Nanotube structure and electronic properties probed by scanning tunneling microscopy

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Scanning tunneling microscopy (STM) has been used to investigate the structure and electronic properties of carbon nanotubes produced from a discharge between graphite electrodes. STM images of the nanotubes deposited onto polycrystalline gold substrates resolve the three-dimensional structure of the nanotubes and show that these tubes often exist as tightly packed bundles. In addition, bias-voltage dependent imaging studies indicate that the nanotubes studied are semiconductors. The implications of these new data to the application of nanotubes in structural composites and nanoelectronics is discussed.

The discovery of carbon nanotubes in the deposit produced from a direct current discharge between two graphite electrodes has added an exciting new dimension to fullerene research.[1–3] Nanotubes, which consist of concentric tubes of graphene sheets,[1,4] may be an especially interesting and important form of carbon since they are expected to be mechanically stiffer than any presently available carbon fiber material.[3,5] Furthermore, electronic structure calculations have predicted that nanotubes will exhibit metallic or semiconducting electronic properties depending on the diameter, length, and helicity of the tube.[6–8] Underlying potential technological applications of these fascinating materials is an understanding of the structure and electronic properties of the tubes. To date, electron microscopy has been used to structurally identify nanotubes.[1,2,4] Transmission electron microscopy (TEM) studies have addressed the nature of the stacking of concentric carbon layers within the nanotubes and the closure of the tube ends. Resistivity measurements made on the crude carbon product containing nanotubes also indicates that the tubes may have a high conductivity.[2] However, the surface structure, solid-state packing and potentially novel electronic properties of the nanotubes have not been clearly determined. Herein, we report real-space images of nanotubes obtained by scanning tunneling microscopy (STM). The STM images resolve directly the three-dimensional structure of the tubes and are consistent with the structures inferred from TEM. Our STM data also demonstrate that the nanotubes often exist as tightly packed and stable fiber bundles. In addition, similar images acquired over a range of bias voltages indicate that nanotubes are small band-gap semiconductors.

Carbon nanotubes were grown in a standard fullerene reaction chamber. A direct current arc-discharge between 1.2 and 0.6 cm carbon rods in 400 Torr of He produced an elongated deposit on the large (negative) carbon electrode.[1,2] The core of the deposit, which contains the nanotubes,[2] was mechanically ground and ultrasonically cleaned in methanol and 1,2,3,5-tetramethylbenzene (TMB). Samples for STM and TEM were prepared by suspending (ultrasonically) the tubes in TMB, and then allowing single drops of the suspension to evaporate on the STM substrate and TEM grid. TEM studies[9] show that our nanotubes exhibit the same concentric carbon shell structure that was first reported by Iijima.[1] The diameters of the nanotubes determined from the analysis of our TEM images range from 5–25 nm; the three-dimensional structure and packing of the tubes cannot, however, be clearly determined by TEM.

To elucidate further the structural properties of the nanotubes we have used STM. It is important in STM studies of macromolecular species that the substrate does not exhibit features that could mimic the expected structure of the adsorbed material.[10] We find that evaporated polycrystalline gold films represent an ideal substrate for imaging the quasi-one-dimensional nanotubes since the films consist of roughly circular grains which are easily distinguished from the tubes. A typical image of a 50 nm thick polycrystalline Au film evaporated onto a Si(111) single crystal is shown in Fig. 1(a). The average grain size of our Au films was found to be ≈60 nm; no tubelike features are detected on these substrates. Nanotubes were deposited onto the Au substrates by allowing a drop of the TMB/nanotube suspension to evaporate at room tempera-

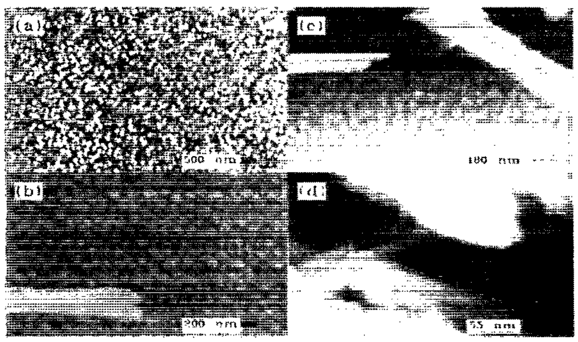

FIG. 1. (a) STM images of a 50 nm polycrystalline gold film deposited on a Si(111) crystal. (b)–(d) Images of gold substrates after deposition of TMB/nanotube suspensions. The polycrystalline gold substrate is clearly visible in images (a) and (c) and serves as an internal reference. The images were recorded in air in the constant current mode using a commercial instrument (Nanoscope, Digital Instruments, Inc.) and mechanically formed Pt-Ir alloy (80%–20%) tips. The bias voltages (with respect to the sample) used to record images (a), (b), (c), and (d) were 400, 400, 400, and 200 mV, respectively; a tunneling current of 1 nA was used in these experiments.

ture. Typical images of the deposited nanotubes are shown in Fig. 1(b)–1(d). In general, the density of tube structures increases as the number of drops of the nanotube suspension deposited on the surface is increased. For example, Fig. 1(b), which shows an isolated bundle of tubes, corresponds to deposition of a single drop of suspension. In contrast, Fig. 1(d), which exhibits a dense structure of tubes, corresponds to a deposition of several drops of suspension. In addition, the tubes observed in the STM images exhibit the same range of diameters as those inferred from the TEM analysis of the same samples. Hence, there is little doubt that the STM data correspond to images of carbon nanotubes.

The STM images can be used to address both the three-dimensional packing and detailed structure of the nanotubes. In general, the STM images of the nanotubes show both oriented bundles and isolated tubes. A low-resolution image of one bundle of tubes is shown in Fig. 1(b). This bundle has a length $>0.5\ \mu m$ (i.e., only one end of the fiber is imaged) and a total diameter of $\approx 0.1\ \mu m$. Inspection of this image indicates that the bundle is made up of closely packed nanotubes. A higher resolution STM image of two bundles is illustrated in Fig. 1(c). This image demonstrates clearly that the large bundles consist of closely packed nanotubes with diameters on the order of 10 nm. Statistical analysis of a number of different bundles of tubes shows that the tube diameters range from 6–26 nm with an average ± 1 SD of 15 ± 5 nm. These diameters are close to the range (5–25 nm) determined by TEM analysis of the same samples. Several additional points can be gleaned from the STM studies of the bundles. First, the bundles of tubes are very stable to repetitive scanning and are not damaged by the tip. These results are indicative of strong intertube binding. Second, the ends of individual nanotubes start and terminate at random positions along the bundle [e.g., Fig. 1(c).] This structural morphology may enable fiber bundles to have lengths exceeding that of individual nanotubes, although additional large scale images are needed to confirm this point. Lastly, obvious structural defects have not been observed along the outer bodies of these nanotubes. These data thus suggest that the nanotube fiber bundles should indeed be a unique reinforcing material for composites.

The images also may be used to address the structure of individual nanotubes in greater detail; the ends of several nanotubes are shown in Fig. 2. A high-resolution zoom of three of these nanotubes shows clearly the tubular structure of this material [Fig. 2(b)]. The cross section taken along the line *c*-*c*′ illustrates the curved outer surface of the nanotubes, while the section taken along *d*-*d*′ shows the contour of the end of the tube. Interestingly, the section over the end of the tube [Fig. 2(d)] indicates that this tube may be closed by a hemispherical cap. However, it is not possible to quantitatively determine the contour of the cap since the tube is oriented ca. parallel to the substrate (i.e., STM cannot reliably image an undercut surface and the tip shape is convoluted with the nanotube end shape). Nevertheless, it is apparent that the ends of these nanotubes do not taper slowly to closure.

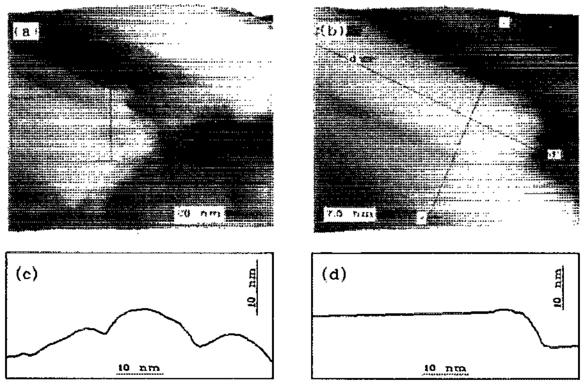

FIG. 2. (a) Perspective view of the end of a bundle that consists of several nanotubes. The image was recorded in the constant current mode with a bias voltage of 400 mV and a tunneling current of 1 nA. The rectangular box outlines the image region that is expanded in (b). The lines in (b) highlight the directions along which the topographic sections in (c) and (d) are taken. (c) A plot of the nanotube structure taken along the line *c*-*c*′. (d) A plot of the topography taken along the line *d*-*d*′.

In addition, it is important to note that the diameters of the tubes estimated from the heights of the cross-sectional plot *c*-*c*′ are consistent with diameters estimated from the linear widths of the tubes. Qualitatively these results suggest that the tubes have a relatively high conductivity at finite bias voltage.[11] These observations are also consistent with the relatively high conductivity indicated by resistivity measurements made on samples containing nanotubes and other carbon products.[2] To further probe the electronic nature of the nanotubes we have carried out bias voltage dependent imaging studies. Images acquired between 200 and 600 mV exhibit no differences in the structural features. The voltage dependent data show that the nanotubes are conducting for voltages >200 mV. Below 200 mV, however, tunneling is unstable. These latter results suggest that there is a gap in the nanotube density of states. We believe that the instability and gap can be associated with the smallest (6 nm diam) nanotubes in the bundles. Theoretical studies of small tubes have suggested that nanotubes may be metallic[6] or exhibit size dependent electronic properties (either metallic or semiconducting).[7,8] Our results do not directly address the single tube electronic properties, but do suggest that the nanotube bundles (and probably some individual tubes) imaged in this study are semiconducting.

In conclusion, we have used STM to elucidate the morphology and packing of nanotube bundles and the three-dimensional structure of individual nanotubes. Voltage dependent imaging studies have also indicated that the nanotubes are small band-gap semiconductors, although additional work is needed to fully elucidate their electronic properties. Since we have shown that nanotubes can be readily imaged it should be possible in the future to illuminate quantitatively the electronic properties of individual tubes as a function of diameter and helicity using atom-resolved tunneling spectroscopy. Such results would provide further motivation for the development of these materials in nanoelectronics.

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[11] The observed similarity in the heights and widths indicate that the density of states of the nanotubes at finite bias voltage (i.e., >200 mV) are similar to that of a metal. If the density of states were low, then the measured heights would be less than the widths.