論文

ＴＦＴＲ黒鉛プローブ表面のＸＰＳ−ＳＩＭＳによる分析

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Surface Characterization of TFTR Graphite Probe by XPS-SIMS

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Abstract

Deposition probe measurements using a cylindrical 4D C-C composite was conducted to investigate the deposition layers on the graphite first wall of TFTR (Tokamak Fusion Test Reactor), *Princeton University*. XPS measurements revealed that the surface atomic compositions of probe areas differed from each other. This indicates that the probe surface was covered with deposits. SIMS measurements detected lithium, carbon, oxygen and deuterium. Lithium was found even at the depth ranging up to 7 - 8 µm far beyond the expected depth and/or thickness of the deposits. This suggests that Li atoms diffused to the bulk along grain boundaries of the probe. Another characteristic feature of SIMS spectra is the appearance of Li-relating signals such as M/e = 28 ($^6Li_2O$), 29 ($^6Li^7LiO$) and 30 ($^7Li_2O$), whereas M/e = 22

and 44 (^{6}LiO and ^{6}Li$_2$O$_2$) were not observed. It is concluded that the surface of the TFTR graphite probe was covered with carbon deposits containing Li, H, D and O with a trace amount of Cr and Fe from stainless steel.

1. Introduction

It has been widely recognized that wall conditioning is essential to achieve high-performance plasma confinement in a magnetic fusion device. Over the past several years, in TFTR lithium pellet injection has been used for carbon wall conditioning and has enabled the enhanced super-shot mode in which the energy confinement time is significantly extended[1]. To date lithium injection is the only wall conditioning technique that clearly affects energy confinement. It is, therefore, of considerable interest to understand the mechanism of improved confinement.

From this point of view, many efforts have been made to investigate the physics of lithium pellet injected plasmas[2,3]. On the other hand, little has been done to understand the role of lithium-painted walls interacting with edge plasmas, other than speculations that lithium might reduce the recycling of oxygen and hydrogen particles, and so on.

To obtain basic data on surface characteristics of lithium-painted walls, a cylindrical probe made of C-C (carbon-carbon) composite has been inserted into the edge region in TFTR during ohmically heated D-D confinement plasmas with lithium pellet injection. The analysis of the exposed probe has been done in a multi-institutional collaboration, including: *Princeton Univ., Sandia National Labs., Univ. of California, San Diego* and *Toyama Univ.* In this paper, the data taken at Toyama Univ. using the SIMS and XPS analysis facility at the Hydrogen Isotope Research Center will be reported in detail. The data taken from other facilities will be separately reported in the near future[4].

2. Experimental

2.1. TFTR graphite probe

Figure 1(a) shows the deposition probe used in the present work. The probe was made of 4-dimensional C-C composite (manufactured by Fiber Materials Inc.), machined into a cylinder with a diameter of 64 mm and a length of 95 mm. This was the same material as that used for the TFTR bumper limiter tiles. This probe was inserted into the TFTR boundary plasma region via a Bay-D port during D-D confinement discharges.

For the SIMS and XPS analysis, as shown in Fig.1(b), the probe was cut into disks with dimensions of about 10 x 10 x (1 - 2) mm in a glove-box. The samples cut from the probe facing the ion-drift and the electron-drift sides will be referred to as "i" and "e"-sample in the remainder of this paper, respectively.
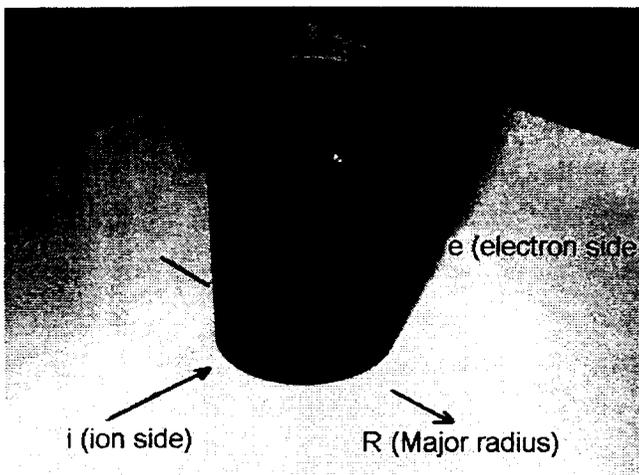

Fig.1(a). Photographic view of a cylindrical 4D C-C composite probe. Arrows indicate ion and electron drift side, and the direction of major radius from inner to outer side.

2.2. Surface Analysis by XPS and SIMS

Those samples were mounted on a rotatable stainless steel holder that could be positioned for the SIMS and XPS optics, both installed in an ultra-high vacuum chamber. To minimize the effect of residual gas adsorption, the vacuum chamber was evacuated below 1×10^{-6} Pa prior to analysis

XPS measurements were done by use of a 400 W MgKα X-ray source with the energy of 1253.6 eV. The photoelectron energy was measured with use of a cylindrical mirror analyzer (PHI 12-255). The binding energy readout was calibrated using the Au4f$_{7/2}$ peak center to be 87.3 eV as the reference[5].

Fig.1(b). Schematic drawing of surface portion of the TFTR graphite probe used for XPS-SIMS measurements.

Argon ion etching at 5 keV was done for the depth profile analysis with SIMS by use of a back-fill type ion gun. The Ar gas was purchased from Nippon Sanso Co. and the purity was 99.999%, which required no further purification. Both positive and negative secondary
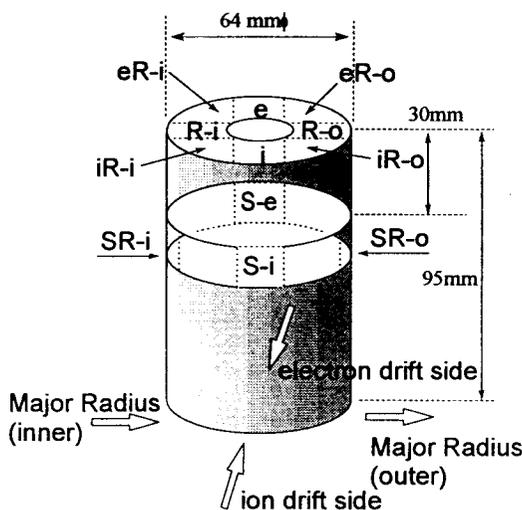
ions were analyzed to ensure a wide range of material detection, using a quadrupole mass spectrometer (Extranuclear Lab., 19 mm rod with 1.5 MHz).

3. Results and discussion

3.1. XPS analysis

Figure 2 shows a comparison of wide range XPS spectra taken from the "i" and the "e" samples cut from the probe (see Fig.1(b)). For both of the samples, the carbon (C1s) and oxygen (O1s) peaks were observed. However, as opposed to the SIMS data to be described later, the lithium peak (Li1s) is not clearly seen in these spectra, presumably due to its low sensitivity. In addition, a virgin C-C composite showed almost the same spectrum to that of "e" sample.

Shown in Fig.3 are the details of the C1s and the O1s spectra, respectively, both taken from the "i" sample. Notice that the C1s spectrum has a compound structure with the main component at 284.4 eV and a small shoulder peaking at around 285 eV. According to the literature[4], the former is indicative of 1s-electrons in carbon in the graphite structure,
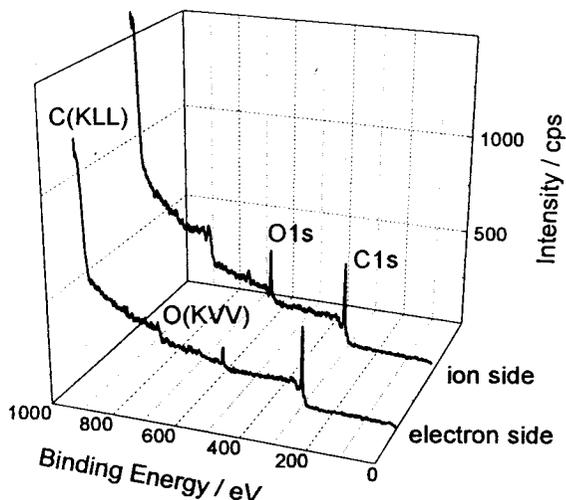
Fig.2. Wide range XPS spectra of 4D C-C composite probe exposed to TFTR boundary D-D plasma region. Samples were cut from the front surface of ion and electron drift side.
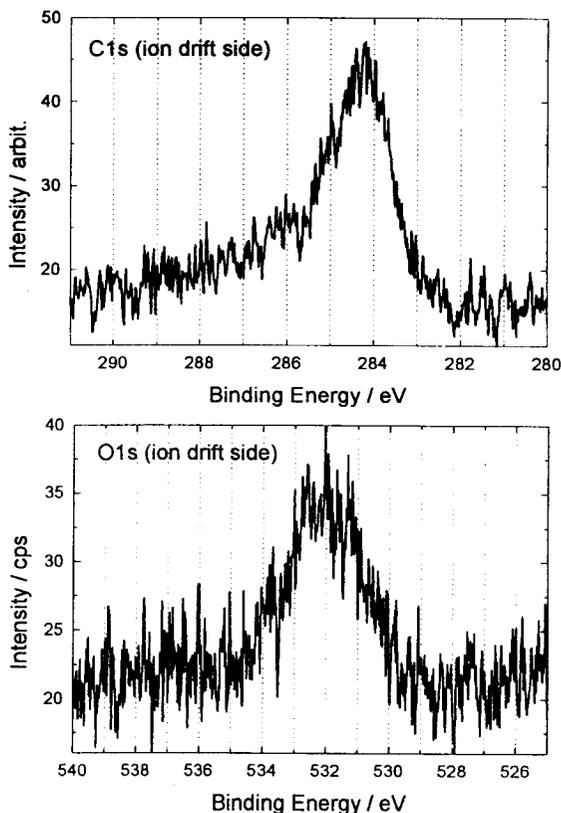
Fig.3. Narrow range XPS spectra of C1s (upperr), and O1s (lower) core electrons for the "i" sample.

whereas the latter may be related to those in carbon, chemically bound to hydrogen and/or oxygen.

The O1s peak also suggests a compound structure, having several small components in addition to the main component peaking at 532 eV. In fact, its apparent Full Width at Half Maximum (FWHM) is about 3 eV, which is over 1.5 times larger than that observed for metal oxides[6]. From the literature[5] and SIMS data to be described later, the O1s peak may be deconvoluted into small components that are related to 1s-electrons in oxygen in the form of -CO, -OH and metal-oxide.

The "e" sample showed basically the same C1s and O1s spectra as those seen for the "i" sample. From the numerical integration of peak areas, the atomic compositions was evaluated to be C : O = 84 : 16 and 87 : 13 for the "i" and the "e" samples, respectively.

3.2. SIMS measurements

Figure 4 shows the positive and negative SIMS spectra taken for the virgin 4D C-C composite graphite sample, the material used for the probe. Because of their high secondary ion emission efficiencies, the major peaks seen in the positive SIMS spectrum were impurities such as $^{23}Na^+$, $^{27}Al^+$, $^{39}K^+$ and $^{41}K^+$. The observed intensity ratio of ^{39}K to ^{41}K was about 15 : 1, which agrees well with the
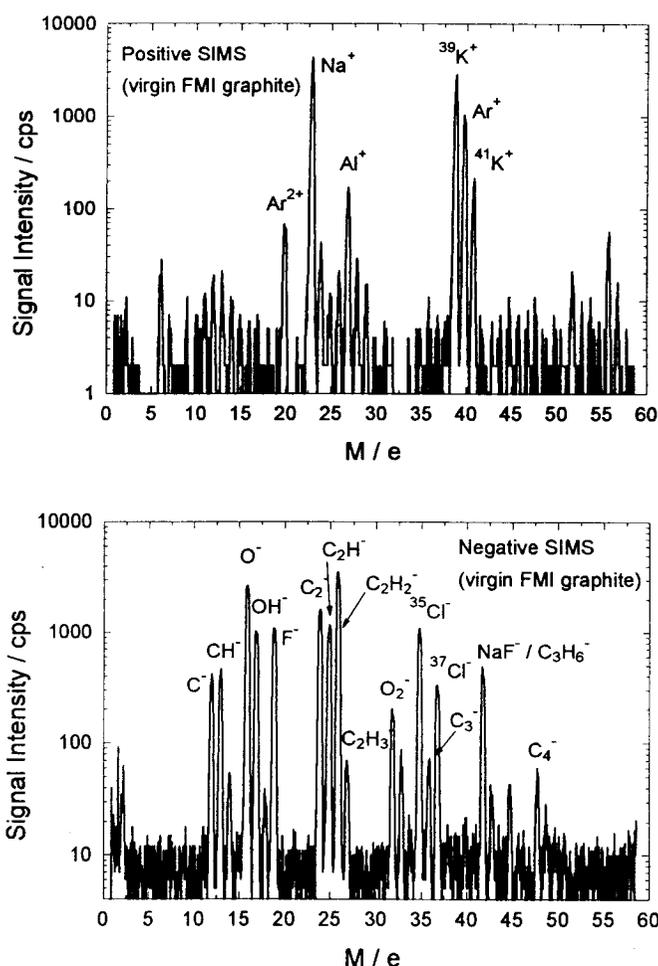

Fig.4. Positive (upper) and negative (lower) SIMS spectra of the virgin FMI graphite sample.

natural abundance ratio[7]. It indicates that observed intensity ratio of neighboring isotope peaks in SIMS spectrum could be regarded as an actual ratio on the sample. The peak at the (M/e) ratio of 40 is from Ar^+ used as the probe ions SIMS.

On the other hand, in the negative SIMS spectrum one can easily identify several predictable elements including, carbon (C), hydrogen (H) and also impurities such as oxygen (O). The peaks at the (M/e) ratios of 19, 35, 37 are indicative of fluorine (F) and chlorine ($^{35}Cl^-$ and $^{37}Cl^-$), typical additives to carbon-based materials in the manufacture processing.

Concerning the cluster species such as C_n^- and $C_nH_m^-$ in the negative SIMS spectrum for the virgin FMI C-C composite sample, data taken here were in good agreement with previous SIMS data taken for graphite[8]. In our previous data[8], $C_nH_m^-$ peaks are considered due to inherent hydrogen rather than due to adsorbed surface impurities. Thermal desorption measurements revealed that the hydrogen content in the virgin FMI C-C composite sample was estimated to be about 10^{18} [H_2-molecules/g][9], agreeing well with the reported data for different C-C composite materials[10].

Oxygen-bound species such as OH^- and O^- were also observed at high intensities for both of the virgin and the TFTR-exposed samples, indicating a large quantity of -C-OH and -C=O. One might attribute those species to H_2O and CO molecules adsorbed on the surface or to the formation of intercalation
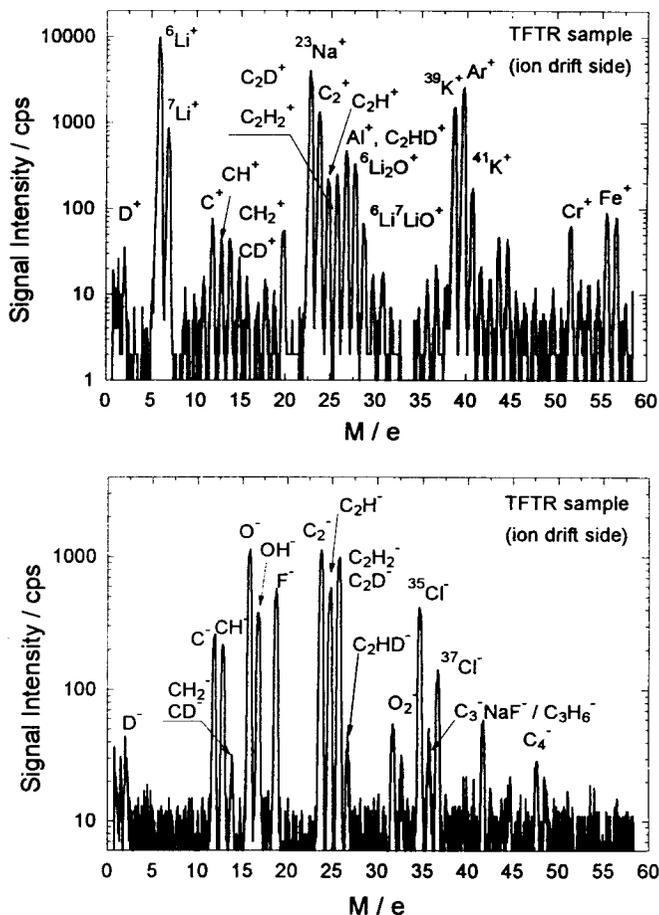

Fig. 5. Positive (upper) and negative (lower) SIMS spectra of the "i" sample.

compounds of 'graphite oxides'. The solid-state carbon oxides can be formed using a strong aqueous oxidizing agent and its stoichiometry is expressed as C_8O_2OH[11].

Figure 5 shows the positive and negative SIMS data taken from the "i" sample, respectively. Lithium (Li), deuterium (D), aluminum (Al), chromium (Cr) and iron (Fe) were identified in the positive SIMS spectrum. Clearly, Li is due to the lithium pellet injection. The probe was exposed to plasma, where 95% enriched ^6Li pellets were injected to minimize the resonance absorption of ion heating power by ^7Li. Therefore, the peaks at M/e = 6 and 7 in positive SIMS spectra are most likely ^6Li and ^7Li. The intensity ratio is about $^6Li : ^7Li = 10 : 1$ though one would expect a ratio of 20 : 1. This discrepancy is due to the recycling of ^7Li implanted from previous discharges. Although intensities of Li peaks were rather small, the "e" sample showed intrinsically the same SIMS spectra to that of the "i" sample. This finding clearly indicates the material (re-)deposition. Another sign pointing to material redeposition in the XPS data is different surface atomic composition between "e" and "i" samples. In addition, a trace amount of tritium was detected[12], presumably due to the particle recycling in the TFTR. Therefore, it is concluded that the probe was re-deposited with carbon which contains impurity, whose amount depended on the direction of the probe faced.

From the SIMS depth profile analysis, lithium was detected even at the depth ranging up to 7 - 8 μm, far beyond the expected depth from a simple deposition mechanism and a diffusion theory. Similarly to the hypothesis made for oxygen, one might attribute this deep penetration of lithium is formation of Li-intercalation compounds[11], C_6Li_{11}. It is important to note here that the positive SIMS spectrum includes a number of peaks related to oxygen-bound lithium, such as M/e = 28 ($^6Li_2O$), 29 ($^6Li^7LiO$) and 30 ($^7Li_2O$), consistent with the XPS data. As to the effect of lithium on the thermal release of inherent hydrogen, one predicts that Li would enhance the recombination. This has been observed in the TDS data[9]. Finally, the cross-examination of the SIMS-XPS data has provided a support for the hypothesis that deposited lithium is in the form of oxide. It is well known that lithium can react with oxygen and water vapor in the following manner:

$$4Li + O_2 \quad \rightarrow \quad 2Li_2O \tag{1}$$

$$2Li + 2H_2O \quad \rightarrow \quad 2LiOH + H_2. \tag{2}$$
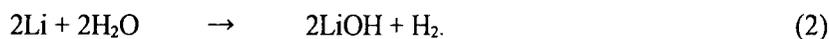
Reaction (2), however, probably does not apply in the present study, because OH⁻ was seen in the SIMS data taken from both of the virgin and the plasma exposed samples, meaning that OH⁻ is not characteristic for the Li-painted graphite surface. Therefore, one assumes that deposited lithium is bound to oxygen.

4. Conclusions

Only carbon (C1s) and oxygen (O1s) peaks were observed for the TFTR graphite probe by XPS measurements. No lithium peak (Li1s) was detected because of its very low sensitivity against XPS. The surface atomic compositions of "i" and "e" samples were evaluated as C : O = 84 : 16 and 87 : 13, respectively. From the shouldered C1s peak, it is concluded that there are two different chemical states of carbon atoms: namely, graphite and impurity-containing carbon deposits. On the other hand, the observed O1s peak suggests that it consists of -CO, -OH and metal-oxide type oxygen.

The appearance of intense OH⁻ and O⁻ peaks in SIMS spectra indicates that a large quantity of -C-OH and -C=O were contained in both of the virgin composite and the TFTR graphite probe. One plausible interpretation of such observations is the formation of intercalation compound of 'graphite oxide', C_8O_2OH. SIMS measurements also revealed that lithium is distributed far beyond the expected depth from the surface (7 - 8 μm from the surface). The results could be explained, assuming that Li diffused thermally along grain boundaries or channels between the layers of lamellar structure of graphite to form Li-intercalation compound, C_6Li. In either case, Li atoms would work as surface trap sites of hydrogen and hence thermal desorption behavior of hydrogen and/or its isotopes is anticipated to be altered. Another characteristic feature of SIMS spectra is the appearance of Li-oxide signals such as M/e = 28 ($^6Li_2O$), 29 ($^6Li^7LiO$) and 30 ($^7Li_2O$), whereas M/e = 22 and 44 (^6LiO and $^6Li_2O_2$) are not found.

References

1. J.T.Terry, E.S.Marmar, R.B.Howell, M.Bell, A.Cavallo, E.Fredrickson, A.Ramsey, G.L.Schmidt, B.Stratton, G.Taylor, M.E.Mauel, Review of Scientific Instruments, **vol.61**, No.10 part 2 (1990) 2908, (8th Topical Conference on High Temperature Plasma Diagnostics, Hyannis, MA, USA, 6-10 May 1990.)

2. D.K.Mansfield, J.D.Strachan, M.G.Bell, S.D.Scott, R.Budny, E.S.Marmar, J.A.Snipes, J.L.Terry, S.Batha, R.E.Bell, M.Bitter, C.E.Bush, Z.Chang, D.S.Darrow, D.Ernst, E.Fredrickson, B.Grek, H.W.Herrmann, K.W.Hill, A.Janos, D.L.Jassby, F.C.Jobes, D.W.Johnson, L.C.Johnson, F.W.Levinton, D.R.Mikkelsen, D.Mueller, D.K.Owens, H.Park, A.T.Ramsey, A.L.Roquemore, C.H.Skinner, T.Stevenson, B.C.Stratton, E.Synakowski, G.Taylor, A. von Halle, S. von Goeler, K.L.Wong, S.J.Zweben, Phys. Plasamas, **2** (1995) 4252.

3. D.K.Mansfield, K.W.Hill, J.D.Strachan, M.G.Bell, S.D.Scott, R.Budny, E.S.Marmar, J.A.Snipes, J.L.Terry, S.Batha, R.E.Bell, M.Bitter, C.E.Bush, Z.Chang, D.S.Darrow, D.Ernst, E.Fredrickson, B.Grek, H.W.Herrmann, A.Janos, D.L.Jassby, F.C.Jobes, D.W.Johnson, L.C.Johnson, F.M.Levinton, D.R.Mikkelsen, D.Mueller, D.K.Owens, H.Park, A.T.Ramsey, A.L.Roquemore, C.H.Skinner, T.Stevenson, B.C.Stratton, E.Synakowski, G.Taylor, A von Halle, S. von Goeler, K.L.Wong, S.J.Zweben, Phys. Plasmas, **3** (1996) 1892.

4. Y.Hirooka, K.Ashida, H.Kugel, M.Bell, M.Hara, S.Luckhardt, M.Matsuyama, D.Mueller, C.Skinner, D.Walsh, W.Wampler, K.Watanabe, to be presented at the 13th Int. Conf. on "Plasma-Surface Interactions in Controlled Fusion Devices", San Diego, California, USA, May 18-22, 1998.

5. G.E.Muilenberg, "Handbook of X-ray Photoelectron Spectroscopy", Perkin-Elmer, 1979.

6. K.Ichimura, K.Ashida and K.Watanabe, J. Vac. Sci. Technol., **A3** (1985) 346.

7. R.C.Weast and M.J.Astle, "CRC Handbook of Chemistry and Physics", 62nd edition, CRC press, Inc., 1981-1982.

8. K.Ashida, K.Kanamori and K.Watanabe, J. Vac. Sci. Technol., **A6** (1988) 2232.

9. unpublished data.

10. Y.Hirohata, M.Okita, T.Hino and T.Yamashina, Carbon, **32** (1994) 280.

11. F.A.Cotton and G.Wilkinson, "Advanced Inorganic Chemistry", 5th edition, John Wiley & Sons, 1988.

12. M.Hara, K.Ashida, M.Matsuyama, K.Watanabe and Y.Hirooka, in this Annual Report of Hydrogen Isotope Research Center, Toyama Univ.