Catalyst-Free GaN Nanorods Grown by Metalorganic Molecular Beam Epitaxy

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***Abstract*—High-density GaN nanorods with outstanding crystal quality were grown on c-sapphire substrates by radio-frequency plasma-assisted metalorganic molecular beam epitaxy under catalyst- and template-free growth condition. Morphological and structural characterization of the GaN nanorods was employed by X-ray diffraction, energy dispersive X-ray spectroscopy, scanning electron microscopy, and high-resolution transmission electron microscopy (HRTEM). These results indicate that the rod number density can reach 1×10^{10} cm^{-2} and the nanorods are well-aligned with preferentially oriented in the *c*-axis direction. Meanwhile, no metallic (Ga) droplet was observed at the end of the rods, which is the intrinsic feature of vapor-liquid-solid method. Nanorods with no traces of any extended defects, as confirmed by TEM, were obtained as well. In addition, optical investigation was carried out by temperature- and power-dependent micro-photoluminescence (μ-PL). The PL peak energies are red-shifted with increasing excitation power, which is attributed to many-body effects of free carriers under high excitation intensity. The growth mechanism is discussed on the basis of the experimental results. Catalyst-free GaN nanorods presented here might have a high potential for applications in nanoscale photonic devices.**

***Index Terms*—Catalyst free, GaN nanorod, metalorganic molecular-beam epitaxy, nanotechnology.**

I. Introduction

RECENTLY, the fabrication of nanostructures is driven by fundamental research referring to the associated dimensional dependent physical and chemical phenomena [1]–[4]. III-Nitrides have raised a great deal of interest during the last decade due to their excellent properties as blue and ultraviolet emitters and detectors. Among them, the wurtzite GaN is an important direct bandgap semiconductor, which is used extensively in the electronics industry. Because of the wide bandgap and strongly emissive properties, GaN is of interest for UV or blue emitters, detectors, and high-temperature/power electronic devices [5]–[7]. Additionally, one-dimensional (1-D) semiconductors can be utilized as components in nanometer-scale optoelectronic devices. The quantum size effects associated with the low-dimensional nanostructures would enhance radiative recombination because they can increase the density of states at the band edges and confine the carriers. This, along with the desire to understand fundamental 1-D physics and material processes, has motivated extensive research in 1-D nanotechnology. For example, the electrically driven nanolasers have been realized by fabricating heterojunctions between CdS and Si substrates [8].

With the advent of the nitride material system, attention quickly turned to the plausibility of GaN 1-D nanostructure growth. For the past several years, a considerable amount of work has been done on the synthesis of 1-D nanostructured GaN by various methods such as laser-assisted catalytic growth [9], sublimation [10], template or catalyst assisted synthesis [11], [12], metal oxide catalyzed growth [13], pyrolysis [14], and direct reaction of Ga with flowing ammonia [15], [16]. Recently, Risic *et al.* reported self-assembled GaN nanorods grown by plasma-assisted molecular beam epitaxy (PAMBE) [17]. For most reports on GaN nanorods growth, the vapor–liquid–solid (VLS) process has been used [2], [18]. The intrinsic feature of the VLS growth method is that at the top of the rods there are always catalytic-impurity particles that could be undesirable for device fabrication. In addition, high-density, well-ordered, and high-quality GaN nanostructures will be needed for practical applications in the future.

In this paper, GaN nanorods were grown by RF-MOMBE on c-sapphire substrates without any catalyst or template treatment. The structural and optical properties of GaN nanorods were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and micro-photoluminescence (μ-PL) measurements. All experimental results indicate that isolated high-density, high-quality, and high-orientated GaN nanorods are successfully self-assembled without extra catalytic assistance.

II. Experiment

Wurtzite GaN epitaxial nanorods were grown on nitridated c-sapphire substrates without buffers by RF-MOMBE. Triethylgallium (TEG) and atomic nitrogen generated by a radio frequency (rf) plasma were used as the group-III precursor and N source. Prior to the growth of GaN, the substrate was heated to 950 °C and then exposed to nitrogen plasma for 10 min in order to clean the surface and also form a thin nitridated layer. After the growth process, a light yellow layer was found on the substrate.

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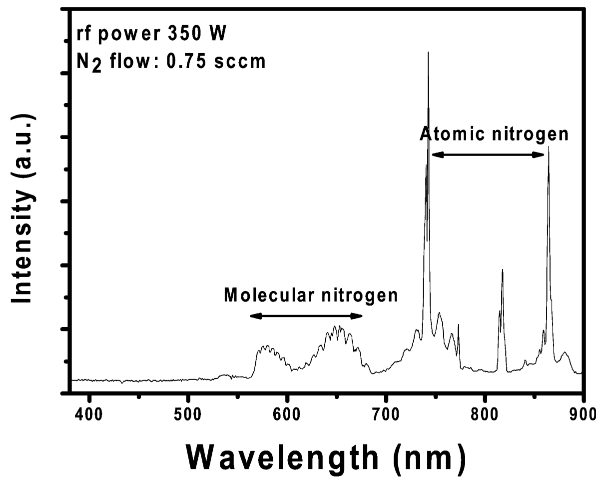

Fig. 1. Typical optical emission spectrum of nitrogen rf-plasma. Dominant emission peaks at 740, 820, and 860 nm indicate that significant amount of atomic nitrogen is produced.

The crystal structures of samples were analyzed using XRD with $\mathrm{CuK}\alpha_1$ radiation. Surface morphology of nanorods is studied by TEM and FESEM. For SEM observation, the samples were directly mounted on copper stubs with conductive gold paint. In addition, the TEM samples were prepared using focused ion beam (FIB) milling techniques. The excitation power- and temperature-dependent μ-PL emission spectra of GaN nanorods were measured by a commercial microscopy system. A 325-nm He–Cd laser was used as the excitation source. The focused spot size on the sample was approximately 1 μm in diameter, which corresponds to approximately 300 illuminated nanorods.

III. Results and Discussion

Shown in Fig. 1 is the typical optical emission spectrum of the nitrogen rf-plasma operating at 350 W and 0.75 sccm of nitrogen flow rate in the growth chamber. A number of emission peaks associated with molecular and atomic nitrogen transitions were observed. The light emission from the rf nitrogen plasma source appears bright orange to the eyes when operated under suitable conditions. Atomic nitrogen generated by an rf plasma will provide efficient nitrogen activation as a group V precursor and hence improve the growth rate and crystalline quality.

Fig. 2 shows a typical θ–2θ XRD pattern of the straight and well-aligned GaN nanorods, where the peaks of (0006) reflection from the sapphire substrate were subtracted. Two peaks are indexed as (0002) and (0004) of the wurtzite structure of GaN. The full-width at half-maximum (FWHM) value of XRD rocking curves of (0002) planes reveals the distribution of the tilt angle between the c axes of the rods and the substrate normal. A rocking curve is shown in the inset of Fig. 2. The FWHM value of the rocking curve was measured to be 900 arcsec. For rods grown on c-sapphire substrates, peaks due to the GaN(0002) and (0004) crystal planes were obtained, from which the lattice constant of 5.175 Å was estimated, being close to the bulk lattice constant along the c axis.

The cross-sectional and plan view SEM images of the GaN nanorods are shown in Fig. 3(a) and (b). The areal density and the average diameter of the GaN nanorods are about 10^{10} cm^{-2} and 50 nm. As shown in Fig. 3(b), the cylindrical shape was observed at the end of RF-MOMBE-grown GaN nanorods. Moreover, it is noted that no Ga droplet was observed at the end of any nanorod.

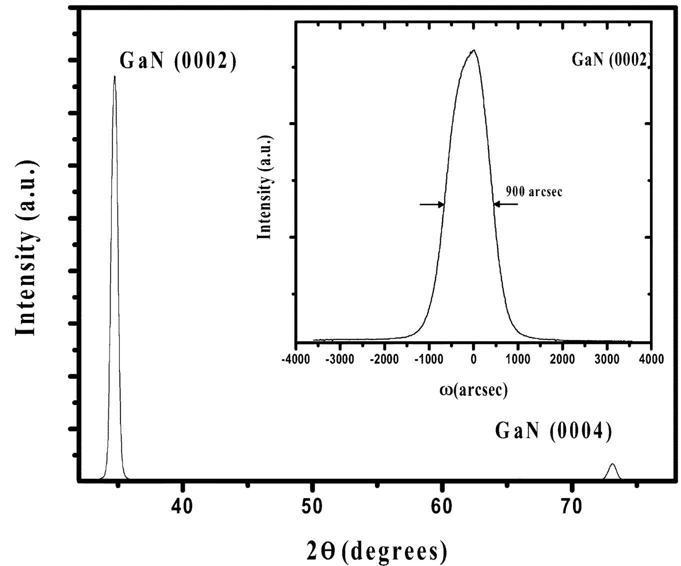

Fig. 2. XRD 2θ scan of GaN naorod on c-sapphire substrate. Insert is corresponding rocking curve of the (0002) reflection. Indexed peaks are those of GaN wurtzite structure.

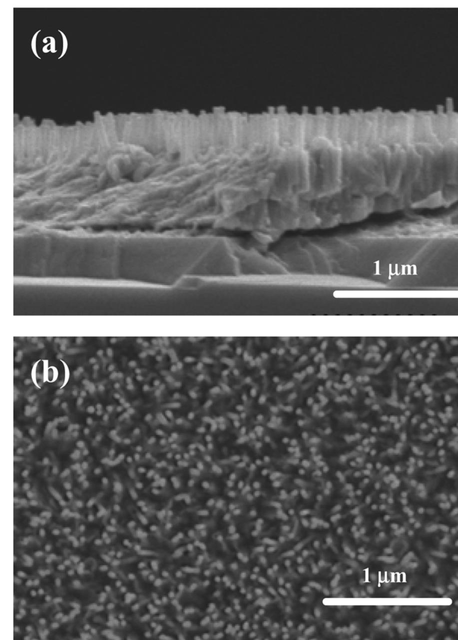

Fig. 3. SEM images of GaN nanorods grown on c-sapphire at 900 °C: (a) cross-sectional view and (b) plane view.

To explore the composition of these samples, the nanorod tips were also investigated by energy dispersive X-ray (EDX) analysis. EDX analysis, as exhibited in Fig. 4(a), revealed that gallium and nitrogen are the only detectable elements, supporting the expectation that no other metal elements are helping to catalyze the observed nanorod growth. Although no metallic particle was seen on the top, we still cannot rule out completely

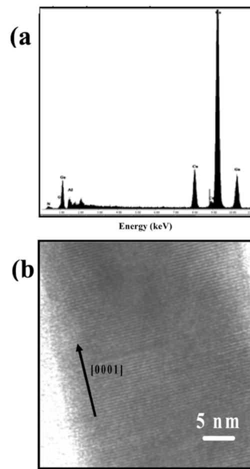

Fig. 4. (a) EDX spectrum at tip of single-crystalline GaN nanorod. (b) High-resolution TEM image of single-crystalline GaN nanorod. No evident discrepancy is observed in top and middle of nanorods.

the possibility of VLS-like mechanism, since Ga might desorb away at high temperature. For further confirmation, we have fabricated a 1-D GaN nonorod at the growth temperature of 750 °C, which is below the temperature for vapor pressure at 10^{-6} torr for a Ga element, and the electron microscopy observations reveal the same results. Fig. 4(b) shows a high-resolution TEM image of a GaN nanorod. It can be seen clearly that the [0001] direction was parallel to the long axis of the rods, indicating that the [0001] direction is the growth direction for the GaN nanorods. The lattice image of a nanorod reveals the perfection of the rod structure, and no dislocation is observed as well. Besides, the clear lattice images were found in many regions of GaN nanorods. The (0001) fringes aligned to the growth direction are separated by about 5.2 Å, which is close to that of bulk GaN (5.18 Å). The TEM results are consistent with those of XRD measurement, and this also demonstrates that the nanorod is single-crystal wurtzite GaN. The discrepancy between our data and accepted bulk data might come from the overestimated XRD angles and spacing of lattice fringes.

The temperature-dependent μ-PL spectra of GaN nanorods are shown in Fig. 5(a). Obviously, the emission spectra are asymmetric. The phenomenon could originate from the coexistence of the nanorods and the formation of films at the bottom of nanorods, and SEM images of Fig. 3 might support this assumption accordingly. Besides, there is not any significant blue shift of the emission peaks compared to the GaN bulk sample. It can be seen obviously that the emission energies blue shift with decreasing temperatures from 300 K to 77 K. From our temperature-dependent PL measurement, we can obtaine a linear shrinkage temperature coefficient of $\partial E/\partial T = -5 \times 10^{-5}$ eV $\cdot$ K^{-1}, which is one order magnitude smaller than those reported for bulk GaN (from -4×10^{-4} eV $\cdot K^{-1}$ to -6×10^{-4} eV $\cdot K^{-1}$) [19]. In addition, the intensity of UV emission increases due to more efficient radiative recombination. The variation of the peak position with temperature can be attributed to the effect of extension of the lattice and electron lattice interaction. Furthermore, the temperature insensitivity of bandgap is characteristic to a

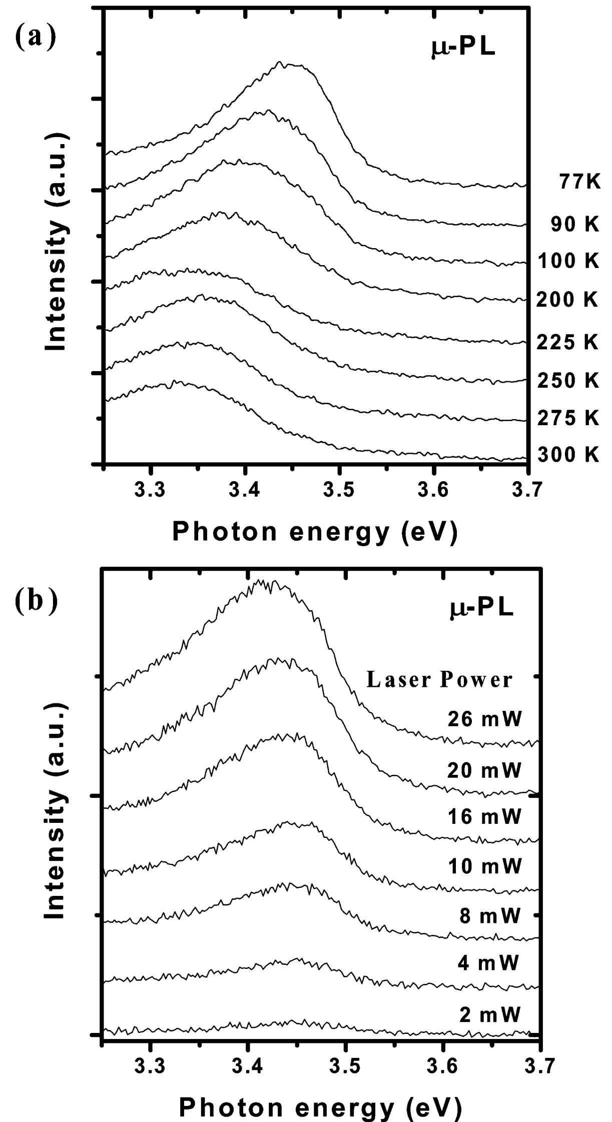

Fig. 5. (a) Temperature-dependent μ-PL spectra under low excitation intensity. (b) Excitation power-dependent μ-PL spectra at 77 K.

quantum size effect as well. The broad half-width of the PL spectra probably reflects the broad size distribution of GaN nanorods revealed by the SEM pictures, as shown in FWHM of the band is about 150 meV, possibly due to the size effect and unintentionally doped shallow impurity [20].

Shown in Fig. 5(b) are the excitation power-dependent μ-PL spectra taken at 77 K. It is interesting to note that the peak position shifts to lower energy as increasing excitation power, where the emission peak energy decreases 75 meV per decade power. Contrary to the bandfilling and free-carrier screen effect observed in other quantum structures, our samples exhibit reduction of the bandgap under high-excitation intensity. The most important reason for the phenomenon is the many body effects of free carriers, which lower the electron energies, as compared to a noninteracting carrier system. The interaction becomes dominate at small carrier-to-carrier distance, i.e., at high carrier concentration. Besides, creation of additional carriers due to thermal heating by pumping would be minimal due to no obvious broadening of the emission line, which reflects

a change in sample temperature. However, further studies are needed to clarify the suspicion.

From the XRD, SEM, TEM, and μ-PL results mentioned previously, the vertically aligned GaN nanorods in the [0001] orientation were demonstrated. HRTEM images reveal that the nanostructures are hexagonal single crystals with no visible dislocations but do not exclude point defects. A possible cause for such dislocation-free growth is as follows. First, initial GaN seeds can grow without dislocations, even with high strain due to the small interface region between GaN seeds and sapphire substrates. Then, following the tiny GaN seeds, GaN nanorods independently grow without coalescing with each other. For this reason, dislocations may not exist in nanorods. The recent work of Peng *et al.* [21] showed that the GaN nanowire with the [0001] growth direction is synthesized at a lower temperature than those with the [10–11] growth direction. The lesser strain of the nanowires grown with the [0001] growth direction implies that the [0001] growth would be more thermodynamically favorable than the others. Therefore, we also expect that the [0001] growth would be dominant at the formation of GaN nanorods. Furthermore, this dislocation-free growth of high-density and well-aligned GaN nanorods should directly result in excellent performance for future photonic devices.

IV. Conclusion

Arrays of well-aligned GaN nanorods have been grown on c-sapphire substrates at 950 °C by a catalyst-free RF-MOMBE method. SEM images show that these rods have an average diameter of 50 nm, and the rod number density can reach 1×10^{10} cm^{-2}. XRD and SEM measurements also show that the rods have grown along the [0001] direction, parallel to the substrate normal. Furthermore, the high crystalline quality of the nanorods, showing no traces of extended defects, has been proven by HRTEM measurements. From the excitation power-dependent μ-PL results, we have observed the reduction in bandgap energy with increasing excitation intensity. This phenomenon might result from the many body effects of a free carrier under high-excitation intensity. The high-quality and high-density nanorods allow us to perform basic research and open new potentials for further optoelectronic device applications.

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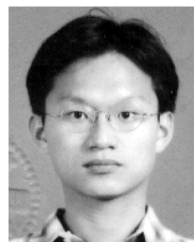

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