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<th>著者別名</th>
<th>木塚 徳志</th>
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<td>書誌情報</td>
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<td>本誌名</td>
<td>Applied physics letters</td>
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<td>巻</td>
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<td>071912</td>
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<td>年</td>
<td>2006-08</td>
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<td>URL</td>
<td><a href="http://hdl.handle.net/2241/103935">http://hdl.handle.net/2241/103935</a></td>
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<td>doi</td>
<td>10.1063/1.2336590</td>
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Buckling of C$_{60}$ whiskers

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(Received 25 April 2006; accepted 26 June 2006; published online 17 August 2006)

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.

DOI: 10.1063/1.2336590

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 $\mu$m.$^{13-16}$ 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.

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The intermolecular distance of the nearest neighbors in the bulk crystals with a face-centered-cubic structure is reported to be 1.002 nm. 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. 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, as shown in Figs. 2(e) and 5. 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.

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

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

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. 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
coefficient \( k \) for the fixed-free end condition is 0.25. 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. The bulk modulus and hardness of C\(_{60}\) bulk crystals increase due to molecular polymerization induced by high-pressure treatment or photoillumination. 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. 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.

This study was partly supported by funds for the Special Research Project on Nanoscience and the University Research Projects of the University of Tsukuba and by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan.