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Investigations of negative oxygen ions in pulsed rf plasmas

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Abstract. The spatial and temporal distributions of electrons and ions in an inductively-coupled plasma (GEC reference cell) and a large diffusion chamber connected to a helicon plasma source were studied. The investigations were focussed on the production and loss processes of negative oxygen ions in argon-oxygen mixtures. Laser-induced photodetachment of the negative oxygen ions using of a frequency-doubled Nd:Yag laser along with a Langmuir probe was applied to diagnose the O^- ions. In the early afterglow the probe measurements of the detached electrons are expected to be less reliable. Therefore, we applied as a novel method photodetachment in the combination with time-resolved (about 1 μs) measurements of the electron density by means of a 1mm microwave interferometer whose beam was collinearly adjusted to the laser beam within the plasma. The results obtained from the two methods exhibit similar evolutions of the negative ion densities. The negative ion density was found to increase in the afterglow at high plasma densities. This increase is supposed to be caused by dissociative attachment to metastable oxygen molecules.

1. Introduction

Radio frequency discharges in oxygen and oxygen/argon mixtures are of considerable technological relevance. Measurements and theoretical predictions for the properties of oxygen RF discharges with inductive coupling [1] show that atomic oxygen and metastable oxygen molecules $O_2(a^1\Delta_g)$ as well as mutual neutralization of negative ions can strongly affect the density of negative ions. Therefore, the resulting negative ion density and the spatial structure depend on a number of parameters. There was an ongoing controversial discussion whether other formation channels for negative ions can play a role in addition to dissociative attachment to oxygen molecules in the electronic ground state. To clarify this issue, quantitative determination of the density of negative ions is decisive. Measurements of the negative ions by photodetachment and detection of the generated electrons by a Langmuir probe have to be regarded with some criticism. A non-intrusive method for measuring negative ions is therefore highly desirable. Cavity ring-down spectroscopy has already been demonstrated to be able to detect negative ions. However, the detection of O^- ions is limited due to the low detachment absorption cross-section [2]. First measurements with another method based on microwave interferometry [3] combined with collinear photo-detachment of negative ions are presented (Fig.1).

2. Experimental set-up

The measurements in noble gas/oxygen mixtures were performed at an inductively rf discharge (GEC reference cell) [4] and in the diffusion chamber of a helicon discharge [3]. The negative ions are detected by photo-detachment whereby the generated electrons are collected by a Langmuir probe. The frequency doubled output of an Nd:YAG laser (532nm) enters the discharge chamber after alignment of a combination of two mirrors which allow varying the beam height. The Langmuir probe is irradiated coaxially. The Langmuir probe has to be operated with a sufficiently high positive bias in order to collect the electrons generated in the detachment process so that the generated negative ions can be determined quantitatively. To avoid destruction of the probe at plasma densities higher than $5x10^{10}cm^{-3}$, the probe was pulsed in face with a laser pulse [5] (pulse length of the probe voltage 30µs, amplitude of probe voltage 0 – +50 V; see Fig.2). A new 1mm microwave interferometer [3] combined with collinear detachment of the negative ions by an 8 mm Nd:YAG laser beam (Fig.1) was performed to detect the electrons released by photodetachment with a time-resolution of less than 1 µs.

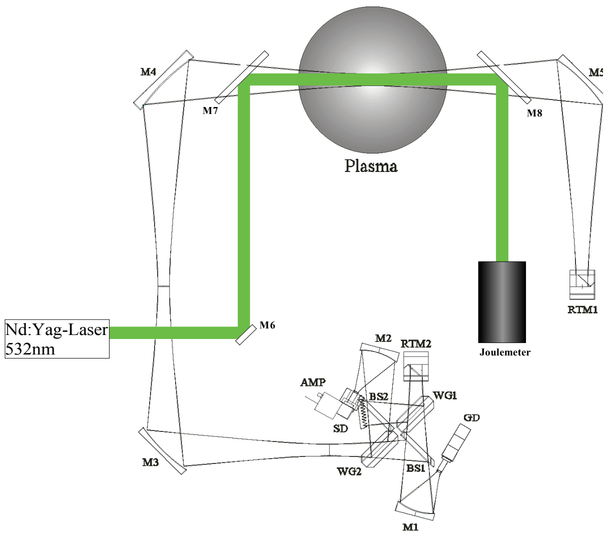

Fig.1. Microwave interferometer and laser photodetachment set up.

3. Results

Fig.3 shows the axial density profile of the charge carriers in the GEC discharge before the shut-off of the discharge; during the afterglow similar profiles are found. The negative ions are confined in the centre of the discharge as well in the afterglow as long as transition to an electron-free plasma is not established [1]. The density profile of the electrons is flat both during the discharge and the afterglow. This can be explained by the reduced ambipolar electric field due to existence of negative ions. Fig. 4 shows an example of the time dependencies of negative ions densities in pulsed Ar/O_2 discharges in the centre of the GEC discharge. We found that the negative ion density increases in the afterglow at high plasma densities. The formation of negative ions according to e + $O_2 \rightarrow O^- + O$ can be excluded for the afterglow (small T_e), since dissociative attachment has a high energy threshold. A new generation channel without threshold behaviour for negative ions is reported by Hayashi and Kadota [6]. They proposed that negative oxygen ions are generated through metastable oxygen molecules, $e + O_2^M \rightarrow O^- + O$, $O_2^M = O_2(A^3\Sigma_u^+, C^3\Delta_u, c^1\Sigma_u^-)$, whereby the attachment cross-section increases with decreasing electron temperature. This channel may lead to an increase of the negative ion density during the decay phase of the discharge. Our global model calculations show that, at electron temperatures of 3 eV or higher, this formation channel becomes unimportant as compared to the formation of negative ions by dissociative attachment of O_2 molecules in the electronic ground state. Only in the afterglow, where the electron temperature decreases, the formation channel via metastable oxygen molecules is efficient.

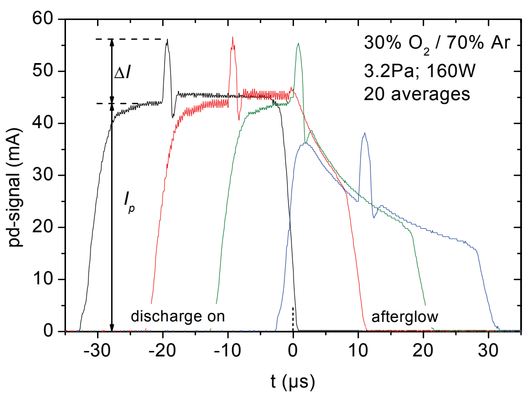

Fig.2. Electron saturation currents, I_p, and photo detachment signal, ΔI, at the pulsed probe measured 20, 10 and 1 µs before and 10 µs after the rf turn-off.

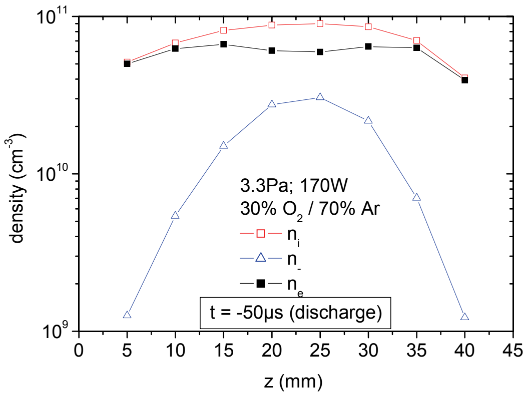

Fig.3. Axial density profiles before rf turn-off; n_e, n_i, n_-: densities of electrons, positive and negative ions, lower electrode (z = 0 mm), coil, (z = 45 mm).

First measurements of negative ions by laser irradiation of a Langmuir probe also reveal (Fig.5) a slight density increase in the diffusion chamber of the helicon discharge. The slower increase of the negative ion density can be explained by a much slower decrease of the electron temperature. The analysis of the probe characteristics in the GEC cell as well as in the helicon diffusion chamber has to be considered with some doubts since the electron temperature changes by a factor 10 at the transition to the early afterglow and, moreover, the plasma potential strongly drops; this can be a source of error. However, first line-integrated measurements with the combined laser-induced photodetachment and microwave interferometry also evidenced a slight increase of the negative ion density. The comparison with global model calculations shows that in the early afterglow of both discharges at plasma densities above approximately 8×10^{10} cm^{-3} the strong destruction of the O^- ions by mutual neutralization can be compensated by dissociative attachment of the O_2^M molecules. In the late afterglow, this attachment reaction decreases due to the finite life-time of the O_2^M molecules (quenching collisions with Ar and O_2). The destruction of O^- ions via collisions with atomic oxygen, $O^- + O \rightarrow e + O + O$, then becomes increasingly important. The comparison with global model calculations shows that, at higher oxygen content in argon-oxygen mixtures, collisions with $O_2(a^1\Delta_g)$ are the dominant volume loss mechanism for negative oxygen ions in the very late afterglow, $O^- + O_2(a^1\Delta_g) \rightarrow e + O_3$.

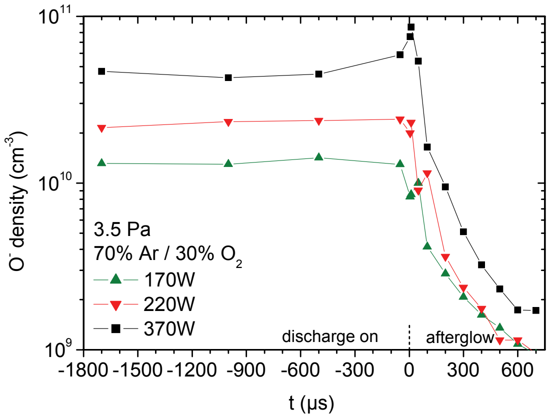

Fig. 4. Density of the negative ions vs. time for different rf powers in an Ar/O₂ mixture.

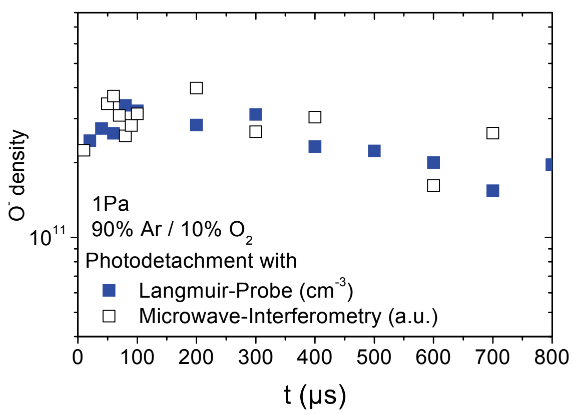

Fig.5. Density of the negative ions in the helicon diffusion chamber vs. time.

4. Summary

The measurements presented show that in oxygen discharges with a high noble gases admixture and at high plasma densities the density of negative ions should decrease by mutual neutralization much faster than experimentally observed. An increase of the negative ion density in the early afterglow is found with the photodetachment technique in combination with a Langmuir probe in the GEC cell as well as in the diffusion chamber of the helicon discharge. Apparently, there is a formation channel for negative ions that becomes efficient with reduced electron temperature at high plasma density and low neutral densities. First measurements with a new non-invasive diagnostic of negative ions combining laser photodetachment with microwave interferometry show also an increase of the negative ions in the early afterglow.

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