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Spatio-temporal dynamics of a pulsed microwave argon plasma: ignition and afterglow

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Abstract

In this paper, a detailed investigation of the spatio-temporal dynamics of a pulsed microwave plasma is presented. The plasma is ignited inside a dielectric tube in a repetitively pulsed regime at pressures ranging from 1 up to 100 mbar with pulse repetition frequencies from 200 Hz up to 500 kHz. Various diagnostic techniques are employed to obtain the main plasma parameters both spatially and with high temporal resolution. Thomson scattering is used to obtain the electron density and mean electron energy at fixed positions in the dielectric tube. The temporal evolution of the two resonant and two metastable argon 4s states are measured by laser diode absorption spectroscopy. Nanosecond time-resolved imaging of the discharge allows us to follow the spatio-temporal evolution of the discharge with high temporal and spatial resolution. Finally, the temporal evolution of argon 4p and higher states is measured by optical emission spectroscopy.

The combination of these various diagnostics techniques gives deeper insight on the plasma dynamics during pulsed microwave plasma operation from low to high pressure regimes. The effects of the pulse repetition frequency on the plasma ignition dynamics are discussed and the plasma-off time is found to be the relevant parameter for the observed ignition modes. Depending on the delay between two plasma pulses, the dynamics of the ionization front are found to be changing dramatically. This is also reflected in the dynamics of the electron density and temperature and argon line emission from the plasma. On the other hand, the (quasi) steady state properties of the plasma are found to depend only weakly on the pulse repetition frequency and the afterglow kinetics present an uniform spatio-temporal behavior. However, compared to continuous operation, the time-averaged metastable and resonant state 4s densities are found to be significantly larger around a few kHz pulsing frequency.

Keywords: microwave plasmas, pulsed plasmas, spatio-temporal dynamics, Thomson scattering, optical emission spectroscopy, laser diode absorption spectroscopy

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

1. Introduction

Non-equilibrium plasmas have a wide range of applications due to their large flexibility in modifying the ratio between fluxes of different species as well as other plasma parameters. Despite an already large number of control parameters such as power, pressure and gas composition, time modulation of the plasma has proven to be beneficial for certain applications [1–3]. Most notably, power interruption was found to be suitable for reducing gas heating while keeping relatively similar radical/ion fluxes compared to the steady state situation [4]. The ratio of the excited species’ densities and fluxes...
to the wall can also be tuned by power interruption of the plasma. Midha et al. [5] showed for instance that pulsing an inductively coupled plasma (ICP) in chlorine allow the increase of the time-averaged chlorine negative ion Cl\(^-\) density because of electron attachment in the temporal afterglow. Lazzaroni et al. [6] investigated an argon–oxygen plasma by global plasma modeling and demonstrated the possibility of tuning the time averaged atomic oxygen versus electron/ion fluxes to the wall. Numerical modeling by Lieberman et al. [7] of low pressure ICP discharges predicted that pulsed operation can allow one to obtain higher plasma densities than in continuous wave (CW) operation mode. Ashida et al. [8] demonstrated theoretically the possibility of increasing averaged plasma densities while applying a power modulation on a low pressure argon capacitively coupled source. Although the global dynamic plasma response to power interruption is fairly well understood, many details are still not well described, particularly the time–space coupling during the ignition phase of the plasma. It is also possible to change the ratio between different species’ densities and electron energy distributions while changing the duty cycle, the pulse frequency and the rise time of the power pulse [9]. Power interruption is also a quite popular method for the investigation of species kinetics from the study of the decay of their densities and temperatures in the afterglow [10, 11]. In this paper, one of our main aims will be to extend such investigations to microwave plasmas.

In the case of pulsed microwave plasmas, there have been far fewer studies, especially using fast switching power supplies (rise time <1 \(\mu\)s). Measurements reported in the literature are typically focused on pulsed measurements with rise times in the range of 2–20 \(\mu\)s [1, 12, 13]. It is thus of particular interest to study how the steep increase in power input coupled into the plasma region (but not necessary the plasma itself) can change the plasma dynamics. In a previous study [14], we showed that the ignition delay is significantly longer than the power input rise time. The pulse repetition frequency, however, strongly changes the plasma breakdown behavior.

An easy way to study the evolution of a pulsed plasma is to monitor the light emission from the plasma. However, in this case, good knowledge of the excitation kinetics populating high-lying states is needed in order to deduce which temporally varying internal parameters are responsible for the observed changes in the density of particles in these specific states [15]. In high-density discharges, such treatment usually requires a cumbersome analysis of the data which in turn relies also on accurate knowledge of cross section values. To circumvent these limitations, one can use electrical probes and laser Thomson scattering to measure directly the electron density and temperature. Laser or broadband absorption spectroscopy can also be used to measure absolute densities of species in their ground state [16–18] or in highly populated metastable and resonant states of the rare gases [19] which cannot be detected by optical emission spectroscopy.

An analogy between fast pulsing and the application of an ac voltage is often made [20]. Going from low to high driving frequency plasmas usually helps to facilitate the breakdown and increase the densities of some active species, and particularly the electrons [21] in the steady state. As microwave plasmas are often compared in terms of behavior to dc glow discharges [22–24], it is interesting to see whether applying a temporal modulation of the power can modify the time averaged properties of the plasma in a similar way as in an ac or pulsed dc field [25, 26]. Tailored voltage waveforms have recently received a lot of interest in separately controlling the ions’ energy and flux in capacitively coupled discharges [27]. The use of multiple harmonics of the fundamental driving frequency in RF discharges has been proposed and investigated as well [28]. Similarly, it is of interest to study the effect of pulsing microwave plasmas, in which case, a slow frequency is superimposed on the microwave frequency to tune the spatio-temporal creation and destruction of species inside the plasma volume.

In this paper, we consider a surface wave discharge that was previously studied extensively in its steady state by laser Thomson scattering (see [29, 30] and references therein). The ignition dynamics in pure argon were also analyzed using nanosecond time-resolved imaging with an intensified charge-coupled device (iCCD) camera using an ultrastable pulsed microwave power supply [14]. Recently, we also studied its afterglow by Thomson scattering while adding molecular gases such as \(\text{N}_2\), \(\text{CO}_2\) and \(\text{H}_2\) with argon as the carrier gas [31]. We present here a detailed experimental investigation of the spatio-temporal dynamics of this discharge in the case of pure argon. Thomson scattering measurements of the electron density and mean energy are presented and reviewed with previous results on the same discharge. The spatial evolution of the discharge both during ignition and the afterglow is presented with nanosecond imaging. Additionally, the temporal evolution of all argon 4s states is measured by laser diode absorption spectroscopy. The temporal evolutions of some selected argon 4p and higher states are finally presented. We end the paper with a discussion of the main processes leading to the production and destruction of different species in the plasma during pulsed operation. The experimental results highlight the effects of the pulse repetition frequency on the discharge dynamics. The combination of different diagnostic methods finally allows us to obtain a thorough insight in the mechanisms at play for the discharge generation and afterglow dynamics.

2. Plasma source and diagnostic techniques

The experiments presented in this paper are performed on a surfatron discharge driven by 2.45 GHz microwave power [32, 33]. The cylindrical quartz plasma tube, with an inner radius of 3 mm, is placed inside the surfatron launcher (see figure 1 for a schematic of the discharge). The results presented here are for pure argon in the pressure range of 1–100 mbar.

An amplitude adjustable oscillator produces a continuous microwave power. This output is then modulated with a fast switch, gated by a function generator, before amplification. A microwave power amplifier, AM87(-2.45S-57-57R) from Microwave Amplifiers Ltd is then used to amplify the microwave power from 10 up to 120 W. The rise time of the power pulse is only 30 ns (i.e. from 0 to 90% peak power
it takes less than 100 ns) and the pulse has an almost perfect square shape. The power pulsing frequency ranges from 1 Hz up to 5 MHz, approximately. Considering the much better temporal properties of this pulsed microwave generator, we will use it exclusively in this study and briefly compare the new results with those obtained for the same discharge with another generator and published previously by Hübner et al [34]. In that study, the microwave power pulses were directly produced by pulsing the microwave power supply.

For the laser scattering experiments, a Nd : YAG 532 nm laser is aligned along the surfatron tube axis [29]. The photons of the laser beam are scattered on either bound or free electrons, which create, respectively, Rayleigh and Thomson scattered photons. The number of scattered photons is directly proportional to the number density of scattering particles, thus proportional to the electron density \( n_e \) in the case of Thomson scattering. On the other hand the Doppler broadening of the scattered photons by free electrons gives insight in the electron energy distribution, and more particularly the mean electron energy \( \langle E_e \rangle \) [30]. The Rayleigh scattering and stray light created by the scattering of the laser beam on nearby solid surfaces need to be filtered out, since they are usually more intense and partially overlap with the Thomson signal. In order to resolve this issue, we use a triple grating spectrograph (TGS) in which the two first gratings form a notch filter for the spectral range of 532 ± 0.2 nm. Only the spectrally broader signal of the Thomson scattered photons can pass through this filter [35]. After the subsequent re-dispersion by the third grating, the photons are collected by an iCCD camera (Andor iStar 734). In our previous work, reported in [34], another Andor camera (DH534) with a lower sensitivity was used. The new camera has a much lower thermal noise and a quantum efficiency of 0.49 which increases the signal-to-noise ratio by almost a factor of ten. The detection limit and accuracy of the measurements are thus significantly improved. Systematic and relative errors were estimated to be in the order of 8% and 5% respectively [29], leading to an absolute accuracy of the electron density measurements better than 15%, the latter stemming mostly from uncertainties in the Raman cross section for the absolute calibration.

For the optical emission measurements, a Jarrell-Ash monochromator with a concave grating and 0.5 m focal length is used. The spectrally resolved photons are collected with a photomultiplier and the signal is recorded with an Agilent 1000 Series oscilloscope. The entrance slit of the monochromator was adjusted to maximize the signal while avoiding the collection of more than one atomic line at once. A system of mirrors and lenses allows the collection of the radially averaged light emission with an axial resolution along a plasma slab of about 1 mm. In the results presented here, the relative spectral response of the detection system is not performed as only the temporal variation of the emission intensities is of interest. Atomic lines in the range of 300–900 nm can be detected.

Three different tunable diode lasers (TDLs) are used to measure by laser absorption the radially averaged densities of argon atoms in their metastable and resonance 4s states at different axial positions. The set-up used for these measurements has already been described in detail in [19]. The laser TDL-1 (Littman configuration, TEC 500; Sacher Lasertechnik) can be tuned to the 772.38 nm and 772.42 nm argon lines to probe metastable atoms in 1s5 and 1s3 states (in Paschen’s notation), respectively. The TDL-2 (Littrow configuration, DL100, Toptica), is tuned to the argon 810.37 nm line, to probe atoms in the resonant 1s4 state. And additionally, a third laser TDL-3 (Littman configuration, TEC 500 Lion; Sacher Lasertechnik), tuned to the 826.45 nm argon line is used to measure the atoms’ density in the resonant 1s2 state. The three beams from the TDLs are perfectly superimposed by use of two cube beam splitters to form a single beam. This beam crosses a 10 mm thick optical plate, which by partial reflections on its faces, provides two weak secondary beams. One of these beams is directed through a low pressure argon discharge tube and the transmitted signal allows the setting of the laser wavelengths at the center of the corresponding absorption lines. The second weak beam crosses a 25 cm long confocal Fabry–Perot interferometer (300 MHz free spectral range (FSR)) and the signal from the photodiode (PD) backing it serves to control the spectral quality of the laser beams and the mode-hop free tuning of
the TDLs when adjusting their wavelengths. After passing the optical plate, the main beam crosses successively a diaphragm, which limits the beam diameter to 1 mm, and an attenuator, which reduces the power to less than 0.3 µW for each of the lasers. The main beam then crosses the plasma tube radially before being detected by an avalanche PD (APD) backed by a 10^5 V A^{-1} transimpedance amplifier. The APD system has a detection sensitivity of 0.5 V µW^{-1} and its response time is less than 10 ns. A high-pass optical filter located in front of the APD blocks photons below 750 nm and limits the detected plasma light to the infrared transitions of argon from 4p states. The absorption signal from the APD is averaged over 1000 plasma cycles by a digital oscilloscope (Lecroy 44Xi Waverunner) triggered by the same function generator which drives the plasma pulses. When recording the absorption signal relative to each of the four 4s states, the beams of the two other TDLs are blocked, letting only one laser beam cross the plasma tube and be detected by the APD. To obtain the transmitted laser intensity, from which the radially averaged density of atoms in the monitored 4s state is deduced, the APD signal is corrected for the plasma emission and laser induced fluorescence lights, following the procedure detailed in [19, 36].

3. Temporal evolution of the density and mean energy of electrons by Thomson scattering

In an earlier study [34], Thomson scattering measurements were performed 2 cm away from the launcher for pressures between 8 and 70 mbar. Some examples of the temporal responses that were obtained in that paper are shown in figure 2 with a pulse repetition frequency of 81 Hz and 31 Hz respectively and with an off-time of about 7 ms in both cases. At low pressure, the electron density started to rise rapidly while at 70 mbar a delay of almost 1 ms was observed. Electron temperatures as high as 4.4 eV were found during the ignition which then decreased while the electron density increased. Growth with an exponential law after breakdown, the electron density exceeded its steady state value for the same CW (peak) power value by about 30%. With the solid state power supply used in the present study, no overshoot of the electron density compared to the steady state is observed (see figure 3) although the applied microwave power has a much shorter rise time. As mentioned in the previous section, the solid state microwave power supply delivers an almost perfect square wave power to the plasma. To understand this discrepancy, a careful re-checking of the shape of the square power input of the previously used Opthos microwave generator was performed. The presence of a power overshoot in the early stages of the pulse was then discovered. Indeed, the fast response of the diode measuring the microwave power is essentially nonlinear and logarithmic. Taking that into account, an overshoot of about 30% during the power switch on of the Opthos microwave power supply is measured and hence the power decreases linearly toward its steady state value. This is then very similar to the overshoot seen in the electron density for the 8 mbar measurements. In figure 2 as well as in [34], the overshoot in electron density finally relaxes to reach its steady state value. The latter value is found to be the same as in the continuous mode for the same peak power. The previously reported overshoot in electron density in [34] was then purely due to the microwave power overshoot delivered by the microwave generator. It is interesting to note that the overshoot is less pronounced in the case of the 70 mbar argon plasma. This can be explained by the longer time it takes for the plasma to ignite. This delay decreases the absorption of the power during the early stages of the plasma ignition [37].

With the Opthos power supply, the electron temperature was observed to decay within 10 µs when the power was switched off. This corresponded actually to the decay of the microwave power itself. The electron density on the other hand decayed more slowly and the decay was representative of the main loss channels of electrons. At low pressure, it is defined by ambipolar diffusion losses whereas at high pressure, i.e. \( p > 20 \) mbar, volume recombination losses dominate, mainly by dissociative recombination (DR) of molecular ion \( \text{Ar}_2^+ \), as discussed in section 7.2 and in [29, 34].

To investigate in more detail the plasma behavior during the ignition and post-discharge periods, in this work we use exclusively a solid state power supply which has a rise time of 30 ns and a perfectly flat square shape (below 1% deviation). Some typical Thomson scattering results are shown in figure 3. The temporal behavior of the electron temperature from these new results is quite different from that
The rise time of the power supply is decreased by a factor 100. Up to electron density, and also electron temperature, although the changes in the ignition behavior are found in terms of the at 40 mbar are now found.

The new iCCD camera used for our measurements leads to a much improved background subtraction. Before the maximum electron temperature is now measured, with a maximum electron energy distribution function (EEDF) is depleted. On the other hand, an increase of the mean electron energy was observed and correlated with modeling (see [30] for more details). The overshoot in the temperature of the bulk electrons cannot be directly associated to a higher effective electron temperature as only the electrons of the tail of the distribution can contribute to extra ionization events. A higher mean electron energy $E_e = 3/2T_e$ does not necessarily correspond to a higher effective excitation or ionization rate. We will come back to this point in section 7.1.

In figure 4, the effects of the pulse repetition frequency at a pressure of 20 mbar and a duty cycle of 50% are examined. As in the case of figure 3, one can see a moderate overshoot of the electron temperature at a repetition frequency of 5 kHz. For a pulse repetition rate of 50 kHz (see figure 4(b)), the electron density is almost not modulated any longer whereas the electron temperature still decays in the afterglow to values close to 0.2 eV. At 500 kHz (see figure 4(c)), the electron temperature is only slightly modulated. The electron temperature takes a few microseconds to reach its steady state value at 50 and 500 kHz and does not overshoot its quasi-steady state value (i.e. its value at the end of the plasma pulse). On the other hand, the plateau value of the electron density tends to slightly decrease with increasing pulse repetition frequency and is no longer modulated at the highest pulse repetition frequency. Conversely, the maximum electron temperature is found to slightly increase, from 1.15 eV at 5 kHz up to 1.4 eV at 500 kHz.

4. Nanosecond spatially resolved imaging of the plasma evolution

In a previous paper [14], we presented already a detailed investigation of the spatio-temporal evolution of the plasma light during ignition as a function of pressure and pulse repetition frequency. It was found that the effect of the pulse repetition frequency and duty cycle were combined in only one parameter, which is the time $\tau_{\text{off}}$ during which the discharge is off. Several discharge ignition modes were found as a function of $\tau_{\text{off}}$. We will not discuss them again in detail here but will present the general characteristics of the spatio-temporal evolution of the plasma in the ignition and the afterglow. The plasma induced argon emission is dominated by infrared lines from 4p states but the camera also receives emission from the 5p and higher states and has a rather high sensitivity to photons in the blue range. The time-resolved images using the iCCD camera thus mostly provide information about the shape of the ionization front and plasma propagation.

At low pulse repetition frequencies (i.e. large $\tau_{\text{off}}$ values and $f < 5$ kHz), an ionization front propagates from the launcher to the end of the column, as illustrated in figure 5. At low pressure, such as 2 mbar, a standing wave structure is found to propagate with the ionization front head. This structure was not observed at higher pressures by iCCD imaging (without any

![Image](image_url)
Figure 4. Temporal evolution of the electron density and temperature for pulse frequencies of 5, 50 and 500 kHz at fixed pressure of 20 mbar, a peak power of 50 W and a duty cycle of 50%. The measurements are performed 2 cm downstream of the launcher.

(filter). However, such a structure is also seen in the intensity of lines from the 5p states even at high pressures but not in those from 4p states, which usually dominate the plasma emission spectrum at high pressures (see section 6 for more details). On the other hand, a standing wave structure, which is fixed by the position of the launcher, is also observed in the plasma light emission even in steady state at all pressures (see for instance the first frame in figure 7).

Figure 5. Temporal evolution of the plasma light during plasma ignition at 2 mbar. The iCCD camera was positioned far away and records from the launcher to about 15 cm downstream of the launcher. The input power is 46 W with a 1 kHz pulsing frequency and 50% duty cycle. Each frame is a single shot picture with a gate of 50 ns.

Figure 6. Temporal evolution of the plasma light as a function of the duty cycle (time off) for a plasma at 100 mbar and a pulse frequency of 500 Hz. The iCCD camera covers the first 25 cm of the quartz tube. For the last frame (97% duty cycle), the plasma was slid down by 18 cm to cover the end of the plasma column. Each frame is a single shot picture with a gate width of 30 ns.

In figure 6, the morphology of the ionization front at 100 mbar and for a pulse repetition frequency of 500 Hz is shown for different duty cycles, varying from 10 up to 97%. One can see various ignition modes which correspond to those reported in [14]. For long τoff values, the plasma is not homogeneous and ignites while forming finger-like structures. They seem to form preferentially along the plasma tube, especially for not too long τoff times. For shorter τoff times, plasma bullet-like shapes are observed. For duty cycles from 90% to 95%, the plasma bullet elongates back to the launcher.
and only volume ignition is then observed at a duty cycle of 97% (bottom image in figure 6 which corresponds to the same ignition mode as in figure 2(d) in [14]). From low to high pulse repetition frequencies, there is most notably a transition from a traveling ionization front mode toward a volume ignition mode. The latter is usually the one associated with low pressure discharges such as inductively coupled discharges. The time dependent behavior of these discharges is usually advantageously described with volume averaged time dependent plasma models [38]. However, from these results, one can already see that a time dependent modeling approach with averaging over the volume will not be able to describe the plasma behavior below a pulse repetition frequency of a few kHz.

The spatio-temporal behavior of the light emission in the plasma afterglow for the same conditions as in figure 5 is presented in figure 7. As expected, one can see that the plasma light decreases homogeneously everywhere in the plasma volume. No spatially dependent features were found even at higher pressures nor in the early afterglow during the switching off of the microwave power supply. As will be discussed in section 7.2, the afterglow kinetics depend only on the local particle balances and species densities.

5. Time-resolved metastable and resonant 4s states densities

In figure 8, the temporal evolution of all four 4s states of argon are presented for pulse repetition frequencies of 5 and 50 kHz (50% duty cycle) at a fixed pressure of 20 mbar. These are the same conditions as in figures 4(a) and (b) where the temporal evolutions of the electron density and temperature are given.

In the early afterglow, after an initial dip, the 4s states’ densities are found to increase, up to a factor 10 in the case of the 1s2 state (in Paschen’s notation), at a 5 kHz repetition frequency (and 20 mbar), compared to the steady state discharge. The peak density arrives after about 25 µs in the afterglow. In the case of the 50 kHz pulsing rate, the overall increase of the 4s densities is lower because the afterglow period is too short to permit the 4s atoms’ densities to reach their peak value due to the electron recombination processes before the re-ignition of the discharge.

In figure 9, the temporal evolution of the relative densities in 4s states are shown in the plasma afterglow at 1 kHz and 50% duty cycles, and 50 W peak power for pressures of 5 mbar and 40 mbar, respectively. As observed in the previous cases, the initial dip in each density is followed by an overshoot and a slow decay. At 5 mbar, the dip is much more significant compared to the results obtained at 20 and 40 mbar. On the other hand, compared to the steady state value, the peak density in the afterglow is much less pronounced at 5 mbar than at 40 mbar. It is also interesting to note that the population ratio of the 1s4 and 1s5 states normalized to their steady state values is inversed going from 5 to 40 mbar.
The measurements are performed 3 cm downstream of the launcher. The plasma light increases at higher pressures and that it can be correlated with the shorter off-times of the discharge and therefore the higher electron and metastable densities at the start of the subsequent plasma pulse. The power switch-off time (~100 ns from 100% to 5% of the input power) is also much faster than the relaxation time of the electron density and temperature. Changing the pulse frequency does not much affect the decay phase of the plasma. This is indeed expected as it is an ionizing plasma (i.e. excitation rates of species by electron impact will decrease much faster than their losses in the afterglow) and it has the time to reach a quasi-steady state value before switching off for frequencies of 10 kHz and below.

In figure 11, the temporal evolution of the light emission from argon 420 nm lines (5p states) is shown for two different pressures (5 and 30 mbar) and recorded for different positions along the plasma column. One can see the increasing delay before the plasma breakdown increases significantly with pressure. As shown in the previous section, at high pressures it takes more time for the generation of an electron avalanche which leads also to a delay in the plasma light emission. On the other hand, the light intensity decreases due to the collisional quenching by Ar atoms.

In figure 12, the temporal evolution of the light emission intensity before switching off for frequencies of 10 kHz and below. The most significant one is the increase by almost a factor of 20 of the 1s3 density at 5 kHz. The fast increase in densities during the ignition of the plasma column. One can see the increasing delay before the ionization front reach the observation point (given as a distance from the launcher) but also that the rise time of the plasma light increases at higher pressure and that it changes along the plasma column. Clear temporal oscillations of the 420 nm lines’ intensities can be seen while they are absent for the 4p lines. This is due to their higher sensitivity to small variations of the plasma electron temperature [39] (see section 7.1 for more details).

The temporal variation of the intensity of various atomic lines in the ignition and afterglow phases originating from high-lying argon states is shown in figure 13. In both phases, line intensities from different 4p states behave relatively similarly but the amplitude of the overshoots significantly increases.

The most dominant emission lines of an argon plasma in the visible and near infrared are transitions from 4p states back to the 4s states. They are widely used to monitor and investigate argon plasmas. In this section we will present and briefly discuss their temporal evolution for various pressures and along the plasma column. The spatio-temporal behavior of lines from 5p states and some higher states which could be detected as well are also presented.

In the steady state, the emission intensities are found to decrease with pressure and weakly depend on the electron density. As seen in figure 7, the light intensity decreases slightly along the plasma column with decreasing electron density. In figure 10, the temporal variation of the 738 nm line (from the 2p3 state in Paschen’s notation) intensity is shown during the ignition and the afterglow phases of a 1 mbar plasma at pulse frequencies of 1 and 20 kHz and a 50% duty cycle. The ignition delay is found to be shorter for higher pulse repetition frequencies and the rise time of the light intensity is also slightly faster. However, this rise time of about 1 μs is considerably slower than the 30 ns rise time of the power supply. Under these conditions, a significant overshoot in emission intensity is observed before it slowly approaches its steady state. The reduction of the ignition delay time can be correlated with the shorter off-times of the discharge and therefore the higher electron and metastable densities at the start of the subsequent plasma pulse. The power switch-off time (~100 ns from 100% to 5% of the input power) is also much faster than the relaxation time of the electron density and temperature. Changing the pulse frequency does not much affect the decay phase of the plasma. This is indeed expected as it is an ionizing plasma (i.e. excitation rates of species by electron impact will decrease much faster than their losses in the afterglow) and it has the time to reach a quasi-steady state value before switching off for frequencies of 10 kHz and below.

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6. Time-resolved optical emission spectroscopy

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In figure 12, the temporal evolution of the light emission intensity before switching off for frequencies of 10 kHz and below. The most significant one is the increase by almost a factor of 20 of the 1s3 density at 5 kHz. The fast increase in densities during the ignition of the plasma column. One can see the increasing delay before the ionization front reach the observation point (given as a distance from the launcher) but also that the rise time of the plasma light increases at higher pressure and that it changes along the plasma column. Clear temporal oscillations of the 420 nm lines’ intensities can be seen while they are absent for the 4p lines. This is due to their higher sensitivity to small variations of the plasma electron temperature [39] (see section 7.1 for more details).

The temporal variation of the intensity of various atomic lines in the ignition and afterglow phases originating from high-lying argon states is shown in figure 13. In both phases, line intensities from different 4p states behave relatively similarly but the amplitude of the overshoots significantly increases.

6. Time-resolved optical emission spectroscopy

The most dominant emission lines of an argon plasma in the visible and near infrared are transitions from 4p states back to the 4s states. They are widely used to monitor and investigate argon plasmas. In this section we will present and briefly discuss their temporal evolution for various pressures and along the plasma column. The spatio-temporal behavior of lines from 5p states and some higher states which could be detected as well are also presented.

Figure 9. Evolution in the plasma afterglow of the relative densities of the two resonant and two metastable 4s states. The plasma is generated with 50 W peak power, at a 1 kHz repetition frequency and 50% duty cycle. The pressure is 5 mbar (top) and 40 mbar (bottom) and the plasma lengths are 36 cm and 15 cm, respectively. The measurements are performed 3 cm downstream of the launcher. Densities are normalized to their values in the steady state, which stops at 0 s.

During the discharge ignition, starting at $t = 100 \mu s$ and $t = 10 \mu s$ for 5 and 50 kHz respectively in figure 8, an overshoot in 4s densities is observed for both repetition rates. The most significant one is the increase by almost a factor of 20 of the 1s3 density at 5 kHz. The fast increase in densities during the ignition of the discharge comes from the high energetic electrons produced in the ionization front. Later, with increasing electron density and lowering of $T_e$, the effective ionization rates of atoms in 4s states (and the states above them) overcome the total excitation rates of 4s states from the ground state and leads to the observed decay of 4s atoms’ densities. The decay time of 4s densities toward the steady state is a couple of microseconds at 50 kHz, much faster than the tens of microseconds observed in the 5 kHz case.

Figure 9. Evolution in the plasma afterglow of the relative densities of the two resonant and two metastable 4s states. The plasma is generated with 50 W peak power, at a 1 kHz repetition frequency and 50% duty cycle. The pressure is 5 mbar (top) and 40 mbar (bottom) and the plasma lengths are 36 cm and 15 cm, respectively. The measurements are performed 3 cm downstream of the launcher. Densities are normalized to their values in the steady state, which stops at $t = 0$ s.
for excited states with higher principal and angular quantum numbers. The rise and decay times are found to be similar for all lines. For the state with the highest energy level that could be detected and which belongs to the 7s group, its intensity increases up to 100% in the afterglow and more than eight times during breakdown compared to its steady state value. If we compare the different temporal behaviors of the 4p lines presented in this paper, one may see some small differences as well. These differences originate from differences in excitation rates and losses and possibly some radiation trapping as well. This is, however, beyond the scope of this study and does not affect the discussion of the overall behavior of different groups of argon lines as the variations are minimal.

The propagation velocity of the ionization front along the tube can be deduced from the delay in ignition between adjacent axial positions along the plasma column. The resulting velocities plotted for two pressures and powers in figure 14 show a significant decrease of the plasma front velocity with increasing pressure and decreasing applied power. The plasma front velocity also decreases by almost an order of magnitude along the plasma column. The local ionization front velocity then depends strongly on the local power density which is carried along the surface wave during
breakdown and on the gas pressure. The ignition of the plasma can be delayed by up to several hundreds of microseconds in the region of the tube corresponding to the end of the plasma column in the steady state. This is due to the finite bulk propagation velocity of the ionization front. We may stress here that, when the plasma has been stopped for tens of seconds, the first ignition after switching on the microwave power pulses is not spontaneous. This is because the amplitude of the microwave field is not high enough to initiate the primary breakdown. Primary electrons, produced by a small spark (kitchen lighter) in the vicinity of the set-up is needed to initiate the first plasma breakdown.

7. General discussion

In the case of a simple square pulse power modulation and for a given position along the plasma column, the time evolution of the plasma can be divided into three main phases: the ignition, when the power is injected in the plasma volume with a certain rise time, the transient ‘on-phase’, when the power is constant and the plasma will reach a steady state if the pulse is long enough and the ‘switching-off’ phase (or afterglow), when the power is stopped and the plasma is decaying, losing its charged and excited species. In this section we will successively discuss the ignition and the afterglow plasma kinetics. Finally, the effect of the pulse repetition frequency on averaged plasma quantities will be discussed briefly in section 7.3.

7.1. Ignition of the plasma

If the plasma has been stopped for a long period, only a few free electrons generated by the background cosmic radiation are present in the gas [40]. When an electromagnetic wave is coupled into the discharge region, these electrons start to oscillate and gain momentum and randomize it by collisions with atoms, resulting in their heating. They create, in turn, new electrons which will, by avalanche, lead to the formation of a plasma. In the case of repetitively pulsed discharge, the situation is different as electrons from the previous pulse will still be present when the power is coupled again into the volume. This is shown for instance in figure 4, where a significant number of electrons created by the previous pulse are still present at the onset of the next plasma discharge. So, the memory effect from the previous afterglow is important while discussing the plasma ignition dynamics. This is illustrated in figure 6 where various ignition modes are found as a function of the duty cycle at 100 mbar and a pulse repetition frequency of 500 Hz. One can see that the ionization front morphology is a strong function of the time during which the plasma was switched off. Variations in the gas temperature during the plasma pulse can have some effect as well. However, gas heating being relatively moderate [41] and the heat transport to the walls being a relatively slow process in the example cited above (τ about 10 ms at 100 mbar), the gas temperature remains almost constant during the cycle. Consequently, we do not expect it to play any important role.
In the early ignition phase of the plasma, one can expect an initial large electron temperature while the electron density rapidly rises by electron impact ionization of argon atoms. This is moreover expected to strongly depend on the rise speed of the applied power [8]. For faster switchings, higher $T_e$ values are expected in the beginning of the plasma ignition while for a very smooth and slow (several microseconds) rise time of the power, no large overshoot in $T_e$ is expected [42]. As discussed in section 3, this was not observed experimentally using Thomson scattering when comparing results for two different power supplies. The delay time before ignition is actually several orders of magnitude longer than the rise time of the power supply used in this study (see [14] for a detailed description). Measurements could not be performed directly inside the microwave cavity but one can see that the electron density takes, in all cases, at least several microseconds to reach its quasi-steady value for all the cases. The rise time of the electron density is roughly inversely proportional to the pressure and a value of about 25 $\mu$s is measured at 5 mbar, for example.

Using different techniques, very large delays in ignition time were found as a function of pressure but also power (see also [14]). The background ionization and remaining metastables from the previous pulse play, without doubt, an important role. However, one should keep in mind that the measurement points are at least 1 or 2 cm away from the launcher depending on the conditions and diagnostic techniques.4 The plasma ionization front velocity follows the same trends and may vary fast inside the surfatron region. Without a more detailed analysis taking into account this effect, it is thus not straightforward to try to deduce some physical quantities out of these ignition delay times. Consequently, we will not discuss them further here.

In figures 3 and 4, we observe an initial overshoot of the bulk electron temperature at low pulse frequencies (5 kHz and lower). However, as discussed in [30], we do not measure the ‘electron temperature’ but the temperature of the bulk electrons from the EEDF. In the case of the steady state for this microwave discharge, it was found that the tail of the EEDF is depleted. For the same ionization rate, an EEDF with a depleted tail requires thus a higher mean electron energy than its corresponding Maxwellian EEDF. Deviations from Maxwellian equilibrium (and consequently higher mean electron energy) were found to be inversely proportional to the ionization degree of the plasma. If we translate these steady state results to the pulsed plasma, the highest depletion of the EEDF tail should occur in the early phase of the plasma ignition and higher mean electron energies should be measured by Thomson scattering. This is indeed what we see at low pulse repetition frequencies. However, in figure 8, we can also see strong overshoots in the argon 4s state densities during the early ignition. These can only be produced by direct electron impact excitation from the ground state. Consequently, the overshoot in the mean electron energy seen by Thomson scattering corresponds also to an overshoot in the effective electron temperature. The mean electron energy increases but also the tail of the EEDF is higher populated during the plasma breakdown. This indicates that the EEDF’s temporal evolution during microwave plasma breakdown cannot be derived simply from quasi-steady state (and spatially integrated) assumptions. If any spatial effect is present, we, however, expect that the EEDF can still be treated locally with no differences in spatio-temporal evolution for different parts of the EEDF. Such effects due to fast transport were observed in pulsed low pressure (about 20 mTorr) inductively coupled discharges [44] but the mean free path of electrons (even in the tail) is small compared to the radius of the discharge in this study. At higher pulse frequencies of 50 and 500 kHz (figure 4), the bulk electron temperature is not found to overshoot its steady state value. This can be correlated to the higher electron density at the end of the afterglow of the previous pulse.

As shown in figure 12 for the emission intensity of the 420 nm line from the 3p5 state, an ionization front propagates from the launcher to the end of the plasma column (as defined in the steady state). The density of atoms in the 3p5 state is mostly sensitive to the electron temperature [39]. From the 420 nm line intensity and Thomson scattering measurements, one can deduce that the overshoot in the electron temperature is located within a small region of the ionization front. Moreover, this overshoot decreases towards the end of the plasma and no overshoot at all is seen close to the steady state end of the plasma column.

Similarly, an overshoot in the 4p states densities is observed in figure 10 for 1 kHz pulsing at 1 mbar. The rise time of the 4p states density is much faster than that of the electron density (a few tens of $\mu$s or less compared to a few hundreds of $\mu$s for the electron density close to the launcher). At very low frequencies, we shall note that the light intensity from the plasma does not overshoot its steady state value, a phenomenon which starts to occur only for pulse frequencies of 1 kHz and above [45]. This is correlated with the inhomogeneous ionization front observed under these conditions [14]. The overshoot seems to be well correlated with a decrease of the afterglow period. However, its magnitude is found to decrease away from the launcher and no overshoot is now observed at the position corresponding to the steady state end of the plasma column (see figure 12). The initial electron and metastable densities before the re-ignition seem to play a critical role here.

During the plasma ignition, electromagnetic waves are launched from the surfatron and propagate along the quartz tube. Mohanty et al [47] found that at high power, pulsed microwave discharges generate acoustic waves due to the propagation of the plasma along the column. By comparing different gases (argon and nitrogen), they concluded that these acoustic waves were related to periodic ionization/energy coupling to the gas. This conclusion is indeed demonstrated in this work by observing the space and time evolution of different plasma parameters ($n_e$, $T_e$, Ar, and the plasma emission) by various diagnostic techniques. Gamero et al [48] investigated...
the propagation of the radial component $E_r$ of the electric field and the light emission along the plasma column of a pulsed low pressure surfatron discharge. They found that the plasma induced light emission propagation velocity is maximum close to the launcher with values up to $10^8$ m s$^{-1}$ at 0.8 Torr. On the other hand, Garcia et al [49] found a maximum velocity of $2.5 \times 10^7$ m s$^{-1}$ at atmospheric pressure which decreases along the column. In this study, we find the same trends as seen in figure 14.

An oscillation of the 3p$_5$ light intensity can also be clearly seen in figure 12 behind the ionization front, following it during the plasma propagation, but its amplitude is damped along the plasma column. If we take the period of this oscillation and multiply it by the ionization front velocity (see figure 14), a characteristic length of approximately 10 cm is found. This corresponds roughly to the microwave wavelength after correction due to the change in permittivity of the plasma medium compared to vacuum. Although less clear, such a pattern is actually seen in the iCCD images in figure 5 as well. The 5p states are more sensitive to the electron temperature compared to the 4p states and the 3p$_5$ state can be used as a probe for the electron temperature [39]. The oscillations in the 3p$_3$ line can be associated to the higher mean electric field values corresponding to a wave pattern following the ionization front propagation. In the case of microwave plasmas [24], the electron temperature is usually correlated with the electric field as $T_e \propto |E|^2$ and a tiny oscillation in $T_e$ is indeed observed by Thomson scattering as well (see figures 3(a) and 4(a)). This pattern is likely to have been created by the reflection of the EM wave at the end of the ionization front back toward the launcher. This reflection is stronger at the early stage of the discharge when the total electron density is not large enough to absorb all the microwave power coupled inside the cavity. Toward the end of the plasma column, the amplitude of the reflected wave decreases because of the slabs of plasma in front of it that will dissipate the power from the EM field. The oscillatory pattern amplitude then decreases with the distance from the launcher before disappearing completely.

At low pressure, the ionization front velocity is found to approach streamer velocities. Chaudhury et al [51] modeled the high power microwave breakdown at atmospheric pressure of an array of plasma filaments parallel to the electric field that propagates toward the microwave source. They showed in their plasma configuration that large $E$ field values are preceding the plasma ionization front due to the strong gradient in space charge. This field (which varies during the microwave period) sustains the propagation of the plasma front. For a surface wave discharge very similar to the one studied here, Garcia et al [49] also showed experimentally a delay between the temporal rise of the $|E_r|^2$ and the light emission. The higher electron temperature and production rate of argon 4s states at the tip of the plasma front seen in our experiments indicate that such effects may play an important role during the ignition of this discharge as well. Interestingly, at low pulse repetition frequencies, the ionization front is found to be strongly inhomogeneous which indicates that stochastic processes play an important role. This can be correlated to the lower ionization degree remaining from the previous pulse. A detailed description of the ignition of this pulsed surface wave discharge would need a time dependent, two-dimensional model of the discharge [52] coupled with a particle-in-cell code to take into account the non-uniformity of the ionization front [53].

In the early phase of the ignition, the electron temperature is found to be smaller than its peak value despite lower electron densities (see figure 3). This trend can be compared to the results obtained by Murohashi et al [54] in pulsed microwave ring slot antenna while using a Langmuir probe. The conditions were however quite different and it is hard to make any direct comparison. However, Böhle et al [37] showed that during the breakdown, the microwave power is initially coupled into the discharge volume but radiates in the surroundings. We expect that such an effect may contribute to this particular behavior of the electron temperature. Furthermore, ohmic heating will be less efficient for lower electron temperatures [55]. A high $T_e$ at the start of the ignition is not seen in figure 4 at 50 and 500 kHz pulsing frequencies. This is because, at the time when the microwave power is applied, the densities of the 4s states are high enough to favor stepwise ionization processes. This also explains why almost no overshoot occurs on 4s atoms densities. So, the $T_e$ does not need to overshoot during ignition to compensate by direct excitation from the ground state (to the 4s states) the loss of electrons during the off period. But later on, the atoms’ density in 4s states decreases, as does the stepwise ionization, and $T_e$ must increase to sustain the operation of the plasma.

7.2. The afterglow phase

In steady state operation, excitation and ionization processes in an ionizing plasma compensate for the losses of excited species. In the case of an argon microwave plasma, the power density that is coupled locally to the plasma is such that ionization will be sufficient to compensate for the electron–ion pair losses by diffusion and volume recombination [24]. The temporal evolution of excited species has been already extensively studied in the case of pulsed ICP. Fey et al [56] studied the partial Boltzmann and Saha equilibrium for ionization and recombination processes for atomic species in an atmospheric pressure ICP plasma. Similarly, the afterglow of low pressure argon ICP discharges have been studied and the importance of electron ion recombination processes discussed [57, 58]. Pulsed dc glow discharges have been extensively studied as well [59, 60]. In a previous paper, we studied the electron recombination kinetics by Thomson scattering on this surfatron discharge at high pressure [34]. For pressures above 10 mbar, it was shown that the main loss mechanism of electrons in the early afterglow is the DR of molecular ions Ar$_2^+$. Similar results were obtained by Cotrino et al [61] by microwave interferometry measurements and they also studied the influence of the tube radius. We will therefore not discuss it in more detail here.

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5 For higher pressures, such an oscillatory pattern could not be distinguished by fast iCCD imaging although one can clearly see it in figure 12(b) for the 5p line at 30 mbar. This is due to the fact that the camera is collecting all the light from the 4p and 5p lines of the plasma and some temporal features are then averaged out. Moreover, the electron temperature decreases at higher pressure and the 5p states are strongly quenched by heavy particle collisions [50].
In figure 9(a), the different temporal phases of argon atoms in their resonant and metastable 4s states are visible. Initially, at the moment of the power switch off, their densities rapidly decay. This is because the fast drop in electron temperature cuts the production of argon 4s atoms by direct excitation from the ground state but the stepwise ionization via excited states of argon, which requires only a few eV, still continues for a few µs during which the $T_e$ is close to 1 eV. But after some microseconds a minimum is reached and all densities rise again due to a new production term by electron–ion recombination.

In argon plasmas, the primary ions are Ar$^+$ but in three-body collisions part of them are converted into molecular ions Ar$_2^+$

$$\text{Ar}^+ + \text{Ar} + \text{Ar} \longrightarrow \text{Ar}_2^+ + \text{Ar}.$$ \hfill (1)

Excited states of argon atoms can be populated by collisional–radiative (CR) recombination of Ar$^+$ ions

$$\text{Ar}^+ + e^- + e^- \longrightarrow \text{Ar}^+ + e^-$$ \hfill (2)

and by DR of Ar$_2^+$ ions

$$\text{Ar}_2^+ + e^- \longrightarrow \text{Ar}^+ + \text{Ar}.$$ \hfill (3)

The well-known theoretical CR recombination coefficient of Ar$^+$ ions derived from the Thomson formula is [57]

$$\alpha_{th}(\text{CR}) = 1.29 \times 10^{-38} \cdot n_e \cdot T_e^{-4.45}$$ \hfill (4)

in which $n_e$ is in m$^{-3}$ and $T_e$ in eV. Celik et al [57] have extended the model to take into account the Stark splitting of Rydberg states by the plasma microfield but this refinement is out of the scope of the order of magnitude comparison of different production rates of this work.

For the DR of Ar$_2^+$ ions, Mehr and Biondi measured $\alpha_2(\text{DR}) = 8.5 \times 10^{-13}$ m$^3$ s$^{-1}$ in an afterglow plasma at room temperature and proposed a $T_e^{-0.67}$ dependence for it [62]. A formula accounting for the temperature of Ar$_2^+$ ions (gas temperature) on DR toward Ar (4s) states is given in table 6 of [43]. To estimate the relative contributions of these two recombination mechanisms in the production of argon 4s states in the afterglow, different reaction rates of ions are summarized in table 1 for gas pressures of 5, 20 and 40 mbar. These pressures correspond to the experimental conditions for which the time evolution of the atoms’ density in Ar (4s) states are reported in figures 8 and 9. The gas temperature, $T_g$, and the total atom density in all four Ar (4s) states reported in this table are the steady state values measured by laser absorption spectroscopy [19]. At each pressure, the electron densities and the highest electron temperatures are also steady state values measured by Thomson scattering under the same plasma conditions [29]. At each pressure, two lower $T_e$ values are also considered. $\nu_{IC}$ is the conversion frequency of Ar$^+$ ions into Ar$_2^+$, $\nu(\text{CR}_{th})$ is the loss frequency of Ar$^+$ ions when the theoretical CR recombination rate given in equation (4) is considered and $\nu(\text{CR}_{exp})$ is the frequency if we consider the experimental value reported by Chen [63] at $n_e = 6.4 \times 10^{19}$ m$^{-3}$ and $T_e = 0.7$ eV and scaled for other $n_e$ and $T_e$ values according to the dependence on them of $\alpha(\text{CR})$ given by equation (4) and $\nu_{DR}$ is the loss frequency of Ar$_2^+$ ions by DR. In table 1, for all considered afterglow conditions $\nu_{DR}$ is in the range or above $1 \times 10^9$ s$^{-1}$ and as the time evolution of $n_e$ is much slower (see figure 4) one can conclude that the density of Ar$_2^+$ ions will always remain much lower than $n_e$.

This results from the bottleneck on the production of Ar$_2^+$ ions by ion conversion. The density of these dimer ions can be deduced from the balance between their production and losses

$$\frac{\partial [\text{Ar}_2^+]}{\partial t} = k_{IC} [\text{Ar}^+] \cdot [\text{Ar}]^2 - \alpha_{DR} \cdot [\text{Ar}_2^+] \cdot n_e \approx 0.$$ \hfill (5)

The density of Ar$_2^+$ ions, deduced from the balance equation (5) is also reported in table 1 and, as expected, it remains almost two orders of magnitude smaller than $n_e$.

The three subsequent lines of table 1 report electron–ion recombination events (m$^{-3}$ s$^{-1}$). Ar$^+$ (CR$_{th}$) and Ar$^+$ (CR$_{exp}$) are the production rates when the theoretical CR recombination coefficient of reaction (2) or the $\alpha_{exp}$ (CR) of Chen [63] are considered. The latter seems to be about 10 times the value of $\alpha_{th}$ (CR). Finally, $\alpha^*$ (DR) is the production rate of Ar$^*$ atoms by DR, which is in fact limited by the bottleneck in the production rate of Ar$_2^+$ ions by the conversion reaction (1). Considering the 1.25 eV dissociation energy of Ar$_2^+$ ions [64], the DR reaction can mainly populate Ar states below 14.51 eV (i.e. 4s, 3d, 5s, 4p and a few 5p states), which are less subject to ionization in the afterglow.

A reasonable assumption is to consider that before ending in the ground state, the majority of excited argon atoms produced in the afterglow will pass through the 4s states. As seen in table 1, even with the largest experimental recombination coefficient of Chen $\alpha_{exp}(\text{CR})$, in favor of the $T_e^{-4.5}$ dependence for the e–Ar$^+$ recombination, DR dominates the production rate of Ar (4s) atoms in the start of the afterglow and for $T_e$ down to about 0.6 eV at 5 mbar, 0.4 eV at 20 mbar and 0.3 eV at 40 mbar. For electron temperatures below these values, the Ar (4s) atom production rate by CR recombination becomes dominant. However, with the theoretical $\alpha_{th}$ (CR) (Thomson’s formula), the DR remains dominant for all pressures with $T_e$ down to 0.3 eV.

To estimate the loss rate of Ar (4s) atoms, we assume that electron impact collisions mix the population density of all four Ar (4s) states which then achieve statistical equilibrium (see [19]) and their global population is mainly lost by radiation from the resonant 1s4 and 1s2 states to the ground state. The apparent radiative lifetimes of these states, calculated following the method described in [65] according to Holstein’s model [66, 67], are in the range of 8.0 µs and 1.9 µs, respectively. Accounting for the statistical weight of the states, we deduce a loss frequency $\nu_{loss}$ of about $1.6 \times 10^6$ s$^{-1}$ for the radiative decay of mixed Ar (4s) states, from which the losses, Ar$^*(4s)_{loss}$ (m$^{-3}$ s$^{-1}$) in table 1 are deduced for the steady state.

The balance between Ar$^*(4s)_{loss}$ and the production rate by electron–ion recombination defines the behavior of the density variation in the Ar (4s) states in the early afterglow. At 5 mbar, when the discharge is stopped, the loss rate is well above the production rate as seen in figure 9. Normalized to their steady state values, all Ar (4s) atom densities decay immediately with initial decay times of about...
1.5/2.0/2.2/2.8 \mu s for the 1s_2/1s_1/1s_3/1s_5 states, respectively. The observed closeness of the decay times of resonance and metastable states is a justification for the strong collisional coupling of the Ar (4s) states. Also, with the rate coefficients we have recently published for the electron impact transfer from 1s_3 to 1s_1 and from coupled 1s_2,3 to coupled 1s_3,5 states [36], the corresponding rate frequencies are about 20 and 2 × 10^6 s^{-1}, much faster than the global radiative loss frequency, \nu_{max} = 1.6 × 10^8 s^{-1} of 4s states. Moreover, the observed decay frequency of the states (about 5 × 10^6 s^{-1} as measured in the start of the afterglow in figure 9) is about three times the above calculated \nu_{max}, indicating the presence of another destruction mechanism for Ar (4s) atoms. The latter is likely to be stepwise ionization of these states by bulk electrons whose temperature remains above 1 eV for about 6 \mu s in the afterglow of the 5 mbar plasma, if scaled by a factor 20/5 = 4 for elastic cooling from figure 4, which is for p = 20 mbar.

At 20 and 40 mbar, Ar^{+}(DR) should always dominate the production rate of Ar (4s) atoms but small dips are seen at the discharge switch off in figures 8 and 9. As pointed out before, this should be due to the stepwise ionization of Ar (4s) atoms by the hot bulk electrons in the early afterglow. At 20 mbar (figure 8), the more important dip at 50 kHz, compared to 5 kHz, is certainly related to slightly higher T_e in the former case, which results in less production by electron–ion recombination.

The importance of stepwise ionization during the plasma-on period and of excited argon atom production by electron–ion recombination in the afterglow is demonstrated in figure 13 which shows the evolution of several argon line intensities for a pulsed 5 mbar plasma. We shall note that all intensities are normalized relative to their steady state values in the plasma-on period. First, all intensities drop with the interruption of the microwave power and after a minimum they show an overshoot due to the population of excited states by electron–ion recombination. The high-lying 5d and 7s states, which are at about 0.6 eV below the ionization limit, are highly subject to ionization during the plasma-on period and consequently the intensities of the 603.2 and 545.2 nm lines, which are low during this period, show important enhancements in the afterglow; these levels being efficiently populated by e^-–Ar^* recombination after the cooling down of T_e. In contrast, during the plasma-on period the 4p states are efficiently populated via electron impact excitation from the ground state, as well as from the 4s states. The fast elimination of energetic electrons when the microwave power stops eliminates this source of excitation and electron–ion recombination results in only a weak overshoot on the intensity of 696.5 and 811.5 nm lines. The time variation of the intensity of the 420.1 nm line from a 5p state shows the intermediate case because of its less efficient direct excitation (relative to 4p states) and stepwise ionization (relative to 5d and 7s states) in the discharge. The temporal shapes observed for the 4p and 5p states follow those seen for the 4s states which underline, as expected, their common production terms.

In the late afterglow, the 4s states are fed, according to their respective statistical weights, by both CR recombinations and DRs and their destruction will essentially be by radiative losses to the ground state via the resonant states. So their time evolution will result from an equilibrium between these processes. However, with the continuous decay of T_e in the late afterglow, mixing between them by electron collisions will become less and less effective and consequently their lifetimes will diverge. This explains the slower decay (faster decay) of the population density of the metastable 1s_5 (resonant 1s_2) states in the late afterglow, as seen in figure 9(b). A complete model of the afterglow should be used to discuss the observed trends in more detail. This is, however, out of the scope of this study.

7.3. Tuning averaged plasma quantities by power interruption

As discussed in section 1, one of the main reasons for power interruption is to tune the time-averaged species’ densities.

Pulsing the plasma is found to have very little effect on the Quasi-steady state electron density as is shown in figure 4. For a given peak power density, the maximum electron density does not exceed its value reached in continuous power operation. The time-averaged electron density is proportional to the time-averaged power density injected in the plasma and insensitive

### Table 1. Computation of the main reaction rates for the production and losses of argon 4s states for different pressures and electron temperatures in the temporal afterglow (see text for the definition of parameters).

<table>
<thead>
<tr>
<th>p (mbar)</th>
<th>( T_e ) (eV)</th>
<th>( T_g ) (K)</th>
<th>( n_e ) (m^{-3})</th>
<th>( \nu_{Ar^*} ) (m^{-1})</th>
<th>( v_1(CR_{th}) )</th>
<th>( v_1(CR_{inh}) )</th>
<th>( v_2(CR_{inh}) )</th>
<th>( v_2(DR) )</th>
<th>( \nu_{Ar}^+ ) (m^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>20</td>
<td>550</td>
<td>2 × 10^{19}</td>
<td>6 × 10^{17}</td>
<td>13 000</td>
<td>19.0 × 10^{6}</td>
<td>9.0 × 10^{6}</td>
<td>110</td>
<td>980</td>
</tr>
<tr>
<td>1.1</td>
<td>0.6</td>
<td>550</td>
<td>4 × 10^{19}</td>
<td>1.2 × 10^{17}</td>
<td>13 000</td>
<td>4.9 × 10^{6}</td>
<td>4600</td>
<td>210</td>
<td>980</td>
</tr>
<tr>
<td>1.0</td>
<td>0.3</td>
<td>550</td>
<td>1.2 × 10^{17}</td>
<td>1.8 × 10^{17}</td>
<td>52 000</td>
<td>4.9 × 10^{6}</td>
<td>4600</td>
<td>210</td>
<td>52 000</td>
</tr>
<tr>
<td>1.0</td>
<td>0.6</td>
<td>550</td>
<td>4 × 10^{19}</td>
<td>1.2 × 10^{17}</td>
<td>13 000</td>
<td>4.9 × 10^{6}</td>
<td>4600</td>
<td>210</td>
<td>52 000</td>
</tr>
</tbody>
</table>

\( a \) In s^{-1}, \( b \) In m^{-3} s^{-1}.
to the duty cycle (if ignition delay times are neglected). However, with increasing repetition frequency, the electron density slightly decreases whereas the electron temperature slightly increases. The reduction in electron density is then compensated by an increase in electron temperature. On the other hand, an increase of the quasi-steady state Ar (4s) densities is observed (see figure 15) although the quasi-steady state is not achieved at frequencies above a few kHz for some of the species (e.g. the electrons) present in the plasma. Their densities are higher due to the increase of their effective production rate from the ground state because of the higher mean electron energy/temperature. The reason behind this slow self-consistent adaptation of the ionization rate and densities with respect to the (fast) electric field modulation is, however, not completely clear.

However, ions are not the only interesting species in the plasma. Long lived excited neutral species can be important for plasma processing as well. Our results show that the density of atoms in Ar (4s) states have much larger averaged densities in the pulsed mode than in continuous plasma. This is illustrated in figure 15. The averaged absorbance ($A = \ln(I_0/I)$) gives values of (0.256; 0.151) for the 1s5, and (0.146; 0.11) for the 1s2 state for the pulse repetition frequencies of 5 kHz and 50 kHz respectively. The absorbance values taken at the end of the discharge pulse at 5 kHz corresponding to the steady state (which is at $t = 0 \mu s$) gives values of $\langle A(1s5) \rangle = 0.072$ and $\langle A(1s2) \rangle = 0.059$, respectively. This corresponds to increases by factors of seven and five for the 1s1 and 1s2 states while normalizing to the total discharge power input. It is then possible to adjust the power input and its pulsing conditions to obtain the required amount of argon atoms in 4s states and hence to tune the relative fluxes of charged and neutral reactive species of interest for applications. This is possible because the production of charged particles stops in the afterglow whereas the neutral reactive species continue to be produced in this phase of the plasma by electron–ion recombination processes.

To conclude, it is interesting to note, that extrapolations from optical emission measurements (and even electron density measurements) [68, 69] are not necessarily sufficient to evaluate experimentally whether pulsed operation can be beneficial for applications or not. This will be particularly true in the cases where important amounts of neutral reactive species are produced in the afterglow through specific production channels.

8. Conclusions and perspectives

Pulsed surface wave argon discharges were produced by means of an ultrafast pulsed microwave generator and the time variation, during the pulse period, of the charged and excited species of argon were investigated using various techniques. The effect of pulse repetition frequency, pressure and power, and their effect on averaged plasma properties are discussed.

The use of an ultrafast pulsed microwave power supply does not show any significant differences in the ignition and afterglow behaviors compared to a more conventional microwave power supply (magnetron) used in [34]. New insights into the propagation mechanism of the ionization wave are obtained. The effective electron temperature at the tip of the ionization front is higher than in the bulk of the plasma. However, under some plasma and pulsing conditions the ionization front is no longer homogeneous. A self-consistent fluid hybrid (two- or three-dimensional) time dependent model would be needed to shed more light on the mechanisms responsible for microwave plasma propagation.

In the afterglow, large amounts of argon atoms in the metastable and resonant states are produced. Depending on the pulse repetition frequency and duty cycle, the kinetics in the post-discharge also influence the re-ignition of the discharge. The production rates in the afterglow of Ar atoms in 4s and higher states are analyzed and attributed to recombination of electrons with Ar+ and Ar2+ ions. For sufficiently short afterglow times, the 4s states’ densities still remain very high at the beginning of the subsequent plasma pulse. Much higher time-averaged Ar (4s) atom densities relative to the steady state operation are also observed at 5 kHz pulsing frequency.

In conclusion, we have gathered a large amount of data in this and previous papers [14, 29, 30] that can be used for an in-depth theoretical investigation of low power, pulsed microwave plasmas. These data can of course be complemented with earlier studies on this type of discharge such as the work of Böhle et al [37]. To understand the ignition mechanism of the plasma, detailed numerical investigation will be needed. Up to now, only high power density microwave plasmas were studied by modeling and further investigations for low power pulsed microwave plasmas are needed. The temporal evolution of the afterglow of various plasma parameters could also be used to validate time dependent global models of argon plasma afterglows.

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