# DIAGNOSTICS OF LOW-PRESSURE RF OXYGEN PLASMA SUITABLE FOR TREATMENT OF SENSITIVE SURFACES

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## ABSTRACT

We have created an asymmetric CCP plasma reactor that operates at 13.56 MHz for the purpose of large scale plasma treatment of sensitive samples such as textiles or seeds. In order to be able to optimise parameters for different treatments one should determine chemical composition of plasma in detail. Here we will present results obtained by optical actinometry that was used to determine concentration of oxygen atoms. In addition, mass spectrometry was used to estimate relative number of metastable and excited oxygen atoms and molecules.

## 1. INTRODUCTION

Due to relative simplicity of parameter control of low pressure plasmas they are widely used in industry for processes such as deposition and etching [1]. Plasma source that was developed in our laboratory is, due to its geometry, especially suitable for treatments of sensitive samples like textile, wool or seeds [2] as its asymmetry ascertains reduced energy of ions hitting the outer walls. When it comes to pre-treatment of seeds, plasma is an effective tool for improvement of germination and, also, an excellent sterilization agent [3]. With plasma treatment both problems could be solved simultaneously by choosing the correct set of treatment parameters for desired plasma chemistry.

Knowledge of active species produced in the plasma is required to plan its effects on materials. Especially important species for biomedical applications are radical oxygen species (neutral oxygen atoms, singlet delta oxygen molecules etc.) and oxygen ions. Optical actinometry was used in order to obtain absolute concentrations of atomic oxygen in our plasma. This is a simple, non-intrusive experimental tool, but at the same time one should be aware of its limits [4, 5]. Here we will present results of integrated absolute density of atomic oxygen obtained for pressures of 300 mTorr and 450 mTorr for the range of powers from 200 W up to 500 W.

Since optical actinometry can give us information only about absolute concentrations of neutral oxygen atoms, we have used mass-energy analyser in order to obtain the relative number of excited and metastable oxygen species. For example one of the most important signal molecules and at the same time oxidants is the metastable state of oxygen molecule ($^1\Delta_g O_2$) [6]. Apart from this molecule, excited and metastable oxygen atoms and ions also actively participate in plasma-biosurface interactions.

## 2. EXPERIMENTAL SETUP

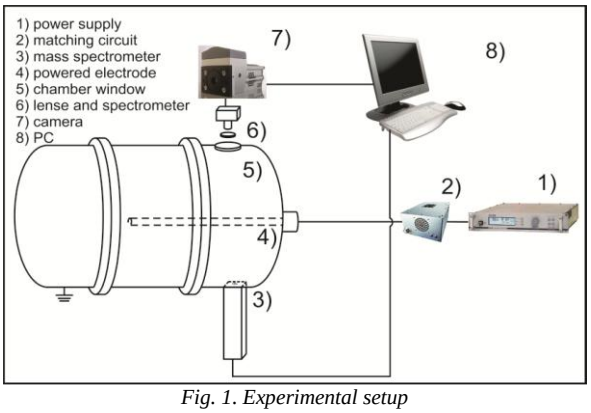


*Fig. 1. Experimental setup*

Diagnostics and treatments of sensitive samples were performed in RF plasma system that can be used for industrial applications if necessary. Power to this asymmetric capacitively coupled system operated at 13.56 MHz was supplied by Dressler Cesar 1310 through Variomatch

matching network (*Fig. 1*). Cylindrically shaped outer wall made of stainless steel served as grounded electrode. The reactor chamber was 2.5 m long and had a diameter of 1.17 m. Powered electrode was 1.5 m long aluminum rod (3 cm in diameter) placed along the central axis of the chamber.

Plasma emission in visible spectral range was recorded side-on through a window positioned at the level of the rod electrode. In focus of a lens, an entrance slit of monochromator Oriel MS127i was placed equipped with i-Star Andor ICCD camera as a detector. This way, the spectroscopic system recorded spatially integrated light coming from the region around electrode to the side window of the chamber. Recording time of the spectra was several hundred ms, so light emission from many RF periods was integrated. The emission intensity of two characteristic lines of oxygen (777 and 844 nm) and Ar (750 and 811 nm) were traced for different powers and pressures. Intensity ratios of 844 nm and 811 nm lines were used for actinometry calculations.

HIDEN EQP mass spectrometer was positioned side-on and the distance of the mass spectrometer orifice from the powered electrode was 30 cm. The number of oxygen atoms and molecules was measured as a function of electron energies coming from the filament of mass spectrometer. The range of electron energies covered was from 4 to 35 eV with resolution of 0.1 eV. Apart from neutrals we have measured energy distribution of $O^+$ ions. The working gas mixture was 99% of oxygen and 1% of argon, added as an actinometer gas.

## 3. RESULTS AND DISCUSSION

*Optical emission measurements*

Absolute densities of oxygen atoms can be determined from actinometry calculations by using optical emission intensity ratios of O and Ar atoms. Generally, for the intensity ratio to be proportional to the densities of excited species, conditions regarding cross section shape and thresholds as well as (de)excitation levels should be fulfilled [4]. Since these conditions are not generally satisfied in plasmas, utilization of the method for a particular experimental system depends on the evaluation of the conditions.

In case of oxygen, processes relevant for emission of O-844 nm line are direct and dissociative excitation, radiative decay and quenching of excited atoms. Rate coefficients for direct ($k(O)_{dir}$) and dissociative excitation ($k(O)_{dis}$) shown in Fig. 2 were calculated using emission cross sections from literature [7, 8] and assuming Maxwell distribution of electron energy. An error introduced to the rates by using Maxwell distribution function and disregarding cascading transitions is not larger than a factor of 2 [9]. Rate for direct excitation of oxygen atoms is more than 50 times higher than the rate for excitation through the dissociative channel at the temperature around 3 eV, which is the temperature of electrons obtained in our reactor. Rate coefficient for direct excitation of Ar ($k(Ar)_{dir}$) [10] is also shown (*Fig. 2*).

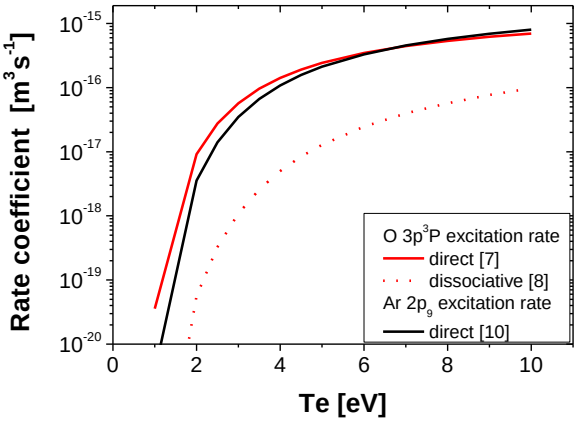


*Fig. 2 Rate coefficients for direct excitation of Ar and O atoms (full lines) and dissociative excitation of O (dashed line)*

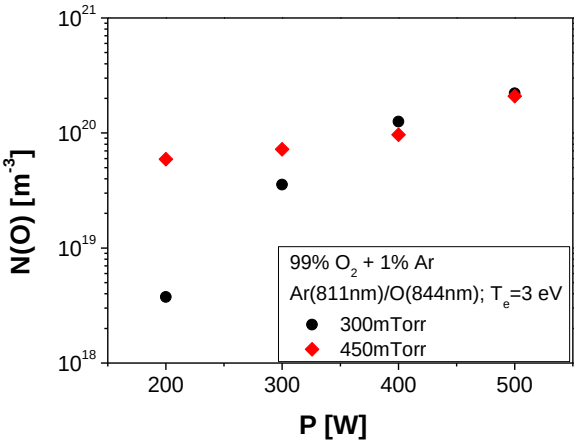


*Fig. 3 Densities of oxygen atoms produced in 99% O2 + 1% Ar plasma at 300 mTorr and 450 mTorr obtained from actinometry*

All processes relevant for emission of O-844 nm and Ar-811 nm lines ($I_O$ and $I_{Ar}$) are included in actinometry formula:

$$N_O = N_{Ar} \frac{I_O}{I_{Ar}} \gamma \frac{k_{Ar}^{dir}}{k_O^{dir}} - N_{O_2} \frac{k_O^{dis}}{k_O^{dir}} \qquad (1)$$

with

$$\gamma = C_{em}\frac{A_{Ari}(\Sigma_j A_{Oj}+q^{O}_{O_2}N_{O_2})}{A_{Oj}(\Sigma_i A_{Ari}+q^{Ar}_{O_2}N_{O_2})} \quad (2)$$

where coefficient $C_{em}$ contains all calibration factors of the optical system, $A_{Ari}$ and $A_{Oj}$ are transition probabilities [11] and $q^{X}_{O_2}$ are coefficients for atom quenching with $O_2$ [12]. Stepwise excitations through metastable states were disregarded in this calculation.

In Fig. 3 we show densities of atomic oxygen calculated from actinometry measurements for two pressures: 300 mTorr and 450 mTorr. Densities of O rise steady with power for both pressures, starting from around $5\cdot10^{19}$ $m^{-3}$ and going up to $2.2\cdot10^{20}$ $m^{-3}$ at maximum power of 500 W. There is not much differences between densities obtained for two pressures in case of higher powers. For powers bellow 400 W the density of neutral oxygen atoms is lower at lower pressure.

*Mass spectrometry measurements*

Mass spectrometry can give us information about chemical composition of the plasma system and its behaviour depending on the type of measurements conducted. When measuring the composition of neutral molecules and atoms, ionisation takes place inside the ionisation source of mass-energy analyser. We have measured mass spectra of the plasma with the energy of the electrons in the ionisation source set to 70 eV. The most abundant molecule and atoms were $O_2$ and O. We detected small amount of nitrogen molecules and atoms due to only mechanical pumping that was used in experiment. From these measurements dissociation degree was estimated and in our case dissociation degree goes up to 1 %. This result is in general agreement with the dissociation degree obtained by actinometry. Having said that we have to bear in mind that the two techniques average out properties differently, one throughout the system the other just samples in front of the orifice.

Number of oxygen atoms and molecules detected by the mass energy analyser is shown as a function of the energy of the electrons in ionization source (*Fig 4*). When plasma is not ignited, the signal for O atoms originates only from the dissociation of the oxygen molecules inside the ionisation source. In case when plasma is ignited, we can see that the signal for oxygen atoms is obtained even for energies of electrons lower than dissociation threshold of $O_2$ (20 eV [14]) and ionisation threshold of O (13.6 eV [15]). This indicates that all these atoms, which can be ionised by the electrons with lower energy then the ionisation threshold, are entering ionisation source already in the excited or metastable state. The slight increase in the signal around 10 eV correspond to the two metastable states of O atom.

Similar measurements were made for the oxygen molecule. This molecule and its metastable states are very important in interaction of plasma with the cells - $^1\Delta_gO_2$ is recognized as one of the most important signal molecules and oxidant [6]. We can see that when plasma is ignited significant amount of molecules are detected below the threshold energy for ionisation of oxygen molecule (13 eV). As in case of oxygen atoms, this signal is obtained by ionisation of excited and metastable molecules coming from the plasma into the ionisation source. Slight increase in the signal can be observed around 12 eV and this can be attributed to the metastable state of $O_2$ ($^1\Delta_gO_2$).

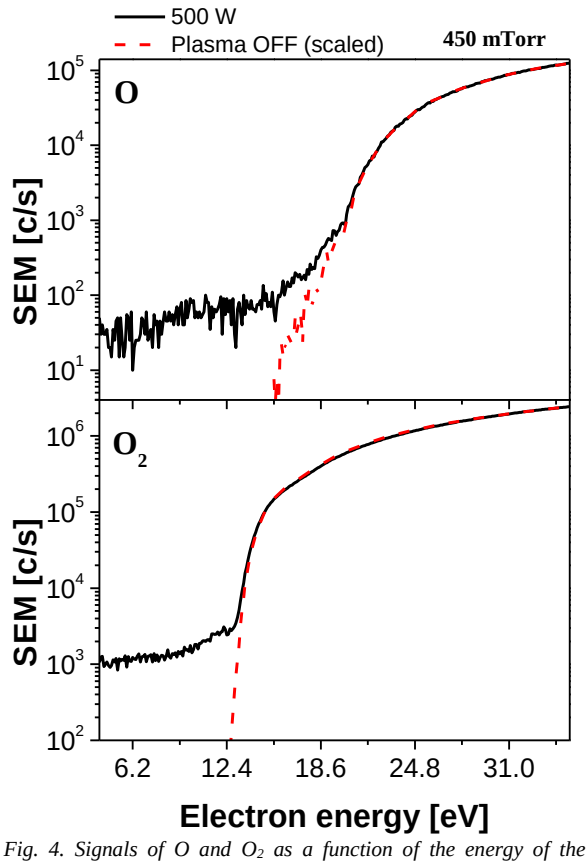


*Fig. 4. Signals of O and $O_2$ as a function of the energy of the electrons in the ionisation source. Black curve represents signal when plasma is ignited (500W) and red one when there is no plasma. Pressure was 450 mTorr.*

The relative number of excited and metastable oxygen atoms and molecules as a function of power is presented in Fig. 5. The values presented are obtained by integration of the recorder signal for the range of energies from 4 eV to 13.62 eV for oxygen atom and for the range 4-13 eV for $O_2$. We can see that number of excited and metastable atoms/molecules increases with power. Number of excited species increases with pressure.

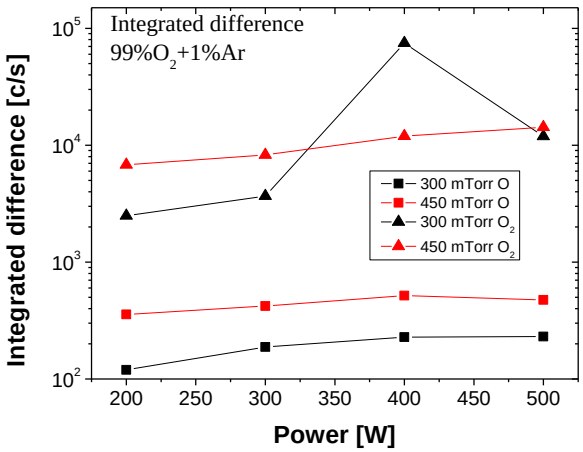


*Fig. 5 Integrated difference of excited states count for atomic and molecular oxygen at 300 and 450 mTorr for various powers.*

## 4. CONCLUSION

We found from actinometry measurements-calculations that in our reactor atomic O densities (around $10^{20}$ $m^{-3}$) show similar, steady rise with power for both pressures. The dissociation degree around 1% at the highest power of 500 W agrees reasonably with the results obtained by mass spectrometry. Furthermore, the relative number of excited and metastable oxygen atoms and molecules increases with power and pressure. Number of excited and metastable species was estimated from the measured number of O and $O_2$ as a function of the energy of electrons in the ionization source of mass spectrometer.

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