Auger and electron spectroscopy of the surface of solid tubular C_{60+18n}

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Auger spectra and electron energy-loss spectra have been measured by probing the surface of the nanofilament carbon material described previously {Z. Ya. Kosakovskaya *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **56**, 26 (1992) [JETP Lett. **56**, 26 (1992)]} with an electron beam. The results indicate C_{60} soccer-ball lids on the surface of nanotube carbon molecules.

The solid phase of C_{60} molecules,[2] which have the shape of a truncated icosahedron, has attracted considerable interest because it exhibits a high-T_c superconductivity when doped with alkali metals, and it also exhibits a high adsorption activity.[3] A solid of a new type was recently produced.[1] It consists of carbon molecules which are extended formations 1 nm in diameter with end caps or lids tentatively identified as having the shape of the C_{60} fullerene. In this letter we are reporting a study of the surfaces of films of this material by Auger spectroscopy and electron energy-loss spectroscopy (the electron penetration depth was < 5 Å). The results support the interpretation just mentioned.

Samples in which the "tubes" were oriented perpendicular to the substrate surface were prepared by a known procedure.[1] The substrate was (110) silicon. The film thickness was varied from 5 to 50 nm. The measurements were carried out in ultrahigh vacuum (5×10^{-10} Torr) on a high-resolution electron spectrometer ($\Delta E/E = 0.2\%$). The current density of the exciting electrons was kept below 10^{-7} Å/cm^2 in order to avoid changing the surface structure of the films during the electron bombardment. The resulting Auger spectra were processed numerically by a procedure described previously.[4]

Figure 1a shows a distribution of the density of electron states found from a carbon Auger line on the surface of a thin (50-Å) film. This film completely covered the substrate, as is indicated by the absence of characteristic lines of silicon from the Auger spectrum. This $n(E)$ distribution is reproducible quite well over five films of various thicknesses (up to 500 nm) grown by the same procedure. The experimental curve was compared with a theoretical curve generated for the purpose of approximating the experimental data. Specifically, this theoretical curve was generated by smearing the theoretical spectrum of the C_{60} fullerene[5] by means of a Gaussian curve with a width of 1 eV (Ref. 4). The first three peaks on the theoretical curve are associated with π orbitals of the C_{60} "sphere." We see that the experimental spectrum reproduces

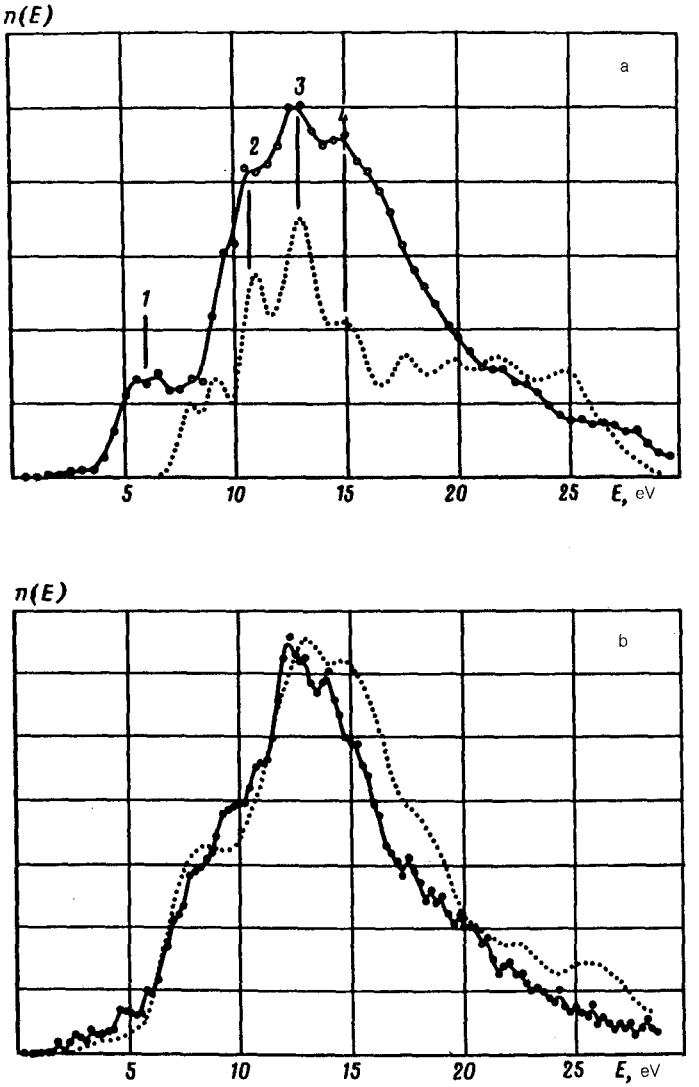

FIG. 1. Spectra of the density of electron states, $n(E)$. a: Solid line—For the surface of a nanofilament carbon film; dotted line—theoretical spectrum for C_{60}. b: Solid line—For a film after ion bombardment; dotted line—for well-ordered graphite. The energy E is reckoned from the vacuum level.

the theoretical spectrum for C_{60} qualitatively well, while it is quite different from the spectrum of well-ordered graphite, obtained by a similar experimental procedure (the dashed line in Fig. 1b). The peaks in the first part of the spectrum (reference line 1) can be attributed to ruptured and deformed π orbitals on tubes "without lids." These incomplete tubes can be seen on the scanning tunneling micrograph of a film in Fig. 2 of Ref. 1. Next comes a rise, without the characteristic peak at ~ 8 eV associated with the π orbitals of graphite (cf. Fig. 1b). On this rise and at the crest, three peaks

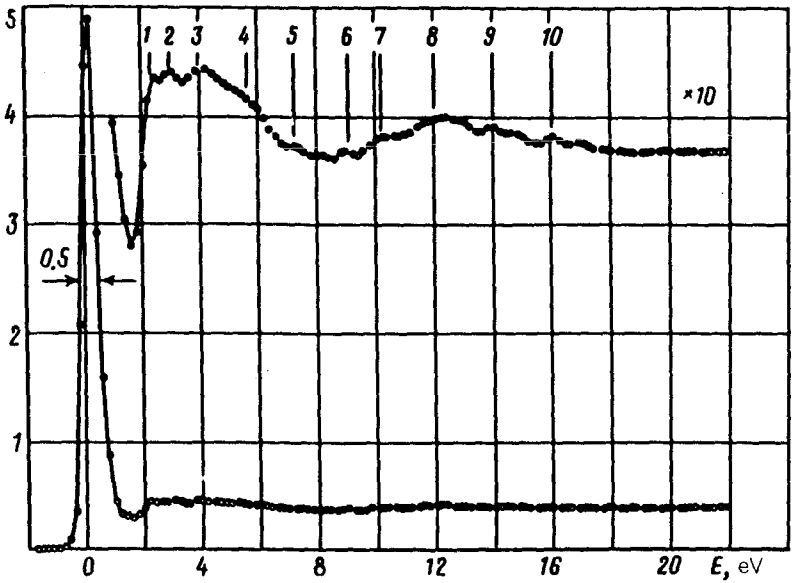

FIG. 2. Characteristic electron-energy loss spectrum at the surface of a nanofilament carbon film on a Si substrate. The primary-electron energy is 200 eV.

characteristic of C_{60} can be seen (*2*, *3*, and *4* in Fig. 1a). Bombardment with 30-keV krypton ions in a dose of 10^{17} ions/cm^2 changes the $n(E)$ spectrum of the film substantially (the solid line in Fig. 1b). Specifically, all the structural features characteristic of the C_{60} valence band disappear, as do the peaks at 5–7 eV corresponding to the ruptured orbitals. On the whole, the spectrum of the density of states in this case is similar to that of graphite (the dotted line). This similarity means that the bombardment disrupts the C_{60}-like surface of the tubelite and leads to the formation of a graphite-like structure.

The electron loss spectrum was recorded at a low electron excitation energy, $E = 200$ eV, below the threshold for the excitation of bulk plasmons. For the given experimental geometry, this circumstance lowers the cross section for the excitation of π plasmons ($\sim$8 eV) and that for σ plasmons ($\sim$20 eV), so that the losses which occur upon one-electron excitation can be seen. A high-resolution spectrum (the width at half-maximum of the elastic-reflection peak is 0.5 eV) reveals ten well-resolved structural features (Fig. 2 and Table I). The point at which the curve begins to rise, $\sim$1.8 eV, can be linked with the width of an interband transition between a filled

TABLE I.

EELS peak of surface of nanofilament carbon structure	1	2	3	4	5	6	7	8	9	10
E (eV)	2.3	3.0	4.0	5.5	7.3	9.1	10.2	12.0	14.0	16.0
C_{60} fullerite[5]	2.1	2.8	3.7	6.1	7.5	9.5	10.7		15.0	18.0

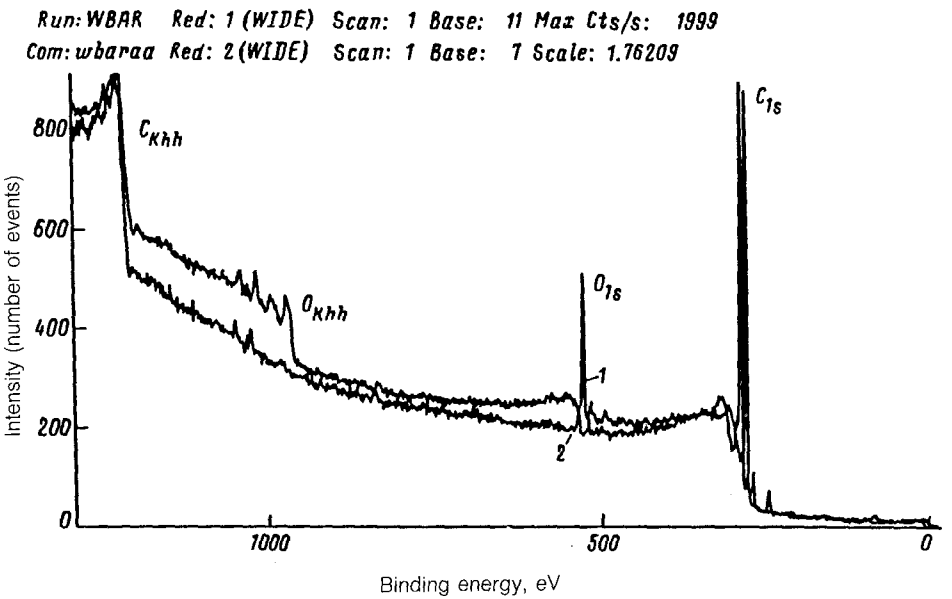

FIG. 3. Photoelectron spectra of (*1*) the original carbon film and (*2*) the film after ion bombardment (a relative displacment of the spectra has been introduced for clarity).

upper electron state and an unfilled lower state, in agreement with experimental and theoretical evaluations of the gap width of C_{60} (1.4–1.8 eV; Refs. 5 and 6). The peaks found for the surface of the nanotube carbon structure can be associated with characteristic peaks of solid C_{60} (Ref. 6; see also Table I of the present paper). Up to 9 eV, the peaks of the structure under study here are shifted toward higher energies, while above 9 eV they are shifted toward lower energies. These shifts can apparently be explained on the basis that the interatomic bonds on the surface of the C_{60+18n} ($n \gg 1$) tubelene[7,1] are stronger than those in C_{60}. This tubelene is a graphite tube consisting of n belts of nine carbon hexagons with end caps or lids consisting of halves of a C_{60} fullerene.

Our results thus indicate a C_{60}-like arrangement of atoms on the surface of a structure consisting of extended macromolecules with a diameter of 1 nm, which is close to that of C_{60} (Ref. 2). In other words, these results support our earlier interpretation of this new carbon structure.[1] This interpretation is also supported by photoelectron spectroscopy (Fig. 3), which shows that a tubelite film, which has spent some time in air, has a significant amount of oxygen on its surface; C_{60} tends to adsorb oxygen. In other words, the surface of this nanofilament carbon structure has a chemical activity comparable to that of a C_{60} fullerite. After graphitization of the structure by ion bombardment (as discussed above), the surface is free of oxygen.

A comprehensive comparison of the results found here with the model will of course become possible after a theoretical calculation of the electronic spectrum of

solid C_{60+18n} and after direct observation of the arrangement of atoms on an individual tubelene.

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