The role of the singlet metastables in capacitively coupled oxygen discharges

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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)

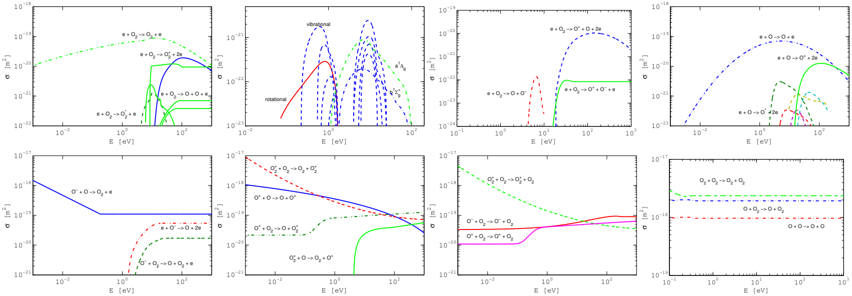
The oxygen discharge

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), and **24** 035016 (2015)

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

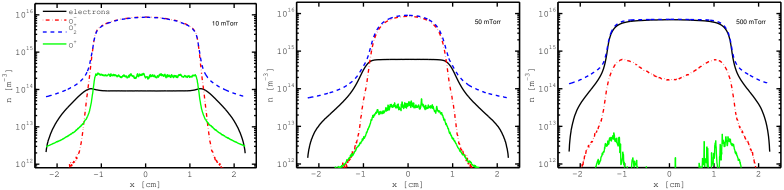
Capacitively Coupled Oxygen Discharge at 13.56 MHz

- 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

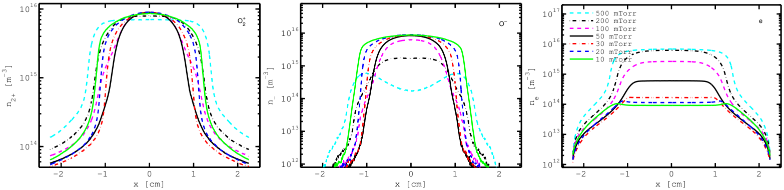
Capacitively Coupled Oxygen Discharge at 13.56 MHz



- 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

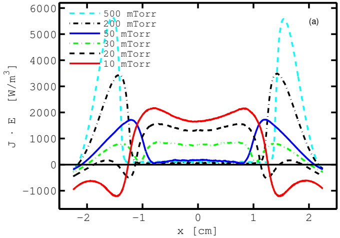


- The sheath width decreases as the pressure is decreased in the pressure range from 50 mTorr to 10 mTorr
- The sheath widths are largest at 50 mTorr
- As the pressure is increased from 50 mTorr up to 500 mTorr the sheath width decreases
- This agrees with what has been observed experimentally in the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

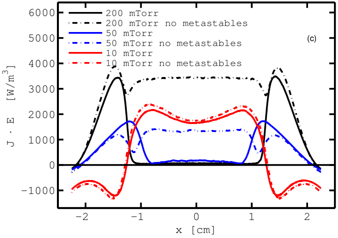
- The electron heating profile $\mathbf{J}_\mathrm{e} \cdot \mathbf{E}$
- In the pressure range 50 - 500 mTorr the electron heating occurs almost solely in the sheath region
- As the pressure is decreased the Ohmic heating contribution in the plasma bulk increases and sheath heating decreases



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

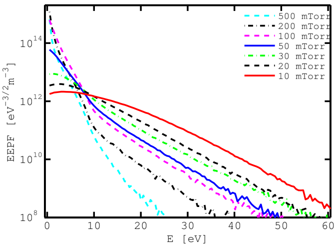


Gudmundsson and Ventéjou (2015) JAP **118** 153302

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

Capacitively Coupled Oxygen Discharge at 13.56 MHz

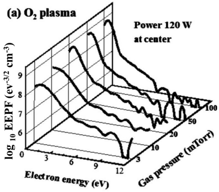
- At low pressure the EEPF is convex, the population of low energy electrons is relatively low
- As the pressure is increased the number of low energy electrons increases and the number of higher energy electrons (> 10 eV) decreases
- Thus the EEPF develops a concave shape or becomes bi-Maxwellian as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



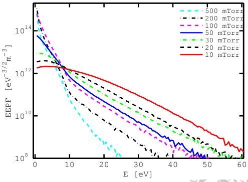
Gudmundsson and Ventéjou (2015) JAP **118** 153302

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

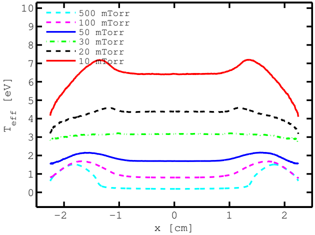


Gudmundsson and Ventéjou (2015) JAP **118** 153302

Capacitively Coupled Oxygen Discharge at 13.56 MHz

- The effective electron temperature drops as the pressure is increased
- We had seen earlier that 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

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



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

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

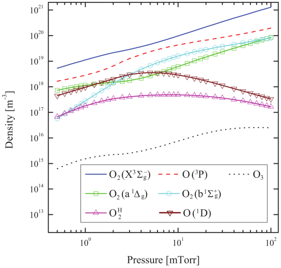
Capacitively Coupled Oxygen Discharge at 13.56 MHz

- 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

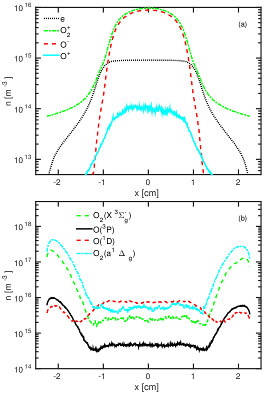
- Recent global model study indicates there is a significant density of $O_2(b^1\Sigma_g)$ in the oxygen discharge
- The $O_2(b^1\Sigma_g)$ is mainly created through

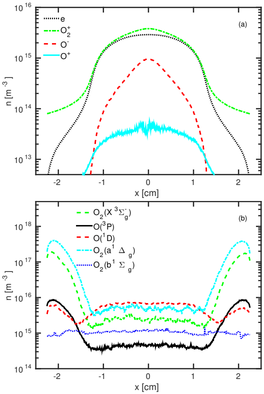
$$O_2(X^3\Sigma_g^-) + O(^1D) \longrightarrow O_2(b^1\Sigma_g) + O(^3P)$$



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

Capacitively Coupled Oxygen Discharge at 13.56 MHz

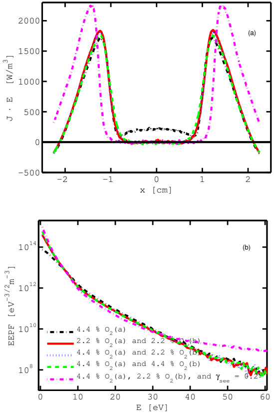




- The density profiles of charged particles and fast neutrals comparing including $O_2(a^1\Delta_g)$ (left) and $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g)$ (right) at 50 mTorr

Capacitively Coupled Oxygen Discharge at 13.56 MHz

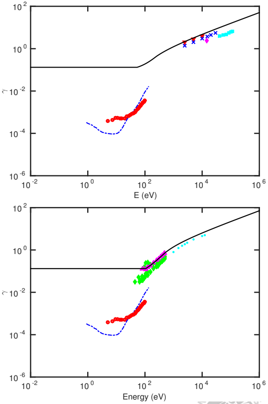
- The number of cold electrons increases as $O_2(b^1\Sigma_g)$ is added to the discharge model
- The electron heating in the bulk drops to zero
- The EEPF is roughly independent of the pratial pressure of $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g)$ while both are included
- Adding secondary electron emission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



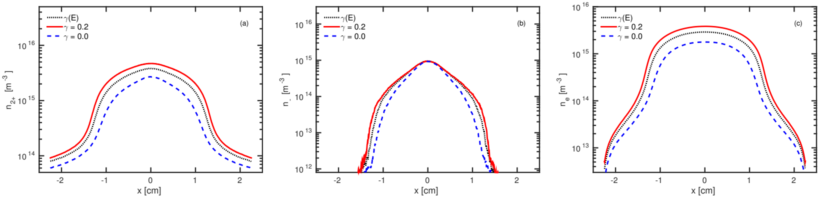
Capacitively Coupled Oxygen Discharge at 13.56 MHz – including secondary electron emission

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



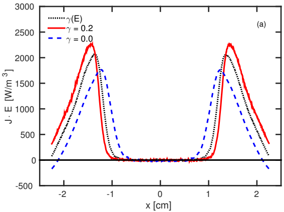
Capacitively Coupled Oxygen Discharge at 13.56 MHz

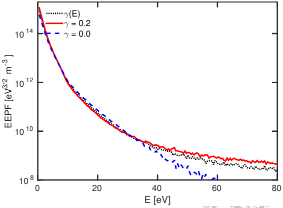


- The O_2^+, O^- and electron density profiles for $\gamma_{\mathrm{see}} = 0.0$, $\gamma_{\mathrm{see}} = 0.2$, and energy dependent secondary electron emission yield
- The electron density increases with increased secondary electron emission yield

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





Summary

Summary

- We explored a capcacitively coupled oxygen disharge using particle-in-cell/Monte Carlo collision simulation
- The reaction set includes
  - Oxygen atoms $O(^3P)$ and O^+-ions
  - The metastables $O(^1D)$, $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g)$
- 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

Thank you for your attention

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The slides can be downloaded at

http://langmuir.raunvis.hi.is/∼tumi/plasma.html

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