Atmospheric-pressure diffuse dielectric barrier discharges in Ar/O₂ gas mixture using 200 kHz/13.56 MHz dual frequency excitation

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Abstract

Atmospheric-pressure diffuse dielectric barrier discharges (DBDs) were obtained in Ar/O₂ gas mixture using dual-frequency (DF) excitation at 200 kHz low frequency (LF) and 13.56 MHz radio frequency (RF). The excitation dynamics and the plasma generation mechanism were studied by means of electrical characterization and phase resolved optical emission spectroscopy (PROES). The DF excitation results in a time-varying electric field which is determined by the total LF and RF gas voltage and the spatial ion distribution which only responds to the LF component. By tuning the amplitude ratio of the superimposed LF and RF signals, the effect of each frequency component on the DF discharge mechanism was analysed. The LF excitation results in a transient plasma with the formation of an electrode sheath and therefore a pronounced excitation near the substrate. The RF oscillation allows the electron trapping in the gas gap and helps to improve the plasma uniformity by contributing to the pre-ionization and by controlling the discharge development. The possibility of temporally modifying the electric field and thus the plasma generation mechanism in the DF discharge exhibits potential applications in plasma-assisted surface processing and plasma-assisted gas phase chemical conversion.

Keywords: atmospheric pressure, dielectric barrier discharge, dual frequency, excitation dynamics

(Some figures may appear in colour only in the online journal)
also known as ‘corona’ in industrial applications related to the surface treatment [1, 2, 4]. However, a DBD is typically filamentary resulting in a strong spatial non-uniformity of the plasma restricting its use for demanding applications e.g. deposition of high quality thin films. The less common diffuse modes of the DBD expand the novel application fields in plasma-assisted surface engineering and are therefore in focus of scientific and industrial interest [6–10].

The properties of an atmospheric-pressure high-current diffuse DBD operating at 200kHz frequency in low cost N\textsubscript{2}/O\textsubscript{2}/Ar gas mixtures were investigated in [11–14]. According to the fast imaging analysis, during the single current pulse, this transient discharge evolved from a ‘Townsend-like’ mode to a ‘glow-like’ mode for each half cycle of the electric field [11, 12]. It was also demonstrated that application of such a diffuse discharge as a plasma source for the roll-to-roll AP-PECVD process in conjunction with organosilicon precursors results in high quality inorganic silica-like thin films, which can be deposited on thermally sensitive polymeric substrates [14–16].

In this process, the increased discharge power density allows the synthesis of silica-like films with improved microstructure, lower impurities level and excellent gas diffusion barrier properties [16, 17]. Moreover, a higher power density is also required to increase the deposition rate and therefore the throughput of the PECVD process. However, when the input power increases, one of the biggest challenges is to prevent the transition from the homogeneous to the filamentary discharge or even a high current arc which will damage the polymeric substrate. One approach to increase the discharge power without generating arcs can be to modulate the electric field by applying a high frequency (HF) voltage to a low frequency (LF) voltage.

This dual frequency (DF) excitation was previously investigated in low-pressure inductively coupled plasmas (ICPs) [18, 19], capacitively coupled plasmas (CCPs) [20–22] and dielectric barrier discharges (DBDs) [23, 24].

It was found that in low-pressure plasmas the LF and HF component can facilitate separate control of the ion energy and ion flux to the surface [19, 20, 25, 26]. Under atmospheric pressure, however, the collision rate between ions and gas molecules becomes so high that the incident ions have nearly thermal energy (with certain reservations [27]), thus depriving any meaningful scope for manipulating the ion energy [28]. The effects of the DF excitation in an atmospheric-pressure plasma are focused on tailoring the electron energy distribution function (EEDF) and controlling the plasma parameters e.g. electron density, gas temperature and ion flux to the sample [29, 30]. The HF voltage allows to trap the electrons in the plasma bulk with less electron loss at the surface, which helps to maintain a high plasma density [28]. On the other hand, electron trapping results in more power coupled into elastic collisions and therefore a higher gas temperature and a lower electron energy [31]. Usually the DF plasma is generated with two frequencies both in the range of MHz, the DF combination in the kHz and MHz domain, however, was not widely studied. Zhou et al studied an atmospheric-pressure 50kHz/2 MHz DF plasma jet which exhibits the advantages of both the LF and RF plasma, namely, a long plasma plume and a high electron density [32]. By applying a MHz power to one electrode and a kHz power to the counter electrode, Massines et al investigated the DF discharge behaviour and the thin film deposition. The combination of low and high frequencies led to the synthesis of a denser film with an improved microstructure compared to the pure RF DBD excitation [23, 33].

For cold atmospheric-pressure discharges electrons are the key to plasma dynamics, and wall fluxes of plasma species are influenced by those generated in the boundary layer of the electrode [28]. The plasma chemistry, and thus the concentrations of reactive species, is predominantly driven by energetic electrons [34]. The electron dynamics, governing dissociation, excitation and ionization processes, is therefore of crucial significance in plasma processing [34]. In the previous work of Gans et al [35, 36], phase-resolved optical emission spectroscopy (PROES) was used as a non-intrusive and sensitive way to investigate the EEDF of RF plasmas. Highly excited states in atoms or molecules are excited by electrons in the tail of the EEDF. PROES therefore is sensitive to the dynamics of high energetic electrons ($E \geq 11.7 \text{eV}$) and yields information on the plasma parameters with high temporal and spatial resolution [37].

In this study, it was demonstrated for the first time that the dual frequency (200kHz + 13.56 MHz) excitation can produce homogeneous, filament-free DBDs at atmospheric pressure in Ar/O\textsubscript{2} gas mixture. The focus of the present work is to study the excitation dynamics of the DF plasma and to explore the potential approaches to enhance the plasma-assisted processing efficiency. The paper is structured in the following way: the experimental setup and the diagnostic methods are introduced in section 2. The presentation of results in section 3 is divided into two parts. First, the electrical characteristics including the voltage–current waveforms and the Lissajous figures are investigated. Second, the time-integrated emission and the spatiotemporal excitation dynamics deduced from the PROES of 750.4 nm and 751.5 nm (corresponding to the emission from Ar 2p\textsubscript{1} state and Ar 2p\textsubscript{5} state, respectively [38]) with nanosecond time resolution are studied. From these studies, direct insight into the excitation dynamics and the plasma generation mechanism of LF, RF and DF discharges are obtained. Finally, conclusions are drawn in section 4.

2. Experimental setup

The schematic picture of the atmospheric-pressure roll-to-roll plasma reactor is presented in figure 1. The discharge was ignited between a flat bottom electrode with a length of 100 mm and a width of 45 mm and a curved top electrode with a radius of 60 mm and a width of 45 mm, both the electrodes were covered by 0.1 mm thick PET (polyethyleneterephthalate) foils as the dielectrics. The electrode temperature was sustained at 30 ºC by means of an oil circulation system. The smallest distance between the two electrodes was 1.0 mm. The gas mixture was injected from the left side of the discharge area in figure 1 while the substrates were transported at 40 mm min\textsuperscript{−1} in the same direction as the gas flow. The flow rate of the gas mixture (Ar/O\textsubscript{2}) was controlled at 10 slm/0.1
slm (standard litre per minute). The DBD was excited by a 200kHz LF (SEREN L1001) and a 13.56 MHz RF (SEREN R601) power source which were connected to a home-made matching circuit. The tunable matching network helps to stabilize the discharge and reduce the reflected power of both the power sources. To reduce the power load to the plasma, the injected power of both power sources was modulated at 625 Hz with a pulse width of 800 µs and a duty cycle of 50%. The discharge voltage and current were measured by a high voltage probe (Tektronix P6015A) with 75 MHz bandwidth and a current transformer (Pearson model 4100), respectively. An intensified charge-coupled device (ICCD) camera (PI MAX3), triggered by the applied voltage, was employed to collect the discharge emission from the side view of the gas gap with a macro lens (Tamron AF 90 mm). A spectral filter (Andover Corporation 750FS10-50) at 750 nm with 10 nm bandwidth was mounted in front of the camera which allows discrimination of emission lines from Ar $2p_1$ and Ar $2p_5$ excited states (750.4 nm and 751.5 nm). These lines are ideally suited to probe the excitation and ionization dynamics due to their short natural lifetime, negligible contributions of step-wise excitation out of metastable excited states, and small cascade contributions from higher excited states [35].

3. Results and discussion

3.1. Electrical characteristics

3.1.1. Voltage–current waveforms. Electrical characterization is a powerful tool to study the discharge mechanism. Figure 2 shows the representative voltage and current oscillograms recorded for the fixed electrode configuration and gas mixture operating in LF, RF and DF discharge modes. Usually the waveforms of the DBD driven by a single frequency voltage in the kHz range can be characterized by single or multi current pulses during each half cycle [39]. From figure 2(a), the single smooth discharge current peak can be clearly identified from the measured current which also contains the displacement component. In the RF discharge, the displacement current is so high that identifying the discharge component from the measured current becomes very difficult, see figure 2(b). In the DF discharge, both the current and the voltage contain the LF component and the RF oscillation. Depending on the ratio of the input power, the amplitudes of the LF and RF signals are varied. By doing fast Fourier transform (FFT) filtering of the original waveforms, signals above 10 MHz including the RF component can be removed, and the LF component in the voltage and current can be extracted, see figures 2(c)–(e).

3.1.2. Lissajous figures. To further analyse the electrical characteristics, the $Q$–$V$ plots or the Lissajous figures are studied, as illustrated in figure 3. The Lissajous figure of the LF discharge has approximately the form of a parallelogram, see figure 3(a). Two distinct phases can be identified [40]. Lines DA and BC represent the phase when no plasma is ignited. Hence there is only a displacement current, and the slope $dQ/dV$ corresponds to the total reactor capacitance. Lines AB and CD represent the phase when the plasma is formed in the gas gap, and the slope of these lines can approximately indicate the total capacitance of the dielectrics [41]. The Lissajous figure of the RF discharge has approximately an oval shape since the RF plasma is in a continuous mode, and therefore the ‘plasma-off’ phase cannot be distinguished, see figure 3(b). The capacitances in the DBD reactor cannot be obtained from the Lissajous figure under these conditions. The Lissajous figures of the DF discharges are rather complex due to the RF oscillation. Fast Fourier transform (FFT) filtering is used to extract the LF-induced $Q$–$V$ plots, see figures 3(c)–(e). The equivalent capacitances of the dielectrics and the total reactor are estimated from the FFT-filtered Lissajous figures which have the characteristic LF shape but are affected by the RF.

The capacitances, the charge transferred through the gas gap per LF half cycle ($Q_{trans}$) and the averaged power ($P$) of the LF, RF and DF discharges are summarized in table 1.
It should to be noted that due to the curved electrode configuration in this work, the plasma cannot cover the available discharge area. To simplify the discussion, the influence of partial surface discharging on the electrical characterization of the discharges [42] is not considered in this study. The geometrically determined dielectric capacitance $C_{\text{diel}}$ can be estimated according to the equation:

$$C_{\text{diel}} = \varepsilon_{\text{PET}} \cdot \varepsilon_0 \cdot S / 2d,$$

(1)

where $\varepsilon_{\text{PET}}$ is the relative permittivity of the dielectrics (~3.4), $\varepsilon_0$ is the vacuum permittivity ($8.85 \times 10^{-12}$ F·m$^{-1}$), $S$ is the dielectric area which can be estimated according to width of the discharge area in figure 5, and $d$ is the thickness of the dielectrics (0.1 mm). To distinguish between $C_{\text{diel}}$ and the slopes of AB and CD in the $Q$–$V$ parallelograms, the latter will be referred to as the temporally-varied equivalent capacitance $\zeta_{\text{diel}} (t)$. Similarly, the geometrically determined reactor cell capacitance and the slopes of DA and CB in

![Figure 2. Voltage–current waveforms of (a) LF ($P_{\text{LF}} = 120$ W), (b) RF ($P_{\text{RF}} = 100$ W), (c) DF ($P_{\text{LF}} = 115$ W and $P_{\text{RF}} = 13$ W), (d) DF ($P_{\text{LF}} = 10$ W and $P_{\text{RF}} = 107$ W) and (e) DF ($P_{\text{LF}} = 95$ W and $P_{\text{RF}} = 100$ W) discharges.](image)
the $Q$–$V$ parallelograms are represented as $C_{\text{cell}}$ and $\zeta_{\text{cell}}(t)$, respectively.

The equivalent electrical circuit of the LF discharge is illustrated in figure 4(b). The effective capacitance of both the dielectrics is considered as a single lumped element $C_{\text{dell}}$ equal to the serial connection of two single layer capacitors. The LF discharge is represented as a gas capacitance $C_{\text{gas}}$ in parallel with a variable resistor $R_{\text{LF}}(t)$ [42, 43]. In this case, the time-averaged equivalent capacitance of the dielectrics

\[ \zeta_{\text{dell}} = C_{\text{dell}} \approx 170 \text{ pF} \]

\[ \zeta_{\text{cell}} = C_{\text{cell}} \approx 15 \text{ pF} \]

therefore $\zeta_{\text{gas}} = C_{\text{gas}} \approx 16 \text{ pF}$.

The equivalent electrical circuit of the DF discharge is illustrated in figure 4(c). In the DF discharges, the fast varying RF electric field works as an external capacitance which stores
electric charge. Here the equivalent capacitance of the RF field is represented as a temporally varied $\zeta_{\text{RF}}(t)$ which is in parallel with the gas gap capacitance $C_{\text{gas}}$. Moreover, a temporally varied ohmic resistor $R_{\text{RF}}(t)$ in parallel to $R_{\text{LF}}(t)$ is introduced to the equivalent circuit. Unlike the LF discharge in which the plasma can be regarded as a pure resistor $R_{\text{LF}}(t)$ during the ‘plasma-on’ period (AB and CD) of the DF discharges, the equivalent capacitance of the RF field $\zeta_{\text{RF}}(t)$ still exists in the circuit. In cases (d) and (e), the equivalent capacitance of the dielectrics $\zeta_{\text{cell}}(t)$ is lower than $C_{\text{cell}}$. In case (e), with a low RF power ($P_{\text{RF}} = 13$ W), the effect of the RF field during the discharging phase (AB and CD) is negligible. As a result, $\zeta_{\text{cell}}$ is not affected which yields the same value as $C_{\text{cell}}$.

### Table 1. Estimated values of capacitances, transferred charge and averaged discharge power of the LF, RF and DF discharges.

| Case | Power source | $P_{\text{LF}}$ (W) | $P_{\text{RF}}$ (W) | $S$ (mm$^2$) | $C_{\text{diel}}$ (pF) | $\zeta_{\text{diel}}$ | $\zeta_{\text{cell}}$ (nC) | $P_{\text{LF}}$ (W) | $P_{\text{RF}}$ (W) |
|------|--------------|---------------------|---------------------|-------------|------------------|----------------|---------------------|----------------|----------------|
| (a) | LF | 120 | 0 | 1125 | 170 | 170 | 15 | | |
| (b) | RF | 0 | 100 | — | — | — | — | | 82.5 | — |
| (c) | DF | 115 | 13 | 1125 | 170 | 170 | 20 | | 70 | — |
| (d) | DF | 10 | 107 | 600 | 90 | 70 | 35 | 35 | 7 | — |
| (e) | DF | 95 | 100 | 1190 | 180 | 140 | 30 | 280 | 65 | — |

**Figure 4.** (a) The DBD configuration with curved electrodes, (b) the equivalent circuit of the LF discharge, and (c) the equivalent circuit of the DF discharge.

**Figure 5.** Integrated discharge emission of Ar (750.4 nm and 751.5 nm) with 8 ms exposure time for LF, RF and DF discharges. The dashed region corresponds to the discharge area.

Furthermore, for the LF and DF discharges, the charge transferred through the gas gap per LF half cycle ($Q_{\text{trans}}$) can be deduced from the $Q$–$V$ plot [43]. For the RF discharge, the
plasma is in a continuous mode, the conductively transferred charge cannot be separated from the total measured charge. The transferred charge per half cycle of the LF discharge \((Q_{\text{trans}})\) is about 250 nC, see figure 3(a). For the DF discharge, with a high LF power \((P_{\text{LF}} = 115 \text{ W})\) and a low RF power \((P_{\text{RF}} = 13 \text{ W})\), \(Q_{\text{trans}}\) yields the same value (250 nC) as in the case of the LF discharge \((P_{\text{LF}} = 120 \text{ W})\), see figure 3(c). From figure 3(d), with a high RF power \((P_{\text{RF}} = 107 \text{ W})\) and a low LF power \((P_{\text{LF}} = 10 \text{ W})\), \(Q_{\text{trans}}\) is only about 35 nC due to the weak charge extraction by the LF voltage. With comparable high level of the LF and RF powers \((P_{\text{LF}} = 95 \text{ W}, P_{\text{RF}} = 100 \text{ W})\), \(Q_{\text{trans}}\) is increased to 280 nC which is probably induced by the increase of the charge density in the discharge area and thus the charge delivered to the surface, see figure 3(e).

The discharge power of the single LF or RF discharge \((P_{\text{LF}}\) or \(P_{\text{RF}}\) can be calculated according to the enclosed area of the Lissajous figures. However, the power measurement of the DF discharges is not possible because of the overlapping of adjacent RF waveforms, especially under the conditions with a low LF power, see figure 3(d). The averaged LF input power \((P_{\text{LF}})\) of the DF discharges can be estimated according to the FFT filtered Lissajous figures, as presented in table 1. The total DF discharge power \((P_{\text{LF+RF}})\) can be determined from the measurements of the voltage \((U_{\text{LF+RF}})\) and current \((I_{\text{LF+RF}})\) over one LF cycle \((T)\) [23]:

\[
P = \frac{1}{T} \int_{t}^{t+T} U_{\text{LF+RF}} \cdot I_{\text{LF+RF}} \, dt.
\]

Under these conditions, however, this standard power equation does not deliver a correct value for the DF discharge. This is probably due to the phase shift induced by the probes or the cables and the inaccuracy of the triggering in the acquisition of at least 2 LF periods on the RF signal. Therefore extra efforts are necessary to acquire correct current and voltage measurements to calculate the power.

### 3.2. Time-integrated plasma emission

The time-integrated 2D spatially-resolved emission of Ar (750.4 nm and 751.5 nm) with 8 ms integration time of the LF, RF and DF discharges are presented in figure 5. The discharges remain homogeneous and filament-free under all the tested conditions. Both the maximal and the total emission intensities are normalized to those of the LF discharge. As mentioned before, these emission lines are caused by the electron impact excitation from the ground state of Ar. The emission intensity therefore indicate the information of the high-energy electrons in the tail of the EEDF (13.5 eV and 13.3 eV in this study).

From figure 5, the LF discharge \((P_{\text{LF}} = 120 \text{ W})\) can be characterized as operating in ‘glow-like’ mode with maximal emission intensity close to the electrodes, as previously studied in [11] using nitrogen/oxygen gas mixtures. The RF discharge mode depends on the amplitude of the input power. At a low power \((P_{\text{RF}} = 100 \text{ W})\), the discharge only occupies the region from the centre of the electrodes to the gas outlet. This is mainly induced by the gas flow which displaces the ions and metastables in the inlet region and causes a preferential discharge in the centre and the downstream of the curved electrode where the density of ions and metastables is sufficiently high. The discharge is identified as \(\alpha\) mode with two layers, indicating the electron heating at the interface between the sheath and the bulk [44]. At a higher power \((P_{\text{RF}} = 150 \text{ W})\), the RF discharge transits into the \(\alpha\)-\(\gamma\) coexisting mode with two extra luminous layers restricted to the region near the centre of the electrodes. These regions are characterized as the \(\gamma\) mode where the maximal intensity is much higher than the emission of the \(\alpha\) mode. Due to the electrode configuration, the \(\gamma\) breakdown tends to ignite near the centre of the electrodes where the electric field is particularly high. The pure \(\gamma\) mode, however, cannot be observed under these conditions. The DF discharge with an extra low RF power \((P_{\text{LF}} = 115 \text{ W}, P_{\text{RF}} = 13 \text{ W})\) is similar to the LF discharge but with a higher maximal and total intensity. With a low LF power \((P_{\text{LF}} = 10 \text{ W})\) and a high RF power \((P_{\text{RF}} = 107 \text{ W})\), the discharge area is more expanded around the centre of the electrodes and has a much higher intensity than the 100 W \(\alpha\) mode RF discharge. Under the condition with a comparable high amplitude of the LF and RF power \((P_{\text{LF}} = 95 \text{ W}, P_{\text{RF}} = 100 \text{ W})\), the discharge intensity is enhanced in both the bulk and the regions adjacent to the electrodes.

### 3.3. Phase-resolved electron impact excitation

By controlling the delay between the camera gate and the voltage, the single shot ICCD emission of Ar (750.4 nm and 751.5 nm) with gate width of 5 ns was obtained at various phases of the voltage cycle. The emission profiles in the discharge area were integrated in the horizontal direction \((x)\) direction in figure 5), and the PROES was then obtained by collating and reconstructing the results. The spatiotemporal electron impact excitation \((E_{0i}(t,z))\) from the ground state to the excited state can be directly determined from the PROES \((I_{0i}(t,z))\) by the following equation [45]:

\[
E_{0i}(t,z) \propto I_{0i}(t,z) + \tau_{\text{eff}} \frac{dI_{0i}(t,z)}{dt},
\]

\[
\tau_{\text{eff}} = \frac{n_{q}}{k_{q} + n_{q}},
\]

where \(t\) is the time, \(z\) is the distance from the grounded electrode. \(\tau_{\text{eff}}\) and \(\tau_{n}\) are the effective and natural lifetime of the excited states, respectively. \(k_{q}\) is the quenching rate constant with the species \(q\) of density \(n_{q}\). In this study, \(\tau_{n}\) is taken as 24 ns for Ar 2\(p_{1}\) and Ar 2\(p_{3}\) states [46], \(k_{q}\) for both the excited states by O\(_{2}\) molecules is about \(7.4 \times 10^{-10} \text{ cm}^{3} \text{ s}^{-1} \) [46]. \(n_{q}\) is calculated from \(n_{q} = p_{q}/k_{q}T\), where \(p_{q}\) is the partial pressure of O\(_{2}\) (0.01 atm), \(k_{q}\) is the Boltzmann constant \((1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1})\) and \(T\) is the absolute temperature \((\sim 450 \text{ K})\) in this study.

In this way \(\tau_{\text{eff}}\) for the excited state of Ar 2\(p_{1}\) and Ar 2\(p_{3}\) is estimated at about 6.3 ns.

#### 3.3.1. LF discharge

Figure 6(I) shows the phase-resolved excitation of the single LF (200 kHz) discharge within one voltage cycle \((5 \mu s)\) with an input power \(P_{\text{LF}} = 120 \text{ W}\). The flat grounded electrode is situated at \(z = 0 \text{ mm}\), and the centred of the curved powered electrode is situated at \(z = 1 \text{ mm}\) where the gap distance is the smallest. Figure 6(II) shows...
the corresponding gas voltage, current and excitation rate integrated in the direction of z. The optical emission from Ar $^2p_1$ and Ar $^2p_3$ states in the discharge gap was observed for approximately 40% of the LF cycle. The apparent asymmetry of the excitation between two opposite polarities of the applied voltage is caused by the different shapes of the top and bottom electrodes (see figure 1). In this case and the following sections the excitation rates are normalized to the maxima of the LF excitation in figures 6(I) and (II). The characteristic transverse excitation intensity profiles corresponding to phase (1) and (2) in figure 6 are presented in figure 7.

As previously studied by Starostin et al for similar conditions in an N$_2$/O$_2$ gas mixture, the LF discharge is initiated by the Townsend breakdown mechanism [11]. The space charge produced from the preceding half cycle would affect the electric field and reduce the breakdown voltage at the ignition of the next discharge. In the stable discharge, the amplitude of the gas breakdown voltage was estimated at about 700 V. According to Townsend’s theory the electron density grows exponentially from the cathode to the anode producing a higher density of excited states and noticeable light emission in the anode region [47], and this is observed during phase (1) in figure 7. As the discharge develops, the positive space charge, initially accumulated in the anode region due to the difference in the mobility of electrons and positive ions, will start to affect the electric field profile. This will lead to an enhancement of the electric field and ionization rate in the direction to the cathode, resulting in the formation of a fast propagating ionization wave directed from the anode to the cathode [48]. Finally a significant space charge is formed by the positive ions that can localize the electric field in the instantaneous cathode region. The formation of the cathode voltage fall induces the gas voltage decrease and enhances the ionization rate close to the cathode where the electric field is at maximum. This leads to the transition from the ‘Townsend-like’ discharge into the ‘glow-like’ structure with a characteristic light emission profile, showing regions which can be attributed to the negative glow and the positive column [48], as shown in phase (2) in figure 7.

3.3.2. RF discharge. For the single RF discharge under atmospheric pressure, different ionization mechanisms including sheath expansion, sheath collapse and sheath gas breakdown can be involved [49, 50]. The dominant mechanism depends on the amplitude of the voltage or the input power [51]. In this study, the first breakdown of the plasma cannot be obtained by the single RF voltage, an additional LF voltage must be supplied in order to produce a stable RF discharge. According to the literature, the amplitude of electron oscillation $A$ can be estimated [44, 52]:

$$A \approx 1.414 \langle \mu_e \rangle \frac{V}{\omega d},$$

(5)

where $\langle \mu_e \rangle$ is the average electron mobility over the time varying electric field strength, $V$ is the voltage amplitude, $\omega$ (=2$\pi$f) is the angular frequency, $d$ is the gap distance. The electron mobility under standard atmospheric pressure for argon gas is about 430 cm$^2$/V s [47]. The influence of oxygen concentration (1%) on the electron mobility is ignored. In this way, the electron oscillation amplitude $A$ in the centre of the electrodes is estimated at about 0.5 mm which is smaller than the gas gap distance ($d = 1$ mm), indicating that the electrons are trapped in the plasma bulk.

3.3.2.1. $\alpha$ mode. As previously discussed in section 3.2, the RF discharge with an input power of 100 W can be attributed to the $\alpha$ mode. In the $\alpha$ mode, the discharge is sustained by the volumetric ionization processes in the bulk [44]. In this case the secondary ion–electron emission on the electrodes is not essential for the existence of the self-sustained plasma. The bulk electrons usually have a relatively low mean energy because of the low local electric field value; nevertheless, this Ohmic heating is sufficient to sustain the plasma [44]. Due to the high excitation energy threshold of Ar $^2p_1$ and Ar $^2p_3$ states (13.5 eV and 13.3 eV, respectively), the phase-resolved
The excitation rate of Ar in α mode is too weak to detect under these conditions.

3.3.2.2. α-γ coexisting mode. Figure 8 shows the phase-resolved excitation of the α-γ coexisting discharge with an input power of 150 W. Unlike the α mode discharge which is sustained by volumetric ionization processes, the γ mode discharge is sustained by the sheath gas breakdown allowing substantial ionic flux to the instantaneous cathode and a strong secondary electron emission [44]. The electron avalanches are created in the high electric field of the sheath with a particularly high excitation rate near the substrate, see figure 8.

3.3.3. DF discharges. The DF discharge mechanism is rather complex as the excitation is modulated by the time varying LF and RF electric field. At the same time, the ions, which respond to the average electric field mainly determined by the LF component, also play an important role in the discharge generation. Depending on the amplitude ratio of the LF and RF signals, the excitation dynamics and the discharge mechanism are expected to exhibit a different behaviour.

3.3.3.1. High LF power and low RF power. The time and space resolved DF excitation during one LF cycle with $P_{LF} = 115$ W and $P_{RF} = 13$ W is shown in figure 9(I). In this case, the maximum of DF gas voltage ($U_{LF}$) is about 900 V, while the amplitude of the RF voltage ($U_{RF}$) is about 150 V, see figure 9(II). Similar to the single LF discharge in figure 6, the DF excitation operates in a pulsed transient mode. The plasma ignites and extinguishes during each half LF cycle, and the light emission from Ar 2$p_1$ and Ar 2$^2$S states can be observed for approximately 40% of the LF period time. The LF gas voltage decreases after the breakdown, indicating the formation of a cathode voltage fall with a high ion density close to the cathode. Moreover, the oscillation of the excitation indicates the electric field modulation by the RF voltage.

3.3.3.2. Low LF power and high RF power. The time and space resolved excitation of the DF discharge during one LF cycle with $P_{LF} = 10$ W and $P_{RF} = 107$ W is shown in figure 11. Unlike the transient mode in the last section, under the present conditions, the discharge is in a continuous mode.
which is modulated by both the LF and the RF electric field. The amplitude of the LF voltage \( (U_{LF}) \) is about 250 V, while that of the RF voltage \( (U_{RF}) \) is about 300 V. Depending on the phase of the LF voltage, the RF oscillation results in a different discharge mechanism. Figure 12 shows the detailed time-resolved excitation during phase (1) and (2) of figure 11.

From figure 12(a), the discharge is in an approximately symmetrical ‘γ-like’ mode exhibiting a sheath breakdown in both the positive and the negative half cycle of the RF. As previously discussed, the ‘γ-like’ structure is caused by the electrons accelerated in the sheath electric field and the electron avalanches within the sheath [44]. The transient sheath electric field is determined by the total gas voltage \( (U_{LF} + U_{RF}) \) and the spatial distribution of ions which can only respond to the LF voltage due to their large mass. The ions from the preceding LF half cycle generates a self-induced electric field in the gas gap that neutralizes the electric field of the LF gas voltage at this moment (phase (1)). The discharge therefore is mainly driven by the RF electric field and exhibits a symmetrical ‘γ-like’ structure. Besides, from figure 12(a), the discharge in the bulk area can also be characterized. According to literature, the bulk discharge in this study can be attributed to the sheath expansion and the sheath collapse structures [50, 53]. The sheath expansion is induced by the excitation/ionization near the sheath edge caused by the energetic electrons which are accelerated by sheath oscillations toward the opposite electrode [44]. When the sheath collapses, the collision rate at atmospheric-pressure is so high that the generated electrons cannot instantaneously follow the retreating sheath merely by diffusion. Instead, a self-consistent electric field builds up to drive the electrons, creating a region of negative space charge. The resulting electric field accelerates the electrons toward the electrode and heats the electrons in the process [30, 54].

In figure 12(b), corresponding to phase (2), the amplitude of the total gas voltage \( (U_{LF} + U_{RF}) \) yields from \(-500 \text{ V} \) to \(100 \text{ V} \). Due to the difference in mobility, the electrons can follow the fast varying RF field, while the ions can only react to the LF field and can be regarded as approximately static within the RF period (~74 ns). The asymmetric LF component of the gas voltage leads to the ion accumulation near the instantaneous cathode (top electrode in this case). As a result, the electric field and thus the excitation rate in this phase exhibits an asymmetric structure. In the negative half cycle of the RF voltage, the sheath electric field and the ion-impact secondary electron emission are enhanced, resulting in a more pronounced excitation/ionization in the sheath and the bulk regions. In the positive half cycle of the RF voltage, the discharge is not obviously influenced in either the sheath or the bulk region compared to phase (1) in figure 12(a).

By applying a low LF power to the RF power, the ion flux and the electron energy in the sheath region can be manipulated.
This helps to increase the concentration of reactive species in the boundary layer of the electrode and to enhance the plasma chemistry compared to a single RF discharge, as discussed in [23]. Moreover, the LF voltage transfers charge in the space within each half LF cycle, which induces a more uniform distribution of ions and thus a more uniform plasma compared to the single RF discharge in which the ions can be regarded as static.

3.3.3.3. LF and RF power with comparable high amplitude. Figure 13 shows the time and space resolved excitation during one LF cycle with \( P_{LF} = 95 \) W and \( P_{RF} = 100 \) W. The amplitude of the LF voltage (\( U_{LF} \)) is about 700 V, while the RF voltage (\( U_{RF} \)) is about 300 V. The DF excitation reveals both the transient property of the LF breakdown and the continuous behaviour of the RF excitation. Under these conditions, three distinct regimes can be identified from the time-resolved excitation profile, as shown in figure 14.

In figure 14(a), the discharge is characterized as an ‘\( \alpha \)-like’ mode with excitation in the bulk during both the negative and the positive half cycle of the RF electric field. In this phase, the self-induced electric field of the spatial ions neutralizes the electric field of the LF gas voltage (\( U_{LF} \sim -500 \) V). The electron energy gain is mainly driven by the rapid RF electric field oscillation in the bulk [44]. The excitation therefore has an approximately symmetrical ‘\( \alpha \)-like’ mode which contains both the sheath expansion and the sheath collapse structures.

In figure 14(b), corresponding to phase (2), the spatial ions generate a higher electric field than the LF gas voltage (\( U_{LF} = -250 \) V ~ -100 V). As a result, the ‘\( \alpha \)-like’ excitation mode exhibits an asymmetrical structure with a more pronounced bulk excitation during the positive half cycle while no discharge is observed during the negative half cycle of the RF electric field.

As the discharge further develops, in figure 14(c), the polarity of the LF gas voltage reverses with an amplitude of about 150–200 V. The electric field in the gas gap, determined by both spatial ions and \( U_{LF} \), reaches a maximum. The sheath electric field and thus the ion-impact secondary electron emission is enhanced, resulting in the sheath gas breakdown with a particularly high excitation rate.

Under these conditions, the DF excitation exhibits the characteristics of both the LF and RF discharge, namely, a strong excitation/ionization near the instantaneous cathode, and an extended discharge period. Since the excitation is continuous even between the LF half cycles, the residual charges in the volume, which are generated and trapped by the RF voltage, contribute to the pre-ionization before the breakdown. A high
breakdown voltage, which may induce a rapid multiplication of electrons and lead to the formation of streamers or filamentary arcs, can be avoided. The DF excitation therefore could be an approach to improve the plasma uniformity together with a higher concentration of reactive species near the substrate.

According to the phase-resolved electron impact excitation caused by the high-energy tail of the EEDF, the single LF or RF discharge exhibits limited modification of the excitation dynamics. The DF excitation however reveals the capability of modifying the electric field and thus the EEDF [30]. By applying a low RF power to a high LF power, the electric field can be modified and the plasma uniformity can be improved by reducing the gas breakdown voltage and controlling the discharge development. By applying a low LF power to a high RF power, the ion flux and the electron energy in the sheath region can be manipulated, which helps to increase the concentration of reactive species in the boundary layer of the electrodes and to potentially improve the efficiency of plasma-assisted surface engineering processes. By combining an LF power and an RF power with comparable high amplitudes, the advantages of both discharges, namely, a strong excitation/ionization near the cathode, and an extended ignition period or a continuous excitation, can be achieved. The DF excitation therefore can be a potential approach to enhance the efficiency of surface functionalization or the productivity of thin film deposition via PECVD. Furthermore, the DF discharge can also bring a substantial advantage in the plasma-assisted gas phase chemical conversion in which high energy efficiency and high conversion efficiency are needed [55, 56]. This includes CO₂ decomposition into CO and O₂ in CO₂-neutral energetics cycle [56], methane conversion [57], nitrogen fixation [58], hazardous waste gases reduction

Figure 14. Detailed phase resolved electron impact excitation and corresponding gas voltage, LF discharge current and integrated excitation rate of (a) phase (1), (b) phase (2), and (c) phase (3) in figure 13.
etc. The energetic electrons are required to sustain the ionization, however the subsequent dissociative recombination is energetically an inefficient way of initiating chemical reactions [56]. The possibility of tuning the EEDF in the atmospheric-pressure DF discharge can boost the efficiency of plasma chemistry in molecular gases when compared to standard corona-type DBD [3, 60]. At the same time the non-thermal character of the plasma as well as the large area operation can enable efficient utilisation of catalytic surfaces.

4. Conclusions

In this study, a homogeneous dielectric barrier discharge was obtained in atmospheric-pressure Ar/O2 gas mixture excited by a dual frequency (200kHz + 13.56 MHz) power source system for the first time. Electrical characteristics and phase-resolved optical emission spectroscopy (PROES) with nanosecond time resolution were employed to investigate the excitation dynamics and the plasma generation mechanism. The DF excitation results in a time-varying electric field which is determined by the total LF and RF gas voltage and the spatial ion distribution which only responds to the LF component. The LF component transfers the charge from the bulk to the surface and leads to excitation/ionization processes near the substrate, while the RF component allows charge trapping in the gas gap. This mechanism is supported by the analysis of Lissajous figures (Q–V plots) for the equivalent capacitances and the transferred charge in the gas gap. Either single LF or single RF discharge has limited modulation of the excitation dynamics, while the DF discharge reveals capability of temporally modulating the electric field and thus the excitation/ionization mechanism by tuning the amplitude ratio of the superimposed LF and RF signals. The DF discharge exhibits potential applications in plasma-assisted surface processing as well as in other fields such as plasma-assisted gas phase chemical conversion in which control of the electron energy distribution function (EEDF) is required.

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