Vol 16 No 5, May 2007
1009-1963/2007/16(05)/1405-05

Chinese Physics

© 2007 Chin. Phys. Soc.
and IOP Publishing Ltd

Synthesis of flower-shape clustering GaN nanorods by ammoniating Ga_2O_3 films*

Xue Shou-Bin(薛守斌), Zhuang Hui-Zhao(庄惠照)†,
Xue Cheng-Shan(薛成山), Hu Li-Jun(胡丽君),
Li Bao-Li(李保理), and Zhang Shi-Ying(张士英)

Institute of Semiconductors, Shandong Normal University, Jinan 250014, *China*

(Received 3 August 2006; revised manuscript received 15 January 2007)

Flower-shape clustering GaN nanorods are successfully synthesized on Si(111) substrates through ammoniating Ga_2O_3/ZnO films at 950°C. The as-grown products are characterized by x-ray diffraction (XRD), scanning electron microscope (SEM), field-emission transmission electron microscope (FETEM), Fourier transform infrared spectrum (FTIR) and fluorescence spectrophotometer. The SEM images demonstrate that the products consist of flower-shape clustering GaN nanorods. The XRD indicates that the reflections of the samples can be indexed to the hexagonal GaN phase and HRTEM shows that the nanorods are of pure hexagonal GaN single crystal. The photoluminescence (PL) spectrum indicates that the GaN nanorods have a good emission property. The growth mechanism is also briefly discussed.

Keywords: GaN, magnetron sputtering, ammoniate
PACC: 6146

1. Introduction

In the fields of electronics and optoelectronics, the intensive research on GaN semiconductors has grown rapidly in the last decade due to their unique properties, showing that they have strong points in various aspects.[1−6] On the other hand, with the ever-increasing demand of size shrinkage of modern devices, nanotechnologies are developing at an unprecedented pace. Previous reports on GaN nano-scale structures included columnar structures[7−9] or pyramidal hillocks.[10] Many studies have utilized catalytic or nanostructure-assisted growth through vapour–liquid–solid (VLS) growth mechanism,[11−13]carbon nanotube,[14] or anodic alumina membrane,[15] for example.

In this paper, we report on an effective method of synthesizing the flower-shape clustering GaN nanorods on Si(111) substrates. This growth method is applicable to continuous synthesis and able to produce a large number of single-crystalline GaN nanorods with a relatively high purity and at a low cost. Therefore, it may be significant for commercial-scale production.

2. Experiments

In our experiment, the flower-shape clustering GaN nanorods were prepared by self-assembly of Ga_2O_3films in their reaction with NH_3. The process could be fallen into two steps. The first step was to sputter ZnO target by a JCK-500A radio frequency magnetron sputtering system to form the ZnO layer on the Si substrates. The sputtering condition was as follows: a background pressure was 6.6×10^{-4} Pa; the output voltage of steady current device was 200 V and the output current was 220 mA; the working pressure of Ar gas (99.999%) was 2 Pa and the sputtering time was 90 min for a film with a thickness of about 400 nm.

The second step was to deposit Ga_2O_3 films and synthesize GaN nanorods. The Ga_2O_3 thin films were deposited on the ZnO/Si substrates by sputtering the Ga_2O_3 target in the same system. The sputtering chamber was evacuated by a turbomolecular pump to a base pressure of 3.0×10^{-4}Pa, and then Ar gas was introduced into the chamber at a pressure of 3 Pa. When the pressure of the chamber was stabilized, the radio frequency generator was set to 150 W. The tar-

*Project supported by the State Key Program of the National Natural Science Foundation of China (Grant No 90201025) and the National Natural Science Foundation of China (Grant No 90301002).
†E-mail: zhuanghuizhao@sdnu.edu.cn

get was used as a cathode and the substrates as an anode. Then Ga_2O_3 films were deposited at room temperature after cleaning the target with Ar plasma for 5 min, and the sputtering time was 90 min. The thickness of Ga_2O_3 film was about 500 nm.

Subsequently, the quartz boat loaded with the samples was placed into a constant temperature region for ammoniating. Above all, the flowing N_2 was introduced into the tube to flush out the residual air for 5 min, and then ammonia was introduced into the tube with a flow rate of 500 mL/min for 15 min at 950°C while the N_2 flow was switched off. After being ammoniated, the samples were taken out for characterization.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of the samples are measured by a Rigaku D/max-rB X-ray diffractometer with Cu Kα-line. Figure 1 shows the XRD pattern of the GaN nanorods ammoniated at 950°C. Four peaks of (100), (002), (101) and (102) of GaN are located at 32.36°, 34.54°, 36.78°, and 48.02°, demonstrating that the reflections can be indexed to the hexagonal GaN phase with the lattice constants of $a = 0.318$ nm and $c = 0.518$ nm, which are consistent with the reported values for bulk GaN.[16] The only other peak at $2\theta = 28.5°$ corresponds to the refection of the Si substrate. There appear no peaks of ZnO,[17] Zn_3N_2[18] and Ga_2O_3,[19] indicating that the ZnO buffer layer has decomposed completely at the temperature of NH_3 ambient, there is no indication of the formation of Zn_3N_2 and the Ga_2O_3films have completely reacted with NH_3.

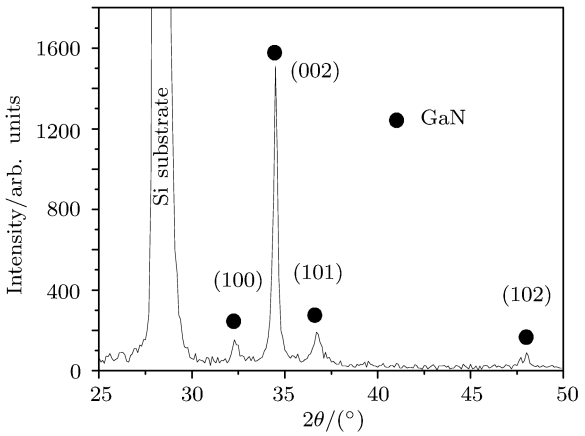


Fig.1. XRD pattern of the GaN nanorods ammoniated at 950°C.

3.2. FTIR analysis

Tensor 27 Fourier transform infrared (FTIR) system is used to measure the chemical states of products. Figure 2 shows the FTIR spectrum of the GaN nanorods. Four prominent absorption bands are observed at 561.1 cm^{-1}, 608.8 cm^{-1}, 1105.9 $cm^{-1}$and 1238.9 cm^{-1}. The absorption band at 561.1 cm^{-1} corresponds to Ga–N stretching vibration in hexagonal-type GaN crystal.[20] The absorption band at 608.8 cm^{-1} is associated with the local vibration of substitutional carbon in the Si crystal lattice.[21] According to Ref.[22] the bands at 1105.9 cm^{-1} and 1238.9 cm^{-1} are related to the Si–O–Si asymmetric stretching vibration mode, which is ascribed to extremely thin oxide layer on the Si surface. There appears no Zn–O absorption band in Fig.2,[23] which reveals that hexagonal ZnO does not exist and volatilizes totally, and Ga_2O_3 absorption band does not exist either,[24] proving that the Ga_2O_3 film has reacted with NH_3 entirely. The FTIR spectrum further confirms that the GaN is definitely obtained under this condition.

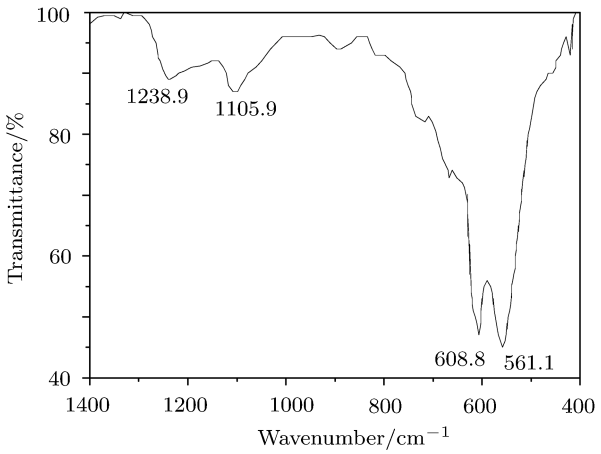


Fig.2. FTIR spectrum of the GaN nanorods ammoniated at 950°C.

3.3. SEM and HRTEM analysis

The morphologies of the products are characterized by a Hitachi S-570 scanning electron microscopy (SEM) at room temperature. The SEM images (Fig.3) show that the flower clusters are composed of nanorods, which display an actinomorphic structure. These nanorods are not parallel to the substrates and all come out of the same site. Figure 3(a) is the SEM image of a cluster of flower-like GaN nanorods. Although several rods are straight, most of them are

curved. Their diameters and the lengths are not uniform, varying from 300 to 900 nm, and from 1 to 8 μm, respectively. Figure 3(b) clearly shows the magnified SEM image of another area of the sample, which indicates that each nanorod is not very smooth and has a slightly rough surface. Besides the cluster, there are a large number of crystal grains on the surface, which have not formed into the rods but agglomerated into micrograins.

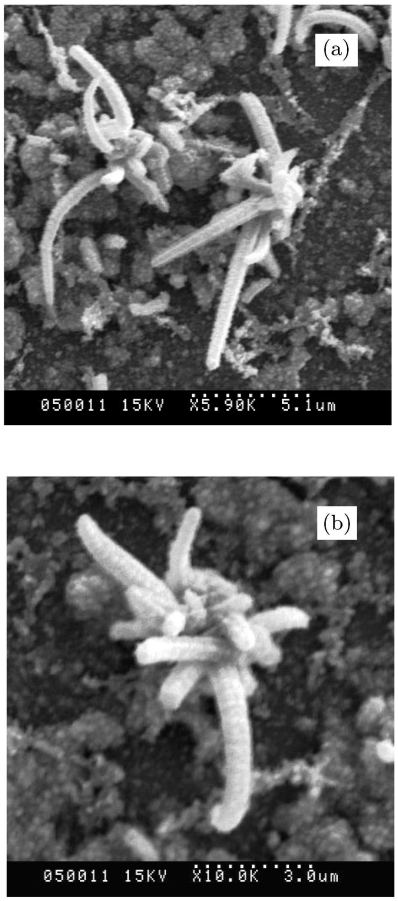


Fig.3. (a) SEM image of the flower-like GaN nanorods obtained at 950°C; (b) Magnified SEM image of another area of the sample.

Philips TECNAI F30 field-emission transmission electron microscope (FETEM) is used at room temperature to measure the microstructures of samples. Figure 4(a) shows the HRTEM morphology of the GaN nanorod, which is as long as several micrometres with an average diameter of about 500 nm. Slightly rough sidewalls are also found in the HRTEM observation, indicating that the nanorod probably has defects. Figure 4(b) shows the HRTEM lattice image and the corresponding selected area electron diffraction (SAED) pattern of the single nanorod. The clear lattice fringes confirm that the synthesized nanorods are of single-crystal GaN. The interplanar spacing is about 0.242 nm, which is close to the value of the {101} plane spacing of hexagonal GaN, indicating that the growth direction of the nanorod tilts with respect to the fringes of the (101) plane by about 27°. However, there are also many defects in the rods as illustrated by the HRTEM lattice image (indicated by an arrow). The single-crystal GaN nanorod can also be identified from the SAED pattern shown in the inset of Fig.4(b), which can be ascribed to the reflection of hexagonal wurtzite GaN single crystal.

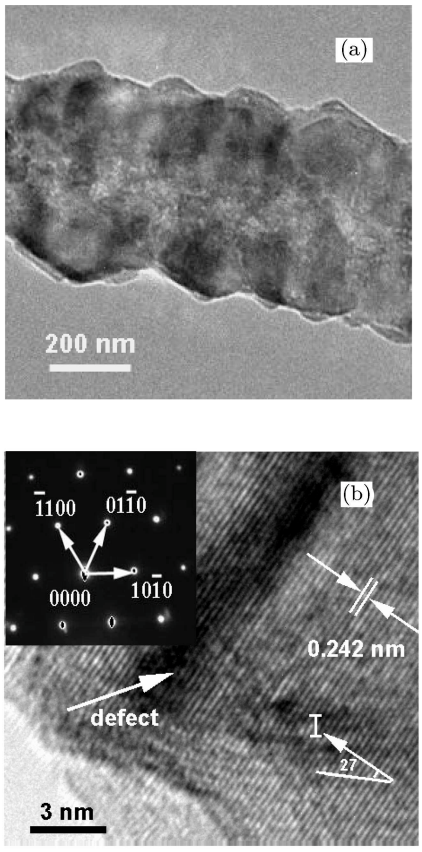


Fig.4. (a) HRTEM image of a single GaN nanorod; (b) HRTEM lattice image of the GaN nanorod. Inset: the corresponding selected area electron diffraction pattern.

3.4. PL analysis

For the optical property, the measurement of PL spectrum is performed by using the LS50-B fluorescence spectrophotometer with a Xe lamp used as the excitation source (with a wavelength of 298 nm) at room temperature. Figure 5 shows the PL spectrum of the as-grown GaN nanorods. Band-edge emission is observed in these nanorod samples to be located at

372.5 nm. Because the as-grown GaN nanorods are too large for quantum confinement effects, and the diameter of the thinnest nanorod is even much larger than the Bohr exciton radius (11 nm) of GaN,[25] the UV light emission has no blue shift from the band-gap emission compared with that of bulk GaN.[26] Other peaks at 436.4 nm and 474.9 nm may be ascribed to the existence of defects or surface states.[27−29] The GaN nanorods show a very good emission property, which will be a great advantage in their applying to laser device. However, further work is needed to investigate the PL mechanism of the GaN nanorods.

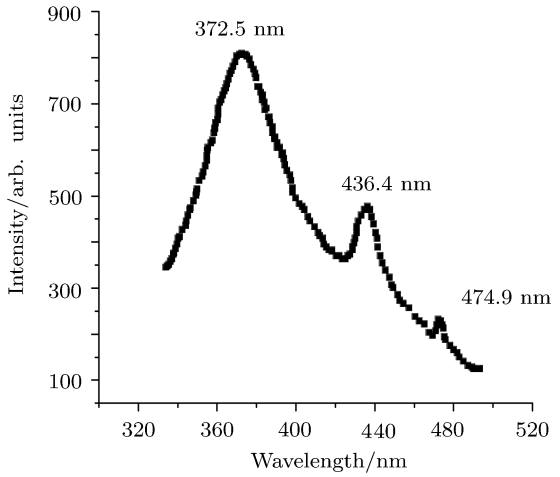


Fig.5. PL spectrum of the as-grown GaN nanorods ammoniated at 950°C.

3.5. Discussion about growth process

According to the above analyses, to the growth mechanism of GaN nanorods, we can give a brief explanation as follows: when the temperature is above 650°C, the ZnO films can volatilize in the ammoniating process. ZnO films react with NH_3 to produce Zn, NO_2 (or NO), and water vapour in the interface between ZnO layer and Ga_2O_3 layer. Zn sublimes at the high temperature and is brought downstream by NH_3 gas to the inner wall in the tube.[30] The volatilization process may experience the following reaction:

$$ZnO + NH_3 \rightarrow Zn + NO_2(\text{or NO}) + H_2O.$$

The Ga_2O_3 layer falls on the next ZnO layer so as to decrease the interfacial energy (The result is similar to that in the interface between Si and ZnO layers). At the end, the GaN nanostructured film will fall on the Si substrates directly. Despite the volatilization of ZnO, self-organized nanometre-sized holes are formed, which can subsequently be used as a mask to fabricate the flower-like GaN nanorods or act as potential nucleation sites for the GaN nanostructures. It is well known that when the ammoniating temperature is above 850°C, NH_3 decomposes stepwise to NH_2, NH, H_2 and N.[31] The Ga_2O_3 particles come out and subsequently react with H_2 to form Ga_2O vapour. The GaN molecules are finally generated through the reaction of Ga_2O with ammonia. All the reactions can be expressed as

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

These GaN molecules continuously come out and agglomerate into micrograins. When the growth directions of the micrograins are all orientated to the same direction, the single-crystal GaN nanorods are formed. It can be seen that the high temperature, ammonia, ZnO layer and Ga_2O_3 are crucial to the growth of GaN nanorods. However, the specific function of the ZnO buffer layer in growing the GaN nanorods should be further studied.

4. Conclusion

In summary, flower-like GaN nanorods have been successfully synthesized on Si (111) substrates through the reaction between the Ga_2O_3 films and ammonia at 950°C in a quartz tube. The structure, morphology and optical properties of the as-prepared GaN nanorods are studied by XRD, SEM, HRTEM, FTIR and PL. The results show that the nanorods have pure hexagonal GaN single-crystal structures with lengths of about several micrometres and diameters ranging from 300 nm to 900 nm. The growth mechanism is briefly discussed.

References

[1] Morkoc H and Mohammad S N 1995 *Science* **267** 51
[2] Zhang H, Lu H, Ye Z, Zhao B, Wang L and Que D 1999 *Acta Phys. Sin.* **48** 1315 (in Chinese)
[3] Li Z, Yu T, Yang Z, Feng Y, Zhang G, Guo B and Niu H 2005 *Chin. Phys.* **14** 830
[4] Chang Y, Zhang Y and Zhang Y 2006 *Chin. Phys.* **15** 636

[5] Nakamura S 1998 *Science* **281** 956
[6] Tu L W, Tsao P H, Lee K H, Lo I, Bai S J, Wu C C, Hsieh K Y and Sheu J K 2001 *Appl. Phys. Lett.* **79** 4589
[7] Yoshizawa M, Kikuchi A, Fujita N, Kushi K, Sasamoto H and Kishino K 1998 *J. Cryst. Growth* 1**89/190** 138
[8] Calleja E, Sánchez-García M A, Sánchez F J, Calle F, Naranjo F B and Munõz E 2000 *Phys. Rev.* B **62** 16826
[9] Araki T, Chiba Y, Nobata M, Nishioka Y and Nanishi Y 2000 *J. Cryst. Growth* **209** 368
[10] Romano L T and Myers T H 1997 *Appl. Phys. Lett.* **71** 3486
[11] Morales A M and Lieber C M 1998 *Science* **279** 208
[12] Chen C C, Yeh C C , Chen C H, Yu M Y, Liu H L, Wu J J, Chen K H, Chen L C, Peng J Y and Chen Y F 2001 *J. Am. Chem. Soc.* **123** 2791
[13] Huang Y, Duan X, Cui Y and Lieber C M 2002 *Nano Lett.* **2** 101
[14] Han W, Fan S, Li Q and Hu Y 1997 *Science* **277** 1287
[15] Zhang J, Zhang L D, Wang X F, Liang C H, Peng X S and Wang Y W 2001 *J. Chem. Phys.* **115** 5714
[16] Perlin P, Jauberthiecarillon C, Itie J P, Miguel A S, Grzegory I and Polian A 1992 *Phys. Rev.* B **45** 83
[17] Goldberger J, He R, Zhang Y F, Lee S K, Yan H Q and Yang P D 2003 *Nature* **422** 599
[18] Masanobu F, Katsuaki Y and Osamu T 1998 *Thin Solid Films* **322** 274
[19] Yang Y, Ma H, Xue C, Zhuang H, Hao X, Ma J and Teng S 2002 *Appl. Sur. Sci.* **193** 254
[20] Yang L, Xue C, Zhuang H, Li H and Wei Q 2002 *Int. J. Mod. Phys.* B **46** 1639
[21] Sun Y, Miyasato J T and Wigmore K 1999 *J. Appl. Phys.* **85** 3377
[22] Meng G W, Zhang L D, Qin Y, Mo C M and Phillipp F 1999 *Nanostruct. Mater.* **12** 1003
[23] Bachari E M, Baud G, Ben Amor S and Jacquet M 1999 *Thin Solid Film* **348** (1-2) 165
[24] Xiao H, Ma H, Xue C, Hu W, Ma J, Zong F, Zhang X and Ji F 2005 *Diamond and Related Materials* **14** 1730
[25] Ridley B K 1982 *Quantum Process in Semiconductors* (Oxford: Clarendon) pp62–66
[26] Monemar B 1974 *Phys. Rev.* B **10** 676
[27] Chen X, Li J, Cao Y, Lan Y, Li H, He M, Wang C, Zhang Z and Qiao Z 2000 *Adv. Mater.* **12** (19) 1432
[28] Shi W S, Zheng Y F, Wang N, Lee C S and Lee S T 2001 *Chem. Phys. Lett.* **345** 377
[29] Peng H Y, Zhou X T, Wang N, Zheng Y F, Liao L S, Shi W S, Lee C S and Lee S T 2000 *Chem. Phys. Lett.* **327** 263
[30] Gao H, Zhuang H, Xue C, Wang S, Dong Z and He J 2005 *Rare Metals* **24** (3) 267
[31] Xue C, Wu Y, Zhuang H, Tian D, Liu Y, Zhang X, Ai Y, Sun L and Wang F 2005 *Physica* E **30** 179