DETERMINATION OF $N_2(A)$ POPULATION FROM OPTICAL EMISSION SPECTRA

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Introduction

Microwave discharges containing nitrogen are commonly used both in the research and the technology. Often it is advantageous for the given function (deposition, etching, plasma treatment, etc.) to exploit the processes in the afterglow rather than those in the active discharge. In most published works the authors used relatively low peak power in the range of hundreds of watts. However, in our apparatus we use very short pulses with peak power around 10^5 W, which is challenging from both theoretical and experimental point of view.

Interferometer diagnostics and spectroscopic measurements of pulse excited plasmas may give interesting results, concerning the loss, excitation and deexcitation processes as we have shown in our previous papers[1–4]. However, in many common experimental setups the interaction between the plasma and the walls is very difficult to account for. Therefore we carried out our experiments in the device with suppressed influence of surface processes. The processes involving nitrogen molecules in $A^3\Sigma^+_u$ metastable state are studied using time resolved optical emission spectroscopy of decaying plasma. The paper proposes a way to determine the absolute density of nitrogen metastable molecules at the end of the discharge pulse from relative intensity of second positive system ($N_2(C^3\Pi_u\text{-}B^3\Pi_g)$) emission in the afterglow.

Experimental set-up

We have developed the apparatus, where the volume processes are significant and the interaction of the plasma with the walls can be neglected. Plasma is produced in spherical glass vessel with inner diameter of 0.5 m, on one side covered by reflection foil, which reflects and focuses the microwaves radiated on another side by horn antenna. Microwaves (10 GHz, X-band) are generated by pulse magnetron. The 100 kW pulses have duration 2.5 μs and are repeated 400 times per second.

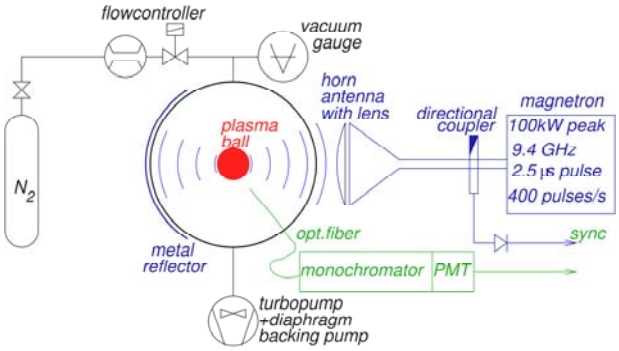

Fig. 1. **Experimental set-up**

The electric field is just in front of the horn antenna not high enough to produce a breakdown at reduced gas pressure. Only after focusing, the field has a maximum in the centre of the glass vessel and therefore a plasma ball is formed there. A pressure is measured by a Pirani/Penning full-range gauge and controlled by a gas flow meter and by varying rotation speed of a turbo pump. We use nitrogen as working gas and the operating pressure is in the range 20–2000 Pa.

The light emitted from plasma was collected into the optical fiber made from fused silica (see Fig. 1). Spectral analysis was made by Zeiss SPM2 monochromator equipped with EMI 6255B photomultiplier tube. Output signals from photomultiplier are digitalized via 50 Ω inputs by HP Infinium 500 MHz digital oscilloscope. Relatively large buffers of this device permitted us to record data points during the whole pulse with a time step of 10 ns. The synchronization pulses are taken from the 70 dB directional coupler. To perform sensitive measurements was quite a challenge and careful shielding, wiring and grounding had to be employed.

Results and discussion

In discharges containing nitrogen, $N_2(A)$ metastables are of relatively high population and therefore they strongly influence the plasma kinetics. In order to determine the concentration of $A^3\Sigma^+_u$ metastable state of N_2 we should discuss the processes relevant for their production and loss.

Regarding the literature we can find that it is possible to generate nitrogen neutral metastables by electronic collisions, radiative cascade, electronic ionic recombination and neutral atomic recombination. As we follow the evolution of spectral intensity in the afterglow, the collisions with electrons are not important due to their rapid cooling[5]. As the intermediary states in radiative cascade have permitted transitions, the process is very fast and need not to be accounted for in the afterglow. Using the NO titration experiment[6] we found that [N] is under our detection limit, i.e. lower than 10^{13} cm^{-3}. Considering this low atomic density and low rate constant for volume atom reassociation, we neglect this process, too. Using the values of electron density and recombination coefficient from[1] we conclude that contribution of electron – ion recombination on population of nitrogen metastables is low. Therefore, all production processes taken into account may be successfully neglected and we should deal only with the loss

processes.

In literature[7] we can find many sources of destruction for the $N_2(A^3\Sigma^+_u)$ metastables, such as

- quenching by N_2 ($l_1 = 3\cdot10^{-16}$ cm^3 s^{-1}),
- quenching by N ($l_2 = 4\cdot10^{-11}(300/T)^{2/3}$ cm^3 s^{-1}),
- energy pooling to B and C states ($l_3+l_4 = 2.6\cdot10^{-10}$ cm^3 s^{-1}),
- quenching by N_2^+ (l_5 unknown).

It is possible to write the following kinetic equation for our problem

$$\frac{d[N_2(A)]}{dt} = -\left(l_1[N_2(X)] + l_2[N(^4S)] + l_5[N_2^+]\right)[N_2(A)] - (l_3 + l_4)[N_2(A)]^2 - D\nabla^2[N_2(A)]$$

where the reaction coefficients l are explained above, D is the diffusion coefficient for nitrogen metastables and $[N_2(A)]$ is the $N_2(A^3\Sigma^+_u)$ metastable concentration.

We can make following assumptions:

- It is possible to neglect the effect of diffusion since the times we are dealing with in our experiment are on the microsecond scale.
- It is possible to neglect the quenching by N_2 and by N because their rates are low compared with energy pooling reactions and the concentration of $N(^4S)$ is relatively low compared with the concentration of $N_2(A)$
- Since the l_5 coefficient is not known (we could not find it in any publication), we will solve this matter later demonstrating that it is possible to neglect the quenching by ions, too. Let us work now with the hypothesis that l_5 is low enough to be neglected.

Neglecting the above mentioned, it reduces the previous equation to following

$$\frac{d[N_2(A)]}{dt} = -(l_3+l_4)[N_2(A)]^2 = -l[N_2(A)]^2$$

which can be easily solved, giving us the following solution:

$$[N_2(A)](t) = \frac{[N_2(A)]_{t=0}}{1 + l[N_2(A)]_{t=0}t}$$

where t = 0 corresponds to the end of the discharge pulse, i.e. the beginning of the afterglow. Then we can apply this to the temporal evolution profiles we have found experimentally for the second positive system of N_2. Assuming that the $N_2(C)$ state is populated by the energy pooling reaction only, the intensity of the second positive system is proportional to the squared concentration of $N_2(A)$ metastables

$$I(2^{nd}\ positive) \approx \frac{([N_2(A)]_{t=0})^2}{(1 + l[N_2(A)]_{t=0}t)^2} \qquad (1)$$

We measured the intensities of the electronic-vibrational transitions 0–2, 1–3 and 2–4 from $N_2(C^3\Pi_u)$ to $N_2(B^3\Pi_g)$ for several pressures. Typical curve is presented in Fig. 2, which also demonstrates excellent agreement between experimental data and the theoretical curve (Eq. (*1*)). For each pressure the nonlinear fitting of experimental data to Eq. (*1*) was performed and as a result, the value of initial $N_2(A)$ metastables concentration was found.

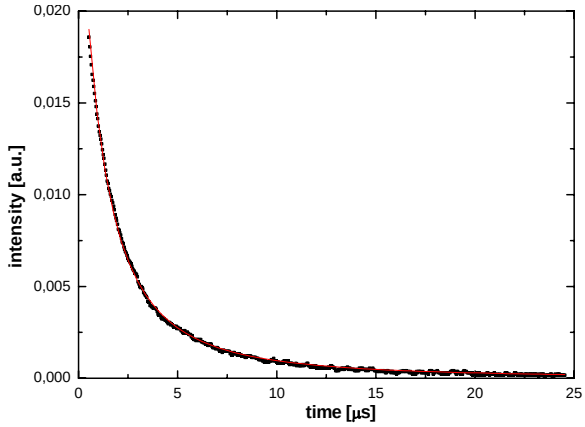

Fig. 2. **Measured data of the 0–2 2nd positive system evolution in afterglow (points) and fit by Eq. (*1*) (line)**

The dependence of the initial value (i.e. the concentration at the end of the microwave pulse and at the beginning of the afterglow) is plotted in Fig. 3. The error bars were calculated from the three independent values obtained from 0–2, 1–3 and 2–4 transitions measured for each pressure.

Now, if we have not neglected the ion quenching (which we assume is also responsible for production of excited molecular ions), it would be possible to find an expression for intensity of the 1st negative system of nitrogen

$$I(1^{st}\ negative) \approx \frac{[N_2(A)]_{t=0}}{(1 + l[N_2(A)]_{t=0}t)} \frac{[N_2^+]_{t=0}}{(1 + r[N_2^+]_{t=0}t)}$$

since the intensity of the ionic band is proportional to the metastable concentration and to the ground state ion concentration. The constant r corresponds to the electron-ion recombination coefficient.

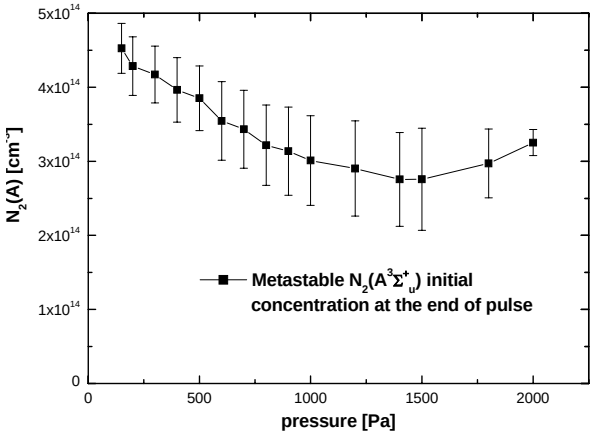

Fig. 3. **Density of $N_2(A^3\Sigma_u^+)$ metastable molecules produced by the microwave pulse**

Let us now demonstrate that we can neglect the quenching by the ions. We normalize the intensities of *I(2nd positive)* and *I(1st negative)* by their initial values (at t = 0). In such way we can follow the evolution of both band intensities in the same plot (Fig. 4). For pressures increasing up to 1500 Pa the metastable initial concentration decreases (see Fig. 3) and so our normalized intensity of second positive system must increase at any time in the afterglow, as normalized *I(2nd positive)* is

$$\frac{I(2^{nd}\ positive)}{([N_2(A)]_{t=0})^2} \approx \frac{1}{(1+l[N_2(A)]_{t=0}t)^2}$$

In our previous paper[1] we found that electron concentration at the beginning of the afterglow also decreases with pressure. Due to plasma neutrality, the ion density should also decrease. From the similar reasoning as above we can see that normalized *I(1st negative)*

$$\frac{I(1^{st}\ negative)}{[N_2(A)]_{t=0}\cdot[N_2^+]_{t=0}} \approx \frac{1}{(1+l[N_2(A)]_{t=0}t)}\frac{1}{(1+r[N_2^+]_{t=0}t)}$$

must also increase with the increasing pressure, as both the initial metastable concentration and initial ion concentration decrease with pressure. In Fig. 4 we can see that the behavior of the neutral lines is the one expected, but the ion lines behave in the opposite manner. This means that the excitation of ions by collision with metastables molecules is not the main process responsible for 1st negative system.

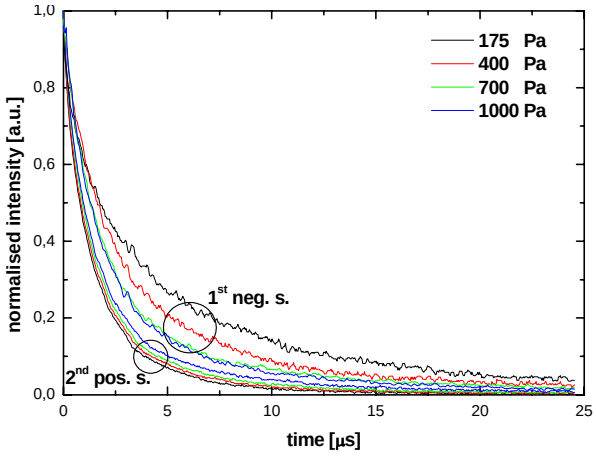

Fig. 4. **Time evolution of 2nd positive and 1st negative systems in the afterglow.** All intensities have been normalized by the initial value

Consequently, this process should not be important for the quenching of metastables molecules.

Conclusion

We carried out complex diagnostics of the afterglow of short pulse high power low pressure nitrogen discharge. From the temporal evolution of the second positive system of nitrogen we calculated concentration of nitrogen molecules in $A^3\Sigma^+_u$ metastable state.

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We studied the low pressure high power pulsed microwave discharge produced in the experimental device with suppressed influence of wall reactions. This work is focused on the afterglow. Using the experimental results, the elementary plasma processes in such type of discharge are discussed, mainly the kinetics of metastable states. It enables us to derive absolute density of nitrogen metastable molecules from relative evolution of emission of second positive system of N_2.