

Characterization of a large-volume Oxygen RF discharge suitable for low-pressure treatment of sensitive samples

K. Spasić, N. Puač, N Škoro, G. Malović and Z.Lj. Petrović

Institute of Physics, University of Belgrade, Pregrevica 118, 11000 Belgrade, Serbia

We have created plasma reactor that is prototype of a commercial device for industrial applications, in order to enable large scale treatment of sensitive samples. Strong asymmetry of electrodes and large volume are suitable for achieving streamer free and generally mild plasma. In order to optimize treatment conditions and make them as energy efficient as possible plasma characterization has to be performed. For that purpose we have used mass energy analyzer, optical emission spectrometry and actinometry in an oxygen-argon plasma at pressures of 300, 450, and 600 mTorr with applied powers between 100 and 700 W.

1. Introduction

Applications of low pressure plasmas are distributed over wide range of industries, mostly for processes such as etching and deposition. This is understandable if one bears in mind that they are easily controllable and fairly cheap to use [1]

The effect of non-equilibrium plasmas are also well-known and used in fields such as medicine and biology [2, 3, 4, 5]. It is shown that after being exposed to gas discharges some seeds may improve their germination rate [6, 7, 8]. Effects can be noticeable even when seeds start to sprout since treated seedlings grow faster than those which were not treated [9]. Some seeds, usually due to bad storage conditions, can be infected with malignant bacteria and fungi that can affect their germination rate and growth. If that happens, plasma can be used for pre-saw sterilization, but discharge conditions have to be carefully set to avoid damage of seeds.

Having that in mind, a large scale plasma reactor, which can be used for treatment of sensitive samples, have been constructed in our laboratory. So far, it has been used for treatment of both seeds and textile [10, 11].

Getting well acquainted with plasma chemistry and the ability to tune plasma parameters of the discharge that is used for treatments is very important in order to make it as effective and energy efficient as possible. For that purpose we have used mass-energy spectrometry, optical emission spectrometry and actinometry.

2. Experimental set-up

In order to provide a device for industrial scale treatment of sensitive samples, we have created large volume plasma reactor with asymmetric electrodes. It is 2.5 m long cylinder with the diameter of 1.17 m. Powered electrode is made of

aluminum and it is placed along the central axis of the reactor. The cylindrical electrode is 1.5 m long and 3 cm in diameter. Chamber wall serves as a grounded electrode. Samples are placed on a flat metal platform lying at the bottom of the chamber below the powered electrode. Power is supplied via matching box at 13.56 MHz by Dressler Cesar 1310 power supply that can deliver up to 1000 W. Due to the fact that electrode surface ratio is very big we can accomplish plasma conditions that are streamer free and hence suitable for treatment of samples that cannot withstand high currents or temperatures.

Gases are introduced over two separate lines, each controlled by a flow meter, while two mechanical pumps were used to achieve and maintain vacuum. Oxygen and argon are mixed at the ratio of 99:1. Total flows were set to 110 sccm for 300 mTorr, 200 sccm for 450 mTorr and 290 sccm for 600 mTorr.

Mass-energy analyzer, HIDEN EQP, was placed side-on into the chamber. Its orifice is positioned at a fixed distance of 30 cm from the powered electrode. Energy of ionizing electrons emanating from the hot filament, which are required for detection of neutral species, can be controlled with resolution of 0.1 eV, starting from 4 eV. Number of neutral atoms or molecules can be measured as a function of energy of these electrons.

In a single scan, measurements performed at low power have very low signal. Therefore, we had low signal to noise ratio. In order to increase precision, 12 measurements were performed for each condition in accumulation mode resulting in a significant signal to noise improvement.

Optical emission spectra were obtained by using Oriel MS127i monochromator coupled with an ICCD camera. The spectrometer was positioned end-on, with a focusing lens collecting light along

axis of the vessel at two different levels: at the electrode level, facing the electrode tip, and at the platform level, 40 cm below the electrode. Since spectra recording times were several hundred ms, time and space integrated light emission was obtained in visual spectral range. Experimental set-up and positioning of the measurement equipment is shown in Figure 1.

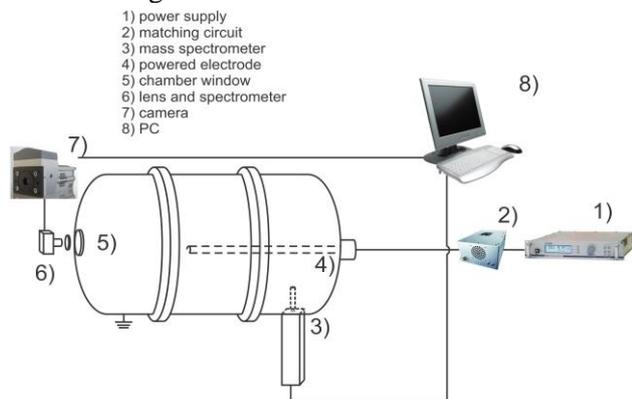


Figure 1. Experimental set-up schematics where devices are numbered as: 1) power supply, 2) matching box, 3) Mass spectrometer, 4) powered electrode, 5) chamber window, 6) lens and spectrometer, 7) camera and 8) PC.

3. Results

3.1. Mass spectroscopy

Mass spectroscopy is an indispensable tool for analyzing plasma sources. We have measured counts of oxygen molecules as a function of energy of ionizing electrons from the ionizer of the mass-energy analyzer. Measurements were performed at three different pressures: 300, 450 and 600 mTorr. Typical results are shown in Figure 2.

Oxygen molecules are of great interest due to their role in biochemical pathways in cells. Especially important signal molecule is O_2^- that is, among other places in cell, created at the cell membrane by ionizing O_2 metastable. In oxygen plasma we have a rich environment for this kind of reaction due to the presence of excited species and metastables. One should be aware that one of the most abundant metastables of oxygen, the $O_2(a^1\Delta_g)$ state, has threshold energy below 1 eV and thus the extension of the signal below 5 eV of the electron energy in Figure 2 is not surprising. With power set to 0 W (plasma not ignited) we can see only those molecules which were ionized inside mass spectrometer. Only neutral oxygen molecules in ground state are present. Therefore nothing is detected below the ionization energy which is 12.3 eV [12]. When discharge is turned on, a lot of molecules are detected below the threshold energy because, when they reach mass-energy analyzer

from plasma, they are already in excited or in metastable state. Signal obtained from these molecules can be seen in Figure 2 for the electron energies below the threshold. The fact that signal below threshold decreases with increasing power probably means that the reduction is due to electron quenching of metastables and increasing electron density with power.

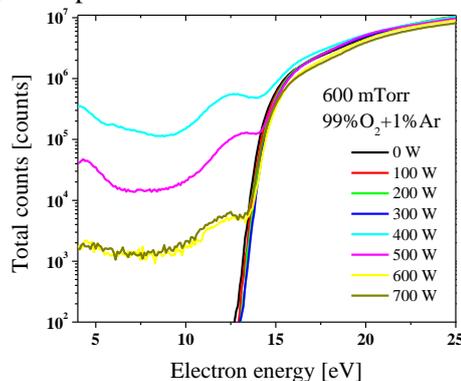


Figure 2. Counts of oxygen molecules, recorded as a function of electron energy at 600 mTorr at powers ranging from 0 to 700 W.

By integrating one curve up to the energy of 12 eV, we can get total number of molecules that are excited in the plasma and that arrived at the orifice of mass energy analyzer in excited/metastable state. We have chosen 12 eV as the limit for integration in order to be safely below the ionization threshold. Summarized results for excited and metastable oxygen molecules are shown in Figure 3.

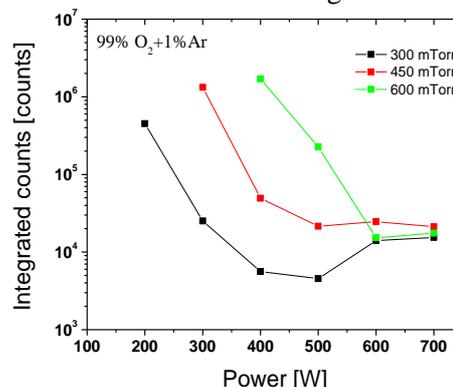


Figure 3. Counts of oxygen molecules integrated from device limit to ionization energy, recorded at various powers at pressures of 300, 450 and 600 mTorr

For all pressures that we used in these experiments plasma ignites for powers lower than 10 W. On the other hand, due to the large volume and cylindrical geometry of our reactor we have a range of power and pressure dependent conditions when excited and metastable molecules could not be detected by mass spectrometer for present position of the orifice. In order to obtain the signal below the

ionization threshold of O₂ more power has to be supplied to the system at higher pressures. Thus there appears to be a considerable loss of excited species between the active region of the plasma and the orifice of the mass analyzer especially at higher pressures. In addition there is a relative depletion towards the higher powers which may be associated by further excitation/ionization of the excited species.

We can see in Figure 3 that maximum counts are recorded at the lowest powers for each pressure. With the increase in applied power we observe the decrease in counts. At all three pressures we have a minimum that is a few orders of magnitude lower. For the highest powers there is an increase in the total counts up to the plateau that is common for all pressures.

3.2. Optical emission spectra and actinometry

In order to check the density of excited atomic oxygen species we recorded optical emission spectra of the discharge in the visual and near IR range for three different pressures and powers from 100 to 700 W. In figure 4 part of the spectrum between 740 – 850 nm is shown with characteristic atomic and molecular lines marked. The strongest lines in this wavelength range belong to O atoms produced in the discharge. Emission band coming from oxygen molecule is also present. Additionally, due to the admixture of 1% Ar, weak Ar lines are also visible.

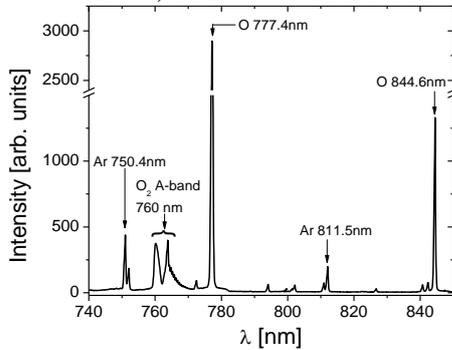


Figure 4. Part of the visual emission spectrum of O₂/Ar discharge at 200 W and 450 mTorr with characteristic oxygen and argon lines labeled in the plot

Addition of a small amount of Ar allowed us to use optical actinometry – simple and straightforward technique for determining concentration of neutral species in low-pressure plasmas [13]. Employing this technique, ratio of the observed emission intensities for selected transitions from the upper excited atomic states of oxygen and argon can be related to the concentration ratio of ground states of these atoms.

Main assumption in actinometry is that emitter atoms are excited from the ground state in collisions with electrons. However, with atomic O lines in some cases, large extent of emission could originate from dissociative excitation and not from direct atom excitation [14]. Thus, in principle, dissociative excitation has to be taken into account as well as all other important excitation (through metastables, three-body collisions etc.) and de-excitation (spontaneous emission, quenching) channels [15, 16]. In our calculations, contribution of the dissociative excitation has been included.

Using appropriate rate coefficients (k) [17], spectroscopic constants (transition probabilities, geometric constants: $C(\lambda_{Ar})$, $C(\lambda_O)$) and measured line intensities (I_O , I_{Ar}) the dissociation degree of oxygen is calculated as:

$$x = \left(\frac{N_{Ar}}{N_{O_2}^0} \frac{I_O}{I_{Ar}} \gamma \frac{k_{Ar}^{dir}}{k_O^{dir}} - \frac{k_O^{dis}}{k_O^{dir}} \right) / \left(2 - \frac{k_O^{dis}}{k_O^{dir}} \right) \quad (1)$$

where

$$\gamma = \frac{C(\lambda_{Ar}) \lambda_O A_{Arp} (\sum_j A_{Oji})}{C(\lambda_O) \lambda_{Ar} A_{Oj} (\sum_p A_{Arpq})}$$

In numerator of equation (1) the first term represents contribution of direct excitation and the second one describes dissociative excitation channel. For calculations we used rate coefficients obtained assuming Maxwell distribution of electron energy and mean electron energy of 3 eV.

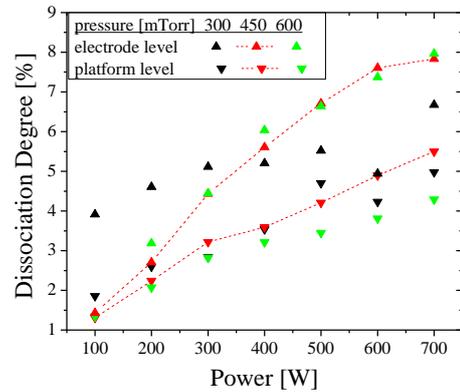


Figure 5. Dissociation degree of O₂/Ar discharge at 300, 450 and 600 mTorr calculated by using actinometry formula and emission line intensities (O-844 nm, Ar-811 nm) obtained at two different window positions.

In figure 5 we show the extent of O₂ dissociation at three different pressures calculated by using data of oxygen 844 nm and Ar 811 nm lines obtained for two different positions of the spectrometer. The spectra were recorded for discharge conditions (pressure and power) at two windows placed at different positions with the respect to the central cylinder axis. The first one, in the center, opposite

to the very bright volume around the electrode (marked as electrode level in the plot) and the other, at the platform level, close to the wall of the reactor (marked as platform level). Due to small size of the windows, emission of the lines recorded at these positions mostly originates from the volumes lengthwise the reactor facing the appropriate window.

At low powers, the dissociation degree is similar for all pressures and at both window levels. As power increases, number of dissociative products grows steadily at all pressures and for both positions. Degree of dissociation in the central region around the electrode increases much faster comparing to the degree obtained away from the electrode, at the platform level. At maximum power of 700 W the degree of dissociation reaches 8% in the region around electrode while at the platform it is around 5%. Variation of the dissociation degree for different pressures is small and almost within error bars of the technique.

From equation (1) we were able to estimate contribution of the dissociation excitation channel to the calculation of dissociation degree. For the data obtained at platform level, we estimate that dissociative excitation contributes up to 30% of the O atom emission at lowest powers while it decreases to 15% with increasing power. At the electrode level, this contribution is lower than 20% at lower powers and around 10% at the highest power.

3. Conclusion

We have used mass-energy analyzer to measure counts of oxygen molecules as a function of energy of ionizing electrons in 99% oxygen and 1% argon plasma. It is shown that the highest presence of excited and metastable oxygen molecules is obtained for minimum power in the range where signals are observable, at every pressure. Also, maximum counts are moving to higher powers at higher pressures. Optical actinometry measurements enabled us to determine dissociation degree of oxygen molecules in zone around the electrode and at the platform level. At both levels dissociation is rising with power and this increase is more pronounced near the powered electrode. The dissociation degree obtained from the space-time integrated measurements is in the range between 1 and 8 % and it has a very weak pressure dependence between 300 mTorr and 600 mTorr.

4. References

[1] T. Makabe and Z. Lj. Petrovic, *PLASMA ELECTRONICS: Applications in Micro Electronic*

Device Fabrication, Taylor & Francis Group, (2006).

[2] K. Kutasi, B. Saoudi, C.D. Pintassiglo, J. Loureiro, M. Moisan, *Plasma Processes and Polymers*, **5** (2008) 840.

[3] R.J. Reece, D.M. Sherman, R.B. Gadri, F. Karakaya, Z. Chen, T.C. Montie, K.W. Kimberly, and PP-Y. Tsai, *Plasma Science, IEEE Transactions on* **28** 1 (2000) 56.

[4] G. Fridman et al, *Plasma Processes and Polymers Special Issue: Special Issue on Plasma Medicine*, **5** 6 (2008) 503.

[5] M. Laroussi, M. Kong, G. Morfill and W. Stolz, *Plasma Medicine: applications of low-temperature gas plasmas in medicine and biology*, University Press, Cambridge (2012)

[6] S. Živković, N. Puač, Z. Giba, D. Grubišić, Z.Lj. Petrović, *Seed Science and Technology*, **32** 3 (2004) 693.

[7] N. Puač, Z.Lj. Petrović, S. Živković, Z. Giba, D. Grubišić and A.R. Đorđević, *Low-Temperature Plasma Treatment of Dry Empress-Tree Seeds*, in *Plasma Processes and Polymers*, Wiley-VCH Verlag GmbH & Co. KGaA (2005).

[8] I. Filatova, V. Azharonok, V. Lushkevich, A. Zhukovsky, G. Gadzhieva, K. Spasić, S. Živković, N. Puač, S. Lazović, G. Malović and Z.Lj. Petrović, *31st ICPIG* (2013).

[9] I. Filatova, V. Azharonok, E. Gorodetskaya, L. Mel'nikova, O. Shedikova, and A. Shik, *19th ISPC* (2009) 26.

[10] S. Živković, N. Puač, Z. Giba, D. Grubišić, Z.Lj. Petrović, *Seed Science and Technology*, **32** 3 (2004) 693.

[11] N. Puač, Z.Lj. Petrović, M. Radetić, A. Djordjević, *Materials Science Forum* **494** (2005) 494.

[12] J. T. Gudmundsson and E. G. Thorsteinsson, *Plasma Sources Sci. Technol.* **16** (2007) 399.

[13] J. W. Cobrun, M. Chen, *J. Appl. Phys.* **51** (1980) 3134.

[14] H. M. Katsch, A. Tewes, E. Quandt, A. Goehlich, T. Kawetzki, H. F. Doebele, *J. Appl. Phys.* **88** (2000) 6232.

[15] L. Zhongwei, L. Sen, C. Qiang, Y. Lizhen, W. Zhengduo, *Plasma Sci Technol* **13** (2011) 458.

[16] S. Radovanov, B. Tomčik, Z. Lj. Petrović, B.M. Jelenković, *J. Appl. Phys.* **67** 1 (1990) 97.

[17] N.C.M. Fuller, M.V. Malyshev, V.M. Donnelly and I.P. Herman, *Plasma Sources Sci. Technol.* **9** (2000) 116.