Extended Abstracts of the 2007 International Conference on Solid State Devices and Materials, Tsukuba, 2007, pp. 704-705

P-13-8

In Situ Transmission Electron Microscopy of Deformation of Crystalline C_{60} Nanotubes

Kazuma Saito[1], Ryoei Kato[1], Kun'ichi Miyazawa[2], Tokushi Kizuka[1]

[1] Institute of Material Science, University of Tsukuba, Tsukuba 305-8753, Japan
[2] National Institute for Materials Science, Namiki, Tsukuba 305-0044, Japan
E-mail: kizuka@ims.tsukuba.ac.jp

1. Introduction

Since bulk crystals composed of fullerene C_{60} molecules were first synthesized in 1990 [1], their crystal structure and mechanical properties have been investigated [2-12]. At room temperature, C_{60} molecules crystallize in a face-centered-cubic structure by van der Waals forces with a lattice constant of 1.417 nm [2, 3]. The Young's modulus of bulk C_{60} crystals has been measured to be 8.3 - 20 GPa [8-12]. In 2001, Miyazawa *et al.* synthesized crystalline C_{60} nanowhiskers with high aspect ratios of length to diameter [13-16]. Furthermore, they found that tubular C_{60} nanowhiskers, i.e., crystalline C_{60} nanotubes are fabricated by the same method as that for filling crystalline C_{60} nanowhiskers [17]. Asaka *et al.* reported that the Young's modulus of C_{60} nanowhiskers is higher than that of crystalline C_{60} plates [18]. These nanowhiskers and nanotubes are expected to be applied to nanometer-scale functional and structural devices. In this paper, to estimate the Young's modulus of individual C_{60} nanotubes, we performed the bending tests by *in situ* transmission electron microscopy (TEM).

2. Experiment

We synthesized C_{60} nanotubes by a liquid-liquid interfacial precipitation method using a saturated solution of C_{60} molecules in pyridine and isopropyl alcohol [13-16]. The solution including precipitated nanotubes was dropped on a microgrid as used for TEM. The microgrid was mounted on a specimen holder on a transmission electron microscope equipped with a piezo manipulation system. A nanometer-sized tip of a silicon microcantilever was fixed onto another specimen holder. Then, we deformed individual C_{60} nanotubes using the cantilever tip inside the microscope. The deformation process was observed *in situ* using a television system.

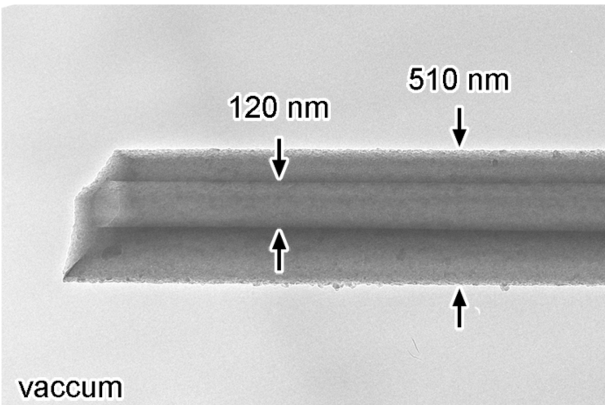

Fig. 1 TEM image of C_{60} nanotube. The outer diameter is 510 nm and the inner diameter is 120 nm.

3. Result and Discussion

Figure 1 shows a TEM image of a C_{60} nanotube protruding from an edge of the microgrid. A inner linear cavity is observed at the center axis of the nanotube. The outer diameter of the nanotube is 510 nm and inner diameter is 120 nm. From selected-area electron diffraction,

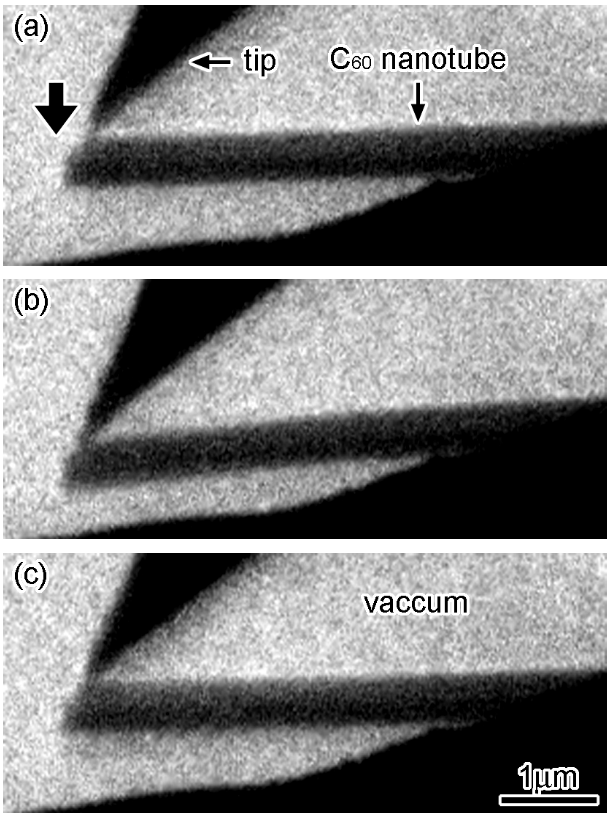

Fig. 2 (a) - (c) Time-sequential images of bending deformation of C_{60} nanotube as observed in Fig. 1. The effective length for bending is 4.8 ± 0.2 μm.

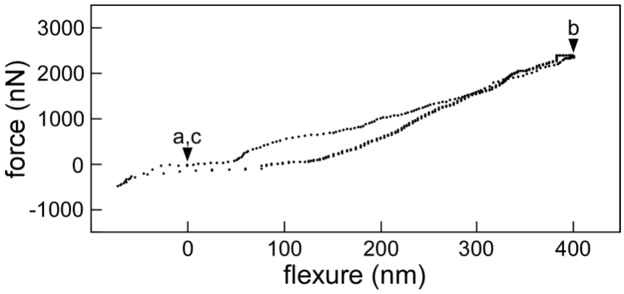

Fig. 3 Flexure - force curve of nanotube during bending observed in Fig. 2. The points indicated by arrowheads a-c correspond to the TEM images in Fig. 2 (a) – (c).

we found that the crystal structure of the nanotubes is a body-centered tetragonal structure with lattice constants of a = 0.876 nm and c = 1.66 nm. The longer growth axes of C_{60} nanotubes are aligned parallel to <100>.

Figure 2 shows time-sequential TEM images of the deformation process of the nanotube observed in Fig. 1. The length of a deformed part is 4.8 ± 0.2 μm. The dark triangular region in the top of each frame in Fig. 2 is the cantilever tip and the dark region in the bottom is the edge of the microgrid. The bright region is a vacuum. Figure 3 shows the relationship between the flexure of the nanotube and force during the bending shown in Fig. 2. The points indicated by arrowheads a - c in Fig. 3 correspond to the states at which Figs. 2(a) - 2(c) were observed. First, cantilever tip was placed to contact with the nanotube tip as shown in Fig. 2(a) and 3(a). Then, the nanotube was pressed along the direction indicated by the bigger arrow in Fig. 2(a). The nanotube was bent as shown in Fig. 2(b). At this state, the maximum flexure of the nanotube was 400 nm with a force of 2300 nN as indicated by arrow b in Fig. 3. Subsequently, the tip was retracted, and the nanotube recovered its initial straight shape as shown in Fig. 2(c) and point c in Fig. 3. Thus, this observation indicates that the bending is an elastic deformation. The curve in Fig. 3 shows a hysteresis owing to the friction on the contact boundary between the cantilever tip and the nanotube,

From the *in situ* bending test, we estimated the Young's modulus of the nanotube to be 61 - 105 GPa. This value is 110 % - 330 % larger than that of C_{60} nanowhiskers [18]. Therefore, it is deduced that the increase in the Young's modulus of the C_{60} nanotubes results from the change in shape; strengthening by formation of the internal surfaces.

4. Conclusions

We performed bending test for individual C_{60} nanotubes by *in situ* TEM. The maximum flexure of a C_{60} nanotube was 400 nm with a force of 2300 nN. The Young modulus of the C_{60} nanotube was estimated to be 61 - 105 GPa.

Acknowledgements

This work was partly supported by funds for the Special Research Project on Nanoscience and the University Research Projects of the University of Tsukuba, and Grants-in-Aid from the Ministry of Education, Culture, Sport Science and Technology, Japan (Nos. 18310075 and 19651047).

References

[1] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman: Nature (London) **347** (1990) 354.

[2] J. E. Fischer, P. A. Heiney, A. R. McGhie, W. J. Romanow, A. M. Denenstein, J. P. McCauley, Jr., and A. B. Smith III: Science **252** (1991) 1288.

[3] P. A. Heiney, J. E. Fischer, A. R. McGhie, W. J. Romanow, A. M. Denenstein, J. P. McCauley Jr., A. B. Smith III, and D. E. Cox: Phys. Rev. Lett. **66** (1991) 2911.

[4] W. I. F. David, R. M. Ibberson, J. C. Matthewman, K. Prassides, T. J. S. Dennis, J. P. Hare, H. W. Kroto, R. Taylor, and D. R. M. Walton: Nature (London) **353** (1991) 147.

[5] S. J. Duclos, K. Brister, R. C. Haddon, A. R. Kortan, and F. A. Thiel: Nature (London) **351** (1991) 380.

[6] Y. A. Ossipyan, V. S. Bobrov, Y. S. Grushko, R. A. Dilanyan, O. V. Zharilov, M. A. Lebyodkin, and V. S. Sheckhtman: Appl. Phys. A: Solids Surf. **56** (1993) 413.

[7] M. Tachibana, M. Michiyama, K. Kikuchi, Y. Achiba, and K. Kojima, Phys. Rev. B **49** (1994) 14945.

[8] X. D. Shi, A. R. Kortan, J. M. Williams, A. M. Kini, B. M. Savall, and P. M. Chaikin: Phys. Rev. Lett. **68** (1992) 827.

[9] S. Hoen, N. G. Chopra, X.-D. Xiang, R. Mostovoy, J. Hou, W. A. Vareka, and A. Zettl: Phys. Rev. B **46** (1992) 12737.

[10] H. Coufal, K. Meyer, R. K. Grygier, M. de Vries, D. Jenrich, and P. Hess: Appl. Phys. A: Solids Surf. **59** (1994) 83.

[11] D. Fioretto, G. Carlotti, G. Socino, S. Modesti, C. Cepek, L. Giovannini, O. Donzelli, and F. Nizzoli: Phys. Rev. B **52** (1995) R8707.

[12] N. P. Kobelev, R. K. Nikolaev, Ya. M. Soifer, and S. S. Khasanov, Chem. Phys. Lett. **276** (1997) 263.

[13] K. Miyazawa, A. Obayashi, and M. Kuwabara, J. Am. Ceram. Soc. **84** (2001) 3037.

[14] K. Miyazawa, Y. Kuwasaki, A. Obayashi, and M. Kuwabara: J. Mater. Res. **17** (2002) 83.

[15] K. Miyazawa, Y. Yuwasaki, K. Hamamoto, S. Nagata, A. Obatashi, and M. Kuwabara: Surf. Interface Anal. **35** (2003) 117.

[16] K. Miyazawa, K. Hamamoto, S. Nagata, and T. Suga: J. Mater. Res. **18** (2003) 1096.

[17] J. Minato, K. Miyazawa: Diamond and Related Materials **15** (2006) 1151.

[18] K. Asaka, R. Kato, K. Miyazawa and T. Kizuka: Appl. Phy. Lett. **89** (2006) 071912.