Suppression of hydrogenated carbon film deposition by scavenger techniques and their application to the tritium inventory control of fusion devices.

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Abstract: The well-known radical and ion scavenger techniques of application in amorphous hydrogenated carbon film deposition studies are investigated in relation with the mechanism of tritium and deuterium co-deposition in carbon-dominated fusion devices. A particularly successful scheme results from the injection of nitrogen into methane/hydrogen plasmas for conditions close to those prevailing in the divertor region of present fusion devices. A complete suppression of the a-C: H film deposition has been achieved for N_2/CH_4 ratios close to one in methane (5%)/hydrogen DC plasma. The implications of these findings in the tritium retention control in future fusion reactors are addressed.

One of the main concerns in nuclear fusion research is the performance of the plasma facing materials in relation with long pulse operation in the next step devices¹. To date, carbon based materials have shown, together with the low intrinsic Z value, the best general behavior against high thermal loads, thermal shock and other aggressive conditions expected in the proximity of the divertor plates and limiters for reactor-relevant scenarios. Unfortunately, the high reactivity of carbon with hydrogenic isotopes, especially at high temperatures, leads to strong chemical sputtering of impact on material lifetime and formation of co-deposits with the plasma fuel². Although re-deposition of the chemically eroded C is expected to strongly alleviate the first problem, activation of the reactor by tritium retention has emerged as a serious constraint for the operation of ITER³. Co deposits have been preferentially found in regions hidden from direct exposure to the plasma, both in limiter and divertor plasmas⁴. Although the present understanding of the deposition process is far from complete, it is believed that hydrocarbon migration from the regions of net-erosion plays a major role. Ion and radicals are probably involved in the re-deposition process. In that respect, it is worth noting that very recently, plasmas of $T_e \sim 10$ eV and $n_e \sim 10^{11}-10^{13}$ cm⁻³ have been detected in the sub-divertor region of the Asdex-U device, where strong evidence of ion mediated deposition has been observed⁵. Techniques oriented to the reduction of the sticking probability of the precursor radicals in hidden areas of the divertor⁶ together with the development of doped graphites⁷ with a lower chemical sputtering yield are presently in progress. Also, a strong effort is presently devoted to the removal of these T-rich layers by several methods⁸. To date, oxidation of the co deposits at temperatures above 250 °C seems to be the fastest way for "between-shots" removal of tritium⁷. However, this solution poses important problems in the recovering of the oxygen-free conditions for regular plasma operation.

In the present work a completely new approach is proposed, namely, the use of scavengers for the *in-situ*, shot to shot control of the deposition of T/C layers in fusion devices.

Scavengers of both, ions and radicals have been traditionally used in the study of the mechanism of film formation, particularly in the field of plasma assisted Diamond Like Carbon (DLC) film deposition, under a very broad range of experimental conditions. Thus for example, Vandertop *et al*⁹ injected NO in a pure methane

RF plasma at ~ 70 mTorr. A drastic decrease of the film growth rate was observed in the powered electrode at NO concentrations below 10%. For a 20% of NO, no deposition took place in that electrode, although the formation of a soft, N and O containing polymeric film was detected in the grounded electrode. Other radical scavengers suitable for methyl radical removal are iodine and halogen hydrides, among others¹⁰. In the same type of plasmas, ion scavengers such as ammonia (also used as a radical scavenger¹¹), molecular oxygen and nitrogen, all having a strong proton affinity, have been applied (12 and refs. therein). The use of molecular nitrogen is particularly well documented. It has been successfully used for the precluding of film formation not only in pure methane plasmas, but also with other film precursors. Complete suppression of the deposition has been observed for nitrogen concentrations equal to that of methane, and gradually decaying growth rates of softer, almost N free films have been reported for lower N_2 plasma content. The critical concentration of the scavenger in the plasmas depends on the total power, and lower values are needed for film suppression at higher powers¹². Although the topic is still controversial, it is believed that gas phase ion reactions can promote the formation of stable molecules from the film precursors. The role of plasma film interaction in the film suppression has not been clarified yet. Some scavenger techniques could in principle be extrapolated to the typical pressures (few Pa) and hydrocarbon dilution conditions of divertor plasmas where T, D/C co deposition is observed¹³. To check that, we have undertaken the study of hydrogen plasmas with low concentrations ($<5\%$) of methane at total pressures of 1-3 Pa. In the present work, the main results of nitrogen injection in such plasmas are presented. A description of their implications in the mechanism of film formation/inhibition will be presented elsewhere.

A DC glow discharge reactor similar to that used in previous deposition studies¹⁴ was used to produce H_2 /methane plasmas with variable N_2 content ($N_2/CH_4 < 1.0$ for the deposition) at total currents of $50 < I_p < 300$ mA. Typical voltages were between 350 and 550 V, the higher values corresponding to pure N_2/H_2 plasmas. The deposition was monitored by inserting metal and silicon samples into the plasma at room temperature. XPS depth profile and profilometry were used for the characterization of the film growth. Mass spectrometry of neutrals and ions was performed by differentially pumped spectrometers (Balzers, QMS125, calibrated for the relevant species and PPM 421, respectively). Optical emission spectra in the range of 370 to 500 nm were recorded by means of an OMA (Oriel,) through a glass window. The discharges were readily initiated at the operation

pressure by means of an electron gun. At the total pressure of 1.2 Pa typically used, a residence time of ~50 ms for methane and nitrogen was estimated. For the results reported here, a partially coated metal wall was used in the reactor. Figure 1 shows the mass spectra of deposition plasmas with a variable ratio of N_2/CH_4 , and a constant CH_4/H_2 ratio of 5%. For the constant plasma current of 250 mA used, a constant cracking fraction of ~15% for methane was measured in the plasma, regardless of the relative N_2 content. As seen, a systematic increase of the C_2H_x hydrocarbons peaks ($x=2,4,6$) mostly represented by masses at $m/q=26,27$ and 28, is observed for increasing N_2 content, the peaks at 26 and 27 reaching a plateau at N_2/CH_4 ratios >0.5 . Also shown is the film thickness deposited in metal samples at a constant deposition time of 30'. No deposition at all was recorded for N_2/CH_4 ratio of 0.9, even when the depletion of methane from the gas phase would imply a film thickness of 120 nm. This thickness value is in excellent agreement with the mass balance of C atoms assuming a geometrical deposition area of 2000 cm² and the loss of C by C_2 hydrocarbon formation in pure H_2 plasmas¹⁴.

In order to check the contribution of wall release species by N_2 ions in the results shown above, pure N_2/H_2 plasmas were run on a fresh, plasma-deposited a-C:H film. A linear increase of C_2 peaks was observed as the N_2 fraction is increased in the same range as used in the deposition. The main released species changed from methane at low N_2 fraction to C_2H_2 at higher values. No peaks corresponding to C_2N_2 molecules were detected. Absolute values between 25 to 35% of those shown in fig.1 were found at the maximum N_2 fraction. Mass balance from the released hydrocarbons can account for the effect of both contributions within the calibration uncertainties.

Optical emission spectroscopy was used for the recording of some relevant excited species. In particular, the bands at 428 nm (N_2^+) and 431nm (CH) were followed for a wide range of plasma conditions, including N_2/CH_4 ratios >3 . Figure 2 shows the results for constant plasma current of 250 mA. As it can be seen, the emission from the N_2 ion line is basically proportional to the amount of injected nitrogen, and almost insensitive to the presence of methane in the plasma. Thus for example, a variation of $\pm 10\%$ in the 428 nm band is observed from no methane (top) to $N_2=CH_4$ plasmas, at $P_{N_2}=3.10^{-4}$ Torr. Similarly, the CH band emission shows a good proportionality with the amount of injected methane, for any relative concentration of nitrogen. Since the CH emission is a good indicator of methane cracking by the plasma¹⁴, this finding is consistent with the insensitivity of

methane depletion from the gas phase to the injection of nitrogen reported above.

Ions at total energies up to the plasma potential (300-400 V) and with a very narrow energy distribution (2 eV) were detected and mass analyzed. The results for three extreme cases, nitrogen, methane and a 1:1 mixture of both in a 95% hydrogen plasma were compared. A clear increase in the ion masses with strong or exclusive contribution from C_xN_y compounds takes place for the 1:1 mixture. This is the case for ions at amu =30 (CH_4N^+), 42($C_2H_4N^+$), 44 ($CH_4N_2^+$), 52, 54 and 56 ($C_2N_2H_n^+$, $n=0,2,4$, respectively). A drastic decrease in amu 18 (NH_4^+) was also detected upon addition of methane to the N_2/H_2 plasma. From all these findings, it is concluded that nitrogen-related species (ions) play an important role in the fate of the products resulting from the cracking of methane molecules by electron impact. These species favor the formation of volatile, stable molecules, which could eventually be condensed in the cold surface of a divertor pump. In this point, it must be recalled that nitrogen injection into the divertor and plasma periphery is one of the best methods for thermal load control in plasma facing components¹⁵. Moreover, its use has been recently proposed for giant ELM (Edge Localized Mode) suppression in fusion reactors¹⁶. Optimization of the injection point respect to the main divertor plasma and puffing rate will be required for the complete suppression of the C/D, T redeposition in hidden areas. Experiments on different type of film precursors in fusion devices, such as C_2 hydrocarbons² and other type of ion/radical scavengers are presently in progress.

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Figure captions.

Figure 1. Evolution of mass spectrometer peaks (left) and deposited film thickness (right) in H₂/CH₄/N₂ (100:5:0-5%) plasmas vs. nitrogen/methane ratio. Lines are drawn only for clarity.

Figure 2. Emission intensity of the CH (431nm) and N₂⁺(428nm) bands vs. the methane (bottom) and nitrogen (top) pressures, respectively, at a constant plasma current of 250 mA in mixtures of arbitrary relative concentrations (see text).