

Communications

CVD Growth of Boron Nitride Nanotubes

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Received February 22, 2000

Revised Manuscript Received May 9, 2000

We describe BN-nanotube growth by chemical vapor deposition (CVD) using the precursor borazine ($B_3N_3H_6$),¹ which is generated in situ.² Multiwalled BN nanotubes are observed to form in dense thickets on and about nickel boride catalyst particles at ~ 1100 °C. The BN nanotubes resemble those grown by the higher temperature arc-discharge^{3–6} and laser-ablation methods,⁷ except for a preponderance of bulbous, club-like, and flag-like tip closures, which to our knowledge have been observed in only one prior study.⁸ The results suggest a root-growth mechanism in which the nanotubes are extended by BN addition at their roots, where the nanotubes are attached to the catalyst particles.

In contrast to their all-carbon analogues, boron nitride nanotubes are predicted to exhibit electronic properties that are insensitive to tube diameter and chirality.⁹ Boron nitride nanotubes are known to have a wide band gap of ~ 5 eV and to thus be insulating.¹⁰ A comparison of the mechanical properties (tensile, bending, and flattening) of boron nitride and carbon nanotubes is also of interest.^{11,12} Previous attempts to grow BN nanotubes by CVD or related chemical methods produced materials having internally closed, segmented (bamboo-like), or other irregular structures, having poorly crystalline or polycrystalline walls, and/or having carbon incorpor-

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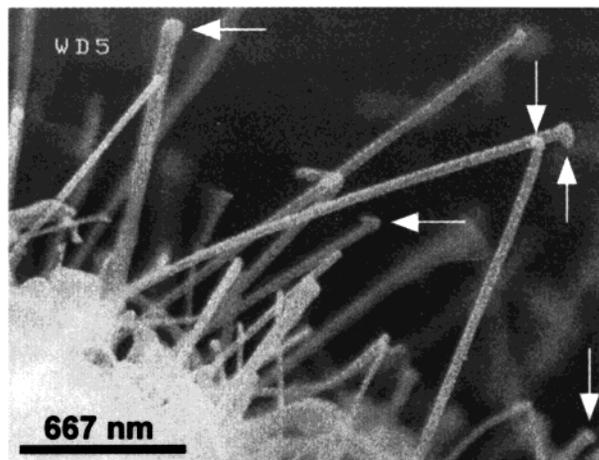


Figure 1. SEM image from a BN-nanotube deposit. The arrows identify bulbous tip features, which are present on many nanotubes.

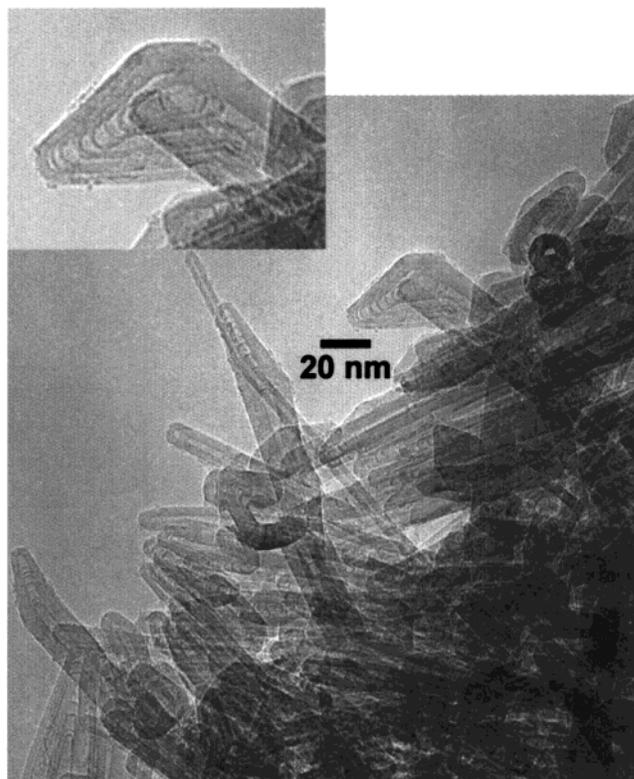


Figure 2. TEM image showing the variety of BN-nanotube tip closures present. Inset: magnified view of the club-shaped tip from the upper right.

ation.^{13–18} The method described here produces carbon-free BN nanotubes with concentric-tube structures that do not contain internal wall closures or internal cap structures and that possess crystallinities and lengths

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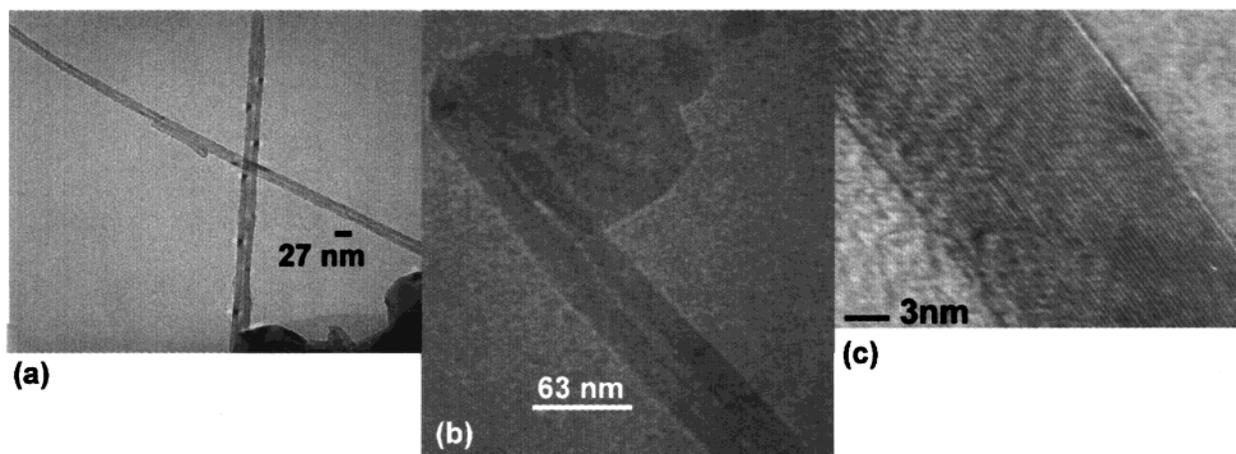
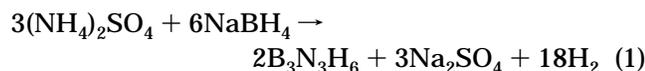


Figure 3. TEM images of and from BN nanotubes: (a) two long, crystalline nanotube sections; the dark spots evident in the walls are presumably buckling sites resulting from bending strain; (b) ragged nanotube terminus that appears to consist of incomplete BN layers and is proposed to be the nanotube growth root; and (c) high-magnification view of a nanotube wall.

comparable to those produced by the arc-discharge or laser-ablation syntheses.^{3–7}

We adapted a standard borazine preparation² (eq 1) for the in-situ generation of borazine. We found in-situ generation convenient because isolation and storage of borazine, which slowly decomposes at room temperature and is prone to polymerization,^{1,2} was bypassed. A solid mixture of $(\text{NH}_4)_2\text{SO}_4$ and NaBH_4 was slowly and intermittently added to a flask containing Co_3O_4 at 300–400 °C. A dark-purple, molten-salt mixture was generated, which evolved gas vigorously and emitted a small amount of a white aerosol. The evolved gas contained borazine, related BN precursor species, and H_2 , which were swept into a tube-furnace reactor by a N_2 carrier-gas flow.¹⁹ A diagram of the borazine generator and CVD reactor is provided in Figure S1 (Supporting Information). The aerosol collected as a trace white powder in the transfer tubing and was found to consist primarily of $(\text{NH}_4)_2\text{S}_2\text{O}_3$, a minor side product, by X-ray powder diffraction. The use of carbon-free reagents and the carbon-free molten-salt reaction medium precluded carbon incorporation into the BN nanotubes.



Nanotube growth was achieved from Co, Ni, NiB, and Ni_2B particulate catalysts. The nickel boride catalysts produced the best results, which appeared to be indistinguishable and are described here. Commercial NiB or Ni_2B powder was ball-milled or ground in a mortar

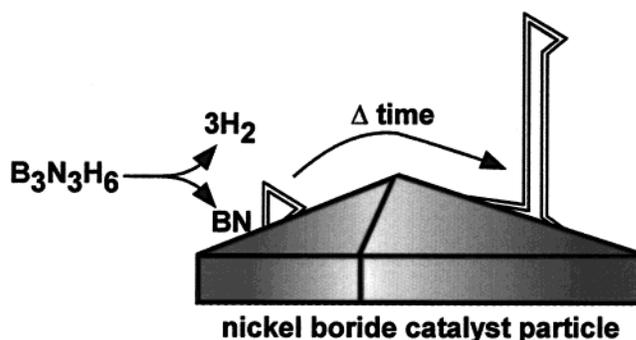


Figure 4. A depiction of the proposed root-growth mechanism. Left: nanotube-cap nucleation. Right: at a later stage of growth; note the flag-like initial cap, the conventional nanotube middle section, and the root at the nanotube-catalyst junction consisting of incomplete BN layers.

and pestle to micrometer-range particle sizes, and applied as an EtOH slurry to a silicon-wafer substrate having a 250 nm thermally grown SiO_2 passivation layer. The substrate and NiB or Ni_2B were placed in the center of the tube-furnace reactor, which was heated to 1000–1100 °C. The substrate and catalyst were exposed to the borazine-containing carrier-gas flow for ~30 min. After this exposure, white deposits were observed on the substrate by an unaided eye and optical microscopy.

Examination of these deposits by SEM revealed dense coatings of BN nanotubes radiating from and between most or all of the nickel boride particles (Figure 1). Many nanotube tips were bulbous (Figure 1). TEM images of nanotubes scraped from the substrates revealed that these bulbous tips often possessed club-like or flag-like geometries (Figure 2), which were enlarged extensions of the nanotubes,⁸ not attached nickel-boride-catalyst nanoparticles. The TEM images established that the structures were hollow, crystalline nanotubes (Figure 3a) that exhibited the parallel-fringe patterns characteristic of multiwalled C and BN nanotubes (Figure 3c).^{3–7} The nanotube lengths were up to ~5 μm . Electron-energy-loss spectroscopy (EELS) confirmed the BN composition of the nanotubes, giving B:N ratios in the range of 1.0–1.3 (Figure S2). Some nanotubes contained isolated deposits of amorphous material (*not* internal closures) within their hollow interiors, which

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(19) **Caution:** The reaction generates significant amounts of H_2 , which should be continuously removed from the apparatus by an efficient N_2 flow. Additionally, the borazine generation described here is potentially hazardous and must be conducted in accordance with the safety measures described in the Supporting Information.

appeared to be composed only of B, or B and N, because energy-dispersive X-ray spectroscopy and EELS did not detect other elements.

TEM images also revealed that one nanotube end was often either fractured or ragged, in the latter cases appearing to consist of flared, incomplete shells (Figure 3b). These were presumably the nanotube ends that had been attached to the catalyst particle on the substrate. The results were consistent with a root-growth mechanism in which nanotubes nucleated on a nickel boride particle with often irregular (bulbous, club-like, flag-like, or other) initiation caps and grew by incorporation of additional BN at the catalyst–nanotube junctions, such that growth separated the initiation caps from the catalytic surface (Figure 4). At the termination of growth the nanotubes apparently remained attached by roots consisting of incomplete BN layers adhering to the large nickel boride particles on the substrate.

We are currently attempting to prepare monodispersed nickel boride particles having nanometer-scale dimensions to control BN nanotube diameters and wall thicknesses. We are also working to develop this method

for bulk production of BN nanotubes, and for the growth of uniform BN nanotube films to be evaluated as potential low-*k* dielectrics.^{20,21}

Acknowledgment. This work was funded by the Semiconductor Research Corporation (Research ID 651) and NSF grants CHE-9709104 (to W.E.B.) and DMR-9704644 (to R.S.R.). C.R.J. was partially supported by a Department of Education GAANN grant (P200A98 0221). We thank Thomas Kelly and Richard Casper (University of Wisconsin) for help with electron microscopy, Ping Jiang for help with GC-MS, Hui Huang (Cornell University) for providing the passivated silicon substrates, and David McIlroy (University of Idaho) for suggesting and providing the ball-milled NiB catalyst.

Supporting Information Available: Figures S1 and S2, experimental (procedural) details, and safety precautions (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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