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Nitrogen-assisted removal of deuterated carbon layers

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ABSTRACT

Deuterated carbon films prepared in laboratory and boronised films prepared in the TEXTOR tokamak were exposed to hydrogen–nitrogen plasmas in order to determine erosion characteristics and fuel removal efficiency. Exposures were performed in: (i) TEXTOR tokamak during ion cyclotron heated wall conditioning discharges (ICWC) and (ii) TOMAS magnetic plasma facility in radio frequency-assisted glow discharges. The essential results are: (i) films exposed in TEXTOR are not affected: deuterium and carbon content does not decrease and the morphology is unchanged, and (ii) deuterium and carbon contents in films exposed in TOMAS is reduced by 30–60% after 2 h of cleaning and topographical changes are noted. The study shows that while exposure to H_2–N_2 laboratory plasma removes a-C:D films, no effect is seen at the position of the sample exposure during tokamak ICWC plasmas. It also indicates that the removal efficiency is only weakly related to nitrogen, since the highest removal efficiency is seen with pure hydrogen plasma. A comparison to oxygen-assisted fuel removal is given.

1. Introduction

The reduction of long-term fuel inventory in plasma-facing components (PFC) is one of the most critical and challenging issues to be resolved in order to ensure safe and economical operation of a reactor-class device [1,2]. Therefore, efficient methods for removal of hydrogen isotopes and co-deposited layers are to be developed and tested. In this process, three aspects must be taken into account for each technique: (i) removal efficiency of fuel and co-deposits, (ii) impact on the surface state of the PFC and (iii) dust formation caused by destruction/disintegration of co-deposits. To date, fuel removal by glow discharge in hydrogen and helium [3], oxidative [4–6] and photonic methods with lasers [7,8] and flash lamp have been tried [9]. Nitrogen-assisted fuel removal is also considered a candidate method, and encouraging results have been obtained in laboratory experiments [10–14]. This work provides an account of experiments performed in nitrogen-assisted discharges in the TEXTOR tokamak and in the TOMAS experimental plasma device, a toroidal laboratory low temperature plasma experiment to study wall conditioning. This experimental program allowed for covering a broad range of conditions.

2. Experimental

2.1. Experiments in TEXTOR

The study was performed using silicon substrates with two types of films: (a) pure amorphous deuterated carbon films (a-C:D) with a thickness of 150–300 nm prepared under laboratory conditions in a radio frequency-assisted glow discharge in a CD_4–D_2 mixture [15] and (b) boron layers (approximately 15 nm thick) deposited on Si substrates during routine boronisation of the TEXTOR tokamak with hydrogenated diborane (B_2H_6) [16]. Not precoated witness sample made of Inconel® was also exposed. These probes were mounted on holders using steel stripe for fixing. The stripe was shadowing a small part of the probe. Therefore, on each sample there was a region not accessible by the plasma. In surface studies after the exposure this region is referred to as "unexposed". The holders were inserted into the tokamak using transfer systems, so-called limiter locks, positioned at a radius equivalent to the TEXTOR wall. One set of probes were inserted from the bottom (Limiter Lock 1) and another from the top (Limiter Lock 3). The probes were exposed to special wall conditioning discharges in hydrogen–nitrogen (H_2–N_2) produced by ion cyclotron resonance heated (ICRH) pulses, i.e. ion cyclotron heated wall conditioning (ICWC). This technique is being develop for ITER as it can be used in the presence of the toroidal and vertical magnetic field [17]. The ICRH antenna system was located about 45° away form the limiter lock systems at the low field side of the device. The experiment used 25 discharges with a total ICRF time of 40 s.

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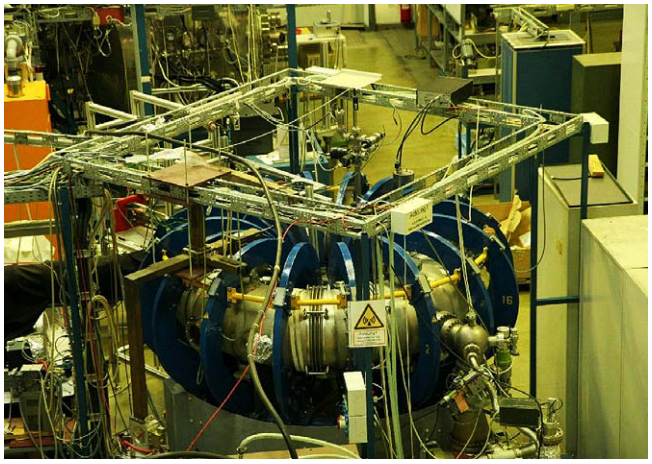

Fig. 1. View of the TOMAS plasma facility.

2.2. Experiments in TOMAS

TOMAS (TOroidal MAgnetic System) is a low temperature plasma device with a major radius of 0.78 m, a minor radius of 0.26 m and maximum toroidal field of 120 mT. The device is shown in Fig. 1, whereas technical details can be found in [18]. Two basic series of exposures to H_2–N_2 plasma have been made to check the impact of gas mixture composition (0–100% N_2) and temperature (40–290 °C) on the removal efficiency of carbon and deuterium from laboratory-prepared pure amorphous carbon films (a-C:D) deposited on silicon substrates. A summary of experimental conditions is given in Table 1. Most experiments were performed using glow discharge assisted by radio frequency (RF). In addition, one exposure was performed with microwave heated plasma to assess the effect of plasma heating. The temperature 200 °C was chosen because it is also the wall temperature foreseen for ITER; it is also the wall temperature of TEXTOR, thus making comparison easier. The pressure during GDC was around 10^{-2} mbar and an accelerating voltage of 330 V was applied. When using pure hydrogen, the pressure was about a factor two higher – this was necessary to ensure plasma stability. The total plasma current was around 0.8 A, Except for the pure nitrogen case when the current was about 1.6 A. Since the total surface area of TOMAS is around 10 m^2, this corresponds to 80 and 160 mA m^{-2}, respectively, or a flux density of 5×10^{13} and 1×10^{14} $cm^{-2}s^{-1}$. With the exposure normalized to 2 h (7200 s), the samples were exposed to 3.6×10^{17} and 7.2×10^{17} incident ions, respectively. With the dissociation energy for N_2 of 9.5 eV and for H_2 of 5 eV, and ionization energy at 14.5 and 13.6 eV respectively, it may be assumed that the impinging ions contains H^+ and N^+ ions in quantities proportional to the percentage of a given species in the H_2–N_2 gas mixture feeding discharges in TOMAS. During microwave heated exposures, a biasing voltage of −200 V was applied to the holder. In these discharges, the pressure was lower (3.8×10^{-3} mbar) because of heating limitations. Taking into account parameters (i.e. bias and ion flux density) in types of experiments the power deposition to the samples was in the range from 16 W m^{-2} to 32 W m^{-2}. Gas phase composition was continuously monitored with a quadrupole mass spectrometry (QMS).

Table 1
Experimental condition in TOMAS.

Exp.	Discharge	Pressure (10^{-2} mbar)	Gas mix (% N_2)	Temp (°C)	Flux density (10^{13} $cm^{-2}s^{-1}$)
1	GD + RF	1.8	0	200	10
2	GD + RF	0.9	10	200	5
3	GD + RF	0.9	25	200	5
4	GD + RF	0.9	50	200	5
5	GD + RF	0.9	75	200	5
6	GD + RF	0.9	100	200	10
7	GD + RF	0.9	50	40	5
8	GD + RF	0.9	50	100	5
9	GD + RF	0.9	50	290	5
10	Microwave	0.4	25	200	5

2.3. Ex-situ examination of surface morphology

After experiments, exposed and unexposed parts of the layers were examined using accelerator-based ion beam analysis (IBA) methods. Nuclear reaction analysis (NRA) with a 2 MeV $^3He^+$ beam was used to determine the content of deuterium [^{3}He(d,p)^{4}He] and a 2 MeV proton beam for the determination of boron [^{11}B(p,α)^{8}Be]. The same proton beam allowed studies of carbon content by enhanced proton scattering (EPS): ^{12}C(p,p)^{12}C. The other methods were: high resolution scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and sputter-assisted X-ray photoelectron spectroscopy (XPS) with an erosion rate of 0.5 nm s^{-1} by an Ar^+ beam. In the case of materials exposed in TOMAS, all layers were pre-characterized using optical microscopy and profilometry to assure that the layers were uniform and not peeling-off.

3. Results and discussion

3.1. Exposures in H_2–N_2 ICRH-assisted plasma in TEXTOR

Deuterium and carbon contents before and after exposure are summarized in Table 2. This table also provides a comparison to cleaning by He–O_2 GD in TEXTOR [4]. The results of exposures to the hydrogen–nitrogen mixture show no decrease in C or D from the films under laboratory conditions. On the contrary, the amount of both species slightly increases on samples from both limiter locks. This is best noted in the case of carbon content on pre-boronised surfaces. The effect has been also observed after exposures of such boronised probes to the helium–oxygen glow. It is most likely related to the re-deposition of carbon eroded by glow discharge from the graphite plasma-facing components of TEXTOR.

SEM images recorded on the Si probes exposed in TEXTOR have shown smooth surfaces before and after exposure. There have been small differences in contrast probably due to deposited carbon. Also EDS has not revealed any noticeable changes in the elemental composition but the sensitivity of this technique for light elements

Table 2
Removal of carbon and deuterium by exposure to TEXTOR plasma.

Plasma	Probes	Initial D (10^{15} at/cm^2)	Change of D content	Initial C (10^{15} at/cm^2)	Change of C content
H_2–N_2 glow & ICRF pulses	a-C:D (Lab)	654	No change	993.5	Increase 14%
	Pre-boronized In TEXTOR	2	Increase 25%	108	Increase 36%
He–O_2 glow [4]	a-C:D (Lab)	525	Removed 99%	885	Removed 98%
	Pre-boronized in TEXTOR	17	Removed 88%	12	Increase 138%

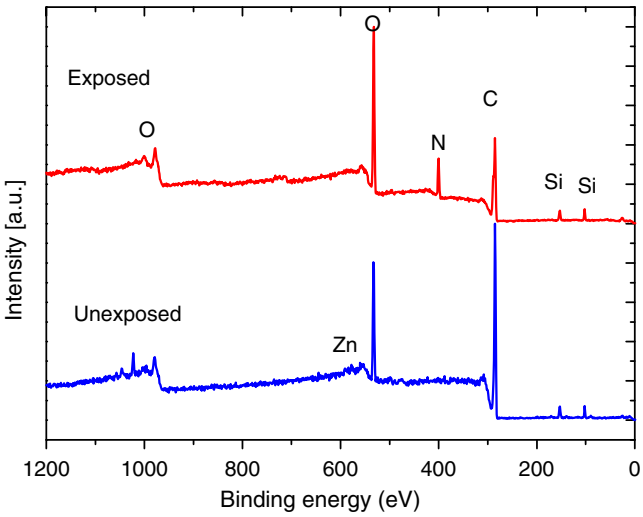

Fig. 2. X-ray photoelectron survey spectra for a-C:D films on silicon recorded before and after exposure to the H_2–N_2 plasma in the TOMAS facility.

is small. However, the change of chemical composition has been recorded with XPS. The presence of nitrogen has been detected on all surfaces (including an Inconel® witness sample) exposed to the H_2–N_2 mixture. A clear peak has been observed on samples before and after 45 min of sputtering with Ar^+. Fig. 2 shows an XPS survey spectrum with a clear 1s N photoelectron line in the a-C:D film (on Si substrate) treated with the ICWC discharges.

In summary, one notices major difference when comparing the impact of nitrogen- with oxygen-assisted cleaning on the removal of laboratory-prepared a-C:D layers. The exposures in the nitrogen-containing environment lead only to some changes of the layer chemical composition, whereas He–O_2 glow plasma in TEXTOR resulted in the removal of the whole amorphous films, as confirmed earlier by IBA, EDS and XPS [4].

3.2. Exposures in TOMAS

Amorphous carbon films prepared in laboratory were used for all experiments reported below. As received samples have shown very smooth featureless surfaces as observed with high resolution SEM. An exposure to GDC in TOMAS caused a change in the layer structure. Results for all experiments at different target temperature and gas composition are summarized in Table 3. Plots in Fig. 3(a) and (b) show the change of D and C contents in the main series of experiments in RF-assisted glow discharge: dependence on gas composition (10–100% N_2) and temperature (40–290 °C) with the $H_2/N_2 = 1$ mixture, respectively. The results have been normalized with respect to the exposure time (7200 s) and ion current measured on targets during the exposure. QMS measurements detected H, N, N_2 as the main components. Smaller signals associated with $M = 16$ (CH_4, O, NH_2), $M = 17$ (OH, NH_3) and H_2O ($M = 18$) were noticed. Only trace signals were recorded at $M = 26$ (CN) and $M = 27$ (HCN) thus showing that the involvement of chemical processes between nitrogen and carbon has rather negligible impact on the removal efficiency of D and C.

Following main results have been obtained in exposures to different gas composition at constant temperature:

(i) in each exposure, the removal rates of deuterium and carbon are approximately the same;
(ii) 2 h exposures at 200 °C to the H_2–N_2 mixture (10–100% N_2) result in removal of 20–30% of the layer with the maximum recorded for 25% N_2 when 31% deuterium and 33% carbon was removed; but at other gas compositions no clear trend could be detected;
(iii) the erosion rate is increased by a factor of 2 with microwave heating, to 58% deuterium and 52% carbon removed using 25% N_2, although this experiment is not exactly comparable to the others;
(iv) in the reference exposures using only hydrogen, ~60% of the layers were removed in 2 h.

Table 3
Removal of carbon and deuterium by exposure H_2–N_2 plasma in TOMAS.

Discharge	Gas mix (% N_2)	Temp (°C)	Initial D (10^{15} at/cm^2)	Removed (% D)	Initial C (10^{15} at/cm^2)	Removed (% C)
RF + glow	0	200	1261	48	1986	59
RF + glow	10	200	1174	24	1832	19
RF + glow	25	200	855	31	1431	33
RF + glow	50	200	1114	23	1655	19
RF + glow	75	200	1170	30	1840	21
RF + glow	100	200	981	24	1534	23
RF + glow	50	40	916	29	1414	32
RF + glow	50	100	1071	27	1775	25
RF + glow	50	290	1031	26	1669	14
Microwave heated	25	200	1288	58	2051	52

In summary, the greatest removal efficiency is measured in pure hydrogen plasma due to chemical erosion and physical sputtering of the films by hydrogen flux. However, in the case of H_2–N_2 gas mixture there is little influence of the gas composition on the

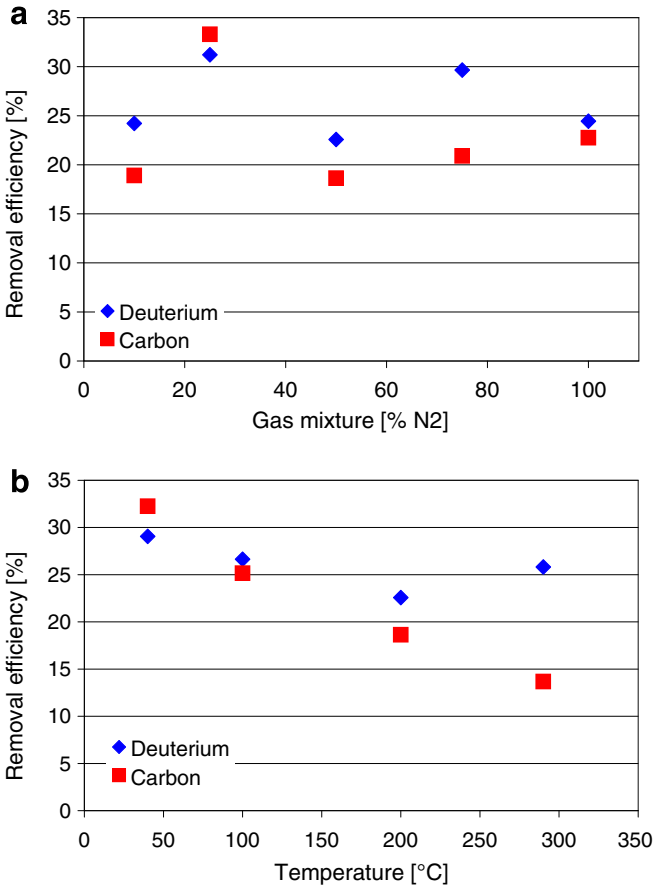

Fig. 3. Deuterium and carbon removal efficiency as a function of: (a) nitrogen content in H_2–N_2 plasma and (b) target temperature.

removal efficiency of deuterated carbon films. One can tentatively state that the erosion (chemical and physical) caused by H and the physical sputtering mainly by nitrogen somewhat compensate each other leading to the rather flat profile. It can also be noted that 2 h exposure to TOMAS plasma with an ion flux density of in the range from $5 \times 10^{13}\,cm^{-2}s^{-1}$ to $10^{14}\,cm^{-2}s^{-1}$ is not enough to erode approximately 250 nm thick layer. The experiments at the constant 50–50 gas mixture but increasing temperature (40–290 °C) show a decrease in the removal efficiency of carbon when the temperature rises. The efficiency of deuterium removal decreases up to 200 °C and then the increase is noted again at 290 °C. While the increased rate of D removal when the temperature rises from 200 °C to 290 °C can be attributed to thermal release, the other results - especially for carbon – are still to be better understood and clarified in future experiments in TOMAS and studies of the exposed layers with XPS. This is because the tendency in target temperature impact on the erosion of amorphous carbon films by H_2–N_2 is opposite than that measured for such films under the bombardment with hydrogen or deuterium atoms or energetic ions [19,20].

4. Conclusion

The experiments performed under a broad range of conditions in with H_2–N_2 mixture have shown that: (i) no or little erosion of carbon and deuterium is induced by glow discharge ICRH-assisted pulses in TEXTOR; (ii) the erosion of a-C:D films measured after the exposures in TOMAS varies, but even in the best case (25% of N_2 in the mixture) the efficiency does not exceed 35% for a 200–300 nm thick layer after 2 h treatment by RF-assisted glow discharge at 200 °C; (iii) greater efficiency, though not better than 60% is determined in pure hydrogen and in discharges heated by microwaves. The results indicate that the major erosion mechanism is physical sputtering, which depends on the ion energy, i.e. the acceleration voltage under experimental conditions.

For the hydrogen–nitrogen mixture in TOMAS with ion flux of $5 \times 10^{13}\,cm^{-2}s^{-1}$ in RF-assisted glow discharge the removal rate for carbon (see Table 3) was in the range 0.8–1.3 C atom per incident ion which is very higher than 0.5 C/ion given in [11] for nitrogen bombardment of carbon. The effective removal rate of the layers is around 0.01 nm s^{-1} for most exposures, very similar rates have been reported in [13]. This value, which is a figure of merit in the assessment of deposit and fuel removal methods, is much lower than the growth rate of co-deposited layers in carbon wall tokamaks like TEXTOR where the rates of 3 and 10 nm s^{-1} were determined for deposits on the main toroidal limiter and the neutralizer plates, respectively [21,22]. Therefore, the results obtained do not lead to optimistic conclusions regarding the application of H_2–N_2 glow plasma for the removal of co-deposits from large areas in a device with carbon PFC.

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