Nanofilament carbon structure

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A new solid phase of carbon has been observed. It consists of tubular clusters 1 nm in size which form a filamentary structure.

Carbon clusters of extended shapes have recently been attracting interest because of properties[1–4] which differ from those of the well-known spheroidal C_{60} cluster (fullerene). Foremost among these differences is an anisotropy of possible solid structures. Experiments indicate that clusters of extended shape form under extreme conditions (during bombardment of a C_{60} film by a 400-keV electron beam[4]). We have now observed a new carbon structure in the solid phase, in which the atoms are assembled into long macromolecules which are tubes with a diameter $d_t \simeq 1$ nm with "sealed-off" ends. These tubes are in turn gathered in filaments with a diameter $d_F \simeq 5$ nm (Fig. 1). Examination by electron microscopy and by tunneling microscopy (Fig. 2) leads us to believe that the carbon structures obtained here are made up of tubular clusters of C_{60+18n} ($n \gg 1$) or "tubelenes,"[2] each of which consists of a cylindrical fragment of a graphite surface. The fragment is closed at both ends by hemispheres which are halves of the fullerene C_{60} (Fig. 3). These conclusions are supported by electron diffraction and electron spectroscopy, the results of which will be published later.

Films of nanofilament carbon were produced by a known method[6] of electron-beam evaporation in a vacuum of 10^{-5} torr. Highly pure (99.99%) reactor graphite was evaporated on a substrate at room temperature. As substrates we used silicon, quartz, anodized aluminum, graphite, and a ceramic, all polished to a mirror finish. The film thickness was varied from 0.01 to 10 μm. Figure 2 shows a micrograph of a section of a film recorded on a JEM-6 electron microscope. We see the characteristic filamentary structure. At high resolution, we can see filaments ~ 5 nm in diameter over essentially the entire thickness of the film ($L_t \sim 0.1$–0.01 μm). These filaments are collected into "cables" 10–30 nm long. Scanning tunneling microscopy shows that the structure consists of extended entities with a characteristic diameter of 10 Å. Figure 2 is a scanning tunneling micrograph of a carbon film with a thickness ~ 50 Å recorded during the initial stage of the deposition. In addition, electron and Auger spectroscopy of surface atomic layers shows that the electron energy spectrum and the density of states are almost exactly the same as the known properties of C_{60} fullerites. The electron diffraction pattern of the surface of a film with the normal texture indi-

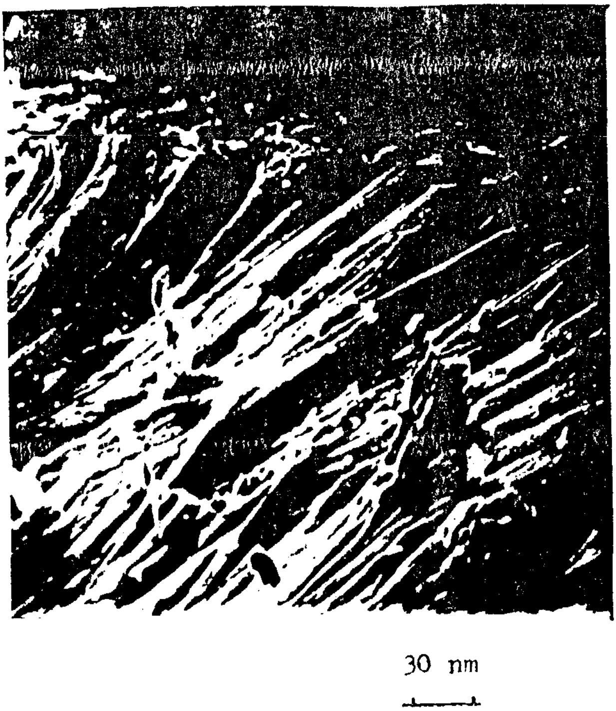


FIG. 1. Electron micrograph of a nanofilament carbon structure with a 45°-slope texture.

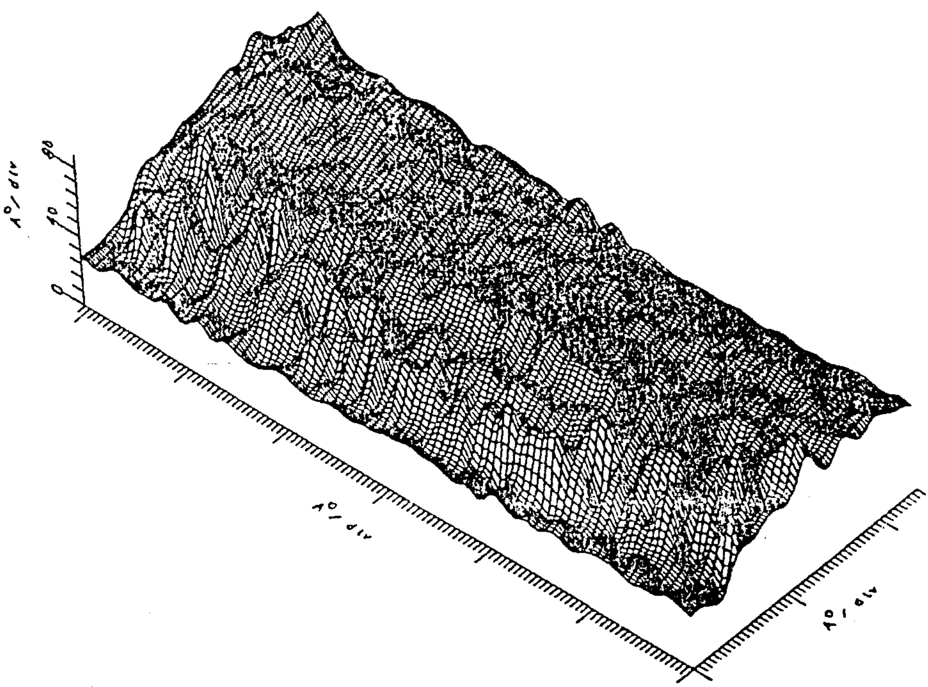
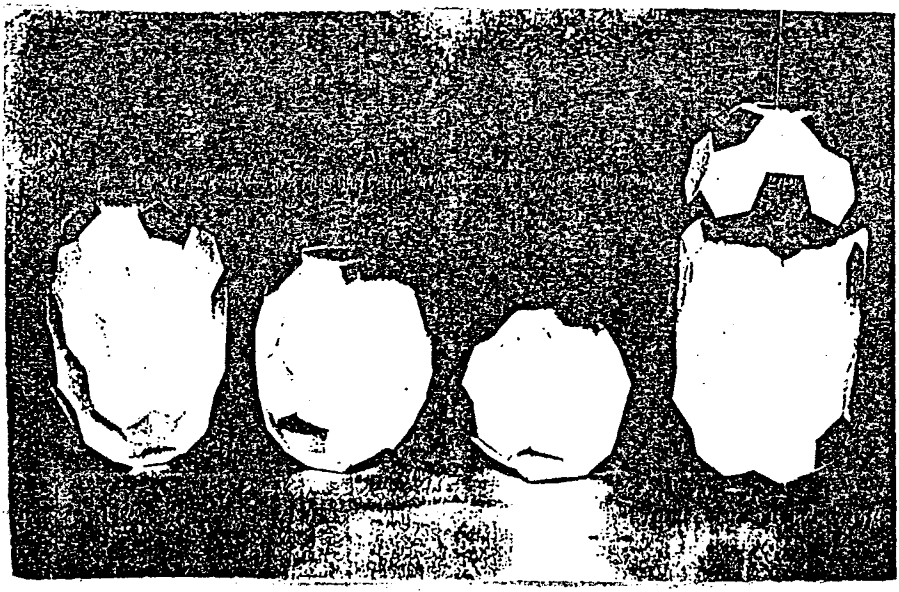


FIG. 2. Scanning tunneling micrograph of an ultrathin carbon nanostructure on a graphite (001) surface.



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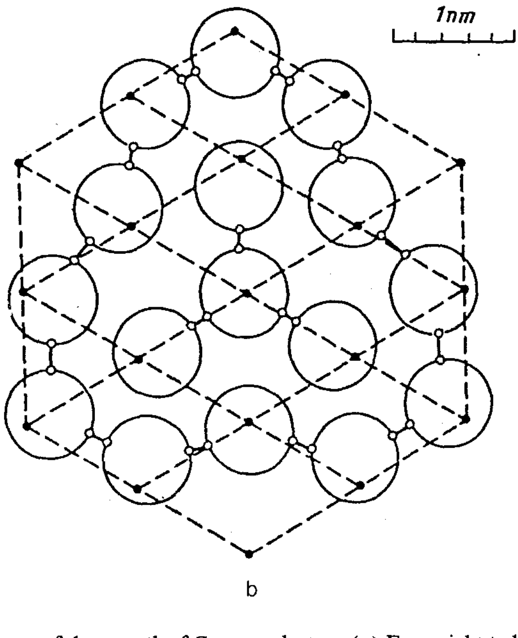

b

FIG. 3. Schematic diagram of the growth of C_{60+18n} clusters. (a) From right to left: tubelene, C_{60}, C_{78}, and C_{96}. (b) Schematic diagram of a section through a filament consisting of 16 tubelenes connected by covalent bonds O—O ($\simeq 2$ Å long[5]) along lines on which the atoms have a nearly ideal ($\simeq 330°$) tetragonal configuration (the sum of the C—C—C angles is 328°).[2] The size of the filament is $d_F \simeq 5d_t$ and is approximately the same as that in Fig. 1. The dashed lines show a hexagonal packing of 19 tubelenes in a molecular binding. The filaments may gather into a "cable" with a similar hexagonal structure ($d_c \simeq 5d_F \simeq 200$–$300$ Å).

cates threefold and sixfold symmetries in the arrangement of atoms in these layers.

These facts lead us to suggest the following scenario for the formation of a structure of C_{60+18n} clusters. The flux of carbon particles reaching the surface of the substrate is reflected from it. The reflected particles collide with newly arriving particles and form a gaseous surface layer of elevated pressure. When 100 torr is reached, this layer promotes a nucleation of C_{60} clusters, as occurs in a laser plasma or spark in the presence of gaseous helium.[7,8] Fragments of the stablest cluster structure, the fullerene C_{60}, thus begin to form on the surface during a certain initial time interval. However, the construction of the spherical cluster is not brought to completion, because of the directed influx of high-energy carbon particles into this layer. These particles lead to a growth of tubular structures in the direction of the incoming flux (along the threefold symmetry axis of the C_{60+18n} "lid").

By varying the direction of the flux of carbon particles with respect to the substrate surface we were able to grow some inclined tubular textures (the inclination angles ranged from 0 to 45° from the normal). Such a texture reveals the anisotropy in the properties of the nanofilament structures, in a transverse thermoelectric effect: When a temperature gradient of 10 K/m is set up in the bulk of the film by a heat flux of 1 kW/m^2, a transverse thermal emf of 5–7 mV arises. These structures differ from fullerite (an insulator) in having a fairly high conductivity at room temperature. For example, in films 0.3 μm thick with a 40° inclined texture, with electrons 1 cm apart, we observe an anisotropy of the resistance in the plane of the film. Specifically, we find $R_x = 1.73$ kΩ along the direction of the projected axis of the texture, while in the transverse direction we find $R_y = 1.24$ kΩ. These results suggest that electrons on a graphite-like fragment of a tubular cluster (Fig. 3) are contributing substantially to the conductivity. This interpretation is indicated by calculations on "infinite" C_{12n} and C_{20n} ($n \rightarrow \infty$) carbon tubes,[1,9] which suggest that these tubes are semimetallic. In these new nanofilament carbon structures we would expect an anisotropy in other physical properties (thermal, magnetic, etc.) also, and we would expect a fairly high superconductivity with a "chain" doping by metal atoms both inside the tubes and in the space between tubes, because of the quasi-1D electron–phonon coupling.[2]

In particular, we would like to call attention to the considerable hardness of the structures produced in this study. Specifically, the microhardness of a film 0.5 μm thick on a substrate of the hard alloy T15K6 is 4000 kgf/mm^2. This figure is greater than the microhardness of the substrate, which is 2500 kgf/mm^2 (Ref. 10).

Similar carbon nanostructures (and apparently nanostructures of silicon also) might be formed from tubular or barrel-shaped $C_{60+18(\text{or } 12)n}$ ($n = 0,1,2,\ldots$) by other methods which are capable of generating a directed flux of particles, e.g., laser, magnetron, and ion-beam methods.

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