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XPS study of the process of oxygen gettering by thin films of PACVD boron

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Abstract

Numerous collector samples have been exposed in the TdeV tokamak, either to plasma assisted chemical vapor boronization only, or to boronization plus tokamak power discharges. They have been analyzed by X-ray photoelectron spectroscopy (XPS) in order to characterize and better understand the process by which the boron-rich film getter ambient oxygen. It was found that the state of oxidation of the samples after boronization is the most reliable predictor of subsequent machine performance. The gettering capacity is high, on the order of 10^{21} O/m^2, and affects a surprisingly thick layer (~100 nm), but the oxide always remains substoichiometric (with a formula BO_x, $x < 1$). The oxidation is clearly activated by the plasma, during both glow discharge deposition and power discharges, but in this respect the latter are much more effective than the former. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Plasma assisted chemical vapor deposition (PACVD) of boron-rich thin films on tokamak walls has led to remarkable improvements in operational performance ever since its demonstration on TEXTOR [1] and its adoption on practically all tokamaks. In particular, boronization has considerably reduced the oxygen impurity content of the plasma, through a gettering reaction between ambient oxygen and deposited boron, leading to oxygen 'burial' in the film as a solid oxide.

The process itself has not been studied in great detail previously. In the TCA tokamak, Hollenstein et al. [2] found appreciable oxygen (7–18 at.%) trapped in fresh B/C films deposited at room temperature by a He/B_2H_6/CH_4 glow discharge. In TEXTOR, von Seggern et al. [3] found essentially no O in similar films deposited at 150°C; however, O was found to be collected together with B on carbon probes inserted normal to field lines during subsequent tokamak shots [4]. In laboratory simulations, Zehringer et al. [5] studied the oxidation of B and B_4C by molecular O_2 and O^+ ions, and observed gettering of residual oxygen during ion carbidization of boron. Yamage et al. [6] and Noda et al. [7] measured the gettering capacity of B, B/C and B/N films in the presence of He/O_2 glow discharges.

In this paper we report an X-ray photoelectron spectroscopy (XPS) study of boron film oxidation, both during deposition itself and during power discharges on the TdeV tokamak. Many more details, such as spatial asymmetries in deposition, erosion and redeposition, are to be found in Ennaceur [8]. Although such details vary considerably among tokamaks with different magnetic geometries, wall materials, type and level of auxiliary plasma heating, etc., the basics of the chemical processes taking place in the films are undoubtedly the same in all machines. The results reported herein are thus, hopefully, of general interest.

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2. Experimental details

2.1. Machine

At the time of these experiments, TdeV was a double-null poloidal divertor tokamak with triplets of internal coils, major radius 0.87 m, minor radius 0.27 m, plasma volume 1 m^3. The 4 m^3 non-bakeable vacuum chamber was made of stainless steel with an Inconel liner, the divertor tiles and guard limiters of graphite (CL 5890PT). A number of vacuum seals were made of viton. Pumping relied on two turbomolecar pumps (2000 l/s each) and liquid helium cryosorption pumps (total of ~10 000 l/s for water). The base pressure was $\sim 1 \times 10^{-5}$ Pa, and the residual gas consisted of water, hydrogen isotopes, carbon oxides and hydrocarbons. An original feature of TdeV was the capability of biasing the divertor plates up to several hundred volts. The plasma was heated either ohmically (typical current 200 kA, $q \sim 3$), or by RF waves at the lower hybrid frequency (3.7 GHz, $\leqslant 0.8$ MW). Typically, 30 to 60 one-second deuterium power discharges were performed per day, 3 days a week.

2.2. Wall conditioning and boronization

After a period at atmospheric pressure, the walls were first cleaned for days or weeks by deuterium and/or helium dc glow discharges (GD). Next a film of boron nominally 100-nm thick was deposited using a GD in a mixture of deuterated diborane B_2D_6 (5%) and He (95%) at a total pressure of ~1 Pa (gas flow 180 sccm). Only turbopumping was used during boronization of course. The dc GD was sustained by applying ~350 V through a current regulated power supply to two diametrically opposed anodes inserted deep into the torus, assisted by 2.45 GHz microwaves to increase ionisation, giving an average current density of ~10 μA/cm^2 on the wall which acts as the cathode. These conditions give dense films that are mechanically and chemically stable even when deposited at room temperature [9]; the films did not peel off or change color after storage in air or in vacuum (1 Pa) for long periods, indicating no change in thickness or refractive index [10]. Boronization was repeated almost every week of operation. Frequent He GD conditioning was applied, either for a few minutes between shots, or for longer periods as needed, to exhaust wall hydrogen (deuterium).

2.3. Collector samples

Two types of Inconel collector samples have been analyzed by XPS after exposure in the tokamak. First, short term samples (STS) could be inserted through a vacuum lock for as little as one shot or only during boronization. They were positioned near the midplane at the same major radius as the liner. Second, 14 toroidally distributed long term samples (LTS) were attached to the liner near the midplane, whenever the vacuum chamber was opened, and retrieved at the next opening. The samples were generally transported in an argon filled plastic bag and analyzed overnight by XPS and other means (Auger electron spectroscopy, scanning electron microscopy), or stored in a primary vacuum (~1 Pa) for a few days before analysis. Some early samples were transfered in a 'vacuum suitcase' ($\sim 10^{-4}$ Pa) but since only minor surface oxidation was found on samples shortly exposed to air, this cumbersome and time consuming operation was discontinued (one of our goals was to give immediate feedback to tokamak operators).

2.4. XPS analysis

High resolution (0.4 eV) photoelectron spectra and depth profiles were acquired using an ESCALAB 220i-XL, with a monochromatic Al Kα (1486.6 eV) source and a 5 keV argon ion gun. The base vacuum of this system is in the 10^{-8}–10^{-9} Pa range and is equipped with a double vacuum lock for sample introduction; high purity argon is used for depth profiling. For quantification, standard sensitivity factors provided by the instrument manufacturer were used. For the depth scale, standard sputtering yields were used, with an atomic density of 5×10^{28} m^{-3} [3,11]. Pure boron, carbon, B_2O_3 and B_4C samples were available as references. In order to eliminate the effect of surface charging the binding energy scales were always referenced to the C 1s line of graphitic carbon. Our main interest is the B 1s line at 187.7 eV. It shifts up by 0.5 eV in B_4C (while the C 1s line shifts down by 1.8 eV); in B_2O_3, the B 1s chemical shift is very large and equal to +5.8 eV with respect to pure B (in accordance with the large value of the bond energy, 806 kJ/mol [12]).

Upon inspection of the spectra, such as in Fig. 1, it became evident that the B 1s line was too broad to be

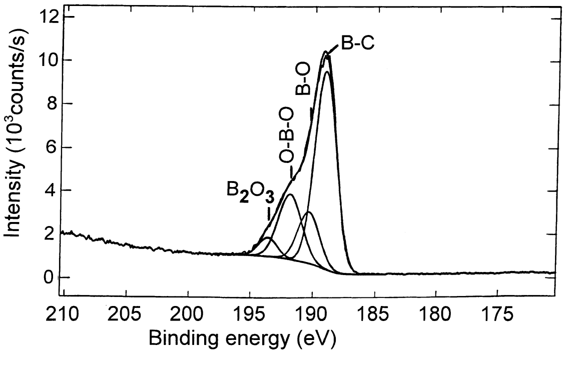

Fig. 1. Deconvolution of the B 1s line of a freshly boronized sample.

Table 1
XPS determination of the chemical composition and thickness of 10 fresh boronization layers deposited on different occasions during one year of operation

Sample #	B (at.%)	C (at.%)	O (at.%)	O (10^{20} m^{-2})	Thickness (nm)
1	82	8	6	5	113
2	87	7	5	2	52
3	75	16	7	13	247
4	49	23	26	14	72
5	60	22	17	7	55
6	76	13	9	6	92
7	85	6	8	4.6	77
8	77	6	16	10	88
9	84	6	7	7	138
10	84	5	9	8	123

described by a mixture of stoichiometric oxide and carbide (plus, perhaps, unbound B). The line shows a very wide tail on the high binding energy (oxidic) side. We hypothesized [8], therefore, that the films were composed in large part of non-stoichiometric oxides and assumed three equally spaced subpeaks, shown in the figure, corresponding to a B atom bound to one, two or three O neighbors, respectively, the last coinciding with the nominal B_2O_3 peak. Zehringer [5] has found similar line shapes in some cases, while Wienhold [4] has observed a narrow peak at 191 eV corresponding to our 'B–O'.

3. Film oxidation during deposition

3.1. Experiment; general composition

In the course of a year, during which the chamber was vented a first time for 3 days and a second time for 2 months, a total of 10 boronizations were investigated by way of STS insertion just before boronization and removal immediately after.

The sample compositions are shown in Table 1. Note that hydrogen isotopes, undetected by XPS and unaccounted for here, are also undoubtedly present at a level of tens of % [3,13]. The depth profiles show that the composition is uniform (until the substrate is reached), indicating that the oxygen is gettered at a constant rate as the film grows, not unlike other results [2,5]. Samples #4 and #5 were obtained immediately after the 2 month vent. Though not saturated in the sense of having a stoichiometric B_2O_3 composition, these samples contain, probably not coincidentally, nearly the same total oxygen ($1.3–1.4 \times 10^{21}$ O/m^2) as the saturation ($1.2–1.5 \times 10^{21}$ O/m^2) found in laboratory experiments with PACVD boron films subsequently exposed to O_2/He glow discharges [6,7]. Similarly, sample #8 was obtained following an attempt to recover favorable operating conditions by boronizing after an episode of disruptive high power RF discharges. Saturated films cannot getter more oxygen, and not surprisingly, conditions still proved to be unsatisfactory in either of these two cases. We have found that quick surface analysis (by Auger electron spectroscopy) was a more reliable indication of the adequacy of boronization than simple residual gas analysis and have used it systematically thereafter to determine whether more and/or different conditioning was required. Finally note that a high oxygen content is frequently correlated with a high carbon content; this may due to chemical sputtering of carbon by oxygen followed by C redeposition (the 'CO vicious circle'), and to direct gettering of CO and CO_2 by the growing film from the residual gas.

3.2. Nature of the oxide

A separate boronization experiment was performed with a substrate heated at 120°C. The resulting film contained the least C and O. This fact confirms the beneficial effect of higher temperatures on the purity and stability of plasma deposited boron films [9,14,15]. The B 1s line of this sample was narrow and practically coincided with that of pure boron. For this reason we have used it as a reference. It is shown in Fig. 2 together with the B1s lines for sample #4, just mentioned in Section 3.1, and sample #10, obtained under excellent operating conditions at the end of the campaign (an intermediate case with 'typical' conditions was shown in Fig. 1). The line for sample #10 is seen to consist of a narrow peak (a mix of 'pure' [2] and 'carbidized' B), and a relatively weak but wide oxidic tail. For sample #4, on the contrary, the

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[2] We have found no data regarding the chemical shift induced by B–H bonds; the strength of this bond (338 kJ/mol) being less than that of the C–B bond (448 kJ/mol) [12] and nonpolar, the shift is probably small and undetectable in the present case.

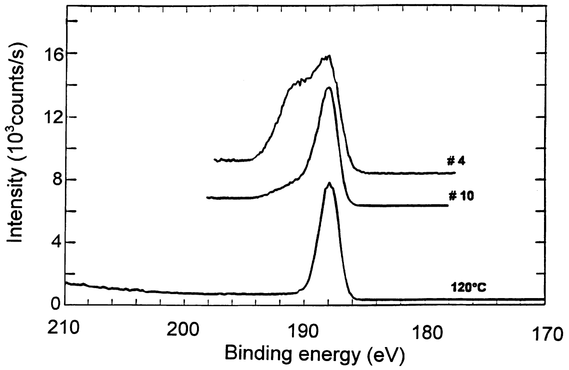

Fig. 2. B 1s lines for freshly boronized samples #4 and #10, and a reference sample boronized at 120°C. The quasi oxygen-saturated sample #4 indicates improper conditions for operation, whereas sample #10 indicates excellent conditions.

oxides dominate but, as noted, true saturation as B_2O_3 did not take place.

4. Oxidation during high power tokamak discharges

4.1. Experiment

In order to avoid the difficulty of interpreting the cumulative effects of long experimental campaigns, a special experiment was performed. LTS's were installed, the chamber was closed, conditioned by 12 days of He GD, and boronized, and finally only two days of power discharges followed before recovering the samples. This occasion was the first where deuterated diborane was used in TdeV rather than trimethylboron [16]. During boronization, a STS was inserted through the vacuum lock; this sample is taken as a reference and is considered to be representative of the state of the wall before the power discharges; indeed its composition is similar to that of the typical non-saturated boronized samples discussed in the previous section (compare 'ref'of Fig. 3 with '#10' of Fig. 2). The first day of power discharges consisted of 25 ohmic plasmas at an electron density of 2.5×10^{19} m^{-3}, and with negative biasing of the divertor plates. The second day consisted of 21 discharges at the same density but with various levels of RF power applied (no biasing).

4.2. Results

The B 1s line for several of the LTS's and the reference (STS, only boronized) are shown in Fig. 3. Obviously, the LTS's are already very strongly oxidized on the surface after 46 tokamak shots only. Depth profiles were not acquired; it is supposed that there is underneath the surface a remaining capacity for oxygen gettering because TdeV can normally operate for ~100–200 shots before conditions degrade. (Nevertheless, this is rather short and reflects the relatively poor vacuum conditions of this unbakeable chamber.) The very existence of this underlying capacity is remarkable; it is consistent with Noda's evidence [7] for a ~100-nm thick 'oxidable layer' in PACVD boron exposed to a He/O_2 GD. Also note the wide discrepancies between different toroidal locations, although all LTSs are at the same minor radius. Since the seemingly more 'active' parts of the wall saturate rapidly, the gettering capacity of other parts remains unused, with a loss in efficiency. As an example, the deconvolution of the B 1s line for one of the most heavily oxidized samples is shown in Fig. 4. The most abundant species is 'O–B–O'. A third bond is possibly made with a H(D) atom; indeed, boronization layers contain 20–30 at.% of H(D) after exposure to tokamak plasmas [13]. But B_2O_3 is definitely not dominant.

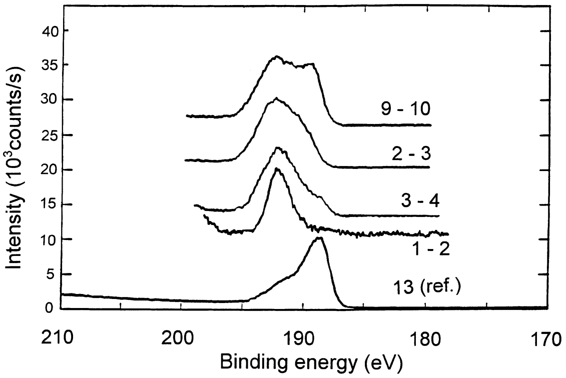

Fig. 3. B 1s lines for several samples located at different toroidal positions (identified by the diagnostic bay numbers between which they are located), after one boronization followed by 46 tokamak shots; the reference is a freshly boronized sample.

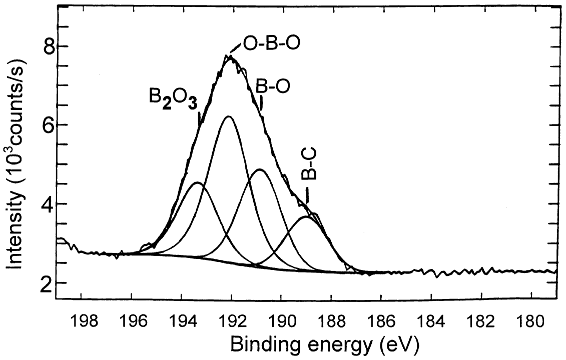

Fig. 4. Deconvolution of the B 1s line for the sample located between bays 3 and 4.

5. Discussion and conclusion

(1) Why is the oxide non-stoichiometric? In the literature, B_2O_3 was reported to be neatly synthesized only in the case of prolonged bombardment (>30 min, current unknown) of pure B and B_4C with 400 eV O^+ ions [5]; interestingly, for shorter bombardment times, wide oxidic tails similar to ours appeared in their XPS B 1s spectra. On tokamak collector probes in TEXTOR [4], co-deposited B and O apparently formed an oxide characterized by a surprisingly narrow peak at 191 eV, interpreted as B bound to a single O atom in our scheme. Whether during deposition or during tokamak shots, plasma particles are deposited at random and bonds between new neighbors are similarly established at random. The formation of the stoichiometric oxide (with possibly phase precipitation) is thermodynamically favored by the very large bond energy compared to competing bonds, i.e., 806 kJ/mol for B–O, 448 kJ/mol for B–C, 338 kJ/mol for B–H and 297 kJ/mol for B–B [12]. However, it requires overcoming energetic, entropic and kinetic barriers. Apparently, thermal agitation, even assisted by plasma particle impact, is generally insufficient for this purpose.

(2) How is subsurface ($\sim$100 nm) oxidation possible? This is puzzling in view of the fact that oxygen ions with a few hundred eV of energy only penetrate a few nanometers in matter and that the atomic mobility is apparently reduced, according to (1) above. However, one must make distinctions. Formation of B_2O_3 implies relative motions between closely packed neighbors so as to break existing B–H(D) and B–C bonds and to position the B and O atoms at the right steric angles; this clearly involves severe energetic and entropic barriers. In contrast, diffusion in depth may only be limited by kinetics if it takes place on internal surfaces. Typical PACVD films (a-C, a-Si, etc.) are nanoporous.

Another possibility could be atomic mixing through erosion/redeposition. It would require that roughly 100 nm of wall material be eroded and redeposited during the experiment. Besides the fact that 100 nm of erosion is an order of magnitude larger than any reasonable estimate for 46 discharges, this possibility is further weakened by the observation of net erosion (little redeposition) on LT wall samples [8].

(3) Why is oxidation more pronounced under 46 s of tokamak plasma than under 2 h of glow discharge? Indeed, based on the confinement time (10 ms) and the plasma density, the total wall fluence during the 46 discharges is at most on the order of 10^{21} m^{-2}; moreover, this estimate neglects the fact that the greater part of the fast particle flux flows to the divertor. On the other hand, based on the discharge current and its duration, the total ion fluence on the wall during boronization is on the order of 10^{22} m^{-2}. This is at least an order of magnitude larger than the wall fluence during the 46 shots. In both cases, for the numbers to make sense, most of the gettered oxygen must come from the ambient gas (or maybe neutral radicals) rather than from plasma ions, which are too few. Since boron is inert at room temperature in the presence of molecular oxygen [5] or water, the oxidation process must be activated by plasma impact. The relative degrees of oxidation under the two types of plasma thus imply that the tokamak-type discharges are more effective 'oxidation activators' than the He/B_2D_6 GD, by at least an order of magnitude. This is surprising because the walls have little direct interaction with the hot plasma, from which they are magnetically insulated. They interact with the so-called scrape-off layer. Typical SOL plasma temperature and density at the wall radius are $T_e \sim$ few eV , $n_e \sim 10^{18}$ m^{-3}, whereas for the GD they are respectively, $\sim$1 eV, 10^{17} m^{-3}. It is not evident that these differences are significant enough to explain the results. In addition, the glow discharge features a 350 V cathode drop, which accelerates the ions to the corresponding energy, a fact that would enhance its activation potency. The tokamak plasmas, for their part, bombard the walls with charge-exchange deuterium neutrals, with energies up to $\sim$1 keV, and a copious flux of X and UV radiation, on the order of 10–100 kW/m^2, depending on plasma heating and other conditions. Which of these factors is the most significant cannot be determined without a reliable chemical model and a precise knowledge of all particle fluxes.

In summary, we have found informative and reliable correlations between the composition of boronization layers and the wall preparedness for power discharges. We propose that quick surface analysis before operation would be well worth the effort, given the operating costs of large tokamaks. The boron film getters oxygen from the residual gas during deposition and during tokamak power discharges. A favorable aspect of the process is that a rather thick layer ($\sim$100 nm) with a capacity of $\sim 10^{21}$ O/m^2 is involved, implying that the process is not limited by diffusion through the layer. On the other hand, the oxide always remains substoichiometric, possibly due to the low probability of forming properly oriented B_2O_3 bonds at ambient temperature, even if amorphous. The oxidation reaction is undoubtedly activated by the plasma, and for this purpose the power discharges are very much more effective than the glow discharges, although the reasons for this are not trivially simple.

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