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Mechanisms of the \( \alpha \) and \( \gamma \) modes in radio-frequency atmospheric glow discharges

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Large-volume and uniform atmospheric glow discharges are finding a vast range of processing applications, many of which have been traditionally addressed with the vacuum plasma technology. When excited at kilohertz or above, these atmospheric plasmas operate typically at low current densities below 30 mA/cm\(^2\) and often they are perceived to have very similar properties regardless of their operation conditions. Recently a radio-frequency (rf) atmospheric glow discharge was observed at high current density of up to 1 A/cm\(^2\), thus suggesting a previously overlooked and potentially different operation regime. Through a computational study of rf atmospheric glow discharges over a wide range of current density, this paper presents evidence of at least two glow modes, namely, the \( \alpha \) mode and the \( \gamma \) mode. It is shown that gas ionization in the \( \alpha \) mode is volumetric occurring throughout the electrode gap whereas in the \( \gamma \) mode it is dominated by localized events near the boundary between the sheath and the plasma bulk. Secondary electron emission strongly influences gas ionization in the \( \gamma \) mode yet matters little in the \( \alpha \) mode. These findings suggest a wider operation range of atmospheric glow plasmas than previously believed. The contrasting dynamic behaviors of the two glow modes highlight both the potential to preferentially match the operation regime of atmospheric glow discharges to the specific requirements of their intended applications and the importance to develop diagnostics strategies appropriate for their operation regimes. © 2005 American Institute of Physics. [DOI: 10.1063/1.1834978]

I. INTRODUCTION

Atmospheric pressure glow discharges (APGD) have recently commanded much attention, fuelled by their promise to rival the widely used low-pressure glow discharges and their facilitation of numerous applications through the removal of the usually indispensable vacuum chamber. They are capacitive nonthermal plasmas generated between two parallel electrodes that are either metallic or coated with a dielectric layer, and their generation has been achieved over a very wide spectrum from dc through kilohertz and megahertz to microwave. They can also be generated as surface-wave discharges. Today APGD are finding wide-ranging applications including etching, deposition, surface modification, and sterilization. The progress of their fundamental understanding, on the other hand, lags markedly behind their technological advancement largely due to comparatively few theoretical studies so far. One common perception is that atmospheric pressure glow discharges may possess similar properties regardless of their operation conditions. Yet it is known that glow discharges at low and medium pressures have different operation modes of contrasting behaviors in, for example, their ionization mechanisms and current–voltage characteristics. If glow discharges at atmospheric pressure are also found to possess distinctively different operation modes, there will be important implications to their future development strategies, not least of which is the possibility to preferentially match the operation regime of APGD to the specific requirements of their intended applications. Therefore it is important to establish whether different glow modes exist in atmospheric discharges.

In this paper, we aim to substantiate the existence of different APGD modes through a study of their dynamics and ionization mechanisms. Our work is based on rf APGD, for which studies have been reported of their current–voltage characteristics, optical emission, and reaction chemistry. Most experimental and computational studies reported so far suggest that rf APGD may operate only in a regime of low current density typically below 30 mA/cm\(^2\) and a significant increase in current density tends to evolve the discharge directly into an arc plasma, thus bypassing the \( \gamma \) mode of larger current density commonly seen in medium-pressure glow discharges. Recently this view has been challenged by our experimental observation of a stable rf glow mode in atmospheric helium at large current density of up to 1 A/cm\(^2\), thus suggesting a possible existence of both the \( \alpha \) and \( \gamma \) modes in atmospheric pressure glow discharges. To explore this observation further with an unambiguous interpretation, a theoretical study is preferred since it allows for access to information on dynamic evolution of many key physical quantities, such as electric field, densities of plasma species, and electron production rates that are at present either difficult or expensive to access experimentally. As a result, we have developed a fluid model of rf APGD and employed it to study their ionization mechanisms over a wide range of current density from 5 to 100 mA/cm\(^2\). It is shown that both the \( \alpha \) and \( \gamma \) modes indeed exist in atmospheric pressure glow discharges, and...
that gas ionization in the α mode is volumetric occurring throughout the plasma, whereas in the γ mode it is dominated by localized events near the boundary between the sheath and the plasma bulk. It is further demonstrated that plasma chemistry does not affect the presence of the two glow modes but strongly influences the transition voltage from the α mode to the γ mode.

II. COMPUTATIONAL MODEL

As a test vehicle to demonstrate the existence of different glow modes in atmospheric plasmas, we consider a rf glow discharge in atmospheric helium. Given that impurity gases, such as nitrogen, are known to be important in helium APGD,\textsuperscript{11,12} we consider both a pure helium APGD model and a He–N\textsubscript{2} APGD model so as to contrast out the generic characteristics of possible APGD modes. Our pure-He plasma model considers six species, namely, electrons \( e \), helium ions He\textsuperscript{+}, excited helium atoms He\textsuperscript{*}, dimer helium ions He\textsubscript{2}\textsuperscript{+}, excited dimer He\textsubscript{2}\textsuperscript{*}, and background helium atoms He. Similar to a comparable numerical study of the rf APGD,\textsuperscript{11} our model include nine chemical reactions among these plasma species including direct ionization, excitation, deexcitation, charge transfer from atomic helium ions to dimer helium ions, the stepwise ionization through He\textsuperscript{*}, and recombination. Rates for all other reactions are identical to those used in Ref. 11.

Our plasma model is a self-consistent and continuum model. Its governing equations consist of the mass conservation equations to determine the densities of each plasma species, the current continuity equation for calculation of the electric field, and the electron energy conservation equation for the electron mean energy. Specifically they are given below:

\[
\frac{\partial n_e}{\partial t} = -\frac{\partial I_e}{\partial x} + K_{ij}(e)n_in_j, \tag{1a}
\]

\[
\frac{\partial n_{e+}}{\partial t} = -\frac{\partial I_{e+}}{\partial x} + K_{ij}(e)n_in_j, \tag{1b}
\]

\[
J(t) = e\frac{\partial E}{\partial x} - (-e\Gamma_{e} + e\sum_{p} \Gamma_{e+p}), \tag{1c}
\]

\[
\frac{\partial (n_eE)}{\partial t} = -\frac{\partial E}{\partial x} + e\Gamma_{e}E - K_{Lij}(e)n_in_j
- \frac{3m_{e}}{m_{neut}}NK_{e}m_{e}k(T_e - T_{neut}), \tag{1d}
\]

where \( n \) and \( \Gamma \) are the density and flux of species, \( e \) the electron mean energy, and \( J \) the current density. \( K_{ij} \) and \( K_{Lij} \) are, respectively, the reaction rate and the energy gain/loss rate due to a reaction between species \( i \) and \( j \). \( K_{e} \) is the momentum-transfer frequency corresponding to the elastic collision between electrons and background gas atoms. \( D \) is the diffusion coefficient, \( \mu \) the mobility, and \( E \) the electric field. \( m \) is the mass of a plasma species and \( T \) is the temperature of a plasma species. Subscripts \( e, +, *, \) and \( \text{neut} \) denote, respectively, electrons, ions, metastables, and neutral particles. \( p \) represents different plasma species considered in the model. Fluxes of all plasma species are given below:

\[
\Gamma_{e} = -D_{e}(e)\frac{\partial n_e}{\partial x} - \mu_e n_e E, \tag{2a}
\]

\[
\Gamma_{e+} = -D_{e+}(e)\frac{\partial n_{e+}}{\partial x} + \mu_{e+} n_{e+} E, \tag{2b}
\]

\[
\Gamma = -D_{\Gamma}(\Gamma)\frac{\partial \Gamma}{\partial x}, \tag{2c}
\]

\[
\Gamma_{e} = \frac{5}{3} \Gamma_{e} - n_{e}D_{e}(e)\frac{\partial e}{\partial x}, \tag{2d}
\]

Transport properties are the same as those used in literature.\textsuperscript{11} The ionization coefficient is calculated as a function of the electron mean energy rather than the local electric field. Our model is one dimensional with the governing equations solved in the direction perpendicular to the electrode plane. We assume that the gas temperature is 393 K\textsuperscript{11,16} and the externally applied rf current is of sinusoidal waveform at 13.56 MHz.

The boundary conditions for electrons at the surface of both electrodes are

\[
\Gamma_{e} = -\gamma\Sigma_{p} \Gamma_{e+p}, \tag{3}
\]

where \( \gamma \) is the secondary emission coefficient. For neutral particles, positive ions, and metastable, the flux at the electrodes is dominated by drift and the diffusive flux is negligible:

\[
\frac{\partial n_{e}}{\partial x} = 0, \quad \frac{\partial n_{e+}}{\partial x} = 0. \tag{4}
\]

The electron mean energy at the electrode surface is fixed at 0.5 eV.

To include impurity nitrogen, we have also developed a He–N\textsubscript{2} plasma model by adding nitrogen molecules N\textsubscript{2}, nitrogen atoms N, atomic nitrogen ions N\textsuperscript{+}, and dimer nitrogen ions N\textsubscript{2}\textsuperscript{+} to the six plasma species in the pure-He plasma model. As a result, we have five nitrogen-only reactions including electron-impact dissociation of nitrogen molecules, electron-impact ionization of nitrogen atoms and molecules, recombination of nitrogen ions; and six nitrogen–helium coupling reactions including Penning ionization of nitrogen molecules by helium metastables and charge transfers from helium ions to nitrogen ions. These additional reactions and their rates are identical to those used in Ref. 11. With their inclusion via \( K_{ij} \) and \( K_{Lij} \), the governing equations of the He–N\textsubscript{2} plasma model are also given in Eqs. (1) and (2).

For validation of our plasma models, we consider a 13.56 MHz APGD in a 600 Torr helium–nitrogen mixture with their electrode gap at 2.4 mm and the secondary electron emission coefficient at 0.03. The choice of these parameters is to compare our simulated current–voltage relationship with the available experimental\textsuperscript{16} and numerical data\textsuperscript{11} obtained under the same operation conditions. The nitrogen content is set at 0.16 ppm in our simulation. This is within
the range of impurity nitrogen that can be realistically expected for the comparison experiment, though it is less than 5 ppm used in the numerical study. As shown in Fig. 1, the agreement is in general very favorable and particularly so with the experimental results, suggesting that our plasma model is capable of accurately capturing the main features of rf APGD and as such is reliable for the study of their operation modes. Further simulation with a smaller secondary electron emission coefficient at 0.01 leads to an almost identical current–voltage relationship to that in Fig. 1 with an emission coefficient of 0.03, thus suggesting the insignificance of secondary electrons in the case of Fig. 1.

III. DIFFERENT APGD MODES AND THEIR MECHANISMS

A. Evidence of different APGD operation regimes

We consider possible operation regimes in pure-helium APGD using our pure-He plasma model. Figure 2 shows the variation of the maximum electron density as a function of the rf voltage amplitude for an atmospheric helium discharge generated at 13.56 MHz and with a secondary electron emission coefficient of 0.1. When the rf voltage amplitude is less than 410 V, the electron density increases approximately linear with the rf voltage at a rate of $1.0 \times 10^9$ cm$^{-3}$/V. As the rf voltage amplitude becomes greater than 410 V, the electron density increases much more significantly. In other words, the rf voltage amplitude at 410 V appears to be a transition point that divides two distinctly different APGD regimes. Significantly the distinct change in the voltage dependence of the electron density resembles that of the glow discharges at medium pressures, suggesting the existence of two different APGD modes. Similar to the medium-pressure glow discharges, the regime of gradual density change below 410 V in Fig. 2 is the $\alpha$ mode and that of rapid density change above 410 V is the $\gamma$ mode. It is also interesting to note the last data point of Fig. 2 at 4.2 $\times 10^{13}$ cm$^{-3}$, which is in the $\gamma$ mode and has a smaller rf voltage of 406 V than 410 V of the $\alpha$-$\gamma$ transition point at $3.6 \times 10^{13}$ cm$^{-3}$. This voltage decrease is very similar to the voltage drop accompanying the $\alpha$-$\gamma$ transition in medium-pressure glow discharges.

B. Ionization mechanisms

To understand the different behaviors of these two glow modes, we consider their ionization and calculate their electron production rate. In Fig. 3(a), we plot the dynamic evolution of the normalized electron production rate across the interelectrode gap over one cycle of the applied voltage, at a current density of (a) 10 mA/cm$^2$ in the $\alpha$ mode; and (b) 70 mA/cm$^2$ in the $\gamma$ mode. The maximum rate in (a) and (b) are $4.1 \times 10^{16}$ cm$^{-3}$s$^{-1}$ and $8.5 \times 10^{18}$ cm$^{-3}$s$^{-1}$, respectively. The dashed curve shows the boundary between the sheath region and the plasma bulk.
and very similar to the plasma bulk region. So gas ionization is volumetric (electron production occurs both within the sheath region and the plasma bulk region). The maximum rates of electron production are \(4.1 \times 10^{10} \text{ cm}^{-3} \text{ s}^{-1}\) and \(8.5 \times 10^{18} \text{ cm}^{-3} \text{ s}^{-1}\), respectively.

Electrode gap when the current-density amplitude is 10 mA/cm\(^2\). This case is representative of the \(\alpha\) mode, and corresponds to the first point in Fig. 2 where the maximum electron density is \(4.6 \times 10^{10} \text{ cm}^{-3}\) and the rf voltage amplitude is 217 V. The dashed curve indicates the boundary between the sheath and the plasma bulk, estimated using a technique reported recently.\(^{19}\) It is evident that significant electron production occurs both within the sheath region (e.g., between the sheath boundary and its nearest electrode) and the plasma bulk region. So gas ionization is volumetric and very similar to the \(\alpha\) mode of glow discharges in medium pressures.\(^{14,18}\) As an example of the \(\gamma\) mode, Fig. 3(b) plots the evolution of the normalized electron production rate across the electrode gap when the peak current density is 70 mA/cm\(^2\). This corresponds to the last point in Fig. 2 for which the maximum electron density is \(4.2 \times 10^{11} \text{ cm}^{-3}\). It is clear that electron production is largely confined in the boundary area between the sheath and the plasma bulk and intriguingly this is very similar to the behaviors of medium-pressure glow discharges in their \(\gamma\) mode.\(^{18}\)

To provide further insight into electron production, we plot in Fig. 4 the spatial profile of the electron mean energy when the electric field in the sheath is the largest, with the peak current density at 10 mA/cm\(^2\) in the \(\alpha\) mode (solid line) and 70 mA/cm\(^2\) in the \(\gamma\) mode (dashed line). Their maximum rates of electron production are \(4.1 \times 10^{10} \text{ cm}^{-3} \text{ s}^{-1}\) and \(8.5 \times 10^{18} \text{ cm}^{-3} \text{ s}^{-1}\), respectively.

C. Effects of secondary electrons

To further support the hypothesis that the operation regime above 410 V in Fig. 2 is in the \(\gamma\) mode, we plot the voltage dependence of the electron density for different secondary electron emission coefficients in Fig. 5. With a large secondary emission coefficient, more electrons are available to be accelerated to the helium ionization energy within the sheath, thus resulting in a large space-charge field to be established at a relatively low rf voltage. Again this is very similar to that in medium-pressure glow discharges,\(^{18}\) and responsible for an early onset of the \(\gamma\) mode in Fig. 5 when the secondary emission coefficient is 0.3. Also when the current density is sufficiently small, for example, less than 30 mA/cm\(^2\), that corresponds to a rf voltage of about 300 V in Fig. 5, secondary electron emission does not significantly influence the electron density and indeed other electrical characteristics. So the ionization by secondary electrons emitted from the electrodes is not important in the \(\alpha\) mode and instead primary electrons accelerated by the oscillating field of the applied voltage dominate the ionization. This also plasma stability and this is partly why most reported experiments of the rf APGD were operated in this mode.\(^{3,7,16,17}\)

For the 70 mA/cm\(^2\) case in the \(\gamma\)-mode region, the maximum electron mean energy is seen to be at 10.3 eV, much greater than 4.7 eV in the \(\alpha\) mode case of Fig. 3(a). Therefore, compared to the \(\alpha\) mode case, significantly more electrons can now reach the helium ionization energy within the sheath, thus resulting in most ionization events being confined to the sheath-bulk boundary region as indicated in Fig. 3(b). The more frequent ionization events in the sheath suggest a more rapid energy loss among more energetic electrons, leading to a smaller electron mean energy of 0.7 eV in the plasma bulk compared to 1.9 eV in the 10 mA/cm\(^2\) case. These observations are consistent to behaviors of medium-pressure glow discharges in their \(\gamma\) mode and as such offers further evidence of the existence of the \(\gamma\) mode in APGD. An important point to note is the rapid electron density increase of the \(\gamma\) mode in Fig. 2, which in practice relates to a similarly rapid increase of power dissipation in the plasma. Without restriction this sharp power increase can cause considerable gas heating and thus rapidly evolve the glow discharge into the arc plasma. This is partly why the \(\gamma\) mode is difficult to be observed in some rf APGD experiments.\(^{3,16}\) On the other hand if the current density is appropriately restricted, by means of resistive elements in the discharge circuitry, for example, rf APGD can be safely operated in their \(\gamma\) mode without undue gas heating,\(^{14}\) thus expanding their operation range beyond previously believed.

An ability to restrict the discharge current is important not only for the control of glow-to-arc transition but also for achieving the highest possible plasma density that are often beneficial for applications. Figure 2 shows clearly that larger electron density is achieved in the \(\gamma\) mode. Given that reactive plasma species tend to be more abundant at large electron density, a controlled operation of APGD in their \(\gamma\) mode is desirable especially for applications in which processing efficiency is important.

FIG. 4. Spatial profile of electron mean energy when the electric field in the sheath is the largest, with the peak current density at 10 mA/cm\(^2\) in the \(\alpha\) mode (solid line) and 70 mA/cm\(^2\) in the \(\gamma\) mode (dashed line). Their maximum rates of electron production are \(4.1 \times 10^{10} \text{ cm}^{-3} \text{ s}^{-1}\) and \(8.5 \times 10^{18} \text{ cm}^{-3} \text{ s}^{-1}\), respectively.
contributes to the volumetric nature of gas ionization in the \( \alpha \) mode. In other words, effects of secondary electrons are insignificant when rf APGD operates with low current densities\(^{16}\) and in the \( \alpha \) mode.

**IV. EFFECTS OF REACTION CHEMISTRY**

To establish whether the presence of the two APGD modes is generic, we use our He–N\(_2\) plasma model to study a 13.56-MHz APGD in a helium–nitrogen mixture with N\(_2\) content at 0.16 ppm. Again the electrode gap is 2.4 mm and the secondary emission coefficient is 0.1. Figure 6 shows the maximum electron density as a function of the peak rf voltage, and the division between the \( \alpha \) mode and the \( \gamma \) mode is distinct at a rf voltage amplitude of 284 V. Further numerical simulation is then used to study the regions of the most significant electron production and the effects of secondary electron emission, and its results resemble that in Figs. 3 and 5, respectively, thus confirming the existence of both APGD modes. The early onset of the \( \gamma \) mode at a smaller rf voltage in the He–N\(_2\) rf APGD is related to the fact that its gas ionization is considerably enhanced by the Penning ionization of nitrogen by helium metastables. Therefore, even at a modest rf voltage, adequate electron production is achieved in the sheath to set up a significant space-charge field there for the transition from the \( \alpha \) mode to the \( \gamma \) mode. From the standpoint of electron production, the more significant gas ionization in the He–N\(_2\) plasma is equivalent to a larger secondary emission coefficient in the pure-helium APGD of Fig. 5. In summary, plasma chemistry does not affect the presence of the two glow modes but influences strongly the transition voltage from the \( \alpha \) mode to the \( \gamma \) mode.

For both diagnostics and applications of APGD, larger electron density of the \( \gamma \) mode is desirable since this usually leads to more abundant reactive species. Figure 7 shows the time-averaged spatial profile of helium ions and metastables, for the first point of the He–N\(_2\) curve in Fig. 6 \((J = 20 \text{ mA/cm}^2)\) and for the last point of the curve \((J = 70 \text{ mA/cm}^2)\). It is seen that as the APGD operation evolves from the \( \alpha \) mode to the \( \gamma \) mode densities of all the plasma species increase. Intriguingly, atomic species increase much more significantly than molecular species. Table I shows the maximum densities of helium ions, nitrogen ions, and helium metastables at the two current densities. It is clear that in the \( \alpha \) mode the molecular species are more abundant, by at least one order of magnitude, than their atomic counterparts. So if APGD operates in the \( \alpha \) mode, it is advantageous to base both plasma diagnostics and application strategies on molecular species. In the \( \gamma \) mode on the other hand, atomic and molecular species are similarly abundant and so it is important to consider both when developing their diagnostic meth-
tolologies and their applications. In general the contrasting features of the two modes offer the potential to preferentially match the operation regime of APGD to the specific requirements of their applications and underline the importance to develop diagnostics strategies appropriate for their operation regimes.

V. CONCLUSION

A self-consistent computational study is presented to substantiate the existence of both the $\alpha$ mode and the $\gamma$ mode in rf APGD and to unravel their ionization mechanisms. It is established that gas ionization in the $\gamma$ mode is localized whereas that in the $\alpha$ mode is volumetric. Secondary electron emission strongly affects gas ionization in the $\gamma$ mode but matters little in the $\alpha$ mode. It is also shown that if the current density is restricted appropriately rf APGD can be operated in their $\gamma$ mode safely without the danger of evolving into arc plasmas. These findings suggest a wider operation range of rf APGD than previously believed. Furthermore the distinctively different dynamic behaviors of the two glow modes both offer the potential to preferentially match the operation regime of APGD to the specific requirements of their intended applications and emphasize the importance to develop diagnostics strategies appropriate for their operation regimes.


<table>
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<th>70 mA/cm²</th>
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