Influence of a square pulse voltage on argon-ethyl lactate discharges and their plasma-deposited coatings using time-resolved spectroscopy and surface characterization

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ABSTRACT
By comparing time-resolved optical emission spectroscopy measurements and the predictions of a collisional-radiative model, the evolutions of electron temperature (T_e) and number density of argon metastable atoms (n(Ar^m)) were determined in argon-ethyl lactate dielectric barrier discharges. The influence of a square pulse power supply on T_e, n(Ar^m), and the discharge current is evaluated and correlated to the chemistry and the topography of the plasma-deposited coatings. Pulsed discharges were found to have shorter (100 ns) but stronger (1 A) current peaks and higher electron temperatures (0.7 eV) than when using a 35 kHz sinusoidal power supply (2 µs, 30 mA, 0.3 eV). The n(Ar^m) values seemed rather stable around 10^{11} cm^{-3} with a sinus power supply. On the contrary, with a pulse power supply with long time off (i.e. time without discharge) between each pulse, a progressive increase of n(Ar^m) from 10^{11} cm^{-3} up to 10^{12} - 10^{13} cm^{-3} was observed. When the time off was reduced, these increases were measured in sync with the current peak. The chemical composition of the coatings was not significantly affected by using a pulse signal whereas the topography was strongly influenced and led to powder formations when reducing the time off.

KEYWORDS
dielectric barrier discharge (DBD), electron temperature, argon metastable, time-resolved optical emission spectroscopy, pulsed discharge, ethyl lactate

CITATION

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1 INTRODUCTION

Over the last decade, many studies have examined the influence of pulse input signals on the plasma polymerization dynamics [1–4]. The general observation is that, thanks to their short but
strong discharge current peaks accompanied by long time off, pulse discharges usually lead to a more chemically conventional polymerization, which minimize plasma-induced crosslinking effects. Electrical models have further demonstrated that they can also significantly improve the power transfer efficiency from the power supply to the plasma [5,6]. In addition, the duty cycle in pulse discharges represents a very interesting knob to control plasma-on and plasma-off times, which can obviously play a very important role in the plasma polymerization dynamics.

To compare different discharges in terms of energy and chemistry, most studies focus on determining key plasma parameters such as the electron number density \(n_e\) and temperature \(T_e\) and the number density of reactive species [7–10]. When working at atmospheric pressure, spectroscopy is usually the method of choice to extract those parameters because it is non-invasive and provides easy-to-use data in a very short period of time [11]. In particular, optical emission spectroscopy (OES) can give access to real time emission spectra of atoms and molecules in the plasma during their transitions from an excited state to a lower energy state. The emission intensities gathered by OES can then be combined with a collisional-radiative (CR) model that can compute the populations of the excited states leading to the observed emission intensities. The strategy consists in solving a set of particle balance equations considering all population and depopulation processes for at least two energy levels to determine their number density ratio and thus the corresponding line ratio. In most cases, the electron temperature is the only unknown variable in this ratio: \(T_e\) can therefore be extracted from a simple line ratio measurement [12–15]. However, when stepwise excitation processes involving long-lived species such as metastable states start to play an important role in the population kinetics, line ratios become also dependent on the population of these long-lived species. In these cases, more than one line ratio is necessary to determine \(T_e\) and the population of this long-lived species. The most accurate solution is then to exploit a maximum number of emission lines originating from various excited states [9,15,16].

In the literature, only a few studies have reported values of the electron temperature and the number densities of long-lived species in pulse discharges at atmospheric pressure. Balcon et al. determined \(T_e\) in argon discharges powered by a pulse RF generator by using line ratio measurements [7]. Panousis et al. investigated the densities of active species using OES in the afterglow of a nitrogen dielectric barrier discharge (DBD) using two modes of pulse high voltage excitation [17,18]. Tao et al. estimated \(T_e\) and \(n_e\) in a nanosecond-pulse air DBD from calculations. [19]. Walsh et al. used time-resolved optical diagnostics to characterize a 3-nanosecond-pulse argon microplasma in terms of gas temperature, electron density and excitation temperature (with similar trend as \(T_e\)) [20]. Among those works, none was completed under plasma enhanced chemical vapor deposition conditions, which means that it is not possible to convincingly correlate those fundamental findings to the physico-chemical properties of plasma-deposited coatings.

This work examines the influence of a square pulse power supply on an argon-ethyl lactate dielectric barrier discharge. When used as precursor, ethyl lactate has already shown its potential to deposit poly(lactic acid)-like coatings that could be used in biomedical applications.[21–23] This study first aims at evaluating the influence of the excitation mode (with various duty cycles) on the electron temperature \((T_e)\), number density of argon metastable atoms \((n(\text{Ar}^m))\), and the discharge current \((I_d)\). These discharge characteristics were obtained from the combination of OES, an argon collisional-radiative model, and a detailed analysis of the electrical response of the discharge. The collisional-radiative model used in this work is based on a detailed analysis of 4p-to-4s argon transitions [10]. It considers electron-impact processes, excitation transfers, spontaneous emission, collision quenching, and radiation trapping effects [10,24]. The second part of the work focuses on correlating these discharge characteristics with the physicochemical properties of the plasma-deposited layers. The topography of the coatings was characterized by atomic force microscopy, while their chemistry was assessed using Fourier Transform Infrared spectroscopy and X-ray Photoelectron spectroscopy.
2 EXPERIMENTAL SETUP

2.1 Atmospheric pressure plasma conditions

2.1.1 The plasma reactor

The plane-to-plane dielectric barrier discharge reactor used, previously described elsewhere, is schematized Figure 1 [10]. Briefly, argon (Ar, 99.999 %, Alphagaz 1) was used to fill the enclosure at atmospheric pressure (760 Torr) and then introduced at a flow rate of 2 L/min between the 3.9 × 3 cm² electrodes covered with two 0.64 mm-thick alumina plates used as dielectrics. The gas gap (g) was varied between 1.1 and 2.1 mm but to facilitate the reading, those gas gaps will later on be referred to as 1 and 2 mm respectively.

![Figure 1. Scheme of the experimental setup](image)

2.1.2 The power supplies

For low-frequency measurements, a 35 kHz sinusoidal voltage was generated (Agilent, LXI) and amplified with a linear amplifier (Crest Audio model 4801) whose output was applied to the primary winding of a transformer (Boige et Vignal, ratio 1:30). The applied voltage was measured using a high-voltage probe (Tektronix P6015A) and a 220 nF capacitor in series with the cell discharge was used to monitor the electric charge.

Alternatively, a square pulse voltage was generated (Agilent, LXI) at 10 kHz, with duty cycles $(DC (\%) = \frac{t_{ON}}{t_{ON}+t_{OFF}} \times 100)$ of 1, 10, and 50 %. It was connected with a high voltage pulse generator (Directed Energy Inc., PVX-4110) that could send unipolar square voltage with a fixed rising time of 130 ns and amplified with a Technix power supply (0-10 kV, 0-120 mA, SR 10KV-1.2kW).

A digital oscilloscope (Teledyne Lecroy, WaveRunner 8404M-MS, bandwidth: 4 GHz, 40 GS/s) was used to visualize these signals. The discharge currents were obtained by subtracting the displacement currents (due to cable, dielectric, and gas capacitances), which were extracted by applying the same voltage without discharge (in air) to the total current measured with a discharge [6]. The dissipated discharge power $P_w$ per surface unit (W/cm²) was calculated using Q-V Lissajous plots [25]. Correlation between coating properties and plasma experimental parameters was performed by calculating the energy density $E$ transmitted to the atoms and molecules in the plasma (corresponding to the energy per volume unit) using equation 1, with $P_w$, g and t being the dissipated...
power by surface unit ($P_w = P/S$), the interelectrode gap and the mean residence time of atoms and molecules in the plasma, respectively [22].

$$E(J \cdot \text{cm}^{-3}) = \frac{P_w \text{W} \cdot \text{cm}^{-2}}{g \text{ cm}^{-1}} \cdot t_r(s)$$

(1)

2.2 Optical emission spectroscopy (OES)

OES was used to analyze the argon discharge in deposition conditions (with ethyl lactate) to study the variations depending on the way the discharge was powered up.

The optical system comprised a spectrometer from Princeton Instruments (Acton) coupled with a PI-Max3 camera also from Princeton Instruments. An optical fiber was used to collect the light coming from the plasma perpendicularly to the 1 mm-thick quartz block guiding the gas flow at about 1 cm from the gas entrance in the plasma zone (and 2 cm from its exit). A BLZ 300 monochromator was used to gather spectra from 650 to 950 nm. For each plasma condition studied, a set of time resolved OES spectra was measured. For the discharges obtained using low frequency sinusoidal voltage generator, each time-resolved spectrum was recorded successively with 100 ns gate, so that the whole period of time around the discharge peak was covered. For all analyses made using a pulse power supply, each spectrum was recorded successively for a 20 ns gate to observe the evolution during the faster discharge current peak. Each spectrum represents the sum of 1000 spectra with the 35 kHz sine waveform and 70 spectra with the square pulse waveform taken at the same time with respect to the current voltage curves. For each spectrum, the wavelength axis was centered according to the 763 nm peak and the overall spectral intensity was corrected to take into account for the optical response of the optical fiber and spectrometer.

2.3 Collisional-radiative (CR) model

The most probable pair of electron temperature ($T_e$) and number density of argon metastable atoms ($n(Ar^m)$) was determined through a comparison between measured emission intensities from Ar 3p4p-to-3p4s transitions (2p-to-1s in Paschen notation) and those calculated using an argon collisional-radiative model described elsewhere [10,24].

Briefly and using the Paschen notation, this model solves the particle balance equation for the 10 argon 2p levels. It takes into account the following population processes: 1) electron impact with a ground state argon atom to populate a 2p level; 2) electron impact with an excited 1s state to populate a 2p level; 3) excitation transfer with 2p-ground state collisions to populate another 2p level; 4) radiation trapping of argon 2p-to-1s transitions. The depopulation processes considered are: 1) spontaneous emission of argon 4p states; 2) collisional quenching of argon 2p states by ground state argon atoms and impurities. Of note, argon 1s states were treated as a block (i.e. their populations were assumed equal for all conditions).

The measured emission intensities were then fitted with this model using the electron temperature ($T_e$) and the number density of Ar 1s states ($n(Ar^m)$) as the only adjustable fitting parameters. The theoretical emission intensities were calculated over a wide range of $T_e$ and $n(Ar^m)$ values and the relative standard error between measured and theoretical emission intensities was calculated. The values of $T_e$ and $n(Ar^m)$ that minimized the relative standard error were then attributed to the corresponding set of experimental conditions with an error of ±5% attributed to these $T_e$ and $n(Ar^m)$ calculated values. Twelve argon 2p-to-1s transitions were considered based on availability of cross sections for the processes involved and the spectral resolution of the monochromator. Only the lines distinguishable from the background noise by at least 50% of the calculated background were considered in the fitting operation. $T_e$ and $n(Ar^m)$ were not considered when less than 12 lines were available from the measured spectra (due to low emission signals). Finally, the pairs of $T_e$ and $n(Ar^m)$
were averaged between three timepoints (t0 - gate, t0, t0 + gate) and were plotted as a mean with the corresponding standard deviation.

2.4 Surface characterization

The glass coated samples were divided in three identical areas of about 1×1 cm\(^2\) along the gas flow (as represented by the red crosses in Figure 1), to follow the surface chemistry of the ethyl lactate plasma polymers (EL-PP) throughout various plasma regions. Three measurements were performed on each of these 1 cm\(^2\) sample areas to ensure reproducibility.

2.4.1 Atomic Force Microscopy (AFM)

A Dimension 3100 Atomic Force Microscope from Digital Instruments was used in tapping mode supplied with a NCHV probe from Bruker. Surface topography of 10 x 10 µm\(^2\) representative AFM images were analyzed using NanoScope Analysis v.1.40 software from Bruker. The average roughness (Ra) was calculated for all surfaces.

2.4.2 X-ray Photoelectron Spectrometry (XPS)

A PHI 5600-ci spectrometer (Physical Electronics) was used with an anode aluminum standard source (1486.6 eV) operated at 200 W and a charge neutralizer to record X-ray photoelectron survey spectra between 0 and 1200 eV.

2.4.3 Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR)

Infrared spectra were recorded from 4000 to 400 cm\(^{-1}\) with a spectrometer (Cary 660, Agilent Technologies, DLaTGS, KBr) equipped with a SplitPeaTM ATR microsampler (UNS-ATR-0E, Harrick Scientific Products, Si crystal). More details can be found elsewhere.[10]

3 RESULTS AND DISCUSSION

3.1 Discharge electrical characteristics

When gathering the electrical data of the discharges obtained using a pulse voltage, large exponentially decreasing oscillations were observed on the measured current response following the voltage rising and falling edges. This phenomenon was identically noticed by Boscher et al. who attributed it to a discharge peak surrounded by satellite peaks due to the discharge breakdown.[4] However, in the present study, the same oscillations were observed when the discharge was off. It can therefore be hypothesized that this response is in fact due to parasitic capacitive coupling from the circuit (enhanced by the fast voltage variation), which is hiding the actual discharge current peak. In this context, our results revealed part of those oscillations can be removed after subtraction of the displacement current component from the total measured current to obtain the corresponding discharge current, which is how the data was treated to obtain Figure 2. In addition, impedance matching could help lessening these oscillations [5,6].

The first obvious difference observed when using a pulse power supply was the duration of the discharge current peak which, as expected, was much shorter (around 100 ns) compared to a more standard low frequency sinus voltage (a few microseconds). This observation is in agreement with previous studies from several groups, which all reported current peaks of about 100 ns [4,6,5]. This fast discharge peak was explained by Pan et al. by the fast increase of the charged particle density on the dielectric during the discharge current peak, which led to an increase of the dielectric voltage,
and consequently to a decrease of the gas voltage until the discharge can no longer be sustained [26].

A second difference is that, compared to a sinus study in similar conditions, a much stronger current was observed, with maximum current values of 1 to 2 A. This was also reported by Liu and Neiger with a current of 0.2 A (when using 2 kV, air, 50 mbar, 4 mm gap) [5] and by Laroussi et al. with a current of 20 to 30 A (when using 10 kV, helium + 1 % air, atmospheric pressure, 2.5 mm gap) [6].

Figure 2. Voltage-current curves of argon-ethyl lactate discharges generated using 1 mm gap and a 10 kHz square pulse voltage with duty cycles of a) 50 % and b) 1 %. The current plotted (in red) is the calculated discharge current and the OES gate (in blue) corresponds to the exposure time of the camera linked to the spectrometer.

Figure 2 displays the voltage (in black) and discharge current (in red) curves synchronized with the OES camera gate (in blue) for discharges supplied with a 10 kHz square pulse voltage using duty cycles (DC) of 50 % (a) and 1 % (b). As shown by this figure, the current peak following the voltage increase from 0 to 2 kV was similar in time and intensity at 50 % and 1 % duty cycles, with a 1.2 A peak appearing about 300 ns after the voltage reached 2 kV and lasting for about 130 ns. A similar peak of 1.2 A was observed 300 ns following the drop of voltage from 2 to 0 kV when using a 50 % DC. However, when reducing the duty cycle down to 1 %, the current peak reached its minimum at 1.8 A 10 ns before the voltage reached 0 kV with a peak duration of only 70 ns. Interestingly, this phenomenon was also observed when using a 10 % DC since the second discharge peak appeared 280 ns after the voltage drop (compared to 300 ns during the positive half cycle). Table 1 shows the evolution of the duration of the discharges (tON d1/2) and the duration between the discharges (tOFF 1-2/1-2) for all investigated conditions. The calculated tOFF 1 2 value corresponds to the voltage ON time (tON) or half period in sinus subtracted by the discharge ON time of the first peak (tON d1). On the other hand, the calculated tOFF 2-1 value corresponds to the voltage OFF time (tOFF) (or half period in sinus) subtracted by the discharge ON time of the second peak (tON d2). This table demonstrates that by reducing enough the duty cycle, the time off between two discharges becomes so low that it influences the behavior of the second discharge. For the 1 % DC 10 kHz pulse power supply with a 1 mm gap, the shortest theoretical time off (1 % of the half period-duration of the first discharge, cf. Calc. tOFF 1-2 in Table 1) was 900 ns as compared to 49.9 µs when using the same frequency at 50 % DC. This corresponds to the calculated time after which the second discharge peak should appear. Instead, this peak appeared only 600 ns after the first one, and with an intensity 1.5 times greater. With voltage pulses of about 500 ns in both Liu’s [5] and
Laroussi’s [6] studies, the second current peaks were also observed earlier than the ones happening after the voltage increase. This can be explained by a lower breakdown voltage for the second discharge due to the presence of residual charged species from the previous discharge in the gas gap and/or at the surface of the dielectric[6]. This was corroborated by the fact that this phenomenon was even stronger when increasing the interelectrode gap. Lu et al. also reported a significant influence of the pulse width on the discharge current, in particular with pulse widths or pulse breaks below 600 ns when using a 1 kHz pulse repetition and a 6 mm gap.[27]

Table 1. Duration of the first (t_{ON d1}) and second (t_{ON d2}) discharge peaks. Comparison between the calculated and the observed values of the duration between the first and second discharges (t_{OFF 1-2}) and between the second discharge and the first one of the next cycle (t_{OFF 2-1}) for all conditions studied.

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<th>Waveform &amp; frequency</th>
<th>DC (%)</th>
<th>Gap (mm)</th>
<th>Voltage ON/OFF duration (µs)</th>
<th>Discharge ON/OFF duration (µs)</th>
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<td>Square pulse 10 kHz</td>
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3.2 Plasma composition

Figure 3a displays a typical set of time-resolved OES spectra taken around the discharge current peak during the deposition of ethyl lactate plasma polymers when using a pulse power supply at 10 kHz with a 50% duty cycle (EL-PP-Pulse-10 kHz-50 % DC). The emission lines visible between 650 and 950 nm originated from transitions from the excited levels 2p1 to 2p10 in the Paschen notation with energies between 12.91 and 13.48 eV), to the metastable (1s_{3} and 1s_{5}) and resonant (1s_{2} and 1s_{4}) levels with energies between 11.55 to 11.83 eV as detailed in [10]. The intensity of each emission line increased up to a maximum (i.e. maximum population of 2p species) near the highest current density zone and decreased once the discharge current peak extinguished. As mentioned in [10], this peak intensity variation was identical for both current peak directions (positive and negative) and rather symmetrical around the discharge peak time when using a sine waveform.
Figure 3. Time-resolved optical emission spectra of argon-based discharges. Spectra recorded during the deposition of a) EL-PP-Pulse-10 kHz-50 % DC with the peak attributions and b) EL-PP-Pulse-10 kHz-1 % DC. The gap is fixed to 1 mm.

Comparing this trend with a square pulse power supply at 10 kHz, a similar behavior was observed when using duty cycles of 50 % and 10 %. However, as shown in Figure 3b, when reaching a duty cycle of 1 %, the increase and decrease slopes of the emission intensities did not exhibit the same behavior between the first positive current peak (first one after the long off period) and the second one. Similarly to the behavior with a 50 % duty cycle, the rise and decline of the intensities with a 1% duty cycle had a comparable variation rate during the positive current peak. When looking at the negative current peak (coming only 900 nanoseconds after the positive one), in concordance with the discharge current behavior observed, the concentration of emitting Ar species increased much faster compared to the one occurring during the first peak, while the decrease variation rate was similar to what is observed at 50% or 10% duty cycle.

Of note, when using the 1% duty cycle, the lines linked to a deexcitation from the 2p\(_2\) level (at 696.54, 727.29, 772.42, and 826.45 nm as detailed in [10]) reached approximately the same maximum intensity in both cycles whereas the other lines had generally a lower maximum intensity during the negative cycle compared to their positive homologues. This means that the Ar 2p\(_2\) species seems to be the only ones to reach approximately the same population in both discharges when working at 1% duty cycle.
3.3 Variation of the electron temperature and the argon metastable density with the current

By comparing the measured and calculated line emission intensities using a collisional-radiative model, the spectra presented in 3.2 were converted into variations of the electron temperature $T_e$ and argon metastable number density $n(\text{Ar}^m)$.

![Graph](image)

Figure 4. Correlation of the electron temperature (blue triangles) and argon metastable number density (black circles) with the discharge current peak (red curve) using a 2 kV$_{pp}$ sinus voltage (black curve) at 35 kHz using a 1 mm gap. The total intensity gathered by the spectrometer is plotted in green. a) Positive half cycle and b) negative half cycle of the same discharge.

The evolution of $T_e$ (top graphs, blue triangles) and $n(\text{Ar}^m)$ (top graphs, black rounds) for a discharge supplied by a 2 kV$_{pp}$ sinus voltage at 35 kHz (Figure 4) and a 10 kHz 50 % DC square pulse voltage (Figure 5) are displayed. For comparison, the total light emission intensity (integration over all wavelengths between 650 and 950 nm) is also shown (top graphs, green area). In the bottom graphs, the corresponding current-voltage curves are plotted over the same time scale. In both power supply conditions (all using a 1 mm gap) and for both half cycles, the increase of light emission was observed simultaneously with the increase of the discharge current peak.

The maximum population of argon metastable atoms during the discharge ranged between $10^{11}$ cm$^{-3}$ for DBD with the low frequency sinus voltage power supply and $10^{12}$ cm$^{-3}$ for DBD with the pulse power supply. These values are in agreement with the $10^{11}$ to $10^{13}$ cm$^{-3}$ values reported by Massines et al. in argon-ammonia discharges over a wide range of frequencies, and thus of discharge regimes [28].

In addition, the maximum observed current density were around 2 mA/cm$^2$ for the low frequency sinus discharge and went up to 100 mA/cm$^2$ for the discharges obtained with the pulsed power supply. According to the maximum current densities reviewed by Massines et al. for the different regimes observed in atmospheric discharges, this could indicate a transition from a glow discharge to a glow-like discharge regime described by Starostin et al. [28,29] This would also be in concordance with the shorter discharge duration and higher currents observed.

The mean electron temperature was around 0.3 eV for a discharge with a 35 kHz sinus power supply and went up to 0.7 eV for a DBD with a 10 kHz pulse signal. The higher $T_e$ values observed in pulse discharge could be attributed to many factors, including higher electric fields or a change in the ionization kinetics. These $T_e$ values are slightly lower than those usually reported for low frequency and pulse DBD (between 0.8 and 8 eV), although a radiofrequency DBD can go down as low as 0.5 eV [28,30]. In argon-based discharges at atmospheric pressure, $T_e$ values are usually around 1 eV. For instance, the electron temperature was estimated to 1.3 eV in pulse radiofrequency
argon discharges operated in a glow mode [7]. Similarly, Zhu et al. reported electron temperatures between 0.8 and 1.6 eV in argon micro discharges sustained by microwave electromagnetic fields [31]. Sarani et al. used a line ratio technique to estimate an electron temperature of 0.97 eV in an argon plasma jet [32]. Interestingly, they noticed that adding water vapor to the feed gas led to a sharp decrease of $T_e$ (down to 0.2 eV). This is consistent with the lower $T_e$ observed in the present study that could be due to the presence of a precursor.

Since $T_e$ and $n(Ar^m)$ remained fairly constant for the DBD with a sinus power supply, one concludes that it is mostly the electron density (linked to the discharge current) that varies during the discharge ignition and extinction. On the other hand, for the DBD with a pulse voltage with 50% DC, all parameters ($n_e$, $T_e$, and $n(Ar^m)$) seem to vary during the discharge evolution. While higher electron temperatures can be observed early in the discharge cycle, these values decreased when the electron density and thus the number density of argon metastable increased. Overall, in these conditions, $T_e$ and $n(Ar^m)$ thus vary by compensating one another. A similar behavior was previously reported for helium DBDs [9,33] and argon-ammonia discharges [10,24].

Figure 5. Correlation of the electron temperature (blue triangles) and argon metastable number density (black circles) with the discharge current peak (red curve) for a square pulse discharge powered by a 2 kV voltage (black curve) at 10 kHz with a 50% duty cycle using a 1 mm gap. The total intensity gathered by the spectrophotometer is plotted in green. a) Positive half cycle and b) negative half cycle of the same discharge.

Figure 6 presents the results for a 10 kHz pulsed discharge using a 1% duty cycle and a 1 mm gap. The mean electron temperature measured with the CR model for the 1% duty cycle was the same as the 50% DC 0.7 eV. As for the mean metastable number density, higher values up to about $2\times10^{12}$ cm$^{-3}$ were achieved.

As mentioned in 3.1, when using such a low duty cycle, the second current peak was formed in advance compared to the positive one. This phenomenon was also observed in the optical emission (Figure 6 top) that reached its maxima simultaneously with the discharge current peaks (Figure 6 bottom).

This was translated by two behaviors in terms of electron temperature and metastable density. While the positive peak showed a synchronized increase of both $T_e$ and $n(Ar^m)$ immediately after the discharge current, the second peak revealed the reverse trend for $T_e$ with again a rise for $n(Ar^m)$. The behavior of the second peak appears to be similar to the one described above for 50% DC (and thus smaller off times between each discharge peaks). This observation suggests the presence of a memory effect due to residual active plasma species between the first positive and the second negative discharge peak and its absence between the second negative and the next positive
These residual active species would be either at the surface of the dielectric that charged during the previous discharge (leading to its extinction but facilitating its next ignition after the change of polarity) or inside the gas gap, under the form of long lifetime species (i.e. metastable). For example, metastable helium atoms are typically characterized by lifetimes of a few milliseconds under atmospheric-pressure conditions [35] such that their creation in a DBD can facilitate the development of subsequent discharges by lowering the breakdown voltage. For metastable argon atoms at atmospheric pressure, assuming that these species are mostly lost through the formation of excited dimers (singlet and triplet) \( \text{Ar}^m + \text{Ar} + \text{Ar} = \text{Ar}_2^* + \text{Ar} \), their pressure-dependent lifetime decreases to 0.19 \( \mu \)s when we consider the law given by Coll: \( \tau_A = 1/(9*p^2) \) (where \( p \) is the pressure in mmHg) [38] or 0.24 \( \mu \)s according to Fig. 8 from [39]. This means that these species would barely be present for the second discharge peak, which happened 0.5 to 0.6 \( \mu \)s after the first one at 1\% DC (cf. Table 1). However, the metastable triplet dimers triplet \( \text{Ar}_2(3^*) \) also represents a significant energy reservoir in argon-based discharges at high pressure. In particular, these species were reported to have a pressure-independent lifetime of about 3 \( \mu \)s [36,38,39]. This means that \( \text{Ar}_2(3^*) \) species are likely to play an important role in the formation dynamics of argon-based DBDs. In particular, as discussed in [40], these species could be involved in the formation dynamics of charged species either by Penning ionization or by electron-impact ionization with very low-energy electrons. In both cases, this would imply much lower \( T_e \) values than in plasmas relying on electron-impact ionization on ground and metastable argon atoms. This is in very good agreement with our experiments for both sinus and pulse voltage waveforms. The contribution of residual \( \text{Ar}_2(3^*) \) species at 1\% DC is further supported by the fact that no difference between the first positive and second negative discharge peaks was observed at 10\% DC, which corresponds to a 9.9 \( \mu \)s time off between two similar discharges. This confirms that the metastable \( \text{Ar}_2(3^*) \) species helping in the development of the second negative discharge at 1\% DC were mostly gone before the development of the subsequent first positive discharge for which the time off was much larger than 10 \( \mu \)s.

The formation of dimer ions \( \text{Ar}^+ + \text{Ar} + X = \text{Ar}_2^+ + X \) was also reported to happen in less than 10 ns in argon plasmas at atmospheric pressure [28,40]. This could imply that \( \text{Ar}_2^+ \) is the dominant positive ion, even in our plasma enhanced chemical vapor deposition experimental conditions. For example, if one considers the reaction rates from [40], and the \( \text{Ar} \) and \( \text{Ar}^+ \) densities proposed in [28]: assuming a reaction rate of 5\( \times \)10\(^{-10} \) cm\(^3\)/s for Penning ionization, a population of argon metastable atoms of 10\(^{12} \) cm\(^{-3} \) (in case of a 10 kHz square pulse voltage), and a precursor population of 5.8\( \times \)10\(^{15} \) cm\(^{-3} \) (250 ppm), this yields a production rate of the ethyl lactate ion (EL+) 2.9\( \times \)10\(^{18} \) cm\(^{-3} \)·s\(^{-1} \) via Penning ionization. On the other hand, assuming a population of charged species of 10\(^{11} \) cm\(^{-3} \) for glow discharges and a reaction rate of 2.5\( \times \)10\(^{31} \) cm\(^6\)/s for the production of dimer ions by collisions with two \( \text{Ar} \) atoms at a population of 2.3\( \times \)10\(^{19} \) cm\(^{-3} \), this leads to a creation rate of \( \text{Ar}_2^+ \) of 1.3\( \times \)10\(^{19} \) cm\(^{-3} \)·s\(^{-1} \). Considering then a reaction rate of 10\(^{-32} \) cm\(^9\)/s for the formation of \( \text{Ar}_2(3^*) \) with a three-body reaction described in the previous paragraph, a 5.3\( \times \)10\(^{18} \) cm\(^{-3} \)·s\(^{-1} \) production rate would be expected. Of course, these calculations do not take into account any loss reaction nor synthesis through multiple routes.
When increasing the gap from 1 to 2 mm while using a 10 kHz signal with 1 % duty cycle, the first current peak was observed 500 ns after the voltage reached 2 kV and reached a maximum of 0.5 A as shown in Figure 7. This was 200 ns later and less than half of the maximum current value with respect to the homologous discharge obtained using a 1 mm gap. In addition, the discharge achieved with a 2 mm gap lasted about 230 ns, which is 100 ns more than when using a 1 mm gap. The light emission observed by OES also lasted longer (about 500 ns for the first peak) and was observed simultaneously with the current peak. The second discharge peak was observed barely 200 ns after the first one, which corresponds to 100 ns after the beginning of the voltage drop and 30 ns before it reached 0 V. It lasted 120 ns according to the emission peak. The mean values of electron temperature and metastable species density were 0.6 eV and $10^{12}$ cm$^{-3}$, respectively.

During the first current peak, the metastable density was close to $10^{10}$ cm$^{-3}$ until the maximum of current was reached. Right after, the n(Arm) rose around $10^{12}$ cm$^{-3}$ for 140 ns, and then went slowly down to $4 \times 10^{10}$ cm$^{-3}$ once the current was back to 0 A. When the second discharge peak arose, the metastable number density increased again up to $10^{12}$ cm$^{-3}$ for at least 120 ns. Meanwhile, $T_e$ stayed stable around 0.6 eV before going up to 0.7 eV synchronized with the decrease of the first metastable population peak, once the current went down to zero. During the second discharge peak, no variation of $T_e$ was observed, it stayed around 0.6 eV.

The strong influence of the gap increase observed on the current density can be explained by a higher breakdown voltage leading to a delayed first discharge peak (appearance 200 ns later at 2 mm compared to 1 mm). By delaying the first current peak, the time between both discharges decreased, which means that even more metastable species were still present in the gas, hence enabling a stronger second discharge. This is supported by the fact that in the case of a 10 kHz, 1 % DC with a 2 mm gap, the emission from the discharge never became null in between both discharges.
3.4 Coating properties

3.4.1 Chemical composition

On a coating point of view, the use of a pulse power supply did not have a strong influence on the layer topography or chemistry. XPS analyses of the different coatings are presented in Figure 8 in terms of %oxygen / %carbon ratio.

Figure 8. Oxygen-to-carbon ratio obtained from XPS for coatings obtained with either a 35 kHz sinewave or a 10 kHz square pulse power supply as a function of the energy density dissipated in the plasma.
No major difference in composition between the coating obtained using a 35 kHz sinus power supply and the ones achieved using a 10 kHz square pulse power supply, even at lower duty cycles. A slight decrease of the oxygen content (relatively to the carbon content) was observed when the gap increased from 1 to 2 mm. However, it is worth mentioning that the energy densities were also slightly higher than the ones achieved at 1 mm, since the breakdown voltage at 2 mm was above the voltage initially used at 1 mm. This difference in energy would likely influence the coating deposition towards a more carbonated coating as already described in [22].

Figure 9. Infrared spectra of coatings obtained with either a 35 kHz sinewave or a 10 kHz square pulse power supply

The infrared analysis, presented in Figure 9, supported these results since no obvious difference was observed between the spectra of the coatings.

3.4.2 Roughness analysis

If no major influence on the coating chemistry was observed, the changes observed on the discharge when decreasing the duty cycle were translated in the topography of the coatings deposited, especially at larger gaps.

AFM analyses of the ethyl lactate plasma polymer (EL-PP) coatings obtained in argon-based discharges are presented in Figure 10. When using a 1 mm gap, a significant difference in roughness was observed at the exit side of the discharge along the gas flow lines. The arithmetic average roughness (Ra) was 0.3±0.1 nm for all positions of the 35 kHz sinus coating. When using the 10 kHz square pulse power supply, the values were also close to 0.3 nm with, however, an important roughness increase at the exit of the discharge to reach a value of 0.8 nm and 1.2 nm for the 50 % DC and 1 % DC, respectively.
More obvious variations were observed when using a 2 mm gap. As can be seen on Figure 11, a rougher surface was obtained when decreasing the duty cycle, with average Ra going from 0.3±0.2 nm for the 50 % DC coating up to 1.2±0.6 nm for the 1 % DC coating. Looking at the AFM images, it is obvious that decreasing the duty cycle led to an increase of powder formation.
Figure 11. AFM images of coatings obtained at a 2 mm gap, with a square pulse signal at 10 kHz and duty cycles of 1%, 10%, and 50% for many positions along the gas flow lines.

The powder created at low duty cycles could be explained by the increase of energy locally available right after the second and larger current peak. In addition, this powder formation demonstrated the absence of polymerization (in a chemical sense) of the ethyl lactate molecule, but rather the agglomeration of reactive species.

Other studies made with polymerizable precursors such as acrylates showed that longer time off could induce radical polymerization and hence smoother coatings [2–4]. This was not observed in this study since the chemical structure of ethyl lactate cannot enable conventional polymerization. Instead, it is likely that the main deposition was happening during the “on” time of the discharge, which would be mainly influenced by the energy density available inside the discharge as presented in a previous paper [22]. Discharges with regular activation times should then be considered for smooth ethyl lactate coatings.

4 CONCLUSIONS

The aim of this study was to compare the influence of a square pulse voltage on the electron temperature, argon metastable number density, and current shape of an argon-ethyl lactate discharge with the one of a more traditional sinewave voltage. This was correlated with physicochemical properties of the ethyl lactate plasma-deposited coatings.

The use of a square pulse voltage power supply enabled to strongly shorten the discharge duration while increasing the maximum intensity of the current peak. Higher electron temperatures than the low frequency sinus power supply studied along with noticeable variations in the number
densities of argon metastable species were also reported. In addition, the duty cycle was found to have a major influence on the discharge behavior. More specifically, when lowering the time between the first and negative discharge peak (or equivalently when increasing the off time between the negative discharge peak and the subsequent positive discharge peak), differences were observed in the time evolution of $T_e$ and $n(Ar^m)$ between the first and second discharge peaks. This was linked to a loss of the so-called memory effect involving long lifetime Ar$_2$ triplet dimers at longer off times between two subsequent discharges.

This variation in the discharge properties as a function of the duty cycle did not influence significantly the chemistry of the deposited coatings but did have an influence on their topography. The amount of powder found on the ethyl lactate-based coatings kept increasing when decreasing the time between the first positive and the second negative discharges. This was attributed to the absence of polymerization of ethyl lactate since it is not a conventional polymerizable molecule. Instead, all activated ethyl lactate-based species likely formed clusters in the gas phase and at the surface and ended up as powder on the layer. Further studies using polymerizable precursors could be of interest to compare the influence of a radical polymerization on the discharge physics.

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