123

Graphitic Nanotubes and Aligned Nanotubes Films

D. Ugarte[1], W.S. Bacsa[2], B. Doudin[2], L. Forro[3] and W. A. de Heer[2]

[1] *Laboratório Nacional de Luz Síncrotron (CNPq/MCT)*

Cx. Postal 6192, 13081-970 Campinas SP, Brazil

[2] *Institut de Physique Expérimentale*

Ecole Polytechnique Fédérale de Lausanne

PHB Ecublens, CH-1015 Lausanne, Switzerland

[3] *Lab. de Phys. des Solides Semicristallins*

Ecole Polytechnique Fédérale de Lausanne

PHB Ecublens, CH-1015 Lausanne, Switzerland

Carbon nanotubes are easily produced in macroscopic quantities, however their characterisation and possible applications are still rather limited. We have developed a new method to make aligned nanotube films which open new opportunities, not only for basic research but also for eventual applications. With this method the tubes can be aligned either parallel or perpendicular to the surface. We give a short review of the microscopic properties of single tubes and the bulk properties of the aligned films.

I. Introduction

Carbon nanostructures are produced in a wide variety of shapes and sizes, as is evidenced by a extremely rich literature. The ideal fullerene, C_{60}, was originally discovered by Kroto and Smalley's group[1] in 1985 using a complex molecular beams apparatus, where graphite rods were laser vaporised. The remarkable stability of this molecule, was explained by suggesting a single spherical shell of sp^2 bonded carbon, consisting of hexagons and pentagons of carbon atoms. Topological considerations request that closed three dimensional surface cannot be exclusively composed of hexagons, and must also contain 12 pentagons. This general principle has been known for very long time, and this particular arrangement was used in different domes projects by the American architect and inventor W. Buckminster Fuller, after who the C_{60} molecule is now named. At present, we know that C_{60} is only one member of a large class of molecules formed by a closed graphitic surface: the fullerenes.

In addition to spheroidal single shell fullerenes, a second class of molecules, consisting of concentric graphitic layers (multiple shells) was discovered. These fullerene related large molecules have received names as onions or hyperfullerenes for the case of concentric spheroidal graphitic shells[2,3], or high aspect ratio tubular structures called nanotubes[4]. In particular, these tubules are usually formed by very long (on the order of microns) concentric graphitic tubes, with a hollow centre. Typical diameters are in the range of one to several tens of nanometers.

As for most of the fullerenes and related molecules, highly energetic conditions are necessary for a efficient formation. The traditional electric arc discharge run in a inert gas atmosphere has been the key experiment in the recent development of fullerene research[5,6]. Fullerenes and nanotubes are spontaneously formed in macroscopic quantities in a carbon arc. The intriguing question of why they are formed is still hotly debated, and, as for C_{60}, the production is still poorly understood. An important modification of the electric arc may be prepared by adding a transition metal to the graphitic electrodes which yields micrometer long single shell tubular structures with a typical diameter of 1-2 nm[7,8], but apparently formed by a undetermined catalytic reaction. Here, we will not discuss the production of nanotubes in detail, but rather the recent

development in the characterisation on electronic and optical properties of nanotubes.

II. General properties

Since nanotube discovery and until quite recently the associated research was mainly focused on the use of electron microscopy techniques. Numerous works showed beautiful high resolution microscopy images of various types of graphitic nanotubes with different forms, straight[4] (Fig. 1a), spring shaped[9], etc. The number of layers forming the tube varies from two shells to about 100. Electron diffraction studies have revealed that individual tubule layer present a helicity[4].
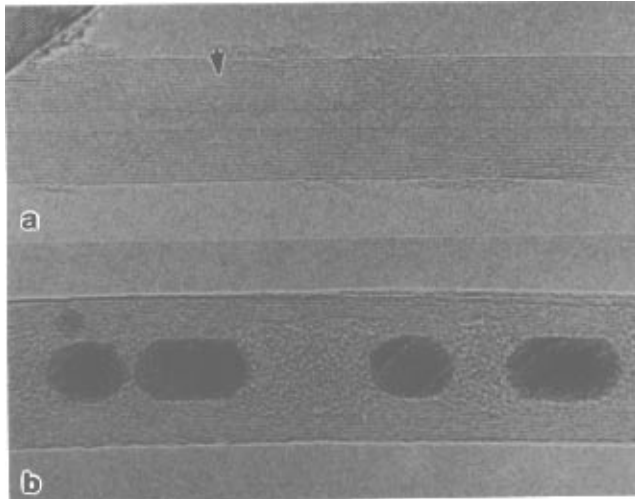

Figure 1. High resolution electron micrographs of carbon nanotubes. a) as generated in the electric arc, note the bamboo-like defect (marked with an arrow); b) nanotube whose inner cavity (5 nm in diameter) has been filled with liquid silver nitrate, subsequently reduced to silver metal particles; note that the inner tube layes have been eroded during the chemical reaction. Distance between nanotube layers is 3.4 Å.

Recently, some methods have been developed to fill the inner empty space in tubes with metals or oxides[10,11]. In Fig. 1b, we show a silver filled tube which was opened and subsequently capillarity filled with pure liquid silver nitrate; the following step consisted of a heath treatment to reduce the nitrate, resulting in isolated silver droplets inside the tube[12]. Note how the chemical reaction has eroded the inner shells of the tube.

Concerning the mechanical properties of nanotubes, theoretical calculations predict that they are extremely stiff[13], nevertheless bent nanotubes are often observed in electron microscopy studies. A bent nanotube is

shown in Fig. 2, note the regular pattern on the compression region of the deformed tube.
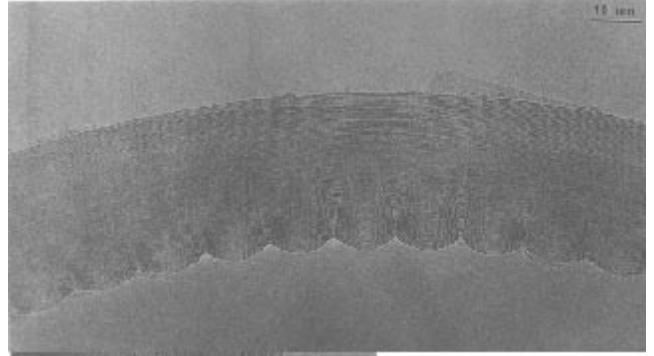

Figure 2. Deformation of a thick graphitic nanotube. Note the buckling of the compression region of the bent tube.

Theoretical predictions of nanotube electronic properties suggest that single shelled tubes may either be semi conductors, or semi metals, depending on geometrical factor such as diameter and helicity[14−16]. However there have been few predictions concerning properties of multi shelled nanotubes, the sample which is usually studied experimentally, nevertheless it is assumed that they reflect up to some degree the properties of the constituent tubules.

III. Aligned nanotubes films

With the exception of electron microscopy evidence, rather little experimental data is available on the properties of the nanotubes. The main reason being that it is quite difficult to prepare reasonably pure monodispersed samples of nanotubes: a typical sample usually contains 30- 50 % of polyhedral onion-like graphitic particles, and a rather large size distribution is present. In order to be able to study nanotube properties (optical, electronic magnetic, etc.), it is essential that the performed experiments are sensitive to possible anisotropic effects expected for such a high aspect ratio structure. Then in conclusion, it is highly desirable to dispose of aligned nanotubes. We have recently succeeded in generating aligned nanotube films[17]. Fig. 3 shows the surfaces of aligned nanotube films, one where the tubes are oriented perpendicular to the thin film surface (β aligned) and the other where they lie flat parallel the surface (α aligned). These films can be studied with standard spectroscopic methods in order to determine the nanotubes properties.
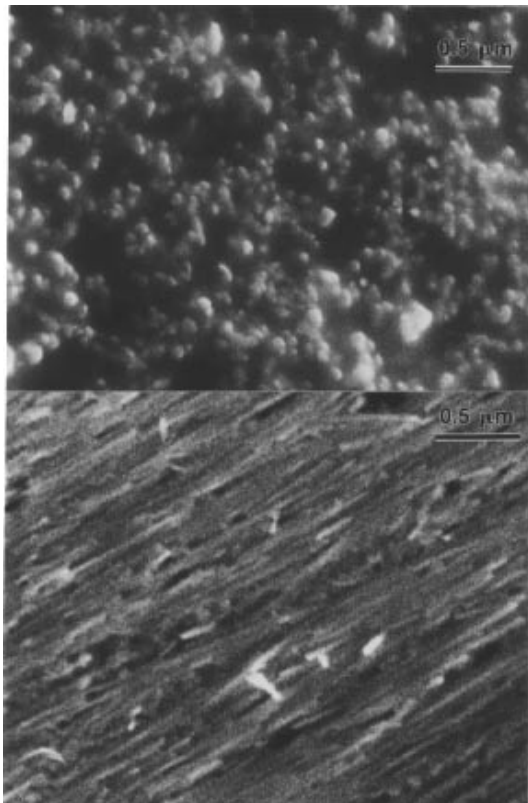
Figure 3. Scanning electron micrographs of the surface of aligned carbon nanotube films. (A) β aligned, with tubes perpendicular to the film surface so that only the tips are visible. (B) α aligned films: rubbing the surface, the surface changes dramatically and becomes densely covered with nanotubes lying flat on the surface; the tubes are aligned in the direction of the rubbing.

Figure 4. Dielectric functions of nanotube films as determined from ellipsometry (dashed lines real part ϵ_1, continuous lines imaginary part ϵ_2). α aligned surfaces are birefringent ($\alpha_\parallel$, $\alpha_\perp$, parallel and perpendicular to the tubes). The dielectric function of the β aligned surface is isotropic and resembles that of glassy carbon.

We have determined the optical properties of these films by ellipsometry; the measured dielectric functions ϵ_1 and ϵ_2, i.e. the real and imaginary part of the dielectric function are shown in Fig. 4. These dielectric functions may be compared with the those ones of graphite[18]. As expected, the α aligned nanotube films display a anisotropic dielectric function: it depends if the polarisation of the light is perpendicular or parallel to the nanotubes. In particular when the polarisation is parallel to the tubes ($\alpha_\parallel$), the dielectric function closely resembles planar graphite. For example, the peak observed at 4.61 eV is related to an similar peak in graphite. When the polarisation is perpendicular to the tubes ($\alpha_\perp$), this peak is diminished. The importance of this peak diminishes even further in the β aligned case, where one is primarily observing the tips of the nanotubes, and electronically they are quite different compared with the planar sheets. The β aligned surface dielectric function displays a striking resemblance to glassy carbon[19].
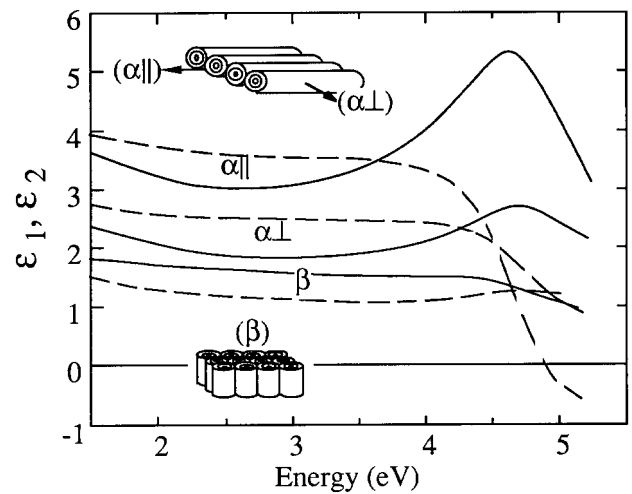
The anisotropical structure of the aligned nanotubes films is also evidenced in resistivity measurements, where the resistivity in the direction parallel to the tubes is considerably lower than perpendicular to them (see Fig. 5). When the electrons travel a certain distance along the surface, they need to hop from tube to tube, and evidently fewer hops are required when the electron follow the tubes direction, than when they hop in the direction perpendicular to the tube alignment. At low temperatures the hopping becomes thermally activated[20], hence we observe a large increase in resistivity.

Graphitic nanotubes present a high diamagnetic magnetic susceptibility, a property which they share with planar graphite (see Fig. 6). Anisotropy effects are also rather large: the susceptibility is larger when the applied magnetic field is parallel to the tube axis than in the perpendicular configuration[21]. We may note that the susceptibility temperature dependence is rather similar to what is observed for planar graphite in both parallel and perpendicular cases. The susceptibilities values are also of the same order as the graphite one along the c direction (i.e. perpendicular to the graphitic planes).

Our observations contradict several predictions relating to single shelled nanotubes[22,23]. In any case, the larger diamagnetism with the applied field parallel

to the tubes is likely to be due to persistent ring current which may be seen as a response of the conduction electrons where diamagnetic currents circulate around the tube axes.
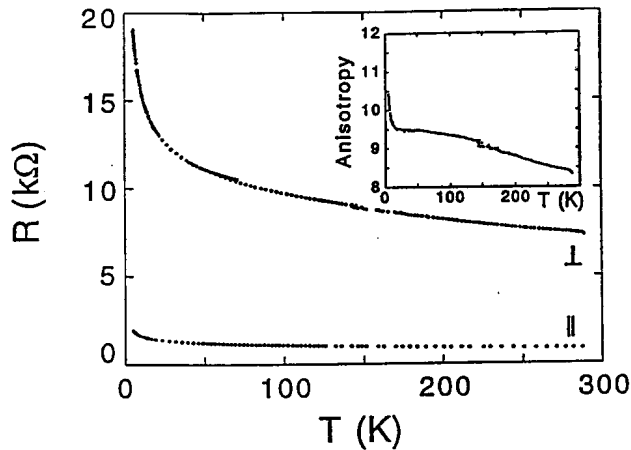

Figure 5. Resistivities of carbon nanotubes films from 4 K to 300 K (film size 5 mm square, $\approx 1\mu$m thick), and resistivity anisotropy $\rho_\perp/\rho_\parallel$ (inset). The high resistivities and their relatively small increase with decreasing temperature are indicative of a disordered conductor whose resistivity is determined by the mean free path of the delocalized electrons. The stronger increase of the resistivities at very low temperatures may be caused by localization of electrons on the tubes.

If the tubes are not aligned but are randomly oriented and touch each other, the diamagnetic behaviour is completely different to what is observed when the tubes are aligned[24]. In the random aligned case, a much larger diamagnetism is observed and also the temperature dependence is different (see Fig. 6). We speculate that this enhancement is due to diamagnetic currents which are induced by the applied field, but involving large closed loops of connected nanotubes. The induced magnetic moment is the product of the current times the area, so a loop which encompass a large area generates a larger diamagnetic moment. We must note that this suggested mechanism does not account for the rather anomalous temperature dependence.

In summary, the development of a method to align carbon nanotubes has allowed the study of several properties of this nanostructures. Besides the examples given here, we also have preliminary results on the spin susceptibilities, magneto resistance, Hall coefficients, infrared absorption, and photo emission. The analysis of this data is in progress and the results will be presented in future publications.
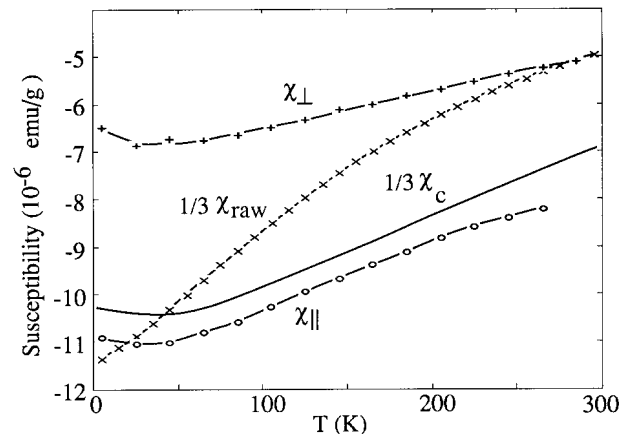

Figure 6. Static magnetic susceptibilities of carbon nanotubes vs. Temperature, for field parallel $(\chi_\parallel)$ and perpendicular $(\chi_\perp)$ to the tubes. Raw nanotube containing material (χ_{raw}) extracted form the electrode deposit. Planar graphite (χ_c) from Ref. [24].

Acknowlegements

References

1. H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl and R.E. Smalley, Nature **318**, 162 (1985).
2. S. Iijima, J. Cryst. Growth **50**, 675 (1980).
3. D. Ugarte, Nature **359**, 707 (1992).
4. S. Iijima, Nature **354**, 56 (1991).
5. W. Kratschmer, L.D. Lamb, K. Foristopoulos, and D.R. Huffman, Nature **347**, 354 (1990).
6. T.W. Ebbesen and P.M. Ajayan, Nature **358**, 220 (1992).
7. S. Iijima and T. Ishihashi, Nature **363**, 603 (1993).
8. D. Bethune, et al, Nature **363**, 605 (1993).
9. X. B. Zhang, et al., Europhys. Lett. **27**, 141 (1994).
10. P. M. Ajayan and S. Iijima, Nature **361**, 333 (1993).
11. S. C. Tsang, Y. K. Chen, P.J.F. Harris and M.L.H. Green, Nature **372**, 159 (1994).
12. D. Ugarte, W. Bacsa, A. Chatelain and W. A. de Heer, unpublished.
13. T. Overney, W. Zhong and D. Tománek, Z. Phys. D **27**, 93 (1993).
14. J. W. Mintmire, B.I. Dunlap and C. T. White, Phys. Rev. Lett. **68**, 631 (1992).

15. N. Hamada, S. Sawada and A. Oshiyama, Phys. Rev. Lett. **68**, 1579 (1992).

16. R. Saito, M. Fujita, G. Dresselhaus and M. S. Dresselhaus, Appl. Phys. Lett. **60**, 2204 (1992).

17. W. A. de Heer, et al., Science **268**, 845 (1995).

18. E. A. Taft and H. R. Philpps, Phys. Rev. **138**, A197 (1965).

19. M. W. Williams and E. T. Arakawa, J. Appl. Phys. **43**, 3460 (1972).

20. L. Langer, J. Mater. Res. **9**, 927 (1994).

21. O. Chauvet, et al, Phys. Rev. B**52**, R6963 (1995)

22. J. P. Lui, Phys. Rev. Lett. **74**, 1123 (1995).

23. J.-Y. Yi, and J. Bernholc, Phys. Rev. **B 47**, 1708 (1993).

24. A. P. Ramirez, et al., Science **265**, 84 (1994).