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Crystalline Boron Nanowires

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We report growth of boron nanowires by chemical vapor deposition (CVD). The nanowires have diameters in the range of 20−200 nm, lengths of several μm, and are crystalline as grown. Conductivity measurements establish that the nanowires are semiconducting and exhibit electrical properties consistent with those of elemental boron.

Much attention has focused on carbon nanotubes for their potential as nanowires, that is, as nanoscale electrically conducting interconnects for molecular electronics.[7] However, the electrical properties of carbon nanotubes depend on diameter and chirality,[7,8] and only ~33% in a synthetic mixture exhibit metallic conductivity.[7] Nanowires composed of metals are dramatically susceptible to electromigration failure at diameters of <60 nm.[9] We propose that ideal 1D nanoscale interconnects would be composed of electrically conductive ceramics or refractory elements possessing high crystallinities, high conductivities irrespective of chirality or crystallographic orientation, and covalent bonding, which should reduce susceptibilities to electron-wind-induced[9] thinning and failure.

Recent theoretical studies suggest that boron nanotubes, resembling carbon nanotubes except having deltahedral rather than graphene wall structures, should be stable.[10,11] Moreover, boron nanotubes are predicted to have high metallic conductivities, exceeding those of carbon nanotubes, in both zigzag and armchair structures.[11] Consequently, we sought to prepare 1D boron nanostructures to investigate their structural and electrical properties. Our initial results are described here. While our work was in progress, Yang and co-workers reported the VLS growth of amorphous boron nanowires, which were used to prepare MgB_2 nanowires.[12] Additionally, Cao and co-workers reported the growth of amorphous boron nanowires by magnetron sputtering.[13] The electrical behavior of the amorphous boron nanowires was not described.[12,13]

In our procedure, a 5% diborane-(B_2H_6)-in-Ar gas mixture (13 mL/min) further diluted with pure Ar (15 mL/min) was passed over NiB powder on an alumina substrate in a hot-wall, fused-silica reactor tube held at 1100 °C in a tube furnace. The B_2H_6−Ar gas mixture was delivered to the reactor through stainless steel tubing for 30 min. Upon cooling, the substrate was removed from the reactor tube and inspected. The NiB particles were found to have partially melted and fused together, forming a slag that adhered to the substrate.

SEM images of the slag were either recorded directly or after peeling the brittle slag from the substrate using tweezers. The images revealed dense entanglements of nanowires (Figure 1a), which appeared in various, separated regions on the slag at an estimated surface coverage of up to ~40%. The nanowires were generally at least several micrometers in length, appearing to grow both in long straight segments and in curly tufts.

Representative TEM images of nanowires are shown in Figure 1b and c. The nanowire diameters ranged from 20 to 200 nm (mean value ~60 nm). Most nanowire images contained a prominent line lying along the nanowire long axis (Figure 1b, c), resulting from a twinning plane rather than a central hollow space. Electron diffraction established that the nanowires were crystalline; the doubling of spots and parallel streaks between spots in the patterns confirmed the twinning (Figure 1d). An orthorhombic unit cell with a = 9.4 Å, b = 7.1 Å, and c = 5.4 Å was consistent with nanodiffraction data. The twinned halves of each nanowire were found to share a common c axis. Hence, the nanowires were dense, twinned, whisker crystals rather than nanotubes.

The lattice parameters given above did not match those of any known boron polymorph or boron-rich compound we found in a search of the literature. Elemental analysis by energy-dispersive X-ray spectroscopy (EDS) and parallel electron-energy-loss spectroscopy (PEELS) in the TEM, detected carbon, which we assigned to adventitious surface deposits (see below), but did not detect Ni or other elements (detection limits ≈ 1−3%). However, the propensity of boron to incorporate impurity elements and to form boron-rich compounds with other elements at levels possibly below our detection limits precluded a conclusion that the nanowires constitute a new allotrope of boron.[14,15]

PEELS analyses established that the carbon concentration in the nanowires scaled with their diameters. As shown in Figure 2, the measured carbon levels generally increased with decreasing diameter, which is inconsistent with a uniform carbon distribution throughout the nanowire volume in the form of a boron-rich compound or solid solution. To evaluate if the observed diameter dependence was consistent with carbon as a surface deposit, we conducted stoichiometric calculations on hypothetical nanowires having C surface coatings of various thickness surrounding a dense, cylindrical B core. Our model calculations produced the curves in Figure 2, which compared closely to the experimental data. Additionally, element maps constructed from energy-filtered TEM images showed carbon concentration at the peripheries of the nanowires, and amorphous coatings were evident in some normal TEM images (Supporting Information). The diffuse background scattering about the center of Figure 1d is also of proper form and intensity to have been generated by a thin amorphous carbon layer on the surface of the crystalline nanowire. The source of the surface carbon is uncertain; however, carbon is environmentally ubiquitous, and can be deposited by e-beam decomposition of residual hydrocarbon in the SEM or TEM or both.[16,17,18]

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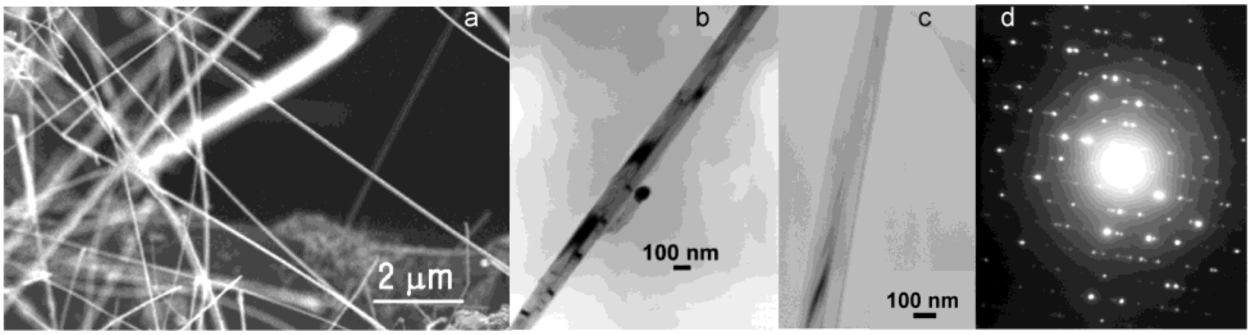

Figure 1. (a) SEM image of B nanowires, (b) and (c) TEM images, (d) electron-diffraction pattern of nanowire in (c).

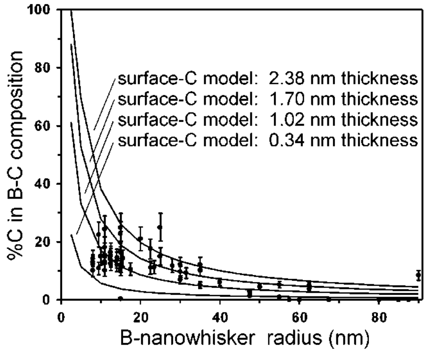

Figure 2. C content of B nanowires vs radius, as determined by TEM/PEELS (data points). The curves were obtained from surface-C model calculations and correspond to layer thicknesses of 1, 3, 5, and 7 carbon van der Waals diameters (0.34, 1.02, 1.70, and 2.38 nm, respectively).

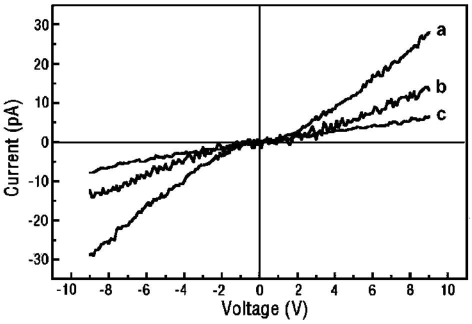

Figure 3. $I-V$ data for three B nanowires. The diameters (d), distances between the PtIr probes (l), and conductivities (σ) determined were: (a) $d = 46 \pm 2$ nm, $l = 2740 \pm 37$ nm, $\sigma = (5.5 \pm 0.4) \times 10^{-5}$ (ohm cm)$^{-1}$; (b) $d = 115 \pm 33$ nm, $l = 8400 \pm 81$ nm, $\sigma = (1.3 \pm 0.5) \times 10^{-5}$ (ohm cm)$^{-1}$; (c) $d = 58 \pm 4$ nm, $l = 4817 \pm 30$ nm, $\sigma = (1.4 \pm 0.2) \times 10^{-5}$ (ohm cm)$^{-1}$.

Individual B nanowires were manipulated by and suspended between two PtIr probe tips in an SEM (LEO 1530) to enable electrical measurements. The $I-V$ curves for three nanowires are plotted in Figure 3. The nonlinearity in the central region of each curve results from nonohmic electrode contacts and is characteristic of semiconducting nanowires.[19,20] The nanowire conductivities were extracted by least-squares fitting of the linear regions of the curves, giving the values in Figure 3, which must be interpreted as lower limits because of the unknown contact resistances associated with the two-probe measurements. The observed values of $1.3-5.5 \times 10^{-5}$ (ohm cm)$^{-1}$ fit the range reported for bulk B: $10^{-4}-10^{-7}$ (ohm cm)$^{-1}$.[21] Interestingly, the room-temperature conductivities for the bulk boron carbides $B_{1-x}C_x$ ($x = 0.1-0.2$),[22] and C-doped bulk B[23] fall in the range of 10^0-10^2 (ohm cm)$^{-1}$, well-separated from our measured values, which suggests that the nanowires are neither carbide phases nor C-doped phases. If the nanowires had been metallic conductors, the contact resistances should have vanished, resulting in fully linear $I-V$ data and conductivity values in the metallic regime, which we did not observe. Thus, the B nanowires we synthesized were semiconductors. Bulk B is a semiconductor having a band gap of 1.6 eV.[24]

In summary, crystalline, semiconducting B nanowires have been grown by a simple CVD method. We expect that the nanowire conductivities can be enhanced to metallic levels through doping, as has been demonstrated for Si nanowires,[20] and bulk B.[23,25] Furthermore, if stable B nano*tubes* may exist, they are likely to be found at smaller diameters than those obtained here, as is the case for C,[7,8] Au,[26] and other nanotubes. Investigations of these issues are in progress to realize the goal of refractory, covalently bonded, highly conductive nanowires.

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Supporting Information Available: EELS and EDS data, element maps, nanodiffraction pattern, and so forth. (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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