Symmetry Breaking in Boron Nitride Nanotubes

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We have imaged boron nitride nanotubes with atomic scale resolution using scanning tunneling microscopy. While some nanotubes show the expected triangular lattice pattern, the majority of the nanotubes show unusual stripe patterns which break the underlying symmetry of the boron nitride lattice. We identify the origin of the symmetry breaking and demonstrate that conventional STM imaging analysis is inadequate for boron nitride nanotubes.

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Boron-nitride nanotubes (BNNTs) are inorganic analogues of carbon nanotubes (CNTs) and possess physical properties suitable for a broad variety of applications [1]. BNNTs have a high Young’s modulus [2] and are good thermal conductors [3] much like CNTs, but possess radically different electronic properties. Unlike CNTs, previous calculations [4,5] have shown that electronic properties of BNNTs are uniform and not dependent on their chiral angles or diameters [6]. Since there are no synthesis techniques to control chiral angles and diameters of CNTs, BNNTs are considered to be better suited for some electronics applications in which the uniform electronic property is desirable [7].

In this Letter, we report atomic scale features resolved on BNNTs using scanning tunneling microscopy (STM). Surprisingly, only 10% of nanotubes studied show the expected triangular lattice pattern while the majority appear with a stripe pattern which breaks the symmetry of the underlying hexagonal boron nitride lattice. We account for the symmetry breaking by analyzing the electron transport problem at the tunneling junction using detailed ab initio calculations.

The BNNTs used in this study were produced using an arc-discharge technique [8]. As-grown soot was then ultrasonically suspended in 1, 2-dichloroethane and deposited from the suspension on Au(111) surfaces. The nanotubes in our STM samples were mostly double walled with diameters of 27 ± 3 Å as determined from transmission electron microscopy and atomic force microscopy. The samples were outgassed at 623 to 723 K for 3 hours in ultrahigh vacuum prior to the STM investigations. The experiment was performed using a homemade ultrahigh vacuum low-temperature STM operated at 7 K. We find that the BNNTs are less susceptible to imaging-induced damages at negative sample voltages.

Atomic scale features can be resolved only when the nanotubes appear cylindrical at sample bias voltages higher than 3 to 4 V. The noncylindrical appearance of the nanotubes at low bias voltages is due to the giant Stark effect (GSE) [9,10]. Nominal height variations of these on-tube features are 0.2 Å. 10% of the nanotubes display the expected triangular lattice pattern with the approximate lattice constant of 2.5 Å as shown in Fig. 1. Figures 2(a)–2(c) show representative STM images of the stripe pattern which appears on the majority of the nanotubes. The periodicity of the stripe pattern is 2.3 ± 0.49 Å. Orientation angles of the stripe pattern with respect to the axis of the nanotubes measured in the clockwise direction range from −41 ± 9° to +38 ± 9° [12]. The stripe pattern has no bias dependence and the nanotubes displaying the stripe pattern never display the triangular lattice pattern under varied tunneling parameters.

What is the origin of the broken symmetry in BNNTs? We have systematically ruled out anomalous tip shapes, and other extrinsic imaging effects as causes for the unusual patterns [14]. Instead, the double barrier electron transport [23] at the tunneling junction is responsible for the observed features. We show that the stripe patterns are due to the loss of the triangular symmetry in the tunneling current rather than in the local charge densities. In addition, the orientation angles of the stripe patterns are found to be the chiral angles of the BNNTs.

FIG. 1 (color online). Constant current STM image of a BNNT appearing with a triangular lattice pattern. $V_{\text{sample}} = −4.8$ V and $I_{\text{tunnel}} = 1.0$ nA.
and (4,16) single-walled nanotubes. The STM images are developed for the double barrier tunneling problem self-consistently determined by the procedure formally. Chemical potentials of the tip, nanotube, and substrate are relative chemical potentials of the tip and the substrate.

\[ \Theta(\mu_{\text{tip}} - \epsilon_n) \Theta(\epsilon_n - \mu_{\text{substrate}}) \frac{\rho_{n,\text{tip}} \rho_{n,\text{substrate}}}{\rho_{n,\text{tip}} + \rho_{n,\text{substrate}}} \]

where \( \Theta \) is the unit step function and \( \mu_{\text{tip}} \) and \( \mu_{\text{substrate}} \) are relative chemical potentials of the tip and the substrate. Chemical potentials of the tip, nanotube, and substrate are self-consistently determined by the procedure formally developed for the double barrier tunneling problem.

We have calculated theoretical STM images for (20,20) and (4,16) single-walled nanotubes. The STM images are calculated using the density functional theory within the local density approximation. For the (20,20) nanotube the calculations are performed using a local combination of atomic orbitals (LCAO) with double zeta polarized basis in the SIESTA code. For the (4,16) nanotube we use a plane wave basis with real pseudopotential using the PARATEC code. Some of the conduction band states of a BNNT are nearly free electron like and are poorly described by an LCAO basis. However, our calculations based on a plane wave basis find that these states redistribute to the close proximity of either the tip with negative sample bias voltages or the substrate with positive sample bias voltages and hence participate only weakly in the transport across the tunneling junction. Therefore, both of our calculation methods are sufficient for analyzing the experiment.

Our calculations find that STM images acquired with high negative sample bias voltages are dominated by the conduction band states at the bottom of the conduction band for both (20,20) and (4,16) nanotubes. These conduction band electronic states are located far from the substrate due to the GSE and cannot hybridize with the substrate electronic states. Therefore, the conventional methods for calculating STM images of substrate-hybridized adsorbates do not apply in the present problem. Figure 3(a) shows an unweighted STM image of a (20,20) nanotube calculated without including the tunneling probabilities to the substrate. The image displays a triangular lattice pattern which retains the underlying symmetry of the hexagonal boron nitride lattice. Therefore, the GSE does not disturb the triangular symmetry of the spatial distribution of the electronic states and the stripe patterns are not explained by the GSE alone. A weighted STM image calculated including the proper tunneling probabilities is shown in Fig. 3(b). A vertical stripe pattern, parallel to the nanotube axis with a periodicity of 2.17 Å, is clearly visible. The calculated image reproduces the stripe pattern seen in the experiment and is similar to what is shown in Fig. 2(c). For chiral BNNTs, stripe patterns also appear when the tunneling probabilities are included in the calculation.
The orientation angle of a stripe pattern is the same as the chiral angle of a given nanotube. Figure 4 shows our weighted theoretical STM image for the (4,16) nanotube displaying a stripe pattern oriented at 19.1° from the tube axis. The calculation was performed with a theoretical sample bias voltage of −4 volts.

The mechanism for the appearance of stripe patterns in weighted theoretical STM images can be explained using the zone folding approach. Figure 5 shows the first Brillouin zone for a sheet of hexagonal boron nitride. Conduction band minima are at Γ, M, and K. The nearly free electron state discussed previously is at Γ. There are 2 K points (K = (1/3, 2/3) and \( \hat{K} = (2/3, 1/3) \)) and 3 M points which we call \( M_1 = (0, ±1) \), \( M_2 = (±1, 0) \), and \( M_3 = ±(1/2, 1/2) \). The STM tip-induced electric potential on the tube is given by \( V(\theta) = V_0 \cos(\theta) \), where \( \theta \) is the circumferential coordinate of nanotubes. This slowly varying electric field confines electronic states in the direction of the tip-induced electric field along the wrapping vector for a nanotube. Using the Wentzel-Krammer-Brillouin method, the decay length of a state being confined by this potential is proportional to \( 1/\sqrt{m_{\text{eff}}} \), where \( m_{\text{eff}} \) is the effective mass of the state in the direction of the applied electric field. Effective masses at M points are smaller than those at Γ and K points. Furthermore, the lightest effective mass is found to be in the direction towards the Γ point at the M points. Since the applied electric field is most parallel to the M point direction, the electronic state at the M point is the most dominant contributor to the tunneling current.

As calculated by both the PARATEC and the SIESTA code, the tunneling current at high negative bias voltages is derived primarily from the conduction band states. These conduction band states originate from \( p_z \) orbitals of boron atoms. There are six nearest neighbor boron atoms to a given boron atom, “A”, located at (0,0). These atoms can be grouped into 3 sets of atoms located at \( P_1 = (±a, 0) \), \( P_2 = (0, ±a) \), and \( P_3 = (±a, ±a) \), where \( a \) is the lattice constant of hexagonal boron nitride. Boron \( p_z \) orbitals at the \( P_3 \) point are related to the electronic state at the \( M_3 \) point in the momentum space. The intensity of a bond between A and \( P_3 \) is proportional to

\[
|1 + e^{i(k_1x_1 + k_2x_2)}|^2 = 2[1 + \cos(k_1x_1 + k_2x_2)],
\]

where \( (k_1, k_2) \) is the coordinate in the momentum space for the \( M_3 \) point and \( (x_1, x_2) \) is the coordinate in the real space for the \( P_3 \) atoms. Equation (2) shows that the \( M_3 \) state interferes constructively producing a stripe pattern which connects A and \( P_3 \) atoms. The orientation angle is given by

\[
\sin(\phi) = \frac{n - m}{2\sqrt{m^2 + n^2 + mn}},
\]

where \( \phi \) is the angle relative to the tube axis. The angle coincides with the chiral angle of nanotubes [35]. Equation (3) dictates that the angle should be between −30° and +30°, consistent with the experimental observation.

The stripe patterns, appearing on 90% of the BNNTs, are due to the combination of the GSE and the tunneling probabilities of each electronic state to the substrate. If there are conducting impurities present in the tunneling junction and these tunneling probabilities can be disregarded, the triangular lattice patterns are seen instead.

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[6] BNNTs with smaller diameters are predicted to have narrower band gaps, but these diameters are not experimentally seen.


[10] The GSE, induced by the applied local electric field of the STM tip, shifts the spatial distribution of electronic states in the BNNTs. As a result, only electronic states located near the substrate can contribute to the tunneling current at lower sample bias voltages and the nanotubes appear as noncylindrical, “rain gutter”-like, structures in STM images [11]. Atomic scale features on the top of nanotubes deposited on the substrate, accessible by the STM tip, can only be resolved when the nanotubes appear cylindrical at higher sample bias voltages.


[12] The angles for these stripe patterns are determined by using the procedure determined in [13] from STM images. Raw data from the images are ($a$) $+30.9^\circ$, ($b$) $+12.5^\circ$, and ($c$) $-2^\circ$.


[14] In addition, we have also ruled out other possible structural and electronic origins for the stripe pattern. Gas molecules are expected to desorb at lower temperatures than degassing temperatures prior to our experiments [15–17]. Moiré pattern formed by the inner and outer layers of the nanotubes cannot produce sufficiently small periodicities to explain the stripe pattern [18,19]. Finally the degenerate electronic states [20,21], which interfere with each other to form the similar pattern in STM images of carbon nanotubes, do not exist in the BNNTs [22].


[27] It is important to note that, in addition, the tip is located ($a$) and ($b$) nanotubes, ($c$) nanotubes appear cylindrical at higher sample bias voltages.


[35] In ($n$, 0) nanotubes, $M_1$ and $M_3$ states are equivalent and two stripe patterns angled 60° from each other should appear simultaneously.