Loss mechanisms of negative oxygen ions in an inductively coupled rf discharge

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A high fraction of negative ions (approx. 90%) is observed in a pulsed oxygen rf discharge (13.56 MHz, 10 Pa). At the end of a discharge pulse of 1 ms duration both the axial and the radial density profiles of the negative ions coincide in the centre of the discharge with the density profile of the positive charge carriers. The dominant loss reactions - in particular of the negative ions - can be found from measurements of the temporal decay of the positive and negative charge carriers in the afterglow. Recombination with positive oxygen ions and collisions with atomic oxygen dominate the decay of the negative ions. These observations are consistent with the determination of the atomic oxygen density and determinations of the ion species (plasma monitor). Probe measurements indicate a production of electrons during this late phase. This can be explained by collisions of negative oxygen ions with atoms, whereby oxygen molecules are formed.

Introduction

Plasmas of electronegative gases can produce a high fraction of negative ions. Energy coupling and loss of charge carriers can be strongly modified by negative ions [1]. As a result the structure of electropositive plasmas can differ from the structure of electropositive plasmas. The significant production mechanism of negative ions (dissociative attachment) is well known for oxygen plasmas, yet the loss mechanisms can differ with the type of the discharge. Results with capacively coupled rf discharges have shown [2] [3] [4], that the following reactions play the dominant role for the destruction of negative ions in these discharges:

\[ \text{O}^- + \text{O} \rightarrow \text{O} + \text{e}^- \]
\[ \text{O}^- + \text{O}_2 (\text{a}^3\Delta_g) \rightarrow \text{O}_3 + \text{e}^- \]

Since the charge carrier density in an inductively coupled discharge is expected to be higher by two orders of magnitude, the following reactions have to be taken into account, too:

\[ \text{O}^- + \text{e}^- \rightarrow \text{O} + \text{e}^- + \text{e}^- \]
\[ \text{O}^- + \text{O}_2^+ \rightarrow \text{O}_3 \]

It is an open question, which one of these loss mechanisms is dominant in an inductive coupled oxygen plasma and which densities of the negative ions appear. It will be shown that these questions can be answered exceptionally well for a pulsed discharge.

Experimental set up and diagnostics

All measurements are done on a GEC reference cell, which is extensively described in the literature [5] [6]. The experiments are performed with a pulsed inductively coupled 13.56 MHz rf plasma at a gas pressure of 10 Pa and a power of 250 W.
A ½ m monochromator is used for emission spectroscopy. The light of the discharge is focussed with a short focus quartz lens into a quartz fibre which leads to the entrance slit of the monochromator. The focusing unit can be displaced in z- and r-direction, so that a two-dimensional spatial resolution can be achieved. The Langmuir probe measurements are done with a commercial probe system (Smart Probe System). The boxcar mode of the system allows time resolved probe measurements. A second uncompensated probe is used for the measurement of the density of the negative ions. Both probes can be displaced in z- and r-directions. The negative ions are destroyed by photodetachment. The produced electrons are detected by the cylindrical probe and are a measure of the density of the negative ions. A Nd:YAG laser system (Quantel YG 571 G) is available for photodetachment. It provides an output energy of 310 mJ at \( \lambda = 532 \) nm. At a sufficient photon flux of about 160 mJ / cm\(^2\) [2] all negative ions in the range of the probe can be destroyed (saturation) [7]. A plasma monitor (Balzers PPM 421) is used to detect the plasma ions and their energy distribution by mass spectroscopy.

**Measurements and results**

**Fig. 1: Radial density profiles**

**Fig. 2: Axial density profiles (z = 0 mm : lower electrode)**

In fig. 1 and 2 the measured radial and axial density profiles of oxygen (plasma density \( n_p \) and density of the negative ions \( n_n \)) and for comparison of argon (plasma density \( n_{n p} \)) are shown.

The radial density profiles (fig. 1) show a comparatively flat gradient towards the wall both in argon and in oxygen, whereas the argon discharge shows a significant higher density. The high density of the negative oxygen ions, which nearly coincides with the plasma density, is remarkable. Since the negative ions should drift to the centre of the discharge due to the positive plasma potential \( U_p \) (fig. 3), a much higher density of the negative ions is expected in the centre of the discharge. This is obviously not the case. It is, therefore, assumed that the lifetime of the negative ions is too short to reach the centre of the discharge. This is confirmed by calculations of the loss reactions of the negative ions - see below. Computer simulations by Kushner [8] yield a much stronger density gradient of the negative ions towards the centre of the discharge. These predictions could not be confirmed.
The axial profile of the charge carrier densities (fig. 2) shows significant differences between the oxygen and the argon discharges. The density of the argon plasma has a weaker density gradient towards the lower electrode. The differences can be explained by volume recombination of the oxygen plasma charge carriers - see below.

Fig. 4 shows the plasma potential and the floating potential versus time in the post discharge. The plasma potential has a value of +14 V during the discharge and decreases to about +4 V in the post discharge. 500 µs after the switch-off of the plasma an ion-ion-plasma has not been established. The still existing electrons cause a positive plasma potential.

The ratio of the negative ion density to plasma density is shown in fig. 5. 500 µs after the switch-off of the plasma a low amount of electrons still exists in accordance with the positive plasma potential in the post discharge.

Fig. 6 shows the measured and calculated densities of the negative ions versus time in the post discharge. The calculation is based on the assumption that the negative ions are trapped by the positive plasma potential and are being destroyed by the reactions

\[
O^- + O_2^+ \rightarrow O_3
\]
(rate coefficient \( K_{O^- O_2^+} = 1.4 \times 10^{-7} \text{ cm}^3 \text{s}^{-1} \)) and

\[
O^- + O \rightarrow O + O + e^-
\]
(rate coefficient \( K_{O^- O} = 1.4 \times 10^{-10} \text{ cm}^3 \text{s}^{-1} \)).

Consequently, the density of the negative ions, \(n_-(t)\), is determined by

\[
\frac{dn_-}{dt} = -K_{O^- O_2^+} n_+ n_-(t) - K_{O^- O} n_- n_0(t)
\]

The temporal decay of the density of the atomic oxygen \(n_0(t)\) has been determined by emission spectroscopy and the density of atomic oxygen, \(n_o\), at the end of the discharge pulse by actinometry (ratio of \( \frac{n_o}{n_0 + n_0} = 2\% \) [9]). The fraction of molecular oxygen ions \(O_2^+\),

\[
\frac{n_{O_2^+}}{n_{O_2^+} + n_{O^+_0}} = 98\%
\]

has been measured with the plasma monitor.
The comparison of calculation and experiment shows that the dominant loss process of O-ions is the recombination with O$_2^+$-ions during the discharge and in the beginning of the post discharge. The loss reaction with atomic oxygen, which produces additional electrons, is of lower significance. The theoretically expected state of an ion-ion-plasma in early post discharge, 100 μs after the switch-off of the discharge, cannot be observed until 500 μs after the switch-off due to the production of electrons.

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References


