

Study of characteristic fragmentation of nanocarbon by the scanning atom probe

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Six nine purity graphite and single-walled carbon nanotube (SWCNT), double-walled carbon nanotube (DWCNT), multiple-walled carbon nanotube (MWCNT) are mass analyzed by the scanning atom probe. Surface atoms well exposed to the external field are field evaporated and individual evaporated fragment ions are detected. Each specimen exhibits a characteristic mass spectrum of fragmented cluster ions. The SWCNT exhibits the cleanest mass spectrum with a small amount of hydrogen. The commercially available DWCNT shows two types of mass spectra: one is fairly clean and the other with many $C_{15}(H_2O)_m$ clusters. The laboratory grown MWCNT shows various doubly and triply ionized cluster ions indicating strong bonding between the atoms forming the clusters. The sharper the mass peak is and the higher the multiplicity of charge is, the stronger the binding between atoms forming the clusters. The commercially available pure graphite shows three types of mass spectra, fairly clean spectra without large C-H clusters, spectra with various C-H clusters with a large mass peak of $C_{28}H_4$, and spectra with larger clusters such as $C_{38}H_n$. The magic number forming the clusters is discussed. © 2008 American Vacuum Society. [DOI: 10.1116/1.2832364]

I. INTRODUCTION

Presently most carbon nanowires such as carbon nanotubes (CNTs),¹ graphite nanofibers (GNFs),² and ultrananocrystalline diamond³ are grown in the source gases, H_2 , CH_4 , C_2H_4 , and CO . Thus, it is highly probable that these nanowires contain a significant amount of impurities, mostly hydrogen and oxygen. The impurities may impede the utilization of their unique physical properties. Accordingly it is the basic requirement to know the amount and distribution of the impurities in the nanoscale point of view because each nanowire serves as a key component of an electronic device. However, no atomic level analysis has been conducted to clarify how these impurities are distributed in the nanowires and how strongly bound with carbon.

We have realized that the scanning atom probe^{4,5} (SAP) is one of the most suitable instrument to investigate individual nanowires because the analyzed area is a few nanometer square and the successive field evaporation of a nanowire allows to clarify the composition of the fiber at atomic level resolution. Following this idea, GNF and commercially available multiwalled CNT (CA-MWCNT) are analyzed and their characteristic fragmentation due to hydrogen was found.^{6,7} Thus, the purpose of this study is to extend the SAP analysis to evaluate the quality of single-walled CNT (SWCNT), double-walled CNT (DWCNT), MWCNT, and commercially available pure graphite and shed light on the binding between carbon and impurity atoms.

II. EXPERIMENT

The structure of the SAP is described elsewhere.⁴ For the SAP mass analysis, a positive pulsed voltage V_p of 5 ns wide is superposed on a positive dc voltage V_{dc} . The ratio of V_p to $(V_{dc} + V_p)$ is set at 20%. Flight times of the field evaporated ions are measured by the timer with 1 ns accuracy. Accordingly, the mass resolution $m/\Delta m$ of the SAP is better than 1000. Preceding the SAP analysis, the SAP is operated as a field emission microscope applying a negative voltage to the specimen in order to estimate the work function.⁶

Purity of the commercially available (CA) pure graphite is 6 nines. A graphite block is grounded to small grains and silver pasted on a dull tungsten tip. SWCNT produced by the high pressure carbon monoxide process is supplied from Carbon Nanotechnology Laboratory of Rice University.⁸ SWCNT and commercially available double-walled carbon nanotubes (CA-DWCNTs) are silver pasted on a tungsten tip. MWCNT from Nagoya University is attached to a tungsten tip by electrophoresis.⁹

Sharp apexes of CNT and graphite powder protrude on the silver paste and confine the high field required for the field evaporation of carbon atoms in a minute space between the apexes and the small open hole of the extraction electrode. No contamination by the silver paste is noticed. Occasionally, silver ions are detected after the analysis of CNT.

The field evaporation proceeds not as smooth as metals because the covalent binding is directional and irregular by the contaminants. Accordingly, the evaporation rate is intentionally lowered, less than a few thousand pulses per ion.

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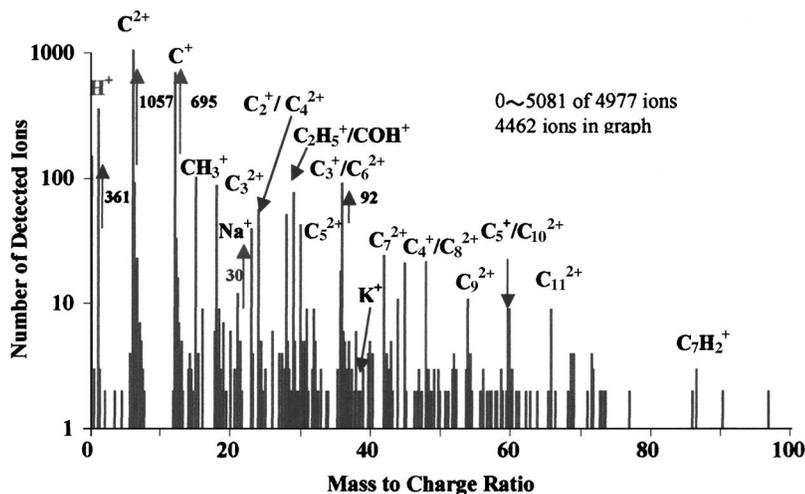


FIG. 1. Mass spectrum of SWCNT. The number beside an upward arrow indicates the number of detected ions. Most ions are doubly charged and the number of C–H clusters is small. The total number of detected ions from this specimen is 5081 and 4462 ions are plotted in this figure. The small letters on the right below 820.821SWCNT is the code number of these data indicating the dates of analysis and specimen.

III. RESULTS

A. SWCNT

Figure 1 is the mass spectrum of SWCNT. The largest mass peak is C^{2+} and C^+ is the second. The number of detected ions decreased with the number of clustering carbon atoms and the clusters of odd numbered carbon atoms are more abundant than those of the even numbered. Most carbon clusters are doubly charged indicating strong C–C bonds. Although H^+ and a few C–H clusters are detected, the total number is significantly smaller than other CNTs, about 10% of the ions plotted in Fig. 1. No mass peaks are observed in the mass range larger than 100.

Masses 54 and 56 are detected. However, these ions may not be iron because iron is usually field evaporated as doubly charged ions and the numbers of detected ions with masses 56 and 54 do not agree with the isotope abundance ratio of iron. Several ions with mass to charge ratios of 28 and 27 are also detected. However, the numbers are too small to designate the ion species.

More than 20 specimens are analyzed. Every specimen shows a similar mass spectrum. However, sodium and potassium ions are detected from a few specimens as shown in Fig. 1. It is told that they are added during the handling process.

B. DWCNT

CA-DWCNT exhibits two types of mass spectra. The largest mass peak of type 1 is C^{2+} and C^+ follows as SWCNT (Fig. 2). Most other ions are singly charged and each major mass peak has satellite mass peaks indicating the detection of various C_nH_m , where n and m are integers. No mass peaks are observed in the range of mass to charge ratio larger than 100.

Many other specimens exhibit utterly different type 2 spectra as shown in Fig. 3. The largest mass peak is H^+ and various C_nH_m clusters are plotted. Furthermore, $C_{15}(H_2O)_n^{2+}$ and $C_{15}(H_2O)_n^+$ are detected. The broad $C_{15}(H_2O)_n^{2+}$ mass peaks (Fig. 4) indicate the dissociation of weakly bound hydrogen atoms from these clusters before the evaporated clusters arrive at the ion detector.⁴

C. MWCNT

MWCNT grown by thermal chemical vapor deposition⁸ exhibits a small number of mass peaks of singly charged C–H cluster in the range of mass to charge ratio less than 100 (Fig. 5). The mass peaks are very sharp indicating strong C–H bonds. An interesting point is that larger clusters are doubly and triply charged (Fig. 6). Because of the strong C–H bonds, every mass peak is sharp enough to identify

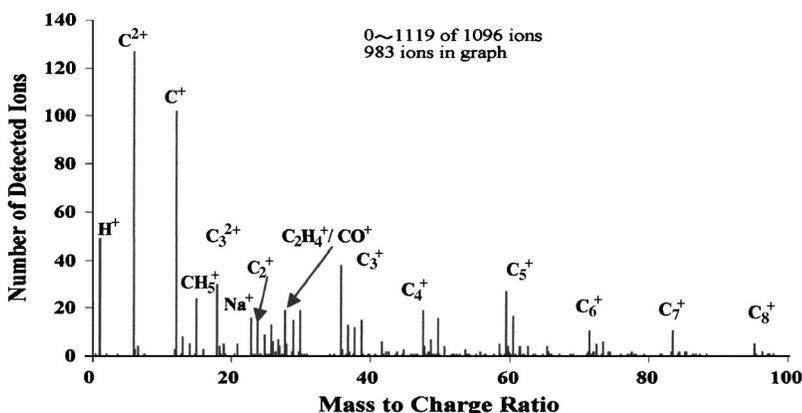


FIG. 2. Mass spectrum of type 1 DWCNT. Although C^{2+} is the largest peak, most ions are singly charged $C_nH_m^+$, where $n=1,2,3,\dots$ and $m=0,1,2,\dots$

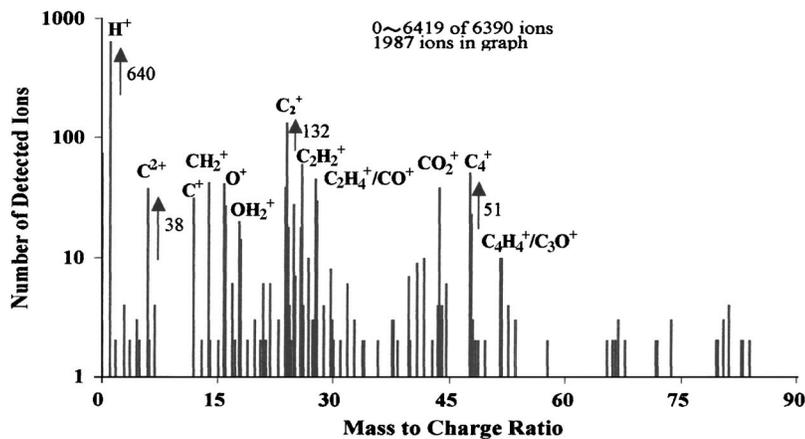


FIG. 3. Mass spectrum of type 2 DWCNT. Range of mass to charge ratio (M/n): 0–90. The number beside an upward arrow is the number of detected ions. H^+ is the largest peak and C_2^+ follows.

major mass peaks: $C_{18}H_n^{2+}$, $C_{19}H_n^{2+}$, $C_{37}H_n^{2+}$, $C_{38}H_n^{2+}$, $C_{37}H_n^{3+}$, $C_{38}H_n^{3+}$, and $C_{76}H_n^{3+}$. Small numbers of singly charged $C_{28}H_n^+$, $C_{29}H_n^+$, C_{36}^+ , and $C_{38}H_n^+$ are also detected.

D. Pure graphite

Mass spectra of pure graphite can be classified into three types. Type 1 is as clean as SWCNT. The mass spectra of types 2 and 3 are quite similar showing various C–H clusters (Fig. 7). The sharpness of the mass peaks indicates strong C–H bonds. The difference between types 2 and 3 is in the large clusters. Type 2 shows a large mass peak of $C_{28}H_4^+$ as CA-MWCNT.⁶ However, the broadness of the peak indicates

that the C–H bond of the pure graphite is significantly weaker than that of the MWCNT. Type 3 has $C_{38}H_n^{2+}$, $C_{40}H_n^{2+}$, and $C_{23}H_n^+$ (Fig. 8). The mass peaks are fairly sharp indicating strong C–H bonds.

IV. DISCUSSIONS AND CONCLUSIONS

Major mass peaks of analyzed specimens including CA-MWCNT (Ref. 8) and GNF (Ref. 7) are compiled in Table I. From the hydrogen content and charge multiplicity point of view, SWCNT is the most solidly constructed clean specimen, and type 1 of pure graphite follows. The drastic difference in the mass spectra between SWCNT and other CNTs

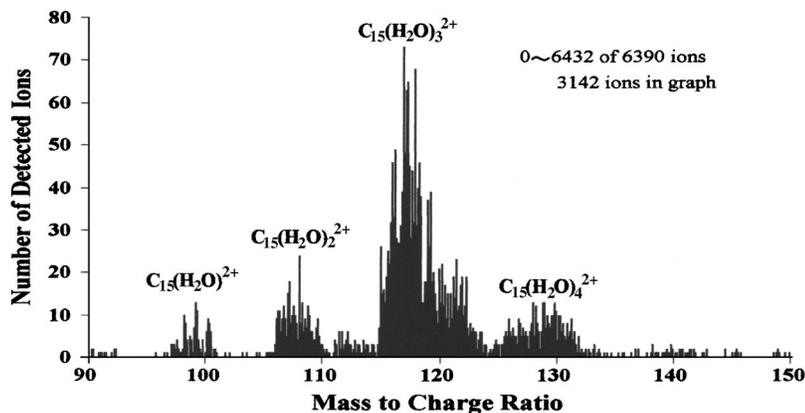


FIG. 4. Mass spectrum of type 2 DWCNT. M/n : 90–150. The broadness of $C_{15}(H_2O)_m^{2+}$ peaks indicates that the hydrogen attached to the clusters is weakly bound.

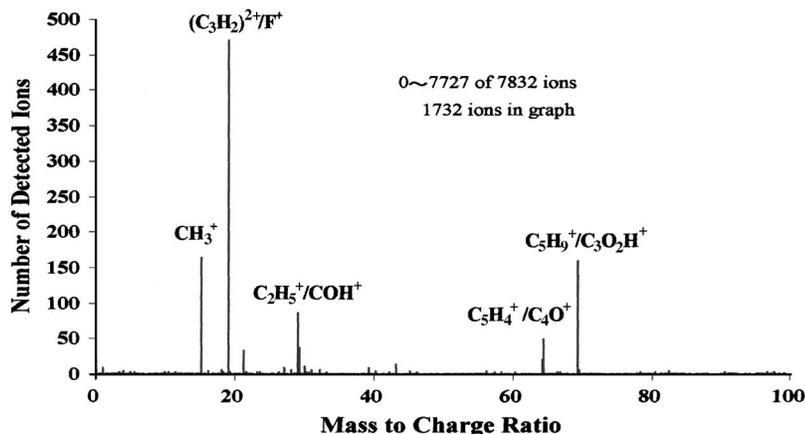


FIG. 5. Mass spectrum of MWCNT. Range of mass to charge ratio: 0–100.

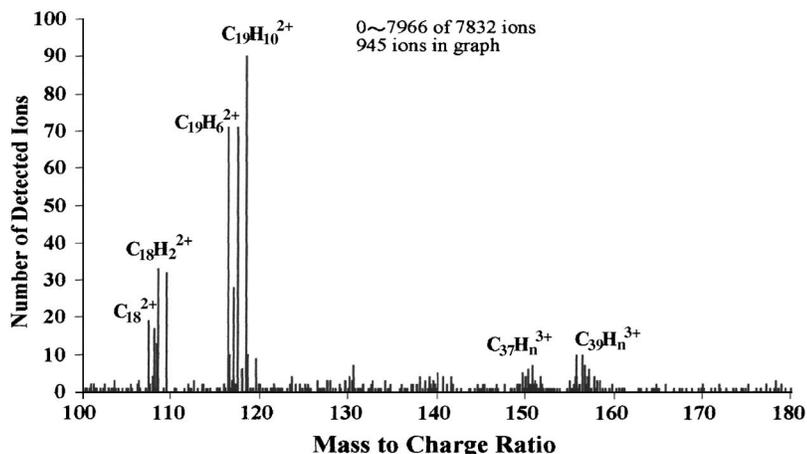


FIG. 6. Mass spectrum of MWCNT. Range of mass to charge ratio: 100–180. The mass differences between mass peaks, $0.5M/n$ and $0.3M/n$, indicate that these mass peaks are formed by doubly and triply charged cluster ions. Sharp mass peaks indicates strong C–H bonds.

could be due to the difference in the amount of contaminants and not by the difference in the structures. Furthermore, the most important requirement for the nanosize carbon specimens is in the homogeneity of the specimens. Thus, the SWCNT could be the most reliable CNT.

Although the charge multiplicity of MWCNT is high, it contains a significant amount of hydrogen. The study suggests to mass analyze this specimen attached by silver paste.

All large clusters are C_nH_m and the number of clustering carbon atoms n is not random but appears to be magic num-

bers. $C_{28}H_4$ and $C_{28}H_m$ are detected from CA-MWCNT, MWCNT, and type 2 pure graphite. Double and triple of $C_{19}H_m$, $C_{38}H_m$, and $C_{76}H_m$, respectively, are found from MWCNT and type 3 pure graphite. Strongly bound hydrogen atoms are orderly distributed and form the characteristic structures as suggested by the previous work.^{6,7}

The present study clearly suggests that the carbon specimens are not homogeneous in nanodimension and most specimens contain a noticeable amount of hydrogen and oxygen for the utilization as electronic elements. Extensive and

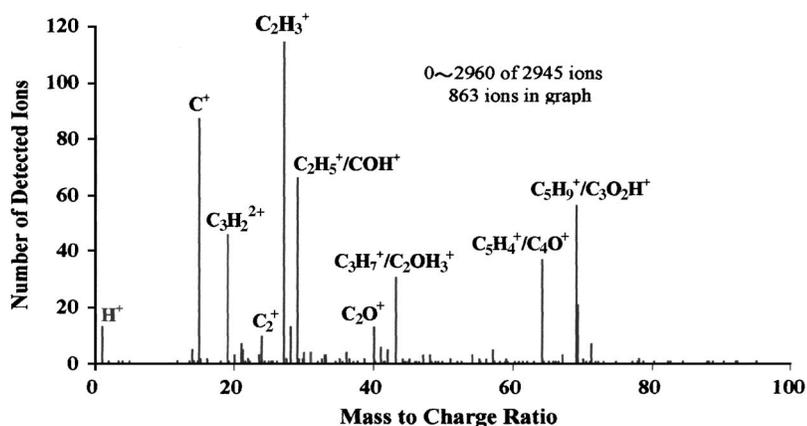


FIG. 7. Mass spectrum of type 3 pure graphite. Range of mass to charge ratio: 0–100. Almost all ions are singly charged C–H cluster.

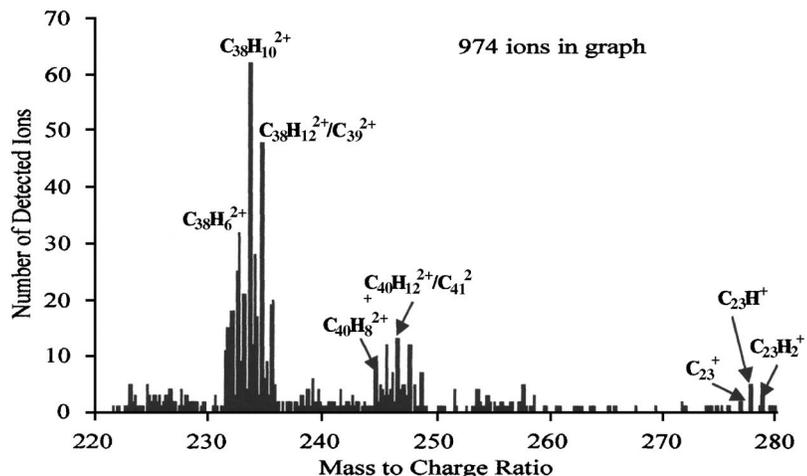


FIG. 8. Mass spectrum of type 3 pure graphite. Range of mass to charge ratio: 220–280. The mass peaks of $C_{38}H_m^{2+}$ and $C_{40}H_m^{2+}$ are sharp.

TABLE I. Major mass peaks of analyzed carbon specimens. Some characteristic small mass peaks are also listed. Underlined clusters have a broad mass peak because of weak C–H bonds.

Specimens	Major mass peaks					
SWCNT	C ²⁺ , C ⁺ , H ⁺ , CH ₃ ⁺	C ₃ ⁺ /C ₆ ²⁺	C ₅ ⁺²⁺ , C ₇ ²⁺ (small peaks)			
Type 1 CA-DWCNT	C ²⁺ , CH _m ⁺ , (m=0, 1, 2, ...)	C ₅ H _m ⁺ , C ₅ H _m ⁺ (small peaks)				
Type 2 CA-DWCNT	H ⁺ , C ₂ H _m ⁺		<u>C₁₅(H₂O)_m⁺</u> <u>C₁₅(H₂O)_m²⁺</u>			
CA-MWCNT	H ⁺ , H ₂ ⁺ , CH ₃ ⁺ C ₂ H ₅ ⁺ /COH ⁺			C ₂₈ H ₄ ⁺		
MWCNT	CH ₃ ⁺ /C ₃ H ₂ ²⁺	C ₅ H ₉ ⁺ /C ₃ O ₂ H ⁺	C ₁₉ H _m ²⁺	C ₂₈ H _m ⁺ C ₂₉ H _m ⁺ (small peaks)	C ₃₈ H _m ²⁺ C ₃₈ H _m ³⁺	C ₇₆ H _m ³⁺ (small peaks)
GNF	C ₂ H ₅ ⁺ /COH ⁺ C ₂ OH ₃ ⁺			<u>C₂₃H₄⁺</u>		
Type 1 pure graphite	C ²⁺ , C ⁺	C ₃ ⁺ (small peak)				
Type 2 pure graphite	C ₂ H ₅ ⁺ /COH ⁺	C ₄ H ₉ ⁺ /C ₂ O ₂ H ⁺		<u>C₂₈H₄⁺</u>		
Type 3 pure graphite	CH ₃ ⁺ , C ₂ H ₃ ⁺	C ₅ H ₉ ⁺ /C ₃ O ₂ H ⁺			C ₃₈ H _m ²⁺	

systematic study of carbon specimens will be conducted for the development of an improved growth process of the high quality carbon nanowires.

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