

# Direct Synthesis of Gallium Nitride Nanowires Coated with Boron Carbonitride Layers

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*Received: January 1, 2003; In Final Form: April 30, 2003*

Gallium nitride nanowires coated with boron carbonitride layers were directly synthesized by thermal chemical deposition using the reaction of gallium, gallium oxide, boron oxide, and carbon nanotubes under an ammonia atmosphere. The average diameter is 30 nm, and the length is up to 1 mm. Less than 20 graphitic sheets coat the single-crystalline wurtzite-structured gallium nitride nanowires. The graphitic outerlayers are composed of boron, carbon, and nitrogen atoms with a ratio of about 1:2:1. The photoluminescence exhibits a broad band in the energy range 2.1–3.6 eV, suggesting a contribution of the emission from the graphitic boron carbonitride outerlayers.

## 1. Introduction

Since the discovery of carbon nanotubes (CNTs), much technological and scientific excitement has been raised by the discovery of various forms of nanostructures.<sup>1–4</sup> There has recently been a great deal of interest in the preparation and characterization of gallium nitride (GaN) nanowires and their nanocomposites because the GaN material is one of the important semiconductors in many applications including UV or blue emitters and detectors, high-speed field-effect transistors, and high-temperature microelectronic devices.<sup>5–7</sup> A number of research groups succeeded in synthesizing GaN nanowires using various methods such as carbon-nanotube-confined reaction,<sup>8</sup> arc discharge,<sup>9</sup> laser ablation,<sup>10</sup> sublimation,<sup>11</sup> pyrolysis,<sup>12</sup> and chemical vapor deposition (CVD).<sup>13–18</sup> The synthesis of a GaN–carbon nanocomposite was first demonstrated by the arc discharge method, producing GaN nanorods coated with carbon multilayers.<sup>8</sup> Han and Zettl reported the synthesis of GaN nanorods coated with graphitic layers by the deposition of carbon layers on preproduced GaN nanorods.<sup>19</sup> They also synthesized GaN nanorods coated with boron nitride (BN) layers.<sup>20</sup> The mixture of Ga, gallium oxide (Ga<sub>2</sub>O<sub>3</sub>), and amorphous boron powder reacts with flowing NH<sub>3</sub>. The synthesis of not only GaN nanowires but also many other semiconductor (e.g., Si, SiC, Ge) nanorods coated with graphite or BN layers was reported.<sup>21–24</sup>

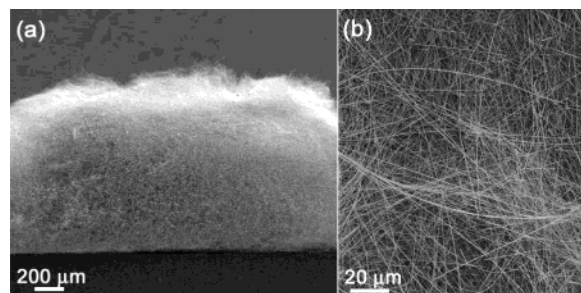
In this paper, we first report on boron carbonitride (BCN) layers coated on GaN nanowires. The bulk quantity of GaN nanowires coated with graphitic BCN multilayers has been synthesized directly via a thermal CVD method. The reaction of a Ga source (Ga and ball-milled Ga<sub>2</sub>O<sub>3</sub> mixture) with NH<sub>3</sub> in the presence of ball-milled boron oxide (B<sub>2</sub>O<sub>3</sub>) and multiwalled CNTs produces exclusively coated GaN nanowires on

a large area of iron (Fe) nanoparticle deposited alumina substrates. The structural and optical properties of the coated GaN nanowires have been investigated using scanning electron microscopy (SEM), transmission electron microscopy (TEM), electron diffraction (ED), electron energy loss spectroscopy (EELS), X-ray diffraction (XRD), Raman spectroscopy, and photoluminescence (PL).

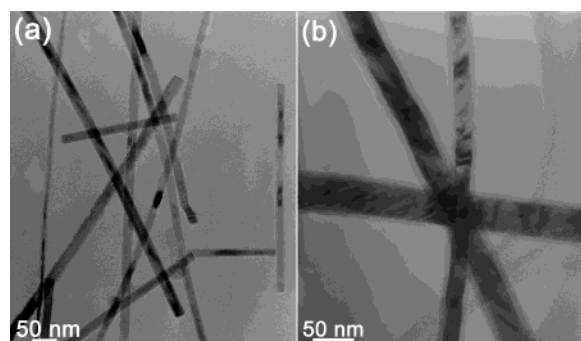
## 2. Experimental Section

Ga<sub>2</sub>O<sub>3</sub> (99.9999%, Mateck) and B<sub>2</sub>O<sub>3</sub> (99.9%, Aldrich) were separately ball-milled for 20 h, using a mechanical ball mill system (Spex 8000M). The multiwalled CNTs were grown using a thermal CVD of acetylene at 900 °C. The diameter is in the range of 20–60 nm, and the length is about 30 μm. About 0.5 g of Ga (99.999%, Aldrich), ball-milled Ga<sub>2</sub>O<sub>3</sub>, ball-milled B<sub>2</sub>O<sub>3</sub>, and CNTs mixed with the same volume ratio were placed inside a 2.5 cm diameter and 80 cm long quartz tube reactor. Alumina substrate (1 cm × 2 cm) was dipped into 0.1 M FeCl<sub>2</sub>·4H<sub>2</sub>O (99%, Aldrich) ethanol solution prepared in an argon (Ar)-filled glovebox and dried by Ar. The substrate was transferred at a distance of 5–10 cm from the Ga source. The temperature of the source was set at 1100 °C, and that of the substrate was approximately 950 °C. While the temperature was raised, Ar flowed at a rate of 500 sccm using a mass-flow controller. NH<sub>3</sub> (99.999%, Solkatrionic) was introduced at a rate of 200 sccm. The growth time was 1 h. SEM (Hitachi S-4300), TEM (JEOL JEM-2010, 200 kV), ED, and EELS (GATAN GIF-2000) coupled with TEM (Philips CM200, 200 kV) were employed to examine the morphology and structure of the products. XRD (Philips X'PERT MPD) patterns and Raman spectra (Renishaw 1000) excited by the 514.5 nm line of an argon ion laser were measured. The PL measurement was conducted using a 325 nm helium–cadmium (He–Cd) laser as the excitation source.

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**Figure 1.** SEM micrographs showing (a) the wool-like GaN nanowires grown on a large area of the alumina substrate and (b) the high-density pure GaN nanowires.



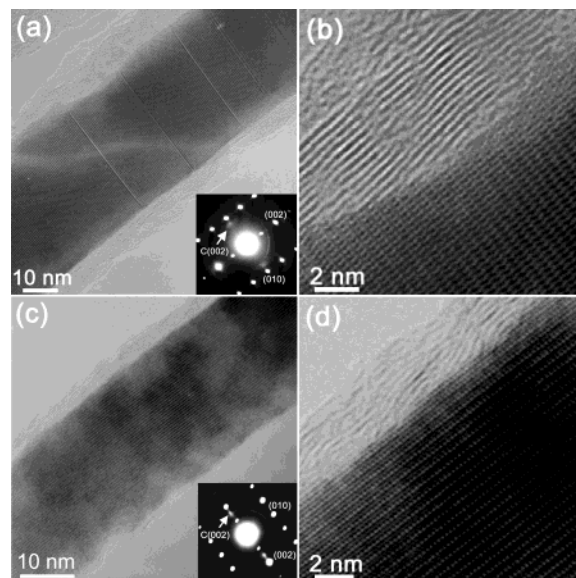
**Figure 2.** (a) TEM image showing the general morphology of the GaN nanowires in which all of them are straight and coated with the layers. The average diameter is 30 nm. (b) An enlarged view revealing the homogeneous coating of the GaN nanowires.

### 3. Results and Discussion

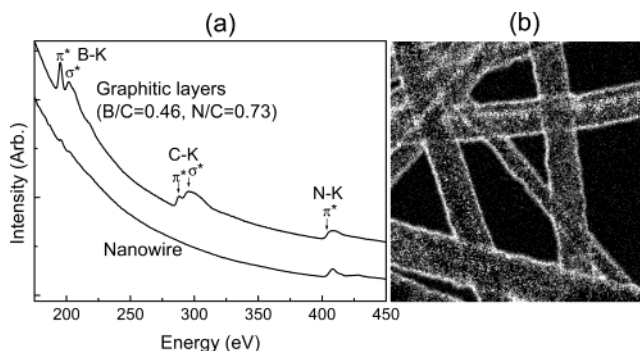
Wool-like product with a light gray color was homogeneously deposited on a large area of the alumina substrates with a visible thickness. Figure 1a shows a low-magnification SEM image of such products. The high-density nanowires are grown with a length up to 1 mm. A magnified view reveals the high purity of GaN nanowires without any nanoparticles (Figure 1b).

TEM images show a typical morphology of the GaN nanowires in which thin layers coat the straight nanowires along the entire length (Figure 2a). The diameter is 10–50 nm with an average value of 30 nm. The thickness of the outerlayer is less than 5 nm (Figure 2b). The nanowires are rotated along the wire axis, showing that the diameter is not much changed. The cylindrical nanowires are thus uniformly coated with the layers.

The high-resolution TEM (HRTEM) images reveal the detailed features for an individual GaN nanowire. Figure 3a shows that the highly crystalline GaN nanowire is coated with  $\sim 15$  sheets of the graphitic layers. The inset is the corresponding selected-area ED (SAED) pattern, which is consistent with that of the wurtzite GaN structure recorded along the  $\langle 210 \rangle$  zone axis. The growth direction is  $[001]$ . It also shows the  $[002]$  direction of the graphitic layers indicated by the arrow. The pattern is essentially identical over the entire nanowire, confirming the single-crystalline wurtzite structure. The fringes of the crystalline graphitic layers are separated by 0.33–0.34 nm (Figure 3b). In the nanowire part, the distance between neighboring  $(001)$  planes is 0.52 nm, which is approximately the same as that of the bulk wurtzite GaN crystal.<sup>25</sup> A few stacking faults exist along the stacking of the  $(001)$  planes. Figure 3c corresponds to the HRTEM image of another GaN nanowire coated with about seven graphitic sheets. The growth direction of the GaN nanowire is  $[010]$ . The ED pattern clearly shows the  $[002]$  direction of the graphitic layers indicated by



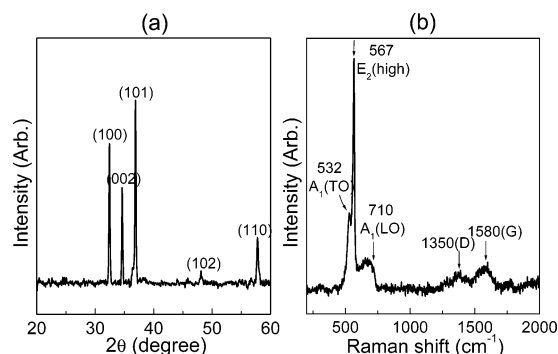
**Figure 3.** (a) HRTEM image of a wurtzite GaN nanowire grown in the  $[001]$  growth direction. The SAED pattern shows the  $[002]$  direction of the graphitic layers indicated by an arrow (inset). (b) The fringes of the crystalline graphitic layers are separated by 0.33–0.34 nm. (c) HRTEM image and SAED pattern of another GaN nanowire whose growth direction is  $[010]$ . The arrow indicates the obvious  $[002]$  direction of the graphitic layers (inset). (d) Atomic-resolved view revealing the nearly defect free GaN  $(001)$  plane and low degree of crystalline perfection of the graphitic outerlayers.



**Figure 4.** (a) EELS data for the coated GaN nanowire. The graphitic outerlayers show the K shell ionization edges of boron (B-K), nitrogen (N-K), and carbon (C-K) at 188, 280, and 400 eV, respectively. The atomic ratios B/C and N/C are 0.46 and 0.73, respectively. The nanowire part shows only N-K edges. (b) Element map of carbon obtained using the inelastic electrons corresponding to the energy loss of K shell edges of carbon.

the arrow (inset). Figure 3d is an enlarged image for part of Figure 3c, showing that the graphitic sheets are waved over a short range and thus are more defective than those of the nanowires shown in Figure 3b. The growth direction of the nanowires is not uniform, and the degree of the crystalline perfection of the graphitic layers also varies, but all GaN nanowires are nevertheless coated with the graphitic layers.

The EELS data of the GaN nanowire are shown in Figure 4a. They are taken from two regions, the GaN nanowire and the graphitic outerlayer parts. The spot size of the electron probe is about 2 nm. The graphitic outerlayer part shows three distinct absorption features starting at 188, 280, and 400 eV, corresponding to the known K-shell ionization edges for boron (B-K), carbon (C-K), and nitrogen (N-K), respectively. A detailed inspection of the near-edge fine structure confirms the  $sp^2$  hybridization state for boron, distinguished by the sharply defined  $\pi^*$  features. For the C-K edge, a defining  $\pi^*$  peak at



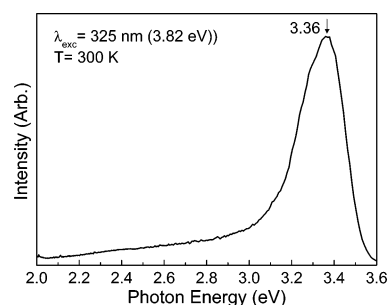
**Figure 5.** (a) XRD pattern and (b) Raman scattering spectrum of the GaN nanowires coated with BCN layers. The excitation wavelength is 514.5 nm from the argon ion laser.

288 eV corresponds to the graphitic carbons. For the N-K edge, the  $\pi^*$  peak at around 405 eV is not completely split with the  $\sigma^*$  peak, which is probably due to the contribution of the GaN nanowire. The relative atomic ratios B/C and N/C are 0.46 and 0.73, respectively. The ratio B/C varies in the range 0.4–0.5, while the ratio N/C varies in the range 0.4–0.7, depending on the nanowires. In the GaN nanowire part, only the N-K edge appears. The data suggest that the GaN nanowires would be coated with the graphitic BCN layers whose composition ratio is approximately B/C/N = 1/2/1. The EELS (or energy-filtered TEM) imaging of the nanowires has been obtained using the inelastic electrons corresponding to C-K edges. Figure 4b shows the C elemental map for the GaN nanowires coated with BCN layers. The brighter points represent a higher concentration of the element. This element mapping confirms that all of the nanowires are homogeneously coated with the C element.

We irradiated the electron beam of the microscope onto the graphitic overlayers for about 30 min, and found that the overlayers were not removed but the nanowires were collapsed instead. Han and Zettl reported the removal of the carbon layers by irradiation for several minutes. The BCN composition probably enhances the susceptibility to the electron beam damage.<sup>19</sup> The BCN layers would act as better protecting layers than the carbon layers for the GaN nanowires.

The XRD pattern shows the peaks of the wurtzite GaN crystal for the nanowires detached from the substrate (Figure 5a). The peak from the other crystalline phase is negligible. The Miller indices are indicated on each peak. A careful examination of the peak position reveals that the (100), (002), and (101) peaks shift to higher angles from those of the commercial GaN powders (99.999%, Aldrich) by 0.1–0.15°. A similar value of the angle shift was also observed from the uncoated GaN nanowires that were previously reported by our group.<sup>17</sup> Since the nanowires are randomly oriented on the substrate, the XRD can reflect mostly the separation of the lattice planes parallel to the growth direction. The reduction of lattice constants suggests that the nanowires would experience compressive strains toward the radial direction and tensile strains induced along the growth direction.

The Raman scattering spectrum of the GaN nanowires is displayed in Figure 5b. The first-order phonon frequencies of A<sub>1</sub>(TO), E<sub>2</sub>(high), and A<sub>1</sub>(LO) are known to be 533, 570, and 740 cm<sup>-1</sup>, respectively.<sup>26,27</sup> The peaks at 532, 567, and 710 cm<sup>-1</sup> can be assigned to the A<sub>1</sub>(TO), E<sub>2</sub>(high), and A<sub>1</sub>(LO) modes, respectively. The shift of the E<sub>2</sub>(high) peak to the lower frequency region from that of the bulk would be correlated with the tensile strain inside the nanowires, which is consistent with the results of the uncoated GaN nanowires.<sup>17,28</sup> The first-order Raman peak of the BCN film or multiwalled BCN nanotubes



**Figure 6.** PL spectrum of the BCN layer coated GaN nanowires measured at room temperature (300 K). The excitation laser is the 325 nm line of a He–Cd laser.

usually consists of two bands at ~1580 cm<sup>-1</sup> (G band) and ~1350 cm<sup>-1</sup> (D band).<sup>29,30</sup> The G band originates from the Raman active E<sub>2g</sub> mode due to in-plane atomic displacements. The origin of the D band has been explained as a disorder-induced feature due to the finite particle size effect or lattice distortion. Two bands at ~1580 and ~1350 cm<sup>-1</sup> can be the G and D bands, respectively. The appearance of two bands provides another indication for the coated BCN multilayers.

The PL spectrum obtained from the BCN layer coated GaN nanowires at 300 K shows a broad band in the energy range of 2.1–3.6 eV with the peak at 3.36 eV (Figure 6). The well-known yellow band centered at 2.2–2.3 eV is not noticeable.<sup>31</sup> The PL of uncoated GaN nanowires was observed in the broader range 2.9–3.6 eV with the peak at lower energy compared to that of the epilayer.<sup>17</sup> The results were interpreted by the change of the band gap energy due to the strains predicted from the data of XRD and the Raman spectrum. The various strengths of the strain would shift the band gap in the broader range. The tensile strains are dominant, resulting in the reduction of the band gap energy. The PL properties of the present GaN nanowires are also probably related to such a band gap change.

However, the weak emission in the lower energy range 2.1–2.9 eV was not found from the uncoated GaN nanowires. This may be related to defects such as atomic vacancies, existing possibly at the interface of the nanowires with the BCN layers. Another possible origin is the graphitic BCN layers. The PL from the layered BC<sub>2</sub>N compounds shows a peak at 2.1 eV at room temperature.<sup>32,33</sup> The BCN films showed a shift of the PL peak from 2.80 to 3.4 eV with increasing B content.<sup>34</sup> The peak of the BCN film appears in the broad range 2.0–3.6 eV. Recently, the blue-violet PL of the highly aligned BCN nanofibers in the range of 2.6–3.2 eV was reported.<sup>35</sup> When the B content increases, the peak centers shift to higher energy. Therefore, the emission from the BCN layers would add to the PL of the GaN nanowires.

It is known that when a Ga and Ga<sub>2</sub>O<sub>3</sub> mixture is used, Ga<sub>2</sub>O vapor is generated as follows: 4Ga(l) + Ga<sub>2</sub>O<sub>3</sub>(s) → 3Ga<sub>2</sub>O(g).<sup>36</sup> The ball-milled Ga<sub>2</sub>O<sub>3</sub> powders are nearly amorphous, so they can produce a sufficient vapor pressure of Ga<sub>2</sub>O to grow the GaN nanowires on a large scale. The reaction involved in the growth of the nanowires is probably Ga<sub>2</sub>O(g) + 2NH<sub>3</sub>(g) → 2GaN(s) + H<sub>2</sub>O(g) + 2H<sub>2</sub>(g).<sup>37</sup> Since the growth of nanowires is negligible without the catalyst, it would follow a typical vapor–liquid–solid (VLS) growth mechanism.<sup>3</sup> The Ga<sub>2</sub>O vapor deposits on the Fe catalytic nanoparticles, forming a miscible liquid alloy. The continuous dissolving of the Ga and N sources would lead to the precipitation of GaN. Our group synthesized the GaN nanobelts using B<sub>2</sub>O<sub>3</sub> as a catalyst under NH<sub>3</sub> flow.<sup>38,39</sup> No BN overlayers exist on those nanobelts. In this experiment the multiwalled CNTs provide the C source to react with B<sub>2</sub>O<sub>3</sub> and NH<sub>3</sub>, depositing the multiwalled BCN



outerlayers on the GaN nanowires. The reaction may be  $4\text{C(g)} + \text{B}_2\text{O}_3\text{(g)} + 2\text{NH}_3\text{(g)} \rightarrow 2\text{BC}_2\text{N(s)} + 3\text{H}_2\text{O(g)}$ . The GaN nanowire can play as a template for the growth of the graphitic BCN layers. The result suggests that the formation of BCN layers would be more efficient than that of BN layers under our growth conditions.

#### 4. Conclusions

The graphitic BCN layer coated GaN nanowires were synthesized in large quantity by the thermal CVD method. The mixture of Ga, ball-milled  $\text{Ga}_2\text{O}_3$ , and  $\text{B}_2\text{O}_3$  powders, and multiwalled CNTs reacts under  $\text{NH}_3$  atmosphere. The temperature of the source was maintained as 1100 °C, and the nanowires were grown on the Fe nanoparticle deposited alumina substrates at 950 °C. The light-gray-colored wool-like nanowires were produced with a visible thickness. The average diameter is 30 nm, and the length is up to 1 mm.

The TEM, ED, and EELS analyses show that less than 20 graphitic sheets coat the single-crystalline wurtzite-structured GaN nanowires whose growth direction is not uniform. For the graphitic outerlayers, the EELS estimates the atomic ratio B/C/N to be about 1/2/1. XRD and Raman spectroscopy confirm the high crystallinity of the wurtzite GaN crystals and the existence of graphitic BCN layers. They also suggests that the lattice constants of the nanowires would be changed via the strains. The PL exhibits a broad band in the energy range 2.1–3.6 eV, excited by the 325 nm line of a He–Cd laser. The results are possibly explained in terms of the band gap decrease due to the dominant tensile strains. The emission from the BCN outerlayers may contribute to the PL in the lower energy range 2.1–2.9 eV. The GaN nanowires would grow following the VLS mechanism. They probably act as template for the formation of the graphitic BCN outerlayers.

**Acknowledgment.** The National R&D Project for Nano Science and Technology (KISTEP) supported the present work. SEM and XRD analyses were performed at the Basic Science Research Center in Seoul. We thank Dr. S. Y. Lee and Dr. J. C. Park (Hynix) for the EELS data.

#### References and Notes

- (1) Iijima, S. *Nature* **1991**, 354, 56.
- (2) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Science* **1995**, 270, 1335.
- (3) Hu, J.; Odom, T. W.; Lieber, C. M. *Acc. Chem. Res.* **1999**, 32, 435.
- (4) Pan, Z. W.; Dai, Z. R.; Wang, Z. L. *Science* **2001**, 291, 1947.
- (5) Mohammad, S. N.; Morkoç, H. *Prog. Quantum Electron.* **1996**, 20, 361.
- (6) Ponce, F. A.; Bour, D. P. *Nature (London)* **1997**, 386, 351.
- (7) Nakamura, S. *Science* **1998**, 281, 956.
- (8) Han, W.; Fan, S.; Li, Q.; Hu, Y. *Science* **1997**, 277, 1287.
- (9) Han, W.; Redlich, P.; Ernst, F.; Rühle, M. *Appl. Phys. Lett.* **2000**, 76, 652.
- (10) Duan, X.; Lieber, C. M. *J. Am. Chem. Soc.* **2000**, 122, 188.
- (11) Li, J. Y.; Chen, X. L.; Qiao, Z. Y.; Cao, Y. G.; Lan, Y. C. *J. Cryst. Growth* **2000**, 213, 408.
- (12) Han, W.-Q.; Zettl, A. *Appl. Phys. Lett.* **2002**, 80, 303.
- (13) Chen, X.; Li, J.; Cao, Y.; Lan, Y.; Li, H.; He, M.; Wang, C.; Zhang, Z.; Qiao, Z. *Adv. Mater.* **2000**, 12, 1432.
- (14) Chen, C.-C.; Yeh, C.-H.; Chen, C.-H.; Yu, M.-Y.; Liu, H.-L.; Wu, J.-J.; Chen, K.-H.; Chen, L.-C.; Peng, J.-Y.; Chen, Y.-F. *J. Am. Chem. Soc.* **2001**, 123, 2791.
- (15) Zhang, J.; Zhang, L. D.; Wang, X. F.; Liang, C. H.; Peng, X. S.; Wang, Y. W. *J. Chem. Phys.* **2001**, 115, 5714.
- (16) Lee, M. W.; Twu, H. Z.; Chen, C.-C.; Chen, C.-H. *Appl. Phys. Lett.* **2001**, 79, 3693.
- (17) Seo, H. W.; Bae, S. Y.; Park, J.; Yang, H.; Park, K. S.; Kim, S. J. *J. Chem. Phys.* **2002**, 116, 9492.
- (18) Kim, H.-M.; Kim, D. S.; Park, Y. S.; Kim, D. Y.; Kang, T. W.; Chung, K. S. *Adv. Mater.* **2002**, 14, 991.
- (19) Han, W.; Zettl, A. *Adv. Mater.* **2002**, 14, 1560.
- (20) Han, W.; Zettl, A. *Appl. Phys. Lett.* **2002**, 81, 5051.
- (21) Zhang, Y.; Suenaga, K.; Colliex, C.; Iijima, S. *Science* **1998**, 281, 973.
- (22) Tang, C.; Bando, Y.; Sato, T.; Kurashima, K. *Adv. Mater.* **2002**, 14, 1046.
- (23) Sun, X.-H.; Li, C.-P.; Wong, W.-K.; Wong, N.-B.; Lee, C.-S.; Lee, S.-T.; Teo, B.-K. *J. Am. Chem. Soc.* **2002**, 124, 14464.
- (24) Wu, Y.; Yang, P. *Adv. Mater.* **2001**, 13, 520.
- (25) Neumayer, D. A.; Ekerdt, J. G. *Chem. Mater.* **1996**, 8, 9.
- (26) Azuhata, T.; Sota, T.; Suzuki, K.; Nakamura, S. *J. Phys.: Condens. Matter* **1995**, 7, L129.
- (27) Davydov, V. Yu.; Kitaev, Yu. E.; Goncharuk, I. N.; Smirnov, A. N.; Graul, J.; Semchinova, O.; Uffmann, D.; Smirnov, M. B.; Mirgorodsky, A. P.; Evarestov, R. A. *Phys. Rev. B* **1998**, 58, 12899.
- (28) Klose, M.; Wieser, N.; Rohr, G. C.; Dassow, R.; Scholz, F.; Off, J. *J. Cryst. Growth* **1998**, 189/190, 634.
- (29) Yap, Y. K.; Yoshimura, M.; Mori, Y.; Sasaki, T. *Appl. Phys. Lett.* **2002**, 80, 2559.
- (30) Zhi, C. Y.; Bai, X. D.; Wang, E. G. *Appl. Phys. Lett.* **2002**, 80, 3590.
- (31) Chen, H. M.; Chen, Y. F.; Lee, M. C.; Feng, M. S. *Phys. Rev. B* **1997**, 56, 6942.
- (32) Watanabe, M. O.; Itoh, S.; Sasaki, T.; Mizushima, K. *Phys. Rev. Lett.* **1996**, 77, 187.
- (33) Chen, Y.; Barnard, J. C.; Palmer, R. E.; Watanabe, M. O.; Sasaki, T. *Phys. Rev. Lett.* **1999**, 83, 2406.
- (34) Yu, J.; Wang, E. G.; Ahn, J.; Yoon, S. F.; Zhang, Q.; Cui, J.; Yu, M. B. *J. Appl. Phys.* **2000**, 87, 4022.
- (35) Bai, X. D.; Wang, E. G.; Yu, J.; Yang, H. *Appl. Phys. Lett.* **2000**, 77, 67.
- (36) Frosch, C. J.; Thurmond, C. D. *J. Phys. Chem.* **1962**, 66, 877.
- (37) Balkaş, C.; Davis, R. F. *J. Am. Ceram. Soc.* **1996**, 79, 2309.
- (38) Bae, S. Y.; Seo, H. W.; Park, J.; Yang, H.; Park, J. C.; Lee, S. Y. *Appl. Phys. Lett.* **2002**, 81, 126.
- (39) Bae, S. Y.; Seo, H. W.; Park, J.; Yang, H.; Song, S. A. *Chem. Phys. Lett.* **2002**, 365, 525.