

Comparison of spatial distributions of atomic oxygen and hydrogen in ICP by means of catalytic probes and actinometry



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ABSTRACT

Low pressure inductively coupled plasma was investigated with a combination of two diagnostic techniques: catalytic probes and optical emission spectroscopy (actinometry). Three working gases were used: oxygen, oxygen–argon mixture and hydrogen. Concentrations of oxygen and hydrogen atoms were determined in a wide range of plasma parameters, with pressure ranging from 10 Pa to 70 Pa, applied power in the range from 50 to 250 W and at many different positions throughout the system (including the coil and afterglow in sample chamber). Concentrations of oxygen atoms were measured to be $1.3 \times 10^{15} \text{ cm}^{-3}$ in the middle of the coil and $4 \times 10^{12} \text{ cm}^{-3}$ in the regions of the chamber furthest from the coil. These spatially resolved concentrations are very important in plasma processing of materials, because radical concentrations over the sample determine plasma–material interactions. This work demonstrates that a relatively simple detection system can be practical and sufficiently successful in many plasma applications.

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1. Introduction

Deeper understanding of plasma properties and processes is important for numerous applications, ranging from biology and medicine [1] to materials processing [2,3]. Even though the current focus in biomedical applications is on atmospheric plasma processing [4], low pressure plasma processing is still quite challenging [5–7]. Insight into the plasma processes is enabled by a wide range of different plasma diagnostic techniques; sometimes just a basic investigation of main characteristics (composition, temperatures, pressures) is enough, but for a complete understanding experimental results have to be combined with modelling and simulations. The most widely used methods include emission [8,9] and absorption spectroscopy [10,11], Langmuir probes [12,13], hairpin probes [14], catalytic probes [15] and other active probes (probes that are immersed into plasma [16]). Most often their combination is sought, where complementarity of their characteristics can be utilized. Even though this direction is generally the best path of research, it can sometimes lead to addition of numerous diagnostics which are not always necessary for every experiment and it will only drive the costs up. In this work we are combining two

low-cost detection techniques: actinometry (using low cost CCD spectrometer with a quartz rod) and catalytic probes. Results obtained previously with catalytic probes have been compared with TALIF [17] (for nitrogen), NO-titration [18] and actinometry [19] (only for hydrogen). In this work results obtained by catalytic probes and actinometry are spatially resolved and include oxygen plasma for the first time. Oxygen and hydrogen neutral atom concentrations were measured at various pressures and applied powers of the RF inductively coupled low pressure (RF ICP) system. We show that this combination of diagnostic methods can be utilized for a detailed description of the whole plasma system, because oxygen and hydrogen neutral atom concentrations vary significantly throughout the system and their exact values are important for materials processing in RF ICP.

2. Experimental

The experimental set-up is shown in Fig. 1. Low-pressure inductively coupled plasma was created inside a borosilicate glass tube whose length was 80 cm with an outer diameter of 4 cm and the inner one of 3.6 cm. Borosilicate glass has a good optical transparency from 300 nm to IR. The glass tube protruded into a specially built stainless steel vacuum chamber. The chamber was cylindrical with a diameter of 16 cm, equipped with multiple windows for optical emission spectroscopy. For OES

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Fig. 2(a) shows the current through the coil and voltage across the coil with respect to applied power. Effective values of current I_{rms} and voltage U_{rms} were measured ($I_{\text{rms}} = \frac{I}{\sqrt{2}}$). Rather pronounced growth of both features with applied power can be observed. It is clear that such a change in current increases induced electrical field responsible for acceleration of electrons and because of this, higher powers lead to higher electron concentrations, thereby concentrations of other particles (atoms and radicals in excited states). Phase shift ϕ between these two quantities was also measured, from it the power delivered to the plasma can be determined. Fig. 2(b) shows the phase between voltage and current with respect to applied power, for different pressures. Power delivered to plasma is shown in Fig. 2(c). The phase shift is very close to 90° , therefore the delivered power is similar to the applied power. As the applied power was measured on the amplifier, before the coil (as a difference between forwarded and reflected powers) the observed discrepancies with the delivered power are not

unexpected. Fig. 2(d) shows sinusoidal signals of current and voltage, it can be seen that there are no distortions and the situation is similar for all other cases (lower powers and higher pressures).

3. Results and discussion

3.1. Concentrations of oxygen atoms

Catalytic probes, described in the preceding section, have been used to measure oxygen atom concentrations in our system. Measurements have been performed in a wide range of applied powers (ten different powers) and pressures (four pressures), as well as over 30 positions inside the chamber and the tube. Measurements were also performed for the prepared mixture of oxygen and argon (98% O_2 – 2% Ar – actinometric mixture). Similar measurements were performed for hydrogen plasma, but with somewhat smaller set of different parameters (two pressures, ten powers and twenty positions). It is important to note that concentrations were

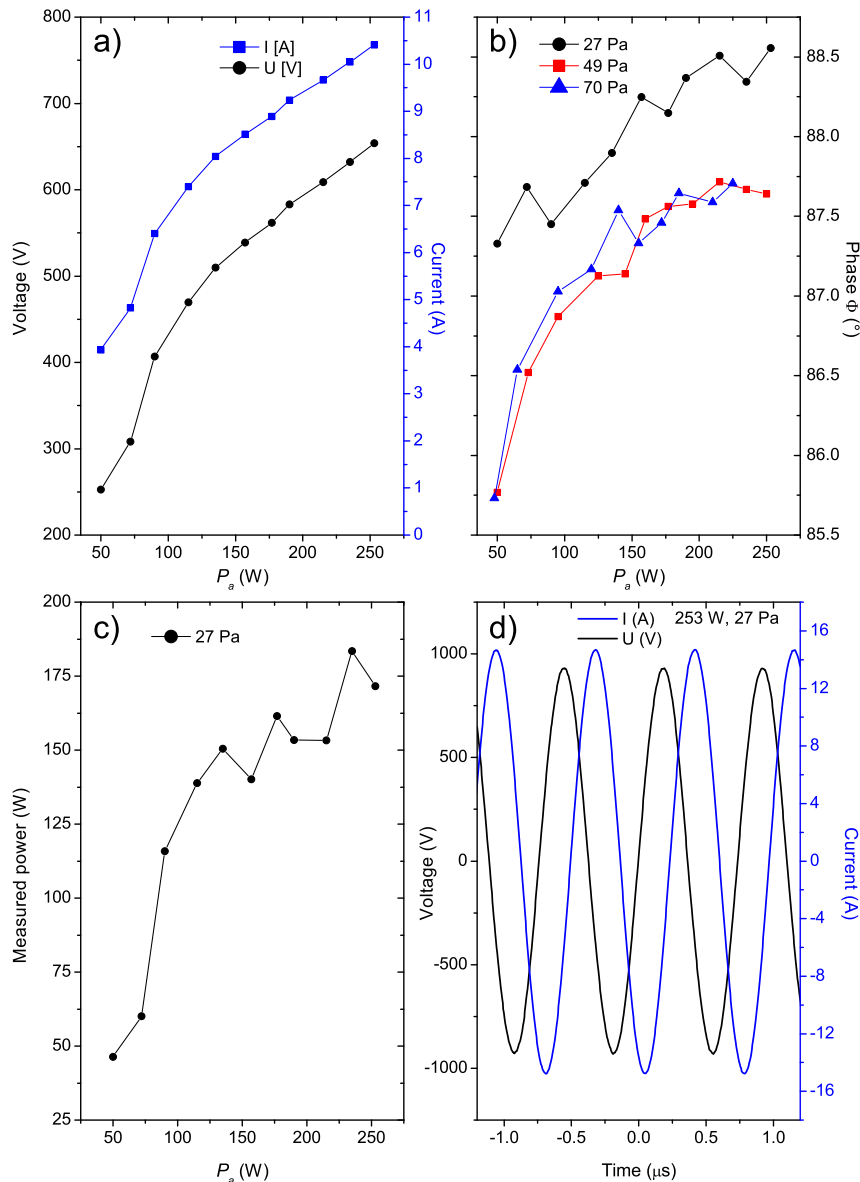


Fig. 2. (a) Current and voltage with respect to applied power P_a , for 27 Pa of oxygen plasma. (b) Phase between current and voltage, (c) measured power with respect to P_a , (d) Temporal evolution of current and voltage, for 27 Pa of oxygen plasma and 253 W of P_a .

measured for both plasma modes (E and H) in oxygen and in hydrogen plasma.

The catalytic probe was oriented and moved as shown in Fig. 1 (in direction of the tube and perpendicularly to it). Concentrations were measured with a better spatial resolution inside the chamber as more detailed characterization was required (sample placement). The probe measurement reliability was checked at a constant pressure (29 Pa) and applied power (250 W). Fig. 3 shows a sequence of probe temperatures for pure oxygen and for an actinometric mixture of oxygen and argon. Measured concentrations and associated standard errors for different gases at the position $z = 0$ cm are shown in Table 2.

One can notice quite small relative error for oxygen (under 2%) and somewhat larger for hydrogen (around 5%). The reason for this is that under these conditions, concentrations of hydrogen are smaller and that leads to lower probe temperatures, i.e. bigger influence of fluctuations. Several measurements for every set of parameters were not practical (one measurement with statistics takes over 2000 s). Because of this, in all results a somewhat higher standard error of 5% was used. Error bars are presented only in Fig. 4, while in others, for the sake of clarity, they are not presented. Concentrations of neutral oxygen atoms at the same set of parameters (power, pressure) are same to within the experimental error for both oxygen gases (pure oxygen and oxygen–argon mixture).

In Fig. 4 a substantial rise of concentration at higher applied powers can be observed, which is actually quite consistent with Fig. 2, but only for higher powers. At lower powers plasma is barely approaching the centre of the chamber ($z = 0$ cm), therefore the concentrations are significantly lower. At these low powers (below 100 W) plasma is practically not visible (or detectable by a spectrometer). This shows that a non negligible oxygen concentration persists in all parts of the system even if it is not detectable by emission spectroscopy.

Spatial distribution of neutral oxygen atom concentration, for three pressures (27, 49 and 70 Pa) and six applied powers, is presented in Fig. 5. Range of concentrations is more than two orders of magnitude (from $7 \cdot 10^{12} \text{ cm}^{-3}$ to $2 \cdot 10^{15} \text{ cm}^{-3}$). Very steep decrease in concentration can be observed inside the chamber (especially after the end of tube). This steep fall inside the chamber is expected, because recombination coefficient is much bigger for steel than glass [23]. These results show that the spatial characterization of the sample chamber is very important because already at small scale (around 1 cm) variation in concentration is quite significant. Therefore, this has to be taken into account during sample treatment and small sample sizes are advisable if spatially homogeneous interaction is desirable.

As oxygen is a molecular gas and its pressure (before plasma ignition) is well known, from the measured concentration n_0 dissociation degree η can be calculated:

Table 2
Concentrations and their relative standard errors (position $z = 0$ cm).

Gas	O ₂ (29 Pa)	O ₂ + Ar (29 Pa)	O ₂ + Ar (15 Pa)	H ₂ (39 Pa)
n (10^{14} cm^{-3})	4.23 ± 0.08	3.8 ± 0.07	2.84 ± 0.02	0.53 ± 0.03
R (%)	1.9	1.8	0.7	5.6

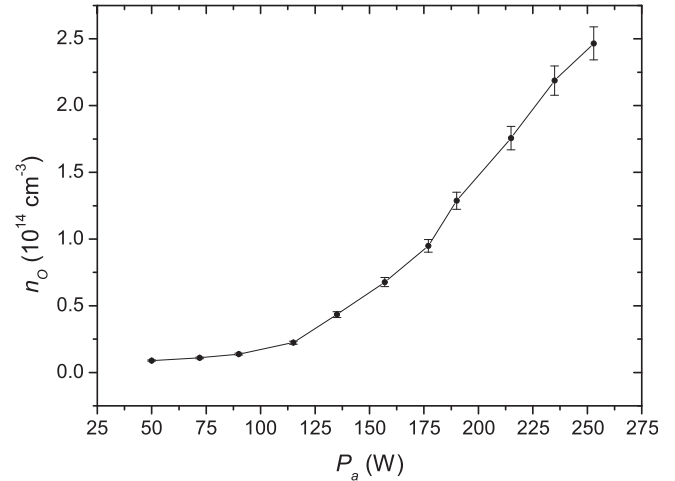


Fig. 4. Concentration of oxygen atoms obtained by catalytic probe at the position $z = 0$ cm and pressure of 49 Pa, with respect to applied power P_a .

$$\eta = \frac{n_0 \cdot k \cdot T}{2 \cdot p_{0, O_2}} \quad (2)$$

From Eq. (2) and concentrations from Fig. 5 spatially resolved dissociation degree η at the pressure of 49 Pa was obtained (Fig. 6). Temperature of the gas was estimated to be 350 K [24], and relatively constant along the coil. Even at the highest concentrations, near the excitation coil, the dissociation degree does not exceed 10%. Actually, it is shown that outside the coil, dissociation degree is quite low.

Measurements of concentration have been also performed inside the chamber perpendicularly to the tube axis. They are shown in Fig. 7, where R_0 is the dimension denoted in Fig. 1. In this direction the measured concentrations are rather symmetric, which is a noteworthy result considering that on one side (negative side of R_0) a pump exit is situated, and therefore the gas flow is preferentially to that side. Also the fall of concentration towards high values of R_0 is overly pronounced. In fact, it can be assumed with a high degree of certainty that the concentration of oxygen atoms along the diameter of the tube (3.6 cm) is quite constant. This is due

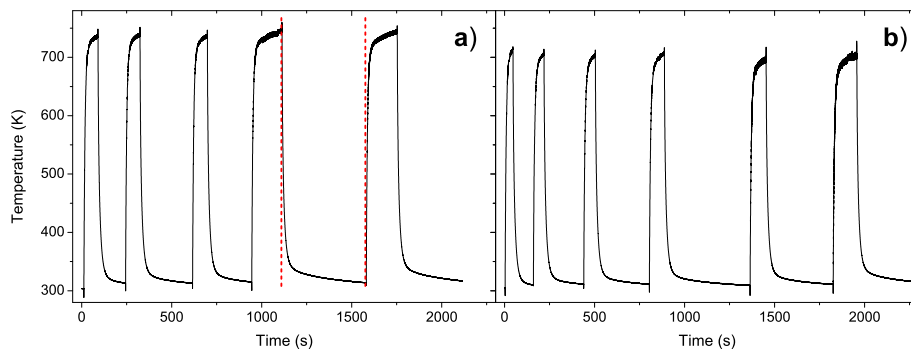


Fig. 3. Sequence of temperatures of the Ni probe with respect to time at the pressure of 27 Pa and applied power P_a of 250 W: (a) pure oxygen (b) oxygen–argon mixture. Dashed lines denote one interval of probe cooling, from which concentration is calculated.

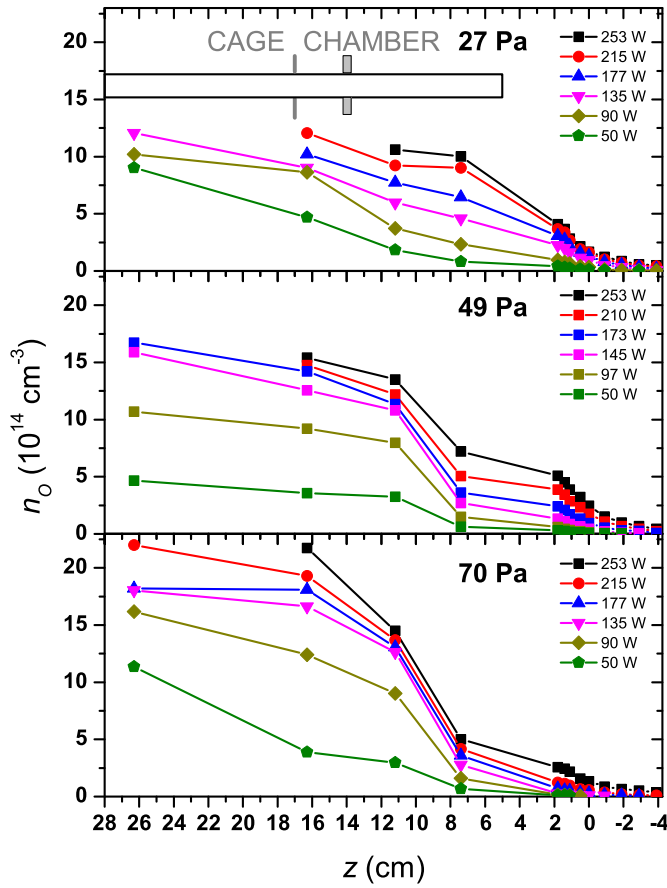


Fig. 5. Spatial distribution of O-atom concentration obtained by catalytic probe, different applied powers, at three O_2 pressures. Measured in the direction of the tube. Positions of the tube and chamber walls are denoted.

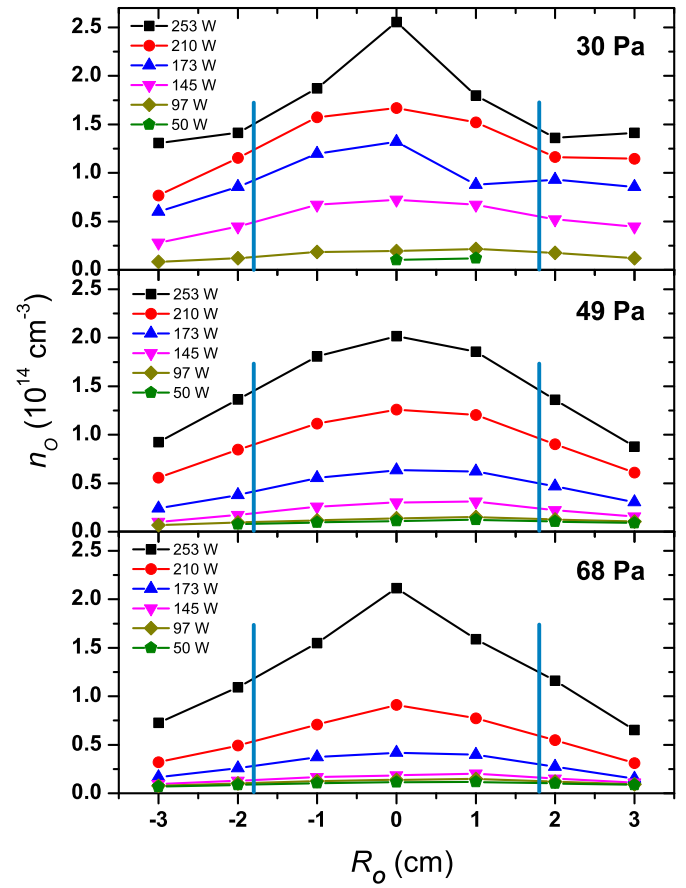


Fig. 7. Spatial distribution of O-atom concentration obtained by catalytic probe, different applied powers, at three O_2 pressures. Measured perpendicularly to the tube, inside the chamber. Vertical lines denote the diameter of the tube.

to the fact that plasma expands after the end of tube (this measurement was performed at 3 cm in z direction from the tube end), so we can make a reasonable assumption that the homogeneity inside the tube can only be better than these measurements.

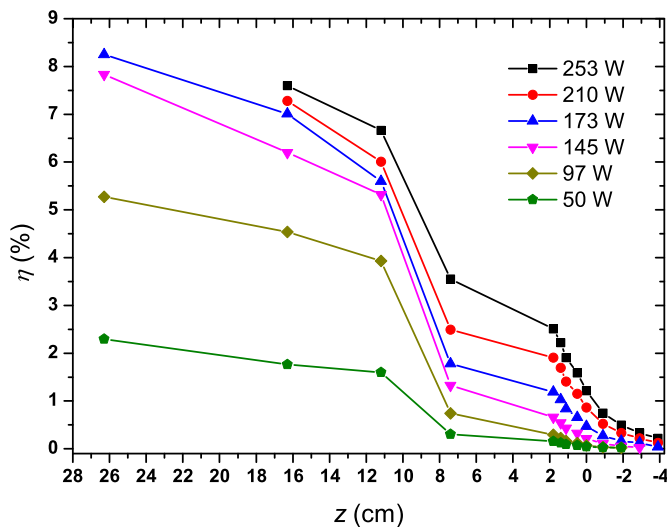


Fig. 6. Dissociation degree η at different applied powers, at O_2 pressure of 49 Pa. Measured in the direction of the tube. Positions of the tube and chamber walls are denoted.

Measurements of concentrations inside the coil were made with a small modification to the system. Additional band-pass filter was placed on the thermocouple to minimize the RF interference (which is rather high when the probe is inside the coil). Also, the pressure was lowered to 15 Pa and only the highest applied power was used. Therefore, it was possible for plasma to transit into H-mode, as shown in Fig. 8. A steep fall in concentration is quite

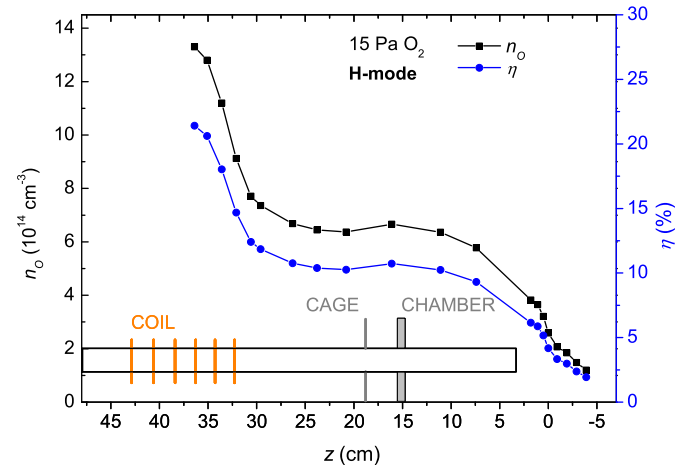


Fig. 8. O-atom concentration in H-mode obtained by catalytic probe, at 15 Pa, and dissociation degree η in the same case.

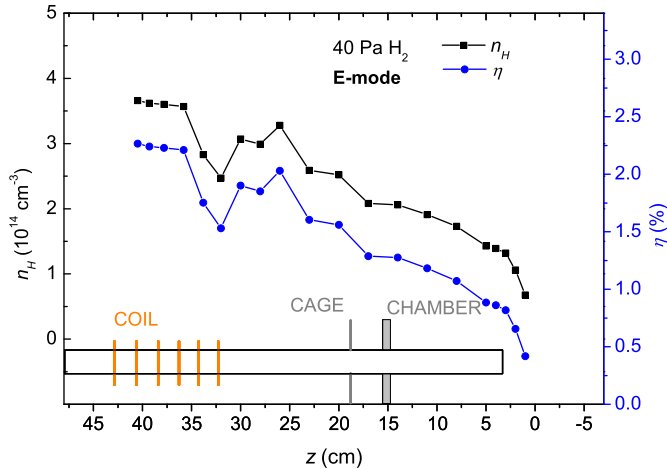


Fig. 9. H-atom concentration in E-mode obtained by catalytic probe, at 39 Pa, and dissociation degree η in the same case.

apparent immediately outside the coil. This shape of spatial profile was previously observed in emission intensity of oxygen lines [25]. Results therefore show that, for an optically thin medium, intensity of an emission line is directly proportional to the concentration. Dissociation degree measured towards the centre of the coil is higher (>20%) than in all other measurements.

3.2. Concentrations of hydrogen atoms

Concentrations of hydrogen atoms in hydrogen plasma have been measured by the gold catalytic probe. In similar manner as before, the probe was moved in the z -direction. Gold probe was movable even further than the nickel probe, through the whole length of the coil (as RF interference was smaller). Spatially resolved concentration of hydrogen atoms is presented in Figs. 9 and 10, for both plasma modes (E and H). Again, spatial profiles are similar to the intensity profiles (Balmer series) of hydrogen atoms (not shown in this paper). Both concentration and intensity exhibit a decrease towards the end of the tube in E-mode. In H-mode a steep decrease followed by relatively constant value towards the end of the tube can be observed. Associated dissociation degrees are also presented and they are couple times lower than the ones in oxygen plasma.

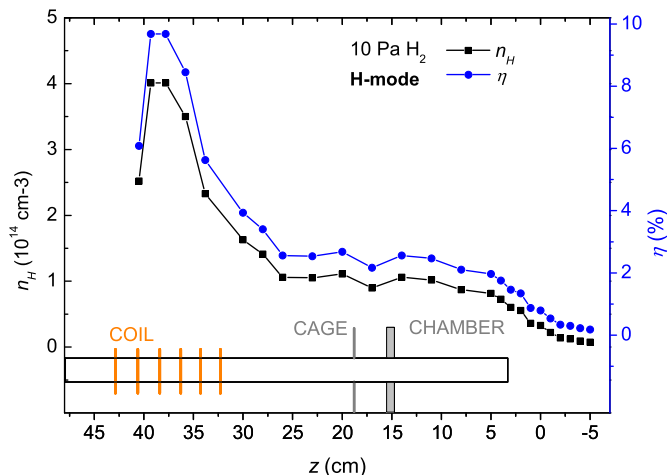


Fig. 10. H-atom concentration in H-mode obtained by catalytic probe, at 10 Pa, and dissociation degree η in the same case.

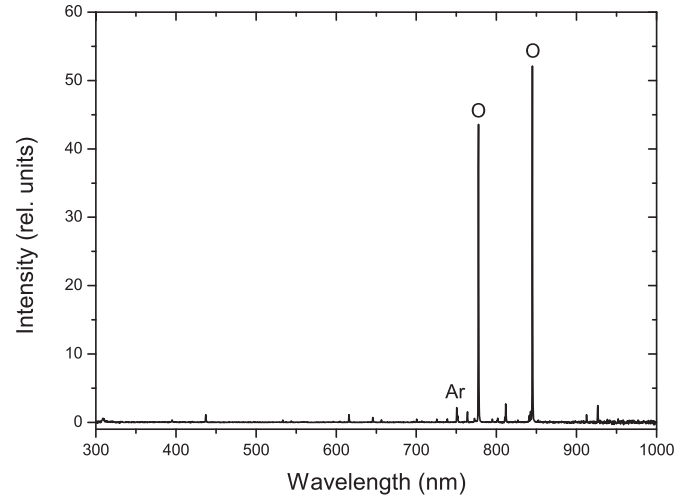


Fig. 11. Calibrated emission spectrum of oxygen argon mixture, at $z = 32$ cm, with applied power of 250 W, at 15 Pa. Lines used for actinometry are denoted on the graph.

3.3. Actinometry

For comparison with concentrations of oxygen atoms measured using catalytic probes, actinometry method was introduced [26]. Oxygen–argon mixture was used (98% O_2 and 2% Ar) and spectra were measured via the quartz rod at the same positions as with catalytic probes. Fig. 11 shows a typical spectrum of oxygen–argon mixture measured with the Avantes spectrometer. It is important to use a spectrometer that can measure intensity of lines of interest in all conditions, without the saturation of oxygen lines (777 and 844 nm) and with a strong enough signal for argon line (750 nm).

As the exact values of electronic temperatures are not known in our system, it is obvious that actinometry will exhibit a certain discrepancy. However, electronic temperature is usually around 3 eV, as noted in very similar RF plasma systems [27,28], and at these temperatures direct excitation is more pronounced for 844 nm line than for 777 nm line. Therefore, 844/750 nm ratio is more similar to probe measurements. Fig. 12 shows that inside and near the coil spatial distribution of concentration is rather similar for both methods, even though the measured values are not

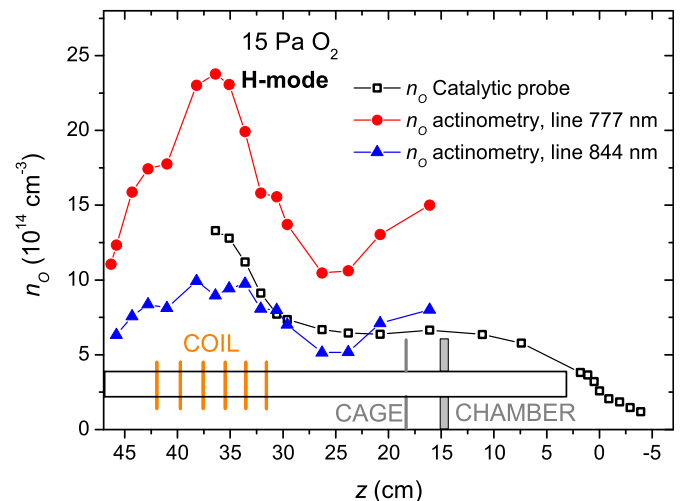


Fig. 12. O-atom concentrations obtained by actinometry (ratios 777/750 nm and 844/750 nm) compared to the ones obtained by catalytic probe.

completely similar. At positions more distant from the coil a larger difference in spatial profiles can be observed. Concentration obtained by actinometry rises, while the one obtained by probes remains constant. It can be assumed that further away from the coil, there is a larger change in electronic temperature and this leads to change in concentrations (only one T_e has been used in calculations). Actinometry results will rarely be completely quantitative, but they give a satisfactory range of concentrations for basic measurements and comparisons, for instance in vaguely described commercial plasmas in various applications. It is interesting to note that the spatial change of concentration is quite comparable to the one obtained using probes and that gives an additional applicability to the method [29].

4. Conclusions

Low pressure inductively coupled oxygen and hydrogen plasmas were investigated by optical emission spectroscopy and catalytic probes in a first spatially resolved comparison of neutral oxygen atom concentrations. Concentrations of oxygen and hydrogen atoms were measured at a large number of positions in the ICP system, including very detailed examination of multiple positions inside the steel chamber. Detailed knowledge of neutral atom concentrations inside the sample chamber is important for sample placement during treatment as it was measured that the oxygen concentration varies around 50% over 1 cm. Concentrations were measured in both modes of plasma (E- and H-mode), ranging from $4 \times 10^{12} \text{ cm}^{-3}$ to $1.3 \times 10^{15} \text{ cm}^{-3}$. These detection methods were chosen for their relative simplicity of use and to demonstrate that they can be effectively combined to produce a good description of a typical ICP system designed for materials processing.

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