Auger Investigation of Fullerene Nanowhiskers Heat-treated at 400-800 Degrees Centigrade

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Abstract. Fullerene nanowhiskers were prepared from a toluene solution of C\(_{60}\) and isopropyl alcohol by a liquid-liquid precipitation method. The samples on the silicon (100) wafer were heated at the elevated temperatures ranging from 400°C through 800°C by an electron beam bombardment in an ultra-high vacuum, and their thermal stability was investigated with a scanning Auger-electron microprobe. At 400°C fullerene nanowhiskers already got thinner, while bulky fullerene crystals still remained even at 800°C. And many craters were observed around the fullerene crystals on the Si(100) substrate.

1. Introduction
Since the discovery of third carbon allotrope fullerene C\(_{60}\) [1], many fullerene families including carbon nanotubes [2] and endohedral metallofullerenes M@C\(_{60}\) [3] have been extensively investigated for their unusual properties. And various forms of C\(_{60}\) crystals were found to be generated from their liquid solutions. K. Miyazawa reported a fine fibrous structure of C\(_{60}\), formed at room temperature [4]. Needle-like crystals of C\(_{60}\) precipitated from an interface between a toluene solution of C\(_{60}\) and isopropyl alcohol, and they typically grew more than 100 \(\mu\)m long with a sub-micron diameter, called nanowhiskers [5]. The C\(_{60}\) nanowhiskers are considered to exhibit a higher strength and a higher electrical conductivity through polymerization [6]. However the detailed properties of C\(_{60}\) nanowhiskers are still unknown and intensive studies are now under way. In this study the thermal stability of the C\(_{60}\) nanowhiskers at the elevated temperatures, ranging 400-800 degrees Centigrade, was investigated by scanning Auger-electron microprobe (SAM).

2. Experimental
2.1. Sample preparation of fullerene nanowhiskers
The C\(_{60}\) nanowhiskers were fabricated by a liquid-liquid interfacial precipitation method, as described [5]. A toluene (99.5 %, Wako Pure Chemical Industries, Ltd., Japan) solution of fullerene C\(_{60}\) (>99.9 %, Tokyo Kasei Kogyo Co. Ltd., Japan) powder with a concentration of 0.1 mass% was prepared. Solubility of C\(_{60}\) in toluene was reported 2.8 mg/mL (ca. 0.3 mass%) [7], and its concentration was less than saturation. This toluene solution of 2 mL was poured into a 5 mL glass bottle, and 2 mL isopropyl alcohol (99.5 %, Wako Pure Chemical Industries, Ltd., Japan) was added.

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gently. Since the densities of toluene and isopropyl alcohol are 0.86 and 0.79 g/mL respectively, the isopropyl alcohol layer was formed over the toluene layer. Around the interface many seed crystals were generated. The sample bottle was kept at room temperature (approximately 23 °C) till they grew to needlelike whiskers.

2.2. Thermal stability of fullerene nanowhiskers
Morphological and elemental analyses of the samples were performed with an equipment of scanning Auger microprobe (Ulvac PHI, SAM650). The C_{60} nanowhisker solution was dropped on the Si(100) wafer (p-type, 280 μm thick, Furuuchi Chemical Corporation), and used for SAM observations after its solvent promptly evaporated. To investigate the thermal stability of C_{60} nanowhiskers, the samples were heated at 400-800 °C stepwise by using a sample heater with electron beam bombardment. The heating temperature was monitored with an infrared radiation thermometer (CHINO Corporation). After the sample was heated at fixed temperatures (400, 500, 600, 700 and 800 °C for 10 minutes each) in the irradiation chamber, it was transferred into the measurement chamber. All measurements were done at room temperature under an ultra high vacuum of 10^{-7} Pa or better. During the heat treatment the pressure temporarily went up to 10^{-6} Pa.

3. Results and discussions
The scanning electron microscopic (SEM) observation was done for the samples prepared. Figure 1(a) shows a SEM image (5 kV, ×160) of the sample as prepared (that is, no heat treatment). There seem many C_{60} nanowhiskers entangled and particulate C_{60} crystals. The SEM images of the samples after heated at 400 - 800 °C for 10 minutes are shown in Figures 1(b)-(f). This result shows that most of C_{60} nanowhiskers already got thinner at 400 °C, and that only traces of C_{60} nanowhiskers can be seen after a heat treatment at 800 °C. On the other hand, the bulky C_{60} crystals gradually get smaller with an increase of the heating temperature, but many C_{60} crystals still remains at 800 °C. Since the remaining carbon materials are not determined as C_{60} crystals, strictly they should be written as the remnants of C_{60} crystals. This result means that the thermal stability of C_{60} nanowhiskers is considered lower than that of bulky C_{60} crystals.

![SEM images](image_url)

Figure 1. The SEM images of the C_{60} nanowhiskers (5 kV, ×160): (a) no heat treatment, and after the heat treatment at (b) 400 °C, (c) 500 °C, (d) 600 °C, (e) 700 °C, and (f) 800 °C for 10 minutes each.
Then the C\textsubscript{60} nanowhisker samples were observed by scanning Auger microprobe for elemental analyses. The C\textsubscript{60} nanowhiskers heated at 600 °C is shown in Figure 2(a) (5 kV, × 1000). There seem one large C\textsubscript{60} crystal and two lines, the supposed traces of C\textsubscript{60} nanowhiskers. Two points, one on a trace line of C\textsubscript{60} nanowhisker and the other on the Si substrate, were measured by Auger. As shown in Figure 2(b), the Auger spectrum of the Si substrate presents silicon, oxygen, and carbon peaks, indicating the silicon oxide layer and the residual organic solvents. The spectrum of the trace line includes more carbon and less oxygen than the Si substrate, and so it means that the trace line must originate from the C\textsubscript{60} nanowhisker. Such a framework of the C\textsubscript{60} nanowhisker seems to be retained after a heat treatment at 800 °C, which may be a fullerene shell tube [8].

![Figure 2](image)

(a) SEM image (b) Auger spectra

Figure 2 The C\textsubscript{60} nanowhisker sample heated at 600 °C: (a) SEM image and (b) Auger spectra.

Figure 3 shows the Auger mapping of the large C\textsubscript{60} crystals remained after a heat treatment at 800 °C, where (a), (b), and (c) represent the Auger maps of carbon (C KLL), oxygen (O KLL), and silicon (Si KLL), respectively (5 kV, × 2000). The large crystals mainly consist of carbon, while the substrate is composed of silicon and oxygen. Here it is noted again that the large C\textsubscript{60} crystals are much more stable to the temperature than the C\textsubscript{60} nanowhiskers. And there are also observed many craters on the Si substrate like a white spot in the Figure 3(c). Since the crater consists of silicon, the silicon oxide layer is considered to disappear anyhow. In fact the enlarged SEM image of this crater in Figure 4(a) confirms this. Their Auger spectra in Figure 4(b) show that the crater is the silicon (100) substrate itself and that the island observed in the middle of the crater is the remnant of the C\textsubscript{60} crystal. Here it is noted again that the remnant carbon materials are not necessarily C\textsubscript{60} crystals. The thermal decomposition of SiO\textsubscript{2} layer on Si were often reported, where the reaction of SiO\textsubscript{2} + Si → 2SiO ↑ occurs [9,10]. But in our investigation a thickness of SiO\textsubscript{2} layer is estimated as thin as 2 nm by ellipsometry and the craters are usually observed with C\textsubscript{60} crystals in the center. And so it suggests that the bulky C\textsubscript{60} crystals play some role in a crater formation, but further study is to be done for clarifying the mechanism.
Figure 3 The Auger mapping of the C60 crystals heated at 800 °C: (a) carbon, (b) oxygen, and (c) silicon.

Figure 4 The crater on the Si(100) substrate: (a) an enlarged SEM image and (b) Auger spectra.

4. Conclusions
The C60 nanowhiskers and large crystals were formed with a liquid-liquid precipitation method. Their thermal stability is rather different. Almost all nanowhiskers already got thinner at 400 °C, while bulky C60 crystals still remained even at 800 °C. So the thermal stability of C60 nanowhiskers is lower than that of C60 crystals. And many craters were generated around the C60 crystals on the Si(100) substrate and it may be inferred that the C60 crystals should be a help towards the crater formation of the silicon oxide layer.

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