Studies of the removal of hydrogenated carbon films by nitrogen glow discharges

J.A. Ferreira¹, F.L. Tabarés¹

¹Association EURATOM-CIEMAT, Avda. Complutense 22 Ed6 P2.07, 28040
Madrid, Spain

E-mail: ja.ferreira@ciemat.es

Abstract. In the present work the erosion of laboratory-produced a-C:H layers by H₂/N₂ plasmas is addressed. Hard hydrocarbon films were deposited using He/CH₄ plasmas. These layers were exposed to H₂/N₂ plasmas, showing a high erosion rate, above 4 nm/min. However, thermal desorption of the films after exposure to the erosion plasmas indicates that some modifications of the binding states of H took place, leading to an increase of the temperature of desorption. The studies reported in the present work include the characterization of the plasma chemistry by differentially pumped mass spectrometry and Cryotrapping-Assisted Mass Spectrometry, erosion rates by laser interferometry and characterization of the binding states by thermal desorption spectroscopy. The detection of acetonitrile in the reaction products provides a clear indication of chemical reactions being involved in the film removal mechanism under the reported conditions.

1. Introduction
The use of carbon facing materials in ITER [1] is hampered by the formation of significant amounts of re-deposited carbon layers, resulting in tritium retention, and hence, a potential environmental risk during accidental vacuum loss. Therefore the development of new techniques for preventing the formation or for removing these layers is highly desirable [2]. Among these techniques the most appealing candidates are oxygen-containing plasmas and thermal oxidation. Oxygen plasmas can achieve high cleaning rates and could be able to reach even remote areas of the reactor [3]. On the other hand thermal oxidation can achieve high cleaning efficiencies, but at temperatures not compatible with the present ITER design [1].

The presence of Be (strong oxygen getter) as first wall material in ITER can limit the use of oxygen-bearing molecules as oxidizing agents. In addition, the deleterious side effect of highly corrosive T₂O formation in oxidizing atmospheres represents a serious drawback for the use of these techniques in a reactor. Other chemical active agents as nitrogen or ammonia could become an attractive alternative to oxygen. Nitrogen, either as a molecular or atomic ion or in its atomic form, shows a high reactivity with carbon, comparable to that of oxygen. In its mixture with hydrogen it has been proven especially efficient for the removal of carbon layers, either in DC [4] or ECRH [5] glow discharge plasmas. In addition, nitrogen does not react with metals at low temperatures, thus preventing the non-carbon first wall materials from chemical modification. However, a systematic use of glow discharges in nitrogen will not be possible until other side effects are ruled out. In the present work, the erosion of a-C: H films due to hydrogen/nitrogen dc glow discharges is studied by mass
spectrometry, cryotrap-assisted mass spectrometry (CTAMS), laser interferometry and thermal desorption spectroscopy (TDS).

2. Experimental set-up

Figure 1 shows the setup used in the present studies. Two different chambers were used. The deposition chamber was used to deposit the carbon films from a He/CH\textsubscript{4} plasma. The walls of this chamber were completely coated by carbon. In this chamber, experiments of total etching of the film by H\textsubscript{2}/N\textsubscript{2} were carried out. A silicon sample was introduced to measure both deposition and erosion rates by laser interferometry. A He/Ne laser ($\lambda = 632.8$ nm), at normal incidence, was used to produce interference fringes. Each interference fringe is related to the thickness change $d$ by $d = \lambda/2n$. A value of the refraction index of $n = 2.2$ typical of hard a-C:H films [6] was assumed. This chamber was connected to a differential mass spectrometer (SRS RGA 200) to monitor the residual gas during plasma operation. A tee with a liquid nitrogen trap was place between both chambers for CTAMS analysis [7]. Typical plasma conditions were the following: total pressure 5 mTorr, plasma current 100 mA and discharge voltage 300-600 V. The gas mixtures were He/CH\textsubscript{4} (65:35 ratio) for the a-C:H films deposition and H\textsubscript{2}/N\textsubscript{2} (80:20 ratio) for the erosion.

A clean second chamber (metallic walls) was used to expose samples to H\textsubscript{2}/N\textsubscript{2} glow discharges, under the same conditions as described before, and to analyze these samples by TDS before and after nitrogen exposure using a mass spectrometer directly fitted to the chamber.

3. Results

A layer was deposited on the walls of the deposition chamber by a He/CH\textsubscript{4} plasma. The rate was measured by laser interferometry resulting in ~6.6 nm/min, in good agreement with carbon balance analysis. A total thickness of 200 nm was deposited, showing typical properties of a hard a-C:H coating as measured in previous reports [6]. This film was exposed to a H\textsubscript{2}/N\textsubscript{2} plasma until its complete depletion. Figure 2 and 3 show the mass spectrometric data of the exhausted gases from the plasma. The main masses observed are 27, 26 and 25. Mass 27 was ascribed to HCN and mass 25 due to contribution of C\textsubscript{2}H\textsubscript{2}. The signal at mass 26 can be reconstructed assuming that it is the sum of the contributions of both molecules, using their cracking patterns. Mass 52 is assigned to C\textsubscript{2}N\textsubscript{2} that is produced as a minority product, but that contributes twice to carbon balance. These three products follow the same time behavior, and their concentrations are nearly constant during the film erosion, finally diminishing as the layer is being fully removed. At this time, masses 17 and 16 assigned to NH\textsubscript{3} raise, indicating a higher recombination of N and H species in the carbon-free surface conditions.

Total film erosion takes around 3400 s, which yields a mean erosion rate of ~4nm/min. This value is in excellent agreement with that measured by laser interferometry. From the total plasma current and exposure area, an erosion yield of 2 C/ion is deduced, so that it cannot be only due to a pure physical sputtering process and other mechanisms must be present as well.
CTAMS was used for a detailed analysis of the residual gases. Figure 4 and 5 show some traces measured with this technique. The presence of HCN as main product of the erosion is again confirmed. Also some contribution of C$_2$H$_2$ is present. Again C$_2$N$_2$ and NH$_3$ are unequivocally recorded. The most prominent result obtained from CTAMS is shown in figure 5. The cracking pattern of masses 39 to 42 can only be ascribed to CH$_3$CN, acetonitrile or it isomer methyl isocyanide.

In another run of experiments two a-C: H layers of ~80 nm each were deposited under the same conditions as the previously described. These layers were transferred under air to a clean chamber and analyzed by TDS in a similar set-up as in [3]. Two thermal desorption spectra (TDS) were compared. one of a fresh layer and the other after exposing the layer to a H$_2$/N$_2$ plasma (identical to that used before) for 15 minutes. Both are shown in figures 6 and 7. The TDS analysis of the plasma-exposed layer shows a reduction of an 80% of the desorbed methane (mass 15), indicating the etching of the film. Desorbed hydrogen is also reduced, but its desorption maximum occurs at a higher temperatures than those obtained after etching in He/O$_2$ plasmas [3] or from fresh deposited layers, thus indicating that the binding state of hydrogen has increased upon the exposure to the N$_2$/H$_2$ plasma. Unfortunately, temperature ramps up to higher values, unavailable with the present set-up, will be needed for the accurate characterization of the binding states.
4. Discussion and conclusions

The use of N\textsubscript{2}/H\textsubscript{2} plasmas for the removal of organic films has been a subject of interest in microelectronics since long [9]. For their application to the tritium inventory control in fusion, previous experiments [4,5,8] have shown a high potential. However, little is known about the detailed mechanism underlying their high efficiency. Thus, for example, studies of the correlation between etching rate of organic films and atomic composition of the plasmas, performed by H. Nagai et al [9] indicated that H atoms and N ions are the active species responsible for the etching in an ICP reactor at low pressure, and no direct etching by N radicals takes place. The maximum rate at 30\% N\textsubscript{2} a in the gas mixture (also reported in ref. 5) is explained in terms of enhanced H production by changes in the plasma parameters. Detailed analysis of the reaction products by CTAMS indicate that HCN is the main product in DC glow discharges, but C\textsubscript{2} hydrocarbons were also recorded [10]. In this respect, the detection of acetonitrile, an obvious outcome of the direct recombination of CH\textsubscript{3} and CN radicals of high relevance in C/N containing plasmas, provides a direct evidence of the role that chemical processes (as opposed to pure sputtering) play in the etching process and it stresses the need of devoted studies in order to validate the technique for its application to the ITER complex scenario.

In conclusion: H\textsubscript{2}/N\textsubscript{2} plasmas show high erosion yields (4 nm/min) for carbon deposits cleaning, demonstrating the feasibility of these techniques to clean pure carbon layers. The findings of new species those are present (HCN, C\textsubscript{2}N\textsubscript{2} and mainly CH\textsubscript{3}CN) in these plasmas, and the high rate of erosion, that can not be explained only by pure physical methods, emphasize the role of chemical processes in this type of cleaning at low energy. More experiments are necessary, but if chemical reactions between neutral species are the main pathway for erosion then, it could be possible to reach hidden parts of a fusion reactor, like the subdivertor region, that could contribute to the mitigation of the tritium retention.

References
[1] G. Federici et al. Nucl. Fus. 41(2001), 1967
[2] G. Counsell et al. Plasma Phys. Control. Fusion 48(2006), B189-B199
[3] J.A. Ferreira et al. J. Vac. Sci. Technol. A 25(4) (2007), 746
[4] F.L. Tabarés et al. Plasma Phys. Control. Fusion 46(2004), B381-B395
[5] T. Schwarth-Selinger et al. J.Nucl. Mater. 363-365 (2007) 174
[6] W.L. Hsu. J. Vac. Sci. Technol. A 7(3) (1988), 1047
[7] J.A. Ferreira and F.L. Tabarés J. Vac. Sci. Technol. A 25(2) (2007), 246-251
[8] J.A. Ferreira et al. J. Nucl. Mater. 363-365 (2007), 888-892
[9] H.Nagai, S. Tajashima, M. Hiramatsu et al. J. Appl. Phys. 91 (2002) 2615
[10] F.L. Tabarés et al Chem.Vap.Dep. 13 (2007) 335