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Optimization of non-oxidative carbon-removal techniques by nitrogen-containing plasmas

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ABSTRACT

The continuous control of tritium inventory in ITER calls for the development of new conditioning techniques [G. Federici et al., Nucl. Fus. 41 (2001) 1967]. For carbon plasma-facing components, this implies the removal of the T-rich carbon co-deposits. In the presence of strong oxygen getters, such Be, the use of oxygen-based techniques will be discouraged. In addition, tritiated water generated by these techniques poses extra problems in terms of safety issues [G. Saji, Fus. Eng. Des. 69 (2003) 631; G. Bellanger, J.J. Rameau, Fus. Technol. 32 (1997) 196; T. Hayashi, et al., Fus. Eng. Des. 81 (2006) 1365]. In the present work, oxygen-free (nitrogen and ammonia) glow discharge plasmas for carbon film removal were investigated. The following gas mixtures were fed into a DC glow discharge running in a ~200 nm carbon film coated chamber. Erosion rate was measured in situ by laser interferometry, RGA (Residual Gas Analysis) and CTAMS (Cryotrapping Assisted Mass Spectrometry) [J.A. Ferreira, F.L. Tabarés, J. Vac. Sci. Technol. A25(2) (2007) 246] were used for the characterization of the reaction products. Very high erosion rates (similar to those obtained in helium–oxygen glow discharge [J.A. Ferreira et al., J. Nucl. Mater. 363–365 (2007) 252]) were recorded for ammonia glow discharge.

1. Introduction

The use of carbon facing components in the high flux region of fusion devices is constrained by the formation of co-deposits that migrate to remote areas not reached by the fusion plasma. Oxygen containing methods have been suggested for carbon removal [1]. Among these techniques high temperature oxidation and glow discharge-driven erosion have been considered for tritium removal in ITER. But formation of tritiated water poses extra problems concerning safety [2–4]. The presence of oxygen getters in the vacuum vessel also could limit the use of oxygen but this only occurs at a significant rate at high temperatures (>600 °C) [7].

Chemical affinity between nitrogen and carbon was widely reported [8–11]. Nitrogen reacts with carbon to form very stable volatile species as HCN or C_2N_2. In the present work, DC glow discharges in different gas mixtures were tested, with nitrogen and ammonia as the active gas and hydrogen or helium as carrier gas.

2. Experimental set-up

Experiments were carried out at room temperature in a deposition chamber, previously described [6]. The residual gas was analyzed using a differential pumped mass spectrometer (QMS) while the reaction products were also determined by Cryotrapping Assisted Mass Spectrometry (CTAMS) [5] which consists of the controlled desorption of condensed gases on a liquid nitrogen trap. This chamber was covered with a hard carbon film (~200 nm) deposited using a helium–methane or a helium–ethylene DC glow discharge. A grounded silicon sample was introduced into the vessel and film thickness was monitored during deposition or erosion (both in situ) by laser interferometry [12] (Fig. 1). The set-up consists on a diode laser (wavelength 670 nm) and a photodiode to collect the reflected light. At near normal incidence to the sample one fringe is related to a film thickness change d by

$$d = \frac{\lambda}{2n}. \tag{1}$$

Some information can be extracted from the laser signal during the deposition. Using a non-linear least squares method and the Eq. (2) to adjust normalized reflectance [13] it is possible to fit experimental data and recover information about refraction index n and extinction coefficient k of the layer, and deposition rate v.

$$R = \left| \frac{n_2(n_1 - n_3)\cos(2\pi n_2 vt/\lambda) + i(n_1 n_3 - n_2^2)\sin(2\pi n_2 vt/\lambda)}{n_2(n_1 + n_3)\cos(2\pi n_2 vt/\lambda) + i(n_1 n_3 + n_2^2)\sin(2\pi n_2 vt/\lambda)} \right|^2, \tag{2}$$

where n_1 states for refraction index of the medium (in vacuum $n_1 = 1$), n_3 refraction index of the substrate (including the complex

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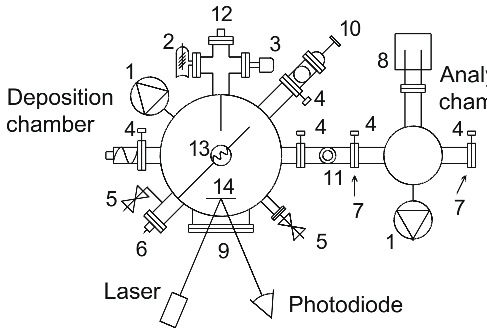

Fig. 1. Experimental set-up. Top view. (1) Pumping system (turbo pump and rotary pump), (2) manometer (Bayard Alpert), (3) capacitance manometer, (4) isolation valve, (5) flow controllers, (6) anode, (7) diaphragm (differential pumping), (8) quadrupole mass spectrometer, (9) optical port, (10) sample manipulator, (11) cryogenic (LN_2) trap, (12) Langmuir probe, (13) electron gun, and (14) silicon sample.

part), $n_2 = n + ik$ (complex refraction index), t deposition time and λ wavelength of the incident light.

The optical properties of carbon layers are related with other properties as hydrogen content [14]. The real part of refraction index estimated by this technique was 1.9 ± 0.1 in the case of methane as the source gas, and 2.0 ± 0.1 in the case of ethylene, that correspond to hydrogen contents H/(H + C) of 0.35–0.4. These figures agree with ERD (Elastic Recoil Detection) analysis [15] and allow us to conclude that both films are similar.

3. Results

The first mixture to be tested was a hydrogen-nitrogen mixture (10 mTorr). Two different ratios were used. First a hydrogen flow of 9.0 sccm and a nitrogen flow of 5.6 sccm (38%) was injected in a glow discharge with a current of 100 mA (~0.02 mA/cm^2, 640 V).The resulting erosion rate was 3.6 nm/min. The second mixture consists of a flow of 7.3 sccm of hydrogen and 12.4 sccm of nitrogen (63%). Characteristics of the glow discharge were 100 mA and 450 V, resulting in an erosion rate of 3.2 nm/min. The main products measured by the QMS were hydrogen cyanide (HCN) and acetylene (C_2H_2). Some ammonia (NH_3) and cyanogen (C_2N_2) was also recorded. Fig. 2 shows masses of products as measured by the QMS in the second mixture. The laser trace is also shown. The products species were univocally identified by using CTMAS technique (see Fig. 3). Some traces of acetonitrile (CH_3CN) were also detected.

A rise of ammonia peak (amu 17) is observed at the end of the discharge, suggesting that some nitrogen recombines with the available hydrogen, although it is simultaneously consumed by the carbon film, its concentration recovering only after full carbon depletion. The ratio between main products (HCN and C_2H_2) is 2.3 in the first example and 1.6 in the second one. This ratio is related to the carbon eroded by nitrogen (with HCN as final product [8–10]) to the ratio of hydrocarbons (mainly acetylene) formed by chemical sputtering.

The second mixture (see Fig. 4) to be tested was a helium–nitrogen mixture (10 mTorr) with 23.5 sccm and 5.40 sccm (19%), respectively. Glow discharge conditions were 100 mA, 620 V and 5 mTorr (total pressure). The resulting erosion rate was 2.61 nm/s. The main products are HCN and C_2N_2. The production of C_2N_2 is twice than the case of hydrogen-nitrogen but HCN production is similar to that case. Neither ammonia nor C_2H_2 was observed. This observation was confirmed by the CTAMS technique.

Different mixtures of helium and ammonia were tested resulting in very high erosion rates. The results are summarized in the Table 1. As an example Figs. 5 and 6 shows masses registered in the case of higher erosion rate (He 18.8 sccm, NH_3 13.50 sccm

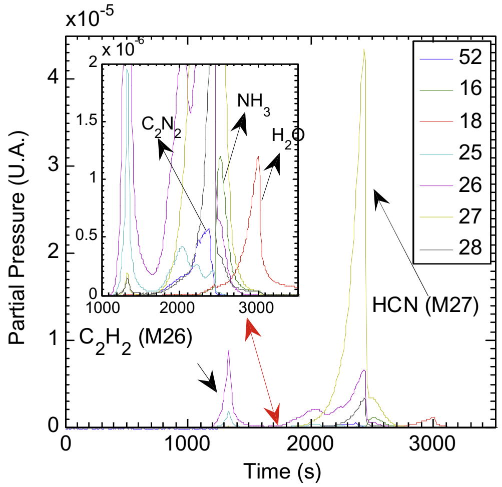

Fig. 3. CTAMS spectrum of a H_2/N_2 mixture.

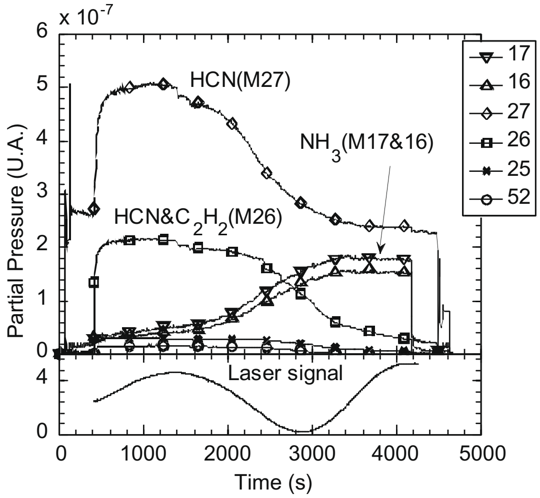

Fig. 2. Product masses measured by QMS (top) for a H_2/N_2 (7.3 sccm/12.4 sccm) glow discharge. Bottom, laser signal.

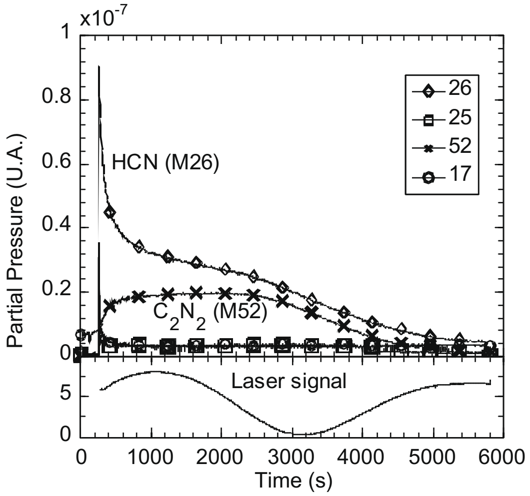

Fig. 4. Product masses measured by QMS (top) for a He/N_2 (23.5 sccm/5.4 sccm) glow discharge. Bottom, laser signal.

Table 1
Summary of results on helium–ammonia mixtures.

%NH_3	42	73	19	42	42
He (sccm)	18.8	7.6	27.7	18.8	18.8
NH_3 (sccm)	13.5	20.6	6.7	13.5	13.5
I (mA)	100	100	100	200	100
V (volts)	400	450	400	450	475
P_{total} (mTorr)	20.2	20	15.6	26.7	19
Erosion rate (nm/min)	11.64	13.24	8.66	16.68	9.99
HCN/C_2H_2	4.9	4.6	4.08	4.7	Metallic walls

(43%), 200 mA, 450 V, total pressure during glow discharge 26.7 mTorr). The main products of the etching are HCN, C_2H_2 (Fig. 5) and H_2 (Fig. 6). Hydrogen is produced by cracking of the ammonia molecule but also some hydrogen is released by the film, because mass two decays after the film depletion. HCN:C_2H_2 ratio is near 4 as is shown in Table 1. The CTAMS technique could not be applied because ammonia is a condensable gas at liquid nitrogen temperature, thus hiding the main product. The resulting erosion rates are over 10 nm/min and the best erosion rate (16.68 nm/min) was obtained for the results shown in Figs. 5 and 6 (fourth column in Table 1). In these experiments the chamber walls were coated with a a-C:H layer including the silicon sample. One experiment was carried out moving the sample to a next chamber (under vacuum) and cleaning the main chamber until remain a metallic (stainless steel) environment. The silicon sample (coated) was reintroduced and exposed to an ammonia plasma, different loss rate of the species at the surface could affect to the erosion rate (competition) but no effect was observed.

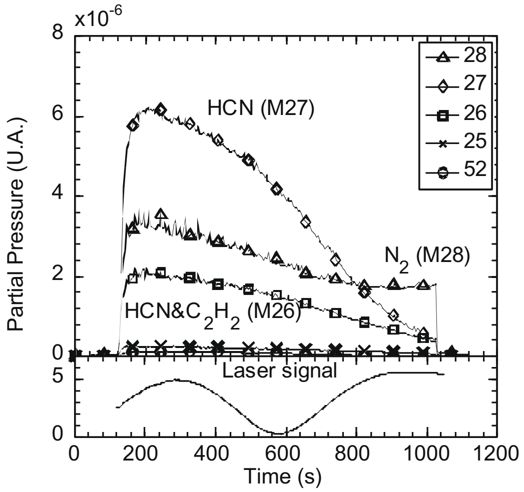

Fig. 5. Products of the erosion of a 200 nm carbon film by a helium–ammonia mixture (top). Laser signal (bottom).

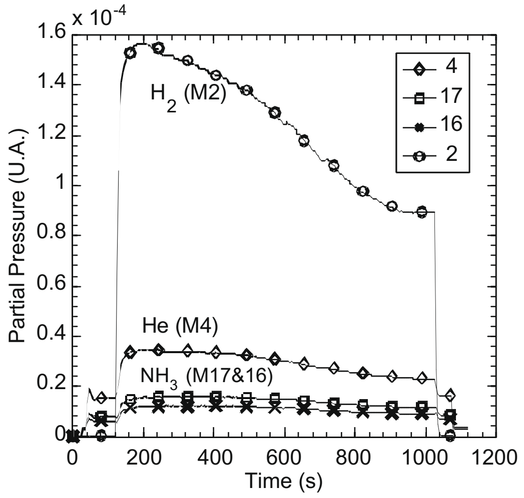

Fig. 6. Main masses for a helium–ammonia mixture.

4. Discussion

Different nitrogen-containing mixtures were tested for the removal of carbon layers produced by helium–hydrocarbon (CH_4 or C_2H_4) mixtures. When nitrogen gas is used as the nitrogen source reactions rates are significantly lower (~2–3 nm/min compared to ~10 nm/min) than mixtures with ammonia. Hydrogen cyanide was the main product that results from the film erosion. The presence of hydrogen in the mixture yields the formation of some acetylene. Other products that were detected this mixtures are cyanogen (which production rises when hydrogen concentration is low) and other minor products as acetonitrile (CH_3CN) detected by CTAMS [16] in N_2 mixtures.

The dependence of the erosion rate with chemical form of the injected gas only can be explained if chemical reactions have a major role. A mechanism of enhanced chemical erosion by ion bombardment damage and simultaneous chemical erosion by hydrogen cannot explain the large differences observed between nitrogen and ammonia mixtures. This suggests that nitrogen has a chemical role but does not exclude a role related to ion bombardment as the erosion rate rises whit current. However, this dependence could be explained either in terms of bond damage in the carbon film by the ion bombardment or in terms of higher cracking and formation of active species (NH_x) from the injected gas.

Discharges in H_2/N_2 mixtures led to the formation of some ammonia (Fig. 2) that rises as the carbon film is depleted, thus indicating that ammonia was simultaneously being produced and consumed as the carbon layer was eroded. Strong variations of ammonia concentration in the plasma doesn't change erosion rates significantly (from ~9 to 13 nm/min) but an increase in the plasma current produces a higher erosion rate (from ~12 to 17 nm/min for the same concentration). All the detected products are formed by endothermic reactions (HCN has a formation enthalpy of 132 kJ/mol, C_2N_2 307.2 kJ/mol, C_2H_2 kJ/mol, CH_3CN 71.5 kJ/mol [17]), so part of the energy supplied to the plasma is consumed in the formation of these products. This could be partially responsible of the dependence with plasma current, but further research is needed to assess this point.

It should be pointed out that ammonia-containing glow discharges have higher erosion rates than those observed in helium–oxygen glow discharges in similar conditions [6]. It has also the advantage of being free from water production [2–4]. In a hypothetical reactor, the use of ammonia would lead to the formation of tritiated ammonia, but tritium recovery from ammonia is an efficient process at low pressure and high temperature (~800 °C) and is easily decomposed to H_2 and N_2 catalyzed by iron or nickel [17].

$$2NH_3 \rightarrow N_2 + 3H_2 \quad \Delta H_{298} = +91.86\ \text{kJ/mol}. \tag{3}$$

5. Conclusions

High erosion rate (>10 nm/s) was observed in nitrogen-containing glow discharges comparables to those rates obtained with helium–oxygen (12 nm/s) plasmas. The high sensitivity of the removal to the chemical form of injected nitrogen indicates that erosion is dominated by chemical reactions between plasma species and the carbon layer. Also it was observed in hydrogen–nitrogen plasmas when the film is completely etched that ammonia concentration rises (because it is not being consumed by the carbon layer). This could be linked to the use of ammonia as a better precursor for etching of carbon films. The main products that are produced in these conditions are hydrogen cyanide and acetylene. In the literature [2–4] HCN and CH_3CN used to be the main product of carbon–nitrogen reactions in presence of hydrogen.

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