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C_{76} thin films grown on mica and NaCl substrates

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Submicrometer-thick C_{76} films were prepared by vacuum deposition on air-cleaved mica and NaCl substrates held at 430 K, and the crystal structure and textures of the films were studied by transmission electron microscopy (TEM). C_{76} formed the fcc lattice with a lattice parameter $a = 1.53 \pm 0.02$ nm on both substrates. A film grown on mica exhibited a single-crystalline pattern in electron diffraction, though local variations in thickness and orientation were suggested by high-resolution TEM. On NaCl, polycrystalline films consisting of small grains (10–20 nm) were formed. Electron diffraction experiments at low temperatures showed no structural transformation down to 110 K.

I. INTRODUCTION

Studies on physical and chemical properties of fullerenes in the solid state are carried out for the most part by using film samples prepared by vacuum deposition or crystals prepared by sublimation. Thin-film growth of fullerenes has been widely studied by using electron microscopy,[1–6] scanning tunneling microscopy,[7–12] and reflection high-energy electron diffraction.[13,14] Most such studies are restricted to C_{60} and C_{70}, but recently thin films of larger fullerenes such as C_{76}, C_{78}, C_{82}, and C_{84} are beginning to be prepared[9,15,16] and used for studying their physical properties.[15,17]

C_{60} and C_{70} produced by the Krätschmer-Huffman method[18] have only one isomer each. On the other hand, higher fullerenes consisting of over 70 carbon atoms in general have various structural isomers; e.g., three isomers (C'_{2v}, C_{2v}, and D_3) for C_{78}, at least three isomers (C_2, C_{2v}, C_{3v}) for C_{82}, and two isomers (D_2 and D_{2d}) for C_{84}.[19] However, C_{76} is an exceptional molecule among higher fullerenes in that the molecules isolated by chromatography are isomerically pure, i.e., ^{13}C NMR of C_{76} shows only one isomer with D_2 symmetry.[20] The structure (Fig. 1) is uniquely determined from the symmetry and the size (number of carbon atoms) of the molecule under the restriction of the isolated pentagon rule.[21] The structure of D_2-C_{76} is chiral, and its racemization (a state in which the left- and right-handed forms are mixed with an equal amount of each other) has been found through an investigation of circular dichroism.[22]

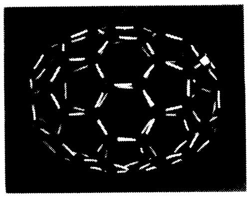

FIG. 1. Ball-and-stick model of D_2-C_{76}. A view along the middle length axis (the long and the short axis are perpendicular to the view direction).

In recent ultraviolet photoelectron spectroscopy[15,23] electron energy loss spectroscopy[17] studies on C_{84} films attempting to determine the structure of a D_2 isomer out of four candidates, an assumption on a mixture of isomers (D_2 and D_{2d}) intervened in the comparison between the experiments and theories, and made it difficult to derive a definite conclusion. Similar problems concerning the structure will occur for other higher fullerenes. However, spectroscopic data of C_{76} are expected to be compared directly with theoretical predictions without any assumption on the structure since the geometric structure of C_{76} is known. Furthermore, theoretically calculated energy values, e.g., band gap and work function, can be calibrated by comparing with the corresponding experimental data. Therefore, C_{76} is a key fullerene to develop further studies on the other higher fullerenes.

The shape of D_2-C_{76} is fairly flat and deviates from a sphere; the length of three principal axes is calculated to be 0.875, 0.750, and 0.654 nm.[23] It is interesting to investigate the crystal structure of C_{76} whose eccentricity of the molecular shape from a sphere is larger than that for C_{70}. It is known that C_{70} in a crystalline state forms a close-packed lattice at high temperature (at 440 K), indicating free rotation of molecules at this temperature. When C_{70} was deposited on mica substrate at elevated temperature (above 370 K), a single-crystalline epitaxial film with fcc structure was formed.[6]

In the present study, we produced submicrometer-thick films of C_{76} on mica and NaCl, and the structure and texture of the films were investigated by transmission electron microscopy (TEM).

II. EXPERIMENT

The fullerene-rich carbon soot containing C_{76} was produced by arc burning of a graphite electrode. The resulting soot was extracted with carbon disulfide. The separation and isolation of C_{76} were performed by high-pressure liquid chromatography (HPLC) with CS_2 eluent. Detailed procedures are described elsewhere.[24] Purity of the C_{76} sample was more than 99%, as checked by HPLC. The separated C_{76} was washed with toluene to remove CS_2, and then dried to obtain powder.

Mica and NaCl substrates were cleaved in air and were mounted on an aluminum plate, and pure C_{76} powder (3 mg) was loaded on a molybdenum boat (evaporation source). The substrates and the source were placed in a vacuum chamber of 2×10^{-6} Torr evacuated with an oil diffusion pump backed by a rotary pump. The evaporation source was heated to 1000 K. The temperature of the substrates was measured by a thermocouple and held at 430 K. The thickness of the grown films was monitored by a quartz oscillator placed close to the substrates. The deposition rate was 9.7×10^{-7} g/cm^2 min, which corresponds to 5.9 nm/min under an assumed density of 1.64 g/cm^3. The pressure in the vacuum chamber was 6×10^{-6} Torr during the evaporation. The thickness of the films prepared was 45 nm.

The films grown on mica and NaCl were separated in water and mounted on a specimen-supporting mesh covered with perforated carbon film, a so-called microgrid, for TEM. The specimens thus prepared were examined mostly at room temperature with electron microscopes, Hitachi H-800 operated at 200 kV and Philips EM400 operated at 120 kV. A cooling stage was also used for investigating phase transition at low temperatures.

For an accurate measurement of the lattice constant, electron diffraction patterns from C_{76} and gold (standard sample for the calibration of camera length) were taken simultaneously by using C_{76} films on which gold was deposited.

Energy dispersive x-ray analysis of the prepared films showed no signal due to sulfur, indicating that the amount of CS_2 in the films is not more than one molecule per three C_{76} if CS_2 is present.

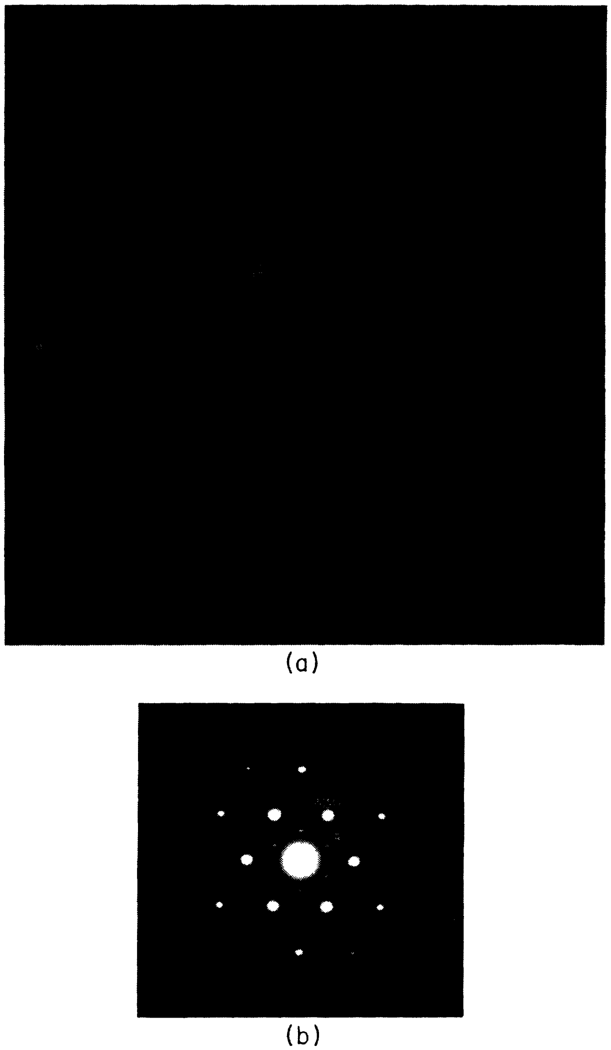

FIG. 2. (a) High-resolution TEM image of a C_{76} film grown on mica. The image was taken along the normal of the (111) film. (220) lattice fringes with a spacing 0.54 nm are observed along the three equivalent directions. Contrast of C_{76} columns changes from domain to domain (see text). (b) The corresponding diffraction pattern, showing the [111] zone-axis pattern of the fcc structure. One of the irrational reflections $(\frac{4}{3}, \frac{2}{3}, \frac{2}{3})$ is marked by E.

III. RESULTS AND DISCUSSION

Figures 2(a) and 2(b) show a typical TEM image of a C_{76} film grown on mica and the corresponding diffraction pattern. The diffraction pattern indicates the film is a single crystal. The strong first-order reflections are (220) type which is expected for molecules arranged in a fcc lattice with a [111] orientation normal to the film. Diffraction patterns taken from various directions by tilting the film could be interpreted with the fcc structure ($a = 1.53 \pm 0.02$ nm).

Analogous epitaxial growth of fullerene films on mica has been reported for C_{60}, C_{70}, and C_{84}.[6,16] In previous studies of fullerene films, epitaxial growth on mica with the following orientational relationship was observed for all the fullerenes studied:[6,16] $(111)_F \parallel (001)_{\rm mica}$, $[\bar{1}10]_F \parallel [100]_{\rm mica}$, where subscript F stands for fullerenes, C_{60}, C_{70}, and C_{84}. Though in the present study we have not investigated the orientational relationship between the C_{76} film and the mica substrate, the above relationship observed for the other fullerenes is strongly supposed to hold for the present C_{76} and mica substrate.

The cleaved plane of mica is characterized by hexagonal arrays of SiO_4 tetrahedra. The in-plane periodicity of these hexagonal arrays is 0.52 nm. The nearest-neighbor distance of C_{76} molecules in the closed-packed plane is 1.08 nm, which should be compared with twice the periodicity of the mica surface. The misfit between the mica and the C_{76} crystal is calculated to be only 3.9%. This small misfit indicates that the mica substrate acts as a template for the arrangement of C_{76} molecules.

The faint innermost reflections, which are indicated by letter E in Fig. 2(b), are extra ones for the fcc structure, being indexed as $(\frac{4}{3}, \frac{2}{3}, \frac{2}{3})$. The irrational reflections were observed for C_{60}, C_{70}, and C_{84} as well. These extra spots originate from the (111) reciprocal-lattice spots

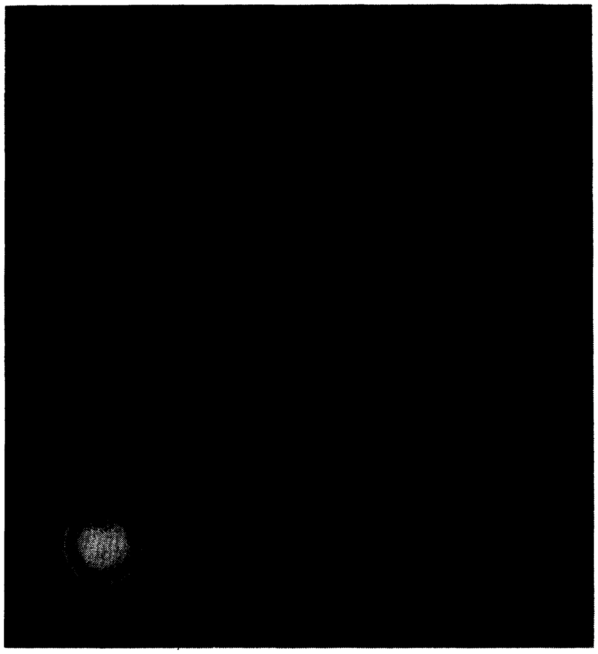

FIG. 3. TEM image of a C_{76} film grown on NaCl. The image was taken along the film normal. The corresponding diffraction pattern (in the inset) shows that the film is polycrystalline.

elongated toward the direction of the film normal. The elongation is considered to be due to the existence of many stacking faults or twin planes parallel to the film plane and/or extra layers on the film surfaces.[3]

Though the diffraction pattern shows the film is single crystalline, the TEM picture in Fig. 2(a) does not show a uniform image of the lattice over an entire area of view, but reveals that the appearance of the lattice image differs from region to region whose sizes are typically 10–20 nm; e.g., in some regions bright dots arranged in a hexagonal net are well recognized [see a domain indicated by arrow A in Fig. 2(a)], and in other regions dark rings are arranged in the hexagonal net (arrow B). Furthermore, in a certain region the hexagonal array of spots is not observed but only one set of (220) lattice fringes is strongly observed (arrow C). These variations in contrast are caused by local changes in thickness and orientation of the film. Slight undulations of the (220) fringes due to the misorientation between domains are also observed [which is well recognized when Fig. 2(a) is viewed obliquely along the direction of the lattice fringes].

Figure 3 shows a TEM image of a C_{76} film grown on NaCl at 430 K and the corresponding diffraction pattern (in the inset). The diffraction pattern reveals that the film is polycrystalline with the fcc structure ($a = 1.53 \pm 0.02$ nm). The image shows the size of domains ranges from 10 to 20 nm. The polycrystalline nature of fullerene films grown on NaCl is commonly observed for C_{60} and C_{70}.[6]

Electron diffraction experiments at low temperatures showed no structural transformation down to 110 K; the fcc structure was retained and no super-reflections were observed in the present range of temperature (from 110 to 350 K). Adiabatic calorimetry of C_{76} power carried out by Tanaka *et al.*[25] showed no definite phase transition between room temperature and 10 K, consistent with the present experiment. The transformation temperatures at which the free rotation of fullerenes is hindered are 260 K for C_{60} and 337 K for C_{70}. The corresponding transformation temperature for C_{76} is expected to be higher than that for C_{70}. Therefore, it is inferred that the free rotation of C_{76} is already hindered at room temperature, and so no phase change was observed at the lower temperatures within the sensitivity of the electron diffraction technique in the present experiment.

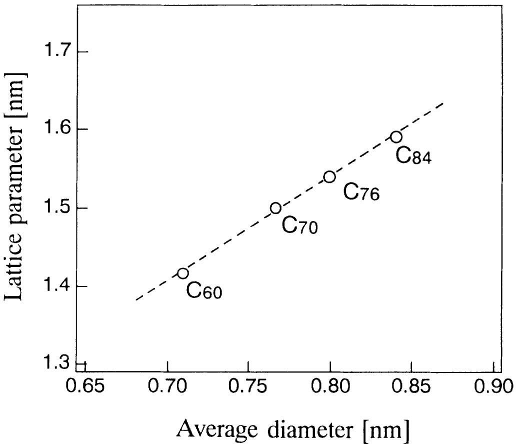

FIG. 4. Lattice parameters of fcc C_{60}, C_{70}, C_{76}, and C_{84} plotted against the average diameters of the fullerenes.

Finally, it should be noted that the lattice parameters of fcc C_{60}, C_{70}, C_{76}, and C_{84} plotted against the diameter of the fullerenes lie on a straight line as shown in Fig. 4. The diameter of the fullerenes C_n used here is defined as follows: $d(C_n) = 0.71 \times (n/60)^{1/2}$ (nm), which is based on a diameter 0.71 nm for C_{60}. $d(C_{70}) = 0.767$ nm, $d(C_{76}) = 0.799$ nm, and $d(C_{84}) = 0.840$ nm are obtained. These diameters were first introduced to discuss the relation between the lattice parameters and the fullerene sizes in our previous report for C_{84}.[16] The diameter thus obtained is a kind of average diameter, being averaged over all the orientations of a fullerene whose shape deviates from a sphere. The linear relation between the lattice parameters and the average diameters seems to indicate that the orientation of fullerenes is disordered dynamically or statically, though the physical meaning of this linear relationship is not clear. The finding that even C_{76} whose eccentricity is large obeys the linear relation between the lattice parameters and the average diameters shows that the idea of the average diameter can be used conveniently to describe a linear dimension of fullerenes.

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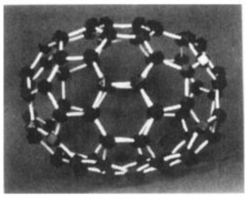

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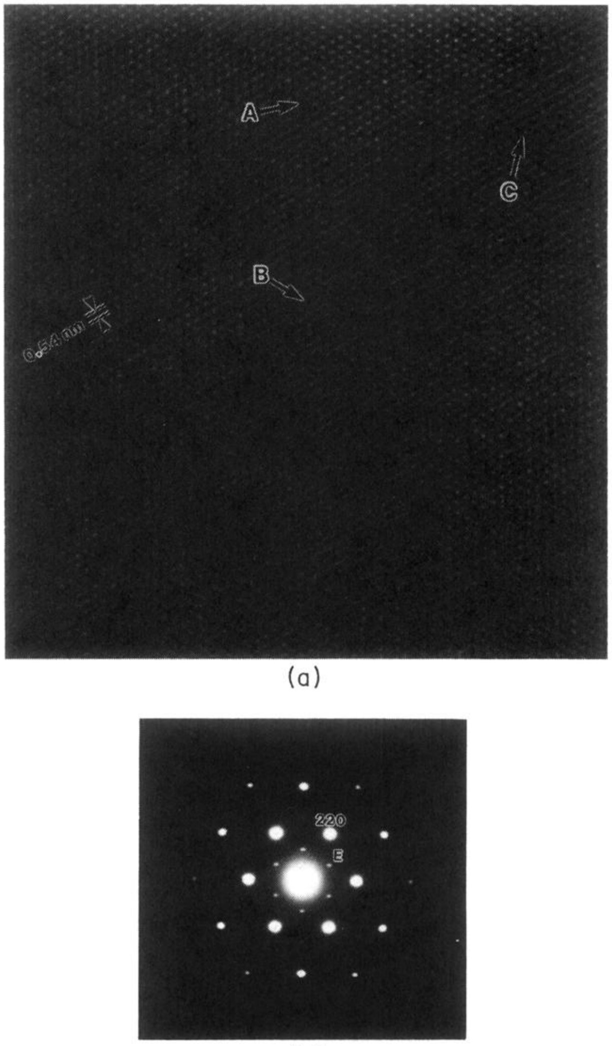

(a)

(b)

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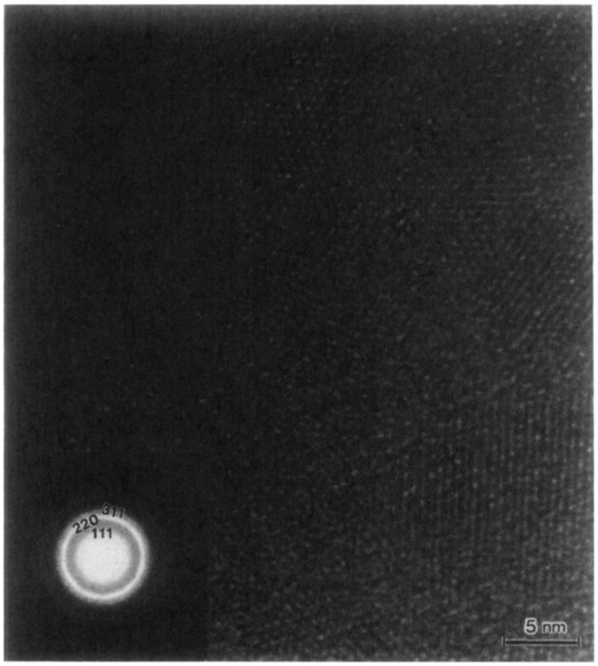

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