Laser-Assisted Catalytic Growth of Single Crystal GaN Nanowires

Xiangfeng Duan and Charles M. Lieber*

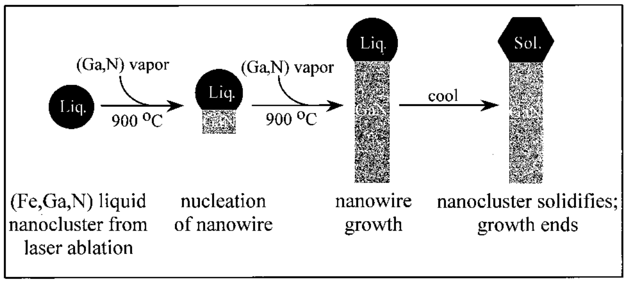
Department of Chemistry and Chemical Biology
Harvard University, Cambridge, Massachusetts 02138

Received October 18, 1999

Herein we report the bulk synthesis of single crystalline GaN nanowires. Laser ablation of a composite target of GaN and a catalytic metal generates liquid nanoclusters that serve as reactive sites confining and directing the growth of crystalline nanowires. Field emission scanning electron microscopy (FE-SEM) shows that the product primarily consists of wire-like structures. Powder X-ray diffraction (PXRD) analyses of a bulk nanowire sample can be indexed to the GaN wurtzite structure, and indicate >95% phase purity. Transmission electron microscopy (TEM), convergent beam electron diffraction (CBED), and energy-dispersive X-ray fluorescence (EDX) analyses of individual nanowires show that they are GaN single crystals with a [100] growth direction.

Nanostructured GaN materials have attracted extensive interest over the past decade due to their significant potential for optoelectronics.[1] These studies have primarily focused on zero-dimensional (0D) quantum dots[2−7] and two-dimensional (2D) quantum well structures,[8−11] which can be readily synthesized using established methods. Investigations of one-dimensional (1D) GaN nanowires, which could enable unique opportunities in fundamental and applied research,[12,13] have been limited due to difficulties associated with their synthesis. Specifically, there has been only one report of GaN nanowire growth.[14,15] In this work, carbon nanotubes were used as templates in the presence of Ga-oxide and NH_3 vapor to yield GaN nanowires. We have exploited the predictable synthetic approach for GaN nanowire growth called laser-assisted catalytic growth (LCG).[12,16,17] In this method, a pulsed laser is used to vaporize a solid target containing desired material and a catalyst, and the resulting liquid nanoclusters formed at elevated temperature direct the growth and define the diameter of crystalline nanowires through a vapor−liquid−solid growth mechanism.[12,16−18] A key feature of this method is that the catalyst used to define 1D growth can be selected from phase diagram data and/or knowledge of chemical reactivity. A related approach termed solution−liquid−solid phase growth has been used by Buhro and co-workers to prepare nanowires of several III−V materials in solution,[19] although not nitrides.[20]

Scheme 1



In the case of GaN, detailed information on ternary phase diagrams relevant to LCG (i.e., catalyst−Ga−N) is unavailable. However, we can use the knowledge of the growth process to choose a catalyst rationally. Specifically, the catalyst should form a miscible liquid phase with GaN but not form a more stable solid phase under the nanowire growth conditions. The guiding principle suggests that Fe, which dissolves both Ga and N,[21] and does not form a more stable compound than GaN will be a good catalyst for GaN nanowire growth by LCG. The overall evolution of nanowire growth following the generation of the catalytic nanocluster by laser ablation is illustrated in Scheme 1.

Significantly, we find that LCG using a GaN/Fe target produces a high yield of nanometer diameter wire-like structures. A typical FE-SEM image of the product produced by LCG[22] (Figure 1a) shows that the product consists primarily of 1D structures with diameters on the orders of 10 nm and lengths greatly exceeding 1 μm, that is, high aspect ratio nanowires. The FE-SEM data also show that the products consist of ca. 90% nanowires, with the remaining being nanoparticles. We have also assessed the overall crystal structure and phase purity of the bulk nanowire samples using PXRD (Figure 1b). All the relatively sharp diffraction peaks in the PXRD pattern can be indexed to a wurtzite structure with

---

(1) (a) Nakamura, S.; Mukai, T.; Senoh, M. *Jpn. J. Appl. Phys.* **1991**, *30*, L1998. (b) Rigby, P. *Nature* **1996**, *384*, 610. (c) Fasol, G. *Science* **1996**, *272*, 1751. (d) Nakamura, S.; Senoh, M.; Nagahama, S.; Iwasa, N.; Yamada, T.; Matsushita, T.; Sugimoto, Y.; Kiyoku, H. *Appl. Phys. Lett.* **1996**, *69*, 3034. (e) Nakamura, S. *Science* **1998**, *281*, 956. (f) Someya, T.; Werner, R.; Forchel, A.; Catalano, M.; Cingolani, R.; Arakawa, Y. *Science* **1999**, *285*, 1905.

(2) Frank, A. C.; Stowwasser, F.; Sussek, H.; Pritzkow, H.; Miskys, C. R.; Ambacher, O.; Giersig, M.; Fisher, R. A. *J. Am. Chem. Soc.* **1998**, *120*, 3512.

(3) Micic, O. I.; Ahrenkiel, S. P.; Bertram, D.; Nozik, A. J. *Appl. Phys. Lett.* **1999**, *75*, 478.

(4) Xie, Y.; Qian, Y.; Wang, W.; Zhang, S.; Zhang, Y. *Science* **1996**, *272*, 1926.

(5) Daudin, B.; Widmann, F.; Feuillet, G.; Adelmann, S.; Samson, Y.; Arlery, M. *Mater. Sci. Eng. B* **1997**, *50*, 8.

(6) Ramvall, P.; Tanaka, S.; Nomura, S.; Riblet, P.; Aoyagi, Y. *Appl. Phys. Lett.* **1998**, *73*, 1104.

(7) Goodwin, T. J.; Leppert, V. J.; Risbud, S. H.; Kennedy, I. M.; Lee, H. W. H. *Appl. Phys. Lett.* **1997**, *70*, 3122.

(8) Xiao, R. F.; Liao, H. B.; Cue, N.; Sun, X. W.; Kwok, H. S. *J. Appl. Phys.* **1996**, *80*, 4226.

(9) Vispute, R. D.; Talyansky, V.; Sharma, R. P.; Choopun, S.; Downes, M.; Jones, K. A.; Lliadis, A. A.; Khan, M. A.; Yang, J. W. *Appl. Phys. Lett.* **1997**, *71*, 102.

(10) Mesrine, M.; Grandjean, N.; Massies, J. *Appl. Phys. Lett.* **1998**, *72*, 350.

(11) Ran, C. A.; Osinski, A.; Karlicek, R. F.; Berishev, I. *Appl. Phys. Lett.* **1999**, *75*, 1494.

(12) (a) Lieber, C. M.; Morales, A. M.; Sheehan, P. E.; Wong, E. W.; Yang, P. In *Proceeedings of the Robert A. Welch 40th Conference on Chemical Research: Chemistry on the Nanometer Scale*; R. A. Welch Foundation: Houston, 1997; pp 165−187. (b) Lieber, C. M. *Solid State Commun.* **1998**, *107*, 607. (c) Hu, J.; Odom, T. W.; Lieber C. M. *Acc. Chem. Res.* **1999**, *32*, 435.

(13) (a) Brus, L. E. *J. Phys. Chem.* **1994**, *98*, 3575. (b) Snoke, D. *Science* **1996**, *273*, 1351. (c) Yacobson, B. I.; Smalley, R. E. *Am. Sci.* **1997**, *85*, 324. (d) Dekker, C. *Phys. Today* **1999**, *52*, 22.

(14) (a) Han, H.; Fan, S.; Li, Q.; Hu, Y. *Science* **1997**, *277*, 1287. (b) Zhu, J.; Fan, S. *J. Mater. Res.* **1999**, *14*, 1175.

(15) Carbon nanotube templates have also been used in the growth of Si_3N_4 nanorods: Han, H.; Fan, S.; Li, Q.; Gu, B.; Zhang, X.; Yu, D. *Appl. Phys. Lett.* **1997**, *71*, 2271.

(16) Morales, A.; Lieber, C. M. *Science* **1998**, *279*, 208.

(17) Duan, X.; Lieber, C. M. *Adv. Mater.* In press.

(18) Wagner, R. S.; Ellis, W. C. *Appl. Phys. Lett.* **1964**, *4*, 89.

(19) (a) Trentler, T. J.; Hickman, K. M.; Goel, S. C.; Viano, A. M.; Gibbons, P. C.; Buhro, W. E. *Science* **1995**, *270*, 1791. (b) Trentler, T. J.; Goel, S. C.; Hickman, K. M.; Viano, A. M.; Chiang, M. Y.; Beatty, A. M.; Gibbons, P. C.; Buhro, W. E. *J. Am. Chem. Soc.* **1997**, *119*, 2172.

(20) Buhro and co-workers have also produced AlN nanowhiskers at high temperatures by a proposed vapor−solid mechanism: (a) Haber, J. A.; Gibbons, P. C.; Buhro, W. E. *J. Am. Chem. Soc.* **1997**, *119*, 5455. (b) Haber, J. A.; Gibbons, P. C.; Buhro, W. E. *Chem. Mater.* **1998**, *10*, 4062.

(21) Massalski, T. B. *Binary Alloy Phase Diagrams*; Scott, W. W., Tr. American Society for Metals: Metals Park, OH, 1986; Vol. 1, pp 1063−1064 and 1079−1083.

(22) The LCG experimental apparatus is similar to that reported previously.[16] A GaN/Fe (atomic ratio (GaN):Fe = 0.95:0.05) composite target was positioned with a quartz tube at the center of a furnace. The experimental system was evacuated to 30 mTorr, and then refilled with anhydrous ammonia gas. While the pressure and flow rate were maintained at ca. 250 Torr and 80 sccm, respectively, the furnace temperature was increased to 900 °C at 30 deg/min. A pulsed Nd:YAG laser (1064 nm, 8 ns pulse width, 10 Hz repetition, 2.5 W average power) was then used to ablate the target with a typical ablation duration of 5 min. After ablation, the furnace was turned off and allowed to cool to room temperature. The system was then vented and light yellowish powders were collected from the end of the inner quartz tube wall. The product was used directly for FE-SEM and PXRD studies. The product was suspended in ethanol and then transferred onto TEM grids for TEM, CBED, and EDX measurements.

10.1021/ja993713u CCC: $19.00

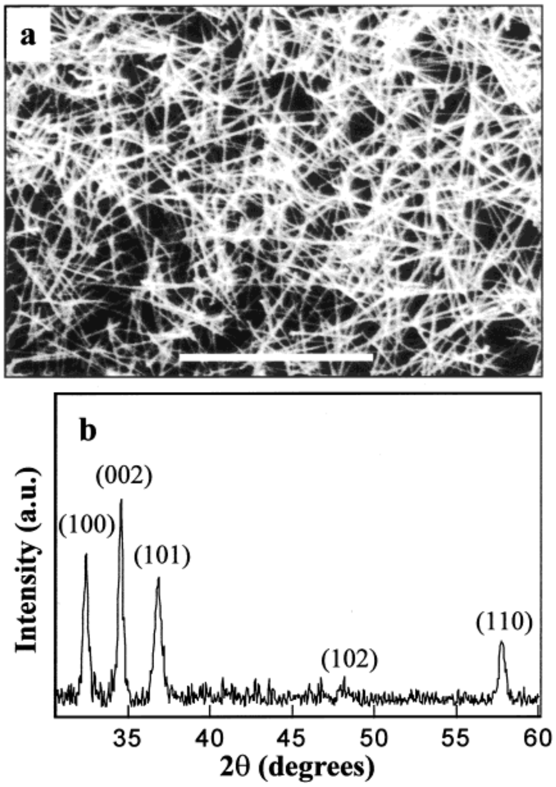


Figure 1. (a) FE-SEM (LEO 982) image of bulk GaN nanowires synthesized by LCG. The scale bar corresponds to 1 μm. (b) PXRD (Scintag, XDS2000) pattern recorded on bulk GaN nanowires. The numbers above the peaks correspond to the (*hkl*) values of the wurtzite structure.

lattice constants of $a = 3.187$ Å and $c = 5.178$ Å. These values are in good agreement with literature values for bulk GaN: $a = 3.189$ Å and $c = 5.182$ Å.[23] In addition, comparison of the background signal and observed peaks indicates that the GaN wurtzite phase represents >95% of the crystalline material produced in our syntheses.

The morphology, structure, and composition of the GaN nanowires have been characterized in further detail using TEM, CBED, and EDX. TEM studies show that the nanowires are straight with uniform diameters, and typically terminate in a nanoparticle at one end. Figure 2a shows a representative diffraction contrast image of one nanowire. The uniform contrast along the wire axis indicates that the nanowire is a single crystal. The nanoparticle (dark, high contrast feature) observed at the nanowire end is faceted as expected following crystallization of the liquid nanocluster (Scheme 1). We have also used EDX to address the composition of the nanowires and terminal nanoparticles. Data recorded on the nanowire show only Ga and N in a ratio ca. the same as a GaN standard, while the nanoparticles contain Ga, N, and Fe. The presence of Fe (with Ga and N) only in the terminal nanoparticle confirms the catalytic nature of Fe in the synthesis.

To probe further the importance of the catalyst, we have also investigated GaN nanowire growth using a Au catalyst. Gold has been used recently as a catalyst for growth of a number of nanowires of III−V and II−VI material,[17] and as such might be expected to also function effectively in the growth of GaN nanowires. However, Au exhibits poor solubility of N[24] and thus may not transport N efficiently to the liquid/solid growth interface. Consistent with this analysis, we have been unable to obtain GaN nanowire using the Au catalyst. We believe that this highlights the important role of the catalyst and how it can be rationally chosen.

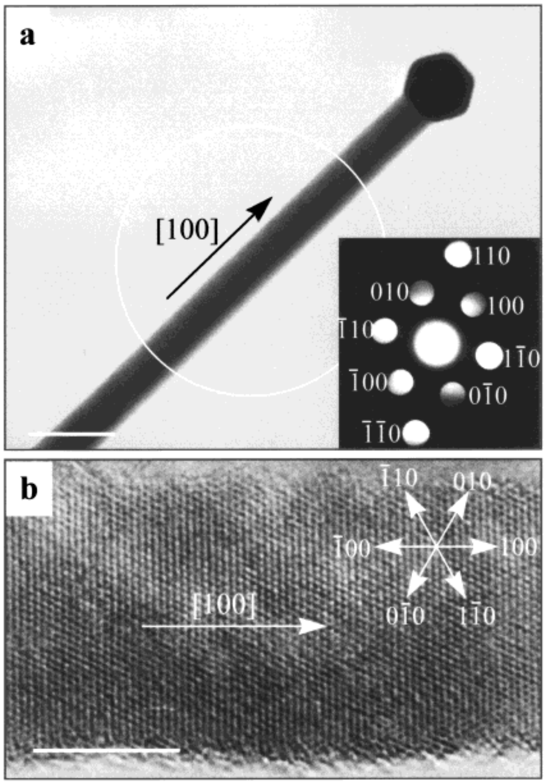


Figure 2. (a) Diffraction contrast TEM (Philips, EM420) image of a GaN nanowire that terminates in a faceted nanoparticle of higher (darker) contrast. (Inset) CBED pattern recorded along the ⟨001⟩ zone axis over the region indicated by the white circle. The white scale bar corresponds to 50 nm. (b) HRTEM (JEOL 2010) image of another GaN nanowire with a diameter of ca. 10 nm. The image was taken along the ⟨001⟩ zone axis. The [100], [010], and [−110] directions are indicated with the [100] parallel to the wire axis. The white scale bar corresponds to 5 nm.

Last, we have characterized the structure of GaN nanowires in greater detail using CBED and high-resolution TEM (HRTEM). A typical CBED pattern (inset, Figure 2a) of a nanowire exhibits a sharp diffraction pattern consistent with the single-crystal structure inferred from the diffraction contrast images. Indexing this pattern further demonstrates that the [100] direction is aligned along the wire axis. In addition, Figure 2b shows a lattice resolved HRTEM image of a GaN nanowire with an ca. 10 nm diameter. The image, which was recorded along the ⟨001⟩ zone axis, shows clearly the single-crystal structure of the nanowire and the lattice planes along the [100], [010], and [−110] directions. This image demonstrates that the [100] direction runs parallel to the wire axis, and thus confirms the [100] growth direction in GaN nanowires.

In conclusion, we have exploited the LCG method for the rational synthesis of GaN nanowires. Highly pure GaN nanowires were obtained as single crystals with a unique [100] growth direction. We believe that this approach, which is based on the predictable choice of catalyst and growth conditions, can be readily extended to the synthesis of InN, (GaIn)N alloys, and related nitride nanowires. The synthesis of bulk quantities of single-crystal nanowires of GaN and other technologically important semiconducting nitride materials is expected to open up many opportunities for further fundamental studies and applications.

Acknowledgment. We thank M. Frongillo and Y. Lu for help with TEM. C.M.L. thanks the Office of Naval Research and the National Science Foundation for support of this work.

JA993713U

---

(23) Ross, J.; Rubin, M.; Gustafson, T. K. *J. Mater. Res.* **1993**, *8*, 2613.
(24) Massalski, T. B. *Binary Alloy Phase Diagrams*; Scott, W. W. Tr.; American Society for Metals: Metals Park, OH, 1986; Vol. 1, p 283.