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Core–Shell Nanowire Light-Emitting Diodes**

By Oliver Hayden,* Andrew B. Greytak,
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Semiconducting nanowires have attracted much attention for potential applications in nanophotonics.^[1] Electrically driven nanometer-scale light-emitting diodes (LEDs) have

been fabricated using both internanowire p–n junctions formed at the crossing point of two oppositely doped nanowires, and intranowire p–n junctions formed by axial or radial (core–shell) modulation doping.^[2] However, these approaches still face challenges of device fabrication, which could hinder progress towards application. Crossed nanowire structures often require time-consuming electron-beam lithography to define metal contacts. In modulation-doped core–shell structures, it is difficult to contact the core and the shell separately because of the lack of a selective wet-etch for the shell material.^[3] It is therefore of interest to synthesize radially heterostructured nanowires which allow a simpler approach to nanowire LED (nanoLED) fabrication, by using a chemically selective etch to separately contact the oppositely doped core and shell.

In many direct bandgap semiconductors, it can be difficult to achieve good conductivity for both n-type and p-type doping in the same material, due to compensation effects. This is the case for a wide range of II–VI compounds which are of interest for visible-light-emitting devices.^[4] Intranowire p–n heterojunctions are therefore an attractive option. Previously reported approaches to constructing radially heterostructured nanowires for photonic applications include chemical vapor deposition (CVD)^[5] and thermal evaporation of semiconductor powders,^[6] both of which face limitations. The elevated substrate temperatures typically required for CVD growth can lead to island formation if the lattice constants of the core and shell do not match,^[7] while thermal evaporation of compound semiconductors such as metal sulfides and selenides is susceptible to the formation of non-stoichiometric shells.^[8] These defects can lead to broad emission spectra, which are not attractive for potential nanowire applications, such as nanoLEDs for fluorescence spectroscopy.

Here, we present a novel concept for fabricating radially heterostructured nanowires, using pulsed-laser deposition (PLD) to synthesize polycrystalline nanowire shells. Nanowires consisting of a p-type Si core and n-type CdS shell were synthesized, and were used for the fabrication of nanoLEDs. The synthesis of the core–shell nanowires and the device fabrication steps are schematically shown in Figure 1.

PLD is a well-known, versatile technique for the deposition of thin films, with the key advantage of producing nearly identical transfer of the target stoichiometry to the substrate.^[9] This process should be applicable as an alternative technique for nanowire coatings for a broad range of semiconductors, despite large lattice mismatches. Core–shell nanowires of Si and CdS were synthesized in two steps. Boron-doped Si nanowire cores were grown by CVD, using gold nanoclusters to catalyze axial growth via the vapor–liquid–solid (VLS) growth mechanism.^[10] The Si nanowires were immediately overcoated with CdS via PLD. The use of an inert atmosphere of Ar during the PLD coating step, in which the substrate was placed upstream of the target, allowed the formation of a conformal shell rather than the anisotropic deposition that would be expected in the molecular-transport regime under high vacuum.^[11] Previous studies in which PLD was used as a reac-

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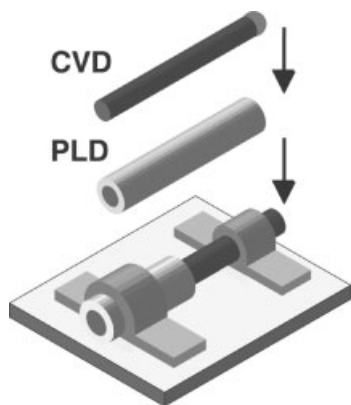


Figure 1. Scheme of the core-shell nanowire synthesis and the nanoLED fabrication. The CVD-grown Si nanowire is coated with CdS using PLD. Selective etching of the shell is followed by the deposition of metal electrodes.

tant source for axial growth of compound semiconductor nanowires via the VLS approach reported the transfer of the target stoichiometry to the product material even in the presence of carrier gas pressure as high as several hundred torr (1 torr \approx 133 Pa).^[12]

The transmission electron microscopy (TEM) image in Figure 2a shows a \sim 60 nm thick polycrystalline CdS shell around a 80 nm Si core. High-resolution TEM revealed the sharp interface between the single-crystal core and the shell (Fig. 2b). Energy-dispersive X-ray spectroscopy (EDS) was used to study the spatial distribution of elements in the nanowire (Figs. 2c,d) and confirmed that a uniform CdS shell was grown. The TEM results prove that PLD can be used to form continuous polycrystalline CdS coatings that completely cover the Si core over the whole length of a nanowire, despite the large lattice mismatch.

Since CdS films grown without intentional doping are typically n-type,^[13] we expect a radial p-n junction to be formed with the p-type Si core. The band alignment of Si and CdS suggests that the barrier for electron transport is lower than that for holes in our devices, so that a significant amount of recombination may be expected to occur non-radiatively in the Si core. Nonetheless, strong light emission has been demonstrated previously in n-CdS/p-Si crossed nanowire structures, indicating that this material system is a promising one for the further development of nanoLEDs.^[14]

Single-nanowire diode devices were fabricated by using electron-beam lithography to open windows in a resist layer in order to selectively etch the CdS shell with hydrochloric acid. The selectivity of the HCl etch for CdS is important, since it allows the complete removal of the shell from the exposed region of the wire without harming the Si

core. After a second electron-beam writing step to define the contact to an unetched portion of the nanowire shell, a Pd/Ti contact metallization was applied to both the core and the shell. We would like to point out that, in principle, photolithography can be used for these fabrication processes as well. Transport data recorded across the core-shell interface showed the rectifying behavior of a p-n diode, with the p-Si core acting as the anode (Fig. 3a). A rectification ratio of 130 was observed at 2.2 V bias. Figure 3b shows transport measurements obtained on control devices with contacts to only the core, or only the shell, of the heterostructured nanowires. In both cases, the current-voltage (I - V) curves are linear or nearly linear, indicating that the Pd/Ti metal contacts to both the core and the shell were ohmic. Electroluminescence (EL) from the core-shell diode devices was observed at an onset of \sim 2 V forward bias. For the spectroscopic measurements, we applied a bias of 4 V to obtain a higher light intensity. Green-light emission was observed close to the electrode contact to the CdS shell. The EL peak at room temperature was centered at 528 nm with a full width at half maximum of 20 nm (Fig. 3c). Deep-level luminescence around 600 nm was hardly observed, suggesting good stoichiometry and high pur-

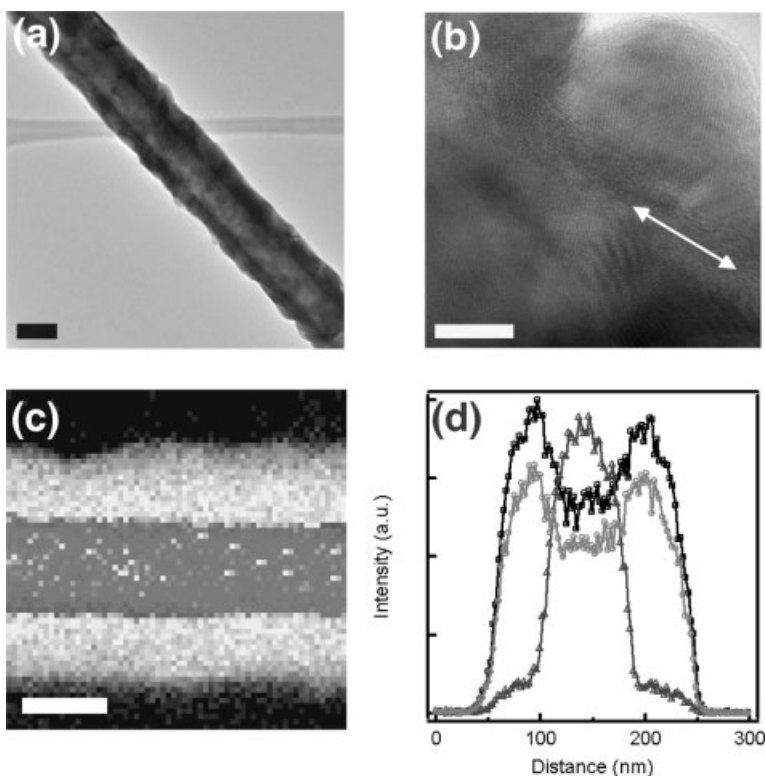


Figure 2. a) TEM image of the Si/CdS core-shell nanowire. Scale bar: 100 nm. b) High-resolution TEM image illustrating the core-shell interface. The arrow highlights the position of the interface between the single-crystalline Si core and the polycrystalline PLD-deposited CdS shell. Scale bar: 10 nm. c) Elemental mapping with EDS. Overlay of the spatial distributions of Si (K-line) and Cd (L-line) along the nanowire, illustrating the Si core and CdS shell. Scale bar: 50 nm. d) Cross-sectional line scan of the nanowire, highlighting the profiles of Si (Δ), Cd (\square), and S (\circ) across the core-shell nanowire.

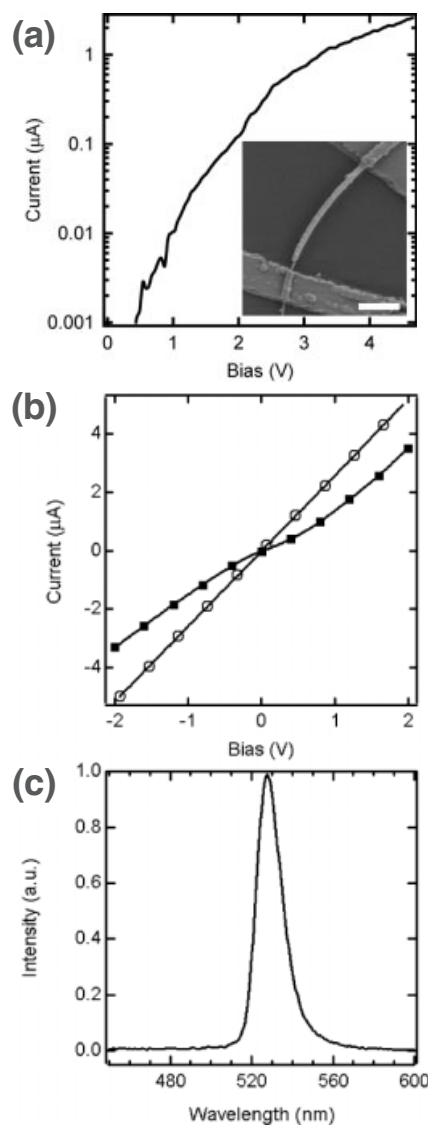


Figure 3. a) Transport measurement of the p–n core–shell junction, showing a rectifying I – V curve. The inset shows a scanning electron micrograph of the device. Scale bar: 2 μm . b) Transport measurements of the Si core (○: both contact regions etched) and the CdS shell (■: no etching). c) EL spectrum of the core–shell nanowire nanoLED.

ity in the polycrystalline CdS shell. However, the near band-edge emission was significantly red-shifted by ~ 15 nm, compared to reported luminescence results.^[15] The narrow EL peak, strong light emission, and rectifying I – V relationship demonstrate clearly that good electronic and optical properties can be achieved with this material system. Electron transport appeared to occur readily in the shell, despite the presence of grain boundaries. Further studies could help to determine the roles played by impurities and interfacial phenomena in electronic and optical properties of the CdS shell,^[16] and this, in connection with improved synthetic procedures, could lead to higher quantum yields and an even narrower EL spectrum. At present, the internal quantum yield of these preliminary core–shell nanoLEDs is ~ 0.01 %.

In conclusion, nanoLEDs from core–shell nanowires have been fabricated, despite large lattice mismatches, by introducing PLD as a novel approach for the deposition of nanowire shells. Though this heterostructure has not been optimized, the devices show near band-edge EL with a high spectral purity. These materials can potentially be applied to arrays of nanoLEDs on a single nanowire using photolithography, along with predefined p–n junctions. We expect that a variety of nanowire materials with a heterostructured core–shell interface can be synthesized using PLD overcoating, which is a flexible method compared with existing approaches to fabricating nanowire LEDs.

Experimental

Nanowire Synthesis and Characterization: Si nanowires were synthesized catalytically by VLS growth using 80 nm gold colloids (Ted Pella) which were dispersed on an oxidized silicon substrate. The growth substrate was placed in the center of a quartz tube furnace. The evacuated furnace (less than 3 mtorr) was heated up to 460 °C for 10 min followed by being kept for 30 min at 30 torr with a 40 sccm flow of SiH₄ (10 % in He) and a 10 sccm flow of B₂H₆ (100 ppm in He), resulting in the synthesis of silicon nanowires.

The growth substrate with the Si nanowires was used immediately for deposition of the CdS shell in order to prevent the formation of silicon oxide. The CdS target for PLD was placed in the center of a second tube furnace. The Si nanowire growth substrate was placed 2 cm upstream of the target. The tube was heated up to 250 °C in Ar at 10 mtorr. Laser ablation of CdS was performed using a pulsed Nd:yttrium aluminum garnet (YAG) laser ($\lambda = 1064$ nm; 10 Hz pulse rate; 0.5 W average power) for 1 min with a Ar flow rate of 1 sccm. The Si/CdS core–shell nanowires were characterized by TEM (JEOL 2010) and field-emission scanning electron microscopy (FESEM) (LEO 982).

Device Fabrication and Electrical Characterization: Electrical contacts to individual wires were defined using electron-beam lithography (JEOL 6400). The core–shell nanowires were supported on oxidized Si substrates (600 nm SiO₂). The CdS shells were etched with 20 % HCl. Electrode contacts consisting of 5 nm Pd and 200 nm Ti were deposited using a home-built electron-beam evaporator system. Electrical-transport measurements were made using a computer-controlled home-built system.

Electroluminescence Characterization: Room temperature EL spectra and images were recorded with a home-built microscope, a liquid-nitrogen-cooled CCD (Princeton Instruments Spec-10) and a spectrometer with a 1200 lines/mm grating blazed at 500 nm (Acton Scientific 300i).

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Hierarchical Mesoporous Carbon/Silica Nanocomposites from Phenyl-Bridged Organosilane**

By Jiebin Pang, Vijay T. John, Douglas A. Loy, Zhenzhong Yang, and Yunfeng Lu*

Mesoporous silica is of great interest for many applications.^[1,2] The past decade of research enables precise mesostructural control through tuning the co-assembly of surfactant and silicate. Functionalization of mesoporous silica, a process that imparts functionality to the pore surface or pore wall, is essential to convert the relatively inert silica into various functional materials.^[3,4] Until now, functionalization of

mesoporous silica has often been achieved by post-grafting methods,^[5,6] direct-synthesis methods,^[7,8] or by using functional surfactants.^[9] The direct-synthesis method provides mesoporous silica with functionalities through co-assembly of surfactants with organosilane precursors that contain non-hydrolyzable pendant or bridged organic ligands.^[6–8,10–13] Current research in this area has been focused on the synthesis of functionalized mesoporous silica with organic or metallic moieties.^[3,14]

This communication reports the synthesis of ordered mesoporous carbon/silica composites with unique pore walls that are composed of molecularly integrated silica and carbon. This is achieved by co-assembling octadecyltrimethylammonium bromide (OTAB) with 1,4-bis(triethoxysilyl)benzene (BTEB),^[13] followed by a carbonization process that decomposes the surfactant and converts the phenylene moieties into carbon. The incorporation of carbon into the pore wall not only results in interesting mesoporous carbon/silica nanocomposites, but also may provide materials with improved thermal, chemical, and mechanical properties. Furthermore, removal of the silica from the carbon/silica nanocomposites results in mesoporous carbon materials that can positively replicate the mesostructure of the silica template. Compared with the conventional two-step synthesis of mesoporous carbon^[15] in which mesoporous carbon (an inverse replica of silica) is prepared by the infiltration of carbon precursors into preformed mesoporous silica followed by carbonization and silica removal, this method provides a direct method to synthesize mesoporous carbon for hydrogen storage, catalysts, fuel cells, and other applications.

Figure 1 shows the X-ray diffraction (XRD) patterns of the phenylene/silica/surfactant hybrid powders before the removal of surfactant (curve a), after the removal of surfactant by solvent extraction (curve b), and after the carbonization in N₂ at 900 °C (curve c). Similar to previously reported results,^[13] the phenylene/silica hybrid materials before and after surfactant removal exhibit typical low-angle diffraction peaks that correspond to a hexagonal mesostructure with a *d*₁₀₀ spacing of 4.8 nm. The high-angle diffraction peaks (curves a,b) demonstrate the periodic crystal-like structure

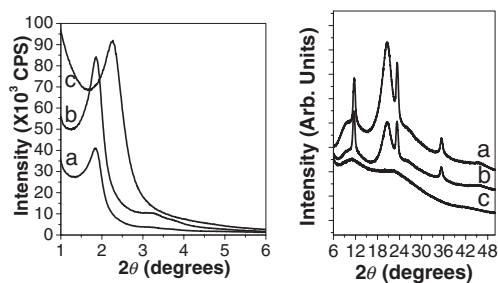


Figure 1. Low-angle (left) and high-angle (right) XRD patterns of the phenylene/silica/surfactant hybrid powders before the removal of surfactant (curve a), after the removal of surfactant by solvent extraction (curve b), and after the carbonization in N₂ at 900 °C (curve c). (CPS: counts per second.)

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