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Synthesis of $B_xC_yN_z$ nanotubules

Z. Weng-Sieh
Department of Materials Science and Mineral Engineering, University of California at Berkeley, Berkeley, California 94720 and Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

K. Cherrey, Nasreen G. Chopra, X. Blase, Yoshiyuki Miyamoto,* Angel Rubio,† Marvin L. Cohen, Steven G. Louie, and A. Zettl
Department of Physics, University of California at Berkeley, Berkeley, California 94720 and Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

R. Gronsky
Department of Materials Science and Mineral Engineering, University of California at Berkeley, Berkeley, California 94720 and Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720
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We report the successful synthesis of $B_xC_yN_z$ nanotubes. Arc-discharge methods were used to produce stable nanotubule structures identified by high-resolution transmission-electron microscopy. Local electron-energy-loss spectroscopy of K-edge absorptions for B, C, and N atoms was used to determine the atomic compositions of individual tubules. Tubes of stoichiometry BC_2N and BC_3 have been observed, in agreement with theoretical predictions.

The discovery of tubule forms of graphitic carbon[1] has motivated interest about their atomic and electronic structures, and possibilities for technological applications. Motivated by graphitic analogs, such as hexagonal BN, BC_3, and BC_2N, the existence of $B_xC_yN_z$ nanotubes has been proposed and studied theoretically.[2–5] For example, *ab initio* total-energy calculations[3] shows that the wrapping of a BN hexagonal sheet onto a tubular shape is energetically more favorable than in the case of graphite, suggesting that $B_xC_yN_z$ nanotubes may be metastable. We report in this paper on the synthesis of $B_xC_yN_z$ nanotubes.[6] The samples were prepared using arc-discharged carbon/BN anodes. Transmission-electron microscopy (TEM) was used to confirm the tubule forms and electron-energy-loss spectroscopy (EELS) of K-edge absorptions for B, C, and N atoms was used to determine the atomic compositions of the samples.

Synthesis of $B_xC_yN_z$ nanotubules was carried out using arc-discharge methods similar to those used previously for pure carbon nanotubes.[1] Anode rods of different structure and B-C-N composition were prepared, and subsequently arced against pure graphite cathodes in a helium gas environment. A number of anode-type, arc current, and helium pressure combinations were investigated. To produce the $B_xC_yN_z$ nanotubules described below, a high-purity graphite rod (0.250-in. diam) was center drilled to slip-fit a high-purity, hot-pressed BN rod (0.125-in. diam) inside. This composite rod was arced next to a larger (0.750-in. diam) graphite cathode at low current (30–40 A dc) in a relatively high-pressure helium environment of 650 torr. The arc gap was maintained as close as possible without extinguishing the arc (gap typically <1 mm). A cathodic deposit formed with a diameter of approximately 0.375 in. Unlike the result using pure graphite electrodes, this deposit did not have a soft inner core with a hard outer sheath. The deposit easily scratched glass and was somewhat denser along the central axis. Transmission-electron-microscopy and electron-energy-loss-spectroscopy studies were conducted on the denser inner region. We note that a slightly lower helium pressure of 450 torr and an increased arc current of 55–60 A dc with a similar anode configuration did not produce a cathodic deposit with B- or N-containing nanotubules. A similar anode instead containing a 0.188-in.-diam high-purity, hot-pressed BN rod failed to vaporize completely at any current setting (the graphite burned without sustained melting of BN). We also note that although cobalt-catalyzed single-wall nanotubes have been reported[7] for pure carbon nanotubes, introduction of cobalt into our graphite/BN anodes produced no corresponding evidence for single-wall $B_xC_yN_z$ nanotubules.

Specimens for TEM were prepared by crushing the inner, denser region of the deposit between two glass slides and by dispersing the resultant fine particles onto a copper grid covered with a holey carbon film. TEM imaging, EELS measurements, and electron-diffraction analyses were performed at 200 keV in a JEOL JEM 200CX TEM equipped with a Gatan 666 parallel collection electron-energy-loss spectrometer. All spectra were acquired using an $\sim$5-nm probe size, and recorded with an energy dispersion of 0.5 eV per channel in the core-loss (K-edge) regime or 0.1 eV per channel in the low-loss (plasmon peak) regime. Spectral analyses were performed on the inner-shell ionizations for chemical fingerprinting, on the near-edge fine structure for bonding and structure information, and on the plasmon peaks for electron-density and coupling information.

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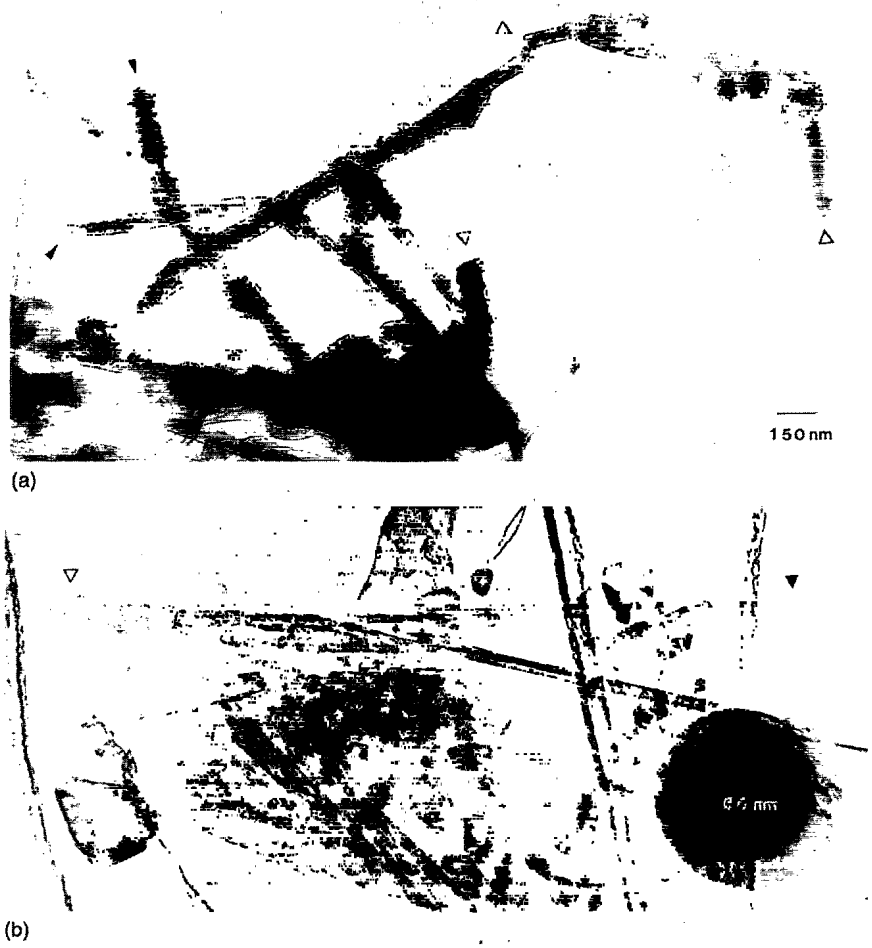

FIG. 1. (a) TEM image of BC_2N (filled arrow) and BC_3 (hollow arrow) tubes. The image, taken in the out-of-focus condition, clearly indicates tube morphologies, including large tube walls and small inner-tube diameters. (b) TEM image of a single tube with BC_3 composition on one end (hollow arrow) and a carbon composition on the other (filled arrow).

TEM images of the arc-discharge deposited material reveal an assortment of tubule, platelet, and sheet morphologies. Figures 1(a) and 1(b) show a typical assortment of nanotubules with diameters ranging from 10 nm to 0.1 μm and lengths ranging from 0.1 to 0.3 μm. Some of the tubules exhibit tapered, needlelike tips, as previously observed in conventional carbon nanotubules,[1] while others have distinctively capped blunt ends.

EELS spectra obtained from blunt-edged tubules reveal two different atomic compositions: boron-carbon-nitride [Fig. 2(a)] and boron carbide [Fig. 2(b)]. Spectra obtained from tubules indicated by the hollow arrowheads in Figs. 1(a) and 1(b) exhibit ionization edges[8] at approximately 188 and 284 eV,[8,9] corresponding to the characteristic K-shell ionization edges of boron and carbon, respectively, in addition to a nitrogen K-edge ionization at approximately 414 eV in Fig. 2. For both the boron-carbon-nitrogen and the boron carbide tubules, the near-edge finite structures of both the boron and carbon K edges consist of distinct π^* and σ^* graphitic features. The separations of the measured π^* and σ^* energy levels observed for boron-carbon-nitrogen (at 8.0, 7.0, and 6.0 eV for B, C, and N, respectively) and for the boron carbide tubes (9.5 eV for B and 7.5 eV for C) are comparable to those predicted by density-of-states calculations of the BC_2N and BC_3 layer structures.[10,11] For the BC_3 tubules, both the π and π^* bands are calculated to be unoccupied, in contrast to other compound and carbon tubules.[4] Although the present EELS spectrum taken from the sample around the area with atomic composition of BC_3 does not show a clear peak for the $1s \rightarrow \pi$ transition, we expect that the peak could be observed with higher resolution.

The sharply defined π^* and σ^* pre-ionization-edge fine-structure features, associated with π^* and σ^* antibonding orbitals, are the well-known signatures of the sp^2 hybridization seen in graphitic structures. However, the nitrogen K-edge structure found in the boron-carbon-nitrogen spectra deviates from the ideal sp^2 hybridization. This deviation can be explained in terms of atomic relaxation in the tubular structure. A recent calculation[3] suggests that the BN tubules are stabilized by a buckled configuration of the B-N bonds. Consistent with the present experimental results, this buckling brings the $\widehat{NBN}$ angles to a nearly perfect 120° (i.e., the signature of the sp^2 hybridization), while N atoms relax towards an s^2p^3 geometry. Since such a buckling effect is related to ionicity differences between B and N atoms, a similar buckling is expected to occur in the BC_2N tubules.[5] We

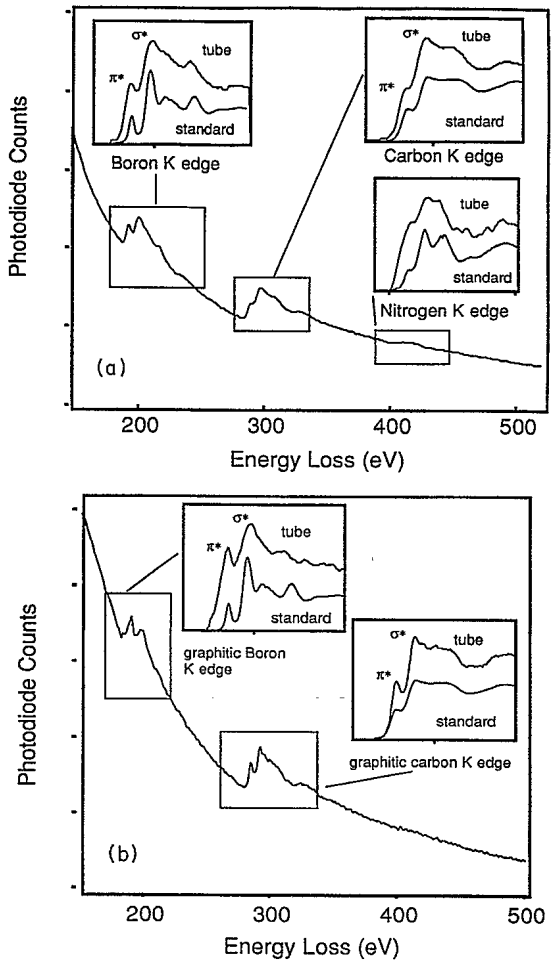

FIG. 2. EELS spectra of (a) a B-C-N tube and (b) a boron carbide tube. Insets show the background-subtracted K edges of (a) boron, carbon, and nitrogen for the B-C-N tube (top spectra), for bulk hexagonal boron-nitride and carbon fullerene tube standards (bottom spectra), and (b) of boron and carbon for the boron carbide tube (top spectra). The boron, carbon, and nitrogen K edges obtained from the $B_xC_yN_z$ tubes exhibit distinct π^* and σ^* features, indicating a graphitic structure.

note that selected area diffraction patterns recorded from carbon, boron carbide, and boron-carbon-nitride tubule structures depict interplanar spacings of approximately 3.35±0.1 Å, which is close to the 3.35-Å interplanar spacing of graphitic carbon and consistent with the theoretical findings. This suggests that the atomic displacement from the ideal cylindrical shape is small compared to the observed interwall distance and that the atoms remain close to the ideal hexagonal symmetry of the planar sheet. Furthermore, in all cases, two plasmon peaks are observed in the EELS data corresponding to the π and $\sigma+\pi$ plasmon excitations of the graphiticlike structure.

Quantitative determination of the chemical composition of the nanotubules by EELS is possible using a method described by Egerton,[8] which assumes hydrogenic cross sections and has an associated error in the range of 10–15 %. For the boron-carbon-nitride tubules, this analysis reveals a relative boron-carbon-nitrogen (B:C:N) ratio of 23:60:17, which is close to the predicted BC_2N structure described by Miyamoto *et al.*[5] and similar to the bulk structure proposed by Liu *et al.*[10] and Kouvetakis *et al.*[12] Quantitative analysis of the boron carbide tubule spectra suggests a B/C ratio of approximately 0.3 or, equivalently, a BC_3 stoichiometry. We also note the interesting observation that a single nanotubule may have a variable atomic composition along its length. For example, in Fig. 1(b), the single tubule with a needlelike cap on one end (hollow arrow) and a blunted cap on the other (filled arrow) has, by localized EELS analysis, a pure carbon composition on the needlelike end and a B-C composition on the blunt edge. This suggests a strong sensitivity of tube composition on sample growth conditions.

The most obvious differences in morphology between the pure carbon tubules and compound tubules is the capping structure which closes the ends of the tubules. Carbon tubules have sharp, needlelike tubule ends that are believed to be formed by pentagon defects on the honeycomb network of the tubule walls.[13] However, all of the compound tubules observed have blunt ends, which may be rationalized by their chemical frustration in forming fivefold rings.

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*Permanent address: Fundamental Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba 305, Japan.

†Permanent address: Departmento de Fisica Teórica, Universidad de Vallodolid, E-47011 Valladolid, Spain.

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