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Production of molecules on surface under plasma exposure: Example of NO on pyrex

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Abstract: We propose a new experimental approach to the study of surface-catalyzed nitric oxide production under plasma exposure. Stable nitrogen species are grafted to the surface of pyrex discharge tube during N₂ plasma pretreatment. These species are trapped by surface active sites and being exposed to O₂ plasma, they initiate production of NO molecules, which are detected using tunable diode laser absorption spectroscopy. Supposing that nitrogen species are adsorbed N atoms, we estimate the initial surface coverage $[N_{\text{ads}}]=3\cdot 10^{13} \text{ cm}^{-2}$. That gives an assessment of the lower boundary of the surface active sites density.

1. Introduction

Extensive experimental and theoretical studies of NO_x production in low pressure ($p < 400$ Pa) N_2/O_2 containing plasmas in continuous [1,2], pulse-periodic [3] and single-pulse mode [4,5] have been performed in the last years because of a great interest with respect to environmental problems and plasma chemistry in general. Low pressure conditions provide temporally and spatially stable plasma, which can be most readily modeled, even if the modeling implies very complex coupled kinetics of a large amount of species. At the same time, when decreasing the pressure some heterogeneous processes start to dominate over gas phase reactions introducing a new degree of complexity into the system. It is well known, that surface atomic recombination [6-12] is the main mechanism of atom losses in low pressure plasma applications. However, surface re-association of chemically different atoms is rather poorly studied, although it presents a particular interest because it leads to the production of new plasma species. For example, the important role of nitric oxide formation from surface recombination of oxygen and nitrogen atoms has been evidenced in [3,5,10,13-15].

In [3,4] it was found that NO concentration in pulsed DC discharge in air scales as a function of time averaged current and this scaling is well described by simplified kinetic model. However, lower calculated values compared to experimental ones are obtained for low currents and authors suppose that NO formation on the tube wall that is not included in the model may be responsible for this discrepancy. More recent self consistent simulation taking into account gas phase kinetics [5] for experimental conditions [4] also exhibit underestimation of [NO] at low currents while showing good agreement for higher currents, indicating that some NO formation channels may be missing in the model.

In a series of experimental and theoretical works [15 and references therein] dealing with an expanding thermal plasma source, Authors demonstrate the major role of surface reactions for molecular conversion in recombining plasmas at low pressure. From the comparison between measured and calculated concentrations of the main stable plasma species it is shown that surface production accounts for about 99% of NO observed in an Ar cascade arc jet expansion into $\text{N}_2\text{-O}_2$ background gas at 100 Pa.

Copeland *et al.* [13] and later Pejaković *et al.* [14] present the direct evidence of surface-catalyzed production of nitric oxide from the recombination of oxygen and nitrogen atoms on quartz. In [14] spatial profiles of N and O atoms concentration in a diffusion-tube side-arm reactor are studied using two-photon laser induced fluorescence technique. Comparison between measured and calculated concentrations showed that in given conditions the rate of recombination $(\text{N}+\text{O})_{\text{wall}} \rightarrow \text{NO}$ has the same order of magnitude as $(\text{O}+\text{O})_{\text{wall}} \rightarrow \text{O}_2$ and $(\text{N}+\text{N})_{\text{wall}} \rightarrow \text{N}_2$.

Numerous experimental and theoretical efforts have been made in order to improve our understanding of surface catalyzed atomic recombination because of its great importance for atomic sources [8], heat shielding on reusable space vehicles [7,13,14,16] and various plasma-chemical applications [6,9]. Authors [8] point out that the surface exposed to plasma presents itself a complex kinetic system and it cannot be considered as a simple boundary condition for bulk plasma. It is usually assumed that dielectric surface incorporates a small fraction of active sites, which irreversibly hold chemisorbed atoms [6-9] and recombination takes place between chemisorbed atoms and gas phase or adsorbed atoms arriving on the active site. Detailed modeling of surface recombination usually implies introduction of the whole set of kinetic constants of relevant elementary processes (sticking, diffusion, desorption, recombination) and surface parameters (active sites density, roughness), which are not known *a priori*.

We propose a new approach to the study of surface recombination, and namely NO production via surface catalyzed recombination. Since chemically adsorbed atoms that play the major role in heterogeneous recombination are irreversibly trapped by the active sites, one can expect that they remain on the surface long after plasma exposure. In this way we can separate in time two essential steps required for NO surface formation. We use RF discharge in pure N_2 or O_2 to graft atoms to the pyrex tube surface. Then the plasma feed gas is changed ($\text{N}_2 \leftrightarrow \text{O}_2$) and surface NO production is observed.

2. Experiment

2.1 Discharge set up

The discharge is generated in a pyrex tube 60 cm long and 2 cm inner diameter. In order to eliminate the influence of metallic electrodes on NO surface kinetics, we use CCP discharge with ring electrodes placed outside the tube. Schematic diagram of the experimental set up is shown on figure 1. In the current configuration discharge zone occupies about 85% of the tube length. Industrial frequency (13.56 MHz) RF generator, which can run in either pulsed or continuous mode, is matched to discharge impedance with a push-pull configuration resonant circuit. Incident and reflected power is measured by an in-line power meter before the matchbox. RF voltage across the discharge is measured with Tektronix P6015A voltage probe and then digitalized by LeCroy LT374L 500 MHz oscilloscope. Discharge power is deduced using subtractive method [17], taking into account power dissipation in matching network and transmission line. Depending on the conditions 40-60% of incident power is absorbed by plasma.

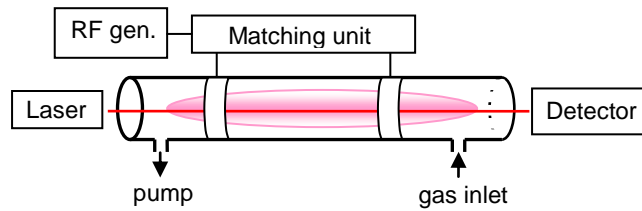


Figure 1. Schematic diagram of RF discharge and IR laser beam across the plasma.

Vacuum system is evacuated by a rotary pump to a base pressure of 0.1 Pa, typical gas pressure during the measurements is 50 Pa. Experiments may be carried out in a closed reactor (no gas flow) or under flowing conditions.

2.2 Laser absorption spectroscopy

In situ tunable diode laser absorption spectroscopy (TDLAS) is performed to measure NO concentration in a single path through the discharge tube. Absorption spectra are acquired with 2 MHz fast acquisition board and then processed by TDL Wintel software. Time resolution down to 1 ms is achieved in the “burst mode” in which all the spectra are collected during the plasma pulse and then processed by the computer during the plasma OFF phase. Concentrations down to 10^{12} cm^{-3} could be detected. Detailed description of the diode laser system can be found elsewhere [4].

The absorption line used for the ground state $\text{NO}(X^2\Pi_{3/2})$ detection is unresolved multiplet located at 1894.15 cm^{-1} (R(4.5) transition of $v=1 \leftarrow v=0$ band). The absolute concentration is deduced from the well known relation between frequency integrated absorption coefficient K and the total concentration of absorbing species n :

$$K = \int k_\nu d\nu = \frac{1}{L} \int \ln\left(\frac{I_0}{I}\right) d\nu = nS(T) \quad (1)$$

where I is the transmitted radiation intensity, I_0 is the incident intensity on the sample, k_ν is the absorption coefficient per unit length, L is the total absorption path length and $S(T)$ is the line strength of the observed transition as a function of gas temperature. Temperature dependence of $S(T)$ is mainly caused by the redistribution of absorbing molecules over the rotational levels of the lower vibrational state. If we neglect stimulated emission, which contributes to less than 0.5% of absorption [18] in our conditions, temperature dependence of $S(T)$ can be expressed as follows:

$$S(T) = S(T_{ref}) \frac{Q(T_{ref})}{Q(T)} \frac{\exp(-E''/k_B T)}{\exp(-E''/k_B T_{ref})} \quad (2)$$

where k_B is the Boltzmann constant, $Q(T)$ is the partition function, E'' is the energy of the lower state. All the parameters of chosen absorption line and tabulated partition function are available in the HITRAN database [19]. Relative variation of $S(T)$ is shown on figure 2. As it appears from the graph, the change of the line strength is not negligible and it can be used for neutral gas temperature determination in pulsed plasmas studied by TDLAS [18,20].

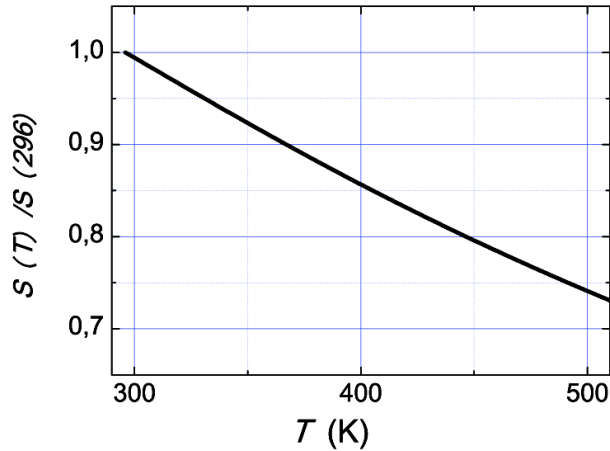


Figure 2. Relative variation of $S(T)$ calculated using equation (2).

2.3 Experimental procedure

The basic idea of experimental approach developed in this work is to separate surface and volume processes leading to NO formation in plasma. First, the tube is prepared by flowing RF discharge in pure N_2 , which leaves adsorbed nitrogen species on the surface. Then the reactor is evacuated and filled with pure oxygen. Nitric oxide production is observed when O_2 discharge (“probe discharge”) is started in the closed reactor. Figure 3 illustrates the sequence of manipulations.

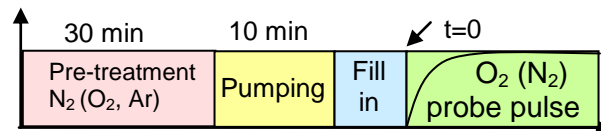


Figure 3. Schematic diagram of the experimental procedure.

Pretreatment and probe discharge parameters are listed in Table 1 and in the following they will be called “standard”. The influence of these parameters on the resulting NO production is discussed below.

	Pretreatment	Probe
Gas	N_2	O_2
Pressure, Pa	53	53
Flow, sccm	10	closed tube
P_{pl}^a , W	16	17

^a P_{pl} - power dissipated in plasma.

After being pretreated, the tube is continuously pumped for 10 minutes to get rid of gas phase N_2 and to cool down the reactor to the room temperature. In order to reach surface steady state during pretreatment

and avoid memory effects in a series of measurements 30-minute pretreatment duration is chosen. This allows us to obtain good reproducibility during several months of experiments. Day-to-day reproducibility also ensures that the surface is not irreversibly modified by plasma exposure.

3. Results and discussion

3.1 NO production in a single pulse

After 30 minutes of standard N₂ plasma pretreatment, the tube is evacuated and filled with pure O₂ at p=53 Pa. No nitric oxide production is detected until the discharge is switched on. That indicates that active oxygen species are required to promote the reaction. Figure 4 shows evolution of NO concentration in a single O₂ plasma pulse for 100-800 ms pulse duration recorded with 5 ms time resolution.

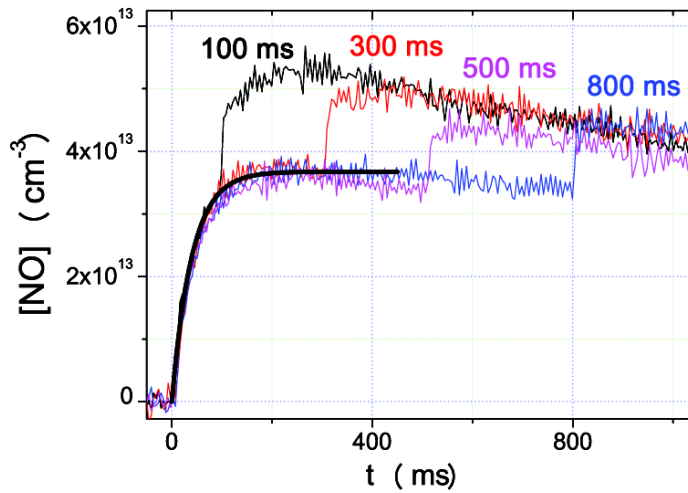


Figure 4. NO production in 100-800 ms O₂ plasma pulse after a standard N₂ pretreatment. The initial phase is fitted by $N_0(1 - \exp(-t/\tau))$ with $\tau=40$ ms. Abrupt jumps of measured concentration correspond to discharge switching-off.

As the discharge is switched on, we observe production of NO originating from nitrogen species grafted to the tube surface. Time behaviour of [NO] during plasma ON phase can be well described by a single exponent expression $N_0(1 - \exp(-t/\tau))$ with $\tau=40$ ms. When the discharge is stopped, measured concentration undergoes a fast jump caused by the gas cooling and abovementioned temperature dependence of the absorption line strength. This essentially diagnostic effect is discussed in the next section. For 100 ms pulses an increase of [NO] after the end of the discharge is still observed. This is caused by the long-lived nature of reacting species and will be discussed in section 3.5.

In the post discharge NO concentration is decreasing with characteristic time of about 4 s. This relatively slow decrease may be due to heterogeneous losses of NO or oxidation by O₃ produced in the discharge. But these reactions may be discarded when processes with characteristic time of 40 ms are being considered.

3.2 Validity of the diagnostics

Before passing to the discussion of the physics lying behind NO production observed on figure 4, it is

necessary to address the reliability of the diagnostics used to monitor NO. Namely, we need to take into account the effect of the gas temperature on measured concentrations. The characteristic time of temperature relaxation in our conditions can be estimated using the following expression [18]:

$$\tau = \frac{\Lambda^2}{\chi / \rho c} \quad (3)$$

where $\Lambda=R/2.4$ is the diffusion length of the tube, R - tube radius, χ - gas thermal conductivity, ρ – gas density, c – heat capacitance of the gas. Calculation with (3) yields $\tau \approx 1$ ms, i.e. gas temperature reaches steady state when the discharge is switched on or off within $3 \cdot \tau \approx 3$ ms. This time scale is of the same order as the temporal resolution of our diagnostics, so we are unable to follow temperature transition. That leads to an observed abrupt jump of measured concentration when the discharge is stopped (see figure 4).

Since the reactor volume is closed and the total NO number density can be considered constant during the fast cooling process, the change of measured [NO] corresponds solely to the temperature variation of the absorption coefficient. Absorption coefficient in the discharge drops to 77% of its room temperature value, thus giving an average gas temperature across the laser beam $T_g=470$ K. Gas temperature used by TDL Wintel for fitting absorption spectra is the ambient one; hence the correct absolute concentrations are obtained only when the discharge is switched off. It means that the values obtained during the plasma ON phase are underestimated and they must be fitted to the concentration measured after the cooling down of the gas. Nevertheless, NO formation kinetics in discharge pulses longer than 20 ms that will be considered below is correctly described.

3.3 Kinetics of nitrogen oxides

A question may arise if NO that we observe is the main nitrogen oxide present in the discharge, or other species should be taken into account to establish the balance of nitrogen atoms. It is well known that plasma in N_2 - O_2 containing mixtures is capable of production of various nitrogen oxides (NO, NO_2 , N_2O , N_2O_3 , N_2O_5), but at low pressure NO, NO_2 and N_2O are the most abundant [21,22]. While N_2O is expected in the excess of nitrogen, in our oxygen-rich conditions NO and NO_2 are the most plausible products. Analysis of the possible $NO \leftrightarrow NO_2$ conversion channels showed that in O_2 plasma NO can be oxidized into NO_2 via reactions R1 and R2, but this oxidation is balanced by an efficient inverse process R3 (see Table 2) [3,5].

Table 2. Relevant NO_2 production and destruction reactions.

Reaction	Rate constant
R1 $NO+O+M \rightarrow NO_2+M$	$k_1= 8.6 \cdot 10^{-32} \text{ cm}^6 \text{ s}^{-1}$
R2 $NO+O_3 \rightarrow NO_2+O_2$	$k_2=1.8 \cdot 10^{-12} e^{-1370/T} \text{ cm}^3 \text{ s}^{-1}$
R3 $NO_2+O \rightarrow NO+O_2$	$k_3=9.3 \cdot 10^{-12} \text{ cm}^3 \text{ s}^{-1}$

Heterogeneous oxidation of NO by O atoms may also take place, but this reaction is much slower than R1-R2 as it was found in [21,22]. Furthermore, reaction R2 may be ignored because in low pressure oxygen discharge conditions concentration of O_3 is too low [23]. Hence it is possible to estimate the fraction of NO_2 in the discharge steady state from the balance between R1 and R3 which doesn't depend on the O atoms concentration:

$$\frac{[NO_2]}{[NO]} = \frac{k_1[M]}{k_3} \approx 10^{-4}$$

this confirms that NO is the only significant nitrogen oxide in the discharge active phase and in the early afterglow while O atoms concentration is still high. It is worth noting that reaction R2 may be responsible for observed NO destruction in the post discharge.

3.4 Adsorbed nitrogen species

It is evident that nitrogen required for NO production is stored on the discharge tube surface during the

N_2 plasma pretreatment. If we neglect NO destruction in oxygen plasma and assume that every N atom from the surface gives NO molecule in the gas phase, we can estimate the initial surface density of nitrogen atoms. Using the maximum NO number density from figure 4 $[NO]_{\max}=5 \cdot 10^{13} \text{ cm}^{-3}$ and surface to volume ratio of the tube, we get $[N_{\text{ads}}]=3 \cdot 10^{13} \text{ cm}^{-2}$. It is worth noting that both adsorbed molecular and atomic nitrogen may contribute to this value. Although N_2 is not strongly adsorbed on pyrex surface at room temperature [24], it should be taken into account since obtained surface coverage is also small and corresponds to less than 1% of a monolayer.

To verify the role of molecular nitrogen in observed NO production, standard N_2 plasma pretreatment is replaced by neutral N_2 flow. In this way the tube is prepared with Ar flowing discharge during 1 hour in order to clean the surface and then it is exposed to the flow of N_2 at 53 Pa during 5 min. Figure 5 shows NO production in 100 ms standard O_2 pulse after this neutral pretreatment. As it follows from the graph, much smaller NO production is observed in this case and it doesn't exceed 10% of the values measured after N_2 plasma pretreatment. This confirms that N_2 adsorption on pyrex is not significant.

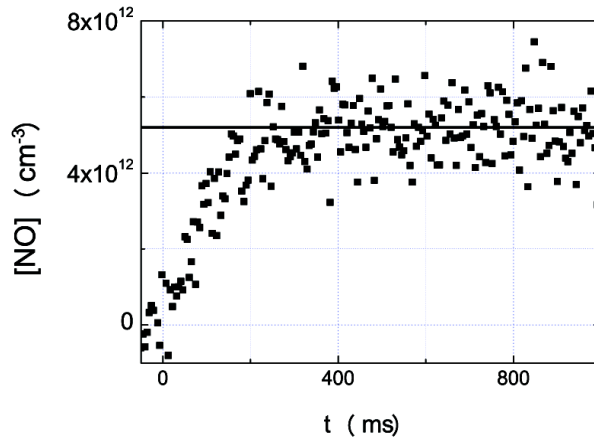
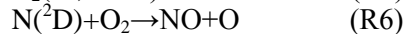
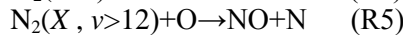
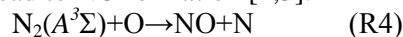


Figure 5. NO production in 100 ms probe pulse after N_2 neutral flux pretreatment.

However, one may argue that pretreatment conditions in N_2 discharge differ from those in the neutral N_2 flux and plasma exposure can enhance adsorption of N_2 molecules. Assuming that adsorbed molecular nitrogen is an important source of nitric oxide in the conditions presented on figure 4, let us consider the possible reaction pathways that may lead to NO formation [1,3]:



In all these cases excited nitrogen is required, so it seems unlikely that processes (R4-R6) occur directly on the surface. Therefore prior to produce NO, N_2 molecules should be first desorbed and then excited in the bulk plasma. In principle, N atoms may be also desorbed by plasma and then form NO in the reaction R6. Therefore, we can distinguish two possible ways of NO production:

- i) Surface reaction between adsorbed N atoms and impinging active oxygen species.
- ii) N_2 or N desorption followed by gas phase reactions R4-R6.

The question that should be answered here is which of these ways dominate in our conditions. In order to evaluate the efficiency of nitrogen species desorption by plasma, three 100 ms discharge pulses in argon are applied after standard pretreatment. It is found that additional pretreatment by non-reactive Ar plasma doesn't remove adsorbed nitrogen species and no appreciable depletion in the subsequent NO production is observed.

At the same time, as it follows from figure 4, 100 ms O₂ discharge produces 5·10¹³ cm⁻³ NO molecules, i.e. it removes from the surface an equivalent of 3·10¹³ of N atoms per cm².

The fact that adsorbed nitrogen species are stable upon argon discharge exposure and react easily in oxygen plasma allows us to suggest that NO is not produced via the channel (ii), but rather directly on the surface via (i). It means that in our conditions adsorbed nitrogen species are mainly chemisorbed N atoms and they form NO in surface reactions with oxygen radicals produced in the probe discharge.

3.5 Active oxygen species

As it was mentioned above, active oxygen species are involved in NO surface production. Analysis of NO formation kinetics can provide valuable information on the nature of reacting particles. Figure 6 shows a closer view on NO formation in a 20 ms O₂ plasma pulse. One can note that NO concentration is rising during several tens of milliseconds in the afterglow. The growth of measured concentration on this timescale could be attributed neither to the gas cooling nor to the diffusion of the molecules from the wall into the volume since in our conditions these processes have characteristic times of about 1 ms.

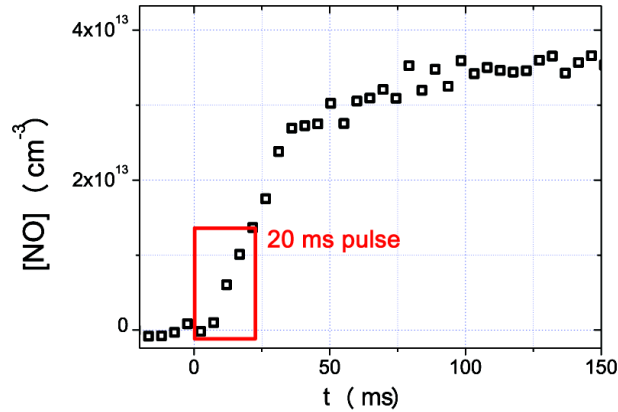


Figure 6. NO production in 20 ms probe pulse after standard pretreatment procedure (a closer view).

The fact that NO formation persists in the afterglow can be explained if we assume that NO is produced in the reaction of long-lived active oxygen species with adsorbed N atoms. Among all the long-lived active oxygen species formed in the discharge only O atoms and metastable O₂(a¹Δ) molecules have significant population. G. Gousset *et al* [23] report relative concentrations [O]/[O₂] and [O₂(a¹Δ)]/[O₂] about 10 % in DC discharge in pure oxygen in similar discharge geometry, gas pressure and deposited power as in this work. Based on the present experimental results we are unable to determine relative yield of these two species. Nevertheless it should be taken into account that atomic oxygen is chemically more active and it seems reasonable that it plays the major role in NO production on the surface in our conditions.

3.6 Estimation of surface active sites density

Based on the previous discussion we can conclude that after N₂ plasma pretreatment tube surface is covered with adsorbed N atoms having surface density [N_{ads}]_≈3·10¹³ cm⁻². One should note that this value corresponds to the apparent surface not taking into account surface roughness. The value of [N_{ads}] can be considered as the lower boundary of the surface active sites density because some of the sites may be still vacant after N₂ plasma treatment. Furthermore, conversion of adsorbed atoms into NO molecules is not complete due to NO destruction in the discharge.

The nature of active sites for atomic adsorption on glass surface is still unclear and it is not discussed in the majority of works devoted to heterogeneous atomic recombination. It is widely accepted [6-10,12,25] that

active sites cover only a small fraction of the surface $\varphi=0.2 - 6 \%$ and they hold adsorbed atoms with binding energy $E_d= 2.6 - 5.9 \text{ eV}$. If we take the total density of surface atoms 10^{16} cm^{-2} as proposed in [9], the obtained $[N_{\text{ads}}]$ will correspond to $\varphi \approx 0.3\%$, i.e. it provides a plausible estimation of the lower limit of φ .

The validity of $[N_{\text{ads}}]$ as an assessment of surface active site density depends on the fractional coverage of the sites after the pretreatment. Today there is no common opinion in the literature concerning this question. Some authors [6,7,9] assume that all the available active sites are occupied with adsorbed atoms during atomic flux exposure from the plasma. However, in [8] Cartry *et al* suggest that a significant fraction of active sites are vacant after plasma treatment. Moreover, the total amount of active sites may be also modified by plasma as was proposed in [11]. Present work doesn't **claim** to answer all these questions; **however, it is** worth mentioning that our approach **allows probing** the state of the surface after various pretreatment procedures **that** can provide a wealth of information in future studies.

3.7 The role of pretreatment parameters

In this section the influence of pretreatment conditions on N atoms surface coverage is studied while keeping standard probe discharge parameters. It is found that $[N_{\text{ads}}]$ depends on the deposited power; on figure 7 shown NO production after 7 W, 16 W and 28 W N_2 plasma pretreatment. The last two curves nearly coincide indicating that $[N_{\text{ads}}]$ reaches saturation with increasing the power. It is possible to assume that saturation is attained when all the available surface sites are occupied.

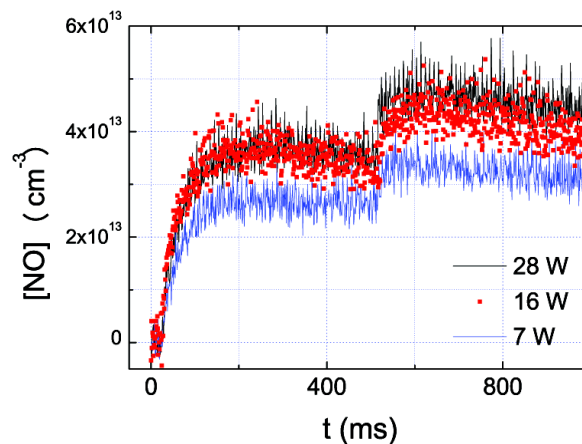


Figure 7. NO production in 500 ms probe pulse after N_2 plasma pretreatment with different power: $P_{\text{pl}}=7 \text{ W}$ (lower solid curve), 16 W (scatter) and 28 W (upper solid curve).

Variation of the gas flow (10 – 60 sccm) and pretreatment duration (5 – 120 min) doesn't lead to any notable differences in NO production. The influence of the time lag between the end of pretreatment and the start of O_2 plasma has been also verified. No significant changes are found for delay times from 10 min to 10 hours. The last confirms that N atoms don't undergo thermal desorption at room temperature.

Geometry of the experiment allows us to change the length of N_2 plasma column therefore changing the pretreated surface area. Figure 8 demonstrates direct proportionality between the length of the pretreated part of the tube and resulting maximum NO concentration. This result proves that N atoms are present only on the pretreated part of the tube.

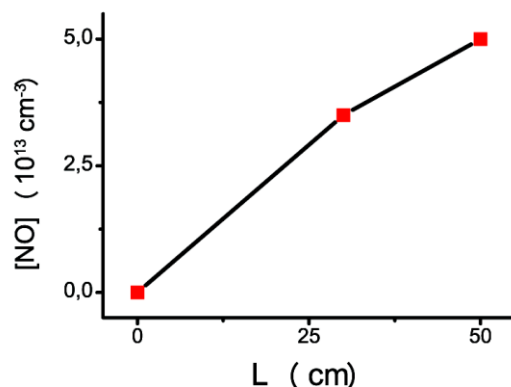


Figure 8. Dependence between the pretreated length and resulting NO production.

We have tried also to observe nitric oxide production in N₂ probe discharge after O₂ plasma pretreatment, but it was impossible to attain detectable concentration of NO in this case. The most likely explanation of this asymmetry is the fast NO destruction in N₂ plasma due to collisions with N atoms [3,5]. It is worth noting that small quantities of NO are always present in pure N₂ discharges sustained in glass tubes. This NO originates from the oxygen precipitated in the glass and can be readily observed by NO(γ) emission [26], which provides higher sensitivity than single-pass IR absorption.

4. Conclusions

Direct evidence of heterogeneous NO production on pyrex has been obtained. It was shown that after N₂ RF discharge pretreatment pyrex surface remains covered by irreversibly adsorbed N atoms. Being exposed to O₂ plasma these atoms produce nitric oxide via reactions with active oxygen species impinging the surface. It was shown that adsorbed N₂ accounts to less than 10% NO production in our conditions. With the use of the maximum detected NO concentration the density of adsorbed N atoms $[N_{\text{ads}}]=3 \cdot 10^{13} \text{ cm}^{-2}$ was estimated. That gave the lower boundary of the surface active sites density.

The novel experimental approach developed in this work is found to be a promising tool for the studies of heterogeneous processes in molecular plasmas.

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Table captions.

Table 1. Standard experimental conditions.

	Pretreatment	Probe
Gas	N ₂	O ₂
Pressure, Pa	53	53
Flow, sccm	10	closed tube
P _{pl} ^a , W	16	17

^aP_{pl} - power dissipated in the plasma.

Table 2. Relevant NO₂ production and destruction reactions.

Reaction	Rate constant
R1 NO+O+M → NO ₂ +M	$k_1 = 8.6 \cdot 10^{-32} \text{ cm}^6 \text{ s}^{-1}$
R2 NO+O ₃ → NO ₂ +O ₂	$k_2 = 1.8 \cdot 10^{-12} e^{-1370/T} \text{ cm}^3 \text{ s}^{-1}$
R3 NO ₂ +O → NO+O ₂	$k_3 = 9.3 \cdot 10^{-12} \text{ cm}^3 \text{ s}^{-1}$