Plasma Chemistry and Kinetics in Low Pressure Oxygen Discharges: The significance of metastable states

Jón Tómas Guðmundsson[1,2]

[1] Science Institute, University of Iceland, Reykjavik, Iceland
[2]Department of Space and Plasma Physics, School of Electrical Engineering, KTH Royal Institute of Technology, SE-100 44, Stockholm, Sweden

tumi@hi.is

Laboratoire de Physique et Technologie des Plasmas, Ecole Polytechnique, Palaiseau, France
March 31., 2016

Outline

- A. Global (volume averaged) chemistry models
  - A1 The oxygen discharge
    - chlorine dilution
- B. 1D particle-in-cell/Monte Carlo collision simulation
  - B.1 Capacitively Coupled Oxygen Discharge at 13.56 MHz – Voltage Source – pressure dependence
- C. Summary

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

A.1 Global (volume averaged) chemistry models – oxygen

The oxygen discharge

- The oxygen discharge is of significance in various materials processing applications including
  - etching of polymer films
  - ashing of photoresist
  - oxidation
- The oxygen chemistry is complicated due to the presence of metastable atomic and molecular species
- It is in particular the two low lying metastable molecular states designated by $a^1\Delta_g$ and $b^1\Sigma_g^+$, which are located 0.98 and 1.627 eV above the ground state, respectively
- It is well established that collisions with these metastable states have in many cases larger cross sections and thus higher reaction rates than corresponding collisions with the ground state molecule

The global (volume averaged) model

- A steady state global (volume averaged) model was developed for the oxygen discharge
- The following species are included
  - electrons
  - the ground state oxygen molecule $O_2(X\,^3\Sigma_g^-, v = 0)$,
  - The metastable oxygen molecules $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g^+)$ and the metastable Herzberg states $O_2(A^3\Sigma_u^+$, $A'^3\Delta_u$, $c^1\Sigma_u^-)$
  - the ground state oxygen atom $O(^3P)$
  - the metastable oxygen atom $O(^1D)$
  - the negative oxygen ions O^- and O_2^-
  - the positive oxygen ions O^+ and O_2^+
  - Ozone O_3 and its ions O_3^+ and O_3^-
- The content of the chamber is assumed to be nearly spatially uniform and the power is deposited uniformly into the plasma bulk

Toneli et al., *J. Phys. D.*, **48** (2015) 325202 and Gudmundsson and Thorsteinsson, *PSST*, **16** (2007) 399

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

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

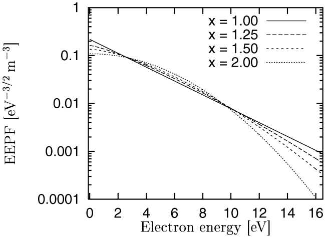
is based on a one-region flat topped electronegative profile

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

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

The global (volume averaged) model

- 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

The global (volume averaged) model

- The diffusional losses of the neutral oxygen atoms (ground state and metastable) to the reactor walls are given by

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

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

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

- The wall recombination coefficient γ_{rec} is one of the most important parameter in oxygen 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
- The pressure dependence on the wall recombination coefficient was achieved by fitting all the available data for stainless steel surfaces
- The same wall recombination coefficient was used for $O(^1D)$ as no data is available

Gudmundsson and Thorsteinsson, *PSST*, **16** (2007) 399

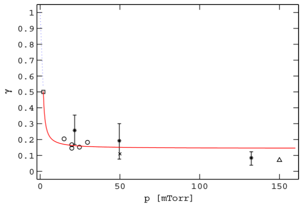


Figure 1. The recombination coefficient of oxygen atoms at the chamber walls for stainless steel as a function of pressure. The measured data is taken from, o Singh *et al* [47], × Matsushita *et al* [90], △ Mozetič and Zalar [91], □ Booth and Sadeghi [44] and ∗ Gomez *et al* [46]. The solid line shows a fit to the measured data and the dotted line is a linear extrapolation from $\gamma = 0.5$ at 2 mTorr to $\gamma = 1.0$ at vacuum.

The wall recombination coefficient for oxygen atoms on stainless steel surfaces depends on pressure through

$$\gamma_{\text{rec}} = 0.1438 \exp(2.5069/p) \quad p > 2 \text{ mTorr}$$

$$\gamma_{\text{rec}} = -0.25p + 1 \quad p < 2 \text{ mTorr}$$

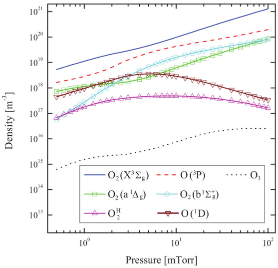
A.2.3 Particle densities

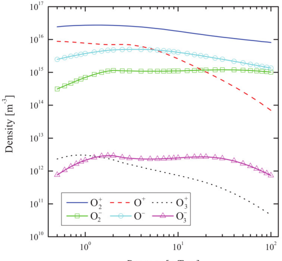
Particle densities

- The dominant species is the oxygen molecule in the ground state $O_2(X^3\Sigma_g)$ followed by the oxygen atom in the ground state $O(^3P)$
- The singlet metastable states $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ and the metastable atom $O(^1D)$ are also present in the plasma in significant amounts
- a cylindrical stainless steel chamber

radius R = 15 cm and length L = 30 cm P_{abs} = 500 W

Toneli et al., *J. Phys. D*, **48** (2015) 325202



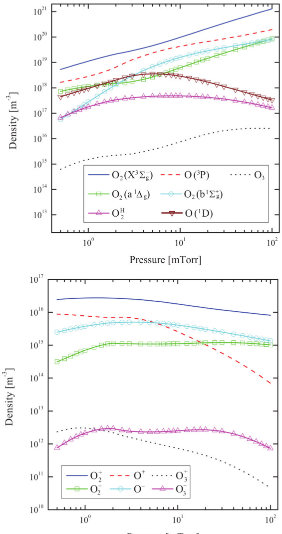


Particle densities

- The $O_2(b^1\Sigma_g^+)$ density overcomes the $O_2(a^1\Delta_g)$ density in the pressure range from 2.5 to 80 mTorr
- The O_2^+ ions are in majority among the positive ions
- The O^+ density has a sharp decrease for pressures above 4 mTorr
- The ratio $[O^-]/[O_2^-]$ is 5.3 at 1 mTorr, and 1.3 at 100 mTorr
- a cylindrical stainless steel chamber

  radius R = 15 cm and length L = 30 cm P_{abs} = 500 W

Toneli et al., *J. Phys. D*, **48** (2015) 325202



Creation of metastable $O_2(a^1\Delta_g)$ molecules

- Electron impact excitation (17)

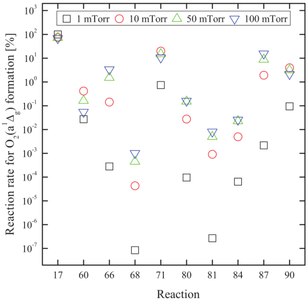
$$e + O_2(X^3\Sigma_g^-) \longrightarrow O_2(a^1\Delta_g) + e$$

has 100 % contribution at 1 mTorr and 68.2 % at 100 mTorr

- The role of quenching of the metastable atom $O(^1D)$ to create the metastable oxygen molecule (71)

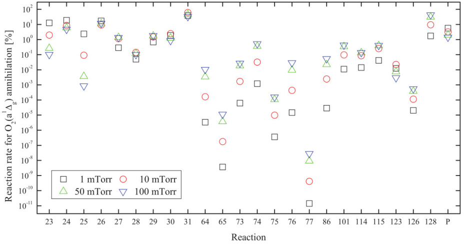
$$O(^1D) + O_2(X^3\Sigma_g^-) \longrightarrow O_2(a^1\Delta_g) + O(^3P)$$

reaches a maximum value, 20.1 % contribution at 12.5 mTorr, and 10.5 % at 100 mTorr



Toneli et al., *J. Phys. D*, **48** (2015) 325202

Destruction of metastable $O_2(a^1\Delta_g)$ molecules



- Electron impact dissociation (31,24)

$$e + O_2(a^1\Delta_g) \longrightarrow O(^1D) + O(^3P) + e$$

$$e + O_2(a^1\Delta_g) \longrightarrow O(^3P) + O(^3P) + e$$

are the most important channels for destruction of the metastable $O_2(a^1\Delta_g)$ molecules, 57.2 % contribution at 1 mTorr and 38.1 % at 100 mTorr

Toneli et al., *J. Phys. D*, **48** (2015) 325202

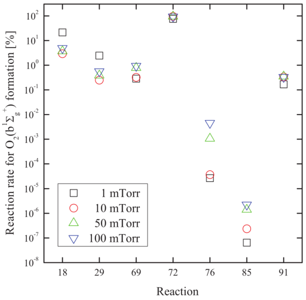
Creation of metastable $O_2(b^1\Sigma_g)$ molecules

- The most important contributor to the formation of the metastable oxygen molecule $O_2(b^1\Sigma_g)$ is reaction 72

$$O(^1D)+O_2(X^3\Sigma_g^-) \longrightarrow O_2(b^1\Sigma_g)+O(^3P)$$

  which has 75.7 % contribution at 1 mTorr and 93.2 % at 100 mTorr

- This reaction has been suggested in the past to be a major contributor to the formation of $b^1\Sigma_g^+$ state in the atmosphere



Toneli et al., *J. Phys. D*, **48** (2015) 325202

Destruction of metastable $O_2(b^1\Sigma_g)$ molecules

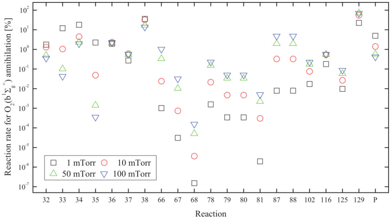
- Wall quenching is an important loss process for $O_2(b^1\Sigma_g)$
- Electron impact dissociation (38,34)

$$e + O_2(b^1\Sigma_g) \longrightarrow O(^1D) + O(^3P) + e$$

$$e + O_2(b^1\Sigma_g) \longrightarrow O(^3P) + O(^3P) + e$$

are the most important channels for destruction along with electron impact ionization (33)

$$e + O_2(b^1\Sigma_g) \longrightarrow O_2^+ + 2e$$



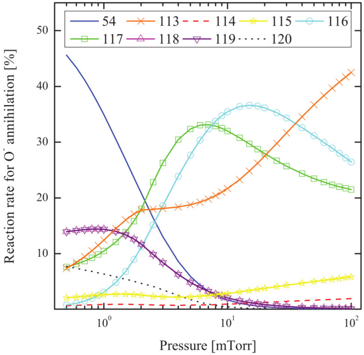
Toneli et al., *J. Phys. D*, **48** (2015) 325202

Destruction of the negative ion O^-

- At low pressure that the electron impact detachment (54),

$$e + O^- \longrightarrow O(^3P) + 2e$$

  is the main contributor
- Ion-ion mutual neutralization is also important
- As pressure increases, the contributions of these reactions become negligible



Toneli et al., *J. Phys. D*, **48** (2015) 325202

Destruction of the negative ion O^-

- As the pressure increases charge exchange (113)

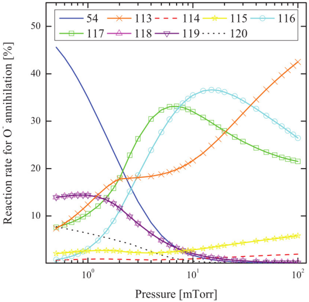
$$O^- + O_2(X^3\Sigma_g^-) \longrightarrow O(^3P) + O_2^-$$

and detachment by collision with $O(^3P)$ (117)

$$O^- + O(^3P) \longrightarrow O_2(X^3\Sigma_g^-) + e$$

have increased contribution as well as detachment by collision with $O_2(b^1\Sigma_g)$ (reaction 116)

$$O^- + O_2(b^1\Sigma_g) \longrightarrow O(^3P) + O_2(X^3\Sigma_g^-) + e$$

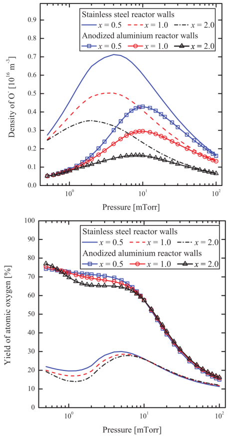


Toneli et al., *J. Phys. D*, **48** (2015) 325202

A.2.4 Influence of chamber wall and EEDF

Influence of chamber wall and EEDF

- The parameter x defines the shape of the electron energy distribution
  - $x = 0.5$ is concave or bi-Maxwellian
  - $x = 1$ is a Maxwellian distribution
  - $x = 2$ is Druyvesteyn distribution
- For anodized aluminium reactor walls, the recombination coefficient for oxygen atoms at the walls is assumed to be a constant $\gamma_{\mathrm{O}} = 0.06$ based on the measurements of Guha et al. (2008)
- The chamber wall has a significant influence on the dissociation fraction

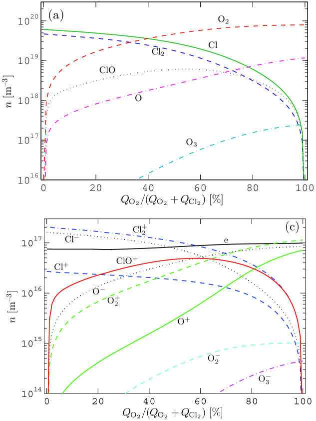


Toneli et al., *J. Phys. D*, **48** (2015) 495203

A.2.5 Chlorine dilution

Chlorine dilution – Particle densities

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

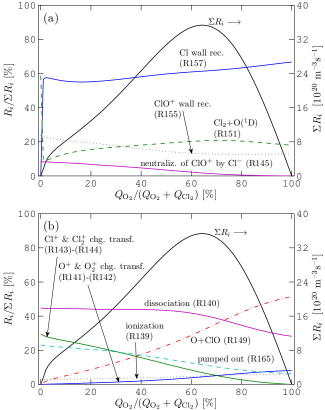


Thorsteinsson and Gudmundsson, *Plasma Sources Sci. Technol.*, **19** 055008 (2010)

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 O_2, and Cl_2/O_2 discharges has been applied to explore the creation and destruction of the singlet metastable molecules $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g^+)$
- The singlet delta state $O_2(a^1\Delta_g)$ is created mainly by lectron impact excitation

$$e + O_2(X^3\Sigma_g^-) \longrightarrow O_2(a^1\Delta_g) + e$$

- The singlet delta state $O_2(b^1\Sigma_g^+)$ is created mainly by

$$O(^1D) + O_2(X^3\Sigma_g^-) \longrightarrow O_2(b^1\Sigma_g) + O(^3P)$$

- At low pressure that the electron impact detachment

$$e + O^- \longrightarrow O(^3P) + 2e$$

is the main contributor to the loss of O^-
- 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 – pressure dependence
  - 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)

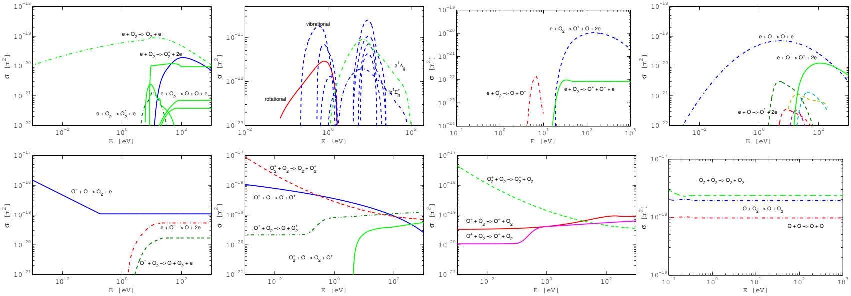
B.1. The oxygen discharge

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 metastable oxygen molecule $O_2(b^1\Sigma_g)$
  - 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^+
- We apply a global model[1] beforehand to calculate the partial pressure of the various neutrals

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

The oxygen discharge



- The reaction set for the oxygen is comprehensive and for this study includes 67 reactions

Gudmundsson et al., *Plasma Sources Sci. Technol.*, **22** 035011 (2013), and **24** 035016 (2015)

B. 1. 1. Capacitively Coupled Oxygen Discharge at 13.56 MHz – pressure dependence – including $O_2(a^1\Delta_g)$

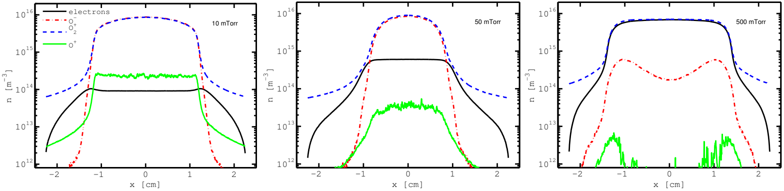
Capacitively Coupled Oxygen Discharge at 13.56 MHz

- 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 $V_{\mathrm{rf}} = 222$ V and $f = 13.56$ MHz
- The neutrals (O_2 and O) are treated as background gas at $T_{\mathrm{g}} = 300$ K with a Maxwellian distribution
- The dissociation fraction and the metastable fraction is found using a global model
- The pressure is varied from 10 – 500 mTorr

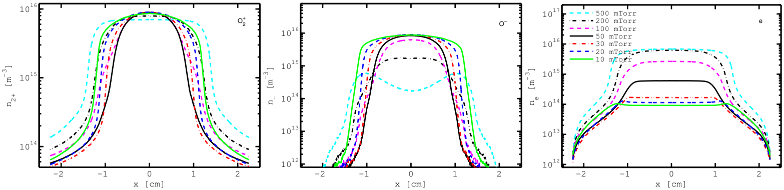
Capacitively Coupled Oxygen Discharge at 13.56 MHz



- 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
  - O^--ion density profile
  - electron density profile

Gudmundsson and Ventéjou (2015) JAP **118** 153302

Capacitively Coupled Oxygen Discharge at 13.56 MHz

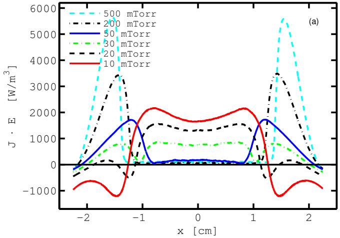


- The sheath width decreases as the pressure is decreased in the pressure range from 50 mTorr to 10 mTorr
- The sheath widths are largest at 50 mTorr
- As the pressure is increased from 50 mTorr up to 500 mTorr the sheath width decreases
- This agrees with what has been observed experimentally in the pressure range 40 – 375 mTorr

Mutsukura et al. (1990) JAP **68** 2657 and van Roosmalen et al. (1985) JAP **58** 653

Capacitively Coupled Oxygen Discharge at 13.56 MHz

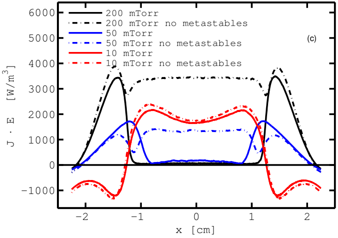
- The electron heating profile $\mathbf{J}_e \cdot \mathbf{E}$
- In the pressure range 50 - 500 mTorr the electron heating occurs almost solely in the sheath region
- As the pressure is decreased the Ohmic heating contribution in the plasma bulk increases and sheath heating decreases



Gudmundsson and Ventéjou (2015) JAP **118** 153302

Capacitively Coupled Oxygen Discharge at 13.56 MHz

- At 10 mTorr excluding the metastable states in the simulation has very small influence on the heating mechanism
- At 50 mTorr the metastable states have a significant influence on the heating mechanism
- The role of the metastables is even more significant at 200 mTorr

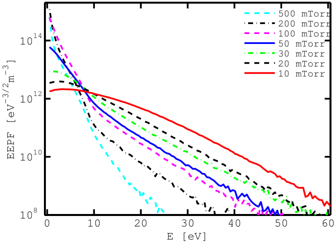


Gudmundsson and Ventéjou (2015) JAP **118** 153302

Gudmundsson and Lieberman (2015) PSST **24** 035016

Capacitively Coupled Oxygen Discharge at 13.56 MHz

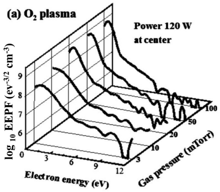
- At low pressure the EEPF is convex, the population of low energy electrons is relatively low
- As the pressure is increased the number of low energy electrons increases and the number of higher energy electrons (> 10 eV) decreases
- Thus the EEPF develops a concave shape or becomes bi-Maxwellian as the pressure is increased



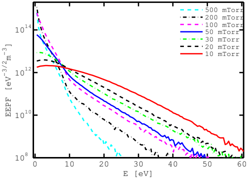
Gudmundsson and Ventéjou (2015) JAP **118** 153302

Capacitively Coupled Oxygen Discharge at 13.56 MHz

- Our results agree with the measurements of Lee et al. (2010) which explored experimentally the evolution of the EEPF with pressure in a capacitively coupled oxygen discharge in the pressure range 3 – 100 mTorr
- They find that the EEPF became more distinctly bi-Maxwellian and the density of low energy electrons increases as the gas pressure is increased



Lee et al. (2010) PRE **81** 046402

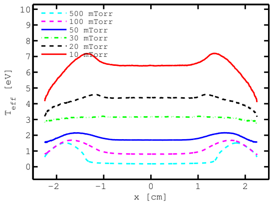


Gudmundsson and Ventéjou (2015) JAP **118** 153302

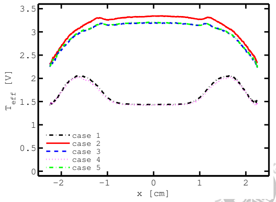
Capacitively Coupled Oxygen Discharge at 13.56 MHz

- The effective electron temperature drops as the pressure is increased
- When the metastable singlet oxygen molecule $O_2(a^1\Delta_g)$ is added to the discharge model the effective electron temperature drops, in particular in the electronegative core due to detachment by the metastable $O_2(a^1\Delta_g)$ molecule

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



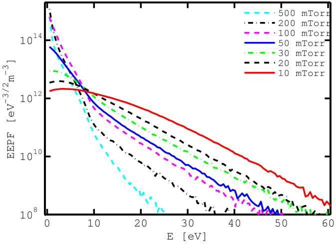
Gudmundsson and Ventéjou (2015) JAP **118** 153302



Gudmundsson and Lieberman (2015) PSST **24** 035016

Capacitively Coupled Oxygen Discharge at 13.56 MHz

- At low pressure the EEPF is convex and develops a concave shape or becomes bi-Maxwellian as the pressure is increased
- These results contradict what is commonly found for the capacitively coupled argon discharge where the EEPF evolves from being concave at low pressure to being convex at high pressure



Gudmundsson and Ventéjou (2015) JAP **118** 153302

B. 1. 2. Capacitively Coupled Oxygen Discharge at 13.56 MHz – pressure dependence – including $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g)$ and $\gamma_{\rm see}(E)$

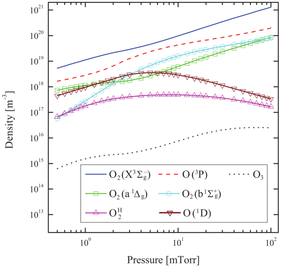
Capacitively Coupled Oxygen Discharge at 13.56 MHz

- It has been known for decades that the metastable oxygen molecule $O_2(b^1\Sigma_g)$ plays an important role in the oxygen discharge

  Thompson (1961) *Proc. Royal Soc. A 262*(1311) 519

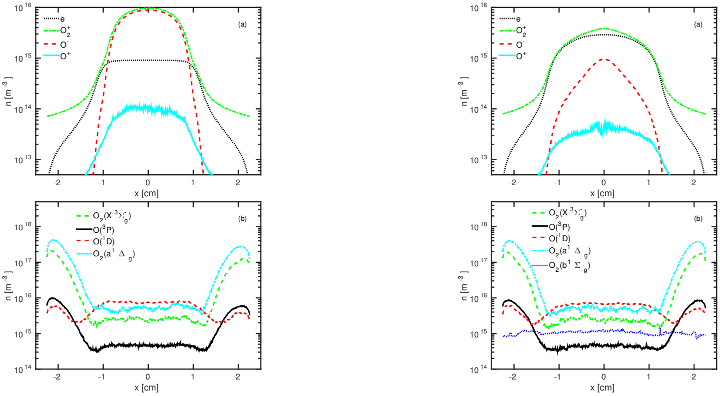
- Recent global model study indicates there is a significant density of $O_2(b^1\Sigma_g)$ in the oxygen discharge
- The $O_2(b^1\Sigma_g)$ is mainly created through

$$O_2(X^3\Sigma_g^-) + O(^1D) \longrightarrow O_2(b^1\Sigma_g) + O(^3P)$$



Toneli et al., *J. Phys. D*, **48** 325202 (2015)

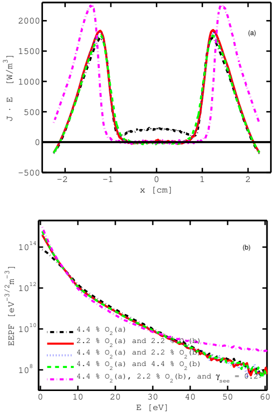
Capacitively Coupled Oxygen Discharge at 13.56 MHz



- The density profiles of charged particles and fast neutrals comparing including $O_2(a^1\Delta_g)$ (left) and $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g)$ (right) at 50 mTorr

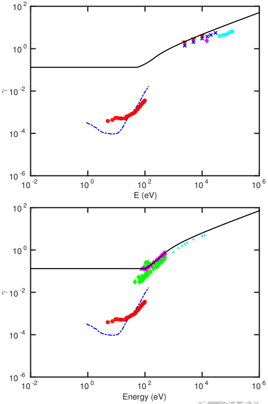
Capacitively Coupled Oxygen Discharge at 13.56 MHz

- The number of cold electrons increases as $O_2(b^1\Sigma_g)$ is added to the discharge model
- The electron heating in the bulk drops to zero
- The EEPF is roughly independent of the pratial pressure of $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g)$ while both are included
- Adding secondary electron emission ($\gamma_{see} = 0.2$) leads to a high energy tail in the EEPF

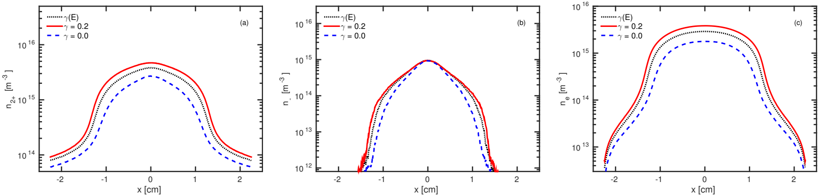


Capacitively Coupled Oxygen Discharge at 13.56 MHz

- We have compiled experimental data from the literature on secondary electron emission yields for the species O_2^+, O^+, O_2 and O bombarding various metals and substances
- A fit was made through the available experimental data



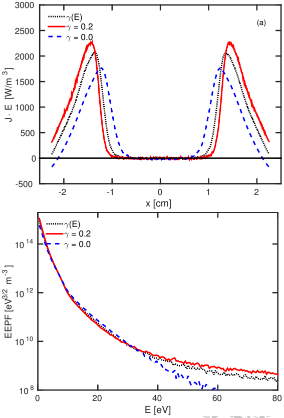
Capacitively Coupled Oxygen Discharge at 13.56 MHz



- The O_2^+, O^- and electron density profiles for $\gamma_{\rm see} = 0.0$, $\gamma_{\rm see} = 0.2$, and energy dependent secondary electron emission yield
- The electron density increases with increased secondary electron emission yield

Capacitively Coupled Oxygen Discharge at 13.56 MHz

- Increased secondary electron emission yield increases the electron heating rate in the sheath region and the sheath region becomes narrower



Capacitively Coupled Oxygen Discharge at 13.56 MHz

- Comparison to experimental findings:

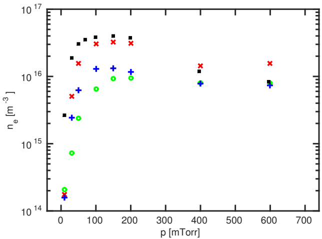
  o $\gamma_{\rm see} = 0.0$,
  4.4 % $O_2(a^1\Delta_g)$

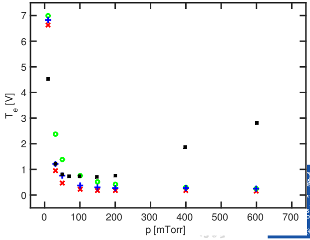
  + $\gamma_{\rm see} = 0.0$,
  4.4 % $O_2(a^1\Delta_g)$ and 4.4 % $O_2(b^1\Sigma_g)$

  x $\gamma_{\rm see} = \gamma_{\rm see}(E)$,
  4.4 % $O_2(a^1\Delta_g)$ and 4.4 % $O_2(b^1\Sigma_g)$

  - Experimental findings by Keckar

  (Ph.D. Thesis, Dublin City University, January 2015)





Summary

- We demonstrated particle-in-cell/Monte Carlo collision simulation of a capcacitively coupled disharge
- In an oxygen discharge at low pressure the EEPF is convex and develops a concave shape or becomes bi-Maxwellian as the pressure is increased
- These results contradict what is commonly found for the capacitively coupled argon discharge where the EEPF evolves from being concave at low pressure to being convex at high pressure

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)

Overall Summary

- There is clearly a need for basic experimental work on capacitively coupled oxygen discharges
  - Langmuir probe measurements, EEDF, $T_{\rm eff}$, $n_{\rm e}$ versus pressure and applied voltage
  - Electronegativity for various pressures and applied voltage
- The rate coefficient for detachment by $O_2(b^1\Sigma_g)$ has to be reevaluated
- What is the role of electron impact dissociative attachment from vibrationally excited molecular states ?
- What is the role of the metastable Herzberg states $O_2(A^3\Sigma_u^+$, $A'^3\Delta_u$, $c^1\Sigma_u^-)$?
- Measurements of the wall quenching coefficient of $O_2(b^1\Sigma_g)$ are needed

Acknowledgements

The slides can be downloaded at
`http://langmuir.raunvis.hi.is/~tumi/ranns.html`
Much of this work was made by

- Eyþór Gísli Þorsteinsson (Univ. of Iceland)
- Shuo Huang (UM-SJTU, Shanghai)
- David A. Toneli (ITA, São José dos Campos, Brazil)
- Hólmfríður Hannesdóttir (Univ. of Iceland)

in collaboration with

- prof. Michael A. Lieberman (UC Berkeley)
- prof. Allan J. Lichtenberg (UC Berkeley)
- prof. John P. Verboncoeur (Michigan State)
- Dr. Emi Kawamura (UC Berkeley)

and funded by Icelandic Research Fund grants no. 130029 and 163086 and the Swedish Government Agency for Innovation Systems (VINNOVA) contract no. 2014-04876

References

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. and E. G. Thorsteinsson (2007). Oxygen discharges diluted with argon: dissociation processes. *Plasma Sources Science and Technology 16*(2), 399–412.

Gudmundsson, J. T. and M. A. Lieberman (2015). On the role of metastables in capacitively coupled oxygen discharges. *Plasma Sources Science and Technology 24*(3), 035016.

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.

Gudmundsson, J. T. and B. Ventéjou (2015). The pressure dependence of the discharge properties in a capacitively coupled oxygen discharge. *Journal of Applied Physics 118*(15), 153302.

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

Kechkar., S. (2015, January). *Experimental investigation of a low pressure capacitively-coupled discharge*. Ph. D. thesis, Dublin City University.

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.

References

Lee, M.-H., H.-C. Lee, and C.-W. Chung (2010). Comparison of pressure dependence of electron energy distributions in oxygen capacitively and inductively coupled plasmas. *Physical Review E 81*(4), 046402.

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.

Mutsukura, N., K. Kobayashi, and Y. Machi (1990). Plasma sheath thickness in radio-frequency discharges. *Journal of Applied Physics 68*(6), 2657–2660.

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.

Thompson, J. B. (1961). The ion balance of the oxygen d.c. glow discharge. *Proceedings of the Royal Society A 262*(1311), 519–528.

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.

Toneli, D. A., R. S. Pessoa, M. Roberto, and J. T. Gudmundsson (2015a). On the formation and annihilation of the singlet molecular metastables in an oxygen discharge. *Journal of Physics D: Applied Physics 48*(32), 325202.

Toneli, D. A., R. S. Pessoa, M. Roberto, and J. T. Gudmundsson (2015b). A volume averaged global model study of the influence of the electron energy distribution and the wall material on an oxygen discharge. *Journal of Physics D: Applied Physics 48*(49), 495203.

van Roosmalen, A. J., W. G. M. van den Hoek, and H. Kalter (1985). Electrical properties of planar rf discharges for dry etching. *Journal of Applied Physics 58*(2), 653–658.