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# Fabrication of High-Density GaN Nanowires through Ammoniating $Ga_2O_3$/Nb Films

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High-density GaN nanowires were successfully synthesized on Si(111) substrates through ammoniating $Ga_2O_3$/Nb films under flowing ammonia atmosphere at 950°C. The as-synthesized GaN nanowires are characterized by X-ray diffraction, selected-area-electron diffraction, Fourier transform infrared, scanning electron microscopy, and field-emission transmission electron microscopy. The results show that the synthesized nanowires are single-crystal hexagonal wurtzite GaN with diameters ranging from 30 to 100 nm and lengths up to several microns. The photoluminescence spectra measured at room temperature only exhibit a strong and broad emission peak at 367.8 nm. Finally, the growth mechanism of GaN nanowires is discussed.

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## 1. Introduction

Nanowires of gallium nitride and other related nitrides with direct band gaps, large breakdown fields, and high saturation velocities are the ideal candidates for efficient nanoscale ultraviolet/visible light emitters, detectors, and radiation hard, high temperature nanoelectronic devices. GaN nanowires were first synthesized using carbon nanotubes as the templates [1]. Direct band-gap group III-nitride (Al/Ga/In-N) semiconducting nanowires with their unique properties [2] are emerging as the most promising candidates for realizing these types of devices. chamber was pumped down to aboutSince then, several works on the growth of GaN nanowires by the vapor–liquid–solid (VLS) [3] or vapor–solid (VS) [4] methods have been reported. Progress has been made in the synthesis of

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ordered GaN nanowires with controlled cross-section, length, and diameter [5]. Applications of GaN nanowires for single nanowire laser [6] and individual device fabrication [7–11] have also been demonstrated. In recent years, our group develops a novel method for synthesizing one-dimensional GaN materials through ammoniating $Ga_2O_3$ films [12], $Ga_2O_3/Al_2O_3$ films [13] and $Ga_2O_3$/SiC films [14] and $Ga_2O_3$/ZnO films [15], $Ga_2O_3$/MgO films [16], which are deposited by rf magnetron sputtering. However, the yield and the quality of the synthesized GaN nanowires are still in need of optimization for the application of GaN nanowires to nanoelectronic devices. Niobium materials are presently of great interest in heterogeneous catalysis where they are used as catalyst components or are added in small amounts to catalysts [17]. However, the yield and the quality of the synthesized GaN nanowires are still in need of optimization for the application of GaN nanowires to nanoelectronic devices. Based on the above-mentioned demand, in this paper we report that GaN nanowires have been successfully produced on Si(111) substrates through ammoniating $Ga_2O_3$/Nb films under flowing ammonia atmosphere at 950°C in a quartz tube.

## 2. Experimental procedure

In our experiment, GaN nanowires were prepared by self-assembling of $Ga_2O_3$ films in their reaction with $NH_3$. The $Ga_2O_3$ films were deposited by magnetron sputtering on the Nb layer on Si(111) substrates. The first step was the process of forming Nb layer. Nb films were deposited to Si substrates by the progress of direct current (dc) sputtering with JCK-500A magnetron sputtering system. The conditions of sputtering were as follows: the sputtering time was 0.5 min; the sputtering chamber was pumped down to about $7.4 \times 10^{-4}$ Pa; the distance between targets and substrates was 8 cm; the pressure of Ar ($\geq 99.99\%$) was 2 Pa; the output voltage of WLY steady current device was 260 V and the output current was 160 mA.

The second step was to deposit $Ga_2O_3$ films and synthesize GaN nanowires. $Ga_2O_3$ was deposited on the Nb layer on Si(111) substrates by radio frequency (rf) magnetron sputtering. Compared with the first step, the different conditions were as follows: the sputtering power was fixed at 150 W and the frequency was 13.56 MHz. After 90 min, $Ga_2O_3$ films with a thickness of about 500 nm were obtained. Then the samples were placed into the reaction system. $N_2$ was introduced into the system for 5 min to expel air. Subsequently, $NH_3$ ($\geq 99.999\%$) with a flux of 500 ml/min was introduced into the system. The reaction lasted for 15 min at 950°C.

A RigakuD/max-rB X-ray diffraction (XRD) meter with a Cu $K_\alpha$ line, a Hitachi S-570 scanning electron microscope (SEM) and a Philips TECNAIF30 field-emission transmission electron microscope (FETEM) were applied to investigate the structure and surface morphology properties of the GaN nanowires. Tensor 27 Fourier transform infrared (FTIR) system was used to measure the chemical

states of products. Room-temperature photoluminescence (PL) measurements of as-synthesized GaN nanowires obtained were carried out by using a He–Cd laser (excitation wavelength = 325 nm).

### 3. Results and discussion

Figure 1 shows the typical XRD pattern of the sample at 950°C. The peaks positioned at $2\theta = 32.31°$, $34.45°$ and $36.78°$ correspond to the reflections of GaN (100), GaN (002) and GaN (101), respectively. The other strong diffraction peaks in the XRD pattern can be easily indexed to the hexagonal GaN phase with lattice constants of $a = 3.181$ Å and $c = 5.165$ Å, which agree well with the previously reported values for bulk GaN [18]. The low-intensity (002) peak, which is consistent with that of Ref. [19], may be ascribed to a small quantity of nanowires grown along the [001] direction. The XRD results suggest that the as-synthesized product is pure, hexagonal wurtzite structured GaN.

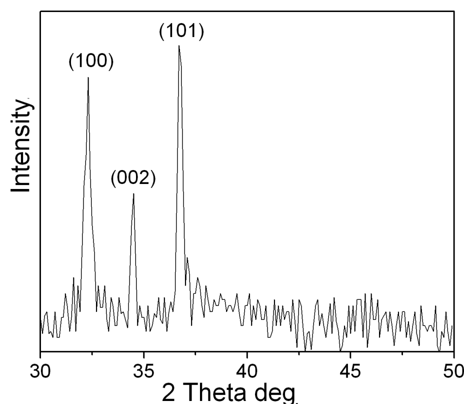



Fig. 1. The typical XRD pattern of GaN nanowires at 950°C.

The morphologies of the product are characterized by SEM. Figure 2a shows a typical SEM image of the high-density GaN nanowires grown on the substrate. In fact, the whole surface of the substrate is found to be covered with very dense fibriform products by the full-scale observation of SEM. Figure 2b exhibits a magnified image, showing that the individual nanowires possess a very smooth and a relatively straight morphology with diameters in the range of 30–100 nm, and lengths of typically several microns, displaying an aspect ratio exceeding 50:1.

Morphology and crystal structure of the GaN nanowires are further studied through high-resolution transmission electron microscopy (HRTEM) analysis. Figure 3a depicts a single nanowire with diameter 50 nm collected from the samples shown in Fig. 2b. The surface of the nanowire is quite straight and smooth without any particles, which is in good agreement with the corresponding SEM image shown in Fig. 2b. Figure 3b shows the HRTEM image of a GaN nanowire

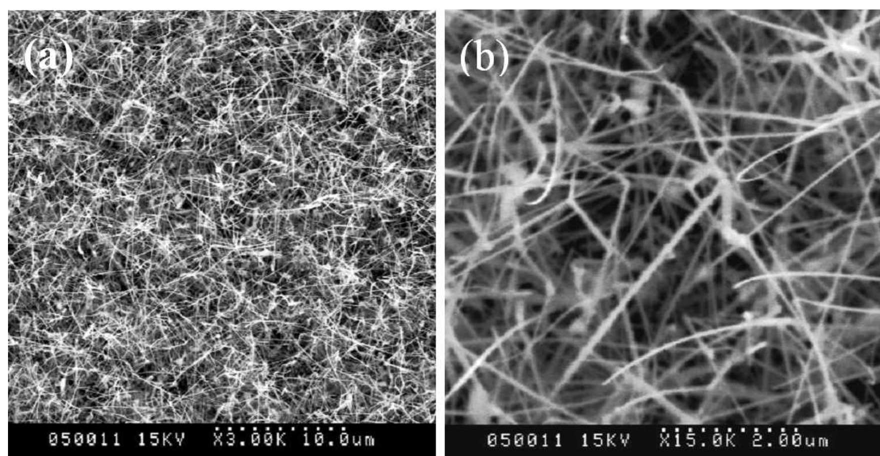



Fig. 2. (a) SEM view of high-density GaN nanowires grown on the substrate surface; (b) magnified view of the sample.

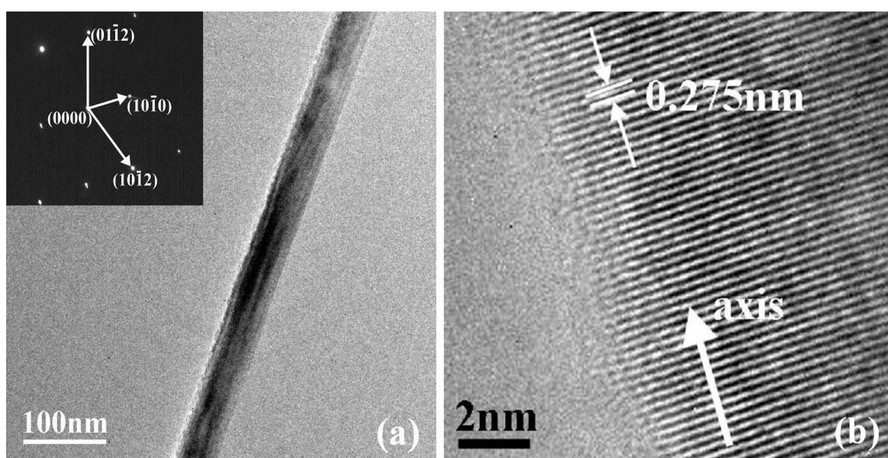



Fig. 3. (a) Low-magnification TEM image of a single GaN nanowire. Inset is the corresponding SAED pattern. (b) HRTEM lattice image.

and the corresponding selected-area-electron diffraction (SAED) image is shown in the inset in Fig. 3a. The lattice spacing of 2.75 Å, as shown in HRTEM image, corresponds to the spacing of (100) crystal planes of hexagonal GaN, indicating that the growth direction of the nanowire is perpendicular to the fringes of (100) plane.

Tensor 27 FTIR system is used to measure the chemical states of products. Figure 4 shows the FTIR spectrum of the GaN nanowires. Three prominent absorption bands are observed at 562.5 $cm^{-1}$, 609.5 $cm^{-1}$, and 1110.4 $cm^{-1}$, respectively. In the light of the reported band of Ga–N stretching vibration in hexagonal

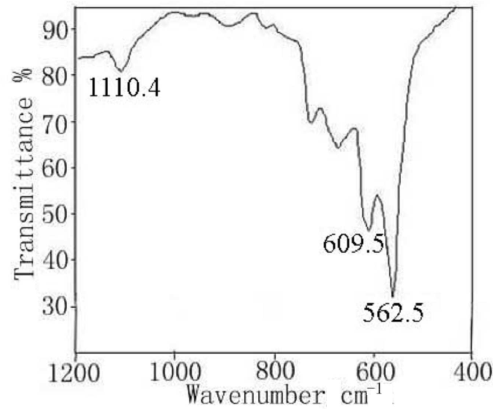



Fig. 4. FTIR spectrum of the GaN nanowires ammoniated at 950°C.

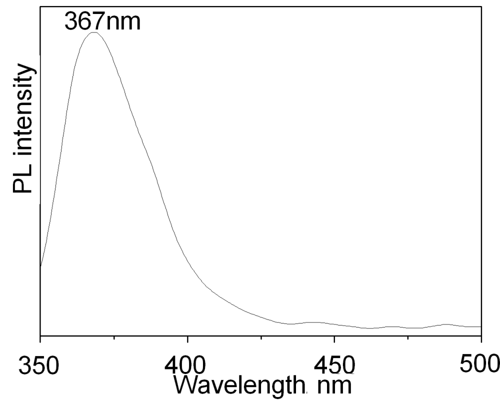



Fig. 5. PL spectrum of GaN nanowires ammoniated at 950°C.

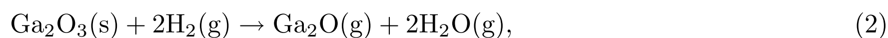
type GaN 560.45 $cm^{-1}$ [20], the absorption band at 562.5 $cm^{-1}$ corresponds to Ga–N stretching vibration peak. The absorption band at 609.5 $cm^{-1}$ is associated with the local vibration of substitutional carbon in the Si crystal lattice [21]. The band at 1110.4 $cm^{-1}$ is attributed to the Si–O–Si asymmetric stretching vibration mode, which is ascribed to extremely thin oxide layer on the Si surface [22]. $Ga_2O_3$ absorption band does not exist, proving that the $Ga_2O_3$ films have reacted with $NH_3$ entirely.

The PL measurement was conducted using a 325 nm He–Cd laser as the excitation source. Figure 5 shows only a strong and broad UV light emission peak at 367 nm (3.39 eV), which is associated with the near-band-edge emission of GaN. Because the as-prepared GaN nanowires are too large for quantum confinement effects, and even the thinnest GaN nanowire,s diameter is much larger than the Bohr exciton radius (11 nm) [23] of GaN. The UV light emission peak has no

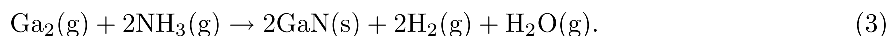
blue shift of the band-gap emission compared with the bulk GaN [24]. The GaN nanowires show a good emission property due to the excellent crystallinity of nanowires, which will have a good advantage for applications in laser devices using one-dimensional structures. However, further work is needed to investigate the PL mechanism of the GaN nanowires.

A detailed investigation of the growth mechanism is currently in progress. However, based on the above analysis and the observation, we might briefly describe the process as follows. In our experiment, there are probably several chemical reactions involved in our approach to synthesize GaN nanowires. $NH_3$ decomposes step by step to $NH_2$, NH, and N at temperatures above 850°C [25]. Therefore, $H_2$ can be assumed to present in our system. $Ga_2O_3$ will be reduced to $Ga_2O$ through the following reactions [26]. The reaction of $Ga_2O$ with ammonia results in the formation of GaN crystal nuclei [27]. In the process of ammoniating reaction, the main chemical reaction taking place in our system can be expressed as follows:

$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g), \tag{1}$$



$$Ga_2O_3(s) + 2H_2(g) \rightarrow Ga_2O(g) + 2H_2O(g), \tag{2}$$



$$Ga_2(g) + 2NH_3(g) \rightarrow 2GaN(s) + 2H_2(g) + H_2O(g). \tag{3}$$

where g means gaseous and s — solid.

There are $SiO_2$ layers (the thickness is about 12 nm) on the surface of Si(111) substrate before the deposition. When niobium is deposited on oxide supports, such as $SiO_2$, it forms a dispersed niobium oxide surface phase [28]. The surface niobium oxide phase has a pronounced catalysis effect on the above-mentioned three chemical reactions and the growth of GaN nanowires. Because of the decomposition of $Ga_2O_3$, parts of dispersed niobium oxide surface phase may leak out on the surface of substrate. The $Ga_2O$ vapor evaporates at reaction temperature and transfers from chemical reactions sites to substrate, where catalytic reaction takes place. At the same time, atomic nitrogen is produced by the catalytic decomposition of NH3 introduced into the quartz tube. Dissolving into the dispersed niobium oxide surface phase layer, Nb–O–Si–Ga–N liquid alloy nanoparticles are thus formed. The Nb–O–Si–Ga–N transition alloy maintains a liquid phase while the catalytic reaction proceeds. When the concentration of Ga–N exceeds a saturation point in the liquid phase Nb–O–Si–Ga–N alloy droplet, GaN begins to grow from liquid phase and deposits to form nanowires. Therefore, the GaN nanowires formed through the catalysts on the substrate gradually increase, as shown in Fig. 6. Why we do not find sign of any metal or alloy droplets at the end of the nanowires? It is well known that the nano-sized dispersed niobium oxide surface phase layer (Nb–O–Si layer) have very specific properties [17]. On the other hand, because of sublimation of GaN, the catalyst particle was displaced to the Si substrate but this did not impact the overall morphology. In order to identify the catalytic effect of Nb, we also ammoniated a sample which only deposited a

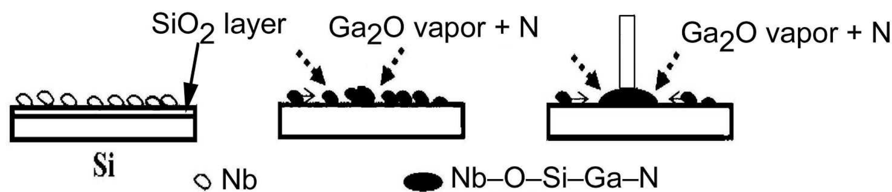



Fig. 6. A proposed mechanism for forming the nanorods.

$Ga_2O_3$ film on Si substrates with the same conditions. As a result, no nanowires are observed. It is proved that Nb plays an important role in the growth process of GaN nanowires. It can be seen that the high temperature, ammonia, Nb layer, and $Ga_2O_3$ are crucial in the growth of GaN nanowires. However, the further functions of the Nb in the growth of GaN nanowires and more details are under study.

## 4. Conclusions

High-density GaN nanowires have been successfully synthesized on Si(111) substrates through ammoniating $Ga_2O_3$/Nb films under flowing ammonia atmosphere at 950°C. XRD and SAED results showed that the product is crystalline GaN with hexagonal structure. SEM and HRTEM observations demonstrated that the GaN nanowires have a smooth surface with diameters of the nanowires 30–100 nm and lengths up to several microns and the nanowires grew along the [100] direction. The present results suggest that Nb can be a good candidate catalyst for the growth of high-quality GaN nanowires.

## Acknowledgments

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