

Synthesis of GaN nanowires by ammoniating Ga₂O₃/BN

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GaN nanowires were successfully prepared on Si (111) substrate through ammoniating Ga₂O₃/BN films deposited by radio frequency magnetron sputtering system. The synthesized nanowires were confirmed as hexagonal wurtzite GaN by X-ray diffraction, selected-area electron diffraction and Fourier transform infrared spectra. Scanning electron microscopy and transmission electron microscopy revealed that the grown GaN nanowires have a smooth and clean surface with diameters ranging from 40 to 160 nm and lengths typically up to several tens of micrometers. The representative photoluminescence spectrum at room temperature exhibited a strong UV light emission band centered at 363 nm and a relative weak purple light emission peak at 422 nm. The growth mechanism is discussed briefly.

Keywords: Sputtering; GaN; Photolumines.

1. INTRODUCTION

GaN has been considered to be the most promising optoelectronic material for such applications as light emitting diodes (LEDs), laser diodes (LDs) as well as high power electronic devices, due to its large direct energy band gap of 3.39 eV at room temperature and strongly emissive properties [1,2]. In the past decade, one-dimensional GaN nanomaterials have attracted extensive attention owing to their great uses in the novel nanoelectronic devices and the quantum devices [3]. Up to the present, several techniques have been developed to prepare one-dimensional GaN nanomaterials such as carbon nanotube-confined reaction[4], template-based growth method^[5], catalytic growth^[6] and direct reaction of metal Ga with NH₃ [7]. Furthermore, Huang *et al.* have reported successful fabrication of logic gates and demonstrated the computation capabilities from assembled *p*-Si and *n*-GaN crossed nanowire junctions [8]. However, the synthesis of high-quality GaN nanowires with a large-scale on Si

substrate is very important for the application of GaN nanowires, and needs to be optimized. In this paper, we report a successful synthesis of highly crystalline GaN nanowires through ammoniating Ga₂O₃/BN films on Si (111) substrate deposited by radio frequency (RF) magnetron sputtering system. We chose hexagonal BN on Si (denoted BN/Si) as a substrate for hexagonal GaN films growth because of the reasonably low lattice mismatch (8%)[9] and higher thermal conductivity than that of sapphire; the latter is insulating and is poorly lattice matched (16%). Moreover, if GaN can be prepared on BN/Si, it will offer a very attractive way to incorporate future GaN optoelectronic devices into silicon-based very large-scale integrated circuits.

2. EXPERIMENT

The GaN nanowires were prepared by a two-step method. The first step was to deposit Ga₂O₃/BN films on Si(111) substrate in turn using a JCK-500A RF magnetron sputtering system (13.56 MHz). The targets for depositing BN films and Ga₂O₃ films were hot-pressed BN with a purity of 99.9% and sintered Ga₂O₃ with a purity of 99.99%. The base pressure before sputtering was about 6.4×10^{-4} Pa. The working gas was pure argon and the working pressure was 2 Pa. During deposition, the substrate' temperature was fixed at 300 K by a water-cooled pipe, and the RF power was adjusted to 150 W. The distance between the target and substrate was 8 cm, and the deposition time was about 20 min for BN films and 90 min for Ga₂O₃ films.

Subsequently, the samples were ammoniated under flowing ammonia atmosphere in an open tube furnace. When the furnace reached the equilibrium temperature of 950°C, the quartz boat with the samples was pushed into the constant temperature region of the furnace. Flowing N₂ was first introduced into the tube for 5 min to flush out the residual air. Then NH₃ was flowed into the tube for 15 min at a flow rate of 800 mL/min while the N₂ was switched off. At the end of the ammoniating process, the NH₃ was flushed out by N₂ before the boat was taken out of the furnace.

A scanning electron microscope (SEM, Hitachi S-570), transmission electron microscope (TEM, Hitachi H-800) and high-resolution transmission electron microscope (HRTEM, Philips TECNAI-20) were used to observe the morphology of the synthesized samples. X-ray diffraction (XRD, Rigaku D/max-rB Cu K α) and Fourier transform infrared spectroscopy (FTIR, TENSOR27) were used to examine the crystalline structure and elemental state of the samples. The photoluminescence (PL) spectra of the samples were measured in an FLS920 fluorescence spectrophotometer at room temperature.

3. RESULTS AND DISCUSSION

Figure 1 shows the typical SEM images of the synthesized samples at different magnifications. At low magnification, it can be clearly observed from Fig. 1(a) that a great deal of micrometre sized spheres with diameters ranging from 2 to 27 μ m is sparsely distributed over a large area on the Si substrate. In fact, the whole surface of the substrate is found to be covered with spheres by the full-scale observation of SEM. And the further observation reveals that each sphere consists of a large cluster of high-density nanowires as shown in the high magnification image (Fig. 1(b)). The SEM image of Fig. 1(c) demonstrates that the nanowires possess a very smooth surface and a relatively straight morphology with a diameter of about 40—160 nm and a length of about several tens of micrometers, which is possibly favorable for the future

applications of nanodevice.

Figure 2 shows the typical XRD pattern of the samples. All the reflection peaks can be indexed to a hexagonal wurtzite GaN phase with lattice constants of $a = 0.3186$ nm and $c = 0.5178$ nm, which are well consistent with the reported values for one-dimensional GaN nanomaterials [10]. The low-intensity (0002) peak, in comparison with that of ref. [10], may be attributed to a small quantity of nanowires grown along the [0001] direction. No diffraction peaks from Ga_2O_3 , BN or other crystalline impurities were found in any of our samples, indicating that the sample was of high purity. And the sharp diffraction peaks also revealed that the GaN nanowires thus prepared had a high crystalline quality.

Figure 3(a) shows the TEM image of a single GaN nanowire with a diameter of about 60 nm, providing more structural information. It is straight and has a fairly clean surface without any particles. Figure 3(b) shows an HRTEM lattice image of another GaN nanowire. The distinct lattice fringes indicate that the nanowire is single crystal. No defect was observed in the lattice image, revealing that the nanowire has a high-quality crystal lattice. The spacing between two conjoint planes is about 0.243 nm, which corresponds to the {10 11} planes of hexagonal GaN, indicating that the growth plane of the nanowire is one of the {10 11} planes. The single crystalline nature of the nanowire can also be identified from the corresponding selected area electron diffraction (SAED) pattern taken by the fast Fourier transform (FFT) techniques (Fig. 3(c), which can be indexed to the reflection of the hexagonal wurtzite GaN along the [1213] axis.

Figure 4 shows the FTIR transmission spectrum of the synthesized GaN nanowires. Four prominent IR absorption bands were observed at 563 (band 1), 609 (band 2), 670 (band 3) and 1105 cm^{-1} (band 4), respectively. According to refs. [9,10], band 1 corresponds to Ga-N stretching vibration ($E_1(\text{TO})$ mode) in the hexagonal type GaN crystals, indicating that hexagonal GaN was obtained under current conditions, which accords with the results of XRD and SAED. Bands 2—4 are relevant to the Si substrate. Band 2 is associated with a local vibration of substitutional carbon in the Si crystal lattice [11,12]. Band 3 is related to the absorption by Si-C bonds in amorphous phase, illustrating the diffusion of carbon impurity into the Si substrate during the film growth. And band 4 is due to the Si-O-Si asymmetric stretching vibration in the SiO_2 resulting from oxygenation of Si substrate surface [13].

Under 300 nm photoexcitation, a strong and broad UV light emission band centered at 363 nm and a relatively weak purple light emission peak at 422 nm are observed as shown in Figure 5. 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)[14] of GaN, the bandgap emission at 363 nm has no blue shift compared with the bulk GaN^[15]. Another purple light emission peak might be ascribed to the existence of defects or surface states [16]. However, further work is needed to understand the PL mechanism of the GaN nanowires.

Although the detailed growth mechanism of the GaN nanowires is still not fully understood, we might briefly describe the process based on the above observation and the analysis. It is well known that Ga_2O_3 begins to decompose into Ga_2O and Ga above 800°C and NH_3 decomposes stepwise into NH_2 , NH and N at 850°C [7] in the ammoniating period. GaN molecules are subsequently formed through the reaction of Ga_2O with NH_3 or the reaction of Ga atoms with N atoms. First, the GaN molecules diffuse and agglomerate into the GaN micrograins. Then the very small GaN micrograins grow up with the progress of the

ammoniating and accordingly lay the foundations for the growth of nanostructured GaN. Thus, the temperature, ammonia and Ga₂O₃ are all crucial in the growth progress of nanostructured GaN. However, as the intermedium between Si substrate and Ga₂O₃ films, BN films are also very important for the fabrication of GaN nanostructure. To test this conclusion, we also ammoniated a sample with only a deposited Ga₂O₃ layer on Si(111) substrate under the same condition and duration of time, and found no such nanowires formed. A study of the detailed role of the BN films during the growth of GaN nanowires is still in progress.

4. CONCLUSION

In summary, single-crystal GaN nanowires were successfully prepared by ammoniating Ga₂O₃/BN films at 950°C. SEM and TEM observations demonstrate that the as-synthesized GaN nanowires have a smooth surface with diameters ranging from 40 to 160 nm and lengths up to several tens of micrometers, which may be applied in the future nanodevices. XRD, FTIR and SAED analyses revealed that the nanowires are hexagonal wurtzite GaN. The PL spectrum at room temperature exhibited a strong emission at 363 nm and a relatively weak emission at 422 nm.

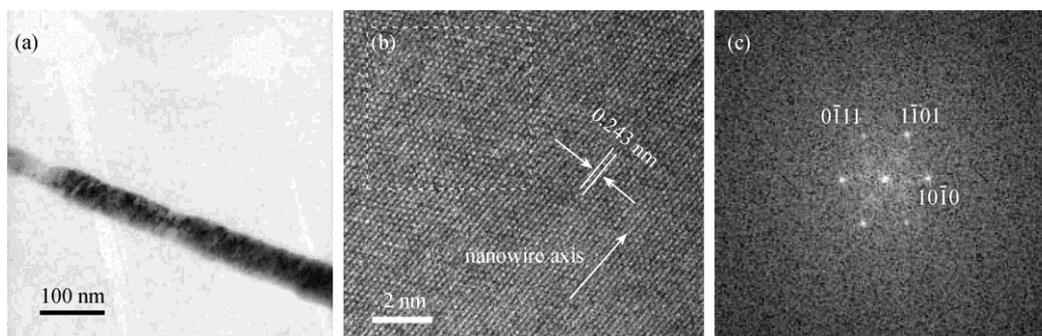


Fig. 3 (a) TEM image of a single GaN nanowire; (b) HRTEM lattice image of GaN nanowire; (c) SAED pattern taken by FFT techniques.

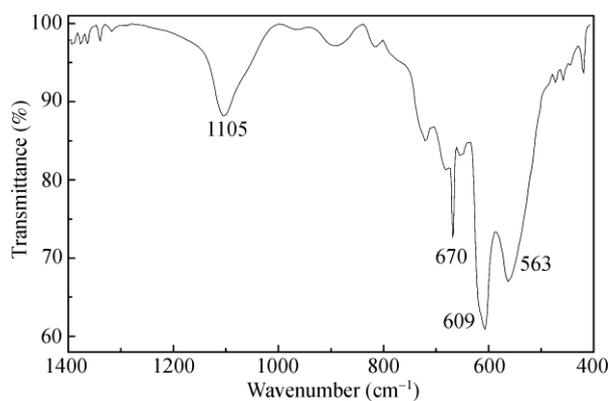
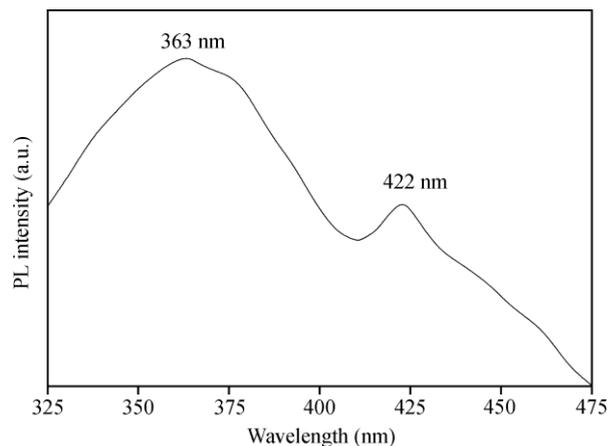


Fig. 4. FTIR transmission spectrum of the synthesized GaN nanowires.**Fig. 5.** PL spectrum of the synthesized GaN nanowires.

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