Imaging the interlayer interactions of multiwall carbon nanotubes using scanning tunneling microscopy and spectroscopy

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Using atomically-resolved scanning tunneling microscopy and spectroscopy, we probe the nature of interwall interactions within multiwall carbon nanotubes at room temperature. We find that, at low bias voltages, the tunnel current depends strongly on the atomic position, introducing visibility differences between adjacent lattice sites. Since all atoms are equally visible in analogous measurements on single-wall nanotubes, we conclude that these modulations are introduced by the interwall interactions and provide unique information about the stacking nature. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1427743]

Single-wall (SWCNTs) and multiwall (MWCNTs) carbon nanotubes exhibit a wealth of extraordinary properties, making them ideal candidates for device applications.[1] Particular attention has been paid to their electronic properties, since small variations in diameter or chiral angle cause profound changes in their conductance.[2–5] This unique behavior, coupled with the small diameter, large aspect ratio, and atomic perfections of carbon nanotubes has made it possible to construct new nanoscale devices, such as field effect transistors,[6] diodes, and field emitters.[7] Nevertheless, the full potential of nanotubes in high performance devices remains to be explored.

Transport measurements in MWCNTs have been performed to understand the nature of electronic conduction in these quasi-1D systems. Conductance quantization has been observed in both multiwall[8] and single-wall[9] nanotubes. Still, little is known about the effect of interlayer interactions on the nature of electronic states near the Fermi level in MWCNTs.

In this letter, we present a comparative study of structural and electronic properties of MWCNTs and SWCNTs using atomic-resolution scanning tunneling microscopy (STM) at room temperature. In order to probe the inter-wall interactions in MWCNTs, we utilize the current imaging tunneling spectroscopy (CITS) to probe locally the electronic structure at specific atomic sites along the nanotube walls. High-resolution STM scans of MWCNTs, with a previously unachievable atomic resolution at room temperature, reveal visibility differences between carbon atoms of the outer wall of the tubes. These observations find a remarkable counterpart in scanning tunneling spectroscopy (STS) measurements indicating that the current versus bias voltage characteristics depends strongly on the atomic locations. Neither effect has been observed in SWCNTs. As the measurements on SWCNTs and MWCNTs are performed under same conditions for all samples, we suggest that these visibility asymmetries have an electronic origin in the weak inter-wall interaction in MWCNTs, in analogy to a similar effect observed in pristine graphite.[10]

The SWCNT and MWCNT samples of this study were synthesized using the arc discharge method.[1] A mat of the generated soot was sonicated in ethyl alcohol for a few minutes prior to being cast onto a highly oriented pyrolytic graphite (HOPG) substrate for STM measurements. We have carried out STM measurements using a Digital Instruments Nanoscope IIIa instrument equipped with a customized vibration isolation, operated at room temperature in ambient conditions. High quality images revealing the atomic structure of MWCNTs, SWCNTSs, and of HOPG were obtained by recording the distance between the Pt-Ir tip and the substrate at constant current, with the STM operated at a typical tunnel current of 300 pA and a bias voltage of 50 mV. The images presented here have not been processed in any way. STS measurements in the CITS mode were performed by interrupting the lateral scans, as well as the feed-back loop, and measuring the current (I) as a function of the tip-sample voltage (V) at a fixed tip-sample distance. A combination of STM and STS measurements on individual nanotubes allowed us to investigate both their structural and electronic properties. We first focus in the interpretation of the atomic resolution STM images of SWNTs and MWNTs. Then, we discuss the CITS results, revealing the nature of the interwall interactions.

In Fig. 1 we show atomic resolution images of (a) a

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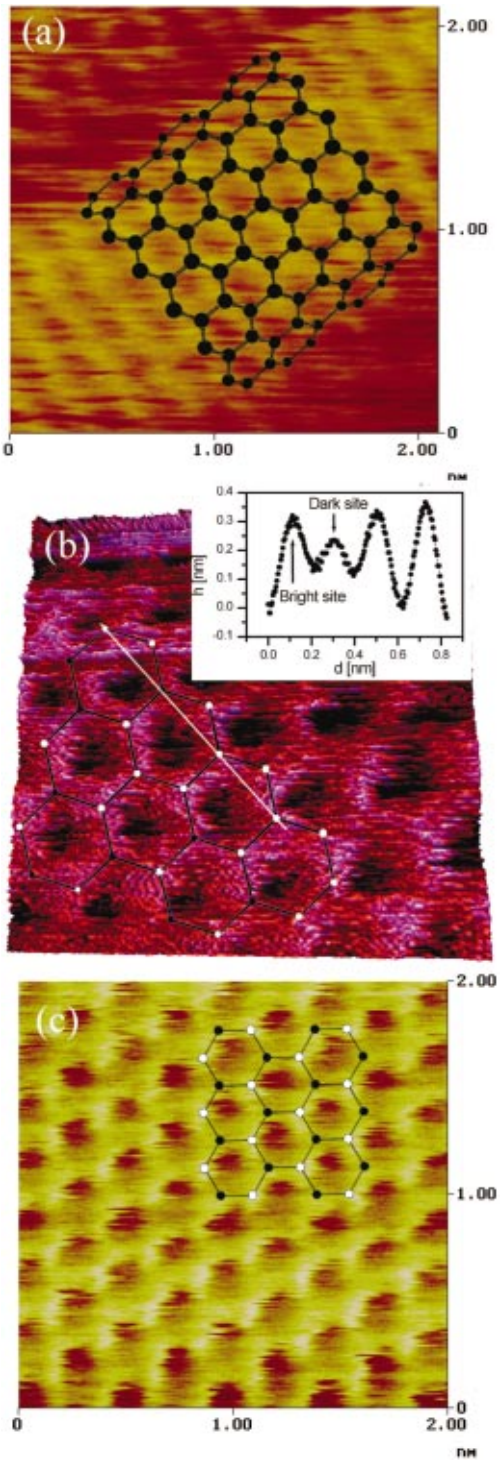

FIG. 1. (Color) Room temperature topographic STM images with true atomic-resolution of a (a) zigzag SWCNT with a diameter of 1.3 nm, a (b) zigzag MWCNT with a diameter of 2.3 nm and (c) highly oriented pyrolytic graphite (HOPG). In all cases the darkest areas correspond to centers of the carbon hexagons and brighter areas mark the location of carbon atoms. In HOPG and MWCNTs, the brightest spots indicate atoms with no neighbor in the adjacent layer below, whereas atoms with such neighbors appear darker. This asymmetry is caused by spatial variations in the local electronic density of states which occur both in MWCNTs and HOPG, but are absent in SWCNTs. The inset in (b) is a line profile taken along the highlighted line in the main image, where differences in peaks height are clearly visible.

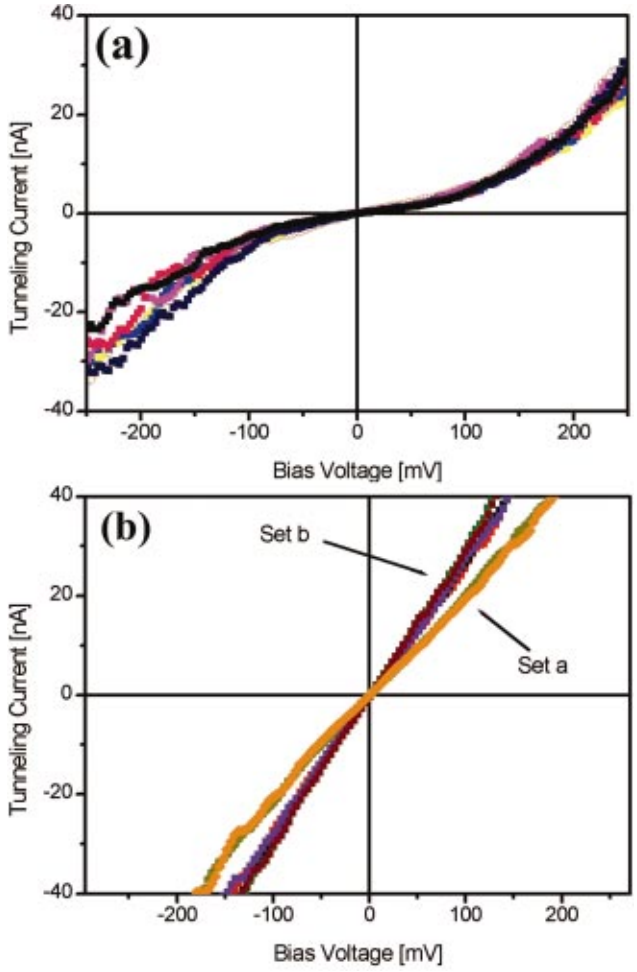

FIG. 2. (Color) Scanning tunneling spectra of carbon nanotubes. For SWCNTs (a), the current–voltage ($I-V$) curves show remarkable reproducibility, independent of the atomic site. For MWCNTs (b), two sets of $I-V$ data can be distinguished. $I-V$ spectra of "set *b*" are obtained at bright sites, whereas spectra of "set *a* " are correlated with atomic sites that appear darker.

zigzag SWNT with a diameter of 1.3 nm, and (b) a zigzag MWNT with a diameter of 2.3 nm. In both cases, the dark areas correspond to the center of the carbon hexagons, which are arranged in a triangular lattice on the cylindrical tube surface. The distance between neighboring dark spots is 0.25 nm, which compares well with that of HOPG shown in Fig. 1(c). The hexagon centers appear elongated along the tube circumference due to the geometrical distortion arising from the locally changing tip-sample arrangement due to the tube morphology.[11] The measuring conditions in (a), (b), and (c) are identical.

Next, we examined more carefully the signal intensity at different atomic sites of MWNTs in Fig. 1(b) and found that some atoms are clearly more visible than others. This effect is not seen in the case of SWNTs in Fig. 1(a), but is reminiscent of the site asymmetry in HOPG.[10] The topographic STM image of HOPG in Fig. 1(c) shows two triangular sublattices with a markedly different visibility within the honeycomb atomic lattice of the graphite layer. The origin of this effect lies in the atomic stacking nature of hexagonal graphite, which places half the atoms directly on top of each other in adjacent layers (*A* sites, solid circles), whereas the remaining atoms (*B* sites, open circles) have no such neighbors. Due to the local crystal symmetry, the only interlayer interaction due to the π states, which are imaged by the STM due to their proximity to the Fermi level, occurs normal to the graphite layers. This distinguishes the sublattices of *A* and *B*

sites in pristine HOPG with a hexagonal or a rhombohedral stacking of graphene layers. The interlayer interactions cause an energy dispersion of almost 1 eV along the chains of *A* atoms normal to the layers, whereas the negligible interlayer interaction along the analogous chains of *B* atoms yields no such dispersion.[10] Consequently, one observes a sharp peak near E_F in the local density of states at the *B* sites, which spreads into a band at the *A* sites. In low biased ($<$50 meV) STM experiments, we therefore expect the *B* sites (with no neighbors in the adjacent layer below) to be more visible than the *A* sites. Then, the STM image will show a triangular rather than a honeycomb pattern.

The above elucidation is consistent with the fact that all atoms are equally visible within the honeycomb lattice of a SWNT, as seen in Fig. 1(a). The STM image of a MWNT, shown in Fig. 1(b), exhibits a more complex structure, with some sites considerably more visible than others. This difference in visibility even between adjacent atomic sites on the same nanotube is a consequence of spatial variations in the local density of states, originating in the inter-wall interaction. Following the previous arguments about STM images of HOPG, the discernible differences in the local electronic density of states provide information about the relative stacking (or the relative atomic arrangement) in the outermost tube walls. This means that a comparison of local intensities identifies not only those atoms which have a neighbor in the adjacent layer below, but also provides an indirect information about the chirality of the second outermost wall. Furthermore, the stability of the intensity modulation pattern provides a clear evidence that individual tubes do not rotate freely even at room temperature.

To understand the origin of the visibility difference, we have performed atomically resolved scanning tunneling spectroscopy measurements on both single- and multiwall carbon nanotubes. Data obtained from SWCNTs, presented in Fig. 2(a), do not show any site-to-site variations in the $I-V$ characteristics. Data obtained from MWCNTs, on the other hand, exhibit two very different types of $I-V$ characteristics, as shown in Fig. 2(b). ''Set *b*'' of $I-V$ curves, taken at the bright sites, is markedly different from data of ''set *a*,'' taken at less visible sites on MWNTs. The larger slope of the $I-V$ curves of ''set *b*'' reflects a higher electronic density of states near the Fermi level at these sites. This is consistent with our assessment that the brighter sites, called ''*B* sites'' in HOPG, have no neighbors in the adjacent layer below. The lower slope of the $I-V$ curves of ''set *a*'' indicates a lower density of states, caused by the hybridization with atoms in the adjacent layer located directly below.

The complementarity of the information obtained using scanning tunneling microscopy and spectroscopy indicates that these techniques are unique probes of the inter-wall interaction in carbon nanotubes. Combining STM and STS measurements allows us to detect not only the atomic stacking in the outermost tube walls, but also the site-dependence of the inter-wall interaction.

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[1] M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, Science of Fullerenes and Carbon Nanotubes (Academic, San Diego, 1996).
[2] Jeroen W. G. Wildoer, Liesbeth C. Venema, Andrew G. Rinzler, Richard E. Smalley, and Cees Dekker, Nature (London) **391**, 59 (1998).
[3] Teri Wang Odom, Jin-Lin Huang, Philip Kim, and Charles M. Lieber, Nature (London) **391**, 62 (1998).
[4] A. Hassanien, M. Tokumoto, Y. Kumazawa, H. Kataura, Y. Maniwa, S. Suzuki, and Y. Achiba, Appl. Phys. Lett. **73**, 3839 (1998).
[5] A. Hassanien, M. Tokumoto, S. Ohshima, Y. Kuriki, F. Ikazaki, K. Uchida, and M. Yumura, Appl. Phys. Lett. **75**, 2755 (1999).
[6] Y. Saito, K. Hamaguchi, S. Uemura, K. Uchida, Y. Tasaka, F. Ikazaki, Y. Yumura, A. Kasuya, and Y. Nishina, Appl. Phys. A **67**, 95 (1998).
[7] Sander J. Trans, Alwin R. M. Verschueren, and Cess Dekker, Nature (London) **393**, 49 (1998).
[8] S. Frank, P. Poncharal, Z. L. Wang, and W. A. de Heer, Science **280**, 1744 (1998).
[9] S. J. Tans, M. H. Devoret, H. J. Dai, A. Thess, R. E. Smalley, L. J. Geerligs, C. Dekker, Nature (London) **386**, 474 (1997).
[10] D. Tománek, S. G. Louie, H. J. Mamin, D. W. Abraham, R. E. Thomson, E. Ganz, and J. Clarke, Phys. Rev. B **35**, 7790 (1987); D. Tománek and S. G. Louie, Phys. Rev. B **37**, 8327 (1988).
[11] V. Meunier and Ph. Lambin, Phys. Rev. Lett. **81**, 5588 (1998).