On the Significance of Metastable States in Low Pressure Capacitively Coupled Oxygen Discharge

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69$^{\text{th}}$ Gaseous Electronics Conference, Bochum, Germany
October 14. 2016

Introduction

- Oxygen is a weakly electronegative gas and the presence of negative ions has a strong influence on the kinetics and dynamics of the oxygen discharge
- The oxygen discharge is of vital importance in various materials processing applications such as
  - ashing of photoresist
  - etching of polymer films
  - oxidation and deposition of thin film oxides
- 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

Outline

- The 1D particle-in-cell/Monte Carlo collision simulation
- The oxygen discharge
- Capacitively Coupled Oxygen Discharge at 13.56 MHz
    - Pressure dependence – including $O_2(a^1\Delta_g)$
    - Including both $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g)$
    - Including secondary electron emission
- Summary

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

The oopd1 1d-3v PIC/MCC code

- We use the `oopd1` (objective oriented plasma device for one dimension) code to simulate the discharge
- The `oopd1` code was originally developed at the Plasma Theory and Simulation Group at UC Berkeley
- It has 1 dimension in space and 3 velocity components for particles (1d-3v)
- The `oopd1` code is supposed to replace the widely used `xpdx1` series (`xpdp1`, `xpdc1` and `xpds1`)
- It is developed to simulate various types of plasmas, including processing discharges, accelerators and beams
  - Modular structure
  - Includes relativistic kinematics
  - Particles can have different weights

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

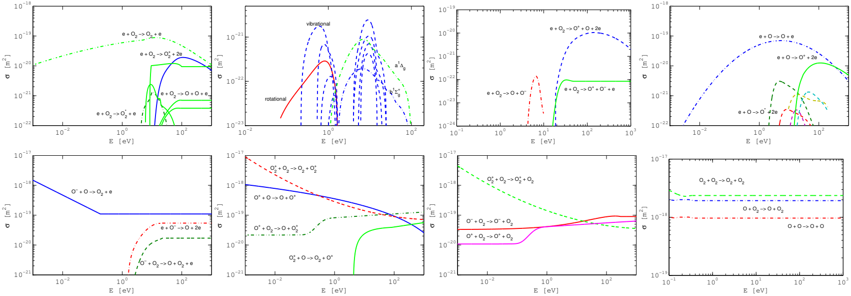
The oxygen discharge

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), **24** 035016 (2015) and **25** 055002 (2016)

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

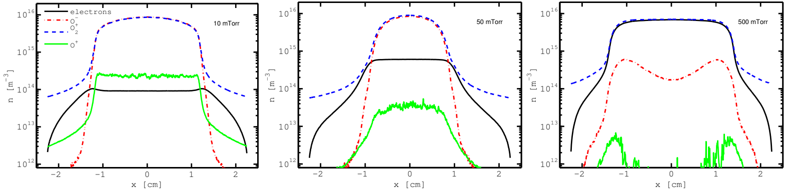
Capacitively Coupled Oxygen Discharge at 13.56 MHz

- 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_{rf} = 222 V and f = 13.56 MHz
- The neutrals (O_2 and O) are treated as background gas at T_{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

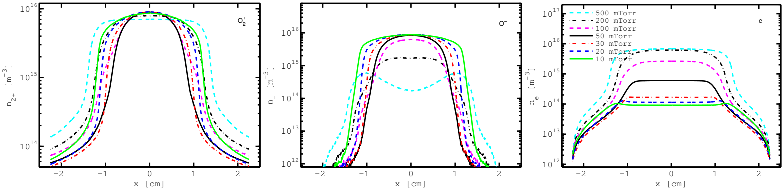
Capacitively Coupled Oxygen Discharge at 13.56 MHz



- 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

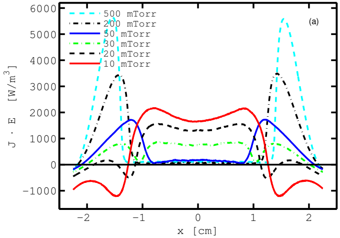


- The sheath width decreases as the pressure is decreased in the pressure range from 50 mTorr to 10 mTorr
- The sheath widths are largest at 50 mTorr
- As the pressure is increased from 50 mTorr up to 500 mTorr the sheath width decreases
- This agrees with what has been observed experimentally in the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

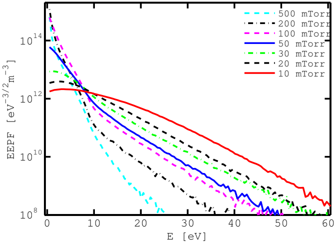
- The electron heating profile $\mathbf{J}_e \cdot \mathbf{E}$
- In the pressure range 50 - 500 mTorr the electron heating occurs almost solely in the sheath region
- As the pressure is decreased the Ohmic heating contribution in the plasma bulk increases and sheath heating decreases



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

Capacitively Coupled Oxygen Discharge at 13.56 MHz

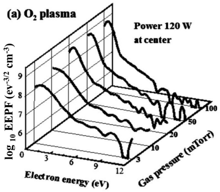
- At low pressure the EEPF is convex, the population of low energy electrons is relatively low
- As the pressure is increased the number of low energy electrons increases and the number of higher energy electrons (> 10 eV) decreases
- Thus the EEPF develops a concave shape or becomes bi-Maxwellian as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



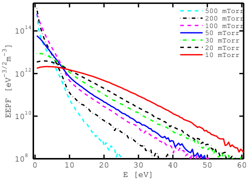
Gudmundsson and Ventéjou (2015) JAP **118** 153302

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

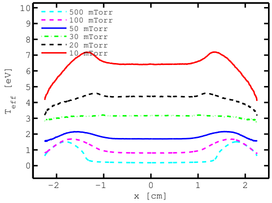


Gudmundsson and Ventéjou (2015) JAP **118** 153302

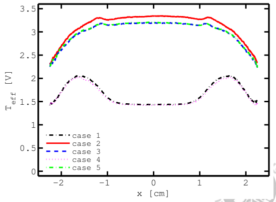
Capacitively Coupled Oxygen Discharge at 13.56 MHz

- 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

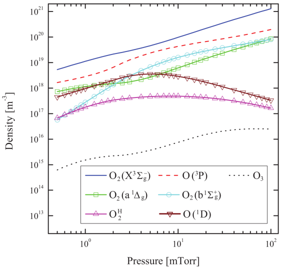
B. 1. 2. Capacitively Coupled Oxygen Discharge at 13.56 MHz – pressure dependence – including $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g)$ and $\gamma_{\rm see}(E)$

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

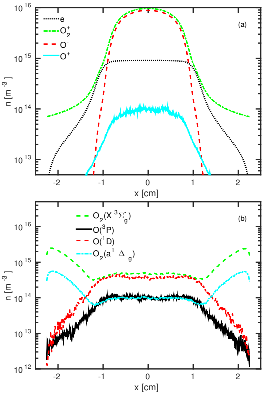
- Recent global model study indicates there is a significant density of $O_2(b^1\Sigma_g)$ in the oxygen discharge
- The $O_2(b^1\Sigma_g)$ is mainly created through

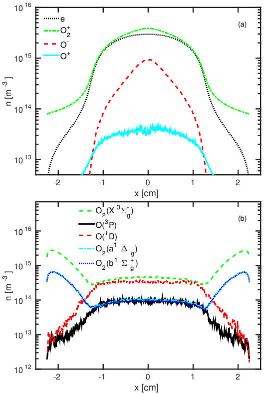


Toneli et al., *J. Phys. D*, **48** 325202 (2015)

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

Capacitively Coupled Oxygen Discharge at 13.56 MHz

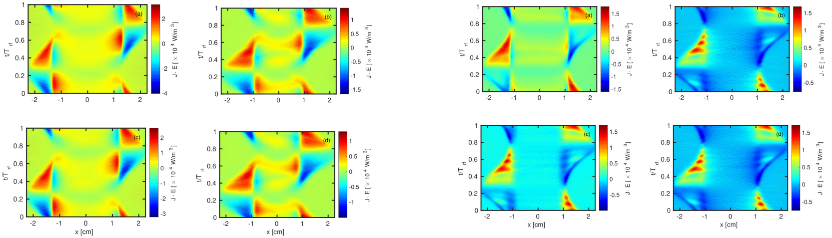




Hannesdottir and Gudmundsson, PSST, **25** 055002 (2016)

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

Capacitively Coupled Oxygen Discharge at 13.56 MHz

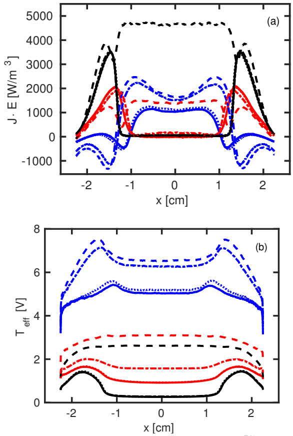


Gudmundsson and Hannesdottir, AIP Conf. Proc. accepted 2016

- The spatio-temporal electron heating at 10 mTorr (left) and 50 mTorr (right)
- The four cases explored are:
  - (a) detachment neither by $O_2(a^1\Delta_g)$ nor $O_2(b^1\Sigma_g^+)$
  - (b) only detachment by $O_2(b^1\Sigma_g^+)$ included
  - (c) only detachment by $O_2(a^1\Delta_g)$ included
  - (d) both detachment by $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ included

Capacitively Coupled Oxygen Discharge at 13.56 MHz

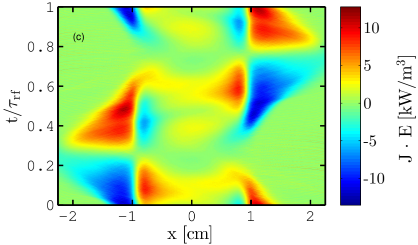
- The number of cold electrons increases as $O_2(b^1\Sigma_g)$ is added to the discharge model
- The electron heating in the bulk drops to zero
- The effective electron temperature profile changes significantly when detachment by singlet metastables is added to the reaction set
- 10 mTorr, 50 mTorr and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

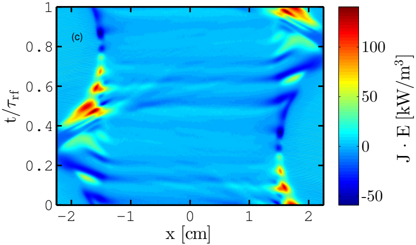


Gudmundsson and Hannesdottir,

AIP Conf. Proc. accepted 2016

Capacitively Coupled Oxygen Discharge at 13.56 or 27.12 MHz

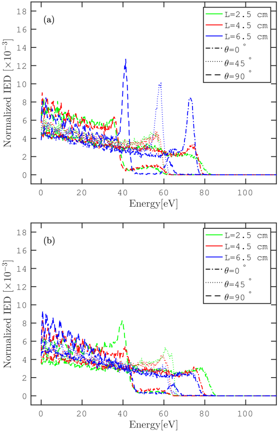




- The spatio-temporal electron heating at 10 mTorr with a gap separation of 4.5 cm driven by a 222 V voltage source at 13.56 MHz (left) and 27.12 MHz (right)

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, (2016) to be submitted

Capacitively Coupled Oxygen Discharge at 13.56 MHz

- Comparison to experimental findings:

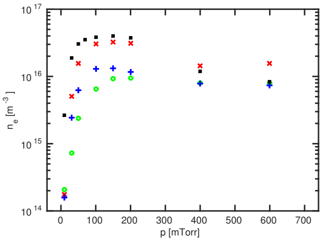
  o $\gamma_{\rm see} = 0.0$,
  4.4 % $O_2(a^1\Delta_g)$

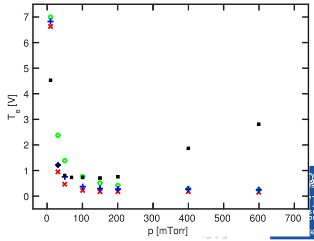
  + $\gamma_{\rm see} = 0.0$,
  4.4 % $O_2(a^1\Delta_g)$ and 4.4 % $O_2(b^1\Sigma_g)$

  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 Kechkar

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





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

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
- Including the detachment processes by the singlet metastable states has a strong influence on the effective electron temperature and electronegativity in the oxygen discharge

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 now Men & Mice)
- Shuo Huang (UM-SJTU, Shanghai now University of Michigan)
- David A. Toneli (ITA, São José dos Campos, Brazil)
- Hólmfríður Hannesdóttir (Univ. of Iceland now Harvard Univ.)

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

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.

Gudmundsson, J. T. and H. Hannesdottir (accepted 2016). On the significance of metastable states in low pressure oxygen discharges. *AIP Conference Proceedings*.

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.

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.

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

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 (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.

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.