The effect of singlet metastable states on the ion energy distribution in capacitively coupled oxygen discharges

Jón Tómas Guðmundsson[1,2], Davíð I. Snorrason[1] and Hólmfríður Hannesdóttir[1]

[1]Science Institute, University of Iceland, Reykjavík, Iceland
[2]Department of Space and Plasma Physics, School of Electrical Engineering, KTH – Royal Institute of Technology, Stockholm, Sweden

tumi@hi.is

23rd International Symposium on Plasma Chemistry
Montréal, Canada, August 3, 2017

Introduction

- Oxygen forms a weakly electronegative discharge
- The oxygen chemistry is rather involved, in particular due to the presence of **metastable molecular and atomic** oxygen and their role in dissociative attachment and detachment processes
- We use the `oopd1` (objective oriented plasma device for one dimension) **particle-in-cell Monte Carlo collision** code to simulate the discharge
- It has 1 dimension in space and 3 velocity components for particles (1d-3v)
- 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)

Outline

- The oxygen discharge
- Capacitively Coupled Oxygen Discharge at 13.56 MHz
  - Pressure dependence
  - Frequency dependence
    - including both $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g)$
    - including secondary electron emission
  - Dual Frequency at 13.56 MHz + 27.12 MHz
- Summary

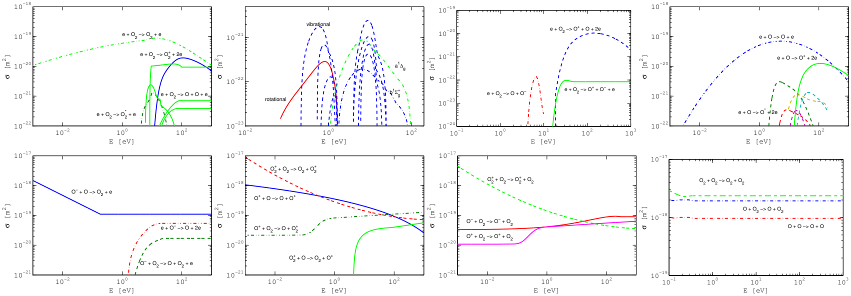
The oxygen discharge

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
- In most PIC/MCC simulations of oxygen discharges to date only O_2^+, O^- and electrons have been tracked

[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 up to 67 reactions

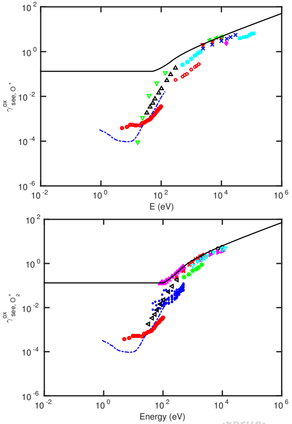
Gudmundsson et al., *Plasma Sources Sci. Technol.*, **22** 035011 (2013)

Gudmundsson and Lieberman, *Plasma Sources Sci. Technol.*, **24** 035016 (2015)

Hannesdottir and Gudmundsson, *Plasma Sources Sci. Technol.*, **25** 055002 (2016)

The oxygen discharge

- The discharge model also includes energy dependent secondary electron emission yield
- 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



Hannesdottir and Gudmundsson (2016) PSST, **25** 055002

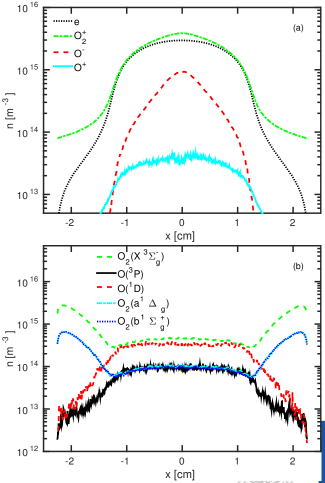
Capacitively Coupled Oxygen Discharge
single frequency at 13.56 MHz

– 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

- The density profiles
  - (a) Charged particles
  - (b) Fast neutrals
- For a parallel plate capacitively coupled oxygen discharge at
  - 50 mTorr
  - electrode separation 4.5 cm
  - voltage amplitude 222 V
  - frequency 13.56 MHz
- If the kinetic energy of the neutrals reaches a certain threshold they are tracked

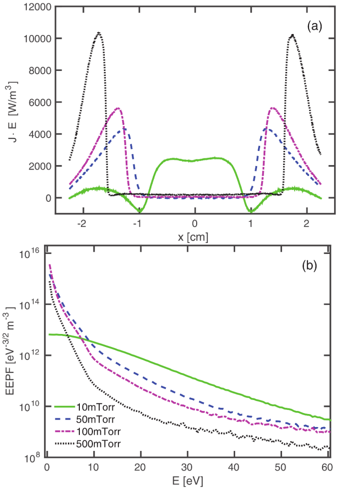


Hannesdottir and Gudmundsson (2016) PSST, **25** 055002

Capacitively Coupled Oxygen Discharge at 13.56 MHz

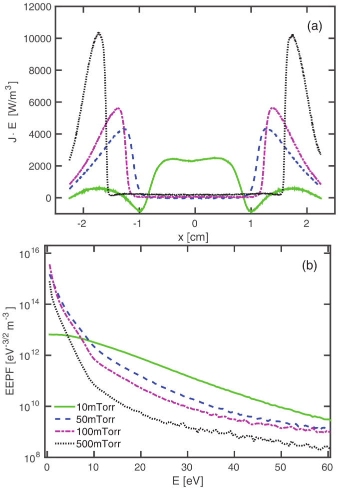
- The electron heating profile $\mathbf{J}_{\mathrm{e}} \cdot \mathbf{E}$
- In the pressure range 50 – 500 mTorr the electron heating occurs almost solely in the sheath region
- As the pressure is decreased the Ohmic heating contribution in the plasma bulk increases and sheath heating decreases

Hannesdottir and Gudmundsson (2016) PSST, **25** 055002



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

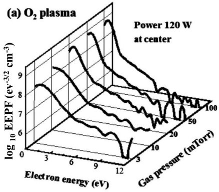


Hannesdottir and Gudmundsson (2016) PSST, **25** 055002

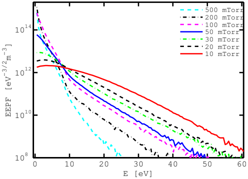
Gudmundsson and Ventéjou (2015) JAP **118** 153302

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

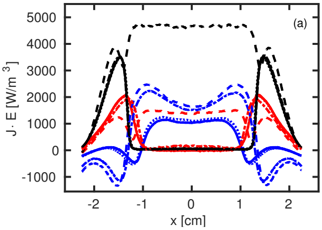


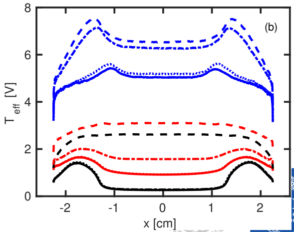
Gudmundsson and Ventéjou (2015) JAP **118** 153302

Capacitively Coupled Oxygen Discharge at 13.56 MHz

- The number of cold electrons increases as the metastables $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g)$ are added to the discharge model
- The electron heating in the bulk drops to zero at the higher pressures
- The effective electron temperature profile changes significantly when detachment by singlet metastables is added to the reaction set
- **10 mTorr**, **50 mTorr** and **200 mTorr**

Gudmundsson and Hannesdottir, AIP Conf. Proc. **1811** 120001 (2017)





Capacitively Coupled Oxygen Discharge at 13.56 MHz

- Comparison to experimental findings:

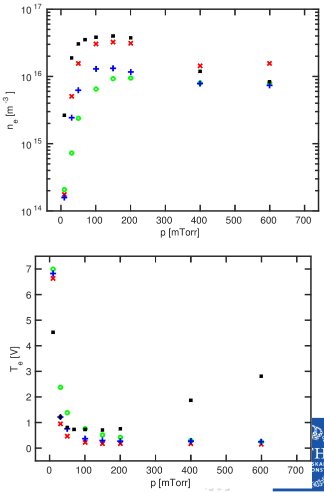
  o $\gamma_{see} = 0.0$,
  4.4 % $O_2(a^1\Delta_g)$

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

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

  - Experimental findings by Kechkar

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

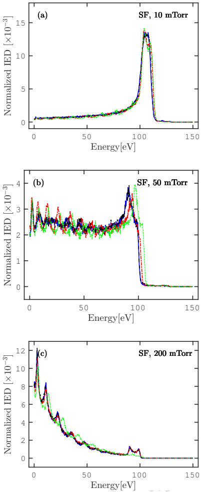


Hannesdottir and Gudmundsson (2016) PSST **25** 055002

Capacitively Coupled Oxygen Discharge at 13.56 MHz

- The ion energy distribution (IED) of O_2^+ at the powered electrode
- The four cases explored are:
  - detachment neither by $O_2(a^1\Delta_g)$ nor $O_2(b^1\Sigma_g^+)$ ($\cdots$)
  - detachment by $O_2(a^1\Delta_g)$ only ($- \cdot -$)
  - detachment by $O_2(b^1\Sigma_g^+)$ only ($--$)
  - both detachment by $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ included (full reaction set) (—)

Hannesdottir and Gudmundsson (2017) JPD **50** 175201



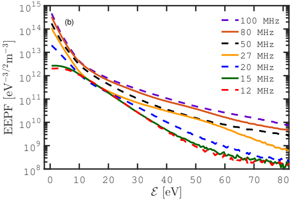
Capacitively Coupled Oxygen Discharge single frequency at 10 mTorr

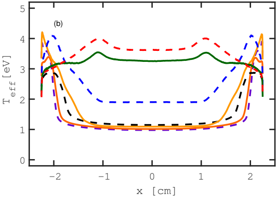
– driving frequency dependence –

including $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g)$ and $\gamma_{\rm see}(E)$

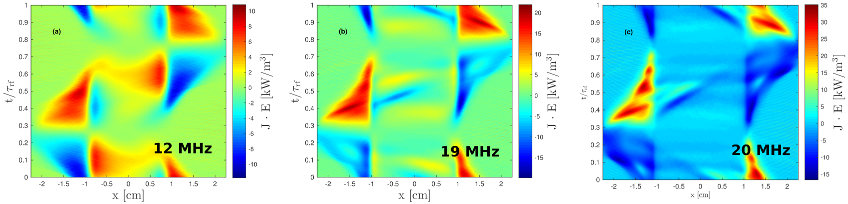
Capacitively Coupled Oxygen Discharge at 10 mTorr

- At low driving frequency the EEPF is convex, the population of low energy electrons is relatively low
- The EEPF remains convex for driving frequency up to 15 MHz and has transitioned to concave or bi-Maxwellian shape at 20 MHz
- Increasing the driving frequency enhances the high energy tail as the number of high energy electrons increases



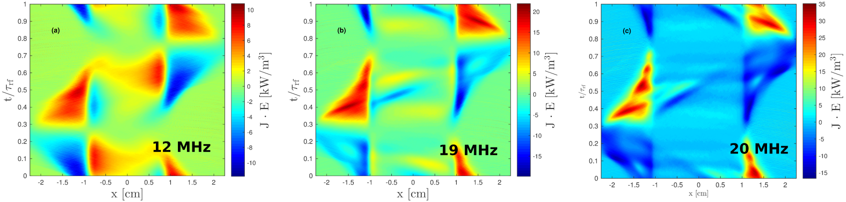


Capacitively Coupled Oxygen Discharge at 10 mTorr



- At 12 MHz the heating is observed in the sheath region, during sheath expansion, and the cooling is observed during the sheath collapse
- Here significant energy gain (red and yellow areas) are evident in the plasma bulk region

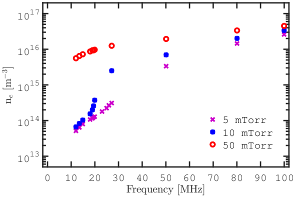
Capacitively Coupled Oxygen Discharge at 10 mTorr

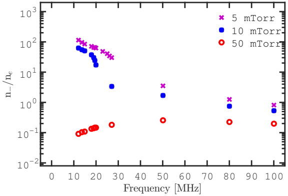


- At 19 MHz the heating and cooling in the sheath regions has increased, however there is contribution to the electron heating in the bulk region (note the change in scale)
- Between 19 and 20 MHhz there is a transition in the heating processes
- At 20 MHz the electron heating rate in the sheath region has increased, there is almost no electron heating in the plasma bulk

Capacitively Coupled Oxygen Discharge at 10 mTorr

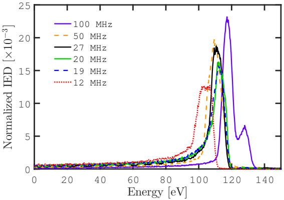
- At 10 mTorr there is a jump in the center electron density between 20 and 27 MHz
- At 10 mTorr $n_e \propto f^{2.11}$ at low frequency, below 18 MHz, and $n_e \propto f^{2.00}$ at higher frequencies, 27.12 MHz and above
- At 50 mTorr $n_e \propto f^{0.93}$ over the entire frequency range explored and no transition is observed
- We see that at 5 and 10 mTorr the electronegativity decreases with increasing driving frequency

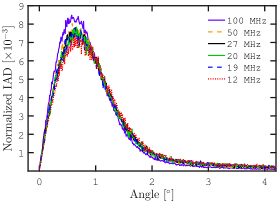




Capacitively Coupled Oxygen Discharge at 10 mTorr

- The ion energy distribution (IED) and the ion angular distribution (IAD) at the grounded electrode at 10 mTorr
- The ion energy increases with increased driving frequency
- The ion angular distribution shifts only very slightly to lower angle with increased driving frequency





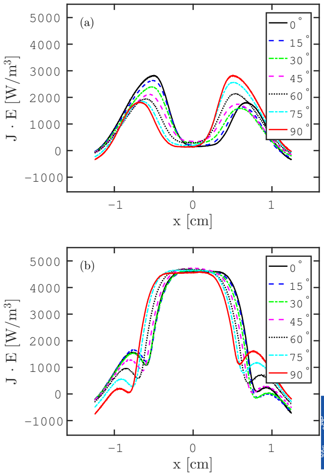
Capacitively Coupled Oxygen Discharge

– Dual Frequency at 13.56 MHz + 27.12 MHz –

including $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g)$ and $\gamma_{\rm see}(E)$

Capacitively Coupled Oxygen Discharge Dual Frequency at 13.56 MHz + 27.12 MHz

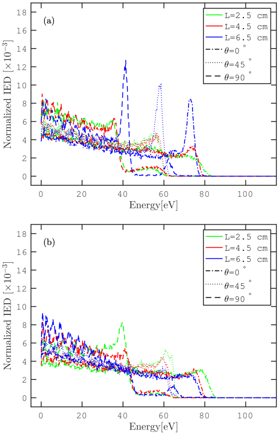
- The time averaged electron heating rate profile for a discharge
  - gap of 2.5 cm, dual frequency 13.56 MHz + 27.12 MHz and 75 mTorr
- Adding detachment reactions shifts the electron heating from mostly ohmic bulk heating to collisionless heating in the sheaths
- Increasing the phase from 0° to 90° decreases the sheath width at the powered electrode and increases the sheath width at the grounded electrode



Hannesdottir and Gudmundsson (2017) JPD **50** 175201

Capacitively Coupled Oxygen Discharge Dual Frequency at 13.56 MHz + 27.12 MHz

- The ion energy distribution (IED)
- A dual frequency (13.56 MHz + 27.12 MHz) parallel plate capacitively coupled oxygen discharge at 75 mTorr
  - (a) Detachment by $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g)$ included
  - (b) Detachment by $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g)$ excluded
- For a larger discharge gap (L = 6.5 cm), the peak in the IED is much more apparent in the case where the full reaction set is used in the discharge model

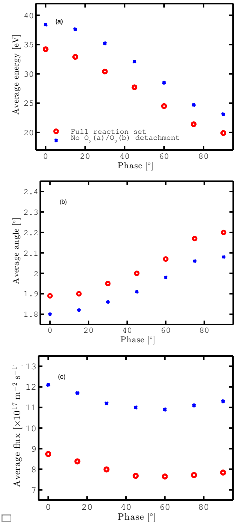


Hannesdottir and Gudmundsson (2017) JPD **50** 175201

Capacitively Coupled Oxygen Discharge Dual Frequency at 13.56 MHz + 27.12 MHz

- O_2^+-ion flux on the powered electrode
  - (a) average ion bombarding energy
  - (b) the average ion angle
  - (c) the average ion flux
- A parallel plate capacitively coupled oxygen discharge with a gap separation of 2.5 cm operated at a dual frequency of 13.56 MHz (75 V voltage source) and 27.12 MHz (75 V voltage source), at 75 mTorr pressure

Hannesdottir and Gudmundsson (2017) JPD **50** 175201



Summary

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 or driving frequency is increased
- Including the detachment processes by the singlet metastable states has a strong influence on the effective electron temperature and electronegativity in the oxygen discharge
- Including the detachment processes by the singlet metastable states lowers the average ion bombarding energy and the ion flux

Acknowledgements

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

- David A. Toneli (ITA, São José dos Campos, Brazil)
- Bruno Ventéjou (LPGP, Université Paris-Sud, Orsay, France)

in collaboration with

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

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

References

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., 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.

Gudmundsson, J. T. and H. Hannesdottir (2017). On the role of metastable states in low pressure oxygen discharge. *AIP Conference Proceedings*, *1811*(5), 120001.

Hannesdottir, H. and J. T. Gudmundsson (2016). The role of the metastable $O_2(b^1\Sigma_g^+)$ and energy-dependent secondary electron emission yields in capacitively coupled oxygen discharges. *Plasma Sources Science and Technology*, *25*(5), 055002.

Hannesdottir, H. and J. T. Gudmundsson (2017). On singlet metastable states, ion flux and ion energy in single and dual frequency capacitively coupled oxygen discharges. *Journal of Physics D: Applied Physics 50*(17), 175201.

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

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.

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.