Ammonia Production, Isotopic Exchange and Sticking on Materials Relevant to Fusion Reactors: Tungsten and 316L Stainless Steel

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AMMONIA PRODUCTION, ISOTOPIC EXCHANGE AND STICKING ON MATERIALS RELEVANT TO FUSION REACTORS: TUNGSTEN AND 316L STAINLESS STEEL

Focus on ammonia production from tungsten

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Abstract

Injection of nitrogen into the edge plasma of fusion reactors is envisioned to dissipate part of the exhaust power. ITER will use a fuel mixture containing radioactive tritium, thus, production of tritiated ammonia would be expected. Quantification of this ammonia production is important to evaluate the tritium inventory in ITER. The paper reports a systematic study that quantifies ammonia production on W materials relevant for ITER and that sheds light on the mechanism for ammonia formation. Sequential co-implantation of nitrogen and deuterium in polycrystalline tungsten is analysed with temperature programmed desorption. Ammonia production is observed during thermo-desorption between 350 K and 650 K, in synchrony with the deuterium desorption. In contrast, nitrogen desorption occurs above 800 K. Significantly large production of ammonia is obtained only when the nitrogen layer created by ion implantation is saturated. The amount of nitrogen lost to ammonia production is only a few percent of the N layer content. This result is understood by repeating cycles of deuterium implantation and thermo-desorption below the desorption temperature of a saturated nitrogen layer. The decaying amount of ammonia production at each cycle demonstrates that nitrogen diffusion to the surface is negligible and that ammonia formation occurs at the outermost surface layer. The maximum quantity of ammonia produced from the present N implanted layer is below 2x10^{19} NDs m^{-2}, which is limited by the nitrogen atom surface density.

1. INTRODUCTION

For high-power operations in ITER, it is foreseen to inject extrinsic impurities into the edge plasma to dissipate part of the plasma exhaust power through radiation and maintain the power fluxes to the plasma-facing components (PFCs) within tolerable limits (10 MW m^{-2}). To date, the best compromise between radiative efficiency [1] and hot plasma performance [2, 3] has been achieved with the injection of molecular nitrogen in the edge plasma region. However, injection of nitrogen (N) in a divertor plasma environment next to metallic components leads to the conversion of ~10% of the injected nitrogen into ammonia (NH₃) [4, 5]. In ITER, ammonia production will be concurrent with a deuterium/tritium plasma thus radioactive tritiated ammonia is expected.

The formation of large quantities of tritiated ammonia has consequences for several aspects of the ITER plant operation in terms of tritium retention, gas processing and duty cycle. It is well known that ammonia is a polar molecule and could stick on shadowed metallic in-vessel components as well as on pumping ducts. This represents an issue for the tritium recycling plant operated to retrieve tritium from cryopumps and exhaust gases. Recently, using molecular beam techniques, we have reported the absolute sticking probability of NH₃ on tungsten (W) and stainless steel 316-L surfaces as they will be used in ITER, i.e. covered with natural impurities such as carbon and oxygen. We were able to reproduce our well-controlled experiments with a Generalized and Separable Kisliuk kinetic model that can be used to forecast the coverage of NH₃ on W and 316-L surfaces as a function of the surface temperature and the ammonia flux [6].

However, it is currently unclear how and where NH₃ formation predominantly occurs in fusion devices, which makes it difficult to predict the ammonia formation rate in ITER and thus the ammonia flux expected on areas in the vacuum vessel where ammonia might accumulate. While it was shown a significant NH₃ formation in ASDEX-Upgrade [4] and JET [5] tokamaks during N-seeded discharge, recent experiments in the full-W
tokamak WEST [7] evidenced an absence of ammonia formation concurrent with PFCs that are still able to pump nitrogen. This result in WEST suggests that the N wall reservoir needs to be saturated in order to produce ammonia in significant quantities.

In the present work, we performed a systematic study of the production of deuterated ammonia (ND₃) from polycrystalline W samples co-implanted sequentially with N and deuterium (D) ions. In Section 2, we describe the experimental setup and the methodology used to co-implant N and D in tungsten and to measure the production of ND₃ during thermo-desorption experiments. In Section 3, we discuss the obtained results and their interpretation in terms of ammonia formation mechanism. This paper ends on a summary and a perspective on future studies that could contribute further to the estimation of the tritium inventory from tritiated ammonia in ITER.

2. EXPERIMENTAL METHODS

Tungsten PFCs in ITER are made of polycrystalline tungsten with specific grain elongation to optimize heat transfer to the cooling structures [8]. However, in our experimental approach we use model samples which can withstand multiple implantations and thermo-desorption cycles without structure evolution that could affect either its deuterium retention or its thermal release of molecules containing hydrogen isotopes [9-11]. Therefore, we used recrystallized and mirror-like polished polycrystalline W samples from A.L.M.T. Corp. (Japan) with 99.99 wt.% purity and with dimensions of 10×10×0.4 mm³. Two W samples from the same batch were used in this study, giving identical results.

All experiments were conducted in the CAMITER set-up [11] located at PIM laboratory (Aix-Marseille University – CNRS). The experimental apparatus consists in two interconnected ultra-high vacuum (UHV) chambers: a differentially-pumped load-lock/storage chamber (base pressure < 3×10⁻⁹ mbar) and an implantation/temperature programmed desorption (TPD) chamber (base pressure < 2×10⁻⁹ mbar). The implantation/TPD chamber is equipped with an OMICRON ISE 10 ion source, a PID/thermocouple-controlled radiative (tungsten filament) oven and a differentially-pumped chamber (base pressure < 1×10⁻¹⁰ mbar) containing the quadrupole mass spectrometer (HIDEN 3F/PIC, noted QMS in the following) which is located in a line-of-sight 2 mm above the sample. An all-metal leak valve connected to the ion source controls the D₂ or N₂ gas flow. The created D⁺⁺ or N⁺⁺ ions are accelerated to a kinetic energy of 500 eV and impinge the sample with an incidence angle of 45° through a collimating pinhole defining an elliptical projected area of 0.5 cm². A single ion source has been used to ensure an optimal overlap of the two ion beams footprints on the W sample. Thus, a thorough pumping/dgassing of the ion source is performed after each switching of the gas feed, with the W sample located in the load-lock/storage chamber. To move samples between UHV chambers, tungsten samples are mounted on a molybdenum transfer platen. The ion flux is determined by measuring the current on the sample with a picoammeter (Keithley 410A). The total incident fluence is calculated by converting the sample current into particle flux and by multiplying the particle flux with the duration of the implantation.

Once W samples were introduced in the load-lock/storage chamber from air, they were subjected to a degassing procedure consisting of at least two linear temperature ramp of 1 K s⁻¹ up to 1300 K followed by a 10 min annealing at 1300 K. This procedure removes most of hydrocarbons impurities and leaves the native oxide of tungsten on the surface [10]. A sequential co-implantation/TPD experiment consists in first implanting the W sample with N ions at a constant flux of ~ 1×10¹⁶ N⁺ m⁻² s⁻¹ for a certain duration to obtain the desired N fluence. After a thorough ion source degassing, the N-implanted W sample is bombarded with D ions at a constant flux of ~ 1.6×10¹⁶ D⁺ m⁻² s⁻¹ for a given duration to reach the desired D fluence. The sample is then moved to the load-lock/storage chamber in order to degas the oven on which the sample was mounted during implantation. Indeed, during N (D) ion implantation a significant neutral N₂ (D₂) flux is also present, which dissociates and adsorbs on the oven assembly. Once the oven is nitrogen and deuterium-free and cooled down to room temperature (typically after 2 hours), the sample is finally inserted on-top the oven and the TPD is performed. During TPD, the sample temperature is increased linearly with a ramp of 1 K s⁻¹ and its value is recorded simultaneously with the desorption rates measured by the multiplexed QMS at m/z = 3, 4, 14, 15, 16, 17, 18, 19, 20 and 28.

Usually, D retention is determined through a temporal integration of the rate of desorption of molecules containing deuterium (m/z=3, 4 and 20 for, respectively, HD, D₂ and ND₃) during the TPD. Our method for conversion of the QMS signals into desorption rates from the sample has been detailed and has been checked with Nuclear Reaction Analysis (NRA) in [9]. In the present paper, we will not discuss the D retention in N co-implanted W but focus instead on N retention and ND₃ production. Nitrogen retention is determined in a similar
way than for D retention, using m/z=14 (instead of m/z=28 which is perturbed by the concomitant emission of CO molecules from the hot oven) and m/z=20 for quantifying, respectively, N\textsubscript{2} and ND\textsubscript{3} products. Finally, deuterated ammonia production is evaluated using solely m/z=20, since NH\textsubscript{2}D (m/z=19) and NH\textsubscript{2}D (m/z=18) products are overwhelmed with, respectively, the fluorine background from the QMS ionization head and the water background from the UHV chamber. Thus, deuterated ammonia production reported in this work are to be considered as lower limits. For calibration of the ND\textsubscript{3} production, we used the calibration realized for D and N retention corrected from relative partial ionization cross sections at the ionizing energy of 50 eV [12-13].

3. RESULTS AND DISCUSSION

3.1. Nitrogen retention in polycrystalline tungsten

Fig. 1 presents the evolution of the nitrogen retention in polycrystalline tungsten at room temperature as a function of the nitrogen ionfluence. As the nitrogen fluence is increased from 1×10\textsuperscript{19} N\textsuperscript{+} m\textsuperscript{-2} to 4×10\textsuperscript{20} N\textsuperscript{+} m\textsuperscript{-2}, the nitrogen retention increases linearly with the N ion fluence, indicating a negligible nitrogen diffusion at the implantation temperature of 300 K and resulting in an apparent implantation probability of about 10 %. Then, the nitrogen retention saturates at a value of 3.9±0.9×10\textsuperscript{19} N m\textsuperscript{-2}. The nitrogen fluence necessary to achieve the saturation of N retention is comprised between 4.5×10\textsuperscript{20} N\textsuperscript{+} m\textsuperscript{-2} and 1.1×10\textsuperscript{21} N\textsuperscript{+} m\textsuperscript{-2}.

These results are consistent with the work of Meisl et al. [14], who showed with X-ray photoelectron spectroscopy and NRA quantification of N retention, that room temperature implantation of 2500 eV/N and 500 eV/N ions resulted in a saturation of the N retention to values of 1.8×10\textsuperscript{20} N m\textsuperscript{-2} and 1.1×10\textsuperscript{20} N m\textsuperscript{-2}, respectively, for an ion fluence above ~1×10\textsuperscript{21} N\textsuperscript{+} m\textsuperscript{-2} and ~6×10\textsuperscript{20} N\textsuperscript{+} m\textsuperscript{-2}, respectively. Considering that in the present study the kinetic energy per nitrogen nuclei is further reduced to 250 eV/N, the measured reduction of the saturation of N retention to ~0.4×10\textsuperscript{20} N m\textsuperscript{-2} confirms that nitrogen diffusion is negligible at room temperature and thus saturation of retention is the result of a balance between the depth profile of N implantation and the erosion of nitrogen by physical sputtering.

3.2. Deuterated ammonia production from polycrystalline tungsten sequentially co-implanted with nitrogen and deuterium

3.2.1. Identification of deuterated ammonia production
Prior to study the production of ND₃, we have performed a series of control experiments dedicated to confirm that the signal observed at m/z=20 originates from deuterated ammonia and not, for example, deuterated water that could be created subsequently to D implantation because of the native oxide presents on the tungsten surface.

Fig. 2 shows the comparison between two (co-)implantation experiments. Open symbols represent the desorption rates of products at m/z=14 (blue) and m/z=20 (red) after a D ion implantation of 2.8×10¹⁹ D⁺ m⁻². Clearly, after D ion implantation there is no peak of desorption for the N₂ product (m/z=14) nor for D₂O or ND₃ products (m/z=20). Solid symbols show the desorption rates of products at m/z=14 (blue) and m/z=20 (red) after a sequential co-implantation of N ions (1.2×10¹⁹ N⁺ m⁻²) and D ions (2.8×10¹⁹ D⁺ m⁻²). Now, two peaks of desorption are observed, one peak for m/z=14 between 800 K and 1050 K, ascribed to N₂ desorption, and one peak for m/z=20 between 350 K and 650 K. Since the desorption peak for m/z=20 is observed only when both deuterium and nitrogen ions were co-implanted, we demonstrate that the product at m/z=20 must be attributed to ND₃ in our experimental conditions.

Note that ND₃ desorption occurs in synchrony with the D₂ product (black solid symbols in Fig. 2) while N₂ desorption starts only above 800 K. The separation in temperature of the release of the deuterated products, D₂ and ND₃, from the N₂ product will be exploited in section 3.2.3. to gain information on the formation mechanism of ND₃ on tungsten.

3.2.2. Quantification of deuterated ammonia production

First, we have compared the production of ND₃ during a TPD ramp from a near-saturated nitrogen layer (fluence of 4.5×10²⁰ N⁺ m⁻²) for different D ion fluence (Fig. 3, solid green squares). When the deuterium fluence is increased it is found that the production of ND₃ increases up to a maximum production of about 4×10¹⁷ ND₃ m⁻². This saturation of the deuterated ammonia production is reached for a D ion fluence of ~1×10²⁰ D⁺ m⁻². The maximum production of ND₃ during a TPD ramp contains about 4×10¹⁷ N m⁻² and 1.2×10¹⁸ D m⁻², which are small quantities compared to the content of the near-saturated nitrogen layer (~3×10¹⁹ N m⁻²) and the D ion fluence (~1×10²⁰ D⁺ m⁻²). The amount of implanted nitrogen consumed during the TPD ramp that produces ND₃ is very small, i.e. only 1% of the near-saturated N layer. Furthermore, one can note that the amount of deuterium found in ND₃ products is at most 10 % of the tungsten atoms surface density (a tungsten monolayer being about 1.2×10¹⁹ W m⁻²). This order of magnitude suggests that one may consider the production
of ND$_3$ products over the course of a TDS ramp to happen solely on the tungsten surface. This hypothesis will be tested in section 3.2.3.

![Graph](image)

**FIG. 3.** The production of ND$_3$ as a function of D ion fluence for three different nitrogen layers. The open blue circle is the result for a third-of-a-saturated nitrogen layer (1.4±0.4x10$^{19}$ N m$^{-2}$). Solid green squares are results for the near-saturated nitrogen layer (2.9±0.8x10$^{19}$ N m$^{-2}$). The open red triangle is the result for a saturated nitrogen layer (3.9±0.9x10$^{19}$ N m$^{-2}$). Data points with error bars are the average of at least two experiments.

We have also compared the production of ND$_3$ during a TPD ramp at a low and high D ion fluence for different nitrogen-implanted tungsten layers. First, a low D ion fluence of 2.8x10$^{19}$ D$^+$ m$^{-2}$ was implanted in two different N layers: one near-saturation (fluence of 4.5x10$^{20}$ N$^+$ m$^{-2}$) and one at a third of the saturation of the nitrogen (fluence of 1.2x10$^{20}$ N$^+$ m$^{-2}$). Results are presented as the solid green square and the blue open circle on the left of Fig. 3, respectively. For this low D ion fluence, when the nitrogen density is decreased by a factor of 2.5, it is found that the ND$_3$ production is decreased by about a factor of 2. Thus, near-saturation of the nitrogen layer is necessary to obtain a significantly large ND$_3$ production. Second, a high D ion fluence of 2-3x10$^{20}$ D$^+$ m$^{-2}$ was implanted in two different N layers: one near-saturation (fluence of 4.5x10$^{20}$ N$^+$ m$^{-2}$) and one at saturation of the N layer (fluence of 1.0 x 10$^{21}$ N$^+$ m$^{-2}$). Results are presented as a solid green square and an open red triangle in the middle of Fig. 3, respectively. For this higher D ion fluence, when the nitrogen density is near or at the saturation of the layer, there is no change of the ND$_3$ production which remains at the ~4x10$^{19}$ ND$_3$ m$^{-2}$ level. Therefore, once the N layer is approaching saturation, ND$_3$ production is maximum.

### 3.2.3. The formation mechanism of deuterated ammonia on tungsten

In the previous section, we found that the saturated amount of produced ND$_3$ during a TDS ramp was small (~4x10$^{19}$ ND$_3$ m$^{-2}$) relatively to the amount of nitrogen present in the (near-)saturated nitrogen layer (3-4x10$^{19}$ N/m$^2$). These numbers indicate that only a small fraction of the available nitrogen (1.4% in average) is consumed to produce ND$_3$ products (desorbing below 650 K), the rest producing N$_2$ molecules (desorbing above 800 K). This result could be interpreted in two ways. On the one hand, in the hypothesis where ND$_3$ precursors could be formed within the nitrogen layer, it would mean that the process of deuterium binding to nitrogen within the bulk, or the process of diffusion of ND$_3$ precursors, would be inefficient. On the other hand, if ND$_3$ precursors can only be formed at the tungsten surface, it would mean that the nitrogen concentration in the surface layer would be small or that a competition between ND$_3$ production and D$_2$ production occurs. At first glance, the two latter explanations of a surface-assisted production of ND$_3$ sounds mechanistically most simples. Furthermore, we have shown in section 3.2.2 that the amount of deuterium found in ND$_3$ products is well below the tungsten atoms surface density (about 10%) and thus does not contradict the surface-production hypothesis. Thus in the following we will test this surface-production hypothesis.
Since N$_2$ desorption occurs after D$_2$ and ND$_3$ desorption, with no overlap in desorption temperature range, we were able to test the surface-production hypothesis by using interrupted TDS ramp with the following cycles experiments. For the first cycle, we performed a sequential co-implantation of N$_2^+$ / D$_2^+$ followed by a TPD ramp interrupted at 750 K, i.e. not desorbing the N implanted layer. For the second and next cycles, we realized a D$_2^+$ implantation (same fluence as the first cycle) followed by a TPD ramp interrupted again at 750 K to keep the N implanted layer in W. Cycles experiments were performed for a near-saturated N layer (fluence of 4.5×10$^{20}$ N$^+$ m$^{-2}$, green solid squares in Fig. 4) and a saturated N layer (fluence of 1.0×10$^{21}$ N$^+$ m$^{-2}$, red open triangles in Fig. 4) with D ion fluence of 2.3×10$^{21}$ D$^+$ m$^{-2}$ and 3.0×10$^{21}$ D$^+$ m$^{-2}$, respectively.

![Diagram](image1)

**FIG. 4.** The production of ND$_3$ in near-saturated (green solid squares) and saturated (red open triangles) nitrogen layers in tungsten obtained by successive cycles of D$_2^+$ implantation and TPD up to 750 K (i.e. below the nitrogen desorption temperature).

Fig. 4 presents the results of these cycles experiments and evidences that more than the initial ~4×10$^{17}$ ND$_3$ m$^{-2}$ can be produced from a (near-) saturated N layer. In particular, it is observed for the two investigated N/D fluences a common behaviour: the ND$_3$ production rate decreases monotonously with the cycle number. Using a linear fit for these decays, we find that an absence of ND$_3$ production should be observed after 4 and 5 cycles of implantation/interrupted TPD for the near-saturated N layer and the saturated N layer, respectively. Summing up the total quantity of ND$_3$ produced within these cycles for these N layers, we estimate that no more than 1×10$^{18}$ ND$_3$ m$^{-2}$ could be produced. Using a more conservative estimate for the decay of ND$_3$ production with increasing the cycle number, i.e. an exponential decay, we found that for the saturated N layer there should not be any detectable ND$_3$ production after 7 cycles of implantation/interrupted TPD. In this case the total quantity of ND$_3$ produced would be < 2×10$^{18}$ ND$_3$ m$^{-2}$. Thus, less than 5% of the total nitrogen present in the saturated N layer can be consumed during these cycles of D implantation and thermal release up to 750 K. This striking result demonstrates that not all nitrogen in the N layer is mobilized for ND$_3$ production, even with a temperature sweep to 750 K and thus it points towards a surface-limited mechanism for ND$_3$ production on tungsten.

Assuming that for a saturated N layer on W at most 2×10$^{18}$ ND$_3$ m$^{-2}$ can be produced and that the consumed nitrogen is only the one at the surface (with an atomic W surface density of 1.2×10$^{19}$ m$^{-2}$), we can estimate that about 17% of the surface atoms at the N saturated W samples are Nitrogen atoms. This result is consistent with SD.TRIM calculations performed by Meisl et al. [14], whom estimate the nitrogen concentration in the first layer of tungsten to be on the order of 20% for similar implantation conditions.

4. SUMMARY AND PERSPECTIVES

To evaluate quantitatively ND$_3$ production from co-implanted N and D ions in W as well as to understand its formation mechanism, systematic sequential implantation of N$_2^+$ and D$_2^+$ ions at 300 K were performed in an ultra-high vacuum environment and temperature programmed desorption was used to quantify N$_2$ and ND$_3$ production rates.
We observed that the production of ND3 molecules on W occurs at a surface temperature above 350 K (Fig. 2). Furthermore, we showed in Fig. 3 that significant ND3 production can be obtained with N-implanted tungsten materials only if a near-saturated N layer is present. Finally, we demonstrated that the quantity of ND3 produced from a near-saturated N layer is limited by the N density at the outermost layer of the surface of W (Section 3.2.3). Note that these results have been obtained for N layers held between 300 K and 750 K and that we measured the onset of N2 desorption at 800 K (Fig. 2). These results are important for quantifying ammonia production in tokamaks operating with W plasma-facing components and N-seeded plasma discharge. The present set of results implies that significantly large ND3 production from bulk W PFCs should be limited to W components having a surface temperature in the range 350 – 800 K and which have been subjected, while being in this temperature range, to a N ion fluence leading to a N retention \( > 4 \times 10^{19} \text{ N m}^{-2} \). The N exposure conditions necessary for significant ammonia production on W materials being clarified, one should analyse past and future experiments in WEST and ASDEX-Upgrade with this dual N retention / surface temperature conditions in mind. In that respect, the search for spatial correlations between the temperature of plasma-facing components and the presence of ND fragments by spectroscopy could test the interpretation of the present results.

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