Scanning tunneling microscopy current–voltage characteristics of carbon nanotubes

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Scanning tunneling microscopy (STM) has been used to obtain images and current–voltage ($I-V$) curves of carbon nanotubes produced by arc discharge of carbon electrodes. The STM $I-V$ curves indicate that carbon nanotubes with diameters from 2.0 to 5.1 nm have a metallic density of states. Using STM, we also observe nanometer-size graphene sheets which are four graphite layers thick. The STM images of carbon nanotubes are in good agreement with transmission electron microscope images.

I. INTRODUCTION

The recent discovery of the existence of carbon nanotubes in the soot produced from the arc discharge of carbon electrodes,[1] as well as the production of nanotubes in macroscopic quantities,[2,3] has stimulated intensive research concerning the structural and electronic properties of these interesting structures. Potential applications of carbon nanotubes include nanometer-size electronic and optical devices, and fiber reinforced materials.[4,5] There has recently been much theoretical work concerning the electronic structure of carbon nanotubes. It has been predicted that carbon nanotubes are metallic or semiconducting depending on the diameter and chirality of the nanotubes.[6–8] Recently, scanning tunneling microscopy (STM)[9,10] and atomic force microscopy (AFM)[9] have been used to image carbon nanotubes. In this paper, we present STM images and STM current versus voltage ($I-V$) curves of carbon nanotubes which show that nanotubes with diameters from 2.0 to 5.1 nm have a metallic density of states.

II. EXPERIMENT

The scanning tunneling microscope used was made by Burleigh Instruments, Inc.[11] Carbon nanotubes were grown using arc discharge of carbon electrodes at 500 Torr of He. The nanotube samples were prepared for STM imaging by sonicating the carbon soot from the arc discharge in methanol and placing a few drops on a highly oriented pyrolytic graphite (HOPG) substrate. The use of a metallic HOPG substrate instead of a semiconducting substrate, such as Si,[9] allowed us to measure the $I-V$ curves of nanotubes without interference from the band gap of the substrate. In addition, the high lateral conductivity of HOPG allowed us to measure the $I-V$ curves of nanotubes at small tip-sample voltages. The STM imaging and $I-V$ spectroscopy were performed in air using a mechanically cut Pt-Ir tip. Typical tip-sample voltages and tunneling currents used for imaging were 75 mV and 1.0 nA, respectively. The $I-V$ curves were obtained by disengaging the feedback loop of the scanning tunneling microscope and measuring the tunneling current versus tip-sample voltage at a fixed tip-sample distance. The tunneling current was measured using a 12-bit analog-to-digital converter.

Transmission electron microscopy (TEM) images of carbon nanotubes were obtained using a JEOL 100CX and a Hitachi H9000 high-resolution 300 keV transmission electron microscope. The nanotube samples were prepared for TEM imaging using the procedure described above for STM imaging except a thin amorphous carbon film was used as the substrate.

III. RESULTS

Figure 1(a) shows a low magnification TEM image of the carbon soot from the arc discharge. Granular carbon material and filament-like structures corresponding to carbon nanotubes are observed. Figure 1(b) shows a higher-resolution TEM image of the carbon nanotubes. The nanotubes in Fig. 1(b) have diameters on the order of 5 nm and greater. Figure 1(c) shows a TEM image of nanotubes sticking out of the granular carbon material.

Figure 2(a) shows a top view STM image of a 1×1 μm area of a carbon nanotube sample prepared as described above on a HOPG substrate. The STM image shows a high contrast between the carbon soot material and the smooth surface of the HOPG. The clumping of the soot material is similar to that observed in the TEM image of Fig. 1(a). Figure 2(a) reveals the existence, in the region indicated by the arrow, of aligned nanotubes approximately 110–140 nm in length. The nanotubes stick out of the carbon soot material in a manner similar to that observed in the TEM images of Figs. 1(a) and 1(c). Therefore, we do not believe these nanotubes are spurious structures from the HOPG substrate. Such spurious structures have been reported to resemble biological structures such as DNA.[12] Figure 2(b) shows a higher-resolution three-dimensional topographic STM image of the region indicated by the arrow in Fig. 2(a). From Fig. 2(b),

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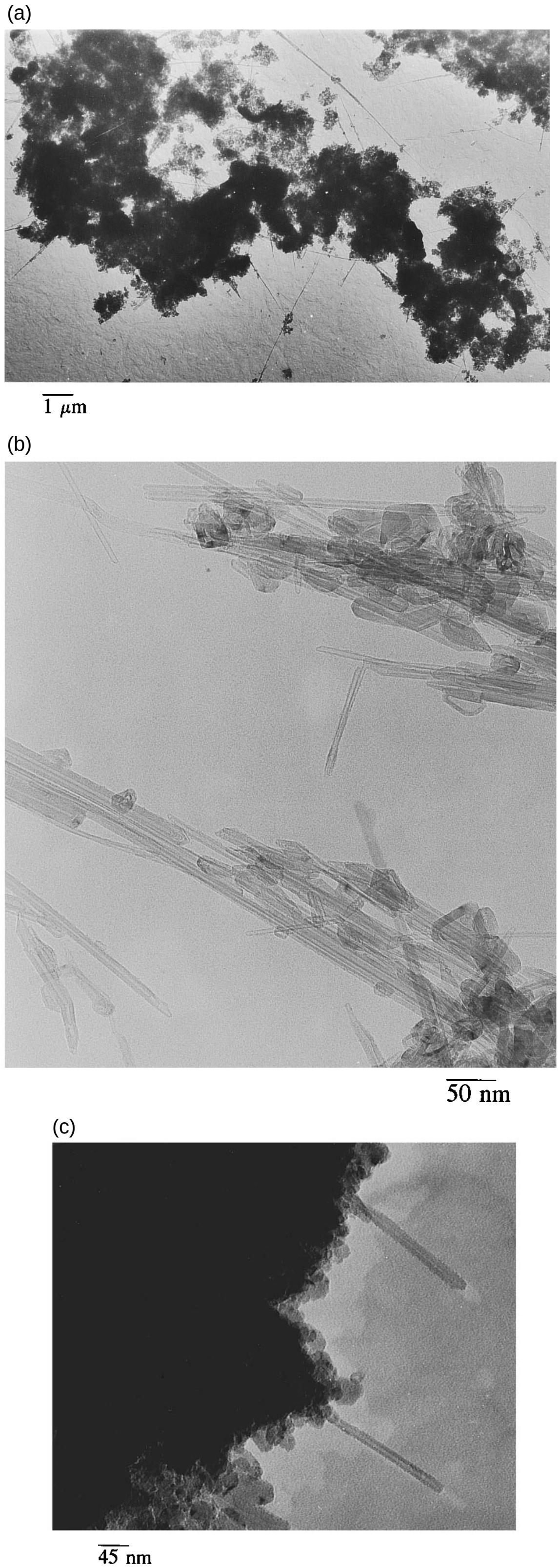

FIG. 1. (a) TEM image of carbon soot showing granular carbon material and carbon nanotubes. (b) Higher-resolution TEM image of carbon nanotubes. (c) TEM image of carbon nanotubes sticking out of the granular carbon material.

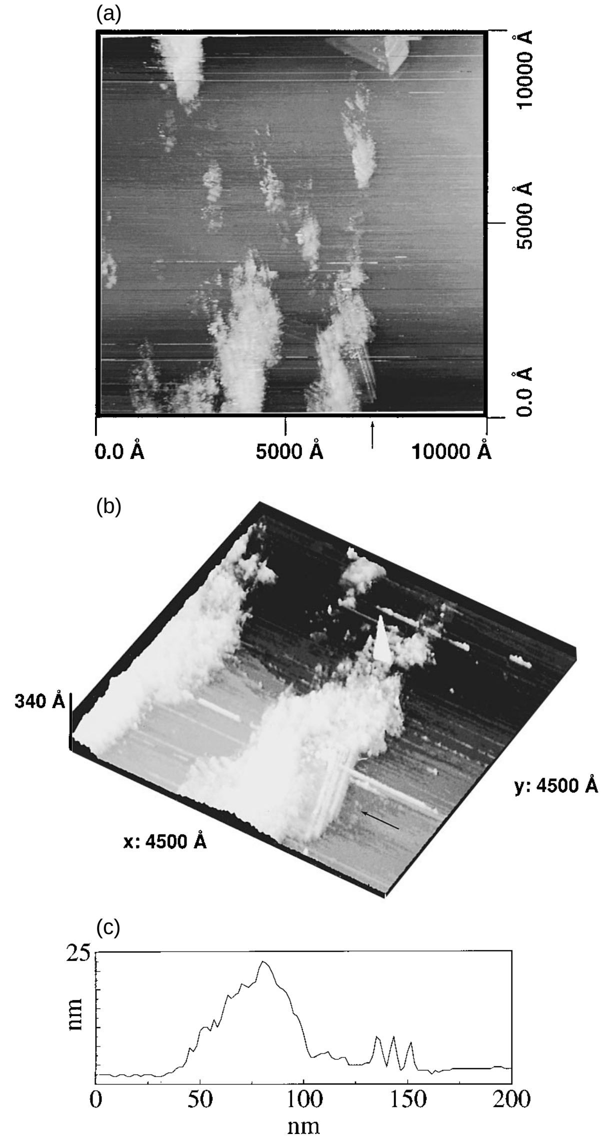

FIG. 2. Top view STM image of carbon soot from the arc discharge deposited on a HOPG substrate. Carbon nanotubes are observed sticking out of the carbon soot in the region indicated by the arrow. (b) Higher-resolution three-dimensional STM image of the region indicated by the arrow in (a). The observed nanotubes have diameters between 5.0 and 7.0 nm. (c) Line scan starting at the point indicated by the arrow and going horizontally across the surface. Three nanotubes are observed on the right with dimensions consistent with the TEM results.

the diameters of the nanotubes are measured to be from 5.0 to 7.0 nm. Figure 2(c) shows a STM line scan starting at the point indicated by the arrow in Fig. 2(b) and going horizontally across the surface. The line scan clearly shows the soot material to the right and three nanotubes to the left with dimensions consistent with the TEM results. The nanotubes in Fig. 2(b) have a cross angle of ~110°C with the two steps of the HOPG substrate at the left center of the image. Although 120 is one of the characteristic value of the angle between steps on the surface of HOPG, we do not believe the nanotubes are steps because the nanotubes do not have a topography corresponding to steps, as shown in the line scan. Figure 3(a) shows a top view STM image of several aligned nanotubes. Figure 3(b) shows a higher-resolution STM image of the nanotubes in Fig. 3(a). The diameters of the nanotubes in Fig. 3(b) are from 2.0 to 5.1 nm. Figure 3(c) shows an STM line scan starting at the point indicated by the arrow

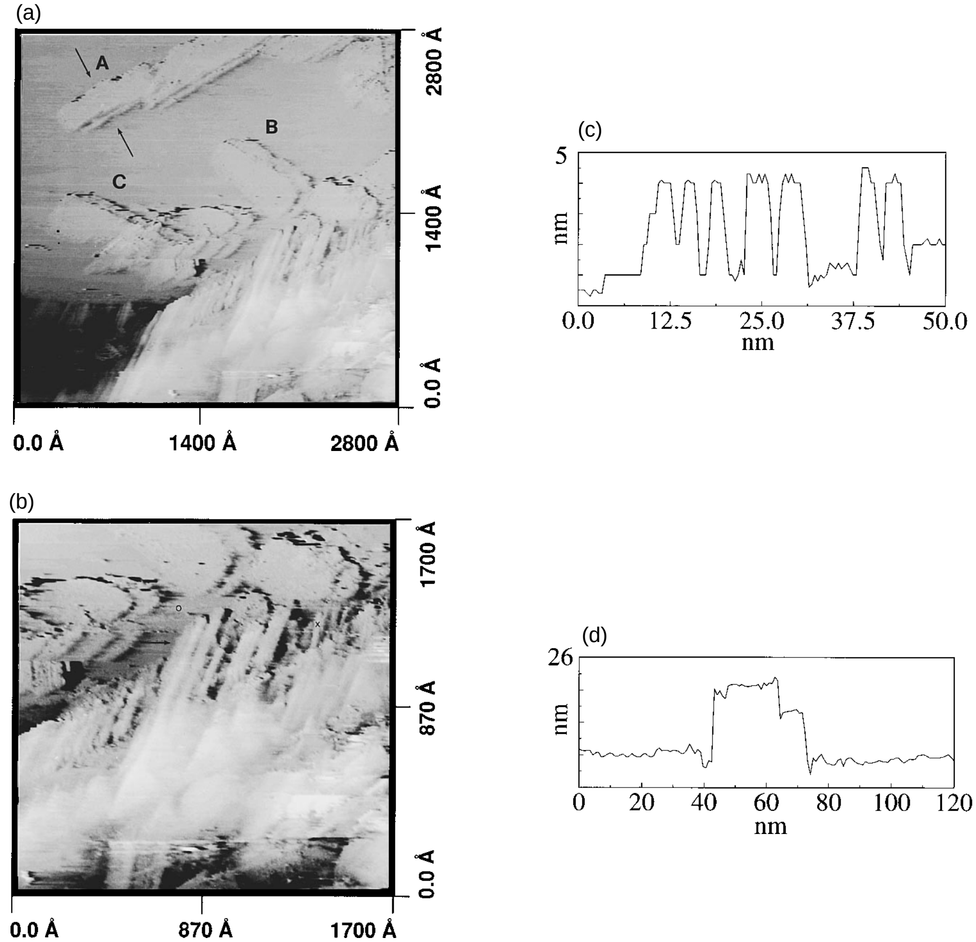

FIG. 3. (a) Top view STM image of several aligned nanotubes having different diameters. Regions labelled A, B, and C contain graphene sheets which are four graphite layers thick. (b) Higher-resolution top view STM image of the nanotubes in (a). Empty circle denotes location on the HOPG where the $I-V$ curve was measured. "X" denotes location on carbon nanotube where the $I-V$ curve was measured. (c) Line scan starting at the point indiated by the arrow in (b) and going horizontally across the surface. The line scan shows the nanotube structure. (d) Line scan taken between the two arrows near region A in (a). The line scan shows the graphene sheet structure.

in Fig. 3(b) and going horizontally across the surface. The line scan clearly shows the nanotube structure.

The fact that the above nanotubes were imaged using low tip-sample voltages of 75 mV, typically used for metals, is evidence that these nanotubes are metallic. To directly test this hypothesis, we measured the $I-V$ curves of individual nanotubes. From the $I-V$ curves, one can determine the conductivity dI/dV and electronic density of states (DOS) ρ from the expression $\rho \propto (dI/dV)/(I/V)$.[13] It is well known that for a metal one has a linear $I-V$ curve about the Fermi level at a tip-sample voltage of 0 V, whereas the DOS of a semiconductor leads to the absence of tunneling current about the Fermi level due to the band gap.[13] $I-V$ spectroscopy has been used to study the band structure of metal[14] and quantum well[15] nanostructures and the electronic structure of passivated and nonpassivated Si[16] and GaAs[17] surfaces in air.

$I-V$ curves were measured for all the nanotubes in Fig. 3(b), and the HOPG substrate. Figure 4(a) shows the $I-V$ curve for a carbon nanotube with diameter of 2.0 nm measured at the location indicated by the "X" in Fig. 3(b). A linear relationship for tip-sample voltage from -80 to 80 mV about the Fermi level at 0 V is observed, indicating a metallic DOS. The $I-V$ curves for all nanotubes in Fig. 3(b) with diameters from 2.0 to 5.1 nm were similar in shape and slope. Figure 4(b) shows the $I-V$ curve for the HOPG substrate measured at the location indicated by the empty circle in Fig. 3(b). A linear relationship is observed, as expected. Semiconducting nanotubes were not observed. However, since $I-V$ spectroscopy measures surface rather than bulk electronic structure, the presence of surface states on the nanotubes may produce $I-V$ curves similar to those displayed here. In addition, energy band bending induced by the tunnel tip may yield a spectrum similar to that shown here. Recently, it was reported, using STM imaging, that carbon nanotubes with diameters of 5 nm deposited on a thin polycrystalline gold film on Si were semiconducting and had a band gap of 200 mV.[10] However, it should be pointed out that thin polycrystalline gold films on Si have very poor conductivity for STM imaging at such low voltages,[18] and that $I-V$ curves for the nanotubes were not measured.

Also observed in Fig. 3(a), near the regions labeled A, B, and C, are nanometer-size rectangular structures which we identify as graphene sheets. These structures are approximately 50 nm in width and several hundred nanometers in length. The heights of all of these structures were approximately 13.5 Å, in good agreement with the thickness of four

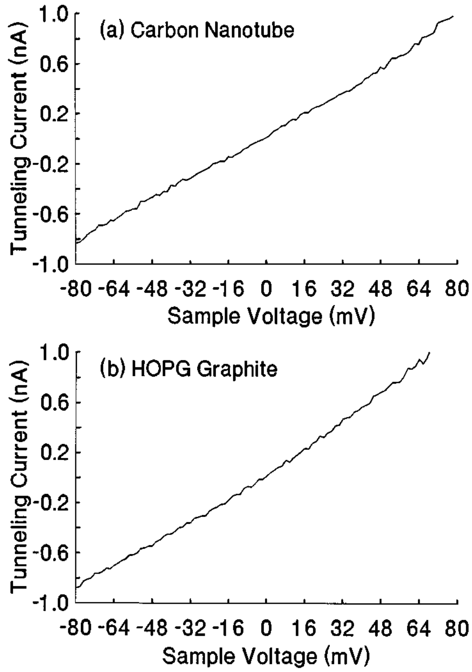

FIG. 4. (a) Tunneling current vs sample voltage curve for the carbon nanotube with diameter of 2.0 nm, showing linear behavior about 0 V, indicating a metallic density of states. (b) Tunneling current vs sample voltage curve for the metallic HOPG substrate showing linear behavior about 0 V, indicating a metallic density of states.

graphite layers (the interlayer distance in graphite being 3.4 Å). Figure 3(d) shows a line scan taken between the two arrows near region A in Fig. 3(a). The line scan clearly shows the graphene sheet structure. Graphene sheets have been conjectured to be produced during the arc discharge,[19] but have not yet been reported. These thin structures lying on the surface would be difficult to observe using TEM, but would easily be observed using STM which is highly sensitive to surface topography.

In conclusion, we have used STM and STM $I-V$ curves to study the structural and electronic properties of individual carbon nanotubes. Our results show that nanotubes with diameters from 2.0 to 5.1 nm have a metallic DOS. We also observe in the carbon soot nanometer-size graphene sheets which are approximately four graphite layers thick.

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