Introduction to Non-thermal Reactive Plasmas

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DFG Collaborative Research Centre Transregio 24 „Fundamentals of Complex Plasmas“
Outline

● Reactive plasmas – Overview
● Non-thermal plasmas
● Plasma boundary – plasma sheath
● Example oxygen cc-rf plasma
● Example fluorocarbon cc-rf plasma
● Outlook
Reactive plasmas

- Reactive plasmas are a demanding, complex and highly application-oriented field which needs fundamental knowledge of plasma processes and plasma-surface interaction.

- The situation is complicated due to the fact that reactive plasmas represent a cross-disciplinary field which requires knowledge in the fields of
  
  Plasma physics, 
  Plasma chemistry, and 
  Materials science.

- But above all, reactive plasmas represent a field with a fascinating variety of well-established processes and novel potential applications.
## Overview

### Low-temperature plasma applications

<table>
<thead>
<tr>
<th>Application</th>
<th>Plasma acts as</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>electrical switches</td>
<td>conductor</td>
<td>vacuum switches, gas pressure switches</td>
</tr>
<tr>
<td>light sources</td>
<td>radiation source</td>
<td>low pressure: fluorescent lamp, sodium lamp</td>
</tr>
<tr>
<td></td>
<td></td>
<td>high pressure: Hg, Xe, Na lamp, Halogen-metal-vapor lamp, gas lasers (CO₂, He)</td>
</tr>
<tr>
<td>material treatment</td>
<td>heat source</td>
<td>welding, melting (steel production), cutting, ....</td>
</tr>
<tr>
<td>deposition</td>
<td>particle source</td>
<td>sputtering, thin film deposition</td>
</tr>
<tr>
<td>surface modification</td>
<td>particle source</td>
<td>treatment of textiles, treatment of polymers</td>
</tr>
<tr>
<td>etching</td>
<td>particle source</td>
<td>dry etching of semiconductors</td>
</tr>
<tr>
<td>electrical gas cleaning</td>
<td>particle source</td>
<td>electrical filters (dust filters in exhaust of power plants)</td>
</tr>
<tr>
<td>plasma chemistry, thermal</td>
<td></td>
<td>remediation of toxic waste</td>
</tr>
<tr>
<td>plasma chemistry, non-thermal</td>
<td></td>
<td>synthesis of chemical compounds (e.g. ozone production)</td>
</tr>
</tbody>
</table>
Overview

Multitude of scales in time and space

- Plasma bulk
- Plasma striations
- Plasma sheath
- Particles
- Thin surface layers, clusters
- Atoms, molecules

- 10^{-1} m
- 10^{-3} m
- 10^{-6} m
- 10^{-9} m
- 10^{-10} m
- 10^{-12} m

- 10^{0} s
- 10^{-3} s
- 10^{-6} s
- 10^{-9} s
- 10^{-12} s

- Diffusion, collective behavior of particles, phase transitions
- Radical reactions, chemical processes
- Dynamic ion processes
- Excitation, ionization, attachment, dissociation
- Electron energy relaxation

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**Problem**

**Multi species plasma**
positive/negative ions, electrons, excited and reactive neutral species, nano/micro particles, plasma radiation (photons)

**Plasma boundary**
metal, alloy, semiconductor, insulator (polymer, ceramics, glass)
Reactive plasma

Overview

Ionisation, attachment, excitation, dissociation, ion-molecule-reactions, radical reactions

Plasma sheath - charged species transport

Plasma boundary

Adsorption/desorption, reflection, sputtering
Recombination, dissociation, diffusion, radical reactions, secondary species formation

Kinetic/internal energy, momentum, charge, mass

Reflected and secondary species, reactions products, sputtered species

Charged atoms and molecules, reactive species, photons

L

\( \lambda_{\text{De}} \)

\( \delta \)

\( d \)

PLASMA

SOLID

Interface

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Overview

Carrier gases - precursors

Rare gases
Ar, He,…

Simple molecular gases
O₂, N₂, H₂,…

Hydrocarbons
CH₄, C₂H₂,…

Fluorocarbons, gases containing halogens
CF₄, C₂F₄, C₂F₆, C₃F₈, C₄F₈, NF₃, CHF₃, CCl₄, CHCl₃,…

Silane, organosilicons
SiH₄, HMDSO, HMDSN,…

Hydrocarbons with specific functional groups
Acrylic acid (-COOH), Ethylene glycol (-OH), Ethylene diamine / Allyl amine (-NH₂),…
Reactive Plasma – Surface Interaction

Surface properties

Super-hydrophobic surface
self-assembling
reflectivity
micro turbulence

functional groups
Nano/micro-structured surface
Nanoparticles
thin film

barrier films
membranes
sensors

Thin film properties
Nano- and micro-structured surfaces

- Erosion / etching of surface material
- Interaction deposition / etching
- Cluster-, particle deposition
Overview

Chemical modification of material surfaces

- Surfaces with specific molecular groups
  e.g. C-OH, -COOH, -C=O, -NH$_2$, -CH$_3$, -CF$_3$

- Synthesis of functional thin films
  e.g. a-C:F, a-C:H, -Si-O-Si-, SiO$_x$, -Si-NH-Si-

- Composite films with nanoparticles
  e.g. organic thin film with TiO$_2$ nanoparticles
Overview

Partially hydrophilic surface

Plasma treatment of hydrophobic polyvinylidenfluoride (water drops Ø 1.25 mm)

Membrane from PP HMDSO

Porous polymer (polysulfone) and 200 nm thin pinhole free plasma polymer film (top) from hexamethyldisiloxane.

C. Oehr, Fraunhofer-Institut für Grenzflächen- und Bioverfahrenstechnik, Stuttgart
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Non-thermal plasma

Temperature – Density – Plot

Low-temperature Plasma

relativistic plasmas
$kT = m_e c^2 = 511$ keV

ideal plasmas

technologies

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Non-thermal plasma

Low-temperature plasmas

Thermal plasma
local thermodynamic equilibrium (LTE)
$T_e = T_{ion} = T_{gas} \leq 10^4 \text{ K}$

Non-thermal plasma
non-equilibrium plasma
$T_e \sim 10^4 \text{ K} \gg T_{ion} \sim T_{gas}$

$10^4 \text{ K} \approx 1 \text{ eV}$

Electric gas discharge plasmas at
high pressure atmospheric pressure low pressure

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Non-thermal conditions

Two important consequences are due to the large difference in the mass of the electrons and ions ($m_e / m_p \approx 1 / 2000$):

(1) Electrons have at the same energy a much higher velocity than the heavy particles and react much more readily to external fields.

(2) The energy transfer in elastic collisions between electrons and heavy particles (ions, neutrals) is very low

- a large number of elastic e − i and e − n collisions is required to equilibrate the energy.

As a consequence of point 2 **low-pressure plasmas are not in thermal equilibrium** because the externally applied energy is coupled to the electrons and they do not significantly heat the heavy particles.

While the electrons are hot ($T_e \approx 1$ to $10$ eV) the heavy particles retain more or less the temperature of the surrounding walls. Therefore, low-pressure plasmas are also often called **non-equilibrium plasmas** or **cold plasmas**.
Non-thermal plasma

Momentum gain of neutral species in an elastic electron - neutral collision:

\[ \Delta p_n = m_e \cdot \Delta v_e \]

Increase of the kinetic energy of a neutral species of the mass (m)

\[
\frac{\Delta p_n^2}{2m} = \frac{(m_e \cdot \Delta v_e)^2}{2m} = \frac{m_e}{m} \cdot \left( \frac{m_e}{2} \cdot \Delta v_e^2 \right) = \frac{m_e}{m} \cdot \Delta \varepsilon_T^e \propto 10^{-5} \cdot \Delta \varepsilon_T^e
\]

\[
n_e \cdot v_e \cdot \frac{m_e}{m} \cdot \Delta \varepsilon_T^e = n_e \cdot v_e \cdot \frac{m_e}{m} \cdot 3 \cdot k_B (T_e - T) = P_{abs}^e = \frac{e^2 \cdot n_e \cdot v_e}{m_e \cdot (\omega^2 + v_e^2)} \cdot E_{eff}^2
\]

Temperature difference (two temperature model)

\[
T_e - T = \frac{e^2 \cdot m \cdot E_{eff}^2}{3 \cdot k_B \cdot m_e^2 \cdot (\omega^2 + v_e^2)} \sim \frac{E_{eff}^2}{(\omega^2 + v_e^2)} \sim \frac{E_{eff}^2}{(\omega^2 + c_1 \cdot p^2)}
\]
Non-thermal plasma

Transition from non-thermal to thermal plasma due to pressure increase
Non-thermal plasma

**Why non-thermal plasmas?**

- allows non-equilibrium processes for synthesis of novel materials
  - thin amorphous films/plasma polymers
  - composite films containing nano-particles

- allows treatment of sensitive materials
  (e.g. polymers, living human and animal tissues!)

- enables processes which are not possible with conventional thermo-chemistry or would require a much higher effort

- in general good environmental compatibility due to low material turnover

  ➔ Non-thermal low-pressure plasmas (rf discharge, glow discharge)
  ➔ Non-thermal atmospheric pressure plasmas (DBD, Corona)
Non-thermal plasma

Gas discharges - plasma sources

Townsend discharge  
Glow discharge  
Arc discharge

Townsend-Mechanism

Barrier discharge (DBD)  
Corona discharge  
Spark discharge

Microdischarges, streamers

Radio frequency plasma (CCP/ICP, single/dual frequency)

Microwave plasma / surface wave

Electrons in high-frequency electric field

Magnetised plasma

Magnetron, Microwave - ECR, RF- Helicon

Cyclotron motion, ExB-drift, wave heating, resonances
Non-thermal plasma

Experiment, Diagnostics Modelling, Simulation

Plasma, plasma sheath

- Microwave interferometry, probes
- Spectroscopy (VUV, vis, IR)
  Emission, absorption, laser
- Mass spectrometry
  Ions (energy resolved), neutrals
  Threshold-, attachment-MS
- Kinetic modelling
  BMGL (electrons), PIC-MC
- Fluid models (heavy species)
- Hybrid models
- Global models, macroscopic kinetics,
  reactor parameter, YASUDA-parameter

Interface, thin film

- In situ: ellipsometry, FTIR,
  microgravimetry, ...
- Ex situ: surface analysis
  (XPS, XRD, SIMS, AFM, SEM, ...)
- Adsorption models, MC (TRIM)
  Species fluence, sticking coefficients
  Chemical sputtering, ...
- MD-Simulations
Non-thermal plasma

**Kinetics of non-equilibrium plasmas**

*BOLZMANN equation – single particle distribution function $f_i$*

$$
\frac{df_i}{dt} = \frac{\partial f_i}{\partial t} + \vec{v}_i \cdot \frac{\partial f_i}{\partial \vec{r}} + \frac{\vec{F}}{m_i} \cdot \frac{\partial f_i}{\partial \vec{v}} = \left( \frac{\partial f_i}{\partial t} \right)_{\text{coll}} = \sum_{klmn} \left[ \int d\Omega d\vec{\nu}_l \cdot \vec{v}_i - \vec{v}_k \right] \cdot \sigma_{klmn} (v, \vartheta) \cdot \left( f_m f_n - f_i f_k \right) \right]^{(i)}
$$

**Differential operator**
- flow term → particle movement in phase space

**Integral operator**
- collision term → velocity variation, due to collisions, generation/destruction of particles

external electric and magnetic fields, macroscopic space charge field

micro fields and quantum physics of atomic or molecular interactions at short distances

binary collisions

$A_k + B_l \rightarrow C_m + D_n$

$\Delta E_{klmn}$

$A_k$ $f_k$, $C_m$ $f_m$, $B_l$ $f_l$, $D_n$ $f_n$
Non-thermal plasma

**Macroscopic: particle balance equation – rate coefficient**

\[
\frac{\partial n_i}{\partial t} + \text{div} \, j_i = S_i - L_i
\]

**Elementary processes**

Chemical reactions

\[
N_A + N_B \xleftrightarrow[k_{AB}]{} N_C + N_D
\]

\[k_{AB} \neq k_{CD}!\]

**Rate coefficient:**

\[
k_{AB} = \langle \sigma_{AB} \cdot v_{AB} \rangle = \int \sigma_{AB} \cdot v_{AB} \cdot f(v_{AB}) \cdot dv_{AB}
\]

e.g. production of charged particles by electron impact (source term)

\[
e + Ar \rightarrow Ar^+ + 2e
\]

\[
\left[ \frac{dn_e}{dt} \right]_{ion} = n_e \cdot v_{ion} = n_{Ar} \cdot n_e \cdot k_{ion} = n_{Ar} \cdot n_e \cdot \langle \sigma_{ion} \cdot v \rangle
\]
Non-thermal plasma

**Elementary processes in plasma / gas phase**

- generation of charged and neutral reactive species due to inelastic electron – neutral collisions
  
  \[
  \begin{align*}
  \text{e} & + \text{O}_2 \rightarrow \text{O}^+ + \text{O} + 2\text{e} \\
  \text{e} & + \text{CF}_4 \rightarrow \text{CF}_3^+ + \text{F} + 2\text{e} \\
  \text{e} & + \text{CF}_4 \rightarrow \text{CF}_3^- + \text{F}^-
  \end{align*}
  \]

- ion – molecule reactions
  
  \[
  \begin{align*}
  \text{O}_2^{\text{fast}} & + \text{O}_2^{\text{therm}} \rightarrow \text{O}_2^{\text{fast}} + \text{O}_2^{\text{therm}} \\
  \text{H}_2^{+} & + \text{H}_2 \rightarrow \text{H}_3^{+} + \text{H}
  \end{align*}
  \]

- radical – radical reactions
  
  \[
  \text{CF} + \text{F}_2 \rightarrow \text{CF}_2 + \text{F}
  \]

**Macrosopic**

Plasma chemical gas conversion
- formation of new stable gas molecules
- formation of nano- and micro-particles
Example: non-thermal oxygen plasma

Reactions between plasma species:

\[\begin{align*}
  &O, \, O_2, \, O_3 \\
  &O^+, \, O_2^+, \, O_3^+ \\
  &O^-, \, O_2^-, \, O_3^- \\
  &O_2 (a^1\Delta), \, ... \\
  &\text{electrons}
\end{align*}\]

more than 100 elementary reactions!
Non-thermal plasma

some elementary processes with electrons

<table>
<thead>
<tr>
<th>Process</th>
<th>Rate coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \ e + O_2 \rightarrow O^- + O$</td>
<td>$f(E/N)$</td>
</tr>
<tr>
<td>$2 \ e + O_2 \rightarrow e + O_2(a^1\Delta)$</td>
<td>$f(E/N)$</td>
</tr>
<tr>
<td>$3 \ e + O_2 \rightarrow e + O_2(b^1\Sigma)$</td>
<td>$f(E/N)$</td>
</tr>
<tr>
<td>$4 \ e + O_2(a^1\Delta) \rightarrow O^- + O$</td>
<td>$1.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ [7]</td>
</tr>
<tr>
<td>$5 \ e + O_2 \rightarrow O_2^+ + 2e$</td>
<td>$f(E/N)$</td>
</tr>
<tr>
<td>$6 \ e + O_2 \rightarrow e + O + O$</td>
<td>$f(E/N)$</td>
</tr>
<tr>
<td>$7 \ e + O_2(a^1\Delta) \rightarrow e + O + O$</td>
<td>$f(E/N)$</td>
</tr>
<tr>
<td>$8 \ e + O_2(b^1\Sigma) \rightarrow e + O + O$</td>
<td>$f(E/N)$</td>
</tr>
<tr>
<td>$9 \ e + O_3 \rightarrow e + O + O_2$</td>
<td>$f(E/N)$</td>
</tr>
<tr>
<td>$10 \ e + O_2^+ \rightarrow O + O$</td>
<td>$5.2 \times 10^{-9}/T_e \text{ cm}^3 \text{ s}^{-1}$ [29]</td>
</tr>
<tr>
<td>$11 \ e + O^- \rightarrow O + 2e$</td>
<td>$2 \times 10^{-7} \exp(-5.5/T_e) \text{ cm}^3 \text{ s}^{-1}$ [33]</td>
</tr>
<tr>
<td>$12 \ e + O_2(a^1\Delta) \rightarrow O_2^+ + 2e$</td>
<td>$f(E/N)$</td>
</tr>
<tr>
<td>$13 \ e + O_2(b^1\Sigma) \rightarrow O_2^+ + 2e$</td>
<td>$f(E/N)$</td>
</tr>
<tr>
<td>$14 \ e + O_3 \rightarrow O^- + O_2$</td>
<td>$10^{-11} \text{ cm}^3 \text{ s}^{-1}$ [29]</td>
</tr>
<tr>
<td>$15 \ e + O + O_2 \rightarrow O^- + O_2$</td>
<td>$10^{-31} \text{ cm}^6 \text{ s}^{-1}$ [33]</td>
</tr>
<tr>
<td>$16 \ e + O_2 + O_2 \rightarrow O_2^- + O_2$</td>
<td>$1.4 \times 10^{-29}(0.026/T_e) \times \exp(100/T_e - 0.061/T_e) \text{ cm}^6 \text{ s}^{-1}$ [29]</td>
</tr>
<tr>
<td>$17 \ e + O + O_2 \rightarrow O + O_2^-$</td>
<td>$10^{-31} \text{ cm}^6 \text{ s}^{-1}$ [29]</td>
</tr>
<tr>
<td>$18 \ e + O_3 \rightarrow O_2^- + O$</td>
<td>$10^{-9} \text{ cm}^3 \text{ s}^{-1}$ [29]</td>
</tr>
<tr>
<td>$19 \ e + O_2 \rightarrow O^- + O^+ + e$</td>
<td>$7.1 \times 10^{-11}T_e^{0.5} \exp(-17/T_e) \text{ cm}^3 \text{ s}^{-1}$ [28]</td>
</tr>
<tr>
<td>$20 \ e + O_2 \rightarrow O + O^+ + 2e$</td>
<td>$5.3 \times 10^{-10}T_e^{0.9} \exp(-20/T_e) \text{ cm}^3 \text{ s}^{-1}$ [28]</td>
</tr>
<tr>
<td>$21 \ e + O \rightarrow O^+ + 2e$</td>
<td>$9 \times 10^{-9}T_e^{0.7} \exp(-13.6/T_e) \text{ cm}^3 \text{ s}^{-1}$ [28]</td>
</tr>
<tr>
<td>$22 \ e + O^+ + O_2 \rightarrow O + O_2$</td>
<td>$10^{-26} \text{ cm}^6 \text{ s}^{-1}$ [28]</td>
</tr>
</tbody>
</table>
Some elementary processes with neutrals and ions

<table>
<thead>
<tr>
<th>Processes</th>
<th>Rate coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}_2(a^1\Delta) + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2 + \text{O}$</td>
<td>$9.7 \times 10^{-13} \exp(-1564/T_g) \text{ cm}^3 \text{ s}^{-1}$ [29]</td>
</tr>
<tr>
<td>$\text{O}_2(b^1\Sigma) + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2 + \text{O}$</td>
<td>$1.8 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ [29]</td>
</tr>
<tr>
<td>$\text{O} + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2(a^1\Delta)$</td>
<td>$10^{-11} \exp(-2300/T_g) \text{ cm}^3 \text{ s}^{-1}$ [33]</td>
</tr>
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<td>$\text{O} + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2$</td>
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<tr>
<td>$\text{O} + \text{O}_2 + \text{O}_2 \rightarrow \text{O}_2 + \text{O}_3$</td>
<td>$6.4 \times 10^{-35} \exp(663/T_g) \text{ cm}^6 \text{ s}^{-1}$ [33]</td>
</tr>
<tr>
<td>$\text{O}_2(a^1\Delta) + \text{O}_2 \rightarrow \text{O}_2 + \text{O}_2$</td>
<td>$2.2 \times 10^{-18}(T_g/300)^{0.8} \text{ cm}^3 \text{ s}^{-1}$ [29]</td>
</tr>
<tr>
<td>$\text{O}_2(a^1\Delta) + \text{O} \rightarrow \text{O}_2 + \text{O}$</td>
<td>$7 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ [29]</td>
</tr>
<tr>
<td>$\text{O}_2(b^1\Sigma) + \text{O}_2 \rightarrow \text{O}_2(a^1\Delta) + \text{O}_2$</td>
<td>$4.3 \times 10^{-22}T_g^{2.4} \exp(-241/T_g) \text{ cm}^3 \text{ s}^{-1}$ [29]</td>
</tr>
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<td>$\text{O}_2(b^1\Sigma) + \text{O} \rightarrow \text{O}_2(a^1\Delta) + \text{O}$</td>
<td>$8 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ [29]</td>
</tr>
<tr>
<td>$\text{O}_2 + \text{O}_3 \rightarrow \text{O} + \text{O}_2 + \text{O}_2$</td>
<td>$3.322 \times 10^{-12} \exp(-11726/T_g) \text{ cm}^3 \text{ s}^{-1}$ [30]</td>
</tr>
<tr>
<td>$\text{O}_2 + \text{O}_2 \rightarrow \text{O} + \text{O}_3$</td>
<td>$7.972 \times 10^{-12} \exp(-49824/T_g) \text{ cm}^3 \text{ s}^{-1}$ [30]</td>
</tr>
<tr>
<td>$\text{O} + \text{O} + \text{O}_2 \rightarrow \text{O}_2 + \text{O}_2$</td>
<td>$3.8 \times 10^{-30}T_g^{-1} \exp(-170/T_g) \text{ cm}^6 \text{ s}^{-1}$ [33]</td>
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<td>$\text{O}^+ + \text{O} \rightarrow \text{e} + \text{O}_2$</td>
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<td>$\text{O}^- + \text{O}_2(a^1\Delta) \rightarrow \text{e} + \text{O}_3$</td>
<td>$1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ [33]</td>
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<td>$\text{O}^- + \text{O}_2 \rightarrow \text{e} + \text{O}_3$</td>
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<td>$\text{O}^- + \text{O}_2^+ \rightarrow \text{O}_2 + \text{O}$</td>
<td>$2 \times 10^{-7}(300/T_g)^{0.5} \text{ cm}^3 \text{ s}^{-1}$ [29]</td>
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● Example fluorocarbon cc-rf plasma
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Plasma boundary

**Plasma sheath**

Assumptions
- stationary plasma sheath
- no collisions
- completely absorbing surface
- MAXWELLian electrons
- single charged positive ions
- \( k_B T_e = 2...3 \text{ eV} \gg k_B T_+ \)

**BOHM criterion:**

\[
\frac{m_+}{2} \cdot \frac{V_{bohm}^2}{e} = \frac{1}{2} k_B T_e = |e| \cdot \Delta \varphi_{bohm}
\]

**Surface on floating potential:**

\[
\varphi_{pl} - \varphi_s = \Delta \varphi_{Bohm} + \Delta \varphi_{Sheath} = \frac{1}{2} k_B T_e \ln \left( \frac{0.43 \cdot m_+}{m_e} \right)
\]

\( \sim 10...15 \text{ V} \)

\[
\rho_+ = 0.61 |e| n_{pl} \sqrt{\frac{k_B T_e}{m_+}}
\]
High-voltage plasma sheath, $e\Delta\varphi >> k_B T_e$

Powered electrode in rf plasma (ccp)

$\lambda_+ << s$  no collisions

$$\bar{j}_+ = |e| n_0 \cdot v_{bohm} = C_+ \cdot \varepsilon_0 \cdot \left( \frac{2 \cdot |e|}{m_+} \right)^{1/2} \frac{\phi_s^{3/2}}{s_{\text{max}}}$$

$\lambda_+ \geq s$  transition regime

$$\bar{j}_+ = |e| n_0 \cdot v_{bohm} \approx 1.68 \cdot \varepsilon_0 \cdot \left( \frac{2 \cdot |e|}{m_+} \right)^{1/2} \frac{\phi_s^{3/2} \lambda_+^{1/2}}{s_{\text{max}}^{5/2}}$$

$\lambda_+ < s$  collisions

$$\bar{j}_+ = |e| n_0 \cdot v_{bohm} \approx \frac{9}{8} \cdot \varepsilon_0 \cdot \frac{b_{+0} \cdot \phi_s^2}{p \cdot s_{\text{coll}}^3}$$
Ion energy distribution at rf discharge electrodes

Asymmetric rf plasma 13.56 MHz

Capacitive rf sheath

M. Zeuner, H. Neumann and J. Meichsner
J. Appl. Phys. 81(1997)2985
Plasma boundary

\[ \Theta = \frac{\omega_{p^+}}{\omega} = 0.25 \]

\[ \lambda = \frac{\lambda_{ex}}{\lambda_D} = 10 \]

\[ \Phi_{rf} = \frac{e \cdot U_{rf}}{k_B \cdot T_e} = 20 \]

Overlapping sattle-shaped structure charge exchange collisions
Outline

- Reactive plasmas – Overview
- Non-thermal plasmas
- Plasma boundary – plasma sheath
- Example oxygen cc-rf plasma
- Example fluorocarbon cc-rf plasma
- Outlook
Plasma diagnostics

Oxygen rf plasma

Probe, MW interferometry, MS, OES, TALIF

Capacitively coupled unconfined rf plasma (CCP)

13.56 MHz
Oxygen rf plasma

Plasma density (Langmuir-probe)

\[ n_e = 10^9 \ldots 10^{10} \text{ cm}^{-3} \]

\( p = 5 \text{ Pa}, \ U_{pp} = 800 \text{ V} \)

Oxygen rf plasma

160 GHz Microwave interferometry, \textit{GAUSSian} optics

Talk: C. Küllig
Poster

Electron density Instabilities Negative oxygen ions

\textbf{Line integrated electron density}

\begin{itemize}
\item 10Pa
\item 20Pa
\item 50Pa
\item 100Pa
\end{itemize}

Oxygen rf plasma
Mass spectrometry - ion analysis: oxygen rf plasma

Oxygen rf plasma

RF-Plasma

Monochromator
ICCD

Power supply
Screening
Electrode

RF-Plasma

Chamber

Energy
analyser

Penning gauge

Channeltron

13.56 MHz
CCP
asymm.

Ion analysis

HIDEN EQP 300
1 – 300 amu
1 – 1000 eV

O₂⁺  O⁺
O₂⁻  O⁻
Energetic positive ions at the powered rf electrode
13.56 MHz plasma (CCP) in oxygen

\[ \text{O}_2^+ \]

\[ \text{O}^+ \]
Energetic negative ions at the grounded electrode
13.56 MHz plasma (CCP) in oxygen

Oxygen rf plasma

Intensity [cps]

Ion energy [eV]

Intensity [cps]

Ion energy [eV]

p = 7 Pa
Q = 2 sccm
d = 2 cm

13 Pa
11 Pa
9 Pa
7 Pa
5 Pa
3 Pa

U_{SB} = 800 V
Q = 2 sccm
d = 2.5 cm
Oxygen rf plasma

Ground state atomic oxygen density

Two photon absorption laser induced fluorescence - TALIF

Axial O-density distribution

\[ \frac{p \cdot U_b \cdot z^2}{d} \] similarity

S. Peters et al
Contrib. Plasma Phys. 45, No. 5-6, 373 (2005)

\[ U_{SB} = -350 \text{ V} \]

\[ \text{flame} \]

\[ 3 \cdot 10^{13} \text{ cm}^{-3} \]

\[ d = 25 \ldots 90 \text{ mm} \]

\[ p = 20 \ldots 100 \text{ Pa} \]

\[ U_{SB} = 100 \ldots 500 \text{ V} \]
Oxygen rf plasma

**VUV plasma radiation**

Breaking of chemical bonds in organic materials by energetic photons, $\lambda < 200$ nm, and initiation of radical reactions.

13.56 MHz plasma, CCP

Spectral distribution of emission intensity for different gases

Integral emission intensity (115 nm – 160 nm)
Oxygen rf plasma

Emission spectrum rf oxygen plasma (CCP)

- **p = 60 Pa**
- **P = 60 W**
- Atmospheric band **760 nm**
- **3s 5S**
- **3p 3P_{1,2,0}**
- **3p 5P_{1,2,3}**
- **844.6 nm**
- **777.4 nm**

Wave length [nm]

Intensity [a.u.]

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Oxygen rf plasma

Space and time resolved optical emission spectroscopy

Monochromator
ICCD

axial resolution < 1 mm
spectral resolution < 0.1 nm
temporal resolution < 2 ns

Monochromator:
0.5 m
3 grids g = 600, 1200 & 1800

ICCD-Kamera
(PI-MAX, Gen II RB)
512 x 512 Pixel
Quantum efficiency:
≈ 2% (800nm).......15% (500nm)

Ion analysis
\[ O_2^+ \quad O^+ \quad O^- \quad O_2^- \quad O^- \]

HIDEN EQP 300
1 – 300 amu
1 – 1000 eV

13,56 MHz
CCP asymm.

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Oxygen rf plasma

74 pictures
74 measurements
< 2 ns
Objective
Filter
ICCD-camera
Pulse Delay
0...74 ns
74 pictures

PC

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Sheath dynamics – excitation patterns

I  rf sheath heating  III  field reversal
II  secondary electrons  IV  heavy particle excitation

S. Nemschokmichal, IEEE, 2008

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Oxygen rf plasma

**Increasing total pressure**

Increasing modulation of the excitation rate for heavy species excitation:

\( \Rightarrow \) ion flux modulation

**Transition**

\( \alpha \Rightarrow \gamma \) mode
Oxygen rf plasma

**PIC-MCC Simulation**

- Equations of motion: $F_i \Rightarrow v_i^* \Rightarrow x_i$
- Weighting: $E_j \Rightarrow F_i$
- Field equations: $\rho_j \Rightarrow E_j$
- Weighting: $x_i \Rightarrow \rho_i$
- Particles loss, gain boundaries
- Monte-Carlo collisions: $v_i \Rightarrow v_i^*$

\[
\frac{d\mathbf{x}}{dt} = \mathbf{v} \\
\frac{d\mathbf{v}}{dt} = \frac{q}{m} (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \\
\mathbf{E} = -\nabla \phi \\
\Delta \phi = -\frac{1}{\epsilon_0} \rho(\mathbf{x})
\]

\[
\rho = \sum_i \frac{q_i}{\Delta x \Delta y} S(x - x_i)
\]

\[
S(x) = \begin{cases} 
1 - \frac{|x|}{\Delta x} & \text{for } |x| \leq \Delta x \\
1 - \frac{|y|}{\Delta y} & \text{for } |y| \leq \Delta y \\
0 & \text{otherwise}
\end{cases}
\]

K. Matyasch, D. Tskhakaya, R. Schneider

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Oxygen rf plasma

PIC-MC simulation + Experiment

Included elementary processes

<table>
<thead>
<tr>
<th>Elastic scattering</th>
<th>Coulomb scattering</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $e + e \rightarrow e + e$</td>
<td></td>
</tr>
<tr>
<td>(2) $O^- + O^- \rightarrow O^- + O^-$</td>
<td></td>
</tr>
<tr>
<td>(3) $O_2^+ + O_2^+ \rightarrow O_2^+ + O_2^+$</td>
<td></td>
</tr>
<tr>
<td>(4) $e + O_2 \rightarrow e + O_2$</td>
<td>Elastic scattering</td>
</tr>
<tr>
<td>(5) $O_2^+ + O_2 \rightarrow O_2^+ + O_2$</td>
<td>Elastic scattering</td>
</tr>
<tr>
<td>(6) $O^- + O_2 \rightarrow O^- + O_2$</td>
<td>Elastic scattering</td>
</tr>
<tr>
<td>(7) $O_2^+ + O_2 \rightarrow O_2 + O_2^+$</td>
<td>Charge exchange</td>
</tr>
</tbody>
</table>

Electron energy loss scattering

| (8) $e + O_2 \rightarrow e + O_2$ ($\nu = 1, ..., 4$) | Vibrational excitation |
| (9) $e + O_2 \rightarrow e + O_2$(Ryd) | Rydberg excitation |
| (10) $e + O_2 \rightarrow e + O$(3P) + O(3P) | Dissociation (6.4 eV) |
| (11) $e + O_2 \rightarrow e + O$(3P) + O(1D) | Dissociation (8.6 eV) |
| (12) $e + O_2 \rightarrow e + O_2(a^1\Delta_g)$ | Meta-stable excitation |
| (13) $e + O_2 \rightarrow e + O_2(b^1\Sigma_g)$ | Meta-stable excitation |

Electron and ion production and loss

| (14) $e + O_2^+ \rightarrow O + O$ | Dissociative recombination |
| (15) $O^- + O_2^+ \rightarrow O + O_2$ | Neutralization |
| (16) $e + O_2 \rightarrow O + O^-$ | Dissociative attachment |
| (17) $O^- + O_2 \rightarrow O + O_2 + e$ | Direct detachment |
| (18) $O^- + O_2(a^1\Delta_g) \rightarrow O_3 + e$ | Associative detachment |
| (19) $e + O_2 \rightarrow 2e + O_2^+$ | Electron impact ionization |
| (20) $e + O^- \rightarrow O + 2e$ | Electron impact detachment |

3 paper series:
F.X. Bronold, K Dittmann, D Drozdov, H Fehske, B Krames, K Matyash, J Meichsner, R Schneider, D Tskhakaya

K. Dittmann, K. Matyash
S. Nemshokmichal,
J. Meichsner, and R. Schneider
*Contrib. Plasma Phys, 2010, accepted*
Oxygen rf plasma

**Experiment**

- 60 Pa
- 60 W
- -350 V\(_{\text{Bias}}\)

**Phase-resolved OES**

- \(e + O_2 \rightarrow e + O(3P) + O(3P)\)
- \(O_2^+ + O_2 \rightarrow O(3P) + X\)

**PIC-MC Simulation**

- 60 Pa

**Time-averaged OES**

- 60 Pa
- selfbias voltage
  - -100 V
  - -200 V
  - -250 V
  - -350 V
  - -400 V

---

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Oxygen rf plasma

Ion energy distribution $O_2^+$ at the powered electrode

PIC-MC simulation

Experiment

$O_2^+$ ions
5 Pa, $U_{RF} = 1000$ V

5 Pa $U_{RF} = 1000$ V

$5 \text{ Pa } U_{RF} = 1000 \text{ V}$

$E_{i} [\text{eV}]$

$E [\text{eV}]$
Plasma modification of polymer surfaces

In-situ FTIR spectroscopy

Polyethylene - PE

- CH₂ -
Oxygen rf plasma

**In situ FTIR-ATR (Attenuated Total Reflection)**

**Principle of the measurement**

- 45° ATR-Element IRG 100 (Ge-Sb-Se glass)
- Number of reflections: 34, in the sample region 13
- Effective thickness of the sample: $d_{\text{eff}} \sim 1.9 \ d_{\text{Probe}}$
- Efficiency in comparison with transmission experiment: 25

---

N J Harrick
Internal Reflection Spectroscopy, Interscience, New York, 1975]
Oxygen rf plasma

**Interaction O$_2$-plasma – polyethylene (PE)**

**in situ FTIR (ATR) analysis**

**ratio spectra**

![Graph showing normalized absorbance vs. wave number for Polyethylene - PE](image)

- **C=O formation**
- **CH$_2$ loss**

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Oxygen rf plasma

⇒ Thin plasma modified surface layer

TRIM Simulation
Oxygen ions ⇒ PE

Spectroscopic ellipsometry

![Graphs showing depth distribution and refractive index](image)

In steady state:
etching and surface modification (oxydation) take place simultaneously!

---

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Oxygen rf plasma

**Characteristic penetration depth of species in polymers**

<table>
<thead>
<tr>
<th>Plasma species</th>
<th>Energy</th>
<th>Interaction</th>
<th>Depth</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ions, Fast neutrals</strong></td>
<td>$10^2$ - $10^3$ eV</td>
<td>Elastic collisions, sputtering, chemical reactions</td>
<td>2-5 nm</td>
</tr>
<tr>
<td></td>
<td>...10 eV...</td>
<td>Adsorbate sputtering, chemical reactions</td>
<td>Top monolayer</td>
</tr>
<tr>
<td><strong>Electrons (!)</strong></td>
<td>5 -10 eV</td>
<td>Inelastic collisions, Dissociation/ionisation on the surface</td>
<td>...1 nm ...</td>
</tr>
<tr>
<td><strong>Reactive neutrals: - atoms, - molecules</strong></td>
<td>thermal Energy, 0,05 eV</td>
<td>Adsorption, chemical surface reactions, Formation of functional groups, production of low molecular (volatile) compounds</td>
<td>Top monolayer</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Diffusion and chemical reactions</td>
<td>Volume</td>
</tr>
<tr>
<td><strong>Photons</strong></td>
<td>$&gt; 5$ eV (VUV)</td>
<td>Photochemical reactions</td>
<td>... 10 - 50 nm ...</td>
</tr>
<tr>
<td></td>
<td>&lt; 5 eV (UV)</td>
<td>Secondary processes</td>
<td>µm-scale</td>
</tr>
</tbody>
</table>
Influence of polyethylene treatment on plasma composition

Difference ion mass spectra at the grounded electrode

Intensity [cps] vs. Mass [u]

- H₂O⁺
- CO⁺
- CO₂⁺

Difference neutral mass spectra at the grounded electrode

Intensity [cps] vs. Mass [u]

- H₂O
- CO
- CO₂

Difference ion mass spectra at the powered electrode

Intensity [cps] vs. Mass [u]

- H₂O⁺
- CO⁺
- CO₂⁺

Difference neutral mass spectra at the powered electrode

Intensity [cps] vs. Mass [u]

- H₂O
- CO
- CO₂

Oxygen rf plasma

56
Outline

● Reactive plasmas – Overview
● Non-thermal plasmas
● Plasma boundary – plasma sheath
● Example oxygen CCP rf plasma
● Example fluorocarbon cc-rf plasma
● Outlook
Fluorocarbon rf plasma

Transient species

Stable reaction products

Precursors

Plasma sheath

a-C:F thin film

Substrate/wall

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Fluorocarbon rf plasma

Fluorocarbon plasmas for etching/thin film deposition, and surface modification

A. Sanakaran, P Subramonium
U. of Illinois, 2003

Many activities over the last decades

... Winters, d`Agostino, Oehrlein, Kushner, Graves, Booth, Meichsner, ...
Fluorocarbon rf plasma

**Plasma chemical gas conversion**

- stable gaseous reaction products
- contamination of reactor walls

**Graphs**

- CF$_4$
- C$_3$F$_8$

- Deposited mass at reactor wall

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Silicon etching and film deposition, simultaneously

In situ microgravimetry

\[ \Delta m > 1 \mu g \]

Polymer film thickness of between 1 nm to 5 nm

H-U Poll, J Meichsner
*Thin Solid Films*, 1985

Fluorocarbon rf plasma
Fluorocarbon rf plasma

MgO-Mask

SiO$_2$ 1 µm plasma polymer, side wall protection

CF$_4$  C$_2$F$_6$  C$_3$F$_8$

anisotropy
Fluorocarbon rf plasma

Influence on the reaction kinetics due to hydrogen admixture

\[ \text{CF}_4 + e \rightarrow \text{CF} + \text{CF}_2 + \text{CF}_3 \text{ ions} \]

\[ \text{H}_2 \text{admixture} \]

\[ \begin{align*}
\text{Reducing of fluorine due to production of HF} \\
\rightarrow \text{Increasing of CF}_x \text{ radical densities} \\
\rightarrow \text{Formation of unsaturated and saturated fluorocarbons, film deposition}
\end{align*} \]
Transient species diagnostics – film deposition /etching

Fluorocarbon rf plasma

Ellipsometry

Polarizer

Analyzer

Si substrate

IR TDLAS

IR beam

Vacuum pump

RF electrode

Matching unit

RF generator

Process gases

$C_xF_y$

$H_2$

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Infrared Tunable Diode Laser Absorption Spectroscopy (IR-TDLAS)

Fluorocarbon rf plasma

Stable molecules:
- CF: 1308.5 cm\(^{-1}\) (\(^2\Pi_{1/2}\ R_{7.5}\))
- CF\(_2\): 1096-3433 cm\(^{-1}\) (P\(_2\)(21))
- CF\(_3\): 1261,307 cm\(^{-1}\)
- CF\(_4\): 1250-1300 cm\(^{-1}\)
- C\(_2\)F\(_4\): 1180 cm\(^{-1}\)
- C\(_2\)F\(_6\): at 1180 cm\(^{-1}\)

Radicals:
- CF\(_2\)
- CF\(_3\)
- CF\(_4\)
- C\(_2\)F\(_4\)
- C\(_2\)F\(_6\)

Spectral resolution: 10\(^{-3}\) cm\(^{-1}\)
Temporal resolution: 1 ms
Fluorocarbon rf plasma

State of reactor walls on CF$_2$ kinetics in pulsed CF$_4$ plasma

\[
\frac{dn}{dt} = -k_1 n - 2k_2 n^2 
\]

Wall with a-C:F layer:
second order reaction ($k_1 = 0$)

\[
C F_2 + C F_2 \xrightarrow{+Wall?} 2k_2 C_2 F_4
\]

50 Pa, 50 W, 10 sccm CF$_4$
Fluorocarbon rf plasma

Thin film growth ↔ FC species in gas phase

100 W
50 Pa
33% CF₄
67% H₂
no gas flow
Thin film growth ↔ FC species in gas phase vs H₂ admixture

50 Pa, 50 W, 0.1Hz, 50% duty cycle,
total Gas flow rate 10 sccm
Outline

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Outlook

Challenge: Microplasmas

- Small dimensions
  Scaling laws
- Role of boundaries
  Surface charge & temperature
  Secondary species
  Quantum effects
- Discharge stability
  Operation modes

Plasma boundary physics
Atmospheric pressure plasma

Coupling of surface and volume processes, chemical micro-reactors

K. Tachibana, Kyoto

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Outlook

**Syntheses of new functional materials**

- Preparation of metal-polymer composites
- Plasma processes and energetic ions for material modification
- Nanostructuring of surfaces

TR24, Project B13, University of Kiel
Outlook

Challenge: Plasma meets medicine

Plasmas for cleaning / sterilisation

Plasmas for biocompatible surfaces

e.g. coated implants with increased cell adhesion and anti-microbial properties

→ Thin plasmapolymer film with NH₂ functional groups and metallic nanoparticles.

Plasmas for tissue treatment → PLASMA MEDICINE
Thank you for attention!

K. Dittmann, S. Nemschokmichal, C. Küllig, B. Krames,
S. Stepanov, O. Gabriel, K. Li, S. Peters, K. Matyasch, R. Schneider