NEXAFS and XPS Study on Carbon Nanotube Formation Process by Surface Decomposition of SiC

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1 Introduction
Carbon nanotube (CNT) growth by surface decomposition of SiC is a unique growth technique, because zigzag-type CNTs are selectively formed only by heating SiC crystals in a vacuum without any catalysts. At the initial stage of CNT formation, nanosized hemispherical structures composed of carbon atoms are formed on SiC surface [1]. These “carbon nanocaps” determined the structure of CNTs, such as the number of walls, diameter and chirality [2]. Therefore, clarifying the formation process of carbon nanocaps would lead to control of the CNT structure. In this study, we carried out XPS and NEXAFS measurements at high temperature to investigate the formation process of carbon nanocaps.

2 Experiment
After HF etching, 6H-SiC(000-1) substrates were placed in a high vacuum chamber. Then, the samples were gradually heated to an intended temperature, followed by annealing under a H₂ ambient for 30 min. The sample temperature was monitored with a pyrometer. After exhausting the H₂ gas, XPS and C K edge NEXAFS spectra were measured at BL-7A, keeping the sample at the heating temperature. The photon energy used for XPS measurements was 430 eV.

3 Results and Discussion
Decomposition process of SiC surface was investigated by XPS measurements. Fig. 1 shows the variation of intensity ratio of Si 2p peak to C 1s peak in XPS spectra measured for SiC(000-1) surfaces, as a function of the heating time. The heating temperatures measured by the pyrometer are also shown. The relative intensity of Si 2p peak decreased rapidly above 1230°C, which was caused by desorption of Si atoms. At 1380°C, the Si peak became negligible, indicating that the surface of SiC was covered with carbon layers. Taking into account the escape length of photoelectron, the thickness of carbon layer were estimated to be larger than 5 nm at this temperature, indicating the formation of carbon nanocaps.

To investigate the crystallization process of carbon nanocaps, we carried out NEXAFS measurements for SiC(000-1) surfaces. In this measurements, we carried out NEXAFS measurements at two incidence angles (30° and 90°), to estimate the orientation of C-C bonds on the SiC surface. Fig. 2 shows the intensity ratios of π* peaks measured at 30° to that at 90° as a function of the heating temperature. Below 1200°C, the relative intensity of normal incidence was weaker than that at 30°. As the temperature increased, the former became larger than the latter, indicating the change of C-C bond orientation. That is, the C-C bonds were parallel to the surface at first, but they inclined and became perpendicular to the SiC surface, as the temperature rose. Taking into account the results of the QM/MD calculation [3], we consider that the graphene flakes formed on the surface were curved by the dangling-bonds on SiC(000-1) face, leading to the orientation change of the C-C bond and that this induced the formation of carbon nanocaps.

References
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