Growth kinetics of GaAs nanoneedles on silicon and sapphire substrates

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(Received 23 December 2010; accepted 21 March 2011; published online 14 April 2011)

We study theoretically and experimentally the time evolution of GaAs nanoneedles grown by metal organic chemical vapor deposition on silicon and sapphire substrates. A theoretical model is presented which provides explicitly the nanoneedle length as a function of growth time under the assumption of a fixed aspect ratio. Experimental data confirms that the aspect ratio remains approximately constant during the growth. From fitting the experimental length-time dependences, we estimate the effective arrival rates and the Ga diffusion lengths as being 3.5 nm/min and 80 nm on the silicon and 2.9 nm/min and 400 nm on the sapphire substrates, respectively. © 2011 American Institute of Physics. [doi:10.1063/1.3575556]

Due to a very efficient relaxation of elastic stress on free sidewalls, laterally confined nanostructures, such as quantum dots (QDs) (Refs. 1 and 2) and nanowires (NWs),3–5 enable a radical increase in critical thickness for dislocation-free growth in lattice mismatched material systems. Stress relaxation is most efficient in NWs, where the critical thickness increases infinitely when the NW is smaller than a certain critical diameter.6 A coherent growth can, therefore, be more easily realized in NW geometry with a small footprint being dictated by the metal particle catalyzing the vapor-liquid-solid (VLS) process.7 NWs thus offer much wider opportunities for band gap engineering and substrate selection compared to thin films and even QDs, which is vital for numerous optoelectronic applications.3,8,9 However, VLS III-V NWs may suffer from several drawbacks. First, a 11.6% mismatched InAs/Si system10,11 catalyst droplet could lead to unwanted Au contamination.12 Second, the Au diffusion from the catalyst droplet could lead to unwanted Au contamination.12 Third, VLS grown III-V NWs often feature spontaneous zincblende-wurtzite polytypism13,14 and, despite many efforts in this field,15–17 the desired phase purity is still difficult to achieve. Fourth, GaAs NWs require a high growth temperature15,17 (or at least a high temperature step in order to initiate the VLS process18) that is incompatible in integrating with existing CMOS technologies.

The above issues have led to many attempts to develop catalyst-free procedures for the fabrication of highly anisotropic nanostructures. In Ref. 19, catalyst-free, single crystalline wurtzite GaAs nanoneedles (NNs) with 6°–9° hexagonal pyramid shape and an ultrasharp tip were obtained by molecular organic chemical vapor deposition (MOCVD) on roughened Si substrates. Later on, coherent GaAs NNs were grown by MOCVD on sapphire substrates with an extreme mismatch of 46% with no preliminary surface treatment.20 The model proposed in Ref. 21 shows that the energetically preferred aspect ratio of GaAs NNs is acquired at the nucleation stage and maintained throughout the subsequent growth stage by growing in a core-shell fashion. As in the case of NWs,17,22–25 theoretical and experimental studies of growth chronology may provide important information regarding the physical properties and kinetic constants of III-V NNs. In this work, we present a theoretical and experimental study of growth kinetics of GaAs NNs obtained by MOCVD on silicon and sapphire substrates.

Growth model of a single GaAs NN is shown in Fig. 1. The NN has a pyramidal shape with length L, base dimension D and regular hexagonal cross-section.19–21 The aspect ratio \( \beta = L / D \) and the corresponding taper angle \( \theta \) are assumed as being constant at any time \( t \). The growth under As-rich condition is assumed as being Ga-limited. The NN grows due to (i) direct impingement onto the sidewalls of surface area \( S_W = (3/2)\beta \sqrt{1+3/(16\beta^2)L^2} \) and (ii) migration of Ge adatoms from the diffusion ring of width \( \lambda \), giving a diffusion area \( S_D = (3\sqrt{3}/2)(R+\lambda)^2-R^2 \) around the NN base (see Fig. 1). The quantity \( \lambda \) is essentially the effective diffusion length of Ge on the surface,21,22 Re-evaporation processes are neglected, which is reasonable at a low surface.

FIG. 1. (Color online) NN growth model with the parameters described in the text. Left insert shows the scanning electron microscopy (SEM) image of GaAs NN on sapphire. Right insert schematizes the surface layer of height \( H = V_{Ge}t \) burying the NN root.
temperature. The total change in NN volume, \( \Omega = (3/8\lambda^2)L^3 \), per unit time is given by

\[
d\Omega/dt = \chi_W V_S + \chi_S V_S D.
\]  

(1)

The first term represents the volume of GaAs pairs adsorbed by the sidewalls, the second stands for the volume of GaAs pairs originating from Ga adatoms migrating from the diffusion ring on the substrate surface. The quantity \( V \) is the arrival rate, \( \chi_W \) and \( \chi_S \) are the pyrolysis efficiencies at the corresponding surfaces, thus the \( \chi_S V \) term gives the effective deposition rate.

Using the above definitions, Eq. (1) can be put in the dimensionless form

\[
\frac{dx}{dh} = \frac{a^2 x^2 + 4\beta x + 4\beta^2}{x^2},
\]  

(2)

where \( x = L/\lambda \) is the normalized length, \( h = (\chi_S V t)/\lambda \) is the normalized deposition thickness, and \( a = (\chi_W/\chi_S)^{1/3} (16\beta^2/3) - 1 - V_S/(\chi_S V) \). The quantity \( V_S \) represents the vertical growth rate of a surface layer (see Fig. 1). Integration of Eq. (2) with the initial condition \( x(h=0)=0 \) readily gives the reverse dependence \( h(x) \)

\[
h = \frac{x^2}{a^2} 2\beta \ln \left( \frac{a^2 x^2 + 4\beta x + 4\beta^2}{4\beta^2} \right)
\]  

\[
- \frac{2\beta}{a^2} \left[ \arctg \left( \frac{ax + 2\beta}{2\beta a - 1} \right) - \arctg \left( \frac{1}{a - 1} \right) \right].
\]  

(3)

The asymptotes at small and large lengths follow directly from Eq. (2)

\[
L \approx \lambda^{2/3} (12\beta^2 \chi_S V t)^{1/3}, \quad L \ll \lambda;
\]

\[
L \approx \left[ (16\beta^2/3) - 1 \chi_W V - V_S \right] t, \quad L \gg \lambda.
\]  

(4)

The first asymptote shows that the NN grows primarily by the surface diffusion as long as \( L \) is much smaller than \( \lambda \), with the length scaling with time as \( t^{1/3} \). At \( L \gg \lambda \), the diffusion-induced contribution disappears and the length becomes proportional to \( t \). Since NNs extend in both vertical and lateral directions, the exponential \( L(t) \) dependence [typical for straight NWs (Refs. 17 and 22–25)] is absent.

We now turn to the description of our growth experiments and the comparison of theoretical and experimental length-time dependences. The MOCVD growth procedure is the following. The silicon or sapphire substrates were first cleaned with acetone, methanol, and water. The growth was carried out in an Emcore D75 MOCVD reactor using tertiarybutylarsine (TBA) and triethylgallium (TEGa) as group V and III sources, respectively. The growth temperature was between 385 and 415 °C. The TBA and TEGa mole fractions were kept constant at 5.42×10⁻⁴ and 1.12×10⁻⁵, respectively, in a 12 l/min hydrogen carrier gas flow. More growth details can be found in Refs. 19 and 20.

Figure 2 shows 30° tilted SEM images of GaAs NNs obtained on the Si(111) substrates at \( T=400 \) °C after different growth times. Table I summarizes the details of NN growth evolution at \( T=400 \) °C. The data on the length and diameter are the average values of 15–20 NNs from the same sample (except for the smallest NNs where the results are averaged over only 5 NNs). In agreement with the model of Ref. 21, the aspect ratios for a given growth run are indeed approximately constant. The linear fits to the data presented in Table I yields the mean values of \( \beta=6.7 \) on the silicon and 5.7 on the sapphire substrate.

Experimental length-time curves were fitted by Eq. (3) with the above aspect ratios, \( \chi_S=\chi_W=1 \) and \( V_S=0 \). Theoretical \( L(t) \) dependence contains two fitting parameters: the arrival rate \( V \) and the diffusion length on the substrate surface \( \lambda \). From the best fits shown in Fig. 3, we deduce the parameters summarized in Table II. Investigation of parameter robustness shows that the fits are less sensitive to \( \lambda \) than to \( V \).

**Fig. 2.** GaAs NNs on Si(111) substrate at \( t=6 \) (a), 15 (b), 38 (c), 60 (d) and 90 (e) min.

**Fig. 3.** (Color online) Time evolution of GaAs NN length on Si and sapphire substrates.
TABLE II. Growth parameters of GaAs NNs.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$\beta$ (nm/min)</th>
<th>$V$ (nm/min)</th>
<th>$\lambda$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>6.7</td>
<td>3.5</td>
<td>80</td>
</tr>
<tr>
<td>Sapphire</td>
<td>5.7</td>
<td>2.9</td>
<td>400</td>
</tr>
</tbody>
</table>

so that 20% variation in $\lambda$ at fixed $V$ does not change significantly the curves shown in Fig. 3. This is well understood intuitively, because most of the time NNs grow due to the sidewall impingement, while the diffusion-induced contribution is important only at the very beginning of growth. The obtained value of 80 nm for the effective diffusion length of Ga on Si substrate is consistent with previously published data on the group III element diffusion during the NW growth (from tens to one hundred nanometers), while the 400 nm value on sapphire substrate is noticeably larger. A smaller diffusion length on the Si substrate is probably explained by the preliminary roughening. As for the arrival rate, the obtained values of 2.9–3.5 nm/min are rather small, yielding only 174–210 nm equivalent heights of a two-dimensional layer growing in 1 h. The NNs grow much faster, with average vertical growth rates of 46 nm/min on sapphire and 58 nm/min on Si, because their developed lateral surfaces absorb surrounding vapors very efficiently.

To conclude, we have developed theoretical model and presented the experimental data describing the growth kinetics of GaAs NNs on Si and sapphire substrates. It has been shown that GaAs NNs grow with a fixed aspect ratio determined by the material systems and the growth conditions. At the beginning of growth, the NN length scales with the time as $\lambda \sim t^{1/3}$. When the contribution from the surface diffusion disappears, the NN length becomes proportional to $t$. Numerical fits of experimental data allow us to deduce the arrival rate and diffusion length as being 3.5 nm/min and 80 nm on Si, and 2.9 nm/min and 400 nm on sapphire substrate, respectively.

This work was partially supported by contracts No. 02.740.11.0383, 2010-1.2.1-101-003-19 and 14.740.11.0592 with Russian Ministry of Education, scientific programs of Russian Academy of Sciences, grants No. 10-02-93107-a, 11-02-00445-a and 11-02-00727-a of Russian Foundation for Basic Research, Chang Jiang Scholar Endowed Chair Professorship at Tsinghua University, China, Li Ka Shing Foundation Women in Science Research Grants, and U.S. Department of Defense National Security Science and Engineering Faculty Fellowship.