Particle-in-cell Monte Carlo collision simulation of a capacitively coupled discharge in oxygen

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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 is dissociative attachment and detachment processes

Outline

- The 1D particle-in-cell/Monte Carlo collision simulation
- The oxygen discharge
- Benchmark oopd1 vs xpdp1
- Capacitively Coupled Oxygen Discharge at 13.56 MHz – Voltage Source
- 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

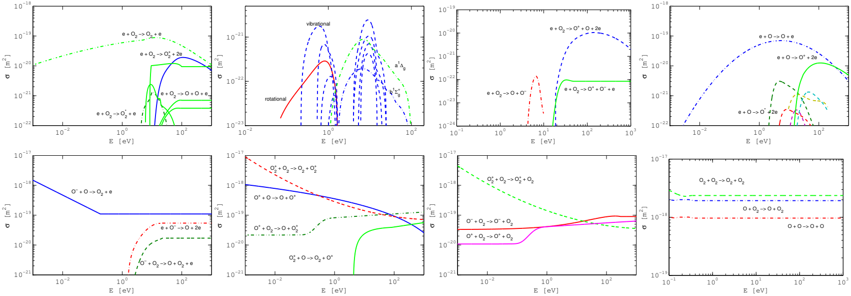
- We consider a discharge that consists of:
  - electrons
  - the ground state oxygen molecule $O_2(X^3\Sigma_g^-)$
  - the metastable oxygen molecule $O_2(a^1\Delta_g)$
  - the ground state oxygen atom $O(^3P)$
  - the metastable oxygen atom $O(^1D)$
  - the negative oxygen ion O^-
  - the positive oxygen ions O^+ and O_2^+

The oxygen discharge

- In the oxygen discharge, the density of the metastable oxygen molecule $O_2(a^1\Delta_g)$, oxygen atom in the ground state $O(^3P)$ and the metastable oxygen atom $O(^1D)$ is much larger than the number of charged species
- Thus, we apply a global model[1] beforehand to calculate the fraction of the O atoms and the metastables $O_2(a^1\Delta_g)$ and $O(^1D)$ under certain control parameters including the discharge pressure, absorbed power and the gap length between two electrodes
- The absorbed power found in the PIC/MCC simulation is used as an input parameter in the global model iteratively
- Both O_2 molecules and O atoms and the metastables are treated as the initial background gas in the simulation

[1] Thorsteinsson and Gudmundsson, *Plasma Sources Sci. Technol.*, **19** 055008 (2010)

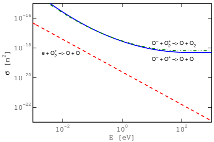
The oxygen discharge

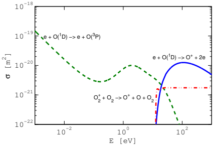


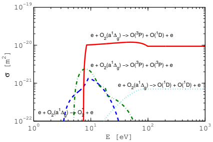
- The reaction set for the oxygen is comprehensive and includes 53 reactions

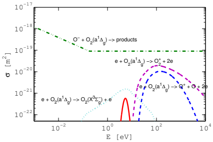
Gudmundsson et al., *Plasma Sources Sci. Technol.*, **22** 035011 (2013)

The oxygen discharge









- We know from global model calculation that dissociative attachment of the oxygen molecule is almost the sole source of O^- in the discharge and the metastable oxygen molecules play a major role for the creation of negative ions in an oxygen discharge
- We use the rate coefficient for the detachment by the metastable $O_2(a^1\Delta_g)$ that was measured by Belostotsky et al. (2005) to estimate a cross section

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

Belostotsky et al., *Plasma Sources Sci. Technol.*, **14** 532 (2005)

The oxygen discharge

- Detachment by the metastable O_2 molecules has been considered a major contributor to the loss of negative ions in oxygen discharges

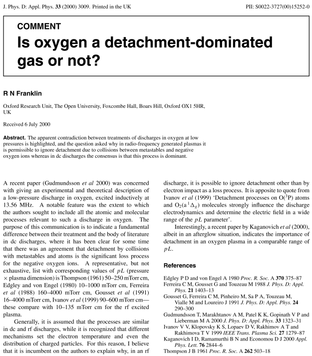
  Thompson, *Proc. R. Soc. A*, **262** 503 (1961)

  Ivanov et al, *IEEE TPS*, **27** 1279 (1999)

- However, in the high density inductivley coupled plasma (ICP) discharges we found the contribution to be relatively small

  Gudmundsson et al., *J. Phys D.*, **33** 1323 (2000)

  Gudmundsson and Thorsteinsson, *PSST*, 399 (2007)



J. Phys. D: Appl. Phys. **33** (2000) 3009. Printed in the UK PII: S0022-3727(00)15252-0

COMMENT

Is oxygen a detachment-dominated gas or not?

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Abstract. The apparent contradiction between treatments of discharges in oxygen at low pressures is highlighted, and the question asked why in radio-frequency generated plasmas it is permissible to ignore detachment due to collisions between metastables and negative oxygen ions whereas in dc discharges the consensus is that this process is dominant.

A recent paper (Gudmundsson *et al* 2000) was concerned with giving an experimental and theoretical description of a low-pressure discharge in oxygen, excited inductively at 13.56 MHz. A notable feature was the extent to which the authors sought to include all the atomic and molecular processes relevant to such a discharge in oxygen. The purpose of this communication is to indicate a fundamental difference between their treatment and the body of literature in dc discharges, where it has been clear for some time that there was an agreement that detachment by collisions with metastables and atoms is the significant loss process for the negative oxygen ions. A representative, but not exhaustive, list with corresponding values of pL (pressure × plasma dimension) is Thompson (1961) 50–250 mTorr cm, Edgley and von Engel (1980) 10–1000 mTorr cm, Ferreira *et al* (1988) 160–4000 mTorr cm, Gousset *et al* (1991) 16–4000 mTorr cm, Ivanov *et al* (1999) 90–600 mTorr cm—these compare with 10–135 mTorr cm for the rf excited plasma.

Generally, it is assumed that the processes are similar in dc and rf discharges, while it is recognized that different mechanisms set the electron temperature and even the distribution of charged particles. For this reason, I believe that it is incumbent on the authors to explain why, in an rf discharge, it is possible to ignore detachment other than by electron impact as a loss process. It is apposite to quote from Ivanov *et al* (1999) 'Detachment processes on $O(^3P)$ atoms and $O_2(a\,^1\Delta_g)$ molecules strongly influence the discharge electrodynamics and determine the electric field in a wide range of the pL parameter'.

Interestingly, a recent paper by Kaganovich *et al* (2000), albeit in an afterglow situation, indicates the importance of detachment in an oxygen plasma in a comparable range of pL.

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Gousset G, Ferreira C M, Pinheiro M, Sa P A, Touzeau M, Vialle M and Loureiro J 1991 *J. Phys. D: Appl. Phys.* **24** 290–300
Gudmundsson T, Marakhtanov A M, Patel K K, Gopinath V P and Lieberman M A 2000 *J. Phys. D: Appl. Phys.* **33** 1323–31
Ivanov V V, Klopovsky K S, Lopaev D V, Rakhimov A T and Rakhimova T V 1999 *IEEE Trans. Plasma Sci.* **27** 1279–87
Kaganovich I D, Ramamurthi B N and Economou D J 2000 *Appl. Phys. Lett.* **76** 2844–6
Thompson J B 1961 *Proc. R. Soc.* A **262** 503–18

Franklin, *J. Phys D.*, **33** 3009 (2000)

The oxygen discharge

- We found that ion–ion recombination is the dominating loss process for negative ions in oxygen discharges at low pressures
- The figure shows critical pressure where the contributions of recombination reactions and detachment reactions are equal

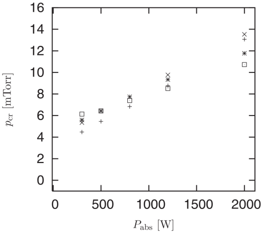


Figure 6. The critical gas pressure where $D_{\mathrm{tot}}/R_{\mathrm{tot}} = 1$ versus power applied to the plasma for various conditions: + ($\gamma_{\mathrm{O}} = 0.5$, $T_{\mathrm{g}} = 600$ K and $q = 50$ sccm), ∗ ($\gamma_{\mathrm{O}} = 0.5$, $T_{\mathrm{g}} = 1500$ K and $q = 50$ sccm), × ($\gamma_{\mathrm{O}} = 1.0$, $T_{\mathrm{g}} = 600$ K and $q = 50$ sccm) and ⊡ ($\gamma_{\mathrm{O}} = 0.5$, $T_{\mathrm{g}} = 600$ K and $q = 500$ sccm).

Gudmundsson, *J. Phys D.*, **37** 2073 (2004)

The oxygen discharge

- Experimental findings for cpapcitively coupled oxygen discharge
  - At 2.54 cm separation and 100 mTorr and 150 V
    - $\alpha_0 = 2.33$
  - At 2.54 cm separation and 100 mTorr and 280 V
    - $\alpha_0 =< 1$

    Katch et al., *Plasma Sources Sci. Technol.*, **9** 323 (2000)
  - At 2 – 10 cm separation and 22 – 220 mTorr and ($n_{\rm e} < 10^{15}$ cm^{-3}.
    - $\alpha_0 \sim 10$

    Berezhnoj et al., *Appl. Phys. Lett.*, **77** 800 (2000)
- Earlier particle-in-cell/Monte Carlo collision simulations have indicated a significant role of the metastable molecule $O_2(\mathrm{a}^1\Delta_g)$

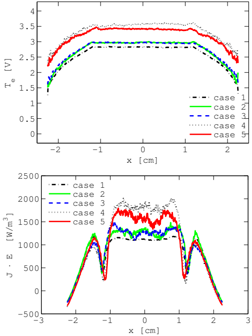
  Bronold et al., *J. Phys. D.*, **40** 6583 (2007)

Benchmark oopd1 vs xpdp1

Benchmark oopd1 vs xpdp1

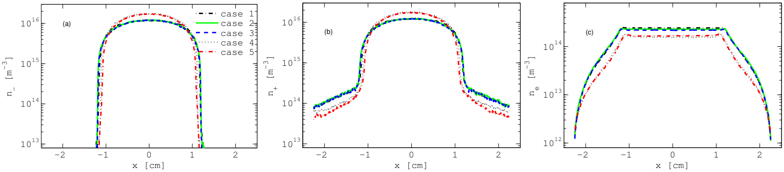
- For the benchmark study we used a simplified reaction set including
  - electrons
  - the ground state oxygen molecule $O_2(X^3\Sigma_g^-)$
  - the negative oxygen ion O^-
  - the positive oxygen ion O_2^+

Case	Code	Cross section set	Electron kinematics
1	xpdp1	xpdp1	xpdp1
2	oopd1	xpdp1	xpdp1
3	oopd1	xpdp1	oopd1
4	oopd1	oopd1 limited	oopd1
5	oopd1	oopd1 full	oopd1



Gudmundsson et al., *PSST*, **22** 035011 (2013)

Benchmark oopd1 vs xpdp1



- 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^--ion density profile,
    - O_2^+-ion density profile,
    - electron density profile

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

Capacitively Coupled Oxygen Discharge at 13.56 MHz

Capacitively Coupled Oxygen Discharge at 13.56 MHz

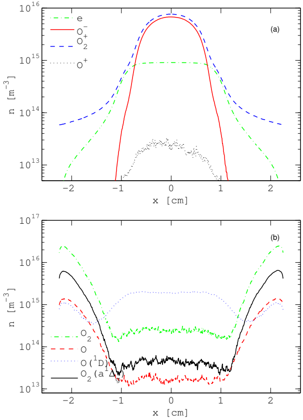
- We apply a voltage source with a single frequency

$$V(t) = V_{\mathrm{rf}} \sin(2\pi f t)$$

- 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 is found using a global model
- The metastable fraction is found using a global model
- The pressure is 50 mTorr

Capacitively Coupled Oxygen Discharge at 13.56 MHz

- In the center of the discharge the O_2^+-ion density is slightly higher than the O^- density and have parabolic profile
- The ground state molecule $O_2(X^3\Sigma_g^-)$ with $\mathcal{E} > 1$ eV and the metastable $O_2(a^1\Delta_g)$ with $\mathcal{E} > 0.5$ eV
- For the oxygen atom in the ground state $O(^3P)$ with $\mathcal{E} > 1$ eV and the metastable oxygen atom $O(^1D)$ with $\mathcal{E} > 0.1$



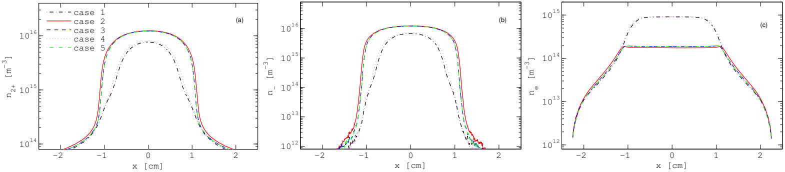
Capacitively Coupled Oxygen Discharge at 13.56 MHz

- The five cases explored in this study are
  - Case 1 – is the basic case explored – the complete reaction set is used that includes both the metastable O(^{1}D) atom and the metastable $O_2(a^1\Delta_g)$ molecule
  - Case 2 – is the same as case 1 except that the reaction

    $$\mathrm{O}^- + \mathrm{O}_2(a^1\Delta_g) \rightarrow \text{products}$$

    is neglected
  - Case 3 – includes only the metastable O(^{1}D) atom and the corresponding reactions
  - Case 4 – includes only the metastable $O_2(a^1\Delta_g)$ molecule and the corresponding reactions
  - Case 5 – includes no metastables

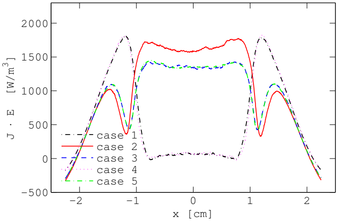
Capacitively Coupled Oxygen Discharge at 13.56 MHz



- 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
  - electron density profile
- The center electronegativity α_0 changes from about 7 for full reaction set to 70 when detachment by $O_2(a^1\Delta_g)$ is neglected

Capacitively Coupled Oxygen Discharge at 13.56 MHz

- The detachment by the metastable $O_2(a^1\Delta_g)$ has a significant influence on the heating mechanism in the discharge
- Neglecting detachment by $O_2(a^1\Delta_g)$ electron heating appears both in the sheath region and in the bulk
- When this process is included electron heating exists only in the sheath region, sheath-oscillation heating dominates



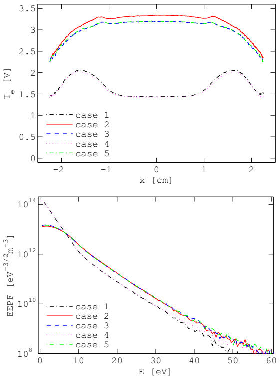
Neglecting the reaction

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

has a significant influence

Capacitively Coupled Oxygen Discharge at 13.56 MHz

- The effective electron temperature drops when including the metastable oxygen molecule $O_2(a^1\Delta_g)$, in particular in the electronegative core
- The number of low energy electrons increases and the number of higher energy electrons (> 10 eV) decreases, and the EEPF develops a concave shape or becomes bi-Maxwellian



Summary

- We explored a capcacitively coupled oxygen disharge using particle-in-cell/Monte Carlo collision simulation
- Oxygen atoms O(^{3}P) and O$^+$-ions are included in the reaction set
- The metastables O(^{1}D) and O$_2$(a$^1\Delta_g$) are included in the reaction set
- Detachment by the metastable O$_2$(a$^1\Delta_g$) molecule

  $$\mathrm{O}^- + \mathrm{O}_2(a^1\Delta_g) \;\rightarrow\; \mathrm{products}$$

  has a significant influence of the overall discharge

Thank you for your attention

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

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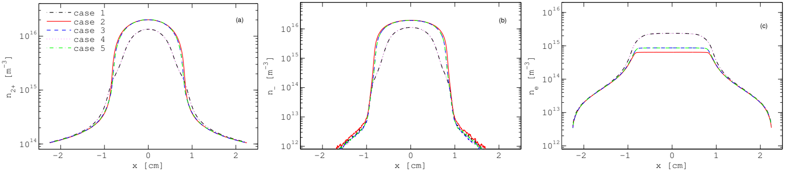
Capacitively Coupled Oxygen Discharge at 13.56 MHz



- For a parallel plate capacitively coupled oxygen discharge at 50 mTorr with with a gap separation of 4.5 cm by a 500 V voltage source at 13.56 MHz
    - O_2^+-ion density profile
    - O^--ion density profile
    - electron density profile
- The center electronegativity α_0 changes from about 5 to 31 when detachment by $O_2(a^1\Delta_g)$ is neglected

Capacitively Coupled Oxygen Discharge at 13.56 MHz

- For higher applied voltage (500 V) neglecting the reaction

  $$\mathrm{O}^- + \mathrm{O}_2(a^1\Delta_g) \rightarrow \text{products}$$

  increases the bulk heating in the discharge but less
- This leads to higher effective electron temperature