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Gallium Nitride-Based Nanowire Radial Heterostructures for Nanophotonics

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ABSTRACT

We report a new and general strategy for efficient injection of carriers in active nanophotonic devices involving the synthesis of well-defined doped core/shell/shell (CSS) nanowire heterostructures. n-GaN/InGaN/p-GaN CSS nanowire structures were grown by metal-organic chemical vapor deposition. Electron microscopy images reveal that the CSS nanowires are defect-free single crystalline structures, while energy-dispersive X-ray linescan profile studies confirm that shell thickness and composition can be well controlled during synthesis. Photoluminescence data further show that the optical properties are controlled by the CSS structure with strong emission from the InGaN shell centered at 448 nm. Importantly, electrical devices made by simultaneously contacting the n-type core and outer p-type shell of the CSS nanowires demonstrate that in forward bias these individual nanowires behave as light-emitting diodes (LEDs) with bright blue emission from the InGaN shell. The ability to rationally synthesize gallium nitride-based radial heterostructures should open up new opportunities for nanophotonics, including multicolor LEDs and lasers.

Semiconductor nanowires are emerging as versatile building blocks for photonic devices,[1] including photodectors,[2] light-emitting diodes (LEDs),[3−6] and lasers.[7−10] The ability to assemble and electrically interconnect these building blocks is especially critical since it represents an approach to active devices that could emit light over a wide range of wavelengths on a single chip, in contrast to conventional technologies. Previous studies have shown that the n- and p-type materials required in active devices can be realized in crossed[3,5] and axial[4,6] structures, yet the nanoscale p−n junctions in these structures limit significantly injection currents. Here we report a new and general strategy involving the metal−organic chemical vapor deposition (MOCVD) synthesis of well-defined doped core/shell/shell (CSS) nanowire heterostructures that overcomes these limitations.

We have focused on GaN-based materials since alloys of (Al−Ga−In)N are direct band gap semiconductors with potential for light emission from the ultraviolet through visible regions of the electromagnetic spectrum.[11] Previous studies of planar LEDs have shown that n-GaN/InGaN/p-GaN and related double heterostructures exhibit enhanced light emission efficiency compared to simple n-GaN/p-GaN diode structures,[11−13] and thus suggest that CSS versus core/shell (CS) structures would be ideal candidates for GaN-based active nanowire devices. The nanowire CSS structures also have potentially significant differences compared to planar heterostructures beyond that of dimensionality. In particular, because nanowire synthesis is essentially substrate-free it should prevent formation of dislocations originating from lattice mismatch between GaN and growth substrates, and thereby reduce nonradiative recombination (at these defects) relative to planar structures.

Our approach for preparing the GaN-based CSS structures (Figure 1) involves initial metal nanocluster mediated vapor−liquid−solid (VLS) growth[1] of an n-type GaN core followed by sequential radial growth of intrinsic InGaN and p-type GaN shells. The general concept of controlled, sequential growth of CS structures was described recently for the case of silicon and germanium materials,[14] although this earlier work did not realize structures with selective n- and p-type doping that are crucial to active photonic devices. To investigate the more complex nanowire structures required for active CSS devices, we exploited MOCVD, which is a technique used extensively for the growth of planar GaN-based heterostructures,[11] as a means of delivering Ga and In reactants as well as silicon (n-type) and magnesium (p-type) dopants in a highly controlled and reproducible manner.[15]

Scanning electron microscopy (SEM) images of Si-doped GaN nanowires obtained following axial elongation (Figure 2a) reveal a high yield of uniform nanowire cores. The lengths of the nanowire cores used in these studies, which depend directly on growth time, were 10−20 μm. A bright

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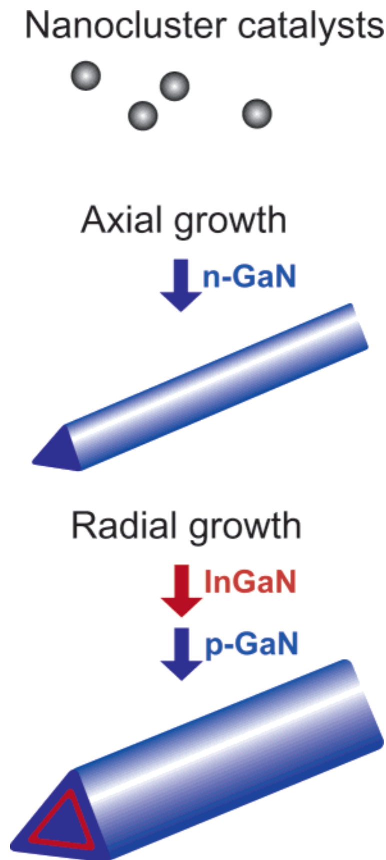

Figure 1. Synthesis of CSS nanowire heterostructures. Catalytic metal nanoclusters lead to one-dimensional GaN nanowire (blue) growth via a VLS mechanism. Subsequently, conditions are changed to favor uniform surface deposition, which enables growth of controlled thickness InGaN (red) and GaN (blue) shells epitaxially on the GaN nanowire cores.

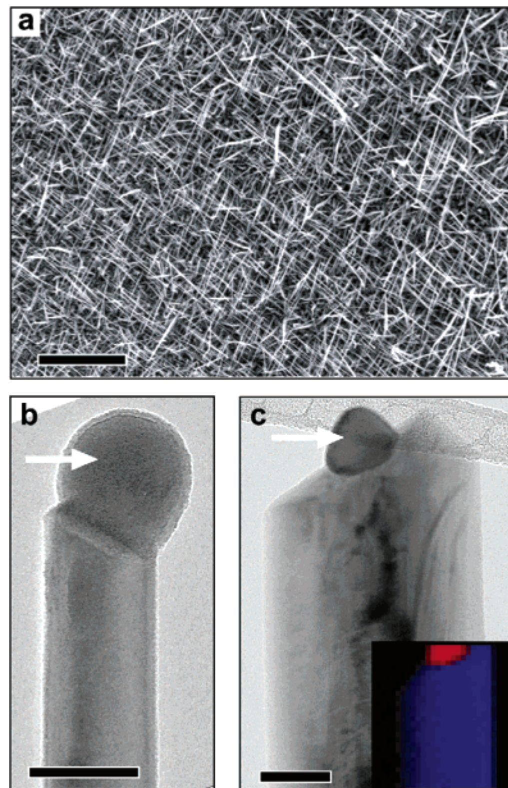

Figure 2. Structures of n-GaN and n-GaN/InGaN CS nanowires. (a) SEM image of n-GaN nanowires grown using nickel nanoclusters. Scale bar is 20 μm. (b) Bright-field TEM image of n-GaN nanowire core. The diameter of the nanowire is the same as the diameter of the corresponding nanocluster; the white arrow highlights the nanocluster. Scale bar is 50 nm. (c) Bright-field TEM image of n-GaN/InGaN CS nanowire; the white arrow highlights the nanocluster. Scale bar is 50 nm. Inset: EDX map of nickel (red) and gallium (blue) for this same nanowire.

field transmission electron microscopy (TEM) image of a representative n-GaN core (Figure 2b) shows that the nanowire diameter is essentially the same as the nickel nanocluster diameter as expected for the VLS process.[1] Corresponding TEM images of n-GaN/InGaN CS nanowires demonstrate that the overall diameters increase following InGaN shell growth. Examination of a representative CS nanowire end (Figure 2c) shows that the overall diameter is substantially larger than that of the nanocluster, in contrast to the core nanowires (Figure 2b), and that the nanowire has a triangular cross section. The triangular cross section is similar to that reported recently for undoped GaN nanowires grown by MOCVD.[16] Energy-dispersive X-ray spectroscopy (EDX) mapping (inset, Figure 2c) demonstrates that nanoclusters at the CS nanowire ends are nickel while the larger core–shell nanowire structure contains Ga, In, and N. The TEM data also show that the InGaN shell grows uniformly with smooth surfaces and maintains the overall triangular cross section of the core nanowire (Figure S1, Supporting Information). Taken together, these results strongly suggest that shell growth is epitaxial as required for efficient devices.

High-resolution TEM and EDX have been used to characterize in greater detail the CS and CSS nanowires. Lattice-resolved images obtained from n-GaN/InGaN/p-GaN CSS nanowires containing a nominal 20% In in the InGaN shell (Figure 3a) demonstrate that the CSS nanowires have a single crystalline structure, while lower resolution bright-field images show no evidence of either dislocations or other defects following growth of the inner InGaN and outer p-GaN shells; these results imply that strain at the GaN/InGaN interface is not relaxed. Electron diffraction data recorded along the [0001] zone axis (inset, Figure 3a) can be indexed to the GaN wurtzite structure and enable assignment of the nanowire growth direction to be ⟨11−20⟩. The CSS nanowire maintains the triangular cross section observed for CS structures, and angle dependent imaging studies further demonstrate that the three lateral facets consist of (0001) and two {1−101} crystallographic planes. The observed crystallographic planes are consistent with lateral facets that are stable in selectively grown GaN with substrates patterned in the ⟨11−20⟩ direction for different carrier gas compositions,[17] temperatures, and pressures.[18] However, the shell boundaries and thicknesses are not obvious from projection TEM images of these triangular nanowires.

To characterize the CS and CSS nanowires further we have recorded and analyzed EDX compositional line profiles[19] (Figure 3b,c). Overall, the EDX data show clearly distinct differences in the spatial profiles of In and Ga that are

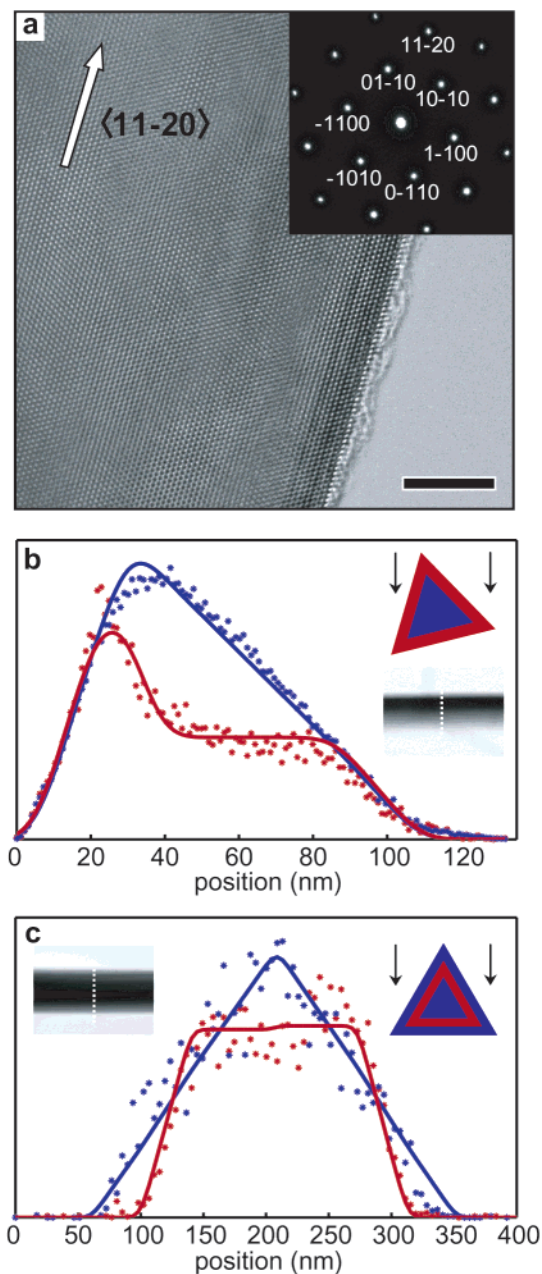

Figure 3. Crystalline structure and composition profiles of n-GaN/InGaN CS and n-GaN/InGaN/p-GaN CSS nanowires. (a) High-resolution TEM image of single crystalline n-GaN/InGaN/p-GaN CSS nanowire taken along the [0001] zone axis. The white arrow highlights the ⟨11−20⟩ growth direction for the CSS nanowire. Scale bar is 5 nm. Inset: corresponding electron diffraction pattern indexed for the [0001] zone axis. (b) and (c) Normalized EDX line profiles for gallium (blue symbols) and indium (red symbols) recorded on n-GaN/InGaN CS and n-GaN/InGaN/p-GaN CSS nanowires, respectively. Insets: scanning TEM images of the nanowires, and models for the nanowire cross-sections (blue and red regions represent GaN and InGaN, respectively). The models were used to fit the experimental line profiles (solid lines); the black arrows in the insets indicate the orientation of the electron beam relative to the triangular nanowires.

qualitatively consistent with well-defined InGaN shells in the CS and CSS structures. The composition profiles depend on the orientation of the triangular nanowire samples relative to the electron beam, and this dependence was taken into account in modeling these data[19] to obtain quantitative information about shell thicknesses. The analysis of the In and Ga profiles obtained on an n-GaN/InGaN CS structure (Figure 3b) reveals excellent fits with a nanowire core diameter of 69 nm, shell thickness of 12 nm, and tilt relative to the electron beam of 17°; the tilt angle is in agreement with that determined independently from angle-dependent images. The data at the sample edge also provides an estimate of the In composition, 20%, in the InGaN shell that is consistent with growth conditions and photoluminescence (PL) measurements (Y.L., F.Q., S.G., C.M.L., unpublished results). Analysis of the In and Ga profiles obtained on an n-GaN/InGaN/p-GaN CSS structure (Figure 3c) yields a nanowire core diameter of 131 nm, InGaN shell thickness of 22 nm, a p-GaN shell thickness of 24 nm, and a tilt angle of 0.5°. The outer shell thickness and tilt angle obtained from the fit are in good agreement with the thickness estimated from the onset of the In signal (after the outer GaN shell) and the orientation angle determined from images, respectively. Taken together, these TEM and EDX studies provide strong evidence for the growth of single-crystal GaN/InGaN CS and GaN/InGaN/GaN CSS nanowire structures with well-defined and controllable shell thicknesses and composition.

These GaN-based CSS nanowires have been further characterized by optical, electrical, and optoelectronic measurements.[20] PL spectra recorded on n-GaN and n-GaN/InGaN/p-GaN CSS nanowire structures (Figure 4a) demonstrate several important points. The data recorded from a n-GaN core nanowire structure show a sharp, 12 nm full width at half-maximum (fwhm), peak at 367 nm that is consistent with band-edge emission from GaN.[11] The position, sharpness and absence of longer wavelength emission demonstrate the excellent crystalline quality of the n-GaN core. Significantly, the PL spectra obtained from n-GaN/InGaN/p-GaN CSS structures show a dominant emission peak at 448 nm. This wavelength is consistent with band-edge emission from an InGaN structure of composition $In_{0.18}Ga_{0.82}N$.[21] The InGaN emission is approximately 20 times stronger than the small GaN band-edge emission peak also present in the PL spectrum, which shows that the much smaller volume InGaN shell in our CSS structures provides an efficient region for radiative recombination. The InGaN emission peak is also broader, fwhm = 40 nm, than the peak observed for the GaN nanowires. We suggest that this broadening may reflect strain in the InGaN shell by comparison to broadening reported for planar InGaN single quantum well LEDs,[11,13] although further work will be needed to prove this point. Last, these PL data show that impurity or defect-related emission at wavelengths longer than the InGaN band-edge peak are not significant, and thus demonstrate that the CSS nanowires have very good optical quality.

The n-GaN/InGaN/p-GaN CSS nanowire heterostructures have been used to prepare functional nanoscale LEDs. Electrical transport measurements made in a field-effect transistor configuration[5,22] (Figure S2, Supporting Information) demonstrate that the Si-doped GaN nanowires and the Mg-doped GaN outer shells of the CSS nanowires are n-type and p-type, respectively. These results are consistent with

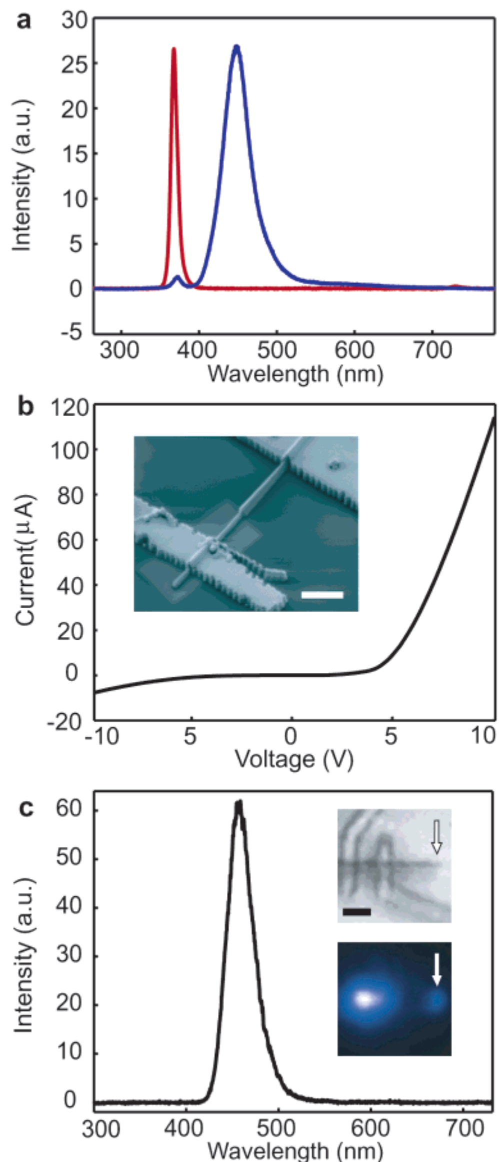

Figure 4. Optoelectronic properties of n-GaN/InGaN/p-GaN CSS nanowires. (a) Normalized PL spectra obtained from single n-GaN (red) and n-GaN/InGaN/p-GaN CSS (blue) nanowire. (b) Current vs voltage data recorded on a n-GaN/InGaN/p-GaN CSS nanowire device. Inset: field emission SEM image of a representative CSS nanowire device prepared using the FIB technique to selectively etch the outer shells from one end (lower right) of the CSS nanowire prior to contact deposition. Scale bar is 1 μm. (c) EL spectrum recorded from a forward-biased CSS p−n junction at 7 V. Insets: bright field (upper) and EL (lower) images of a CSS structures. The EL image was recorded at 4 K with a forward bias of 12 V. White arrows in both images highlight the end of the CSS nanowire. Scale bar is 2 μm.

our previous studies of homogeneous n- and p-type nanowires,[5,22] and planar materials.[11] Simultaneous electrical contacts to both the n-type core and p-type outer shell of individual CSS nanowires, which are required to inject electrons and holes into the InGaN shell, were achieved using a focused ion beam microscope[23] to etch and expose selectively the core at one end of the CSS nanowires (inset, Figure 4b). Current versus voltage data recorded between contacts to the n-type core and p-type shell (Figure 4b) show current rectification with a sharp onset at ca. 4 V in forward bias that is characteristic of a p−n diode.

Notably, the electroluminescence (EL) spectrum collected from a representative forward biased n-GaN/InGaN/p-GaN CSS nanowire device (Figure 4c) exhibits an intense peak at 456 nm with a fwhm of 50 nm. These values are in good agreement with the PL spectra recorded from similar CSS nanowires. In addition, no emission is observed at the GaN band edge or longer wavelengths associated with defect or impurity states.[11,13,24] These results show that injected electrons and holes recombine in an $In_{0.18}Ga_{0.82}N$ active shell in these new nanowire heterostructures. Images of the EL from CSS nanowire devices were also recorded (inset, Figure 4c) and typically show peaks at two spatial locations. Comparison of these peaks to bright field images (inset, Figure 4c) demonstrates that the most intense EL peak originates between the two metal contacts and that the less intense peak is located at the remote free-end of the CCS nanowire structure. Remarkably, the blue light emitted from many of the forward-biased single CSS nanowire devices is sufficiently intense to be visible to the naked eye (Figure S3, Supporting Information) and thus suggests that these nanoscale LEDs could be developed as local excitation sources. The EL observed at the end of the CSS structure also shows that these nanowires can serve as optical waveguides and could function as the optical cavity needed for single nanowire injection lasers.[10]

In summary, we have demonstrated the growth of single crystalline n-GaN/InGaN/p-GaN CSS nanowire heterostructures. PL measurements have shown that strong blue light emission is due to radiative recombination in the InGaN shell, and moreover, electrical measurements with separate contacts to the core and outer shell have demonstrated that these CSS nanowires behave as p−n diodes with blue light emission arising from electron−hole recombination in the InGaN layer. We believe that these electrically driven nanoscale blue LEDs could find uses in a number of areas, such as sources for lab-on-a-chip devices and optical information storage. More generally, we believe that present studies open up a number of opportunities in nanoscale photonics, for example, by exploiting the efficient injection possible in the CSS geometry to create electrically driven nanoscale lasers. Because the emission color of CSS nanowire could vary over a broad range of the electromagnetic spectrum in (Al−In−Ga)N alloys during nanowire synthesis, it should also be possible via assembly of different composition CSS building blocks to make multiccolor LED and laser arrays not possible with conventional planar processing today.

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Supporting Information Available: Triangular faceting of GaN/InGaN CS nanowires (Figure S1), electrical characterization of a core nanowire and CSS nanowire outer shell (Figure S2), and digital photograph of high brightness CSS nanoLED device in forward bias (Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) CSS nanowires were synthesized on a c-plane sapphire in a MOCVD reactor (Thomas Swan Scientific Equipment Ltd.) using trimethylgallium (TMG), trimethylindium (TMI), and ammonia (NH_3) as Ga, In, and N sources, respectively, and deposited 0.01 M nickel(II) nitrate solution[5] as the nickel nanocluster precursor. n-Type GaN cores were grown at 775 °C and 100 Torr using TMG (5 standard cubic centimeters per minute, sccm) and NH_3 (1300 sccm); silane (100 ppm, 0.3 sccm) was used as the n-type dopant. Shell growth was carried out using constant NH_3 flow (6500 sccm) at 400 Torr. Intrinsic InGaN shells were deposited at 700 °C using TMG (0.55 sccm) and TMI (140 sccm). p-Type GaN shells were grown at 960 °C using TMG (5 sccm) and biscyclopentadienylmagnesium (990 sccm) as the Mg dopant source.
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(19) For TEM studies, nanowires were transferred to copper/holey carbon grids and characterized using a field emission system (JEOL 2010F) operated at 200 kV. EDX elemental line profiles were collected in the scanning TEM mode. EDX profiles were analyzed as follows neglecting absorption effects. Geometrical models of CS and CSS structures were made having triangular cross sections defined by three 60° angles, as an approximation to the experimentally determined cross section of GaN nanowires defined by one (0001) and two {1−101} crystallographic planes, which define a triangle with two 62° and one 56° angles. These models were then used to fit experimental line profiles taking into account a Gaussian electron probe profile of 2.5 nm fwhm, where the core and shell thicknesses, as well as the nanowire tilt angle relative to the electron beam, were parameters.
(20) For electrical and optoelectronic measurements nanowires were dispersed on oxidized silicon substrates (600 nm oxide, 1−10 Ω·cm resistivity), and electrical contacts were defined by electron beam lithography as described previously.[3−5] Etching of nanowires was performed using a focused ion beam microscope equipped with field-emission electron beam and a liquid-gallium ion beam (FEI Dual Beam DB235/SEM). The nanowire milling was carried out at 30 kV with a beam current of 10 pA. The alignment of the system was carried out in SEM mode prior to ion etching to avoid ion damage to the nanowire. Source-drain contacts were deposited by thermal evaporation of nickel/gold (200/50 nm) and annealed in nitrogen at 450 °C for 2 min. PL images and spectra were obtained using a home-built, far-field epifluorescence microscope.[2,3] A frequency-tripled Ti:sapphire laser at 273 nm was focused by a microscope objective (numerical aperture = 0.7) to a 30 μm spot at 1 kW/cm^2 onto the nanowires dispersed onto the oxidized surface of a silicon substrate. PL and EL data were recorded using a 300 mm spectrometer (150 lines/min grating) and a liquid nitrogen cooled charge-coupled device detector; images were obtained with the same system by replacing the grating with a mirror.
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