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Electrical Conducting Properties of Amorphous Carbon Nanowhiskers Studied by *In Situ* High-Resolution Transmission Electron Microscopy

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1. Introduction

Fullerene C_{60} molecules crystallize in films and plates [1]. Superconductivity, electrical conductivity, hardness and deformation of single crystalline C_{60} films and plates have been studied [2-5]. Recently, the synthesis method of single crystalline C_{60} whiskers with a face-centered-cubic structure was discovered by Miyazawa *et al.* [6]. The diameter and length of the whiskers are submicrometer and longer than 100 μm, respectively. The electrical resistivity of the C_{60} whiskers is in the range from 10^6 to 10^8 Ωm, which is the same order as that of other C_{60} crystalline films and plates [7]. The structure of the crystalline C_{60} whiskers transforms to amorphous by heating at 1373 K in a high vacuum.

In this report, we studied the electrical conduction properties of heated whiskers of single crystalline C_{60} whiskers, i.e., amorphous carbon nanowhiskers (a-CNWs), by combined high-resolution transmission electron microscopy (TEM) with the functions of scanning probe microscopy.

2. Method

We synthesized single crystalline C_{60} whiskers by a liquid-liquid interfacial precipitation method using a toluene solution saturated with fullerene powders of C_{60} and isopropyl alcohol [6-7]. The C_{60} whiskers were heated in a high vacuum at 1373 K for 30 min. The atomistic structural dynamics and electrical properties of the heated whiskers were simultaneously analyzed by the *in situ* TEM [8]. The heated whiskers were fixed on an edge of a silver electrode of 50 μm in thickness with a rectangular shape. Then the electrode was mounted on a specimen holder on the microscope. The tip of a silicon cantilever, coated with a thin silver film, as used for atomic force microscopy, was fixed in front of a tube-type piezo on another specimen holder. The cantilever tip was manipulated by a piezo-driven system and brought into contact with an edge of C_{60} whiskers. Then, bias voltage was applied between the cantilever and the electrode at room temperature in a vacuum of 1×10^{-5} Pa. The conductance was measured by a two-terminal method. The atomistic structural variation was simultaneously observed by *in situ* high-resolution TEM using a television rate system. The microscope was operated at an acceleration voltage of 200 kV. The high-resolution images were recorded on videotapes at a time resolution of 17 ms.

3. Results and Discussion

Figures 1(a) and 1(b) show a low-magnification image and an electron diffraction pattern of a heated whisker, respectively. The regions in the right-hand and left-hand sides of Fig. 1(a) are the cantilever tip and the edge of the electrode, respectively. The diameter and length of the whisker lying between the tip and the electrode are 1.1 μm and longer than 8.3 μm, respectively. The electron diffraction pattern in Fig. 1(b) is a hallow pattern, indicating that the structure of the heated whisker is

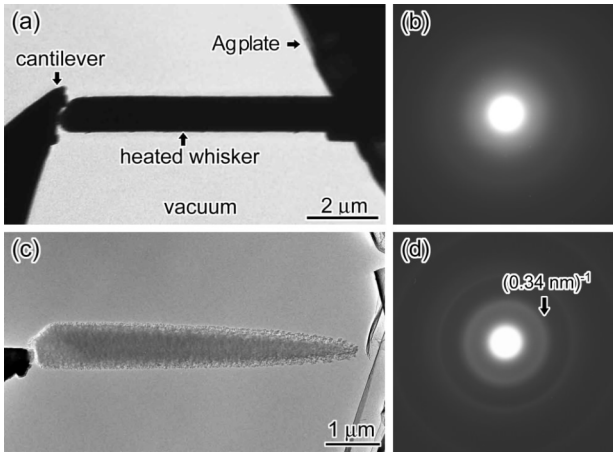

Fig. 1 (a) Low-magnification image and (b) electron diffraction pattern of whisker prepared by heating of C_{60} whisker. (c) Low-magnification image and (d) electron diffraction pattern of whisker after structural change owing to impressive current.

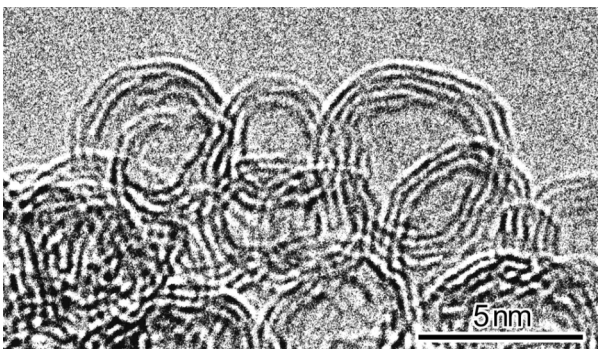

Fig. 2 High-resolution image of surface of whisker observed in Fig. 1(c). The whisker is composed of multilayered hollow carbon capsules of smaller than ten nanometers in diameter.

amorphous. Subsequently, bias voltage was applied to both edges of the whisker observed in Fig. 1(a). The current-voltage curve is shown in Fig. 3. The current increases gradually from 0 to 3.5 V. At 4.0 V, the current abruptly increases to 0.89 mA, and then decreases to zero at 4.5 V. Thus, the electrical resistivity decreases from 9.8 x 10^{-4} to 4.4 x 10^{-4} Ωm. These values are much smaller than that of pristine crystalline C_{60} whiskers [3]. After a bias voltage of 4.5 V was applied in the whisker in Fig. 1(a), a low-magnification image and an electron diffraction pattern were taken as shown in Figs. 1(c) and 1(d), respectively. The whisker gradually becomes narrow toward the right-hand side in Fig. 1(c) and the contact with the electrode completely fractures. The Debye rings in Fig. 1(d) are broad. The width of the smallest Debye ring corresponds to around $(0.34\ \text{nm})^{-1}$ and is close to that of the 00・2 reflections from graphite. Figure 2 shows a high-resolution image of the surface of the whisker shown in Fig. 1(c). It is found that the carbon hollow capsules surrounded with carbon shells of a few atomic layers are synthesized. The capsules are observed on the whole surfaces of the whisker. The spacing of the atomic layers is 0.34 ± 0.05 nm, corresponding to the interlayer spacing of graphite. The number of the layers is 2 ~ 4. The outer diameter of the capsules ranges from 3 to 8 nm. The TEM observation showed that the structural change from the amorphous to the capsules started from a bias voltage of 3.5 V. The electrical resistivity also starts to increase from the same voltage. Thus, the increase in resistivity is caused by the structural transformation. It was reported that similar capsule structures were produced by heating of carbon soot at 2373 K [9]. The molecular dynamics simulation regarding the nucleation mechanism of the fullerene C_{60} also showed that randomly arranged carbon atoms start to form spherical clusters surrounded with hexagonal rings at 2000 K [10]. In this study, we did not perform any heat treatment. However, resistive Joule heating occurs owing to the impressive current inside the microscope. Therefore, it is deduced that the formation of the capsules results from an increase in temperature owing to the resistive Joule heating.

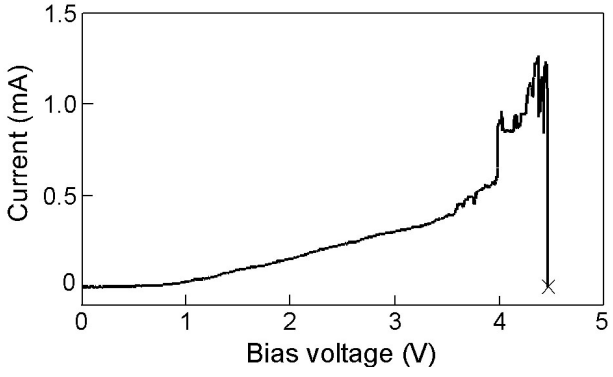

Fig. 3 Current-voltage curve of whisker shown in Fig. 1(c). The abrupt increase of current at the bias voltage of 4V indicates that the structural change occurs. A cross indicates the fracture of the contact.

4. Conclusions

We synthesized amorphous carbon whiskers by heating of single crystalline C_{60} whiskers. It was found that the structural transformation from the amorphous whiskers to carbon nanocapsule whiskers occurs by applying current at a bias voltage of 4 V. After the transformation, the electrical resistivity decreases from 9.8 x 10^{-4} to 4.4 x 10^{-4} Ωm. Thus, we can easily synthesize the conductive carbon filaments using the C_{60} whiskers as starting materials.

Acknowledgements

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