom of the nanowire. For low Ga rates, no tapering is observed, which means that the diameter is homogeneous throughout the wire length. For the highest Ga rates, the diameter tends to increase during growth because the Ga droplet increases in size due to the large arrival rate of Ga adatoms. (c) Schematics of the nomenclature used for the tapering description.

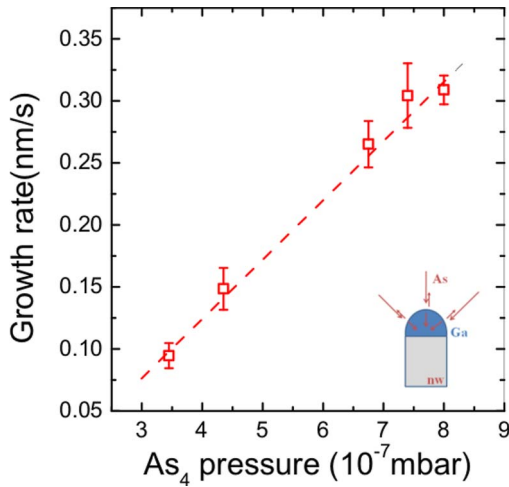


FIG. 4. (Color online) Growth rate of GaAs nanowires as a function of the  $As_4$  pressure. The inset schematically shows the  $As_4$  arrival, diffusion, as well as desorption from the Ga droplet.

$$\Gamma_{NW} = -7.37 \times 10^{-2} + 5.26 \times 10^5 P_{As_4}, \quad (1)$$

where the pressure of  $As_4$  is expressed in mbar and the growth rate in nm/s. From this expression, it is possible to deduce that  $1.4 \times 10^{-7}$  mbar is the  $As_4$  partial pressure at which the growth rate of the nanowires should be zero. This means that the growth of the nanowires cannot occur for  $As_4$  pressures below this value. The value of this minimum pressure for the existence of nanowire growth is related to the vapor pressure of arsenic at the surface of the Ga droplet. In the inset of Fig. 4, we show a model which can explain the growth of the nanowires. The  $As_4$  molecules impinge on the Ga droplet, decompose into As atoms, and diffuse through the droplet following the As gradient until they reach the interface with the nanowire. There, they alloy with the Ga atoms and form GaAs. The fact that the  $As_4$  vapor pressure at the Ga droplet surface is nonzero indicates that a small fraction of the impinging  $As_4$  molecules desorb before diffusing through the droplet and do not contribute to the growth. When the pressure of the impinging  $As_4$  equals the vapor pressure, the Ga droplet is in equilibrium and the growth of nanowires cannot occur.

By further increasing the  $As_4$  partial pressure up to  $4 \times 10^{-6}$  mbar, the nanowires still grow. However, for pressures between  $1 \times 10^{-6}$  and  $4 \times 10^{-6}$  mbar, we observe a large distribution of lengths. From those conditions, it is difficult to obtain any statistical trend in the axial growth rate. If the  $As_4$  partial pressure is further increased, then the growth of nanowires stops and only GaAs polycrystalline particles are observed.

The evolution of the diameter during growth was also studied for the growth conditions presented above. For Ga rates  $\leq 0.25$  Å/s, the diameter of the nanowires appears to be homogeneous through the length of the nanowire and tends to increase with time. An example is presented in Fig. 5, where the diameter of the nanowires grown with an  $As_4$  partial pressure of  $2.3 \times 10^{-6}$  mbar and a Ga rate of  $0.25$  Å/s is presented. The radial growth rate is  $0.07$  Å/s. Clearly, the

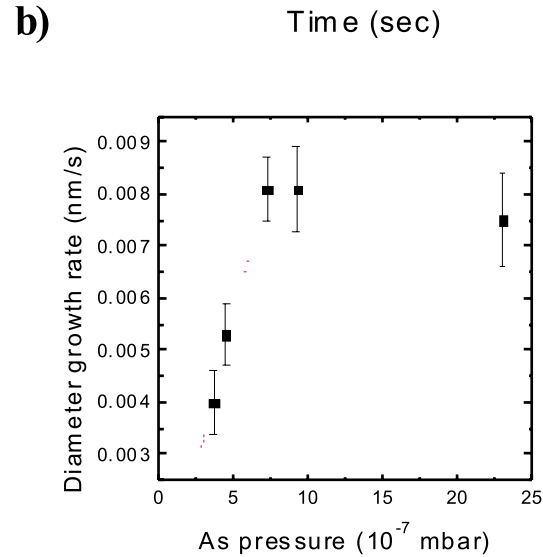
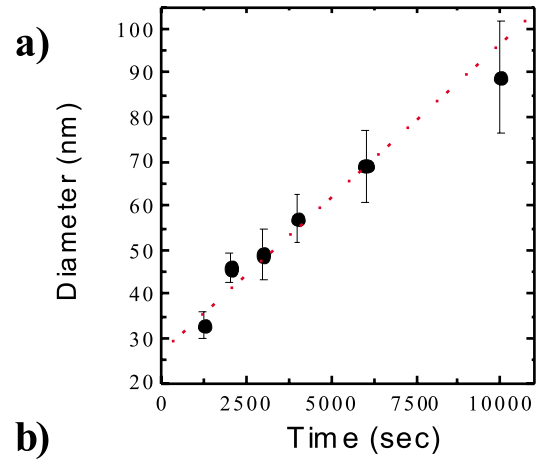


FIG. 5. (Color online) (a) Increase of the diameter of the nanowires as a function of the deposition time for an  $As_4 = 2 \times 10^{-6}$  mbar pressure. (b) Radial growth rate of the nanowires as a function of the  $As_4$  pressure. Saturation is achieved with  $As_4$  pressures higher than  $7 \times 10^{-7}$  mbar.

radial growth is a very small effect, but for long growth times, it cannot be neglected. The existence of a radial growth rate means that the impinging  $As_4$  molecules on the side facets of the nanowires also contribute to a relatively slow lateral growth. The growth rate can be translated into a characteristic incorporation time for Ga atoms,  $\tau_a$ ,

$$\tau_a = \frac{d_{ML}}{\Gamma_r} = \frac{0.14}{0.07} = 20 \text{ s}. \quad (2)$$

Here,  $d_{ML}$  is the distance between two Ga atoms and  $\Gamma_r$  is the radial growth rate.

This time is extremely long compared to a typical thin film growth. For  $As_4$  pressure up to  $7 \times 10^{-7}$  mbar, the radial growth rate linearly increases with the  $As_4$  pressure. For higher  $As_4$  pressures, the radial growth rate saturates. As was done for the axial growth rate, one could also, in principle, deduce the  $As_4$  vapor pressure on the (110) facet from the linear dependence of the radial growth rate. As shown in Fig. 5(b) a pressure of about  $1 \times 10^{-7}$  mbar would be deduced. This value is, however, much lower than the tabulated vapor

pressure of  $\text{As}_4$  on (110) facets, which is about  $4 \times 10^{-5}$  mbar.<sup>15</sup> We believe that this indicates that the facets of the nanowires may be continuously covered by a thin Ga layer. More specific investigations should be realized to confirm this, although they would confront significant technical difficulties.

#### IV. DISCUSSION

In this section, we provide a theoretical basis to explain the above exposed results, which concern the As-limited type of growth and the highly increased axial growth rate of the nanowires with respect to thin film growth. Equally important, our model should also provide information on some of the limits of this type of growth, e.g., what is the maximum length that can be obtained?

Some general considerations such as the role of the surface oxide and the growth temperature should be discussed before the model is presented in detail. As presented elsewhere, one of the key roles of the oxide is to provide a site for nucleation, as well as to offer wetting characteristics that favor the formation of Ga droplets.<sup>6</sup> Moreover, it has been shown that for temperatures of 630 °C, the sticking coefficient of Ga adatoms on  $\text{SiO}_2$  is close to zero due to a combination of an increase in the desorption rate and the diffusion length.<sup>16</sup> The consequence of this is that Ga adatoms are mobile on the  $\text{SiO}_2$  surfaces and can diffuse toward GaAs regions, where they can be incorporated. In this way, the atoms impinging on the substrate are supposed to diffuse through the oxide and then along the nanowire sidewalls and to the tip of the nanowire contributing to the Ga droplet.<sup>17,18</sup> During their path along the nanowire facets, they can also be incorporated or desorb. Schematics of these above presented processes are shown in Fig. 6. In stationary conditions, the diffusion of Ga adatoms along the facets toward the tip of the nanowire is described with the following equation:

$$D_f \frac{\partial^2 \eta}{\partial z^2} - \frac{\eta + 1}{\tau_f} - \frac{1}{\tau_a} = 0, \quad (3)$$

where  $D_f$  is the diffusion coefficient,  $\eta$  is the supersaturation of Ga atoms, and  $\tau_f$  and  $\tau_a$  are the characteristic times for desorption and for incorporation, respectively. As the incorporation time (20 s) is several orders of magnitude larger than the desorption time ( $10^{-4}$  s), the last term of Eq. (3) can be neglected and the process is assumed to take place with a constant diameter. The boundary conditions are (i) constant flux at the bottom of the nanowire and (ii) constant supersaturation at the top. The flux at the bottom resulting from the collection of Ga adatoms diffusing from the  $\text{SiO}_2$  region is equal to

$$W = -D_f 2\pi R n_{eq} \left. \frac{\partial \eta}{\partial z} \right|_{z=0}. \quad (4)$$

By considering a nominal Ga deposition rate  $\gamma_{\text{Ga}}$  of 0.25 Å/s, a collecting area  $r_c$  for each nanowire with a radius of about 0.5  $\mu\text{m}$ , and a volume per Ga atom in the GaAs zinc blende structure  $\Omega$  of 43.90 Å<sup>3</sup>, we have

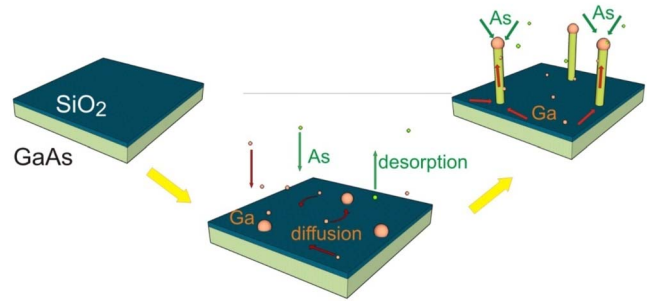


FIG. 6. (Color online) Cartoon of the proposed growth model. On the  $\text{SiO}_2$ , the seeds of the GaAs nanowires nucleate and grow, being continuously fed by the Ga adatoms that diffuse from the neighboring  $\text{SiO}_2$  surface, and form a droplet on top of the nanowires. The  $\text{As}_4$  molecules impinging on the Ga top droplet contribute to the axial growth of the nanowires.

$$W = \frac{\gamma_{\text{Ga}} \pi r_c^2}{\Omega} = 4.5 \times 10^5 \text{ atoms/s}. \quad (5)$$

$\eta(z)$  can be obtained by solving the diffusion equation with these boundary conditions. From this equation, the flux of Ga atoms along the nanowire is expressed as

$$J(z) = -D_f 2\pi R n_{eq} \frac{\partial \eta}{\partial z}. \quad (6)$$

As the diffusion coefficient  $D_f$  of Ga atoms on the GaAs (110) surface is about  $1.6 \times 10^5$  Å<sup>2</sup>/s at a growth temperature around 600 °C, the equilibrium concentration  $n_{eq}$  is equal to  $2.27 \times 10^{-4}$  atoms/Å<sup>2</sup> and a typical value for the nanowire radius  $R$  is 30 nm.<sup>18</sup> This flux provides Ga atoms to the catalytic droplet in order to keep it liquid and it is not the growth limiting factor; otherwise, a decrease in the growth rate should be observed for longer nanowires due to the reduction in the incoming flux. The flux of Ga atoms at the top of the nanowire decreases as the nanowire grows, as shown in Fig. 7. In order to maintain the same axial growth rate, the Ga diffusing flux at the top of the nanowire  $J(L)$  has to be equal to or higher than the incorporation rate  $\Gamma$  of Ga atoms from the liquid droplet into the nanowire. This incorporation rate can be easily estimated with this formula,

$$\Gamma_{IN} = \frac{\Gamma_{NW} \pi R^2}{\Omega} \approx 1.8 \times 10^4 \text{ atoms/s}, \quad (7)$$

where  $\Gamma_{NW}$  is the axial growth rate,  $R$  is the nanowire radius, and  $\Omega$  is the volume per Ga atom in the GaAs zinc blende crystal structure. The condition  $J(L) = \Gamma_{IN}$  is reached for a nanowire of about 40  $\mu\text{m}$  long. For longer nanowires, the flux  $J(L)$  is not able to keep the size of the droplet. Then, the droplet should diminish in size, resulting in a tapering of the nanowire. After the droplet is completely consumed, the axial growth rate should stop.<sup>19</sup>

#### V. CONCLUSION

The key parameters governing the Ga-assisted growth of GaAs nanowires obtained by molecular beam epitaxy have

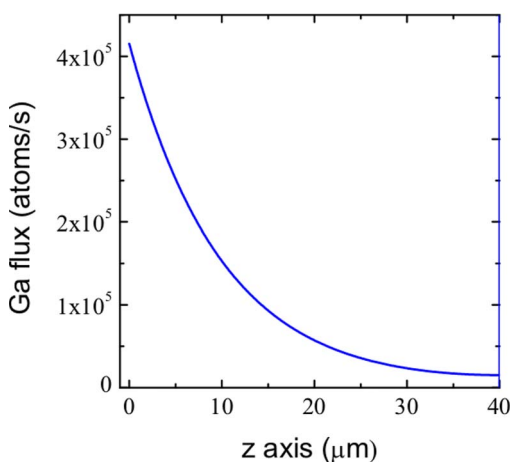


FIG. 7. (Color online) Flux of Ga atoms along the sidewall of a 40  $\mu\text{m}$  nanowire with respect to the axial coordinate  $z$ . Moving toward the tip of the nanowire, the flux decreases due to the desorption process.

been presented. The axial growth rate of the nanowires is shown to be arsenic limited; it is controlled by the  $\text{As}_4$  pressure. Due to the collection of Ga adatoms at the Ga droplet at the top of the wires, the growth rate of the nanowire is severalfold larger than the nominal Ga rate. The radial growth rate of the nanowires is on the contrary very slow, namely, more than 2 orders of magnitude lower than the axial growth rate. Our experimental results are explained by a theoretical model that also predicts a maximum length of nontapered nanowires of 40  $\mu\text{m}$ .

#### ACKNOWLEDGMENTS

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- <sup>19</sup>In the model, we have assumed the collection area around the nanowire to have a radius of 500 nm. The radius of the nanowire is 30 nm, which means that the ratio of the atoms directly impinging on the droplet is 0.36% of the total flux contributing to the formation of the Ga droplet. We therefore consider that the effect on the impingement of the Ga atoms on the maximum length for the growth of a nontapered nanowire is negligible.