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ABSTRACT

Tailored voltage waveforms, formed by a fundamental frequency waveform superimposed with higher harmonics, show promise in realizing independent control and optimization of plasma parameters in conventional atmospheric dielectric barrier discharge systems (DBDs). In this paper, a self-consistent fluid model developed by a semi-kinetic treatment of electrons is applied to study the dependency of the electron energy and density distributions on the number of applied higher harmonics, applied fundamental frequency, and contributions from secondary electron emission—in a DBD system driven by tailored voltage waveforms. The mechanisms for achieving selective control over the modulated parameters are proposed, which allow for optimal selection of applied parameters for various downstream applications. This work exhibits dual-advantages for its novelty in presenting practical methods to modulate atmospheric plasma parameters, while in-depth analysis and discussions reveal underlying theoretical principles for the modulation of plasma parameters in atmospheric pressure discharges driven by tailored voltage waveforms.

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I. INTRODUCTION

In recent decades, cold atmospheric non-equilibrium plasmas (CAPs) have been a subject of rigorous study due to their numerous inherent technical advantages, including the flexibility to initiate processes without expensive vacuum systems and the ability to selectively generate high densities of chemically reactive species, based on the feedstock gases introduced in these systems. For chemically reactive plasmas generated in the atmospheric regime, applications across multiple domains have been found in non-converging and independent fields such as materials processing,^{1–3} environmental engineering,^{4–6} plasma chemistry,⁷ and other emerging fields of treatment and modification of biological samples (plasma medicine/surgery).^{8–10} One of the most commonly employed methods to generate atmospheric plasmas is through the utilization of a dielectric barrier discharge (DBD) configuration. The DBD is an indispensable plasma source with relatively high plasma densities, decreased gas temperatures, and stable effective

discharges over large areas. It also generates substantial reactive chemical species of interest for specific applications and constrains the growth of the discharge current to suppress unstable arc discharge modes.

Recent studies featuring DBD systems mainly revolve around work in the following verticals: (1) methods contributing to effective parameter modulation,¹¹ (2) typical physical processes in DBD systems,¹² and (3) applications of DBD systems.^{13,14} The significance of investigation of DBDs applied in various configurations can be seen as follows: First, a novel phenomenon may be induced and observed in the process of attaining effective modulation of plasma parameters, which gives rise to unraveling of rich physics behind the discharges. Second, in the variety of industrial applications that deploy DBDs, different plasma parameters may be tailored to prescribed optimized values in order to meet the requirements of the processes involved. Hence, methods to obtain precise control over plasma parameters may

be classified as one of the most important scientific and technical areas of interest in atmospheric plasma applications. For example, in the biomedical field, many treated samples are cellular systems including tissues and organs, which are extremely sensitive to the temperature of the environment. Under such circumstances, processing performance is improved significantly through enhancement of plasma densities with effective control of gas temperatures to curb and mitigate irreversible cellular and tissue damage caused by excessive temperatures. In the field of surface processing, different requirements for plasma parameters are introduced, e.g., higher plasma density and gas temperatures for higher processing efficiencies and optimized reaction pathways. It is therefore relevant that technologies working on the modulation of plasma parameters in DBDs provide not only an in-depth understanding of such discharges but also practical solutions for the promotion of the deployment of these atmospheric plasma sources in large-scale industrial applications.

For the case of atmospheric non-equilibrium cold plasmas, the most employed method for parametric control is complex waveform modulation. Such methods exploit superimposed modulation of pulses and/or a superposition of multi-frequency waveforms. In the case of the former, the modulation is enabled by control of energy storage in the discharge process by adjusting the duty cycle of the applied pulse, serving to reduce the overall gas temperature, where substantial results have been reported in recent years. In contrast, other researchers have applied dual-frequency (DF) modulated discharge methods to atmospheric pressure plasmas, and significant findings have been reported. For instance, Massines *et al.*¹⁵ adopted a hybrid 50 kHz/9 MHz frequency combination to drive a DBD system to study how the electron energy distribution evolves as the ratio of the applied voltage amplitudes is modulated. More recently, Liu *et al.*¹⁶ employed a 200 kHz/13.56 MHz frequency combination to drive a DBD system to study the spatial uniformity of the plasma by introducing an additional low-frequency source. In previous work,¹⁷ we used numerical methods to assess how the plasma parameters of the DF driven DBD system could be modulated. The results then revealed a strong nonlinear synergistic behavior by adding an extra low-frequency source (LF, 2 MHz) on the fundamental frequency (HF, 13.56 MHz). Based on that effect, the plasma density was shown to have been enhanced substantially, without any noticeable influence on the gas temperature, which is in contrast to the observations made in the case of the DBD being driven by a single HF source. Clearly, DF driven DBD systems allow for wider windows for operation and give rise to unprecedented access to theoretical possibilities and independent control of the obtainable discharge parameters for numerous practical applications.

Despite the advantages discussed above, plasma parameters modulated by DF excitation depend on applied parameters, such as the ratio of frequencies or amplitudes.¹⁸ In order to solve the problem and address the challenges of de-coupling the inter-dependencies in these systems, Heil *et al.* developed a wave modulation method by the superposition of a fundamental frequency with a number of higher harmonics.¹⁹ Significant control over discharge parameters, particularly under low pressure discharge conditions, has been reported.^{20–25} Our recent work further applied this modulation technology to the atmospheric pressure regime²⁶ and studied the influence of plasma parameters by altering the number of added harmonics and phase shifts. Relevant results preliminarily verified the feasibility of directional optimization and independent control of plasma parameters by

using this tailored waveform modulation methodology under atmospheric pressure conditions. In 2019, Korolov *et al.* used the tailored voltage waveform and also effective control of electron dynamics and metastable species generation at atmospheric pressure.^{27–29}

The above-mentioned modulation technology is still in its early phase of theoretical and laboratory studies, as well as feasibility studies for translation to other downstream technological applications. Associated modulation mechanisms still require significant and thorough investigation and analysis for clearer understanding of the physics involved. Thus, in this paper, we focus on the effects on the electron energy and density distributions as various parameters are varied, i.e., added harmonic numbers, fundamental frequency, fundamental phase angle, and secondary electron emission (SEE) coefficient. A self-consistent fluid model is used to describe a globally diffusive argon DBD driven by the tailored voltage waveforms. The driving waveform is composed of a superposition of a fundamental radio frequency (RF) wave and additional high harmonics. This study reveals the modulating mechanism of the specified tailored waveforms and provides a theoretical foundation for achieving directional optimization and independent parametric control of desired plasma parameters in atmospheric pressure discharges. This paper is organized as follows: The model and simulation setup are introduced in Sec. II. In Sec. III, results and discussions of the numerical study are presented, and the paper is finally concluded with a summary.

II. MODEL AND COMPUTATIONAL IMPLEMENTATION

In this paper, the discharge under investigation is generated and sustained between two parallel plates, whereby both electrodes are covered by insulating layers with a dielectric constant $\epsilon = 4.8$. The discharge channel of the DBD system is on the order of several millimeters. In the atmospheric pressure regime, the collisions between particles are frequent, and thus, non-local effects are assumed to be negligible.^{20,30,31}

A. Discharge model

Therefore, a one-dimensional fluid model with a semi-kinetic treatment of electrons is a good description for such a DBD process. In the drift diffusion approximation, governing equations in SI units are written as follows:

$$\frac{\partial n_e(x, t)}{\partial t} + \nabla \cdot \Gamma_e = S_e, \quad (1)$$

$$\frac{\partial n_i(x, t)}{\partial t} + \nabla \cdot \Gamma_i = S_i, \quad (2)$$

$$\nabla \cdot \Gamma_e = -n_e \mu_e E - D_e \nabla n_e, \quad (3)$$

$$\nabla \cdot \Gamma_i = n_i \mu_i E - D_i \nabla n_i, \quad (4)$$

$$\nabla \cdot (\epsilon E) = e(n_i - n_e), \quad (5)$$

where n_e , n_i , and Γ_e , Γ_i represent the number densities and fluxes of electrons and the i th species of ions, respectively. Additionally, E is the electric field, S_e and S_i are the electron and ion source terms for creation and recombination of particles, and e is the elementary charge. This can be further expressed as

$$S(x, t) = \mp \alpha \mu_{e,i} E(x, t) n_{e,i}(x, t) - \beta n_{e,i}(x, t). \quad (6)$$

Here, α and β represent the Townsend ionization coefficient and recombination coefficient, respectively, and μ_e and μ_i are the electron

TABLE I. Species and associated transport coefficients used in this model.

Species	ε_{th} (eV)	$\mu_p N$	$D_p N$ (m ⁻¹ s ⁻¹)	References
e	0	$\mu_p N(\varepsilon)$	Einstein	35
Ar^*	11.55	...	6.45×10^{20}	36
Ar^+	15.76	$\mu_{\text{Ar}^+} N(E/N)$	Einstein	37
Ar_2^+	14.5	$\mu_{\text{Ar}_2^+} N(E/N)$	Einstein	37, 38

and ion mobility coefficients as functions of the local reduced electric field, E/p —obtained using the Boltzmann equation solver BOLSIG.³² The electron and ion diffusion coefficients D_e and D_i are obtained from the Einstein relation: $D = k_B T \mu / e$, where k_B is the Boltzmann constant, T is the electron temperature (set at 2 eV initially), and the gas temperature is 450 K.³³

At the dielectric surface, the surface charge density can be calculated by integrating the charged particle flux density toward the surface during the discharge development as

$$\sigma(t) = e \int ((1 + \gamma_{\text{sec}}) \Gamma_i - \Gamma_e) dt, \quad (7)$$

where γ_{sec} is the SEE coefficient. Hence, the flux density can be rewritten as

$$\Gamma_e = -n_e \mu_e E + n_e v_{e,\text{th}}/4 - \gamma_{\text{sec}} \Gamma_i, \quad (8)$$

$$\Gamma_i = n_i \mu_i E + n_i v_{i,\text{th}}/4, \quad (9)$$

where $v_{e,\text{th}}$ and $v_{i,\text{th}}$ are the thermal speeds of the electrons and ions, respectively. The system is driven by a tailored voltage waveform, comprising a fundamental radio frequency wave and a number of higher harmonics. The tailored waveform can be described in detail through the satisfaction of the following equation:

$$V_{\text{AC}}(t) = V_0 \sum_{k=1}^n \frac{1}{k} \sin(k\omega t + \Theta), \quad (10)$$

where V_0 is the fundamental amplitude (set as the desired peak-to-peak voltage V_{pp}), n is the number of added harmonics, ω is the

angular frequency, and Θ is the phase shift with respect to the fundamental, for all harmonics. The nonlinear equations mentioned above are then solved using a semi-implicit Scharfetter–Gummel scheme.³⁴

In this simulation, the working gas is argon at a pressure of 760 Torr, and 4 species (i.e., electrons, Ar^+ , Ar_2^+ , and Ar^*) are considered in the description of the argon chemistry. These species and the related (transport coefficients) parametric inputs are shown in Table I.

The ion mobility is experimentally determined as a function of the reduced electric field. The diffusion coefficient for the metastable particle, Ar^* , is calculated using a collision integral method, which is evaluated at the gas temperature. The electron mobility is calculated as a function of the mean electron energy from the electron energy distribution function (EEDF), using the Boltzmann solver BOLSIG+, from which the chemical reaction rate coefficients involving electrons are also obtained. The detailed associated reaction equations and chemical reaction rate coefficients in this model are shown in Table II. The processes include excitation (R1), de-excitation (R2), stepwise ionization (R3), direct ionization (R4), metastable to metastable ionization (R5 and R6), atomic to molecular (R7), molecular to atomic (R8), ion conversions and dissociative recombination (R9), three-body recombination (R10 and R11), and radiative decay (R12).^{39,40}

B. DC self-bias analysis model

Using the tailored waveforms, a DC self-bias arises in the system due to the asymmetry of the RF sheath. In order to obtain conditions allowing for the DC self-bias, a method based on an analytical model for RF discharges⁴⁵ was adopted in the simulation. Here, only the results for DC self-bias are used for reference,

$$\eta = -\frac{\phi_{\text{max}} + \kappa \phi_{\text{min}}}{1 + \kappa}, \quad (11)$$

where ϕ_{max} and ϕ_{min} are the maximum and minimum values of the applied driving voltages,

$$\kappa = \left| \frac{\phi_{\text{sheath,g}}}{\phi_{\text{sheath,p}}} \right|. \quad (12)$$

TABLE II. Reaction equations and associated rate coefficients used in this model.

No.	Reaction equations	Rate coefficients	References
R1	$e + \text{Ar} \rightarrow \text{Ar}^* + e$	$k_1(\varepsilon)$	35,41
R2	$e + \text{Ar}^* \rightarrow \text{Ar} + e$	$k_2(\varepsilon)$	35,41
R3	$e + \text{Ar}^* \rightarrow \text{Ar}^+ + e + e$	$k_3(\varepsilon)$	1,35
R4	$e + \text{Ar} \rightarrow \text{Ar}^+ + e + e$	$k_4(\varepsilon)$	35,41
R5	$\text{Ar}^* + \text{Ar}^* \rightarrow \text{Ar}^+ + e + \text{Ar}$	$5.16 \times 10^{-16} \text{ cm}^{-3} \cdot \text{s}^{-1}$	42
R6	$\text{Ar}^* + \text{Ar}^* \rightarrow \text{Ar}_2^+ + e$	$4.64 \times 10^{-16} \text{ m}^{-3} \cdot \text{s}^{-1}$	42
R7	$\text{Ar}^+ + \text{Ar} + \text{Ar} \rightarrow \text{Ar}_2^+ + \text{Ar}$	$2.5 \times 10^{-43} [300/T(K)]^{3/2} \text{ m}^6 \cdot \text{s}^{-1}$	43
R8	$\text{Ar}_2^+ + \text{Ar} \rightarrow \text{Ar}^+ + \text{Ar} + \text{Ar}$	$5.22 \times 10^{-16} T(\text{eV})^{-1} \exp[-1.304/T(\text{eV})] \text{ m}^3 \cdot \text{s}^{-1}$	43
R9	$e + \text{Ar}_2^+ \rightarrow \text{Ar}^* + \text{Ar}$	$7 \times 10^{-13} \cdot [300/T_e(K)]^{1/2} \text{ m}^3 \cdot \text{s}^{-1}$	43
R10	$e + \text{Ar}^+ + e \rightarrow \text{Ar} + e$	$8.75 \times 10^{-39} \cdot T_e(\text{eV})^{-9/2} \text{ m}^6 \cdot \text{s}^{-1}$	43
R11	$e + \text{Ar}^+ + \text{Ar} \rightarrow \text{Ar} + \text{Ar}$	$1.5 \times 10^{-40} \cdot [300/T(K)]^{2.5} \text{ m}^6 \cdot \text{s}^{-1}$	44
R12	$\text{Ar}^* \rightarrow \text{Ar} + h\nu$	$6.24 \times 10^5 \text{ s}^{-1}$	37

Here, κ is the symmetry parameter defined and determined by the ratio of the maximum and minimum of the sheath voltages at both the grounded and powered electrodes. Additionally, $\phi_{\text{sheath,g}}$ and $\phi_{\text{sheath,p}}$ are the sheath voltage drops of the grounded and powered electrodes.

In the simulation, the input parameters that are modulated are the fundamental frequency, the number of added harmonics, and the SEE coefficient.

III. RESULTS AND DISCUSSION

It has been demonstrated previously that RF DBDs enable the generation of stable glow discharges over large areas at atmospheric pressure. In this work, the gas gap between the two insulating layers is fixed at $d_g = 2$ mm, the thickness of the dielectric layers covering the electrodes is $d_B = 1$ mm with a relative permittivity of 4.8, and the SEE coefficient is initially set as 0.01. Figure 1 shows two complete periods of the applied voltage waveforms evolving over time according to Eq. (10), as the number of harmonics is modulated from $n = 1$ to 4. In the figure, we see that the waveform is influenced by the number of added harmonics, n . When $n = 1$, the discharge waveform is purely sinusoidal. With the increase in n , the magnitude of the positive slope of the waveforms increases, whereas the magnitude of the negative slope decreases in the oscillations, respectively. According to previous studies,²⁴ the plasma sheath motion exhibits strong correlation with the discharge waveforms. When constrained through the study in an asymmetric modulation condition, the sheath is characterized by contrasting properties observed at both electrodes with a fast sheath expansion and a slow sheath collapse for one electrode and a reverse tendency observed at the other electrode. This induces asymmetry in the power absorption of the electrons and the impact ionization rates of electrons in the system.

To derive deeper insights, Fig. 2 shows the typical temporal behavior of the discharge current density, applied voltage, and gas

FIG. 1. Tailored voltage waveforms generated as governed by Eq. (10). The peak to peak voltage is set at $V_{pp} = 3$ kV, the fundamental frequency $f = 2$ MHz, and the phase shift of fundamentals $\Theta = 0$.

FIG. 2. Spatiotemporal evolution of (a) the electron impact ionization rate, (b) the current density, and (c) the applied voltage and gas voltage, in two complete periods where the discharge condition is set as $f = 2$ MHz, $\Theta = 0$, and $V_{pp} = 3$ kV with $n = 3$. The location of the grounded electrode is at $y = 0$.

voltage of the DBD (driven by voltage waveforms with the number of harmonics set at $n = 3$ and the peak to peak voltage maintained at $V_{pp} = 3$ kV). The spatiotemporal electron impact ionization rates under the corresponding conditions can also be correlated and are displayed in parallel. A classical waveform of the discharge current and the corresponding gas voltage is observed with the argon-based discharge driven by tailored voltage waveforms as shown in Figs. 2(b) and 2(c). The discharge current is modulated in phases. It is worth noting that the discharge current exhibits unique properties, with clear distinctions from the pulsed modulated single-RF source sinusoidal signal. Further observations also illustrate that the discharge current peak corresponds to the occurrence of the sheath expansion at the grounded electrode. At the powered electrode, the existence of two sub-maximal impact ionization spots is observed. It manifests in the form of two “weaker” peaks in the discharge current that corresponds to the sheath expansion region. These vastly different impact ionization structures in the two sheath regions suggest the observation and production of an electrical asymmetric effect (EAE) in the system. In low pressure plasma discharges,^{20,21} an EAE can induce a strong DC self-bias to independently control plasma parameters. This therefore

suggests that the formation of EAE structures allows for the effective modulation of plasma parameters in atmospheric DBDs.

Figure 3 provides insights into energy control through outlining the evolution of the space averaged phase dependent EEDF based on Eq. (10) with $n = 3$. The phase range is an entire period from 0 to 2π , with five demarcated instances corresponding to either local maxima or minima in the current density in Fig. 2. This is also illustrated by the vertical dashed lines capped with the Roman numerals (i)–(v). Considering EEDFs at (i) and (iii) for the two local “weaker” peaks, we find that the EEDFs are quasi-Maxwellian, corresponding to characteristics resulting from regular Ohmic heating. For EEDFs at (ii) and (iv) corresponding to the two local points of minima, the profiles are approximately bi-Maxwellian with a “low energy peak” and a marked reduction in the “high energy tail” (particularly for the curve resulting from instance (iv)). The EEDF at (v) however exhibits significant deviations as compared to EEDFs of the others. Therefore, from Fig. 3 alone, we deduce that a tailored voltage waveform method may have a significant impact on the phase dependent EEDF. This opens up technological opportunities to deterministically tailor the time-averaged EEDF and thus the chemical kinetics of the plasma.

A. Effect of the harmonic number

In previous studies in low pressure discharge regimes, the electrical asymmetric effect can induce a DC self-bias voltage to cause different effective mean particle densities in both sheaths due to the particle flux continuity.⁴⁶ Similar results can also be found in atmospheric pressure discharge plasmas. Figure 4 shows the spatial electron density distribution in discharges featuring different numbers of added harmonics. In the figure, we see the existence of a favorable spatially symmetric distribution of the electrons when $n = 1$. Within the plasma bulk region where the electron density is approximately equal to the ion density, a “flattened” or saturated distribution is formed. This is because in atmospheric pressure discharges, the electrons have a very short mean free path. This implies that only fast electrons can be easily

FIG. 3. Phase dependent EEDFs for tailored voltage waveforms corresponding to the instances as marked in Fig. 2 by the dashed lines (i)–(v).

FIG. 4. Spatial electron density distribution as the number of added harmonics is varied. The discharge condition is set as $f = 2$ MHz, $\Theta = 0$, and $V_{pp} = 2.4$ kV.

accelerated within the sheath region to cause ionization of the neutral feedstock gas. Similar density profiles can be found in atmospheric pressure capacitive coupled argon discharges driven by single frequency sources.⁴⁹ It is also worth noting that this is described as the main loss mechanism of charged particles in the sheath region.

As the number of superimposed harmonics increases, the spatial electron density distribution evolves to give rise to an asymmetrical structure that deviates further from symmetry with the number of added harmonics. Meanwhile, the spatial location of the peak density exhibits bipolar features. It is worth noting that as the “dual-peaks” appear as the number of added harmonics increases, the peak density in the side of the powered electrode is larger than that of the grounded electrode. This indicates that an EAE can be induced by increasing the number of added harmonics. As the harmonic number increases to $n = 4$, the spatial distribution of the electron density deviates slightly to resemble a concave profile, possibly caused by the polar drift of electrons.

Figure 5 shows the time-averaged EEDF with added harmonics from $n = 1$ to 4. The EEDF is plotted over an energy range of 0–20 eV, which reveals the primary chemical kinetics of typical macrodischarges in argon plasmas. In Fig. 5, a quasi-Maxwellian distribution can be observed as the number of superimposed harmonics is varied. This satisfies the strong collisional condition found in typical atmospheric pressure discharge plasmas. Additionally, we can see significant changes in the EEDF profile, with the low energy peak shifting with the added harmonics. The EEDF profiles almost overlap within the range of 12.5–20 eV. This implies that the added superimposed harmonics has the ability to selectively induce a significant effect on the time-averaged EEDF profiles in the low energy domain.

B. Effect of the fundamental frequency

Figure 6 shows the absolute value of the normalized DC self-bias voltage as a function of the applied fundamental frequency, obtained at $\Theta = 0$. In this figure, we see a profile with three prominently distinct

FIG. 5. Time averaged EEDF as the number of added harmonics is varied from $n = 1$ to 4.

regimes as the fundamental driving frequency increases. Inflection points appear at $f = 5.5$ and 27 MHz, respectively. From the given profile in Fig. 6, we can see that for a given phase shift at fixed voltage amplitudes, we can classify the behavior of the dependence of the DC self-bias on the applied fundamental frequency into three regimes. In the first regime, the normalized DC self-bias increases logarithmically with the frequency until the first inflection point at $f = 5.5$ MHz. As the fundamental frequency continues to increase in the second regime, the slope of the profile increases substantially. As the frequency increases further to the second point of inflection at $f = 27$ MHz, the

FIG. 6. Absolute value of the normalized DC self-bias as a function of the fundamental frequency. The discharge condition is set as $V_{pp} = 2.4$ kV, $n = 3$, and $\Theta = 0$.

curve transits into the third regime with a gradual and less aggressive slope.

In order to derive further insights, Fig. 7 shows the spatiotemporal distributions of the electron heating—evolving with the selected frequencies of 1, 5.5, 13.56, 40.68, and 60 MHz, respectively. These selected parameters also correspond to the points as marked in Fig. 6. In this figure, we can see that the discharge operates primarily in α -mode, where the primary electron heating phenomenon is largely dominated by the expansion and collapse of the sheaths.⁴⁷ At a low frequency (1 MHz), the strongest heating occurs within the plasma bulk, coinciding with typical features obtained at atmospheric pressure. Different heating processes in each half cycle give rise to the occurrence of an asymmetric electron heating phenomenon when the system is driven by such tailored voltage waveforms. The heating effects are observed to occur closer to the grounded electrode, indicating an enhanced electrical asymmetry. When the fundamental frequency is increased to 40.68 MHz, the electron heating distribution deviates significantly from the distributions obtained from low frequency excitation sources. In the figure, we can see that the heating occurs not only within the plasma bulk region but also within the plasma sheath of the powered electrode. As compared to the electron heating near the grounded electrode, the heating at the powered electrode becomes more prominent, which further enhances the electrical asymmetric structure and increases the DC self-bias as a result.

Figure 8 shows the obtained DC self-bias voltage as a function of the phase shift of the fundamental frequencies (where $n = 3$). The selected corresponding fundamental frequencies are also marked as points within Fig. 6 for comparison and analysis. In all cases, similar profiles are observed and in good agreement with results from low pressure discharges in both PIC simulations^{23,48} and experimental measurements.⁴⁶ From the figure, we observe that the DC self-bias can be controlled by tuning the phase shift of the fundamentals. The control range of the DC self-bias is significantly reduced at lower frequencies. This is because the electron impact excitation at the two sheaths differs from each other significantly when the system is driven under lower frequency conditions. This enhances the space charge dynamics and reduces the DC self-bias voltage accordingly. At higher frequencies, electron trapping becomes more significant. As electrons are bounded near the sheath, the dynamics of the electrons become suppressed, which in turn causes the DC self-bias voltage to rise. We also note that for all cases, a crossover point of convergence is found at about 30° when the fundamental phase shift changes monotonically from 0° to 90° . This is due in two parts to contributions from both phase shifts and modulated frequencies on the dynamics of the discharge. As mentioned, the DC self-bias voltage is determined by the extreme value of the applied voltage and the coefficient of asymmetry, as given in Eq. (11). For a given frequency, with the tuning of the phase shift, the maximum and minimum values of the applied voltage vary gradually, and the waveform transits from either a sawtooth to inverse-sawtooth profile or vice versa. On the other hand, for a given phase angle, as the fundamental frequency varies, the corresponding effect on V_{max} and V_{min} does not appear to change significantly. However, the asymmetric coefficient decreases sharply as the fundamental frequency increases. A balance between these two effects can therefore be found at $\Theta \approx 30^\circ$, according to the figure.

In contrast, the attainable range of the averaged electron density in discharge conditions at higher frequencies is relatively wide but

FIG. 7. Spatiotemporal distributions of the electron heating effect as the fundamental frequency is varied. The discharge condition is set as $V_{pp} = 2.4$ kV, $n = 3$, and $\Theta = 0$. The powered electrode is located at $y = 0$.

does not therein present opportunities for precise control. The averaged electron energy, for both powered and grounded electrodes, has similar ranges for control at different fundamental frequencies. The findings from this subsection above imply that the EAE can be effectively used to control the averaged electron density and energy in tailored voltage driven DBDs at higher fundamental frequencies.

It is also worth noting that results from this study are in good agreement with earlier work by Czarnetzki *et al.*,⁴⁵ which documented how a DC self-bias could be generated in a geometrically symmetrical configuration, through exploitation of asymmetry in the system arising from charged particle dynamics. Through the variation of the phase shifts in the driving fundamental frequency, sheath symmetry in systems that are otherwise symmetric in geometry can be broken and controlled. The asymmetry results from total uncompensated charges from losses to the electrodes, and they have contributions due to loss of ions due to Bohm fluxes and electron loss to electrodes as the sheath collapses. Czarnetzki demonstrated how a DC self-bias could be obtained electrically (instead of through the more conventional method of creating asymmetry geometrically) in a symmetric setup (linearly with a $\pm 25\%$ operational window) by tuning the phase shifts from 0 to 90° . This correlates positively with the model and results developed in this work and show great promise for applications in

large area atmospheric DBD systems (which are considered to be geometrically symmetric) but require symmetry from sheaths to be broken electrically in order to realize independent control over particle densities, particle fluxes, and mean particle energies.

C. Secondary emission electron effect

As mentioned, the asymmetric effect in the plasma sheaths is the dominant mechanism, which allows for the modulation of plasma parameters. For atmospheric pressure DBD systems, the SEE coefficient is also a very important parameter. Hence, changing the SEE coefficient, γ_{sec} , affects the generation of a self-bias and the corresponding variations of the electron energy and density. A higher SEE coefficient leads to stronger discharge asymmetry via the influence of secondary electrons on the ionization dynamics.

Figure 9 shows the absolute value of the DC self-bias voltage as a function of the SEE coefficient. In the figure, we can see that the DC self-bias voltage increases with the number of added harmonics and the SEE coefficient. Though the increase with the SEE coefficient is not as pronounced as the increase due to the added harmonics, it is worth noting that the SEE coefficient still has an impact on the manifestation of the EAE. Moreover, the presence of secondary electrons improves the

FIG. 8. The DC self-bias voltage as a function of the phase shift of fundamentals, ranging from 1 to 60 MHz. The peak to peak voltage is fixed at $V_{pp} = 2.4$ kV with the harmonic number $n = 3$.

distribution of charged particles and aids in effectively modulating the spatiotemporal distribution of the electron density and electron energy.

Figure 10 shows the averaged electron density and electron energy as functions of the number of added superimposed harmonics with the SEE coefficients set as $\gamma_{sec} = 0.01$ and 0.04 . In the figure, we can observe that the averaged electron density and energy vary with the increment of added harmonics. In particular, for the case when $\gamma_{sec} = 0.01$, the averaged electron density rises from $0.23 \times 10^{13} \text{ cm}^{-3}$ for $n = 1$ to $4.6 \times 10^{13} \text{ cm}^{-3}$ for $n = 4$. With specific references to the

FIG. 9. The absolute value of DC self-bias voltage as a function of the number of added harmonics as represented by different SEE coefficients. The discharge condition is set as $f = 2$ MHz, $\Theta = 0$, and $V_{pp} = 2.4$ kV.

FIG. 10. Averaged electron density and electron energy as functions of the number of added superimposed harmonics with different SEE coefficients. The discharge condition is set as $f = 2$ MHz, $\Theta = 0$, and $V_{pp} = 2.4$ kV.

two cases where $n = 4$ ($\gamma_{sec} = 0.01$ and 0.04 accordingly), it is also suggested that the SEE coefficient has an impact on the time-averaged electron energy and density. With a larger SEE coefficient, the amount of added harmonics appears to have a more significant impact on the electron density, but this effect is not obvious for the electron energy.

To further this investigation, the time-averaged spatial distribution of the electron density for different SEE coefficients is illustrated in Fig. 11. The shaded area represents the density distribution within the sheath region. In the figure, we can see that the maximum density increases with γ_{sec} , as the sheath region is significantly compressed. The ratio of the mean electron density at the ground electrode and powered electrode, n_{sg}/n_{sp} , also changes from 0.517 to 0.439 . This indicates a rapid growth of the electron density in the region near the powered electrode with a larger SEE coefficient.

IV. CONCLUSIONS

In summary, by using a fluid model with semi-kinetic treatment, a DBD system driven by tailored voltage waveforms is investigated in this work. The proposed method for the parametric modulation of plasma parameters demonstrates potential and feasibility in achieving directional optimization and selective control over both electron energy and electron density via exploitation of the EAE. The main conclusions of this work are as follows:

1. By varying applied input discharge parameters of waveforms that are tailored, including the number of added harmonics, fundamental frequency, and its phase shift, as well as the SEE coefficient, the time-averaged spatial distribution of the electron energy and density can be modulated and controlled significantly based on the EAE.
2. The increase in added harmonics induces an EAE, which is shown to influence the spatial electron density distribution and time-averaged EEDFs of the plasma. This has critical implications over the effects on actual chemical kinetics and suggests a possibility of achieving enhanced control of plasma chemistry for downstream applications.

FIG. 11. Spatial electron density distribution with different SEE coefficients (a) for $\gamma_{\text{sec}} = 0.01$ and (b) for $\gamma_{\text{sec}} = 0.04$. The discharge conditions is set as $n = 3$, $f = 2$ MHz, and $\Theta = 0$. The vertical dashed lines indicate the position of the sheath edges at the powered and grounded electrodes, respectively.

3. The fundamental driving frequency and the phase shift influence the DC self-bias and heating process significantly. The absolute magnitude of the DC self-bias increases with the fundamental frequency due to the charge dynamics at the sheaths of both electrodes. A wide range of attainable magnitudes for the DC self-bias is also attainable at higher fundamental frequencies.
4. The SEE coefficient plays a significant role in the manifestation of the EAE in DBD systems. It exhibits influence on the DC self-bias voltage and distribution of charged particles and thus has the potential to modulate the spatiotemporal distribution of the electron density and energy effectively.

In conclusion, although work on understanding the EAE phenomenon is still in early phases of research in the domain of atmospheric pressure discharges, this work demonstrates that there are possibilities to realize selective control of plasma properties in atmospheric pressure conditions. Moreover, the control range can be modulated by careful selection of applied processing parameters, such as the added harmonic number, fundamental frequency, and the accorded phase shifts. It is then prospected that tailored voltage waveform modulation techniques will remain to become a promising emerging alternative approach to realize independent control of key plasma parameters under atmospheric pressure.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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