Pyrolysis approach to the synthesis of gallium nitride nanorods

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Herein we describe a pyrolysis route to the synthesis of gallium nitride (GaN) nanorods. GaN nanorods have been grown by the pyrolysis of gallium dimethylamide and ferrocene under an ammonia atmosphere. High-resolution transmission electron microscopy and energy dispersive x-ray spectrometer show that they are GaN single crystals, the sizes of which vary from 3 to 30 μm in length and 15 to 70 nm in diameter. Iron acts as an important catalyst for the GaN nanorod growth. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1431401]

In recent years, GaN and other group-III-nitride based wide–band gap semiconductor films have emerged as the leading material for the production of blue light-emitting devices, blue laser diodes, and nonoptoelectronic applications.[1,2] One-dimensional structures with nanometer sized diameters have great potential for playing an important role in the testing and understanding of fundamental concepts of the role of dimensionality and size in physical properties.[3] Since the first work of GaN nanorods was prepared using a carbon-nanotube-confined reaction,[4] many efforts have been devoted to developing different approaches for synthesizing GaN nanorods. These include metal-catalyzed growth assisted by laser ablation,[5] template-induced growth,[6] hot filament chemical vapor deposition,[7] and gallium oxide reacted with ammonia.[8–11] GaN nanorods and carbon nanotubes filled with GaN nanorods have also been synthesized by an arc discharge route.[12] Inorganic gallium sources, such as Ga and Ga_2O, and inorganic catalysts are typically used for the growth of GaN nanorods. The pyrolysis of organometallic precursors has already been demonstrated to be a powerful route to the synthesis of nanotubes and filled nanotubes.[13–16] In the present study, we describe the use of a pyrolysis route to prepare GaN nanorods where both the Ga and the catalyst come from organic sources.

In order to prepare the GaN nanorods by the pyrolysis route, we employed a two-stage furnace system fitted with temperature controllers.[13–16] The flow rate of gases was controlled by using mass flow controllers. A (1:2) mixture (by weight) of powdered gallium dimethylamide ($Ga_2([N(CH_3)_2]_6$ Alfa 99.9%) and ferrocene (Bis(cyclopentadienyl)iron, $(C_2H_5)_2Fe$, Aldrich 98%) was introduced into a quartz tube (inner diameter, ~9 mm). Ammonia gas passed through the quartz tube (~20–30 ml/min) during the whole process. The part of the quartz tube which contained ferrocene and gallium dimethylamide was moved from a cold zone outside of the first stage of the furnace to the high temperature zone of the first stage. The first and second stages were kept at the temperatures of 1000 °C and 900 °C, respectively, for 15 min. Subsequently, the system was allowed to cool to room temperature and soot-like deposits were collected from the quartz tube at the second stage of the furnace. The resulting sample was characterized by high-resolution transmission electron microscopy (HRTEM) using a Philips CM-200 FEG equipped with energy dispersive x-ray spectrometer (EDS).

To reveal the growth process of the product, HRTEM was used to examine the general morphology. In Fig. 1(a), we show the typical low-magnification image of the nanorods. The sizes of the nanorods are typically 3 to 30 μm in length and 15 to 70 nm in diameter. The nanorods are usually straight and uniform. Carbon nanotubes are also found in the product. The compositions of nanorods are checked by EDS, which shows that the nanorods are GaN and the elemental

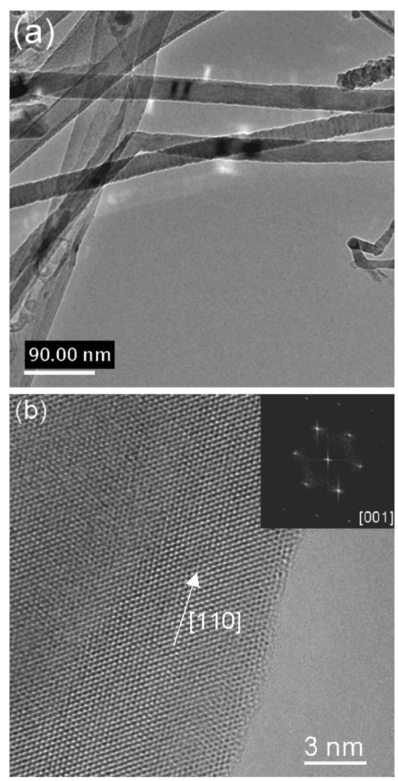

FIG. 1. (a) Low-magnification TEM image showing a general view of the GaN nanorods and the carbon nanotubes in the product and (b) high-magnification image of part of a nanorod. Inset is the corresponding diffraction patterns taken by FHT techniques. The incidence direction of the electron beam is along ⟨001⟩ direction.

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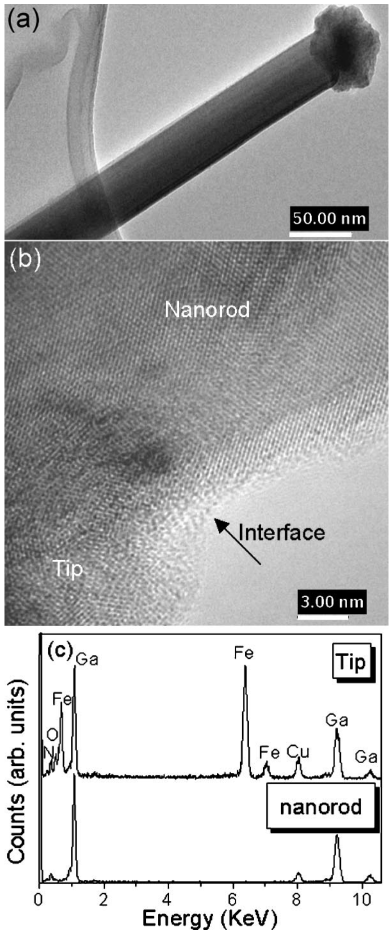

FIG. 2. (a) Low-magnification image of a GaN nanorod including its tip, (b) a high-magnification image of the interface of the tip and the nanorod, and (c) EDS spectra taken from the tip (upper) and nanorod (down), respectively.

ratio of Ga to N closes to 1. Figure 1(b) shows a high-magnification image of part of a nanorod. Digitized images were then analyzed by fast Hartley transform (FHT) techniques to reveal details of the local structure. The inset of Fig. 1 is the corresponding diffraction patterns taken by FHT, which can be indexed to hexagonal wurtzite GaN. The incidence direction of the electron beam is along ⟨001⟩ direction. The axis direction of the GaN nanorod is [110].

Polygonal- or spherical-shaped particles are frequently found at the tip of the nanorods. Figure 2(a) shows a low-magnification image of a GaN nanorod including its tip. Figure 2(b) shows a high-magnification image of the interface of the tip and the nanorod. It shows that the tip is polycrystalline and the nanorod part is monocrystalline. The compositions of the tip and the nanorod were detected by EDS [Fig. 2(c)]. It shows that there are Fe, Ga, N, and O at the tip and only GaN in the nanorod part. A small amount of oxygen at the tip might have come from the remaining oxygen in the quartz tube although the tube was purged with ammonia. Another possibility is that it may have come from the quartz tube at high temperatures.

Fe, which dissolves both Ga and N and does not form a more stable compound than GaN, is a good catalyst for the growth of GaN nanowires by arc discharge and laser-assisted catalytic methods.[5,12] Ferrocene has been shown to be a successful catalyst for nanotube growth.[13–16] Omission of ferrocene in our initial pyrolysis experiment resulted in no nanorods and nanotubes, which supports the fact that ferrocene plays a crucial catalytic role in the present case. The growth process of GaN nanorods might be described by the so-called vapor–liquid-solid (VLS) mechanism.[17,18] Upon the decomposition of ferrocene, gallium dimethylamide, and ammonia, iron particles are surrounded by N, Ga, C, etc. radicals. In the initial stage, segregation of iron occurs, leading to an increase in the size of iron clusters on the surface of quartz tube. Subsequently, Ga and N are introduced in vapor phase and dissolve in the iron oxide clusters to form liquid catalyst centers.[19] Continuous dissolution of Ga and N leads to a supersaturated solution. GaN nanorod growth takes place by the precipitation from the supersaturated liquid of the catalyst centers. The overall evolution of nanorod growth following the generation of the iron catalytic particles by pyrolysis is illustrated in Fig. 3.

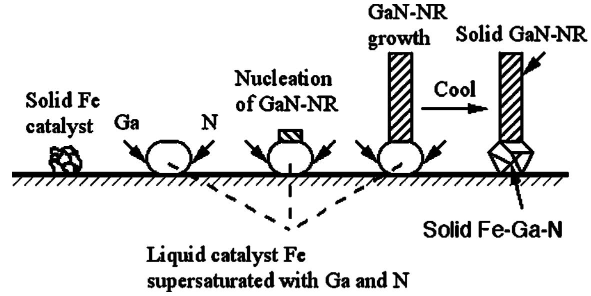

FIG. 3. Schematic illustration of VLS process for GaN nanorod (GaN-NR) growth by a pyrolysis route.

In summary, we have exploited the pyrolysis route for the synthesis of high quality GaN nanorods. We believe that this approach can be readily extended to the synthesis of other group-III-nitride based semiconductor nanorods and also nanorods of other materials which might offer great opportunities for both fundamental research and technological application.

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[1] S. Nakamura and G. Fasol, *The Blue Laser Diode* (Springer, New York, 1997).
[2] J. Pankove and T. Moustakas, *Gallium Nitride (GaN)*, Semiconductors and Semimetals, Vol. 50 (Academic, San Diego, 1998).
[3] C. M. Lieber, Solid State Commun. **107**, 607 (1998).
[4] W. Han, S. Fan, Q. Li, and Y. Hu, Science **277**, 1287 (1997).
[5] X. Duan and C. Lieber, J. Am. Chem. Soc. **122**, 188 (2000).
[6] G. Cheng, L. Zhang, Y. Zhu, G. Fei, L. Li, C. Mo, and Y. Mao, Appl. Phys. Lett. **75**, 2455 (1999).
[7] H. Peng, X. Zhou, N. Wang, Y. Zheng, L. Liao, W. Shi, C. Lee, and S. Lee, Chem. Phys. Lett. **327**, 263 (2000).
[8] C. Chen and C. Yeh, Adv. Mater. **12**, 738 (2000).
[9] C. Tang, S. Fan, H. Dang, P. Li, and Y. Liu, Appl. Phys. Lett. **77**, 1961 (2000).
[10] X. Chen, J. Li, and Y. Cao, Adv. Mater. **12**, 1432 (2000).
[11] M. He, I. Minus, P. Zhou, N. Mohammed, J. Halpern, R. Jacobs, W. L. Sarney, L. Salamanca-Riba, and R. Vispute, Appl. Phys. Lett. **77**, 3731 (2000).

[12] W. Han, P. Redlich, F. Ernst, and M. Ruehle, Appl. Phys. Lett. **76**, 652 (2000).
[13] M. Terrones, N. Grobert, J. Olivares, J. P. Zhang, H. Terrones, K. Kordatos, H. K. Hsu, J. P. Hare, P. D. Townsend, K. Prassides, A. K. Cheetham, H. W. Kroto, and D. R. M. Walton, Nature (London) **388**, 52 (1997).
[14] C. N. R. Rao, R. Sen, B. C. Satishkumar, and J. Govindaraj, J. Chem. Soc. Chem. Commun. **15**, 1525 (1998).
[15] W. Han, P. Kohler-Redlich, F. Ernst, M. Rhle, N. Grobert, W. K. Hsu, B. H. Chang, Y. Q. Zhu, H. W. Kroto, D. R. M. Walton, M. Terrones, and H. Terrones, Appl. Phys. Lett. **77**, 1807 (2000).
[16] W. Han, J. Cumings, and A. Zettl, Appl. Phys. Lett. **78**, 2769 (2001).
[17] R. S, Wagner and W. C. Ellis, Trans. Metall. Soc. AIME **233**, 1054 (1965).
[18] J. V. Milewski, F. D. Gac, J. J. Petrovic, and S. R. Skaggs, J. Mater. Sci. **20**, 1160 (1985).
[19] The melting temperature of Fe is 1538 °C and that of the Fe–Ga alloy is lower than 900 °C. See T. B. Massalski, in *Binary Alloy Phase Diagrams*, edited by W. W. Tr. Scott (American Society for Metals, Metals Park, OH, 1986), Vol. 1, p. 1064.