Observation of the Giant Stark Effect in Boron-Nitride Nanotubes

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Bias dependent scanning tunneling microscopy and scanning tunneling spectroscopy have been used to characterize the influence of transverse electric fields on the electronic properties of boron-nitride nanotubes (BNNTs). We find experimental evidence for the theoretically predicted giant Stark effect. The observed giant Stark effect significantly reduces the band gap of BNNTs and thus greatly enhances the utility of BNNTs for nanoscale electronic, electromechanical, and optoelectronic applications.

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Boron-nitride nanotubes (BNNTs) are inorganic analogues of carbon nanotubes and possess useful physical properties [1]. Much like carbon nanotubes, they have a high Young's modulus [2] and are good thermal conductors [3]. Unlike carbon nanotubes, which are metallic or semiconducting depending on their helicity [4], theoretical calculations using the *GW* method [5,6] show that experimentally observed BNNTs are semiconductors with a band gap of 5.5 eV [7]. Band gaps ranging from 4 to 5 eV have been observed for BNNTs in recent experiments [8,9]. Since the atomic structure of carbon- and boron-nitride nanotubes cannot be controlled at the synthesis level, this structurally independent electronic property of BNNTs is important for electronics applications. Despite the large band gap, electron field emission [10] and field effect transistor action [11] have already been demonstrated for BNNTs.

A recent theoretical calculation [12] predicts that the band gap of BNNTs can be reduced and even completely eliminated by the application of transverse electric fields. This so-called giant Stark effect (GSE) is analogous to the conventional Stark effect for atomic orbitals. With the GSE, mixing of electronic states in BNNTs occurs in transverse electric fields resulting in a field-induced splitting of the electronic bands. A similar effect has also been predicted for carbon nanotubes [13], but in BNNTs the effect is enhanced by the absence of screening afforded by the large band gap. For example, using the local density approximation (LDA) for a (22, 22) BNNT with an intrinsic band gap of 4.5 eV, a transverse electric field of 0.1 V/Å reduces the gap to 2.25 eV and a transverse electric field of 0.19 V/Å eliminates the band gap entirely. In principle, transverse electric fields can be used to continuously tune the electronic properties of BNNTs from nearly insulating to metallic. The GSE renders BNNTs ideal for nanoscale electronic, electromechanical, and optoelectronic devices.

In this Letter, we used the tip in a scanning tunneling microscope (STM) to impose a local transverse electric field onto BNNTs and simultaneously probe the electronic properties. The electric field is generated across the BNNTs in the tunneling junction between the STM tip and the substrate.

The BNNTs used in this study were produced using an arc-discharge technique [14]. As-grown soot was then ultrasonically suspended in 1, 2-dichloroethane and deposited from the suspension onto 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 h in ultrahigh vacuum prior to the STM investigations. The experiment was performed using a homemade ultrahigh vacuum low-temperature STM operated at 7 K. All STM images were acquired using the constant current mode with sample bias voltages ranging from -7 to $+7$ volts.

The STM images acquired at high magnitude sample bias voltages show features consistent with the cylindrical shapes of the nanotubes, as shown in Fig. 1(a). The average apparent diameter of BNNTs in our STM study, determined by measuring heights of the nanotubes relative to the substrate, is 16.3 ± 6 Å, smaller than 27 ± 3 Å as measured using other microscopy techniques. The discrepancy indicates that the distance between the STM tip and the tube surface is on average 10.7 ± 5 Å smaller than the distance between the tip and the gold substrate. Measurements using similar tunneling junction parameters reveal that the clean gold surface has a tunneling barrier height of 0.75 eV. Thus, with these particular tunneling parameters, the typical tip-gold substrate distance is 16 Å [15] and the typical tip-nanotube distance is 5 Å.

The applied bias voltage, tip-substrate distance (h), and shape of the STM tip determine the applied transverse electric field. As discussed in a previous study [16], the tip shape can be estimated from STM images of nanotubes. The resolved tip profile is shallow and the tip radius is large compared to that of the imaged BNNTs. For the representative image shown in Fig. 1(a) and the corresponding

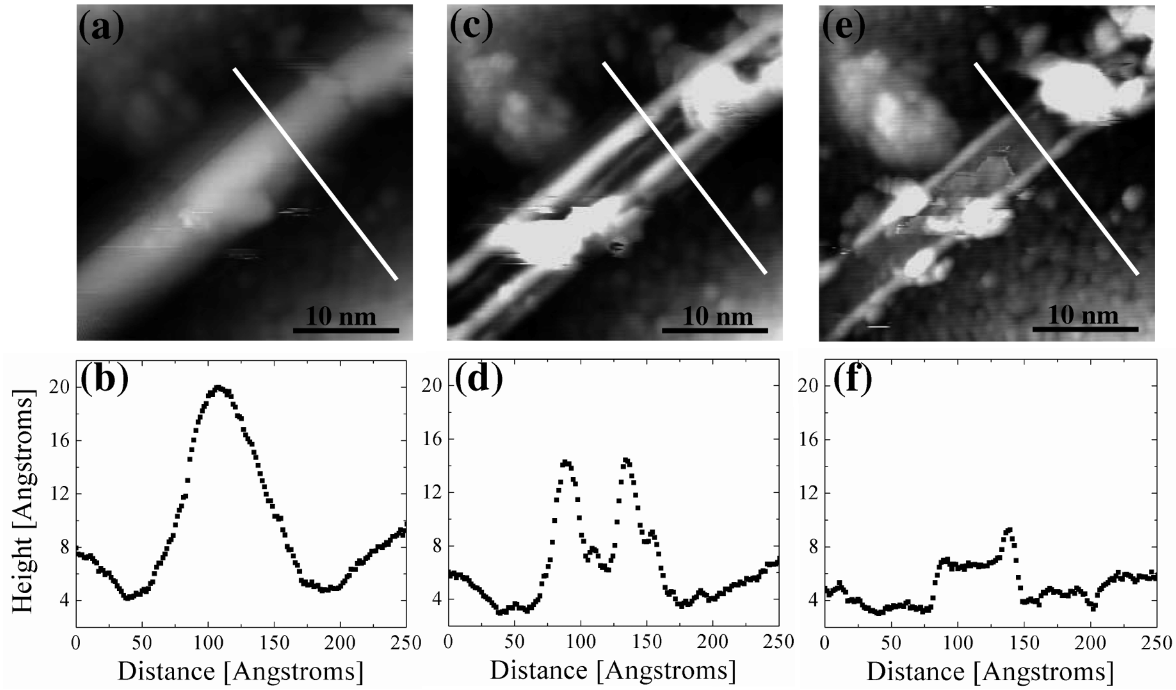

FIG. 1. The top half shows constant current mode STM images of a representative boron-nitride nanotube acquired with (a) $V_{\mathrm{bias}} = -7.0$ V and $I_{\mathrm{tunnel}} = 0.5$ nA. (c) $V_{\mathrm{bias}} = -4.0$ V and $I_{\mathrm{tunnel}} = 0.5$ nA. (e) $V_{\mathrm{bias}} = -2.0$ V and $I_{\mathrm{tunnel}} = 0.5$ nA. The white lines in the images drawn perpendicular to the nanotube are where cross-sectional heights in (b), (d), and (f) are obtained. In order, (b) is associated with (a), (d) with (c), and (f) with (e).

height cross section shown in Fig. 1(b), the determined tip radius is 6 nm. Because of the shallow tip profile, the electric field computed using finite element analysis [17] remains close to V_{bias}/h. The applied electric field when the tip apex is directly over the nanotube in Fig. 1(a) is 0.23 V/Å or 23×10^6 V/cm.

As shown in Figs. 1(c) and 1(e), when the sample bias voltage is lowered below a certain voltage, STM-obtained BNNT images are no longer consistent with cylindrical geometric shapes of the nanotubes. The new features, which all the nanotubes display when imaged at sufficiently low bias voltages, can be described as ''rain gutter'' structures. The threshold voltages below which the nanotubes appear noncylindrical vary between nanotubes and are typically between 3 to 6 V. The same bias dependence is observed with both positive and negative voltages. For the representative nanotube shown in Fig. 1, the magnitude of both negative and positive threshold voltage is 6 V. As shown in Fig. 1(c), the new feature attributed to the nanotube is simply a set of parallel lines along its axis. The height of the parallel lines becomes smaller in images acquired with lower bias voltages as shown in Fig. 1(e).

The tunneling current in an STM is directly proportional to the local electronic density of states (LDOS) integrated from the Fermi level to the applied sample bias voltage [18–20]. Because BNNTs are wide band gap semiconductors, there should be a finite sample bias voltage range corresponding to the energy gap in which no electronic states are available to contribute to the tunneling current. In this voltage range, the nanotubes should simply disappear from the STM images. Therefore, the observed features cannot be explained by the intrinsic properties of the nanotubes and must have an alternate origin, namely, a result of some perturbation specific to our experiment. As inferred from the images, this perturbation enhances the LDOS near the substrate and depletes the LDOS in the nanotube sections further away from the substrate. We identify three plausible causes for the observed perturbation: electron or hole-doping by the substrate, deformation of the nanotubes by the STM tip, and the GSE due to the tip-induced local transverse electric field.

In STM studies of carbon nanotubes, significant hole-doping by the substrate is observed [21]. Since the charge screening length is much longer than the circumferences of the nanotubes, such doping influences the entire nanotube uniformly, even for BNNTs. Thus, the doping by the substrate is unlikely to produce the features observed at low bias voltages.

A theoretical study [22] has shown that radial deformation can reduce the band gap of BNNTs by increasing the curvature of the nanotube walls. The calculated relationship [23] between the curvature and the band gap indicates that the electronic properties are significantly influenced only when the distances between two opposing faces of a flattened BNNT became approximately 5 Å, close to the interlayer spacing of hexagonal boron nitride. Thus, the study implies that the radial deformation required for a substantial effect is approximately 22 Å for the outer shells or 15 Å for the inner shells for the double-walled nanotubes used in this experiment. Although the STM tip does touch and deform the BNNTs when the rain gutter features are being observed, the maximum deformation is always much smaller than the required distances to sufficiently flatten the outer or inner shells of the nanotubes. For example, the maximum deformation for the images in Fig. 1 is 9 Å. Therefore, the effects of radial deformation cannot account for the observed images.

Theoretical calculations predict that the electric field applied on the nanotubes when acquiring the STM images is sufficient to induce the GSE. According to the calculations [12], the GSE redistributes the valence and conduction band states in BNNTs. The valence band states move in the direction of the electric field and the conduction band states move in the opposite direction. As a result, the valence and conduction band states become confined on opposite sides of the nanotubes, and they become spatially separated. The electronic states at the top of the valence band and the bottom of the conduction band are the ones most influenced by the electric field. The field-induced redistribution of the electronic states is more pronounced at a higher electric field. In an STM image acquired with negative sample bias voltages, only valence band states contribute; with positive sample bias voltages, only conduction band states contribute. With the GSE, the STM-visible electronic states should therefore accumulate away from the STM tip, near the substrate, for both negative and positive sample bias voltages. Such redistribution is consistent with the observed rain gutter features.

There are two competing effects that determine the exact bias dependence of the appearance of BNNTs in STM images. When the sample bias voltage is increased, the transverse electric field on BNNTs becomes larger, and the STM-visible electronic states move further away from the tip. At the same time, higher sample bias voltages allow electronic states further away from the Fermi level to contribute to the images. These electronic states are less influenced by the transverse electric field and are more uniformly distributed around the circumference of the nanotube. To properly account for these two competing effects, we have calculated the spatial distributions of the STM-visible electronic states for a $(20, 20)$ nanotube [24] on a gold substrate under increasing sample bias voltages. The calculation is performed using the SIESTA code [25] within the LDA with double-zeta-polarized and single-zeta basis sets. Our computation allows for a self-consistent charge relaxation and accounts for the polarization effects due to applied transverse electric fields and the gold substrate. The charge transfer from the substrate to the nanotube is found to be negligible. The Hartree potential, the substrate Fermi level, and self-consistently calculated nanotube electronic states are used to determine the STM-visible electronic states at each sample bias voltage.

Figure 2 shows calculated spatial distributions of the STM-visible electronic states for -6.9, -4, and -2.1 volts, respectively. As observed in the experiment, BNNTs should contribute cylindrical features to STM images with high sample bias voltage and rain gutter features at low bias voltages. Accounting for the previously discussed difference between the tip-substrate and the tip-nanotube distances, the height cross section data in Fig. 2(e) and 2(f) are also consistent with the experimental data. Furthermore, similar bias dependence is calculated with both positive and negative sample bias voltages, also in agreement with the experiment. The bias dependence of the experimental STM images is fully explained by considering the giant Stark effect. The calculated band gaps for electric fields as in Figs. 2(a)–2(c) are 2.2 eV, 1.2 eV, and 0.49 eV in order. The calculations indicate that the tip-induced

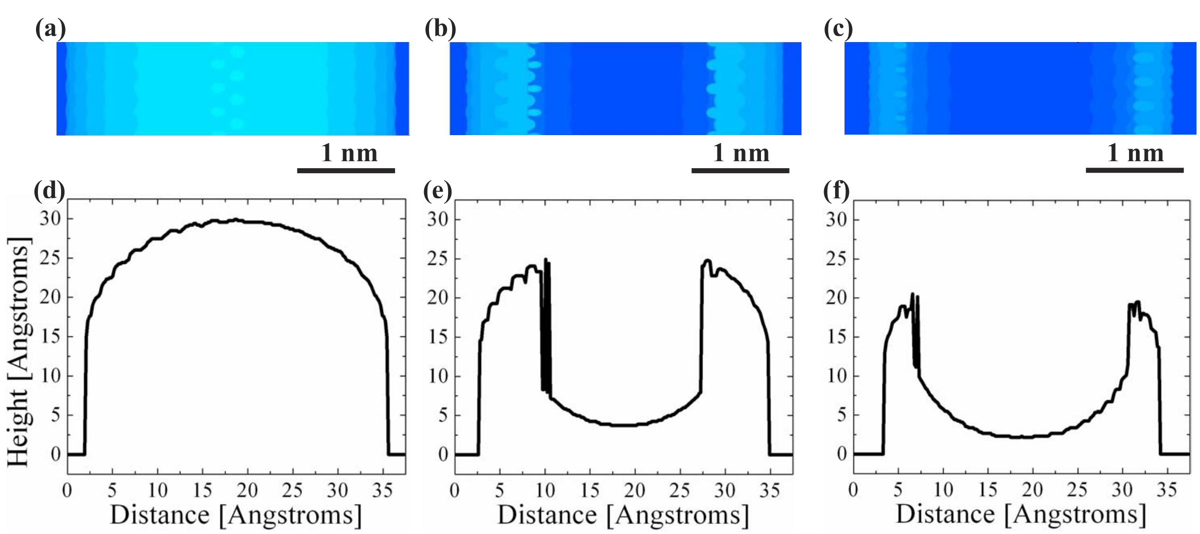

FIG. 2 (color online). Calculated STM images of a $(20, 20)$ BNNT with (a) $V_{\mathrm{bias}} = -6.9$ V, (b) $V_{\mathrm{bias}} = -4.0$ V, and (c) $V_{\mathrm{bias}} = -2.1$ V. (d)–(f) are height cross sections for (a)–(c), respectively.

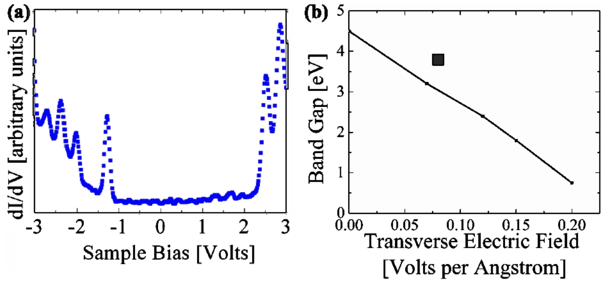

FIG. 3 (color online). (a) A representative scanning tunneling spectrum on a BNNT. (b) Theoretical band gap of a (20, 20) nanotube with respect to transverse electric field. The square indicates the upper bound for the band gap inferred from (a).

electric field is large enough to significantly reduce the band gap of BNNTs.

The GSE also manifests itself in tunneling spectra of BNNTs. Figure 3(a) shows a representative tunneling spectrum on a nanotube with a 23 ± 5 Å diameter. While acquiring the spectrum, the apex of the STM tip is held directly above the axis of the nanotube. The measurement is reproducible along the length of the nanotube. Multiple sets of van Hove singularities are present in the data. At the bias voltages corresponding to the first set of van Hove singularities, the applied electric field is 0.08 V/Å. The apparent band gap is 3.8 eV for this particular nanotube under the influence of the STM-induced transverse electric field. The electronic transport from the substrate, across the nanotube, to the STM tip is complex and the bias voltage does not drop entirely in the tunneling junction between the nanotube and the tip. Thus, the apparent gap represents the upper bound value for the band gap, and the value is indeed lower than 5.5 eV calculated assuming zero electric field using the *GW* method. Furthermore as shown in Fig. 3(b), the theoretical band gap, for a nanotube with a 27.5 Å diameter in varying transverse electric fields calculated using the LDA, is below the experimental datum which is self-consistent.

In summary, the first experimental evidence for the giant Stark effect is obtained by detailed analysis of the bias dependent STM images of BNNTs. Tunneling spectra acquired on BNNTs also support our conclusion. Furthermore, the observed STM topography features imply that the STM tip-induced electric field is sufficient to induce a significant band gap reduction in BNNTs.

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