Plasma Chemistry and Kinetics in Low Pressure Discharges

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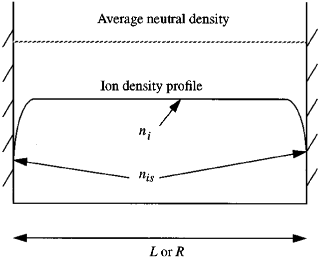
A. Global (volume averaged) chemistry models

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

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

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

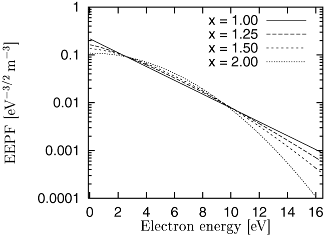
$$\mathrm{e} + \mathrm{Ar} \longrightarrow \mathrm{Ar} + \mathrm{e} \qquad \text{(elastic scattering)}$$

- 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

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

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

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

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

- 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

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

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

- 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

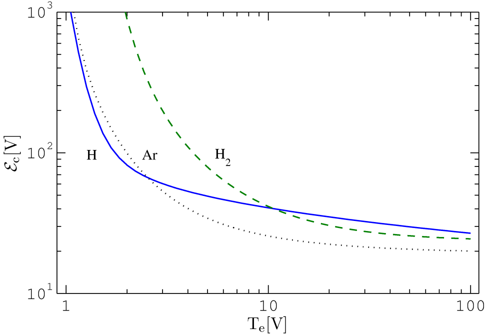
$$\mathcal{E}_\mathrm{i} \approx \bar{V}_\mathrm{s}$$

    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

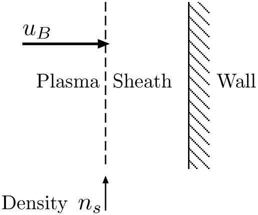
- Ions are lost at the **Bohm velocity** at the plasma-sheath edge

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

assuming Maxwellian energy distribution or more generally

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

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



Argon discharge – Diffusion

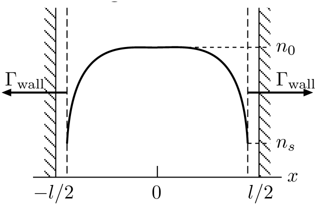
- A low pressure ($<$ 100 mTorr in argon) the plasma density profile is relatively flat in the center and falls sharply near the sheath edge
- Ion and electron loss to the wall is

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

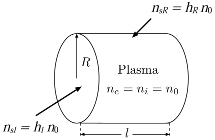
- The **edge-to-center density ratio** is

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

where $\lambda_{\rm i}$ is the ion-neutral mean free path



Argon discharge – Cylindrical discharge



- Loss fluxes to the axial and radial walls are

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

and the edge-to-center density ratios are

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

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

Argon discharge – Cylindrical discharge

- At high pressure

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

  a constant diffusion model is more appropriate

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

- These regimes can be joined heuristically giving

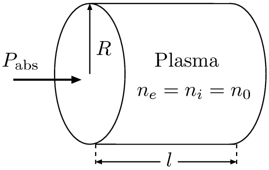
$$h_\ell \approx \frac{0.86}{\left[3 + \ell/2\lambda_{\rm i} + (0.86 R u_{\rm B}/\pi D_{\rm a})^2\right]^{1/2}}$$

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

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

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

Argon discharge – Particle balance

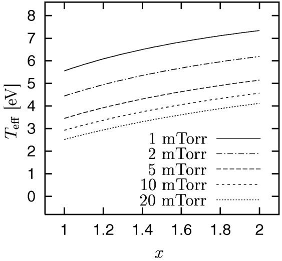
- Rearrange to obtain

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

  where

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

  is an effective plasma size
- So given $n_{\rm g}$ (pressure) and $d_{\rm eff}$ (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

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

- Solve for particle density

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

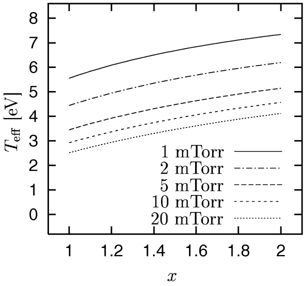
  where

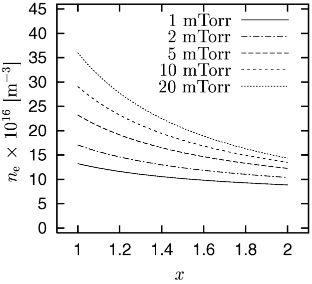
$$A_{\rm eff} = 2\pi R^2 h_\ell + 2\pi R\ell h_{\rm R}$$

  is an effective area for particle loss
- Assume low voltage sheaths at all surfaces

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

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 $\mathrm{Cl}(3p^5\,{}^2P)$
  - 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

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

  - 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

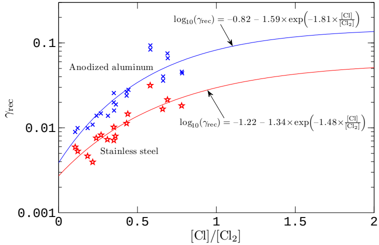
A.2.1 Model parameters

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

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

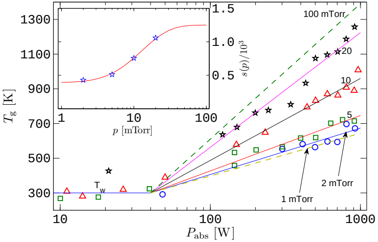
and for stainless steel

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

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

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

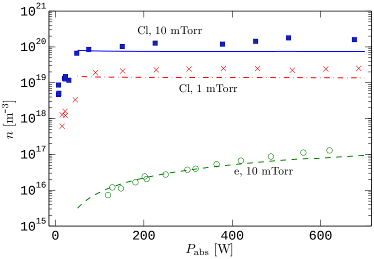
A.2.2 Comparison with experiments

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

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

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



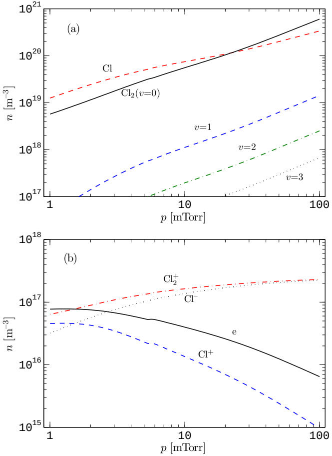
- inductively coupled cylindrical stainless steel chamber
- $L = 20$ cm and $R = 18.5$ cm

A.2.3 Particle densities

Particle densities

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

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



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

Creation and destruction of Cl atoms

- Electron impact dissociation

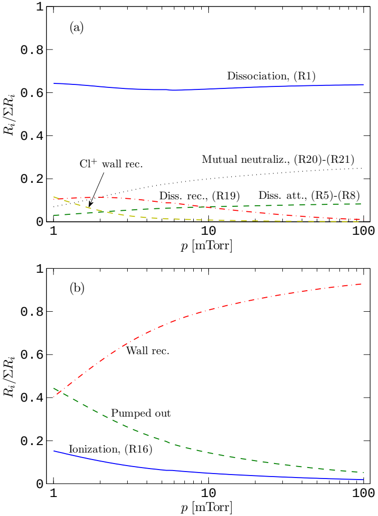
$$e + Cl_2 \longrightarrow Cl + Cl + e$$

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

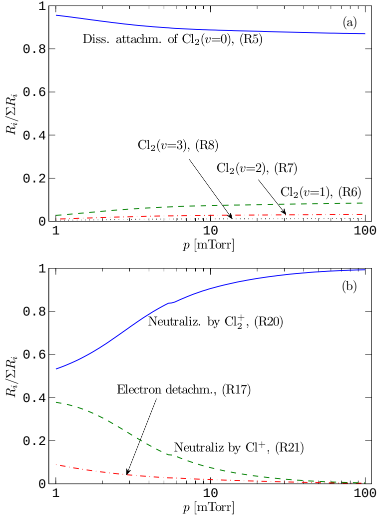
- The production of Cl^--ions is only due to dissociative electron attachment

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

- 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	$\mathrm{T_e}$	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}

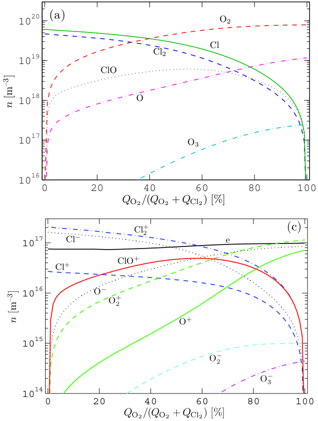
	[Cl]/n_{g}	[Cl$^+$]/n_+	α	T_{e}	n_{e}
γ_{rec}: 10^{-4} – 1	$\downarrow$ 5.75	$\downarrow$ 34.6	$\uparrow$ 4.25	$\uparrow$ 1.13	$\downarrow$ 1.59

- 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 Oxygen dilution

Oxygen dilution – Particle densities

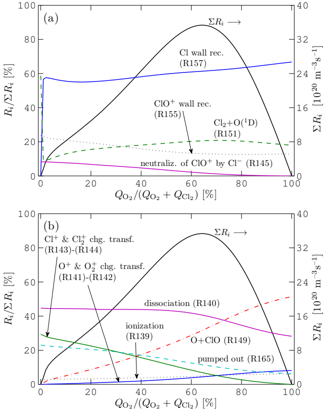
- The Cl^+ density decreases with increased oxygen dilution
- The chlorine-oxide molecule ClO and its ion ClO^+ peak when Cl_2 and O_2 flowrates are roughly equal
- The $O_2(a^1\Delta_g)$ density is about 9 – 10 % of the total O_2 density
- The electron density increases about 30 % between pure chlorine 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 oxygen discharge
    - Capacitively Coupled Oxygen Discharge at 13.56 MHz – Voltage Source
  - The chlorine discharge
    - Capacitively Coupled Chlorine Discharge at 27.12 MHz – Current Source
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  - 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)

B.1. The oxygen discharge

The oxygen discharge

- We consider a discharge that consists of:
  - electrons
  - the ground state oxygen molecule $O_2(X^3\Sigma_g^-)$
  - the metastable oxygen molecule $O_2(a^1\Delta_g)$
  - the ground state oxygen atom $O(^3P)$
  - the metastable oxygen atom $O(^1D)$
  - the negative oxygen ion O^-
  - the positive oxygen ions O^+ and O_2^+

The oxygen discharge

- In the oxygen discharge, the density of the metastable oxygen molecule $O_2(a^1\Delta_g)$, oxygen atom in the ground state $O(^3P)$ and the metastable oxygen atom $O(^1D)$ is much larger than the number of charged species
- Thus, we apply a global model[1] beforehand to calculate the fraction of the O atoms and the metastables $O_2(a^1\Delta_g)$ and $O(^1D)$ 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 O_2 molecules and O atoms and the metastables are treated as the initial background gas in the simulation

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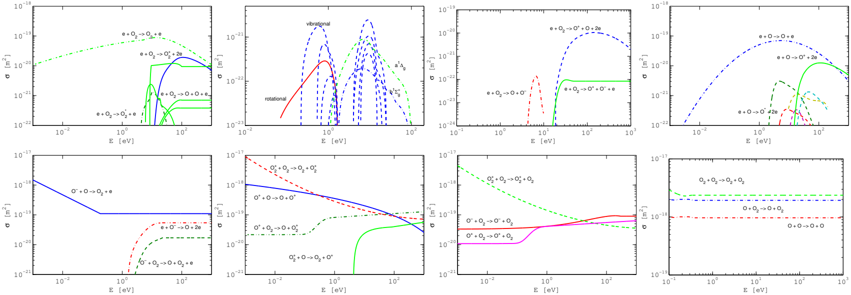
[1] Thorsteinsson and Gudmundsson, *Plasma Sources Sci. Technol.*, **19** 055008 (2010)

The oxygen discharge

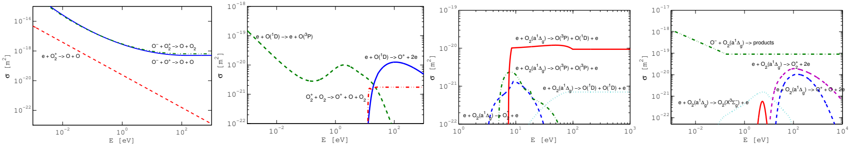


- The reaction set for the oxygen is comprehensive and includes 53 reactions

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

Gudmundsson and Lieberman, *Plasma Sources Sci. Technol.*, accepted (2015)

The oxygen discharge



- We know from global model calculation that dissociative attachment of the oxygen molecule is almost the sole source of O^- in the discharge and the metastable oxygen molecules play a major role for the creation of negative ions in an oxygen discharge
- We use the rate coefficient for the detachment by the metastable $O_2(a^1\Delta_g)$ that was measured by Midey et al. (2008) to estimate a cross section

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

Midey et al., *J. Phys. Chem. A*, **113** 3040 (2008)

The oxygen discharge

- Detachment by the metastable O_2 molecules has been considered a major contributor to the loss of negative ions in oxygen discharges

  Thompson, *Proc. R. Soc. A*, **262** 503 (1961)

  Ivanov et al, *IEEE TPS*, **27** 1279 (1999)

- However, in the high density inductivley coupled plasma (ICP) discharges we found the contribution to be relatively small

  Gudmundsson et al., *J. Phys D.*, **33** 1323 (2000)

  Gudmundsson and Thorsteinsson, *PSST*, 399 (2007)

J. Phys. D: Appl. Phys. **33** (2000) 3009. Printed in the UK PII: S0022-3727(00)15252-0

COMMENT

Is oxygen a detachment-dominated gas or not?

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Abstract. The apparent contradiction between treatments of discharges in oxygen at low pressures is highlighted, and the question asked why in radio-frequency generated plasmas it is permissible to ignore detachment due to collisions between metastables and negative oxygen ions whereas in dc discharges the consensus is that this process is dominant.

A recent paper (Gudmundsson *et al* 2000) was concerned with giving an experimental and theoretical description of a low-pressure discharge in oxygen, excited inductively at 13.56 MHz. A notable feature was the extent to which the authors sought to include all the atomic and molecular processes relevant to such a discharge in oxygen. The purpose of this communication is to indicate a fundamental difference between their treatment and the body of literature in dc discharges, where it has been clear for some time that there was an agreement that detachment by collisions with metastables and atoms is the significant loss process for the negative oxygen ions. A representative, but not exhaustive, list with corresponding values of pL (pressure × plasma dimension) is Thompson (1961) 50–250 mTorr cm, Edgley and von Engel (1980) 10–1000 mTorr cm, Ferreira *et al* (1988) 160–4000 mTorr cm, Gousset *et al* (1991) 16–4000 mTorr cm, Ivanov *et al* (1999) 90–600 mTorr cm—these compare with 10–135 mTorr cm for the rf excited plasma.

Generally, it is assumed that the processes are similar in dc and rf discharges, while it is recognized that different mechanisms set the electron temperature and even the distribution of charged particles. For this reason, I believe that it is incumbent on the authors to explain why, in an rf discharge, it is possible to ignore detachment other than by electron impact as a loss process. It is apposite to quote from Ivanov *et al* (1999) 'Detachment processes on $O(^3P)$ atoms and $O_2(a\,^1\Delta_g)$ molecules strongly influence the discharge electrodynamics and determine the electric field in a wide range of the pL parameter'.

Interestingly, a recent paper by Kaganovich *et al* (2000), albeit in an afterglow situation, indicates the importance of detachment in an oxygen plasma in a comparable range of pL.

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Gudmundsson T, Marakhtanov A M, Patel K K, Gopinath V P and Lieberman M A 2000 *J. Phys. D: Appl. Phys.* **33** 1323–31
Ivanov V V, Klopovsky K S, Lopaev D V, Rakhimov A T and Rakhimova T V 1999 *IEEE Trans. Plasma Sci.* **27** 1279–87
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Franklin, *J. Phys D.*, **33** 3009 (2000)

Capacitively Coupled Oxygen Discharge at 13.56 MHz

Capacitively Coupled Oxygen Discharge at 13.56 MHz

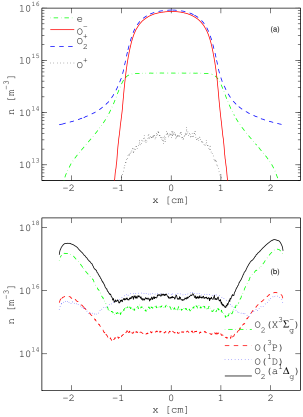
- We apply a voltage source with a single frequency

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

- The electrodes are circular with a diameter of 14.36 cm
- The gap between the electrodes is 4.5 cm
- We set $V_{\rm rf}$ = 222 V and f = 13.56 MHz
- The neutrals (O_2 and O) 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 metastable fraction is found using a global model
- The pressure is 50 mTorr

Capacitively Coupled Oxygen Discharge at 13.56 MHz

- In the center of the discharge the O_2^+-ion density is slightly higher than the O^-density and have parabolic profile
- The ground state molecule $O_2(X^3\Sigma_g^-)$ with $\mathcal{E} > 0.5$ eV and the metastable $O_2(a^1\Delta_g)$ with $\mathcal{E} > 0.1$ eV
- For the oxygen atom in the ground state $O(^3P)$ with $\mathcal{E} > 0.5$ eV and the metastable oxygen atom $O(^1D)$ with $\mathcal{E} > 0.05$



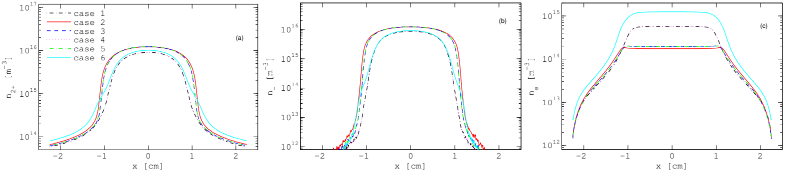
Capacitively Coupled Oxygen Discharge at 13.56 MHz

- The six cases explored in this study are
  - Case 1 – is the basic case explored – the complete reaction set is used that includes both the metastable O(^{1}D) atom and the metastable $O_2(a^1\Delta_g)$ molecule
  - Case 2 – is the same as case 1 except that the reaction

    $$O^- + O_2(a^1\Delta_g) \rightarrow \text{products}$$

    is neglected
  - Case 3 – includes only the metastable O(^{1}D) atom and the corresponding reactions
  - Case 4 – includes only the metastable $O_2(a^1\Delta_g)$ molecule and the corresponding reactions
  - Case 5 – includes no metastables
  - Case 6 – same as case 1 with $\gamma_{\rm see} = 0.2$

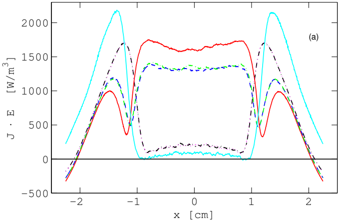
Capacitively Coupled Oxygen Discharge at 13.56 MHz



- For a parallel plate capacitively coupled oxygen discharge at 50 mTorr with with a gap separation of 4.5 cm by a 222 V voltage source at 13.56 MHz
  - O_2^+-ion density profile
  - O^--ion density profile
  - electron density profile
- The center electronegativity α_0 changes from about 15 for full reaction set, 7 for full reaction set and $\gamma_{\rm see} = 0.2$, to 70 when detachment by $O_2(\mathrm{a}^1\Delta_g)$ is neglected

Capacitively Coupled Oxygen Discharge at 13.56 MHz

- The detachment by the metastable $O_2(\mathrm{a}^1\Delta_g)$ has a significant influence on the heating mechanism in the discharge
- Neglecting detachment by $O_2(\mathrm{a}^1\Delta_g)$ electron heating appears both in the sheath region and in the bulk
- When this process is included electron heating exists only in the sheath region, sheath-oscillation heating dominates



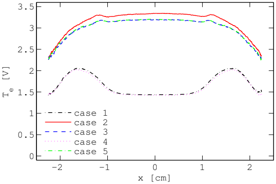
- Neglecting the reaction

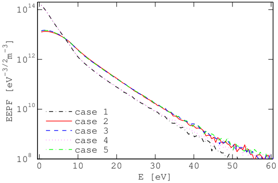
$$\mathrm{O}^- + \mathrm{O}_2(a^1\Delta_g) \rightarrow \text{products}$$

has a significant influence

Capacitively Coupled Oxygen Discharge at 13.56 MHz

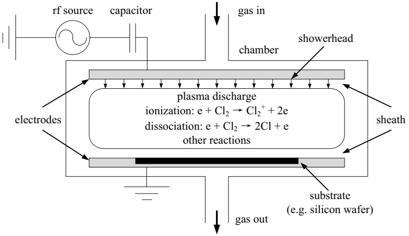
- The effective electron temperature drops when including the metastable oxygen molecule $O_2(\mathrm{a}^1\Delta_g)$, in particular in the electronegative core
- The number of low energy electrons increases and the number of higher energy electrons ($>$ 10 eV) decreases, and the EEPF develops a concave shape or becomes bi-Maxwellian





B.2. The chlorine discharge

The chlorine discharge



- We consider a 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^+

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

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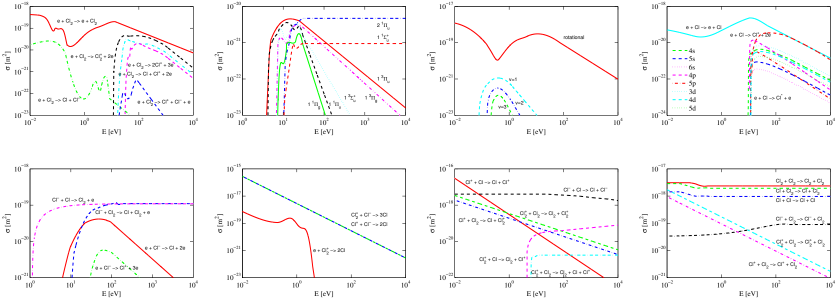
[1] Thorsteinsson and Gudmundsson, *Plasma Sources Sci. Technol.*, **19** 015001 (2010)

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.2.1 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

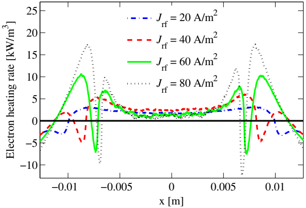
$$J(t) = J_{\mathrm{rf}} \sin(2\pi f t)$$

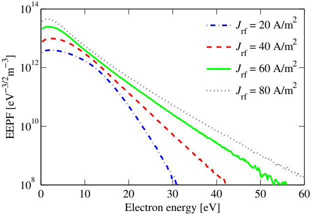
- The electrodes are circular with a diameter of 10.2 cm
- The gap between the electrodes is 2.54 cm
- We set J_{rf} = 20 – 80 A/m^2 and f = 27.12 MHz
- The neutrals (Cl_2 and Cl) are treated as background gas at T_{g} = 300 K with a Maxwellian distribution
- The dissociation fraction is found using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

Huang and Gudmundsson, *Plasma Sources Sci. Technol.*, **23** (2014) 025015

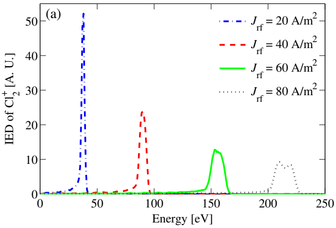
Capacitively Coupled Chlorine Discharge at 27.12 MHz

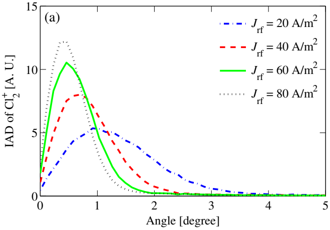
- Stochastic heating in the sheath becomes more prominent as the current increases
- The electron energy distribution function changes from Druyvesteyn to Maxwellian, and then to bi-Maxwellian as the current increases

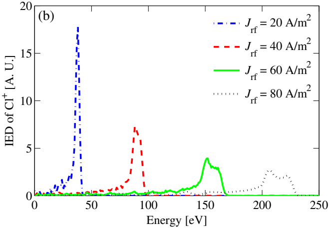


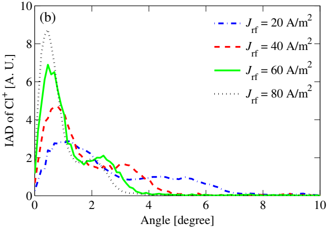


Capacitively Coupled Chlorine Discharge at 27.12 MHz









B.2.2 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

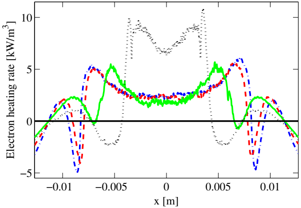
$$J(t) = J_{\mathrm{hf}} \sin(2\pi f_{\mathrm{hf}} t) + J_{\mathrm{lf}} \sin(2\pi f_{\mathrm{lf}} t)$$

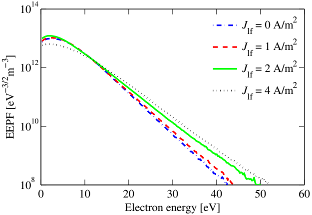
- The electrodes are circular with a diameter of 10.2 cm
- The gap between the electrodes is 2.54 cm
- We set J_{hf} = 40 A/m^2 and f = 27.12 MHz
- We set J_{lf} = 1 – 4 A/m^2 and f = 2 MHz
- The neutrals (Cl_2 and Cl) are treated as background gas at T_{g} = 300 K with a Maxwellian distribution
- The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

Huang and Gudmundsson, *Plasma Sources Sci. Technol.*, **23** (2014) 025015

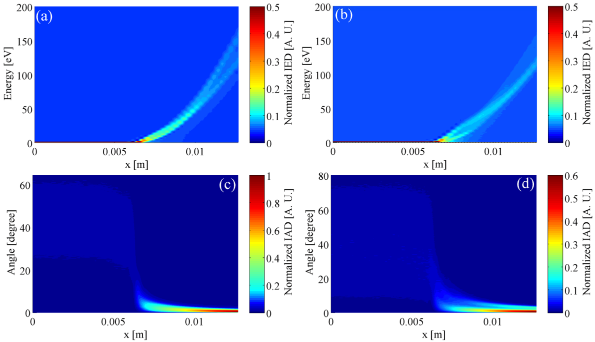
Capacitively Coupled Chlorine Discharge at 27.12 MHz + 2 MHz

- 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





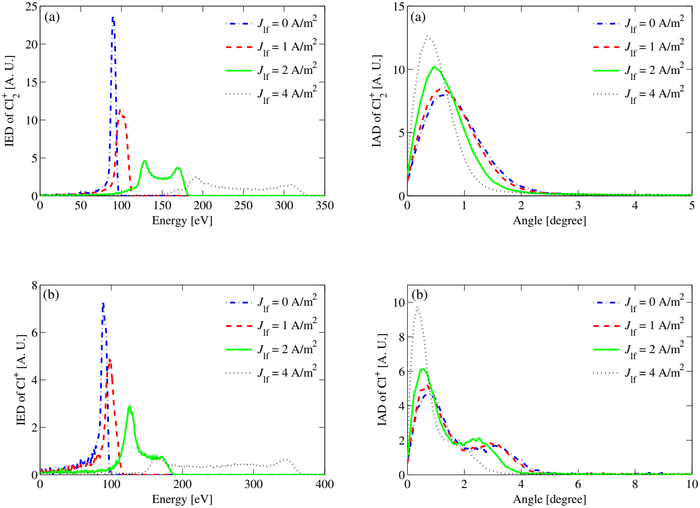
Capacitively Coupled Chlorine Discharge at 27.12 MHz + 2 MHz



- 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

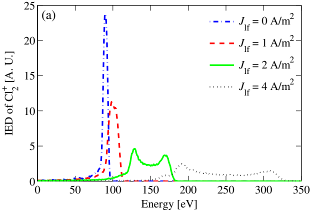
Huang and Gudmundsson, *IEEE Trans. Plasma Science*, **42** (2014) 2854

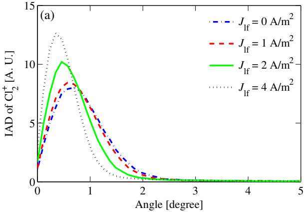
Capacitively Coupled Chlorine Discharge at 27.12 MHz + 2 MHz



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 oxygen and chlorine disharge
- Detachment by the metastable $O_2(a^1\Delta_g)$ molecule

  $$O^- + O_2(a^1\Delta_g) \rightarrow \text{products}$$

  has a significant influence of the overall discharge
- We explored voltage source driven discharge of single frequency and current source driven single and dual frequency discharges
- In dual frequency discharge decreased low frequency current leads to higher ion bombarding energy and decreases the angular spread of the ions

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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- Aron Þór Hjartarson (Univ. of Iceland)

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