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Synthesis of GaN Nanorods with Herringbone Morphology*

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Abstract: Hexagonal GaN nanorods are synthesized on quartz substrates through ammoniating Ga_2O_3 thin films deposited by radio frequency magnetron sputtering. X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and photoluminescence (PL) are used to analyze the synthesized GaN nanorods. Among the products, one-dimensional GaN nanostructures owning protuberances on the surface are detected, which show interesting herringbone morphology. The analysis reveals that the herringbone GaN nanorods are polycrystalline composed of overlapping parallelepiped GaN nanocrystals arranged along the major axis. The large blue shift of yellow PL luminescence of the nanorods is observed at room temperature.

Key words: Ga_2O_3 thin films; GaN nanorods; ammoniate
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1 Introduction

Materials with nanotube and nanowire structures have been extensively studied for their interesting and novel properties from the reduced dimensions of these materials and their promising applications to new devices and technologies[1~3]. GaN is one of the most promising materials for the fabrication of optoelectronic devices operating in the blue and near-ultraviolet (UV) regions, because it has a large direct energy band gap of 3.39eV at room temperature[4~6]. Recently, one-dimensional GaN nanomaterials have received much interest for their potential applications in the development of nanometer optoelectronic devices[7,8]. Over the past few years, several methods have been used to synthesize GaN nanorods or nanowires. Han and his coworkers employed carbon-nanotube-confined reaction to fabricate GaN nanorods, from which blue light emission was observed[2]; Cheng and his coworkers assembled high ordered GaN nanowires with anodic alumina membranes[9]; Duang and Lieber, based on the vapor-liquid-solid (VLS) growth mechanism, developed a new method to fabricate GaN nanowires by laser abating a metal-containing target, in which the metal nanoparticles were used as catalysts[10]; in addition, sublimation method[11], direct reaction of metal gallium with ammonia[12,13], and hot filament chemical-vapor-deposition (CVD)[14] were also applied to synthesize GaN nanowires. Such achieve-

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ments of one-dimensional GaN nanomaterials mentioned above depended either on the assistance of a template or on a catalyst in the process of synthesis which would introduce contaminants unintentionally. Herein we present the successful synthesis of GaN nanorods through ammoniating Ga_2O_3 thin films deposited on quartz substrates by radio frequency (RF) magnetron sputtering without recourse to confined space of a template or involvement of a catalyst. Apart from the straight hexagonal GaN nanorods among the synthesized products, one-dimensional GaN nanostructures with herringbone morphology were observed for the first time. In this paper, we focus on the properties of the synthesized herringbone GaN nanorods.

2 Experiments

The Ga_2O_3 thin films were deposited on the cleaned quartz substrates using a JCK-500A radio frequency magnetron sputtering system. The fused quartz plates were cleaned using acetone, isopropyl alcohol, and deionized water before the deposition. The background pressure of the sputtering chamber was of about 5×10^{-4}Pa and the gas with a ration of Ar : N_2= 10 : 1 under 1Pa was introduced into the chamber during the sputtering process. The purity of both Ar and N_2 was 99.999%. The target was Ga_2O_3(99.999%) and the distance between target and the substrates was 80mm. The radio frequency and power of the sputtering were 13.56MHz and 150W, respectively.

The GaN nanorods were synthesized by ammoniating the Ga_2O_3 thin films in a high purity NH_3(99.999%) ambience with 300mL/min flow rate through a quartz tube. The temperature and duration of the ammoniating were 1000℃ and 10min, respectively.

The morphology and size distribution of samples were characterized using scanning electronic microscope (SEM, Hitachi H-8010). The structure of the rods was determined by an X-ray diffraction spectroscopy (XRD, Rigaku D/max-rB with CuKα line) and a Philips Tecnai-20U-TWIN high-resolution transmission electron microscopy (HRTEM). Photoluminescence (PL) spectra of the samples were measured in the FLS920 fluorescence spectrophotometer at room temperature.

3 Results and discussion

A typical XDR spectrum of the ammoniated products is shown in Fig. 1. The refraction peaks of (100), (002), (101), (102), (110), (103), (200), (112), (201), and (202) correspond to the hexagonal GaN wurtzite structure with lattice constants of a(= 0.318nm) and c(= 0.518nm), in agreement with published values[2] for GaN nanorods. No diffraction peaks corresponding to gallium oxide have been identified. The strong peaks of diffraction relative to the background signal suggest that the material is predominantly GaN in the wurtzite phase.

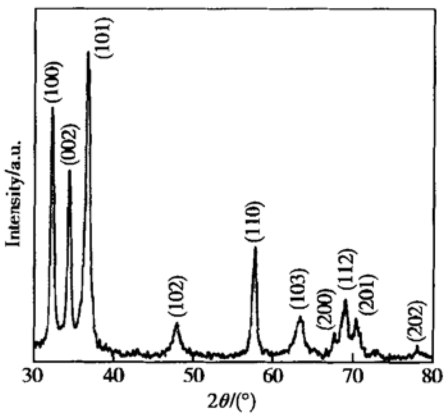

Fig. 1 XRD spectrum of the synthesized products at 1000℃ The numbers above the peaks correspond to the (*hkl*) values of the wurtzite GaN.

Figure 2 shows the typical SEM image of the synthesized nanorods. Most of the synthesized nanorods are straight and smooth, but a few have a faceted surface. Statistical survey shows that the diameters of the GaN nanorods are in the range of 10 to 90nm with an average value of about 60nm, and the lengthes are up to 50μm. A peculiar one-dimensional GaN nanostructure marked by the arrow is shown in the central section of the photo. The rod with a length of ~ 15μm has protuberances on the surface, which gives it an interesting herringbone appearance.

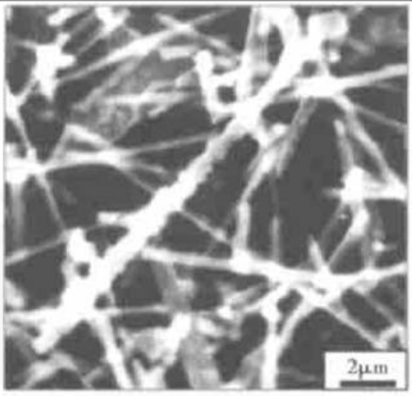

Fig. 2 SEM image of the GaN nanorods An individual herringbone nanorod are shown in the central section.

The detailed structure of the protuberances from the surface of the herringbone GaN nanorods was further revealed by HRTEM image. Figure 3 shows a high-resolution image of a herringbone nanorod in diameter of about 80nm whose morphology has the appearance of overlapping parallels

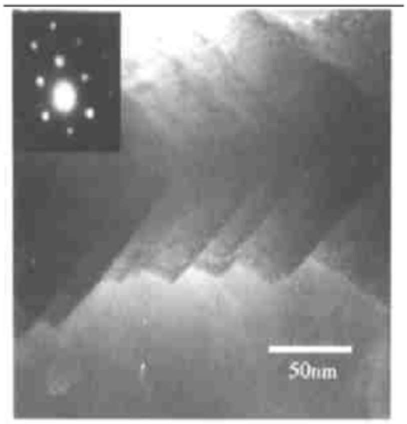

Fig. 3 HRTEM image from a herringbone GaN nanorod and the corresponding SAED pattern of individual crystallite

arranged along the major axis. No adherents such as metal catalyst particles have been detected at the end of the rod. Diffraction pattern recorded from an overlapping parallelepiped crystal particle with size of ~ 70nm × 70nm × 30nm in this sample is shown in the insert. The diffraction pattern indicates that the individual crystallites are single crystal.

The photoluminescence (PL) spectrum of the synthesized GaN nanorods, as shown in Figure 4, was measured at room temperature (22℃). The excitation wavelength at 280nm was used. The PL spectrum consists of one strong emission peak at 370nm and another emission peak at 466nm, which associated with the near-band-edge emission and the well-known yellow luminescence of wurtzite GaN crystal, respectively. Compared with the bulk GaN, the yellow luminescence of the synthesized nanorods had a large blue shift. In general consideration for PL spectra of one-dimensional nanostructure, the blue shift of the PL peaks is mainly attributed to the quantum confinement effect. However, the average diameter (~ 60nm) of GaN nanorods is not small enough to produce such a large blue shift via the quantum confinement effect. Defects, such as point defects and stack faults may be the reason of the large blue shift[15]. The herringbone GaN nanorods, which own peculiar polycrystalline structures, might induce the large blue shift in the PL of the GaN nanorods.

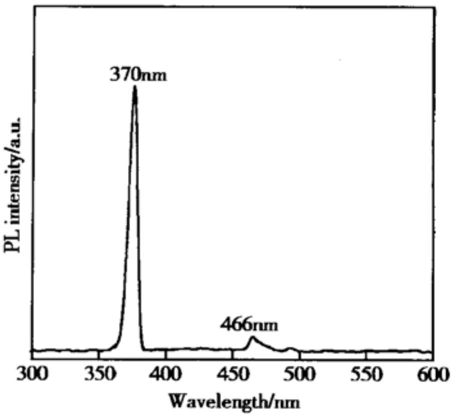

Fig. 4 Typical PL spectrum of GaN nanorods measured at room temperature

4 Conclusion

In summary, we developed a novel method of synthesizing GaN nanorods by ammoniating Ga_2O_3 thin films deposited on quartz by RF magnetron sputtering. Neither metal catalysts nor templates were used in this process. The herringbone one-dimensional GaN nanostructures, which are composed of overlapping parallelepiped hexagonal GaN nanocrystals arranged along the major axis, were observed for the first time, in addition to the straight and smooth GaN nanorods. The large blue shift of the yellow luminescence in GaN nanorods arising from the peculiar herringbone nanostructures was observed at room temperature. The synthesis of GaN nanorods and other one-dimensional GaN nanostructures are very important for the research of nanometer scale photonics and electronics and expected to open up many opportunities for further fundamental studies and applications of nanomaterials.

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References

[1] Morales A M, Lieber C M. A laser ablation method for the synthesis of crystalline semiconductor nanowires. Science, 1998, 279(9): 208

[2] Han Weiqiang, Fan Shoushan, Li Qunqing, et al. Synthesis of gallium nitride nanorods through a carbon nanotube-confined reaction. Science, 1997, 277(29): 1287

[3] An Xia, Zhuang Huizhao, Yang Yingge, et al. Effects of H_2 annealing on silicon carbide films grown on Si (111) by magnetron sputtering method. Chinese Journal of Semiconductors, 2002, 23(6): 593(in Chinese) [安霞, 庄惠照, 杨莺歌, 等. 在Si(111)上磁控溅射碳化硅薄膜的 H_2 退火效应. 半导体学报, 2002, 23(6): 593]

[4] Bi Zhaoxia, Zhang Rong, Li Weiping, et al. GaN MOCVD growth on $ZnAl_2O_4/\alpha$-Al_2O_3 substrates. Chinese Journal of Semiconductors, 2001, 22(8): 1025(in Chinese) [毕朝霞, 张荣, 李卫平, 等. $ZnAl_2O_4/\alpha$-Al_2O_3 衬底上 GaN 的生长. 半导体学报, 2001, 22(8): 1025]

[5] Fu Yi, Sun Yuanping, Shen Xiaoming, et al. Growth of cubic GaN by MOCVD at high temperature. Chinese Journal of Semiconductors, 2002, 23(2): 120

[6] Han Peide, Duan Xiaofeng, Sun Jialong, et al. Difference between GaN films grown on two opposite oriented c-Al_2O_3 substrates. Chinese Journal of Semiconductors, 2001, 22(8): 1030(in Chinese) [韩培德, 段晓峰, 孙家龙, 等. 在蓝宝石衬底两个相反 c 面同时生长氮化镓薄膜的差异. 半导体学报, 2001, 22(8): 1030]

[7] Ponce F A, Bour D P. Nitride-based semiconductors for blue and green light-emitting devices. Nature, 1997, 386(6624): 351

[8] Nakamura S. The roles of structural imperfections in InGaN-based blue light-emitting diodes and laser diodes. Science, 1998, 281: 956

[9] Cheng G S, Chen S H, Zhu X G, et al. Highly ordered nanostructures of sigle crystalline GaN nanowires. Mater Sci Eng A, 2000, 286: 165

[10] Duang X F, Lieber C M. Laser-assisted catalytic growth of single crystal GaN nanowires. J Am Chem Soc, 2000, 122: 188

[11] Li Y J, Qiao Z Y, Chen L X, et al. Morphologies of GaN one-dimensional materials. Appl Phys A, 2000, 71: 587

[12] He M, Minus I, Zhou P Z, et al. Growth of large-scale GaN nanowires and tubes by direct reaction of Ga with NH_3. Appl Phys Lett, 2000, 77(23): 3731

[13] Li J Y, Chen X L, Qiao Z Y, et al. Synthesis of aligned gallium nitride quasi-arrays. Appl Phys A, 2000, 71: 349

[14] Peng Y U, Zhou T X, Wang N, et al. Bulk-quantity GaN nanowires synthesized from hot filament chemical vapor deposition. Chem Phys Lett, 2000, 327: 263

[15] Shi S W, Zheng F Y, Wang N, et al. Oxide-assisted growth and optical characterization of gallium-arsenide nanowires. Appl Phys Lett, 2001, 78(21): 3304

合成鱼骨外形氮化镓纳米棒*

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摘要: 通过氨化射频溅射工艺生长 Ga_2O_3 薄膜, 在石英衬底上成功地合成了六方 GaN 纳米棒. 用 X 射线衍射(XRD)、扫描电镜(SEM)、高分辨率透射电镜(HRTEM)和光致发光光谱(PL)对生成的产物进行了分析. 合成的纳米棒中有部分一维线状结构表面有规则的突起, 呈现鱼骨外形. 这种具有青鱼骨外形的纳米棒由六方单晶 GaN 纳米晶粒沿轴向错落排列而成. 室温下观察到 GaN 纳米棒的黄光发射峰发生了大尺度的蓝移.

关键词: Ga_2O_3 薄膜; GaN 纳米棒; 氨化

PACC: 8115C; 8140G; 6170N; 6480

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