

Preparation and Optical Properties of Prism-Shaped GaN Nanorods

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Large quantities of prism-shaped GaN nanorods were prepared by a thermal CVD reaction between Ga and NH₃ on LaAlO₃ crystal substrates. The distinct morphology of the GaN nanorods lies in their prism-like out shape and most of them have a quadrilateral cross section. The Raman spectrum of the GaN nanorods shows two additional bands at 255 and 419 cm⁻¹. Moreover, a large red shift of A₁(LO) phonon has been observed compared with that of bulk GaN crystals. Room-temperature photoluminescence measurement reveals a broad emission ranging from 2.5 to 3.5 eV with some fine structures, which are believed to be associated with the defect levels.

One-dimensional (1D) nanostructures have become an exciting, intellectually challenging, and rapid expanding research field since the discovery of carbon nanotubes.¹ Over the past several years, considerable efforts have been devoted to the synthesis of 1D nanostructures for semiconductors and metals due to their scientific and technological importance. Wide band gap semiconductor gallium nitride (GaN) has been the subject of intensive research for UV or blue emitters, detectors, high-speed field effect transistors, and high-temperature microelectronic devices.^{2,3} Syntheses of GaN nanowires or nanorods have been achieved by various approaches. Han et al.⁴ first reported the synthesis of GaN nanorods through a carbon nanotube-confined reaction in 1997. Cheng and co-workers⁵ synthesized GaN nanowires using the anodic alumina membrane as template in 1999. Breakthroughs were made to synthesize GaN nanowires without using a template in 2000. In parallel efforts, many groups synthesized GaN nanowires in open space by chemical vapor deposition (CVD),^{6–8} laser ablation,⁹ arc discharge,¹⁰ and sublimation.¹¹ All GaN nanowires grown by those methods are cylindrical in shape. It is known that morphologies of 1D nanostructures are of great importance for their applications. Recently, the belt-shaped 1D nanostructures, i.e., nanobelts or nanoribbons, have attracted great attention because of their interesting geometry and potential applications in technology.^{12–17} The distinctive morphological feature of a nanobelt lies in its rectangular cross section instead of a circular cross section of nanowires. GaN nanobelts have been reported by Bae et al.¹² and our group.¹³ More recently, triangular GaN nanorods synthesized by CVD and MOCVD were reported.^{18,19}

In this study, we report a synthesis of high-yield regular shaped GaN nanorods, which have prism-like morphologies. Most of them have a quadrilateral cross section and diameters ranging from 30 to 200 nm. Raman and photoluminescence (PL) spectra of those unique shaped GaN nanorods were discussed here.

The synthesis process of prism-shaped GaN nanorods was depicted as follows. A long quartz tube mounted in a horizontal resistance furnace was used as reactor. An appropriate amount

of Ga metal was put in a quartz boat placed inside the quartz tube. A single-crystal LaAlO₃ plate with 10 × 5 × 0.5 mm in size was dipped into a Ni(NO₃)₂ ethanol solution with a concentration of about 0.01 M and dried in air. Then, the treated substrate was positioned about 20 mm away from Ga source at the downstream end of quartz tube. The quartz tube was evacuated by a vacuum pump and heated to 900 °C under Ar atmosphere. Then, a steady NH₃ flow of 30 sccm was started and maintained for 5 min. Finally, the system was naturally cooled under an Ar atmosphere. The deposited product was a white layer on the substrate, which was characterized by scanning electron microscopy (SEM, Philips XL 30 FEG), energy-dispersive X-ray spectroscopy (EDX) attached to the SEM and X-ray diffraction (XRD, Rigaku D/max-2400, Cu radiation). The Raman measurement was performed by a multichannel modular triple Raman system (JY-64000) using a 532 nm solid-state laser as excitation source. The photoluminescence spectrum was collected at room temperature with a Hitachi F-4500 spectrofluorometer.

The SEM image with low magnification is shown in Figure 1a, revealing the product consists of a large quantity of nanorods homogeneously distributed on the substrate. The lengths of those nanorods range from several to 20 μm. No tapered rods were observed as described in ref 20. Figure 1b shows a high magnification SEM image of those nanorods. The regular shape of those nanorods can be clearly seen and their diameters vary from 30 to 200 nm. The inset of the Figure 1b shows the cross-section of a GaN nanorod, representing the typical morphology of these nanorods reported here. The inset of Figure 1a is an EDX pattern taken from the product. The peaks of La, Al, and O should originate from the LaAlO₃ substrate. The atom ratio of N/Ga is about 1.4 (N, 43%; Ga, 31%) after deducting the contributions of La, Al, and O from the spectrum, indicating those nanorods are unstoichiometric GaN.

The XRD pattern of the product is shown in Figure 2. Those peaks can be indexed on the basis of a hexagonal cell with the cell parameters of $a = 0.318$ and $c = 0.518$ nm, revealing the deposited product is hexagonal GaN. The strongest peak in the pattern is the reflection of the LaAlO₃ substrate.

Raman scattering of hexagonal GaN has been extensively studied by numerous works. According to previous results,²¹

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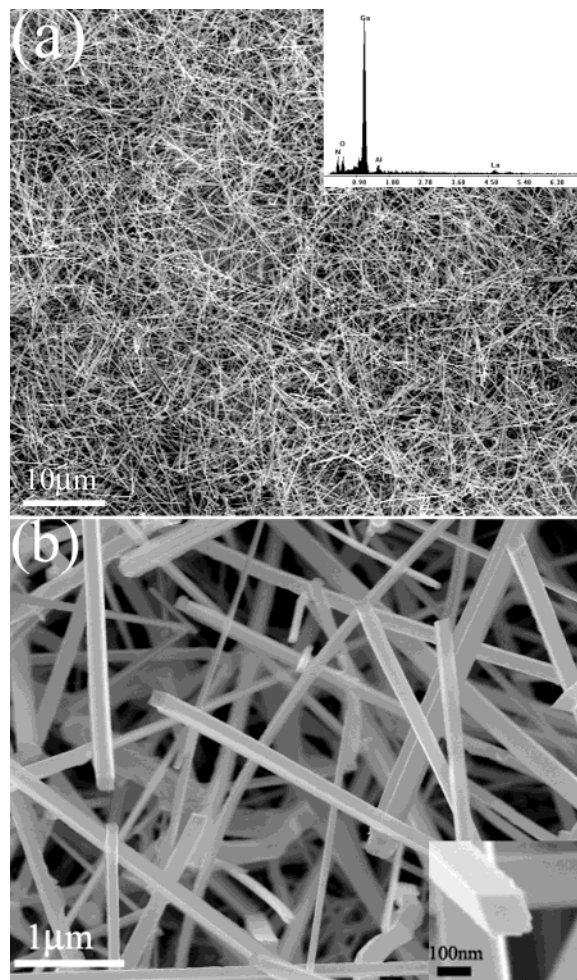


Figure 1. (a) Low magnification SEM image showing quantities of GaN nanorods grown on the substrate. The inset is the EDX pattern of the product. (b) Higher magnified SEM image revealing regular shapes of the GaN nanorods. The inset is an SEM image of the cross-section of an individual GaN nanorod.

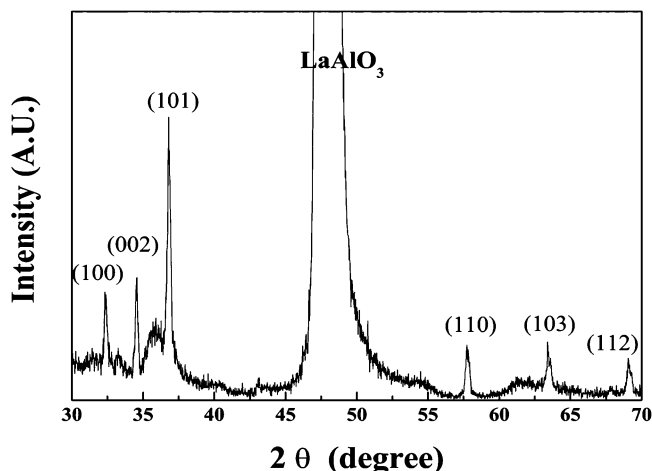


Figure 2. XRD pattern of the GaN nanorods obtained using Cu $K\alpha$ radiation.

perfect bulk GaN (or epilayer) has six first-order Raman active phonons, namely $A_1(\text{TO})$, $A_1(\text{LO})$, $E_1(\text{TO})$, $E_1(\text{LO})$, $E_2(\text{high})$, and $E_2(\text{low})$, with frequencies at 533, 736, 559, 743, 569, and 145 cm^{-1} , respectively. Figure 3 presents the Raman scattering spectrum of the GaN nanorods synthesized here. The bands at 255, 419, 566, and 720 cm^{-1} , can be easily identified. The broad band ranging from 500 to 600 cm^{-1} can be well fitted by three

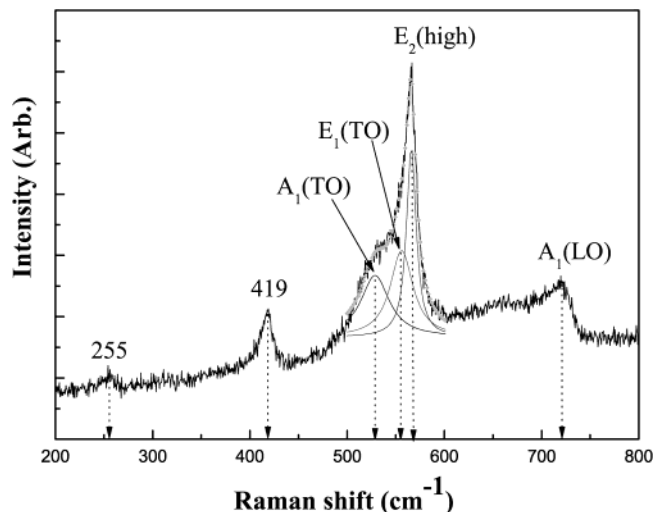


Figure 3. Raman scattering spectrum of the GaN nanorods.

subbands centered at 529, 556, and 566 cm^{-1} , which can be assigned to $A_1(\text{TO})$, $E_1(\text{TO})$, and $E_2(\text{high})$ modes of hexagonal GaN, respectively. The peak at 720 cm^{-1} should be assigned to the $A_1(\text{LO})$ mode. There are two interesting features of the Raman spectrum. First, two additional bands at 255 and 419 cm^{-1} are observed, which are forbidden by $P6_3mc$ space group in first-order Raman-scattering at the zone center. Liu et al.²² observed the two bands and suggested they are zone-boundary phonon activated by surface disorders and finite-size effects, and the acoustic overtone of wurtzite GaN, respectively. Second, $A_1(\text{TO})$, $E_1(\text{TO})$, and $E_2(\text{high})$ modes have negligible shifts compared with previous data, but the $A_1(\text{LO})$ mode has a significantly lower frequency shift of 16 cm^{-1} and is greatly broadened with asymmetric line shape. In general, the phonon confinement effect due to nanocrystalline size can result in soft and broadening of Raman bands. The microcrystal model proposed by Campbell and Fauchet²³ has been widely applied to study the effects of crystal size on one phonon Raman spectra of low dimensional materials. But, the model cannot interpret the present spectrum because the sizes of those nanorods are not thin enough to generate such large shift and broadening of the $A_1(\text{LO})$ mode. We think this perhaps is associated with the unstoichiometry of the GaN nanorods. Kozawa et al.²⁴ studied the Raman spectra of n-type GaN epilayers with different carrier concentrations and pointed out that LO phonon band shifts toward high-frequency side and broadened with an increase in carrier concentration due to the phonon–plasmon coupling. In addition, they found the E_2 mode was not influenced by the carrier concentration. In our case, the GaN nanorods synthesized here are N-rich, as mentioned above. The phonon–plasmon coupling is probably responsible for the low-frequency shift and the broadening of $A_1(\text{LO})$ mode in the spectrum. To verify it, a careful doping dependent investigation is necessary.

A typical room-temperature PL spectrum of the GaN nanorods excited at 220 nm is shown in Figure 4. A well-known yellow luminescence (YL) band (covering from 1.7 to 2.7 eV, centered at 2.25 eV) is often observed in n-type GaN. Here, such a band cannot be seen. It has been pointed out that the YL band is seen in high conductivity GaN (N deficient) and disappears in semi-insulating GaN (N rich). The PL spectrum is consistent with the result of EDX. A very broad band ranging from 2.5 to 3.5 eV is observed. The broad band contains some fine emission peaks at 2.65, 2.74, 2.86, 2.96, 3.10, and 3.27 eV, respectively. The stoichiometry considerations mentioned above imply that those emission peaks are probably associated

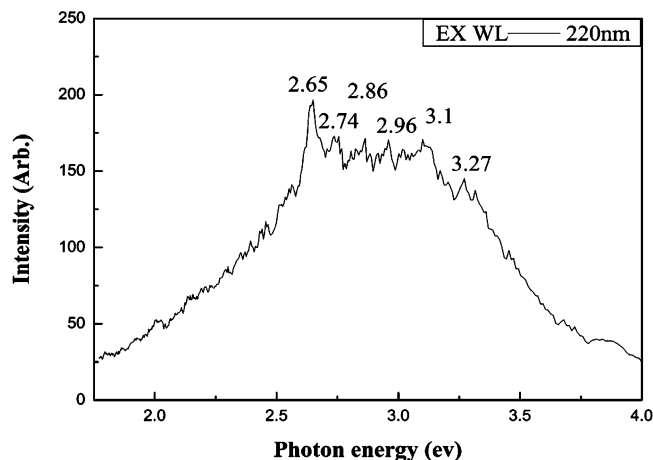


Figure 4. Room-temperature photoluminescence spectrum of the GaN nanorods excited at 220nm.

with the defect levels. In N-rich GaN, we would expect high quantities of the Ga vacancy V_{Ga} , N interstitial N_{i} , and the N antisite N_{Ga} . Furthermore, the incorporation of O is inevitable due to residual air in the system and H_2O vapor absorbed by ammonia. Oxygen point defects in GaN have two forms, i.e., O_{N} (O substituting for N) and O_{i} (isolated O interstitials). It has been demonstrated that the formation energy for O_{N} is several electronvolts lower than for O_{i} .²⁵ Hence, O_{N} is easily formed regarding its low formation energy. The levels of those defects are listed as follows on the basis of results of literature:²⁶ V_{Ga} (acceptor, $E_{\text{V}} + 0.3$ eV), N_{Ga} (acceptor, $E_{\text{V}} + 0.4$ eV), O_{N} (donor, $E_{\text{c}} - 78$ meV), N_{i} (acceptor, $E_{\text{V}} + 1.0$ eV). The strongest peak at 2.65 eV (468 nm) in the PL spectrum has been observed in GaN nanocrystallite solids²⁶ and cylindrical GaN nanowires⁷ before. Ogino et al.²⁷ pointed out that C impurity can form a deep acceptor of $(V_{\text{Ga}} + C_{\text{Ga}})$ complex center and ref 25 ascribes the band to transition from V_{N} or O_{N} to the complex center. Here, the probability can be ruled out because there is no C source in the synthesis. The emission band should involve a deep level that is not clear at present. More detailed work is needed to clarify its origin.

The other smaller blue bands should be attributed to transitions from shallow donors to shallow acceptors and their longitudinal optical phonon replicas. In undoped GaN, blue bands at about 2.9 and 3.27 eV have been reported previously.²⁸ In general, the two bands are assigned to the transition from a shallow donor to a shallow acceptor, which involve some defect levels, such as V_{Ga} , O_{N} , N_{Ga} , or some residual impurities including C, Mg, Si, etc.^{28,29} The transition from O_{N} (donor, $E_{\text{c}} - 78$ meV) to N_{Ga} (acceptor, $E_{\text{V}} + 0.4$ eV) will generate an emission band at about 2.97 eV, which can be identified in the PL spectrum. The band at 3.27 eV is probably attributed to conduction band to V_{Ga} ($e A^0$). Another possibility is the recombination of O_{N} and Si acceptor. Si impurity might be introduced in the product from the quartz boat although it is not detected by EDX. The two transitions are strongly phonon coupled and overlapped each other, causing the broad and complicated line shape of the PL spectrum.

In summary, large quantities of prism-shaped GaN nanorods were synthesized by a thermal CVD reaction between Ga and NH_3 . The diameters of the nanorods range from 30 to 200 nm and the lengths of them range from several to 20 μm . The remarkable feature of morphology of these nanorods lies in its quadrilateral cross section. Raman spectrum of the GaN nanorods reveals two additional modes at 255 and 419 cm^{-1} as compared with Raman modes of bulk GaN. In addition, the $A_1(\text{LO})$ mode has a great low-frequency shift, which may be due to the phonon–plasmon coupling. The room-temperature PL spectrum shows a broad band in the energy range of 2.5 to 3.5 eV. The band and its fine structures were discussed and some defect levels are believed to be responsible for them.

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