Probing adsorption and reactivity of nitrogen atoms on silica surface under plasma exposure

D. Marinov[1(*)], O. Guaitella[1], C. Corbella[2], T. de los Arcos[2], A. von Keudell[2], A. Rousseau[1]

[1]*LPP, Ecole Polytechnique, UPMC, Université Paris Sud-11, CNRS, Palaiseau, France*
[2]*Research Department Plasmas with Complex Interactions, Ruhr-University Bochum, Germany*
(*) daniil.marinov@lpp.polytechnique.fr

Chemisorption and reactive properties of nitrogen atoms on silica surface were investigated. Strongly bound N atoms grafted by low pressure nitrogen plasma were probed using: (i) *ex situ* X-ray Photoelectron Spectroscopy (XPS) (ii) isotopic exchange $^{14}N_{ads} \leftrightarrow {}^{15}N_{gas}$ under $^{30}N_2$ plasma exposure coupled with mass spectrometry, and (iii) exposure of the pre-treated surface to O_2 plasma with *in-situ* laser absorption measurements of NO produced from the recombination reaction $O+N_{ads} \rightarrow NO$. Kinetics of N adsorption on silica surface was investigated by varying the duration of N_2 plasma exposure. The role of N_{ads} as active sites for surface recombination of nitrogen atoms was elucidated based on the measured rates of $^{14}N_{ads} \leftrightarrow {}^{15}N_{gas}$ recombination in the discharge.

At low pressure, reactions on the reactor walls control the density of atoms and lead to production of new species in the plasma [1-6]. It is believed that chemisorbed atoms play a key role in surface catalyzed reactions in reactive plasmas. However, the properties of these atoms are still barely studied. One of the reasons of a relatively poor understanding of the mechanisms of heterogeneous processes is the difficulty of *in situ* surface diagnostics in harsh plasma environment. The aim of this work was to investigate adsorption and reactivity of chemisorbed (i.e. irreversibly trapped) N atoms on silica surface under plasma exposure.

Nitrogen atoms were grafted to the inner surface of a silica discharge tube 60 cm full length and 2 cm inner diameter by a capacitive radiofrequency discharge. Two identical copper ring electrodes were located outside the reactor and were driven symmetrically with a 13.56 MHz generator through a push-pull matching circuit. In the same reactor a pulsed DC discharge could be ignited using a pair of electrodes. The length of both DC and RF discharge columns was identical and equal to 50 cm.

For XPS measurements small silica samples were processed in the reactor and then analysed *ex situ* after different plasma pre-treatments. Recombination between adsorbed N atoms and gas phase O atoms producing NO was evidenced when the pre-treated surface was exposed to O_2 plasma. Time evolution of NO concentration was measured *in-situ* using a tuneable IR diode laser spectrometer. The absorption line at 1900.52 cm^{-1} ($NO(X^2\Pi_{3/2})$ R(6.5), v=0→v=1 transition) was used. Recombination reaction $^{14}N_{ads} \leftrightarrow {}^{15}N_{gas}$ was studied by exposing the reactor surface initially pre-treated by $^{28}N_2$ plasma to a pulsed discharge in $^{30}N_2$ in static conditions. Nitrogen molecules having the mass 29 amu ($^{14}N^{15}N$) were then detected by a quadrupole mass spectrometer (Pfeiffer, PrismaPlus).

First, XPS analysis of treated samples showed that a SiO_xN_y layer is formed on the initial SiO_2 surface under N_2 plasma exposure. Concentration of N in the surface layer probed by XPS (~2 nm) is increasing when the pre-treatment time is increased and reaches 30 at % after 6 hours of plasma exposure. This corresponds to an absolute surface density of nitrogen $[N] \approx 5 \cdot 10^{15}$ cm^{-2} [7]. It was found that the formation of SiO_xN_y layer takes place only under direct plasma exposure. Samples placed in the flowing afterglow zone showed only very small N content (~0.2 at. %) after 1 hour of pre-treatment. Formation of SiO_xN_y layer was inhibited when O_2 was added in the N_2 discharge. These results clearly demonstrate that in pure N_2 plasma recombination of N atoms takes place not on SiO_2 but on SiO_xN_y surface.

The reactivity of N_{ads} was probed by exposing the pre-treated surface to atomic oxygen produced in a single 10 ms DC discharge pulse in O_2. In figure 1, a burst of NO production with characteristic time of ~40 ms can be seen. The maximum obtained concentration of NO was $7 \cdot 10^{13}$ cm^{-3}, corresponding to $\sim 4 \cdot 10^{13}$ cm^{-2} of N_{ads} that participated in the reaction $O+N_{ads} \rightarrow NO$. Using NO production as a probe for reactive adsorbed nitrogen atoms, adsorption and desorption kinetics of N_{ads} was studied. It was found that N_{ads} are very stable and do not undergo thermal desorption for surface temperatures as high as 700K. It was proven that adsorption of N is a relatively slow process and it takes place only under direct N_2 plasma exposure, in accordance with the XPS measurements.

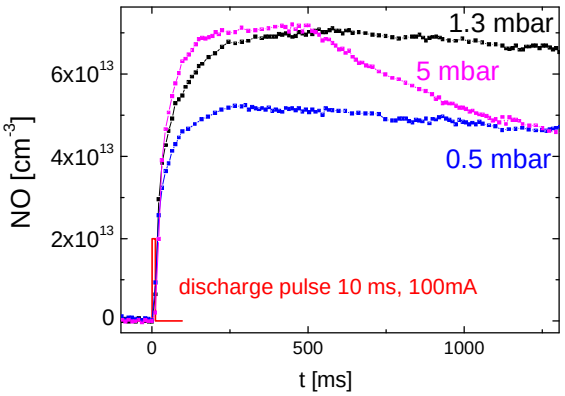

Fig. 1: Production of NO in a single 100 mA discharge pulse in O_2 at different pressures in silica reactor pre-treated by N_2 plasma.

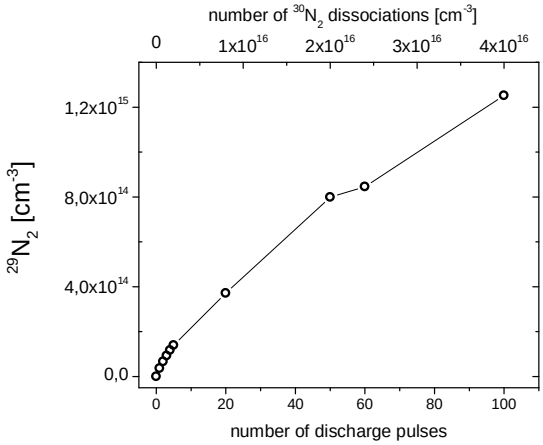

Fig. 2: Production of $^{29}N_2$ in a pulsed DC discharge in $^{30}N_2$ from recombination reaction $^{14}N_{ads}+^{15}N_{gas}\rightarrow{}^{29}N_2$ as a function of the number of discharge pulses. The number of $^{30}N_2$ dissociations was $4\cdot10^{14}$ cm^{-3} per pulse (see text).

In order to assess the role of N_{ads} in surface recombination of N atoms, experiments with nitrogen isotopes were performed. After the pre-treatment with $^{14}N_2$ plasma during 60 min, the reactor was filled with $^{30}N_2$ at 0.53 mbar and short probe discharge pulses (DC, 5 ms, 100 mA) were applied in static conditions. Production of $^{29}N_2$ from recombination $^{14}N_{ads}+^{15}N_{gas}$ as a function of the number of applied discharge pulses is shown in figure 2. One can note that the maximum measured concentration of $^{29}N_2$ is about a factor 20 higher than the concentration of NO in figure 1.The dissociation degree of $^{30}N_2$ in probe discharge pulse was estimated in order to determine the efficiency of $^{29}N_2$ formation on the surface. A mixture composed of $50/50=^{30}N_2/^{28}N_2$ at 0.53 mbar was exposed to 5 ms 100 mA discharge pulses. Production of $^{29}N_2$ was detected using the mass spectrometer. Assuming that $^{29}N_2$ is formed as a result of electron impact dissociation of the initial mixture followed by random recombination of ^{14}N and ^{15}N atoms, it was found that approximately $4\cdot10^{14}$ cm^{-3} N_2 dissociations occur per probe discharge pulse. This result is in reasonable agreement with numerical modelling [8]. Comparison between the amount of $^{29}N_2$ produced on the surface (figure 2) and the number of $^{30}N_2$ dissociations showed that the recombination with $^{14}N_{ads}$ accounts for 5-10% of ^{15}N losses on the surface. The last means that more than 90% of nitrogen atoms recombine via weakly bonded surface complexes that are not detected by the techniques used in this work.

Using $^{29}N_2$ production on the surface as a probe for $^{14}N_{ads}$ the adsorption kinetics of ^{14}N was studied. Obtained absolute values are in accordance with the XPS measurements; surface densities $[^{14}N_{ads}]=10^{15}$-10^{16} cm^{-2} were measured for pre-treatment duration in the range 1-60 min. Much lower values obtained using NO titration technique may be explained by the destruction processes of NO in the discharge. The work is in progress in order to correlate the measurements using NO and $^{29}N_2$ titration.

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