New techniques for of tritium inventory control in carbon-based scenarios by reactive gas injection

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Abstract. The issue of tritium retention in carbon-based plasma facing materials has triggered the development of several techniques of different applicability to the in-situ, non-perturbative control of the tritium inventory in ITER. These techniques are aimed at any of the following aspects of the problem

- 1. Inhibition of co-deposit formation during plasma shots
- 2. Release of T from films at plasma facing areas and gaps between shots
- 3. Release of T from the films formed in remote areas between shots

As a type 1 technique, the scavenger concept offers the possibility of inhibiting the formation of co-deposits during plasma operation. Recently, its application to Asdex Upgrade has led to a reduction of the carbon re-deposition up to 80%. This has been achieved by injecting nitrogen into the subdivertor region, while keeping the plasma parameters unperturbed. Experiments aimed at understanding the underlying mechanism have been carried out at the Ciemat. The characterization of the reaction products by trapping them in a liquid nitrogen cryo-pump, for example, has allowed the discrimination between the sputtering and chemical effects involved in the process, of critical impact on the extrapolation of the technique to ITER-relevant divertor conditions. For the removal of carbon deposits in plasma facing areas (type 2 technique), glow discharges in active gases such as the He/O_2 mixture, seems to be an efficient approach. A surprisingly high efficiency for the removal of carbon coatings in narrow (1mm), 4mm deep gaps has been found in He/O_2 discharges. Moreover, the absolute removal rate for the films was found to be a factor > 50 greater than previous reports. Experiments at the Ciemat show that the survival of atomic species seems to be an important factor to be considered in the application of this technique to ITER. When strong oxygen getters are exposed to the cleaning plasmas, the use of nitrogen containing glow discharges is one of the alternatives. Experiments of carbon removal in the presence of boron by this technique are also described here.

1. Introduction

As it is well known, the use of carbon materials at the divertor plates of ITER is strongly hampered by the deleterious formation of tritium-containing co-deposits from the products of chemical sputtering. These deposits are found at remote areas from the plasma, of difficult access to the plasma-based de-tritiation techniques. To date several ideas have been put forward to solve this problem, with strong impact on safety issues of the reactor plant. A recent review of the topic can be found in [1]. The combination of several of these techniques is presently considered for keeping an acceptable level of in-vessel T inventory. However, in their present form, most of these methods require specific time devoted to the cleaning process and, in some cases, the recovery of plasma normal operation from the strongly perturbed first wall conditions originated by the cleaning procedure. A tentative classification of the presently available techniques can be established based on their efficiency in preventing or removing the T-rich carbon films. So, type one would refer to methods aimed at the full inhibition or removal of the films within the discharge time, type two to plasma-based techniques (regardless of the particular type of plasma) and type three to those techniques requiring long periods of application. Among type one techniques, those aimed at the inhibition of the deposition of tritiated films during normal plasma operation are especial appealing. The scavenger concept is perhaps its main representative [2]. Initially based in the broad experience achieved in the field of Plasma Assisted Chemical Vapour Deposition (PACVD) of nitrogenated carbon films [3], the technique has been tested under actual divertor conditions in JET and Asdex Upgrade (AUG) after preliminary tests in laboratory experiments in low temperature plasmas. A detailed description of these tests can be found in previous publications [2-5]. In summary, although a complete suppression of carbon film formation was readily achieved in glow discharge carbon film deposition in the presence of nitrogen, only a moderate reduction (<30-40%) was seen at JET in type-III Elmy discharges with strong nitrogen seeding. Conversely, injection of moderate fluxes of nitrogen in H-mode discharges at the subdivertor region of AUG led to a 80% reduction in the deposition rate, as evidenced by the quartz micro-balance diagnostic [6]. Since the location of the nitrogen injection was significantly different in both devices, at the SOL in JET and at the PFR in AUG, one possible explanation for the observed effect is the exclusion of direct sputtering by high-energy N ions in the subdivertor region of AUG. New findings about the underlying mechanism responsible for the inhibition, and their implication for the use of the technique in ITER are addressed in the present work.

Plasma assisted cleaning methods are the standard of type 2 techniques. Although their intrinsic efficiency is higher than other, time consuming alternatives, their main drawback comes from a limited access of the plasma to the areas of main co-deposit accumulation. To date, either pure D_2 or He/O_2 mixtures are the main plasma species to be used, depending on their aim, isotope exchange of full carbon removal, respectively [1]. In the presence of strong getters, as it will be the case of ITER with its main wall fully covered by Be, the application of oxidizing plasmas can lead to long-term deleterious effects. Not only the getter has to be de-oxidised with devoted plasma discharges but also the formation of thick oxide layers can lead to enhanced fuel retention during normal operation. For that reason, glow discharges having nitrogen as the active gas have been proposed as alternative [7,8]. Laboratory test by DC [7] or low-pressure ECR [8] plasmas in H_2/N_2 mixtures on carbon films have shown that high etching rates can also be achieved in the absence of oxygen. As the mechanism for film erosion by plasmas implies the interaction of the films with all the species produced by them, care has to be taken when extrapolating laboratory results to new machine scenarios, as it is the case for ITER. Thus for example, the survival of atomic species produces by molecular dissociation in the plasma strongly depends on global wall conditions through the corresponding surface-dependent recombination coefficient. This is particularly relevant when areas of difficult access by plasma ions have to be conditioned. One conspicuous example of this would be the removal of co-deposits from the narrow gaps existing in several regions of the PFC's of ITER. This issue was addressed in a previous work [9] by using a He/O_2 GD on castellated structures. New results are here presented which support the idea of atomic vs. ion cleaning being dominant in the future ITER cleaning scenario.

2. Film Inhibition Techniques. Scavenging.

The fact that the addition of some nitrogen-bearing molecules to carbon film deposition plasmas can lead to the full inhibition of their growth opens the potential use of the concept for the benefit of the Fusion community, in particular, to the tritium retention issue. As it is well known, carbon-based compounds, which include fine grain graphites and Carbon Fiber Composites (CFC), are ideally suited to withstand the high thermal loads delivered by the hot plasma (with steady state values of ~10MW/m^2), while providing local radiation losses able to cool down the divertor plasma in contact with them to electron temperatures of 2-10 eV. Since molecular nitrogen is a candidate for the enhancement of local radiation in divertors, its injection into the area (not directly exposed to the plasma) where chemical processes lead to the formation of the tritium-rich co-deposits could in principle prevent their formation. Experiments aimed at the optimization of the technique of film scavenger were undertaken at CIEMAT. A simple DC glow discharge reactor, previously used for carbon and carbon-boron plasma deposition of interest in first wall conditioning of the TJ-II stellarator [2], was used. Mixtures of $CH_4/N_2/H_2$ (10:0-10:80) were fed into the reactor, and mass spectrometry, optical emission spectroscopy and Langmuir probes were used for the plasma diagnostic. The main finding of these studies was that at N_2/CH_4 ratios of 0.8-1 a complete inhibition of the carbon film was achieved, even when the cracking of methane into the discharge was basically unaffected by the nitrogen addition. An enhanced production of C_2 hydrocarbons and the formation of excited CN radicals were simultaneously recorded. For intermediate nitrogen/methane mixtures, the produced films had low N content, as confirmed by XPS analysis. In addition, etching of the films in a N_2/H_2 plasma was found to yield different products than those recorded during the hindered deposition. Thermal desorption of these films was undertaken in a different experiment [4]. Besides confirming the film growth dependence on injected nitrogen (Figure 1), it was concluded that the films deposited at $N_2/CH_4 < 0.8$ had the same H content as those produced in the absence of nitrogen. The complex mass spectra recorded during these experiments could not be de-convoluted with enough accuracy to assess the exact composition of the reaction products. In a different experiment, full isotopic exchange of the reactants (CD_4 and D_2) was tested [7]. Although acetylene, ethylene and HCN were identified as main components, being the first species dominant, the exact contribution of the N-bearing species (HCN and C_2N_2) to the reaction products could not be assessed. An important finding described in reference [7] was the strong effect that the reactor walls have on the chemistry of the process. Thus, the composition of the plasma was found to evolve during the early stages of the experiments, starting from a clean metallic wall. A full coverage of this wall seems to be required for the scavenger effect to take place in the clean substrate, according to the mass spectrometric data. This suggests that surface losses of the active species are relevant in the overall mechanism of the inhibition. The technique was implemented in two fusion devices with divertor geometry, JET and Asdex Upgrade [10]. While injection at JET was made at the inner SOL region, nitrogen was puffed into the sub-divertor volume (not directly exposed to the plasma) in AUG. Although very high flows of nitrogen were used in the JET case (up to 3.10^{22}e/s), only a moderate effect on the QMB (Quartz Microbalance) diagnostic, at the location showing maximum deposition, was inferred. Significant cooling of the divertor plasma was produced upon the injection, and a top value of 30% for the inhibition efficiency was deduced. Interestingly enough, a decrease of 80% in the shot-by-shot deposition of carbon films, as again recorded by the QMB diagnostic, was observed in AUG [6], even when the injected flows were much lower than in the JET experiment (Figure 2). Consequently, no significant perturbation of the divertor plasma was detected for the small flow of nitrogen used, thus opening the possibility of external, real time control of co-deposit formation in a fusion reactor.

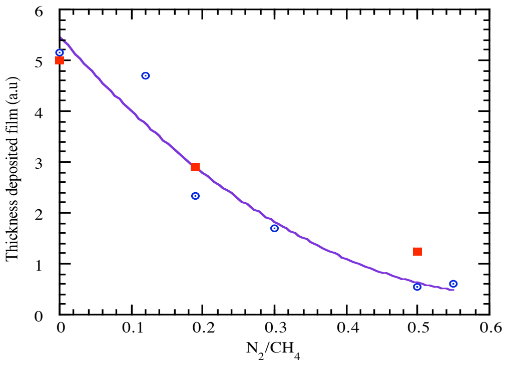

Figure 1. Thickness of carbon film deposited from a CH_4/H_2 plasmas in a constant time (20') as a function of added N_2 to the plasma. From Ref. 4

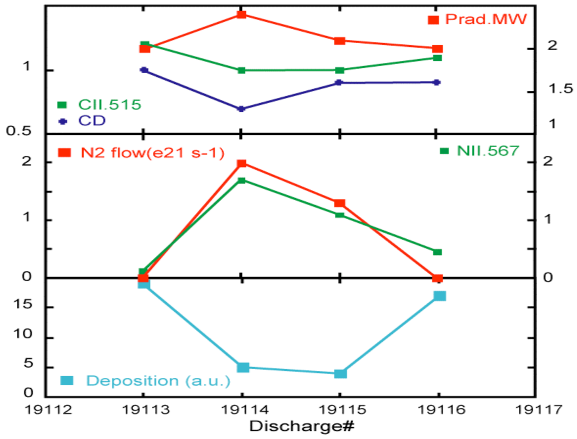

Figure 2. Results of experiments of nitrogen injection in AUG. From Ref. 6

In order to fully validate the technique for its application to ITER, a deeper understanding of the underlying mechanism is mandatory. Of particular relevance is to assess the required composition of impinging plasma species for the film inhibition effect. In that respect, contradictory reports are found in the literature concerning the relative role which chemical sputtering by nitrogen ions and radical chemistry play in the effect, the last one giving its name to the technique. While it is widely accepted that direct interaction of N and N_2 ions with carbon surfaces leads to the formation of volatile products, in particular to HCN for hydrogenated surfaces [11], and therefore to the actual etching of the growing film, the film inhibition effect has also been recorded under conditions where radical chemistry should be dominant [3]. Recently, a high yield and a very low threshold for the etching of a-C: H layers by N_2 ions in laboratory experiments has been reported [12]. However, as described above, our experiments in DC glow discharge plasmas indicate that, even when ion energies of several hundred volts are involved, the production of HCN is only moderate, and very little nitrogen is depleted from the gas phase during the process. In order to clarify this point, new experiments have been carried out very recently at CIEMAT. They profit from the systematic application of the newly developed CTAMS technique [13]**.** It is based on the fact that many of the compounds formed in film deposition plasmas can be readily condensed at the liquid nitrogen temperature, 78 K. The technique takes advantage of both, the cooling and heating cycles. First, the mass spectra are recorded at room temperature during the film deposition in the main reactor by using the differentially pumped MS. Then, the trap is filled with LN_2 and the changes in the spectra are recorded. Finally, the trap is isolated from the reactor, so that all the release gas during the temperature ramping is delivered into the MS chamber through a collimator. Eventually, the process was repeated for singles species, such as acetylene, for absolute calibration purposes. No external heating was used in the release cycle, and the warm-up rate was estimated in ~55 mK/s from the location of the main peaks in the P vs. time curves (see below). The gas mixtures analyzed are summarised in Table I.

Total pressures were measured with a Baratron (MKS, 1 Torr range) and initial compositions were checked with the calibrated RGA system. The rational used for the selection of the plasmas involves cross checking the methane/N_2/H_2 mixture with other systems in which one of the critical components has been removed or substituted by an inert gas. Of particular relevance are the results obtained in the scavenger mixture

Plasma Mixture	**Main Products (T release, K)**	**Secondary Products**	**Characteristic Product Ratios**
$CH_4/N_2/H_2$ 10:10:80	Acetylene (95), Ethylene, HCN (168)	Acetylene (117,122,126) NH_3 (135,168)	$C_2H_2/C_2H_4=3$ $HCN/\Sigma C_2=0.1$
$CH_4/Ar/H_2$ 10:10:80	Acetylene (100), Ethylene	Masses 27-29 (111K)	$C_2H_2/C_2H_4=1$
N_2/H_2 20:80	HCN (156), Acetylene (95)	C_2N_2 (150), NH_3 (157)	$HCN/C_2H_2=4$ $C_2H_2/C_2H_4=1.8$

Table I. Summary of reactive plasmas studied by CTAMS and detected products.

($CH_4/N_2/H_2$, 10:10:80) and the etching plasmas from a N_2/H_2 (20:80) mixture. The corresponding condensation and outgassing cycles are shown in figures 3 and 4. As seen in figure 3 left, in the scavenger mixture, a dominant contribution of acetylene (mass 26 and 25) to the released species can be seen upon plasma initiation. They are followed by mass 27 and mass 29, associated to the formation of N_2H^+ ions in the mass spectrometer ionizer The presence of mass 27 can be mainly attributed either to the formation of C_2 hydrocarbons other than acetylene or to the formation of HCN in the discharge. The introduction of LN_2 into the trap, at 600s, leads to a fast drop of peaks at 26 and 25 (acetylene) and of mass 27. Due to the much lower vapour pressure of HCN compared to that of ethane and ethylene, this drop is a clear indication of a significant presence of this species in the gas phase.

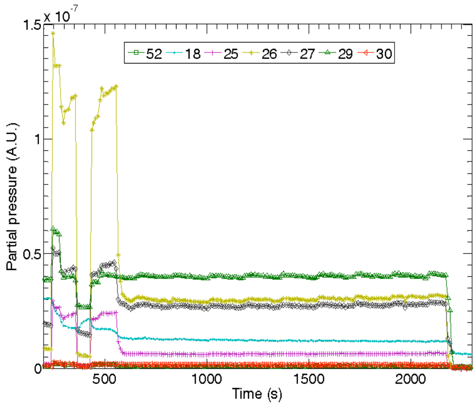

Figure 3a. CTAMS results for the scavenger mixture. LN_2 is added at 600s

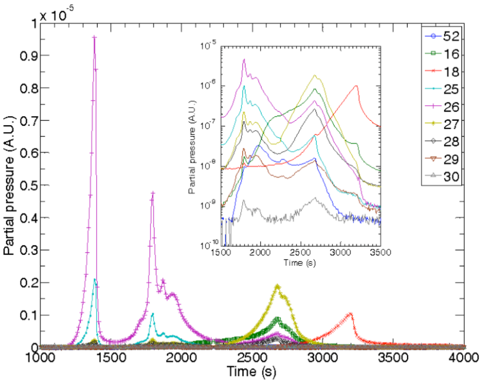

Figure 3b. Desorption of cryo-trapped products from the scavenger plasma

The release of the condensed species during the heating-up of the trap after removal of LN_2 is displayed at the right of the figure. After the evaporation of acetylene starting at t=900s, a second, broader structure, with mass ratios identical to acetylene but at significantly higher times (temperatures) can be clearly seen. Three maxima are evident in the structure, with decaying amplitudes. The data in the insert, again in a logarithmic scale, indicate that only mass 16, among the recorded peaks, is continuously rising during the desorption process. The fact that this kind of spectra are only seen in nitrogen-fed plasmas, and with similar amounts of condensed acetylene, precludes pure instrumental artefacts as their origin. The formation of thermally unstable C-N compounds, which could simply decompose by releasing acetylene to the gas phase at the implied temperatures, is postulated as a possible source of these peaks. A peak of masses 27, 16, 26 and 28 is detected at 2700s. Also, but only apparent in the logarithmic scale, desorption of mass 52 is simultaneously seen. The simplest explanation for this multiple peak is the desorption of HCN (27, 26), C_2N_2 (52) and ammonia (16), the latter starting to desorb earlier. Finally, water outgassing drives the sharp increase of mass 18 at t> 3300s.

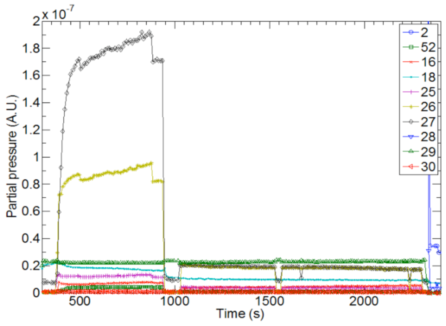

Figure 4a. CTAMS results for the N_2/H_2 mixture. LN_2 is added at 900s

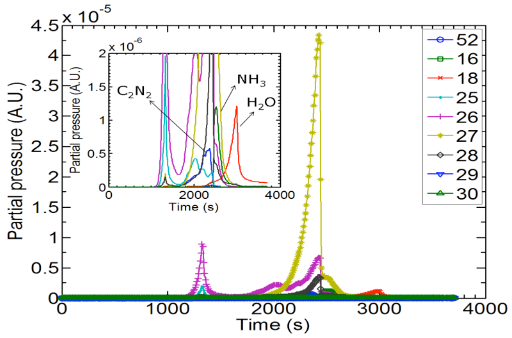

Figure 4b. Desorption of cryo-trapped products from the N_2/H_2 plasma

The results of the CTAMS technique for the N_2/H_2 (20:80) etching plasmas are displayed in Figure 4 in an analogous way as in the scavenger mixture. A conspicuous difference in the reaction products from the two systems can be readily seen. Both, the mass spectra of products during the reaction and the shape of the desorption spectra from the trap afterwards indicate that in the etching mixture HCN formation is dominant, although some acetylene, ammonia and C_2N_2 are also created. A full analysis of the main products, considering the condensation and desorption cycles and the calibration of the system for acetylene, yields the values given in Table I. As seen, only a 5% of the released carbon in the scavenger mixture can be ascribed to the formation of HCN, in strike contrasts with the etching of the film by the N_2/H_2 plasma. A simple hypothesis to explain these findings would be the recombination between the nitrogenated surface products created by the exposure of the film to N_2 ions [11] and the impinging carbon radicals produce from the cracking of methane in the plasma. The possible contribution of atomic N to the perturbed surface chemistry required for the process is still an open question [3,11]. In the absence of methane, the pure chemical sputtering scenario will prevail, and HCN and C_2N_2 molecules are formed and released as expected. On the other hand, the substitution of N_2 by Ar in the scavenger mixture doesn't prevent the film formation at all, even when a significant synergistic effect between the atomic H and the incoming Ar ions is known to lead to enhanced chemical sputtering of the film. Finally, it should be pointed out here that ethylene production was indeed observed in the experiments of N_2 injection at AUG, well correlated with the inhibition effect [6]. Also, CN emission was seen at the outer divertor of JET during N_2 puffing at that location, which corresponds to a net erosion area and characterized by relatively high electron temperatures [10].

3. Cleaning plasmas

The etching of the films by plasmas from reactive mixtures has a very long tradition in microelectronics (dry etching) and its implementation in some fusion devices has open the possibility of becoming a ITER relevant de-tritiation technique. Compared to its use in laboratory systems, its application to the removal of T-rich films in fusion devices with complex structure has to face several challenges, such as full access to the contaminated areas, compatibility with inner components (and materials) and short term recovery of the treated surfaces for normal plasma operation, to mention a few. There are two aspects of the ITER facing components of particular concern: the extensive coverage of the first wall by Be and the presence of narrow gaps. Experiments specifically oriented to these issues have been performed at CIEMAT, and described in previous works [7,9]. In summary, He/O_2 mixtures (at several ratios) and H_2 /N_2 mixtures (20:80) were used in a DC glow discharge plasma in order to remove pure and B-doped a-C: H films. The films were either fully exposed to the plasmas or lying on the bottom of a castellated structure (1mm wide x3mm deep gaps). Low pressures (0.5 Pa) and high oxygen concentration (only tested up to 20%) in the plasma are best suited conditions for the removal, which maximum attained rate was12 nm/min. Cleaning rates were deduced from the full annealing of the remaining film (TDS) before and after the exposure to the plasmas. The cleaning rate for the films lying at the bottom of the 3 mm deep gap was at least 2/3 of the value for fully exposed films. Also, increase of the substrate temperature to 200ºC or of the current density didn't convey any improvement of the cleaning rate. All these findings point to chemical reactions with the active species created in the plasmas, able to reach hidden areas, as the main responsible for the film etching. In fact, much slower rates are deduced from physical sputtering yields models [9]. When a H_2/N_2 glow discharge was used, a cleaning rate of 3,6 nm/min was obtained. Figure 5 shows the complete removal of a 200 nm a-C: H film by this plasma and the chemical composition of the etching products (as in figure 4). The etching rate is lower than the O_2 counterpart, but still high enough for its implementation in a carbonized fusion device. No parametric scan, which could still lead to higher efficiencies, was made for the nitrogen plasmas.

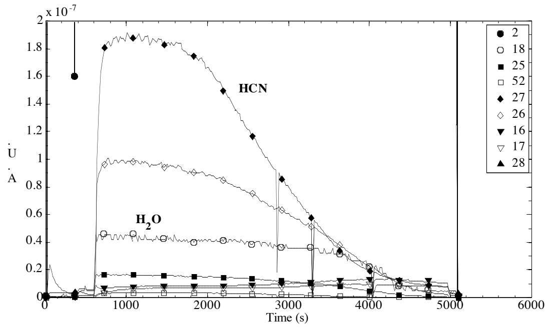

Fig.5. H_2/N_2 treatment over a 200 nm a-C: H layer

Finally, boron-containing films were produced to assess the effect of oxygen getter in the film etching. Either of the two reactive species, N and O, produced much lower etching rates. This fact has also been observed in boronized machines as in AUG and TEXTOR [1], and rather than to the oxygen uptake by the B in the film, it could be due to conversion from sp^2 to sp^3 hybridization in the presence of B, which leads to a lower reactivity.

In order to test the hypothesis of atomic (rather than ion-induced) cleaning a simple experiment was performed. The exposure of the castellated structure, previously used, to the plasma was made upside-down, i.e., the carbon-coated elements to be cleaned were facing the bottom of the chamber, a few centimetres away (see Figure 6). Langmuir probes recorded the floating potential and saturation current in both sides of the structure, and only a very weak plasma was detected between the structure and the chamber bottom. Floating potentials were 350 V (near to the anode-cathode value of 400 V) in the main plasma and 30 V in the plasma seen" the film. TDS studies showed that, in spite of this unfavourable geometry, the cleaning rate was basically identical to the one previously seen, as expected if atomic oxygen survives after a few collisions with the walls.

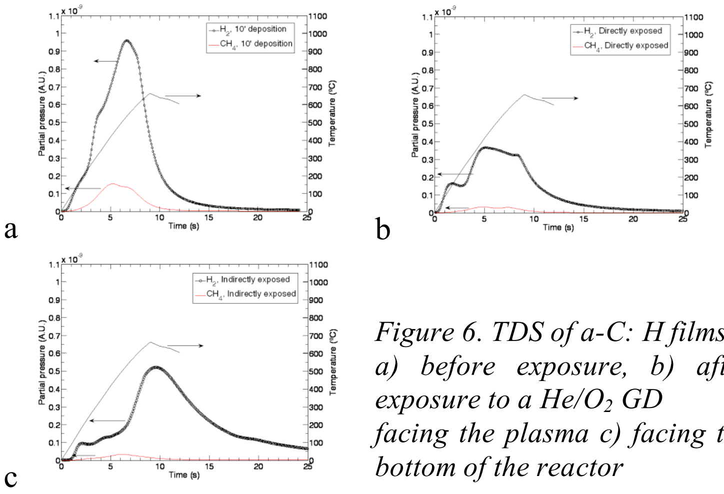

Figure 6. TDS of a-C: H films a) before exposure, b) after exposure to a He/O_2 GD facing the plasma c) facing the bottom of the reactor

When extrapolating these results to a mixed-material scenario, like that of ITER inner wall, care should be taken in predicting the achievable cleaning rates. First, the survival of atomic species produced by the cleaning plasma will be largely given by the actual recombination coefficients at the exposed areas. In the case of ITER, a Be oxide surface layer will likely determine the absolute concentration of atomic oxygen, rather than the restricted divertor surface to be conditioned. Secondly, a high survival probability for the reactive atoms could allow for the expansion of the cleaning effect to areas not directly exposed to the plasma, thus accessing the main re-deposition zones. Experiments aimed to test these important aspects are presently underway at CIEMAT.

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