

## Physical origin of the incubation time of self-induced GaN nanowires

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The nucleation process of self-induced GaN nanowires grown by molecular beam epitaxy has been investigated by reflection high-energy electron diffraction measurements. It is found that stable nuclei in the form of spherical cap-shaped islands develop only after an incubation time that is strongly dependent upon the growth conditions. Its evolution with the growth temperature and gallium rate has been described within standard island nucleation theory, revealing a nucleation energy of  $4.9 \pm 0.1$  eV and a very small nucleus critical size. The consideration of the incubation time is critical for the control of the nanowire morphology. © 2011 American Institute of Physics. [doi:10.1063/1.3610964]

Semiconductor nanowires (NWs) pave the way to the fabrication of promising nanodevices due to their high aspect ratio at nanoscale dimensions and the possibility of integration with silicon-based technology.<sup>1</sup> In particular, GaN NWs are considered as a good candidate for the fabrication of low-cost and highly efficient light emitting diodes.<sup>2,3</sup> A particularly attractive approach to grow GaN NWs with good structural and optical quality is the self-induced growth by molecular beam epitaxy (MBE).<sup>4-6</sup> Typically, in contrast to the deposition of GaN planar layers, highly nitrogen-rich growth conditions are used and often combined with a high growth temperature.<sup>7</sup> The growth process basically follows two consecutive steps: the initial self-induced formation of NW nuclei is followed by their lengthening.<sup>8-10</sup> The control of the initial nucleation phase is critical since it has a strong influence on the GaN NW structural properties such as their diameter or density for instance.<sup>8-11</sup> It has recently been shown that the nucleation phase involves several distinct physical processes: after an incubation time without any growth at all, GaN first nucleates not as NWs but as spherical cap-shaped islands, and the NW nuclei are formed only after the subsequent shape transition(s).<sup>8,9</sup>

Very importantly, the successive steps during the nucleation phase result in a delay for the self-induced formation of GaN NW nuclei.<sup>8-14</sup> Such a delay has also been revealed for the catalyst-induced growth of silicon and GaN NWs and attributed to the time that is necessary for the supersaturation in the catalyst to reach the critical value.<sup>15-19</sup> In contrast, for the self-induced growth of GaN NWs, the physical origin of the delay in nucleation is still open. It is the aim of this paper to cast a light on the very early stages of the nucleation phase by precisely investigating the incubation time and its evolution with the growth temperature and gallium rate by reflection high-energy electron diffraction (RHEED) measurements. These dependences are analyzed in the framework of standard island nucleation theory.<sup>20-23</sup>

GaN NWs were grown on Si(111) substrates by MBE. The active nitrogen species and gallium atoms were supplied

by a SPECS plasma source operating at 500 W power with a 2 sccm flux and by a thermal effusion cell, respectively. Prior to GaN NW growth, a continuous  $\text{Si}_x\text{N}_y$  amorphous interlayer with a thickness of 2 nm was formed by exposing the substrate to an active nitrogen flux for 5 min. The nominal gallium and nitrogen rates correspond to the growth rate of GaN planar layer deposited on SiC(111) substrate under nitrogen or gallium-rich conditions, respectively. The growth temperature and gallium rate were varied in the ranges of 770 to 815 °C and 0.25 to 0.7 Å/s, respectively. The nitrogen rate was equal to 2.8 Å/s: the V/III ratio was thus varied in the range of 4 to 11.2. *In situ* RHEED measurements were performed during the entire growth process with an incident electron beam angle to the substrate of 3°. One RHEED pattern was recorded every 12 s while the RHEED intensity was determined by monitoring *in situ* the diffraction intensity in a fixed rectangular area at a given position that involves several GaN 3D spots. The evolution of the GaN spot intensity was then extracted by integrating and summing the overall area over each GaN 3D spot. It is worth noticing that the background intensity between the GaN 3D spots corresponding to the diffusive contribution was subtracted.

Three typical RHEED patterns recorded at different growth times for the same sample are presented in Fig. 1. Prior to GaN growth, the  $7 \times 7$  surface reconstruction of the Si(111) substrate is revealed as seen in Fig. 1(a) and then vanishes rapidly once the nitridation process is initiated by the opening of only the nitrogen shutter. After 5 min of nitridation, a continuous  $\text{Si}_x\text{N}_y$  amorphous interlayer has been formed with a thickness of about 2 nm and no RHEED signal is detected as seen in Fig. 1(b).<sup>9</sup> Interestingly, once the gallium shutter is opened as well, the nucleation of crystalline GaN does not immediately start: the first GaN 3D spots as seen in Fig. 1(c) appear only after a preliminary incubation time. Thus, the nucleation phase can be divided into two stages, as shown in Fig. 2: stage (I) starts with the opening of the gallium shutter at  $t=0$  s and is associated with the RHEED intensity close to zero. The subsequent increase in the RHEED intensity defines the transition to stage (II). Such a delay in the nucleation process is likely due to massive gallium desorption at the high growth temperature of 780 °C. In particular, it has recently been reported from quadrupole mass spectrometry measurements that the gallium desorption

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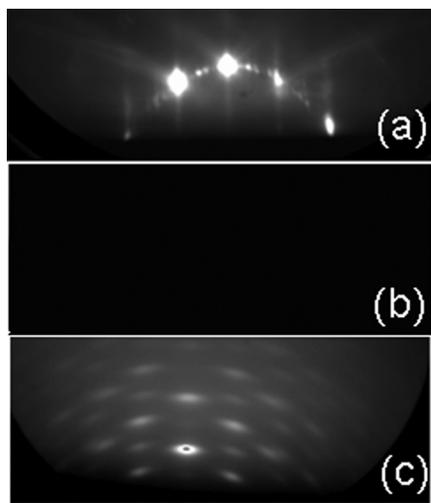


FIG. 1. Three typical RHEED patterns collected (a) prior to GaN growth on the  $7 \times 7$  silicon surface reconstruction, (b) once the nitrogen shutter has been opened for the nitridation process, and (c) once the very first spherical cap-shaped islands have nucleated.

rate cannot be neglected in stage (I).<sup>14</sup> Since gallium adatoms can adsorb onto, desorb from and diffuse on the surface, metastable 2D GaN nuclei could be formed during this period whereas the probability to create a stable nucleus with critical size is low.<sup>8,9</sup> Basically, the extreme growth conditions that combine very high growth temperature with very low gallium rate (i.e., high V/III ratio) are expected to make the incubation time longer. Consequently, the incubation time is a measure of the metastability limit prior to the formation of stable nuclei with critical size.<sup>20</sup>

For the self-induced growth of GaN NWs, it has been found that stable nuclei are actually spherical cap-shaped islands.<sup>8,9</sup> Therefore, the increase in the RHEED intensity in stage (II) as depicted in Fig. 2 is related to the increase in both the density and size of spherical cap-shaped islands. It should be noted that the increase in the RHEED intensity follows a supra-linear behaviour, which is in agreement with the evolution of the x-ray diffraction intensity as described in Ref. 12

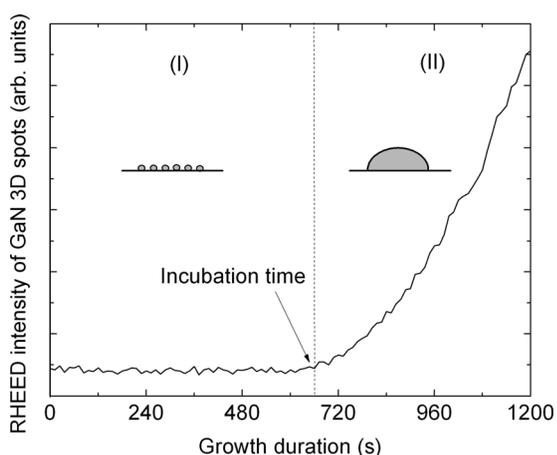


FIG. 2. Evolution of the RHEED intensity as growth proceeds for a growth temperature and gallium rate of  $790^\circ\text{C}$  and  $0.45 \text{ \AA/s}$ , respectively. The gallium shutter was opened at  $t=0$  s. The transition between the two distinct consecutive stages is indicated by the vertical dotted line. The insets represent simple sketches of the GaN island shapes characteristic for the two stages: subcritical nuclei are represented in stage (I), whereas stable nuclei in the form of spherical-cap shaped islands are present in stage (II).

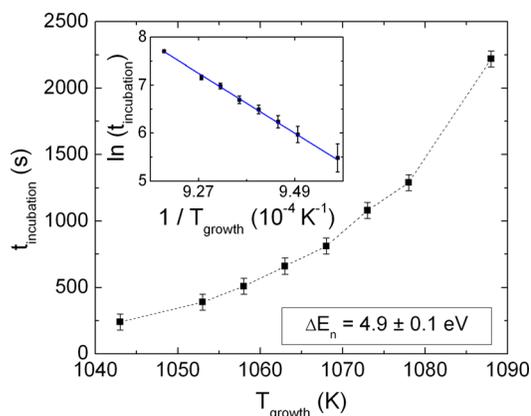


FIG. 3. (Color online) Evolution of the incubation time with the growth temperature. The gallium rate is  $0.45 \text{ \AA/s}$ , which corresponds to a V/III ratio of 6.2. The inset represents the variation of  $\ln(t_{\text{incubation}})$  vs  $1/T_{\text{growth}}$  in which a nucleation energy of  $4.9 \pm 0.1 \text{ eV}$  is inferred from the fit (i.e. solid line) to Eq. (4).

from synchrotron radiation-based experiments. The very first NWs are formed only when the shape transition of spherical cap-shaped islands takes place after a characteristic time called the transition time. The total growth time  $t_{\text{tot}}$  for the self-induced approach is thus defined as the sum of the incubation time  $t_{\text{incubation}}$ , of the transition time  $t_{\text{transition}}$  necessary to induce the transition from spherical cap-shaped islands to NWs, and of the actual growth (i.e. lengthening) time  $t_{\text{actual}}$  corresponding to the growth phase:  $t_{\text{tot}} = t_{\text{incubation}} + t_{\text{transition}} + t_{\text{actual}}$ . As it is shown below, the incubation time can be quite long and has to be taken into account when the growth rate is determined from NW length and growth duration.<sup>24</sup>

Interestingly, the incubation time is highly dependent upon the growth temperature and gallium rate, as shown in Figs. 3 and 4. In particular, the incubation time drastically increases from 240 to 2220 s (i.e. from 4 to 37 min) as the growth temperature is raised from  $770$  to  $815^\circ\text{C}$ . It is expected that the gallium desorption rate increases as the growth temperature is raised, which reduces the probability to form a spherical cap-shaped island with critical size. Similarly, the incubation time significantly decreases from 960 to 210 s (i.e. 16 to 3.5 min), as the gallium rate is increased from  $0.25$  to  $0.7 \text{ \AA/s}$ . An increase in the gallium rate is expected to enhance the probability to form a spherical cap-shaped island

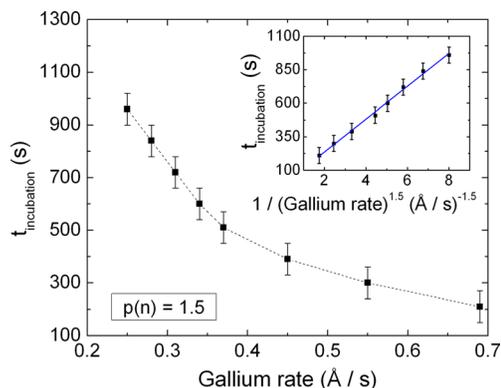


FIG. 4. (Color online) Evolution of the incubation time with the gallium rate. The growth temperature is  $780^\circ\text{C}$ . The inset represents the variation of  $t_{\text{incubation}}$  vs  $1/R^{1.5}$  in which a nucleus critical size-dependent exponent  $p(n)$  of 1.5 is inferred from the fit (i.e. solid line) to Eq. (3).

with critical size. According to standard island nucleation theory, the incubation time is related to the island nucleation rate  $I$  and to the surface area  $S$  considered, as follows:<sup>20</sup>

$$t_{\text{incubation}} = \frac{1}{I \cdot S} \quad (1)$$

For materials deposited by thin film technology, it has been shown that the island nucleation rate  $I$  can be described by the following general relation:<sup>21–23</sup>

$$I = I_0 R^{p(n)} \exp\left(-\frac{\Delta E_n}{k_B T_{\text{growth}}}\right) \quad (2)$$

in which  $R$  is the atom arrival rate per unit surface area and per unit time,  $T_{\text{growth}}$  is the growth temperature,  $I_0$  is a  $R$ - and  $T$ -independent constant, and  $\Delta E_n = (n + 1)E_D - E_{SD} + E_n$  is the nucleation energy, where  $n$  is the critical nucleus size (i.e., its number of atoms),  $E_D$  is the desorption activation energy,  $E_{SD}$  is the surface diffusion activation energy, and  $E_n$  is the dissociation energy of a critical-sized nucleus.  $p(n)$  is a nucleus critical size-dependent exponent.<sup>21–23</sup> Since gallium species are outnumbered by nitrogen species,  $R$  is here proportional in a first approximation to the gallium rate. From Eq. (2), it is expected that the nucleation rate decreases by raising the growth temperature.<sup>21</sup>

By inserting Eq. (2) in Eq. (1), the incubation time can be expressed as

$$t_{\text{incubation}} = \frac{1}{I_0 S \cdot R^{p(n)}} \exp\left(-\frac{\Delta E_n}{k_B T_{\text{growth}}}\right). \quad (3)$$

Therefore, the incubation time follows an Arrhenius-type law such that the formation of spherical cap-shaped islands is especially temperature-dependent. From Eq. (3), it can be deduced that

$$\ln(t_{\text{incubation}}) = \ln\left(\frac{1}{I_0 S \cdot R^{p(n)}}\right) - \frac{\Delta E_n}{k_B T_{\text{growth}}}. \quad (4)$$

By plotting  $\ln(t_{\text{incubation}})$  vs  $1/T_{\text{growth}}$  as shown in the inset of Fig. 3, a nucleation energy of  $4.9 \pm 0.1$  eV is deduced from the slope of the linear fit for a gallium rate of  $0.45 \text{ \AA/s}$ . This activation energy strongly depends on the physical phenomena at work on the surface of the  $\text{Si}_x\text{N}_y$  amorphous interlayer, such as the processes of desorption and surface diffusion.<sup>22,23</sup> Surface defects such as surface steps or surface roughness may also have an influence on this activation energy. Similarly, by plotting  $t_{\text{incubation}}$  vs  $1/R^{p(n)}$  as revealed in the inset of Fig. 4, the nucleus critical size-dependent exponent  $p(n)$  can be determined: an exponent of 1.5 is inferred. The relation between  $p(n)$  and  $n$  is actually not straightforward and still under debate. In a first approximation, it can be assumed that  $p(n) = n$  as mentioned in Ref. 21 or  $p(n) = n + 1$  as reported in Refs. 22 and 23; therefore, a nucleus critical size  $n$  of 1.5 or 0.5 can be deduced. These very small values are in agreement with the very low nucleus critical size of 1 as commonly reported for the MBE growth.<sup>22,23</sup> Its non-integer value may be due to inhomogeneities in temperature and flux as well as surface roughness and defects of the  $\text{Si}_x\text{N}_y$  amorphous interlayer: it is indeed well-known that surface defects results in a decrease in the exponent  $p(n)$ .<sup>22,23</sup> However, it should eventually be noted

that the expression of  $p(n)$  could be more complicated since the conditions involved in the self-induced growth of GaN NWs by MBE are extreme. The main insight obtained from these results is that the incubation time can be predicted by standard island nucleation theory. This finding is crucial for applications since the NW structural properties such as their diameter, length, and density are all dependent upon the selected total growth time.

In conclusion, during the self-induced growth of GaN NWs, stable nuclei as spherical-cap shaped islands form only after an incubation time of considerable length. This incubation time strongly depends on the growth temperature and gallium rate and can be described in the framework of standard island nucleation theory. Under the employed growth conditions, a nucleation energy of  $4.9 \pm 0.1$  eV is found as well as a very small nucleus critical size. For the controlled growth of self-induced GaN NWs with specific properties, it is essential that the incubation time be taken into consideration.

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<sup>1</sup>C. M. Lieber and Z. L. Wang, *MRS Bull.* **32**, 99 (2007).

<sup>2</sup>A. Kikuchi, M. Kawai, M. Tada, and K. Kishino, *Jpn. J. Appl. Phys.* **43**, L1524 (2004).

<sup>3</sup>A. L. Bavecove, G. Tourbot, E. Pougeoise, J. Garcia, P. Gilet, F. Levy, B. André, G. Feuillet, B. Gayral, B. Daudin, and Le Si Dang, *Phys. Status Solidi A* **207**, 1425 (2010).

<sup>4</sup>M. Yoshizawa, A. Kikuchi, M. Mori, N. Fujita, and K. Kishino, *Jpn. J. Appl. Phys.* **36**, L459 (1997).

<sup>5</sup>M. A. Sanchez-García, E. Calleja, E. Monroy, F. J. Sanchez, F. Calle, E. Muñoz, and R. Beresford, *J. Cryst. Growth* **183**, 23 (1998).

<sup>6</sup>C. Chèze, L. Geelhaar, O. Brandt, W. Weber, H. Riechert, S. Münch, R. Rothmund, S. Reitzenstein, A. Forchel, T. Kehagias, P. Komninou, G. P. Dimitrakopoulos, and T. Karakostas, *Nano Res.* **3**, 528 (2010).

<sup>7</sup>S. Fernández-Garrido, J. Grandal, E. Calleja, M. A. Sánchez-García, and D. López-Romero, *J. Appl. Phys.* **106**, 126102 (2009).

<sup>8</sup>V. Consonni, M. Knelangen, L. Geelhaar, A. Trampert, and H. Riechert, *Phys. Rev. B* **81**, 085310 (2010).

<sup>9</sup>V. Consonni, M. Hanke, M. Knelangen, L. Geelhaar, A. Trampert, and H. Riechert, *Phys. Rev. B* **83**, 035310 (2011).

<sup>10</sup>T. Stoica, E. Sutter, R. J. Meijers, R. K. Debnath, R. Calarco, H. Lüth, and D. Grützmacher, *Small* **4**, 751 (2008).

<sup>11</sup>V. Consonni, M. Knelangen, A. Trampert, L. Geelhaar, and H. Riechert, *Appl. Phys. Lett.* **98**, 071913 (2011).

<sup>12</sup>O. Landré, C. Bougerol, H. Renevier, and B. Daudin, *Nanotechnology* **20**, 415602 (2009).

<sup>13</sup>M. Knelangen, V. Consonni, A. Trampert, and H. Riechert, *NanoTechnology* **21**, 245705 (2010).

<sup>14</sup>C. Chèze, L. Geelhaar, A. Trampert, and H. Riechert, *Appl. Phys. Lett.* **97**, 043101 (2010).

<sup>15</sup>T. Clement, S. Ingole, S. Ketharanathan, J. Drucker, and S. T. Picraux, *Appl. Phys. Lett.* **89**, 163125 (2006).

<sup>16</sup>B. Kalache, P. Roca i Cabarrocas, and A. Fontcuberta i Morral, *Jpn. J. Appl. Phys.* **45**, L190 (2006).

<sup>17</sup>B. J. Kim, J. Tersoff, S. Kodambaka, M. C. Reuter, E. A. Stach, and F. M. Ross, *Science* **322**, 1070 (2008).

<sup>18</sup>D. Buttard, T. David, P. Gentile, F. Dhalluin, and T. Baron, *Phys. Status Solidi (RRL)* **3**, 19 (2009).

<sup>19</sup>C. Chèze, L. Geelhaar, A. Trampert, O. Brandt, and H. Riechert, *Nano Lett.* **10**, 3426 (2010).

<sup>20</sup>D. Kashchiev, D. Verdoes, and G. M. Van Rosmalen, *J. Cryst. Growth* **110**, 373 (1991).

<sup>21</sup>C. V. Thompson, *J. Mater. Res.* **14**, 3161 (1999).

<sup>22</sup>J. A. Venables, G. D. T. Spiller, and M. Hanbücken, *Rep. Prog. Phys.* **47**, 399 (1984).

<sup>23</sup>J. A. Venables, *Sur. Sci.* **299–300**, 798 (1994).

<sup>24</sup>C. Chèze, L. Geelhaar, B. Jenichen, and H. Riechert, *Appl. Phys. Lett.* **97**, 153105 (2010).