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ARTICLE

Synthesis of Large-scale GaN Nanowires by Ammoniating Ga_2O_3/V Films

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Abstract: Large-scale GaN nanowires were synthesized on Si(111) substrates through ammoniating Ga_2O_3/V films. The as-grown products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The results reveal that the grown GaN nanowires have a smooth and clean surface with diameters ranging from 20 nm to 60 nm and lengths of about several tens of micrometers. The results of HRTEM and selected-area electron diffraction (SAED) show that the nanowires are pure hexagonal GaN single crystal. The photoluminescence (PL) spectrum indicates that the GaN nanowires have good emission property. The growth mechanism is discussed briefly.

Key words: magnetron sputtering; GaN; nanowires; photoluminescence

GaN single crystal has a wide, direct band gap and is potentially useful to blue and ultraviolet light emission and high temperature, high power electronic devices[1,2]. One-dimensional GaN nanostructures including nanowires, nanorods, and nanotubes have recently attracted much attention because of their potential applications for optoelectronic devices in the nanoscale[3,4]. GaN nanowires have been synthesized by many different nanowire growth methods such as carbon-nanotube-confined reaction, laser-assisted catalytic growth[5], catalytic reaction based on a vapour-liquid-solid mechanism[6], direct reaction of metal gallium with ammonia[7], oxide-assisted growth[8] and thermal chemical vapour deposition. In this paper, we report a successful synthesis of highly crystalline GaN nanowires through ammoniating Ga_2O_3/V films on Si(111) substrates deposited by radio frequency (RF) magnetron sputtering system.

1 Experimental

The GaN nanowires were prepared by a two-step method. The first step was to deposit Ga_2O_3/V films on Si(111) substrate in turn using a JCK-500A magnetron sputtering system (13.56 MHz). The targets for depositing V films and Ga_2O_3 films were the hot-pressed V with purity of 99.9% and the sintered Ga_2O_3 with 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. The distance between the target and the substrate was 8 cm. When V was deposited, the output voltage of WLY steady current device was 320 V and the output current was 160 mA. Ga_2O_3 films were deposited through radio frequency magnetron sputtering. The sputtering power was 150 W. The sputtering progress was maintained at room temperature by the cooling system.

Subsequently, the Ga_2O_3/V films were ammoniated with a flow rate of 500 mL/min in a horizontal tube furnace. The temperature and the duration of the ammoniating were 950 °C and 15 min, respectively.

The samples were characterized with X-ray diffraction (XRD, Rigaku D/max-rB Cu Kα) to specify their crystalline structures. Scanning electron microscopy (SEM, Hitachi S-570) and high-resolution transmission electron microscope (HRTEM, Philips TECNAI-20) were used at room temperature to observe the product morphology and microstructure.

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Photoluminescence (PL) measurements were carried out at room temperature using the He-Cd laser with the wavelength of 325 nm.

2 Results and Discussion

2.1 XRD analysis

Fig.1 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[9]. The low-intensity (002) peak, in comparison with that of ref.[9], may be attributed to a small quantity of nanowires grown along the (002) direction. No diffraction peaks from Ga_2O_3 or other crystalline impurities were detected in any one of our samples, indicating that the sample was of high purity. And the sharp diffraction peaks also revealed that the prepared GaN nanowires have high crystalline quality.

2.2 SEM analysis

Fig.2 shows the typical SEM images of the synthesized samples at different magnifications. At the low magnification, it can be clearly observed from Fig.2a that a great deal of wire-like structure is interlaced each other and randomly distributed on the surface of GaN films. The whole film surfaces are actually covered with a layer of GaN nanowires by the all-around SEM observation. The SEM image of Fig.2b demonstrates that the nanowires possess very smooth surfaces and diameters of about 20~60 nm and lengths of about several tens of micrometers.

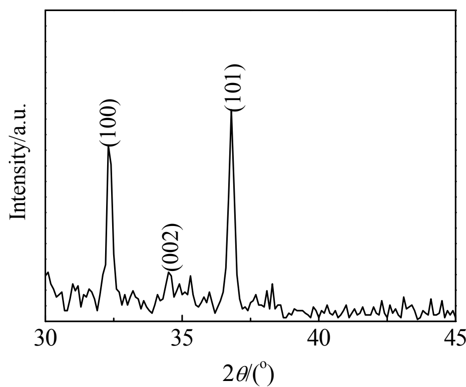

Fig.1 XRD pattern of the synthesized GaN nanowires

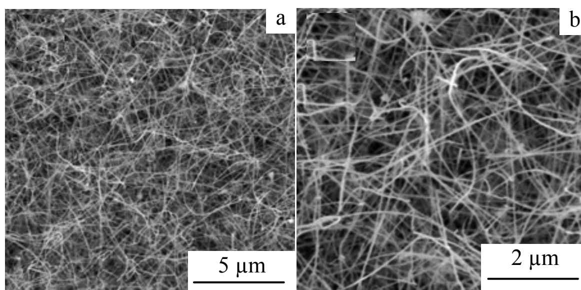

Fig.2 Typical SEM images of the synthesized GaN nanowires at different magnifications

2.3 PL analysis

PL spectrum of GaN product presented in Fig.3 is detected with He-Cd laser used as the excitation source (with a wavelength of 325 nm) at room temperature. Only a broad peak located at 368.5 nm can be activated. 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)[10] of GaN, so the band-gap emission at 368.5 nm has no blue shift compared with the bulk GaN[11]. GaN nanowires show very good emission property, which will be a great advantage in their laser device application. However, further work is needed to investigate the PL mechanism of the GaN nanowires.

2.4 HRTEM analysis

The HRTEM images of the single nanowire are given in Fig.4. Fig.4a shows a low-magnification TEM image of an individual GaN nanowire with a uniform diameter of about 50 nm, which is straight and possesses a fairly clean surface without any particles. Fig.4b shows the HRTEM lattice image and the corresponding selected area electron diffraction (SAED) pattern of the single nanowire. The well-spaced lattice fringes in the image indicate a single crystal structure of the nanowire. The white arrow shows the growth direction of the nanowire. The space between two fringes is about 0.243 nm, which corresponds to the distance between the (101) planes of hexagonal GaN. The single-crystal GaN nanowire can also be identified from the SAED pattern shown in the inset of Fig.4b, which can be ascribed to the reflection of hexagonal wurtzite GaN single crystal.

2.5 Discussion about growth process of GaN

Although the detailed growth mechanism of the GaN nanowires is still not fully clear, we might briefly explain the process as follows. It is well known that Ga_2O_3 begins to de-

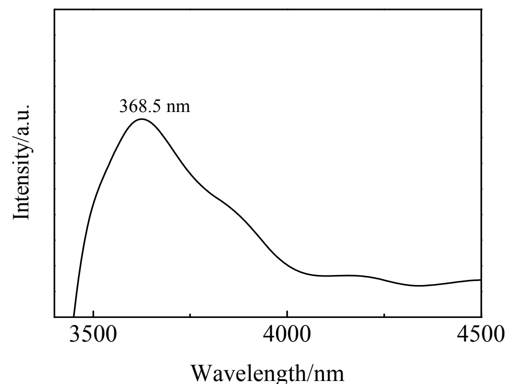

Fig.3 PL spectrum of GaN nanowires at room temperature(the wavelength of He-Cd laser is 325 nm)

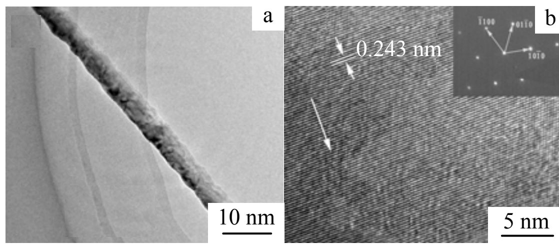

Fig.4 HRTEM image of a single GaN nanowire(a) and HRTEM lattice image of the GaN nanowires(b) (inset: the corresponding selected area electron diffraction pattern)

compose into Ga_2O or Ga above 800 °C and NH_3 decomposes stepwise into NH_2, NH and N in the ammoniating period[12]. GaN molecules would be subsequently formed by the reactions of Ga_2O with NH_3 or N atoms with Ga atoms. The metal V film is very important for the fabrication of GaN nanostructure. In order to make such a test, we also ammoniated Ga_2O_3/Si films under the same condition, and no such nanowires were found, and the XRD peaks of GaN film are much weaker. As we know, the surface energy distribution of a perfect Si substrate is almost identical, which is suitable to form a GaN film. However, the introduction of V makes the surface energy distribution of the substrate uneven and may produce some energetically favored sites for the absorption of gas-phase reactions (Ga_2O)[13]. Firstly, the GaN molecules diffuse and agglomerate into the GaN micrograins. Then the very small GaN micrograins grow up with the ammoniating progress. When the growth directions of the micrograins are all orientated to the same direction, the single-crystal GaN nanowires are formed. However the detailed growth process of GaN nanowires and the reasons for the excellent crystallization of GaN on V middle layer are still under study.

3 Conclusions

1) GaN nanowires can be fabricated by ammoniating technique under flowing ammonia atmosphere at 950 °C.

2) The as-synthesized nanowires are hexagonal wurtzite GaN.

3) GaN nanowires possess diameters ranging from 20 nm to 60 nm and lengths of about several tens of micrometers.

4) A broad peak is located at 368.5 nm.

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氨化 Si 基 Ga_2O_3/V 膜制备 GaN 纳米线

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摘 要：氨化硅基钒应变层氧化镓膜制备了大量氮化镓纳米线, X 射线衍射、扫描电子显微镜和透射电子显微镜观察发现, 纳米线具有十分光滑且干净的表面, 其直径为 20~60 nm 左右, 长度达到十几微米。高分辨透射电子显微镜和选区电子衍射分析结果表明, 制备的氮化稼纳米线为六方纤锌矿结构。光致发光谱显示制备的氮化稼纳米线有良好的发光特性。另外, 简单讨论了氮化稼纳米线的生长机制。

关键词：磁控溅射；氮化镓；纳米线；光致发光

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