Smallest diameter carbon nanotubes

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Mass-selected carbon ion beam deposition (MSIBD) was used to demonstrate that the diameter of a carbon nanotube could be as small as 0.4 nm, the theoretical limit predicted but never experimentally reached so far. The deposition was performed at an elevated temperature much lower than the high temperatures (800–1000 °C) needed for deposition of carbon nanotubes by conventional methods. High-resolution transmission electron microscopy showed that the combination of the stress induced by the ion impact and the C migration at the temperature applied formed graphitic sheets with their normal (c axis) parallel to the surface of the silicon substrate. Some sheets closed to form multiwall nanotubes. The smallest diameter of the innermost tube was found to be 0.4 nm. The novel use of MSIBD (a pure method, catalyst free, low deposition temperature, easily applied to large surfaces without surface pretreatment capable of pattern-writing) may significantly advance the carbon nanostructure technology. © *2000 American Institute of Physics.* [S0003-6951(00)02244-0]

Carbon nanotubes[1–5] have been extensively investigated in the past decade motivated both by the possibility of studying the physics of nanostructured (one-dimensional) materials as well as by their exciting electrical and mechanical applications. The diameter of the carbon nanotubes strongly affects their properties, so that its possible smallest value has been the subject of both theoretical and experimental studies.[6–9] Using a novel technique for fabrication of carbon nanotubes, mass selected carbon ion beam deposition at elevated temperatures, we give high-resolution transmission electron microscopy (HRTEM) evidence that the diameter of a carbon nanotube can be reduced to 0.4 nm, which corresponds to the smallest diameter of a capped carbon nanotube predicted so far.[7]

It has been recently shown[10] that hyperthermal (tens and hundreds electron volt range) carbon ion deposition at elevated temperatures (>150 °C) leads to the formation of graphitic layers with their basal planes perpendicular to the surface (c axis parallel to the surface). This is due to the biaxial stress created by the ion impact, which favors the formation of films aligned so that the most compressible direction is parallel to the stress. This rearrangement of the carbon atoms in sp^2 bonded sites forming graphitic planes necessitates not only energy, but a high enough temperature to allow migration of carbon atoms (at temperatures below 150 °C only amorphous sp^3 films are formed).[11] The alignment of the graphitic layers is constrained only in one dimension, i.e., the normal to the basal planes (c axis) is parallel to the surface, but this normal may have any orientation in the plane parallel to the surface. Some planes may thus close to form multiwall nanotubes. This formation of statistically distributed and oriented graphitic layers, which are subjected to a biaxial stress, enables us to study the minimal size of the innermost nanotube formed in the multiwall carbon tubes. We have thus deposited ~100 nm carbon films by a mass selected ion beam system at Soreq NRC, Israel and have varied the deposition parameters to optimize the formation of closed, circular graphitic layers (multiwalled nanotubes).

Figure 1 is a cross-sectional transmission electron microscopic (TEM) (Philips CM200FEG, 200 kV) image showing

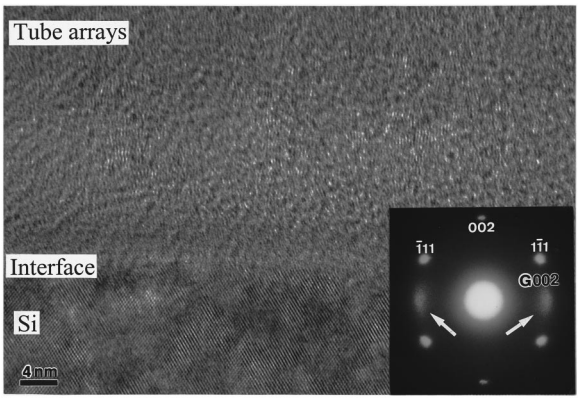

FIG. 1. Cross-sectional TEM image showing the graphitic planes of carbon nanotubes grown on the flat Si (100) surface. Both the contrast of the graphite planes and the SAED pattern (inset) show that the graphitic planes are aligned perpendicular to the Si substrate.

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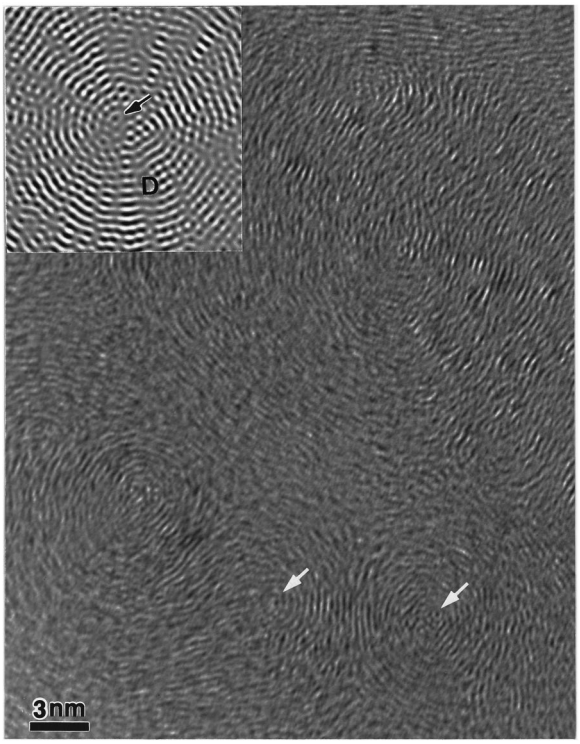

FIG. 2. Plan-view HRTEM image showing the multiwalled carbon nanotubes with ultra small innermost tubes of 0.4 nm in diameter. FT filtered image of individual fingerprint structure is shown in the inset. The arrow illustrates the innermost tubes.

carbon graphitic planes grown perpendicular to the flat Si substrate surface. The inset is the selected-area electron diffraction (SAED) pattern taken along Si [110] direction of this sample in which two arc-like reflections (marked by arrows) have been identified to be the {002} reflections (denoted by G002) originated from the aligned carbon graphitic planes. The absence of diffraction rings indicates that all the graphitic planes are roughly perpendicular to the Si (001) surface. The graphitic planes are continuous along a distance of about 100 nm. The high-resolution plan-view TEM image of Fig. 2 clearly shows an atomic arrangement that contains a multiwall nanotube like structure in which the nanotubes are perpendicular to the Si-carbon interface. This structure is manifested as a fingerprint-like pattern in Fig. 2. Most nanotubes consist of 10–15 shells and the intershell spacing is 0.34 nm. The innermost nanotubes, as marked by the arrows in this figure, are clearly seen to be seamless loops and their diameters are approximately 0.39–0.40 nm. This value is determined by using the graphite $d_{(002)}$ spacing as the internal reference in this figure. The nanotube arrays are very dense, while the graphite sheets having the same orientation to the tube walls fill in the space between them. The Fourier transform (FT) filtered image of the individual nanotube is illustrated in the inset in Fig. 2. (The FT processing was carried out by first Fourier transforming the interested area of the image to obtain a two-dimensional diffraction pattern. The filtered image of multiwalled carbon nanotube was then obtained in the inverse FT by selecting the diffraction ring of graphite {002} and filtering off the noise.) Noted that the innermost tube is seamless, while the shells contain some defects like dislocations (as marked by ''*D*'') resulting in the discontinuity of the fringes.

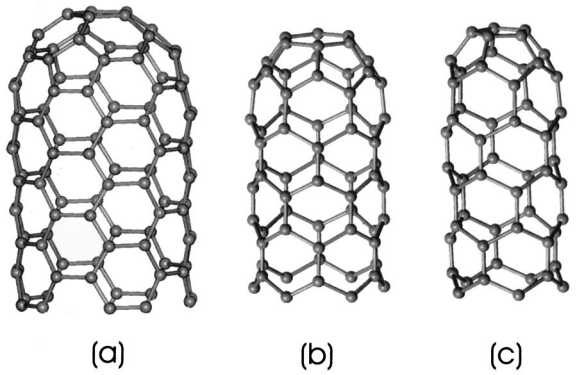

FIG. 3. Single-walled carbon nanotube models constructed by different tip structures of half cages of (a) C_{60}, (b) C_{36}, and (c) C_{20}.

Since the discovery of carbon nanotubes, the peculiar electronic properties of this structure have attracted much attention. It was believed that the smallest nanotube diameter is restricted to the size of the fullerene molecule, which caps the tube. A minimal size of 0.7 nm corresponding to C_{60} was predicted and observed.[8] Their electronic properties have been predicted to depend sensitively on the tube diameter and helicity of the tube lattice. The smallest diameter of carbon nanotubes reported (very recently)[9] is 0.5 nm, the same as that of a C_{36} molecule. Theoretical calculations indicate that carbon nanotubes with a diameter of 0.4 nm are possible since they have lower energies than the graphite sheets.[7] This dimension is the same as that of the possible fullerene C_{20}, which is the smallest carbon cage molecule. The models of carbon nanotubes with diameters of 0.7, 0.47, and 0.39 nm are shown in Fig. 3, in which the caps are half cages of C_{60}, C_{36}, and C_{20}, respectively. Our finding of ultrasmall carbon nanotubes provides definitive evidence that indeed the smallest predicted size is feasible.

In order to find out whether the multiwall carbon nanotubes content affects the overall properties of our films, we performed field emission measurements that indicated a very low turn-on voltage (3 V/μm for 0.01 mA/cm^2). This value is consistent with our measurements of the field emission of regular carbon nanotubes. It suggests that the properties of the carbon nanotubes embedded in the carbon matrix obtained by the present method are similar to those of regular carbon nanotubes.

Conventional methods of carbon nanotube production (arc discharge,[2] thermal deposition,[3] and chemical vapor deposition)[4,5] are all performed at high temperatures (~800–1000 °C), and are difficult to directly apply on a surface and to control. It is an intriguing open question left for future studies if the controllable ion beam deposition could lead to better fabrication methods of carbon nanotubes. This novel technique offers many potential advantages over conventional methods of carbon nanotube productions. They include: (1) high purity with no need of catalyst, (2) simple applicability to most surfaces without pretreatment, (3) low deposition temperature, (4) simple controllability of the nanotube size, structure, and orientation, and (5) patterning and writing options. The combination of all these advantages in a single synthetic approach may open new directions for both basic studies and realization of exciting applications.

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