Probing negative ions and electrons in the afterglow of a low-pressure oxygen radiofrequency plasma using laser-induced photodetachment

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Abstract

This paper reports on the further development and improvement of time-resolved laser-induced photodetachment in concert with microwave cavity resonance spectroscopy. The method is applied to measure—with microsecond time resolution—the decaying density of negative oxygen ions (O$^-$, O$_2^-$, and O$_3^-$) and that of free electrons in the afterglow of a pulsed capacitively coupled radiofrequency-driven oxygen plasma. The afterglow behavior of the electrons shows a significant dependence on the gas pressure between 3 Pa and 6 Pa. For a pressure of 3 Pa, at which the plasma is in the so-called $\gamma$-mode, the decay of the negative ion density is slower than that of the electron density, eventually leading to the occurrence of a negative-ion-positive-ion plasma. At a slightly elevated pressure of 6 Pa (and higher), the plasma transits into the so-called $\alpha$-mode, in which a short period of increased electron density is detected just after switching off the plasma. In the $\alpha$-mode, the negative ion and electron densities decay within similar timescales, leading to the trapping of negative ions. In this pressure range, the decay of the additional electron density released by the photodetachment of negative ions occurs according to two distinct timescales. However, for increasingly elevated pressures above 10 Pa, the photodetachment signal is characterized by decay with an undershoot, which may indicate a temporary local disturbance of the plasma’s quasi-neutrality in the volume irradiated by the laser beam.

Keywords: electronegative plasma, afterglow, laser-induced photodetachment, microwave cavity resonance spectroscopy, MCRS, electron density, negative ions

(Some figures may appear in colour only in the online journal)
1. Introduction

The dynamics of electronegative plasmas have been subject of interest during recent decades [1–4]. In electronegative plasmas, negative ions (often called anions) reside alongside positive ions, electrons, and different neutral species such as metastables and reactive radicals. Such negative ions may be formed due to the significant electron affinity of some specific gaseous species. For instance, in the case of an oxygen plasma—as investigated in this paper—oxygen atoms (O) and oxygen-based molecules (O$_2$, O$_3$) can turn into negative ions, such as O$^-$, O$_2^-$ and O$_3^-$ upon the attachment of a free electron from the plasma. Depending on the experimental configuration and the discharge parameters, the number of free electrons may become significantly suppressed by these attachment processes. This, of course, strongly impacts the overall plasma dynamics.

Oxygen-containing plasmas have been of particular technological importance for decades, mainly due to the presence of negative ions, ozone, and a multitude of excited species. The applications of oxygen plasma include the oxidation of silicon in the semiconductor industry [5], surface cleaning [6], the etching of organic polymers [7,8] and amorphous carbon films [9], as well as the treatment of polymers and polymer composites [10] on industrial scales. The role of oxygen negative ions, in particular, in plasma chemistry and plasma-surface processing, has been studied extensively for such potential applications [11,12], highlighting negative ion formation in the near-surface and sheath regions.

These potential applications and the compounded complexity of electronegative plasmas [13–15] require diagnostic tools that can investigate the formation and destruction mechanisms of negative ions in order to comprehend and model their dynamics under various conditions. To date, an array of diagnostic techniques has been proposed and developed to detect and measure the density and investigate the dynamics of electrons and negative ions in plasmas [16]. Besides the role of free electrons in the overall dynamics of negative ions, the diagnostic methods used with negative ions are, in some cases, dependent on a determination of the electron density.

Langmuir probes have been used as diagnostic tools for negative ions [17]. Nonetheless, the probes’ intrusiveness and their contamination create additional obstacles when operated in chemically reactive discharges. Mass spectrometry [18] is another diagnostic that has been used to probe negative ions. However, in this method, the trapping of negative ions in the positive plasma glow complexifies their extraction and subsequent detection. In addition, laser-induced photodetachment (LIP) has been developed and implemented as a diagnostic tool for various types of electronegative plasma [19]. To obtain absolute values for the negative ion densities, various probes have been combined with the LIP technique, including Langmuir probes [20,21], resonance hairpin probes [22], microwave interferometry [23], and microwave resonant cavities [1].

The dynamics of negative ions have been investigated in various plasma configurations and under various conditions. For instance, the spatial profiles of negative ions in low-pressure oxygen discharges have been documented by Stoffels et al [1]. In that work, the densities of oxygen negative ions at different gas pressures, input gas flows, and plasma powers were measured and compared to a kinetic model. In addition, the (axial) negative ion profiles in oxygen [24] as well as in CC$_2$F$_2$, C$_2$H$_2$ [25], and aniline argon radiofreQUENCY (RF) discharges [26] were provided, while the temporally resolved negative ion and electron densities during the afterglow of a CF$_2$ RF plasma were determined by Kono et al [27]. Moreover, negative ion and electron densities have been probed in a time-resolved fashion in the afterglow of oxygen- and hydrogen-containing RF plasmas driven in both capacitively coupled (CC) [28] and inductively coupled (IC) [29] manners. For instance, LIP in concert with microwave interferometry was used in a pulsed CC-RF plasma [30] and in the afterglow of an IC-RF [31] plasma by Küllig et al. In that work, it was shown that the electronegativity $\alpha = n_\text{e}/n_\text{e}$ (where $n_\text{e}$ and $n_\text{e}$ are the negative ion density and the electron density, respectively) of the plasma was a function of the gas pressure and the plasma input power. In addition, a significant momentary release of electrons was observed during the afterglow in a highly electronegative mode. In all the aforementioned measurements, which were based on the microwave interferometry technique, the lowest electron density detection limit was on the order of $10^{14}$ (m$^{-3}$), rendering a lower detection limit for negative ion densities on the order of $10^{15}$ (m$^{-3}$).

In this article, an experimental investigation of the temporal evolution of the densities of different oxygen anions and electrons in the afterglow of a capacitively coupled pulsed RF oxygen plasma is presented. For this purpose, laser-induced photodetachment in concert with microwave cavity resonance spectroscopy has been further developed and employed with a 50 ns time resolution. The key contribution of this work is that the detection limit for negative ions has been improved by three orders of magnitude—i.e. to the order of $10^{12}$ (m$^{-3}$)—compared to previously published works. This is achieved by increasing the stability of the laser beam energy, by optimizing the microwave cavity resonant method, and by averaging over many LIP events. As a result of the enhanced detection accuracy, negative ions can be detected within prolonged timescales of up to 5.5 ms in the afterglow. This enables us to distinguish between two distinct behaviors of the afterglow phase that have only been predicted numerically in the literature [32,33]: the occurrence of a negative-ion-positive-ion plasma afterglow in the low electronegative mode and the sudden release of secondary electrons by the afterglow in the high electronegative mode, which results in self-trapping of negative ions.

This article is organized as follows. First, the experimental methods, the setup and the data-acquisition hardware are explained in detail in section 2. In section 3, structured time-resolved measurements of the electron density and the relevant negative ion densities in steady-state plasma operation as well as in the afterglow plasma phase are presented. In particular, the variation of the gas pressure enables us to distinguish between the low electronegative mode and the high electronegative mode. Finally, section 4 summarizes and concludes the presented work.
2. Experimental methods

In this section, brief descriptions encompassing the main aspects of MCRS and LIP are provided in sections 2.1 and 2.2, respectively. Following these sections are overviews of the experimental setup (section 2.3), the data acquisition hardware (section 2.4) and the data processing (section 2.5).

2.1 Microwave cavity resonance spectroscopy

The principle of MCRS is based on the fact that a plasma and an associated change in the permittivity \( \varepsilon \) associated with the presence of free electrons are produced inside a hollow metal cylindrical pillbox cavity. In addition to the number and the locations of the free electrons present inside it, the geometry of the designed cavity also determines the resonance frequencies of the resonant eigenmodes that can be excited inside the cavity. Typically, these resonance frequencies are in the GHz frequency range. By precisely monitoring the resonance frequency(ies) of the excited mode(s), accurate information can be retrieved about the free electrons inside the cavity. Over a certain (microwave) frequency range, multiple resonant modes may be excited, of which the ones featuring the desired characteristics may be used as probes. Moreover, the simultaneous application of multiple modes has been demonstrated to even provide opportunities to sample the spatial distribution of electrons over the cavity volume [34].

In MCRS, the temporal evolution of the electron density inside the cavity volume is determined by the difference between the cavity’s resonance frequencies before \( f_0 \) and during \( f(t) \) a particular incident. This incident may be the introduction of plasma in general, or a slight and transient change of the electron density, for instance—in the case of this work—due to photodetachment events. Hence, the time-resolved electron density obtained by MCRS is given by:

\[
\pi_e(t) = \frac{8\pi^2 m_e e^2}{\varepsilon^2} \int E_x^2 E_y^2 f(t) - f_0 \frac{f_0}{f_0},
\]

where \( m_e \) and \( e \) are the electron mass and charge, respectively, and \( \varepsilon_0 \) is the permittivity of free space. It is important to note here that the value of \( \pi_e \) is a microwave electric field weighted electron density, which is averaged over the cavity volume. Taking into account both the spatial distribution of the free electrons over the cavity volume \( \pi_e(\vec{x}) \) and the local value of the electric-field component \( E(\vec{x}) \) of the applied microwave resonant mode, the cavity-averaged and microwave electric field weighted electron density at a certain moment is then given by:

\[
\pi_e = \frac{\int_\text{cavity} \pi_e(\vec{x})E_x^2(\vec{x})d^3\vec{x}}{\int_\text{cavity} E_x^2(\vec{x})d^3\vec{x}}.
\]

Figure 1. Spatial distribution of the resonant microwave field associated with the TM\( \text{\delta}_{10} \) resonant mode in the cavity; the electric and magnetic field directions are represented by red and white arrows, respectively. Calculations were performed using COMSOL®.

Since electrons are not necessarily homogeneously distributed over the cavity volume, \( \pi_e \) means that, depending on the resonant mode used, electrons at different positions in the cavity are probed to various extents. In this work, the resonant mode used is the fundamental resonant mode, (transverse magnetic) TM\( \text{\delta}_{10} \), for which the electric field component \( E_x(\vec{x}) \) is computed (using COMSOL®) and represented in figure 1. The microwave electric field distribution, which has only an axial component that has a radial dependence that is axially symmetric, has been used to obtain the electron density for each subsequent experiment. As can be seen in figure 1, this mode is most sensitive on the axis of the cavity. Typically, the error in the determination of the volume-averaged value \( \pi_e \) using MCRS is on the order of 0.1% [35].

The time resolution with which changes in the electron density can be detected using MCRS is limited by the fundamental response time \( \tau_{\text{fund}} \) of the cavity used, which depends on the resonance frequency \( f_0 \) and the quality factor \( Q \) of the resonant mode used (\( \tau_{\text{fund}} \approx Q/f_0 \)). The quality factor of a resonance peak is determined by:

\[
Q \equiv \frac{f_0}{\Gamma}
\]

where \( \Gamma \) is the full width at half maximum (FWHM) of the resonance peak. For the experiments presented in this work, \( f_0 = 1.3665 \text{ GHz} \) and \( \Gamma \approx 5.91 \text{ MHz} \), which amount to \( Q = 231 \) and, hence, the time resolution was \( \approx 50 \text{ ns} \).

2.2 Laser-induced photodetachment

Laser-induced photodetachment (LIP) is an indirect approach used for the detection of negative ions. In this technique, negative ions are converted into electron–neutral pairs upon the absorption of laser photons with sufficient energy:

\[
X^- + h\nu \rightarrow X + e^-.
\]
Here $X^-$, $h\nu$, and $X + e^-$ signify a negative species, a laser-beam photon, and a photodetached neutral–electron pair, respectively. This process occurs provided that the photon energy $h\nu$ exceeds the binding energy of the electron, i.e. the electron affinity of $X$. During the experiments presented here, we used the fundamental mode (1064 nm, which is equivalent to a photon energy of 1.16 eV) of a Nd:YAG laser to probe the density of $O_3^-$ anions, which has an electron binding energy of 0.45 eV. Using the secondharmonic (i.e. 532 nm, which is equivalent to a photon energy of 2.3 eV) of the same laser system enables us to detect all the anions, i.e. $O^-$, $O_2^-$, and $O_3^-$, which have electron binding energies of 1.46 eV, 0.45 eV, and 2.10 eV, respectively [36–38].

By cleverly taking the difference between the photodetachment signals at 532 nm and those at 1064 nm—including the scaling of the laser pulse power, the photodetachment cross sections, etc. the individual contribution of at least $O_3^-$ can be pinpointed.

First, when the laser wavelength is set to 532 nm, all the negative ions involved—$O^-$, $O_2^-$, and $O_3^-$—contribute to the overall photodetachment signal which can be probed by MCRS and provide information regarding the total negative ion density. The contribution of $O^-$ to the overall photodetachment signal is significant since, first, in such oxygen plasmas, $O^-$ is by far the most dominant negative ion [39] and, second, the photodetachment cross section of $O^-$ is about three to six times higher than the other negative ions’ cross sections at 532 nm. Due to the relatively low concentration of the other negative ions involved ($O_3^-$ roughly constitutes 10% and $O_2^-$ roughly constitutes 1% of the total negative ions), their contribution to the total photodetachment signal is considered marginal.

Subsequently, after setting the laser wavelength to 1064 nm, only $O_3^-$ is vulnerable to LIP, and hence, when the photodetachment signal is probed by MCRS, information can be obtained with respect to the density of $O_3^-$ alone.

The overall impact of the photodetachment event can now consequently be detected by MCRS, i.e. the electron release accompanying the photodetachment of negative ions leads to a sudden local surge of the electron density in the plasma, which is, in turn, directly observed as a change in the resonance frequency. Figure 2(b) represents an exemplary photodetachment incident upon radial laser irradiation of a plasma and the resulting change in resonance frequency during and after this event.

Equation (1) links the additional resonance frequency shift due to the sudden appearance of photodetached electrons to a change in electron density ($\Delta n_e^{phot}$). Assuming that the laser pulse energy is sufficient to convert all the negative ions in the laser beam path, i.e. operation in the saturation regime, a radially averaged negative ion density $n_-$ can be obtained by multiplying $\Delta n_e^{phot}$ by the ratio of the cavity to the laser beam volume, weighted with $E^2$ of the specific microwave mode used:

$$ n_- = \Delta n_e^{phot} \frac{\int \text{cavity} E^2(\vec{x}) d\vec{x}}{S \int_{-R}^{R} E^2(r) dr}, \quad (5) $$

where $R$ is the radius of the cavity ($2R$ is the path taken by the laser beam through the cavity) and $S$ is the geometric cross section of the laser beam. Since the cavity is cylindrical, the electric field of the TM010 mode has only an axial field component given by the Bessel function $J_0(r)$, with only a radial dependence. Furthermore, the integrals in equation (5) have been calculated using the electric fields (see figure 1) associated with the geometrical configuration of the cavity used in the experiments.

In the case in which the saturation regime is not achieved, meaning that the laser beam is only capable of partial conversion of the negative ions into neutral–electron pairs along its path, the photodetached electron density scales exponentially with the laser pulse energy. In this case, the fraction between the photodetached electron density using a specific laser pulse
energy ($\Delta n_e$) and the photodetached electron density in the saturation regime ($\Delta n_{e,\text{sat}}$) is given by:

$$\alpha = \frac{\Delta n_e}{\Delta n_{e,\text{sat}}} = 1 - \exp\left(\frac{-\sigma_{\text{det}} E_{\text{laser}}}{h \nu S}\right)$$

(6)

where $\sigma_{\text{det}}$, $h \nu$, and $E_{\text{laser}}$ denote the photodetachment cross section of a specific anion, the energy of the photons used for irradiation, and the laser pulse energy, respectively.

2.3. Experimental setup

Figure 3 includes a schematic representation of the experimental setup. The experiments were conducted in a cylindrical vacuum vessel, which was 30 cm in diameter and 45 cm in height. It contained two pairs of concentric quartz windows, of which one pair allowed the illumination by laser light, while the other pair enabled the acquisition of plasma radiation. The vessel lid contained a gas inlet connected to a shower-head shaped electrode, ensuring a homogeneous gas flow into the experimental volume. This shower-head electrode was electrically insulated from the rest of the vessel lid by a Teflon ring and was powered with a radiofrequency (RF) voltage signal [25]. The discharge was operated below the powered electrode, while the rest of the cavity electrically served as ground. Therefore, the plasma was operated in an asymmetric capacitively coupled mode.

A grounded aluminum hollow cylindrical resonant pillbox cavity with an internal diameter of 170 mm and an internal height of 67 mm was mounted below the shower-head electrode in an electrically insulated manner. The bottom of this cavity contained 105 holes (0.5 millimeters in diameter) evenly distributed over the full surface to allow the injected gas to leave the cavity without friction and hence to ensure a stable gas pressure inside the measurement volume. The reason for the usage of the cavity was twofold. First, it served to confine the generated plasma inside a well-defined volume below the RF-powered shower-head top electrode (the cavity and confined plasma are illustrated in figure 3). This confined volume appears to be important for the calculation of the absolute anion density values from the experimental data. Second, this cavity was used as a microwave resonant cavity to temporally resolve the plasma electron density and negative ion densities. The plasma had a typical Debye length of $\lambda_D \approx 1$ mm (assuming $T_e = 2.5$ eV and an electron density of a few times $10^{14}$ m$^{-3}$) and the typical sheath thickness was known to be $s \approx 5 - 10 \lambda_D$. Therefore, the holes in the shower head and the bottom plate, which were designed to be as small as possible, did not have any major effect on plasma properties.

A single metal antenna that simultaneously served as both transmitter and receiver for low-power microwave (0.3-8 GHz) signals, was a straight fixed piece of copper wire. This transmitter–receiver antenna was connected to the data-acquisition system, as discussed in the next section. Two 12 cm-diameter circular holes, aligned opposite to each other in the cavity’s circumferential wall and perpendicular to the antenna’s plane, enabled the laser beam to pass through the cavity without hitting the wall and generating secondary
electrons. The diameters of these holes were smaller than wavelength of the excited microwaves, preventing significant leakage of microwaves from the cavity volume.

The injected gas left the vacuum vessel at the bottom and was then pumped out by, respectively, a turbo-molecular pump and a rotary roughing pump. The base pressure inside the vessel was \(3 \times 10^{-4}\) Pa. During the experiments, the pressure inside the vacuum vessel and thus inside the measurement volume was controlled within the pressure range of 2–30 Pa by a butterfly valve (VAT 61.332-KAAH) operated in a vacuum line—bypassing the turbo-molecular pump—between the vacuum vessel and the rotary roughing pump.

An RF generator (Barthel RFG-13-100-L) synchronized with an automatic match box (Barthel MCI-300) delivered a pulsed 13.56 MHz RF signal with a power of 15 W during the plasma-on phase, with self-bias voltages ranging from 72 to 51 V, depending on the operating pressure. A digital delay generator (Stanford Research Systems DG645) was used for temporal modulation of the input RF signals as well as for the synchronization and triggering of the data-acquisition hardware and the LIP laser system.

The LIP experiments were performed using a pulsed Nd:YAG laser (Ekspla SL235) operated either in its fundamental mode at 1064 nm or in its second harmonic at 532 nm. The laser-generated short (150 ps) pulses had an energy of 490 mJ for 1064 nm and 291 mJ for the 532 nm mode at a 5 Hz repetition rate. The laser beam profile was top hat with a diameter of 11.5 mm. Two triggering signals were fed to the laser, one marking the pumping and Q-switch and the other marking the onset of the laser beam, which was used as a reference signal for the synchronization of the other equipment.

While subsequent measurements were performed using the gas pressure as a variable, all other plasma and process parameters were kept constant. The pulse frequency of the plasma was set to 5 Hz, corresponding to the repetition rate of the laser system used, with a duty cycle of 50%. For all experiments, the plasma input power was set to 15 W, and the oxygen input flow was kept constant at 4 SCCM.

2.4. Data-acquisition hardware

The data-acquisition hardware used has been already extensively elaborated in the previous articles published by our group [25, 34]. However, a brief description including recent upgrades will be provided below. A microwave generator (Stanford Research Systems SG386) produced a sinusoidal microwave signal at a power of 16 dBm and an externally set frequency. This output was connected to the input port of a directional coupler (Mini-Circuits ZHDC-10-63-S+) and passed unhindered to its output port, which was connected to the antenna inside the cavity. Therefore, by applying the correct frequency from the microwave generator, resonant modes could be excited in the cavity. If the cavity was not resonating, the power coupling to it was very inefficient, and most of the power reaching the antenna was reflected back to the microwave generator, where it dissipated. If the cavity was resonating, hardly any signal was reflected back, since most of the energy was dissipated by building up the resonant electromagnetic field inside the cavity. This translated into a sharp minimum in the reflected power spectrum at—and very near—the resonance frequency of the excited mode. Note that the total microwave power used (several mW) is negligible with respect to the RF power (\(\sim 15\) W) used to drive the plasma.

In our setup, however, part of the reflected signal (\(\sim 10\%)\) was rerouted by the directional coupler to the measurement leg of the detection system, where it was first converted to a DC signal by a logarithmic power detector (Hittite 602LP4E with 10 ns rise and fall times) and subsequently fed to a high-frequency (up to 250 MHz) transient recorder (Spectrum M4i.4420-x8) inside the measurement PC. The transient recorder continuously sampled its input port and stored the data in its internal memory. Only upon an external trigger, for which the trigger signal was provided by the delay generator used, were the data made available to the user for subsequent analysis. This arrangement offered the possibility of obtaining the MCRS response even before the actual trigger had occurred.

The laser, transient recorder, and RF generation were accurately synchronized by a delay generator. Three pulses with adjustable delay between each pulse were fed to the instruments. At a time \(t_A\), the RF generator was triggered for the plasma to be switched off. The transient recorder was triggered at \(t_B\) to record the cavity’s response during the afterglow and temporally around the photodetachment incident. \(t_B\) indicates the total amount of time during which the MCRS signal was recorded. The laser was set to illuminate the plasma at \(t_c\) with a delay of \(\Delta t\) relative to the beginning of the afterglow (i.e. compared to the moment at which the plasma was switched off). With this delay pattern, as illustrated in figure 4, an arbitrary time interval during the afterglow of the plasma could be investigated.

During the measurements presented in this study, the microwave source was set to a certain frequency and kept at this frequency for the entire duration of a given set of plasma ignitions and LIP pulses, while the cavity’s response was recorded temporally resolved before and after the laser was shot through the cavity. For each set value of the microwave frequency, the delay pattern was repeated (typically 30 times) for the purpose of averaging in order to enhance the signal-to-noise ratio. Just before the pulsed plasma in the cavity was exposed to the next train of LIP pulses, the microwave source was set to the next frequency value. To obtain sufficient accuracy, a resonant peak was probed by 65 measurement frequency steps of 100 kHz, located in the frequency domain close to the resonant frequency.

It is notable that in order to retrieve accurate results, the pulsed plasma needs to be highly reproducible. This has been verified extensively for all measurement settings presented in this study.

2.5. Data processing

In order to calculate the resonance frequency temporally-resolved, the cavity response was recorded as raw data in specific time steps determining the duration of the measurements and
processed accordingly. The cavity response (in mW) was stored as a function of time and microwave frequency for each sequence of measurements. The exact resonance frequency was obtained by a Fourier fit of the peak in the frequency domain for each time step. At an arbitrary time, the fitting function can be formulated as:

\[ V_{\text{fit}}(f) = a_0 + \sum_{n=1}^{4} [a_n \cos(nwf) + b_n \sin(nwf)], \]  

where \( a_0, a_n, b_n \) and \( w \) are fitting parameters. To improve the accuracy of the determined resonance frequency and to account for possible peak asymmetries, four harmonics of the Fourier series were used. As illustrated in figure 2(a), the frequency at which the fit was minimized indicated the resonance frequency (\( f = 1.3733 \) GHz). Since electron density measurements require only the resonance frequency from the raw data, a Fourier fit function was deemed suitable for the measurements presented in this contribution. However, a more sophisticated Lorentzian fit capable of delivering the temporally resolved quality factor \( Q \) (as well as the resonance frequency) could have been used \([40]\), had the measurements been performed in a collisional plasma regime.

3. Results and discussion

In order to get the maximum insight into the behavior of anions in the afterglow of the investigated low-pressure oxygen pulsed RF discharge, the following experiments were conducted. In the first set of experiments, presented in section 3.1, the electron density was measured with high temporal resolution during the full afterglow phase and at two different gas pressures, i.e. at 3 Pa and at 6 Pa, chosen such that the difference between the low electronegative mode and the high electronegative mode is clearly demonstrated experimentally. In the second set of experiments, presented in section 3.2, the overall photodetachment signals (at 532 nm) are measured during steady-state operation, during the afterglow phase of the same discharge at 6 Pa, and at an elevated pressure of 25 Pa. In the third set of experiments, presented in section 3.3, the densities of distinct anion species during the afterglow phase are portrayed. In this section, these measurements are subsequently linked to the presented electron density measurements in section 3.1.

While the subsequent measurements were performed with the gas pressure as a variable, all other plasma and process parameters were kept constant. The pulse frequency of the plasma was set to 5 Hz, corresponding to the repetition rate of the laser pulses, with a duty cycle of 50%. The plasma input power was set to 15 W for all experiments, and the oxygen input flow was kept constant at 4 SCCM.

3.1. Electron density measurements

First, the temporal behavior of the electron density during the afterglow phase at pressures of 3 Pa (blue curve) and 6 Pa (red curve). Figure 5 (blue curve) shows the afterglow decay at a pressure of 3 Pa. In this situation, the decay of the electron density begins at the moment that the RF pulse falls (\( t = t_{\text{off}} \)) and is dominated by plasma diffusion to, and recombination at, the plasma-containment walls, i.e. the resonant cavity walls. At these low pressures, the influence of volume recombination is negligible. Clearly, at a pressure of 3 Pa, the afterglow is comprised of a single stage, during which the electron density decays rapidly. Negative ion densities decrease relatively slower, as will be observed from experiments presented later in this paper (figures 10 and 12). However, as illustrated in figure 5 (red curve), the afterglow at a slightly increased pressure of 6 Pa (and higher) behaves significantly differently, featuring a rampant release of electrons. Initially, right after switching off the plasma,
the electron density shows a minor and brief drop, which is normally due to a decrease in the electron temperature with, as a main result, the termination of ionization events. Afterwards, a rapid release of electrons in the cavity volume causes the electron density to even exceed its value during steady-state plasma operation ($t < t_{\text{off}}$) for a short period of time. Finally, an exponential decay similar to the former case—but much slower—is observed.

The appearance of this temporal increase of the electron density in the afterglow phase is attributed to the detachment of—mainly—negative atomic oxygen ions, $O^-$. As the models by Brockhaus et al. [41] and Küllig et al. [30] suggest, the most important production channel for electrons in this phase is the detachment of electrons from negative ions by collisions with atomic oxygen O, with ground-state molecular oxygen $O_2(X^3 \Sigma^+_g)$, or with metastable oxygen molecules $O_2(a^1 \Delta_g)$.

Under steady-state plasma operation, there is a balance between the production and the loss channels of electrons. In addition to the traditional loss channels, such as those at the plasma-confining walls, electron losses are mainly due to the formation of negative ions through dissociative electron attachment, while, apart from ionization events, electron production mainly occurs via associative electron detachment of negative ions. As will be observed later in this paper, the negative ion densities begin to fall simultaneously with the start of electron detachment (figures 11 and 13).

Upon switching off the plasma, in the case of the measurements in figure 5 (red curve), this balance is changed in favor of electron production, since a lower temperature of the electrons leads to suppression of the electron loss reactions (electron attachments forming negative ions) while maintaining their production through detachment processes. This consequently culminates in a net electron release at the beginning of the afterglow phase.

Upon switching off the plasma, dependent on the pressure, two distinct situations can be observed, as is obvious from figure 5.

At relatively low pressures, i.e. at 3 Pa in the case of the measurement in figure 5 (blue curve), the electron loss mechanisms (i.e. electron attachment forming negative ions in combination with traditional diffusive plasma decay) in the plasma afterglow dominate over the electron production mechanism (i.e. electron detachment from negative ions). This situation is represented in figure 5 by a distinct phase of electron depletion during the full afterglow phase. This ‘mode’ is often called the low electronegative mode or the $\gamma$-mode.

At slightly higher pressures, i.e. at 6 Pa in the case of the measurement in figure 5, in the first part of the afterglow phase, the electron production mechanism (i.e. electron detachment from negative ions) dominates over the electron loss mechanisms (i.e. electron attachment forming negative ions in combination with traditional diffusive plasma decay). This situation is represented in figure 5 (red curve)—after an initial brief and minor decrease in the electron density—by a period of electron density increase, after which, the electron density eventually depletes. This ‘mode’ is often called the high electronegative mode or the $\alpha$-mode.

Under these plasma and process conditions, the transition from the $\gamma$-mode to the $\alpha$-mode was found to occur at a gas pressure of 4 Pa in the direction of increasing pressure. As a result, we report the experimental verification of this transition, which was already previously predicted by numerical simulations [32, 33]. An investigation of the role of the sheath parameters or the positive and negative ion Bohm velocities in the decay of the electron density would require extensive modeling to retrieve accurate results. Therefore, these effects have been omitted in this analysis, since this paper is mainly focused on the experimental measurement of the densities of electrons and negative ions.

### 3.2. Photodetachment signals from a steady-state plasma and its afterglow

In this section, we present ‘bare’ MCRS measurements displaying the effect of LIP on the overall electron density and the resulting response of the plasma. Section 3.2.1 reports on the results for steady-state plasma operating conditions, while section 3.2.2 reports on similar results for the plasma afterglow phase. All experiments have been performed under the same plasma and process conditions as mentioned in the previous sections with—again—the value of the gas pressure as a variable.

#### 3.2.1. Photodetachment signal during steady-state plasma operation

The LIP incident and the associated subsequent plasma response during steady-state plasma operation was monitored using MCRS. The electron densities before, during, and after the laser was shot through the cavity are displayed in figure 6 for two different values (6 Pa and 25 Pa) of the gas pressure.

In these graphs, several distinct stages can be identified. For both pressures, the first stage represents a steep increase in the electron density corresponding to the (almost) instantaneous photodetachment of electrons from the negative oxygen ions. Since the photon energy corresponding to the laser wavelength used, 532 nm, exceeds the threshold energy required for the photodetachment of $O^-$, $O_2^-$ and $O_3^-$ ions, photodetachment of all three ions contributes to the measured value of the additional electron density $\Delta n_e$, which is determined via equation (2).

Following the sudden rise in electron density, there is a subsequent decay of $\Delta n_e$, which eventually reaches the same electron density value as just before the LIP incident took place. This decay, for the case of the relatively low pressure of 6 Pa, appears to occur within the two distinct decay timescales ($\tau_1$ and $\tau_2$)(see figure 6(a)). The first timescale, $\tau_1$, can be attributed to the swift diffusion of the photodetached electrons to the adjacent electronegative plasma as a reaction to the sudden local increase in electron density in the volume irradiated by the laser. In other words, the photodetached electrons are redistributed over the cavity volume. From a macroscopic point of view, the photodetached electrons redistribute to regions where they are probed to a lesser extent by MCRS, since the
Figure 6. Photodetachment signals: responses of steady-state plasmas operating at (a) 6 Pa and (b) 25 Pa to an LIP incident. Each signal is comprised of several distinct stages.

Electric fields of the resonant TM\(_{010}\) mode are lower in the outer regions of the cavity. Hence, this leads to a net decrease in the detected signal. The second timescale, \(\tau_2\), can be attributed to the (re)formation of negative ions in the laser-irradiated volume. Steady-state plasma conditions demand a certain level of negative ion density, which is disturbed by the LIP incident. Recovering this balance by (re)attachment consumes electrons. After both timescales (\(\tau_1\) and \(\tau_2\)), the plasma is restored to its original steady-state. Different threshold energies for the photodetachment of O\(^-\), O\(^{-2}\), and O\(^{-3}\) ions lead to different temperatures of the photodetached electrons gained from the same photon energy. However, this temperature difference could not cause the two observed distinct decay times, \(\tau_1\) and \(\tau_2\), since the photodetachment signal obtained at a 1064 nm laser wavelength (i.e. only exceeding the threshold energy of O\(^{-2}\)) contains the same two distinct decay times.

For the case of a higher gas pressure, i.e. 25 Pa (see figure 6(b)), the second timescale, \(\tau_2\), in particular, becomes shorter and is—at most—comparable to \(\tau_1\). The decrease of \(\tau_2\) can be explained by the increased reaction rate \(k_{\text{att}}\) for electron attachment, which scales linearly with the background gas density \(n_{\text{neutral}}\) (and thus—at constant temperature—also with the background gas pressure):

\[
k_{\text{att}} = \sigma_{\text{att}} n_e n_{\text{neutral}}.
\]

Here, \(\sigma_{\text{att}}\) is the electron attachment cross section. Hence, at elevated pressures, the plasma restores quicker to its initial steady state, as can be concluded when comparing figures 6(a) and (b). The densities of neutral O\(_2\) are reported to be \(10^{20}\, (\text{m}^{-3})\) and \(6 \times 10^{20}\, (\text{m}^{-3})\) in 6 Pa and 25 Pa gas pressure, respectively [1]. Assuming that dissociative attachment reactions to O\(_2\) are dominant, this would lead to a six-times-higher electron attachment rate in a 25 Pa plasma operation (compared to the situation at 6 Pa), therefore resulting in a decrease in the second timescale \(\tau_2\).

Additionally, for the case of 25 Pa, a slight undershoot of the electron density is observed before it finally reaches its initial steady-state value before the LIP event. This undershoot can most likely be ascribed to a local disturbance of the plasma’s quasi-neutrality due to the initiation of a potential barrier in the laser irradiated volume [42, 43].

The photodetachment signal obtained using a laser wavelength of 1064 nm (i.e. where only O\(^{-2}\) contributes to the additional electron density \(\Delta n_e\)), verifiably agrees with the measurements illustrated in figure 6. A decay of the photodetached electrons also occurs on two distinct decay timescales for the case of the relatively low pressure of 6 Pa, as well as for the shorter decay time of the photodetached electrons associated with the case of a higher gas pressure of 25 Pa.

3.2.2. Photodetachment signal during the plasma afterglow. While the measurements presented in the previous section were performed under steady-state plasma conditions, the upcoming measurements in this subsection are conducted during the afterglow phase of the same plasma. As illustrated in figure 7, in this case, the laser pulse is triggered to irradiate the afterglow at specific moments. This enables the detection of negative ions throughout the decaying afterglow phase. In figure 7, these LIP events are shown as electron density peaks. For reference, \(t = t_{\text{off}}\) indicates the moment at which the RF power was switched off, marking the beginning of the afterglow phase.

A gradual decrease of the photodetached electron density as a function of time throughout the afterglow phase was already apparent, implying the afterglow behavior of the negative ions. Remarkably, however, photodetached electrons ( \(1–5 \times 10^{13}\, (\text{m}^{-3})\) are detected, even though the electron density (plotted for reference in the same graph) has already been depleted for a considerable amount of time. This indicates the much longer decay constants associated with negative ions than those associated with electrons.
In the previous sections, we measured the electron density using MCRS and the change thereof upon LIP events. This section presents a structured set of measurements in which the absolute values of negative ions are probed during the afterglow of the oxygen plasma under investigation. The application of two wavelengths of laser irradiation—i.e. 532 nm and 1064 nm—enables us to distinguish the individual contributions of O$_2^-$ to the total negative ion density. It should be recalled (see section 2.2) that O$^-$ is expected to be the dominant ion, while the contribution of O$_3^-$ to the total negative ion density is less than 1%.

In the presented measurements, 532 nm laser light is first applied in order to convert all the negative ions residing in the laser beam volume. Initially, we examined whether the saturation regime—meaning conversion of all the negative ions in the laser beam volume—is achieved. For this purpose, $\alpha$—i.e. the fraction between the photodetached electron density ($\Delta n_e$) at each laser pulse energy and the photodetached electron density in the saturation regime ($\Delta n_{e,sat}$)—is determined using equation (6). Figure 8 illustrates the calculated and measured values of $\alpha$ as a function of laser pulse energy, for a laser operating at a 532 nm wavelength. As can be seen from figure 8, saturation can nearly be reached when the laser pulse is set to $E_{laser} = 291$ mJ, meaning that, in this case, nearly all ($\alpha = 0.99$) of the negative ions within the laser beam are converted into pairs of neutrals and free electrons. The determined values, as observed in figure 8, follow an exponential trend toward saturation, regardless of the fact that only the O$^-$ cross section is used for the calculation (blue line), confirming that the majority of the negative ions consists of O$^-$ ions. Therefore, in this case, to derive the absolute values of the negative ion density, one primarily has to correct for the ratio between the cavity volume and the laser beam volume, weighted by the electric field of the microwave mode used (see equation (5)).

The individual contribution of O$_2^-$ ions to the total negative ion density is determined when 1064 nm laser light is applied. In this case, the maximum laser pulse energy that the laser yields is 490 mJ, which is not capable of saturating the photodetachment signal. This incapability is due to the tiny photodetachment cross section of O$_2^-$ at 1064 nm. According to equation (6)—filling in the photodetachment cross section and the electron binding energy of O$_2^-$—the fraction $\alpha$ for the maximum laser pulse energy is $\alpha = 0.72$. Figure 9 shows the measured values of $\alpha$ as a function of the laser pulse energy when the laser operates at 1064 nm. In conclusion, applying 490 mJ of laser pulse energy at 1064 nm enabled the photodetachment of 72% of the total O$_2^-$ in the laser beam volume. Therefore, the measured photodetachment signal is corrected with $\alpha$ as well as the correction for the laser beam volume.

The error associated with the measurements of the negative ion densities stems from both the instability of the laser pulse energy through successive irradiations of the plasma and the error in the determination of the electron density using MCRS. In order to enhance the accuracy of the negative ion density measurements, the laser pulse energy is first stabilized during the time required for each set of LIP measurements. The laser pulse energies used for each LIP trial are accurate within a standard deviation of $\sigma_{SD} < 1.5\%$. A technique of averaging through successive MCRS measurements and strict control of the plasma parameters (e.g. the gas pressure) is used to obtain accurate electron density values. With this technique, the lower detection limit for the electron density is $10^{10}$ m$^{-3}$. This accuracy in the electron density measurement translates to an accuracy of $10^{12}$ m$^{-3}$ in negative ion density determination.

### 3.3.1. O$^-$ plus O$_3^-$ negative ion density

The absolute values of the total negative ion density excluding O$_2^-$—i.e. O$^-$ plus O$_3^-$—are measured and temporally resolved during the
afterglow phase of the oxygen plasma. To allow a comparison of the afterglow behaviors of the two previously elaborated modes of plasma operation, the electron and negative-ion densities are illustrated in figures 10 (γ-mode) and 11 (α-mode). A one-term exponential decay fit (shown in the figures with a red line) assists in calculating the time (τ) required for the negative ion density to reach 1/2 of its initial value—i.e. the decay time—besides illustrating its decay behavior.

Figure 10 shows the obtained negative ion (O− plus O−3) and electron densities during the afterglow phase at a pressure of 3 Pa, and therefore represents operation in the γ-mode. In this case, the electron density decays to zero within approximately 75 µs, as already discussed in section 3.1. The negative ion densities are initially measured with 10 µs time steps, which are gradually prolonged to 500 µs. This provides sufficient time resolution, since during the first 200 µs of the afterglow phase, the negative ion density decreases rapidly, followed by a decrease at a slower rate. The enhanced detection accuracy enables negative-ion density measurements over extended timescales in the afterglow. At the moment of the first LIP incident, the negative ion (O− plus O−3) density is measured to be \( n_\text{−} = 6.05 \times 10^{15} \text{ m}^{-3} \). Eventually, it falls by three orders of magnitude to \( n_\text{−} = 2.36 \times 10^{12} \text{ m}^{-3} \) after 5.5 ms. According to the exponential fit, the negative ion density decay time is calculated to be \( \tau \approx 504 \text{ µs} \), a value remarkably longer than electron density decay time.

The same set of measurements is performed at a pressure of 6 Pa (figure 11), i.e. operation in the α-mode. In this case, the electron density behaves differently during the afterglow, featuring a rampant release of electrons (as already discussed and explained in section 3.1). The overall decay time associated with electrons in this mode (about 1.65 ms) is much longer, due to the net release of electrons at the beginning of the afterglow phase. Nevertheless, the decay behavior of the (O− plus O−3) negative ion density, is almost identical to that of the γ-mode situation, except for a slightly shorter decay time of \( \tau \approx 480 \text{ µs} \) compared to the previous case.

During the plasma-on phase, an oxygen plasma (due to its electronegativity) is stratified into a core, where almost all negative ions are trapped, surrounded by an electropositive region consisting of positive ions and electrons [44–46]. During the afterglow phase, however, two distinct scenarios may occur, based on the operating mode of the plasma:

- In the γ-mode, while the electron density decays almost instantly after the RF power is cut, negative ions reside in the former discharge region for a much longer period of time. Initially, the electrons at the edge of the plasma diffuse...
rapidly toward the plasma containment walls, due to their higher mobility. With the electron density having decayed entirely after the first 75 \( \mu s \) of the afterglow phase, the plasma is depleted of electrons. The paucity of free electrons and the residence of negative ions in the later afterglow means that a transition to a negative-ion-positive-ion plasma has occurred. Moreover, the sheath voltage as well as the ambipolar electrostatic fields collapse, due to the loss of electrons, trapping negative ions in the core of the cavity [47]. This behavior has only been numerically predicted in the models laid out by Kaganovich et al [32, 33]. In the case of a negative-ion-positive-ion plasma, according to the models, the negative-ion flux to the plasma containment walls increases phenomenally, consequently raising the possibility of negative ion extraction in the afterglow.

- However, in the latter case of the \( \alpha \)-mode, electrons reside in the afterglow phase for an extended period of time as well. As a result, the occurrence of a negative-ion-positive-ion plasma is prevented by the release of secondary electrons. In addition, the temporal increase of the electron density causes the electrostatic fields to build up in the core as well as in the electropositive edge of the plasma, as a result, negative ions stay trapped due to the extended presence of electrons. This phenomenon leads to the obstruction of negative ion fluxes toward the plasma containment walls. This behavior is known as negative-ion self-trapping in the afterglow [32].

3.3.2. \( \text{O}_2^- \) negative ion density. The absolute values of the \( \text{O}_2^- \) negative ion density are subsequently measured. The \( \text{O}_2^- \) densities are measured to be an order of magnitude smaller \( \left(10^{14} \text{ m}^{-3}\right) \) than the total negative ion density of \( \text{O}^- \) plus \( \text{O}_3^- \), underling the fact that \( \text{O}_2^- \) ions constitute about 10\% of the total negative ions in the plasma, as was explained earlier. The \( \text{O}_2^- \) density is measured for both the \( \gamma \)-mode at 3 Pa (figure 12) and the \( \alpha \)-mode at 6 Pa (figure 13) accordingly. It is notable that due to both the much smaller photodetachment cross section of \( \text{O}_2^- \) at 1064 nm and the relatively lower concentrations, the \( \text{O}_2^- \) density falls below the detection limit \( \left(10^{12} \text{ m}^{-3}\right) \) at shorter timescales than the densities in the previous section do. As a result, the \( \text{O}_2^- \) density can only be tracked for 3 ms into the afterglow phase.

First, the \( \text{O}_2^- \) density is measured and time-resolved with 100 \( \mu \)s time steps in the \( \gamma \)-mode of the afterglow phase (see figure 12). Just as in the previous case with \( \text{O}^- \) and \( \text{O}_3^- \), the decay time associated with the negative ions is longer than that associated with the electrons, and the observed electron density decay behavior is similar to previous cases. The decay time of the \( \text{O}_2^- \) density is calculated to be \( \tau = 756 \mu \text{s} \) according to the exponential fit in the same figure 12. Moreover, the longer decay time associated with \( \text{O}_2^- \) (figure 12) when compared to that of \( \text{O}^- \) plus \( \text{O}_3^- \) (figure 10) illustratively indicates that \( \text{O}^- \) constitutes the majority of the negative ions in the plasma.

Subsequently, the same set of measurements is repeated at an elevated pressure of 6 Pa—i.e. in the \( \alpha \)-mode (see figure 13). Here, the \( \text{O}_2^- \) negative ion density decay occurs on a timescale comparable to the decay timescale for the electron density. The decay time for the \( \text{O}_2^- \) density \( \tau = 376 \mu \text{s} \) is calculated according to the exponential fit in the same figure 13.

4. Conclusions

The afterglow phase of a capacitively coupled pulsed RF oxygen plasma is investigated using MCRS and LIP. While electrons decay on significantly different timescales, depending on the gas pressure, the decay timescales associated with oxygen anions are similar. At a pressure of 3 Pa, namely in \( \gamma \)-mode operation, electrons decay rapidly the moment the RF pulse falls. In this case, the decay is dominated by plasma diffusion to, and recombination at, the plasma containment walls. At a slightly elevated pressure of 6 Pa (and higher), the electron density decay...
features a rampant release of electrons caused by the detachment of electrons, mainly from $O^-$. 

The photodetachment signal—i.e. the total number of electrons photodetached from their parent negative ions—is shown to be comprised of different stages, depending on the gas pressure.

The decay of the oxygen negative-ion densities in the two cases of (1) $O^- + O_2^-$ and (2) $O_2^-$, behave similarly during the afterglow phase in both the $\gamma$-mode and the $\alpha$-mode. Negative ions decay, however, on timescales significantly longer than those associated with electrons when operating in the $\gamma$-mode. A transition to a negative-ion-positive-ion plasma occurs in this case upon the total decay of electrons. In $\alpha$-mode operation, the overall decay of the electrons is extended. This leads to an obstruction of negative ion fluxes toward the plasma containment walls, characterized as negative-ion self-trapping in the afterglow.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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References

[1] Stoffels E, Stoffels W W, Venderlag M, Kroesen G M W and de Hoog F J 1995 Negative ions in low pressure discharges Contrib. Plasma Phys. 35 331–57
[2] Franklin R N 2002 Electronegative plasmas why are they so different? Plasma Sources Sci. Technol. 11 A31–7
[3] Agarwal A, Rauf S and Collins K 2012 Extraction of negative ions from pulsed electronegative capacitively coupled plasmas J. Appl. Phys. 112 033303
[4] Tsutsumi T, Greb A, Gibson A R, Hori M, O’Connell D and Gans T 2017 Investigation of the radially resolved oxygen dissociation degree and local mean electron energy in oxygen plasmas in contact with different surface materials J. Appl. Phys. 121 143301
[5] Taylor S, Zhang J F and Eccleston W 1993 A review of the plasma oxidation of silicon and its applications Semicond. Sci. Technol. 8 1426–33
[6] Oehrlein G S, Scilla G J and Jeng S-J 1988 Efficiency of oxygen plasma cleaning of reactive ion damaged silicon surfaces Appl. Phys. Lett. 52 907–9
[7] Collart E, Baggerman J and Visser R 1995 On the role of atomic oxygen in the etching of organic polymers in a radio-frequency oxygen discharge J. Appl. Phys. 78 47–54
[8] Kim J K, Cho S I, Kim N G, Jhon M S, Min K S, Kim C K and Yeom G Y 2013 Study on the etching characteristics of amorphous carbon layer in oxygen plasma with carbonyl sulfide J. Vac. Sci. Technol. A 31 021301
[9] Hefny M M, Necas D, Zajicikova L and Benedikt J 2019 The transport and surface reactivity of $\alpha$ atoms during the atmospheric plasma etching of hydrogenated amorphous carbon films Plasma Sources Sci. Technol. 28 035010
[10] Vesel A, Princ G, Zaplotnik R and Mozetic M 2020 Applications of highly non-equilibrium low-pressure oxygen plasma for treatment of polymers and polymer composites on an industrial scale Plasma Phys. Control. Fusion 62 024008
[11] Stoffels E, Stoffels W W and Kroesen G M W 2001 Plasma chemistry and surface processes of negative ions Plasma Sources Sci. Technol. 10 311–18
[12] Stoffels E, Stoffels W, Kroustilina V, Wagner H-E and Meichsner J 2001 Near-surface generation of negative ions in low-pressure discharges J. Vac. Sci. Technol. A 19 2109–15
[13] Schepers L, Beckers J and IJzerman W 2018 Determination of microparticle characteristics in an etching plasma Contrib. Plasma Phys. 58 985–94
[14] Denyenko I B, Ostrikov K, Xu S, Yu M Y and Diogn C H 2003 Nanopowder management and control of plasma parameters in electronegative $\text{SiH}_x$ plasmas J. Appl. Phys. 94 6097–107
[15] Economou D J 2014 Pulsed plasma etching for semiconductor manufacturing J. Phys. D: Appl. Phys. 47 303001
[16] Tsumori K and Wada M 2017 Diagnostics tools and methods for negative ion source plasmas, a review New J. Phys. 19 045002
[17] Bredin J, Chabert P and Aanesland A 2014 Langmuir probe analysis in electronegative plasmas Phys. Plasmas 21 123502
[18] Dubois J P J, Achkasov K, Kogut D, Ahmad A, Layet J M, Simonin A and Carthy G 2016 Negative-ion surface production in hydrogen plasmas: determination of the negative-ion energy and angle distribution function using mass spectrometry J. Appl. Phys. 119 193301
[19] Bacal M 2000 Photodetachment diagnostic techniques for measuring negative ion densities and temperatures in plasmas Rev. Sci. Instrum. 71 3981–4006
[20] Dodd R, You S, Bryant P M and Bradley J W 2009 Negative ion density measurements in reactive magnetron sputtering Plasma Process. Polym. 6 5615–19
[21] Oudini N, Sirse N, Taccogna F, Ellingboe A R and Bendib A 2016 Photo-detachment signal analysis to accurately determine electronegativity, electron temperature and charged species density Appl. Phys. Lett. 109 124101
[22] Conway J, Sirse N, Karkari S K and Turner M M 2010 Using the resonance hairpin probe and pulsed photodetachment technique as a diagnostic for negative ions in oxygen plasma Plasma Sources Sci. Technol. 19 065002
[23] Küllig C, Dittmann K and Meichsner J 2010 A novel approach for negative ion analysis using 160 GHz microwave interferometry and laser photodetachment in oxygen cc-rf plasmas Plasma Sources Sci. Technol. 19 065011
[24] Vender D, Stoffels W W, Stoffels E, Kroesen G M W and de Hoog F J 1995a Charged-species profiles in electronegative radio-frequency plasmas Phys. Rev. E 51 2436–44
[25] van de Wetering F M J H, Beckers J and Kroesen G M W 2012 Anion dynamics in the first 10 milliseconds of an argon-acetylene radio-frequency plasma J. Phys. D: Appl. Phys. 45 485207
[26] Patty C, Kovacevic E, Strunskus T, Lecas T and Berndt J 2019 Formation and behavior of negative ions in low pressure aniline-containing RF plasmas Sci. Rep. 9 1–9
[27] Kono A, Haverlag M, Kroesen G M W and de Hoog F J 1991 Temporal behavior of the electron and negative ion densities in a pulsed radio-frequency CF4 plasma J. Appl. Phys. 70 2939–46

[28] Meichsner J, Dittmann K and Källig C 2012 Electron and negative ion analysis in oxygen capacitively coupled radio frequency plasma Contrib. Plasma Phys. 52 561–70

[29] Osiac M, Schwarz-Selinger T, Connell D O, Heil B, Petrovic Z L, Turner M M, Gans T and Czarnetzki U 2007 Plasma boundary sheath in the afterglow of a pulsed inductively coupled RF plasma Plasma Sources Sci. Technol. 16 355–63

[30] Källig C, Dittmann K and Meichsner J 2012 Detachment-induced electron production in the early afterglow of pulsed cc-rf oxygen plasmas Phys. Plasmas 19 073517

[31] Wegner T, Källig C and Meichsner J 2017 On the EH transition in inductively coupled radio frequency oxygen plasmas: II. Electronegativity and the impact on particle kinetics Plasma Sources Sci. Technol. 26 025007

[32] Kaganovich I, Ramamurthi B N and Economou D J 2000 Self-trapping of negative ions due to electron detachment in the afterglow of electronegative gas plasmas Appl. Phys. Lett. 76 2844–6

[33] Kaganovich I, Ramamurthi B and Economou D J 2001 Spatiotemporal dynamics of charged species in the afterglow of plasmas containing negative ions Phys. Rev. E 64 036402

[34] Beckers J, van de Wetering F M J H, Platier B, van Ninhuijs M A W, Brussaard G J H, Banine V Y and Luiten O J 2018 Mapping electron dynamics in highly transientEUV photon-induced plasmas: a novel diagnostic approach using multi-mode microwave cavity resonance spectroscopy J. Phys. D: Appl. Phys. 52 034004

[35] Beckers J, Stoffels W W and Kroesen G M W 2009 Temperature dependence of nucleation and growth of nanoparticles in low pressure Ar/CH4 RF discharges J. Phys. D: Appl. Phys. 42 155206

[36] Neumark D M, Lykke K R, Andersen T and Lineberger W C 1985 Laser photodetachment measurement of the electron affinity of atomic oxygen Phys. Rev. A 32 1890–2

[37] Arnold D W, Xu C, Kim E H and Neumark D M 1994 Study of low-lying electronic states of ozone by anion photoelectron spectroscopy of O3− J. Chem. Phys. 101 912–22

[38] Ervin K M, Anusiewicz I, Skurski P, Simons J and Lineberger W C 2003 The only stable state of O3− is the \( \Omega \) \( \pi \_\text{g} \) ground state and it (still!) has an adiabatic electron detachment energy of 0.45 eV J. Phys. Chem. A 107 8521–9

[39] Gudmundsson J, Koznetsos I, Patel K and Lieberman M 2001 Electronegativity of low-pressure high-density oxygen discharges J. Phys. D: Appl. Phys. 34 1100

[40] Platier B, Staps T, Koelman P, Schans M v d, Beckers J and IJzerman W 2020 Probing collisional plasmas with MCRS: opportunities and challenges Appl. Sci. 10 4331

[41] Brockhaus A, Leu G F, Selenin V, Tarnev K and Engemann J 2006 Electron release in the afterglow of a pulsed inductively-coupled radiofrequency oxygen plasma Plasma Sources Sci. Technol. 15 171–7

[42] Oudini N, Taccogna F, Bendib A and Aanesland A 2014 Numerical simulations used for a validity check on the laser induced photo-detachment diagnostic method in electronegative plasmas Phys. Plasmas 21 063515

[43] Sirse N, Karkari S K, Mujawar M A, Conway J and Turner M M 2011 The temporal evolution in plasma potential during laser photo-detachment used to diagnose electronegative plasma Plasma Sources Sci. Technol. 20 055003

[44] Lichtenberg A, Vahedi Y, Lieberman M and Rognlien T 1994 Modeling electronegative plasma discharges J. Appl. Phys. 75 2339–47

[45] Bereznoj S, Shin C, Buddemeier U and Kaganovich I 2000 Charged species profiles in oxygen plasma Appl. Phys. Lett. 77 800–2

[46] Vender D, Stoffels W, Stoffels E, Kroesen G and De Hoog F 1995b Charged-species profiles in electronegative radio-frequency plasmas Phys. Rev. E 51 2436

[47] Ashida S and Lieberman M A 1997 Spatially averaged (global) model of time modulated high density chlorine plasmas Japan. J. Appl. Phys. 36 854