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In situ Observation of the Behavior of C_{60} (Nano)whiskers under Heating by TEM

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Fullerene whiskers are the fiber-like crystals of fullerenes (C_{60}, C_{70} and so on) that have diameters of about from 20 nm to 200 μm. They are called 'fullerene nanowhiskers' especially when their diameter is less than 1 μm. The fullerene whiskers can be fabricated by the liquid-liquid interfacial precipitation method. In order to study unknown thermal properties of the C_{60} nanowhiskers for the application to electrical devices, we observed the C_{60} nanowhiskers heated in TEM. The C_{60} nanowhiskers had a body-centered tetragonal (bct) crystal system with the lattice constants of a=1.0nm and c=2.1nm at room temperature, and became amorphous between 600 to 650°C. The lattice plane spacing of the C_{60} nanowhisker expanded about 14 % in a direction perpendicular to the growth axis during heating, but didn't change along the growth axis by heating. The bonding strength between the C_{60} molecules along the whisker growth axis was stronger than that in a direction perpendicular to it.
Key words: fullerene, C_{60}, nanowhisker, TEM, in situ observation

1. Introduction

Many forms of solution grown C_{60} crystals have been reported, and their structure and properties depend on solvent, temperature, and so on [1-5]. The C_{60} nanowhisker is one of the new forms of C_{60} crystals, whose shape is needle-like. Whiskers of C_{60} were obtained by the liquid-liquid interfacial precipitation method and were precipitated at the interface between a toluene solution of C_{60} and 2-propanol [6]. If majority of them have diameters less than 500 nm and their length is more than 100 μm, they are called the 'C_{60} nanowhisker'. However, their detailed structure and properties have not been understood precisely.

The observation of C_{60} nanowhiskers by using a transmission electron microscopy (TEM) showed that the intermolecular distance of them is shortened in the close-packed direction parallel to the growth axis, compared with that of pristine C_{60} crystals. Also, C_{60} nanowhiskers were composed of thin slabs with a thickness of about 10 nm along the growth axis. It is also reported that C_{60} whiskers with diameters greater than 500 nm were unstable under electron beam irradiation [6].

It has been reported that the C_{60} nanowhiskers are polymerized more easily by a laser beam (532 nm, 100 mW/mm^2) than pristine C_{60} according to Raman spectrum study [7]. Tachibana et al. pointed out that the shortened intermolecular distance of C_{60} nanowhiskers is the result of fast photo-polymerization. The photo-polymerized C_{60} nanowhiskers were insoluble in toluene, while the pristine C_{60} nanowhiskers were highly-soluble [7].

The resistivity of thick C_{60} whiskers was 10^8-10^{10} Ω·cm, which means that the thick C_{60} whiskers are insulators or semiconductors [8]. On the other hand, pristine C_{60} crystals become the C_{60} shells when they are annealed in vacuum at around 580°C [9]. We expected that the C_{60} nanowhiskers could change into C_{60} 'nano'shells of conductive nanowire.

2. Experimental procedure

We have prepared a toluene or m-xylene solution of C_{60} (99.9wt%) powder pulverized in a mortar with concentration of 0.3mass% C_{60} and poured to glass bottles after filtering. Then we added 2-propanol to form a liquid-liquid interface between 2-propanol (upper phase) and the toluene solution of C_{60} (lower phase), and kept it still at room temperature (approximately 20°C). The growth of C_{60} nanowhiskers was carried out under white light illumination. The prepared C_{60} (nano)whiskers were pipetted onto Cu micro grids for observation by TEM.

We observed the C_{60} nanowhiskers by TEM (JEM-2010, 200kV, JEOL) by using a heating holder (EM-31050, JEOL). The C_{60} nanowhiskers on the Cu microgrid coated by carbon membrane were heated from room temperature to about 800°C at the rate of 10 K/min. in the vacuum condition of the TEM (approximately, 10^{-7} Pa).

The C_{60} (nano)whiskers also annealed in a sealed Pyrex glass tube in the furnace under vacuum (approximately 10^{-5} Pa) and held for 2 hours at 600°C. The structure of the annealed C_{60} (nano)whiskers was characterized by TEM and microscopic Raman spectroscopy(NRS-1000, JASCO). The Raman spectra were taken under 532 nm laser with a low power density (40mW/mm^2). The C_{60} (nano)whiskers were also irradiated by 532 nm laser with a high power density of 1.9 W/mm^2.

3. Results and Discussion

The diameter of the C_{60} nanowhisker observed by TEM is about 200 nm. It was found the C_{60} nanowhiskers with this size of diameter were common. Fig. 1 shows the lattice image of the C_{60} nanowhisker at room temperature. The C_{60} nanowhisker had a body-centered tetragonal (bct) crystal system with the lattice constants of a=1.0 nm and c=2.1 nm. But the lattice constant was different from those of previous researches (Table I). In the present research, we could not observe the shortened intermolecular distance compared with pristine C_{60}. More than two kinds of crystal structure were observed in the prepared C_{60} nanowhiskers, which depended on the solution condition such as the size of the particle of C_{60} crystal or oxidation of it before dissolution. The lattice constant of the

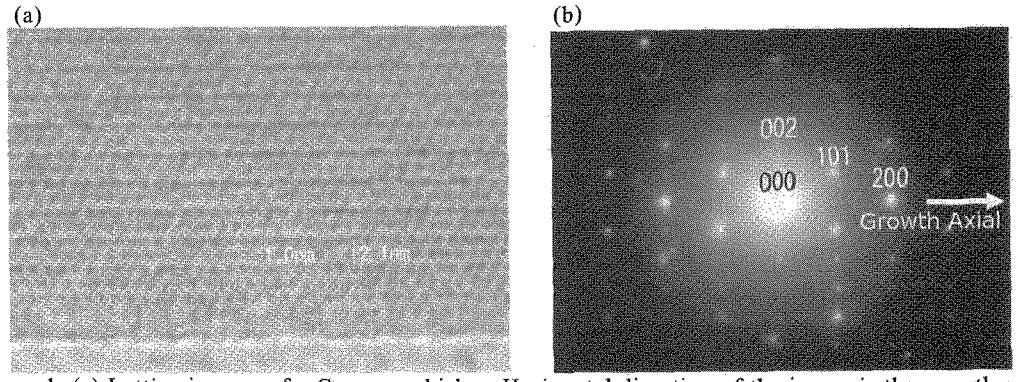

Figure 1. (a) Lattice images of a C_{60} nanowhisker. Horizontal direction of the image is the growth axial of the C_{60} nanowhisker. (b) Selected area electron diffraction pattern of the C_{60} nanowhisker. The SAEDP is indexed with a body centered tetragonal (bct) crystal system and its growth axial is [200].

Table I. Lattice constant of pristine C_{60} crystal and C_{60} nanowhiskers at room temperature

bct axis	pristine C_{60}*[10]	C_{60} nanowhisker	C_{60} nanowhisker [6]	I-doped C_{60} nanowhisker [11]
a	1.01 nm	1.06 nm	0.962 nm	1.01 nm
c	1.43 nm	2.15 nm	1.476 nm	2.01 nm

*pristine C60 has fcc crystal system, and converted as $a_{[fcc]}=1.41a_{[bct]}$

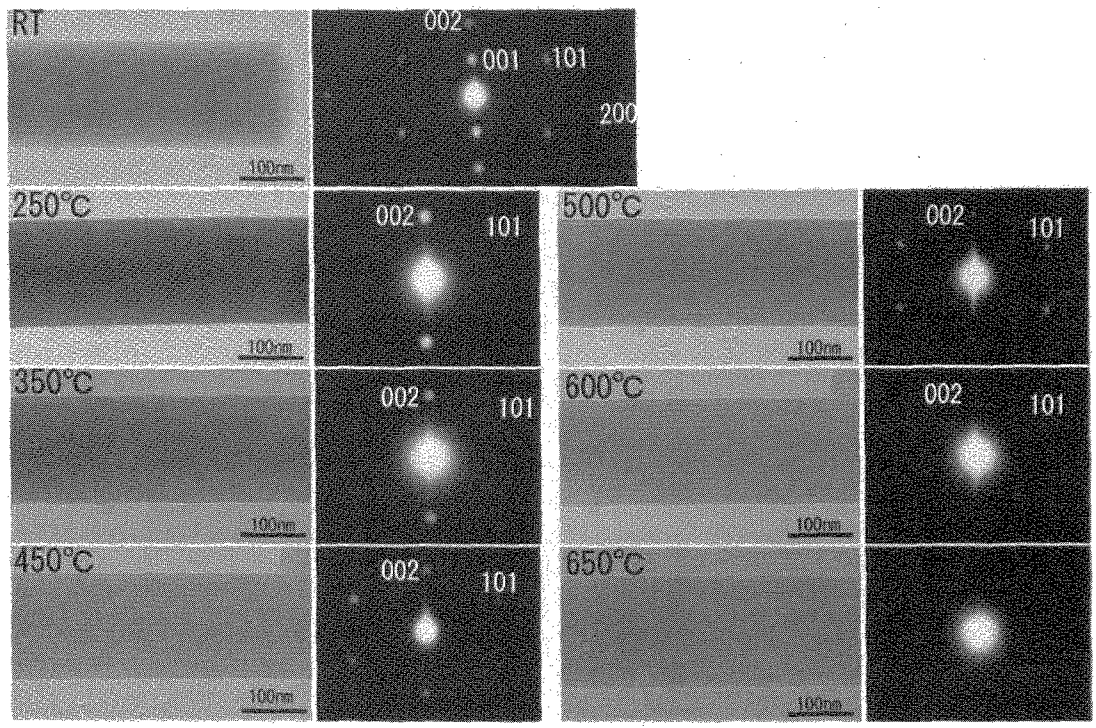

Figure 2. Each bright-field image and selected area electron diffraction pattern of C_{60} nanowhisker from room temperature to 650°C. The diffraction spots were extinguished over 600°C.

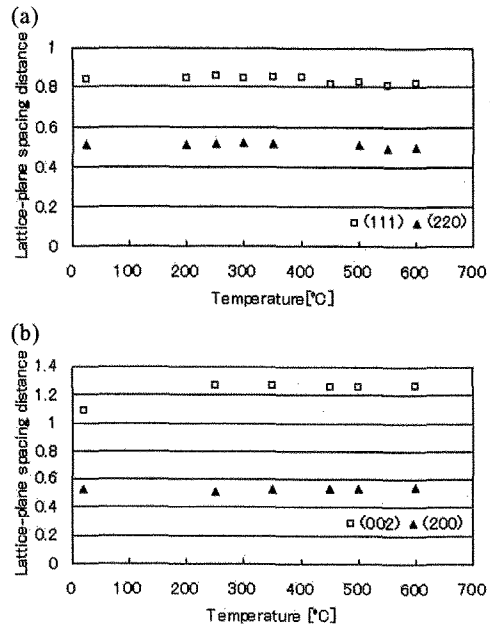

Figure 3. Lattice plane spacing distance of (a) C_{60} nanowhisker and (b) pristine C_{60} crystal.

present C_{60} nanowhisker is almost same as that of the iodine-doped C_{60} nanowhiskers [11]. It is considered that some organic solvents such as toluene/m-xylene or 2-propanol were contained in the C_{60} nanowhisker. The lattice constant a is shortened in former research [6], but the inclusion of solvent could not be confirmed. The crystal form is very sensitive to the precipitating condition including the state of solvent, illumination or temperature. It is necessary to investigate the relation between the lattice constant and precipitating conditions such as illumination or temperature.

Fig. 2 shows the bright-field images and the selected area electron diffraction patterns of the C_{60} nanowhiskers at various temperatures. The appearance of the C_{60} nanowhisker has not been changed at various temperatures, but the crystallinity of the C_{60} nanowhisker disappeared over 650°C, becoming amorphous between 600 and 650°C. Crystallinity was not recovered when it was cooled down to room temperature. The (001) reflection appearing at room temperature disappeared as the C_{60} nanowhisker was heated to 250°C.

The (001) spot is a forbidden reflection in the bct crystal system. The C_{60} nanowhisker was distorted from a perfect bct crystal during precipitation. It is believed that distortion of the crystal was relaxed by heating. It is supposed the distortion was the result of residual organic solvents in the whiskers, and the relaxation of the crystal was caused by their evaporation.

Fig. 3 shows diagrams of lattice plane spacing of each (a) C_{60} nanowhisker and (b) pristine C_{60} powder at various temperatures. The selected area electron diffraction patterns (SAEDPs) of both the C_{60} nanowhisker and pristine C_{60} powder disappeared over 600°C. We measured the lattice plane spacing from these selected area diffraction patterns. The C_{60} nanowhisker showed different thermal expansion depending on the crystallographic direction, i.e., the

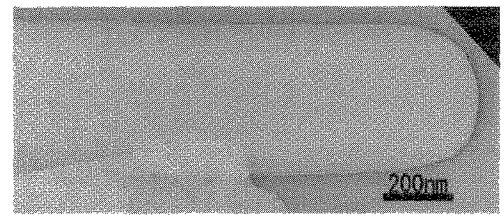

Figure 4. TEM bright-field image of a C_{60} nanowhisker heated at 600°C.

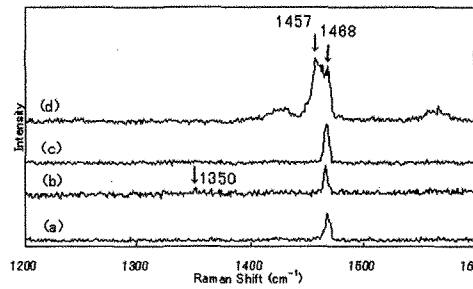

Figure 5. Raman spectra of (a) as-prepared C_{60} nanowhisker, (b)pristine C_{60} crystal annealed at 600°C for 2h in vacuum, (c) C_{60} nanowhisker annealed at 600°C for 2h in vacuum and (d) photo-polymerized C_{60} nanowhisker. Each Raman spectrum was taken by irradiation with a power of 40mWmm^{-2} for 30 sec.

(002) lattice plane spacing measured in the direction perpendicular to the growth axis expanded about 14% from room temperature to 600°C, while the (200) lattice-plane spacing along the growth axis expanded less than 3% in the same temperature range. The thermal expansion of the pristine C_{60} powder was less than 3% in the same temperature range as well. These results suggest that the intermolecular bonding force along the growth axis is stronger than that perpendicular to the growth axis.

Fig. 4 shows the bright-field image of a heated C_{60} nanowhisker. Many voids were formed by the heating. It is considered that the impurity elements in the C_{60} nanowhiskers, such as organic solvents, were evaporated from the whisker surface. But this surface appearance is different from the above-mentioned amorphous C_{60} nanowhiskers which were annealed on the Cu micro grid in TEM. It is supposed that differences of annealing and dispersion conditions of C_{60} nanowhiskers caused the difference of their forms after annealing. But shell-like morphology did not result. According to Ref. [9], it is supposed several treatments such as white light irradiation, air exposure and low temperature annealing at vacuum condition are needed. However, we recently discovered, 'the C_{60} fullerene shell tubes' among the C_{60} nanowhiskers that were heat-treated under evacuation by use of a rotary pump [12].

Fig. 5 shows the Raman spectra of (a) C_{60} nanowhisker, (b) heated pristine C_{60} crystals, (c) heated C_{60} nanowhisker and (d) photo-polymerized C_{60} nanowhiskers. The Raman spectra exhibit an intense peak at 1468 cm^{-1}, but the peak at 1457 cm^{-1} is observed only in the photo-polymerized C_{60} nanowhisker such as

described in Ref. [7]. But this polymerization is not related with the shortened intermolecular distance of the C_{60} nanowhisker which was mentioned in Ref. [7], because the C_{60} nanowhisker observed in this research showed no shrinkage in the lattice constant [Table I]. There is little difference between the spectrum of the annealed C_{60} nanowhisker and that of the as-prepared C_{60} nanowhisker. The main peak at 1468 cm^{-1} corresponds to the $A_g(2)$ [13]. On the other hand, a very broad peak around 1350 cm^{-1} was slightly observed in the annealed pristine C_{60} crystals. This peak corresponds to the peak of amorphous carbon [9], which means that the pristine C_{60} crystals became amorphous by the heating. These results show that the C_{60} nanowhiskers are more heat-resistant than the pristine C_{60} crystals.

4. Conclusion

Various types of lattice constant of the C_{60} nanowhiskers were observed by TEM. The lattice plane spacing of a C_{60} nanowhisker expanded about 14 % in a direction perpendicular to the growth axis during heating, but did not change along the growth axis by the heating. Also the distorted crystal structure at room temperature was relaxed and became the perfect bct system through heating. The C_{60} nanowhiskers became irreversibly amorphous between 600 and 650°C. According to Raman spectroscopy, the C_{60} nanowhiskers retained a higher crystallinity than pristine C_{60} crystals under 600°C annealing.

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References

[1] W. Krätschmer, L. D. Lamb, K. Fostiropolus and D. R. Huffman, *Nature*, 347, 354-358 (1990).
[2] R. M. Fleming, A. R. Kortan, B. Hesse, T. Siegrist, F. A. Thiel, P. Marsh, R. C. Haddon, R. Tycko, G. Dabbagh, M. L. Kaplan and A. M. Mujsce, *Phys. Rev. B*, 44, 888-891 (1991).
[3] Y. Yoshida, *Jpn. J. Appl. Phys.*, 31, L505-507 (1992).
[4] H. Moriyama, H. Kobayashi, A. Kobayashi and T. Watanabe, *Chem. Phys. Lett*, 238, 116-121 (1995).
[5] S. Ogawa, H. Furusawa, T. Watanabe and H. Yamamoto, *J. Phys. Chem. Solids*, 61, 1047-1050 (2000).
[6] K. Miyazawa, Y. Kuwasaki, A. Obayashi and M. Kuwabara, *J. Mater Res*, 17, 83-88 (2002).
[7] M. Tachibana, K. Kobayashi, T. Uchida, K. Kojima, M. Tanimura and K. Miyazawa, *Chem. Phys. Lett*, 374, 279-285 (2003).
[8] K. Miyazawa, Y. Kuwasaki, K. Hamamoto, S. Nagata, A. Obayashi and M. Kuwabara, *Surf. Interface Anal.*, 35, 117-120 (2003).
[9] H. Sakuma, M. Tachibana, H. Sugiura, K. Kojima, S. Ito, T. Sekiguchi and Y. Achiba, *J. Mater Res*, 12, 1545-1550 (1997).
[10] D. McCready and M. Alnajjar, Powder Diffraction File No. 44-558, International Centre for Diffraction Data, Newton Square, PA, (1994).
[11] K. Miyazawa and K. Hamamoto, *J. Mater Res*, 17, 2205-2208 (2002).
[12]K. Miyazawa, C. Nishimura, M. Fujino, T. Suga and T. Yoshii, submitted to MRS-J.
[13] A. M. Rao, P. Z.hou, K.-A. Wang, G. T. Hager, J. M. Holden, Y. Wang, W.-T. Lee, X.-X. Bi, P. C. Elkund, D. S. Cornett, M. A. Duncan and I. J. Amster, *Science*, 259, 955-957 (1993).

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