From nucleation to growth of catalyst-free GaN nanowires on thin AlN buffer layer

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We demonstrate that thin AlN buffer layers improve the orientation of GaN nanowire grown on Si(111). The deposited GaN initially forms into islands which act as a seed for the wires. By raising substrate temperature, the actual amount of grown material decreases but wire density increases and well-separated wires are achieved. Fast wire length growth rate at high growth temperature is assigned to an enhancement of adatom diffusion. The upper limit of length growth rate is determined by the supply rate of active nitrogen.  © 2007 American Institute of Physics.

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For decades, there have been numerous attempts to solve a well-known problem of III-nitride material family, i.e., defects and dislocations due to a lack of proper substrates. The high aspect ratio of nanowires might be a promising solution since it allows the strain in material to relax without dislocation formation. Not only providing a possibility to create a defect-free material, nanowires also open the way to scale down device dimensions. III-N nanowires with excellent crystal quality can be achieved by molecular beam epitaxy (MBE) on Si(111) despite large mismatch.\textsuperscript{1} The strong luminescence observed in such structures\textsuperscript{2} indicates a potential to improve the efficiency of III-N based devices.

In spite of several reports about GaN nanowire growth by MBE,\textsuperscript{3-6} there are very few works focused on the nucleation process.\textsuperscript{5} In addition, even though high substrate temperature and N-rich condition are known to be necessary for the wire growth,\textsuperscript{7} the understanding of wire structural evolution as a function of those parameters are still not completed. Moreover, the quantitative analysis of the wire growth rate enhancement with respect to the planar layer growth rate is also missing. This knowledge could give an insight to the growth mechanism which is important for the fabrication of nanowires.

In this letter, we present detailed analysis of GaN nanowires grown without using external catalyst on thin AlN layer on Si(111) substrate. The nucleation stages are investigated by reflection high energy electron diffraction (RHEED) and scanning electron microscopy (SEM). The structural evolution as a function of growth parameters is systematically studied in terms of diameter and length growth rate and wire density.

GaN nanowires were grown by using radio frequency plasma-assisted MBE on Si(111) substrates under N-rich atmosphere. The substrates were degreased before being passivated by HF (5%) for 2 min. Afterward, they were thermally outgassed until (7×7) reconstruction of clean Si(111) surface appeared. The structure and the density of nanowires were investigated by SEM using a ZEISS Ultra 55.

When GaN was deposited directly on Si(111) at 790 °C, RHEED pattern gradually evolved from a (7×7) streaky feature to a ringlike pattern indicating a disorientation of the grown layer. Continuing GaN deposition, a pattern corresponding to a hexagonal structure appeared overlapping with a faint ringlike pattern, as shown in Fig. 1(a). SEM image in Fig. 1(b) reveals that the nanowires are not well-oriented perpendicular to the substrate surface. The formation of thin SiN\textsubscript{x}, at the beginning of the growth could be a major reason for the disorientation.\textsuperscript{7}

Since AlN is known to improve quality of two dimensional (2D) GaN grown on Si(111),\textsuperscript{8} 2 nm AlN was inserted prior to GaN deposition. A coincidence relationship between AlN and Si(111) lattice\textsuperscript{9} allows the deposited AlN to grow in 2D mode as evidenced by a streaky RHEED pattern. After GaN deposition on AlN, RHEED pattern became slightly spotty (not shown here) and transformed to well-defined spots, as shown in Fig. 1(c). We do not observe any ringlike pattern in this case. Figure 1(d) shows that these nanowires grow perpendicular to the substrate surface.

We investigated structural evolution of GaN grown on AlN thin layer on Si(111) as a function of deposition time ($t_{\text{dep}}$). In this case, the nominal deposition rate ($R_{\text{nom}}$) was 0.33 Å/s as calibrated by RHEED intensity oscillations dur-
ing the growth of GaN 2D layer on GaN thick layer at 765 °C. The substrate temperature was kept at 790 °C. At \( t_{\text{dep}} \) equal to 10 min, a low density of wirelike structure formed together with a high density of GaN islands. The island formation is consistent with spotty RHEED pattern at the initial stage of the deposition. Figures 2(a) and 2(b) are top view and 45° tilted SEM images of the surface at \( t_{\text{dep}} \) equal to 20 and 30 min, respectively. Most of the nanowires grow directly on the top of the three-dimensional islands. There was no clear evidence of island formation when GaN was deposited directly on Si (111).

The average length (\( R_L \)) and diameter (\( R_D \)) growth rate and the wire density are summarized as a function of \( t_{\text{dep}} \) in Figs. 2(c)–2(e). \( R_L \) and \( R_D \) were estimated by dividing the average diameter and height by \( t_{\text{dep}} \). Two regimes can be identified. In the first one, the growth rates in vertical and lateral directions are initially comparable, followed by a rapid drop of \( R_D \) and an increase of \( R_L \) and the wire density. In the second regime indicated by a shaded area in Figs. 2(c)–2(e), the wire density and the growth rates in both directions become constant.

GaN deposited on partially relaxed AlN surface forms into islands via Stranski-Krastanow growth mode. These islands are expected to be preferential sites for further GaN growth due to strain minimization. Thus, the islands could act as a material collector and become a seed of the nanowires. \( R_D \) and \( R_L \) evolutions indicate that the deposited material initially incorporates to the seeds in both lateral and vertical directions and next preferentially participates to the vertical growth.

In the second regime, the nucleation process is complete as evidenced by the saturation of the wire density at 240–275 \( \mu \text{m}^{-2} \). The density possibly saturates due to the growth competition between the adjacent seeds,\(^{10}\) preventing the deposited material to be involved in the nucleation process. Except for those desorbing from the surface, adatoms incorporate to the wires at a constant rate. The ratio between \( R_D \) and \( R_L \) is around 1:32. This value is consistent with that reported in Ref. 6.

We investigated the substrate temperature effect on the nanowires in the regime where the wire density saturates. GaN layers were deposited by using \( R_{\text{nom}} \) equal to 0.35 \( \text{Å/s} \). Figures 3(a)–3(c) are side view SEM images of GaN layers deposited on thin AlN layer at 740, 765, and 780 °C, respectively. Figure 3(d) is a top view image corresponding to Fig. 3(b). At 740 °C, GaN 2D layer with a porous feature is observed together with very few nanowires. The formation of heavily pitted morphology is usually found in GaN grown under N-rich condition.\(^{11}\) At 765 °C, the wire density increases but 2D layer remains at the wire base and the length is substantially higher than the 2D layer thickness. At 780 °C, well-separated wires with high density can be achieved.

The wire density, the wire length growth rate (\( R_L \)), the actual growth rate (\( R_{\text{act}} \)), and the growth rate of 2D layers at the wire base as a function of substrate temperature are displayed in Figs. 4(a) and 4(b). \( R_{\text{act}} \) is approximated by the equivalent 2D thickness of the overall material in the wires and in the 2D area divided by \( t_{\text{dep}} \). The amount of the grown material contributing to the wires is estimated by multiplying the average volume of single nanowire by the wire density. We assume a cylindrical geometry of the wire.

As shown in Fig. 4(a), the wire density increases from 1 to 275 \( \mu \text{m}^{-2} \) with increasing substrate temperature. On the
We changed Ga cell temperature from 850 to 910 °C which at 790 °C provides the highest length growth rate. However, the growth rate of 2D layer and $R_{\text{act}}$ are comparable. In contrast to $R_{\text{act}}$, $R_L$ continually increases by raising the growth temperature.

The dependence of $R_L$ and the wire density on substrate temperature can be explained by the role of Ga diffusion. At low substrate temperature, a short diffusion length of Ga species leads them to incorporate to 2D layer before arriving to wire seeds, resulting in a small amount of Ga atoms contributing to the wire growth. As a consequence, only few seeds could evolve to nanowires and slow $R_L$ is obtained. By raising growth temperature, the diffusion process is enhanced leading larger amount of Ga atoms to contribute to the wire growth. Hence, higher wire density and faster $R_L$ can be achieved.

It is worth to note that well-separated wires form at the temperatures which causes substantial reduction of actual amount of grown material due to significant Ga desorption and GaN decomposition. However, the wire growth rate is continually faster at higher growth temperature [Fig. 4(b)] which corresponds to an increasing amount of Ga atoms participating to the length growth. The absence of 2D layer coinciding with the continual growth of the wires suggests an enhanced diffusion of Ga adatoms toward the wires at such high temperature. Nevertheless, since Ga desorption and GaN decomposition also occur at the wires, $R_L$ can only reach a certain maximum value and then drops when substrate temperature is further increased.

In next experiments, the growth temperature was kept at 790 °C which provides the highest length growth rate. We changed Ga cell temperature from 850 to 910 °C which corresponds to $R_{\text{nom}}$ calibrated at 765 °C ranging from 0.16 to 0.66 Å/s. Well-separated wires form with a density ranging from 140 to 275 μm⁻² by increasing $R_{\text{nom}}$. This observation indicates a general law of cluster nucleation kinetics in which the cluster density increases at higher deposition rate. Nevertheless, the wire density drops to 200 μm⁻² at $R_{\text{nom}}$ equal to 0.66 Å/s due to the wire coalescence.

Figure 5 shows the variations of $R_{\text{nom}}$ calibrated at 765 °C and at 790 °C, $R_L$ and $R_{\text{act}}$ of nanowires grown at 790 °C as a function of Ga cell temperature. $R_{\text{nom}}$ at 790 °C is smaller than that at 765 °C due to Ga desorption and GaN decomposition. By increasing Ga cell temperature, $R_{\text{act}}$ increases but is significantly smaller than $R_{\text{nom}}$ even if the growth rate reduction due to the temperature is taken into account. Approximated from SEM images, only 18%–29% of the deposited material contributes to the growth which is attributed to the enhancement of Ga desorption due to high surface to volume ratio. Even though $R_L$ is larger than $R_{\text{nom}}$ and $R_{\text{act}}$ in all cases, $R_L$ tends to approach GaN growth rate at stoichiometry at higher supply rate of Ga species. The stoichiometry is the point where the supplied number of Ga atoms is roughly equal to the supplied number of active N atoms. In our study, the growth rate at this point is about 1 Å/s.

The larger $R_L$ compared to $R_{\text{nom}}$ also indicates a contribution of the diffusion process to the wire length growth, apart from the direct deposition. The amount of Ga atoms involved in the wire length growth can be altered by changing growth temperature and deposition rate. However, the fact that $R_L$ approaches the growth rate at stoichiometry suggests that the active N atoms impinging on the wire top contribute to the length growth and the contribution of diffusing N atoms is negligible. In other words, the supply rate of active N atoms is the upper limit of GaN nanowire length growth rate. Since the deposition at the wire sidewall is insignificant in MBE, the diffusing Ga atoms mainly travel along the sidewall and incorporate to the wire when they encounter the active N atoms at the wire top. The small amount of active N available at the sidewall leads to the slower growth rate in the lateral direction compared to the vertical one.

In summary, we have shown that GaN nanowire orientation can be improved by using thin AlN buffer layers. Nanowires originate from GaN islands. The length growth rate can be controlled by direct deposition and diffusion process but the upper limit is determined by the supply rate of active N. At high growth temperature at which the actual amount of grown material reduces, the well-separated wires form due to the large diffusion length of Ga atoms.

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