Rare Metal Materials and Engineering
Volume 47, Issue 1, January 2018
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2018, 47(1): 0043-0046.

ARTICLE

Growth and Excellent Field Emission Properties of GaN Nanopencils and Nanotowers

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Abstract: Gallium nitride (GaN) nanopencils and nanotowers have been synthesized by a chemical vapor deposition (CVD) method using the reaction of Ga_2O_3 and ammonia. The observed morphology of GaN nanopencils is divided into two parts: the bottom is a nanowire with large diameter; the top is a nanowire with small diameter. The observed morphology of GaN nanotowers is a layer structure. The formation mechanism of GaN nanopencils and nanotowers is a vapor-liquid-solid (VLS) mechanism. The turn on field of 2.6 V/μm is obtained for GaN nanopencils and the turn on field of 4.1 V/μm is obtained for GaN nanotowers, which are sufficient for field emission flat panel displays and cold electron sources in display devices. This growth of GaN nanopencils and nanotowers will facilitate flexible design of device architectures for nanoelectronics.

Key words: GaN; nanocomposite; field emission properties; functional applications

Gallium nitride (GaN) is a wide band gap (3.4 eV) semiconducting material that has excellent performance, such as optical properties, electrical properties, good thermal stability and mechanical properties. Therefore, GaN has a wide range of applications in optoelectronic and microelectronic devices[1-4]. GaN semiconductor material, a promising cathode material for field emission, has small electron affinity (2.7~3.3 eV), physical and chemical stability, and higher melting point (1500 ºC). GaN nanowires have excellent performance of field emission properties as a kind of one-dimensional nanomaterials with high aspect ratio, applied widely in field emission devices[5-8]. The field emission properties of GaN nanowires are not only related to ratio of length to diameter, but also related to morphology. For example, the needlelike GaN nanowires with bicrystalline structure can enhance the field emission properties, and the sharp ends and rough surfaces of the nanowires are responsible for their good field emission properties[9]. Grass-like, novel durian-like, and dandelion-like GaN nanostructure can improve the field emission characteristics as well[10-12].

In this paper, we have reported the fabrication of GaN nanopencils and nanotowers on a Pt-coated *n*-type Si (111) silicon substrate via CVD method by Ga_2O_3 and ammonia. As-synthesized GaN nanostructures are characterized by X-ray diffraction (XRD) and field emission scanning electron microscope (FESEM). The as-synthesized samples have exhibited impressive field emission properties with a turn-on field (2.6 V/μm and 4.1 V/μm), which will facilitate flexible design of device architectures for nanoelectronics.

1 Experiment

GaN nanopencils and nanotowers have been synthesized on Pt-coated *n*-type Si (111) substrate[13] via CVD method. (1) The fabrication experiment of GaN nanopencils: Ga_2O_3 powders and Pt-coated Si wafer were placed in a quartz boat in the distance of ~2 cm between them and were heated in a constant temperature zone of horizontal tube furnace, and then N_2 was introduced for a certain time to remove remaining gas. Subsequently, the furnace was heated to 1150 °C under a constant flow of NH_3 (400 mL/min) at the same reaction time (20 min). (2) The fabrication experiment of GaN nanotowers: The Ga_2O_3 and C powders were placed into a quartz boat, from which the Pt-coated Si substrate was placed 2 cm away.

Received date: January 12, 2017
Foundation item: National Natural Science Foundation of China (51042010)
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Then the quartz boat was transferred to the central of the horizontal CVD furnace. The horizontal CVD furnace chamber was purged with 300 mL/min of N_2 for 20 min. Next, the chamber was heated from room temperature to 1200 °C, at which Ar with 200 mL/min was firstly introduced in the system for 10 min and then 200 mL/min NH_3 gas was introduced, and maintained 15 min. After reaction, the furnace was cooled down naturally to room temperature, and light yellow products obtained on the substrates were collected and analyzed.

2 Results and Discussion

Fig.1 shows the XRD patterns of GaN nanopencils and nanotowers, which reveal the overall crystal structure and phase purity of the nanostructures. As can be seen from Fig.1a and 1b, the diffraction peaks (100), (002), (101), (102), (110), (103), (112), and (201) are completely consistent with standard card of GaN, and the resulting product has high purity of GaN wurtzite phase[13]. The random orientation of GaN nanowires were caused by lattice mismatch and thermal conductivity between GaN and Si substrate[14].

Electron microscopy observations illustrate that GaN nanostructures are distributed on silicon substrates, as shown in Fig.2. As can be seen from Fig.2a, the piles of GaN nanostructures aligned on the silicon substrate. The inset in Fig.2a is a pile of GaN nanostructure, which likes a hedgehog lying on the silicon substrate. Fig.2b shows a single GaN nanowire with a thin tip, which is like a pencil. Moreover, a Pt catalyst observed at the end of GaN nanowires indicates that the growth mechanism of GaN nanopencils belongs to VLS mechanism[15]. The diameter of GaN nanopencils decreases gradually from ~150 nm to ~50 nm along the wire axis, and the length of GaN nanopencils extends to ten micrometers. Morphology of the sample is similar to that of the GaN nanopencils which has been reported in our research group[15]; however, the diameter of the sample is smaller than that in Ref[15]. The main reason is that the ammonia flow is smaller than that in Ref[15]. As can be seen from Fig.2c, a number of GaN nanostructures are uniformly distributed on silicon substrates, and the length of GaN nanostructures extends to several micrometers. Fig.2d shows the high-magnification FESEM image of GaN nanostructures from Fig.2c. The morphology of GaN nanostructure is a layer sturucture, which is like a tower. The diameter of GaN nanotowers decreases gradually from ~200 nm to ~100 nm along the wire axis. Morphology of the sample is similar to that of the GaN nanowires with layer-structure which has been reported in our research group[13]; however, the diameter of the sample is smaller than that in Ref[13]. The main reason is that the time of ammonia is shorter than that in Ref[13]. The growth mechanism of GaN nanopencils and nanotowers is as the depiction in Ref[13,15].

The field emission properties of the samples were tested by field emission system shown in Fig.3. By defining[16], the turn on field is the electric field required to produce an emission current density of 0.01 mA/cm^2 whereas the threshold field is the electric field required to produce an emission current density of 1 mA/cm^2. The turn on field of 2.6 V/μm and threshold field of 7.1 V/μm are obtained from GaN

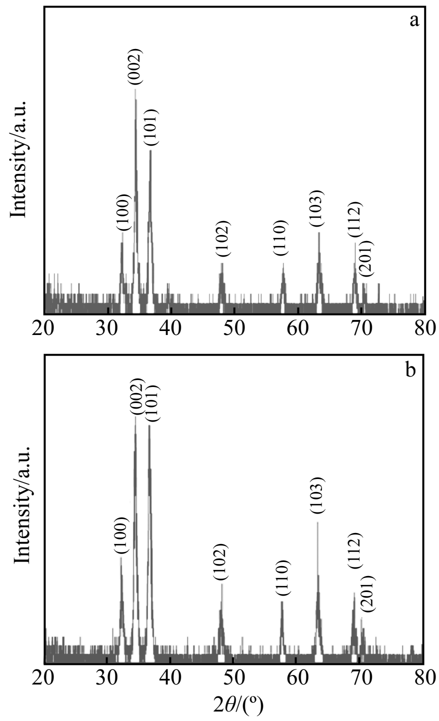

Fig.1 XRD patterns of GaN nanostructures: (a) GaN nanopencils and (b) GaN nanotowers

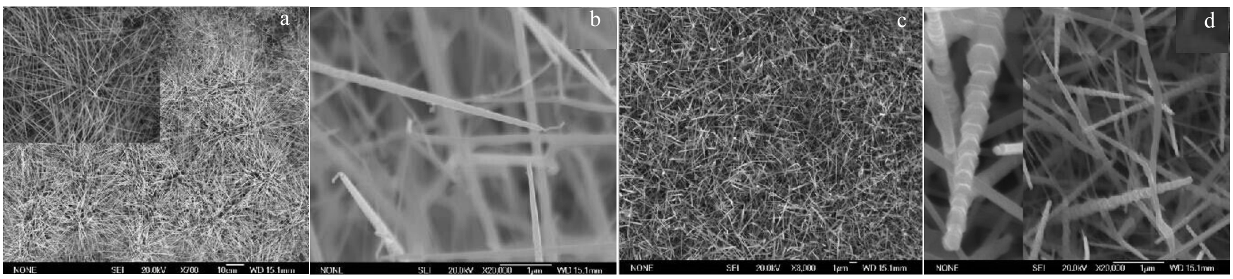

Fig.2 SEM images of GaN nanopencils (a, b) and GaN nanotowers (c, d)

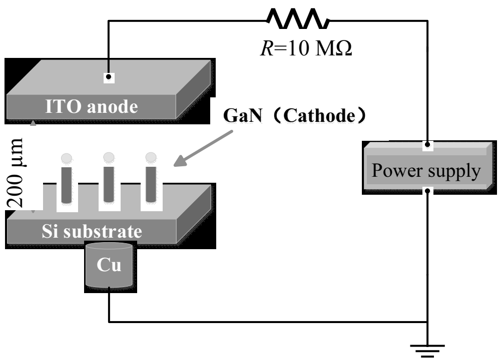

Fig.3 Schematic diagram of field-emission measurements

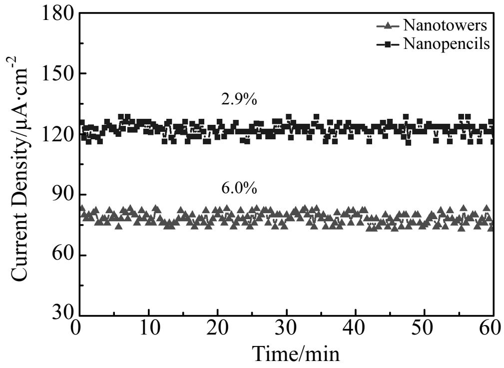

Fig.5 Field emission current density stability of GaN nanopencils and nanotowers

nanopencils as shown in Fig.4a. The turn on field of 4.1 V/μm and threshold field of 8.1 V/μm are obtained from GaN nanotowers as shown in Fig.4b. The field enhancement factors (β) have been calculated to be about 2025 and 1982 for the GaN nanopencils and nanotowers, respectively. The *F-N* curves inset in Fig.4a and Fig.4b are linear approximately, which indicate that the field electron emissions of the samples are caused by vacuum tunneling effect[16].

Fig.5 (blue line) shows the stability of GaN nanopencils within 60 min under an applied electric field of 4.25 V/μm. The initial current density and the average current density are 125.8 μA/cm^2 and 122.2 μA/cm^2, respectively. No notable current density degradation is observed, and the emission current fluctuation is as low as ~2.9 %. Fig.5 (red line) shows the stability of GaN nanotowers within 60 min under an applied electric field of 5.35 V/μm. The initial current density and the average current density are 83.0 and 78.1 μA/cm^2, respectively. No notable current density degradation is observed, and the emission current fluctuation is as low as ~6.0%. The highly stable field emission current makes GaN nanopencils and nanotowers as excellent candidates for the cold electron source for the flat display device. Compared with previous reported values of GaN nanostructure, the turn on field of GaN nanopencils is lower than Ref[5, 8-13,15-23]. We believe this result is due to (1) The morphology of GaN is like a hedgehog, and the sharp ends of GaN nanopencils benefit to electron emission; (2) The surface of the GaN nanotowers is a layer structure, so there are numerous edges on the surface of the GaN nanotowers. The numerous surface edges possess high field enhancement factors because the rough surface can remarkably enhance materials' field emission performance [24,25].

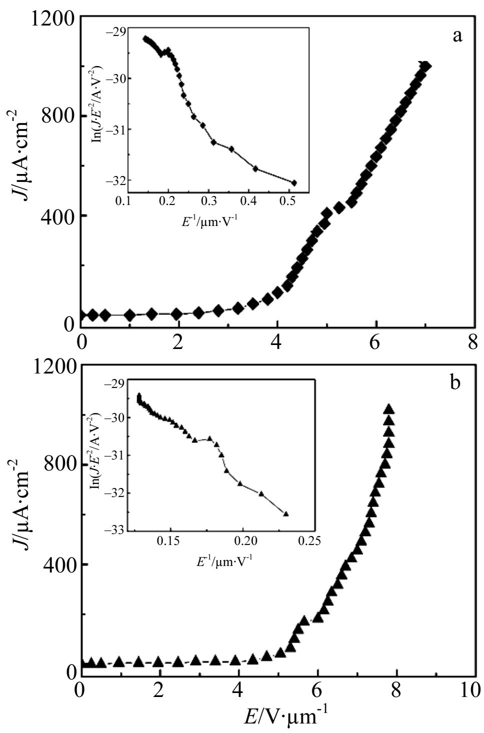

Fig.4 Field emission *J-E* curve and *F-N* curve of GaN nanopencils (a) and GaN nanotowers (b)

3 Conclusions

1) The observed morphology of GaN nanopencils is divided into two parts: the bottom is a nanowire with large diameter; the top is a nanowire with small diameter. The observed morphology of GaN nanotowers is a layer structure.

2) The formation mechanism of GaN nanopencils and nanotowers is a vapor-liquid-solid (VLS) mechanism.

3) GaN nanopencils film possesses a low turn-on field of 2.6 V/μm and GaN nanotowers film possesses a low turn-on field of 4.1 V/μm. The highly stable field emission current density makes nanopencils and nanotowers as a kind of excellent candidate of cold electron source for the flat display device. This growth of GaN nanopencils and nanotowers will facilitate flexible design of device architectures for nanoelectronics.

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氮化镓纳米铅笔与纳米塔制备及优异场发射性能研究

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摘　要：通过化学气相沉积法，用氧化镓和氨气反应成功制备出氮化镓纳米铅笔和纳米塔。通过扫描电镜表征发现氮化镓纳米铅笔分为两个部分：底部是一个大直径的纳米线，顶部是一个小直径的纳米线；氮化镓纳米塔为层状结构。氮化镓纳米铅笔和纳米塔的形成机理是气-液-固机制。场发射性能测试显示氮化镓纳米铅笔的开启电场为 2.6 V/μm，纳米塔的开启电场为 4.1 V/μm，这使得它们可以用于场发射平板显示及显示装置的冷阴极电子源，它们还可以使用于设计复杂纳米电子器件。

关键词：氮化镓；纳米复合材料；场发射；功能应用

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