Scanning tunneling microscopy and spectroscopy of boron nitride nanotubes

Masa Ishigami, Shaul Aloni and A. Zettl

Physics Department, University of California, Berkeley, CA 94720 USA
Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley CA 94720 USA

Abstract. We have investigated electronic properties of boron nitride nanotubes using a low temperature scanning tunneling microscope (STM) operated at 7K. STM images of the tubes reveal hexagonal lattices or stripe patterns, which can be caused by interlayer coupling or scattering of electronic states of the nanotubes. In addition, scanning tunneling spectroscopy measurements indicate that the tubes have band gaps exceeding 4 eV, and reveal van Hove singularities confirming the one-dimensional nature of electronic states of the nanotubes.

INTRODUCTION

Boron nitride nanotubes[1] (BNNTs) can be described as sheets of hexagonal boron nitride (h-BN) rolled into seamless concentric cylinders. Much like carbon nanotubes, they have a high Young's modulus[2] and have been predicted to be exceptionally good thermal conductors. Unlike their carbon analogue, BNNTs are expected to be semiconductors with a 4 to 5 eV band gap irrespective of their chirality[1]. Although BNNTs were first experimentally synthesized in 1995[3], so far no confirmations of these predicted electronic properties have been reported. In the work reported here, we have used a low temperature high resolution scanning tunneling microscope (STM) to investigate this newer class of nanotubes.

EXPERIMENTAL

BNNTs were synthesized using an arc-discharge technique as described elsewhere[4]. Carefully collected as-grown soot was first ultrasonically suspended in 1,2-dichloroethane and then deposited from the solution onto Au(111) surfaces. The nanotubes in our STM samples are mostly double-walled with 3 nm outer diameters as confirmed by atomic force microscopy and transmission electron microscopy. The samples were outgassed at 623 to 723 K for 3 hours in ultra high vacuum prior to the STM investigations. Scanning tunneling microscopy and spectroscopy experiments were preformed in a homemade ultra-high vacuum low-temperature STM operated at 7 K. Scanning tunneling spectroscopy (STS) was performed using a bias modulation lock-in technique. The bias voltage was modulated at 20-50mV at a frequency of ~2.7kHz.

CP685, *Molecular Nanostructures: XVII Int'l. Winterschool/Euroconference on Electronic Properties of Novel Materials,* edited by H. Kuzmany, J. Fink, M. Mehring, and S. Roth

RESULTS AND DISCUSSION

Scanning tunneling microscopy

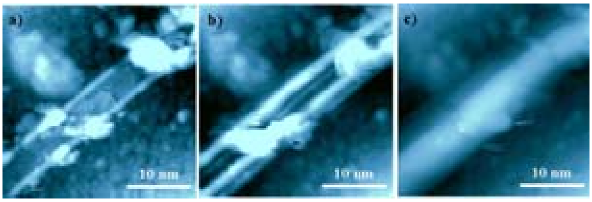

FIGURE 1. Constant current STM images of a boron nitride nanotube taken with –2.0(a), -4.0(b), -7.0(c) volt sample biases respectively with a tunneling current of 0.5 nA.

Fig. 1 shows a typical sample bias dependence of STM images of a BNNT. The nanotube appears as a cylinder when imaged at high positive and negative sample biases. When sample bias magnitude is lowered below threshold of about 4 volts, nanotube-related topographical features diminish in height and eventually reach the substrate corrugation level at a bias magnitude of approximately 1 volt. Below the threshold, the tube appears with a "hollow core", as seen in Fig. 1a and 1b. This structure indicates that no electronic states are available in the nanotube at these energies, suggesting that BNNTs have wide band gaps.

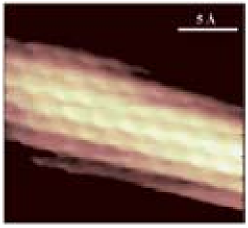

FIGURE 2. A constant current STM image of a boron nitride tube showing a triangular lattice. V_{sample} = -4.8 volts and I_{tunnel} = 1.0 nA.

At high sample bias magnitudes, BNNTs appear as featureless cylinders. When the magnitudes of the sample biases are lowered to values just above the threshold, two types of intramolecular features are resolved. About 10% of the nanotubes display hexagonal patterns 20 pm in height and with lattice constants of 2.5 Å; an example is shown in Fig. 2. The lattice constant is consistent with that of bulk h-BN. The vast majority of the tubes exhibit stripe patterns, as shown in Fig. 3 with periodicities ranging from 2 to 12 Å. In some cases, two different periodicities are observed simultaneously on the same tube as shown in figure 3b.

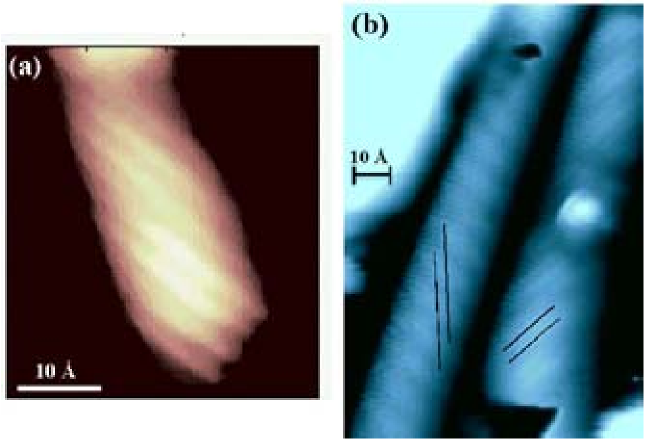

FIGURE 3. a) An STM image of a boron nitride tube showing a stripe pattern. V_{sample} = - 3.2 volts and I_{tunnel} = 0.2 nA. **b)** Two nanotubes displaying two different stripe patterns simultaneously. Two black lines on each tube highlight stripes with smaller periodicities (~ 3 Å). Larger periodicity stripes have periodicities of about 10 Å. V_{sample} = - 4.25 volts and I_{tunnel} = 0.5 nA.

The periodicities of these stripe patterns seem to be unrelated to the h-BN lattice constant. The lack of correlation rules out an adsorbate layer as the cause for the stripes. Furthermore, if the stripes were STM tip-convolutions of the atomic arrangements, the periodicities should depend on chiral angles and would be distributed in a fairly narrow range of values around the h-BN lattice constant[5]. Artifact effects due to tip shapes have also been ruled out because different stripe patterns can be imaged simultaneously with a same tip, as shown in Fig. 3b. The stripes are intrinsic to the nanotubes and reflect spatial variations of local electronic densities of states.

There are two mechanisms which cause similar stripe patterns in graphite or carbon nanotubes. First, as seen on carbon nanotubes[6], the stripe patterns can be interference patterns generated from electrons scattered by tube ends or defects. An example of a defect in a BNNT can be seen as a bright spot on the right tube shown in Fig. 3b. Second, since most of the BNNTs imaged in our experiment are double-walled[4], the stripe patterns may result from interlayer coupling. The observed periodicities would then depend on chiralities, diameters, and relative positions of the outer and the inner tube. We would expect the coupling to create superlattice modulations best described by Moiré patterns. Such modulations from interlayer coupling have been observed in STM of graphite[7] and multi-walled carbon nanotubes[8].

Scanning Tunneling Spectroscopy

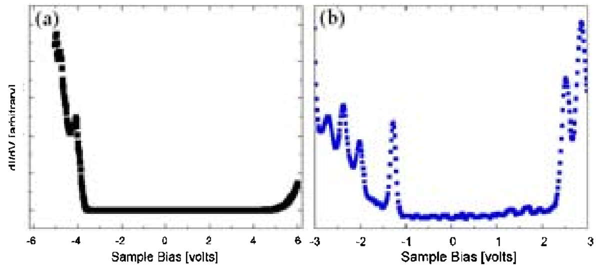

FIGURE 4. A typical scanning tunneling spectra (STS) acquired on a selected BNNts. Both spectra were taken on tubes displaying the stripe patterns.

Fig. 4a shows a tunneling spectrum taken on the majority of the BNNTs. A total lack of features between -3.7V and +5V would naively suggest a band gap of over 8 eV. Such a high band gap value is unexpected for these nanotubes and indeed seems unphysical. Increasing the sensitivity of tunneling spectroscopy by decreasing tip-sample separation did not lead to detection of any additional electronic states in the band gap. In order to understand this unusually large measured band gap, the geometry of our tunnel junction must be considered. In our case, electrons must travel from the tip, through the tube, into the gold substrate. It is likely that bias voltages, applied between the gold substrate and the tip, have not completely fallen in the tip-tube tunneling junction, broadening the apparent gap. Assuming that the tube-substrate contact resistance is low and the tube resistance is comparable to the tunnel junction resistance, the voltage drop in the tunnel junction will be smaller than the applied sample bias. In this case, true band gap of the nanotube can be determined by measuring the exact resistance across the tube. On the other hand, if the tube-gold substrate contact resistance is high, the extraction of the true band gap is more complicated requiring additional considerations of both tip-tube and tube-substrate tunnel junctions. In either case, determination of the band gap requires appropriate theoretical models and additional experiments.

Fig. 4a also shows a sharp peak at -4 volts. Similar sharp features have been observed near the onset of conductance in positive or negative voltages in other spectra. We believe that these are signatures of van Hove singularities, which are manifestation of the one-dimensional electronic structures of the BNNTs.

A few BNNTs revealed spectra which are quite different. As shown in Fig. 4b, in these spectra, van Hove singularities of BNNTs are clearly visible. The first set of the features on this particular spectrum is separated by 3.8 eV. If the locations of these peaks can be interpreted as the onsets of the conduction and the valence bands, the value of the gap is slightly smaller than expected[1]. However, recent theoretical calculations[9] show that an electric field applied across a BNNT can induce a giant Stark effect which reduces the band gap. Field of 1 V/nm is expected to reduce a 4.5 eV band gap of a 3 nm diameter BNNT to 2.8 eV[9]. Therefore, the measured band gap of 3.8 eV maybe reflective of an intrinsic band gap somewhat larger (say 4 to 5 eV) reduced by a tip-induced Stark effect.

REFERENCES

1. Rubio, Angel, Corkill, Jennifer L., and Cohen, Marvin L., *Physical Review B* **49**, 5081-4 (1994).
2. Chopra, N. G., and Zettl, A., *Solid State Communications* **105**, 297-300 (1998).
3. Chopra, N. G., Luyken, R. J., Cherrey, K., Crespi, V. H., Cohen, M. L., Louie, S. G., and Zettl A., *Science* **269**, 966-7 (1995).
4. Cumings, John, and Zettl, A., *Chemical Physics Letters* **316,** 211 (2001)
5. Venema, L. C., Meunier, V., Lambin, Ph., and Dekker, C., *Physical Review B* **61**, 2991-6 (2000).
6. Clauss, W., Bergeron, D. J., and Johnson, A. T., *Physical Review B* **58**, R4266 (1998)
   Kane, C. L., and Mele, E. J., *Physical Review B* **59**, R12759-62 (1999).
7. Xhie, J., Sattler, K., Ge, M., and Venkateswaran N., *Physical Review B* **47**, 15835-41 (1993).
8. Ge M. H. And Sattler K., Science 260 , 515 (1993).
9. Khoo, K. H., Mazzoni, M. S. C., and Louie, S. G., submitted for publication