

Needlelike Bicrystalline GaN Nanowires with Excellent Field Emission Properties

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Large-yield and crystalline GaN nanowires have been synthesized on a Si substrate via a simple thermal evaporation process. The majority of the GaN nanowires has bicrystalline structures with a needlelike shape, a triangular prism morphology, and a uniform diameter of ~ 100 nm. Field-emission measurements show that the bicrystalline GaN nanowires with sharp tips have a lower turn-on field of ~ 7.5 V/ μm and are good candidates for low-cost and large-area electron emitters. It is believed that the excellent field emission property is attributed to the bicrystalline structure defects and sharp tips.

Introduction

One-dimensional (1-D) nanostructured semiconductors have attracted extensive research interest due to their intriguing properties in optics, electronics, optoelectronics, and potential technological applications.^{1,2} Recently, various 1-D nanoscaled materials, such as nanowires, nanorods, nanoribbons (or nanobelts), and nanotubes, have been successfully synthesized via different routines. An interesting and peculiar morphology termed bicrystalline nanostructure has been observed as ZnS nanoribbons,³ Si,⁴ and SiC⁵ nanowires. The unusual bicrystalline nanostructure is an ideal model for basic understanding of the charge and mass transport along single defects in the restricted geometries, as well as the templates for novel device structures.⁴

As an important semiconductor, gallium nitride (GaN), with a wide direct band gap of 3.4 eV at room temperature, is of special interest and importance for its potential application in blue and ultraviolet light emitters and high temperature and high power optoelectronic devices, due to its high melting point, carrier mobility, and electrical break down field.^{6,7} So far, GaN nanostructured materials with various morphologies such as nanowires,⁸ nanorods,¹ nanobelts,⁹ and nanotubes¹⁰ have been successfully synthesized via different routines. Recently, the bicrystalline structure was also found in GaN nanorods prepared by physical vapor deposition.¹¹ However, no further details were reported for microstructure characterization and the dependence of properties on the bicrystalline structure for GaN nanostructured materials. In this paper, we report a novel bicrystalline structure observed in the needlelike GaN nanowires, and the effects of bicrystalline structure defects on field-emission properties for GaN nanowires are also investigated. That is fundamental for understanding the basic concepts and for manufacturing the nanodevices in the future.

Experimental Procedures

GaN bicrystalline nanowires reported here were synthesized via a simple thermal-evaporation process by directly reacting

the starting Ga₂O₃ powders with ammonia in a horizontal resistance. First, the reactants were mechanically mixed and then loaded into the Al₂O₃ boat. A piece of Si wafer coated with a Au film (~ 20 nm) was put on the Al₂O₃ boat, with the Au film directly facing the reactants. Then, the reactants loaded in a quartz tube were moved to a horizontal resistance furnace. When the temperature was increased to 873 K in flowing Ar at a rate of 200 mL/min, NH₃ gas with a rate of 300 mL/min was introduced to replace Ar. After reacting at 1423 K for 30 min, the whole system was cooled to room temperature in the protecting Ar gas. The product deposited on the Si wafer was collected and examined by an X-ray diffractometer (RINT 2200), scanning electron microscope (SEM, JSM-6700F), and transmission electron microscope (TEM, 3000 F) equipped with an X-ray energy dispersive spectrometer (EDS). Field-emission (FE) measurements for the as-synthesized products were conducted in a vacuum chamber at a pressure of 2×10^{-6} Torr at room temperature.

Results and Discussion

Figure 1a shows the X-ray diffraction (XRD) pattern of the as-synthesized product, indicating that the as-synthesized products are well-crystallized. The peaks in the XRD pattern could be well-indexed to wurtzite-type (hexagonal) GaN with lattice constants $a = 0.3185$ nm and $c = 0.5177$ nm. The peak with a strong reflection intensity centered at 70° comes from the Si substrate with a (100) orientation; the Au film could also be detected as displayed in the pattern. A representative low magnification scanning electron microscope (SEM) image of the GaN nanowires, shown in Figure 1b, reveals that GaN nanowire films deposited on the Si substrate with a uniform thickness of about hundreds of micrometers densely cover a large area of about 15×15 mm². Many Au particles are attached on the wires' end, suggesting a catalyzed growth process for these GaN wires. From the high-magnification SEM image, Figure 1c, it could be seen that the GaN nanowires possess a needlelike morphology with the diameter gradually decreasing from ~ 200 nm to ~ 10 nm along the wire axis; the length of the GaN nanowires could extend to several micrometers; the catalyst particles with an average diameter of ~ 10 nm

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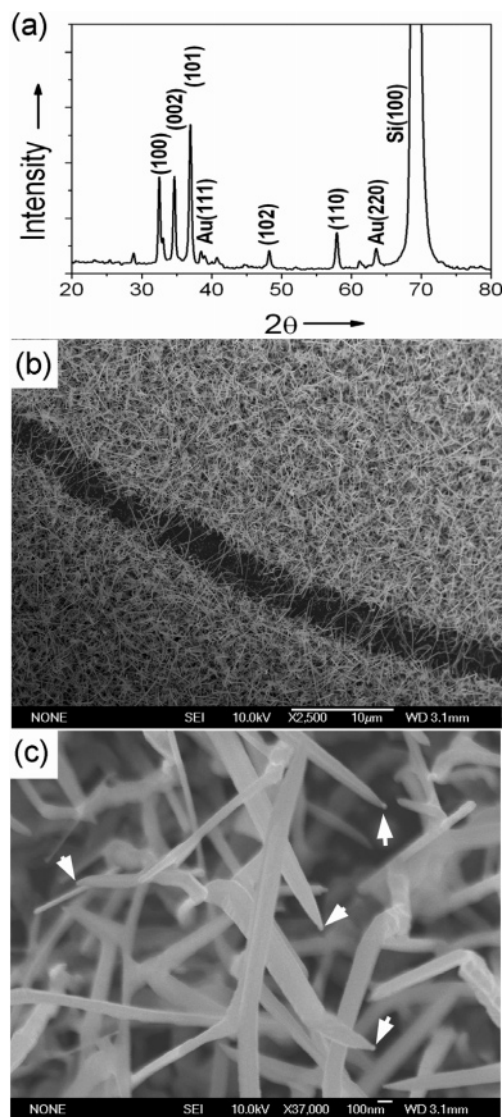


Figure 1. (a) XRD pattern of the as-synthesized GaN nanowires and (b and c) low magnification and magnified SEM images for the needlelike GaN nanowires.

could be clearly found to attach on the tip of the nanowires (as highlighted by the arrows in Figure 1c), which indicates that a well-known vapor–liquid–solid (V–L–S) growth mechanism is involved during the formation of GaN nanowires.

Transmission electron microscope (TEM) images including low-magnification images, high-resolution images, and electronic diffraction (ED) patterns of individual GaN nanowires further demonstrate the microstructures of these materials. Figure 2a shows a representative TEM image for a GaN nanowire. The unique morphology for the bicrystalline structure could be clearly observed for this GaN nanowire. A high-resolution TEM image for the GaN nanowire in this study is presented in Figure 2b. It could be seen that the (010) planes, with a d spacing of ~ 0.275 nm between the adjacent lattice fringes, display a perfect symmetry relationship with (103) as the mirror plane. The angle between the two (010) planes is obtained to be $\sim 150^\circ$, in good agreement with the calculated result. The symmetrical relationship for the bicrystalline GaN nanowire is also well-reflected in the selected area ED pattern, Figure 2c, in which the pattern taken along the $[30\bar{1}]$ axis reveals the good crystallinity of wurtzite-type GaN. Two sets of diffraction patterns, the black ones and the highlighted white ones, coexist and constitute the peculiar bicrystalline structure. The symmetrical relationship of

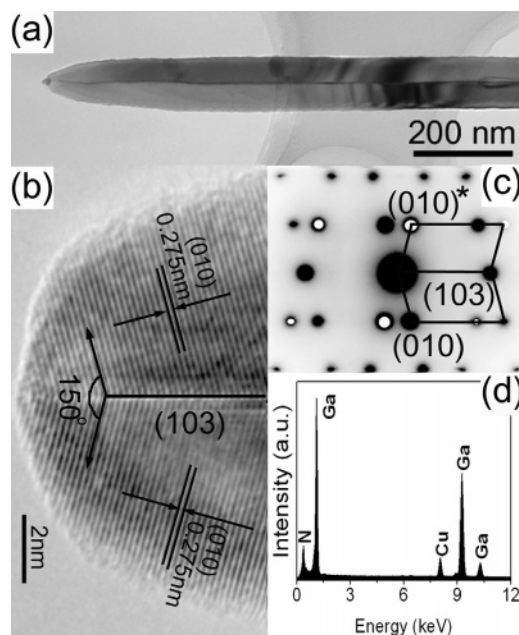


Figure 2. (a) Low magnification TEM image of the bicrystalline GaN nanowires. (b) HRTEM lattice image and (c) corresponding ED pattern taken along the $[30\bar{1}]$ direction of as-synthesized GaN nanowire shown in panel a. Inset of Figure 2c is a schematic model for the bicrystal. (d) EDS spectrum of the GaN nanowires.

the (010) planes reflected by the (103) plane is still well-described by the schematic model; the angle measured between the two (010) planes is consistent with that obtained from the HRTEM image. Several tens of individual GaN nanowires have been examined using this method, and all TEM images and ED patterns confirm the well-crystallized bicrystalline structure in as-synthesized GaN nanowires. The chemical composition of those GaN bicrystalline nanowires is further checked by EDS analysis, as shown in Figure 2d. It confirms that this GaN nanowire is only made of N and Ga (Cu peak originates from a TEM grid). The absence of O or other impurity signals indicates the high purity of the GaN nanowires.

One unique aspect of the current study was that the GaN bicrystalline nanowires prepared using the previous method possess a needlelike shape and a triangular prism morphology, as shown in the SEM image (Figure 1c) and the TEM image (Figure 2a). Figure 3a shows a low-magnification TEM image for a GaN nanowire. The plane facing the twin boundary is usually flat, smooth, and could be clearly observed. A typical HRTEM image, Figure 3b, shows the plane for a GaN nanowire; a well-crystallized characteristic and an interplanar distance of 0.275 nm could be clearly measured, corresponding to the (100) plane in the wurtzite-type GaN. The ED pattern shown in the inset of Figure 3b can be indexed to the $[001]$ zone axis of a GaN crystal. From Figure 3a, the catalyst particle attached on the wire's tip could also be clearly observed, as magnified in the inset. The catalyst particles could be easily found in the tip of each GaN nanowire and have an average diameter of ~ 10 nm. EDS nano-analysis performed on the particle, Figure 3c, confirms that it is mainly made up of Au. The signals of C, Cu, Ga, and Si in the EDS spectrum should result from the carbon film, TEM grid, Ga-contained reactant, and Si substrate, respectively.

On the basis of morphology and composition analysis for the GaN nanowires, the V–L–S growth mechanism is proposed for describing the growing process of the needlelike nanowires as follows: at the first stage, the Ga-containing reactant will

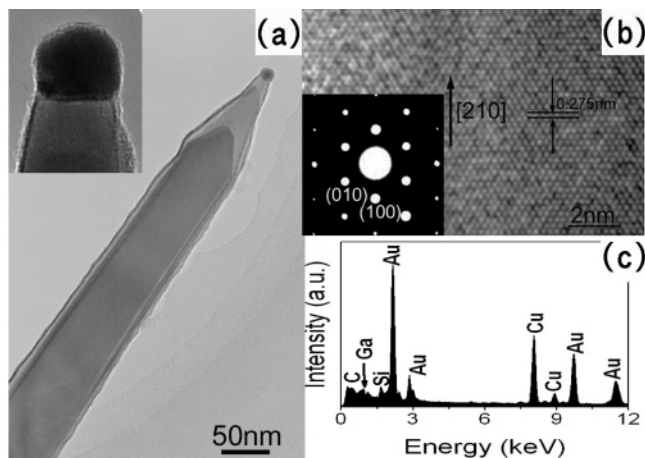
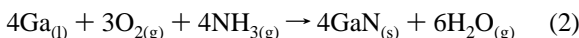
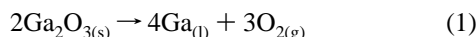


Figure 3. (a) Low magnification TEM image of the needlelike GaN nanowires taken from the bottom plane. Inset shows the magnified tip of GaN nanowires, and the catalyst particle can be clearly observed. (b) HRTEM lattice image for the nanowire shown in panel a. Inset is the ED pattern taken along the [001] direction. (c) EDS spectrum of the catalyst particle attached to the tip of the GaN nanowires.

decompose into some small liquid Ga droplets under the high temperature in NH_3 atmosphere, and then the Ga droplets will be transported to the surface of the Au film by the flowing gas. In the second stage, the liquid Ga droplets will react with NH_3 with the assistance of the Au catalyst and lead to the continuous growth of the GaN nanowires. Detailed growth processes for the GaN nanowires can be described by the following reactions:



It should be noted that the gas flowing rate here plays a key role in the formation of bicrystalline structures. Our extensive experiments indicate that the triangular prism-like bicrystalline structures could only be formed in the large flowing rate of NH_3 (200–400 mL/min). If the NH_3 with a lower flow rate is employed, the product shows nanowire-like morphology. As is known to all, the twin structure defect mainly resulted from the fluctuation of system energy during crystal growth, as reported in ref 12. From the viewpoint of thermal dynamics, it is plausible to assume that the higher gas flow rate will destroy the balance of the system energy for crystal growth during the stage of nucleation. Instability of the system energy will allow the nucleation to first occur at some energetically favorable sites, and then the atoms such as N will be absorbed to the surface of liquid Ga droplets to arrange in some lower energy planes along two different 1-D directions, as described in ref 11. With the subsequent growth, the needlelike bicrystalline GaN nanowires are formed as shown in Figure 2a.

The voltage–current characteristics of field emission from bicrystalline GaN layers are finally investigated. The whole FE measurement systems are composed of a vacuum chamber with a low pressure of $\sim 6 \times 10^{-6}$ Torr; a rodlike Cu probe with a cross-section area of 1 mm², which plays the role of anode; and the needlelike GaN nanowire film as the cathode. A dc voltage increasing from 0 to 1000 V is applied to the GaN film at different anode–cathode separations with an increasing voltage step of 20 V. Figure 4 shows the dependence of field emission–current density (J) on the macroscopic electric field (V) measured at an anode–cathode separation of 125 μm . A turn-on field as low as 7.5 V/ μm was obtained based on its definition for the field to produce an emission current density

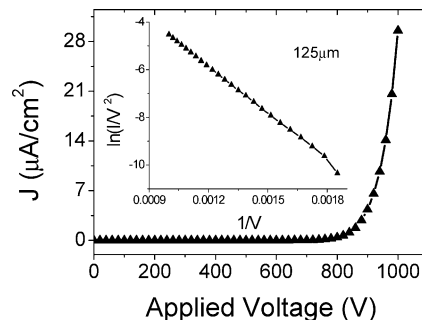


Figure 4. Field-emission J – V curve measured at 125 μm separation between Cu-probe and GaN film (inset is the corresponding F–N plot).

of 0.01 mA/cm². This value is a little lower than the one for the GaN nanowires with uniform diameters.¹³ It is believed that both the bicrystal twin defect and the needlelike morphology are responsible for the superior FE characteristic of GaN nanowires here. The twin boundary is expected to allow the electron emission at a lower voltage from GaN nanowires by increasing the field enhancement factor β , which shows strong dependence on the geometry of materials.¹⁴ Furthermore, the high aspect ratio resulting from the needlelike morphology also contributed to the geometry enhancement factor and greatly enhanced the electron emission as reported for herringbone-like GaN nanobelts.¹⁵ The inset of Figure 4 shows the corresponding Fowler-Nordheim (FN) plots of $\ln(J/E^2)$ versus E^{-1} to the J – E curve.¹⁶ The linearity of the F–N plots indicates that the emission of GaN nanowires is in good agreement with the field emission behavior and follows well with the F–N description.

Conclusion

To summarize, needlelike GaN bicrystalline nanowires with uniform morphology, size, and a large yield have been synthesized on a Au-coated Si substrate via a simple thermal evaporation process. The bicrystalline structure, composed of (001) planes and with a twin angle of $\sim 150^\circ$, was first observed in the wurtzite-type GaN hexagonal structure. Field-emission measurements show that the needlelike bicrystalline GaN nanowires have a lower turn-on field of ~ 7.5 V/ μm . Our experiments confirmed that the present needlelike bicrystalline GaN nanowires with a large yield can be selectively and repeatedly synthesized by adjusting the experimental parameters. This method opens a new way for the controllable growth of other semiconductor nanostructured materials with bicrystalline structures. Excellent field-emission properties suggest that needlelike GaN bicrystalline nanowires are good candidates for low-cost and large-area electron emitters.

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