Publ. Astron. Obs. Belgrade No. 84 (2008), 321 - 324 *Contributed Paper*

DETERMINATION OF NITROGEN DENSITY IN DIRECT CURRENT (dc) GLOW DISCHARGES

D. POPOVIĆ[1], V. MILOSAVLJEVIĆ[2] and S. DANIELS[3]

[1] *Faculty of Physics, University of Belgrade, P.O.B. 368, Belgrade, Serbia*
E–mail: dusan@ff.bg.ac.rs

[2] *Faculty of Physics, University of Belgrade, P.O.B. 368, Belgrade, Serbia*
NCPST, School of Physics, Dublin City University, Dublin 9, Ireland
E–mail: vladimir@ff.bg.ac.rs

[3] *NCPST, School of Electronic Engineering, Dublin City University, Dublin 9, Ireland*
E–mail: daniels@eeng.dcu.ie

Abstract. Measurement of atomic and molecular nitrogen in an oxygen–nitrogen dc plasma has been presented. This is achieved by monitoring the intensities of the atomic nitrogen spectral line at 821.6 nm and the molecular nitrogen bandhead at 337.1 nm, relative to the atomic oxygen spectral line at 844.7 nm. Oxygen is the one of most frequently used gases for surface chemical treatment, including deposition and etching and therefore the ability to measure and control the process and chemical composition of the process is essential.

To validite the oxygen actimometry method for N_2–$x$$O_2$ (where x varies from zero to one) dc plasmas, threshold tests have been performed with Ar actinometry.

1. INTRODUCTION

Nitrogen plays an important role in the synthesis of nitrides owing to its high chemical reactivity. Therefore information regarding the concentration of active species in a nitrogen discharge is essential for the better control of plasma reactions and plasma–surface interactions.

Most plasma diagnostic techniques are either electrical or optical in nature. Among the electrical techniques, the most widely used method is the Langmuir probe because of its easy implementation. However, experimental problems such as contamination of the probe tip and complexities in the theory to interpret the measurements can often lead to erroneous results. Additionally, most modern commercial reactors that use reactive plasmas as processing reagents are not amenable to probes, which are invasive by nature and risk introducing undesirable process shifts. Optical actinometry provides a non–intrusive means of studying a reactive plasma. In this diagnostic technique a small amount (1–2%) of a rare gas is added to the reactive plasma and this serves as the actinometer. The concentration of the actinometer is kept constant and the optical emission derived from it is used to determine the excitation efficiency of the plasma when the discharge parameters are changed. This 'actinometry' method works well when the relative energy dependence of the electron impact excitation of

the rare gas matches that of the emitting species of interest. However, the use of a trace gas as an actinometer in an industrial setting can be problematic, as the requirement for an additional gas line would be outweighed by cost considerations. Also, a rare trace gas dilutes the chemically reactant gases and for many plasma processes this is unwanted. Therefore, the ability to use non–trace gas (like oxygen in our experiment) as the actinometric gas would negate the requirement for additional trace gases and therefore allow this technique to be applied in a manufacturing process. It must be stated, however, that the validity of actinometry is somewhat controversial and the criteria for the utilization of the technique and its limits of validity must be verified in each case (Popović et al. 2007). It is because of this cautionary note that extensive validation measurements have been performed on our system which uses oxygen as the actinometry gas. The validation procedure uses the actinometric technique itself as trace amounts of Ar gas have been added to the N_2–O_2 discharge to confirm the applicability of the technique for a range of N_2–O_2 discharges. The validity of using the non–trace gas as the actinometer should be manifested as an agreement between the oxygen and argon actinometry data under a range of plasma conditions. Once this validation procedure is complete, we no longer use trace gas Ar in the process and can revert back to actinometry measurements using the buffer gas (Milosavljević et al. 2007) of the process (oxygen).

2. EXPERIMENT

A dc discharge is produced in a Pyrex tube of 5 mm inner diameter and effective plasma length of 72 mm.

The discharge tube is evacuated using a rotary vane pump which gives a base pressure of 2 Pa. The working pressures from 50 Pa to 266 Pa are achieved using a gate valve positioned above the rotary pump. Gas flow into the chamber is controlled via mass flow controllers which precisely determine gas content in the discharge tube. The nitrogen and oxygen flow rate is varied up to 200 sccm. The power supply used was a Keithley Model 248 High Voltage Supply with the maximum voltage of 5kV

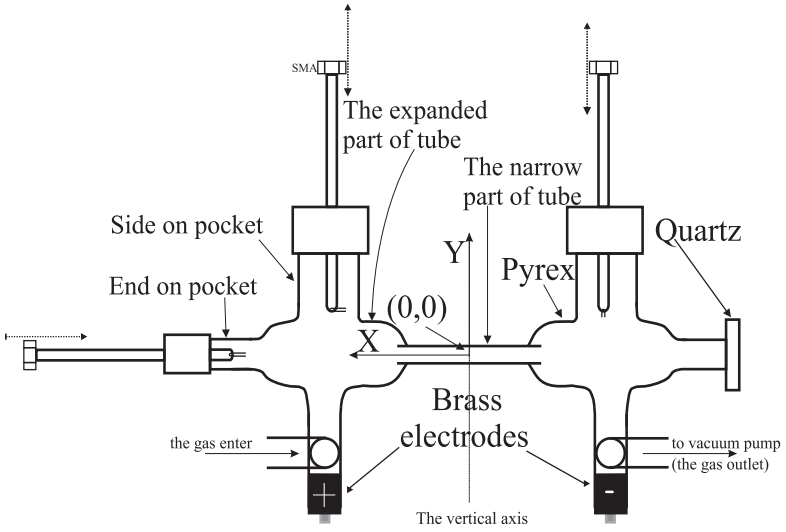

Figure 1: Plasma source with ports for the probes.

and discharge current of 5 mA. For the purposes of this experimental work the maximum voltage is 2.2kV. In fact the large parameter space required of this work meant that a Design of Experiment (DOE) had to be implemented i.e. DC voltage: 700–2200 V, N_2 gas flow rate (4–200 sccm), O_2 gas flow rate: (2–200 sccm) and chamber pressure: 50–266 Pa. The application of this DOE reduced the number of experimental runs to 36. The creation of DOE table is done by The Statistical Discovery software^{TM}, JMP IN^{TM}.

The experimental setup with associated diagnostics is present in Popović et al. (2007).

3. RESULTS AND DISCUSSION

The actinometry atomic oxygen spectral lines are: the 777 nm spectral line from the 3s–3p transition originating from the $^5S^o$–^5P multiplet and the 845 nm spectral line from 3s–3p transition originating from the $^3S^o$–^3P. In the N_2–O_2 mixture only the 845 nm line was used for actinometry since the 777 nm line is embedded in the first positive system of nitrogen molecules. The O I 844.476 nm is also a good choice, since the electron excitation of the ground state of O–atoms is a dominant process (Ricard 1996).

The density of atomic nitrogen is determinated by measuring the emission of the spectral line at 821.634 nm from 3s–3p transition and $^4P_{5/2}$–$^4P^o_{5/2}$ multiplet. While, the density of molecular nitrogen is determinated by the measurement of emission from a second positive system, i.e. 337.1 nm transition $C^3\Pi_u$,v'=0 → $B^3\Pi_g$,v"=0. Transition from second positive system are usually used for this purpose because they are mainly populated by direct electronic excitation from the ground state of N_2, and the excitation energy is close to that of excited nitrogen atom.

As is well known the actinometer should not disturb the discharge but oxygen is, in fact, part of the plasma chemistry used in these experiments. Therefore, argon was required to be employed as an actinometer in trace amounts (about 4% of the total pressure) in order to determine the threshold for actinometry by oxygen in these plasmas. It is essential that as little argon as possible be introduced into the nitrogen–oxygen plasma, only enough to be able to record the argon actinometry line. Argon is commonly chosen as an actinometer, and the 750 nm Ar I spectral line from the 4s–4p transition originating from the $^2[1/2,\ 3/2]^o$–$^2[1/2]$ multiplet is very popular because it is not sensitive to two step excitation. However, for the same reasons as in the case of oxygen actinometry line 777.4 nm, the emission of argon 750.4 nm spectral line is disturbed by the emission of nitrogen. However, this problem can be overcome by using another atomic argon actinometry line 811.531 nm. This line belongs to 4s–4p transition and $^2[3/2]^o_2$–$^2[5/2]_3$ multiplet.

Figure 2 shows a selection of the actinometry results obtained from oxygen and argon as the percentage of oxygen in the nitrogen–oxygen plasma is increased from 0 to 100%.

This plot reveals that in the plasma operating conditions used here, oxygen can be used as an actinometer when the concentration of oxygen in the plasma is not higher then 28%, the DC voltage is less than 1.1 kV and the total pressure is less than 120 Pa. To operate successfully over the full range of dc voltage used in this experiment, pressure and flows, oxygen can only be used as the actinometer if its concentration in the nitrogen–oyxgen plasma is less than 15%.

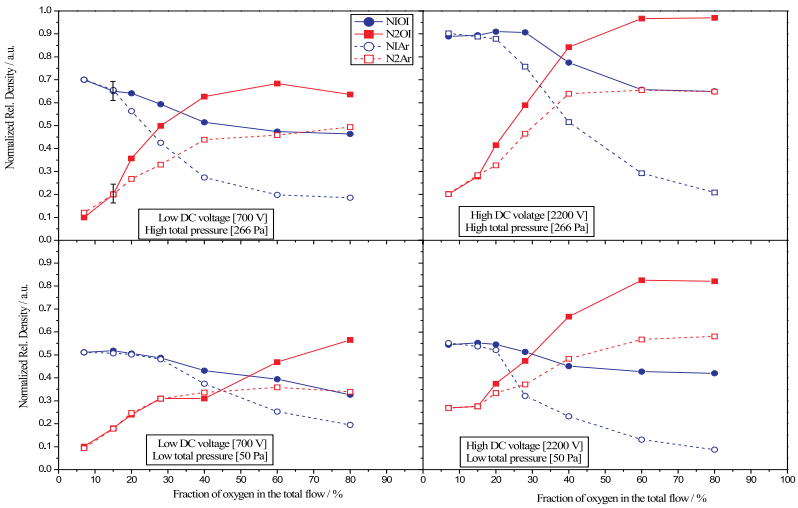

Figure 2: Actinometry results by oxygen (full lines) and by argon (broken line). NIOI and N2OI represent densities of atomic nitrogen and molecular nitrogen, respective, determinate by oxygen as actinometer. NIAr and N2Ar represent densities of atomic nitrogen and molecular nitrogen, respective, determinate by argon as actinometer. The error bar include reproducibility of the measurement.

4. CONCLUSION

We have presented a technique using optical emission spectroscopy for the measurement of nitrogen density in a nitrogen–oxygen DC glow discharge.

The validity of using the non-trace gas (oxygen) as the actinometer was determined by a set of actinometric measurements with argon gas used in trace amounts.

Acknowledgments

This work is a part of the project "Nonlinear dynamical phenomena in photorefractive media, liquid crystals, plasmas and left–handed materials (OI141031)" supported by the Ministry of Science and Environment Protection of the Republic of Serbia.

References

Milosavljević, V., Faulkner, R., Hopkins, M. B.: 2007, *Optical Express*, **15/21**, 13913.
Popović, D., Milosavljević, V., Daniels, S.: 2007, *J. Appl. Phys.*, **102**, 013303.
Ricard, A.: 1996, Reactive Plasmas–SFV Edition, p. 116.