Study of Molecular Reaction on Titanium Oxide by the Scanning Atom Probe *

Masahiro Taniguchi,† Osamu Nishikawa, Shigeto Komata, and Shingo Watanabe
Division of Chemistry, College of Environmental Engineering and Architecture,
Kanazawa Institute of Technology, 7-1 Ohgigaoka, Nonoi, Ishikawa 921-8501, Japan

Akihiko Yamagishi
Department of Earth and Planetary Science, Graduate School of Science,
The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan.

Takayoshi Sasaki
CREST, Japan Science and Technology Agency, and
Nanoscale Materials Center National Institute for Materials Science,
1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
(Received 1 November 2005; Accepted 15 May 2006; Published 3 June 2006)

In this study, we investigated the covalent materials by using a scanning atom probe (SAP) developed by Nishikawa, et al. SAP relaxes the severe requirement of the extremely sharp and slender shaping of sample for an analysis by conventional atom probe (AP). In the application of AP to non-metallic specimens with a low electron conductivity can be overcome by using pulsed laser beam for excitation. Discrete organic molecules and carbon nanotubes (CNT) were examined. CNTs gave mass spectra of few dominant fragments which reflected its one-dimensional homogeneous structure. Discrete molecules showed their molecular ion peaks in their AP mass spectra, which confirmed the softness of the field ionization process. The molecular ion peak disappeared when titania micro crystal was used as substrate in AP measurement. The change in the fragment pattern suggested the emergence of photocatalytic decomposition of adsorbed molecules on titania by laser irradiation. [DOI: 10.1380/ejssnt.2006.521]

Keywords: Scanning atom probe; Field ionization; Mass spectroscopy; Carbon nanotube; Titanium oxide

I. INTRODUCTION

The atom probe analysis is based on its unique mechanism of ionization; the field evaporation/ionization of surface atoms. Since the field evaporation does not put external energy for breaking atomic bonds, it does not disorder surface structure. Evaporated positive ions through the static process reflect the binding state on the surface or preserve the information of surface reaction of specimens.

For the atom probe (AP) analysis of non-metallic materials, there are some difficulties: sample fabrication and low electron conductivity [1, 2]. In a scanning atom probe (SAP) developed by Nishikawa, a funnel-shaped microextraction electrode confines the high field into a small space between a tip apex and an open end of the electrode and relaxes the severe requirement of the sample fabrication in conventional AP. The insufficient electron conductivity can be overcome by irradiating the specimen with a pulsed YAG laser beam.

In this study, we investigated the samples of two different types; solid material of large infinite structure and discrete molecule. As polymer-like sample of infinite structure, commercially available carbon nano-tubes (CNT) were examined in view of binding state. As well defined molecules in chemistry, cationic molecules adsorbed on titania nano-crystal were examined in view of their surface reaction. In the latter case, the interaction between adsorbate and the substrate can be discussed.

II. EXPERIMENTAL

A. Instruments

The structure of the SAP with a reflectron mass spectrometer and the fabrication process of the extraction electrode are described elsewhere[1, 2]. The mass resolution of the reflectron m/Δm is better than 1000. Since the conductivities of the titania nanosheets and organic specimens are low, the field evaporation of these systems were assisted by irradiating a pulsed laser beam. (the second harmonic of a YAG laser λ = 532 nm; pulse width <5 ns; power <3 mJ/shot; repetition rate 15 Hz)

B. Specimens

Carbon Nano-Tubes (CNT)

Two samples of commercial CNTs denoted as (SL) and (S) were analyzed. (SL) CNT was multi wall CNT (MWCNT). (S) CNT was double wall CNT (DWCNT). Small lumps of CNTs were dusted on a Nichrome sheet which is coated by silver paste. The silver paste was dried by heating at 120 °C for 10 min. In the analyses of CNTs, the conventional voltage pulse was used as trigger.

Titania Nanosheet and Organic Molecules

Common forms of titanium dioxide (TiO$_2$) have the three-dimensional structure of octahedron unit, which are...
FIG. 1: Mass spectrum of (SL) MWCNT. The sharp mass peaks reflect the stable C-H bonds.

FIG. 2: Mass spectrum of (S) DWCNT. The tails indicate weak C-H bonds.

not favorable as AP sample material. In this study, ultra thin layer form of titania “Nanosheet”, which was prepared by layer-by-layer delamination process of layered form lepidocrocite[3]. The excessive electrolyte was eliminated by the cycles of dialysis and centrifugation. The nano-sheets suspension was coated on an etched tungsten tip by dipping and drying in the air bath of 150°C for 10 min. The cationic molecules, crystal violet (CV; [C25H30N3]+ = 372, chloride salt) or tetra-n-butyl ammonium hydroxide (TBA; [(n-C4H9)4N]+OH = 242+17 = 259), were coated on tungsten by immersing the etched tungsten tip to the ethanol solution of CV chloride or methanol solution of TBA and dried in the air. The CV was also adsorbed in the same procedure on the titanium oxide nano-sheets supported on tungsten tip.

III. RESULTS AND DISCUSSION

A. CNT

In our previous results, CNT grown at a laboratory and graphite (99.99% purity) contained a large amount of hydrogen but no oxygen was detected[2, 4]. Contrary, the (SL) MWCNT and (S) DWCNTs analyzed here contain a significant amount of hydrogen and oxygen as shown in Fig. 1. The ratio of the number of hydrogen atoms to the total number of detected atoms varies from 3 to more than 57% and that of oxygen from 0.4 to 12.4%. The laboratory grown CNT and graphite are thermally stable and exhibits similar mass spectra before and after heat treatment. The mass spectra of the present MWCNT changed drastically by heat treatment and the number of large clusters decreases significantly.

Contrary, DWCNT of (S) with a small number of oxygen atoms is found to be thermally stable, Fig. 2. While the number of clusters decreases with the number of clustering carbon atoms for the laboratory grown CNT and the pure graphite, the present specimens exhibits utterly different spectra with the strongest mass peak of C5, Fig.1 and C15H8, Fig. 2. The numbers of clustering carbon atoms, 5 and 18, might be related with the structure and the binding state of the CNTs. The long tail observed on the mass peak of C18Hn, to the higher mass side indicates the weak binding between carbon and hydrogen atoms[4].
**B. Titanium Oxide**

Figure 3 demonstrates the mass spectra of titania nanosheets supported on a W tip. Cs\(^+\), K\(^+\) and Na\(^+\) are the remnants cations of the starting material; the lepidocrocite form titanium oxide which is carrying cesium cations between the oxide layers, Fig. 3 (a). In this run, the analysis is extended until the ions of tungsten substrate have been detected. The alkali cations can be eliminated by cycles of dialysis and centrifugation and their mass peaks disappear as shown in Fig. 3 (b). An interesting finding is that all tungsten atoms are detected as oxidized ions, WO\(^+\), WO\(^2+\), WO\(^3+\) and WO\(^4+\), while many titanium atoms are not oxidized. This result may suggest that the oxygen atoms migrate to the substrate tungsten atoms and that the W-O binding is stronger than the Ti-O binding, Fig. 3 (a). Consequently, the ratio of the number of titanium atom to that of oxygen atoms appears to be smaller than 2:1. Another cause of the oxygen deficit may be the neutralization of field evaporated oxygen ions.

**C. Crystal Violet on Tungsten Substrate**

Figure 4 is the mass spectrum of CV molecules on a tungsten tip. Some of CV molecules are not dissociated but desorbed as molecular ions although most of them are detected as dissociated fragment ions. Masses of the fragment ions are not random but highly characteristic related with the structure of CV. No isolated nitrogen ion is detected. C\(_6\)H\(_6\)+ is detected. However, it is not the benzene nucleus because the mass peak of C\(_2\)NH\(_6\)+, 44 amu, is hardly recognizable. The dissociation may be caused by the laser beam with the wave length of 532 nm which is close to the absorption maximum of the CV molecule, 589 nm. The unique feature of this mass spectrum is in the mass difference between adjacent mass peaks, 2 amu.
Furthermore, each mass peak is fairly sharp. This implies that the carbon-hydrogen bond is fairly strong and stable.

D. TBA on Tungsten Substrate

Transparent molecule which has no absorption band in visible region should be little influenced by photo irradiation. Most TBA molecules remain undissociated and desorbed as molecular ion ($([C_4H_9]_4N)^+ = 242$), Fig. 5. TBA is cationic molecule by nature and the spectra shows that TBA desorbs to be detected with no change like alkaline cations. The tailing of the higher mass side reflects the inhomogeneity of the binding state of TBA on surface. Some TBA molecules are dissociated into tri-n-butyl fragments ($([C_4H_9]_3N + C_4H_9 = 185 + 57)$.

E. Crystal Violet on Titanium Oxide Layer

The molecular ion peak disappears and the fragmentation pattern of CV changes when the CV molecules are adsorbed on titania microcrystal supported on tungsten, Fig. 6. All of the CV molecules are dissociated by the photo-catalytic function of titanium oxide. Although the largest fragment $C_{17}N_2H_{20}$ survived, many large fragments such as $C_6NH_6$ and $C_6H_6$ also disappeared. On the other hand the number of $C_4NH_4$ ions becomes extremely large and the fragments $C_7NH_7$ and $C_6NH_6$ increase significantly. The number of hydrogen atoms shown in the mass spectra and that in the molecular structure does not agree possibly due to the attachment and detachment of nearby hydrogen atoms to or from field evaporating fragments. Contrary to Fig. 4, the mass separation between some adjacent peaks is 1 amu. Few mass peaks have a tail to the higher mass side. This implies that the carbon hydrogen bonding is weaker than that of the CV molecules on the tungsten substrate.

F. Coherence between Detected Ions

In the analyses shown above, the TOF data of each analyses are accumulated to draw histograms of mass distribution. If the AP mass data is treated as sequential record of the elements picked up in atom-by-atom manner, one-dimensional depth profile can be drawn as commonly done in SIMS analysis. In AP analysis, the electric field ionizes the surface species in the adiabatic process and the cations are emitted in the radial direction along the
electric field without being fed with the extra energy for
the desorption. Therefore, the AP technique guarantees
us spatial information in the atomic scale.

When AP is applied to metallic samples, the information
of AP can be summarized to the spatial aspect. On
the other hand, the AP results of the molecular systems
discussed here should be bearing other information. The
data of AP is a sequential record of flight time of each ion
evaporated by the application of voltage pulse or laser
pulse. The electric field is controlled so as the ratio of
ion count to number of trigger to be ca. 1:10 or smaller
by controlling the voltage. Therefore, we can say that the
extremely limited number of species are driven by the field
ionization in AP analysis to be fragmented in a step-by-
step manner and some information of the reaction process
might be extracted from the sequence of the detected ions.

In this work, the discrete molecular systems were AP
analyzed. The fragments generated from one molecule or
the fragments correlated in the sequential surface reac-
tion should be detected within a certain period of pulse
sequence. The coherence of fragment ions in the serial
records of AP may reflects the correlation between frag-
ments. To extract the coherence, the distribution of ions
detected within certain neighboring triggers was surveyed
in the whole range of mass analysis data.

Figure 7 shows the distribution of neighboring ions sur-
veyed in the AP data obtained on CV adsorbed on a TiO$_2$
nanosheet supported on a W tip. This map is drawn by
tracking the serial data of AP from the beginning to the
end by searching the key ion. When the key ion was
found, the precedent ions and the antecedent ions de-
tected within 5 triggers were picked up. The value $f(x, y)$
picted in Fig. 7 is the amount of ion count at the point
$(x, y)$. The $x$-coordinate is the mass of search key ion and
the $y$-coordinate is the mass of adjacent (precedent or an-
tecedent) ion in the data sequence. The graph (bottom)
is the conventional histogram showing the distribution of
ions. The pattern distributed symmetrical to the diag-
onal axis from bottom-left corner to top-right corner of
the map. The cross section of this mapping parallel to
FIG. 8: Mapping of the unbalanced factor surveyed in the AP data obtained on CV adsorbed on a TiO$_2$ nanosheet supported on a W tip. The color bar placed on left side of the distribution map is the scale of unbalance factor.

the $x$-axis or $y$-axis will be similar to the inset histogram beneath the mapping if the appearance of the ions is statistically random.

It was difficult to point out the difference right away between the distributions of the precedent ions and the antecedent ions displayed independently in the same way of Fig. 7. To make the visibility better, the unbalance factor defined below was calculated on CV adsorbed on a TiO$_2$ nanosheet supported on a W tip from the same AP data used in Fig. 7.

$$r(i, j) = \frac{\text{Antecedent}(i, j) - \text{Precedent}(j, i)}{\text{Antecedent}(i, j) + \text{Precedent}(j, i)}$$

The unbalance factor $r(i, j)$ varies from 1 to -1 according to the asymmetric abundance of the fragments in sequential record of ion data; the zero value of $r(i, j)$ indicates that the fragments of mass $i$ and mass $j$ appear in random manner. The values of factor $r(i, j)$ are mapped in Fig. 8 using color-scale; the pixels are painted grey where the values are zero or where no coherent ion is found. The blue or orange dots indicate that there are some unbalance between the precedent ions and the antecedent ions in the ion sequence of AP. These non-zero values (non-grey dots) distribute symmetrically from bottom-left corner to top-right corner of the map; the signs of $r(i, j)$ and $r(j, i)$ are opposite.

The ions found around 240 amu show some unbalance against the other ions, Fig. 8. The conventional histogram attached to the bottom of the map shows that the ions of ca. 240 amu is the largest fragment of CV ([$C_{17}N_2H_n]^+$). If the values of $r(i, j)$ for $i \approx 240$ are traced from bottom to top along $y$-direction, the orange colored dots are dominant in the region of $40 < i < 100$ amu. It means that the antecedent ions are superior to the precedent ions in this region which corresponds to the ions of [C$_4$NH$_4]^+$. On the other hand, in the region $j \approx 140$ amu corresponding to [C$_9$NH$_8]^+$, the precedent ions are superior to the antecedent ions against [C$_{17}N_2H_n]^+$. Though the larger fragment desorbs simply after the decomposition of CV into two or three fragments, there might be another surface processes related to the smaller fragments.
IV. CONCLUSION

The commercial CNTs analyzed here show relatively simple mass spectra compared to our previous results. The simplicity of the fragment pattern reflects the uniformity of the samples. The molecules of crystal violet are dissociated even by the laser beam, the wavelength of which is close to the absorption maximum of the molecules. The molecules are completely dissociated by the titanium oxide. The masses of the dissociated fragments are not random but highly characteristic suggesting the correlation with the structure of the molecule. Most of TBA molecules desorb as molecular ions and a small fraction of TBA molecules is dissociated. The dissociation of the organic molecules are highly characteristic exhibiting the binding states in the molecules. The AP data of molecular system contains some information of molecular reaction which can be extracted by searching the ion-ion correlation from the sequential data of AP.

Acknowledgments

This study is supported by Grants-in-Aid from the Ministry of Education and Science of Japan (No. 15310077).

[1] O. Nishikawa, M. Kimoto, M. Iwatsuki, and Y. Ishikawa, J. Vac. Sci. Technol. B 13, 599 (1995).
[2] O. Nishikawa, M. Watanabe, T. Murakami, T. Yagyu and M. Taniguchi, New Diamond and Frontier Carbon Technology 13, 257 (2003).
[3] H. Sato, Y. Hiroe, T. Sasaki, K. Ono, A. Yamagishi, J. Phys. Chem. B 108, 17306 (2004).
[4] O. Nishikawa, T. Murakami, M. Watanabe, M. Taniguchi, T. Kuzumaki and S. Kondo, Jpn. J. Appl. Phys. 42, 4816 (2003).