



Synthesis of GaN nanowires and nanorods via self-growth mode control

S.M. Kang^a, T.I. Shin^a, Duc V. Dinh^b, J.H. Yang^b, S.-W. Kim^c, D.H. Yoon^{a,b,*}

^a School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea

^b Sungkyunkwan Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon 440-746, Republic of Korea

^c School of Advanced Materials and System Engineering, Kumoh National Institute of Technology, Yangho-dong, Gumi, Gyeongbuk 730-701, Republic of Korea

ARTICLE INFO

Available online 9 September 2008

Keywords:

Gallium nitride nanostructures
Vapor–liquid–solid
Vapor–solid

ABSTRACT

The synthesis of hexagonal wurzite one-dimensional (1D) GaN nanostructures on *c*-Al₂O₃ substrates was investigated using a thermal chemical vapor deposition (CVD) process. The diameter of the GaN nanostructures was controlled by varying the growth time using a mixture of GaN powder and Ga metal with the ammonia gas reaction. The morphologies of the GaN nanowires and nanorods were confirmed by field emission scanning electron microscopy. The micro-Raman spectroscopy and X-ray scattering measurements indicated that the GaN nanostructures had a hexagonal wurzite structure without any oxide phases. We investigated the difference in the structural properties between the GaN nanowires and nanorods. Deep-level emission bands were not observed in cathodoluminescence measurements from either the GaN nanowires or nanorods, indicating the incorporation of low-level impurities into our 1D GaN nanostructures.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

In recent years, one-dimensional (1D) semiconductor nanostructures, such as nanowires, nanorods, nanobelts, and nanotubes, have received a great deal of attention for future nanoscale devices. The 1D semiconductor nanostructures have the potential to be used as both interconnect and functional units for the fabrication of electronic, optoelectronic, electrochemical, and electromechanical devices, because of their outstanding electrical, optical, thermal and mechanical properties caused by their size effects [1–4]. Among the various semiconductor nanostructures, gallium nitride (GaN), which has a direct and wide band-gap of 3.4 eV at room temperature, is a promising candidate material for short wavelength optoelectronic devices, such as light emitting diodes (LEDs) and laser diodes (LDs), high power and high temperature operation devices, because of its high melting temperature, high breakdown field, and high saturation drift velocity [5].

Recent reports have intensively investigated low-dimensional GaN-based nanostructures, due to their unique electronic and optical properties, which allow for the fabrication of novel nano-electronic devices and quantum devices with high quantum efficiency [6]. For this reason, a considerable amount of research has been done to synthesize 1D nanostructured GaN. In addition,

the control of the growth direction and size of GaN nanostructures is one of the most important issues in GaN-based nanotechnologies. Metal catalysts such as Au, Ni, Fe are commonly used to initiate 1D nanostructured GaN growth. Various methods have reported that the size of 1D nanostructure growth has been achieved in the catalyst assist growth mode such as the vapor–liquid–solid (VLS) mode [7,8] in which the size of the catalyst nanoparticles determines their final diameter.

Contrary to previous reports, we were able to synthesize GaN nanowires and nanorods on *c*-Al₂O₃ substrates by the direct reaction of molten Ga, GaN powder and ammonia gas using an Au catalyst in a CVD reactor. The diameter of the GaN nanostructures was successfully controlled by varying the growth time. In this study, we compare the structural and optical properties of GaN nanowires and nanorods using various techniques.

2. Experimental procedure

The GaN nanowires and nanorods were synthesized by the thermal CVD method. A mixture of GaN powder (99.999%, High Purity Chem.) and molten Ga (99.9999%, 9Digit Co. Ltd.) at a weight ratio of 1:1 was used as the starting material. The *c*-Al₂O₃ substrate was cleaned by sonication in acetone and then 1 nm-thick Au thin films were coated on it using the thermal evaporation system as a catalyst for the growth of the GaN nanostructure. High purity Ar (99.999%) and NH₃ (99.99%) were introduced into the reactor as a carrier gas and reaction gas, respectively. The Au-coated *c*-Al₂O₃ substrates were placed on

* Corresponding author at: School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea.
Tel.: +82 31 290 7388; fax: +82 31 290 7371.

E-mail address: dhyoon@skku.edu (D.H. Yoon).

GaN powder and molten Ga sources in an alumina boat, placed in the center of the quartz tube. The synthesis experiments were performed at 950 °C. During the main growth of the GaN nanostructure, Ar gas with a flow rate of 1000 sccm and NH₃ gas with flow rate of 20 sccm as a reaction gas were introduced into the quartz tube. The reaction chamber was maintained with a vacuum of 200 Torr. After the main growth, the samples were cooled naturally to RT. The diameter was controlled by varying the growth time.

The shape and morphology of the GaN nanostructures were observed using field emission scanning electron microscopy (FESEM). Micro-Raman spectroscopy was used to observe the microscopic structure using a 514 nm Ar-ion laser. The crystallinity and structure of the GaN nanostructures were investigated by X-ray diffraction (XRD) using a Bruker D8 Discover system with Cu K α radiation. The spatial localization of the emission was determined by monochromatic cathodoluminescence (CL) measurements. CL was performed in a FESEM using a GATAN MONO CL3+ system at RT.

3. Results and discussion

The 1D GaN nanostructures were successfully synthesized using the thermal CVD method. We synthesized GaN nanowires and nanorods with growth times (the time of the NH₃ gas reaction) of 15 and 90 min, respectively. Figs. 1(a) and (c) show the images of the GaN nanowires and Figs. 1(b) and (d) show the images of GaN nanorods grown on the *c*-Al₂O₃ substrates. As shown in Fig. 1, a large number of randomly oriented GaN nanostructures were observed. The morphology of the GaN nanostructures was nearly uniform and straight with a smooth surface being formed all over the Al₂O₃ substrates. The grown GaN nanowires and nanorods had diameters ranging from 40 to 70 nm and from 130 to 160 nm, respectively, and similar length of around

2 μ m. The growth on the lateral facets of the GaN nanowires occurred gradually when the growth time was increased from 15 to 90 min without any length change. The diameter of the GaN nanorods was not affected by the size of the Au catalyst because of the same size with that of the catalyst. The nano-sized Au catalyst was obtained without change of the ramping time to reach the growth temperature of the GaN nanostructure. As shown in the inset image of Fig. 1(c), we could randomly find the metal catalyst or metal alloy at the end of the GaN nanowires. However, we could not find any metal catalyst or metal alloy in the case of the GaN nanorods. The first growth stage of GaN nanowires was attributed to the formation of a liquid phase of the Au–Ga alloy via the VLS process. The Au is used as a metal catalyst to initiate the seed of the GaN nanowires. However, the VLS mechanism alone cannot explain the growth mechanism of the GaN nanorods in this work. Nanorods' growth mechanisms are thought to be a different kind of growth mechanism via the vapor–solid (VS) mechanism accompanied by unknown reaction kinetics and thermodynamics [9,10]. It was concluded that the GaN nanowires were grown via the VLS mechanism by employing an Au catalyst that influenced the initial growth state of the GaN nanowires, after which the GaN nanorods were grown via the VS mechanism. The synthesized GaN nanostructures had a triangular-shaped cross-section, which was attributed to the fact that the triangular GaN nanostructures do not have a six-fold crystallographic symmetry axis as the growth direction, but rather a two-fold crystallographic one.

Fig. 2 shows the XRD patterns used for the structural characterization of the synthesized GaN structures. All of the diffraction patterns were indexed and identified by XRD as the hexagonal wurtzite structure (JCPDS card no. 50-0792), while no cubic phase was found. The GaN diffraction patterns were more easily observed for the GaN nanorods than for the nanowires. The peak intensity of the GaN nanorods was higher than that of the nanowires because of the higher volume ratio of the former. As shown in Fig. 2(a), we observed various diffraction peaks of GaN

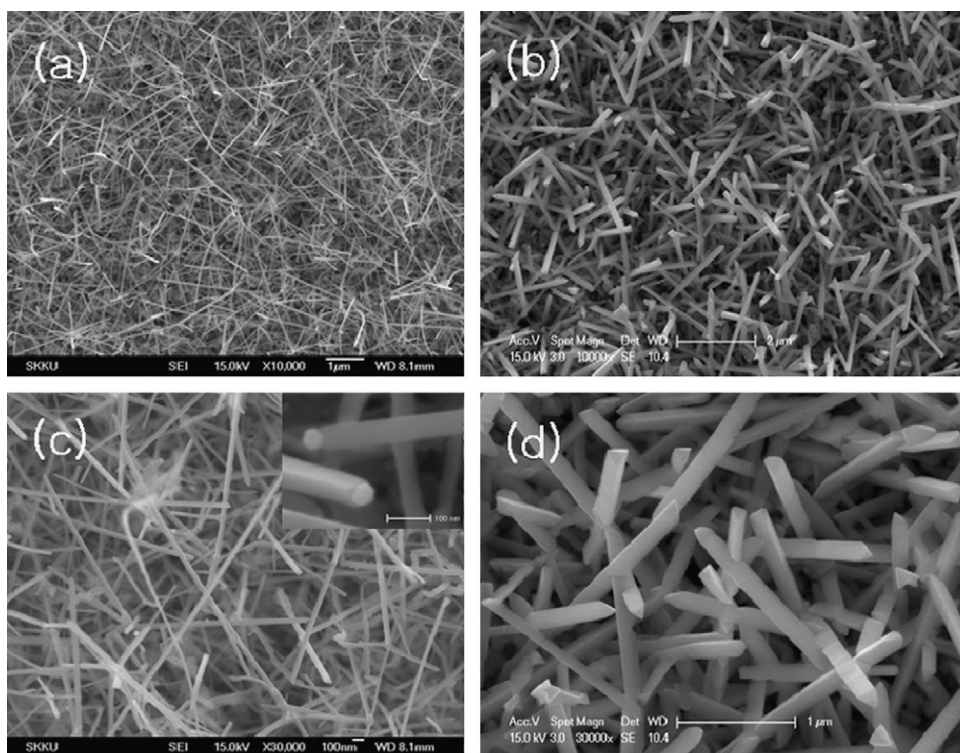


Fig. 1. FESEM images of GaN nanowires and nanorods: (a) low magnification FESEM image of GaN nanowires; (b) low magnification FESEM image of GaN nanorods; (c) high magnification FESEM image of GaN nanowires and inset is the image of catalyst at the end of the nanowires; (d) high magnification FESEM image of GaN nanorods.

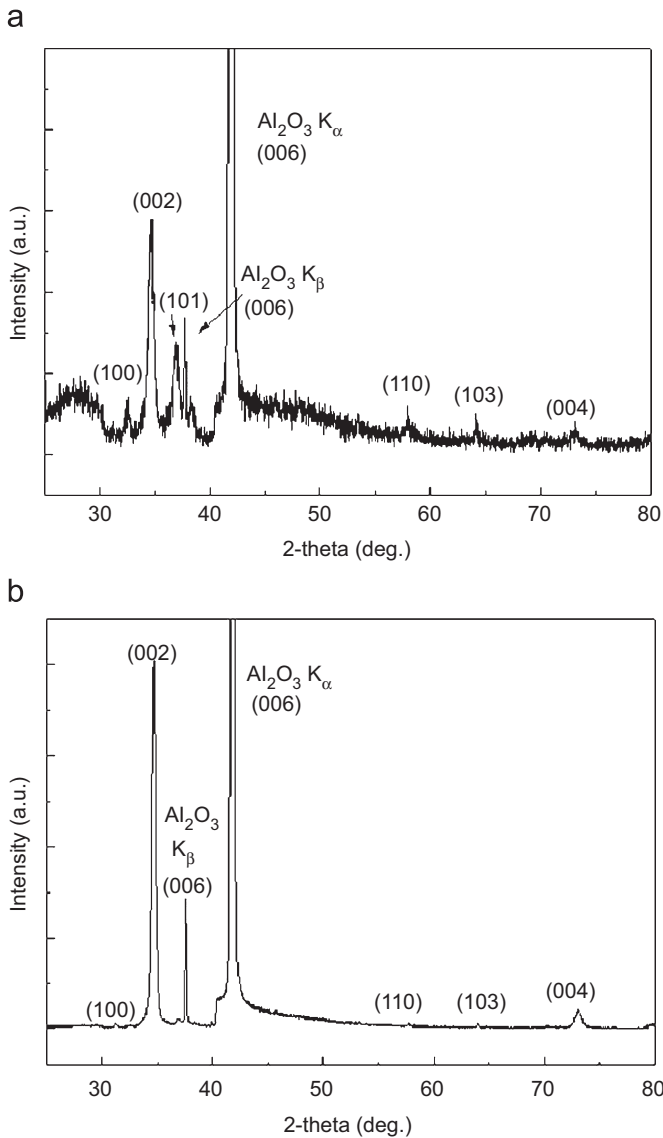


Fig. 2. X-ray diffraction patterns of the synthesized GaN nanostructures: (a) GaN nanowires; (b) GaN nanorods.

such as those for the (100), (002), (101), (110), (103), and (004) reflection peaks. However, we observed intense two peaks at $2\theta = 34.5^\circ$ and $2\theta = 72.9^\circ$ which were attributed to the GaN (002) and (004) plane reflections, respectively, with very small peaks in the case of the GaN nanorods as shown in Fig. 2(b). The intensity of the GaN reflection (002) and (004) peaks increased relative to those of the other peaks with increasing growth time.

Fig. 3 shows the Raman backscattering spectrum of the GaN nanostructures at RT. Only two strong peaks around 565 and 729 cm^{-1} were observed for the GaN nanowires, corresponding to the phonon vibration frequencies of the E_2 (high) and A_1 (LO) modes, respectively, as shown in Fig. 3(a). Their spectrum was obviously different from that of the GaN epitaxial films and GaN nanorods as shown in Fig. 3(b). The peaks were broad and asymmetrical for the GaN nanowires and the intensity of the A_1 (LO) mode was higher than that of the E_2 (high) mode. The unique properties of the GaN nanowires may have resulted from their different morphologies, the effect of the surface states generated by the nanostructures [11], and the plasmon–phonon coupling [12]. In the case of the GaN nanorods, the peaks observed at 531 , 560 , 567 , and 731 cm^{-1} agree with the phonon vibration

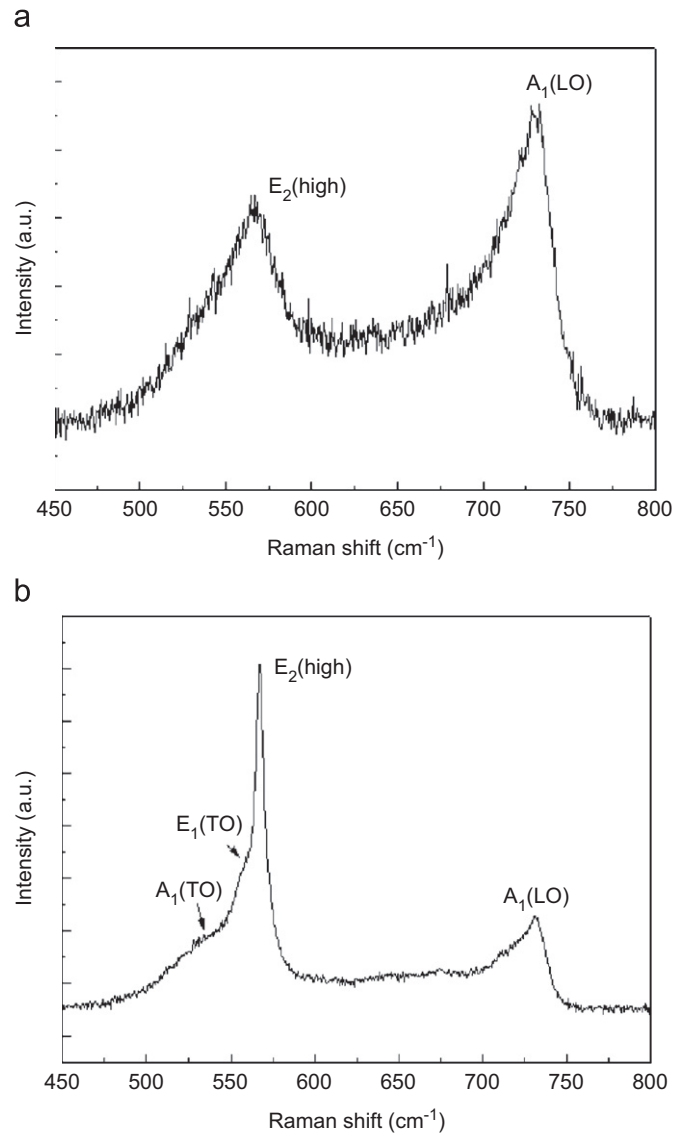


Fig. 3. Raman backscattering spectrum of the GaN nanostructures at RT: (a) GaN nanowires; (b) GaN nanorods.

frequencies corresponding to the A_1 (TO), E_1 (TO), E_2 (high), and A_1 (LO) modes of crystalline wurtzite GaN, respectively. Among these modes, the presence of A_1 (TO) and E_1 (TO) was considered to indicate multi-directional growth.

Fig. 4 shows the CL spectrum of the GaN nanostructures taken at RT. The insets are the FESEM (upper) and CL (bottom) images. A band-edge luminescence was observed at about 365 nm in the ultraviolet range of the spectrum due to the increased excitation rates associated with CL. We could not observe any deep-level (yellow) CL for the GaN nanostructures arising either directly from the atomic structure of the dislocations or associated with the clustering of native point defects (vacancies, interstitials) or impurities (such as carbon) due to the strain and electrochemical lattice distortions induced by the dislocations [13]. This indicated that the GaN nanostructures had fewer defects than bulk GaN. The CL intensity of the GaN nanorods was more than 10 times higher than that of the nanowires under the same CL experiment conditions. The full width at half maximum for the GaN nanorods was smaller than that for the nanowires. In the inset images of Fig. 4, the bright and dark regions in the image represent high and low CL emission intensity, respectively. The lower inset shows

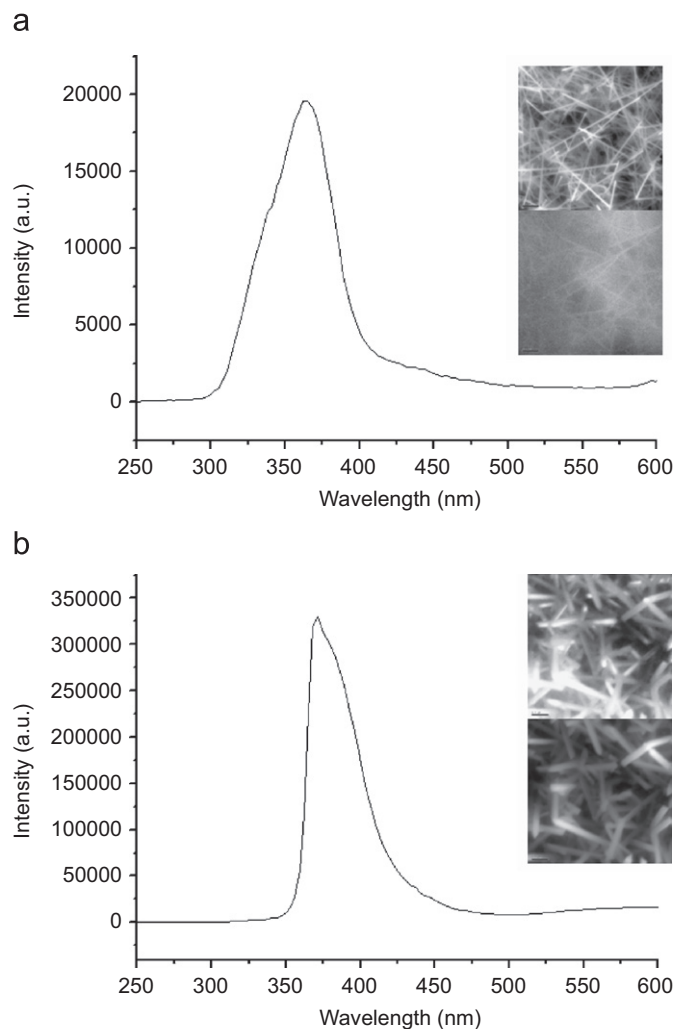


Fig. 4. Cathodoluminescence spectrum of the GaN nanostructures synthesized at RT with inset images showing the FESEM (upper) and CL images (lower): (a) GaN nanowires; (b) GaN nanorods.

a CL image related to the band-edge emission in the same region as that shown in the upper inset FESEM images. The CL image indicated that the luminescence originated all over the nanostructures.

4. Conclusion

In conclusion, we synthesized GaN nanostructures by the direct reaction of molten Ga, GaN powder and NH_3 gas with an Au catalyst using the thermal CVD method. We synthesized GaN nanowires and nanorods with a growth time of 15 and 90 min, respectively. The FESEM images indicated that the GaN nanowires were grown via the VLS mechanism that was affected by the metal catalyst at the initial growth state of the GaN nanostructures. The GaN nanorods were then grown via the VS mechanism. The XRD data indicated that the GaN nanostructures had a hexagonal wurtzite structure. The Raman backscattering spectrum indicated that the peaks were broad and asymmetrical for the GaN nanowires and that the intensity of the A_1 (LO) mode was higher than that of the E_2 (high) mode. The CL spectrum confirmed the high optical properties of the 1D GaN nanostructures.

References

- [1] Y. Xia, P. Yang, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H. Yan, One-dimensional nanostructures: synthesis, characterization, and applications, *Adv. Mater.* 15 (2003) 353–389.
- [2] J. Goldberger, R. He, Y. Zhang, S.-K. Lee, H. Yan, H.-J. Choi, P. Yang, Single-crystal gallium nitride nanotubes, *Nature* 422 (2003) 599–602.
- [3] S.K. Lee, H.J. Choi, P. Pauzauskie, P. Yang, N.K. Cho, H.D. Park, E.K. Suh, K.Y. Lim, H.J. Lee, Gallium nitride nanowires with a metal initiated metal-organic chemical vapor deposition (MOCVD) approach, *Phys. Status Solidi (B)* 241 (2004) 2775–2778.
- [4] H. Dai, A. Javey, E. POP, D. Mann, W. Kim, Y. Lu, Electrical transport properties and field effect transistors of carbon nanotubes, *NANO: Brief Rep. Rev.* 1 (2006) 1–13.
- [5] S. Nakamura, T. Mukai, M. Senoh, Candela-class high-brightness InGaN/AlGaN double-heterostructure blue-light-emitting diodes, *Appl. Phys. Lett.* 64 (1994) 1687–1689.
- [6] A.M. Morales, C.M. Lieber, A laser ablation method for the synthesis of crystalline semiconductor nanowires, *Science* 279 (1998) 208–211.
- [7] G.S. Chen, L.D. Zhang, Y. Zhu, T. Fei, L. Li, C.M. Mo, Y.Q. Mao, Large-scale synthesis of single crystalline gallium nitride nanowires, *Appl. Phys. Lett.* 75 (1999) 2455–2457.
- [8] S. Biswas, S. Kar, T. Ghoshal, V.D. Ashok, S. Chakrabarti, S. Chaudhuri, Fabrication of GaN nanowires and nanoribbons by a catalyst assisted vapor–liquid–solid process, *Mater. Res. Bull.* 42 (2007) 428–436.
- [9] Z.W. Pan, Z.R. Dai, Z.L. Wang, Nanobelts of semiconducting oxides, *Science* 291 (2001) 1947–1949.
- [10] X. Duan, C.M. Lieber, Laser-assisted catalytic growth of single crystal GaN nanowires, *J. Am. Chem. Soc.* 122 (2000) 188–189.
- [11] Z.J. Li, X.L. Chen, H.J. Li, Q.Y. Tu, Z. Yang, Y.P. Xu, B.Q. Hu, Synthesis and Raman scattering of GaN nanorings, nanoribbons and nanowires, *Appl. Phys. A* 72 (2001) 629–632.
- [12] M. Pophristic, F.H. Long, M. Schurman, J. Ramer, I.T. Ferguson, Raman microscopy of lateral epitaxial overgrowth of GaN on sapphire, *Appl. Phys. Lett.* 74 (1999) 3519–3521.
- [13] F.A. Ponce, D.P. Bour, W. Gotz, P.J. Wright, Spatial distribution of the luminescence in GaN thin films, *Appl. Phys. Lett.* 68 (1996) 57–59.