Gallium Nitride Nanotubes

Gallium Nitride Nanotubes by the Conversion of Gallium Oxide Nanotubes**

Junqing Hu, Yoshio Bando, Dmitri Golberg, and Quanlin Liu*

Gallium nitride (GaN), an important semiconductor having a wide direct band gap (3.39 eV at room temperature), is potentially useful in a blue and ultraviolet light emitter, and in high temperature/high power electronic devices.[1] The future of full-colored, flat panel displays, blue lasers, and optical communication is likely to be based on GaN.[2] Nanotubular structures have brought enormous breakthroughs in modern science and technology, including electronics, mechanics, physics, and chemistry.[3] There have been many studies that have focused on compounds characterized by layered structures, for example, graphite,[4] boron nitride,[5] and metal disulfides (MoS_2, WS_2, TiS_2, ZrS_2, and HfS_2).[6] Recent reports indicated that under appropriate experimental conditions, geometrically closed, concentric tubes could be constructed from nonlayered structural materials. Thus far, there has been great progress in the development of new nanotubes; nanotubes of metal oxides (TiO_2,[6] Ga_2O_3, In_2O_3,[8] ZnO,[9] and Al_2O_3[10]), sulfides (CdS and CdSe),[11] and elemental metallic Te,[12] and others [13] were reported.

Along with the development of nanotechnology, 1D structural GaN may find wider applications in many fields. Thus, considerable efforts have been made to fabricate GaN nanowires or nanorods by several routes, such as template-induced growth,[14] metal-catalyzed assisted laser ablation,[15] hot filament vapor–liquid–solid growth,[16] and gallium oxide reacted with ammonia.[17] Although GaN nanotubes were observed in the preparation of GaN nanowires,[18] the synthesis of GaN nanotubes in bulk have not been realized experimentally. Herein we report the growth of GaN nanotubes in bulk by a two-stage process based on a well-controllable conversion of amorphous gallium oxide (Ga_2O) nanotubes.

A dark (or black) material was collected from the C fiber thermo-insulting layer of the induction furnace, in which the deposition temperature was measured to be $\approx$700–800 °C. The yield of the product was estimated to be $\approx$4–5.0 %, based on the amount of the Ga_2O_3 starting material. The phase

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composition and structure of the as-synthesized product were examined by powder XRD (Figure 1a). All of the strong reflection peaks of the XRD pattern can be readily indexed to hexagonal Wurtzite-structured GaN with lattice constants $a =$ 3.185 Å and $c = 5.177$ Å (the standard values from JCPDS

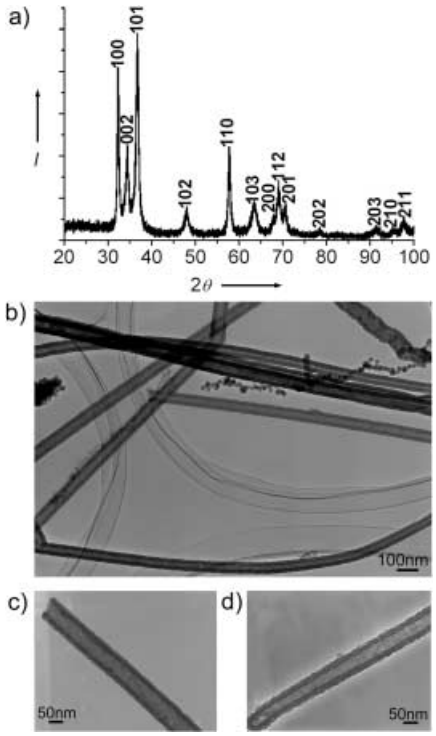

Figure 1. a) An XRD pattern recorded from as-grown GaN nanotubes. b) A typical TEM image of synthesized GaN nanotubes. TEM images showing: c) an open and d) a closed end of GaN nanotubes.

(02–1078): $a = 3.186$ Å and $c = 5.177$ Å), comparable to the literature values for hexagonal GaN.[19] No peaks associated with the other crystalline forms of the gallium oxides can be detected in the pattern. These results suggest that the as-synthesized product contains virtually only one crystalline phase of GaN and the other crystalline phases are below the detection limit (≈5%). The components of Ga and N and the impurities for the sample were further determined by elemental analyses. The amounts (wt%) of Ga and N are 76.80 and 13.40, respectively (calcd for $GaN_{1.00}$:Ga 83.27, N 16.73). This result gives the overall ratio of gallium to nitrogen of 1:0.87 (i.e., not 1:1), which suggests either a gallium-enrichment or nitrogen-deficiency in the synthesized sample. The impurities were (wt%) C 2.1, O 5.0, and the overall metallic elements (such as In, Cu, Zn, Al, Si), 2.7. The black of the synthesized GaN samples is attributed to carbon impurities (from the furnace) and from gallium enrichment (pure h-GaN is pale yellow; the effect of gallium enrichment on the color of the GaN nanocrystals has been demonstrated).[20] The morphology of as-synthesized GaN product was analyzed by transmission electron microscope (TEM; Figure 1b). The clear contrast observed along the lengths of the GaN wirelike product suggests the a tubular structure (the outer part is darker than the inner part). Most of the synthesized GaN nanotubes are straight, although a small quantity are twisted or curved. Typically, the lengths of the GaN nanotubes can reach ≈10 μm. Each tube has a uniform outer diameter and wall thickness (typically ≈80 nm and ≈20 nm, respectively) along its entire length. The TEM images in Figure 1c reveal that some ends of the GaN nanotubes are open and some are closed.

Figure 2a shows a high-magnification TEM image of a segment of a single straight GaN nanotube. A high-resolution TEM image (Figure 2b) of the GaN nanotube wall reveals

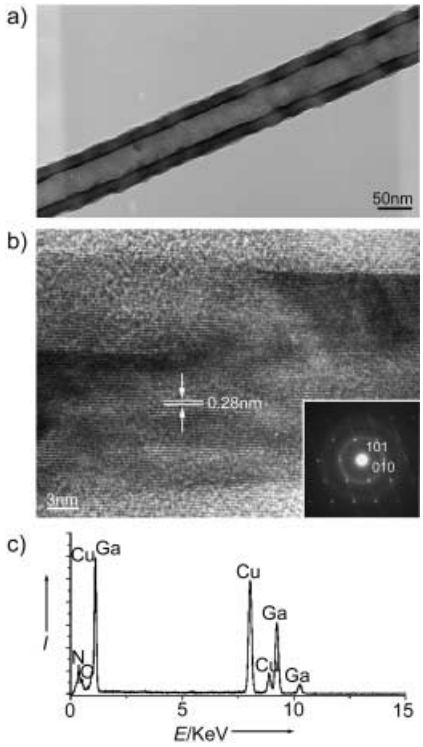

Figure 2. a) A high-magnification TEM image showing a segment of a single straight GaN nanotube. b) A high-resolution TEM image of the GaN nanotube wall as in Figure 2a (lower right inset depicts a corresponding ED pattern). c) An EDS spectrum taken from a single GaN tube.

that the tube is characteristic of a single-crystal. Detailed analysis on the lattice fringes gives an inter-planar spacing of 0.28 nm, which matches well the (101) plane separation of the standard bulk GaN. The lower right inset in Figure 2b depicts the corresponding selected area electron diffraction (ED) pattern; this shows that the brightest diffraction spots can be precisely indexed as the $[10\bar{1}]$ zone axis of hexagonal GaN crystal, whereas the weak diffraction rings may originate from GaN nanocrystallites attached to the tube surface. The phase composition of an individual nanotube was further confirmed by X-ray energy dispersion spectrometry (EDS). The spectrum shown in Figure 2c was recorded from the single GaN tube as in Figure 2a. It reveals the presence of only Ga and N in the nanotubes (Cu signals originate from the TEM grid) with an approximate atomic ratio of 1.00:0.94. A relatively weak oxygen peak in the spectrum probably originates from

unavoidable surface-oxidation and/or surface-adsorption of oxygen on to the tubes arising from exposure to air during sample processing.

Figure 3 shows a room temperature cathodoluminescence spectrum from the synthesized GaN nanotubes. It is clear that one broad emission peak around 505 nm, which is known as the green band, is detected. Compared with the cathodoluminescence behavior (often a yellow band at 550 nm is observed) of the bulk GaN,[21] the peak position of the grown GaN nanotubes displays a blueshift of ≈40 nm, which may be attributed to some intrinsic point defects,[22] such as Ga vacancies, to impurities, such as oxygen or carbon,[23] or to complexes of intrinsic defects and impurities.[24] In addition, one weak peak at ≈370 nm also is detected in this spectrum, which originates from the near band-edge emission.

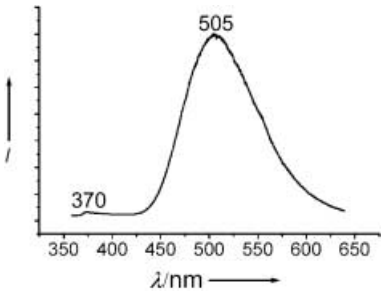

Figure 3. A room temperature cathodoluminescence spectrum of the grown GaN nanotubes.

The reaction of Ga_2O_3 with C (coming from the C crucible) at a synthesis temperature of ≈1250 °C and with pure N_2 as the carrier gas was carried out. The product was examined by using TEM (equipped with a Gatan holder and a twin heating system; Figure 4a and 4b), ED (Figure 4c), and EDS (Figure 4d). These results reveal that the reaction produced amorphous Ga_2O nanotubes (EDS analysis reveals the presence of Ga and O in the tube with an approximate atomic ratio of 2.20:1.00), which were either completely hollow throughout their lengths, or partially filled with Ga.

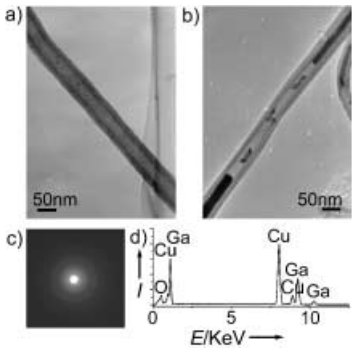

Figure 4. Either hollow a) or partially Ga-filled b) amorphous Ga_2O nanotubes from the reaction of Ga_2O_3 with C at high temperature. c) An ED pattern and (d) an EDS spectrum of the amorphous Ga_2O nanotube as in (a), respectively.

The expansion behavior of a nanoscale liquid Ga column inside an amorphous Ga_2O nanotube has been investigated by TEM, and was demonstrated in carbon nanotubes.[25]. Gaseous Ga_2O forms from the reaction of Ga_2O_3 with C at this reaction temperature: [Eq.(1)][14,16,26]

$$Ga_2O_3 + 2\,C \rightarrow Ga_2O + 2\,CO \quad (1)$$

The formed Ga_2O vapor can be readily transported to the deposition zone by the carrier gas (N_2), and Ga_2O nanotubes forms by a vapor–solid growth mechanism.[27] Meanwhile, the Ga_2O vapor will also react with CO at a desired temperature: [Eq.(2)][25b]

$$2\,Ga_2O + 4\,CO \rightarrow 4\,Ga + C + 3\,CO_2 \quad (2)$$

which will result in liquid Ga filling the Ga_2O nanotubes. Considering the formation of amorphous Ga_2O nanotubes, we speculate that these nanotubes might be converted (or act as a template, thus spatially confining the reaction) into GaN nanotubes through the reaction of Ga_2O with NH_3 at the desired reaction temperature. The reaction can be expressed as: [Eq.(3)]

$$Ga_2O\ (\text{nanotubes}) + 2\,NH_3 \rightarrow 2\,GaN\ (\text{nanotubes}) + H_2O + 2\,H_2 \quad (3)$$

For the synthesis of crystalline GaN nanotubes by the above conversion reaction, a two-stage process was applied by controlling the processing temperature and the carrier gas. In the first stage, a pure N_2 flow was introduced through the quartz tube at a flow rate of 80 sccm (standard cubic centimeter per minute) and at the ambient pressure of the furnace tube. The reactant, Ga_2O_3, was heated to 1250 °C and maintained at this temperature for 1.5 h. The amorphous Ga_2O nanotubes grew at a low temperature, estimated to be around 700 °C. In the second stage, the pure N_2 flow was switched to a pure NH_3 flow with the same flow rate and at ambient pressure in the tube. The furnace was further heated to 1400 °C and kept at this temperature for 1 hour. We speculate that during this stage a significant part of the liquid Ga evaporates out of the Ga_2O nanotube because of the higher reaction temperature. These formed Ga_2O nanotubes serve as energetically favorable sites and enhance NH_3 adsorption on their outer and inner walls (due to the high surface area of these tubes). The reaction shown in Equation (3) may start from the surfaces of the Ga_2O nanotubes, which are thus converted in situ into GaN nanotubes. Therefore, we believe that during the conversion process the formed Ga_2O nanotubes not only are used as a precursor (or an intermediate) but also as a template for confining the reaction in a local space around the nanotubes, which is similar to the synthesis of carbide nanorods with confining reactions by converting carbon nanotubes,[28] except that in present case the Ga_2O nanotubes and GaN nanotubes are both produced from the powdered Ga_2O_3 starting material. The detailed growth mechanisms of Ga_2O nanotubes and GaN nanotubes, however, are not fully understood, and require more systematic investigations.

In summary, GaN nanotubes can be prepared in bulk by a controllable two-stage process that involves the conversion of

Ga_2O nanotubes. An investigation of the properties of the GaN nanotubes synthesized by this route is in progress.

Experimental Section

The amorphous Ga_2O and crystalline GaN nanotubes were synthesized in a vertical induction furnace, as described in detail elsewhere.[29] Briefly, the furnace consists of a fused-quartz tube (50 cm in length, 12 cm in outer diameter, and 0.25 cm in wall thickness) and an induction-heated cylinder (25 cm in length, 4.5 cm in outer diameter, and 3.5 cm in inner diameter) made of a high purity graphite coated with a C fiber thermo-insulating layer. The inductively heated cylinder has one inlet C pipe and outlet C pipe on its top and base, respectively. A graphite crucible containing Ga_2O_3 powder (2.0 g, 99.9 %, Sigma-Aldrich) was placed at the center cylinder zone. After evacuation of the quartz tube to $\approx$1–2 Torr, a two-stage process by controlling the processing temperature and carrier gas was performed as follows: First, a pure N_2 flow was kept introducing through the quartz tube at a flow rate of 80 sccm and the ambient pressure in the tube, and the starting material Ga_2O_3 was heated to and maintained at 1250 °C for 1.5 h. Next, the pure N_2 flow was switched to a pure NH_3 flow with the same flow rate and at the ambient pressure in the tube. The furnace was further heated to and kept at 1400 °C for 1 hour. During the reaction process, an optical pyrometer with an estimated accuracy of $\pm$10 °C was used to monitor the synthesis temperature or deposition temperature. After the reaction was terminated and the furnace cooled to the room temperature, the black resulting product was collected from C fiber thermal insulating layer for characterization using X-ray powder diffractometer (XRD; RINT 2200) with $Cu_{K\alpha}$ radiation and high-resolution transmission electron microscopy (HRTEM; JEM-3000F) with an X-ray energy dispersive spectrometer (EDS). Elemental analyses were performed on a TC-436 (LECO Co., USA) and a CS-444 LS (LECO Co. USA) element simultaneous analytical determinator and an IRIS Advantage ICAP (Nippon Jarrell Ash Co., Ltd., Japan) spectrophotometer. The cathodoluminescence spectra were measured at room temperature in a spectral range of 300–800 nm by using a He–Cd laser with a wavelength of 325 nm as the excitation source.

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[1] a) J. C. Zolper, R. J. Shul, A. G. Baca, R. G. Wilson, S. Pearton, R. A. Stall, *Appl. Phys. Lett.* **1996**, *68*, 2273; b) Q. Chen, M. A. Khan, J. W. Wang, C. J. Sun, M. S. Shur, H. Park, *Appl. Phys. Lett.* **1996**, *69*, 794.

[2] a) S. Nakamura, *Science* **1998**, *281*, 956; b) F. A. Ponce, D. P. Bour, *Nature* **1997**, *386*, 351.

[3] a) M. Harada, M. Adachi, *Adv. Mater.* **2002**, *12*, 839; b) G. Seifert, H. Terrones, M. Terrones, G. Jungnickel, T. Frauenheim, *Phys. Rev. Lett.* **2000**, *85*, 146; c) C. N. R. Rao, M. Nath, *J. Chem. Soc. Dalton. Trans.* **2003**, 1.

[4] See, for example: a) M. T. Woodside, P. L. McEuen, *Science* **2002**, *296*, 1098; b) S. G. Lemay, J. W. Janssen, M. van den Hout, M. Mooij, M. J. Bronikowski, P. A. Willis, R. E. Smalley, L. P. Kouwenhoven, C. Dekker, *Nature* **2001**, *412*, 617; c) M. S. Fuhrer, J. Nygard, L. Shih, M. Forero, Y. G. Yoon, M. S. C. Mazzoni, H. J. Choi, J. Ihm, S. G. Louie, A. Zettl, P. L. McEuen, *Science* **2000**, *288*, 494; d) K. Tsukagoshi, B. W. Alphenaar, H. Ago, *Nature* **1999**, *401*, 572; e) S. S. Wong, E. Joselevich, A. T. Woolley, C. L. Cheung, C. M. Lieber, *Nature* **1998**, *394*, 52; f) S. Iijima, T. Ichihashi, *Nature* **1993**, *363*, 603.

[5] a) E. J. Mele, P. Kral, *Phys. Rev. Lett.* **2002**, *88*, 056803; b) S. S. Alexandre, M. S. C. Mazzoni, H. Chacham, *Appl. Phys. Lett.* **1999**, *75*, 61; c) N. G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie, A. Zettl, *Science* **1995**, *269*, 966; d) E. J. M. Hamilton, S. E. Dolan, C. E. Mann, H. O. Colijin, C. A. McDonald, *Science* **1993**, *260*, 659.

[6] a) R. Tenne, L. Margulis, M. Genut, G. Hodes, *Nature* **1992**, *360*, 444; b) Y. Feldman, E. Wasserman, D. J. Srolovitch, R. Tenne, *Science* **1995**, *267*, 222; c) R. Tenne, M. Homyonfer, Y. Feldman, *Chem. Mater.* **1998**, *10*, 3225; d) P. J. F. Harris, *Carbon Nanotubes and Related Structures*, Cambridge University Press, Cambridge, **1999**; e) M. Nath, A. Govindaraj, C. N. R. Rao, *Adv. Mater.* **2001**, *13*, 283; f) M. Nath, C. N. R. Rao, *Angew. Chem.* **2002**, *114*, 3601; *Angew. Chem. Int. Ed.* **2002**, *41*, 3451.

[7] a) J. H. Jung, H. Kobayashi, K. J. C. van Bommel, S. Shinkai, T. Shimizu, *Chem. Mater.* **2002**, *14*, 1445; b) G. H. Du, Q. Chen, R. C. Che, Z. Y. Yuan, L. M. Peng, *Appl. Phys. Lett.* **2001**, *79*, 3702; c) T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, *Langmuir* **1998**, *14*, 3160; d) P. Hoyer, *Langmuir* **1996**, *12*, 1411.

[8] B. Cheng, E. T. Samulski, *J. Mater. Chem.* **2001**, *11*, 2901.

[9] a) J. J. Wu, S. C. Liu, C. T. Wu, K. H. Chen, L. C. Chen, *Appl. Phys. Lett.* **2002**, *81*, 1312; b) J. Q. Hu, Q. Li, X. M. Meng, C. S. Lee, S. T. Lee, *Chem. Mater.* **2003**, *15*, 305.

[10] L. Pu, X. Bao, J. P. Zou, D. Feng, *Angew. Chem.* **2001**, *113*, 1538; *Angew. Chem. Int. Ed.* **2001**, *40*, 1490.

[11] a) Y. J. Xiong, Y. Xie, J. Yang, R. Zhang, C. Z. Wu, G. A. Du, *J. Mater. Chem.* **2002**, *12*, 3712; b) C. N. R. Rao, A. Govindaraj, F. L. Deepak, N. A. Gunari, M. Nath, *Appl. Phys. Lett.* **2001**, *78*, 1853.

[12] M. S. Mo, J. H. Zeng, X. M. Liu, W. C. Yu, S. Y. Zhang, Y. T. Qian, *Adv. Mater.* **2002**, *14*, 1658.

[13] a) C. R. Martin, *Science* **1994**, *266*, 1961; b) P. M. Ajayan, O. Stephan, P. Redlich, C. Colliex, *Nature* **1995**, *375*, 564; c) O. G. Schmidt, K. Ebert, *Nature*, **2001**, *410*, 168; d) J. She, J. J. Niu, X. Y. Ma, J. Xu, X. B. Zhang, Q. Yang, D. Yang, *Adv. Mater.* **2002**, *14*, 1219.

[14] a) W. Q. Han, S. S. Fan, Q. Q. Li, Y. D. Hu, *Science* **1997**, *277*, 1287; b) G. S. Cheng, L. D. Zhang, Y. Zhu, G. T. Fei, L. Li, C. M. Mo, Y. Q. Mao, *Appl. Phys. Lett.* **1999**, *75*, 2455.

[15] X. F. Duan, C. M. Lieber, *J. Am. Chem. Soc.* **2000**, *122*, 188.

[16] H. Y. Peng, X. T. Zhou, N. Wang, Y. F. Zheng, L. S. Liao, W. S. Shi, C. S. Lee, S. T. Lee, *Chem. Phys. Lett.* **2000**, *327*, 263.

[17] a) C. C. Chen, C. C. Yeh, *Adv. Mater.* **2000**, *12*, 738; b) X. L. Chen, J. Y. Li, Y. G. Cao, Y. C. Lan, H. Li, M. He, C. Y. Wang, Z. Zhang, Z. Y. Qiao, *Adv. Mater.* **2000**, *12*, 1432; c) M. Q. He, I. Minus, P. Z. Zhou, S. N. Mohammed, J. B. Halpern, R. Jacobs, W. L. Sarney, L. Salamanca-Riba, R. D. Vispute, *Appl. Phys. Lett.* **2000**, *77*, 3731.

[18] a) F. L. Deepak, A. Govindaraj, C. N. R. Rao, *J. Nanosci. Nanotechnol.* **2001**, *1*, 303; b) M. Q. He, I. Minus, P. Z. Zhou, S. N. Mohammed, J. B. Halpern, R. Jacobs, W. L. Sarney, L. Salamanca-Riba, R. D. Vispute, *Appl. Phys. Lett.* **2000**, *77*, 3731.

[19] a) Y. Xie, Y. T. Qian, W. Z. Wang, S. Y. Zhang, Y. H. Zhang, *Science* **1996**, *272*,1926; b) J. B. Wiley, R. B. Kaner, *Science* **1992**, *255*, 1093.

[20] a) J. -W, Hwang, S. A. Hanson, D. Britton, J. F. Evans, K. F. Jensen, W. L. Gladfelter, *Chem. Mater.* **1990**, *2*, 342; b) J.-W. Hwang, J. P. Campbell, J. Kozubowski, S. A. Hanson, J. F. Evans, W. L. Gladfelter, *Chem. Mater.* **1995**, *7*, 517; c) A. C. Frank, R. A. Fischer, *Adv. Mater.* **1998**, *10*, 961.

[21] a) H. Lei, H. S. Leipner, J. Schreiber, J. L. Weyher, T. Wosinski, I. Grzegory, *J. Appl. Phys.* **2002**, *92*, 6666; b) Y.-H. Cho, H. M. Kim, T. W. Kang, J. J. Song, W. Yang, *Appl. Phys. Lett.* **2002**, *80*, 1141.

[22] a) L. W. Tu, Y. C. Lee, S. J. Chen, I. Lo, D. Stocker, E. F. Schubert, *Appl. Phys. Lett.* **1998**, *73*, 2802; b) H. Siegle, P.

Thurian, L. Eckey, A. Hoffman, C. Thomsen, B. K. Meyer, H. Amano, I. Akasaki, T. Detchprohm, K. Hiramatsu, *Appl. Phys. Lett.* **1996**, *68*,1265; c) P. Perlin, T. Suski, H. Teiseyre, M. Leszcynsky, I. Grzegory, J. Jun, S. Porowski, P. Boguslawski, J. Bernholc, J. C. Chervin, A. Polian, T. D. Moustakas, *Phys. Rev. Lett.* **1995**, *75*, 296.

[23] a) J. Neugebauer, C. G. Van de Walle, *Appl. Phys. Lett.* **1996**, *69*, 503; b) C. Wetzel, T. Suski, J. W. Ager, E. R. Weber, E. E. Haller, S. Fischer, B. K. Meyer, P. Perlin, *Phys. Rev. Lett.* **1997**, *78*, 3923.

[24] G. Salviati, M. Albrecht, C. Zanotti-Fregonara, N. Armani, M. Mayer, Y. Shreter, M. Guzzi, Yu. V. Melnik, K. Vassilevski, V. A. Dmitriev, H. P. Strunk, *Phys. Status Solidi A* **1999**, *171*, 325.

[25] a) Y. H. Gao, Y. Bando, *Nature* **2002**, *415*, 599; b) Y. H. Gao, Y. Bando, *Appl. Phys. Lett.* **2002**, *81*, 3966.

[26] G. Gundiah, A. Govindaraj, C. N. R. Rao, *Chem. Phys. Lett.* **2002**, *351*, 189.

[27] G. W. Sears, *Acta Metall.* **1956**, *3*, 268.

[28] a) E. W. Wong, B. W. Maynor, L. D. Burns, C. M. Lieber, *Chem. Mater.* **1996**, *8*, 2041; b) H. J. Dai, E. W. Wong, Y. Z. Lu, S. S. Fan, C. M. Lieber, *Nature* **1995**, *375*, 769.

[29] a) D. Golberg, Y. Bando, L. Bourgeois, K. Kurashima, T. Sato, *Carbon* **2000**, *38*, 2017; b) D. Golberg, Y. Bando, W. Q. Han, K. Kurashima, T. Sato, *Chem. Phys. Lett.* **1999**, *308*, 337; c) W. Q. Han, Y. Bando, K. Kurashima, T. Sato, *Appl. Phys. Lett.* **1998**, *73*, 3085.

