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Interlayer spacings in carbon nanotubes

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Electron and x-ray-diffraction studies of nanotubes have revealed that the distances between the graphitic sheets are larger by a few percent than those in bulk graphite. The mean value of the interlayer spacings is 0.344±0.001 nm.

With the advent of the macroscopic preparation of C_{60} and other fullerenes,[1] the production of endohedral metallofullerenes[2,3] and other forms of carbon[4-8] has attracted great interest. Electric arc discharge between graphite rods is commonly used for the production of C_{60} and other higher fullerenes at the present time. Nanotubes[4,5] and polyhedral nanoparticles[6] have been discovered in a slaglike carbonaceous deposit grown on an electrode as a by-product of fullerene-rich soot. Both the polyhedral nanoparticles and nanotubes consist of a few to about 20 layers of graphitic sheets, and they have large cavities inside. Recently, it was revealed by electron diffraction that the spacing between the layers (d_{002}) in nanocapsules is 0.34–0.35 nm,[6] wider by a few percent than that of the ideal graphite crystal (0.3354 nm). This wide d_{002} spacing is due to the turbostratic stacking of graphitic sheets (neighboring graphitic sheets are parallel to each other, but translational and rotational correlations within a sheet plane are random). On the other hand, d_{002} spacing in nanotubes is reported to be 0.34 nm as an approximate value for the graphite crystal.[4] In the present study, by using electron- and x-ray diffraction techniques, we show that d_{002} in nanotubes is also wider than in graphite, which is naturally expected from the turbostratic character in the tubes.[4]

Figure 1 shows an electron-diffraction (ED) pattern from a tubule with an outer diameter of 7 nm. For the tube samples, the reciprocal space consists of annular rings and disks, as illustrated in Fig. 2. The $hk0$ reciprocal rings are appreciably spread toward the radial direction (the direction perpendicular to the tube axis) because the effective number of graphitic layers giving rise to the $hk0$ reflections coherently is smaller, owing to the turbostratic stacking, than the total number of layers making up a tube. Therefore, the $hk0$ reflections can be observed even when the incident electron beam is not perpendiclar to the tube axis. The distance between the origin and the $hk0$ spot varies as $1/(d_{hk0}\times\cos\alpha)$, where α is an angle between the incident electron beam and the tube normal within a plane containing the electron-beam direction and the tube axis. When an ED pattern was recorded with the incident electron beam parallel to the tube normal, $\alpha=0$, the $(hk0)$ spacings can be derived directly from the position of the spots.

On the other hand, the spread of the $00l$ reciprocal spots is not as serious as for the $hk0$ spots as long as the thick tubules consisting of many layers, say more than ten layers, are observed, since all the layers parallel to each other interfere to produce the $00l$ reflection notwithstanding the turbostratic stacking. Furthermore, the $(00l)$ spacing can be measured from its position even when the tube axis is not perpendicular to the electron beam because the region of the graphitic layers giving rise to the $00l$ reflection is still parallel to the incident beam, irrespective of the angle between the tube axis and the incident beam.

To demonstrate the change of the positions of the $hk0$ spots with respect to the angle α, the ratio of d^*_{100} to d^*_{002} as a function of α is shown in Fig. 3, where d^*_{100} and d^*_{002} are the distances between the origin and the 100 and 002 spots in the diffraction pattern, respectively. The 100 reflections used for the measurement of the d^*_{100} were restricted to those appearing in the direction parallel to the

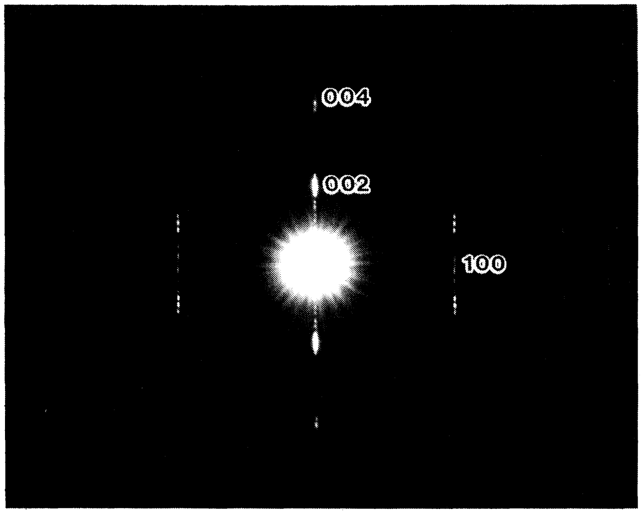

FIG. 1. Electron-diffraction pattern from a single tubule.

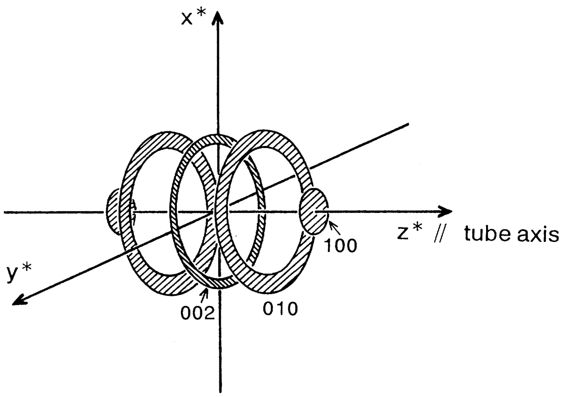

FIG. 2. Schematic drawing of the reciprocal space of a graphitic tube. The 100 annular disks and 002 ring are illustrated. The tube axis is parallel to the z^* axis.

tube axis in order to minimize the effect of the spot elongation on the d^*_{100} measurement.

Since the d^*_{002} is constant irrespective of α and d^*_{100} varies as the inverse of $\cos\alpha$, the ratio d^*_{100}/d^*_{002} is expected to depend on the inverse of $\cos\alpha$. In fact, this behavior is observed in Fig. 3. Therefore, the minimum value of the ratio, 1.616, which is obtained at $\alpha=0$, reflects the real values of the d spacings. The corresponding ratio for the bulk graphite crystal is 1.574.

The large value of the ratio orginates from either the smaller d_{100} spacing or the larger d_{002} spacing in the tubule than in graphite. The interaction between the graphitic layers is of the weak van der Waals type, whereas the bonding between the neighboring carbon atoms in a graphitic sheet is covalent and stiff. Therefore, it is reasonable to conclude that the change of the interlayer spacings is responsible for the observed deviation of the ratio from the bulk value.

Under the assumption that the carbon-carbon bond distance within a graphitic layer is unchanged whether in a tubule or in a graphite crystal, i.e., $d_{100}=0.2131$ nm, we obtain $d_{002}=0.344$ nm. This value of d_{002} is larger by about 0.01 nm (2.6%) than that for the ideal graphite crystal (0.3354 nm). The wide interlayer spacings are commonly encountered in carbon fibers with turbostratic structure.[9]

Figures 4(a) and 4(b) show x-ray diffraction (XRD) profiles of a graphite rod before evaporation and the core of a deposit obtained after evaporation, respectively. The positions of the 002 and 004 reflections from the deposit shift to a lower angle than those from the graphite rod, indicating the wide d_{002} spacings (0.3442 ± 0.0010 nm) of the deposit. Since the core of a deposit consists of tubules and nanoparticles,[5,6] the XRD shows that the tubes and particles have turbostratic structure and thus have large interlayer spacings. This result is consistent with the ED result.

Reflections indexed as 10, 20, and 11 are broad and asymmetric, which is caused by their turbostratic nature, i.e., diffraction from a two-dimensional lattice. From the positions of the 10, 20, and 11 reflections, a lattice parameter $a=0.2468\pm0.0010$ nm is obtained. The value agrees with that of the three-dimensional graphite, and thus supports the assumption mentioned above that the carbon-carbon bond distance within a graphite sheet is unchanged.

In summary, we used ED and XRD techniques to investigate the distance of the graphitic sheets in nanotubes, and both methods revealed that the interlayer spacings are larger by a few percent than that in the bulk graphite crystal. When the properties of nanotubes such as geometric and electronic structures are precisely evaluated, we should keep in mind the wide interlayer spacing of graphitic sheets. The previously reported value of 0.34-nm spacing[4] is an approximate value and should be used with care.

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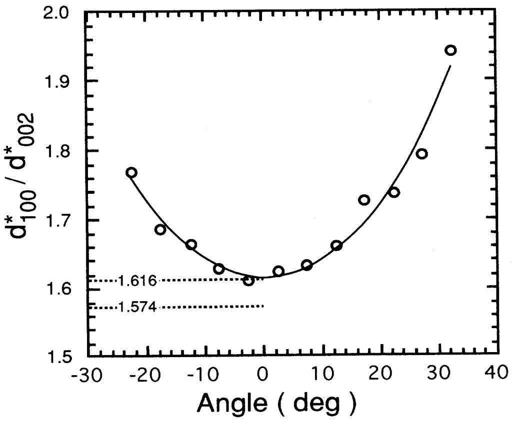

FIG. 3. Ratio of d^*_{100}/d^*_{002} as a function of an angle α. A solid curve is the $1/\cos\alpha$ fitting.

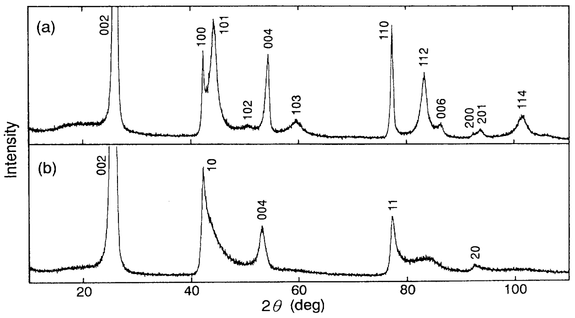

FIG. 4. X-ray diffraction profiles of (a) a graphite rod used as an electrode ($d_{002}=0.3367$ nm) and (b) a core of a deposit grown after arc discharge ($d_{002}=0.3442$ nm). The core consists of bundles of carbon tubules and hollow nanoparticles.

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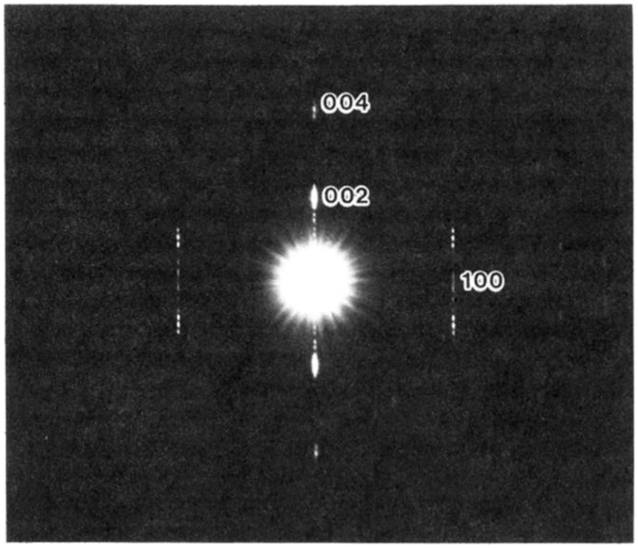

FIG. 1. Electron-diffraction pattern from a single tubule.