Scanning atom probe study of carbon nanotubes and graphite nanofibers with hydrogen terminated defects

O Nishikawa¹, M Taniguchi¹ and M Ushirozawa²

¹ Dept. of Chemistry and Biology, Kanazawa Institute of Technology
7-1 Ohgigaoka, Nononoichi, Ishikawa 921-8501 Japan
² Science and Technical Research Laboratories, NHK
1-10-11 Kinuta, Setagaya-ku, Tokyo 157-8510 Japan

E-mail: nisikawa@neptune.kanazawa-it.ac.jp

Abstract. Graphite nanofibers (GNF) and multi-wall carbon nanotubes (MWCNT) are mass analyzed utilizing the unique capability of the scanning atom probe. Various clusters of carbon and hydrogen are detected from MWCNT. These are mostly H⁺, H₂⁺, C⁺, CH₃⁺ and C₂H₅⁺. Few cluster ions are detected for the mass rang of 100 – 300. The largest mass peak is C₂₈H₄⁺ with two satellite mass peaks. The abundance of the satellites well agrees with the expected abundance of ¹²C₂₇¹³CH₄ and ¹²C₂₆¹³C₂H₄, 28% and 4%, respectively. No H⁺ mass peak was found for GNF but the significant number of the ions such as C₂H₅⁺, C₃H₇⁺ and C₄H₉⁺ are detected. These ions are detected at the beginning of the mass analysis. After the removal of the surface layer, the detection rate of the largest cluster, C₂₃H₂, increases. The proposed structure of the C₂₈H₄ cluster is a rectangle formed three rows by three rows of hexagonal cells and that of C₂₃H₂ is the triangularly arranged six hexagonal cells. Four carbon atoms of C₂₈H₄ and two carbon atoms of C₂₃H₂ clusters are terminated by hydrogen.

1. Introduction

Since the introduction of carbon nanofibers, such as carbon nanotubes (CNT) and graphite nanofibers (GNF), the unique electrical and mechanical properties of these nanofibers have drawn a strong interest in wide fields of scientists and engineers [1,2]. Most nanofibers are synthesized as products of thermal decomposition of hydrocarbons. Accordingly, the nanofibers could contain a large amount of hydrogen which may influence their unique properties. However, few efforts have been paid to investigate the effect of the adsorbed hydrogen because the clarification of the absorbed state of individual hydrogen atom requires the atomic level analysis. It has been realized that the scanning atom probe (SAP) [3,4] has the capability of analyzing these materials by field evaporating individual tube and fiber. The unique feature of field evaporation is in its static process and proceeds by breaking weak bonds forming the materials. Thus, the analysis provides not only the composition of the specimen but also the information about the binding between the atoms. Thus, the purpose of this study is to evaluate the validity of the analysis of the nanofibers by SAP.

2. Experimental

2.1. Apparatus and procedures
The structure of the SAP is described elsewhere [3, 4]. Although the SAP allows to mass analyze a minute specimen on a flat specimen holder, a dull tungsten tip is used as a substrate of the nanofibers. Since the conductivity of the carbon nanofiber is high, a pulsed voltage $V_p$ is superposed on a DC voltage $V_{DC}$ to field evaporated surface atoms in a limited time, a few nanoseconds. The fraction of the pulse voltage, $V_p/(V_{DC}+V_p)$, is 20% of the total voltage applied to the specimen. Flight times of the evaporated ions from the specimen surface to the ion detector are measured in the accuracy of 1 ns. The mass resolution of the SAP, $M/\Delta M$, is better than 1000.

2.2. Specimens
Commercially available multi wall carbon nanotubes (MWCNT) are mass analyzed. Accordingly, the fabrication process of the MWCNT is not informed. Fine grains of the MWCNT are deposited on an apex of a tungsten tip by silver paste.

Graphite nanofibers (GNF) are grown on a SUS304 needle by the thermal CVD method. Source gases were CO (50%) and $H_2$ (50%) at 100 kPa, and growth temperature is 600°C for 20 minutes. The field emission characteristics are also examined by operating the SAP as a field emission microscope.

3. Results

3.1. Mass spectra of MWCNT

Typical mass spectrum obtained by analyzing MWCNT is shown in figures 1 and 2. The range of mass $M$ to charge ratio, $M/n$, of figure 1 is 0 - 100 showing various fragment ions of hydrocarbons. These cluster ions could be ascribed to the incomplete fabrication process of the nanotubes with the source gases. Since the mass resolution of the SAP is not high enough to discriminate the ions with same atomic mass unit (amu) such as $C_2H_5$ and $COH$, these mass peaks are denoted as $C_2H_5/COH$ and $C_3H_5/C_2OH$. Sharpness of the peaks indicates the strong C-H bond [3].

![Figure 1. Mass spectrum of MWCNT.](image)

Few ions in the mass range of 100 – 300 are detected. However, several large peaks are observed in the range of 300 – 450, figure 2. The numbers shown by upward arrows are the number of detected ions, 31.4% and 4.6%, and well agree with the expected ratio from the abundance of the carbon isotope $^{13}C$, 26.2% and 3%.
3.2. Mass spectra of GNF
Contrary to MWCNT H⁺ peak is hardly seen. However, the detected ions are carbon hydride clusters, figure 3. Furthermore, each mass peak has a small tail towards the right side of the mass peaks. This implies that the C-H bonds are not as strong as that of MWCNT [3]. Detection rate of these ions decreases as the field evaporation of surface layer proceeds and that of larger masses increases, especially, C_{23}H_{2}, figure 4. Note that C_{23}H_{2} peak has a wide tail indicating a weak C-H bond. No large mass peak is seen in the mass range of 100 – 200 as for MWCNT.

4. Structures of clustering ions
The abundant and characteristic cluster for MWCNT is C_{28}H_{4} and that for GNF is C_{23}H_{2}. The structures of these clusters should be suitable to construct a tubular structure and a graphene sheet. The proposed structure of C_{28}H_{4} is a rectangle formed by three by three rows of hexagonal cells as shown in figure 5. The assumed structure of C_{23}H_{2} is the triangularly arranged six hexagonal cells. Two corner carbon atoms of the triangle are hydrogen-terminated, as indicated with small circles in figure 6, and third corner carbon atom is bound with an extra carbon atom, denoted by "C". Figure 6 also
shows a hexagonal ring formed by 6 hydrogen atoms terminating the carbon bonds and 6 C atoms forming a hexagon. A similar hydrogen hexagonal ring is seen for a kekulene molecule.

![Figure 4. Mass spectrum of GNF. Mass range: 200 - 300.](image)

**Figure 4.** Mass spectrum of GNF. Mass range: 200 - 300.

**Figure 5.** Proposed structure of C_{26}H_{13} cluster of MWCNT. Eight hexagonal cells are shaded. The terminating hydrogen atoms are shown by small dark circles.

**Figure 6.** Structure of C_{23}H_{2} cluster of GNF. The cluster formed by six hexagonal cells, an extra carbon atom, C, and two hydrogen atoms, small circles, is shaded.

### 5. Conclusions

Following conclusions are drawn by the present analysis. 1. Both MWCNT and GNF contain a significant amount of hydrogen and these hydrogen atoms are terminating a carbon atom’s bond. 2. Hydrogen is orderly distributed forming the characteristic clusters. 3. The C-H bond of MWCNT is stronger than that of GNF. 4. The study clearly demonstrates the high capability of the SAP for the analysis of nanofibers. Variation of the clusters with the fabrication process will be studied by introducing the well defined fabrication process in the future.

[1] Anderson P E, Rodriguez N M 1999 *J. Mater. Res.* **14** 2912
[2] Serp P, Corrias M and Kalck P 2003 *Appl. Catalysis* **253** 337
[3] Nishikawa O, Ohtani Y, Maeda K, Watanabe and Tanaka K 2000 *Material. Character.* **44** 29
[4] Nishikawa O, Watanabe M, Murakami T, Yagyu T and Taniguchi M 2003 *New Diamond and Frontier Carbon Technol.* **13** 257