Plasma Modeling I:
Modeling of plasmas

Annemie Bogaerts

Department of Chemistry,
University of Antwerp (UA),
Research group PLASMANT
Belgium

Annemie.Bogaerts@uantwerpen.be
www.uantwerpen.be/plasmant

20th International School on “Low Temperature Plasma Physics”
Bad Honnef, October 2, 2016
1. General overview of plasma models
   - Explanation of different models
   - Advantages and disadvantages

2. Examples of some models for various applications
   + Typical results
1. General overview of plasma models
A. Analytical model

**Principle:**
Simple analytical formulas, valid for specific range of conditions

e.g.: Condition for self-sustaining discharge:

\[ e^- + A \xrightarrow{\alpha} 2 e^- + A^+ \]

\( \alpha = 1^{\text{st}} \) Townsend coefficient (ionization)

\( \gamma = 2^{\text{nd}} \) Townsend coefficient (sec. e\(^-\) emission)
Electron multiplication in plasma, by electron impact ionisation:

Balance equation: \( \frac{dN_e}{dx} = \alpha N_e \)

Solution: \( N_e = N_{e,0} \exp\left(\int \alpha \, dx\right) \)

At cathode: \( N_{e,0} \)
At anode: \( N_e = N_{e,0} \exp(\alpha L) \)

Hence: for 1 electron at cathode: \( \exp(\alpha L) \) electrons at anode

\[ \Rightarrow \text{Hence formed in plasma: } \exp(\alpha L) - 1 \]

Number of electrons formed = number of ions formed

Secondary electron emission: \( \gamma \)

Number of sec. electrons formed by these ions: \( \gamma \times (\exp(\alpha L) - 1) \)

\[ \Rightarrow \text{Condition “self-sustaining discharge”: } \gamma \times (\exp(\alpha L) - 1) = 1 \]

\[ \Rightarrow \alpha L = \ln\left(1 + \frac{1}{\gamma}\right) \]
A. Analytical model (cont)

**Advantage:** Simple, fast

**Disadvantage:** Approximation, limited validity
Principle:
Rate equations (balance equations) for all species, based on production/loss by chemical reactions:

\[
\frac{\partial n_i}{\partial t} = R_{\text{prod} \ i} - R_{\text{loss} \ i}
\]

\[R_{\text{prod} \ / \ R_{\text{loss}}} = k_{2B} n_1 n_2 \quad (\text{or:} k_{3B} n_1 n_2 n_3, \text{ or:} A n_1)\]

Electron impact reaction rates:
From Boltzmann solver \(\rightarrow\) Look-up tables: \(k(\varepsilon)\)
+ Electron energy balance equation \(\rightarrow \varepsilon\)
B. 0D chemical kinetics model (cont)

**Advantage:**
Simple, fast (detailed chemistry)

**Disadvantage:**
Approximation: No transport (assumes plasma = uniform)

However: based on gas flow velocity:
can deduce spatial behavior from temporal behavior
(equivalence batch reactor – plug flow reactor)
Example: Plasma jet

Plasma jet TU/e
(2 slm Ar gas feed,
6.5 W,
50% relat. air humidity)

Example: Plasma jet

Plasma jet TU/e
(2 slm Ar gas feed,
6.5 W, 50% relat. air humidity)

- O, O₃, O₂(a), OH, H₂O₂
- NO, NO₂, HNO₂, HNO₃
- O↓ at longer distance
- O₃, O₂(a)↑ at longer distance
- OH dimerizes into H₂O₂ (~1.2 cm)
- Cluster formation important in ion chemistry
- O₂⁻ and NO₃⁻ : relatively low (ppb) levels

Example: DBD reactor: filamentary character

Reactor length + gas flow $\rightarrow$ residence time
(correlation spatial – temporal behavior)
B. 0D chemical kinetics model (cont)

Example: DBD reactor: filamentary character

1 microdischarge pulse + afterglow
- $T_e \sim 2-3$ eV
- $N_e \sim 10^{13}$ cm$^{-3}$

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure}
\caption{Graph showing applied voltage and current over time.}
\end{figure}
Example: DBD reactor: filamentary character

5 consecutive pulses: species pass through several filaments (as function of distance, or function of residence time)
Principle:

Moment equations of Boltzmann equation:
Conservation of mass, momentum, energy

Continuity equations (for all species $i$):

$$\frac{\partial n_i(z, r)}{\partial t} + \nabla \cdot \bar{j}_i(z, r) = R_{\text{prod}}_i(z, r) - R_{\text{loss}}_i(z, r)$$

Momentum equation: often drift-diffusion approximation:
→ Transport equations
(drift-diffusion for charged species; diffusion for neutrals):

$$\bar{j}_i(z, r) = \left[ \pm \mu_i n_i(z, r) \bar{E}(z, r) \right] - D_i \nabla n_i(z, r)$$
Electron energy balance equation:
\[
\frac{\partial n_e \varepsilon}{\partial t} + \nabla \cdot j_w = -e j_w \cdot E + \sum_i k_i n_e N_g \Delta \varepsilon_i
\]
\[
j_w = \frac{5}{3} \mu_e n_e \varepsilon \bar{E} - \frac{5}{3} D_e \nabla n_e \varepsilon
\]

Ions, neutrals: assumed $T_g$

**Advantage:** Simple, fast  (detailed chemistry)

Coupling to Poisson equation for self-consistent E-field
\[
\nabla^2 V + \frac{e}{\varepsilon_0} \left( n_{x^+} - n_{x^-} - n_e \right) = 0 \quad | \quad \bar{E} = -\nabla V
\]

**Disadvantage:**
Approximation (assumes species gain more or less same amount of energy from E-field as they lose by collisions
Principle:
Full solution of Boltzmann transport equation
(terms with E-gain, E-loss)

\[ f_j(r, v, t) : \frac{\partial f_j}{\partial t} + \vec{v} \cdot \nabla f_j + \vec{a} \cdot \nabla_v f_j = C_{el}(f_j) + C_{incl}(f_j) \]

Advantage: Accounts for non-equilibrium behavior

Disadvantage: Mathematically complex
→ Typically only used for electron behavior
   (e.g., 2-term approximation): e.g., BOLSIG+
Principle:

• Treats particles on lowest microscopic level
• For every particle – during successive time-steps:
  * trajectory by Newton’s laws:

\[
\begin{align*}
  z &= z_0 + v_{z_0} \Delta t + \frac{qE_{ax}}{2m}(\Delta t)^2 \\
  v_z &= v_{z_0} + \frac{qE_{ax}}{m} \Delta t \\
  x &= x_0 + v_{x_0} \Delta t + \frac{qE_{rad} \cos(\alpha)}{2m}(\Delta t)^2 \\
  v_x &= v_{x_0} + \frac{qE_{rad} \cos(\alpha)}{m} \Delta t \\
  y &= y_0 + v_{y_0} \Delta t + \frac{qE_{rad} \sin(\alpha)}{2m}(\Delta t)^2 \\
  v_y &= v_{y_0} + \frac{qE_{rad} \sin(\alpha)}{m} \Delta t
\end{align*}
\]

* collisions by random numbers
E. Monte Carlo model (cont)

- Probability of collision:
  \[ \text{Prob}_{\text{coll}} = 1 - \exp\left( - \Delta s \Sigma (n\sigma_{\text{coll}}(E)) \right) \]

→ Compare with RN (0 - 1): If Prob < RN => no collision
  If Prob > RN => collision

- Kind of collision: partial collision prob. + compare with RN
E. Monte Carlo model (cont)

- **New energy + direction: scattering formulas + RN, e.g.:**
  - after ionization: \( E_{\text{prim}} = (E_0 - E_{\text{ion}}) \cdot RN \); \( E_{\text{sec}} = E_0 - E_{\text{ion}} - E_{\text{prim}} \)
  
  \[
  RN = \frac{0}{\int_{0}^{0} \sigma_{\text{ion,diff}}(E_0, \varepsilon) d\varepsilon}
  \]

- after excitation: \( E = E - E_{\text{excit}} \)

- **scattering angles (\( \chi \), \( \psi \)):**
  \[
  \cos \chi = 1 - \frac{2 RN}{1 + 8 \varepsilon (1 - RN)} \quad ; \quad \psi = 2\pi RN
  \]

- **new angles (\( \theta \), \( \varphi \)):**
  \[
  \begin{pmatrix}
  \sin(\theta)\cos(\varphi) \\
  \sin(\theta)\sin(\varphi) \\
  \cos(\theta)
  \end{pmatrix}
  =
  \begin{pmatrix}
  \cos(\theta_0)\cos(\varphi_0) & -\sin(\varphi_0) & \sin(\theta_0)\cos(\varphi_0) \\
  \cos(\theta_0)\sin(\varphi_0) & \cos(\varphi_0) & \sin(\theta_0)\sin(\varphi_0) \\
  -\sin(\theta_0) & 0 & \cos(\theta_0)
  \end{pmatrix}
  \begin{pmatrix}
  \sin(\chi)\cos(\psi) \\
  \sin(\chi)\sin(\psi) \\
  \cos(\chi)
  \end{pmatrix}
  \]
**Advantage:**
Accurate (non-equilibrium behavior) + simple
Can be applied for all species

**Disadvantage:**
Long calculation time + not self-consistent
In practice: used for electrons (in hybrid model)
Or for species in sheath (detailed behavior, e.g., EDF)
F. Particle-in-cell / Monte Carlo model

**Principle:**
- Similar to MC model (Newtons’ laws, random numbers)
- But at every time-step: calculation of electric field from positions of charged particles (Poisson equation)

**Advantage:** Accurate + self-consistent

**Disadvantage:** Even longer calculation time
Principle of PIC-MC (cycle):

Real plasma particles: replaced by superparticles
1 superparticle = W real particles (W = weight, e.g. $2 \times 10^7$)

Integration of equation of motion, moving particles
$F_i \rightarrow v_i' \rightarrow x_i$

Particle loss/gain at the boundaries (emission, absorption)

Weighting
$(E,B)_j \rightarrow F_i$
(interpolate field to particles)

MC Collision?

Integration of Poisson's equations on the grid
$(\rho)_i \rightarrow (E)_i$
(interpol. charges to grid)

Weighting
$(x,v)_i \rightarrow (\rho)_i$

Postcoll. velocities
$v_i' \rightarrow v_i$

$\Delta t_{\text{elec}} = 1 \text{ ps}$
$\Delta t_{\text{ion}} = 10 \Delta t_{\text{elec}}$

No

Yes
Which model should I use?
Every model has advantages + disadvantages...

Solution: use combination of models!!
-> “hybrid model”
**G. Hybrid model**

**Principle:**
Because some species = fluid-like, others = particle-like:
→ Combination of above models, e.g.:
• Monte Carlo for fast (non-equilibrium) species
• Fluid model for slow (equilibrium) species + E-field
• (transfer from fast to slow group: if \((E_k + E_p) < \text{threshold}\))

**Advantage:**
• Combines the advantages + avoids the disadvantages
• Accurate + self-consistent + reduced calculation time

**Disadvantage:** /
H. Collisional-radiative model (for excited levels)

Example: Ar: 65 Ar levels (individual or group of levels)

Energy level scheme for Ar* CR model
H. Collisional-radiative model (for excited levels)

For each level: continuity equation (balance equation):

$$\frac{\partial n_{Ar^*}}{\partial t} - D_{Ar^*} \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial n_{Ar^*}}{\partial r} \right) - D_{Ar^*} \frac{\partial^2 n_{Ar^*}}{\partial z^2} = R_{\text{prod}} - R_{\text{loss}}$$

Production + loss processes for each level:
* electron, Ar ion + Ar atom impact excitation, de-excitation, ionization
* electron-ion three-body recombination, radiative recombination
* radiative decay
* Hornbeck-Molnar associative ionization (for Ar* levels with E > 14.7 eV)

Additional processes for 4s levels:
* Ar* - Ar* collisions -> (associative) ionization
* Penning ionization of sputtered atoms
* three-body collisions with Ar atoms
* radiation trapping of resonant radiation
I. Model for plasma-surface interactions: Molecular Dynamics simulations

- Newton’s laws: Calc. of position + velocities of atoms, by interatomic interaction potentials

\[
\begin{align*}
\bar{F} &= -\bar{\nabla} U \\
\bar{a} &= \bar{F} / m \\
\bar{v} &= \bar{v}_0 + \bar{a} \Delta t \\
\bar{r} &= \bar{r}_0 + \bar{v}_0 \Delta t + \frac{1}{2} \bar{a} (\Delta t)^2
\end{align*}
\]

Time-integrated trajectory of impacting C-atom on amorphous C substrate
I. Model for plasma-surface interactions: Molecular Dynamics simulations (cont)

- Interaction potential: empirical potential (parameters)

Potential energy surface for impacting H-atom on diamond \{111\} surface
I. Model for plasma-surface interactions: Molecular Dynamics simulations (cont)

E.g.: C-films: Brenner interaction potential

- Binding energy: sum of binding energies between atoms $i$ and $j$:

$$U_{\text{system}} = \sum_i \sum_{j>i} \left[ V_R(r_{ij}) - b_{ij} V_A(r_{ij}) \right]$$

- Repulsive ($V_R$) and attractive ($V_A$) terms:

$$\begin{cases} 
V_R(r_{ij}) = f_{ij}(r_{ij}) A_{ij} \exp(-\lambda_{ij} r_{ij}) \\
V_A(r_{ij}) = f_{ij}(r_{ij}) B_{ij} \exp(-\mu_{ij} r_{ij})
\end{cases}$$

- ‘Many-body’ chemistry: binding order function $b_{ij}$

$$b_{ij} = f(\text{local binding topology})$$
I. Model for plasma-surface interactions:
Molecular Dynamics simulations (cont)

- Semi-infinite surface: periodic $\pm\{x,y\}$ boundaries
- Time scale $\sim$ ns ($\Delta t \sim 0.1-1$ fs)
  Length scale $\sim$ nm
- Initialisation of the simulation:
  - Define substrate
  - Particle impacts
    » Film growth: sequentially
    » Reaction mechanisms
    » Random orientation +
      $\{x,y\}$ position above surface
  - Bottom layers fixed
  - Heat dissipation by heat bath
Advantage:

• Very accurate + deterministic (self-consistent)

Disadvantage:

Long calculation time…
Illustration of MD simulations for film deposition (diamond like carbon)

- 5-fold coordinated C-atom
- 4-fold coordinated C-atom
- 3-fold coordinated C-atom
- 2-fold coordinated C-atom
- 1-fold coordinated C-atom
- H-atom
Result: Calculated microscopic structure of the film

- 5-fold coordinated C-atom
- 4-fold coordinated C-atom
- 3-fold coordinated C-atom
- 2-fold coordinated C-atom
- 1-fold coordinated C-atom
- H-atom
Illustration of MD simulations for plasma catalysis

CH$_3$ radicals on Ni catalyst surface
Illustration of MD simulations for carbon nanotube growth

Mechanism of cap formation of single walled carbon nanotube on Ni nanoparticle
Illustration of MD simulations for plasma medicine

Breaking of peptidoglycan
(∼ bacterial cell wall damage)
upon impact of O radicals
2. Examples of models for various applications

A. 0D chemical kinetics model: for DBD in CH$_4$/CO$_2$
   Greenhouse gas conversion (plasma chemistry)

B. PIC-MC model: for magnetron discharge

C. MC model for electrons: for magnetron discharge

D. Hybrid model: for glow discharge with sputtering

E. Hybrid model: for ICP etch reactor
A. 0D chemical kinetics model for DBD in CH$_4$/CO$_2$

**Greenhouse gas conversion**

Global warming $\sim$ greenhouse gases
$\rightarrow$ conversion into value-added chemicals

However: greenhouse gases $=$ inert
$\rightarrow$ Classical processes: high $T$, $p$

DBD reactor $=$ very useful: $T_e$ $>>$ $T_{gas}$

Enables reactions that would thermodynamically not occur at low $T_{gas}$
# Plasma chemistry

## 75 species:

<table>
<thead>
<tr>
<th>Molecules</th>
<th>Charged species</th>
<th>Radicals</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>CH₅⁺, CH₄⁺, CH₃⁺, CH₂⁺, CH⁺, C⁺</td>
<td>CH₃, CH₂, CH, C</td>
</tr>
<tr>
<td>C₂H₆, C₂H₄, C₂H₂, C₃H₈, C₃H₆, C₄H₂</td>
<td>C₂H₆⁺, C₂H₅⁺, C₂H₄⁺, C₂H₃⁺, C₂H₂⁺, C₂H⁺, C₂⁺</td>
<td>C₂H₅, C₂H₃, C₂H, C₂, C₃H₇, C₃H₅</td>
</tr>
<tr>
<td>H₂</td>
<td>H₃⁺, H₂⁺, H⁺, H⁻</td>
<td>H</td>
</tr>
<tr>
<td>O₃, O₂</td>
<td>O₄⁺, O₂⁺, O⁺, O₄⁻, O₃⁻, O₂⁻, O⁻</td>
<td>O</td>
</tr>
<tr>
<td>CO₂, CO</td>
<td>CO₂⁺, CO⁺</td>
<td></td>
</tr>
<tr>
<td>H₂O, H₂O₂</td>
<td>H₃O⁺, H₂O⁺, OH⁺, OH⁻</td>
<td>OH, HO₂</td>
</tr>
<tr>
<td>CH₂O, CH₃OH, C₂H₅OH, CH₃CHO, CH₂CO, CH₃OOH, C₂H₅OOH</td>
<td>Electrons</td>
<td>CHO, CH₂OH, CH₃O, C₂H₅O, C₂H₆O, CH₂CHO, CH₃O₂, C₂H₅O₂</td>
</tr>
</tbody>
</table>
Plasma chemistry

1088 reactions taken into account:

165 Electron-neutral collisions
(ionization, excitation, dissociation,...)

\[ \text{e}^- + \text{CH}_4 \rightarrow \text{e}^- + \text{CH}_3 + \text{H} \]

50 Electron-ion recombination reactions

\[ \text{e}^- + \text{O}_2^+ \rightarrow \text{O} + \text{O} \]

873 Ion/neutral chemical reactions

\[ \text{CH}_3 + \text{OH} (+\text{M}) \rightarrow \text{CH}_3\text{OH} (+\text{M}) \]
\[ \text{CH}_4^+ + \text{CH}_4 \rightarrow \text{CH}_5^+ + \text{CH}_3 \]

0D model (DBD in \text{CH}_4/\text{CO}_2: \text{greenhouse gas conversion})
Calculated conversion, yields

\[ \text{CO}_2 + \text{CH}_4 \text{ conversion} + \text{E-efficiency, as f(SEI):} \]
(exp: Tu et al., Univ. Liverpool)

Trade-off: conversion + E-efficiency

Also calculated:
Selectivities of formed products:
At 50/50 \( \text{CO}_2/\text{CH}_4 \):
- \( \text{H}_2 \): 55%
- \( \text{CO} \): 48%
- \( \text{C}_2, \text{C}_3 \): 6%, 30%
- Formaldehyde: 13%
- Methanol: 3%

\[ \Rightarrow \text{Future: plasma catalysis} \]

0D model (DBD in \( \text{CH}_4/\text{CO}_2 \) : greenhouse gas conversion)
Calculated conversion, yields

Computational optimization study (750 simulations):
(Effect of CO₂/CH₄ ratio, power, residence time, frequency)

Max + min obtained total conversion + E-efficiency:

Best results:
- 84% conversion,
- 8.5% E-efficiency

Max. E-efficiency: 15%
(but low conversion...)

⇒ DBD not competitive for industrial implementation
⇒ Plasma catalysis to improve E-efficiency + selectivity

0D model (DBD in CH₄/CO₂ : greenhouse gas conversion)
Comparison CO$_2$/CH$_4$ - CH$_4$/O$_2$

Species densities: Different chemistry

**CO$_2$/CH$_4$:** C$_x$H$_y$, CH$_2$O, CH$_3$CHO, H$_2$/CO $> 1$

**O$_2$/CH$_4$:** H$_2$O, CH$_3$OH, CH$_3$OOH, CO$_2$, H$_2$/CO $< 1$

0D model (DBD in CH$_4$/CO$_2$ : greenhouse gas conversion)
Comparison $\text{CO}_2/\text{CH}_4$ - $\text{CH}_4/O_2$

Different reaction pathways: Explains different product formation

$\text{CO}_2/\text{CH}_4$: $C_xH_y$, $\text{CH}_2\text{O}$

$\text{O}_2/\text{CH}_4$: $\text{H}_2\text{O}$, $\text{CH}_3\text{OH}$, $\text{CH}_3\text{OOH}$, $\text{CO}_2$

0D model (DBD in $\text{CH}_4/\text{CO}_2$: greenhouse gas conversion)
B. PIC-MC model: for magnetron discharge

Reactor geometry + Magnetic field

Br_{max} = 300 – 1100 G
V_{ext} = -400 V
p = 4 - 30 mtorr
Argon

PIC-MC model (magnetron discharge)
Electrons:

Calculated Electron and Ar⁺ Ion Density

Maximum ~ $10^{17}$ m$^{-3}$ at $r = 1.85$ cm (maximum $B_r$)

Ar⁺ ions:

PIC-MC model (magnetron discharge)
Fast Cu Atom Density and Thermal Cu atom density

Fast Cu$^0$ atoms:
Concentrated near cathode
Max $\sim 10^{18}$ m$^{-3}$

Thermal Cu$^0$ atoms:
Broad distribution
Max $\sim 4\times10^{17}$ m$^{-3}$

PIC-MC model (magnetron discharge)
Erosion profile: Calculated - Measured

Good agreement

PIC-MC model (magnetron discharge)
C. MC model for electrons: dual magnetron discharge

Magnetic field

(a) Closed field

(b) Mirror field

Single electron trajectory

Closed field

Mirror field

MC model for electrons (dual magnetron discharge)
Calculated electron density – ionization rate

Closed field:

Mirror field:

MC model for electrons (dual magnetron discharge)
Comparison MC vs PIC-MC model

MC =
• faster (minutes to 1 hour vs. several weeks for PIC)
• complex geometries possible

But: not self-consistent:
- Input B needed (e.g., from Gmsh (http://www.geuz.org/gmsh/)
& GetDP (http://www.geuz.org/getdp/)

- Input E needed (e.g., from PIC-MC model)

MC model for electrons (dual magnetron discharge)
### D. Hybrid model for GD plasma with sputtering

Combination of different models for various species

<table>
<thead>
<tr>
<th>Species:</th>
<th>Model used:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar(^0) atoms</td>
<td>no model (assumed thermalized)</td>
</tr>
<tr>
<td></td>
<td>or: heat conduction equation</td>
</tr>
<tr>
<td>electrons</td>
<td>MC for fast electrons</td>
</tr>
<tr>
<td></td>
<td>fluid for slow electrons</td>
</tr>
<tr>
<td>Ar(^+) ions</td>
<td>fluid (with electrons + Poisson)</td>
</tr>
<tr>
<td></td>
<td>MC in sheath</td>
</tr>
<tr>
<td>Ar(^0_f) fast atoms</td>
<td>MC in sheath</td>
</tr>
<tr>
<td>Ar(^*) excited atoms</td>
<td>collisional-radiative model</td>
</tr>
<tr>
<td>Cu(^0) atoms</td>
<td>thermalization after sputtering: MC</td>
</tr>
<tr>
<td>Cu(^<em>), Cu(^{+(</em>)}), Cu(^{++})</td>
<td>collisional-radiative model</td>
</tr>
<tr>
<td>Cu(^+) ions</td>
<td>MC in sheath</td>
</tr>
</tbody>
</table>
Application: Analysis of solid materials:
Sample to be analyzed = cathode of GD
Sputtering → Excitation, ionization in plasma → OES, MS

E.g.: Depth profiling:
Concentr as f(depth)
**Coupling of the models:**

**“Modeling network”**

- **e⁻ MC model:**
  - \( R_{e,exc,Ar} \), \( R_{e,exc,met} \), \( R_{e,ion,met} \) for \( \text{Ar}^+ \) model
  - \( R_{e,ion,Cu} \) for \( \text{Cu} \) model

- **\( \text{Ar}^+/\text{Ar}^0 \) MC model:**
  - \( R_{i,exc,Ar} \), \( R_{e,exc,Ar} \) for \( \text{Ar}^+ \) model
  - \( f_{\text{Ar}^+(0,E)}, f_{\text{Ar}(0,E)} \) for \( \text{Cu} \) model

- **\( \text{Ar}^+/e^- \) fluid model:**
  - \( n_{\text{Ar}}, n_{\text{e,slow}} \) for \( \text{Ar}^+ \) model
  - \( n_{\text{Ar}^+}, n_{\text{e,slow}} \) for \( \text{Cu}^+ \) model

- **\( \text{Ar}^+ \) CR model:**
  - \( F_T \)

- **\( \text{Cu} \) MC model:**
  - \( n_{\text{Cu}} \)

- **\( \text{Cu}^+ \) MC model:**
  - \( n_{\text{Cu}^+} \)

- **\( \text{Cu}/\text{Cu}^+ \) CR model:**
  - \( f_{\text{Cu}^+(0,E)} \)

**Ar\^+ model:**

- \( n_{\text{Ar}^+} \) for \( R_{e,exc,met} \) and \( R_{e,ion,met} \)
- prod, loss: for \( n_{\text{Ar}^+}, n_{\text{e,slow}} \)

**Cu model:**

- \( n_{\text{Cu}} \) for \( R_{e,ion,Cu} \)
- \( n_{\text{Cu}^+} \) for \( E, V \)
- asymm. CT: for \( n_{\text{Ar}^+} \)
- ioniz. terms: for \( n_{\text{e,slow}} \)

---

**Hybrid model (GD)**
Hybrid model (GD)
Input data for the modeling network

- **Electrical data:**
  - Voltage, pressure, (gas temperature)
  - Electrical current = calculated self-consistently

- **Reactor geometry:**
  - (e.g., cylinder: length, diameter)

- **Gas (mixture)**

- **Cross sections, rate coefficients, transport coefficients,…**

All other quantities: calculated self-consistently

Hybrid model (GD)
Typical calculation results

General calculation results:
* Electrical characteristics (current, voltage, pressure)
* Electric field and potential distribution
* Densities, fluxes, energies of the plasma species
* Information about collisions in the plasma

Results of importance for applications (sputtering, GD-OES, ...):
* Crater profiles, erosion rates at the cathode
* Optical emission intensities
* Effect of cell geometry, operating conditions
Calculated gas temperature:

**VG9000 cell**  
(1000 V, 3 mA, 75 Pa):

**Grimm-type cell**  
(800 V, 50 mA, 400 Pa)  
+ Corresponding Ar gas density:
Potential distribution:
(VG9000 cell
1000 V, 75 Pa, 3 mA)

CDS: ca. 2 mm long
NG: major part (9 V)
Densities: (VG9000: 1000 V, 75 Pa, 3 mA):

**Ar⁺ ions ~ slow electrons:**

**Fast electrons:**

Hybrid model (GD)
Energies:
Electron energy distribution (1000 V, 75 Pa, 3 mA):

Hybrid model (GD)
Energies:
Argon ion energy distribution (1000 V, 75 Pa, 3 mA):

Calculated:

Measured (MS):

Hybrid model (GD)
Energies:
Copper ion energy distribution (1000 V, 75 Pa, 3 mA):

**Calculated:**

**Measured (MS):**

Hybrid model (GD)
Information about sputtering at the cathode: Crater profile after 45 min. sputt. (VG9000: 1000 V, 75 Pa, 3 mA):

**Calculated:**

- Depth vs. radius plot

**Measured:**

- Detailed measurement graph

**Crater edge effect due to anode front plate:**

- Hybrid model (GD)
Grimm cell

Craters more flat
Because equipot.lines // cathode

Hybrid model (GD)
Optical emission intensities:
Ar(I) spectrum
Calculated:

Measured:

Hybrid model (GD)
Optical emission intensities

Calculated

ArI (750.3 nm)

ArI (811.5 nm)

ArII (476.5 nm)

CuI (324.75 nm)

Measured

ArI (750.3 nm)

ArI (811.5 nm)

ArII (476.5 nm)

CuI (324.75 nm)

DC: 0.6 Torr

1.55 mA - 417 V

3.1 mA - 455 V

4.65 mA - 480 V

6.2 mA - 495 V

7.75 mA - 505 V

Hybrid model (GD)
E. Hybrid model for ICP etch reactor

HPEM (M.Kushner, University of Michigan)

- Maxwell equations: $E$, $B$ fields
- Monte Carlo (electrons): $n_e$, $T_e$, EEDF, reaction rates
- Fluid (heavy particles): $n_i$, $\Gamma_i$, $E_s$
- Surface modeling: surface reactions, $\Gamma_Ri$
- Monte Carlo (heavy particles): IEDF, IADF

Hybrid model (ICP etch reactor)
Calculated species densities ($\text{Cl}_2$, $\text{e}^-$)

- $\text{Cl}_2$: Maximum near inlet, then depletion (chemical reactions)
  Fairly uniform density profile
- Electrons: Maximum in center/near coil (ionization degree $\sim 10^{-4}$)

Hybrid model (ICP etch reactor)
Calculated fluxes + angul.distrib. to wafer

- Ion fluxes ± 1000x lower than neutral fluxes
- Ions: narrow angular distribution (directed by E-field)
- Neutrals: wide angular distribution

Hybrid model (ICP etch reactor)
Calculated energy distributions to wafer

- **Ions**: bimodal distribution (rf bias at substrate):
  - Ions “feel” rf bias amplitude ($t_{\text{sheath}} < 1$ rf cycle)
- **Neutrals**: Maxwellian distribution at low $E$

Hybrid model (ICP etch reactor)
Etch profile calculations

Input:

- Fluxes, energy and angular distributions of bombarding species (from plasma model)

- Surface reaction probabilities (etch, oxid, sputt, redepos) of the various species (Cl(+), Cl₂(+), O(+), O₂(+), Ar+) on the various surface sites (Si, SiCl, SiCl₂, SiCl₃, SiO, SiO₂)

Hybrid model (ICP etch reactor)
Plasma modeling:
Most appropriate model depends on application:
- Fluid (1D or 2D) or (0D) chemical kinetics modeling:
  * Detailed information on plasma chemistry
  * Fast
- Particle-in-cell – Monte Carlo simulations:
  * Microscopic – non-equilibrium behavior
- Monte Carlo modeling:
  * Faster, but not self-consistent
- Hybrid Monte Carlo - fluid simulations:
  * Combination: combines the advantages + eliminates the drawbacks of individual models
  * Extra information (etch profiles, OES,...)
- Molecular dynamics simulations: Surface modeling
End of Presentation