Ammonia formation and W coatings interaction with deuterium/nitrogen plasmas in the linear device GyM

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1. Introduction

The seeding of gaseous impurities will be used in ITER to protect the tungsten divertor from local heat loads by means of radiative cooling. One of the candidates is nitrogen [1], which, in a fusion plasma device, can interact with atomic hydrogen and its isotopes leading to formation of ammonia. This reaction may also be catalyzed by the metallic surface of the wall. The presence of ammonia in ITER might be a serious issue for the tritium recovery system. Seeded nitrogen may also be implanted or codeposited onto the tungsten PFC (Plasma Facing Components) of the divertor [2], influencing their physical and chemical properties. Issues of concern are: alteration of melting temperatures and sputtering yields, formation of insulating layers that might induce arcing and alteration of the retention behavior for hydrogen isotopes. It is therefore necessary to investigate if and how much ammonia is formed during a nitrogen-seeded discharge and at the same time how nitrogen interacts with tungsten in divertor-like plasma conditions. This paper reports the first results of experiments aimed to study the formation of W_xN_y compounds on tungsten samples exposed to N_2 seeded D_2 plasma. In the same conditions the ammonia production has been considered and studied. The experiments have been performed on the linear device GyM suitable to simulate a divertor plasma relevant for fusion reactor. Exploiting the fact that GyM can operate in continuous mode, on GyM it is possible to achieve with single experiment discharge high fluences foreseen in fusion device ($\sim 1 \cdot 10^{24}\,m^{-2}$).

The formation of ammonia and its precursors, in N_2 seeded D_2 plasmas, have been monitored by Optical Emission Spectroscopy (OES), while the exhaust, collected by LN_2 trap, has been analyzed with a chromatograph method.

2. Experiments

2.1. Sample preparation

Four samples (1×1 cm) of tungsten with different morphology and structure were prepared using Magnetron Sputtering (MS) [3] and Pulsed Laser Deposition (PLD) [4] methods. Three of them consisted of a tungsten coating of about 1 μm thickness over a ⟨100⟩ silicon substrate (1×1 cm, 400 μm thick), while the forth was a bulk tungsten used as reference materials. Two coatings were prepared by PLD and one by MS. The samples were characterized by Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS) and X-ray Photoelectron Spectroscopy (XPS) analysis.

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2.2. Experimental apparatus

The experiments, to study the formation of W_xN_y compounds and ND_3 in mixed N_2/D_2 plasma, were performed in GyM, a linear plasma device [5] consisting of a cylindrical vacuum vessel (R = 0.125 m, L = 2.11 m) mounted in a linear magnetic field (up to 0.13 T), in which highly reproducible deuterium–nitrogen plas-mas were obtained and steadily sustained by cw microwaves power (1.5 kW, 2.45 GHz). A dedicated sample introduction system was designed and installed as shown in Fig. 1. The samples were located at the center of the plasma column (20 cm of diameter) and exposed normally to magnetic field lines. The GyM plasma parameters used in the experiment were $n_e = 1.6 \cdot 10^{16}\ m^{-3}$, $T_e = 3.3$ eV (on the axis, in correspondence of the sample, as mea-sured by Langmuir probes) and corresponding to an ion flux of $1.22 \cdot 10^{20}\ m^{-2}\ s^{-1}$. These values are comparable to those predicted for divertor of ITER [6]. The sample has been exposed to GyM plasma integrating several discharges in order to reach the required fluence ($\sim 10^{24}\ m^{-2}$); the plasma composition was moni-tored by OES spectra, acquired with a spectral resolution of 0.06 nm, with a line of sight transversal to plasma at 35 cm a part from the sample (see Fig. 1). A liquid nitrogen trap (LN_2), installed between the turbo and rotary pumps of the vacuum system, was used to collect the exhaust produced during the experiments devoted to study the ND_3 formation in N seeded plasma.

2.3. Procedure

In order to study the interaction of nitrogen with tungsten the four samples have been simultaneously exposed to N_2 seeded D_2 plasma discharges (2 sccm of N_2 and 20 sccm of D_2) for a total duration of 120 min to reach a fluence of $8.78 \cdot 10^{23}\ m^{-2}$.

The samples have been characterized before and after plasma exposure. The XPS measurements of W samples were performed in an ultra-high vacuum (10^{-9} mbar) system equipped with a non-monochromatized Al-Kα X-ray source (1486.6 eV). High resolution spectra were acquired in a constant-pass-energy mode (44 eV), which gave an overall energy resolution of 1.05 eV. The recorded spectra were fitted with a routine using Doniac–Sunjic-type curves and a Shirley background subtraction [7–9].

As part of the same experiment, the plasma exhaust of a 90 min discharge, was collected in the LN_2 trap. Furthermore a second discharge, collecting exhaust, of 120 min, without samples but at same plasma parameters, was performed. After each collection the trap, valved off and removed from the vacuum line, was purged by Ar carrier so that the exhaust gas was fluxed into a bubbler containing demineralized water at 10 °C, in this way the ammonia was dissolved into the water following the Eq. (1)

$$ND_3 + H_2O = ND_3H^+ + OH^- \quad (1)$$

The water temperature was kept a 10 °C because the solubility constant increased from 500 to 700 (g of ND_3/kg water) varying temperature form 25 ° Cto10°C respectively. The two solutions so far collected were analyzed by ionic chromatography [10]. The relative concentration of ND_3 in water (ml of ND_3/ml of water) has been determined by using a calibrated standard solution.

3. Results and discussion

3.1. Nitrogen concentration in W samples

Film features (e.g. crystalline domain size, crystallographic phase and composition) play an important role in the production of compounds after plasma exposure [11]. The formation of the

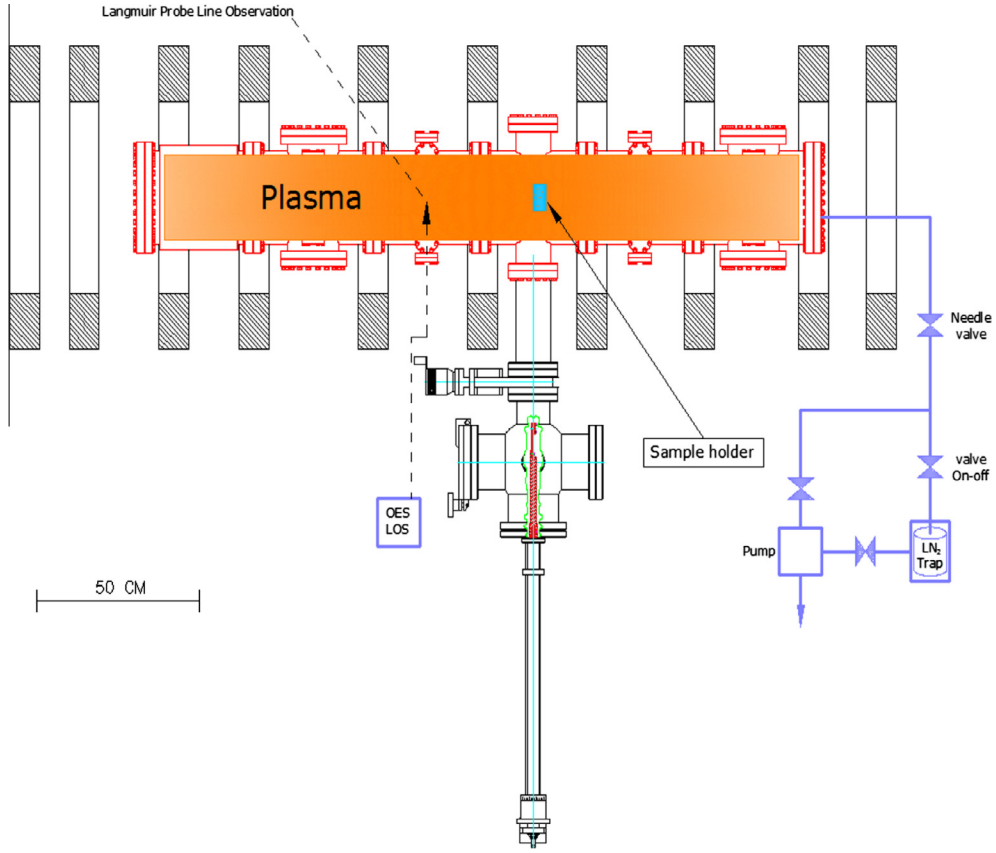

Fig. 1. GyM layout: vacuum chamber and sample introduction system.

mixed W_xN_y layers was investigated on four samples with different W structures exposed to the D_2/N_2 plasma:

- (ms-W) deposited by MS. W polycrystalline film made up of both stable α (bcc lattice) and metastable β phase (A15 cubic lattice). The main crystallographic direction are (1 1 0) for α-W and (2 0 0) for β [12].
- "compact nanocrystalline" tungsten (nc-W), α-W highly oriented along the (1 1 0) crystallographic direction. The film was obtained by PLD method [4]. Structure and morphology of this kind of coating were very similar to those used to cover JET ITER like Wall and ASDEX first wall [13].
- "amorphous-like" tungsten (a-W) with amorphous structure deposited by PLD [4] that resembles redeposited W. This kind of films, due to their full of defect structure, retains high amounts of H_2 gas [14].
- W microcrystalline (bulk) was used as reference sample.

SEM/EDX analysis indicates no morphological changes due to plasma exposure. XPS survey spectra detected W, O and C on the surface of all samples before exposure, while after exposure C disappears and N was revealed together W and O. The absence of C after exposure indicated that its presence was due to a contamination, removed from the surface via plasma sputtering. Information on the relative concentration of nitrogen along the depth was obtained with high-resolution spectra of W*4f* and N*1s* core lines, acquired after three cycles of sputtering with Ar^+ at 3 keV. All the samples exhibits similar spectra, but with different counts. The spectra with the clearer peaks were those from bulk and ms-W samples, which have been used for the detailed analysis of the peaks. At their surface three contributions under W*4f* line have been resolved via deconvolution while two contributions are as well resolved under the N*1s* line. Figs. 2 and 3a show the results obtained from the ms-W sample. Under the N*1s* line, W–N_x bonds was assigned at 397.4 eV of binding energy (B.E.) and the corresponding one under the W*4f* line at 31.42 eV of B.E. A contribution due to nitrogen retained at W grain boundaries was assigned at 400.3 eV in B.E under the N*1s* line and at 33.15 eV in B.E under W*4f* line [15].

Differences in N relative concentrations along the depth, have been found for the four samples, and are reported in Table 1. The thickness of the layer in which nitrogen is retained is about 6 nm. Below 6 nm the N*1s* line was no longer detected. As the four samples were exposed to the same discharges, the differences found in the nitrogen concentration are ascribed to their different morphology and nanostructures. In particular ms-W exhibits the same nitrogen concentration of W bulk. The columnar crystallographically oriented structure of nc-W seems to reduce the amount of W_xN_y in the film: therefore the reaction rate is influenced by the crystal orientation. The lowest nitrogen retention value has been detected in the amorphous-like W sample. Unfortunately the low counts rate under the N*1s* signals did not allow a reliable deconvolution between the contribution of W–N compounds and N retained in the grain boundaries (see Fig. 3b). In general, due to the low photoemission cross section, the N*1s* spectra exhibit a small signal-to-noise ratio and a detailed analysis by peak fitting is often not reliable [2]. The low amount of N in the a-W films can be ascribed to the missing of crystalline or grain structure and to a reduced W–N grain boundary contribution. A similar behavior was also found during the exposure of Rh coatings with different structure to D_2 plasma. Rh films with the same structure of a-W, "amorphous-like" Rh films, lead to the formation of lower amounts of rhodium deuteride (RhD_2) compared with Rh films with higher crystallinity [11]. Although there are many differences

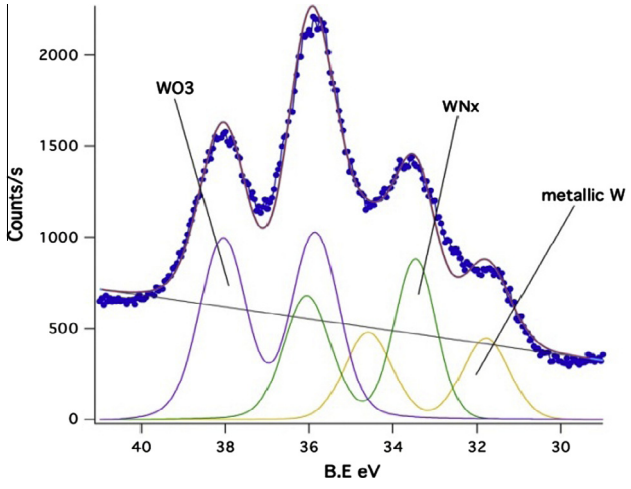

Fig. 2. Deconvolution W*4f* line of ms-W sample.

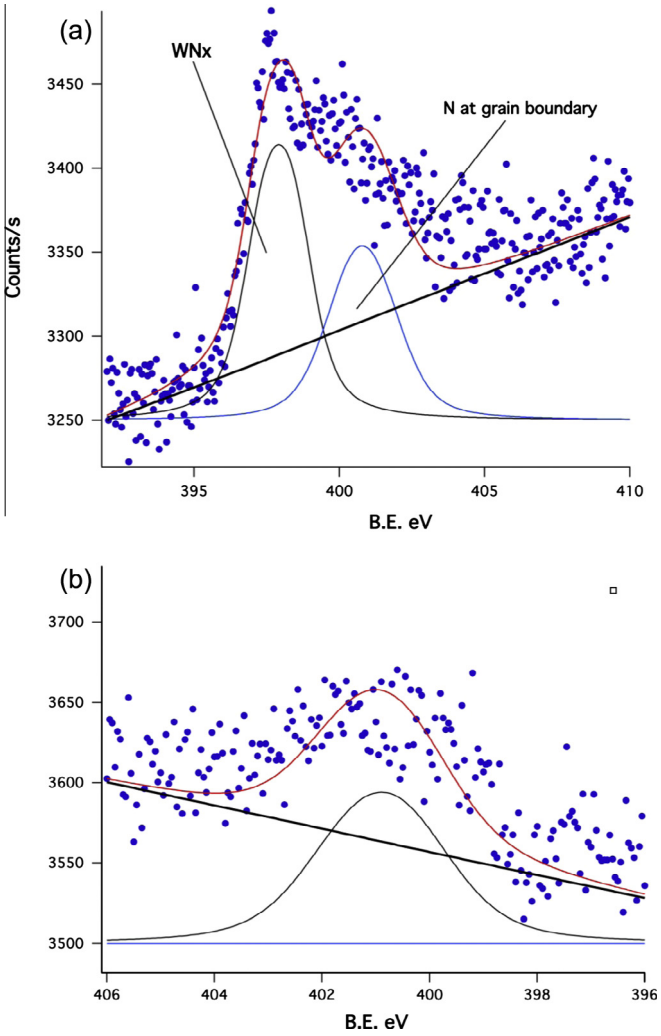

Fig. 3. Deconvolution N1s line of ms-W (a) and a-W (b) samples.

Table 1
Relative N atomic concentration along the depth for the W samples exposed at D_2/N_2 plasma in GyM determined by sputtering XPS.

Depth (nm)	N% in W bulk	N% in ms-W	N% in nc-W	N% in a-W
0	10	9.8	7	4.6
3	3.8	3.8	2.8	3.7
6	1.7	1.6	1.9	1

between the chemical reactivity of N_2 and H_2, it is possible to state (also considering that Rh and W are both transition metals) that the amorphous structure seems to prevent the chemical reactions with the plasma species inhibiting the formation of compounds.

3.2. Ammonia formation in seeded plasma

In Fig. 4 a typical Optical Emission Spectrum acquired in the range between 320–350 nm, is shown. It is possible to distinguish three different signals: two distinct bands emitted from ND radicals at 335.7 and 336.4 nm and one emitted from N_2 molecules at 337.13 nm. ND signals belong to $A^3\Pi$–$X^3\Sigma^-$ system for the transition (0, 0) and (1, 1) respectively. The N_2 signal belongs to the first positive system $B^3\Pi_g$–$A^3\Sigma_u^+$ for the transition (0, 0). The presence of these radicals and molecules is a fingerprint of chemical reactions occurring either in the plasma or at the vessel wall with ND_x as reaction intermediates [16]. In Fig. 5 the liquid ion chromatogram of captured exhaust gas after 90 min of plasma discharge is shown. From the peak of ammonium measured and the relationship with ND_3, reported in Eq. (1), we can deduce that in the collected exhaust the ammonia concentration was 8 ppm. For the 120 min plasma the relative concentration reached 150 ppm. The non-linearity of

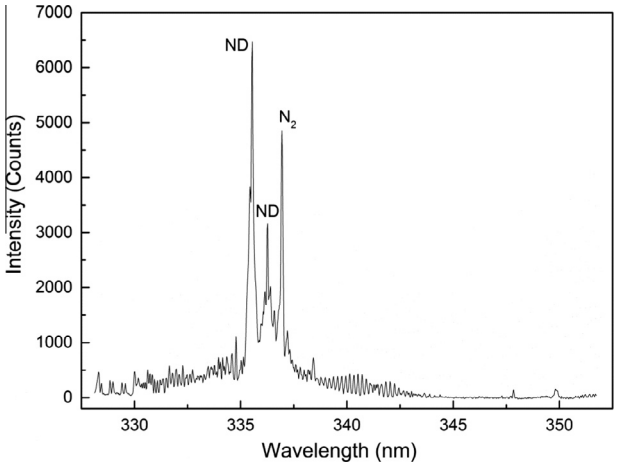

Fig. 4. OES spectrum emitted from ND, belong to $A^3\Pi$–$X^3\Sigma^-$ system for the transition (0,0) and (1,1) respectively, and N_2, belong to the first positive system $B^3\Pi_g$–$A^3\Sigma_u^+$ for the transition (0,0).

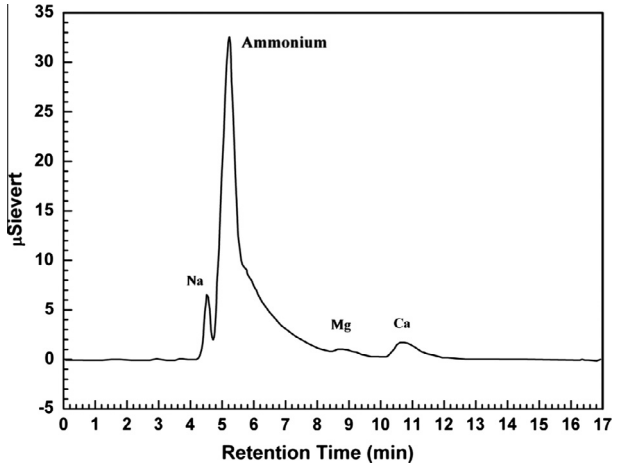

Fig. 5. Chromatogram of the exhaust collected during 120 min of time experiment. Sodium, magnesium and calcium are the natural cations traces of the respective elements contained in the demineralized water used to bubbler the exhaust collected. The retention time is related to the time required to separate in column the different molecules.

these results is not presently explained; a memory effect of the wall can been invoked as in ref [17,18]. The deuterated ammonia formation can be ascribed to two different mechanisms. In the first one N_2 or N_2^+ are formerly physi-or chemisorbed on the surface, and then dissociated by the catalytic effect of the wall. A subsequent reaction with atomic deuterium from the plasma phase (*Eley–Rideal* recombination) or physisorbed deuterium atoms (*Langmuir–Hinshelwood* recombination) will result in the formation of adsorbed ND_x. Further deuteration will lead to formation of ND_3 species which are chemically stable and volatile [16,19,20].

In the second mechanism to be taken in account, atomic N species are already available in the plasma phase and ND_x formation takes place without the catalytic N_2 dissociation effect of the wall [20].

Future experiments will be carried out to investigate which is the dominant mechanism, in order to explain also the non-linearity observed in the amount of ammonia formation as a function of time.

4. Conclusions

From the exposition of W samples with different structures to a deuterium plasma seeded with nitrogen it has been found that N is more retained in bulk W and in polycrystalline W sample, with respect to nanocrystalline and amorphous like film, this last (amorphous) exhibits the lowest retention rate. The depth profile revealed that N compounds are confined up to 6 nm below the surface for all the cases. In the same plasma the ammonia formation has been studied. From OES and ion chromatography of captured exhaust gas the formation of deuterate ammonia has been demonstrated. The amount of formed ammonia is not a linear function of plasma discharge duration, suggesting the relevant role of the metallic wall (via a memory effect) in the mechanisms leading to ND_3 formation. Further experiments are needed to clarify this aspect.

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