

GaN nanorods coated with pure BN

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We report a method to efficiently synthesize gallium nitride (GaN) nanorods coated with insulating boron nitride (BN) layers. The GaN core is crystalline (with either a cubic zincblende or hexagonal wurtzite structure) and has diameters ranging from 10 to 85 nm and lengths up to 60 μm . The outer encapsulating BN shells with typical thicknesses less than 5 nm extend fully over, and adhere well to, the entire nanorod surface. © 2002 American Institute of Physics. [DOI: 10.1063/1.1531836]

Gallium nitride is a scientifically intriguing and technologically important material.^{1,2} Of particular interest are low-dimensional GaN-based structures including nanowires.^{3–6} Because of their low dimensionality and high surface-area-to-volume ratio, nanowires often display unusual electrical characteristics and high chemical reactivity. Often the properties can be dramatically influenced by the surface addition of selected atomic or molecular species (including ultrathin uniform coatings). Such functionalization can lead to dramatic property enhancements for technological application.

Hexagonal boron nitride (BN) is a covalently-bonded system with exceptionally strong sp^2 planar bonds. The material forms the basis of a growing number of nanostructures, including nanotubes^{7–10} and nanococoons.⁹ The desirable mechanical, electronic, thermal, and chemical properties of these materials suggests that BN may form a useful component in other nanosystems, including as a coating material. Indeed, it has been shown that surface addition of BN can greatly enhance the electron field-emission characteristics of carbon nanotubes, Si tips, and GaN films.^{11–13} Several BN- and $B_xC_yN_z$ -coated nanowires have also been demonstrated, including nanotubes filled with carbides, borides, and oxides.^{14–19}

Here, we describe the synthesis and structural characterization of BN-coated GaN nanowires. A simple and highly efficient synthesis process is demonstrated which creates in one step the nanowires together with their coating. The GaN nanowire core is crystalline with either a cubic zincblende or hexagonal wurtzite structure, and can be formed with diameters ranging from 10 to 85 nm and lengths up to 60 μm . The outer coating is typically several BN-layers thick and more or less uniformly covers the entire GaN nanowire. The synthesis process is easily scalable and could produce large amounts of relatively pure material.

To create the coated nanowire Ga_2O_3 and Ga (mol ratio 1:4), amorphous boron powder, and an iron oxide catalyst (supported on an alumina-nanoparticle template) were well-mixed and placed in a quartz boat. The boat was inserted into the hot-zone of a conventional temperature-programmable furnace. We first flowed pure N_2 gas at atmospheric pressure over the boat and linearly ramped the oven temperature from

25 to 800 °C, whereupon a gas flow of pure NH_3 replaced the N_2 . At 1100 °C the oven temperature was held constant for 1 h, still with flowing NH_3 . Thereafter the NH_3 flow was replaced by N_2 and the oven was switched off, allowing it to naturally cool back to room temperature over a period of several hours. The synthesis product was collected from the quartz boat, ultrasonically dispersed in methanol, and dropped onto a holey carbon-coated grid for characterization by high-resolution transmission electron microscopy (HRTEM) using a Philips CM200 FEG equipped with a parallel electron energy-loss spectroscopy (EELS) detector (Gatan PEELS 678) and an energy dispersive x-ray spectrometer (EDS).

Figure 1(a) is a typical low-magnification TEM image of the product, and shows a 34-nm-diameter nanorod with a coating. As we discuss later, the EELS and EDS analyses are consistent with the nanorod core being composed of pure GaN and the coating composed of BN. The thickness of the coating is approximately 3.5 nm (with a modest variation along the length of the nanorod). From a statistical analysis of many similar HRTEM images, we find that the coated nanorods have diameters in the range of 10 to 85 nm and lengths of up to 60 μm . The thickness of the BN coating is usually less than 5 nm.

Figure 1(b) is an expanded HRTEM image of a smaller part of the coated nanorod of Fig. 1(a) [the selected region is indicated by an arrow in Fig. 1(a)]. The lower two-thirds portion of Fig. 1(b) shows the crystalline GaN nanorod, while the upper one-third portion shows the BN coating. Digital TEM images of the GaN region, such as those shown in Fig. 1(b), were analyzed by fast Fourier transform (FFT) techniques to reveal details of the local GaN structure. The inset to Fig. 1(b) is a corresponding diffraction pattern thus obtained for the GaN region of Fig. 1(b). The nanorod structure can be indexed to hexagonal wurtzite GaN. The incident electron beam direction is along $\langle 001 \rangle$ and the long axis of the nanorod is parallel to the crystalline a direction.

The HRTEM image of Fig. 1(b) shows that there are roughly ten BN layers covering the surface of the nanorod in the selected area. These layers are well “graphitized,” but there is also substantial structural disorder present and the concentric shells are certainly not continuous along the length of the nanorod (nor, most likely, even around the nanorod circumference). Nevertheless, the BN coating layers

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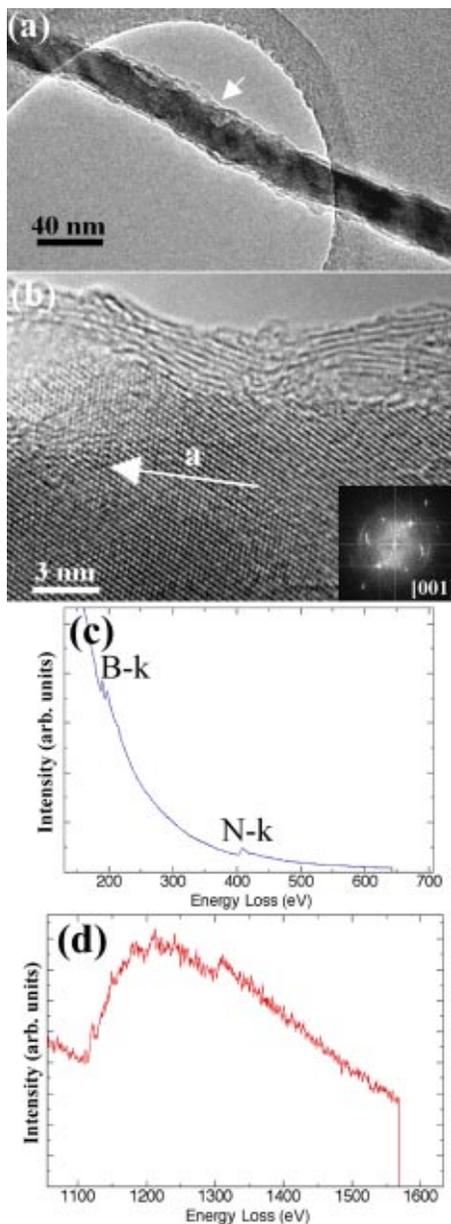


FIG. 1. (a) Low-magnification TEM image of a BN-coated GaN nanorod whose diameter is about 34 nm. (b) HRTEM image of a part of the coated crystalline nanorod indicated by an arrow in (a). The inset is the corresponding diffraction pattern obtained by FFT, indexed to hexagonal wurtzite GaN. The incident direction of the electron beam is along $\langle 001 \rangle$. The long axis of the nanorod is parallel to the crystalline a direction. (c) and (d) show EELS spectra taken from the part of the nanorod indicated by an arrow in (a). (c) indicates prominent B and N peaks, while (d) indicates a Ga peak.

are locally crystalline and very much “nanotube-like,” as opposed to being “herring-bone-like” or lacking layered hexagonal BN structure altogether. The interlayer distance in the BN coating shells is approximately 0.34 nm, in accord with the (002) spacing of bulk hexagonal BN and the inter-wall separation in multiwall BN nanotubes.^{7–10} HRTEM shows that the BN layers extend all along the nanorod and appear to be intimately bonded to the GaN. The BN coating is robust and not easily dislodged from the GaN nanorod core.

EELS spectra taken from the same region of the nanorod indicated by an arrow in Fig. 1(a) are shown in Figs. 1(c) and 1(d). K -edge absorption for B and N, whose distinct absorp-

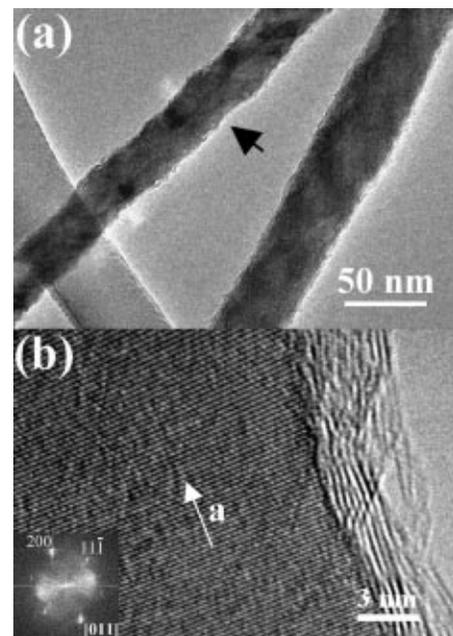


FIG. 2. Low-magnification TEM image of two coated nanorods, whose diameters are about 36 nm and 49 nm. (b) HRTEM image of a part of the coated single crystalline nanorod indicated by an arrow in (a). The inset is the corresponding diffraction pattern taken by FFT, which are indexed to cubic zincblende GaN. The incident direction of the electron beam is along $\langle 011 \rangle$. The long axis of the nanorod is parallel to the crystalline a direction.

tion features start respectively at 188 and 401 eV, are revealed in Fig. 1(c). Figure 1(d) shows an L -edge absorption for the Ga peak that starts at 1.115 keV. The calculated B/N atomic ratio is approximately 0.43, well below the expected 1:1 ratio for isolated hexagonal BN nanostructures. The stoichiometry of the BN coating is almost certainly close to 1:1 and the excess nitrogen in the analysis derives from the N of the overlapping GaN core. A small amount of oxygen is also detected in some coated nanorod specimens.

The synthesis method described above yields predominantly GaN nanorods in the hexagonal wurtzite structure, which is the usual GaN nanorod structure irrespective of synthesis route.^{3–6} However, we have, on occasion, also found in our product BN-coated GaN nanorods displaying the cubic zincblende structure. Figure 2(a) is a low-magnification TEM image of two coated nanorods, whose diameters are about 36 and 49 nm. The thickness of the BN coating for both nanorods is about 3 nm. Figure 2(b) is a HRTEM image of a part of the coated single crystalline nanorod indicated by arrow in Fig. 2(a), and the inset of Fig. 2(b) is again the corresponding diffraction patterns obtained by FFT. The pattern can be indexed as $\langle 011 \rangle$ zone axis of cubic zincblende GaN structure. Two diffraction spots labeled in the inset correspond to planes (200) and $(11\bar{1})$. The long axis of the nanorod is parallel to the crystalline a direction. We note that the cubic zincblende phase of GaN (lattice parameter of about 0.45 nm) is metastable and not easily realized in practice. For GaN films, it is observed only for heteroepitaxial layers on highly mismatched cubic substrates (001)-oriented, for example GaAs, Si, MgO, and cubic SiC.^{5,6} At present it is unclear what local synthesis conditions are responsible for generation of the metastable-phase cubic zincblende GaN nanorods. We have been unable to tune the synthesis param-

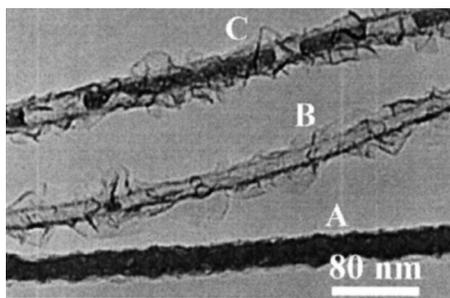


FIG. 3. Low-magnification TEM of (a) GaN nanorods with a well-uniform BN coating (labeled A), (b) an amorphous BN nanotube with rough edges (labeled B), and (c) an amorphous BN nanotube with rough edges and noncontinuous filling (labeled C).

eters to obtain this metastable phase as a dominant fraction of nanorods in the product.

Slight variations in synthesis conditions can lead to different types of coated nanorod structures, including those with very rough edges and discontinuous nanorod filling. Figure 3 shows some examples. This low magnification image shows a well-coated nanorod (labeled as A), an amorphous nanotube with very rough edges (labeled as B), and a nearly amorphous BN nanotube with noncontinuous GaN filling (labeled as C). The well-coated nanorod indicated as A is similar to the coated nanorods shown in Figs. 1 and 2. EELS analysis again showed that the coatings in all three cases was BN and that the filling was GaN. In the virtually “empty” portions of the amorphous BN nanotube housing (as in region C), small amounts of Ga and O were detected. We note that nanorod-like structures with rough surfaces may actually be desirable for some applications, including gas storage, chemical sensors, and “nano-rebar” used in structural composites.

We now turn to a possible growth mechanism for GaN nanorods coated with BN. The Ga, Ga_2O_3 , and B mixture forms gallium oxide (Ga_2O and Ga_2O_3) and boron oxide (B_2O_2 or B_2O_3) vapor at the reaction temperature. The iron oxide nanoparticles act as a catalyst to react gallium oxide and boron oxide with NH_3 to form GaN nanorods and BN “nanotube” coatings. The catalyst is essential, and without it we obtain no BN or GaN one-dimensional nanostructures in the product. We also find metal oxide particles at the tip of coated nanorods and nanotubes, which indicates that the growth process could be described by the so-called vapor-liquid-solid mechanism.^{4,5,20,21} GaN nanorods and amorphous BN nanotubes might first grow separately. During and after the formation of GaN nanorods, they can be fully coated with BN layers adhering to the entire nanorod surface. Meanwhile, during and after formation of amorphous BN nanotubes, the nanotubes can be partially filled with nanorods.

Although the GaN nanorods in our product are single-crystal with few defects, the BN coatings are far less ordered. This may be a result of the relatively low reaction temperature. Previous experiments have demonstrated that highly crystalline BN nanotubes are best produced at temperatures in excess of 1400°C .⁷⁻¹⁰

We find that ammonia is critical in the formation of BN-coated GaN nanorods at the relatively low furnace tempera-

ture of 1100°C . As a comparison, control experiments were performed with identical experimental conditions reported above, except with nitrogen gas replacing NH_3 . No GaN nanorods, with or without coating, were formed. Furthermore, no BN nanotube-like structures, with or without filling, were formed. This agrees with the previous work that ammonia is critical to the synthesis of GaN nanorods or films at relatively low temperature (about 1000°C).^{1-3,6} Because N_2 is much less reactive than ammonia, N_2 is only effective for high temperature reactions, such as arc-discharge.⁵ This is because ammonia is much more chemically active than N_2 .

The synthesis process just described provides a simple, efficient, and unique method to generate GaN nanorods with continuous (though defected) BN coatings. Likely, more so than carbon-layer coatings,⁶ we expect BN-layer coatings to act effectively as chemically and electrically inert protecting layers, and to enhance the stability of GaN nanorods in harsh chemical, thermal, and electrical/optical environments. For example, these coated nanorods might be more immune to photobleaching when used as solid-state nanolasers. Various other physical properties of the BN-coated GaN nanorods, such as electrical conduction and electron field emission characteristics, are obviously of great interest and are the subject of current experiments.

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