

# 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



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

# The oxygen discharge



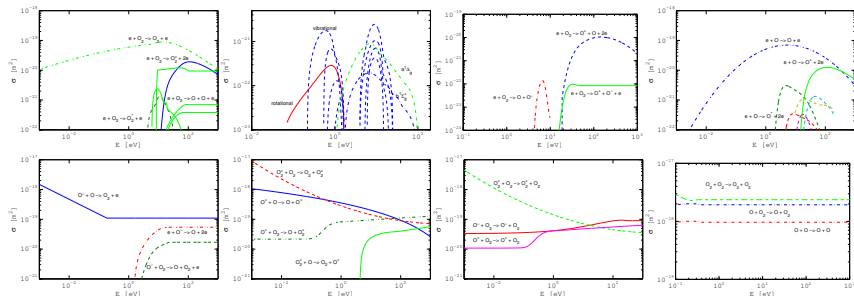
# The oxygen discharge

- 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<sup>1</sup> 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

<sup>1</sup> 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), **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*

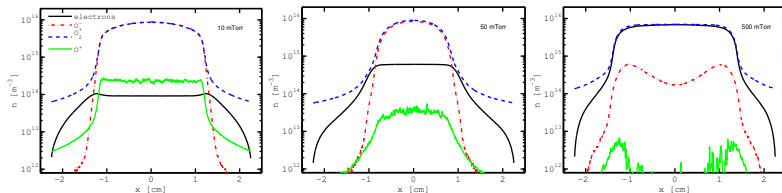
- We apply a voltage source with a single frequency

$$V(t) = V_{\text{rf}} \sin(2\pi ft)$$

- The electrodes are circular with a diameter of 14.36 cm
- The gap between the electrodes is 4.5 cm
- We set  $V_{\text{rf}} = 222$  V and  $f = 13.56$  MHz
- The neutrals ( $\text{O}_2$  and O and the metastables) are treated as background gas at  $T_g = 300$  K with a Maxwellian distribution
- If the kinetic energy of the neutrals reaches a certain threshold they are tracked
- The dissociation fraction and the metastable fraction is found using a global model
- The pressure is varied from 10 – 500 mTorr

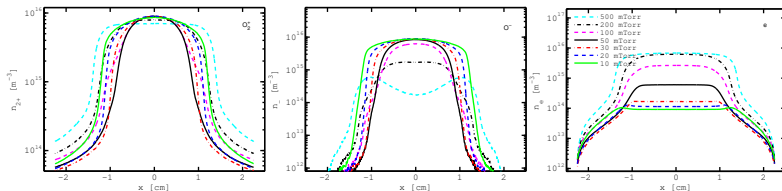


# Capacitively Coupled Oxygen Discharge at 13.56 MHz



- For a parallel plate capacitively coupled oxygen discharge at 50 mTorr with a gap separation of 4.5 cm by a 222 V voltage source at 13.56 MHz
  - $\text{O}_2^+$ -ion density profile
  - $\text{O}^+$ -ion density profile
  - $\text{O}^-$ -ion density profile
  - electron density profile

# Capacitively Coupled Oxygen Discharge at 13.56 MHz

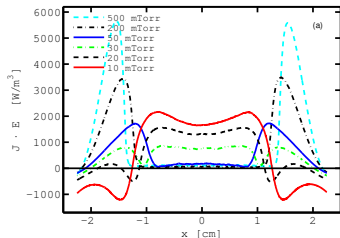


- The sheath width decreases as the pressure is decreased in the pressure range from 50 mTorr to 10 mTorr
- The sheath widths are largest at 50 mTorr
- As the pressure is increased from 50 mTorr up to 500 mTorr the sheath width decreases
- This agrees with what has been observed experimentally in the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

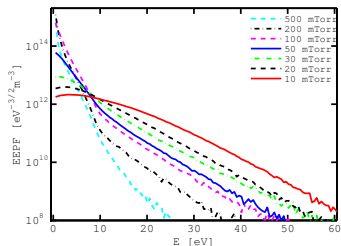
- The electron heating profile  $\mathbf{J_e \cdot E}$
- In the pressure range 50 – 500 mTorr the electron heating occurs almost solely in the sheath region
- As the pressure is decreased the Ohmic heating contribution in the plasma bulk increases and sheath heating decreases



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

# Capacitively Coupled Oxygen Discharge at 13.56 MHz

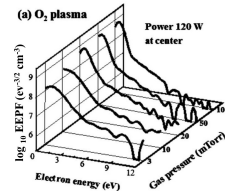
- At low pressure the EEPF is convex, the population of low energy electrons is relatively low
- As the pressure is increased the number of low energy electrons increases and the number of higher energy electrons ( $> 10$  eV) decreases
- Thus the EEPF develops a concave shape or becomes bi-Maxwellian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



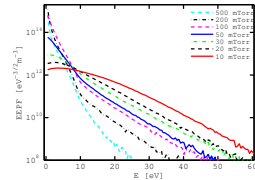
Gudmundsson and Ventéjou (2015) JAP **118** 153302

# 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

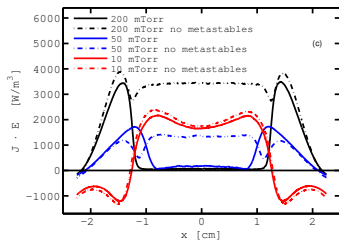


Lee et al. (2010) PRE **81** 046402



# Capacitively Coupled Oxygen Discharge at 13.56 MHz

- At **10 mTorr** excluding the metastable states  $O_2(a^1\Delta_g)$  and  $O(^1D)$  in the simulation has very small influence on the heating mechanism
- At **50 mTorr** the metastable states, in particular  $O_2(a^1\Delta_g)$ , have a significant influence on the heating mechanism
- The role of the metastables is even more significant at **200 mTorr**



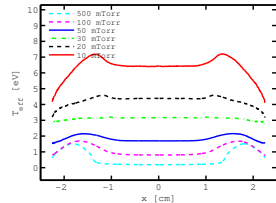
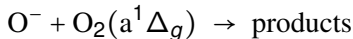
Gudmundsson and Ventéjou (2015) JAP **118** 153302

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

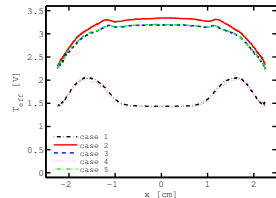


# Capacitively Coupled Oxygen Discharge at 13.56 MHz

- 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



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  $\text{O}_2(\text{a}^1\Delta_g)$ ,  $\text{O}_2(\text{b}^1\Sigma_g)$   
and  $\gamma_{\text{see}}(E)$**

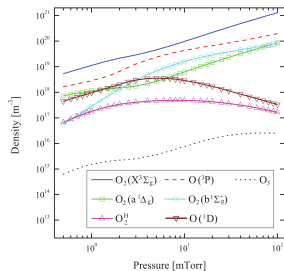
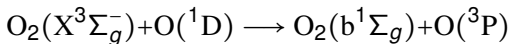


# Capacitively Coupled Oxygen Discharge at 13.56 MHz

- 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

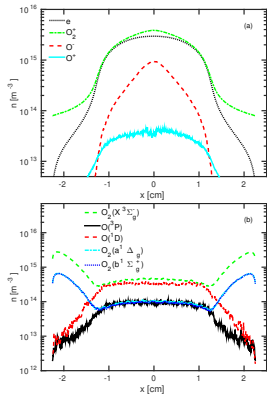
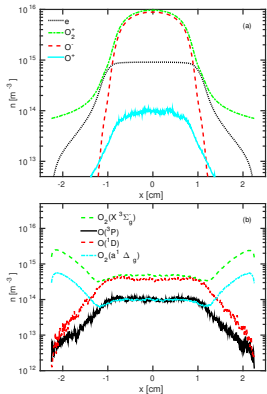
- Recent global model study indicates there is a significant density of  $O_2(b^1\Sigma_g^-)$  in the oxygen discharge
- The  $O_2(b^1\Sigma_g^-)$  is mainly created through



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



# Capacitively Coupled Oxygen Discharge at 13.56 MHz



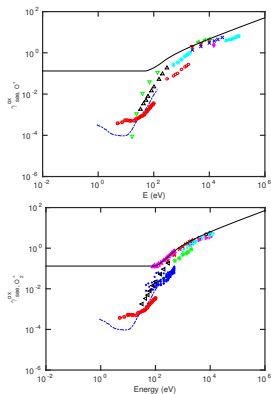
Hannesdottir and Gudmundsson, PSST, **25** 055002 (2016)

- The density profiles of charged particles and fast neutrals comparing including  $\gamma_{\text{see}}(E)$  and O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) (left) and  $\gamma_{\text{see}}(E)$ , O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) and O<sub>2</sub>(b<sup>1</sup>Σ<sub>g</sub>) (right) at 50 mTorr

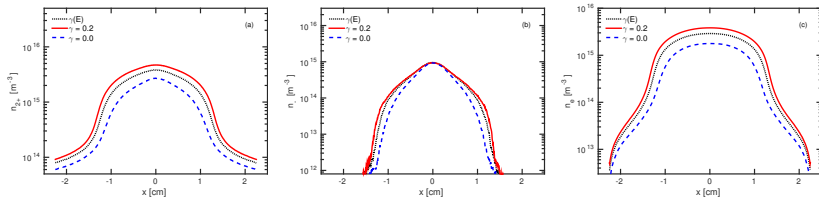


# Capacitively Coupled Oxygen Discharge at 13.56 MHz

- 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



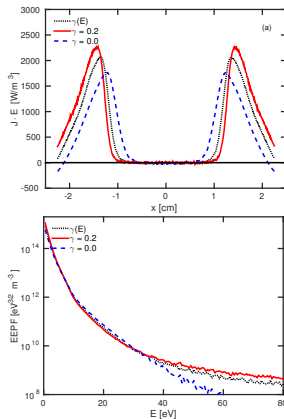
# Capacitively Coupled Oxygen Discharge at 13.56 MHz



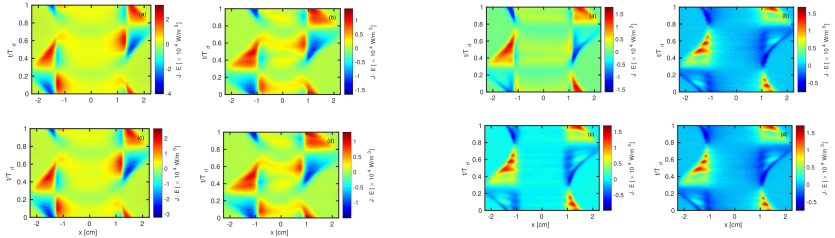
- The  $\text{O}_2^+$ ,  $\text{O}^-$  and electron density profiles for  $\gamma_{\text{see}} = 0.0$ ,  $\gamma_{\text{see}} = 0.2$ , and energy dependent secondary electron emission yield  $\gamma_{\text{see}}(E)$
- The electron density increases with increased secondary electron emission yield

# Capacitively Coupled Oxygen Discharge at 13.56 MHz

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



# Capacitively Coupled Oxygen Discharge at 13.56 MHz



Gudmundsson and Hannesdottir, AIP Conf. Proc. accepted 2016

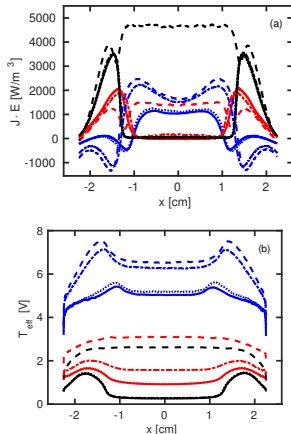
- The spatio-temporal electron heating at 10 mTorr (left) and 50 mTorr (right)
- The four cases explored are:
  - (a) detachment neither by  $O_2(a^1\Delta_g)$  nor  $O_2(b^1\Sigma_g^+)$
  - (b) only detachment by  $O_2(b^1\Sigma_g^+)$  included
  - (c) only detachment by  $O_2(a^1\Delta_g)$  included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



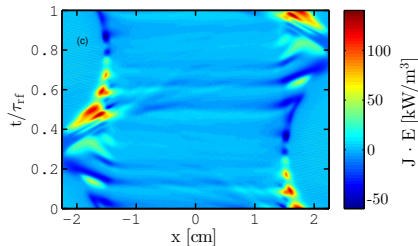
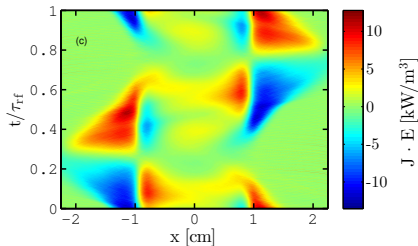


# Capacitively Coupled Oxygen Discharge at 13.56 MHz

- 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 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



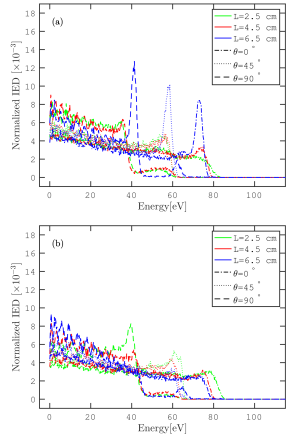
# Capacitively Coupled Oxygen Discharge at 13.56 or 27.12 MHz



- 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



# Capacitively Coupled Oxygen Discharge at 13.56 MHz

## ■ Comparison to experimental findings:

○  $\gamma_{\text{see}} = 0.0$ ,  
4.4 %  $\text{O}_2(\text{a}^1\Delta_{\text{g}})$

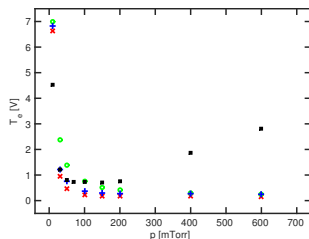
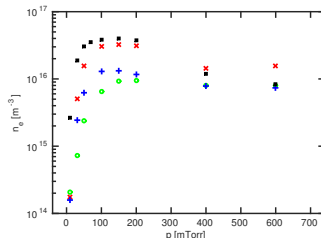
+  $\gamma_{\text{see}} = 0.0$ ,  
4.4 %  $\text{O}_2(\text{a}^1\Delta_{\text{g}})$  and 4.4 %  $\text{O}_2(\text{b}^1\Sigma_{\text{g}})$

×  $\gamma_{\text{see}} = \gamma_{\text{see}}(E)$ ,  
4.4 %  $\text{O}_2(\text{a}^1\Delta_{\text{g}})$  and 4.4 %  $\text{O}_2(\text{b}^1\Sigma_{\text{g}})$

## ■ 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 capacitively coupled discharge
- 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



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The slides can be downloaded at

<http://langmuir.raunvis.hi.is/~tumi/ranns.html>

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- Bruno Ventéjou (LPGP, Université Paris-Su, Orsay, France)

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- prof. Allan J. Lichtenberg (UC Berkeley)
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