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Physical and Electrical Properties of Chemical Vapor Grown GaN Nano/Microstructures

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Wurtzitic gallium nitride nano- and microleaves were controlled grown through a facile chemical vapor deposition method. This is the first report of GaN nanoleaves, a new morphology of GaN nanostructures. The as-grown GaN structures were characterized by means of X-ray powder diffraction, scanning electron microscopy, energy dispersive X-ray, transmission electron microscopy, and selected area electron diffraction. Raman scattering spectra of the GaN leaves were studied. Field effect transistors based on individual GaN nanoleaves were fabricated, and the electrical transport results revealed a pronounced n-type gating effect of the GaN nanostructures.

1. Introduction

Wurtzite structure gallium nitride, a particularly important III−V semiconductor with a direct band gap of 3.4 eV at room temperature, is an ideal material for use as UV or blue emitters, detectors, high-speed field-effect transistors, and high-temperature/high-power electronic devices.[1−6] In the past few years extensive research has been focused on the study of hexagonal GaN nanostuctures such as nanowires (nanorods),[1−6] nanotubes,[7,8] nanoribbons,[9] nanorings, [10] and so forth. Recently, the study on nano-GaN continues at a rapid pace for understanding fundamental optical properties, developing novel nanotechnological applications, and exploiting its significant potential for nano-optoelectronics and nanobiological devices.[11−20]

Nanoleaf is a kind of leaf-shaped nanostucture, and nanoleaves of some compounds such as TiO_2,[21] CuO,[22] C_3N_4,[23] GaAs, [24] and Bi_2S_3[25] have been reported. Herein, we demonstrate that through a facile chemical vapor deposition (CVD) method crystalline GaN nano- and microleaves were grown with controllable locations and shapes on amorphous silicon dioxide on silicon substrates. We believe

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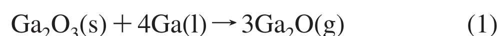
this is the first report of GaN nanoleaves, a new morphology of GaN nanostructures. The as-grown GaN structures were characterized, and their electrical transport and Raman scattering properties were investigated. Controlled growth of GaN nanoleaves will enrich the family of GaN nanostructures and have some potential nanotechnological applications.

2. Experimental Section

The GaN leaves were grown in a chemical vapor deposition system[6] consisting of a horizontal fused quartz tube inside a tube furnace as previously used to prepare GaN nanowires.[26] The source materials were a mixture of elemental gallium (99.999%, Alfa Aesar) and gallium oxide (β-Ga_2O_3) powders (99.999%, Alfa Aesar) with a weight ratio of about 3:2 (molar ratio of 4:1). The source materials reacted with ammonia according to the following scheme



$$Ga_2O_3(s) + 4Ga(l) \rightarrow 3Ga_2O(g) \quad (1)$$

$$Ga_2O(g) + 2NH_3(g) \rightarrow 2GaN(s) + H_2O(g) + 2H_2(g) \quad (2)$$

The substrates were n-type doped silicon with 1 μm thick thermal silicon oxide (Silicon Quest). By physically writing using an iron rod coated with nickel(II) nitrate solution, the catalyst was patterned on an unpolished surface of the substrates. The catalyst-patterned substrates and source materials (precursors) were loaded into a fused quartz boat with a separation of 8−12 cm. The boat was placed inside the horizontal fused quartz tube with the precursors located at the center, the highest temperature zone of the tube furnace. First, the quartz tube was purged through a steady flow of argon (99.99%, National Specialty Gases) at ~1000 sccm for 15 min. Then the furnace was heated under the flow of argon. When 780 °C was reached, a flow of ammonia (99.99%, National Specialty Gases) of about 40 sccm was switched on. The furnace temperature was then raised to 950 °C and kept constant for 3 h. Finally, the furnace was switched off and allowed to cool to room temperature quickly. In order to protect the as-grown GaN from decomposition, the flow of ammonia was maintained during the cooling process.

The morphologies, phase purity, composition, and crystal structure of the as-grown samples were characterized by field emission scanning electron microscopy (FESEM, Philips FEI XL30SFEG), X-ray powder diffraction (XRD, Rigaku Multiflex X-ray diffractometer), transmission electron microscopy (TEM, JEM-2100F FAST TEM), and Raman scattering spectrometry (Jobin Yvon Horiba LabRam-IR systerm).

The individual GaN nanoleaf field effect transistors (FETs) were fabricated by the e-beam lithographic technique[11] described as follows. First, the as-grown GaN nanoleaves were removed from the substrate to form a suspension in acetone by ultrasoundic agitation, and then the suspension of the GaN nanostructures was dispersed on the cleaned 1 μm thick thermal oxide n-type silicon wafers (Silicon Quest). The wafers were cleaned using hot piranha solution, a mixture of 1 part concentrated hydrogen peroxide and 2 parts concentrated H_2SO_4. After that, poly(methyl methacrylate) (PMMA, MW = 200 000 and MW = 950 000) resist layers were spin coated on the wafers, and the patterns were defined on the resist layers by electron irradiation carried out in a SEM (Philips FEI XL30SFEG) at 30 kV. Then, development was made with 1:3 methyl isobutyl ketone (MIBK)/isopropanol solution. After development, Cr/Au (15/45 nm) films were thermally evaporated on the resist, and final pattern formation was accomplished by lift off in acetone. The devices were imaged before the measurement to ensure a single GaN nanoleaf between two metal electrodes. Electrical transport measurements were performed at room temperature on a home-built system that contained two source measure units for source drain and source gate voltages (Keithley 2400 source meters) and a computer-controlled Labview interface.

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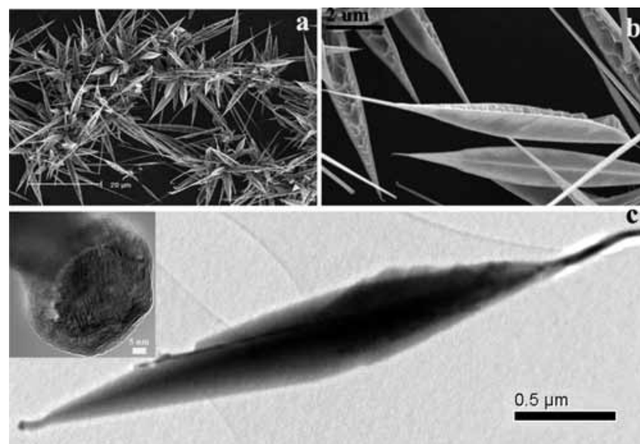

Figure 1. (a) Low-magnification FESEM image of the GaN leaves, and the scale bar is 20 μm. (b) High-magnification FESEM image of the GaN leaves. (c) TEM image of a GaN nanoleaf. (Inset) HRTEM image of the catalyst tip, and the scale bar is 5nm.

3. Results and Discussion

Figure 1a shows a low-magnification FESEM image of the as-grown GaN. It demonstrates that the product consists almost exclusively of leaf-like GaN nano- and microstructures, and most of the GaN leaves are open peapod shaped. The GaN structures were grown with controllable position and only grown on the sites with catalyst. Figure 1b is a high-magnification FESEM image of the GaN structures. It reveals that one side of the leaves is smooth and the other side is rough. The length of the leaves is from several to ~10 μm and the thickness from several tens to hundreds nanometers. The leaves have a nanoparticle attached at one end and a nanowire-like leafstalk at the other end (to connect the substrate surface). Energy dispersive X-ray (EDX) analysis indicates the particles contain catalyst (NiO) (see Figure S1 in the Supporting Information). Figure 1c shows a TEM image of a GaN nanoleaf, and the diameter of the nanoleaf's stalk is 45 nm. The inset of Figure 1c is a high-resolution TEM image of the catalyst particle.

We found that the shapes of the GaN structures could be controlled through adjusting the distance between the substrates and the precursor materials. When the distance between the substrate and the precursors increases, the structures change regularly to longer and narrower structures. Figure 2 is a FESEM image of the "lean" GaN leaves deposited on a substrate ~11 cm downstream from the precursors. The "lean" GaN leaves shown in Figure 2 were simultaneously grown in the same run with the "fat" ones shown in Figure 1, and the distance between the two kinds of leaves is ~3 cm.

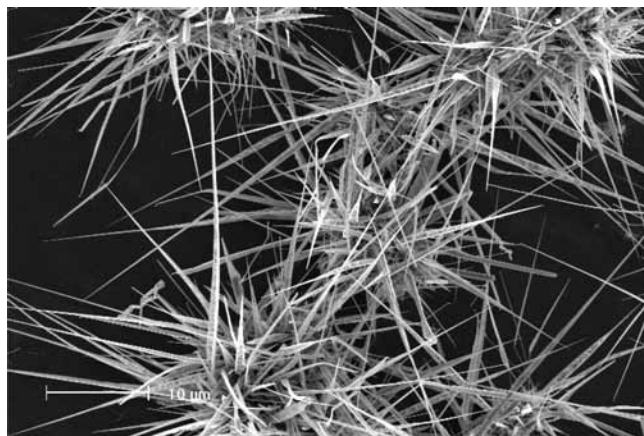

Figure 2. FESEM image of the "lean" GaN leaves, and the scale bar is 10 μm.

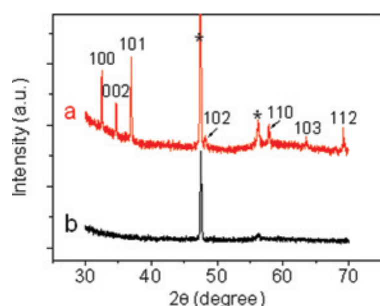

Figure 3. Room-temperature XRD patterns measured using Cu Kα radiation: (a) as-grown GaN leaves on a substrate (the peaks marked with an asterisk in the XRD pattern are from the substrates), and (b) a blank substrate without growing the GaN leaves.

X-ray powder diffraction (XRD) measurements were performed on the samples to assess the overall crystal structure and phase purity of the products. Figure 3a shows a typical powder XRD pattern of the as-grown GaN structures, and the diffraction peaks in Figure 3a were indexed to a hexagonal wurtzite structure of GaN with lattice constants of $a = 0.318$ nm and $c = 0.518$ nm. The data are in good agreement with the reported values of hexagonal GaN (2000 Joint Committee on Powder Diffraction Standards (JCPDS) Card No. 50-0792). The peaks marked with an asterisk in the Figure 3a are from the substrates. The XRD result reveals that the as-grown structures are composed of pure hexagonal structure GaN. To verify the unknown peaks in Figure 3a are from the substrate, an XRD pattern from a blank substrate is shown in Figure 3b, and it validates our hypothesis.

The structure of the GaN was further characterized by high-resolution TEM (HRTEM) and selected area electron diffraction (SAED). Figure 4 is an HRTEM image taken from a GaN nanoleaf, and the two-dimensional atomic structure image can be clearly observed with resolved *d* spacings of 0.276 and 0.244 nm for (100) and (01−1) planes, respectively. The GaN nanoleaves grow along the [01−1] direction. The inset (top right) of Figure 4 is the SAED pattern along the [011] direction. The pattern can be indexed based on a hexagonal cell with lattice parameters of $a = 0.32$ nm and $c = 0.52$ nm, consistent with the above X-ray results. Both

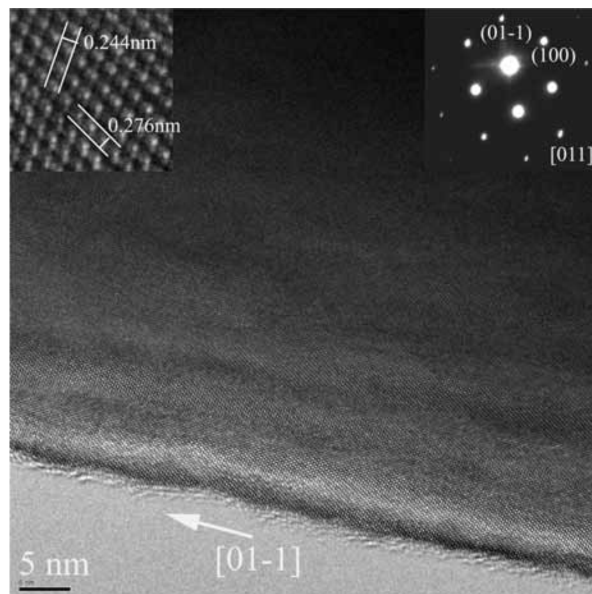

Figure 4. HRTEM image taken from a GaN nanoleaf. (Top left) Lattice-resolved HRTEM image of the nanoleaf. (Top right) Corresponding SAED pattern of the nanoleaf.

HRTEM and SAED results demonstrate that the nanoleaves are single crystals with a wurtzite structure.

The Raman scattering spectrum is also a very useful tool for structure characterization of nanomaterials. Wurtzite structure GaN possesses four atoms per primitive cell, and the space group of the wurtzite structure is C_{6v}^4 ($P6_3mc$) with all atoms occupying the C_{3v} sites. According to the factor group analysis, single-crystal GaN possesses eight sets of optical phonon modes near the zone center. The modes are classified into Raman allowed ($A_1 + E_1 + 2E_2$), infrared allowed ($A_1 + E_1$), and both Raman and infrared silent ($2B_1$). The A_1 and E_1 modes, corresponding to optical phonons, will split into a longitudinal-optical (LO) and a transverse-optical (TO) component due to the macroscopic electrical field associated with the longitudinal vibration.[27,28]

Figure 5 is a Raman spectrum of the GaN structures at frequencies that ranged from 100 to 1000 cm^{-1}. Four first-order Raman-active phonon bands of wurtzite structure GaN are observed. The most intense peak at 567 cm^{-1} corresponds to no-polar optical phonon E_2 (high) of wurtzitic GaN, and it reflects the characteristic of the hexagonal crystal phase of the GaN structures. Other three observed Raman-active phonon bands at 143, 529, and 726 cm^{-1} agree with phonon vibration frequencies of E_2 (low), A_1 (TO), and A_1 (LO) of wurtzitic GaN, respectively. The data agree with that of a previous report on hexagonal GaN nanowires.[4] There are two additional Raman modes at 422 and ~660 cm^{-1}. These two modes are forbidden with the C_{6v}^4 space group in first-order Raman scattering at the zone center, and they were also observed on hexagonal GaN nanowires.[4] The peak mode at 422 cm^{-1} can be attributed to an overtone of transverse-

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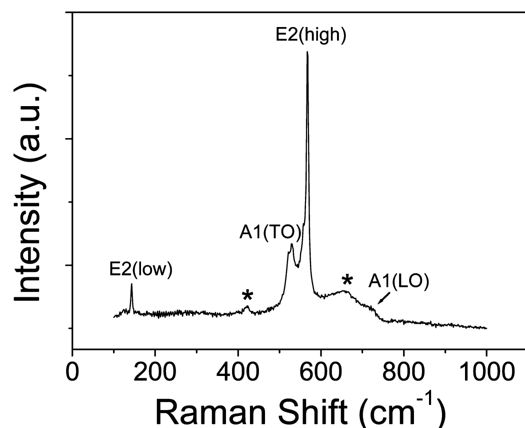

Figure 5. Room-temperature Raman spectrum of the GaN leaves.

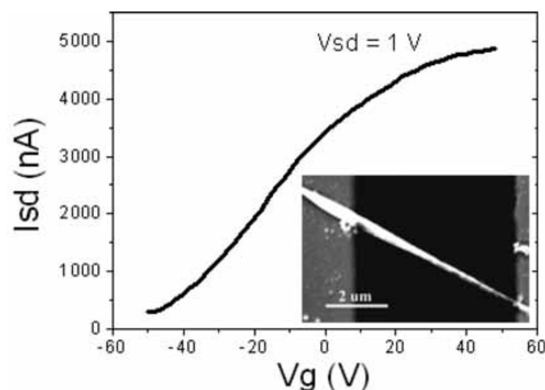

Figure 6. Room-temperature I_{sd} vs V_g curve recorded at V_{sd} = 1 V from an individual GaN nanoleaf FET. (Inset) FESEM image of the individual GaN nanoleaf FET, and the scale bar is 2 μm.

acoustic phonons at the symmetry point *M* in the Brillouin zone of wurtzitic GaN.[4,29] The broad band peaked around 660 cm^{-1} is assigned to a defect level below the GaN conduction band minimum.[4]

Unlike the solution method grown nanoleaves of TiO_2,[21] CuO,[22] C_3N_4,[23] and Bi_2S_3,[25] the GaN leaves reported here have a nanoparticle attached at the tip and a nanowire-like leafstalk at the end to connect the substrate surface. Yang et al. suggested the "leaf-shaped" carbon nitride nanostructures were formed by self-assembly of carbon nitride nanorods because the TEM images in their paper revealed the carbon nitride nanoleaf structures were composed of numerous smaller nanorods.[23] In view of Figure 1c, it is evident that the GaN leaves grow via a different mechanism. A vapor−liquid−solid (VLS) mechanism is common for growth of one-dimensional semiconductor nanowires.[30] There are two typical pieces of evidence in VLS growth: liquid catalyst particles act as the energetically favored sites for absorption of gas-phase reactants and catalyst particles are typically detected at tips of the one-dimensional materials.[30] Typical evidence of the VLS mechanism in GaN leaf growth suggests that the longitudinal (axial) direction growth of the GaN structures reported here occurs via a VLS mechanism. It is known that transition-metal oxides such as nickel and iron oxide can catalyze VLS growth of GaN nanowires.[3,26] As the catalyst precursor, nickel(II) nitrate decomposes to produce nickel(II) oxide at high temperature and nickel(II) oxide catalyzes the VLS growth of the GaN structures. The axial VLS growth of the GaN leaves is confirmed with two typical pieces of evidence as follows. (1) The GaN structures were grown only on the sites with the catalyst precursor nickel(II) nitrate. That is, nothing grows in the absence of the catalyst particles and catalyst is a requirement for growth. (2) Catalyst particles at one end of the leaves can be observed, and EDX analysis indicates the particles contain elements nickel and oxygen (see Figure S1 in the Supporting Information). At the same time as the leaf grows via the VLS mechanism along its axial direction, a vapor−solid (VS) growth along its lateral (radial) direction exists.[31,32] The longitudinal VLS growth influences the lateral VS growth, and an axial perturbation due to fluctuation of growth conditions may cause the bulging of middle region of the structures and result in a leaf-like GaN morphology.[32] A more detailed lateral growth mechanism of the GaN leaves needs further systematic studies.

Since the purpose to grow and study GaN nanomaterials is for their potential applications, individual GaN nanoleave field effect transistors (FETs) were fabricated and their electrical properties measured. Figure 6 shows a source drain current versus gate voltage ($I_{sd}-V_g$) curve obtained from an individual GaN nanoleave field effect transistor (FET) measured at V_{sd} = 1 V. It indicates that the GaN nanoleaves have a pronounced n-type gating effect. The devices operate as n-channel metal-oxide-semiconductor FETs and contain possibilities for applications. This n-type behavior in nominally undoped GaN is believed to be due to the nitrogen vacancies and/or oxygen impurities.[5,33] The inset of Figure 6 is an FESEM image of the individual GaN nanoleaf FET, and the length of the nanoleaf between two electrodes is 6 μm.

4. Conclusions

Hexagonal GaN leaves were grown with controllable locations and shapes on amorphous substrates through a facile CVD process. They were characterized by means of SEM, XRD, EDX, TEM, HRTEM, and SAED. The SEM images show that the product consists almost exclusively of peapod-shaped GaN leaves, and the GaN structures were grown only on the areas with catalysts. XRD, HRTEM, and SAED revealed the leaves were wurtzite structure single-crystalline GaN. Raman scattering spectra of the GaN structures were studied. Four first-order modes of hexagonal GaN at 143, 529, 567, and 726 cm^{-1} were observed, and two additional phonon bands at 422 and 660 cm^{-1} appeared. FETs based on individual nanoleaves were fabricated, and electrical transport measurements reveal that the GaN

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nanoleaves show a pronounced n-type gating effect and the devices operate as n-channel metal-oxide-semiconductor FETs. The controlled growth of GaN nanoleaves will enrich the family of GaN nanostructures and have some potential applications in the novel nanotechnological field.

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Supporting Information Available: EDX spectrum from a catalyst tip of a GaN leaf. This material is available free of charge via the Internet at http://pubs.acs.org.

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