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Studies of a-C: D film inhibition by nitrogen injection in laboratory plasmas and divertors

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Abstract

The injection of nitrogen, as well as other species generally considered as scavengers of the film precursors, in carbon deposition plasmas can completely inhibit the film formation under given plasma conditions, as it has been extensively shown in technical plasmas. Experiments aimed at using this technique to the suppression of tritium/carbon co-deposits in fusion devices have been initiated in several devices. To date, a moderate inhibition (∼40%) of carbon deposition efficiency has been detected in nitrogen-seeded Elmy plasmas at JET. In addition to this, the divertor plasma simulator, Pisces-B, has been used to benchmark the concept under divertor conditions, while maintaining a better control of the experimental parameters. In the present work a review of the state of the art is given. The results from the available experiments are critically analysed in view of the present understanding of the re-deposited film formation in divertors.

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1. Introduction

At present, carbon materials appear to be the best choice for high heat flux areas undergoing strong interaction with the plasma, and they are considered in the present design of the ITER divertor as one of the main constituent. As is well know, the chemical erosion of these materials, when exposed to high particle fluxes of hydrogen isotopes, leads to the formation of re-deposited carbon films, which can incorporate fuel particles up to a ratio of C/H (D, T) of 1:1. The difficulty of T removal from these films by in situ techniques represents a major drawback for the extensive use of any type of carbon material in a fusion reactor [1]. On the other hand, the ample experience gained by the technical plasma community indicates that some chemically active species, which could be acting as scavengers of the film precursors, can lead to the complete suppression of carbon

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film deposition, and the application of one such potential scavenger, molecular nitrogen, was recently proposed for the control of tritium inventory in fusion devices [2]. Laboratory plasma experiments have been initiated in order to fully characterize the underlying mechanism, including the use of the divertor plasma simulator Pisces-B [3]. In addition, a few nitrogen injection experiments have been carried-out in the divertor regions of JET and Asdex Upgrade. The extrapolation of the technique to the reactor conditions is critically evaluated under the light of the present information.

2. Background from film deposition techniques

Ample experience on CN:H film deposition by plasma, generically known as PACVD, and ion assisted techniques points to the existence of a fairly broad range of conditions under which little or no deposition of any kind of film takes place from their gaseous precursors, hydrogen, nitrogen and methane [4]. In fact, this problem also appears at relatively high pressures, as those used in the hot-filament CVD and for other type of precursors, such as ammonia or HCN, for the N component, and several kinds of hydrocarbons for the C component [5]. Although a description of the complex phenomenology involved in these studies is obviously out of the reach of this work, there are several clear findings of direct impact on the application of the technique for divertor chemistry control.

Fig. 1 shows the effect of pressure and gas composition in the deposition rate of a-CN: H films by a RF discharge in the range 0.01–1 Torr [6]. As it can be seen, at pressures below 0.1 Torr and methane/nitrogen ratios below 1 no significant deposition is observed. This finding has been reproduced in other type of plasmas [2,7], although controversial explanations for the inhibition effect of nitrogen exist. A basic insight into some of the processes involved has come from IBAD (ion beam assisted deposition) where it was soon discovered that there is practical upper concentration of <40% for the films created by ion-assisted techniques and that the higher the N concentration, the lower the growing rate of the film was. A large extend of these findings could be well explained for the high chemical sputtering efficiency of nitrogen ions to yield CN and C_2N_2, that for 100 eV N_2^+ impact on graphite is 0.5 C/ion. A threshold value of $E \sim 30$ eV has been found for this erosion process. Moreover, its efficiency is enhanced by the presence of H and by the substrate temperature [4]. Another mechanism that has been claimed is the formation of film-precursor scavengers, and molecular nitrogen ions and ammonia have been put forward as typical examples of them. In an exhaustive study of the chemical background of the film inhibition in CVD reactors at 20 Torr, and using several types of reactants, Ashfold and co-workers [5] identified some of the most likely paths for carbon locking based on fast radical-molecule reactions. Moreover, mass spectrometry of the deposition plasmas at low pressures (in the range of 10^{-2} Torr) has provided additional evidence of the important role of gas-phase chemistry in nitrogen/hydrocarbon mixtures [8].

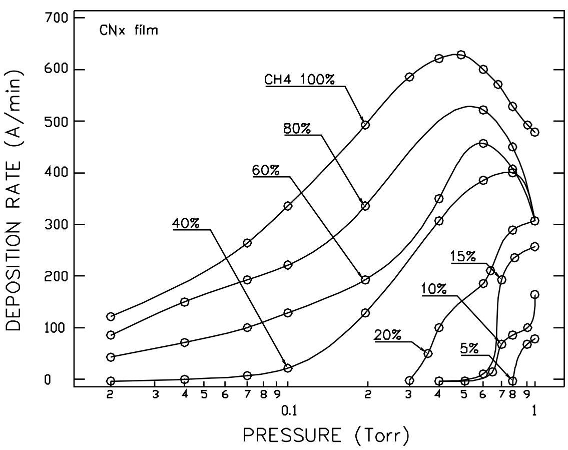

Fig. 1. The deposition rates of a-CN_x: H films as a function of both gas pressure and CH_4/N_2 composition ratio in RF plasmas. From Ref. [6] with permission.

3. Divertor experiments

To date, there have been only a few systematic attempts to validate the scavenger injection technique under real divertor conditions. These attempts have been carried out in the devices JET and Asdex Upgrade, and the quartz microbalance (QMB) was used as deposition monitor in both cases. The experiments at JET were parasitic of the type-III Elmy H-mode with nitrogen-seeded plasmas [9], with nitrogen injection from the inner divertor (GIM 12). Due to the very high sensitivity of the QMB signal and CD photon yield [10] to the exact location of the strike point, only the data from the series #56015–21 and the discharge #58720 (DOC-L configuration, inner strike point at $z = -1.54$ m) are shown. The nitrogen flow upper limit was 3.0×10^{22} e s^{-1}. Exposure times of the QMB to the plasma of 12 s, in the 15–21 series and of 5 s in the 58720 were used. Some relevant optical emission signals were time integrated from the KS3 spectrometer for reference. Fig. 2 shows the evolution of these parameters as a function of the injected nitrogen flow, which in the case of the discharge 58720 reaches its practical upper limit in nitrogen seeded discharges. Several features are evident from the figure. First, a significant decrease of the deposition (normal-

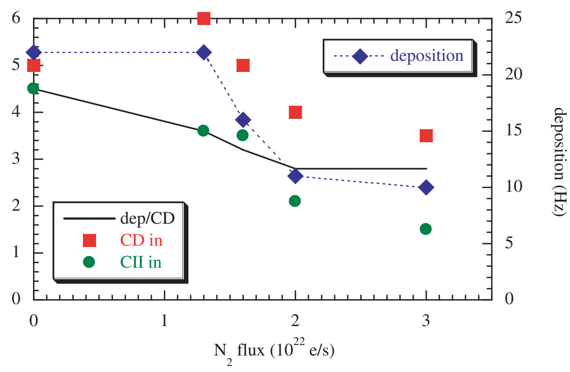

Fig. 2. Evolution of the QMB deposition signal (normalized to 12 s exposure) and some spectroscopic signals from the inner divertor in nitrogen seeded discharges at JET. Dashed line: direct QMB readings in Hz (10 Hz ∼ 1 nm), Solid line: QMB data normalized to the CD emission.

ized to the same time window) at the QMB takes place as the nitrogen flow is increased. Second, a systematic decrease (at least for N_2 flows > 1.3×10^{22} e s^{-1}) can be also observed in all the carbon-related signals at the inner divertor, CD, CII and CIII. Finally, a saturation effect seems to take place at high nitrogen flows.

If no significant erosion from the deposition area (i.e., the QMB in this case) takes place, proportionality between the local concentration of film precursors and deposition rate for constant geometrical conditions would be expected. In the nitrogen-seeded plasmas, the divertor plasma parameters, including flow composition, evolve with injected flow and many effects associated

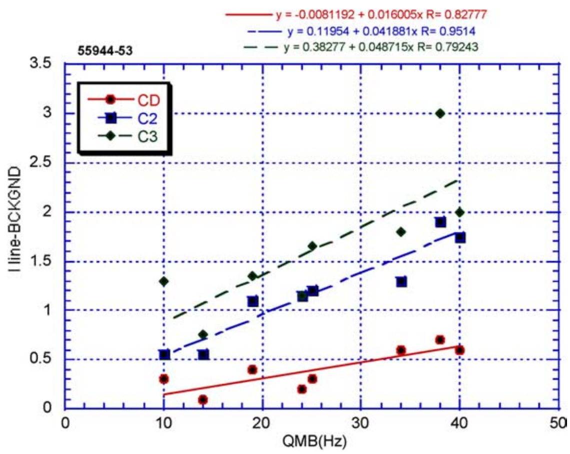

Fig. 3. Evolution of some spectroscopic lines from carbon radiation at the inner divertor versus QMB signal during an edge-parameter scanning in type I Elmy discharges and the same configuration as in Fig. 2.

with these changes could significantly alter the amount of injected film precursors near the deposition monitor. To test this simple picture under conditions close to that used in the experiments of nitrogen feeding, the series #55944–52, devoted to edge characterisation under the DOC-L configuration in type I Elmy plasmas, and implying a scan in injected gas, has been analysed. In Fig. 3, the correlation between the QMB data and some spectroscopic signals from the inner divertor is displayed. As it can be seen a fairly good linear behaviour exists. This allows us to correct the QMB data of the N_2 – seeded discharges for the possible changes of hydrocarbon production that could arise from any extra process of enhanced-decreased erosion under the presence of the injected impurity. As seen in Fig. 2, the data normalized to the CD emission show a decrease of ∼40% in the normalized deposition at the QMB in the full range of nitrogen flows explored.

4. Pisces-B experiments

The Pisces-B facility [3] has been used in the past for divertor-relevant studies of chemical erosion and physical sputtering. The set-up used here is similar to that used in [11]. A gas inlet at −10 (cm towards the plasma side) allowed for the injection of nitrogen, while methane was introduced through the centre of the target plate (TP) in some runs. A deposition monitor (witness plate, WP) is located at −20 cm, and it can be displaced radially. It is electrically isolated from the rest of the chamber. A shield protects the sample from direct irradiation from the plasma while facing the target plate. Polished stainless steel (SS-316) samples were installed in the target plate and in some experiments also in the witness plate. A reciprocating Langmuir probe and optical emission spectroscopy were used as in-situ diagnostics. The samples were weighted after 3 h exposures to the plasma with a 0.05 mg resolution scale. Also, SEM records and EDS analysis of the samples under air were used to characterize the structure and chemical composition of the deposited material. Several configurations of gas inlet (mixed methane and nitrogen, or by separate inlets) and plasma parameters were tried. Total pressures (90% D_2, 5% of each reactant) ranged from 4.5 to 7.5 m Torr. Electron densities of $2.5 < n_e < 3.7$ (10^{12} cm^{-3}) and temperatures of $5 < T_e < 8$ (eV) were measured by the probe. The power and pressure of the discharge were adjusted in order to match the same plasma parameters in the methane and nitrogen/methane mixtures. Deposition on the WP (kept at RT) was only observed when a SS collector sample was used (instead of Si), while deposition on the TP was seen to strongly vary with temperature.

As a systematic feature, deposition at the TP with methane plasmas yielded typical brownish, hard carbon films while those made under the presence of nitrogen

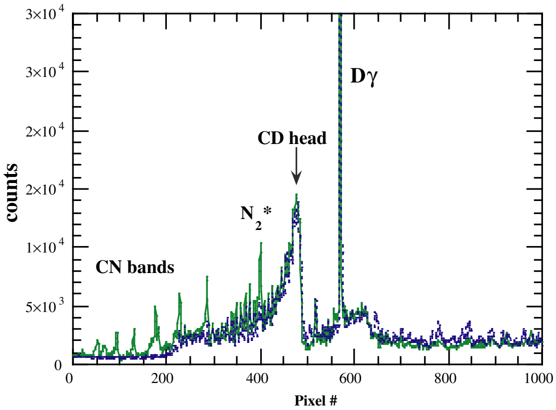

Fig. 4. Emission spectra of methane/deuterium and methane/nitrogen/deuterium plasmas at Pisces-B.

gave softer, easily self-peeling dark films. Particularly remarkable is the comparative run made under a −40 V bias at the TP. A 3× thicker film (0.6 vs. 1.8 mg), but with the characteristic above mentioned, was found in the presence of nitrogen. At the WP, methane plasmas yielded a 0.1 mg carbon film (C = 80%, O = 4%) with clear interference colours indicating a gradual thickening (200 nm maximum) on its closest position to the plasma. On the contrary, a 1.9 mg deposit was found in the nitrogen-containing plasma at the same location. The film was homogeneous, with a yellowish colour. Its chemical composition was 30%N, 60%C and 9%O. The film broke down into flakes upon exposure to the air and pump-down for the EDS analysis. Optical emission spectra were taken during some runs. The wavelength span was limited by the cut-off of the observation window at 390 nm. An example is given in Fig. 4. The spectrum in the range 412–432 nm is displayed for both type of plasmas. They are normalized to the CD band head to allow a better comparison. A clear structure is superimposed to the CD spectrum in the nitrogen case. The identification of many of them indicates a strong contribution of CN radicals (vibrational bands of the B–X transition), as well as excited N_2 molecules (426.97 nm).

5. Discussion and perspectives

In spite of the obvious complexity of the nitrogen-hydrocarbon plasma systems, the different characteristics of the explored scenarios can shed light on some of the prominent features to be considered for the tritium control in re-deposited film under fusion divertor conditions. Perhaps the most striking result corresponds to the work performed at Pisces-B. Although no measurements of the D/C ratio in the deposited films was possible, the fact that more deposition is found under the presence of nitrogen than in pure methane especially in the witness plate, at a considerable distance from the direct plasma contact, points to existence of an operational window leading to the opposed effect to that looked for. The obvious question is in which extend the generated plasmas resemble the expected conditions of a reactor divertor. One of the important issues in this respect is the ion composition and energy spectrum of the injected impurity. Indeed, the low temperatures, and in especial, the low confinement time of the ions in this type of plasmas [12], together with the relatively high ionisation potential of molecular nitrogen, makes it unlikely to reach the chemical etching conditions found in IBAD experiments. On the other hand, gas phase reactions of the 'scavenger type' would in principle require a higher concentration of reactants and the direct injection of the scavenger species such as ammonia (radical molecule reaction) or molecular nitrogen ions (ion–molecule reaction). In this respect it is interesting to note that in the emission spectrum shown in Fig. 4, the band corresponding to this ionic species – at 427.80 nm – is missing, in contrast with the case of the low temperature plasmas where the film inhibition has been recorded [2]. It is also worth noting that the bad quality of the generated films probably indicates that the conditions of their formation are in the threshold of the inhibition scenario, as reported elsewhere [8].

The data from the divertor fuelling at JET deserve also some comments. First of all, the partial decrease of film deposition found in the experiments could in principle be ascribed to the mere decrease of hydrocarbon formation reported for these plasmas [9], which seems to be associated to the lower power flow reaching the divertor under strong impurity radiation. However, if the chemical composition of erosion products is the same as in non-seeded plasmas, the normalized data shown in Fig. 2 imply lower *intrinsic* deposition efficiency in the seeded plasmas. Of particular relevance in this case is the possibility of chemical erosion leading to CN compounds formation. In that respect, evidence of CN emission at the outer divertor in nitrogen seeded discharges at that location, has been reported very recently, thus demonstrating for the first time the chemical contribution to the interaction of nitrogen and carbon elements in a fusion plasma [13], at least for the higher Te plasmas found at the outer divertor. Little is known about the sticking of CN and related species on surfaces, but the formation of these species are common in ammonia/methane mixtures where basically no film is been formed. Finally, the saturation effect observed at high nitrogen flows at JET points to the need of further optimisation of the injection/deposition geometry, together with a better characterisation of the involved chemical processes. Work in this direction is being addressed at Asdex Upgrade now.

In conclusion, all the experimental information presently available indicates that inhibition of co-deposits of T rich carbon films by selective impurity injection in divertors is possible. However, optimisation of the scavenger injection/deposition geometry and a more exhaustive characterisation of the involved species and their energy distribution is still needed. Work in plasma simulators may provide with important answers to the technical requirements, such as type of impurity and minimum energy of the involve ion species. Work in progress in both kinds of plasmas is in progress.

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