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ARTICLE

Synthesis of GaN Nanowires with Tantalum Catalyst by Magnetron Sputtering

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Abstract: Single crystalline wurzite GaN nanowires were synthesized through ammoniating Ga_2O_3/Ta films by RF magnetron sputtering. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), selected-area electron diffraction (SAED) and photoluminescence (PL). The results show that the nanowires have a hexagonal wurtzite structure with diameters ranging from 20 nm to 60 nm and lengths typically up to 10 μm. The PL spectrum exhibits a strong UV light emission at 363 nm. The growth mechanism of the crystalline GaN nanowires is discussed briefly.

Key words: nanostructures; nitrides; sputtering

Gallium nitride (GaN), which has a direct and wide bandgap of 3.4 eV at room temperature, has been considered as an ideal material for the fabrication of blue/green light emitting diodes (LDS), laser diodes (LDS) and high power integrated circuits[1, 2]. In the past decade, nanomaterials have received extensive research interest for their great prospects in the fabrication of new nanoelectronice and development of new nanotechnologies[3]. So far, GaN materials have been synthesized by many different techniques such as carbon nano-tube-confined reaction[4], sublimation method[5], direct reaction of metal Ga and NH_3[6] and metal-catalyzed growth based on the vapor-liquid-solid (VLS) mechanism[7, 8]. But, due to the extensive demand for GaN nanoforms in the field of nanotechnology it is still a challenge to fabricate high quality GaN 1D nanoforms. In this paper, GaN nanowires have been successfully synthesized on Si substrates by RF magnetron sputtering using tantalum as catalyst. This growth method allows a continuous synthesis and produces a large quantity of single-crystal GaN nanowires with relatively high purity and low cost. So, it is to be of interest for commercial-scale production.

1 Experimental

In our experiment, GaN nanorods were prepared by self assembling of Ga_2O_3 films in their reaction with NH_3. There were two steps in the whole process. The first step was that the Ta films and Ga_2O_3 films were deposited in turn on Si (111) substrate in a JCK-500A magnetron sputtering system. The targets for depositing Ta films and Ga_2O_3 films were Ta with purity of 99.9% and sintered Ga_2O_3 with purity of 99.9%. The conditions of sputtering were as follows: the base pressure before sputtering was about 1.8×10^{-3}Pa. The working gas was pure argon(≥99.99%) and the working pressure was 2 Pa. The radio frequency voltage was 900 V and the sputtering power was 150 W. The sputtering time was about 5min for Ta and 90 min for Ga_2O_3.

The second step was that the Ga_2O_3/Ta films were ammoniated for 10 min at 950 °C in the flowing ammonia atmosphere in a horizontal tube furnace. When the tube furnace reached the temperature of 950 °C steadily, the samples were placed into the constant temperature zone of the furnace. Flowing nitrogen with a flux of 500 mL/min was first introduced into the system for 5 min to expel air. Then ammonia with a flux of 500 mL/min flowed into the system for 10 min. Finally, the NH_3 was expelled by N_2 before the samples were removed from the furnace. It could be found that the color of samples turned to be light yellow after ammoniating.

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The crystalline structure information of the as-prepared samples was examined by X-ray diffraction (XRD, Rigaku D/ max-rB Cu Kα, 40 kV). Scanning electron microscope (SEM, Hitachi S-570) and high-resolution transmission electron microscope (HRTEM, Philips TECNAI-20) were used to examine the morphology and microstructure of the products. The photoluminescence (PL) spectrum of the samples was analyzed in an FLS920 flourescence spectro-photometer at room temperature.

2 Results and Discussions

2.1 XRD analysis

Fig.1 shows the typical XRD pattern of the produced nanowires. Four high peaks are found at 2θ=32.26°, 34.44°, 36.72° and 48.52°, respectively. All these peaks could be indexed to a hexagonal wurtzite GaN phase with lattice constants of a=0.3186 nm and c=0.5178 nm, which are the same ones. as the reported value for bulk GaN[9]. No diffraction peaks of Ga_2O_3 or other impurities are found in any of our samples, suggesting that the surface of products is predominantly hexagonal wurtzite GaN.

2.2 SEM analysis

Fig.2a, b show the typical SEM images of the as-synthesized nanowires ammoniated at 950 °C at different magnifications. At low magnification, it can be clearly seen from Fig. 2a that the products consist of a large number of high-density nanowires interlaced with each other. Liquid droplets, which are the remarkable sign of the vapor-liquid-solid (VLS) mechanism, are found on the tips of some nanowires, as shown in the inset Fig. 2a. And further observation demonstrates that the nanowires possess a relatively smooth surface and a relatively straight morphology with diameters ranging from 40 nm to 100 nm and lengths typically up to 10 μm, indicating an aspect ratio about 100:1.

Fig.2c is the typical SEM image of GaN nanorods using TiO_2 as the intermediate layer[10]. The quality and quantity of the as-synthesized nanowires are better than those of Fig. 2c. In addition，no liquid droplets are found on the tips of the nanorods in Fig. 2c. So, the growth mechanisms are different for the two methods.

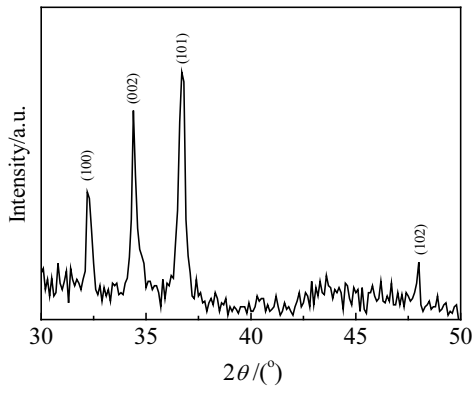

Fig.1 XRD pattern of the synthesized GaN nanowires

2.3 HRTEM analysis

The HRTEM images of a single nanowire are given in Fig. 3. Fig. 3a is the image at lower amplification. It reveals that the GaN nanowire with a uniform diameter of about 70 nm has clean and smooth surface morphology. The inset shows the selected area electron diffraction (SAED) pattern of the single nanowire, where $(0\bar{1}11)$, $(1\bar{1}01)$, $(10\bar{1}0)$ diffraction spots present, which can be indexed to the reflection of hexagonal wurtzite GaN single crystal. Fig.3b is the higher-amplification image of the single nanowire. The clear lattice fringes confirm that the nanowire is high quality hexagonal single-crystal GaN. The distance between the two fringes is 0.276 nm, which is corresponding to the plane distance of GaN (100), indicating the growth direction of the nanowire is perpendicular to the fringes of (100) plane.

2.4 PL analysis

The measurement of PL spectrum performed at room temperature is shown in Fig.4. A strong UV light emission peak at

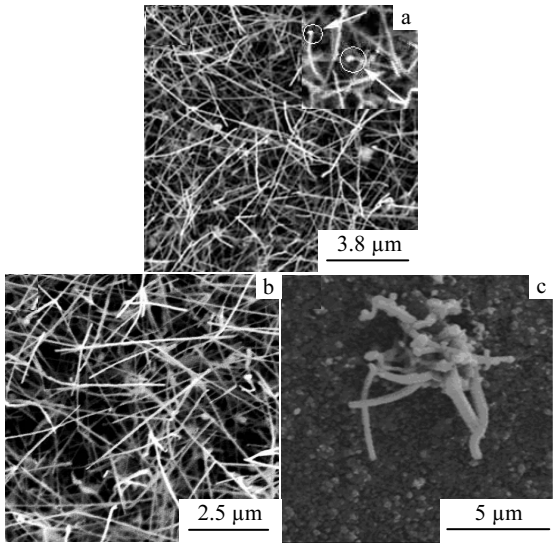

Fig.2 Typical SEM images of GaN nanomaterials at different magnifications: (a) low magnification; (b) higher magnification; and (c) image in Ref[10]

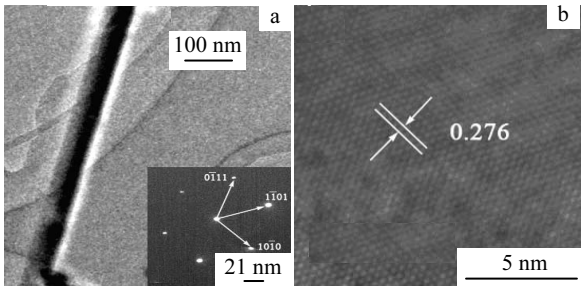

Fig.3 HRTEM images of a single GaN nanowires: (a) lower amplification and (b) higher-amplification

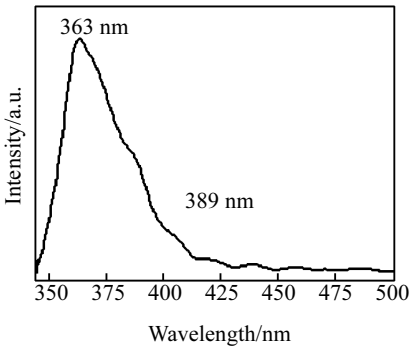

Fig.4 PL spectrum of the synthesized GaN nanowires

363 nm and a very weak light emission band centered at 389 nm can be observed. The UV light emission has tiny blue shift compared with that of bulk GaN[11]. The weak emission band centered at 389 nm might be due to the excitons bound to the surface or other structure defects[12]. However, further work is needed to study the PL mechanism of the GaN nanowires.

2.5 Discussion about growth process of GaN

Although the detailed growth mechanism of the GaN nanowires is still not fully understood, we might briefly explain the process based on the above observations. Ta is very important for the fabrication of GaN nanostructure. To text this, we also ammoniated Ga_2O_3/Ta films under the same condition, and no such nanowires were found. As the fluidization temperature of nanosized catalytic metal particles is lower than the melting point of bulk metal[13], the Ta film broke up, and then the liquid Ta nanodroplets which act as energetically favorable sites for absorption of gas-phase reactants are formed on the Si surface at high temperature. It is well known that Ga_2O_3 can decompose to gaseous Ga_2O or Ga at the temperature above 800 °C [14] and NH_3 decomposes stepwise to NH_2, NH, H_2 and N at 850 °C. Then the gaseous Ga_2O, the atomic Ga, the atomic N and NH_3 could be absorbed in above-mentioned sites to form Ta-Ga-N transition alloys. When the concentration of Ga-N exceeds a saturation point in the liquid phase Ta-Ga-N alloy droplet, GaN begins to grow from liquid phase and deposits to form nanowires. However, the growth mechanism needs to be further studied.

3 Conclusions

1) In summary, GaN nanowires can be prepared through ammoniating Ga_2O_3/Ta films on Si substrate at 950 °C for 10 min.

2) The nanowires are single-crystal wurtzite GaN with diameters ranging from 40 nm to 100 nm and lengths typically up to 10 μm.

3) The PL spectrum exhibited a strong emission peak at 363 nm.

References

1 Yi S N, Jong H N, Kwan H *et al*. *Appl Phys Lett*[J], 2007, 90: 101 901
2 Nakamura S. *Science*[J], 1998, 281: 956
3 Morales A M, Lieber C M. *Science*[J], 1998, 279: 208
4 Han W Q, Fan S S, Li Q Q *et al*. *Science*[J], 1997, 277: 12 879
5 Goldberger J, He R, Zhang Y. *Nature*[J], 2003, 422: 599
6 Duan X F, Lieber C M. *J Am Chem Soc*[J], 2000, 122: 188
7 Zhang J, Zhang L D, Wang X F *et al*. *J Chem Phys*[J], 2001, 115: 5714
8 Lyu S C, Cha O H, Suh E K *et al*. *J Chem Phys Lett*[J], 2003, 367: 136
9 Perlin P, Jauberthiecarillon C *et al*. *Phys Rev B*[J], 1992, 45: 83
10 Sun L, Xue C, Sun C *et al*. *Materials Letters*[J], 2007, 61: 5220
11 Monemar B. *Phys Rev B*[J], 1974, 10: 676
12 Korotkov R Y, Reshchikov M A, Wessels B W. *Physica B*[J], 1999, 273: 80
13 Kim T Y, Lee S H, Mo Y H *et al*. *J Crystal Growth*[J], 2003, 257: 97
14 Xu B S, Zhai L Y, Liang J *et al*. *J Crystal Growth*[J], 2006, 291: 34

钽催化磁控溅射法制备 GaN 纳米线

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摘　要：利用磁控溅射技术通过氨化 Ga_2O_3/Ta 薄膜，合成大量的一维单晶纤锌矿型氮化镓纳米线。用 X 射线衍射、扫描电子显微镜、高分辨透射电子显微镜，选区电子衍射和光致发光谱对制备的氮化镓进行了表征。结果表明：制备的 GaN 纳米线是六方纤锌矿结构，其直径大约 20~60 nm，其最大长度可达 10 μm 左右。室温下光致发光谱测试发现 363 nm 处的较强紫外发光峰。另外，简单讨论了氮化镓纳米线的生长机制。

关键词：纳米结构；氮化物；溅射

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