

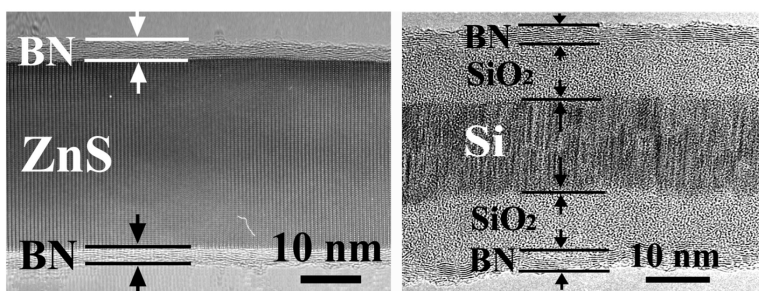
Communication

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Insulating Tubular BN Sheathing on Semiconducting Nanowires

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One-dimensional nanostructures are currently the focus of intensive materials research because of their intriguing properties and a prospective wide range of technological applications.¹ Semiconducting nanowires are of particular interest as the key blocks of nanoscale electronic and photonic devices.^{2,3} Nanoscale materials, e.g., nanowires, often display high chemical reactivity due to their low dimensionality and high surface-to-volume ratio. This chemical reactivity leads to the nanowire oxidation and contamination, resulting in dramatic changes in nanowire structure, morphology, and properties. Thus, it is extremely important to have a protective sheath made of thermally and chemically stable materials on a given nanowire to enhance its performance.

Hexagonal boron nitride (BN), a covalently bonded compound, displays stable insulating properties (a ~ 5.5 -eV band gap) independent of its morphology.⁴ Moreover, graphitic-like BN is chemically inert and remarkably thermally stable.⁵ These advantages are assumed to be inherited on the nanoscale level, and thus a BN nanotube may serve as a naturally insulating and/or protective shield for any nanowire encapsulating within.

Filling BN nanotubes is challenging work. Filling of conventional C nanotubes with various materials by capillarity^{6–8} or wet chemistry methods⁹ has been carried out for a decade. However, all well-established techniques for C tube filling do not properly work for BN nanotubes because of the significant difficulties in wetting a BN graphene-like surface as compared to C.⁵ As a result, to date research on capillarity-induced filling of BN nanotubes has not been widely carried out.¹⁰ The nanotube-templated two-stage process¹¹ and the catalyst-assisted process^{12,13} were performed to synthesize BN-coated nanorods. Recent progress has been made in preparation of BN-sheathed nanowires through a one-step and catalyst-free high-temperature process.¹⁴ This motivates us to probe the possibility of nanowire coating with thermally and chemically stable layered BN at a relatively low temperature. We herein report the successful fabrication and characterization of BN-sheathed semiconducting nanowires.

Semiconducting nanowires composed of ZnS and Si were selected as the objects to be sheathed with BN. ZnS as a wide band gap semiconductor is a well-known luminescence material having prominent applications in displays, sensors, and lasers. Silicon is the most widely used material in the semiconductor industry. It is noted that Si nanowires are often coated with unstable amorphous SiO₂ phase,¹⁵ which, however, cannot effectively protect them. By contrast, the BN-sheathed semiconducting nanowires may find wide applications in nanoelectronics and nanooptics because of their excellent stability. Moreover, the coating method designed in the present communication may be generally applied for the fabrication of any nanostructures sheathed with layered BN.

Experimentally, a precursor was synthesized by dissolving 0.4 mol of boric acid (H₃BO₃) in 1000 mL of water at 100 °C. Melamine (0.2 mol, C₃N₆H₆) was then slowly added into the solution. The white precipitates were dried and calcined at 500 °C in air for 2 h for dehydration. After an additional 1 h of annealing

at 800 °C in nitrogen atmosphere, a yellow-colored powder was obtained as a B–N–O intermediate product; this might be the formula B₄N₃O₂H.¹⁶ The yellow powder was further calcined at 600 °C in air for 2 h; resultantly a white B–N–O product containing more oxygen was obtained.

The as-prepared precursor was put into a BN crucible. A BN disk with semiconductor nanowires¹⁷ was placed above the crucible. The components were enclosed into a graphite susceptor and heated in an induction furnace. The positions of the crucible and disk were adjusted to ensure that the B–N–O precursor was heated at 1600 °C, whereas the nanowires were heated at 700–800 °C. The atmosphere was a N₂/NH₃ flow (N₂ 1.5 L/min, NH₃ 0.05 L/min.) After the process was conducted for 1 h, tubular BN-sheathed nanowires were obtained. The formation of BN may be described using the following chemical reaction: B₂O₃ + 3C (susceptor) + 2NH₃ → 2BN + 3CO + 3H₂O.

The preparation of BN-sheathed nanowires was also carried out in a one-step process when two crucibles were employed. For the preparation of BN-sheathed Si–SiO₂ nanocables, a crucible containing a SiO powder was placed above a crucible containing the B–N–O precursor. The graphite susceptor was heated to 1200 °C in Ar atmosphere to synthesize Si–SiO₂ nanocables¹⁵ and then heated to 1600 °C at N₂/NH₃ atmosphere to sheath the cables with BN. ZnS/BN nanocables can be synthesized through a similar process.

The resultant BN-sheathed nanowires were analyzed using a JEOL-3000F high-resolution 300 kV transmission electron microscope (HRTEM) equipped with a Gatan-766 electron energy-loss spectrometer (EELS) and by a JEOL-3100FEF energy-filtered (Omega filter) 300 kV electron microscope. The EELS line-scan technique was employed in addition to the standard EELS mode.

Figure 1a displays the core–shell structure of a ZnS nanowire coated with uniform BN layers where the BN coating is indicated by parallel lines. The ZnS nanowire reveals clear lattice fringes, and the BN sheath is very uniform over a long range. Figure 1b depicts the magnified image of the nanocable shown in Figure 1a that clearly displays the lattice of the BN sheath with an interlayer spacing of 0.334 nm, which corresponds well to an interplanar distance of the (002) planes of hexagonal BN. The crystal lattice of ZnS has an interplanar spacing $d_{001} = 6.26$ Å. The selected area electron diffraction (SAED) pattern (left inset in Figure 1b) reveals a wurtzite phase with the lattice constants of $a = 0.382$ nm and $c = 0.626$ nm (PDFs: 36–1450). The tubular structure of the BN sheath is clearly seen in the elemental profiles taken across a nanocable (right inset in Figure 1b). The profiles of B and N reveal the tubular geometry, whereas those of Zn and S are consistent with the cylinder geometry.

Figure 2a displays a multilayered coaxial structure that combines a Si nanowire core with SiO₂ and BN sheathes in the radial direction. The magnified image in Figure 2b shows that the nanocable has a crystalline Si core and an amorphous SiO₂ interlayer and a BN outer sheath. The crystal lattice of Si has an interplanar

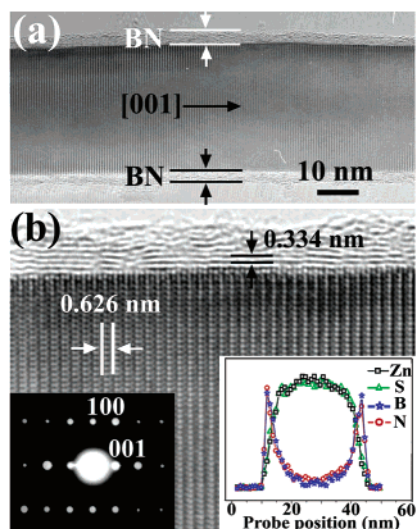


Figure 1. HRTEM images of a BN-sheathed ZnS nanowire. (a) Structure of a nanocable growing along the [001] axis; the parallels indicate BN tubular sheaths. (b) A magnified image of the nanowire in (a). Left inset: SAED pattern. Right inset: elemental profiles across the nanocable.

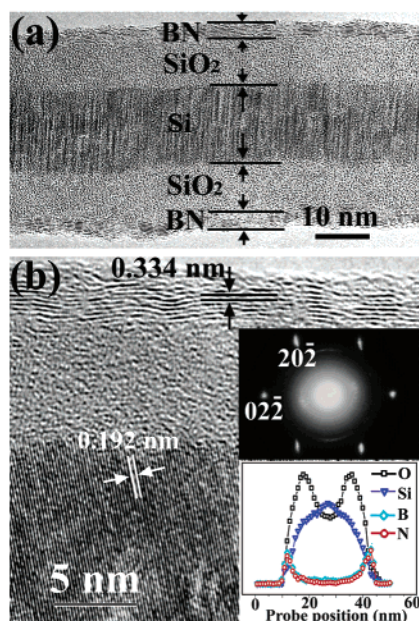


Figure 2. HRTEM images of a BN-sheathed Si-SiO₂ nanowire. (a) Structure of a nanocable. (b) Enlarged image of the nanocable in (a). Top inset: SAED pattern of the nanowire. Bottom inset: elemental profiles across the nanocable.

spacing $d_{220} = 1.92 \text{ \AA}$. The SAED pattern (inset in Figure 2b) indicates that the crystalline core is indeed the cubic Si with a lattice constant of $a = 0.543 \text{ nm}$ recorded along the [111] zone axis (PDFs: 27-1402). The elemental profiles of B, N, and O show two peaks with a central hollow, thus displaying the typical characteristic of a tubular geometry (inset in Figure 2b). The profile of Si is peaked in the center. The atomic ratio of B and N is ca. 1:1 while that of Si and O in the interlayer is ca. 1:2, as measured by EELS analysis using a 1-nm electron probe. The BN sheath on both ZnS and Si-SiO₂ nanowires are crystal hexagonal BN, as confirmed by the long-rang lattice fringes in Figures 1 and 2. Dislocations are observed on the BN sheath.

The present synthesis method has prominent advantages over other methods for the preparation of BN-sheathed nanomaterials. Capillarity-induced filling of BN nanotubes is not so effective due

to the difficulties in wetting a BN graphite-like surface. A template-based two-stage method is more complicated to perform. A catalyst-assisted process unavoidably introduces impurities. The present developed method is effective to sheath variously shaped nanostructures at a relatively low temperature.

The formation process of a BN sheath involves a vapor–solid reaction process. The B–N–O and B₂O₃ vapors were first generated when the B–N–O precursor was heated to 1600 °C, and then B₂O₃ and B–N–O vapors were transported to and deposited on the surface of nanowires. The nanowires, in turn, reacted with other species available in the reaction chamber atmosphere; this finally resulted in the formation of BN sheaths. The formation of a crystalline-layered BN usually requires a high temperature (normally above 1200 °C). The absorption of B₂O₃ and B–N–O on the surface of nanowires may decrease the energy barrier for the formation of BN. Thus, BN sheaths can be formed at a relatively low temperature ($\sim 700\text{--}800 \text{ }^\circ\text{C}$). A wide variety of materials can be sheathed with layered BN at the lower temperatures using the present technique. It is noted that most of the nanowires are sheathed with BN coating (>90%), and some hollow spheres of BN were formed in the coating process.

In summary, an effective method was developed for the generation of insulating tubular BN-sheathed nanostructures. ZnS nanowires and multilayered Si–SiO₂ nanowires were successfully sheathed with insulating tubular BN shells. Both the semiconducting nanowire cores and the BN sheaths are highly crystalline and uniformly structured. The method may be used to sheath nanomaterials of various shapes and geometries. Designed nanostructures for special nanodevices may be sheathed with thermally and chemically stable BN coating (only several nm thick) to form a stable electrical unit. Therefore, we envisage that the method should be particularly important for the fabrication of nanodevices.

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Supporting Information Available: Schema of reaction chamber (S1) and TEM image of the nanocables (S2) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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