Introduction to kinetic modeling in low-temperature plasmas

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2. Plasma processing for semiconductor production equipment makers: $20B/year industry
3. Plasma sources for semiconductor manufacturing
4. Plasma needs to be considered using kinetic theory
5. Particle-in-cell codes
6. Quantum Chemistry Codes
7. Princeton collaborative user facility
8. Conclusions
1. Motivation: Applications of low-temperature plasmas Why low temperature plasma is important?

Multiple multibillion-dollar industries:

- Plasma processing, $15-20 B/year wafer fab equipment for 2T/year semiconductor industry;  
- Thin films;
- Electric propulsion;
- Nanomaterial synthesis;
- Advanced plasma manufacturing (welding, cutting);
- Plasma switches for electric grids and pulsed power.
Low Temperature Plasma Applications

Plasma processing reactor
Plasma cutting tool
Magnetron for thin films
Plasma thruster
Plasma Reactor for nanomaterial synthesis
Gas tube switch

Basic Structure of the Electric System

Subtransmission Customer 330V and 440V
Secondary Customer 440V and 220V
Transmission Customer 220V or 330V
Generator Step Up Transformer
Generating Station
Transmission Line 330, 345, 440, and 720 kV

Color Key:
Blue: Transmission
Green: Distribution
Black: Generation
2. Plasma processing for semiconductor production equipment makers: $20B/year industry

Plasma Enhanced Technologies

A small section of a

Bell Laboratories

Birthplace of solid-state microelectronics:
Bell Laboratories, Murray Hill, NJ

Straight holes like these can be etched with low temperature plasmas.
Plasma processing, $15-20 B/year wafer fab equipment for 2T/year semiconductor industry.

• The CHIPS for America Act includes a range of federal investments to advance U.S. semiconductor manufacturing. The bill also includes a refundable investment tax credit $10 billion for a new federal grant program that would incentivize new domestic semiconductor manufacturing facilities.

• Research is critical to advancing semiconductor innovation in the U.S. American semiconductor design and manufacturing companies invest approximately one-fifth of revenue in R&D, almost $40 billion in 2019 (https://www.semiconductors.org/chips-for-america-act-would-strengthen-u-s-semiconductor-manufacturing-innovation/)

3. Plasma Sources for semiconductor manufacturing

- Capacitively-coupled plasmas CCP
- Inductively-coupled discharges ICP
- Electron and Ion beams

Electron beam generated plasma processing system

* Meager et al., US patent no. 5,874,807 (Feb. 1999)
Plasma needs to be considered using kinetic theory

- Most remote from thermodynamic equilibrium:
  - $T_e$ differs from $T_i$

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Distribution</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>3eV</td>
<td>3 $10^{-2}$ eV</td>
<td>glow discharges</td>
</tr>
<tr>
<td>3 $10^{-3}$ eV</td>
<td>3 $10^{-2}$ eV</td>
<td>afterglow</td>
</tr>
<tr>
<td>10keV</td>
<td>1eV</td>
<td>ECR ion sources</td>
</tr>
</tbody>
</table>

- Electron, ion, photon energy distribution functions (DF) are all nonMaxwellian:
  - Parts of the DFs are very flexible and almost independent.
Plasma parameters in CCP and ICP

- Plasma density $n = 10^9 - 10^{13}$ cm$^{-3}$
- Gas pressure = few mTorr
- Small degree of ionization $< 10^{-4}$
- Electron temperature $T_e = $ few eV
- Ion temperature $T_i = 0.03$ eV
- Spatial scale = mm- m
Global model: particle balance determines $T_e$

Assuming steady-state and a Maxwellian Electron Energy Distribution Function $\Rightarrow$

- Rate of plasma production = rate of plasma loss,
- Ionization frequency = loss frequency to the wall

\[
\nu_{iz} (T_e) = \nu_{loss} (T_e)
\]

\[
\nu_{iz} = n_g V_T \sigma_{iz} e^{-I/T_e},
\]

\[
\nu_{loss} = \gamma C_s / L \quad \text{where} \quad C_s = \sqrt{T_e / M}
\]

\[
n_g V_T \sigma_{iz} e^{-I/T_e} = \gamma \frac{\sqrt{T_e / M}}{L}
\]
V. Godyak’s experiment is benchmark.

The Inductively Coupled Plasmas (ICP) f=0.45-13.56 MHz argon gas pressures 0.3-300 mTorr rf power 6-400 W.

Figure 1. Experimental discharge chamber.

Experiment (left) vs global model (right)

\[
n_g V_T \sigma_{iz} e^{-I/T_e} = \gamma \frac{\sqrt{T_e / M}}{L} \uparrow n_g L \downarrow T_e
\]

T_e as a function of gas pressure at f=6.78 MHz
I need someone well versed in the art of torture—do you know PowerPoint?
### TABLE 1.1. Range of Parameters for rf Diode and High-Density Discharges

<table>
<thead>
<tr>
<th>Parameter</th>
<th>rf Diode</th>
<th>High-Density Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure $p$ (mTorr)</td>
<td>10–1000</td>
<td>0.5–50</td>
</tr>
<tr>
<td>Power $P$ (W)</td>
<td>50–2000</td>
<td>100–5000</td>
</tr>
<tr>
<td>Frequency $f$ (MHz)</td>
<td>0.05–13.56</td>
<td>0–2450</td>
</tr>
<tr>
<td>Volume $V$ (L)</td>
<td>1–10</td>
<td>2–50</td>
</tr>
<tr>
<td>Cross-sectional area $A$ (cm$^2$)</td>
<td>300–2000</td>
<td>300–500</td>
</tr>
<tr>
<td>Magnetic field $B$ (kG)</td>
<td>0</td>
<td>0–1</td>
</tr>
<tr>
<td>Plasma density $n$ (cm$^{-3}$)</td>
<td>$10^9$–$10^{11}$</td>
<td>$10^{10}$–$10^{12}$</td>
</tr>
<tr>
<td>Electron temperature $T_e$ (V)</td>
<td>1–5</td>
<td>2–7</td>
</tr>
<tr>
<td>Ion acceleration energy $E_i$ (V)</td>
<td>200–1000</td>
<td>20–500</td>
</tr>
<tr>
<td>Fractional ionization $x_{iz}$</td>
<td>$10^{-6}$–$10^{-2}$</td>
<td>$10^{-4}$–$10^{-1}$</td>
</tr>
</tbody>
</table>

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**FIGURE 1.13.** The physical model of an rf diode (after Lieberman and Gottscho, 1994).
Discharge modeling needs to be kinetic!

Electron energy distribution functions (EEDF) are non-Maxwellian:

- Parts of the EEDF are very flexible and almost independent.
- An example of a EEDF in capacitive discharge.

Mechanisms of EEDF formation

Cooling is due to energy losses in elastic and inelastic collisions.

\[ e, \varepsilon \rightarrow \Rightarrow \text{ } e, \varepsilon-1 \rightarrow v^* \]

Mixing is due to electron-electron collisions.

\[ e_1, \varepsilon_1 \rightarrow \text{ } e_1, \varepsilon_1+\delta\varepsilon \]
\[ e_2, \varepsilon_2 \rightarrow \text{ } e_2, \varepsilon_2-\delta\varepsilon \]

Electron-electron collisions make EEDF a Maxwellian! =>

If \( v_{ee} >> v^* \) or the degree of ionization, \( n_e/n_g > 10^{-4} \), EEDF is a Maxwellian;

If \( v_{ee} << v^* \) or \( n_e/n_g < 10^{-4} \), EEDF can have any shape,
EEDF in nitrogen, constant electric field

1930 Druyvesteyn’s EEDF for $\lambda$ constant.

$$f \sim \exp(-\varepsilon^2/\varepsilon_0^2)$$

Real cross-sections in N$_2$

Nonlocal, nonlinear electron kinetics

• Formation of non-Maxwellian, non-uniform, \( f(\nu,r,t) \) in self-consistent electric field strongly coupled to plasma density profile through ionization and transport for realistic discharge plasmas.

\[
\left[ \frac{\partial}{\partial t} + (\mathbf{v} \nabla) - e\mathbf{E} \frac{\partial}{m \partial \mathbf{v}} \right] f = \sum_k \left[ v_k^* \frac{\sqrt{u'}}{\sqrt{u}} f(w + w'_k) - v_k^* f \right] + St_{ee},
\]

\[
\frac{\partial n_i}{\partial t} + \nabla (\mathbf{v} n_i) = v_{iz} n_i, \quad v_{iz} n_i = \int_{I} f(u) v \sigma_{iz} \, d\mathbf{v}
\]

\[
\nabla \mathbf{E} = 4\pi e (n_i - n_e)
\]

\[
M_i \left( \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \nabla) \mathbf{v} \right) = e\mathbf{E} - \frac{\nabla p_i}{n_i} - (v_{ia} + v_{iz}) \mathbf{v}
\]

EEDF in decaying plasma

Fig. EEDF afterglow Ar:NF$_3$. E/N=2 $10^{-17}$Vcm$^2$

- 1, 2, 3, 4, 5, 6.
- 0, 0.25, 1, 3, 5, 10 ns.


Strong energy losses due to vibrational excitation

Fig. density as function of time in decaying plasma
5. Particle-in-cell codes (PIC)  
Preferred Computational Tool - PIC

Parallel, implicit particle-in-cell code with energy corrections and noise control is a powerful and versatile tool.

- Ease of coding
- Modular, “easy” for parallelization
- Modern clusters and multi cores PCs are cheap
Selected PPPL computational and scientific accomplishments using PIC

Self-organized structures in magnetized plasmas

A. Powis, et al., 2018

Non-Maxwellian Electron Velocity Distribution in thrusters

D. Sydorenko, I. Kaganovich, et al. 2010

Breakdown in high voltage devices

L. Xu, et al. 2019

Effect of weak magnetic field on radio-frequency discharge

S. Sharma, et al. 2019
3D code for Plasma Panel Modeling

Up to 250 million of ions and electrons on up to 64 processors, up to 150x150x150 meshes

Discharge evolution experiment

Top view

Side view

6. Quantum Chemistry Codes

Quantum chemistry calculations for predictions of carbon and boron nitride nanotube synthesis mechanisms, see nano.pppl.gov

**Carbon chains and fullerenes**

**Carbon diffusion**

**Boron nitride fullerenes**

- B: bombarded with BNH molecules
- T=2000K

**Boron nitride feedstock evolution**

- Pressure 1 atm.
- Solid BN formation
- Boron condensation

- Boron – 45%
- Nitrogen – 55%

**Boron nitride tubes formation**

- Species density, m^3
- Temperature, K
Conclusions

- Plasma processing is a multibillion dollar industry in revenues with inadequately funded fundamental research support.

- Semiconductor equipment requires precise control of plasma surface interaction. Partially-ionized plasmas allows for such control because of great availability in choices of electron, ion and photon energy distribution functions that can be designed and controlled according to required specifications.

- Industry will greatly benefit from innovative methods of designing electron, ion and photon energy distribution functions delivered to required surfaces.

- Examples of such innovative methods for crafting electron, ion and photon energy distribution functions have been recently developed.
PPPL Princeton Collaborative Research Facility

- Established by DOE FES
- PPPL is the lead
- Emphasis: Integrated experimental and modeling efforts on LTP
- Research staff: 6
- Has external research collaboration program (User Program)

Research topics:
- Interactions between plasma and solid state
  - Plasma-induced surface modifications
  - Surface-induced effects on plasma
- Interfacial plasma
  - Plasma-liquid interactions
- Coherent structures
  - Nanoparticles-plasma interactions
  - Turbulence in plasma
Hall Thruster Experiment (HTX) • Total lab space exceeds 5000 sq. ft • Host unique plasma sources and advanced diagnostics for LTP plasmas and applications • Supported by DOE (FES, BES), DOD [http://htx.pppl.gov](http://htx.pppl.gov) & [http://nano.pppl.gov](http://nano.pppl.gov)

Laboratory of Laser Diagnostics

Laboratory for Plasma Nanosynthesis

Surface Science Lab

+ Princeton University Facility, see talk by A. Dogariu
PCRF LTP diagnostics available at PPPL

- Unique combination of ns/DC diagnostics of low to high pressure plasmas, nanoparticles and secondary electron emission & charging

+ Princeton University Diagnostics, see talk by A. Dogariu
Computational Tools for LTP Modeling

• Particle-in-cell codes (2D EDIPIC, 3D PPPL-modified LSP)
  – state of the art collision models and plasma-surface interaction, validated by numerous benchmarks

• Fluid codes (3D ANSYS)
  – implemented sheath models, MHD effects, surface interface

• Molecular Dynamics (DFT-TB)
  – DFT codes: full and tight binding approximation, CMD (classical potentials), KMC –kinetic Monte Carlo, and thermodynamic code for chemical composition.