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C_{84} thin films grown epitaxially on mica

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Single-crystalline C_{84} thin films grown epitaxially on a cleaved surface of mica have been investigated by electron microscopy. The C_{84} molecules formed a face-centered-cubic lattice (lattice parameter $a = 1.59 \pm 0.02$ nm), with the orientation relationship, $(111)[\bar{1}10]_{C_{84}} \| (001)[100]_{\mathrm{mica}}$. Among the fcc C_{60}, C_{70}, and C_{84} crystals, a nearly linear relation between the lattice parameters and the fullerene diameters is found.

I. INTRODUCTION

Crystallographic studies on fullerene thin films prepared by vacuum deposition have been widely carried out,[1–12] but mainly restricted to C_{60} and C_{70} because these are the two fullerenes which are fairly easy to produce in macroscopic quantities.[13] It has been reported that the fcc structure was dominant for both C_{60} (Refs. 4–7) and C_{70} thin films.[10,12] Epitaxial growth of single-crystalline films has been observed for C_{60}/mica,[5,9,12] C_{60}/MoS_2,[8] and C_{70}/mica.[12]

While C_{60} and C_{70} produced by the Krätschmer-Huffmann method[13] have only one isomer each, C_{84} has at least two isomers as has been revealed by ^{13}C NMR.[14] One of the two C_{84} isomers is the D_{2d} C_{84}, whose structure is uniquely defined (model No. 23 in Fig. 4 of Ref. 15). Another is one of the four possible structures with the D_2 symmetry presented in Ref. 15. The determination of the structure out of the four candidates for D_2 is controversial. Recently, initial stage and multilayered adsorption of C_{84} on Si(100) (Ref. 16) and on GaAs(110) surfaces[17] were studied by scanning tunneling microscopy. Hashizume *et al.*[16] observed fcc stacking of C_{84} layers when the substrate temperature was kept at 370–420 K. As a result of their preliminary statistical analysis of individual C_{84} molecules, they suggested that the structure of No. 22 (in Ref. 15), which is energetically favorable,[18] is the most probable among the four D_2 C_{84} candidates. The $D_2(22)$, i.e., D_2 isomer of model No. 22, has other names: D_2(Iowa) (Ref. 18) and D_2(Energy).[19] The structures of the two isomers, D_{2d} and $D_2(22)$ C_{84}, are shown in Fig. 1. It should be noted that the shapes are both rather spherical.

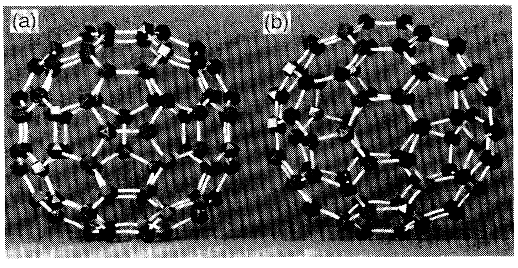

FIG. 1. Ball-and-stick model of two isomers of C_{84}: (a) D_{2d} and (b) $D_2(22)$.

We have hitherto studied the crystal structures and morphology of C_{60} and C_{70} thin films grown on cleaved surfaces of mica and NaCl.[7,12] We extended our studies to C_{84}, and produced submicrometer-thick films of C_{84} on mica. We present here the results of our electron microscope examination of C_{84} films on mica.

II. EXPERIMENT

The method for the production of fullerene-rich carbon soot and purification of C_{84} is described elsewhere.[20,21] Briefly, the crude carbon soot was produced by arc burning of graphite electrodes. The resulting soot was extracted with carbon disulfide. The separation and isolation of C_{84} were performed by high-pressure liquid chromatography (HPLC) with toluene eluent. Purity of the C_{84} sample was 98% and the main impurities were C_{70}, C_{76}, C_{78}, and C_{82}, as checked by laser-desorption mass spectrometry as well as HPLC.

Mica substrates cleaved in air were mounted on an aluminum plate, and pure C_{84} powder was loaded on a molybdenum boat (evaporation source). These were placed in a vacuum chamber evacuated to 2×10^{-6} Torr with an oil diffusion and a mechanical rotary pump. Before sublimation of C_{84}, the boat was heated to about 570 K for a few hours in order to evaporate the solvent occluded in the C_{84} powder. The boat was then heated further to about 970 K, and a shutter between the evaporation source and the substrates was opened. The temperature of the substrates was measured by a thermocouple and was held at 470 and 520 K. The thickness of grown films was monitored by a quartz oscillator placed close to the substrates. The typical deposition rate was 1.65×10^{-6} g/cm^2 min, which corresponds to 10 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.

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The films grown on the mica were separated in water, and mounted on a specimen-supporting mesh covered with a "microgrid" (perforated carbon film). The specimens thus prepared were examined mostly at room temperature with transmission electron microscopes (Philips EM400 and Hitachi H-800). A cooling stage was also used for investigating a low-temperature phase.

Some samples deposited on thin mica films were directly investigated without separation from the substrate. Mica substrates which were thin enough to transmit an electron beam were prepared by repeated cleaving of a mica flake with adhesive tape.

The camera length for electron diffraction was calibrated by Debye-Scherrer rings from gold particles deposited on a C_{84} film.

III. RESULTS AND DISCUSSION

Figure 2(a) shows a transmission electron diffraction pattern of a C_{84} thin film grown on (001) mica held at 520 K. The diffraction pattern indicates the film is a single crystal. The strong first-order reflections are the (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 ($a = 1.59 \pm 0.02$ nm).

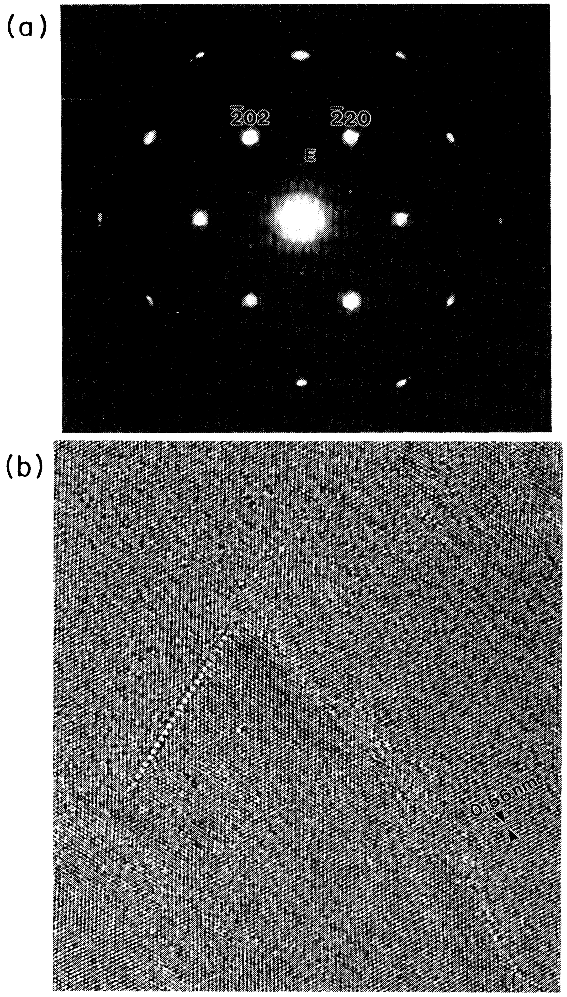


FIG. 2. (a) Transmission electron diffraction pattern of a C_{84} thin film grown on mica, corresponding to the [111] zone-axis pattern of the fcc structure. The incident electron beam is normal to the film. One of the irrational reflections $(\frac{4}{3},\frac{2}{3},\frac{2}{3})$ is marked by *E*. (b) High-resolution electron micrograph of the C_{84} film.

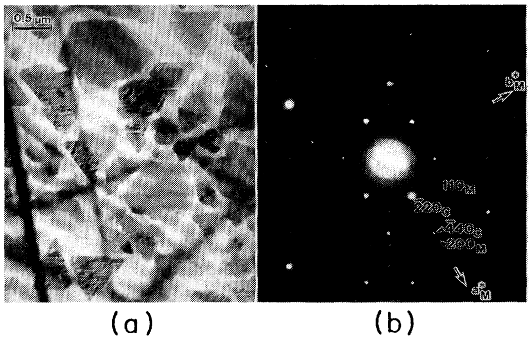
The analogous epitaxial growth of fullerenes on mica has been reported for C_{60} (Refs. 5, 9, and 12) and C_{70}.[12] These results are very similar to earlier investigations where fcc metal films were epitaxially grown on mica held at moderate temperatures.[22] The faint innermost reflections are indexed as $(\frac{4}{3},\frac{2}{3},\frac{2}{3})$ and their higher-order reflections are observed. These irrational reflections were observed for C_{60} and C_{70} as well. The extra spots originate from the (111) reciprocal-lattice points 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.[5,12]

Electron micrographs of the C_{84} films reveal that the film is not perfect, exhibiting defects such as domain boundaries and planar defects as is shown in Fig. 2(b). The size of the domains is 20–30 nm on average.

In order to see an orientation relationship between the C_{84} film and the mica substrate, we took electron diffraction patterns of the deposit together with the mica. Figure 3 shows an electron micrograph and the corresponding diffraction pattern of C_{84} and thin mica. The double positioning of triangular islands is observed, which was commonly found in the earlier investigation of metal films on mica. From the diffraction pattern, the following orientation relationship is derived:

$$(111)_{C_{84}} \| (001)_{\text{mica}} , \quad [\bar{1}10]_{C_{84}} \| [100]_{\text{mica}} .$$

This orientation relationship is the same as that for C_{60}/mica (Refs. 5 and 12) and C_{70}/mica.[12] The cleaved plane of mica is characterized by hexagonal arrays of SiO_4 tetrahedra. The in-plane periodicity of these hexag-



(a) (b)

FIG. 3. (a) Electron micrograph and (b) the corresponding diffraction pattern taken from C_{84} islands together with a thin mica substrate. Black lines in the background are equal inclination contours of the mica film. In the diffraction pattern, indices with subscript *C* and *M* are for C_{84} and mica, respectively. Reflections from the mica substrate are indexed with the monoclinic system.

onal arrays is 0.52 nm. The nearest-neighbor distance of C_{84} molecules in the close-packed plane is 1.12 nm, which should be compared with twice the periodicity of the mica surface. The mismatch between the mica and the C_{84} crystal is calculated to be 7.7%. This value is rather large compared with 3.0% for C_{60}/mica and 2.7% for C_{70}.[12]

The C_{84} molecules are known to be present in at least two different structural isomers (D_2 and D_{2d}). The abundance ratio of D_2 to D_{2d} present in a purified C_{84} sample is reported to be approximately 2:1.[14] The structure of the most abundant isomer (D_2) is still an open question, while the other one (D_{2d}) is uniquely determined. The fcc lattice is characteristic of solids of spherical atoms or molecules. The D_{2d} C_{84} is nearly spherical in shape; the ratio of lengths of the longest principal axis to the shortest one (L/S) is theoretically predicted to be only 1.01.[19] On the other hand, among the four D_2 isomers, $D_2(22)$ is the most spherical (L/S ratio is 1.08).[19] The eccentricities of D_{2d} and $D_2(22)$ C_{84} molecules may be small enough that they could plausibly be rotating isotropically like C_{60} in the solid.[23] This might indicate that the D_2-symmetry isomer has the most nearly spherical $D_2(22)$ configuration.

The D_2 C_{84} has three different diameters along three principal axes, and the D_{2d} C_{84} has two different diameters. For an approximately spherical fullerene, its diameter is proportional to the square root of the surface area of the fullerene (or the number of carbon atoms constituting the fullerene). Therefore, we define here $d(C_N)=0.71\times(N/60)^{1/2}$ (nm) as the diameter of a fullerene C_N, which is based on a diameter 0.71 nm for C_{60}. We obtain $d=0.840$ nm for C_{84} irrespective of the presence of isomers. For C_{70}, the corresponding diameter $d(C_{70})$ becomes 0.767 nm. Using these diameters, the lattice parameters of C_{60}, C_{70}, and C_{84} crystals with the fcc lattice are plotted against the diameters in Fig. 4. The lattice parameters of C_{60} ($a=1.417$ nm) (Ref. 23) and C_{70} ($a=1.501$ nm) (Ref. 10) are those for orientationally disordered phases. A nearly linear relation between the diameters and the lattice parameters is exhibited. The simple relation, which was revealed by using the average diameter, supports the suggestion mentioned above; the orientation of C_{84} is disordered dynamically.

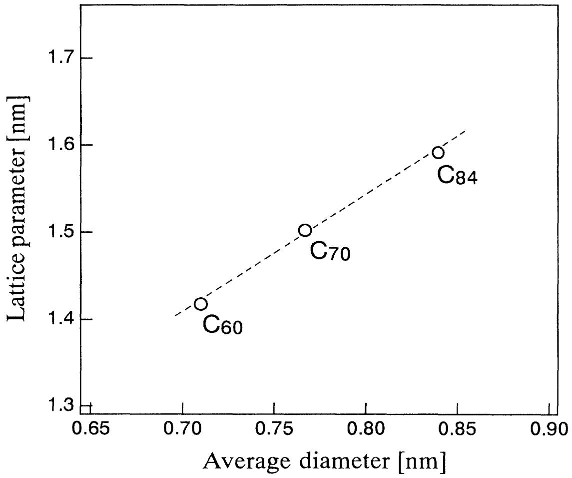


FIG. 4. Lattice parameters of fcc C_{60}, C_{70}, and C_{84} plotted as a function of the average diameters of the fullerenes.

Our preliminary electron diffraction experiments at low temperatures showed no structural transformation down to 160 K; the fcc structure was retained and no super-reflections were observed even at this low temperature. Taking into account the transformation temperatures for C_{60} (250 K) (Ref. 23) and for C_{70} (337 K),[10] the free rotation of C_{84} is expected to be hindered at 160 K. In the case of C_{84}, there exist at least two isomers which randomly occupy four sites in a unit cell of the fcc lattice. Therefore, the orientational potential energy for each molecule differs from site to site. This prohibits molecules from ordering in orientation; the molecular rotation may be frozen at random orientation. Alternatively, we can assume that some short-range orientational order could occur that would not show up in the present electron diffraction, perhaps because the spots that result would be too broad to observe above the background. Further studies, including thermodynamic properties such as heat capacity, are necessary to make clear structural transformation related to orientational ordering in C_{84} crystals.

ACKNOWLEDGMENTS

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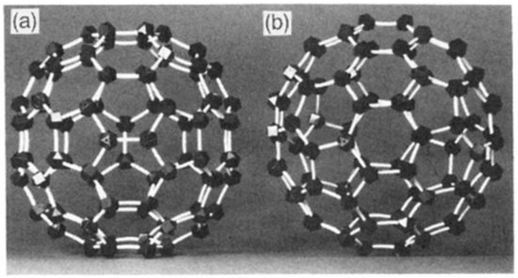

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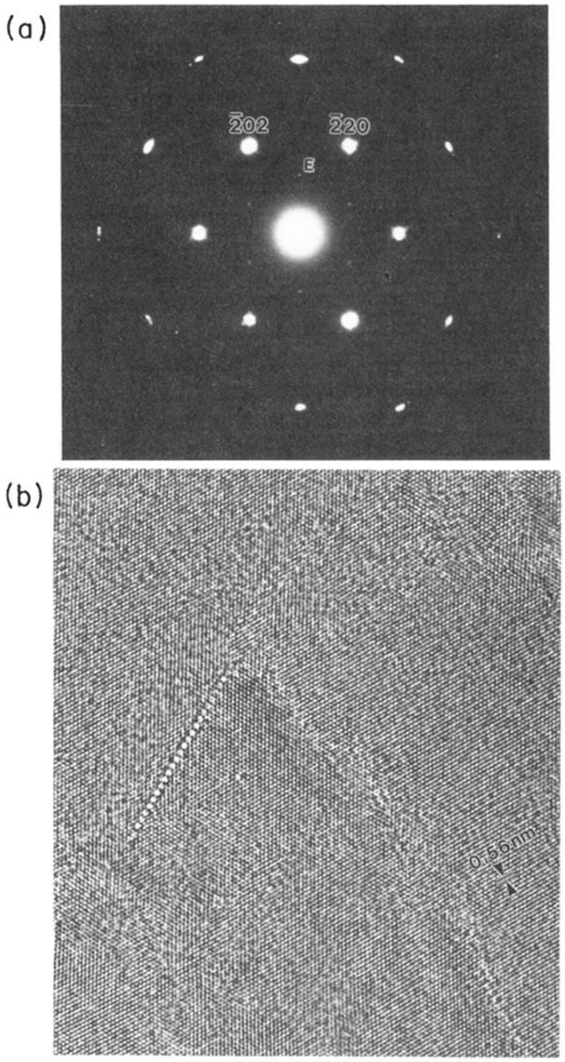

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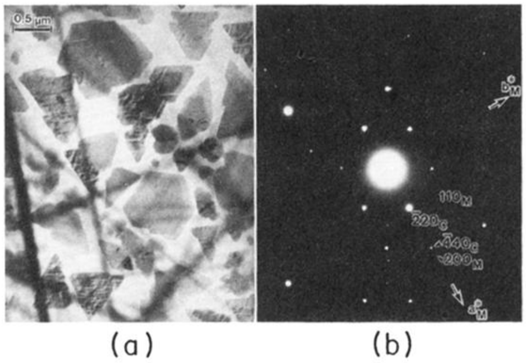

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