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**X-RAY PHOTOELECTRON SPECTROSCOPY
(XPS) STUDIES OF OXYGEN AND CARBON
BONDING TO TOKAMAK WALLS**

BY

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X-ray Photoelectron Spectroscopy (XPS) Studies of Oxygen and Carbon Binding to Tokamak Walls*

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ABSTRACT

The binding energies of surface atoms of stainless steel samples exposed to hydrogen plasma discharges in PDX are measured using X-ray photoelectron spectroscopy. After glow discharges only one O_{1s} line is completely shifted to a higher binding energy which is an indication of the formation of hydroxides. The Fe_{2p} lines show a partial reduction of iron. After high power discharges, the oxygen concentration increases and the binding energy of the deposited O atoms corresponds to a metallic oxide. The deposited limiter material Ti is also completely oxidized. For both kinds of discharges the binding energies of Cr_{2p} and C_{1s} remain essentially unmodified.

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1. Introduction

The occurrence of chemical reactions on the metal wall of tokamaks has become evident in the recent years by the observation of molecular species in the residual gas [1,2,4,]. When used in cleaning procedures, the chemical reactions provide very efficient methods to remove surface contaminants such as C, S, Cl, and O [3,4,5]. Obviously these chemical processes are not restricted to cleaning procedures but also occur during and between normal discharges. The processes involved can be grouped into three steps which are similar to those found for plasma-etching [6].

- (1) The reactive species (H, D, H^+, D^+) are adsorbed and penetrate the surface layer, according to their energy.
- (2) Molecules are formed in the surface layer.
- (3) Some of these molecules can be removed by desorption.

This can be either a spontaneous or an induced (thermal electron, ion, photon) desorption.

The released molecules are eventually pumped out during glow discharge conditioning (GDC), but they contaminate the plasma during high power discharges (HPD). Up to now the elemental composition of the surface has been investigated by Auger Electron Spectroscopy (AES) in a number of devices and are reviewed in [7, 19,20]. Because of the complexity of the samples, no absolutely reliable conclusions concerning the chemical state of the surface could be reached by AES. A first attempt to perform in situ investigations of chemical bondings was done using SXAPS [8]. However

this so-called kinds of Appearance Potential Spectroscopy or Disappearance Potential Spectroscopy, provides complex experimental distributions and their sensitivity varies drastically for different elements. The most adequate method seems to be X-ray photoelectron Spectroscopy (XPS) which is well suited to study complex surfaces and reveals both the elemental composition and the binding energies. The aim of this paper is to demonstrate the usefulness of XPS applied to the study of plasma etched silicon and to present and discuss results obtained from analysis of stainless steel samples exposed to Gaseous EPD plasma. We remark in light of possible molecular reactions.

2. Experimental Arrangement

All the analyses are performed using the Surface Analysis Station (SAS) which is attached to PDX. A detailed description of the equipment is given in [9]. The XPS analyses are performed using a hemispherical LNA with retarding grids (Physical Electronics, model 400). The pass energy is set to 50 eV and corrected to the electron work function $\phi = 1.7$ eV measured on the Au4f lines. The samples are exposed to the Mg-K α photons produced by an X-ray tube run at 17 kV, 20 mA. The calibrations of the binding energies (BE) are done using a graphite (C 1s, BE = 285.4 eV) and a gold sample (Au 4f $_{7/2}$, BE = 83.95 eV). A 4 keV argon ion beam of low current density (1 to 5 $\mu\text{A} \cdot \text{cm}^{-2}$) is used for sputter-cleaning and reduction of oxides.

III. Results and Discussions

The sample, which is the transport tape of the SAS, is made of 304 stainless steel, which is also the major constituent of the PDX-vessel.

3.1. Initial State.

Like all vacuum components of PDX, the sample tape is first chemically cleaned [10]. The resulting major surface impurity is carbon.

Fig. 1 curve a) shows that the BE of Fe 2p_{3/2} is characteristic of a mixture of Fe^{II} and Fe^{III} having BE of 709.7 and 711.2 eV respectively [11]. After Ar⁺ ion bombardment with a fluence of only about $6 \cdot 10^{-4} \text{ C} \cdot \text{cm}^{-2}$ this oxide layer is reduced to Fe_{II} (curve c). This modification is in agreement with observations by other authors [11,12,13]. After longer sputtering times at a fluence of about $1 \cdot 10^{-2} \text{ C} \cdot \text{cm}^{-2}$, the oxide layer has been partly removed and the Fe⁰ state appears at 707.0 eV (curve d) [11,14].

Fig. 2 shows the behavior of oxygen. Initially (curve a) the O_{1s} line consists of two components at 529.8 and 531.5 eV. These components are assumed to correspond to oxide and hydroxide binding respectively and a very similar line shape is observed for Fe OOH [11]. This splitting of the O_{1s} line is also observed on naturally passivated Co metal foils [15] and for similar stainless steel [12]. Like the Fe^{III}, the hydroxide line is very sensitive to Ar⁺ ion bombardment and disappears (curve c) at fluences of $\sim 6 \cdot 10^{-4} \text{ C} \cdot \text{cm}^{-2}$. The remaining line

corresponds to the oxide binding state. The $C_{2p3/2}$ line, also depicted in Fig. 2, is initially weak (curve a). After removal of the C-contamination layer, it is well developed at a BE of 284.6 eV. The same BE value is found in [16] for a C_{2p} film grown on a Cr (111) surface. This line remains unaltered at thicknesses as high as $1 \cdot 10^{-2}$ cm and in contrast with Fe, it is not affected by the glow discharge.

Fig. 3 (curve a) shows the initial state of carbon. The spectrum consists of a major peak at a BE of 284.6 eV which is identical to that of C in graphite (curve c) [14] and of a smaller satellite at 287 $\pm$ 1 eV. This satellite is located at higher binding energy and thus may correspond to hybridization [14].

2. Effect of Glow Discharge Conditioning (GDC).

The GDC procedure is described in [14] and was performed with argon. The sample surface is subjected to continuous bombardment by H^+ and H^- over long periods (up to several hours). The evolution of the Fe_{2p} level are shown in Fig. 4 and are by comparison with the initial state. The Fe^{II} state (with a small Fe^{III} satellite [11]), and Fe^0 is also observed. The appearance of Fe^0 could be understood as the result of the removal of the C contamination layer by the discharge, thus allowing the detection of bulk Fe^0 below the oxide layer. However, Fe^0 is not observed after the Ar bombardment (curve c) which was sufficient to remove the carbon contamination layer. Thus, the presence of Fe^0 has to be the result of a partial reduction of the oxide layer.

The O_{1s} line after GDC shown in Fig. 2 curve b, now consists of the hydroxide component only. The Cr_{2p} line remains again unchanged.

The C_{1s} line is reduced in intensity by a factor of five and shows a complex structure. In addition to the two features observed initially, new satellites are found at higher BE (292.8 and ~295.5 eV) and lower BE (~283.5 eV).

3.3. Effect of High Power Discharges (HPD).

The sample tape was exposed to HPD run of 30 discharges with the following parameters: $B_t = 2T$, $I_p = 340$ kA, $T_e = 1.2$ keV, $\bar{n}_e = 2.5 \times 10^{13} \text{ cm}^{-3}$ and pulse length of ~1s. During such discharges metal is released from the limiter, made of titanium, by arcing, evaporation, and sputtering [7]. Ti is ionized by the plasma, transported along the magnetic field lines and re-deposited over the plasma vessel. The nature of such deposits is shown in Fig. 4 where the O_{1s} and Ti_{2p} transitions are plotted. *The surface was previously cleaned by exposure to (H_2) glow discharge and was free of Ti (curve a). After exposure to the HPD, oxygen had been deposited, but only in the form of oxide (curve b), and Ti was easily observed. For comparison, several BE of $Ti_{2p3/2}$ are indicated as given in [18]. These BE are referred to the O_{1s} line. The comparison makes clear that no Ti^0 is observed, all titanium atoms are chemically bound. If we rely on the BE calibrations, the most abundant oxide is Ti_2O_3 , and TiO is also observed, but not TiH . The calibration used in [18] is different from ours, hence, an uncertainty of ~1 eV may affect the BE values and the Ti_{2p} line could be interpreted as a mixture of Ti_2O_3 and TiH .*

The shape and position of C_{1s} line remain essentially unchanged except for a small shift of ~ 0.5 eV towards higher BE. No evidence of carbide formation was found.

IV. Conclusion

The presented observations underline the importance of chemical effects in plasma-wall interactions and demonstrate the usefulness of XPS for such investigations.

The effects of GDC are (1) the efficient removal of the carbon contamination layer. The remaining carbon is still a graphite-like C, but shows several satellites which are not yet explained; and (2) the hydrolysis and partial reduction of the Fe oxide layer as shown by the complete shift of the O_{1s} line to higher BE, by the disappearance of Fe^{III} and by the appearance of Fe^0 . The chromium oxide is left unaffected. These observations suggest that the oxygen removed during GDC is via hydrolysis of Fe oxides. The hydrogen is evidently introduced in the surface with sufficient energy to induce chemical reactions different from those observed under equilibrium conditions. Possibly, the formation of hydroxides, $Fe(OH)_x$, is followed by that of aquo iron complexes (i.e. $Fe(H_2O)_6$, existing in some alums, from which H_2O can be desorbed.

The effects of HPD are quite different because the surface is oxidized by the discharge and the limiter material (Ti) is deposited in an oxide state. Oxygen rather than hydrogen seems to play the dominant chemical role during HPD.

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Fig. 1. Iron 2p_{3/2} photoelectron line. (a) - initial surface, (b) - after GDC, (c) and (d) - after Ar⁺ bombardment.

Fig. 2. Oxygen 1s and Chromium 2p_{3/2} photoelectron lines. (a) - initial surface, (b) - after GDC and (c) - after Ar⁺ bombardment.

Fig. 3. Carbon 1s photoelectron line. (a) - initial surface, (b) - after GDC and (c) - graphite.

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1. O 1s peak at 533 eV
2. C 1s peak at 285 eV

3. O 1s peak at 533 eV

4. C 1s peak at 285 eV