Properties of Boron Nitride Nanotubes

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Abstract

We examine properties of boron nitride nanotubes and contrast them to those of carbon nanotubes. Boron nitride nanotubes are expected to be as desirable for application as carbon nanotubes. Although boron nitride nanotubes are wide band gap semiconductors and electrically nearly insulating, scanning tunneling microscopy can be used to image and characterize them.

Carbon nanotubes have received considerable research interests because of their remarkable electronic, mechanical, and thermal properties. Single-walled carbon nanotubes (CNTs) are typically 1 nm in diameter and can be either metallic or semiconducting depending on their helicity[1]. So far purification or controlled synthesis of CNTs with selected helicity have not been achieved. This has made electronic device making with CNTs difficult. Thus, researchers have looked to other nanoscale materials such as semiconducting nanowires[2] in order to satisfy the need for smaller circuit components. We have concentrated our efforts on boron nitride nanotubes (BNNTs), which have been predicted[3] to be purely wide band gap semiconducting nanotubes.
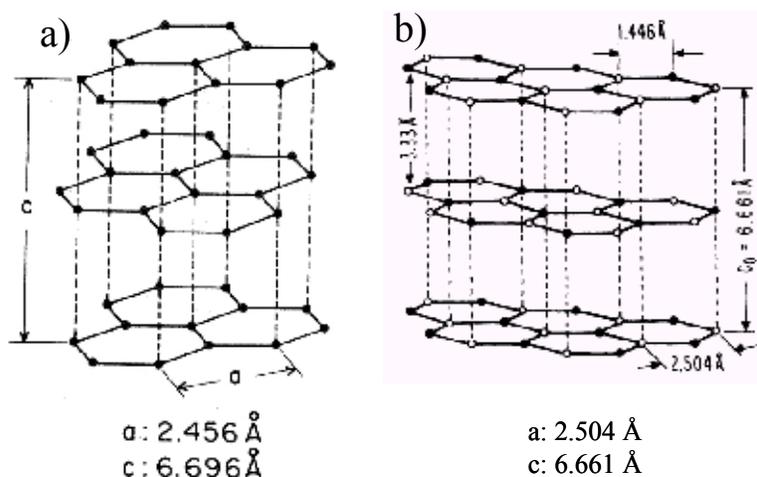

a: 2.456 Å
c: 6.696 Å

a: 2.504 Å
c: 6.661 Å

FIGURE 1. Structures of parent materials. a) Graphite[4]. b) Boron nitride[5].

Structures of graphite and hexagonal boron nitride (h-BN), parent materials for carbon nanotubes and boron nitride nanotubes are quite similar. Fig. 1 compares their structures. They are both layered materials composed of layers of hexagonal lattices; graphite has carbon atoms at all lattice points, while h-BN is composed of alternating atoms of boron and nitrogen. In plane lattice constants are 2.46 Å for graphite[4] and 2.50 Å for h-BN[5]. One minor difference between these materials is in their layer-stacking. In h-BN, layers are arranged so that boron atoms in one layer are located directly on top of nitrogen atoms in neighboring layers and vise versa. As shown in Fig. 1b, the hexagons lie on top of each other. In graphite, the stacking is slightly different; hexagons are offset and do not lie on top of each other. Interlayer distances are similar: 3.35 Å for graphite[4] and 3.33 Å for h-BN[5].
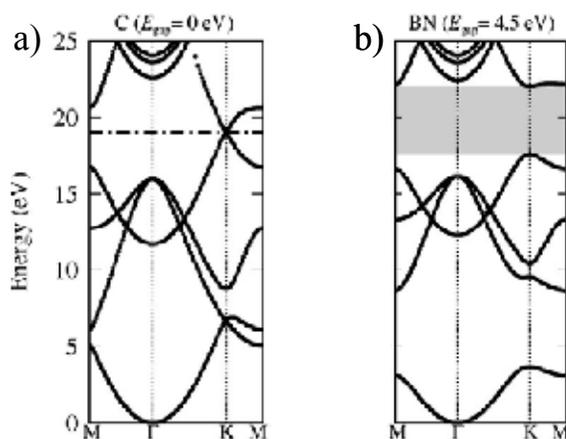

FIGURE 2. Comparison of theoretical band structures of a single layer of a) carbon and b) h-BN[6]

Electronic properties of graphite and h-BN are radically different from each other. Fig. 2 shows theoretical calculations[6] for band structures of a single layer of graphite and h-BN. For a single layer of graphite, a graphene, two bands cross each other at Fermi energy. Thus, a graphene is a semimetal. Unlike a graphene, for a single layer of h-BN, equivalent bands do not cross each other and a 4.5 eV band gap forms. Experimentally, bulk h-BN has been measured to have a band gap of 5.8 eV[7].

Boron nitride nanotubes (BNNTs) can be thought of as a tube rolled from a hexagonal sheet of boron nitride. BNNTs were first synthesized in our laboratory in 1995[8]. Fig. 3[9] shows transmission electron microscopy (TEM) of single to multi-wall BNNTs with six walls. When electron diffractions on individual tubes were performed using in-situ TEM, the tubes were found to be well crystallized[10].
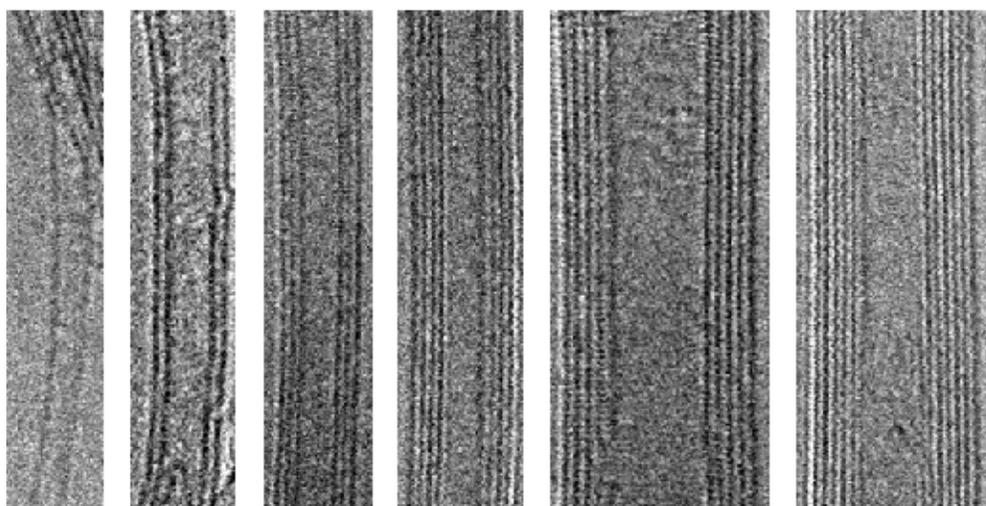
FIGURE 3. Transmission electron micrograph of a single to six-walled boron nitride nanotubes: left to right in succession

Unlike carbon nanotubes, whose electronic properties can be either metallic or semiconducting depending on their chemical structure, BNNTs are expected to have over 4 eV band gaps for observed diameter ranges of over 1 nm. The calculated band structure for a (4,4) BNNT is shown on Fig. 4. This particular tube has an indirect gap. The band structure is quite similar to that of a single layer of h-BN, but is with one notable difference. At the bottom of the conduction band, near Γ point, there is a band, which has energy dispersion close to the free electron gas. This state has been named "nearly free electron" (NFE) state. Although one would naively anticipate the electronic states at the bottom of the conduction band to reside mostly on the boron atomic sites, the NFE state exists approximates 2 Å inside of the nanotube.

	Carbon nanotubes	Boron nitride nanotubes
Electrical properties	Metallic or semiconducting	Always semiconducting [above 4 eV gap]
Mechanical properties [Young's modulus]	1.33 TPa[11]	1.18 TPa[12]
Thermal conductivity	More than 3000 W / m K[13]	High value expected Hexagonal boron nitride : 600 W / m K [in ab plane][14]
Chemical resistance	Stable up to 300 to 400 °C in air	Stable up to 800 °C in air[15]

TABLE 1. Comparison of properties of carbon nanotubes and boron nitride nanotubes

Table 1 compares the properties of CNTs and BNNTs. We have already discussed the differences in electronic properties above. Mechanical properties, measured using Young's modulus, are similar[11, 12] for these materials; they are both ideal for mechanical applications. Thermal conductivity, which is measured to be extremely high value for CNTs[13], is also expected to be as high for BNNTs whose parent material h-BN has exceptional ab-plane thermal conductivity[14]. Chemical resistance is better for BNNTs, which are able to survive in air up to much higher temperature[15]. Over all, BNNTs have properties as desirable for application as carbon nanotubes if not more so. Thus, there is a dire need for experimental investigation of electronic properties of BNNTs. Because of their size scale, scanning tunneling microscope (STM) is the most ideal instrument for the investigation.
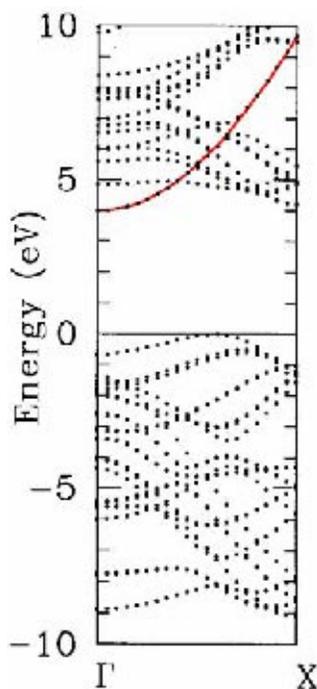

FIGURE 4. Theoretical[3] band structure of a (4,4) BNNT. Highlighted band is the nearly free electron state

When an STM is used to image a large band gap material adsorbed on a metallic surface, one would expect a large range of sample biases in which the material would not be completely visible[16]. Only above a threshold voltage, determined by the band gap and the location of the material's Fermi energy with respect to the Fermi energy of the substrate, should the large band gap material reveal itself. BNNTs behave as expected while we are imaging. Fig. 5a shows an example BNNT imaged at above its threshold voltage; the tube shows its tubular geometry. Below the threshold voltage, the tube appears with a "hollow core" structure as seen on Fig. 5b. Threshold voltages vary from tube to tube, but it is usually about - 4 volts. This is consistent with BNNTs having large band gaps. Similar behavior is seen with positive sample biases.
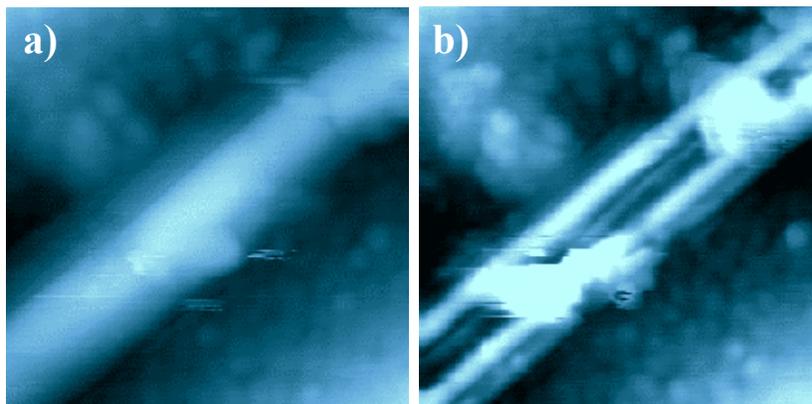
FIGURE 5. An example BNNT imaged at a) –7 volt and b) –4 volt sample biases. Tunneling current used for imaging was both 0.5 nA and the images are 300 Å squares.

When imaging BNNTs with sample biases slightly above threshold voltages, intramolecular features are sometimes revealed. Fig. 6 shows selected STM images of tubes showing such resolutions. Resolved features are triangular lattice having consistent lattice spacing with bulk h-BN. We believe that a triangular lattice is imaged instead of a hexagonal lattice because of charge transfer between boron and nitrogen atoms. Chiral angles in BNNTs are found to be randomly distributed. Surprisingly, these high-resolution images can be obtained with sample biases ranging from 4 to 5 volts. We are in progress of understanding the nature of tunneling at such high sample biases.
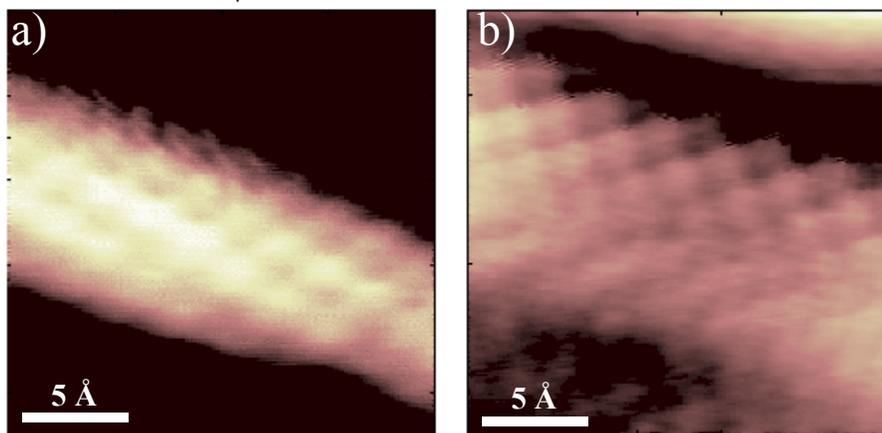

FIGURE 6. Intramolecular resolution achieved on BNNTs. a) V_{sample} = -3.5 volts, I_{tunnel} = 0.4 nA b) V_{sample} = - 4.0 volts, I_{tunnel} = 0.3 nA

Because BNNTs are expected to have large band gaps and to be nearly insulating, it is surprising that we are able to image intramolecular resolution using an STM. We are currently in process of understanding the nature of tunneling into BNNTs. Using scanning tunneling microscopy, we hope to be able to test the theoretical band structure of these tubes calculated nearly a decade ago.

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