Low growth rate synthesis of GaAs nanowires with uniform size

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Abstract
The growth of nanowires (NWs) with uniform sizes is crucial for future NW-based electronics. In this work, an efficient one-step process is introduced for the growth of uniform gallium arsenide NWs on the native oxide surface of Si, which could be even considered as an alternative for expensive and sophisticated patterning approaches. The proposed strategy considers a Ga pre-deposition step leading to the formation of droplets with homogeneous sizes. That is followed by controlled nucleation of gallium arsenide from those droplets only. Our key to controlling the nucleation of gallium arsenide is to perform the NW growth at temperatures above 580 ± 10 °C and low Ga fluxes. By this method, the statistical distribution of the length and diameter of the vertically grown NWs decreased to about 3%–6% of their averaged values. Moreover, 100% epitaxial growth was realized. Besides, the growth of undesired parasitic islands is addressed and accordingly suppressed. Our study focuses on NW low growth rates, which is so far not investigated in the literature and, could be of great interest e.g. for in situ growth studies.

1. Introduction
Gallium arsenide (GaAs) has shown the highest efficiency in single-junction solar cells [1], the best performance among field-effect transistors (higher than carbon nanotubes or graphene) [2], and further applied in photodetectors/sensors [3–5], and light-emitting diodes [6, 7]. Integration of superior GaAs optoelectronics and mature Si technology (CMOS) has shown to be a key toward future NW-based devices [8, 9]. In particular, in the last decades, the growth of self-catalyzed GaAs NWs as the integration method on Si substrates has been vastly studied [10–19].

The Si substrates in such studies are either covered by a thin Si oxide layer (∼1 nm native oxide) or a relatively thicker Si oxide (e.g., >15 nm thermal oxide). The epitaxial NW growth on thicker oxides has opened up the possibility of substrate patterning. That provides defined position and local growth surroundings for NW growth leading to controlled growth of self-catalyzed GaAs NWs onto Si [19–22]. However, patterning techniques require a high demand in terms of equipment, expertise, and time. On the other hand, on native Si oxide substrates, self-assembly of GaAs NWs involves various complex mechanisms and there is still a demand to control the characteristics of the growth [13, 23, 24]. In this work, we report on the growth of self-catalyzed GaAs NWs on Si(111) native oxide at low growth rates. In particular, the NW size distribution is narrowed and parasitic nucleation is suppressed, which are crucial fundamental demands in the production of GaAs NW-based devices. This work is organized as follows. In section 2, a humble review on the uniform growth of GaAs NWs on Si is made by the author, which highlights the line of thinking in the author’s approach and may be useful for the proposal of future studies in the corresponding community. In section 3, the experimental details are presented. In section 4, NW growth on native oxide is discussed. In particular, first, based on experimental results, the limitations of GaAs NW growth with simultaneous supply of Ga and As is explored. Our alternative method is then presented: (i) homogeneous Ga pre-deposition; (2) subsequent controlled NW growth only from the deposited Ga droplets. With a subsection entitled ‘further analysis’, we highlight that the epitaxial growth and density of the over-grown GaAs nano-objects of different types have been highly controlled. In section 5, we conclude our findings.
2. Synthesis of uniform GaAs nanowires in literature

On silicon native oxide substrate, a common approach to grow self-catalyzed GaAs NWs is by the simultaneous supply of As and Ga molecular beams. In this approach, one could tune the NW characteristics on a given sample by altering the substrate temperature, and source material fluxes. Therefore, NW density (0.01–1 μm⁻²) and diameter (10–200 nm) can be manipulated in wide ranges. However, by this approach, it seems not possible to modify the growth density and NW diameter independently; moreover, the number ratio between the NWs and PIs (NW/PI) can not be significantly improved [13, 25–29].

It is widely known that natural openings (pinholes) on native Si oxide are the preferential nucleation sites for Ga and GaAs material [30]. Besides the growth optimization, another degree of freedom to manipulate the NW growth characteristics is by controlling the size of the oxide pinholes. To this end, in literature, it is suggested to treat the native Si oxide substrates prior to the growth by the following general approaches:

(i) The oxide layer is thinned by wet etching or annealing. In this way, aside from a planar oxide removal, the oxide pinholes are largely affected [16, 30–33].

(ii) The oxide is removed at selective positions by a two-step process. First, nano-objects (GaAs crystals or Ga droplets) are grown on a substrate. The grown nano-objects interact with the oxide [34], which leads to the development of new/bigger nano-cavities. Second, by a high-temperature annealing step, the grown objects are removed [15, 16, 23]. In this way, the oxide layer is mostly affected at positions of the nano-objects (see [16] for an atomic force microscopy analysis of the Si oxide surface morphology in this process). Homogeneity of the developing surface nano-cavities (pinholes) might be closely related to the growth characteristics of the nano-objects (e.g., density and size). Because of the improvements in manipulating the mentioned characteristics of the nano-objects, approach (ii) seems to be more controlled as compared to approach (i). The authors in [15] performed the substrate conditioning by growth and annealing of GaAs crystals. Tauchnitz et al [16] performed Ga droplet positioning and removal. Koivusalo et al have combined growth and removal of both Ga droplets and GaAs crystals resulting in a significant narrowing of the NW length distribution and also suppression of the parasitic island (PI) nucleations [23]. PIs are GaAs nanoparticles that undesirably grow in self-catalyzed systems together with the NWs [31, 32]. However, in their case, an intermediate exposure of the substrates to air is used. The authors in [16] have presented an attempt to achieve homogeneous NW sizes without exposing the NWs to air. However, their strategy suffers from the consumption of a significant amount of source material. The latter is, in fact, the general disadvantage of this category of surface conditioning approach (e.g., in [15, 16, 23]) which is unfavorable toward industrial mass production.

As an alternative to surface conditioning, the NW growth characteristics can be controlled by performing a two-step growth protocol: first, nano-objects (Ga droplets or GaAs nano-objects) are pre-deposited; and second, selective growth of NWs takes place at the pre-deposited nano-objects. Following the literature, such approaches can be divided into two categories:

(i) Relatively small GaAs islands are grown. Those nano-objects act as nucleation sites for following selective nucleation of Ga droplets and a consequent NW growth [26, 35].

(ii) Ga droplets are pre-deposited on the Si oxide substrate at high Ga fluxes. Then the Ga flux is decreased for NW growth to minimize further nucleation on the substrate [24].

In both latter categories, one could manipulate the size and number density of the NWs independently. The density of the NWs is related to the density of the pre-deposited nano-objects. The control in the density of the NWs can prevent shadowing effects [36], which is an essential factor in core–shell NWs. Further, one could achieve a high homogeneity in NW length and diameter.

The Ga pre-deposition approach by Küppers et al in 2017 [24] is, in principle, similar to our presented approach, although we collected our data in 2015. Küppers et al however concentrated on decreasing Ga flux to control nucleation [24]. Nevertheless, a report on the interplay of substrate temperature and Ga flux is missing in the literature. An increased substrate temperature can similarly prevent nucleation of the material on the substrate. We report that growth above a critical temperature of 580 ± 10 °C is advantageous likely due to the better interaction of Ga with the silicon oxide. In terms of length homogeneity, the presented results shown in this work are comparable with those achieved in [23, 24]. Also, the diameter and number density of the NWs could be controlled, which are likewise in high demand [16, 23, 24, 26, 35]. The advantage of our method as compared to the literature is that a simple single-step approach is made e.g. with no intermediate step of exposure to air and with little source material usage. Moreover, a significant improvement in the NW/PI ratio is achieved which is another aspect of the current work not addressed in the previous studies. The growth homogeneities along with the low rates of growth are particularly interesting for in situ studies [37, 38].
3. Experimental details

Flux and temperature calibrations were performed by a typical procedure of in situ RHEED (reflection high-energy electron diffraction) monitoring of a Si(100) substrate treatment [39]. Additionally, RHEED was used for in situ characterization of the growth of Ga and GaAs nano-objects in a qualitative manner [40]. In particular, nucleation of the Ga droplets on the surface [41, 42] and the nucleation of the NWs on the substrate [43] could be in situ monitored.

For NW growth, we used Si(111) ± 0.5° n-doped (Ph) wafers covered by a native epiready layer of Si oxide. The samples were received as RCA cleaned by the manufacturer however additionally cleaned using acetone, isopropanol, and deionized water for 5 min at each solvent at an ultrasonic bath followed by nitrogen blowing. The samples were then loaded into a pre-heating chamber and annealed at 300 °C for 1 hour in order to remove the remaining water and volatile carbon species. After transferring the sample to the pMBE chamber, the temperature was ramped up to 660 ± 5 °C, and the sample was annealed for 35 min.

At the first attempts, after the preparation steps explained above, Ga and As molecular beams were simultaneously supplied. Here, mainly, effects of As flux, Ga flux, substrate temperature, and growth duration are presented at otherwise optimized preparation/growth parameters. In the next experiments, Ga was pre-deposited before the simultaneous supply of Ga and As. The Ga deposition was controlled, aiming for narrowing the size distribution of droplets. NW growth was followed, endeavoring for suppression of growth between the Ga droplets. At the mentioned growth conditions, the size and density of the NWs were studied along with statistical analysis of the NWs and PIs. The reproducibility issues have been addressed by repeating experiments by nominally identical growth protocols followed by thorough analysis. SEM was used to study the morphology of the growth using an electron beam with an acceleration voltage of 5 kV detecting secondary scattered electrons.

4. Results and discussion

4.1. Simultaneous supply of As and Ga sources

In the first step, As and Ga were simultaneously supplied to initiate the NW growth. The influences of either the As or Ga fluxes were investigated by keeping the other flux as well as the substrate temperature (570 ± 5 °C) and growth time (1 h) constant. The results of a few selective growth runs are shown in figures 1(a)–(b). Here, panel a and b show the length and diameter evolution of the NWs as a function of As and Ga flux rates, respectively. The SEM images corresponding to the data points in figures 1(a)–(b) are shown in panels A–C and D–F. By increasing the As flux, the length of the NWs increases (see figure 1(a) and A–C). Such a dependency (As limited axial NW growth rate) typically suggests the VLS mechanism of NW growth [29]. At the same time, the maximum As flux results in 100% vertical orientation of the grown NWs (cf figure 1(A)–(C)). Russo-Averchi et al have reported that small V/III ratios result in the occurrence of 3D twinning and a large percentage of discrete growth directions in MBE-based self-catalyzed GaAs NWs on Si [25]. They reported that the NW growth with 100% percentage vertical orientation takes place only at the optimal growth parameters, which highlights the achievement in figure 1(C). In the present work, the average diameter of the NWs within the error bars does not show a significant change by increasing the As rate similar to [29]. In a VLS mechanism of NW growth, first, Ga droplet forms on the substrate; and by the influx of As atoms into the droplet, supersaturation takes place. Finally, GaAs nucleates preferentially at the heterogeneous nucleation sites (the solid substrate surface) [17, 30, 44]. The initial size of the droplet determines the initial NW diameter that is grown. The authors in [18, 33] predict a decreasing NW diameter by increasing the As flux. That is likely because of the accelerated supersaturation rate of the Ga droplet at a higher As influx, meaning that the Ga droplet has less time to grow after Ga droplet nucleation (decreased incubation time). However, the interplay of the radial growth at an extended growth duration can not be neglected in self-catalyzed VLS growth [37, 45]. Therefore, the extended trend in [18, 33] explains the initial stages of NW growth. In contrast, the probability of incorporation of diffusing Ga adatoms onto the side-walls of the NW can increase (enhanced radial growth) by increasing the As flux [17, 46]. Therefore, the interplay of the decreased initial NW diameter and increased radial growth rate has flattened the diameter curve in figure 1(a). In figure 1(b), by increasing the Ga flux from about 25 to 60nm/h, the NW diameter increases whereas the NW length does not change within the error bars. That is in agreement with the findings in [18, 29]. As explained above, the initial diameter of the NW is directly related to the supersaturation time; and at a constant As flux, the increasing Ga influx into the Ga droplet (stable nuclei) increases the initial diameter of the NW [29]. On the other hand, the axial growth rate is affected mainly by arsenic supply and therefore stays unchanged in the present case.

The effects of the substrate temperature on the NW growth can be seen in figure 1(c) and the corresponding SEM images in figure 1(G)–(J). The substrate temperature changes within a range of 560 ± 5–620 ± 5 °C at
otherwise constant conditions (growth duration 1 hour, Ga flux 39 nm/h, As flux 124 nm/h). The overall deposited material decreases by increasing the substrate temperature (cf figure 1 (A)–(D)). Spirkoska et al have reported that above a temperature of 570 °C, the sticking coefficient of GaAs material on Si oxide drastically decreases [47]. That explains the abrupt decrease in the growth density above 570 ± 5 °C in figure 1. On the other hand, by increasing the growth temperature, both NW length and diameter decrease, as shown in figure 1. This can be related to the degradation of the sticking efficiency of both As and Ga molecular beams, which is in agreement with the results in figure 1. The NW/PI ratio increases from 1 at a growth temperature of 550 ± 5 °C up to 3 at 590 ± 5 °C.

To conclude this section, at the presented growth scheme (simultaneous Ga and As supply), the initial diameter of the NW depends on Ga and As fluxes. By growth optimizations, one could elaborate a growth window with controlled NW size and density (not independently in this approach). Moreover, 100% of vertically standing NWs is achieved at high V/III ratios. Nevertheless, the growth of PIs could not be suppressed as is also the case in the literature [13, 25, 29, 33]. To further control the NW growth, an additional Ga pre-deposition step was implemented. That could manipulate the NW diameter, independent from the Ga and As fluxes, and manipulate the NW density, independent from the growth temperature. Moreover, PI growth could be significantly suppressed.

Figure 1. The evolution of the length and diameter of the vertical nanowires as a function of As flux in panel a and Ga flux in panel b by keeping the other flux constant. The growth temperature and duration are constant at 570 ± 5 °C and 1 hour, respectively. The SEM micrographs marked with A–F are taken aftergrowth at a 30° tilted substrate and are corresponding to the data points in panels a and b. (c) The influence of the growth temperature on the vertical NW length and diameter (@growth duration of 1 h, Ga & As flux of 39 & 124 nm/h). The SEM micrographs marked with G–I are taken aftergrowth at a 30° tilted substrate and are corresponding to the data points in panel c (the scale bars are 1 μm). The micrograph marked with J is from a sample grown at 610 °C and disregarded in panel c. The analysis of the density of the grown objects on the samples is shown in table 2. Adapted from [43].
Manipulator have about a 10 different positions on one growth sample. The pyrometer temperature reading revealed that those respective positions on the pMBE temperature within 600 °C. After the preparation steps, similar to the previous section, the substrate temperature was stabilized at a 4.2. Ga pre-deposition

followed by Ga pre-deposition at a substrate temperature of 610 °C. 

桂子等 (111) native oxide for 10 min with a Ga flux of 59 nm/h at a substrate temperature of (a) 600 ± 5 °C and (b) 610 ± 5 °C. Increased substrate temperature results in better size homogeneity visually observed in the panels (see the insets) and statistically reflected in the error bars of the diameter. In panels a and b, the average diameters are 35 ± 10 nm and 39 ± 3 nm, respectively, where the error bars are the statistical standard deviation.

Figure 2. Ga droplet pre-deposition on Si(111) native oxide for 10 min with a Ga flux of 59 nm/h at a substrate temperature of (a) 600 ± 5 °C and (b) 610 ± 5 °C. Increased substrate temperature results in better size homogeneity visually observed in the panels (see the insets) and statistically reflected in the error bars of the diameter. In panels a and b, the average diameters are 35 ± 10 nm and 39 ± 3 nm, respectively, where the error bars are the statistical standard deviation.

4.2. Ga pre-deposition

After the preparation steps, similar to the previous section, the substrate temperature was stabilized at a temperature within 600 ± 5–620 ± 5 °C for Ga pre-deposition. Here, only Ga was supplied for a duration of 10 min. At a substrate temperature of 610 ± 5 °C, Ga was supplied with fluxes of 25, 39, and 59 nm/h. The resulting density and diameter of the deposited Ga droplets were 0.03 ± 0.01 μm⁻² and 48 ± 5 nm, respectively, at a Ga flux of 59 nm/h. Below this Ga flux, the deposition was negligible. Based on the experimental and theoretical reports, Ga droplet formation on Si in vapor phase epitaxy has several steps: i) formation of atomic Ga (adatoms) from molecular Ga (gas) on the substrate, ii) surface diffusion of the Ga adatoms, iii) Ga droplet formation [48–50]. The highest Ga flux (Ga vapor pressure) results in an increasing adatom concentration on the Si surface. In other words, the reaction, $\text{Ga}_{\text{gas}} \leftrightarrow \text{Ga}_{\text{adatom}}$, goes to the right side by increasing $\text{Ga}_{\text{gas}}$. The formation probability of a stable liquid droplet nucleus increases by increasing the adatom concentration on the surface [51], which qualitatively explains the higher formation probability of the Ga droplets at higher Ga fluxes. It is reported that increasing the temperature above 600 ± 5 °C can drastically affect the overall volume of deposited Ga [47]. Therefore, for Ga pre-deposition at higher temperatures, significantly higher Ga fluxes may be required.

The effects of the pre-annealing step (that is prior to the Ga pre-deposition step) are studied at a temperature of 660 °C by varying the annealing duration to 1, 17, and 35 min. The results of the following Ga deposition were compared with the results obtained from a sample without a pre-annealing step. It was discovered that a pre-annealing step significantly increases the density of the deposited Ga droplets (a factor of 10–20) within our growth scheme. That is most likely as a result of the changes in the morphology of the oxide without changing the surface chemistry [16]. On the other hand, the size distribution of the Ga droplets was narrowed as a result of pre-annealing. That suggests an enhanced homogeneity in the distribution of the oxide openings [30].

Pre-deposition of the Ga droplets at higher substrate temperatures showed a narrower droplet size distribution (see figure 2). That can be explained by the enhancement of Oswald ripening at higher temperatures [49]. In simple words, a higher temperature provides the activation energy for the diffusion of the Ga adatoms. Here, the bigger droplets are more stable than the smaller ones because of the decreasing number of dangling bonds at the surface atoms in bigger droplets. Therefore, diffusion of Ga adatoms occurs from the smaller droplets toward the bigger ones. That results in an eventual fading of the small droplets in favor of larger ones leading to larger droplet sizes with a more homogeneous size distribution.

Annealing of the droplets results in even better diameter homogeneity as also observed in [24]; and it provides a longer reaction time for interaction of Ga with Si oxide along with enhanced Ga etching above a temperature of 580 ± 5 °C [34, 52]. The latter facilitates the epitaxial connection of GaAs nano-objects with Si substrates, which decreases the formation energy of GaAs crystals.

In order to manipulate the Ga droplet size, it is suggested to change the pre-deposition time as reported in [24, 53], which was outside our scope.

The best Ga pre-deposition result was achieved using a pre-annealing step for a duration of about 35 min followed by Ga pre-deposition at a substrate temperature of 610 ± 5 °C at a Ga flux of 59 nm/h for 10 min. The sample was then annealed for about 20 min at a temperature of 600 ± 5 °C. The diameter of the deposited droplets, as shown in figure 2(b), is 39 ± 3 nm, and the number density is 0.1–0.5 μm⁻².

Figure 2 are from two different positions on one growth sample. The pyrometer temperature reading revealed that those respective positions on the pMBE manipulator have about a 10° difference in temperature.

1 In order to exclude the uncertainty related to growth on different wafers, the presented results in panels a and b of figure 2 are from two different positions on one growth sample.
After the pre-deposition step, the samples were grown at different growth conditions. After loading the sample afterward, changed to a temperature within 570 °C, the substrate temperature was decreased to a temperature within 600 °C. The enhanced NW nucleation between the Ga droplets can be related to the conditioning of the Si oxide substrate by its interaction with Ga-adsorbed voids.

4.3. Nanowire growth after Ga pre-deposition

After the pre-deposition step, the samples were grown at different growth conditions. After loading the sample into the chamber, the substrate was ramped up to the pre-annealing temperature (660 ± 5 °C, 35 min). Then, the substrate temperature was decreased to a temperature within 600 ± 5–620 ± 5 °C for Ga pre-deposition and afterward, changed to a temperature within 570 ± 5–620 ± 5 °C for NW growth.

In figure 3, the aftergrowth SEM micrographs are taken from the samples grown with and without Ga pre-deposition at otherwise identical conditions (compare panel a with b, and c with d). Figures 3(a) and (b) illustrate two samples grown at a substrate temperature of 570 ± 5 °C. Here, the density of the vertical NWs is 0.6 ± 0.2 μm⁻² without Ga pre-deposition, and that increases up to 1.8 ± 0.5 μm⁻² with Ga pre-deposition. Even if one assumes that the pre-deposited Ga droplets (with a density of 0.1–0.5 μm⁻²) have fully transformed into NWs, the density of the nucleated NWs between the pre-deposited Ga droplets (1.5 ± 0.6 μm⁻²) is by a factor 2 larger compared to that without pre-deposition. The enhanced NW nucleation between the Ga droplets can be related to the conditioning of the Si oxide substrate by its interaction with Ga-adsorbed voids (2D Ga). During Ga pre-deposition, the 2D Ga layers nucleate on the defects at the Si oxide surface, leading to the formation of nanocavities [34]. These nano-cavities are preferential nucleation points for further Ga formation and NW growth during the simultaneous supply of source materials. The 2D Ga layers can be detected by STM as reported by Nitta et al [34] but are invisible in SEM inspection. With Ga pre-deposition, the density of tilted NWs, as well as PIs, is significantly decreased. As a result, the overall number density of the crystallized nano-objects decreased (a full sample density analysis will be presented in table 2). At the same time, NWs grow 50% longer (see table 1) likely due to enhanced collection volume of As source material [34] e.g. by the reemission from the substrate in absence of nucleation sites [35]. That indicates a higher local As influx for the existing NWs (see effects of As flux on the NW growth in figure 1). In other words, the As quota for the NWs increases by decreasing the number density of the PIs. As observed in the inset of figure 3(b), at the right below, thick NWs (37 ± 4 nm) and thin NWs (22 ± 4 nm) are simultaneously present. The average diameter of the thick NWs is comparable with the diameter of the pre-deposited Ga droplets (39 ± 3 nm), and the average diameter of the thin NWs is comparable with the average diameter of the NWs grown on the sample without Ga pre-deposition. Therefore, NWs have nucleated between the pre-deposited Ga droplets along with the NW growth i.e., interstitial NWs. Consequently, as seen in table 1, at a growth temperature of 570 ± 5 °C, the distributions (standard deviation) of the NW diameters and lengths do not significantly change with or without Ga pre-deposition (∼20 % diameter and >30% length). The large standard deviations (distributions) are due to the continuous interstitial NW nucleation during the growth.
The substrate temperature was increased aiming to suppress the interstitial nucleation of NWs, i.e., to hinder the crystallization of material anywhere except at the pre-deposited Ga droplets (see figures 1(c) and panels G–J for the effects of substrate temperature on growth). SEM characterization after the growth indicates negligible NW growth at the sample in figure 3(c) grown at a substrate temperature of 600 ± 5 °C. Similar growth conditions after Ga pre-deposition show NW growth with a number density similar to that of pre-deposited Ga droplets (see figure 3(d)). The data is acquired by averaging within a few mm around the growth location on the sample.

The substrate temperature was increased aiming to suppress the interstitial nucleation of NWs, i.e., to hinder the crystallization of material anywhere except at the pre-deposited Ga droplets (see figures 1(c) and panels G–J for the effects of substrate temperature on growth). SEM characterization after the growth indicates negligible NW growth at the sample in figure 3(c) grown at a substrate temperature of 600 ± 5 °C. Similar growth conditions after Ga pre-deposition show NW growth with a number density similar to that of pre-deposited Ga droplets (see figure 3(d)). That indicates that the main limiting factor for NW nucleation at 600 ± 5 °C is the Ga supply. The SEM cross-sectional side view of this sample is shown in figures 4(a)–(b). The sample is grown for 4 h and 15 min. Figure 4(c) shows the SEM image from another sample grown under identical conditions but for a duration of 34 min. More than 80% of the grown objects on both samples in figure 4 are epitaxially oriented NWs (density analysis will be fully presented in table 2). The NWs/PIs number ratio is significantly increased compared to growth at lower substrate temperatures. Moreover, the standard deviation of the diameter and length decreased to about 3%–6% (see table 1). That means that the nucleation of the nano-objects is suppressed during the NW growth. In other words, the supplied material contributes mainly to the growth of the NWs from the pre-deposited Ga droplets.

It is worth noting that the absolute values of the optimum growth parameters are closely related to the Si oxide morphology and thickness. The reproducibility runs on different wafers showed that the oxide morphological uncertainties seem to be an uncontrolled aspect of the GaAs NW growth on native Si oxide.

*Table 1.* The diameter and length of the grown NWs at different growth temperatures. The growth duration is pointed out (mostly 1 h). The statistical distribution of the NW diameter and length at higher growth temperatures gets narrower. Note that at a growth temperature of 600 ± 5 °C, without Ga pre-deposition, nano-object nucleation is suppressed (see figure 3(c)). The data is acquired by averaging within a few mm around the growth location on the sample.

| Growth Temp | 550 ± 5 °C | 570 ± 5 °C | 570 ± 5 °C | 590 ± 5 °C | 600 ± 5 °C |
|-------------|------------|------------|------------|------------|------------|
|              | no         | no         | with       | no         | with       |
|              | Ga dep.    | Ga dep.    | Ga dep.    | Ga dep.    | Ga dep.    |
|              | 1 h        | 1 h        | 1 h        | 1 h        | 35 min     | 4 h, 15 min |
| avg. NW diameter (nm) | 45 ± 9     | 22 ± 5     | 23 ± 4     | 42 ± 5     | 52 ± 3     | 158 ± 5     |
| standard deviation% | ~20%       | ~23%       | ~17%       | ~12%       | ~6%        | ~3%         |
| avg. NW length (μm)  | 1.2 ± 0.5  | 1 ± 0.4    | 1.5 ± 0.3  | 1.2 ± 0.1  | 0.4 ± 0.03 | 4 ± 0.12    |
| standard deviation%  | ~40%       | ~40%       | ~33%       | ~8%        | ~6%        | ~6%         |

Figure 4. SEM micrographs of the NW growth at the growth temperature of 600 ± 5 °C with Ga pre-deposition. Panels a and b are side-view images at 89° tilted substrate showing the length homogeneity of the grown NWs. The sample is presented above in figure 3(d) where the growth time is 4 hours and 15 min, and the average length of the NWs is 4 ± 0.12 μm. Panel c shows a sample grown at identical growth conditions but for a growth duration time of 34 min.

The growth position has been about 1 cm away from the center of the sample. The pyrometer temperature reading revealed that the corresponding position on the pMBE manipulator had a temperature of about 600 ± 5 °C.

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2 The growth position has been about 1 cm away from the center of the sample. The pyrometer temperature reading revealed that the corresponding position on the pMBE manipulator had a temperature of about 600 ± 5 °C.
substrates. Therefore, our growth parameters should be considered rather qualitative; and a small window for ‘trial and error’ is required for different wafers and growth machines.

4.4. Further analysis (Epitaxial alignment of the overgrown GaAs)

The epitaxial III-V NWs on Si grow mostly in the direction of \(\{111\}\) \([9]\). Additionally, the GaAs NWs can grow on Si along the family of \((111)\) \([156]\) and \((112)\) directions \([14]\). Figure 5 illustrates the epitaxial alignment of the overgrown GaAs nano-objects on Si(111). Here, panels a–b show a top-view SEM image (zero degree tilted substrate) of the sample presented in figure 3(b) (grown @570 ± 5 °C with Ga pre-deposition). The fast Fourier transform (with 90° rotation) at the inset of figure 5(a) indicates the elongation direction of the majority of the overgrown objects. The red ellipsoid in figure 5(a) indicates an object which does not fit the majority growth directions. Figure 5(b) is a high magnification magnification of panel a. The NW facets are extracted from the top-view of the NWs and redrawn by a red hexagon. The NW side-facets in self-catalyzed GaAs NWs are reported to be 6 planes from the \((110)\) family \([37, 57]\): \((1\overline{1}0), (1\overline{1}0), (\overline{1}0\overline{1}), (0\overline{1}0)\), and \((01\overline{1})\), which are perpendicular planes to \((111)\) plane. In figure 5(c), the corresponding NW side-facet surface normals are indicated (from the family of \((110)\) directions). Figure 5(d) shows two examples from the in-plane directions of the NW side-facets (horizontal) and edges (vertical). As indicated, the in-plane directions along the NW edges are the following directions from the family of \((12\overline{1})\): \((2\overline{1}1), (1\overline{2}1), (1\overline{1}2), (2\overline{1}1), (1\overline{2}1)\), and \((1\overline{2}\overline{1})\) (see figure 5(e)). Aside from the in-plane directions of growth, there are three members of the family of \((111)\) \(((1\overline{1}1), (\overline{1}1\overline{1}), and (11\overline{1}))\), which project towards the same direction along \((111)\). That means that the corresponding objects grow outward the Si(111) with an angle of 19° with respect to the surface. From a top-view, those directions project onto the mentioned family of \((12\overline{1})\) directions. At the cross-sectional view, they can have an angle of 19°–90° depending on the in-plane rotational status of the sample in SEM. The cross-sectional SEM imaging revealed that we have NWs grown in both \((1\overline{1}1)\) and \((1\overline{2}1)\) directions (see figure 5(f)). In figure 5, the NW indicated by a red ellipsoid in panel a, as well as the nano-objects at the inset of panel b, does not follow any of the above-mentioned crystallographic directions and therefore, they are considered as non-epitaxial, i.e., without an epitaxial relation to the Si(111) underneath the substrate. Details on how the tilting of the NWs affects the growth process can be found in \([58]\).

Table 2 shows the number density of the grown nano-objects as a function of growth temperature and Ga pre-deposition. The number density of the non-epitaxial nano-objects decreases from \(0.5 ± 0.2 \mu \text{m}^{-2}\) at a growth temperature of 550 ± 5 °C down to zero at a growth temperature of 590 ± 5 °C.

On single-crystalline Si, a passivated layer of native Si oxide forms after exposure to air \([21]\). Notably, NW growth on an amorphous layer like Si oxide is non-epitaxial. Previous STM studies have revealed that on Si oxide, natural holes exist. These holes are the preferential sites for heterogeneous nucleation of Ga droplets \([34, 51]\). The interaction of Ga droplets with the Si oxide results in the formation of bigger nanometer-sized holes underneath the droplets \([34]\). Sublimation of the Si oxide layer can be enhanced at temperatures lower than its evaporation temperature (900 °C) because of the chemical reactions in equations (1)–(3) \([30, 59, 60]\).

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\begin{align*}
2\text{Ga(liquid)} + \text{SiO}_2(\text{solid}) & \rightarrow \text{SiO(gas)} + \text{Ga}_2\text{O(solid/gas)} \quad (1) \\
4\text{Ga(liquid)} + \text{SiO}_2(\text{solid}) & \rightarrow \text{Si(in Ga)} + 2\text{Ga}_2\text{O(solid/gas)} \quad (2)
\end{align*}
\]
Ga droplets oxidize at their interface with Si oxide based on equations (1) and (2). The resulting gallium oxide is volatile in vacuum increasingly at temperatures above 580 °C as reported by Cho in [61]. This process can explain the zero number density of non-epitaxial growth at growth temperatures above 580 °C in our results. On the other hand, the resulting Si oxide evaporates; and the atomic Si is soluble into the Ga droplet above 500 °C based on the Ga-Si phase diagram [62]. The atomic Si can also further react with the Si oxide layer to form volatile species based on equation (3) [61]; and it eventually can etch the Si substrate likely limited to the solubility of Si in Ga [60, 63].

5. Conclusion

This work is a comparative growth study with emphasis on low growth rates. In particular, GaAs self-catalyzed GaAs NWs are firstly studied using a growth scheme by a simultaneous supply of Ga and As source materials. In this growth scheme, in agreement with the literature, the NW size and number density could not be independently modified. Moreover, PI growth could not be suppressed (NW/PI < 5). A Ga pre-deposition step before NW growth provides a new degree of freedom in order to control the NW average diameter. Moreover, after a Ga pre-deposition step and by an interplay of high growth temperature and low Ga flux, the interstitial growth of nano-objects between the Ga droplets is suppressed. In this way, we could narrow the length distribution of the NWs. A high temperature of growth (above 580 ± 5 °C) also fully suppresses the non-epitaxial growth of NWs likely as a result of an enhanced Ga etching effect. Moreover, by our proposed strategy, the NW/PI ratio increases (>30). Aside from the fundamental insights, the achievements of this work can aid in situ studies of NW ensembles. The inherent size fluctuations of the NWs as well as the existence of parasitic

SiO₂(solid) + Si(in Ga) → 2SiO(gas)

(3)
growth can complicate the interpretation of the in situ data. Here, low growth rates are also advantageous to acquire better time resolution. Additionally, our fundamental approach to control the NW growth could be used in other materials systems, i.e. other substrates or other self-catalyzed III-V systems. To this end, further studies could be outlooked.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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