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ARTICLE

Optical and Micro-structural Properties of GaN Nanowires by Ammoniating Ga_2O_3 /Nb Films

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Abstract: Single-crystalline GaN nanowires have been synthesized on Si(111) substrates by magnetron sputtering through ammoniating the Ga_2O_3/Nb films at 900 °C in a quartz tube. The as-prepared nanowires are confirmed as single crystalline GaN with wurtzite structure by X-ray diffraction (XRD), selected-area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM). Transmission electron microscopy (TEM) shows that the GaN nanowires are straight and smooth, and possess the diameters of about 50 nm and lengths up to several microns. When excited by 325 nm helium-cadmium (He-Cd) laser light at room temperature, the GaN nanowires only have a strong ultraviolet luminescence peak located at 367 nm, owing to GaN band-edge emission. Finally, the growth mechanism of GaN nanowires is discussed briefly.

Key words: nanowires; ammoniating; GaN

GaN, a wide and direct band gap semiconductor (3.4 eV at room temperature), is an ideal material for the fabrication of ultraviolet, blue light-emitting diodes and high-power/high- temperature electronics devices[1]. Its one-dimensional 1D nanostructure has been synthesized for potential applications in field emission devices[2,3]. In the last few years, the significant progress in GaN nanowire growth[4,5], and individual device fabrication[6,7] was made. Since Fan and co-workers first synthesized the GaN nanorods through a carbon nanotube-confined reaction of Ga/Ga_2O_3 mixture with NH_3 [8], many efforts have been dedicated to developing different techniques for preparing GaN nanorods. The popular methods include carbon nanotube-confined reaction[8] or template-induced growth[9], metal-catalyzed growth[10], and direct reaction of metal Ga with NH_3 [11,12]. In the last few years, our group developed a novel method for synthesizing one-dimensional GaN materials through ammoniating Ga_2O_3 films[13], Ga_2O_3/SiC films[14], Ga_2O_3/ZnO films[15] and Ga_2O_3/MgO films[16], which were deposited by RF magnetron sputtering. However, the yield and the quality of the synthesized GaN nanowires are still to be optimized for the application of GaN nanowires to nanoelectronic devices. Up to now, there is lack of the information on GaN nanowires synthesizing by ammoniating Ga_2O_3 films on Nb layer deposited on Si(111) substrates. In this paper, we report the successful preparation of GaN nanowires on Si(111) substrates through ammoniating Ga_2O_3/Nb films in flowing ammonia atmosphere at 900 °C in a quartz tube.

1 Experimental Procedure

In our experiment, GaN nanowires were prepared by the reaction of Ga_2O_3 films with NH_3. The nanowires were prepared by a two-step method. The first step was the process of forming Nb layer. Nb films were deposited on Si(111) substrates by the progress of direct current (D.C.) sputtering with JCK-500A magnetron sputtering system. The conditions of sputtering were as follows: the background pressure was 1.2×10^{-3} Pa; the distance between targets and substrates was 8 cm; the pressure of Ar (≥99.99%) was 2 Pa; the output voltage of WLY steady current device was 260 V and the output current was 160 mA. After 10 s, Nb films with a thickness of about 10 nm were obtained.

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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 (r.f.) 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 (≥99.999%) with a flux of 500 mL/min was introduced into the system. The reaction lasted for 10 min at 900 °C.

A RigakuD/max-rB X-ray diffraction (XRD) meter with a Cu Kα line was used to examine the crystalline structure. The microstructure and surface morphology of the GaN nanowires were observed by means of a Hitachi H-800 transmission electron microscope (TEM) and a Philips TECNAIF30 field-emission transmission electron microscope (FETEM). Fourier transform infrared spectroscopy (FTIR, TEN-SOR27) was used to examine the composition information of the samples. Room-temperature photoluminescence (PL) measurements of the obtained GaN nanowires were carried out by a He-Cd laser (excitation wavelength = 325 nm).

2 Results and Discussion

2.1 XRD analysis

Fig.1 shows the XRD pattern of the as-synthesized GaN nanowires. Peaks were found at 32.39°, 34.59°, 36.79° and 48.12° in correspondence with the hexagonal wurtzite GaN. They are due to the (100), (002), (101) and (102) diffraction peaks of hexagonal GaN, respectively. All refraction peaks can be indexed to a hexagonal wurtzite GaN phase with the lattice constants a_0=0.3190 nm and c_0=0.5189 nm, which are in good agreement with the values reported for GaN[17]. The strongest (101) peak of GaN mainly accords with bulk GaN in the XRD pattern[18]. No any other diffraction peaks are observed in any of our samples, indicating that the sample is predominantly polycrystalline hexagonal wurtzite GaN phase with high purity. The sharp diffraction peaks also reveal the high crystallization of the samples prepared in this way.

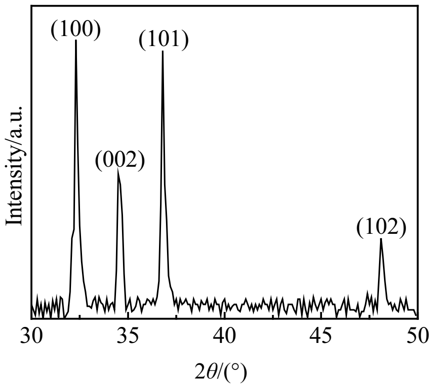

Fig.1 XRD pattern of the nanowires obtained at 900 °C

2.2 TEM analysis

The morphology of the sample was characterized by TEM. Fig.2a shows the typical TEM image of the GaN nanowires ammoniated at 900 °C with high density, and we can see the nanowires cross each other and randomly distribute on the whole surface. These nanowires are straight and smooth with diameters of about 50 nm and lengths up to several microns by statistical survey. And Fig.2b is a TEM image for a single GaN nanowire with a diameter of about 50 nm. It is straight and has a fairly clean surface without any particles.

2.3 HRTEM analysis

Fig. 3 shows the HRTEM lattice image of a single nanowire and the corresponding selected area electron diffraction (SAED) pattern of the single nanowire. The lattice is very perfect and its orientation is clear and uniform. In the image, the distance between the two stripes is 0.275 nm, which is corresponding to the distance between two (100) planes. The HRTEM image reveals that the normal of the nanowire is [001] orientation. The insert in the upper-right-corner of Fig. 3 is the selected area electron diffraction (SAED) pattern of the nanowire sample, which can be indexed to the diffraction of wurtzite GaN crystal along the [021] direction. It is also confirmed that the nanowires are single crystalline GaN.

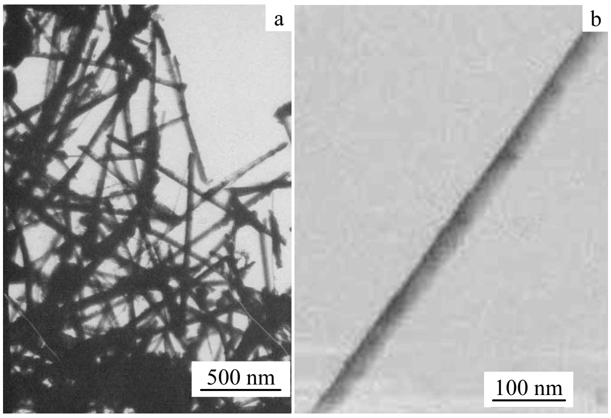

Fig.2 (a) Typical TEM image of the GaN nanowires. (b) TEM image of a single GaN nanowire

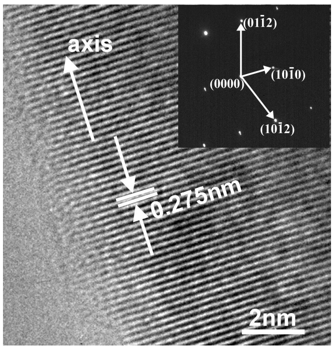

Fig.3 HRTEM lattice image of an individual GaN nanowire and the insert is the SAED pattern

2.4 XPS analysis

The XPS was employed to investigate the chemical composition of the sample. Fig. 4 shows the XPS for the GaN synthesized at the ammoniating temperature of 900 °C. Ga 3d, Ga 3p, Ga3s, Ga LMM Auger peak, C1s, N1s and O1s core level peaks were selected for the investigation in the binding energy between 0 and 600 eV. The peak of N1s is observed at 397.8 eV in Fig.4b. The width and slight asymmetry of the N1s peak can be attributed to the presence of chemisorbed nitrogen along with nitrogen in GaN[19]. Besides, no bonding formation between Ga and O could be attributed to that no satellite peak corresponding to Ga_2O_3[20] shown by Ga3d spectrum. In Fig.4c, the measured value of Ga3d peak of the sample centered at 19.9 eV is in good agreement with the published binding energy values of the Ga3d peak at 19.9 eV of compound GaN[21]. The value in this experiment has a positive shift from element gallium with Ga3d peak centered at 18.5 eV, indicating that the Ga atoms in the sample are in the compound state (GaN). $Ga2p_{3/2}$ and $Ga2p_{1/2}$ peaks for the as-grown GaN nanowires are shown in Fig.4d. The peaks of $Ga2p_{1/2}$ and $Ga2p_{3/2}$ are observed at the binding energies of 1144.9 eV and 1118.1 eV, respectively. The result is in agreement with that observed by Paletal[22]. The core level of Ga has a positive shift from elemental Ga. This shift in binding energies of Ga and N confirms the bonding between Ga and N as well as the absence of elemental gallium. The quantification of the peaks gives the atomic ratio of Ga/N close to 1: 1.

2.5 PL analysis

Fig.5 shows the PL spectrum of GaN nanowires ammoniated at 900 °C. The PL measurement was conducted using a 325 nm helium-cadmium (He-Cd) laser as the excitation source. There is only a strong and broad UV light emission peak at 369 nm (3.36 eV), which is associated with the near-band-edge emission of GaN. Because the as-grown GaN nanowires are too large for quantum confinement effects, and even the diameter of the thinnest GaN nanowires is much larger than the Bohr exciton radius (11nm) of GaN[23], the UV light emission peak has no blue shift of the bandgap emission compared with the bulk GaN[24]. The GaN nanowires show a very excellent good emission property, which will have a good advantage for applications in laser devices using one-dimensional structures. However, for the further work the PL mechanism of the GaN nanowires is to be investigated.

2.6 Discussion about growth process of GaN

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 the temperatures of above 850 °C[5]. So, H_2 can be assumed to present in our system. Ga_2O_3 will be reduced to Ga_2O through the followed reactions[25]. The reaction of Ga_2O with ammonia results in the formation of GaN crystal nuclei. In the process of ammoniating reaction, the main chemical reaction taking place in our system can be expressed as follows[26]:

$2NH_3\ (g) \rightarrow N_2\ (g) + 3H_2\ (g)$

$Ga_2O_3\ (s) + 2H_2\ (g) \rightarrow Ga_2O\ (g) + 2H_2O\ (g)$

$Ga_2O\ (g) + 2NH_3\ (g) \rightarrow 2GaN\ (s) + 2H_2\ (g) + H_2O\ (g)$

There is SiO_2 layer on the surface of the substrate before the deposition. When niobium is deposited on oxide supports, such as SiO_2, a dispersed niobium oxide surface phase will be formed[27]. The surface niobium oxide phase has a pronounced

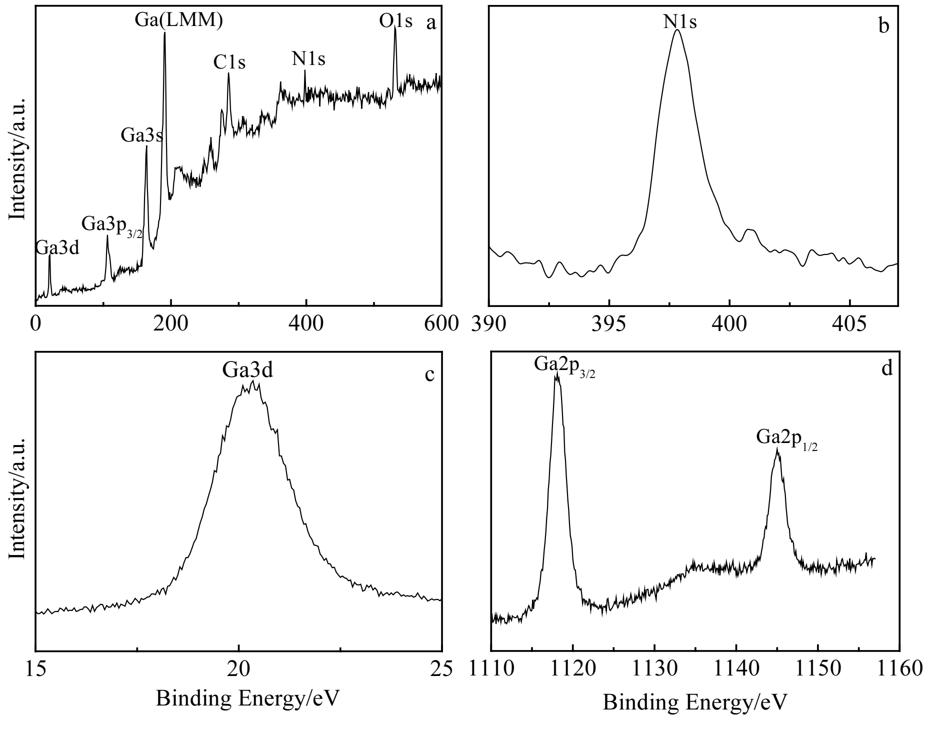

Fig.4 XPS spectra obtained from the sample ammoniated at 900 °C

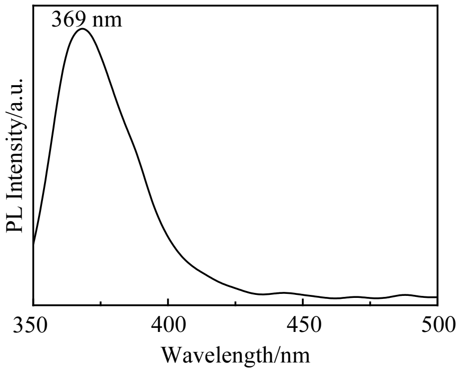

Fig.5 PL spectrum of GaN nanowires ammoniated at 900 °C

catalysis effect on 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 the substrate. The Ga_2O vapor evaporates at the reaction temperature and transfers from chemical reactions sites to the substrate, where catalytic reaction takes place. At the same time, atomic nitrogen is produced by the catalytic decomposition of NH_3 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 is the sign of any metal or alloy droplets not found at the end of the nanorods? Because the nano-sized dispersed niobium oxide surface phase layer (Nb-O-Si layer) has very specific properties[28] on one hand. On the other hand, because of sublimation of GaN, the catalyst particle is displaced to the Si substrate but this does not impact the overall morphology. In order to identify the catalytic effect of Nb, we also ammoniated a sample where only a Ga_2O_3 film was deposited on Si substrates using the same conditions. As a result, no nanowires were 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 function of the Nb in the growth of GaN nanowires and more details are under study.

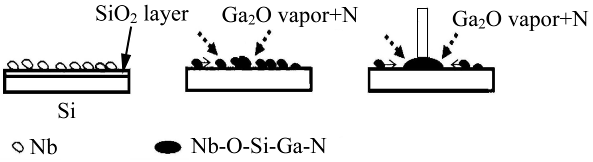

Fig.6 A proposed mechanism for forming the nanowires

3 Conclusion

1) GaN nanowires has been synthesized on Si (111) substrates through ammoniating of Ga_2O_3/Nb films in flowing ammonia atmosphere at 900 °C in quatz tube.

2) The nanowires demonstrate intensive room temperature UV emission, which promises valuable application of the prepared GaN nanwires in optical devices.

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氨化 Ga_2O_3 /Nb 膜制备的 GaN 纳米线的光学和微观结构特性的研究

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摘　要：采用射频磁控溅射技术在硅衬底上制备 Ga_2O_3/Nb 薄膜，然后在 900 °C 下于流动的氨气中进行氨化制备 GaN 纳米线。用 X 射线衍射(XRD)、透射电子显微镜(TEM)和高分辨透射电子显微镜详细分析了 GaN 纳米线的结构和形貌。结果表明：采用此方法得到的 GaN 纳米线有直的形态和光滑的表面，其纳米线的直径大约 50 nm，纳米线的长约几个微米。室温下以 325 nm 波长的光激发样品表面，只显示出一个位于 367 nm 的很强的紫外发光峰。最后，简单讨论了 GaN 纳米线的生长机制。

关键词：纳米线；氨化；GaN

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