Heavy particle impact excitation of atomic oxygen in front of the powered electrode of oxygen rf plasmas – Experiment and PIC-Simulation

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The spatial (axial) and temporal (rf phase) resolved plasma induced optical emission of the atomic oxygen in an asymmetrical oxygen rf plasma (CCP) shows that the electronic excitation of oxygen takes place in two regions, in the transition region rf sheath - bulk plasma, where the excitation is caused by collisions with electrons, and in a narrow zone directly in front of the powered electrode, which could not be explained with electron impact excitation. A particle-in-cell simulation for the oxygen rf plasma confirms the electron impact excitation at the sheath edge very well. For the excitation at the powered electrode a heavy particle impact excitation was assumed. Collision between O_2^+ and the background gas O_2 generate electronically excited atomic oxygen. This assumption follows in a good agreement with the experimental results.

1. Introduction

The inhomogeneous and non-stationary sheath in front of the powered electrode of an asymmetric capacitive coupled rf plasma is of special interest concerning the sheath electron heating, ion acceleration towards the electrode, and secondary particle emission. In particular, the collision dominated rf sheath provides many expectations in generation of fast neutrals by charge transfer collisions and electronically excited species. The accurate measurement of spatially and temporally resolved optical emission intensity from the sheath region and boundary zone to the bulk plasma provides interesting insight into the sheath physics and elementary collision processes. Several papers have already presented results about the plasma induced optical emission from rf plasmas (CCP) for various process gases, e.g. Ar, H_2, N_2, CH_4, O_2 [1, 2, 3, 4, 5, 6 and 7].

In this paper, the focus of the investigations is directed on the measurement of electronically excited atomic oxygen inside rf sheath of a pure oxygen rf plasma (CCP). The spatio-temporally resolved emission intensities were studied to characterise the excitation mechanisms due to collision processes involving electrons and energetic heavy particles. In particular, the rf-phase resolved plasma induced optical emission intensity of atomic oxygen reveals emission pattern immediately in front of the powered electrode which can not be explained by electron impact excitation. The origin of this emission lies in heavy particle collisions. The experimental results were compared with a PIC-(particle-in-cell) simulation for a capacitive coupled oxygen rf plasma to get more information about the excitation mechanisms and to verify the PIC-simulation with experiments.

2. Experimental setup

The investigations were performed at an asymmetric capacitive coupled rf plasma (13.56 MHz) in pure oxygen between two stainless steel parallel plate electrodes of 9 cm in diameter and a distance of 2.5 cm. The typical process parameters are rf power of between 10 and 100 W at corresponding negative self-bias voltages from -100 to -500 V, pressures from 5 to 100 Pa, and constant gas flow rate of 3 sccm.

The plasma induced optical emission from the discharge axis was imaged via a lens and aperture diaphragm onto the entrance slit of a 0.5m-spectrograph (ARC Acton Research Corporation, SpectraPro®-500, 0.5 Meter Triple Grating Spectrograph). The emission intensity is measured with a fast gated ICCD-camera (Princeton Instruments PI-MAX: 512 RB-FG) mounted in the focal plane [Figure 1]. With this setup the resolution is spectral < 0.1 nm, spatial (axial) < 1 mm, and temporal < 2 ns. The time-dependent optical emission intensity is measured for the rf-cycle of 73.75 ns by means of setting the gate of the ICCD to a fixed rf phase position, the accumulation of the optical emission intensity from few thousands rf-cycles at this phase position, then shift the gate 1 ns and running the procedure again.

All intensity measurements presented in this paper were taken from the atomic oxygen transition ($3p^3P \rightarrow 3s^3S^0$) at 844.6 nm. The natural live time of this excited state amounts about 30 ns.

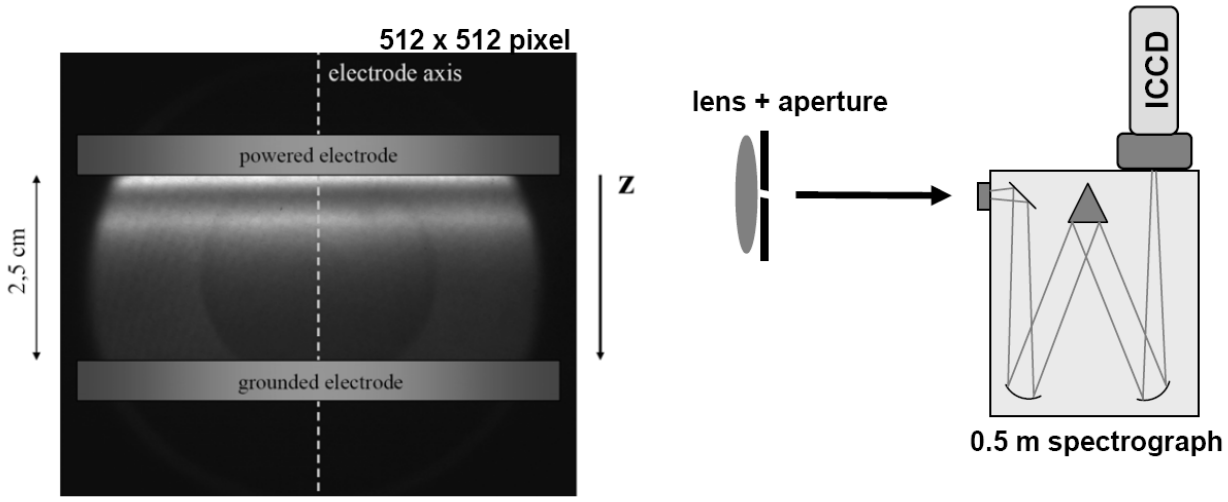

Fig. 1: Side-view of the oxygen rf plasma and schematic of the optical setup.

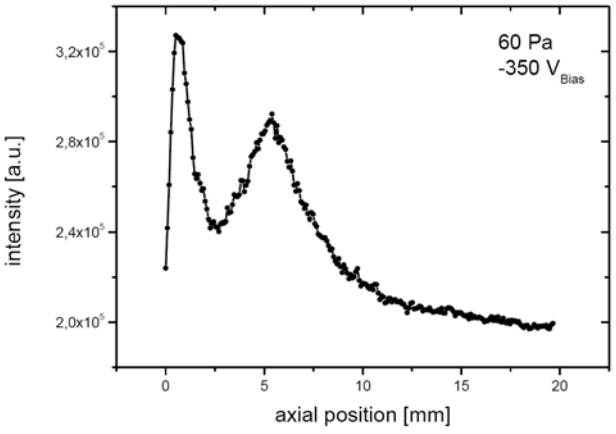

Fig. 2: Time-averaged axial emission pattern of the atomic oxygen transition at 844.6 nm taken from an asymmetric rf plasma in pure oxygen. The powered electrode is located at the axial position of 0 mm.

2. Results & Discussion

The Figure 2 shows an intensity maximum at 5 mm in the time averaged axial emission pattern. The origin of this maximum is from the dissociative excitation of molecular oxygen by sheath electrons, and it represents the position of the mean sheath edge [1, 2]. On the other hand, the increasing emission intensity towards the powered electrode (position 0 mm) reveals excitation due to heavy particle collisions. The observed maximum in front of the rf electrode is caused by shadowing effects of the powered electrode which have influenced the axial intensity measurements for the given optical aperture of the setup. More detailed information was achieved by means of rf phase resolved measurement of the emission intensity. Figure 3 presents exemplarily the measured spatio-temporal emission of atomic oxygen within two rf-cycles for 60 Pa oxygen and a self-bias voltage of -350 V. Similar to the time averaged measurements the excitation of the atomic oxygen takes place mainly in two regions, in a narrow zone directly in front of the powered electrode and in the transition region between rf sheath and bulk plasma. However, it is clearly seen the spot-like electron impact excitation at 5 mm axial position due to the heating of sheath electrons during the sheath expansion phase (at 55 and 130 ns). This excitation process is well understood and discussed in the literature [3, 5, 6].

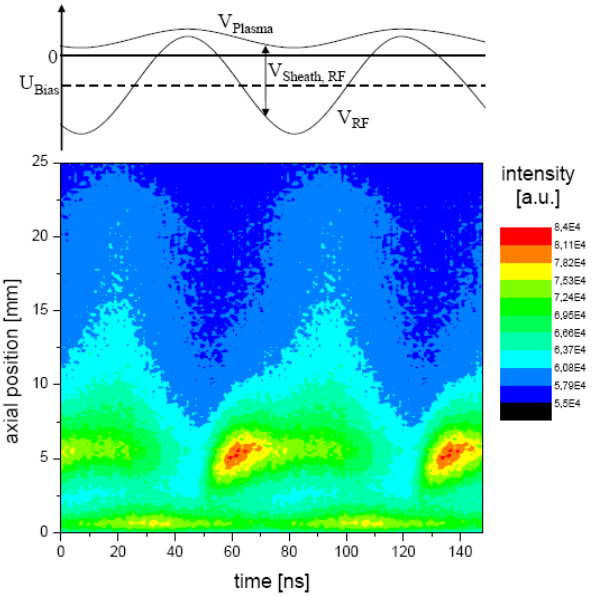

Fig. 3: Spatio-temporally resolved optical emission intensity of atomic oxygen at 844.6 nm for two rf-cycles (axial position: 0 mm powered electrode, 25 mm grounded electrode); pressure 60 Pa, self-bias voltage -350 V. On top: simplified sketch of the applied rf voltage and sheath potential.

The excitation in front of the powered electrode can not be explained by collisions with sheath or secondary electrons. The emission intensity is weakly modulated which is rather untypical for electronic excitation. Thus, it was assumed that this emission is caused by excitation of atomic oxygen due to heavy particle collisions. Generally, near the powered electrode energetic heavy particles are present, e.g. ions, fast neutrals, high-vibrationally excited molecules, which have their origin in acceleration in sheath electric field, charge transfer collisions or surface recombination of atomic oxygen.

Nevertheless, the ordinary collision between positive molecular oxygen ion and molecular oxygen was assumed. From parameter studies, the emission in front of the powered electrode was observed for negative self-bias voltages higher than 100 eV. That means the threshold for atomic oxygen excitation by heavy particles should be in this order of magnitude. Further, this emission intensity is significantly growing with increasing total pressure.

The PIC (particle-in-cell) simulation of the capacitive coupled rf discharge in oxygen was realised according the code described in [8]. Contrary to the experiment the PIC-simulation for the species positive molecular ions, negative atomic ions and electrons is based on a symmetric rf discharge, but the physical parameters in the sheath region at the powered electrode is comparable with the experimental conditions, e.g. self-bias voltage. The involved elementary processes applied for the simulation are listed in Table 1.

Table 1: Reactions included in the PIC simulation

(1) $e + O_2 \Rightarrow e + O_2$
Momentum transfer

(2-5) $e + O_2 \Rightarrow e + O_2(v = n, n= 4)$
Vibrational excitation

(6) $e + O_2 \Rightarrow e + O_2(a^1\Delta_g)$
Meta-stable excitation [0.98 eV]

(7) $e + O_2 \Rightarrow e + O_2(b^1\Sigma^+_g)$
Meta-stable excitation [1.63 eV]

(8) $e + O_2 \Rightarrow e + O^- + O$
Dissociative attachment [4.2 eV]

(9) $e + O_2 \Rightarrow e + O_2(c^1\Sigma^-_u, A^3\Sigma^+_u)$
Meta-stable excitation [4.5 eV]

(10) $e + O_2 \Rightarrow e + O(^3P) + O(^3P)$
Dissociation [6 eV]

(11) $e + O_2 \Rightarrow e + O(^3P) + O(^1D)$
Dissociation [8.4 eV]

(12) $e + O_2 \Rightarrow e + O_2^+ + e$
Ionization [12.06 eV]

(13) $e + O_2^+ \Rightarrow e + O + O$
Dissociative recombination

(14) $e + O^- \Rightarrow e + O + e$
Electron impact detachment

(15) $O^- + O_2^+ \Rightarrow O + O_2$
Mutual neutralization

(16) $O^- + O_2 \Rightarrow O + O_2 + e$
Detachment

(17) $O^- + O_2 \Rightarrow O^- + O_2$
Scattering

(18) $O_2^+ + O_2 \Rightarrow O_2^+ + O_2$
Charge exchange

The implementation of heavy particle collisions for atomic oxygen excitation (19) in PIC simulation allowed the calculation of the spatio-temporally resolved excitation rate of atomic oxygen (Figure 4). The threshold energy was given from the experiment and the excitation cross section was a free fitting parameter in PIC simulation.

(19) $O_2^+ + O_2 \rightarrow O^* + \ldots$

Threshold energy: 100 eV
Cross section (max.): $1.3 \cdot 10^{-20}$ cm^2

The comparison of the emission intensity from the experiment (Figure 3) with the plotted excitation rate from simulation (Figure 4) shows a good agreement.

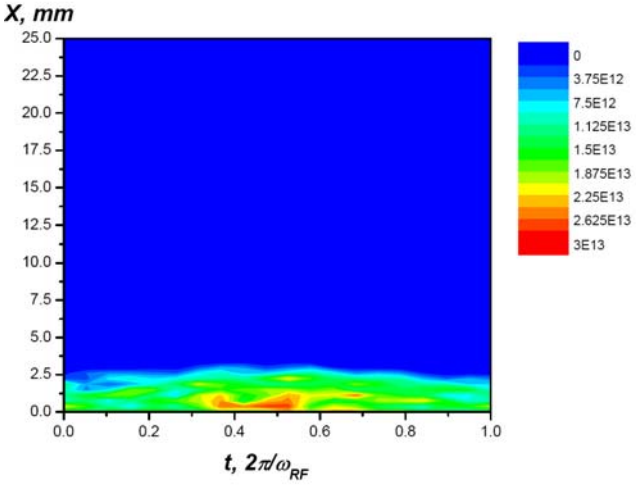

Fig. 4: Excitation rate of atomic oxygen due to the assumed heavy particle collision ($O_2^+ + O_2 \rightarrow O^* + \ldots$) calculated from a PIC-simulation at pressure 60 Pa and self-bias voltage -350 V for one rf-cycle.

4. Acknowledgement

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5. References

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