JMEPEG (2010) 19:1054–1057
DOI: 10.1007/s11665-009-9574-8

1059-9495/$19.00

Catalytic Growth of Large-Scale GaN Nanowires

Jinhua Chen and Chengshan Xue

(Submitted February 22, 2009; in revised form October 16, 2009)

A novel lanthanon seed was employed as the catalyst for the growth of GaN nanowires. Large-scale GaN nanowires have been synthesized successfully through ammoniating Ga_2O_3/Tb films sputtered on Si(111) substrates. Scanning electron microscopy, x-ray diffraction, high-resolution transmission electron microscopy, and Fourier transform infrared spectroscopy were used to characterize the samples. The results demonstrate that the nanowires are single-crystal hexagonal wurtzite GaN. The growth mechanism of GaN nanowires is also discussed.

Keywords ammoniating, magnetron sputtering, nanowires, semiconductor material

1. Introduction

GaN, an attractive wide bandgap (3.4 eV direct gap at room temperature) semiconductor material, has recently attracted considerable attention owing to its innovative physical properties and potential applications. One-dimensional GaN nanostructures have wide applications in the field of high efficient ultraviolet and visible photoelectron devices (Ref 1). Recently, there have been reports on the growth of GaN nanostructures by many methods (Ref 2-7). Among these numerous methods, the metal catalyst-assisted vapor-liquid-solid (VLS) growth is the most successful approach because it can offer simple and size-controllable growth of nanostructures. Some metal catalysts used for the growth of nanostructures, such as Ni (Ref 1), Au (Ref 8), Fe (Ref 9), and In (Ref 10), have been reported. So far as we know, the growth of GaN nanostructures employing lanthanon as catalyst has been reported infrequently. Tb is one of rare earths elements and can be employed as catalyst. This paper presents a novel route via Tb seed for the catalyst-assisted growth of GaN nanowires. This growth method allows a continuous synthesis and produces large-scale single-crystalline GaN nanowires at relatively high purity and low cost. Accordingly, it is obviously advantageous for the applications of nanodevices.

2. Experimental

First, Si(111) substrates were washed with absolute ethyl alcohol and then ultrasonic cleaned in acetone, absolute ethyl alcohol, and de-ionized water for 30 min in sequence. Secondly, Ga_2O_3/Tb thin films were deposited in turn on Si(111) substrates by sputtering a Tb target (99.95%) and a sintered Ga_2O_3 (99.99%) target. The sputtering chamber was evacuated to a background pressure of 1.8×10^{-3} Pa, and then argon gas (99.999%) was introduced into the chamber at a pressure of 2 Pa. The sputtering power was 150 W and the distance between the target and substrates was 8 cm. The sputtering time for Tb and Ga_2O_3 was 5 and 90 min, respectively. Thirdly, as-deposited Ga_2O_3/Tb thin films were placed into a quartz tube of a furnace and ammoniated under flowing NH_3 (flow rate 500 mL/min) at 950 °C for 5 min. After reaction, a light yellow layer was found on the surface of substrate.

The surface morphology, structure, and composition of the samples were examined with scanning electron microscopy (Hitachi S-570, SEM), x-ray diffraction meter (Rigaku D/max-rB Cu k_α, XRD), high-resolution transmission electron microscopy (Philips Tecnai F30, HRTEM), and Fourier transform infrared spectroscopy (Tensor 27, FTIR).

3. Results and Discussion

Figure 1 shows the representative SEM images of the sample, the light-yellow layer is composed of high-density GaN nanowires, crossing each other and distributing homogeneously on the whole surface of Si substrate. Nanoparticles are observed at the top of the rods, lined out with circles in Fig. 1(a). However, no nanoparticles can be detected clearly at the top of some nanowires, because some nanoparticles on the top are destroyed by the sublimation (sublimation temperature about 900 °C) of GaN. Analysis of a number of nanowires shows that the length is about several tens of microns and the diameter ranges from 50 to 100 nm.

Figure 2 shows the XRD pattern of the sample. The four peaks (100), (002), (101), and (102) of GaN nanowires are located at 32.40, 34.54, 36.78, and 48.38°, respectively, demonstrating that the reflections can be indexed to the hexagonal GaN phase with the lattice constants $a = 0.318$ nm and $c = 0.518$ nm, which are consistent with the reported values for bulk GaN (Ref 11). The sharp diffraction peaks reveal that GaN nanowires possess good crystalline quality.

Jinhua Chen, Department of Mechanical Engineering, Zhenjiang Vocational College of Mechanical & Electrical Technology, No. 132 Xuefu Road, Zhenjiang 212016, China; and **Chengshan Xue**, Institute of Semiconductors, College of Physics and Electronics, Shandong Normal University, No. 88 East Culture Road, Ji'nan 250014, China. Contact e-mail: jhch6666@163.com.

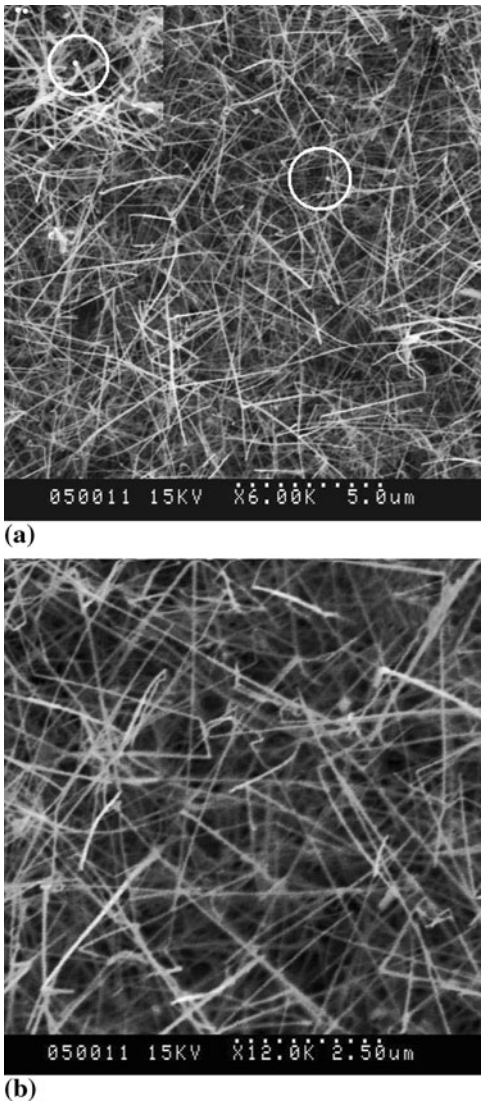

Fig. 1 SEM image of GaN nanowires ammoniated at 950 °C for 5 min

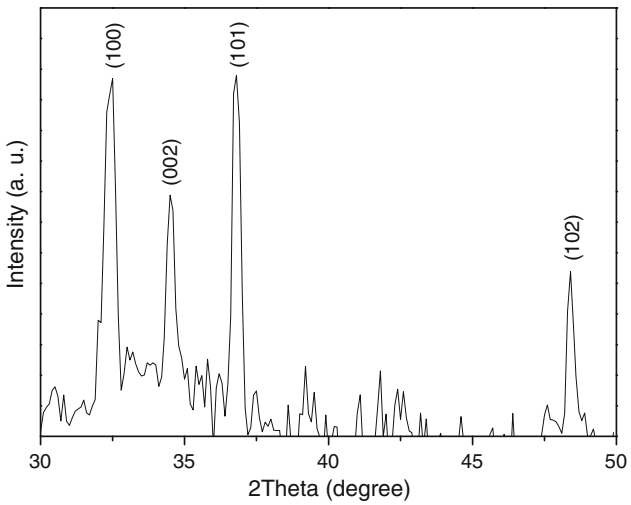

Fig. 2 XRD pattern of as-synthesized sample ammoniated at 950 °C for 5 min

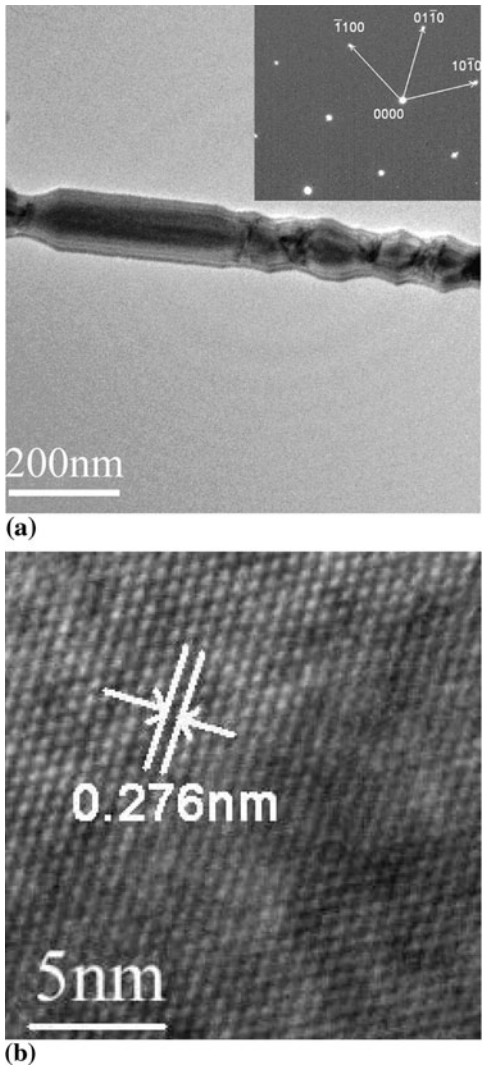

Fig. 3 HRTEM image (a) and HRTEM lattice image (b) of single GaN nanowire. The upper-right-hand inset of (a) is the corresponding SAED pattern

HRTEM (Fig. 3) was carried out for understanding further the structural properties of the nanowires. Figure 3(a) shows the lower-amplified HRTEM image of single nanowire with a diameter of about 100 nm, the inset in the upper-right-hand corner is the selected area electron diffraction (SAED) pattern of the nanowire, which can be indexed to the diffraction of wurtzite GaN crystal along the [001] direction. Meanwhile, it also confirms that the nanostructures are single crystalline GaN nanowires. Figure 3(b) shows the HRTEM lattice image of the same nanowire, the visible lattice image proves that the nanowires are single crystal in nature. The interplanar spacing measured accurately is 0.276 nm, which corresponds to the (100) plane of hexagonal GaN, indicating the growing direction of the nanowire is perpendicular to the (100) plane, which is in accordance with the result of XRD.

Figure 4 shows the FTIR spectrum of GaN nanowires ammoniated at 950 °C for 5 min. Four prominent IR absorption bands are observed at 562.36 cm^{-1} (band 1), 610.91 cm^{-1} (band 2), 728.05 cm^{-1} (band 3), and 1109.23 cm^{-1} (band 4), respectively. In the light of the reported band of Ga-N

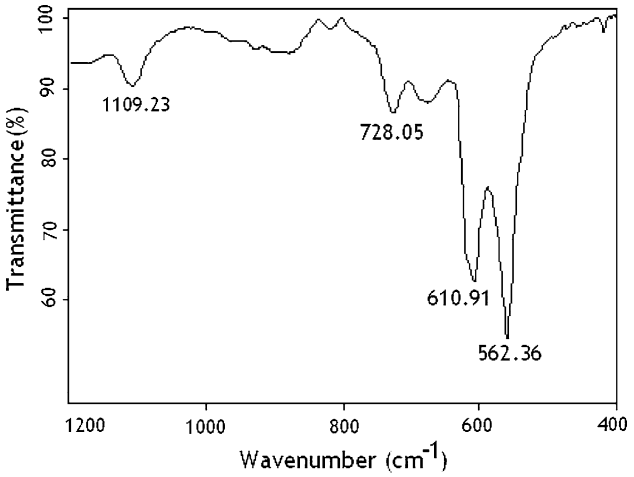

Fig. 4 FTIR spectrum of the sample ammoniated at 950 °C for 5 min

stretching vibration absorption in hexagonal GaN at 560.45 cm^{-1} (Ref 12), band 1 should be a Ga-N stretching vibration absorption peak, illustrating the obtained products are hexagonal GaN, which is in accordance with the results of XRD and HRTEM. Bands 2, 3, and 4 are all related to Si substrate. Band 2 is due to a local vibration of substitutional carbon in Si crystal lattice (Ref 13). Band 3 is associated with amorphous phases in the substrates (Ref 14). Band 4 is attributed to Si-O-Si asymmetric stretching vibration, which ascribes to the extremely thin SiO_2 layer on the surface of Si substrate (Ref 15). FTIR spectrum further confirms that GaN is synthesized under current conditions.

From the above-mentioned SEM pictures, it can be found that the nanowires terminate in nanoparticles with diameter slightly larger than that of the connected nanowires, which is the most remarkable sign (Ref 16) of VLS mechanism. Therefore, the formation of GaN nanowires is dominated probably by Tb catalyst-assisted VLS mechanism. Although the melting point (1360 °C) of bulk metal Tb is higher than the reaction temperature we used, the melting point of nanoparticles is lower than that of the corresponding bulk materials (Ref 17). Tb film breaks up at the reaction temperature and liquid Tb droplets appear on Si substrates, which could act subsequently as the favorable nucleation sites for GaN nanowires. At the same time, NH_3 decomposes step by step to NH_2, NH, H_2, and N when the ammoniating temperature is above 850 °C (Ref 18). The Ga_2O_3 particles are reduced to gaseous Ga_2O by H_2 and then GaN molecules are synthesized through the reaction of Ga_2O and ammonia (Ref 19). All the reactions can be expressed as follows:

$$2NH_3\ (g) \rightarrow N_2\ (g) + 3H_2\ (g),$$
$$Ga_2O_3\ (s) + 2H_2\ (g) \rightarrow Ga_2O\ (g) + 2H_2O\ (g),$$
$$Ga_2O\ (g) + 2NH_3\ (g) \rightarrow 2GaN\ (s) + 2H_2\ (g) + H_2O\ (g).$$

It is thought that Ga_2O and NH_3 gases evaporate and travel to the substrate, where the catalytic reaction takes place. Very miscible Tb-Ga-N alloy liquid droplets could be formed first during the heating process of the reaction. Secondly, Ga_2O and NH_3 gases go on solving into Tb liquid droplets, the supersaturated state of Tb-Ga-N alloy appears and GaN begins to diffuse through the liquid phase to the bottom of droplet, where GaN crystalline nuclei are formed. Finally, with the gases dissolving continuously into Tb liquid droplets, GaN nanowires grow up gradually from the nucleation sites (Ref 11, 20, 21). Consequently, GaN nanowires are produced by the catalytic action of Tb and the growth follows VLS process. However, we think that further detailed investigation is necessary to clarify the growth mechanism of GaN nanowires.

4. Conclusions

In summary, high-quality GaN nanowires have been synthesized successfully on Si(111) substrates by ammoniating Ga_2O_3/Tb films at 950 °C for 5 min. The structure, morphology, and composition of the samples are studied by SEM, XRD, HRTEM, and FTIR. The results show that the nanowires are hexagonal wurtzite single-crystal GaN with length for several tens of microns and diameter for 50-100 nm. The catalytic growth mechanism of GaN nanowires is dominated probably by conventional VLS mechanism.

Acknowledgment

The authors thank the National Natural Science Foundation of China (No. 90201025 and No. 90301002).

References

1. J. Yoo, Y.J. Hong, S.J. An, G.C. Yi, B. Chon, T. Joo, J.W. Kim, and J.S. Lee, Photoluminescent Characteristics of Ni-Catalyzed GaN Nanowires, *Appl. Phys. Lett.*, 2006, **89**, p 043124–043126
2. O. Landre, R. Songmuang, J. Renard, E. Bellet-Amalric, H. Renevier, and B. Daudin, Plasma-Assisted Molecular Beam Epitaxy Growth of GaN Nanowires Using Indium-Enhanced Diffusion, *Appl. Phys. Lett.*, 2008, **93**, p 183109
3. K.H. Lee, P.L. Lo, and I.G. Chen, Synthesis of GaN Nanowires Using Gold Nanoparticles on Plasma-Activated Silicon Substrate, *Nanophoton. Mater.*, 2009, **25**(10), p 79–82
4. W. Han, S. Fan, Q. Li, and Y. Hu, Synthesis of Gallium Nitride Nanorods Through a Carbon Nanotube-Confined Reaction, *Science*, 1997, **277**, p 1287–1289
5. W. Han, P. Redlich, F. Ernst, and M. Ruehle, Synthesis of GaN–Carbon Composite Nanotubes and GaN Nanorods by Arc Discharge in Nitrogen Atmosphere, *Appl. Phys. Lett.*, 2000, **76**, p 652–654
6. X. Duan and C.M. Lieber, Laser-Assisted Catalytic Growth of Single Crystal GaN Nanowires, *J. Am. Chem. Soc.*, 2000, **122**, p 188–189
7. S.D. Hersee, X. Sun, and X. Wang, The Controlled Growth of GaN Nanowires, *Nano Lett.*, 2006, **6**(8), p 1808–1811
8. S.Y. Bae, H.W. Seo, and J. Park, Triangular Gallium Nitride Nanorods, *Appl. Phys. Lett.*, 2003, **82**, p 4564–4566
9. Y. Ohno, T. Shirahama, and S. Takeda, Fe-Catalytic Growth of ZnSe Nanowires on a ZnSe(001) Surface at Low Temperatures by Molecular-Beam Epitaxy, *Appl. Phys. Lett.*, 2005, **87**, p 043105–043107
10. J. Zhang, L.D. Zhang, X.F. Wang, C.H. Liang, X.S. Peng, and Y.W. Wang, Fabrication and Photoluminescence of Ordered GaN Nanowire Arrays, *J. Chem. Phys.*, 2001, **115**, p 5714–5717
11. P. Perlin, C. Jauberthie-Carllon, J.P. Itie, A.S. Miguel, I. Grzegory, and A. Polian, Raman Scattering and X-Ray-Absorption Spectroscopy in Gallium Nitride Under High Pressure, *Phys. Rev. B*, 1992, **45**, p 83–89
12. J.H. Boo, C. Rohr, and W. Ho, MOCVD of BN and GaN Thin Films on Silicon: New Attempt of GaN Growth with BN Buffer Layer, *J. Cryst. Growth*, 1998, **189–190**, p 439–444
13. Y. Sun, T. Miyasato, and J.K. Wigmore, Characterization of Excess Carbon in Cubic SiC Films by Infrared Absorption, *J. Appl. Phys.*, 1999, **85**, p 3377–3379

14. M. Melendez-Lira, J. Menendez, K.M. Kramer, M.O. Thompson, N. Cave, R. Liu, J.W. Christiansen, N.D. Theodore, and J.J. Candelaria, Substitutional Carbon in $Si_{1-y}C_y$ Alloys as Measured with Infrared Absorption and Raman Spectroscopy, *J. Appl. Phys.*, 1997, **82**, p 4246–4252
15. G.W. Meng, L.D. Zhang, Y. Qin, C.M. Mo, and F. Phillipp, Synthesis of β-SiC Nanowires with SiO_2 Wrappers, *Nanostruct. Mater.*, 1999, **12**, p 1003–1006
16. J.K. Jian, X.L. Chen, M. He, W.J. Wang, X.N. Zhang, and F. Shen, Large-Scale GaN Nanobelts and Nanowires Grown from Milled Ga_2O_3 Powders, *Chem. Phys. Lett.*, 2003, **368**, p 416–420
17. B.S. Xu, D. Yang, F. Wang, J. Liang, S.F. Ma, and X.G. Liu, Synthesis of Large-Scale GaN Nanobelts by Chemical Vapor Deposition, *Appl. Phys. Lett.*, 2006, **89**, p 074106–074108
18. B.S. Xu, L.Y. Zhai, J. Liang, S.F. Ma, H.S. Jia, and X.G. Liu, Synthesis and Characterization of High Purity GaN Nanowires, *J. Cryst. Growth*, 2006, **291**, p 34–39
19. S.B. Xue, H.Z. Zhuang, C.S. Xue, and L.J. Hu, Synthesis of GaN Nanorods by Ammoniating Ga_2O_3/ZnO Films, *Chin. Phys. Lett.*, 2006, **23**, p 3055–3057
20. J.B. Schlager, N.A. Sanford, K.A. Bertness, J.M. Barker, A. Roshko, and P.T. Blanchard, Polarization-Resolved Photoluminescence Study of Individual GaN Nanowires Grown by Catalyst-Free Molecular Beam Epitaxy, *Appl. Phys. Lett.*, 2006, **88**, p 213106–213108
21. T.Y. Kim, S.H. Lee, Y.H. Mo, H.W. Shim, K.S. Nahm, E.K. Suh, and G.S. Park, Growth of GaN Nanowires on Si Substrate Using Ni Catalyst in Vertical Chemical Vapor Deposition Reactor, *J. Cryst. Growth*, 2003, **257**, p 97–103