NANO LETTERS

2005
Vol. 5, No. 11
2287−2291

Core/Multishell Nanowire Heterostructures as Multicolor, High-Efficiency Light-Emitting Diodes

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Received August 23, 2005; Revised Manuscript Received September 16, 2005

ABSTRACT

We report the growth and characterization of core/multishell nanowire radial heterostructures, and their implementation as efficient and synthetically tunable multicolor nanophotonic sources. Core/multishell nanowires were prepared by metal-organic chemical vapor deposition with an n-GaN core and $In_xGa_{1-x}N$/GaN/p-AlGaN/p-GaN shells, where variation of indium mole fraction is used to tune emission wavelength. Cross-sectional transmission electron microscopy studies reveal that the core/multishell nanowires are dislocation-free single crystals with a triangular morphology. Energy-dispersive X-ray spectroscopy clearly shows shells with distinct chemical compositions, and quantitatively confirms that the thickness and composition of individual shells can be well controlled during synthesis. Electrical measurements show that the p-AlGaN/p-GaN shell structure yields reproducible hole conduction, and electroluminescence measurements demonstrate that in forward bias the core/multishell nanowires function as light-emitting diodes, with tunable emission from 365 to 600 nm and high quantum efficiencies. The ability to synthesize rationally III-nitride core/multishell nanowire heterostructures opens up significant potential for integrated nanoscale photonic systems, including multicolor lasers.

Semiconductor nanowires[1,2] represent attractive building blocks for active photonic devices, including light-emitting diodes (LEDs)[3−7] and lasers.[8,9] Significantly, the ability to assemble and electrically drive nanoscale building blocks could allow for integrated photonic sources with emission colors spanning from ultraviolet to near-infrared regions of the electromagnetic spectrum. Realizing this potential will require building blocks with emission colors that can be rationally tuned and also integrated into electrical devices. Recent work has demonstrated multicolor, electrically driven emission using monodisperse quantum dots,[10] where the quantum dots were integrated into and excited by a GaN planar device, and using a crossed nanowire architecture,[7] where electron/hole injection occurs directly across the interface between p- and n-type nanowires. These approaches may, however, be limited by inefficiencies due to indirect electrical excitation and/or nonepitaxial nanoscale junctions. Here we demonstrate a general strategy for efficient injection and radiative recombination of carriers in tunable band gap GaN-based core/multishell (CMS) nanowire radial heterostructures.

GaN-based nanowires have several features that make them attractive for optoelectronic devices.[4−6] First, nanowire synthesis is virtually substrate-free, which prevents the formation of dislocations originating from lattice mismatch between GaN and a planar growth substrate. Second, alloys of III-nitrides are direct band gap semiconductors whose emission wavelengths can be tuned through variations in alloy composition.[11] Third, there are few surface states acting as recombination centers in the band gap of GaN and alloys, contrasting related III−V material like GaAs/P, where surface states can dominate the observed behavior.[12] Last, contrary to other wide band gap materials such as ZnO, GaN nanowires can be reproducibly prepared with the n-[6,13] and p-type[4,6] doping required for active, electrically driven photonic devices. To date, GaN-based nanowire LEDs have been realized in p-Si/n-GaN[7] and n-GaN/p-GaN[4] crossed nanowire structures, n-GaN/InGaN multiquantum-well/p-GaN axial nanorod arrays[5] and n-GaN/InGaN/p-GaN core/shell/shell (CSS) radial heterostructures.[6] These previous studies show potential for making electrically driven GaN-based nanowire LEDs, although the structures reported were all single color sources based on relatively simple homo or heterojunctions, which cannot provide efficient confinement of injected carriers.[14] For example, studies of planar LED/laser diode devices[11,15,16] suggest that InGaN/GaN single quantum well (SQW) or multiple quantum wells (MQWs) with an additional AlGaN layer, which confines injected carriers in the recombination region, exhibit enhanced emission efficiency.

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10.1021/nl051689e CCC: $30.25 © 2005 American Chemical Society
Published on Web 09/29/2005

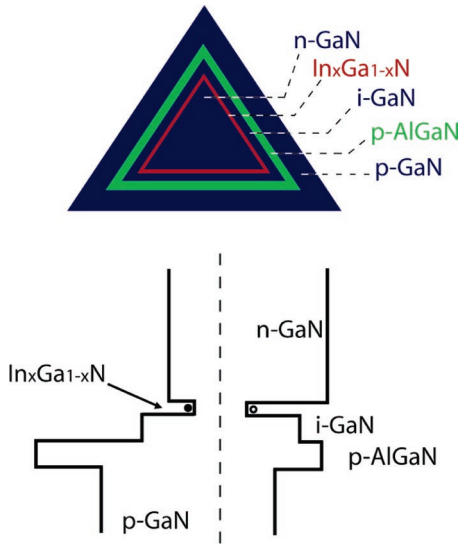

Figure 1. Cross-sectional view of a CMS nanowire structure and the corresponding energy band diagram. The dashed line in the band diagram indicates the position of the Fermi level.

To push the development of nanoscale LED sources with controlled multicolor emission and enhanced efficiencies, we have explored the synthesis and characterization of the CMS nanowire structures shown in Figure 1. The target nanowire structures consist of an inner n-type GaN core, and sequentially deposited i-InGaN, i-GaN, p-AlGaN, and p-type GaN shells. The n-type GaN core and the p-type GaN outer shell serve as electron and hole injection layers, respectively. The $In_xGa_{1-x}N$ layer provides a tunable (with x) band gap well for efficient radiative recombination of injected carriers, while the wider band gap and lower index of refraction AlGaN cladding layer can enhance confinement of both carriers and photons in the InGaN active layer.[11]

n-GaN/$In_xGa_{1-x}N$/GaN/p-AlGaN/p-GaN CMS nanowire radial heterostructures were synthesized by metal−organic chemical vapor deposition (MOCVD),[6,17] using a strategy involving axial elongation by nanocluster catalyzed growth followed by controlled shell deposition onto the nanowire core.[6,18] Significantly, by adjusting the InGaN growth temperature,[19] the indium composition can be systematically tuned and hence used to define the band gap of InGaN and corresponding emission energy. Conventional transmission electron microscopy (TEM) analysis of MOCVD GaN cores has shown that they consist of uniform diameter, single-crystal structures with a ⟨11−20⟩ growth direction. To characterize the chemical composition and thickness of individual shells in the CMS heterostructures, we have exploited cross-sectional imaging with the electron beam parallel (vs perpendicular) to the nanowire axis since this allows direct visualization of the spatial distribution of elements.[20] A bright field cross-sectional TEM image (Figure 2a) of a representative GaN/$In_xGa_{1-x}N$/GaN/AlGaN CMS nanowire taken along the [11−20] zone axis shows that the CMS wire has triangular cross section with smooth facets. No dislocations or boundaries were observed in our studies of a number of nanowires, indicating epitaxial deposition of the shells. Electron diffraction data (inset, Figure 2a) further demonstrates that the CMS nanowire is a single crystal and

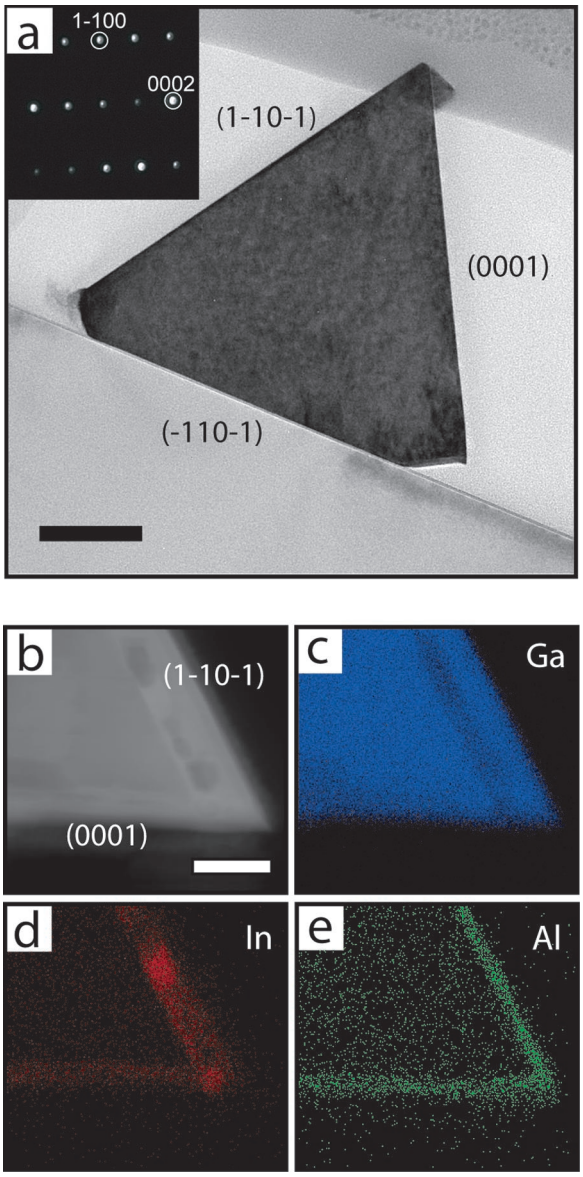

Figure 2. (a) Bright-field TEM cross-sectional image of a GaN/$In_xGa_{1-x}N$/GaN/AlGaN CMS nanowire. Scale bar is 100 nm. Inset: electron diffraction pattern indexed for the [11−20] zone axis. (b) Dark-field STEM image recorded at a nanowire corner with (0001) and (1−10−1) facets. Scale bar is 100 nm. (c−e) Elemental mapping of the same nanowire region, indicating spatial distribution of Ga (blue), In (red), and Al (green), respectively.

that the three lateral facets can be indexed as (0001) and two {1−10−1} crystallographic planes. This result is consistent with our previous report on CSS nanowires.[6]

Additional analysis using dark-field scanning TEM (STEM) (Figure 2b) revealed contrast indicative of variations in the radial chemical composition as expected for the CMS structure. STEM energy-dispersive X-ray spectroscopy (EDS) mapping of the same nanowire region (Figure 2c−e) confirmed this suggestion and defined clearly the spatial distributions of Ga, In, and Al in individual shells that are consistent with targeted CMS structure. Interestingly, the thickness of InGaN shell was larger on the (1−10−1) versus (0001) facet, indicating that shell deposition rate depends on the specific crystalline plane. This can be understood in

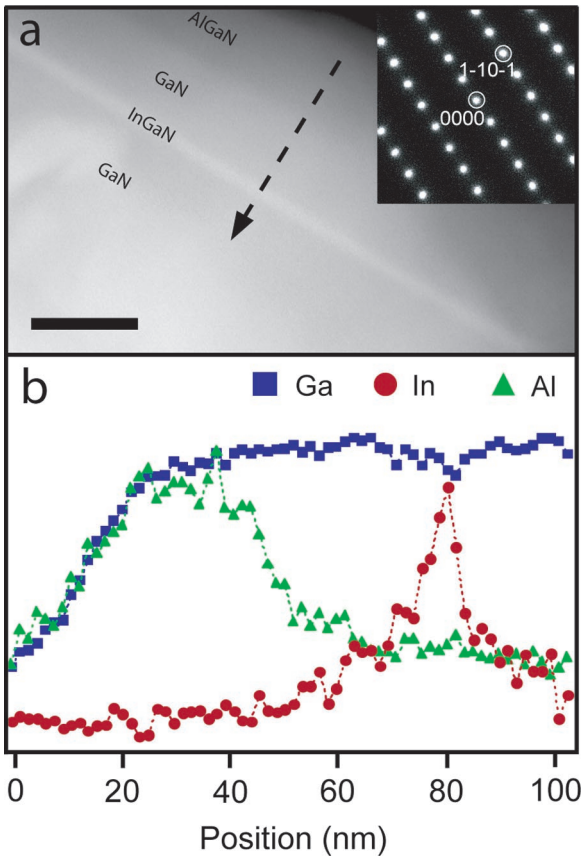

Figure 3. (a) Dark-field scanning TEM image of a cross-sectional GaN/$In_xGa_{1-x}N$/GaN/AlGaN CMS nanowire. Scale bar is 50 nm. Inset: Corresponding electron diffraction pattern confirmed the shown facet was (1−10−1) plane. (b) Normalized EDS line profiles for Ga (blue symbols), In (red symbols), and Al (green symbols), respectively, recorded along the black dashed arrow indicated in Figure 3a.

terms of different surface energies and polarities on nonequivalent facets[21] and suggests that these nanowires could also serve as a model system to study growth kinetics. In addition, localized indium-rich clusters on a scale of 10 to 50 nm were observed in the thicker InGaN layer grown on the (1−10−1) facet; however, we did not observe In segregation in the thinner layer grown on the (0001) facet. Similar indium inhomogeneity has been reported in InGaN-based planar structures and is dependent on several factors, including InGaN layer thickness,[22] as we observe.

To control In segregation in the CMS nanowires, we have focused on the synthesis of heterostructures with thin InGaN layers. Dark-field STEM images (Figure 3a) show that the 8 nm thick InGaN layer is homogeneous (i.e., without obvious segregation), although (sub)nanometer-scale indium compositional fluctuations may exist.[22] In addition, EDS line profiles across the (1−10−1) facet of this CMS nanowire (Figure 3b) confirmed that the observed contrast corresponds to sharp interfaces between InGaN, GaN, and AlGaN shells. Quantitative analysis revealed that the thicknesses of the $In_{0.09}Ga_{0.91}N$, GaN, and $Al_{0.1}Ga_{0.9}N$ shells were 8, 28, and 33 nm, respectively, in agreement with the targeted structure. The ability to prepare a well-defined 8 nm InGaN layer in this structure also suggests that it will be possible to push these results to a quantum well limit in the future. Taken together, these TEM, EDS mapping, and line scan studies demonstrate epitaxial growth of well-defined single-crystal GaN/$In_xGa_{1-x}N$/GaN/AlGaN/GaN nanowire radial heterostructures, where the sequence, thicknesses, and compositions of shells are well-controlled.

In addition, the electrical and optoelectronic properties of the CMS nanowires have been characterized.[23] Electrical measurements made in a field-effect transistor configuration[4,13] have demonstrated that silicon-doped GaN cores are n-type and magnesium-doped GaN outer shells are p-type, respectively (Figure S1). Moreover, control experiments indicate that the additional p-AlGaN confinement shell enhances reproducible p-type behavior in the p-GaN outer shell, which is critical for reliable device studies. To inject holes and electrons simultaneously into the CMS heterostructures, metal contacts were deposited separately onto the p-type outer shell and n-type core at the ends of individual nanowires (inset, Figure 4a). Current versus voltage characteristics (Figure 4a) showed typical p−n diode current rectification with a sharp onset at around 3.5 V in forward bias.

CMS nanowire devices in forward bias yield strong electroluminescence (EL). EL images collected from CMS nanowire LEDs with indium compositions from 1 to 40% showed high brightness and systematic red shifts in emission peak with increasing In composition (Figure 4b). Normalized EL spectra (Figure 4c) collected from five representative CMS nanowires in which only the In composition in the InGaN shells vary, exhibited distinct spectral peaks with maxima at 367, 412, 459, 510, and 577 nm. These results are consistent with band-edge emission from $In_xGa_{1-x}N$ with In compositions of ca. 1, 10, 20, 25, and 35%, respectively.[24] We did not observe emission from impurity or defect states, which typically are observed as a broad band around 550 nm, or from the GaN band edge at ca. 365 nm, showing that injected carriers recombine predominantly in the active InGaN shell. In addition, measurement of the full width at half-maximum (fwhm) yields values of 7, 27, 30, 48, and 61 nm, respectively. The broadening with increasing In concentration is consistent with InGaN-based thin film LEDs[11,15] and has been attributed to increasing strain and In inhomogeneity as the In composition is increased. In addition, compared to previous nanowire LEDs, these new CMS structures exhibit improved emission properties, including narrower peaks and enhanced quantum efficiencies (QEs). The estimated external QE of the CMS nanowire LEDs was on the order of 5.8% at 440 nm and 3.9% at 540 nm. Notably, these values are several times better than the best QEs reported for nanoscale LEDs[3,7,10] and comparable to InGaN-based SQW thin film LEDs at similar emission wavelengths.[11,25] We are encouraged by these QE results since no effort was made to account for the substantial absorption by the metal contact on the p-shell or to optimize the light collection efficiency, and moreover, we expect that further increases in efficiency can be achieved using MQW structures.[14,26]

Last, our studies of the CMS nanowire LEDs also show that some devices exhibit dominant emission from the free

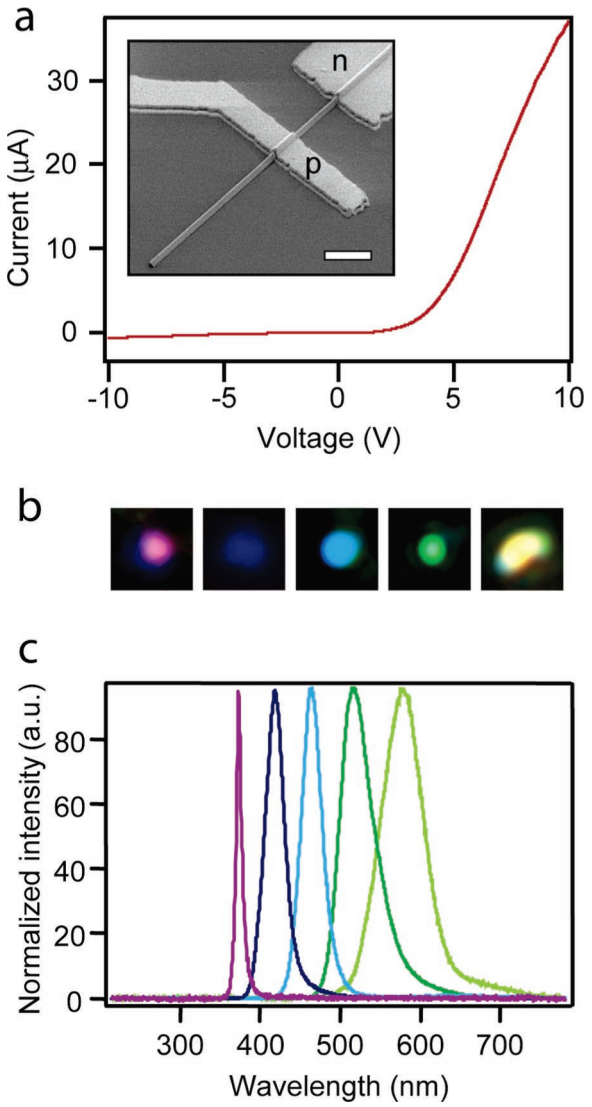

Figure 4. (a) Current versus voltage data recorded on a CMS nanowire device. Inset: field emission scanning electron microscopy image of a representative CMS nanowire device. Scale bar is 2 μm. (b) Optical microscopy images collected from around p-contact of CMS nanowire LEDs in forward bias, showing purple, blue, greenish-blue, green, and yellow emission, respectively. (c) Normalized EL spectra recorded from five representative forward-biased multicolor CMS nanowire LEDs.

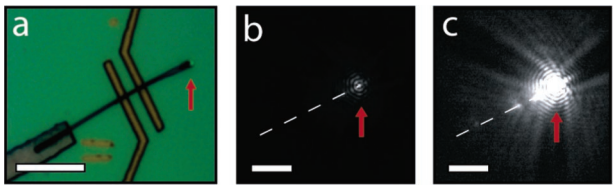

Figure 5. (a) Optical microscopy image showing a 26 μm CMS nanowire device; scale bar is 10 μm. EL images recorded from the same device exhibited dominant end emission in a forward bias at (b) 9 V and (c) 11 V, respectively. The white dashed lines highlight the nanowire position, and red arrows indicate the end of the CMS nanowire.

nanowire ends (Figure 5). These results suggest that a substantial fraction of emitted light is coupled into the guided optical modes of the CMS nanowire structure.[27] The enhanced waveguiding properties of the CMS structures compared to our previous CSS nanowires[6] can be attributed to the improvement in the optical cavity properties of the nanowire cores,[28] as well as better photon confinement due to the AlGaN shells. Significantly, preliminary studies also show that the increase in end emission intensity changes from linear to superlinear as the injection current is increased, while the increase in body emission intensity remains linear over this same range. These results indicate that the CMS nanowire can be driven at least to the point of stimulated emission and thus suggest promise for achieving lasing in the future.

In summary, we have synthesized single-crystal n-GaN/$In_xGa_{1-x}N$/GaN/p-AlGaN/p-GaN CMS nanowire structures, with well-defined radial modulation of doping, composition, and thickness. Transport measurements demonstrate that these nanowires exhibit well-defined and reliable electrical n-type cores and p-type shells and behave as p−n diodes. Moreover, EL measurements showed that in forward bias the CMS nanowires yield intense, color-tunable, and efficient light emission due to radiative recombination in controlled In composition $In_xGa_{1-x}N$ shells. These electrically driven CMS nanowires offer great promises as compact, efficient, reliable building blocks for integrated nanoscale photonic systems, including multicolor LEDs and lasers.

Acknowledgment. We thank R. Schalek for help in TEM sample preparation, A. J. Garratt-Reed for assistance in EDS mapping, and C. J. Barrelet for helpful discussion. S.G. and Y.L. acknowledge the Swiss National Science Foundation and Croucher Foundation for postdoctoral fellowship support, respectively. C.M.L. thanks the Air Force Office of Scientific Research for support of this work and Thomas-Swan Scientific Equipment Ltd. for support of the MOCVD system.

Supporting Information Available: Electrical characterization of a nanowire core and CMS nanowire outer shell (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) 0.01 M nickel nitrate solution was deposited on a sapphire substrate and placed in a MOCVD reactor (Thomas Swan Scientific Equipment Ltd.). n-Type GaN cores were grown at 950 °C in hydrogen (H_2) using trimethylgallium (TMG) and ammonia (NH_3), while silane (100 ppm in H_2) was used as n-type dopant. Intrinsic InGaN layer, GaN layers, and p-AlGaN layer were sequentially deposited in nitrogen at 600−800, 860, and 940 °C, respectively, using TMG, trimethylindium, and trimethylaluminum as Ga, In, and Al sources, respectively. Last, p-GaN outer shell was grown in H_2 at 960 °C using biscyclopentadienylmagnesium as p-type dopant.
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(20) The cross-section TEM samples of CMS nanowires without GaN outer shells were prepared by either mechanical polishing followed by ion-beam milling or ultramicrotomy. For mechanical polishing, nanowires were transferred to Si substrate from which two 2.5 mm wide strips were cut using a low-speed saw and glued together face-to-face. Such samples were mount on a tripod polisher and polished down to a thickness of 10 μm. They were further transferred onto a Cu TEM grid and finally thinned to electron transparency using Ar^+-ion milling. For microtomy, nanowires were transferred to Thermanox plastic coverslips and embedded into an Eponate−Araldite epoxy resin. Embedded samples were cut perpendicular to the nanowire axis into 70−150 nm thick slices using a diamond ultramicrotome knife and then transferred onto Cu/lacey-carbon TEM grids. TEM images and EDS line scans were obtained using a field emission TEM/STEM (JEOL 2010F) operated at 200 kV while EDS elemental mapping was conducted using a VG HB603 STEM.
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(23) For electrical measurements, nanowires were dispersed on silicon substrates (100 nm oxide/200 nm nitride, 1−10 Ω·cm resistivity), and source-drain contact regions were defined by electron beam lithography. Ni/Au (150/50 nm) and Ti/Al/Ti/Au (20/100/30/50 nm) were deposited for p-type contacts on the outer shell and n-type contacts at nanowire ends, respectively, followed by annealing in nitrogen 550 °C for 2 min. This method takes advantage of the following: (i) the n-core is exposed and contacted directly by metal; (ii) the n-type contact metal yields a higher contact resistance to the p-GaN shell; (iii) the p-shell has a much lower (>100×) mobility and correspondingly higher resistivity than the n-GaN core. EL images and spectra were recorded using a 300 mm spectrometer (150 lines·mm^{-1} 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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NL051689E