# On the role of 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
    - Comparing electron heating – at 13.56 and 27.12 MHz
- 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)

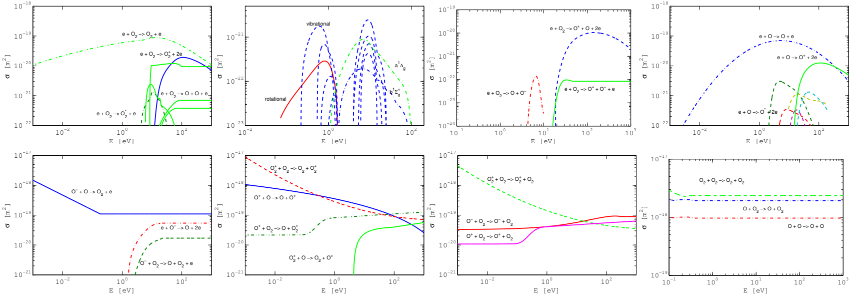
# The oxygen discharge

# *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 up to 67 reactions

Gudmundsson et al., *Plasma Sources Sci. Technol.*, **22** 035011 (2013), **24** 035016 (2015), and **25** 055002 (2016)

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

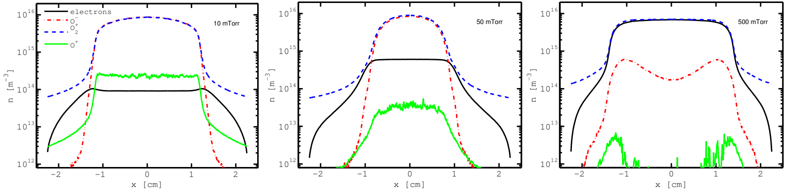
# *Capacitively Coupled Oxygen Discharge at 13.56 MHz*

- 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

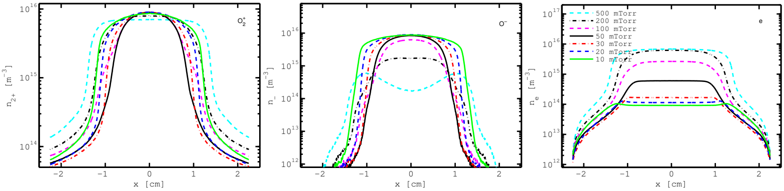
# *Capacitively Coupled Oxygen Discharge at 13.56 MHz*




- 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*

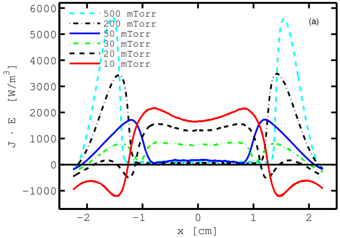



- The sheath width decreases as the pressure is decreased in the pressure range from 50 mTorr to 10 mTorr
- The sheath widths are largest at 50 mTorr
- As the pressure is increased from 50 mTorr up to 500 mTorr the sheath width decreases
- This agrees with what has been observed experimentally in the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

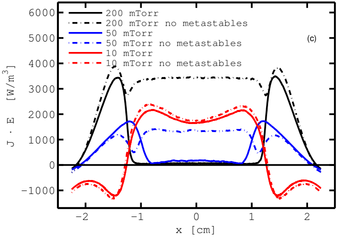
- The electron heating profile $\mathbf{J}_e \cdot \mathbf{E}$
- In the pressure range 50 - 500 mTorr the electron heating occurs almost solely in the sheath region
- As the pressure is decreased the Ohmic heating contribution in the plasma bulk increases and sheath heating decreases




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

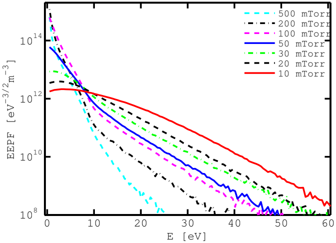



Gudmundsson and Ventéjou (2015) JAP **118** 153302

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

# *Capacitively Coupled Oxygen Discharge at 13.56 MHz*

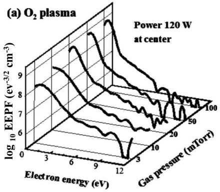
- At low pressure the EEPF is convex, the population of low energy electrons is relatively low
- As the pressure is increased the number of low energy electrons increases and the number of higher energy electrons (> 10 eV) decreases
- Thus the EEPF develops a concave shape or becomes bi-Maxwellian as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



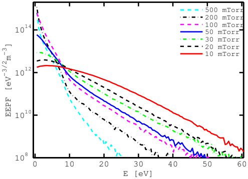

Gudmundsson and Ventéjou (2015) JAP **118** 153302

# *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

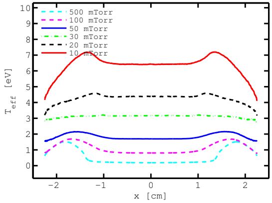



Gudmundsson and Ventéjou (2015) JAP **118** 153302

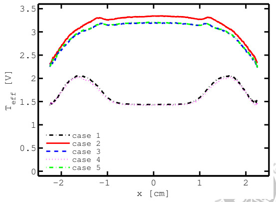
# *Capacitively Coupled Oxygen Discharge at 13.56 MHz*

- 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

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



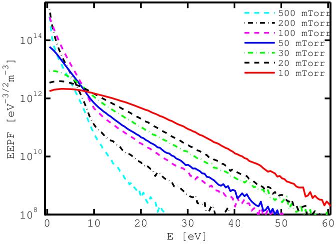

Gudmundsson and Ventéjou (2015) JAP **118** 153302




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

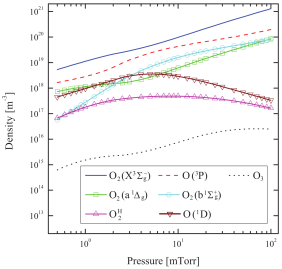
# Capacitively Coupled Oxygen Discharge at 13.56 MHz – pressure dependence – including $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g)$ and $\gamma_{see}(E)$

# *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

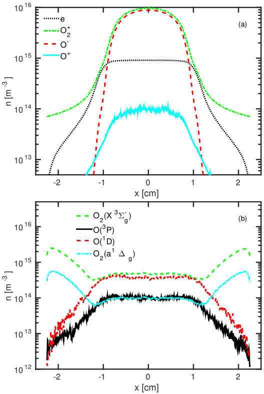
- Recent global model study indicates there is a significant density of $O_2(b^1\Sigma_g)$ in the oxygen discharge
- The $O_2(b^1\Sigma_g)$ is mainly created through

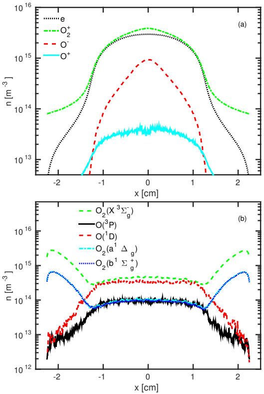



Toneli et al., *J. Phys. D*, **48** 325202 (2015)

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

# *Capacitively Coupled Oxygen Discharge at 13.56 MHz*

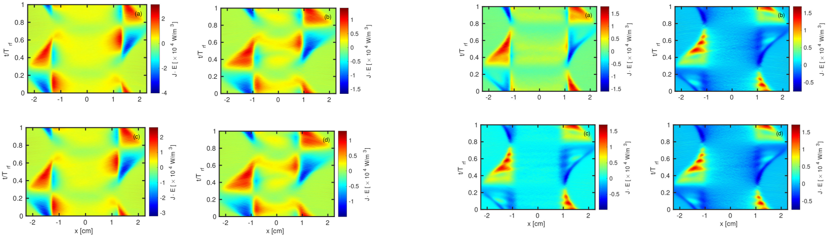



Hannesdottir and Gudmundsson, PSST, **25** 055002 (2016)

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

# *Capacitively Coupled Oxygen Discharge at 13.56 MHz*

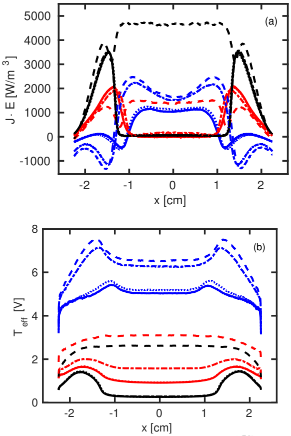



Gudmundsson and Hannesdottir, AIP Conf. Proc. submitted 2016

- 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*

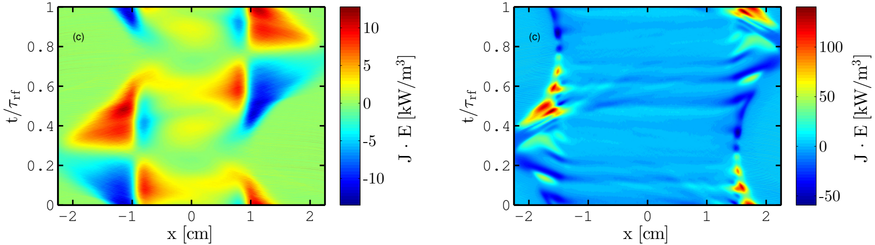
- The number of cold electrons increases as $O_2(b^1\Sigma_g)$ is added to the discharge model
- The electron heating in the bulk drops to zero
- The effective electron temperature profile changes significantly when detachment by singlet metastables is added to the reaction set
- 10 mTorr, 50 mTorr and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




Gudmundsson and Hannesdottir,

AIP Conf. Proc. submitted 2016

# *Capacitively Coupled Oxygen Discharge at 13.56 and 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 at 13.56 MHz*

- Comparison to experimental findings:

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

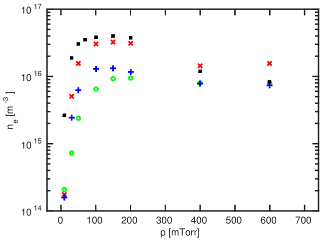
  + $\gamma_{\rm see} = 0.0$,
  4.4 % $O_2(a^1\Delta_g)$ and 4.4 % $O_2(b^1\Sigma_g)$

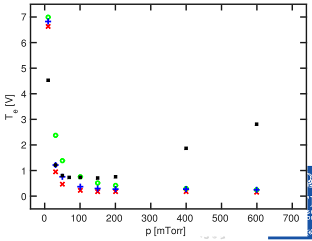
  x $\gamma_{\rm see} = \gamma_{\rm see}(E)$,
  4.4 % $O_2(a^1\Delta_g)$ and 4.4 % $O_2(b^1\Sigma_g)$

  - Experimental findings by Kechkar

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

Hannesdottir and Gudmundsson, 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 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`

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- Shuo Huang (UM-SJTU, Shanghai now Univ. Michigan)
- David A. Toneli (ITA, São José dos Campos, Brazil)
- Bruno Ventéjou, (LPGP, Université Paris Sud)

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