Buckling of C_{60} whiskers

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The authors demonstrated the mechanics of materials for crystalline whiskers composed of C_{60} molecules; compressive deformation of the whiskers was observed by *in situ* transmission electron microscopy with simultaneous force measurement by means of an optical cantilever method, as used in atomic force microscopy. In response to compression along the long axis, the whiskers bent first elastically, then buckled. A whisker with 160 nm diameter fractured brittlely at a strain of 0.08. According to Euler's formula, Young's modulus of the whisker was estimated to be 32–54 GPa, which is 160%–650% of that of C_{60} bulk crystals. © *2006 American Institute of Physics*.
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Since bulk crystals composed of fullerene C_{60} molecules were first synthesized,[1] their crystal structures[2–4] and mechanical properties[5–12] have been investigated. At room temperature, C_{60} molecules bond by van der Waals forces and crystallize in a face-centered-cubic structure with a lattice constant of 1.417 nm.[2,3] Young's modulus of C_{60} bulk crystals has been measured to be 8.3–20 GPa.[8–12] Recently, Miyazawa *et al.* synthesized single crystalline whiskers consisting of C_{60} molecules with a high aspect ratio of length to diameter, typically a submicrometer diameter and a length of more than 100 μm.[13–16] They showed that the flexibility of the C_{60} whiskers is sufficient for applications in nanometer-scale functional and structural devices;[15,16] the deformation behavior and mechanical properties of individual whiskers must be investigated. In this letter, we demonstrate the compressive deformation of the whiskers with simultaneous force measurement to analyze their mechanical properties.

We synthesized C_{60} whiskers by a liquid-liquid interfacial precipitation method using a saturated solution of C_{60} molecules in pyridine and isopropyl alcohol.[13–16] After precipitation, we dropped the whiskers with the solution on a microgrid as used for transmission electron microscopy. The microgrid was mounted on a specimen holder for a transmission electron microscope equipped with an optical lever force measurement system, as used in atomic force microscopes.[17] A microcantilever with a nanometer-sized silicon tip, as used for atomic force microscopes, was coated with a gold film of 5–10 nm in thickness and was then fixed on another specimen holder, while a tube-type piezoelectric element was attached to the specimen holder for manipulation of the cantilever tip. Both specimen holders were inserted into the microscope, and the whiskers were deformed using the cantilever tip as illustrated in Fig. 1. The deformation process was observed *in situ* using a TV rate system. The time resolution of the image observations was 17 ms. Variations in force applied to the whiskers were simultaneously measured by the optical lever method during the deformation.

Figure 2 shows time-sequential of the compressive deformation process of a C_{60} whisker. The compression and retraction process of the cantilever was repeated two times. The dark triangular region at the top of Fig. 2 is the tip of the cantilever, and the dark region at the bottom is the microgrid. The bright regions is a vacuum. First, the whisker was fixed on the microgrid; then, the edge of the whisker was fixed with the cantilever tip. Its diameter was 130 nm. We estimated the effective length for deformation of the whisker from the fixed point to the tip of the cantilever-tip side, i.e., L in Fig. 1, based on the bending shape. The length from the tip of the cantilever tip to the plane of symmetry of bending was half of that to the fixed point, i.e., $L/2$ in Fig. 1. The

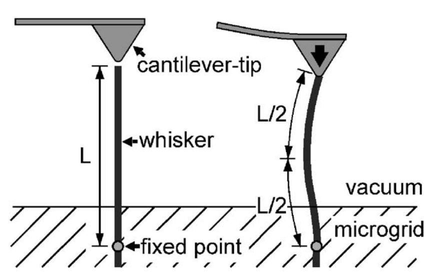

FIG. 1. Illustration of compressive deformation of C_{60} whiskers by transmission electron microscopy equipped with functions of scanning probe microcopy.

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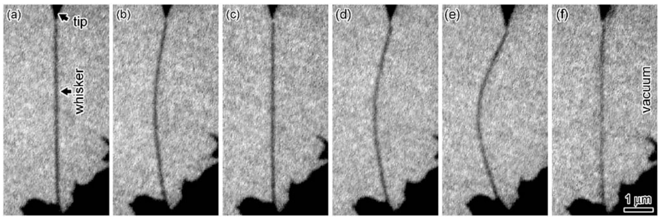

FIG. 2. Time-sequential electron microscopy images of compressive deformation process of a C_{60} whisker. The tip of the cantilever and the edge surface of the microgrid are observed at the top and bottom of the image, respectively. The bright regions is a vacuum.

effective length was estimated to be 7.0 ± 0.2 μm. It was found from the electron diffraction pattern that the whisker is a single crystal with a body-centered tetragonal structure. The lattice parameters are $a=0.97\pm0.05$ nm and $c=1.54\pm0.05$ nm. The long axis of the whisker is parallel to the [100] orientation. The intermolecular distance of the whiskers along the [100] orientation corresponds to the lattice parameter a and is similar to the previous values reported by Miyazawa *et al.*[14–16] The intermolecular distance of the nearest neighbors in the bulk crystals with a face-centered-cubic structure is reported to be 1.002 nm.[2,3] Thus, the intermolecular distance of the present whisker is ~3% smaller than that of the C_{60} bulk crystals. The decrease in the intermolecular distance suggests that polymerization occurs in the whiskers.[14–16] Figure 3 shows the relationship between the cantilever-tip displacement and force during the deformation seen in Fig. 2. The left and right graphs show the relationships at the first and second deformation cycles, respectively. The points indicated by arrowheads a–f in Fig. 3 correspond to those at which Figs. 2(a)–2(f) were observed. First, the cantilever tip was attached to the tip of the whisker [Fig. 2(a)]; then, the whisker was compressed along the long axis. The force rose abruptly from 0 to 29 nN from a in Fig. 3 and then increased gradually up to 36 nN at b in Fig. 3. At a force of 36 nN, the whisker bent to a curvature radius of 12.7 μm [Fig. 2(b)], corresponding to a strain of 0.005. Subsequently, the cantilever tip was retracted toward the top of the image in Fig. 2(c) and the force decreased to 0 nN (c in Fig. 3). The whisker recovered its initial straight shape. During the retraction, the force decreased to a negative value, −5 nN, showing that adhesion occurs between the edge of the whisker and the cantilever tip. We compressed the whisker along the long axis again [Figs. 2(c)–2(e)]. The whisker bent to a curvature radius of 4.4 μm, corresponding to a strain of 0.015 [Fig. 2(e)]. The force showed a maximum of 38 nN and then decreased down to 34 nN. The cantilever tip was retracted and the force decreased to 0 nN [Fig. 3(f)]. The whisker recovered its initial straight shape, as shown in Fig. 2(f). This observation indicates that the bending is elastic. In the second deformation cycles, the compression distance and the amplitude of hysteresis were larger than those in the first.

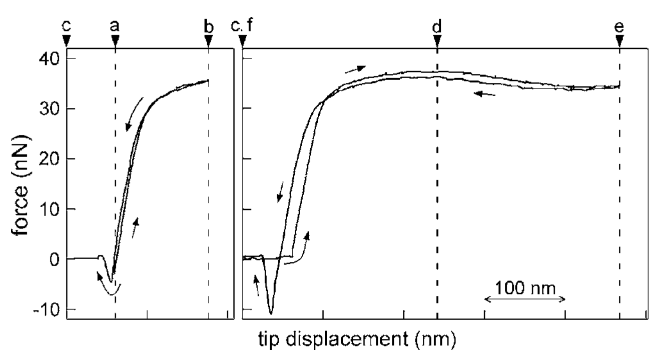

FIG. 3. Variation in force during the deformation in Fig. 2 as a function of cantilever-tip displacement.

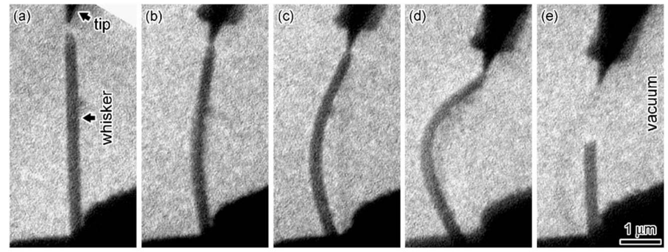

FIG. 4. Time-sequential electron microscopy images of the fracture process of a C_{60} whisker.

Figure 4 shows time-sequential electron microscopy images of the fracture process of a C_{60} whisker. Figure 5 shows variations in force as a function of the strain of the whisker during the deformation in Fig. 4. The diameter of the whisker was 160 nm. The effective length of the whisker from the fixed point to the tip of the cantilever-tip side was estimated based on the bending shape in the same way described as in Fig. 2. The effective length was 3.3 ± 0.3 μm. We compressed the whisker along the long axis as shown in Fig. 4. The force increased from 0 [Fig. 5(a)] to 230 nN [Fig. 5(b)], and buckling occurred in the whisker [Figs. 4(b) and 5(b)]. Due to successive compression, the bending continued as shown Figs. 4(c) and 4(d), and the force decreased down to 160 nN. Finally, as shown in Figs. 4(e) and 5, the whisker fractured brittlely in the middle of its effective length, at a strain of 0.08.

According to Euler's formula, the buckling force P of a material with a columnar shape is given by

$$P = k\frac{\pi^2 EI}{L^2},$$

where k is a fixity coefficient, E is Young's modulus, I is the geometrical moment of inertia, and L is the length of the column.[18] Here, we estimate Young's modulus of the whiskers in Figs. 2 and 4 using Euler's formula. The maximum values of the force, 38 and 230 nN, are used as P. The tip of the whisker on the cantilever-tip side is free and the other is fixed onto the microgrid as seen in Figs. 2 and 4. The fixity

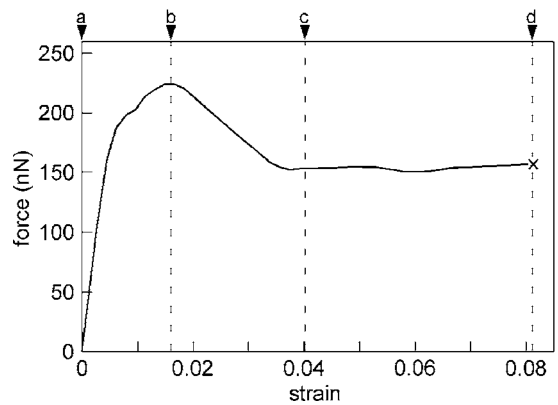

FIG. 5. Variation in force during the deformation of the C_{60} whisker in Fig. 4 as a function of strain.

coefficient k for the fixed-free end condition is 0.25.[18] We selected this value as k of the present deformation. Since the whisker is columnar, I is given by

$$I = \frac{\pi d^4}{64},$$

where d is the diameter of the whisker. As a result, Young's modulus is estimated to be 54 ± 3 GPa for the whisker in Fig. 2 and 32 ± 6 GPa for the whisker in Fig. 4; these values correspond to 160%–650% of those for C_{60} bulk crystals.[8–12] The bulk modulus and hardness of C_{60} bulk crystals increase due to molecular polymerization induced by high-pressure treatment or photoillumination.[19–22] These treatments were not conducted during the synthesis of the present C_{60} whiskers. As described, however, the decrease in the intermolecular distance was observed, suggesting the polymerization of the C_{60} molecules. According to Euler's formula, Young's modulus depends on the whisker shape and is proportional to L^2/d^4. It is also known that the structure of C_{60} bulk crystals is damaged by electron beam irradiation, which reduces their strength.[23] In the present study, however, the initial structure of the C_{60} whiskers was maintained during the observation. It was then deduced that the increase in Young's modulus of the whiskers results from the combined effect of the polymerization and the shape modulation.

In summary, we performed compressive deformation of individual C_{60} whiskers and measured the force acting on them. The present C_{60} whiskers with a higher Young's modulus than that of C_{60} crystals can be utilized for various flexible components of nanometer-sized composites.

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