Boron Nitride Nanotubes with Reduced Numbers of Layers Synthesized by Arc Discharge

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A new route to the successful arc-discharge synthesis of pure boron nitride (BN) nanotubes is presented. The carbon-free plasma is established between HfB_2 electrodes in a nitrogen atmosphere. This technique leads to the formation of BN nanotubes with very few layers including single- and double-layer tubes. Electron-energy-loss spectroscopy yields a B:N ratio of approximately 1. Most tube ends are closed by flat layers perpendicular to the tube axis. A closure by a triangular facet, resulting from three 120° disclinations, is proposed to account for this specific shape. [S0031-9007(96)00494-2]

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The discovery of carbon nanotubes [1] produced by arc discharge between graphite electrodes has generated intense experimental and theoretical interest in these unexpected structures. Nanotubes with new shapes or compositions are obtained by drilling a hole in the anode and filling it with various materials. Abundant production of single-wall nanotubes is achieved when the filling material is a mixture of graphite and cobalt [2], while various mixtures of a metal with graphite were shown to produce nanotubes filled with the corresponding metal or carbides [3]. Finally, the carbon network is partially substituted by boron and nitrogen either by using a mixture of boron and graphite and replacing the usual helium atmosphere by nitrogen [4] or by placing a hot-pressed BN rod inside the drilled anode [5].

The morphology of the ends of carbon tubes is important for practical uses [6] as well as for understanding their growth process. When formed in the arc, they are normally closed at their free end. The tips of carbon tubes are frequently observed to be terminated as cones, with an average apex angle in projection of typically 20° [7]. This angle corresponds to the sharpest cone which can be formed by perfect closure of the honeycomb network, with five pentagons distributed at the tip surface [7,8]. Cones with larger angles [9,10] and more generally a number of different morphologies were observed for the tip surface, and they were attributed to different topological distributions of pentagons at the tip surface [11].

Based upon similarities between carbon and BN-based materials, the existence of boron nitride nanotubes was proposed [12]. Electronic-structure calculations indicate that, contrary to carbon nanotubes, they are constant band-gap materials, which provides interesting possibilities for potential device applications [13]. Boron nitride filaments, with diameters of a few tens of nanometers and a conical rather than cylindrical internal structure, were grown by reaction of N_2 or NH_3 with ZrB_2 or HfB_2 [14]. Very recently, pure boron nitride nanotubes were successfully produced by arc discharge between a BN-packed tungsten anode and a copper cathode [15].

In this Letter, we report on an alternative method to synthesize pure BN nanotubes using arc-discharged hafnium-diboride electrodes. The anode deposit contains a large quantity of pure BN nanotubes, with reduced numbers of layers including single-wall tubes. Specific morphologies are observed for tube ends and are discussed in relation with B-N units.

In the present study, synthesis of BN nanotubes was carried out using an arc-discharge method similar to that used previously for pure carbon nanotubes [3]. The insulating character of BN rods prevents arcing them. Instead, the electrodes consisted of high-purity, hot pressed hafnium-diboride (HfB_2) rods 10 mm in diameter. The evaporation chamber was filled with a nitrogen atmosphere at an initial pressure of 700 mbar. A stable plasma, which lasted for more than 15 min, was established under the electric arc conditions of 60 A dc and 20–40 V. A dark grey soot was produced and deposited on the chamber walls. The electrode deposit was relatively thin, in contrast to the cathode deposit in the carbon-arc case. The anode had a moltenlike tip indicating that temperature at the anode during synthesis was close to the melting temperature of HfB_2, namely, 3650 K. The cathode also had slightly vaporized, and partly broke into pieces.

The deposit formed on the electrodes was ground to a fine powder, ultrasonically dispersed in ethanol, and deposited onto holey carbon grids for characterization by transmission electron microscopy (TEM) with the use of a JEOL 4000 FX equipped with a Gatan 666 parallel collection electron-energy-loss spectrometer. TEM imaging and electron-energy-loss spectroscopy (EELS) measurements were performed at 400 and 200 kV, respectively.

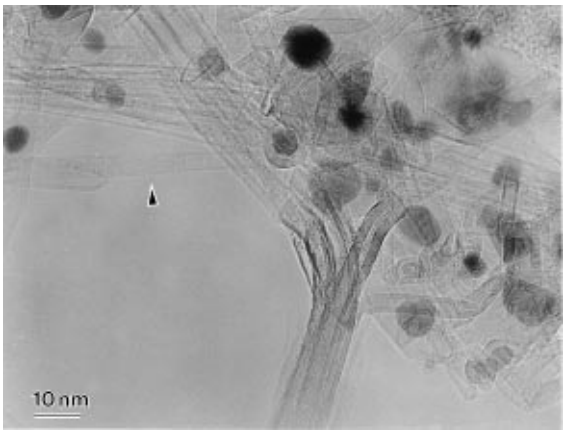

FIG. 1. Low magnification transmission electron micrograph of anode deposit showing abundant BN nanotubes. The arrow indicates filling by amorphouslike material.

All spectra were acquired at liquid nitrogen temperature using probe sizes ranging from 20 to 50 nm. The BN nanotubes described below were observed in the soot collected on the anode, and not on the cathode as usual.

A typical electron micrograph showing a general view of the specimen is reproduced in Fig. 1. Abundant nanotubes form as bundles or as isolated tubules. The dark nanoparticles appearing in Fig. 1 are presumed to be HfB_2 nanocrystals; they are often encapsulated into multiwalled boron-nitride cages. The observed nanotubes have rather small numbers of layers as compared to previously reported boron-nitride nanotubes [15]. Figure 2 illustrates typical tubes having, respectively, six, three, two, and one layers. The length of the tubes may exceed 200 nm. The inner diameters range from ~1.2 to more than 4 nm with a distribution peak close to 2.5 nm. The smallest diameters correspond to tubes with only one or two layers. They are close to the diameter reported for single-layer carbon nanotubes [2,16]. Figure 3 shows that double-layer tubes are not uncommon and have a wide range of diameters. By analogy with previous studies on carbon nanotubes [17], the characteristics of the present tubes, namely, very few layers and small diameters with a wide dispersion, are expected to be intimately related to synthesis conditions, such as catalysts, temperature, and chamber atmosphere. The multiwalled nanotubes—including double-layer tubes—have perfectly straight fringes indicating a well ordered structure. The spacing between layers is approximately 0.34 nm, which is consistent with the interplanar distance of 0.333 nm in bulk hexagonal boron nitride (*h*-BN). By analogy with carbon tubes [10,18], this spacing is likely to be slightly larger in the tubes than in *h*-BN. The walls of single-layer tubes are imaged by wavy lines. This feature may either result from alteration by the electron beam [19], or indicate incomplete ordering during preliminary steps of the growth process. A few tubes are partially filled with amorphouslike material (see Fig. 1), but no filling by metallic nanowire is observed. Boron-nitride nanotubes have also been observed in the soot collected on the cathode; they are less abundant.

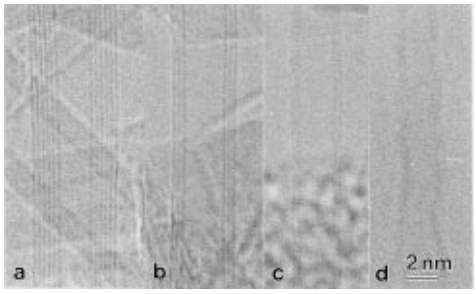

FIG. 2. High-resolution images of typical BN nanotubes, containing, respectively, (a) six, (b) three, (c) two, and (d) one layers. The fringe spacings are approximately 0.34 nm.

The EELS spectra taken from nanotubes show clearly the presence of boron and nitrogen in a B:N ratio of $(1.0 \pm 5)\%$ and the absence of carbon (see Fig. 4). Comparison of the fine structures of B and N *K* edges from BN nanotubes with corresponding spectra from bulk *h*-BN shows that the features are similar with no significant shift in the peak positions but their intensities are not identical. The presence of a sharp π^* peak and the shape of the σ^* peak for both B and N [20] attest for an sp^2 type of bonding as in *h*-BN. Peaks denoted *c*, *d*, and *e* in Fig. 4(b) are significantly damped in the tubes as compared to bulk *h*-BN. These deviations from bulk features are qualitatively similar to what is observed in carbon materials, where they are mainly attributed to modifications in interlayer interactions [21].

A large number of tube ends have been observed (see Fig. 5). Multilayer tubes are always closed at their free end, while single-layer tubes have an end made of amorphouslike material [Fig. 5(d)]. Most of the tubes have a very characteristic end with a flat tip [Figs. 5(a), 5(b), 5(c), and 5(f)] imaged by fringes perpendicular to the tube axis, as clearly seen in Fig. 5(b). The difference in curvature between the capping layers and the cylindrical part of the tube is emphasized by the fact that both kinds of layers are imaged for different focus conditions, as seen from

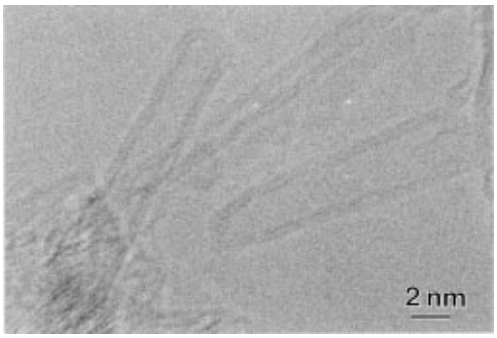

FIG. 3. High-resolution image of a set of double-layer BN nanotubes with a wide range of inner diameters (1.4, 2.7, and 3.4 nm, respectively).

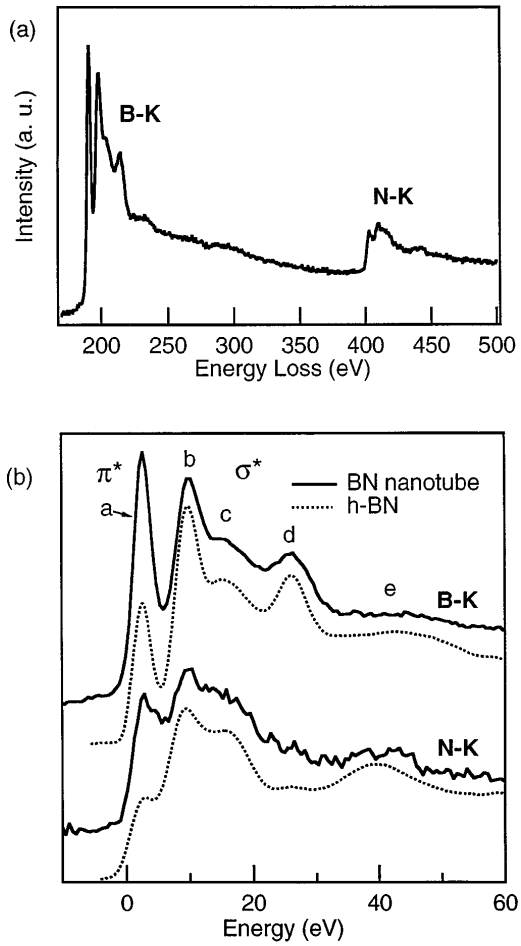

FIG. 4. (a) Core EELS spectra recorded on a nanotube with approximately six layers, showing the *K*-shell excitations of B and N. (b) Fine structures from (a) (continuous line) for B (above) and N (below) compared with that from bulk *h*-BN (dotted line), showing distinct π^* and σ^* features.

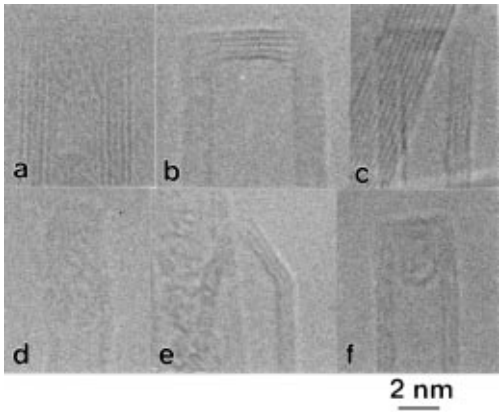

FIG. 5. High-resolution images of tube ends. (a), (b), and (c) Flat tips of tubes with various diameters and number of layers. (d) Amorphouslike termination of a single-layer tube. (e) Conical-shaped end. (f) Nonempty tube end, filled presumably with amorphous BN material.

Figs. 5(b) and 5(c). These tips are very specific compared with carbon-tube tips, which are mostly conelike, although flat tips have also been reported for inner tubes [9,11]. Sharp ends, with a conelike termination, such as the one shown in Fig. 5(e) are not common in the present BN nanotubes. For previously synthesized boron-nitride nanotubes, it was reported that every end contains a dense particle [15], as is the case for carbon tubes produced by catalytic growth. There is no evidence of such ends in the present specimens. The filling material at the end of the tube shown in Fig. 5(f) is likely to be amorphous boron nitride.

We propose that the typical flat ends shown in Fig. 5 correspond to triangular facets, and are the result of three 120° disclinations in the hexagonal BN network. We recall that a set of disclinations, with angles adding up to 2π, is required to close one end of a tube [22]. These disclinations, when positive, are characterized by the angle of the sector which is removed, namely, $n(2\pi/6)$ ($n = 1$, 2, 3, 4, or 5) [7,8]. Because of the B-N alternation in a single layer of *h*-BN, disclinations for odd values of n, such as 60° disclinations ($n = 1$), introduce domain lines, along which unfavorable B-B or N-N bonds are formed. Assuming therefore that only disclinations with even values of n are present because of the chemical frustration induced otherwise, the morphologies of the capped ends of BN tubes are divided into two categories. Type I are conical with two disclinations, of, respectively, 120° ($n = 2$) and 240° ($n = 4$): the sharp tip shown in Fig. 5(e) is compatible with such a shape. Type II have a triangular facet resulting from three 120° disclinations (see Fig. 6). Type II have a more uniformly distributed curvature and therefore a lower elastic energy. The latter is minimized when the cores of the 120° disclinations form a regular triangle (see Fig. 6). Since this particular configuration is the only one where the triangular facet is

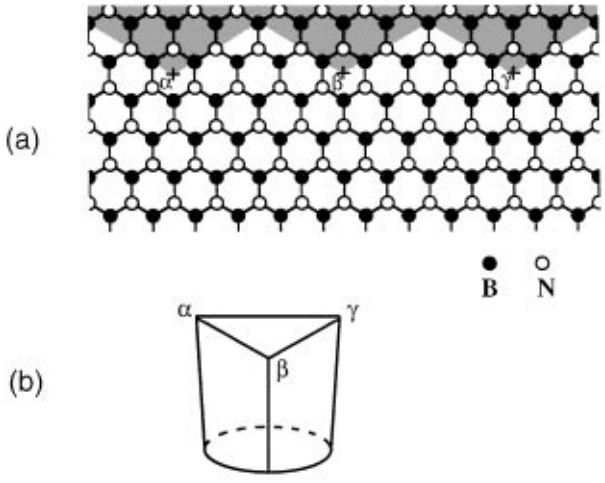

FIG. 6. Formation of a flat tube end. (a) Atomic description illustrated on an unrolled (12,0) tube: the three 120° disclinations are formed by removing shaded portions of the network. (b) Three dimensional geometry of the resulting tip.

perpendicular to the tube axis, it is highly suggested to correspond to the observations in Figs. 5(a), 5(b), and 5(c). The change in projected diameter in Fig. 5(c) is attributed to a distortion to the cylinder induced by the triangular cross section of the tube capping [7,10].

In a polyhedron, the core of a 120° disclination in a hexagonal network corresponds to a square (or two pentagons), whereas a 60° disclination is formed by a pentagon. For small BN clusters, fullerenelike structures with squares instead of pentagons were proposed [23]. These configurations are indeed likely to be more stable, despite the increased curvature, because B-N bonds are preserved. For the same reason, the tube closure by a triangular facet is expected to have a lower energy than tips containing 60° disclinations. When the size is increased, the respective scaling of domain-line and elastic energies should increase the relative stability of the triangular capping. This is consistent with our observations, where the most clearly defined flat terminations correspond to large tubes.

In the case of carbon tubes, it was concluded in Ref. [11] that no preferred morphology exists for tip shapes, and the usual conelike termination has been attributed to the accidental formation of a pentagon during tube growth, suggesting that closure is governed by the growth process [7]. For present BN tubes on the contrary, energy considerations seem to be rather relevant to explain the observed tip morphology.

In conclusion, we have shown that nanotubes with reduced numbers of layers, including single-layer tubes, are also formed with boron nitride. These observations, together with previous synthesis of BN tubes [15], confirm the analogy with carbon found for other fullerenelike structures such as concentric shelled nanoparticles or onions [24,25]. Specific morphologies have been observed for tube ends, which are suggested to result from B-N units. The chemical frustration that five-membered rings—or 60° disclinations—would introduce in BN fullerenelike structures is indeed believed to govern this structural difference with carbon tubes.

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