Nucleation and coalescence effects on the density of self-induced GaN nanowires grown by molecular beam epitaxy

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The evolution of the density of self-induced GaN nanowires as a function of the growth time, gallium rate, and growth temperature has been investigated by scanning and transmission electron microscopy. Nucleation and coalescence effects have been disentangled and quantified by distinguishing between single nanowires and nanowire clusters. Owing to the very specific nanowire nucleation mechanism involving a shape transition from spherical-cap-shaped islands, the nanowire density does not follow the standard island nucleation theory. Furthermore, the detrimental nanowire coalescence process can be significantly reduced by raising the growth temperature. © *2011 American Institute of Physics*. [doi:10.1063/1.3555450]

A particularly attractive approach for the fabrication of GaN nanowires (NWs) is the self-induced growth by molecular beam epitaxy (MBE)[1,2] since it does not require any external collectors or substrate prepatterning. Both the structural and the optical quality of the resulting NWs is furthermore significantly better than for the collector-induced approach.[3,4] Consequently, increasing efforts have been devoted to control the NW structural properties within the self-induced approach. For a wide number of applications, it is critical to tune the NW number density. Within the collector-induced approach, this is easily achieved by adjusting the collector number density. In contrast, for the self-induced approach, the physical mechanisms governing the NW density are unknown. Their clarification is complicated by the NW coalescence process, which superimposes to the evolution of the NW density driven by nucleation effects.[5] Also, for most practical purposes, it is desirable to suppress the coalescence process since it results in the deterioration of the NW structural and optical properties.[6] It is the aim of this paper to elucidate the physical processes that drive the NW density and to determine the optimal growth conditions that lessen the NW coalescence process. In order to disentangle the effects of NW nucleation and coalescence, we carefully distinguish between the evolution of the single NW density and of the NW cluster density: a cluster is defined here as a group of coalesced NWs. Both the cluster and the NWs for which the cluster is composed of are considered.

GaN NWs were grown on Si(111) substrates by MBE. The active nitrogen species and gallium atoms were supplied by a plasma source and by a thermal effusion cell, respectively. Prior to GaN NW growth, the substrates were exposed to an active nitrogen flux for 5 min, resulting in the formation of a continuous Si_xN_y amorphous interlayer with a thickness of about 2 nm. The growth temperature and gallium rate were varied in the ranges of 770–815 °C and 0.25–0.7 Å/s, respectively. The nitrogen rate was equal to 2.8 Å/s, which leads to a V/III ratio in the range of 4–11.2. The total growth time was adjusted such that the effective growth time was systematically 3 h: the gallium shutter was closed 3 h after the end of the incubation time, which is indicated by the appearance of GaN spots in reflection high-energy electron diffraction. Another series of samples was grown with different effective growth times between 1110 and 22 710 s for a substrate temperature and gallium rate of 780 °C and 0.45 Å/s, respectively. Specimens for cross-sectional transmission electron microscopy (TEM) imaging were prepared by mechanical lapping and polishing, followed by argon ion milling according to standard techniques. TEM images were acquired with a JEOL 3010 microscope operating at 300 kV.

Both the cluster density and the NW density were determined from the top-view field-emission scanning electron microscopy (FESEM) images, as shown in the inset of Fig. 1. Edges were detected and particles were counted with the software IMAGEJ to determine the cluster density and the surface area of each cluster: subsequently, the NW density was estimated by dividing the cluster surface area by the NW mean surface area since every NW has an hexagonal base and a very close diameter for a given growth condition. The procedure has been cross-checked by recognizing the NW shape in each cluster. For each sample, a population of more

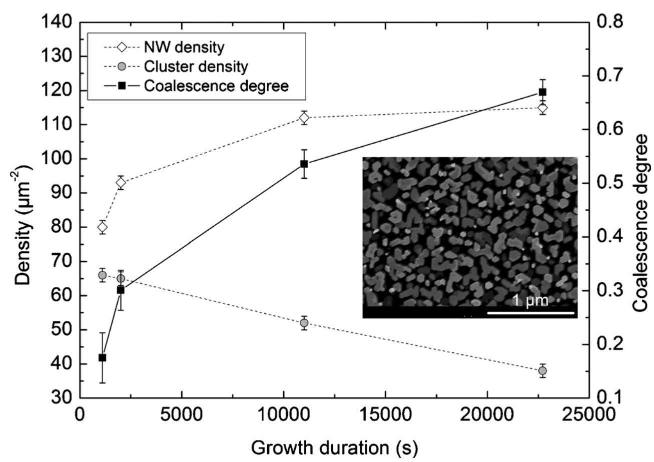

FIG. 1. Evolution of the NW density, the cluster density, and the coalescence degree as a function of the growth time. The growth temperature and gallium rate are 780 °C and 0.45 Å/s, respectively. The corresponding V/III ratio is 6.2. The inset is a top-view FESEM image of NWs after an effective growth time of 3 h.

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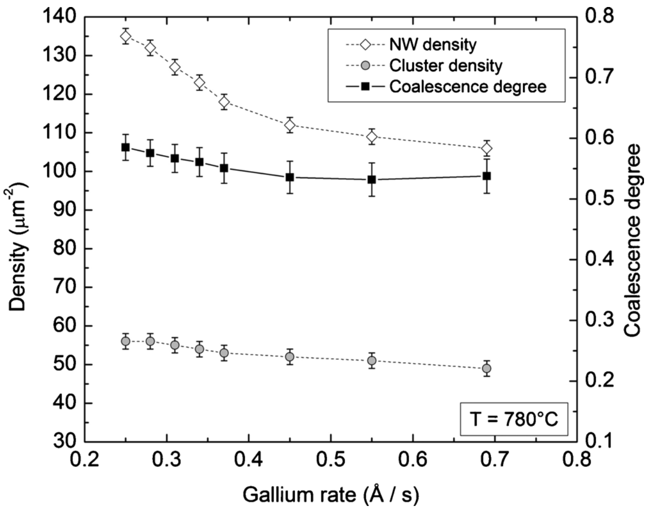

FIG. 2. Evolution of the NW density, the cluster density, and the coalescence degree as a function of the gallium rate. The growth temperature is 780 °C.

than 500 NWs was taken into account. In order to quantify the NW coalescence process, the coalescence degree $\alpha_{\text{coalescence}}$ is defined as $\alpha_{\text{coalescence}}=1-(\rho_{\text{cluster}}/\rho_{\text{NW}})$, where ρ_{cluster} and ρ_{NW} represent the cluster and NW density, respectively. A freestanding NW is also considered as a single cluster. When the coalescence process does not take place (i.e., NWs are perfectly uncoalesced), the cluster density equals the NW density, resulting in a coalescence degree of 0. In contrast, when the coalescence process is strong (i.e., NWs are completely coalesced), the cluster density is much smaller than the NW density, leading to a coalescence degree close to 1.

The evolution of the NW and cluster density and of the coalescence degree is presented in Figs. 1–3 as a function of the growth time, gallium rate, and growth temperature, respectively. By increasing the growth time, the NW density continuously increases and saturates at 115 NWs/μm^2, while the cluster density diminishes. At the same time, the coalescence degree significantly increases due to the small, but not negligible, NW radial growth, which leads to the

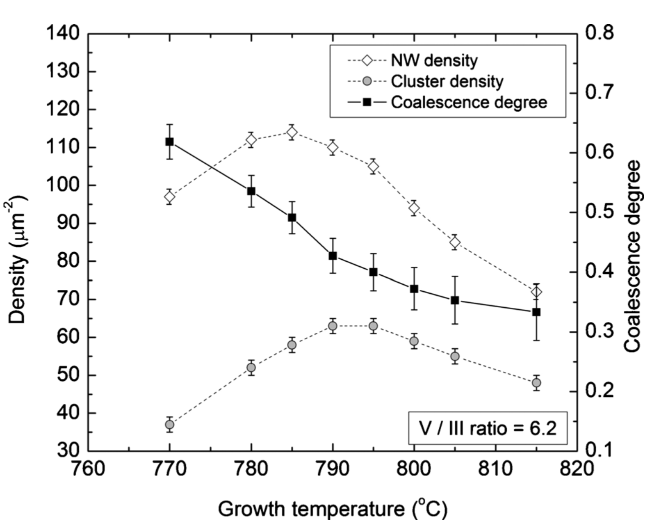

FIG. 3. Evolution of the NW density, the cluster density, and the coalescence degree as a function of the growth temperature. The gallium rate is 0.45 Å/s, which corresponds to a V/III ratio of 6.2.

coalescence of the neighboring NWs. The maximum numerical values for the densities are of the same order of magnitude as reported in Refs. 5 and 7. However, the importance of distinguishing between NWs and clusters is revealed by the comparison between the trends found here in Fig. 1 and in Ref. 5: the decrease in the cluster density seen in Fig. 1 corresponds to the decrease in the NW density observed in Ref. 5 after about 1 h of growth time, while in contrast the NW density as determined here keeps on increasing.

The effects of the gallium rate (i.e., the V/III ratio) are shown in Fig. 2. The NW density continuously decreases as the gallium rate is increased and eventually reaches a plateau. Both the cluster density and the coalescence degree remain almost constant. Since the NW density comparably decreases strongly, which should reduce the coalescence degree, the observed trends may indicate that the NW radial growth rate increases as the gallium rate is increased. Indeed, it is well-known that the growth mode switches from NW growth to planar layer growth for increasing gallium rate,[8] which corresponds to an increase in the radial growth rate and a strengthening of the NW coalescence process. The higher radial growth rate at higher gallium rate has recently been deliberately used to perform a completely two-dimensional layer at the NW top.[9]

More importantly is the growth temperature dependence depicted in Fig. 3. The evolution of the NW density follows two consecutive steps: (i) the NW density initially increases to 114 NWs/μm^2 at about 785 °C and (ii) subsequently, the NW density decreases for higher growth temperatures. The occurrence of a maximum NW density for intermediate growth temperatures is of high interest for technological applications in which increasing the NW density represents a critical point. The trend for the cluster density also exhibits a maximum, although it occurs at a slightly higher growth temperature. In contrast, the coalescence degree is strongly reduced in a monotonous way. It is remarkable that the coalescence degree decreases between 770 and 785 °C, while the NW density increases: this may suggest that the NW radial growth rate decreases as the growth temperature is raised. The thermal decomposition and gallium desorption are significant in such a temperature range: it is deduced from Fig. 3 that the associated decrease in the growth rate is stronger on the m-plane NW vertical sidewalls than on the c-plane top facets. For most practical purposes, it is relevant that the NW coalescence process can be inhibited by raising the growth temperature, which is related to a better structural morphology of the NW ensemble.[6]

The evolution of the NW density as measured in this study only depends on the nucleation phenomena since the coalescence effects were separated by the determination of the cluster density and coalescence degree. According to the standard island nucleation theory, the island density N_I is given by $N_I \sim (\phi_{Ga})^2 \exp[(3\Lambda_S+2E_D)/(k_B T)]$, where ϕ_{Ga} is the gallium flux, T is the growth tempeature, Λ_S is the condensation heat, and E_D is the energy barrier for the adatom diffusion on the substrate surface.[10] The NW density should thus monotonously decrease by raising the growth temperature since the adatom diffusion on the substrate surface is enhanced. Similarly, the NW density should increase by increasing gallium rate since the probability to nucleate an island with critical size is increased. Obviously, the experimental results in Figs. 2 and 3 follow different trends.

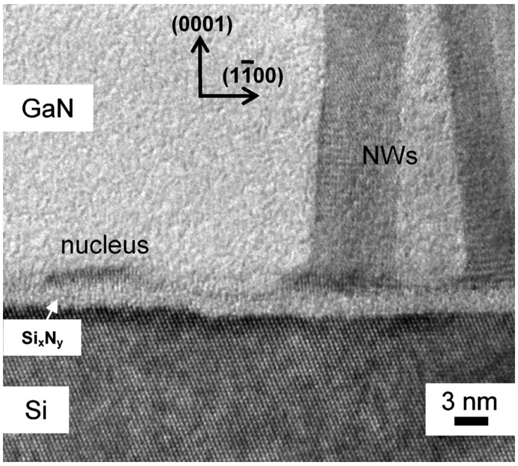

FIG. 4. High resolution TEM image collected on a sample grown for 40 min at a substrate temperature and gallium rate of 780 °C and 0.45 Å/s, respectively. The presence of nuclei as spherical-cap-shaped islands in addition to NWs is clearly shown.

Therefore, the standard island nucleation theory does not suffice to describe the evolution of the NW density.

The seeming disagreement between the experimental evolution of the NW density and the standard island nucleation theory can be reconciled by considering the specific nucleation mechanisms of self-induced GaN NWs. These NWs do not nucleate directly with the NW shape but instead as spherical-cap-shaped islands, while the NW shape is reached only after a shape transition.[11–13] Moreover, it has been argued that the shape transition takes place once an energy barrier related to edge effects is overcome.[13] The TEM image presented in Fig. 4 shows that even after a long effective growth time, spherical caps and NWs coexist: there is one spherical cap for about two to three NWs in Fig. 4. Hence, some spherical caps undergo the shape transition toward the NW morphology only after long growth time and/or spherical caps are consumed by the radial growth of the neighboring NWs and/or spherical caps continue to nucleate. The latter explanation is less likely since the high NW density effectively prevents the impinging fluxes from reaching the substrate surface. At the same time, the prolonged occurrence of the shape transition is consistent with the experimental observation depicted in Fig. 1, showing that the NW density increases even after long effective growth time.

The standard island nucleation theory is only suitable for the formation of the initial spherical caps but not for the subsequent shape transition that governs the NW density. The energy barrier for the shape transition can more easily be overcome at high growth temperatures: in brief, the fraction of spherical caps undergoing the shape transition should drastically increase as the growth temperature is raised for a given gallium rate and effective growth time, accounting for the initial increase in the NW density, as shown in Fig. 3. The subsequent decrease in the NW density for higher growth temperatures is, however, related to the significant decrease in the spherical cap density as predicted by the standard island nucleation theory: although almost all of the spherical caps undergo the shape transition toward the NW morphology for growth temperatures higher than 785 °C, this does not compensate their very low density. Furthermore, the magnitude of the energy barrier itself is expected to be highly dependent on the V/III ratio and thus on the gallium rate: the increase in the NW density by decreasing gallium rate, as seen in Fig. 2, suggests that increasing the V/III ratio may be energetically favorable for the shape transition and hence for the formation of GaN NWs. This interpretation is consistent with the fact that the self-induced growth of GaN NWs requires highly nitrogen-rich conditions, as widely reported.[1–8,11–13]

In conclusion, the evolution of the NW density is strongly affected by the nucleation mechanisms involving a shape transition from spherical caps to NWs. Controlling the NW density both requires to control the spherical cap initial density and their subsequent shape transition. Furthermore, increasing the growth temperature leads to a beneficial reduction of the NW coalescence process.

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[1]M. Yoshizawa, A. Kikuchi, M. Mori, N. Fujita, and K. Kishino, Jpn. J. Appl. Phys., Part 2 **36**, L459 (1997).
[2]M. A. Sanchez-Garcia, E. Calleja, E. Monroy, F. J. Sanchez, F. Calle, E. Muñoz, and R. Beresford, J. Cryst. Growth **183**, 23 (1998).
[3]L. Geelhaar, C. Chèze, W. M. Weber, R. Averbeck, H. Riechert, Th. Kehagias, Ph. Komninou, G. P. Dimitrakopulos, and Th. Karakostas, Appl. Phys. Lett. **91**, 093113 (2007).
[4]C. Chèze, L. Geelhaar, O. Brandt, W. Weber, H. Riechert, S. Münch, R. Rothemund, S. Reitzenstein, A. Forchel, T. Kehagias, P. Komninou, G. P. Dimitrakopulos, and T. Karakostas, Nano Res. **3**, 528 (2010).
[5]R. Calarco, R. Meijers, R. K. Debnath, T. Stoica, E. Sutter, and H. Lüth, Nano Lett. **7**, 2248 (2007).
[6]V. Consonni, M. Knelangen, U. Jahn, A. Trampert, L. Geelhaar, and H. Riechert, Appl. Phys. Lett. **95**, 241910 (2009).
[7]R. Songmuang, O. Landré, and B. Daudin, Appl. Phys. Lett. **91**, 251902 (2007).
[8]S. Fernández-Garrido, J. Grandal, E. Calleja, M. A. Sánchez-García, and D. López-Romero, J. Appl. Phys. **106**, 126102 (2009).
[9]D. Cherns, L. Meshi, I. Griffiths, S. Khongphetsak, S. V. Novikov, R. P. Campion, C. T. Foxon, C. Liu, P. Shields, and W. N. Wang, J. Phys.: Conf. Ser. **209**, 012001 (2010).
[10]V. G. Dubrovskiĭ, I. P. Soshnikov, N. V. Sibirev, G. É. Cirlin, V. M. Ustinov, M. Tchernycheva, and J. C. Harmand, Semiconductors **41**, 865 (2007).
[11]V. Consonni, M. Knelangen, L. Geelhaar, A. Trampert, and H. Riechert, Phys. Rev. B **81**, 085310 (2010).
[12]M. Knelangen, V. Consonni, A. Trampert, and H. Riechert, Nanotechnology **21**, 245705 (2010).
[13]V. Consonni, M. Knelangen, L. Geelhaar, A. Trampert, and H. Riechert, Phys. Rev. B **83**, 035310 (2011).