Plasma Chemistry and Kinetics in Low Pressure Discharges

Jón Tómas Guðmundsson

Science Institute, University of Iceland, Iceland

tumi@hi.is

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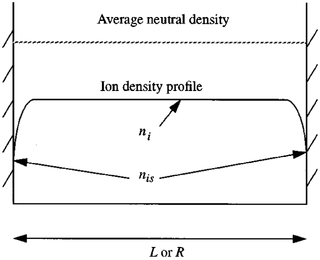
A. Global (volume averaged) chemistry models

Global (volume averaged) chemistry models

- The main idea of a global model is to generate a model that encompasses a large number of reactions in order to model a processing plasma with a limited computing power by neglecting the complexity which arises when spatial variations are considered
- Thus the model does not describe spatial distribution but captures scalings of plasma parameters with control parameters
- The model allows us to investigate various phenomena, such as the effects of excited species, negative ions and particular reactions on the overall discharge

Global (volume averaged) chemistry models

- All densities are assumed to be volume averaged
- For an electropositive discharge the positive-ion densities are assumed to have a uniform profile throughout the discharge except near the wall, where the density is assumed to drop sharply to a sheath-edge density n_{is}
- The electron energy distribution function (EEDF) is assumed (usually Maxwellian)
- The ion and neutral temperature have to be assumed



Lee and Lieberman *JVSTA*, **13** (1995) 368

A.1 Global (volume averaged) chemistry models – argon discharge

Argon discharge – electron - neutral collisions

- In its simplest form argon discharge consists of

$$\mathrm{e}, \mathrm{Ar}, \mathrm{Ar}^+, \mathrm{Ar}^*$$

- There are electron-atom collisions

$$\mathrm{e} + \mathrm{Ar} \longrightarrow \mathrm{Ar}^+ + 2\mathrm{e} \qquad \text{(ionization)}$$

$$\mathrm{e} + \mathrm{Ar} \longrightarrow \mathrm{Ar}^* + \mathrm{e} \longrightarrow \mathrm{Ar} + \mathrm{e} + \text{photon} \qquad \text{(excitation)}$$

$$\mathrm{e} + \mathrm{Ar} \longrightarrow \mathrm{Ar} + \mathrm{e} \qquad \text{(elastic scattering)}$$

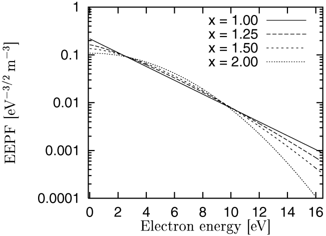
- The reactions are described by **rate coefficients**

$$k(\mathrm{T_e}) = \langle \sigma(v_\mathrm{R}) v_\mathrm{R} \rangle$$

where $\sigma(v_\mathrm{R})$ is the cross section and v_R is the relative velocity of colliding particles

Argon discharge – electron - neutral collisions

- The electron energy distribution function (EEDF) is usually assumed to be Maxwellian
- We can also assume a general electron energy distribution



$$g_{\mathrm{e}}(\mathcal{E}) = c_1 \mathcal{E}^{1/2} \exp\left(-c_2 \mathcal{E}^x\right)$$

$$c_1 = \frac{1}{\langle \mathcal{E} \rangle^{3/2}} \frac{[\Gamma(\xi_2)^{3/2}]}{[\Gamma(\xi_1)^{5/2}]} \quad \text{and} \quad c_2 = \frac{1}{\langle \mathcal{E} \rangle^x} \frac{[\Gamma(\xi_2)]}{[\Gamma(\xi_1)]^x}$$

where $\xi_1 = 3/2x$ and $\xi_2 = 5/2x$

$$g_{\mathrm{p}}(\mathcal{E}) = \frac{g_{\mathrm{e}}(\mathcal{E})}{\mathcal{E}^{1/2}}$$

- Here $x = 1$ and $x = 2$ correspond to Maxwellian and Druyvesteyn electron energy distributions, repectively

Gudmundsson *PSST*, **10** (2001) 76

Argon discharge – ion - neutral collisions

- Argon ions collide with argon atoms

$$\mathrm{Ar}^{+} + \mathrm{Ar} \longrightarrow \mathrm{Ar}^{+} + \mathrm{Ar} \quad \text{(elastic scattering)}$$

$$\mathrm{Ar}^{+} + \mathrm{Ar} \longrightarrow \mathrm{Ar} + \mathrm{Ar}^{+} \quad \text{(charge transfer)}$$

- The total cross section for ions at room temperature

$$\sigma_{\mathrm{i}} \approx 10^{-18}\ \mathrm{m}^2$$

- The ion-neutral mean free path – the distance an ion travels before colliding is

$$\lambda_{\mathrm{i}} = \frac{1}{n_{\mathrm{g}}\sigma_{\mathrm{i}}} = \lambda_{\mathrm{i}}\ [\mathrm{cm}] = \frac{1}{330\ p\ [\mathrm{Torr}]}$$

where n_{g} is the neutral gas density – $\lambda_{\mathrm{i}} \approx 1$ cm at 3 mTorr

Argon discharge – Energy loss processes

- There are three energy loss processes:
  - **Collisional energy** $\mathcal{E}_{\mathrm{c}}$ lost per electron-ion pair created

$$\mathcal{E}_{\mathrm{c}}(\mathrm{T_e}) = \mathcal{E}_{\mathrm{iz}} + \sum_{i=1}^{n} \frac{k_{\mathrm{ex},i}}{k_{\mathrm{iz}}} \mathcal{E}_{\mathrm{ex},i} + \frac{k_{\mathrm{el}}}{k_{\mathrm{iz}}} \frac{3m_{\mathrm{e}}}{M} \mathrm{T_e}$$

  - **Electron kinetic energy** lost to walls

$$\mathcal{E}_{\mathrm{e}} = 2\mathrm{T_e} \quad \text{if Maxwellian EEDF}$$

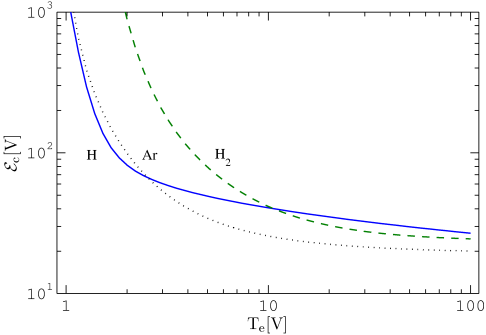
  - **Ion kinetic energy** lost to walls

$$\mathcal{E}_{\mathrm{i}} \approx \bar{V}_{\mathrm{s}}$$

    or mainly the dc potential across the sheath
- The total energy lost per electron-ion pair lost to walls

$$\mathcal{E}_{\mathrm{T}} = \mathcal{E}_{\mathrm{c}} + \mathcal{E}_{\mathrm{e}} + \mathcal{E}_{\mathrm{i}}$$

Argon discharge – Collisional energy losses



- The collisional energy loss per electron-ion pair created for argon, hydrogen atoms and hydrogen molecules assuming Maxwellian EEDF

Hjartarson et al., *Plasma Sources Sci. Technol.*, **19** 065009 (2010)

Argon discharge – Ion loss

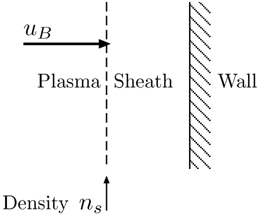
- Ions are lost at the **Bohm velocity** at the plasma-sheath edge

$$u_{\mathrm{i}} = u_{\mathrm{B}} = \left(\frac{k_{\mathrm{B}} T_{\mathrm{e}}}{M}\right)^{1/2}$$

assuming Maxwellian energy distribution or more generally

$$v_{\mathrm{i}} = \langle \mathcal{E} \rangle^{1/2} \left(\frac{2}{M}\right)^{1/2} \frac{[\Gamma(\xi_1)]}{[\Gamma(\xi_2)\Gamma(\xi_3)]^{1/2}}$$

where $\xi_1 = 3/2x$, $\xi_2 = 5/2x$ and $\xi_3 = 1/2x$



Argon discharge – Diffusion

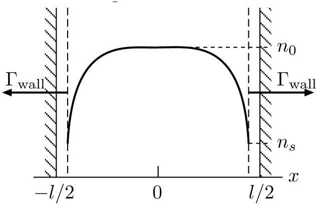
- A low pressure (< 100 mTorr in argon) the plasma density profile is relatively flat in the center and falls sharply near the sheath edge
- Ion and electron loss to the wall is

$$\Gamma_{\mathrm{wall}} = n_{\mathrm{s}} u_{\mathrm{B}} \equiv h_{\ell} n_0 u_{\mathrm{B}}$$

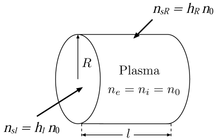
- The **edge-to-center density ratio** is

$$h_{\ell} \equiv \frac{n_{\mathrm{s}}}{n_0} \approx \frac{0.86}{(3 + \ell/2\lambda_{\mathrm{i}})^{1/2}}$$

where λ_{i} is the ion-neutral mean free path



Argon discharge – Cylindrical discharge



- Loss fluxes to the axial and radial walls are

$$\Gamma_{\mathrm{axial}} = h_\ell n_0 u_{\mathrm{B}} \quad \text{and} \quad \Gamma_{\mathrm{radial}} = h_{\mathrm{R}} n_0 u_{\mathrm{B}}$$

and the edge-to-center density ratios are

$$h_\ell \approx \frac{0.86}{(3 + \ell/2\lambda_{\mathrm{i}})^{1/2}} \quad \text{and} \quad h_{\mathrm{R}} \approx \frac{0.8}{(4 + R/\lambda_{\mathrm{i}})^{1/2}}$$

Godyak, *Soviet Radio Frequency Discharge Research* (1986)

Argon discharge – Cylindrical discharge

- At high pressure

$$\ell \frac{T_\mathrm{i}}{T_\mathrm{e}} \geq \lambda_\mathrm{i}$$

a constant diffusion model is more appropriate

$$h_\ell \approx \frac{\pi D_\mathrm{a}}{\ell u_\mathrm{B}}$$

- These regimes can be joined heuristically giving

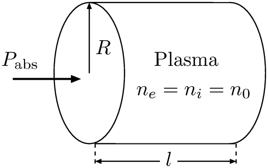
$$h_\ell \approx \frac{0.86}{\left[3 + \ell/2\lambda_\mathrm{i} + (0.86 R u_\mathrm{B}/\pi D_\mathrm{a})^2\right]^{1/2}}$$

$$h_\mathrm{R} \approx \frac{0.8}{\left[4 + R/\lambda_\mathrm{i} + (0.8 R u_\mathrm{B}/\chi_{01} \mathrm{J}_1(\chi_{01}) D_\mathrm{a})^2\right]^{1/2}}$$

Lee and Lieberman *J. Vac. Sci. Technol. A*, **13** (1995) 368

Lieberman and Lichtenberg, *Principles of Plasma Discharges*, 2nd ed., John Wiley & Sons 2005

Argon discharge – Particle balance



- We assume a uniform cylindrical plasma and the absorbed power is $P_{\rm abs}$
- Particle balance

$$\underbrace{n_{\rm g} n_0 k_{\rm iz} R^2 \ell}_{\text{ionization in the bulk plasma}} = \underbrace{(2\pi R^2 h_\ell n_0 + 2\pi R \ell h_{\rm R} n_0) u_{\rm B}}_{\text{ion loss to walls}}$$

Argon discharge – Particle balance

- Rearrange to obtain

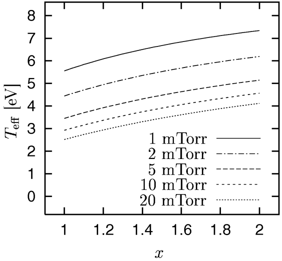
$$\frac{k_{\mathrm{iz}}(T_{\mathrm{e}})}{u_{\mathrm{B}}(T_{\mathrm{e}})} = \frac{1}{n_{\mathrm{g}} d_{\mathrm{eff}}}$$

where

$$d_{\mathrm{eff}} = \frac{1}{2} \frac{R\ell}{Rh_{\ell} + \ell h_R}$$

is an effective plasma size

- So given n_{g} (pressure) and d_{eff} (pressure,dimensions) we know $\mathrm{T_e}$
- The electron temperature is generally in the range 2 – 5 V



$R = 15.24$ cm

$\ell = 7.6$ cm

Gudmundsson *PSST*, **10** (2001) 76

Argon discharge – Power balance

- The power balance is

$$\underbrace{P_{\text{abs}}}_{\text{power in}} = \underbrace{(h_\ell n_0 2\pi R^2 + h_{\text{R}} n_0 2\pi R\ell) u_{\text{B}} e\mathcal{E}_{\text{T}}}_{\text{power lost}}$$

- Solve for particle density

$$n_0 = \frac{P_{\text{abs}}}{A_{\text{eff}} u_{\text{B}} e\mathcal{E}_{\text{T}}}$$

where

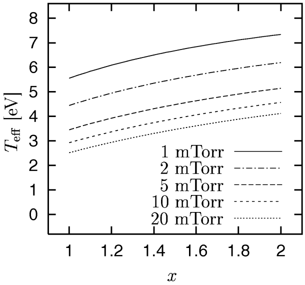
$$A_{\text{eff}} = 2\pi R^2 h_\ell + 2\pi R\ell h_{\text{R}}$$

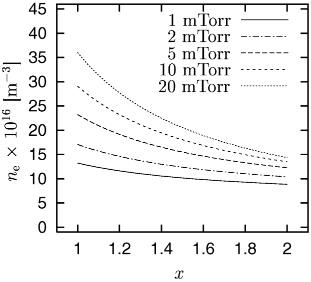
is an effective area for particle loss

- Assume low voltage sheaths at all surfaces

$$\mathcal{E}_{\text{T}} = \mathcal{E}_{\text{c}} + \mathcal{E}_{\text{e}} + \mathcal{E}_{\text{i}} = \mathcal{E}_{\text{c}}(\text{T}_{\text{e}}) + 2\text{T}_{\text{e}} + 5.2\text{T}_{\text{e}}$$

Argon discharge – Power and particle balance





- Particle balance gives the electron temperature
  - only depends on the neutral gas pressure and system dimensions
- Power balance gives the plasma density
  - Once we know the electron temperature

Gudmundsson *Plasma Sources Sci. Technol.*, **10** (2001) 76

A.2 Global (volume averaged) chemistry models – chlorine

The chlorine discharge

- Chlorine is an electronegative diatomic gas that is widely used in plasma etching of both semiconductors and metals, in particular poly-silicon gate and aluminum interconnects
- Chlorine atoms are believed to be the primary reactant in plasma etching
- The chlorine molecule has
  - a low dissociation energy (2.5 eV)
  - a near-zero threshold energy for dissociative attachment
- All electronic excitations of the molecule appear to be dissociative, and no metastable molecular states are of importance

The global (volume averaged) model

- A steady state global (volume averaged) model was developed for the chlorine discharge
- The following species are included
  - electrons
  - the ground state chlorine molecule $\mathrm{Cl_2}(X\,{}^1\Sigma_g^+, v = 0)$,
  - the vibrationally excited ground state chlorine molecules $\mathrm{Cl_2}(X\,{}^1\Sigma_g^+, v = 1 - 3)$
  - the ground state chlorine atom $\mathrm{Cl}(3p^{5\;2}P)$
  - the negative chlorine ion Cl^-
  - the positive chlorine ions Cl^+ and Cl_2^+
- The content of the chamber is assumed to be nearly spatially uniform and the power is deposited uniformly into the plasma bulk

Thorsteinsson and Gudmundsson, *Plasma Sources Sci. Technol.*, **19** (2010) 015001

The global (volume averaged) model

- The particle balance equation for a species X is given

$$\frac{\mathrm{d}n^{(X)}}{\mathrm{d}t} = 0 = \sum_i R^{(X)}_{\mathrm{Generation},i} - \sum_i R^{(X)}_{\mathrm{Loss},i}$$

  where $R^{(X)}_{\mathrm{Generation},i}$ and $R^{(X)}_{\mathrm{Loss},i}$, respectively, are the reaction rates of the various generation and loss processes of the species X

- The power balance equation, which equates the absorbed power P_{abs} to power losses due to elastic and inelastic collisions and losses due to charged particle flow to the walls is given as

$$\frac{1}{V}\left[P_{\mathrm{abs}} - eVn_{\mathrm{e}}\sum_{\alpha} n^{(\alpha)}\mathcal{E}_{\mathrm{c}}^{(\alpha)}k_{\mathrm{iz}}^{(\alpha)} - eu_{\mathrm{B0}}n_{\mathrm{i}}A_{\mathrm{eff}}(\mathcal{E}_{\mathrm{i}} + \mathcal{E}_{\mathrm{e}})\right] = 0$$

The global (volume averaged) model

- For the edge-to-center positive ion density ratio we use

$$h_\ell \simeq \left[\left(\frac{0.86}{(3+\eta L/2\lambda_\mathrm{i})^{1/2}}\frac{1}{1+\alpha_0}\right)^2 + h_\mathrm{c}^2\right]^{1/2}$$

$$h_\mathrm{R} \simeq \left[\left(\frac{0.8}{(4+\eta R/\lambda_\mathrm{i})^{1/2}}\frac{1}{1+\alpha_0}\right)^2 + h_\mathrm{c}^2\right]^{1/2}$$

where $\alpha_0 \approx (3/2)\alpha$ is the central electronegativity, $\eta = 2T_+/(T_+ + T_-)$ and

$$h_\mathrm{c} \simeq \left[\gamma_-^{1/2} + \gamma_+^{1/2}[n_*^{1/2} n_+/n_-^{3/2}]\right]^{-1} \quad \text{and} \quad n_* = \frac{15}{56}\frac{\eta^2}{k_\mathrm{rec}\lambda_\mathrm{i}} v_\mathrm{i}$$

is based on a one-region flat topped electronegative profile

$$\gamma_- = \mathrm{T_e}/\mathrm{T_-} \quad \text{and} \quad \gamma_+ = \mathrm{T_e}/\mathrm{T_+}$$

Kim et al., J. Vac. Sci. Technol. A, **24** (2006) 2025

The global (volume averaged) model

- The diffusional losses of the neutral chlorine atoms to the reactor walls are given by

$$k_{\mathrm{Cl,wall}} = \left[\frac{\Lambda_{\mathrm{Cl}}^2}{D_{\mathrm{Cl}}} + \frac{2V(2-\gamma_{\mathrm{rec}})}{Av_{\mathrm{Cl}}\gamma_{\mathrm{rec}}}\right]^{-1} \quad \mathrm{s}^{-1}$$

  - D_{Cl} is the diffusion coefficient for neutral chlorine atoms
  - $v_{\mathrm{Cl}} = (8eT_{\mathrm{g}}/\pi m_{\mathrm{Cl}})^{1/2}$ is the mean Cl velocity
  - γ_{rec} is the wall recombination coefficient for neutral chlorine atoms on the wall surface
  - Λ_{Cl} is the effective diffusion length of neutral chlorine atoms

$$\Lambda_{\mathrm{Cl}} = \left[\left(\frac{\pi}{L}\right)^2 + \left(\frac{2.405}{R}\right)^2\right]^{-1/2}$$

- The wall recombination coefficient γ_{rec} is one of the most important parameters in chlorine discharge modelling

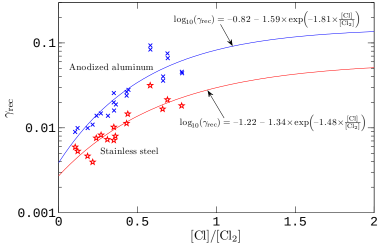
A.2.1 Model parameters

Surface recombination

- The wall recombination probability, γ_{rec}, is a very important quantity in all low pressure molecular discharges
- We use the wall recombination coefficient measured by Stafford et al. (2009) for stainless steel

Guha et al. J. Appl. Phys., **103** (2008) 013306

Stafford et al. J. Phys. D: Appl. Phys. **42** (2009) 055206



A fit to the measured data is for anodized aluminum

$$\log_{10}(\gamma_{\text{rec}}) = -0.82 - 1.59 \exp\left(-1.81 \times \frac{[\text{Cl}]}{[\text{Cl}_2]}\right)$$

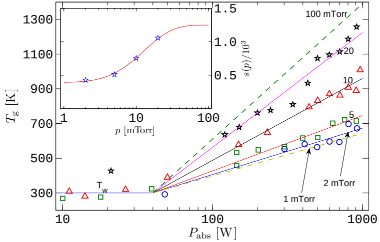
and for stainless steel

$$\log_{10}(\gamma_{\text{rec}}) = -1.22 - 1.34 \exp\left(-1.48 \times \frac{[\text{Cl}]}{[\text{Cl}_2]}\right)$$

Gas temperature

- Donnelly and Malyshev (2000) found that the neutral chlorine gas temperature was between 300 and 1250 K, increasing with power and pressure up to 1000 W and 20 mTorr

Donnelly and Malyshev, Appl. Phys. Lett. **77** 2467 (2000)



A fit through the measured data gives

$$T_g(P_{abs}, p) = 300 + s(p)\frac{\log_{10}(P_{abs}/40)}{\log_{10}(40)}$$

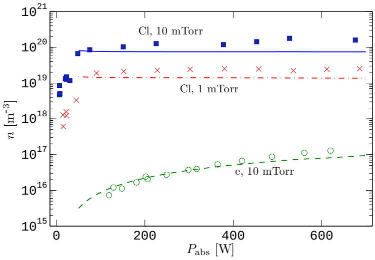
where

$$s(p) = 1250\,(1 - e^{-0.091\times p}) + 400\,e^{-0.337\times p}$$

A.2.2 Comparison with experiments

Comparison with experiments

- Densities of neutral Cl atoms and electrons versus power
- The agreement with the measured electron density is excellent
- The calculated density of atomic chlorine is in a very good agreement with the measured data at both 1 and 10 mTorr



- inductively coupled cylindrical stainless steel chamber
- $L = 20$ cm and $R = 18.5$ cm

Malyshev and Donnelly, J. Appl. Phys. **88** (2000) 6207

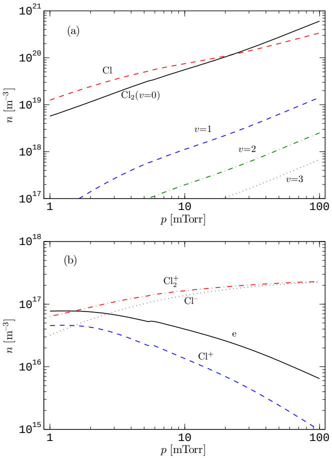
Malyshev and Donnelly, J. Appl. Phys. **90** (2001) 1130

A.2.3 Particle densities

Particle densities

- Atomic chlorine Cl is the dominant particle at low pressure, but the chlorine molecule Cl_2 has a larger density above 20 mTorr
- The density of the atomic ion Cl^+ is always much smaller than the Cl_2^+ density, decreasing with pressure
- a cylindrical stainless steel chamber radius $R = 18.5$ cm and length $L = 20$ cm

  $P_{\text{abs}} = 323$ W



Thorsteinsson and Gudmundsson, *Plasma Sources Sci. Technol.*, **19** (2010) 015001

Creation and destruction of Cl atoms

- Electron impact dissociation

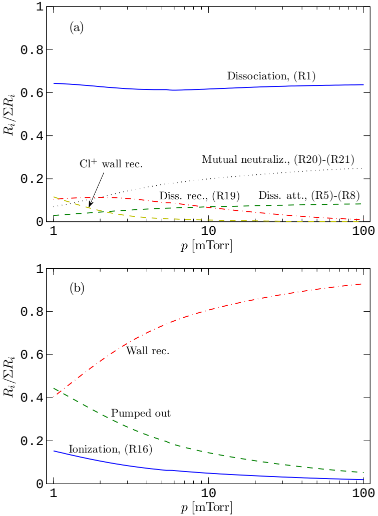
$$e + Cl_2 \longrightarrow Cl + Cl + e$$

is the most important channel for creation of Cl atoms

- Recombination at the wall

$$Cl \longrightarrow \frac{1}{2}Cl_2$$

accounts for 40 – 93 % and is the most important channel for Cl atom loss



Creation and destruction of Cl^- ions

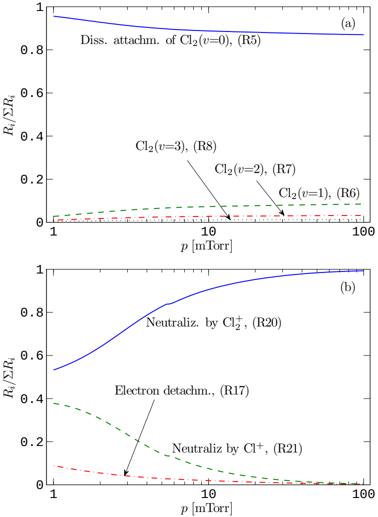
- The production of Cl^--ions is only due to dissociative electron attachment

$$e + Cl_2 \longrightarrow Cl + Cl^-$$

- Vibrational levels contribute at most 14 % at 100 mTorr
- Cl^- ions are primarily lost by mutual neutralization

$$Cl^- + Cl_2^+ \longrightarrow Cl + Cl + Cl$$

$$Cl^- + Cl^+ \longrightarrow Cl + Cl$$



A.2.4 Sensitivity analysis

Sensitivity analysis – EEDF

- The discharge pressure was 10 mTorr and the absorbed power 323 W
- We allow the electron energy distribution function to vary according to the general distribution function

$$g_{\mathrm{e}}(\mathcal{E}) = c_1 \mathcal{E}^{1/2} \exp(-c_2 \mathcal{E}^x)$$

where the coefficients c_1 and c_2 depend on the energy $\mathcal{E}$ and the distribution parameter x

	$[\mathrm{Cl}]/n_{\mathrm{g}}$	$[\mathrm{Cl}^+]/n_+$	α	T_{e}	n_{e}
x: 1 – 2	$\downarrow 1.01$	$\downarrow 1.40$	$\uparrow 1.34$	$\uparrow 1.43$	$\downarrow 1.65$

Gudmundsson et al., *Vacuum*, **86** (2012) 808

Sensitivity analysis – γ_{rec}

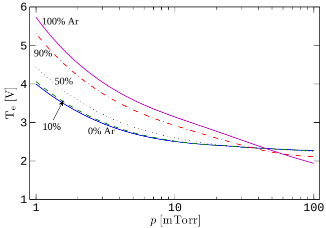
	[Cl]/n_{g}	[Cl^{+}]/n_{+}	α	$\mathrm{T_e}$	n_{e}
γ_{rec}: 10^{-4} – 1	$\downarrow$ 5.75	$\downarrow$ 34.6	$\uparrow$ 4.25	$\uparrow$ 1.13	$\downarrow$ 1.59

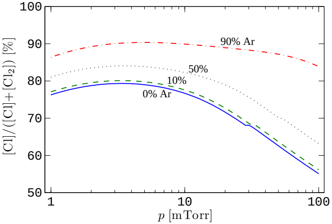
- The wall recombination coefficient γ_{rec} determines the rate coefficient for recombination of neutrals on the wall
- However, varying γ_{rec} has a much larger effect on the atomic ion fraction than on the dissociation fraction

A.2.5 Argon dilution

Argon dilution – Particle densities

- The electron temperature increases with argon content at low and intermediate pressures
- The chlorine dissociation increases with argon content
- The discharge is highly dissociated with Cl atoms being the dominant neutral until the argon content is 60%



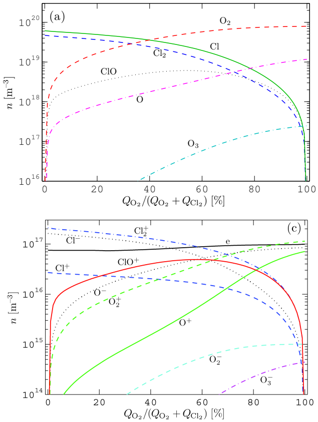


Thorsteinsson and Gudmundsson, *J. Phys. D.*, **43** 115201 (2010)

A.2.6 Oxygen dilution

Oxygen dilution – Particle densities

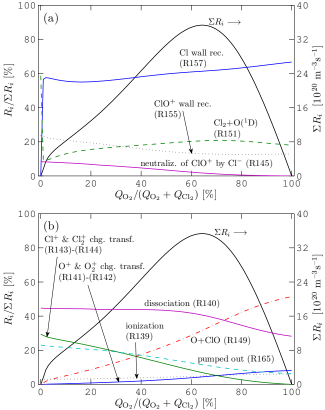
- The Cl^+ density decreases with increased oxygen dilution
- The chlorine-oxide molecule ClO and its ion ClO^+ peak when Cl_2 and O_2 flowrates are roughly equal
- The $O_2(a^1\Delta_g)$ density is about 9 – 10 % of the total O_2 density
- The electron density increases about 30 % between pure chlorine and pure oxygen discharge



A cylindrical stainless steel chamber
L = 10 cm and R = 10 cm
p = 10 mTorr and P_{abs} = 500 W

Oxygen dilution – Particle densities

- The total rate for creation and loss of ClO molecules is at maximum when the oxygen content is 65%.
- Wall recombination of Cl molecules, is the dominating pathway for creation of ClO molecules
- The bulk processes and recombination of ClO^+ ions at the wall account for roughly 33–43% of the total rate for ClO creation, combined



Thorsteinsson and Gudmundsson, *Plasma Sources Sci. Technol.*, **19** 055008 (2010)

A.3 Summary

Summary

- A global model of Cl_2, Cl_2/Ar and Cl_2/O_2 discharges has been developed
- The chlorine discharge remains highly dissociated in all conditions, being over 20 % at the lowest power and highest pressure explored
- Cl^- ions are essentially entirely produced in dissociative attachment of electrons to Cl_2 and lost to mutual neutralization with Cl^+ and Cl_2^+
- The effect of vibrationally excited chlorine molecules $Cl_2(v > 0)$ is not great, at most increasing the Cl^- production by about 14 %
- The Cl^+ density increases with increased argon dilution but decreases with increased oxygen dilution
- The ClO molecule is mainly created by recombination at the discharge wall

B. 1D particle-in-cell/Monte Carlo collision simulation

Outline

- The 1D particle-in-cell/Monte Carlo collision simulation
  - The chlorine discharge
- Comparison with measurements
- Capacitively Coupled Chlorine Discharge at 13.56 MHz – Voltage Source
- Capacitively Coupled Chlorine Discharge at 27.12 MHz – Current Source
- Capacitively Coupled Chlorine Discharge – dual frequency 27.12 MHz and 2 MHz – Current Source
- Summary

The 1D particle-in-cell/Monte Carlo collision simulation

The oopd1 1d-3v PIC/MCC code

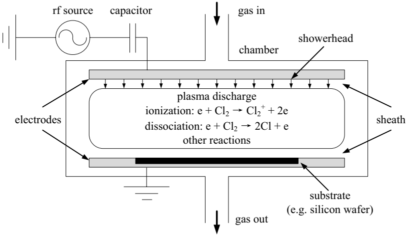
- In particle-in-cell simulation the plasma is represented as a collection of macroparticles
- Each macroparticle is a charged “cloud” representing many real charged particles
- Each macroparticle has the same charge-to-mass ratio (q/m) as the real charged particle
- Equations of motion are solved for each macroparticle
- The electric and magnetic fields are calculated self-consistently using charge densities and currents produced by the macroparticles

The oopd1 1d-3v PIC/MCC code

- 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)
- The `oopd1` code is supposed to replace the widely used `xpdx1` series (`xpdp1`, `xpdc1` and `xpds1`)
- It is developed to simulate various types of plasmas, including processing discharges, accelerators and beams
  - Modular structure
  - Includes relativistic kinematics
  - Particles can have different weights

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

The chlorine discharge



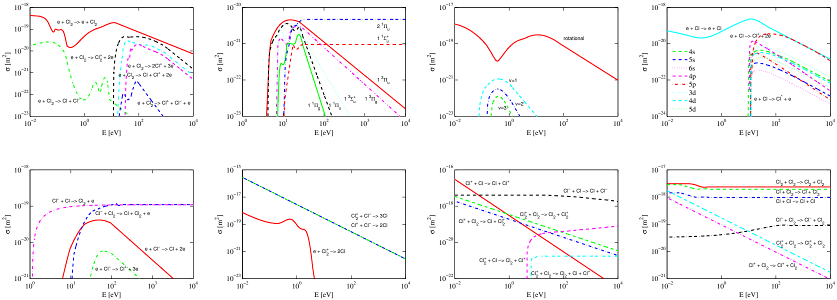
- We consider a discharge that consists of:
  - electrons
  - the ground state chlorine molecule $\mathrm{Cl_2}(X\,^1\Sigma_g^+, v = 0)$,
  - the ground state chlorine atom $\mathrm{Cl(3p^5\,^2P)}$
  - the negative chlorine ion $\mathrm{Cl^-}$
  - the positive chlorine ions $\mathrm{Cl^+}$ and $\mathrm{Cl_2^+}$

The chlorine discharge

- In the chlorine discharge, the number of Cl atoms is much larger than the number of charged species
- Thus, we apply a global model[1] beforehand to calculate the fraction of Cl atoms under certain control parameters including the discharge pressure, absorbed power and the gap length between two electrodes
- The absorbed power found in the PIC/MCC simulation is used as an input parameter in the global model iteratively
- Both Cl_2 molecules and Cl atoms are treated as the initial background gas in the simulation

[1] Thorsteinsson and Gudmundsson, *Plasma Sources Sci. Technol.*, **19** 015001 (2010)

The chlorine discharge



- The reaction set for the chlorine is comprehensive and includes 44 reactions

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

B.1 Capacitively Coupled Chlorine Discharge at 13.56 MHz

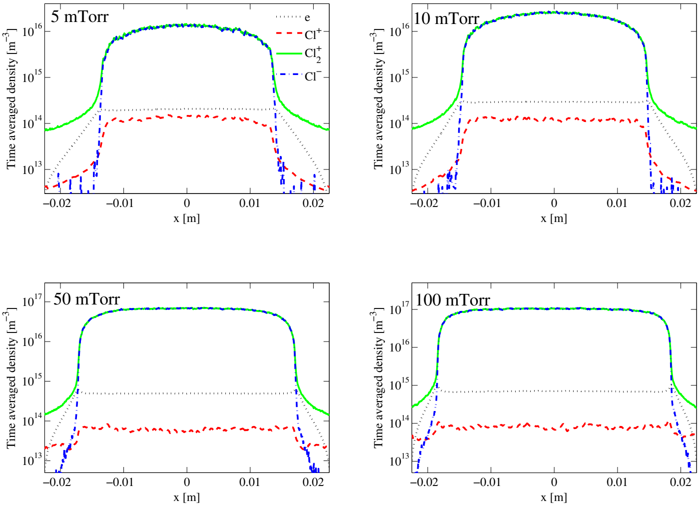
Capacitively Coupled Chlorine Discharge at 13.56 MHz

- We apply a voltage source with a single frequency

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

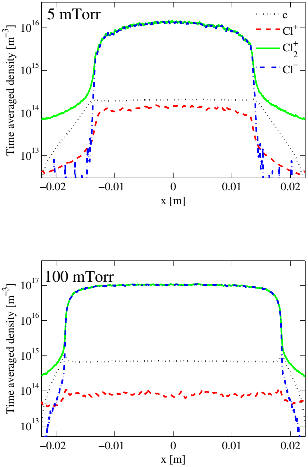
- The electrodes are circular with a diameter of 14.36 cm
- The gap between the electrodes is 4.5 cm
- We set V_{rf} = 222 V and f = 13.56 MHz
- The neutrals (Cl_2 and Cl) are treated as background gas at T_{g} = 300 K with a Maxwellian distribution
- The dissociation fraction is found using a global model
- The explored pressure range is 5 – 100 mTorr

Capacitively Coupled Chlorine Discharge at 13.56 MHz



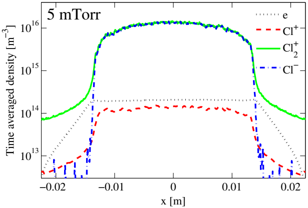
Capacitively Coupled Chlorine Discharge at 13.56 MHz

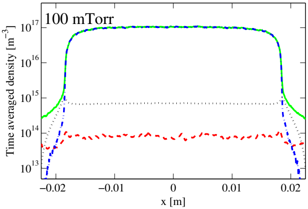
- At low pressures, the profile for Cl_2^+ ions is cosine-like or parabolic since Cl_2^+ ions are lost mainly due to diffusion to the walls
- As the pressure increases, the recombination between Cl_2^+ and Cl^- ions becomes the major loss mechanism for Cl_2^+ ions
- Thus, the density profile for Cl_2^+ and Cl^--ions becomes quite flat in the bulk region



Capacitively Coupled Chlorine Discharge at 13.56 MHz

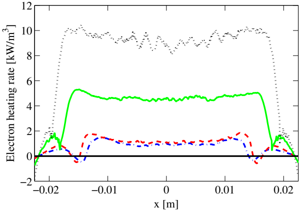
- The density profile for Cl^+-ions is very different from that for Cl_2^+-ions
- In the bulk region the density of Cl^+-ions is uniform at relatively low value
- In the sheath region the density of Cl^+-ions increases with increasing pressure – through non-resonant charge transfer

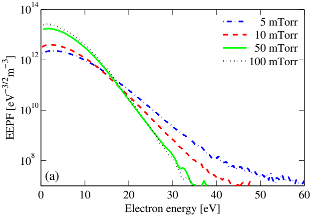




Capacitively Coupled Chlorine Discharge at 13.56 MHz

- At low pressures the power absorbed by the electrons is distributed in the bulk and sheath region through electron–neutral collisions and stochastic heating due to the oscillating sheath, respectively
- At high pressures the power absorbed by the electrons is mainly due to electron–neutral collisions in the bulk





B.2 Capacitively Coupled Chlorine Discharge at 27.12 MHz – Current Source

Capacitively Coupled Chlorine Discharge at 27.12 MHz

- We apply a current source with a single frequency

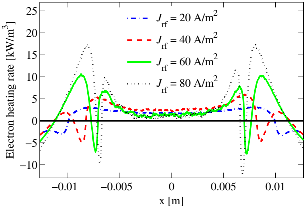
$$J(t) = J_{\mathrm{rf}} \sin(2\pi f t)$$

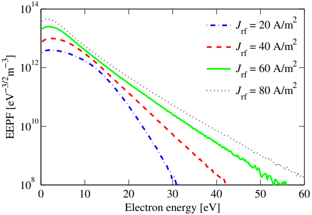
- The electrodes are circular with a diameter of 10.2 cm
- The gap between the electrodes is 2.54 cm
- We set J_{rf} = 20 – 80 A/m^2 and f = 27.12 MHz
- The neutrals (Cl_2 and Cl) are treated as background gas at T_{g} = 300 K with a Maxwellian distribution
- The dissociation fraction is found using a global model
- The pressure is 10 mTorr

Huang and Gudmundsson, *Plasma Sources Sci. Technol.*, submitted 2013

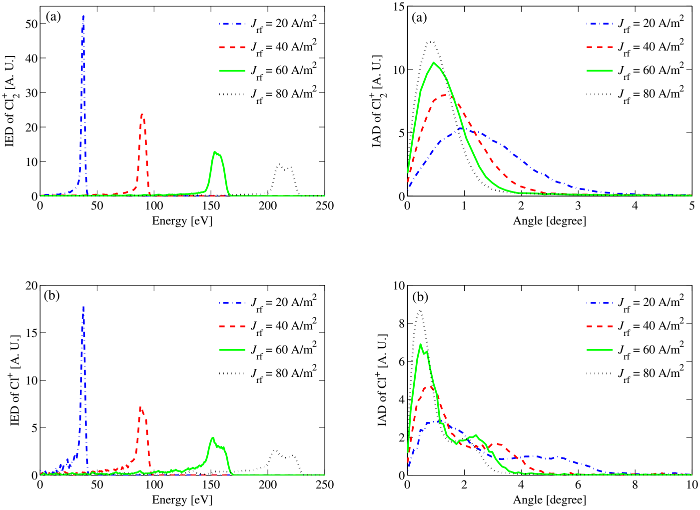
Capacitively Coupled Chlorine Discharge at 27.12 MHz

- Stochastic heating in the sheath becomes more prominent as the current increases
- The electron energy distribution function changes from Druyvesteyn to Maxwellian, and then to bi-Maxwellian as the current increases





Capacitively Coupled Chlorine Discharge at 27.12 MHz



B.3 Capacitively Coupled Chlorine Discharge – dual frequency 27.12 MHz and 2 MHz – Current Source

Capacitively Coupled Chlorine Discharge at 27.12 MHz + 2 MHz

- We apply a current source that consists of two frequency components

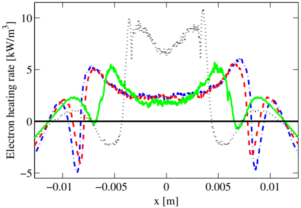
$$J(t) = J_{\rm hf} \sin(2\pi f_{\rm hf} t) + J_{\rm lf} \sin(2\pi f_{\rm lf} t)$$

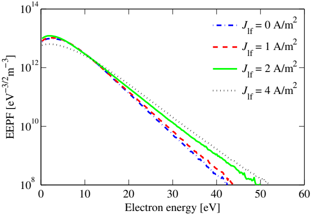
- The electrodes are circular with a diameter of 10.2 cm
- The gap between the electrodes is 2.54 cm
- We set $J_{\rm hf}$ = 40 A/m^2 and f = 27.12 MHz
- We set $J_{\rm lf}$ = 1 – 4 A/m^2 and f = 2 MHz
- The neutrals (Cl_2 and Cl) are treated as background gas at $T_{\rm g}$ = 300 K with a Maxwellian distribution
- The dissociation fraction is found using a global model
- The pressure is 10 mTorr

Huang and Gudmundsson, *Plasma Sources Sci. Technol.*, submitted 2013

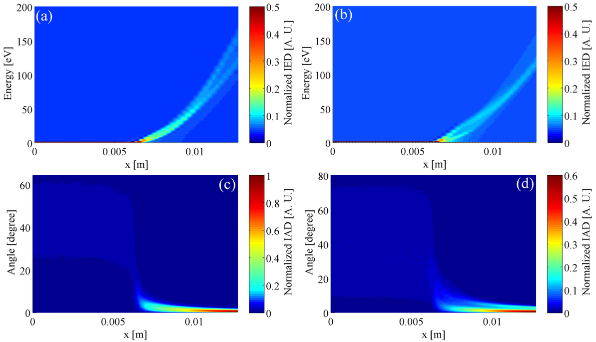
Capacitively Coupled Chlorine Discharge at 27.12 MHz + 2 MHz

- As the low-frequency current increases, the heating in the bulk region first decreases slightly and then increases dramatically
- The number of low-energy electrons first increases and then decreases, while the number of the high-energy electrons increases steadily with increasing low frequency current





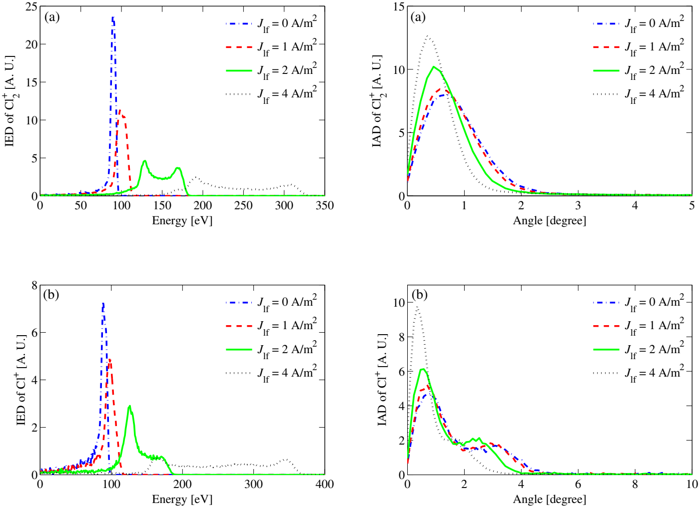
Capacitively Coupled Chlorine Discharge at 27.12 MHz + 2 MHz



- As the ions reach the presheath–sheath boundary they are accelerated across the sheath towards the electrode
- The IEDs become wider and shift from single-peak to bimodal profile

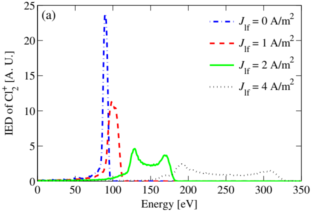
Huang and Gudmundsson, *IEEE Trans. Plasma Science*, submitted 2013

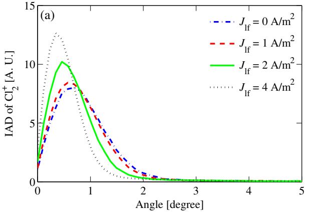
Capacitively Coupled Chlorine Discharge at 27.12 MHz + 2 MHz



Capacitively Coupled Chlorine Discharge at 27.12 MHz + 2 MHz

- The IED becomes wider and extends to the high-energy region with increasing low-frequency current
- The IAD is more concentrated in the small-angle region with increasing low-frequency current





Summary

- We demonstrated particle-in-cell/Monte Carlo collision simulation of a capcacitively coupled chlorine disharge
- Both chlorine atoms and Cl^{+}-ions are considered in the reaction set
- We explored voltage source driven discharge of single frequency and current source driven single and dual frequency discharges

C. Overall Summary

Overall Summary

- A global (volume averaged) model can be used to understand the plasma chemistry
  - Which particles are important
  - Which reactions are important
  - How do the plasma parameters scale with the control parameters – power, pressure, discharge dimensions
- Particle-in-cell/Monte Carlo collision simulations can be used to explore the plasma kinetics
  - To find the electron energy distribution function
  - To find the ion energy distribution (IED) and the ion angular distribution (IAD)

Acknowledgements

The slides can be downloaded at

`http://langmuir.raunvis.hi.is/~tumi/plasma.html`

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References

Donnelly, V. M. and M. V. Malyshev (2000). Diagnostics of inductively coupled chlorine plasmas: Measurements of the neutral gas temperature. *Applied Physics Letters 77*(16), 2467–2469.

Godyak, V. A. (1986). *Soviet Radio Frequency Discharge Research*. Falls Church VA: Delphic Associates.

Gudmundsson, J. T. (2001). On the effect of the electron energy distribution on the plasma parameters of argon discharge: A global (volume averaged) model study. *Plasma Sources Science and Technology 10*(1), 76–81.

Gudmundsson, J. T., A. T. Hjartarson, and E. G. Thorsteinsson (2012). The influence of the electron energy distribution on the low pressure chlorine discharge. *Vacuum 86*(7), 808–812.

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.

Guha, J., V. M. Donnelly, and Y.-K. Pu (2008). Mass and Auger electron spectroscopy studies of the interactions of atomic and molecular chlorine on a plasma reactor wall. *Journal of Applied Physics 103*(1), 013306.

Hjartarson, A. T., E. G. Thorsteinsson, and J. T. Gudmundsson (2010). Low pressure hydrogen discharges diluted with argon explored using a global model. *Plasma Sources Science and Technology 19*(6), 065008.

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

Huang, S. and J. T. Gudmundsson (2013b). Ion energy and angular distributions in a dual-frequency capacitively coupled chlorine discharge. *IEEE Transactions on Plasma Science*, (submitted 2013).

Huang, S. and J. T. Gudmundsson (2013c). A current driven capacitively coupled chlorine discharge. *Plasma Sources Science and Technology*, (submitted 2013).

References

Kim, S., M. A. Lieberman, A. J. Lichtenberg, and J. T. Gudmundsson (2006). Improved volume-averaged model for steady and pulsed-power electronegative discharges. *Journal of Vacuum Science and Technology A 24*(6), 2025–2040.

Lee, C. and M. A. Lieberman (1995). Global model of Ar, O_2, Cl_2 and Ar/O_2 high-density plasma discharges. *Journal of Vacuum Science and Technology A 13*(2), 368–380.

Lieberman, M. A. and A. J. Lichtenberg (2005). *Principles of Plasma Discharges and Materials Processing* (2 ed.). New York: John Wiley & Sons.

Malyshev, M. V. and V. M. Donnelly (2000). Diagnostics of inductively coupled chlorine plasmas: Measurement of Cl_2 and Cl number densities. *Journal of Applied Physics 88*(11), 6207 – 6215.

Malyshev, M. V. and V. M. Donnelly (2001). Diagnostics of inductively coupled chlorine plasmas: Measurement of electron and total positive ion densities. *Journal of Applied Physics 90*(3), 1130–1137.

Stafford, L., R. Khare, J. Guha, V. M. Donnelly, J.-S. Poirier, and J. Margot (2009). Recombination of chlorine atoms on plasma-conditioned stainless steel surfaces in the presence of adsorbed Cl_2. *Journal of Physics D: Applied Physics 42*(5), 055206.

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

Thorsteinsson, E. G. and J. T. Gudmundsson (2010b). The low pressure Cl_2/O_2 discharge and the role of ClO. *Plasma Sources Science and Technology 19*(5), 055008.