Effects of power transfer efficiency and grounded electrode surface on creation of O and O_2 excited species in low pressure plasmas

K. Spasić[1], N. Puač[1], G. Malović[1] and Z. L. Petrović[1,2]

[1]*Institute of Physics, University of Belgrade, Pregrevica 118, 11000 Belgrade, Serbia*
[2]*Serbian Academy of Sciences and Arts, Knez Mihailova 35, 11000 Belgrade, Serbia*

Abstract: We have constructed large volume discharge chamber for streamer free treatments of sensitive samples such are seeds or textiles. Mild plasmas are achieved due to large asymmetry between areas of powered and grounded electrode. Excited species of O and O_2, which participate in the interactions with living cells, were measured by mass spectrometry. Effects of size of grounded electrode and power transfer efficiency on creation of those species was also investigated.

Keywords: plasma chemistry, mass spectrometry, low pressure, power efficiency

1. Introduction

Interest for research of low pressure plasmas stems from their wide range of applications. They are extensively used in manufacturing of electronics, car and plane parts and medical equipment [1-5]. In textile industries they can be used for ecologically acceptable colouring preparation, shrinkage reduction and depositioning of bactericidal material or various microcapsules [6-10]. Relatively new, but quickly expanding field of application is plasma agriculture where they are used to increase seed germination and sprouts growth speed, remove various pathogens or influence enzyme activity [11-14].

Low pressure plasmas are known to be easily controllable and relatively cheap to implement. Due to high number of active species in any plasma and numerous processes in which they can take part, complicated plasma chemistry and treatment effects are very sensitive to even subtle changes in either system geometry or discharge parameters. In this research we will test how does size of grounded electrode influence creation of excited species of oxygen atom and molecule which are important in treatment of biological samples. In addition, relation between abundance of excited species and power transfer efficiency will be explored.

2. Experimental set-up

In order to create plasma reactor that would be suitable for treatment of sensitive samples on an industrial scale, we have crated large volume asymmetrical discharge chamber. Cylindrical geometry was selected so that streamer free discharges can be achieved. Chamber is made out of stainless steel. It is 2.5 m long and 1.17 m wide. Outer wall also serves as grounded electrode while powered electrode is axially placed aluminum rod which is 1.5 m long and 3 cm in diameter. During treatments samples are usually placed on sample holding platform which is 46 cm bellow powered electrode and it is also grounded.

Additional, smaller, grounded electrode is created so that we could test how does different ratio of surfaces of powered to grounded electrode affect plasma composition and power efficiency. It is made of aluminium and it has diameter of 63 cm. It is in electrical contact with both chamber wall and sample holding platform so that ground potential can be maintained. When additional electrode is placed, plasma is ignited only in the volume between powered and smaller grounded electrode. It is schematically presented in Figure 1.

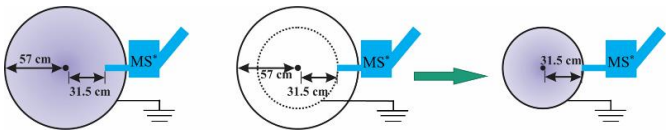

Fig. 1. Placement of additional smaller grounded electrode. MS is mass spectrometer

Pressure inside chamber was controlled by controlling flow of working gasses. They were introduced into the chamber through the system (Figure 2) which allows mixing of up to four different gasses. For this work we have used mixture 99% of oxygen and 1% of argon. Pressures were varied between 300 and 600 mTorr. Vacuum was achieved and maintained by Pfeiffer vacuum Duo 65 mechanical pump.

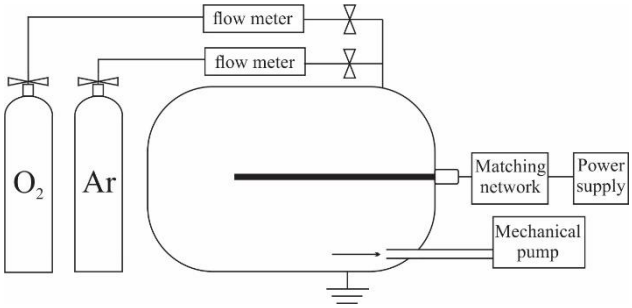

Fig. 2. Electrical and vacuum system

Discharge power was increased up to 700 W at 13.56 MHz and it was provided by Dressler Cesar 1310 power supply. This power supply has maximum output of 1000 W and it is equipped with matching network so we could keep reflected power under 2% of forwarded one.

Mass and energy analysis was performed by HIDEN EQP spectrometer which is placed side-on (see Fig.1.). Distance between powered electrode and sampling orifice of mass energy analyser cannot be changed and it stands at 31.5 cm. In case when smaller grounded electrode was in position, orifice was at the level of grounded electrode as

shown in Fig. 1. When measurements were performed without it (original large chamber wall was grounded electrode), orifice is positioned inside the plasma and 20 cm away from grounded chamber wall.

Since mass spectrometer can manipulate only with ions, ionisation is required for the measurement of neutral species. It is performed inside the internal ionization unit by electrons. The energy of electrons can be adjusted with a step of 0.1 eV with minimum energy of 4 eV. The detection of ionized species can then be performed in two modes. The first mode can give the complete mass spectra (m/Z=1-300 amu) while the energy of ionizing electrons is fixed at specific value. The second mode, which was used in this research, is such that for the fixed m/Z ratio the mass spectrometer is scanning over the specified range of energies of ionizing electrons. In this case, in order to improve low signal to noise ratio at low energies of ionizing electrons, measurements were performed 12 times for each condition.

Assessments of power transfer efficiency were performed by using derivative probes. One example of their construction is shown in Fig. 3. They should be placed as close to powered electrode as possible in order to minimise any power loss between measuring point and plasma itself. In our set-up we were able to position them directly on part of powered electrode which is outside of chamber. They are constructed as a couple of probes. Current probe which is shaped as a coil and voltage probe in a shape of letter T. Power value is obtained by multiplying calibrated current and voltage signals.

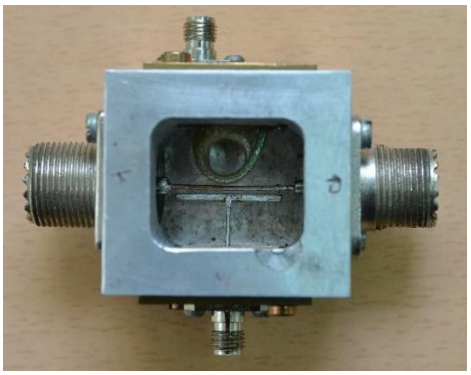

Fig. 3. Derivative probes

3. Results and discussion

Interaction between plasma and plasma treated surface is a complicated set of processes that are defined not only by presence of ions and electrons but of various excited species as well. To detect those species special procedure has to be applied. For that purpose we have applied mass-energy analysis.

Processes of ionization that are required for detection of neutral species by mass spectrometer have certain energy thresholds. Two important reactions of our interest are presented in Table 1. When discharge is turned off, ionizing electrons with energies below these thresholds are not capable of ionization of either molecules or atoms so no detection is taking place. On the other hand when plasma is turned on certain amount of excites species is created. When they enter internal ionization unit they can be ionized with electrons whose energy is well below 13.6 eV for oxygen atoms (m/Z=16) or 12.6 for oxygen molecules (m/Z=32) [15, 16, 17].

$$e + O \rightarrow O^+ + 2e \left(reaction\ threshold\ 13.6\ eV\right)$$

$$e + O_2 \rightarrow O_2^+ + 2e\ (reaction\ threshold\ \ 12.6\ eV)$$

Table 1. Reaction thresholds for creating oxygen ions

In order to count excited particles of certain species it is necessary to fix m/Z ratio to desired value (16 or 32) and perform scan over different energies of ionizing electrons. By integrating that curve up to ionization threshold energy we can get number of all excited particles at selected m/Z that have entered mass-energy analyser.

3.1. Grounded electrode – smaller area

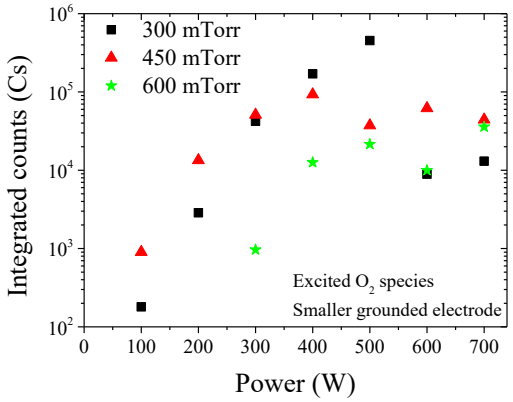

Fig. 4. Excited species of oxygen molecule when smaller grounded electrode was used

Measurements of excited species of oxygen molecule at three different pressures with smaller grounded electrode are presented in Fig. 4. At all three pressures we have certain maximum values after which we have drop in number of excited species with further increase of power. To clarify this situation additional measurements of power transfer efficiency were performed at same discharge conditions and they are presented at Fig. 5.

The most visible feature in Fig. 5 is spike in power transfer efficiency between 400 W and 500 W at pressure of 450 mTorr. It is interesting to note that at the same power we have drop in number of O_2 excited species. On the other hand at lowest pressure of 300 mTorr there is almost constant efficiency up to 500 W which is followed by decline. At that pressure there is an increase in number of excited species up to 500 W with sharp drop in their numbers at higher applied powers. At the highest pressure

of 600 mTorr both power transfer efficiency and number of excited O_2 particles are getting higher at higher powers. We have tried to detect excited oxygen atoms in presence of smaller grounded electrode, but for these conditions their presence is negligible probably due to the recombination on the wall.

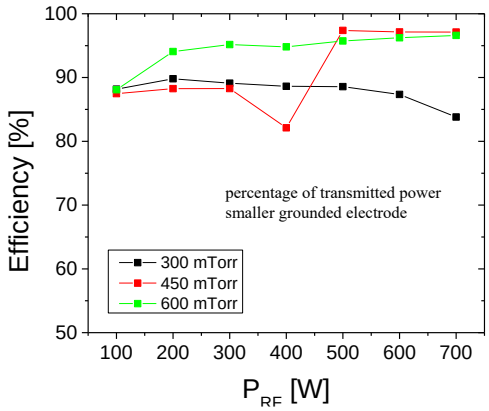

Fig. 5. Power transfer efficiency when smaller grounded electrode was used

3.2. Grounded electrode – larger area

In this configuration the orifice of the mass spectrometer is positioned inside the plasma volume and away of the grounded electrode i.e. chamber wall. Therefore, the influence of the recombination of O atoms due to the presence of the wall is negligible. The measured excited O atoms are presented in Fig. 6. We can see that with the power increase number of excited O atoms reaches the maximum value and then decreases with the position of the minimum depending on the working pressure.

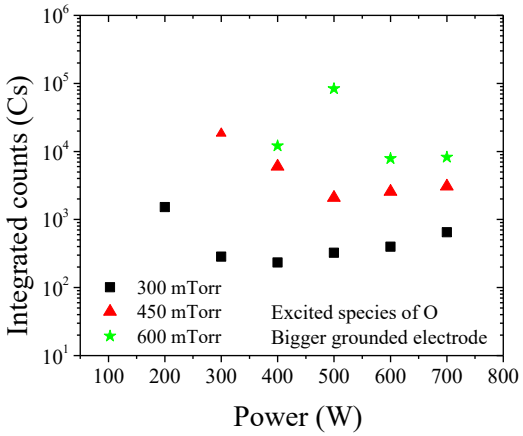

Fig. 6. Excited species of oxygen atom when bigger grounded electrode was used

On the other hand, number of excited oxygen molecules steadily decreases with the power increase (see Fig.7.). As in case of the smaller electrode there can be found the threshold power at which we can detect excited oxygen molecules species. These values of threshold power increase with the increase of the pressure. For the highest powers the number of excited oxygen molecules reaches a plateau for all three applied pressures.

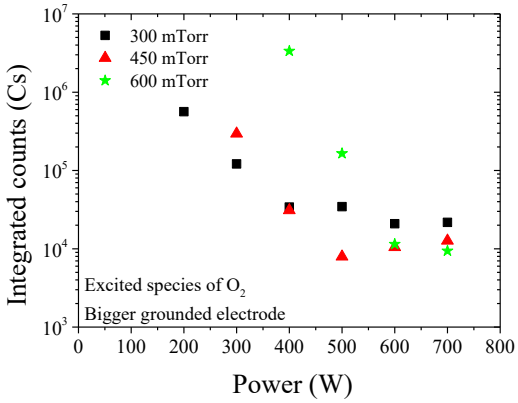

Fig. 7. Excited species of oxygen molecule when bigger grounded electrode was used

In case of large area grounded electrode power transfer efficiency is rising with applied power at all three pressures up to a pressure dependent plateau values after which it goes through a mild decline (see Fig. 8.). Only at the lowest pressure there is a sharper drop of about 10% after 500 W. Higher efficiency is measured at lower pressures. Both atom and molecule species have minimum power below which no detection is possible. At two out of three pressures, maximum number of excited atom species is measured at that minimum power while for molecule species maximal numbers are always detected at minimal powers. Contrary to power transfer efficiency higher number of excited particles are detected at higher pressures. Also in contrast with efficiency, number of excited molecule species are dropping about one order of magnitude with increase in applied RF power before they reach plateau values. Numbers of excited atom species are decreasing to their minimal value which coincide with power efficiency plateau values after which they slowly grow with further increase in power.

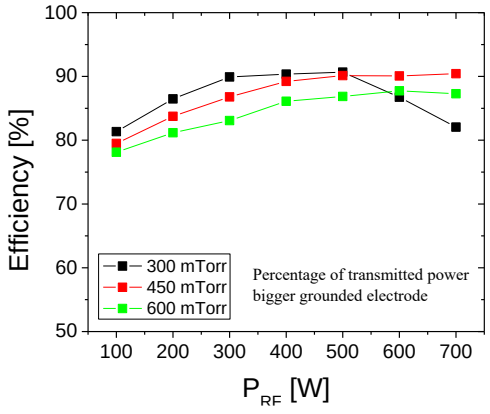

Fig. 8. Power transfer efficiency when bigger grounded electrode was used

4. Conclusion

We have tested influence of the area of the grounded electrode on the power transfer efficiency and creation of excited species of oxygen atoms and molecules in the discharge. It is shown that in case of larger electrode increase in efficiency either due to pressure or applied power leads to drop in number of O and O_2 excited species. On the other hand in case of smaller grounded electrode situation is more complicated due to fact that orifice of the mass spectrometer is at the level of the grounded electrode (i.e. chamber wall). In this case we could not detect any excited oxygen atoms due to the recombination process. Relation between creation of excites species and power efficiency is different at different pressures.

5. References

[1] T. Makabe, Z.L. Petrovic, Plasma electronics: applications in microelectronic device fabrication, CRC Press, (2014).

[2] D.B. Graves, Plasma processing. IEEE transactions on Plasma Science, **1**, 31-42 (1994).

[3] J.L. Shohet, Plasma-aided manufacturing, IEEE Transactions on plasma Science, **5**, 725-33 (1991).

[4] F. Arefi-Khonsari, J. Kurdi, M. Tatoulian, J Amouroux, Surface and coatings Technology, **142,** 437-48 (2001).

[5] C. Oehr, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, **1**, 208, 40-7 (2003).

[6] P. Erra, R. Molina, D. Jocic, M.R. Julia, A. Cuesta, J.M. Tascon, Textile Research Journal, **69**, 11, 811-5 (1999).

[7] M. Radetic, P. Jovancic, N. Puac, Z.L. Petrovic, Journal of physics: conference series, **71**, 1, 012017 (2007).

[8] M.M. Hossain, A.S. Herrmann, D. Hegemann, Plasma Processes and Polymers, **4**, 2, 135-44 (2007).

[9] M. Radetić, V. Ilić, V. Vodnik, S. Dimitrijević, P. Jovančić, Z. Šaponjić, J.M. Nedeljković, Polymers for advanced technologies, **19**, 12, 1816-21 (2008).

[10] M. Gorjanc, M. Mozetič, G. Primc, A. Vesel, K. Spasić, N. Puač, Z. L. Petrović, M. Kert, Applied Surface Science, **419**, 224-34 (2017).

[11] J. C. Volin, F.S. Denes, R.A. Young, S.M. Park, Crop Science, **40**, 6, 1706-18 (2000).

[12] M. Selcuk, L. Oksuz, P. Basaran, Bioresource technology, **99**, 11, 5104-9 (2008).

[13] B. Sera, P. Spatenka, M. Sery, N. Vrchotová, I. Hruskova, IEEE Transactions on Plasma Science, **38**, 10, 2963-8 (2010).

[14] N. Puač, N. Škoro, K. Spasić, S. Živković, M. Milutinović, G. Malović, Z.L. Petrović, Plasma Processes and Polymers, **15**, 2, 1700082 (2018).

[15] Y. Itikawa, A. Ichimura, Journal of Physical and Chemical Reference Data, **19**, 3, 637-51 (1990).

[16] Y. Itikawa, Journal of Physical and Chemical Reference Data, **38**, 1, 1-20 (2009).

[17] NIST database