On the influence of electrode surfaces on the plasma chemistry and striations in a capacitive chlorine discharge

Jón Tómas Guðmundsson[1,2] and Bahram Mahdavipour[2]

[1]Space and Plasma Physics, KTH Royal Institute of Technology,
Stockholm, Sweden
[2] Science Institute, University of Iceland, Reykjavik, Iceland
`tumi@hi.is`

77th Gaseous Electronics Conference
San Diego, California
October 2., 2024

The oopd1 1d-3v PIC/MCC code

- We consider a chlorine discharge that consists of:
  - electrons
  - the ground state chlorine molecule $Cl_2(X\,^1\Sigma_g^+, v = 0)$,
  - the ground state chlorine atom $Cl(3p^5\,^2P)$
  - the negative chlorine ion Cl^-
  - the positive chlorine ions Cl^+ and Cl_2^+

Huang and Gudmundsson (2013) *Plasma Sources Sci. Technol.*, **22**(5) 055020

  - We use the `oopd1` (objective oriented plasma device for one dimension) code to simulate the discharge
  - The `oopd1` code was originally developed at the Plasma Theory and Simulation Group at UC Berkeley
  - It has 1 dimension in space and 3 velocity components for particles (1d-3v)

Gudmundsson et al. (2013) *Plasma Sources Sci. Technol.*, **22**(3) 035011

Wen et al. (2021) *Plasma Sources Sci. Technol.*, **30**(10) 105009

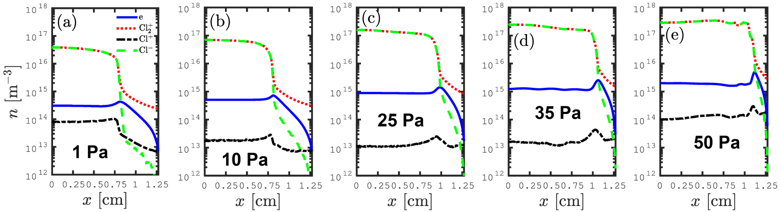
Electron power absorption

Voltage source operated at a single frequency

$$V(t) = V_{\mathrm{rf}} \sin(2\pi f t)$$

gap = 2.54 cm, V_{rf} = 222 V and f = 13.56 MHz

Electron power absorption



Proto and Gudmundsson (2021) PSST **30**(6) 065009

- The time averaged charged particle density profiles of a parallel plate capacitively coupled chlorine discharge
- At low pressures, the profile for Cl$_2^+$ ions is cosine-like or parabolic since Cl$_2^+$ ions are lost mainly due to diffusion to the walls
- As the pressure increases, the recombination between Cl$_2^+$ and Cl$^-$ ions becomes the major loss mechanism for Cl$_2^+$ ions and the density profile for Cl$_2^+$ and Cl$^-$-ions becomes flat in the bulk region

Electron power absorption

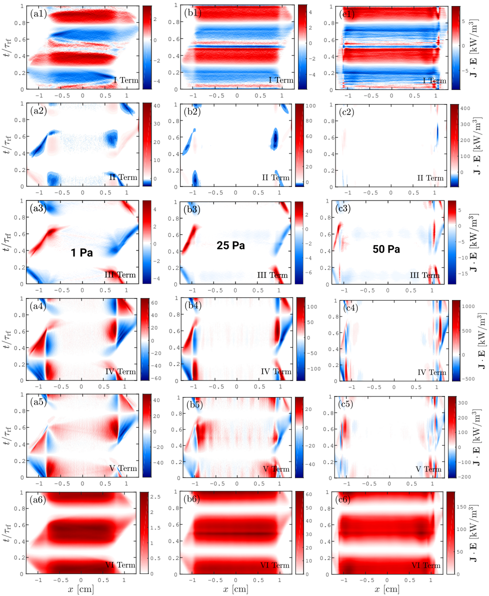
- To determine the electron power absorption mechanisms we apply Boltzman term analysis

$$J_\mathrm{e} \cdot E = \underbrace{m_\mathrm{e} u_\mathrm{e} n_\mathrm{e} \frac{\partial u_\mathrm{e}}{\partial t}}_{\mathrm{I}} - \underbrace{m_\mathrm{e} u_\mathrm{e}^3 \frac{\partial n_\mathrm{e}}{\partial x}}_{\mathrm{II}} - \underbrace{m_\mathrm{e} u_\mathrm{e}^2 \frac{\partial n_\mathrm{e}}{\partial t}}_{\mathrm{III}} + \underbrace{e u_\mathrm{e} T_\mathrm{e} \frac{\partial n_\mathrm{e}}{\partial x}}_{\mathrm{IV}} + \underbrace{e n_\mathrm{e} u_\mathrm{e} \frac{\partial T_\mathrm{e}}{\partial x}}_{\mathrm{V}} + \underbrace{m_\mathrm{e} n_\mathrm{e} \nu_\mathrm{c} u_\mathrm{e}^2}_{\mathrm{VI}} \qquad (1)$$

Surendra and Dalvie (1993) PRE **48**(5) 3914 and Schulze et al. (2018) **27**(5) 055010

- Terms I and III – power absorption due to electron inertia
- Term II – the electron density gradient
- Term IV – ambipolar field – electron density gradient
- Term V – the electron temperature gradient
    - Terms IV and V represent pressure or collisionless heating
- Term VI – electron neutral collisions or Ohmic heating

Electron power absorption



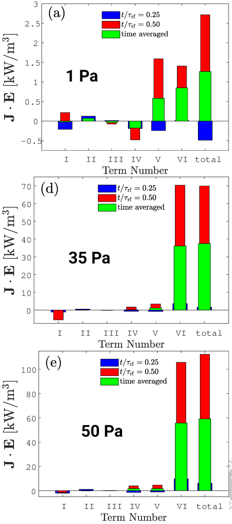
- The spatio temporal behavior of the various terms that constitute the electron power absorption
  - Terms I and III – electron inertia
  - Term II – electron density gradient
  - Terms IV and V – pressure (collisionless) heating
  - Term VI – Ohmic heating

Proto and Gudmundsson (2021) PSST **30**(6) 065009

Electron power absorption

- The space averaged electron power absorption profile terms
  - $t/\tau_{\mathrm{rf}} = 0.25$ blue bar
  - $t/\tau_{\mathrm{rf}} = 0.5$ red bar
  - time averaged green bar
- At 1 Pa the pressure terms and the Ohmic term contribute to the electron power absorption
- At higher pressures Ohmic power absorption dominates

Proto and Gudmundsson (2021) PSST **30**(6) 065009



Surface effects

Voltage source operated at a single frequency

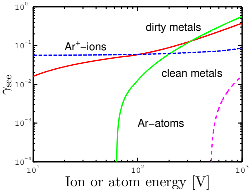
$$V(t) = V_{\mathrm{rf}} \sin(2\pi f t)$$

gap = 2.54 cm, V_{rf} = 222 V and f = 13.56 MHz

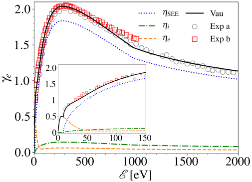
Secondary electron emission

Secondary electron emission due to

- ion bombardment of the electrodes
- neutral bombardment of the electrods
  - Using fits for argon bombardent developed by Phelps and Petrović (1999)
- electron bombardment of the electrodes
  - Using the modified Vaughan method as described by Wen et al. (2023)



based on Phelps and Petrović (1999) PSST **8** R21



Wen et al. (2023) PSST **32** 064001

Secondary electron emission – the cases explored

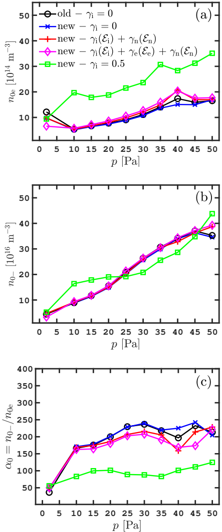
Case	cross section	neutrals	ions	electrons
I	old	0.0	0.0	0.0
II	new	0.0	0.0	0.0
III	new	$\gamma_{\mathrm{see,n}}(\mathcal{E}_{\mathrm{n}})$	$\gamma_{\mathrm{see,i}}(\mathcal{E}_{\mathrm{i}})$	0.0
IV	new	$\gamma_{\mathrm{see,n}}(\mathcal{E}_{\mathrm{n}})$	$\gamma_{\mathrm{see,i}}(\mathcal{E}_{\mathrm{i}})$	$\gamma_{\mathrm{see,e}}(\mathcal{E}_{\mathrm{e}}, \theta)$
V	new	0.0	0.5	0.0

- In Cases I and II the secondary electron emission processes are neglected
- Case III assumes only neutral and ion induced energy dependent secondary electron emission yield
- Case IV has in addition electron induced secondary electron emission
- Case V assumes only a constant ion induced secondary electron emission yield

Secondary electron emission

- The electron density, the Cl$^-$ density, and the electronegativity in the discharge center (α_0) versus pressure
- With increasing pressure the electronegativity in the discharge center α_0 increases before it stabilizes at a relatively constant level
- Secondary electron emission from the electrodes leads to a reduction in electronegativity, which is especially noticeable at higher pressures

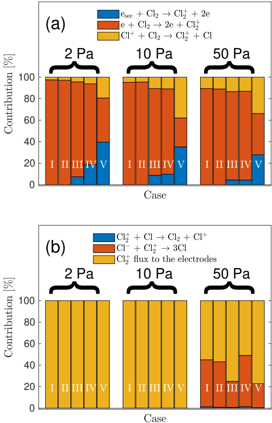
Mahdavipour and Gudmundsson (2024) PSST **33**(6) 065006



Secondary electron emission

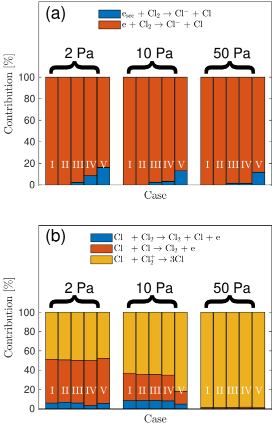
- The creation and loss of Cl_2^+ ions
- Electron impact ionization creates the Cl_2^+ ions
- At the lower pressures the Cl_2^+ ions are almost entirely lost as they bombard the electrodes
- With increasing pressure to 50 Pa the role of ion-ion mutual recombination increases

Mahdavipour and Gudmundsson (2024) PSST **33**(6) 065006



Secondary electron emission

- The creation and loss of Cl^- ions
- The creation of the negative ion Cl^- is almost entirely due to dissociative attachment
- The dominating loss processes for the negative ion Cl^- at 50 Pa is ion-ion mutual neutralization $Cl^- + Cl_2^+$
- Lowering the pressure associative detachment by the Cl atom and detachment by the Cl_2 molecule play an increasing role, with over 50 % contribution at 2 Pa



Mahdavipour and Gudmundsson (2024) PSST **33**(6) 065006

Striations

Voltage source operated at a single frequency

$$V(t) = V_{\mathrm{rf}} \sin(2\pi f t)$$

gap = 2.54 cm, V_{rf} = 222 V and f = 13.56 MHz

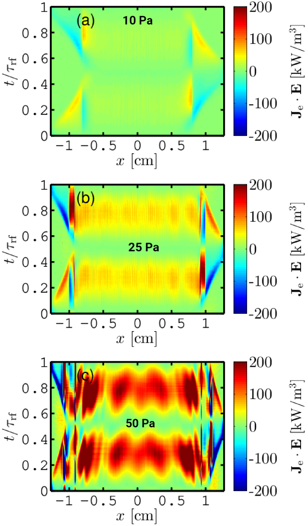
$$\gamma_{\mathrm{i}}(\mathcal{E}_{\mathrm{i}}) + \gamma_{\mathrm{n}}(\mathcal{E}_{\mathrm{n}}) + \gamma_{\mathrm{e}}(\mathcal{E}_{\mathrm{e}}, \theta)$$

Secondary electron emission

- The spatio-temporal behaviour of primary electron power absorption for the most realistic secondary electron emission model

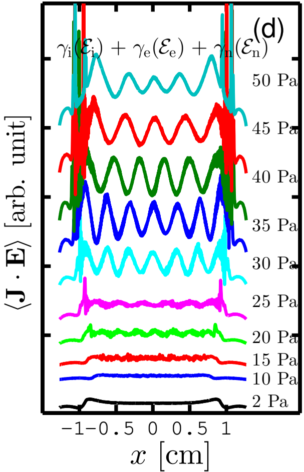
$$\gamma_{\rm total} = \gamma_{\rm i}(\mathcal{E}_{\rm i}) + \gamma_{\rm n}(\mathcal{E}_{\rm n}) + \gamma_{\rm e}(\mathcal{E}_{\rm e}, \theta)$$

- There is a clear indication of the α-mode and the drift-ambipolar (DA) mode
- At higher pressure of 25 and 50 Pa we observe an increase in electron power absorption and pronounced striation structure



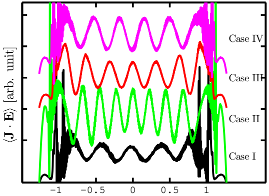
Secondary electron emission

- Primary electron power absorption as the pressure is varied
- We observe striation pattern at 15 Pa
- Above 15 Pa the striation amplitude increases with increased pressure up to 35 Pa, and then decreases
- The number of striations decreases with increased pressure

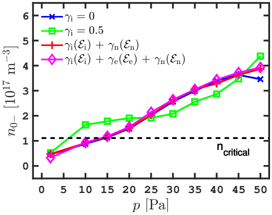


Secondary electron emission

- The primary electron power absorption profiles while varying the secondary emission processes (Cases I – IV) at 40 Pa
- Case II (γ_{i} = 0.5) exhibits the highest number of striations, while Case I (no secondary emission) has the lowest number
- It appears that including secondary electron emission in the discharge model increases both the amplitude and the number of the striations
- This contradicts what has been observed for a cpacitive oxygen (Wang et al., 2019) and CF$_4$ (Wang et al., 2023) discharges



Secondary electron emission



- Striations are known to appear in electronegative discharges when two conditions are simultaneously fulfilled:
  - high enough electronegativity
  - driving frequency that is comparable to the ion plasma frequency
- Based on the ion-ion plasma model striations may appear when $n_\mathrm{ion} > n_\mathrm{critical}$ where the critical density is defined as (Liu et al., 2017)

$$n_\mathrm{critical} = \frac{\omega_\mathrm{rf}^2 \epsilon_0 \mu}{e^2}$$

where $\mu = m_+ m_- / (m_+ + m_-)$ is the reduced mass of the positive and negative ions

Summary

Summary

- The chlorine discharge exhibits high electronegativity
- At the lowest pressure (1 Pa) the electron power absorption is due to both the pressure and the Ohmic terms and at higher pressure Ohmic terms dominate (drift-ambipolar (DA) mode)
- Striations start to appear in the discharge bulk at pressure around 15 Pa and peak in amplitude for pressure around 40 Pa and then decline again
- We find that the amplitude and the number of striations increase with the addition of secondary electron emission to the discharge model

Thank you for your attention

`tumi@hi.is`

References

Gudmundsson, J. T., E. Kawamura, and M. A. Lieberman (2013). A benchmark study of a capacitively coupled oxygen discharge of the oopd1 particle-in-cell Monte Carlo code. *Plasma Sources Science and Technology 22*(3), 035011.

Huang, S. and J. T. Gudmundsson (2013). A particle-in-cell/Monte Carlo simulation of a capacitively coupled chlorine discharge. *Plasma Sources Science and Technology 22*(5), 055020.

Liu, Y.-X., I. Korolov, E. Schüngel, Y.-N. Wang, Z. Donkó, and J. Schulze (2017). Striations in electronegative capacitively coupled radio-frequency plasmas: analysis of the pattern formation and the effect of the driving frequency. *Plasma Sources Science and Technology 26*(5), 055024.

Mahdavipour, B. and J. T. Gudmundsson (2024). On the influence of electrode surfaces on the plasma chemistry of a capacitive chlorine discharge. *Plasma Sources Science and Technology 33*(6), 065006.

Phelps, A. V. and Z. L. Petrović (1999). Cold-cathode discharges and breakdown in argon: surface and gas phase production of secondary electrons. *Plasma Sources Science and Technology 8*(3), R21–R44.

Proto, A. and J. T. Gudmundsson (2021). Electron power absorption in radio frequency driven capacitively coupled chlorine discharge. *Plasma Sources Science and Technology 30*(6), 065009.

Schulze, J., A. Derzsi, K. Dittmann, T. Hemke, J. Meichsner, and Z. Donkó (2011). Ionization by drift and ambipolar electric fields in electronegative capacitive radio frequency plasmas. *Physical Review Letters 107*, 275001.

Schulze, J., Z. Donkó, T. Lafleur, S. Wilczek, and R. P. Brinkmann (2018). Spatio-temporal analysis of the electron power absorption in electropositive capacitive RF plasmas based on moments of the Boltzmann equation. *Plasma Sources Science and Technology 27*(5), 055010.

References

Skarphedinsson, G. A. and J. T. Gudmundsson (2020). Tailored voltage waveforms applied to a capacitively coupled chlorine discharge. *Plasma Sources Science and Technology 29*(8), 084004.

Surendra, M. and M. Dalvie (1993). Moment analysis of rf parallel-plate-discharge simulations using the particle-in-cell with Monte Carlo collisions technique. *Physical Review E 48*(5), 3914–3924.

Thorsteinsson, E. G. and J. T. Gudmundsson (2010). A global (volume averaged) model of a chlorine discharge. *Plasma Sources Science and Technology 19*(1), 015001.

Wang, L., D.-Q. Wen, Q.-Z. Zhang, Y.-H. Song, Y.-R. Zhang, and Y.-N. Wang (2019). Disruption of self-organized striated structure induced by secondary electron emission in capacitive oxygen discharges. *Plasma Sources Science and Technology 28*(5), 055007.

Wang, X.-K., R. Masheyeva, Y.-X. Liu, P. Hartmann, J. Schulze, and Z. Donkó (2023). The electrical asymmetry effect in electronegative CF_4 capacitive RF plasmas operated in the striation mode. *Plasma Sources Science and Technology 32*(8), 085009.

Wen, D.-Q., J. Krek, J. T. Gudmundsson, E. Kawamura, M. A. Lieberman, and J. P. Verboncoeur (2021). Benchmarked and upgraded particle-in-cell simulations of capacitive argon discharge at intermediate pressure: The role of metastable atoms. *Plasma Sources Science and Technology 30*(10), 105009.

Wen, D.-Q., J. Krek, J. T. Gudmundsson, E. Kawamura, M. A. Lieberman, P. Zhang, and J. P. Verboncoeur (2023). On the importance of excited state species in low pressure capacitively coupled plasma argon discharges. *Plasma Sources Science and Technology 32*(6), 064001.