GaN nanowires and nanotubes growth by chemical vapor deposition method at different NH$_3$ flow rate

Pengan Li, Yihe Liu, and Xianquan Meng

Key Laboratory of Artificial Micro-and Nanostructures Ministry of Education and School of Physics and Technology, Wuhan University, Wuhan 430072, Hubei, People’s Republic of China.

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GaN nanowires and nanotubes have been successfully synthesized via the simple chemical vapor deposition method. NH$_3$ flow rate was found to be a crucial factor in the synthesis of different type of GaN which affects the shape and the diameter of generated GaN nanostructures. X-ray diffraction confirms that GaN nanowires grown on Si(111) substrate under 900$^\circ$C and with NH$_3$ flow rate of 50 sccm presents the preferred orientation growth in the (002) direction. It is beneficial to the growth of nanostructure through catalyst annealing. Transmission electron microscopy and scanning electron microscopy were used to measure the size and structures of the samples.

Keywords: GaN; CVD; nanotube; TEM.

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1. Introduction

Gallium nitride (GaN), an important semiconductor with a band-gap of 3.4 eV, has high saturated electron drift velocity and high thermal conductivity [1,2]. GaN nanostructures, for example, nanowires, nanorods and nanotubes have a bright application prospect in UV detector, high-temperature electronic devices, high-speed field-effect transistors, lasers, LEDs and other functional devices [3,4].

The GaN nanowires are very interesting building blocks for the fabrication of various nanoscale devices because of their own superior properties such as the capability of the doping modulation and the selectivity of the carriers [3,5-7]. GaN nanotubes can be obtained through two-step template-assisted methods and direct reaction of metal gallium with flowing NH$_3$. However, the synthesis of high-purity well-structured GaN nanotubes is still a challenge, the mechanical properties of well-crystallized GaN nanotubes are still unknown due to synthetic difficulties [8]. In addition, it is essential to study the Young’s modulus of GaN nanotubes, which differ from GaN nanowires in shape, size, morphology and atomic structure, in order to fully evaluate their possibilities for nanoelectronic mechanical system (NEMS) devices [1,9,10].

Liu et al. [1,11,12] have introduced a complex method to synthesis the GaN nanotubes with mixed powder of Ga$_2$O$_3$ and GaN. He et al. [13] gave the simple synthesis method of CVD, but they did not explore the mechanism. In this paper, we further discussed the influence of different NH$_3$ flow rate on GaN nanowires and nanotubes.

2. Experimental details

In this letter, GaN nanowires and nanotubes were synthesized through direct reaction of metal gallium (Ga,99.99%) vapor with flowing NH$_3$ in an electric furnace. The Si (111) substrate was cleaned by acetone, ethanol, and de-ionized water with ultrasonic bath for 5 min each to remove residual organic contaminations on the surface. Three samples were synthesized at different ammonia concentration using nickel (Ni,~10 nm thick) as a catalyst. The Ga was placed on an quartz boat at the center of the furnace, and the Ni/Si (111) substrates was located about 1 cm downstream to the Ga source. The tube was pumped and filled with N$_2$ for 3 times to clear the residual O$_2$, then was gradually heated to 950$^\circ$C at a rate of 25$^\circ$C/min and kept for 10 min for catalyst annealing, protected by N$_2$. The temperature was dropped to 900$^\circ$C, the tube was bumped, NH$_3$ was introduced at a desired flow rate. The first sample was grown using a NH$_3$ flow rate of 50 sccm for 0.5 h, the second grown using a NH$_3$ flow of 100 sccm for 0.5 h and the third grown using a NH$_3$ flow of 200 sccm for 0.5 h. The growth temperature was maintained for a desired time. Finally the system was cooled down to room temperature in vacuum. GaN products were obtained on the Si (111) substrate.

![XRD pattern of the GaN nanowires in the first sample grown at 900$^\circ$C with NH$_3$ flow of 50 sccm.](image-url)
Figure 2. (a) SEM image of the unannealed nickel, (b) SEM image of the annealed nickel.

Figure 3. (a)(b) the SEM image of the sample 1 under NH$_3$ flow of 50 sccm; (c)(d) the SEM image of the sample 2 under NH$_3$ flow of 100 sccm; (e)(f) the SEM image of the sample 3 under NH$_3$ flow of 200 sccm. (g) the SEM image of Ni catalyst on the tip of GaN nanowire.

Figure 4. (a) TEM of the nanowire from sample 1 under NH$_3$ flow of 50 sccm. (b) TEM of the nanosheet from sample 3 under NH$_3$ flow of 200 sccm. (c) TEM of the nanotube from sample 3 under NH$_3$ flow of 200 sccm.
3. Results and discussion

The first sample grown at 900°C with NH3 flow of 50 sccm is characterized by XRD. Figure 1 shows the XRD patterns of the GaN nanowires and the diffraction peaks show that the GaN nanowires present the preferred growth orientation on the (002) direction and good quality. Because of the lowest surface energy in the (002) crystal plane, the growth of GaN nanostructure tend to (002) crystallographic orientation, while the growth of other direction is subdued.

GaN nanostructure tend to (002) crystallographic orientation, for the GaN nanowires present the preferred growth orientation on the (002) direction. When the NH3 flow rate of 50 sccm present the preferred orientation growth on the (002) direction. When the NH3 flow rate increases to 100 sccm, the products have much wider diameter but shorter length. Continue to increase the NH3 flow rate to 200 sccm, we get nanotubes and nanosheets. This may be because the faster the NH3 flow rate, the greater the tension of the GaN surface. This leads to very easy to form nanosheets. As the temperature is reduced, nanosheets would become the nanotube if they were rolled up properly.

Generally, under the same growth temperature, the faster the NH3 flow rate between 50 and 200 sccm, the larger the nanowires or nanotubes diameter. By the simple method, GaN nanostructures with manifold morphologies, including nanowires, nanorods, nanotubes and nanosheets are fabricated. NH3 flow has great impact on the morphology of the nanostructures. When the flow rate of NH3 is low, GaN nanowires are synthesized based on the VLS mechanism [11]. We get nanowires. As the flow rate increased, on the basis of VLS mechanism, the increase of the NH3 flow rate enhance the lateral growth, which leads to the decreasing of the length to diameter ratio and promoting the formation of nanorods and nanosheets. To date, the direct fabrication of a hexagonal GaN tubular structure free from contamination has been a challenge [12], the nanosheets as showed in Fig. 4(b) were transformed to the nanotubes by rolled up. The work may helpful to achieve the controllable fabrication of GaN nanostructures with varous morphologies.

4. Conclusions

In summary, with different NH3 flow rate between 50 and 200 sccm, large scale GaN nanowires and tubes were formed at the growth temperature of 900°C on Si(111) substrate. The GaN nanowires grown on Si(111) substrate under 900°C and with NH3 flow rate of 50 sccm present the preferred orientation growth on the (002) direction. When the NH3 flow rate increases to 100 sccm, the products have much wider diameter but shorter length. Continue to increase the NH3 flow rate to 200 sccm, we get nanotubes and nanosheets. This may be because the faster the NH3 flow rate, the greater the tension of the GaN surface. This leads to very easy to form nanosheets. As the temperature is reduced, nanosheets would become the nanotube if they were rolled up properly. We are continuing to study other factors which may influence the growth of GaN nanostructures, such as sample location, pressure and trying to gain an better understanding of the detailed growth mechanism.

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