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Metalorganic Chemical Vapor Deposition Route to GaN Nanowires with Triangular Cross Sections

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ABSTRACT

High-quality gallium nitride nanowires have been synthesized via metal-initiated metalorganic chemical vapor deposition for the first time. Excellent substrate coverage was observed for wires prepared on silicon, *c*-plane, and *a*-plane sapphire substrates. The wires were formed via the vapor−liquid−solid mechanism with gold, iron, or nickel as growth initiators and were found to have widths of 15-200 nm. Transmission electron microscopy confirmed that the wires were single-crystalline and were oriented predominantly along the [210] or [110] direction. Wires growing along the [210] orientation were found to have triangular cross-sections. Transport measurements confirmed that the wires were n-type and had electron mobilities of ∼65 cm²/V·s. Photoluminescence measurements showed band edge emission at 3.35 eV (at 5 K), with a marked absence of low-energy emission from impurity defects.

Single-crystalline 1D semiconductor nanostructures have received an enormous amount of attention as building blocks for future nanotechnologies.[1] Gallium nitride is a robust wide-band-gap semiconductor. With a high melting point, high carrier mobility, and high electrical breakdown field, it is a prime candidate for use in future high-performance, high-power optoelectronic devices.[2] Single-crystalline gallium nitride nanowires and nanotubes[3] show promise for realizing photonic and biological nanodevices such as blue-light-emitting diodes (LEDs), short-wavelength ultraviolet nanolasers,[4,5] and nanofluidic biochemical sensors.

Virtually all reported synthetic schemes for GaN-based nanowires to date have employed either laser ablation,[6,7] chemical vapor transport,[2,5,8−10] or hydride vapor epitaxy.[11] Most of these processes use Ga metal as the high-temperature vapor source. Metals such as Ni, Fe, and Au have been used as initiators for vapor−liquid−solid (VLS) nanowire[5−10] growth, although self-catalytic VLS or a direct vapor−solid process can also generate nanowires in this system.[12] The use of a solid Ga source, although technically simple, often yields noncontinuous and nonconstant vapor pressure and is difficult to implement in a continuous-flow reactor. While the growth of GaN thin films predominantly uses metalorganic chemical vapor deposition (MOCVD) process, so far there are no reports on the VLS growth of GaN nanowires using MOCVD. This effort, if successful, would immediately enable the integration of GaN thin film and nanowire technology on the same technical platform. Here we report for the first time the synthesis and characterization of GaN nanowires using a metal-initiated MOCVD approach. Trimethylgallium (TMG) and ammonia source materials were used as Ga and N precursors. A 2−10-nm thin film of Ni, Fe, or Au was thermally evaporated onto a silicon substrate or *c*-plane and *a*-plane sapphire substrates. Subsequent vapor−liquid−solid growth of GaN nanowires occurred at a substrate temperature of 800−1000 °C. The reaction was carried out in an oxygen-free environment at atmospheric pressure. TMG was kept cool in a −10 °C temperature bath. Nitrogen, used as a carrier gas, was percolated through the TMG precursor and coupled with a second nitrogen line to give a total nitrogen flow rate of 250 sccm. These were supplied via a 4-mm i.d. quartz tube. Hydrogen and ammonia sources were supplied via a 22-mm i.d. outer quartz tube at a total flow rate of ∼155 sccm. The placement of the substrates relative to the organic precursor outlet was relatively unimportant, showing thick wire coverage on substrates placed from 1 to 10 cm away. The deposition generally took 5−30 min.

Field-emission scanning electron microscopy (FE-SEM) was used to investigate the nanowire length, shape, and overall substrate coverage. Figure 1a shows an overview of

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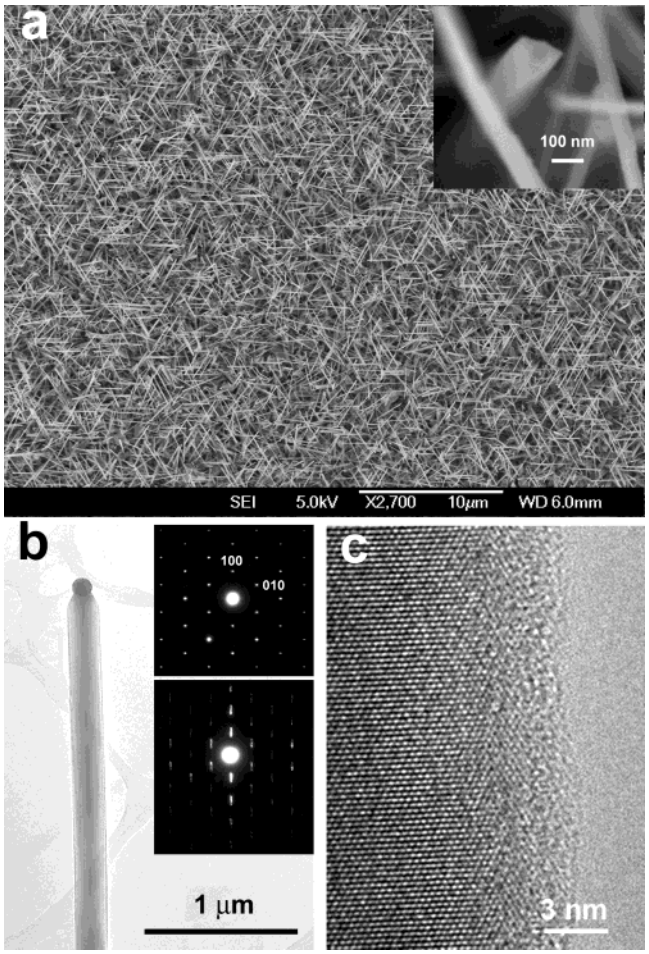

Figure 1. (a) FESEM image of the GaN nanowires grown on a gold-coated *c*-plane sapphire substrate. The inset shows a nanowire with its triangular cross section. (b) TEM image of a GaN nanowire with a gold metal alloy droplet on its tip. Insets are electron diffraction patterns taken along the [001] zone axis. The lower inset is the same electron diffraction pattern but purposely defocused to reveal the wire growth direction. (c) Lattice-resolved TEM image of the nanowire.

GaN nanowire coverage on a gold-coated *c*-plane sapphire substrate. The nanowires have diameters of 15−100 nm and lengths of 1−5 μm. It is also observed that there are preferred nanowire orientations on this substrate, indicating that the epitaxial growth of nanowires on a sapphire substrate is possible. X-ray diffraction recorded on the nanowire arrays can be readily indexed to the wurtzite GaN structure with lattice constants of $a = 0.319$ nm and $c = 0.519$ nm. Interestingly, many of these nanowires have triangular cross sections. Figure 1a (inset) shows an SEM image of a GaN nanowire where two features are apparent: a spherical metal droplet and a triangular cross section.

These nanowires were dispersed on transmission electron microscopy (TEM) grids to carry out additional structural and compositional analyses. Figure 1b shows a TEM image of an individual GaN nanowire, where a metal droplet can be clearly seen on its tip. The composition of the Au metal tip is confirmed with energy-dispersive X-ray spectroscopy. Electron diffraction (insets) along the [001] zone axis indicates that the nanowire grows perpendicular to (100) crystal planes. Figure 1c shows a high-resolution TEM image of the nanowire, showing exactly the (100) lattice plane perpendicular to the wire axis. In addition, electron energy-loss spectroscopy analysis (EELS, Supporting Information) clearly shows the nitrogen peak and the absence of an oxygen peak, confirming the compositional purity of the nanowires. Extensive TEM characterization reveals that the [210] direction is the predominant growth direction, but we have also observed that for a small faction of the nanowires the wire axis can be normal to the (014) or (112) plane and other high-index lattice planes.

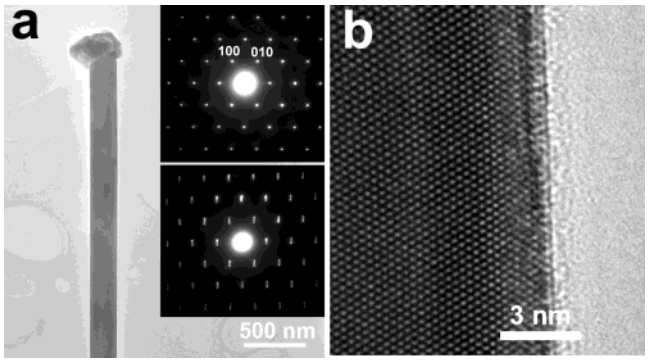

Figure 2. (a) TEM image of a GaN nanowire with an iron metal alloy droplet on its tip. Insets are electron diffraction patterns taken along the [001] zone axis. (b) Lattice-resolved TEM image of the nanowire.

Fe and Ni were also used as metal initiators for GaN nanowire growth. For wires grown on an iron-coated sapphire substrate, the diameter and length are 15−200 nm and 5−20 μm, respectively. However, we found the predominant nanowire growth direction to be [110] instead of [210]. Figure 2a shows a TEM image of such a GaN nanowire with an iron alloy droplet on its tip. Insets show the electron diffraction taken along the [001] zone axis, indicating a [110] growth direction. Figure 2b is the corresponding high-resolution TEM image, showing the (110) lattice plane perpendicular to the wire axis. A global TEM survey of these Fe-initiated GaN nanowires also reveals that a small percentage of the nanowires grow normal to other lattice planes, including the (111) plane.

Figure 3a shows an SEM image of GaN nanowires grown on a Ni-coated sapphire substrate. These wires were also observed to have triangular cross sections with 15- to 100-nm widths and lengths greater than 5 μm. Lattice-resolved, high-resolution TEM images (Figure 3b and c) and electron diffraction data (inset) showed that the nanowires are single-crystalline with the wire axis oriented along the crystallographic [210] direction, the same as for Au-initiated GaN nanowires.

Figure 3d−e shows close-up TEM views of the triangular cross sections of the GaN nanowires. We emphasize that these triangular cross sections are not equilateral (i.e, the observation of these triangular cross sections is not a result of viewing along the 6-fold crystallographic symmetry axis (*c* axis)). Most of these nanowires indeed grow along the [210] direction. This is clearly demonstrated by taking electron diffraction perpendicular to the cross section as

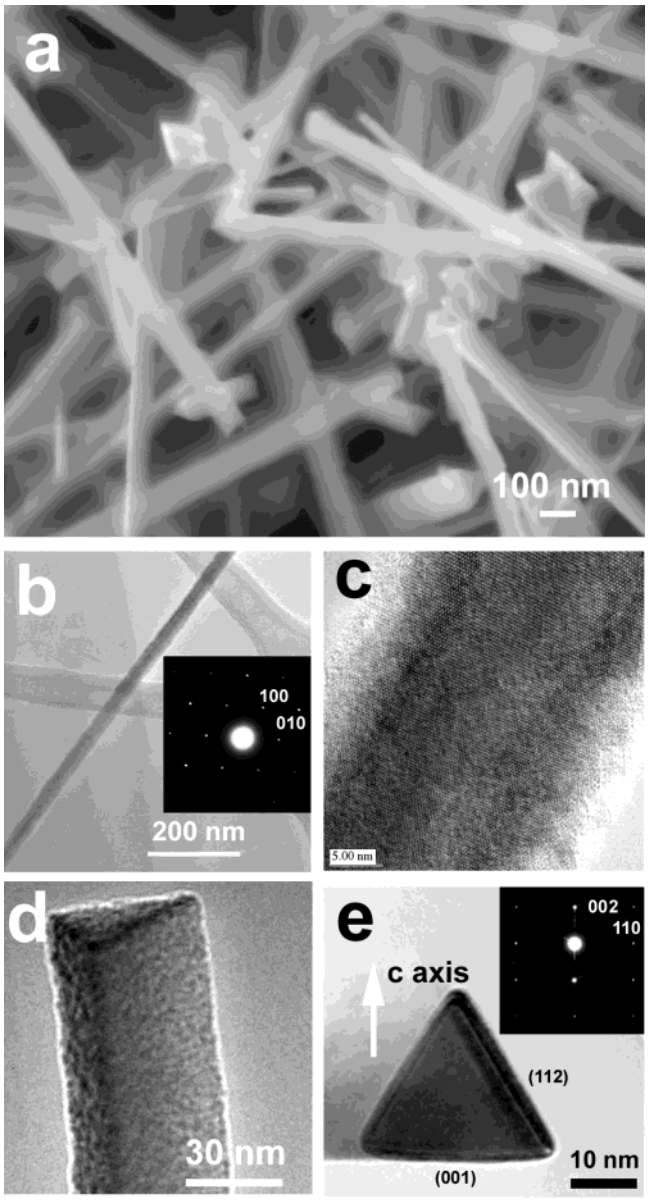

Figure 3. (a) FESEM image of the GaN nanowires grown on a nickel-coated *c*-plane sapphire substrate. (b) TEM image of a GaN nanowire. The inset is an electron diffraction pattern taken along the [001] zone axis. (c) Lattice-resolved TEM image of the nanowire. (d, e) TEM images showing the triangular cross sections of the nanowires. The inset in e shows the electron diffraction pattern taken perpendicular to this cross section along the [1$\bar{1}$0] zone axis. The *c* axis of the wurtzite structure is indicated with an arrow.

shown in Figure 3e (inset). A square electron-diffraction pattern is seen here and can be readily indexed as a [1$\bar{1}$0] zone diffraction pattern (rather than a hexagonal pattern for the [001] zone axis). By indexing this diffraction pattern, we found that these GaN nanowires were enclosed with (112), ($\bar{1}\bar{1}$2), and (001) side planes as marked in Figure 3e. (See Supporting Information for a structural model of the cross section.) The measured angles between these planes (63, 58, 59°) are consistent with those calculated on the basis of the wurtzite GaN crystal structure (63.16, 58.42, 58.42°). Unlike the early GaN nanowire studies,[2,5] we rarely observe nanowires growing along the [001] direction. The triangular

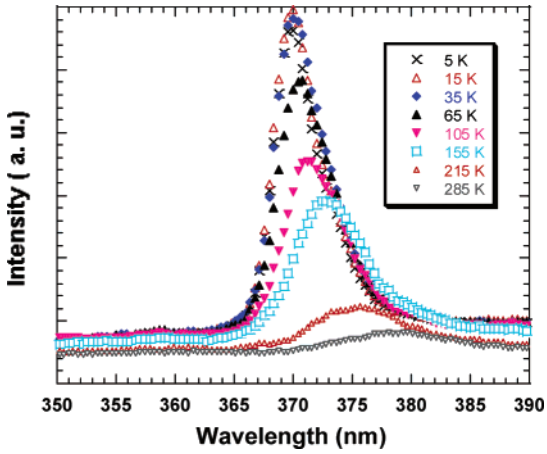

Figure 4. PL spectra of the GaN nanowires as a function of temperature.

cross section is a manifestation of the 2-fold symmetry along the [1$\bar{1}$0] crystallographic direction. Interestingly, this type of cross section has been previously observed in the lateral epitaxial overgrowth of GaN thin films on patterned substrates using MOCVD. It was proposed that the carrier gas (H_2 and N_2) ratio plays an important role in modulating the growth velocity on the (112) and (001) facets. In particular, a hydrogen reaction environment results in triangular cross sections, and the use of nitrogen carrier gas produces a trapezoidal cross section.[13] We believe that a similar facet-regulating mechanism is operating here during our MOCVD nanowire growth.

Photoluminescence (PL) of the nanowires was collected at different temperatures within an optical cryostat. The sample was excited with the 325 nm line of a He−Cd CW laser. The nanowire emission is collected, dispersed with a 0.3 m monochromator (1200 grooves/mm grating), and detected by an intensified CCD detector. Figure 4 shows the PL spectra at eight different temperatures from 5 to 285 K. A broad emission band is observed between 360 and 385 nm. The PL peak positions are 370 nm (3.35 eV) at 5 K and 380 nm (3.26 eV) at 285 K. Importantly, the well-known defect-induced yellow emission band is not observed here, indicating the high optical quality of these GaN nanowires.

The transport properties of the nanowires were investigated using a back-gated two-probe scheme (Figure 5a). The current (I) versus source-drain voltage (V_{sd}) and gate voltage (V_g) were measured to determine the type, mobility, and concentration of the carriers. In general, the nanowire conductance increases for V_g greater than zero and decreases for V_g less than zero (Figure 5b and c), indicating that these MOCVD-derived GaN wires are n-type. The carrier mobility of the nanowire can be estimated from the gate-modulation characteristics with the following equation:

$$\frac{dI}{dV_g} = \mu \cdot \left(\frac{C}{L^2}\right) \cdot V_{sd}$$

where the V_g is the gate voltage, μ is the carrier mobility, and L is the nanowire length. The capacitance (C) is

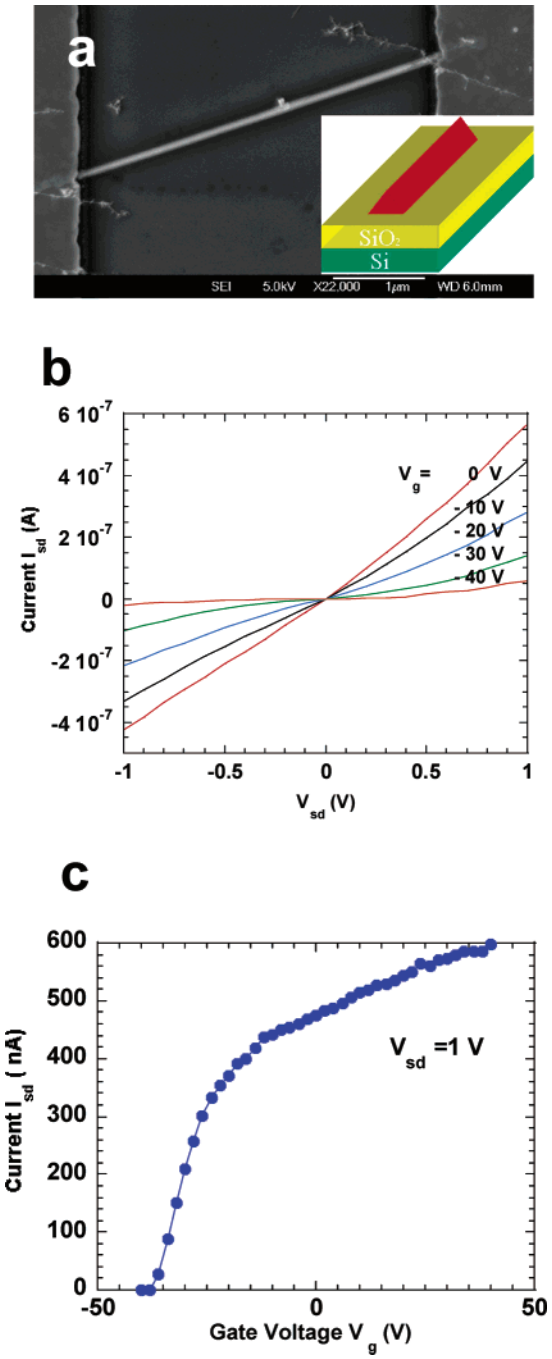

Figure 5. (a) SEM image of a GaN nanowire connected with two electrodes for the transport study. The inset is an illustration of the GaN transistor layout. (b) Current−voltage measurement at different gating voltages for the GaN nanowire. (c) Drain current as a function of the gate voltage (V_g) for the GaN nanowire.

calculated using the following equation with a quasi-circular cross-section approximation:

$$C \approx \frac{2\pi \cdot \epsilon \cdot \epsilon_0 \cdot L}{\ln(4h/a)}$$

where h is the dielectric thickness (400 nm) and a is the width of the GaN nanowires. The carrier mobility (μ) for our nanowires is on the order of 65 cm^2/V·s. In addition, the carrier concentration can be calculated by the following equation:

$$n_e = \frac{Q}{e \cdot 0.433 a^2 \cdot L}$$

where $Q = C \cdot V_{th}$ is the total charge and V_{th} is the threshold voltage required to deplete the nanowire. For our nanowires, the carrier concentration is estimated to be 4×10^{18} cm^{-3}.

Taken together, we report here for the first time the production of high-quality GaN nanowires using a MOCVD process. One unique feature of these MOCVD nanowires is that they are well-facetted and most of them have triangular cross sections. Optical and electrical transport studies indicate that these nanowires are of high optical quality and exhibit high electron mobility. This MOCVD process is compatible with current thin-film technology, which would enable thin film/nanowire integration on the same technical platform. The organometallic precursors offer several advantages over early studies using Ga metal as the source material. First, this MOCVD process can be readily scaled up to wafer-scale production. Second, the MOCVD process would enable facile doping of these GaN nanowires with standard precursors such as Cp_2Mg for p-type doping.

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Supporting Information Available: EELS spectrum collected on individual GaN nanowires and a structural model for the triangular cross section of the GaN nanowire. This material is available free of charge via the Internet at http://pubs.acs.org.

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