Buffer controlled GaN nanorods growth on Si(111) substrates by plasma-assisted molecular beam epitaxy

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Size, shape, and density of self-assembled GaN nanorods grown on Si(111) substrates by plasma-assisted molecular beam epitaxy were successfully controlled by inserting a GaN buffer layer. The structure of the GaN buffer layer plays a vital role in the nanorod growth. Only a broken buffer layer with a suitable opening size can grow nanorods. Evolution of the nanorod is traced to the initial growth stage. Crystal seed grown at the wall of the opening in the buffer layer initiates the beginning of the nanorod, and a self-catalytic vapor-liquid-solid process, triggered by the nanocapillary condensation effect, enhances the GaN nanorod growth. Furthermore, the nanorod density can be largely controlled by using the beam equivalent pressure of the N/Ga ratio. Other GaN nanostructures grown at different growth conditions are also discussed in details. © 2006 American Vacuum Society. [DOI: 10.1116/1.2186342]

I. INTRODUCTION

Low-dimensional nanometer-scale objects have attracted extensive interest in the past decade because of their enormous potential for various electronic and optoelectronic nanodevice applications.1–4 High performance nanodevices based on GaN of high crystal quality are especially attractive as GaN and other related nitrides have many unique properties unavailable from other material systems, such as the wide and direct band gap, chemical stability, high radiation hardness, and capability for high temperature operation,5–10 just to name a few. As reported in the literature, many nanometer-scale GaN structures, for example, nanoparticles,11 nanowires,12,13 nanotubes,14,15 nanopillars,16,17 nanocolumns,18–24 and nanorods,25–27 have been made by various methods. Vertical GaN nanorods and nanocolumns grown on certain substrates are useful material structures, from an application point of view, because well-established traditional multilayered or heterostructural materials can possibly be fabricated on their tops. Practical application of the GaN nanorods includes ultraviolet, blue, green, and white light-emitting diodes (LEDs), laser diodes (LDs), nanosized vertical-cavity surface-emitting laser (VCSEL), and many others.28–30 In order to increase the availability of nanomaterials, many researchers have attempted to control the rod density and lateral width because different specifications have different applications. Dense nanorods can be practically applied to highly luminescent devices, such as high brightness LEDs, because of their highly crystalline quality and large emissive area.28 Isolated nanorods, with rather low rod density, are very suitable to be fabricated as a single nanodevice, and many physical properties can be extracted from a single nano-object.29,30 Although there have been many reports in the literature on the growth of GaN nanocolumns and nanorods, there seems to be no coverage of the full spectrum of evolving nanostructures.18–27 The intricacy of growth conditions in relation to the resultant material structures hence continues to be an intractable problem. Recently, GaN nanorods and nanocolumns grown on different substrates with or without a buffer layer, such as AlN/Al2O3,18–20 GaN/Al2O3,21 AlN/Si(111),21,22 SiO2/Si(001),23 SiC/Si(111),24 Si(111),27 etc., have been studied, but no special differences are observed between the use of these substrates. Appearance of these one-dimensional (1D) nanorodlike structures in their reports is always dominated by changing the beam equivalent pressure (BEP) of the N/Ga ratio and the growth temperature. However, not only these two parameters but also the buffer layer structure can affect the GaN nanorod growth. In previous reports, nanorods grown directly on a substrate or a flat buffer layer controlled by the effective N/BEP/GaBEP ratio could only show relationships of high density to small diameter (highly N-rich condition) and low density to large diameter (slightly N-rich condition).18–27 But the control of specific rod density, diameter, and shape should be studied further. In this article, the GaN nanorod growth was well controlled by inserting a GaN buffer layer under different growth conditions, and many combinations of the rod density and diameter were obtained. Additionally, a comprehensive study has been conducted in an effort to understand the structural evolution from the nearly two-dimensional (2D) epilayer to various sophisticated nanostructures.

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II. EXPERIMENTAL DETAILS

GaN nanorods and related nanostructures were grown on n⁺-Si(111) substrate by plasma-assisted molecular beam epitaxy (PAMBE). The PAMBE instrument is a Veeco-Applied EPI 930 system with liquid nitrogen cryopanel cooling. The growth chamber was evacuated down to a base pressure of $3 \times 10^{-11}$ Torr by a combination of roughing pump, turbomolecular pump, and cryopump. 7N5 pure Ga metal was vaporized with a standard Knudsen effusion cell. 6N pure N₂ was further purified through a chemical purifier (Aeronex) and then fed into a radio-frequency (rf) plasma generator. Both Ga vapor and nitrogen plasma flux were measured with a beam flux gauge. Every effusion cell was equipped with a pneumatic shutter to control the sample growth. The Si substrate was cleaned with acetone, isopropanol, and de-ionized water in an ultrasonic bath to remove residual organic contamination on the surface. To remove surface native oxides, chemical dipping in a HF:H₂O=1:5 solution, the concentration of the HF solution before dilution is 48%, for 5 min was applied. After chemical dipping, the substrate was again cleaned with DI water. After the chemical cleaning process, Si substrate was loaded into the buffer chamber and then transferred into the growth chamber with the transfer arm. The Si substrate was annealed at 900 °C for 30 min in the growth chamber before the growth of GaN nanostructures. A clear (1×1) Si reflection high-energy electron diffraction (RHEED) pattern with Kikuchi lines was observed. After cooling down to 760 °C, the RHEED pattern showed a clear (7×7) surface reconstruction pattern. This pattern indicated that the native oxides had been removed from the Si surface. Then, the GaN nanostructures were grown under different conditions. After the GaN nanostructures’ growth, field-emission scanning electron microscopy (FESEM) was applied to analyze the surface morphology. In order to show more information, these samples were often tilted 20° from the surface’s normal direction or the cross-sectional surface.

III. RESULTS AND DISCUSSIONS

A. Variety of the GaN nanorods controlled by the GaN buffer layer

Various GaN nanorod structures with different sizes, shapes, and densities are shown in Fig. 1 and classified in two different structural groups. One is a dense nanorod structure, and the other structure is isolated nanorods, which are well separated and extruded above the surrounding matrix. Growth conditions and rod structures of these samples (A1–A6) are listed in Table I. Only sample A6 was directly grown on Si(111) substrate with the same rod growth conditions, which were with temperature of 720 °C, growth time of 5 h, and a Nbep/GaBEP ratio of 40. GaBEP values of 2.5×10⁻⁷ and of 8.0×10⁻⁸ Torr were used for the growth of the nanorod and the buffer, respectively, and the Nbep was proportional to the GaBep. The rf power of the nitrogen plasma was always set at 500 W for both the growth of the buffer and nanorod. Among the isolated nanorod structures, the GaN nanorods (sample A3), grown on a suitable buffer layer with a growth temperature of 600 °C, show regular shapes and a uniformly lateral width distribution, but the others (samples A2 and A4) show irregular shapes and a wide lateral width distribution. From the surface FESEM images, regular nanorods show hexagonal shapes with flat surfaces, and they are always accompanied with a sixfold symmetrically V-shaped crater growth. 20 Irregular nanorods have a variety of shapes, such as triangular, rectangular, pentagonal, and hexagonal shapes, and craters with similar shapes also accompanied the rod growth. However, the irregular nanorods are mostly shorter and wider than the regular nanorods. No specific shape can be concluded from the dense nanorods (samples A1, A5, and A6). These nanorods were grown from the substrate surface without a surrounding matrix. This morphological change, the isolated nanorod structure translated into the dense nanorods, is merely due to the use of different buffer structures. This result indicates that the buffer layer has a vital role not only in epifilm growth but also in nanorod growth.

Figure 2(a) shows that the distribution of the GaN nanorod lateral width depends on buffer layer temperature. These statistic results, fitted by a Gaussian formula, show that the nanorods grown on the buffer layer at a temperature of 600 °C (sample A3) have the smallest lateral width and the narrowest width dispersion. The peak of the width distribution curve and the full width at half maximum (FWHM) of the curve which were fitted by a Gaussian formula from sample A3 are 61.1 and 24.2 nm, respectively. As the buffer temperature moves away from 600 °C, both the peak and the FWHM become wider. The rod density, peak, and FWHM of the rod distributions are plotted in Fig. 2(b). As a comparison, sample A6 grown without buffer layer (hollow symbols) is added into Fig. 2(b) and treated as grown on a buffer with a temperature of 720 °C. Densities of the dense nanorods are all almost the same, namely, $2 \times 10^{9}$ cm⁻², but isolated nanorods have rather small densities in the range of $1 \times 10⁷$ to $2 \times 10⁹$ cm⁻², depending on the buffer condition. Conspicuously, only a buffer grown at the medium temperature range promotes isolated nanorod growth with thinner width, better width uniformity, and lower rod density. In earlier reports, 18-22 high density/small diameter (<100 nm) and low density/large diameter (≥100 nm) nanorods were fabricated on different substrates by tuning the effective Nbep/GaBEP ratio. The effective Nbep/GaBEP ratio can be adjusted through adjusting the nominal Nbep/GaBEP ratio, the rf power, and the growth temperature. Furthermore, by inserting a GaN buffer layer, low density/small diameter, low density/large diameter, and high density/large diameter nanorods were achieved in this study.

B. Evolution of the GaN nanorods from buffer layer

Three major morphologies of the GaN buffer layer grown on the Si(111) substrates are shown in Fig. 3. Buffers A1, A3, and A5 grown at temperatures of 460, 600, and 690 °C show a granular structure [Fig. 3(a)], a broken film [Fig. 3(b)], and isolated islands [Fig. 3(c)], respectively. The granular and the isolated island structures lead subsequent films into densely nanorod structures, because the role of these three-
dimensional (3D) islands is to act as nucleation sites to assist the nanorod growth. Figure 3(b) shows that many openings were formed in the buffer layer with sizes in a range of 5–100 nm. In some large openings (<20 nm), a pad grown at the sidewall of the openings may serve as a crystal seed for the isolated nanorod growth. To further study the isolated nanorod growth, different growth times were carried out to trace the regular nanorod growth by using sample A3 growth condition. After 30 min growth, as shown in Figs. 4(a) and 4(b), a large number of rods standing on the sidewall of

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\begin{array}{|c|c|c|c|c|}
\hline
\text{Sample No.} & \text{Temperature (°C)} & \text{N}_{\text{BEP}}/\text{Ga}_{\text{BEP}} \text{ ratio} & \text{Time (min)} & \text{Film structure} \\
\hline
A1 & 460 & 100 & 20 & Dense nanorods & 202.5 \\
A2 & 510 & 100 & 20 & Irregular Nanorods & 105.1 \\
A3 & 600 & 100 & 20 & Regular Nanorods & 61.1 \\
A4 & 620 & 100 & 20 & Irregular Nanorods & 96.6 \\
A5 & 690 & 100 & 20 & Dense nanorods & 168.4 \\
A6 & Without buffer layer & & & Dense nanorods & 150.0 \\
\hline
\end{array}
\]

\(a\) Most rod width: width at the peak of the rod width distribution curve.
craters become prominent with an almost equal height to the surrounding matrix. Figure 4(c) shows the top-view image of a regular hexagonal rod in the center of a crater with a 3 h growth. Both the rod size and the crater size are larger than that obtained after 30 min growth. In Fig. 4(d), a lateral view image shows that the “rod” is embedded inside a large V-shaped opening of a vertical trench. The inset of Fig. 4(d) shows that the root of the rod is in a cave and stands on a pad near the GaN/Si interface. This indicates that the broken buffer film offers a very important environment to promote the nanorod growth inside the large opening.

Figure 5 shows the relationships of matrix thickness, rod height, and rod density with different growth times. Both the matrix and the rods show a linear relationship between the height and growth time, and they keep nearly constant growth rates. The dependence of the densities of nanorods on growth time is nonlinear. The rod density increases very fast when growth time changes from 10 to 30 min. It may be due to the rod height being lower than the matrix thickness for periods less than 10 min, which makes them difficult to be seen and counted. When the rod protrudes above the matrix, it becomes prominent to be identified as shown in Fig. 4(a). The largest rod density is $2.1 \times 10^8$ cm$^{-2}$ after 1 h growth, which is slightly smaller than the density of pads ($3.3 \times 10^8$ cm$^{-2}$) appeared in a large opening. With the increase of the growth time, the nanorod density decreases. The nanorod density decreases about two
orders of magnitude after 20 h growth in comparison to the 30 min growth. This is owing to the fact that some neighboring nanorods coalesce with each other when the distances between these nanorods are too short to grow independently after a long-time growth. This coalescent phenomenon can also be seen in dense nanorods from the cross-sectional SEM images. In summary, the density of pad grown in large openings at 0 min growth, that is, at the buffer layer, is comparable to the maximum density of the nanorods. This result supports the view that the pad serves as a crystal seed to assist the nanorod growth. That is to say, the maximum rod density is determined by the initial growth stage.

C. Role of the \( \frac{\text{NBEP}}{\text{GaBEP}} \) ratio

Various GaN morphologies grown on the same buffer structure (buffer A3) with different \( \frac{\text{NBEP}}{\text{GaBEP}} \) ratios during the nanorod growth are shown in Fig. 6. Their corresponding growth conditions are listed in Table II. These structures vary from matrix only (sample B1) to nanorod with matrix (sample B2), to nanorod with broken matrix (sample B3), and to nanorod with nanocomb structure (sample B4) as the \( \frac{\text{NBEP}}{\text{GaBEP}} \) ratio is changed from 10 to 70. This result reflects that the morphology of the surrounding film is dominated by the surface diffusion length of the Ga adatoms.

Noteworthy, the GaN nanorod that coexisted with the nanocomb structure is quite different from the results of Yoshizawa et al., Calleja et al., and Park et al. because they showed only rodlike structures under N-rich condition. In this series of experiments, basically, the growth rate of the GaN base matrix and nanorod increases as the \( \frac{\text{NBEP}}{\text{GaBEP}} \) ratio increases to 70, and both reach a constant thickness/height at higher \( \frac{\text{NBEP}}{\text{GaBEP}} \) ratios. With respect to rod width, the rod width is between 20 and 100 nm, with most rod widths between 40 and 70 nm when the \( \frac{\text{NBEP}}{\text{GaBEP}} \) ratio is in the range of 30–50. No obvious difference of the rod width is observed in this range of \( \frac{\text{NBEP}}{\text{GaBEP}} \) ratios.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>( \frac{\text{NBEP}}{\text{GaBEP}} ) ratio</th>
<th>Time (h)</th>
<th>Temperature (°C)</th>
<th>Film structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>10</td>
<td>5</td>
<td>720</td>
<td>Matrix only</td>
</tr>
<tr>
<td>B2</td>
<td>30</td>
<td>5</td>
<td>720</td>
<td>Nanorods+matrix</td>
</tr>
<tr>
<td>B3</td>
<td>50</td>
<td>5</td>
<td>720</td>
<td>Nanorods+broken matrix</td>
</tr>
<tr>
<td>B4</td>
<td>70</td>
<td>5</td>
<td>720</td>
<td>Nanorods+nanocomb</td>
</tr>
</tbody>
</table>
a very different phenomenon is that the nanorod density increases one order of magnitude as the $N_{\text{BEP}}/Ga_{\text{BEP}}$ ratio increased from 30 to 50.

Obviously, the $N_{\text{BEP}}/Ga_{\text{BEP}}$ ratio affects both the nanorod and the surrounding matrix growth similar to thin film growth. From a density-functional theory calculation, it was concluded that while Ga is very mobile at typical growth temperatures, diffusion of N is slower by several orders of magnitude. Excess N strongly increases the Ga diffusion barrier, and surface diffusion length of the Ga and the N adatoms dominates the structure evolution. Within an intermediate Ga-rich condition (without Ga droplets), excess Ga forms a steady layer without Ga droplets, and less N adatoms cover the substrate surface and encourage Ga adatoms to travel for a longer distance to promote the film growth with a two-dimensional-like growth mode. Although the GaN film is still grown with a 3D hillock structure, as shown in Fig. 6(a), which is caused by a large lattice mismatch (~17%) between GaN and the Si substrate, the lateral growth rate is high enough to let the nearby 3D islands to coalesce with each other and no nanorod can be grown. On the contrary, with a large amount of N adatoms accumulated on the surface the diffusion of the Ga adatoms under N-rich condition is inhibited, and the matrix becomes a broken film and even develops to a nanocomb structure at higher $N_{\text{BEP}}/Ga_{\text{BEP}}$ ratios. Although a GaN nanorod is grown under N-rich condition, the local environment of the crystal seed in a large opening after the buffer growth can accumulate more Ga adatoms by the nanocapillary condensation effect to form a Ga cluster to start the self-assembled process. A GaN nanorod grows faster along (0001) via the vapor-liquid-solid (VLS) mechanism via reaction of the nitrogen plasma with Ga liquid clusters while its surrounding GaN islands also grow alongside to form the base materials, though at a slower growth rate. Hence, under a slightly N-rich condition, a GaN nanorod grows along the vertical direction with a growth rate $G_{R}$, which is faster than the lateral growth rate of the surrounding matrix $G_{M-L}$, as shown in Figs. 6(b) and 6(c). Furthermore, under highly N-rich condition, though surface diffusion of Ga adatoms is strongly inhibited by the N adatoms, the vertical growth rate of the surrounding matrix is higher than the lateral growth rate, which leads to a nanocomb structure growth, as shown in Fig. 6(d).

Growth diagrams of the GaN nanorod and surrounding matrix are sketched in Fig. 7. At the beginning, the Ga adatoms accumulate on crystal seeds to start a self-catalytic process in large openings triggered via the nanocapillary condensation mechanism [Fig. 7(a)]. Three major morphologies can be discussed via a combination of the parameters of $G_{R}$, $G_{M-L}$, and $G_{M-V}$, the vertical growth rate of the surrounding matrix. When $G_{M-L}$ is bigger than $G_{R}$, no nanorod can protrude above the matrix [Fig. 7(b)]. GaN nanorods start to protrude above the surrounding matrix when $G_{M-L}$ is slightly smaller than $G_{R}$ [Fig. 7(c)]. In Fig. 7(d), $G_{M-L}$ is much smaller than $G_{R}$ and $G_{M-V}$ is similar to $G_{R}$. Utilizing the competition between $G_{R}$ and $G_{M-L}$, a specific nanorod density can be obtained by controlling the $N_{\text{BEP}}/Ga_{\text{BEP}}$ ratio during the nanorod growth. Combined with the buffer structures, the sizes, the shapes, and the densities of the GaN nanorods are more controllable in the self-assembled process, similar to the metal-catalyzed VLS process, in which the diameter of the wire was controlled by the size of the metal catalyst.

**IV. SUMMARY AND CONCLUSIONS**

Various GaN nanorod structures grown on a Si(111) substrate are realized by PAMBE. Evolution of the nanorod structure from isolated regular nanorods, to isolated irregular nanorods, and to dense nanorods is well controlled by the GaN buffer structure. Adding the $N_{\text{BEP}}/Ga_{\text{BEP}}$ ratio parameter to the nanorod growth, the density of the regular nanorods becomes also a controllable item. There are several combinations of rod density and diameter in the nanorod growth. High density/small diameter and low density/large diameter nanorods can be grown directly on the surface without a buffer layer. Low density/small diameter, low density/large diameter, and high density/large diameter nanorods can be achieved by inserting a GaN buffer. A growth mechanism of the isolated nanorods, grown by a buffer assistant, is presented as based on the experimental facts that the crystal seeds grow inside large openings in a broken buffer film and that the nanorods grow faster than the surrounding matrix via self-catalytic VLS process, which is triggered by the nanocapillary condensation.
ACKNOWLEDGMENT

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