Non-invasive measurements of plasma parameters via optical emission spectroscopy

Amy Wendt

Dept. of Electrical and Computer Engineering
University of Wisconsin - Madison

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• Collaborators and students
  ▪ Dr. John Boffard, UW Physics Dept.
  ▪ Prof. Chun C. Lin, UW Physics Dept.
  ▪ Shicong Wang, UW ECE Dept.
  ▪ Cody Culver, UW Materials Science Program
  ▪ Nathaniel Ly, UW ECE Dept.
  ▪ Dr. Ryan Jung, UW Physics Dept. (now at IBM)
  ▪ Lauren Aneskavich, UW ECE Dept. (now at Rockwell Automation)
  ▪ Dr. Svetlana Radovanov, Applied Materials Corp.
  ▪ Dr. Harold Persing, Applied Materials Corp.

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Low-temperature plasma applications

- applications are diverse
- manipulating plasma is a means to control technological outcomes
- diagnostic tools are needed to improve plasma science understanding
LTPs are non-equilibrium systems

- **EM power input**
- **Plasma**
  - $e^{-} (1-10 \text{ eV})$
  - ions (cool)
  - neutrals (cool)

- $e^{-} + A \rightarrow$
  - *excitation (glow)*
  - *ionization (sustains plasma)*
  - *high-T chemistry in low-T gas*

- **energetic electrons are key link in process outcomes**
Electron energy distribution functions

- Maxwellian EEPF appears as straight line -
  - corresponds to thermodynamic equilibrium within electron population
  - characterized by single parameter - $T_e$

- RF inductively coupled plasmas: EEDFs with ‘depleted’ high energy ‘tails’
  - attributed to:
    - inelastic collisions
    - escape to walls

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Godyak et al., PSST 11, 525 (2002)
Presentation Outline: Optical diagnostics for plasma characterization

• Optical emission spectroscopy of argon-containing plasmas
  ▪ emission model for determination of
    ♦ EEDF, $T_{eff}$
    ♦ metastable and resonance level densities
    ♦ electron density - $n_e$
    ♦ Example: non-Maxwellian EEDFs in inductively coupled plasma

• Real-time plasma monitor
  ▪ metastable and resonance level densities - $n_m$ and $n_r$
  ▪ effective electron temperature - $T_{eff}$
  ▪ electron density - $n_e$

• VUV detection
  ▪ resonance level densities - $n_r$ - as a proxy for Ar VUV flux
Each plasma emits distinctive spectrum


- Also, plasmas with the *same* gas changes colors with conditions
Partial Ar energy level diagram

- Allowed transitions resulting in photon emission
• Ultimate Goal: use emission spectra to extract encoded information about plasma conditions
Inductively coupled plasma (ICP)

- Operates in Ar and Ar mixtures at 13.56 MHz
- Electron energy distribution functions (EEDF)
  - Langmuir probes
  - Optical diagnostics
Determining plasma properties from spectrum: emission model

- **Goal:**
  - predict photon emission rate $\Phi_{ij}$ for $i \rightarrow j$

- **Approach:**
  - account for mechanisms that populate emitting state - level $i$
Emission model

• Goal:
  - predict photon emission rate \( \Phi_{ij} \) for \( i \rightarrow j \)

• Include:
  - electron excitation from level \( l \)
    - excitation probability is a function of electron energy
    - measured “cross sections” used to characterize excitation probabilities
Emission model - excitation cross sections

- cross section vs. electron energy
  - measure of electron impact excitation probability
  - key link between emission intensity and EEDF
  - measured by Prof. Chun Lin’s group:
    - excitation from ground state
      - *Ar. Data Nucl. Data Tables* 93, 831 (2007)
    - excitation from metastable levels
• Goal:
  - predict photon emission rate \( \Phi_{ij} \) for \( i \rightarrow j \)

• Include mechanisms for populating level \( i \):
  - electron excitation from level \( l \)
  - radiation trapping: excitation of metastables by photon absorption
Emission model - cascades

- **Goal:**
  - predict photon emission rate $\Phi_{ij}$ for $i \rightarrow j$

- Include mechanisms for populating level $i$:
  - indirect electron excitation from level $l$
  - cascades from higher lying states
  - measured cross sections include cascades
Emission model - electron excitation of metastables

- **Goal:**
  - predict photon emission rate $\Phi_{ij}$ for $i \rightarrow j$

- **Include mechanisms for populating level $i$:**
  - **electron excitation:**
    - from ground state
    - from metastable/resonance levels
  - **photon reabsorption/trapping**
    - from metastable/resonance levels
Excitation from resonance levels $1s_2$ & $1s_4$

- $1s_3$ and $1s_5$ are *metastables*:
  - no radiative losses
  - high concentrations possible
- $1s_2$ and $1s_4$ populations significant when radiation is trapped:
  - $1s_2$ and $1s_4$ resonance levels:
    - have radiative decay channel to ground state
    - generally lower concentrations
    - exception: reabsorption when ground state density is high
  - *Electron impact excitation from resonance levels significant*:
    - cross sections not measured
    - estimates used
Cross sections: variations in threshold and energy dependence used in model

- 419.8 and 420.1 nm - close in wavelength
- difference between ground state and metastable cross sections
- large difference in peak intensities at 1 mTorr vs. 25 mTorr
  - higher ground state contribution at higher $T_e$

Emission model: summary

- **Model goal:**
  - predict photon emission rate $\Phi_{ij}$ for $i \rightarrow j$

- **Effects included:**
  - electron excitation from level $l$
    - cascades
    - metastable contribution
  - radiation trapping

- **Needed inputs**
  - atomic data ($A_{ij}$, cross sections, ...)
  - electron energy distribution function
  - number densities (ground state AND $1s_y$ for argon)
Emission model: intensity of $i \rightarrow j$ transition

$$\Phi_{ij} = Kn_e R_{ij} \left[ \sum_l n_l k_{ij}^l \right]$$

- sum over initial level $l$ (ground state, $1s_2$, $1s_3$, $1s_4$, $1s_5$)
- $k_{ij}^l$ is the electron impact excitation rate
  - depends on cross sections, EEDF

$$k_{ij}^l = \sqrt{\frac{2}{m_e}} \int_0^\infty Q_{ij}^l(E) f_e(E) \sqrt{E} dE$$

- reabsorption correction factor $R_{ij}$ is function of $1s_y$ concentrations
- use ratios to standard line to eliminate $K, n_e$

$$\frac{\Phi_{ij}}{\Phi_{i'j'}} = \frac{R_{ij} \sum_l n_l k_{ij}^l}{R_{i'j'} \sum_l n_l k_{i'j'}^l}$$

- calculate line ratios for multiple trial EEDFs
- seek EEDF giving best match to observed line ratios
Trials for Maxwellian EEDF

- minimum $\chi^2$ gives best fit electron temperature

![Graph showing reduced $\chi^2$ vs. $T_e^{OES}$ for different pressures.]

- $T_e^{OES} = 2.4$ eV at 15 mTorr
- $T_e^{OES} = 5.5$ eV at 2.5 mTorr

Wednesday, December 10, 14
Emission model predictions

- contributions from ground state vs. $1s_y$ levels

**2.5 mTorr**

$T_{\text{eff}} = 5.4 \text{ eV}$

$n_n/n_0 = 1.4 \times 10^{-3}$

**15 mTorr**

$T_{\text{eff}} = 2.7 \text{ eV}$

$n_n/n_0 = 3.2 \times 10^{-4}$
Application:
Non-maxwellian EEDFs in ICPs
Inductively coupled plasma source

- 2.5 turn flat coil antenna
- 13.56 MHz
- 50 cm diameter chamber
- measure emission model inputs
- compare EEDFs with independent measurements

<table>
<thead>
<tr>
<th>gas</th>
<th>variable</th>
<th>pressure (mTorr)</th>
<th>Power (W)</th>
<th>( n_e ) (cm(^{-3}))</th>
<th>( T_e ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>pressure</td>
<td>1-50</td>
<td>600</td>
<td>(10^{10}-10^{12})</td>
<td>2-6</td>
</tr>
<tr>
<td>Ar</td>
<td>power</td>
<td>2.5, 15</td>
<td>20-1000</td>
<td>(10^{9}-10^{12})</td>
<td>5, 3</td>
</tr>
<tr>
<td>Ar/N(_2)</td>
<td>0-86% N(_2)</td>
<td>2.5, 15</td>
<td>600</td>
<td>(10^{10}-10^{11})</td>
<td>5, 3</td>
</tr>
<tr>
<td>Ar/Ne</td>
<td>1-40% Ar</td>
<td>10</td>
<td>600</td>
<td>(10^{10}-10^{11})</td>
<td>3-6</td>
</tr>
<tr>
<td>Ne</td>
<td>pressure</td>
<td>5-25</td>
<td>600</td>
<td>(1-3 \times 10^{10})</td>
<td>5-7</td>
</tr>
</tbody>
</table>

Wednesday, December 10, 14
Model input: ground state density

- $n_0 = \frac{p}{kT_{\text{gas}}}$
- Gas temperature determined with laser absorption spectroscopy
- Doppler width of $3p^54s-3p^54p$ transition line
Model input: optical emission spectrum (OES)

- 300-1600 nm wavelength range
- 0.13 nm resolution
- Detectors:
  - PMT 300-870 nm
  - Ge detector: 300-1600 nm
Model input: $1s_y$ concentrations

- **Method #1**: optical absorption spectroscopy (OAS)
  - white light absorption
  - column density measurement
- **Method #2**: OES (next slide)

![Spectroscopy Diagram]

Transmission vs. Wavelength (nm)

- 25 mTorr
- 1.0 mTorr

Wavelengths:

- 419.83 nm
- 420.07 nm

Transmission values:

- 0.990
- 0.992
- 0.994
- 0.996
- 0.998
- 1.000

- 150 W Xe arc lamp
- 0.5 m spectrometer
- 1024 pixel photodiode array
- 10 cm
- 50 cm path length
- 2.5-turn antenna
- Inductively-coupled 13.56 MHz plasma
Metastable/resonant densities from OES

• Method #2: OES
• OES preferable due to simplified instrumentation
• OES branching fraction technique:
  ▪ takes advantage of reabsorption by 1s_y metastable and resonance levels
  ▪ reabsorption changes branching fractions
  ▪ use ratio of lines from same upper state

\[
\frac{\Phi_{ij}}{\Phi_{ij'}} = \frac{A_{ij}^0}{A_{ij'}^0} \frac{g[\kappa_{ij}(n_j)\rho]}{g[\kappa_{ij'}(n_{j'})\rho]}
\]

▪ extract set of \( n_j \) densities from fit of model to observed ratios of different line pairs

\( \lambda_{ij} \)

\( e^- \) excitation

\( \kappa_{ij} \)

2p_x

1s_y
Metastable/resonant densities from OES

- OES method agrees with OAS over wide parameter range
  - simple, non-invasive method to determine 1s$_y$ densities

![Graph showing comparison of OES and OAS methods]

J. B. Boffard et al., PSST 18:035017 (2009).
Compare emission model with EEDF from Langmuir probe

\[ f_e(V) = \frac{2m_e}{e^2 A} \sqrt{\frac{2eV}{m_e} \frac{d^2 I}{dV^2}} \]

- compare to emission model output
Comparison assuming **Maxwellian** EEDF

- $T_e$ computed from
  - emission model
  - Langmuir probe fit
  - *agreement not great*

- reason for poor fit
  - EEDF is *not* Maxwellian
  - *actually, EEDF “tail” is depleted compared to Maxwellian*

- other (less likely) possibilities:
  - incorrect $n_i$ values
  - incorrect cross sections
Non-Maxwellian EEDF

- Langmuir probe measurement in ICP shows “tail” depletion

![Graph showing electron energy distribution function (EEDF) with Maxwellian fit and probe measurement data. The graph represents the electron energy density (EEPF) in units of cm\(^{-3}\) eV\(^{-3/2}\) as a function of electron energy in eV. The conditions are 20 mTorr and 600 W.]
Representing EEDF in emission model

- Goal: account for non-Maxwellian energy dependence
- use “generalized $x$-form”

$$f_x(E) = c_1 T_x^{-3/2} \sqrt{E} e^{-c_2 (E/T_x)^x}$$

- $T_x$ is an effective electron temperature ($T_x=2/3\langle E \rangle$)
- $c_1$ and $c_2$ are functions of $x$
- $x=1$ corresponds to a Maxwellian
- $x=2$ corresponds to a Druyvesteyn
- $x$-form good fit for most ICP conditions
EEDF with $x=1.2$

- example shows improved fit to Ar probe data
- $x$ ranges from $x=1.2$ to $x=1.6$ for Ar ICP
OES also produces $x=1.2$

- emission model agrees well with measurement*

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Extension to Ar($3p^55p$) emissions - limitations

- $3p_x$ levels have longer radiative lifetimes than $2p_x$ levels
  - $2p_x$ levels: 20-35 ns
  - $3p_x$ levels: 80-160 ns

- Longer radiative lifetime increases chances of electron-atom collision while atom is in excited level
  - electron-quenching: non-radiative decay out of level
  - electron-transfer: excitation from $3p_x$ to another $3p_x'$ level
  - emissions redistributed
  - need modified emission model

- **Bonus**: modified emission model predicts electron density
Emission model including 2p and 3p

- agreement with probe: ±7%

![Graph showing temperature comparison between different mixtures and OES data.](image)
Ar pressure dependence

- Comparison of a) Maxwellian and b) x-form for
  - Probes (solid)
  - OES (open)
  - ‘global’ model (line)
- Global model
  - Volume averaged
  - Particle balance – ionization rate must match wall losses
Conclusions: Non-Maxwellian EEDFS

- Non-Maxwellian EEDFs have been observed using Ar emissions for wide range of ICP conditions
  - sensitive to fairly subtle changes in EEDF
  - “x-form” of EEDF well suited for ICP
    - captures EEDF tail depletion

- OES - BF is a simpler alternative to absorption spectroscopy to determine $1s_y$ concentrations

- Emission model must include contributions from:
  - excitation to higher lying states followed by cascade
  - excitation from metastable/resonance levels
  - reabsorption by metastable and resonance levels
  - electron-driven transfer between emitting levels closely spaced in energy
    - Bonus: allows determination of electron density $n_e$
Real-time monitor of plasma conditions: time-varying and pulse-modulated ICP
OES plasma diagnostics in real time

- Verity spectrograph
  - fast spectra acquisition
  - compact
  - low-resolution (~1 nm) spectra (200-800 nm)
  - similar to systems often included on plasma process equipment
Flow chart for real time measurements

Other

MFC settings

pressure

$T_{gas}$

Ar fraction for gas mixtures

$n_{gs}$

OES measurements

696 nm

707

715

727

738

795

738 nm

750

763

772

795

360 nm

383

750

$n_m, n_r$

OES-BF analysis

emission model

$T_{eff}$

electron-quench Line ratio

$n_e$
Pure Ar: real time/pressure varied

- Computer controlled time-varying Ar pressure; power held fixed at 600 watts
- Plasma parameters evolve in time in response to pressure change
- Solid lines show instantaneous measurements vs. time
- Dots are static measurements made with the same parameter settings
Pure Ar: real-time/powered varied

- Computer controlled time-varying Ar power; pressure held fixed at 15 mTorr
- Plasma parameters evolve in time in response to pressure change
OES plasma diagnostics: gas mixtures

• Challenge: difficult to separate OES lines
  – from neighboring Ar lines
  – from molecular OES features
OES plasma diagnostics in real time

- Computer controlled Ar and N\textsubscript{2} flow rates; pressure held fixed at 15 mTorr, power at 600 W
Detection of VUV in argon-containing ICP
Overview

- VUV flux to wafer matters in plasma processing for integrated circuit manufacturing (and other applications!)

- Diagnostic challenge: no way to non-invasively measure VUV flux directly
  - VUV is *not* transmitted by windows or air

- In Ar containing plasmas, VUV is emitted by resonance level atoms. We posed the following question: can non-invasive measurements of $n_r$ serve as a proxy for VUV?

- Experimental evidence indicates the answer is a *qualified* “yes”…
VUV Photon Flux Detection – 2 methods

- Windowless NIST photodiode installed below ground electrode
- Relative VUV flux detected through visible fluorescence from sodium salicylate coated viewport
Sodium salicylate signal: sensitive at wavelengths beyond photodiode limit

Due to different wavelength dependent sensitivities, relative signal strengths for photodiode and sodium salicylate vary with gas type.

Ar energy levels

104.8 nm
106.7 nm

3p^6 ground state
Non-invasive measurement of resonance level density

Branching Fraction

- Intensity ratios altered by reabsorption in quantifiable way
- Reabsorption is a known function of resonant level density

PSST 18 (2009) 035017
Radiation model predicts VUV signal

• Model elements

  ▪ Local VUV emission is proportional to resonance density

  ▪ Chance of emitted photon reaching VUV photodiode depends on:
    ♦ Geometry – line of sight through pinhole
    ♦ Reabsorption – “escape factor” depends on \( n_{\text{gas}} = \frac{p}{kT_{\text{gas}}} \), thus:
      • Gas pressure, \( p \)
      • Gas temperature, \( T_{\text{gas}} \)

• Both photodiode signal and VUV flux to walls calculated
Non-invasive measurement of gas temperature

Diode laser absorption

Gas density $n = \frac{p}{kT_{gas}}$ decreases as $T_{gas}$ increases.
Pressure scan - Ar

Resonance density

VUV (predicted by model)

VUV flux decreases with pressure due to enhanced reabsorption.
Power scan - Ar

Resonance density

VUV prediction

VUV flux increases with increasing power – rarefaction leads to diminished reabsorption.
VUV photon flux in Ar ICP from photodiode and sodium salicylate agree with model

- At higher pressures, radiation reabsorption increases due to increased ground state atom concentration.

- At constant pressure, VUV photon flux increases with power when excited state densities increase.

- Model is in accord with photodiode and sodium salicylate data
VUV flux at electrode location

VUV photon flux is greater than ion flux for all conditions
Ar/N₂ plasmas - Ar model works due to no N₂ emissions in VUV range
For Ar/H₂, H, H₂ VUV (90-180 nm) emissions add to Ar signals at 104.8 & 106.7 nm.

H₂ contributions decrease with Ar dilution.

H, H₂ emissions dominate sodium salicylate signal.

PD barely sensitive to H, H₂ emissions.

Ar resonance level density increasing.

VUV Photodiode Current (nA)

Sodium Salicylate Signal (arb. units)
VUV: concluding remarks

- Non-invasive VUV detection has been demonstrated

- A radiation model has been developed to infer VUV fluxes:
  - Inputs: measured resonance level density, Ar pressure, gas temperature
  - The model accounts for VUV reabsorption in plasma

- VUV fluxes from model in Ar agree with direct measurements using
  - VUV photodiode
  - Sodium salicylate fluorescence

- For Ar/N\textsubscript{2} mixture, the model works well because only Ar contributes to VUV emissions

- For Ar/H\textsubscript{2} mixture, H and H\textsubscript{2} contribute to VUV emissions – relative contributions inferred by combining Ar model and sodium salicylate measurements
Summary

- OES offers a promising approach to plasma characterization
  - Non-Maxwellian EEDFs, electron density and effective temperature
  - metastable concentrations
  - real-time plasma parameters
  - VUV
  - method is
    - non-invasive
    - applicable in rare gas containing plasmas
    - applicable in conditions where Langmuir probes impractical

- Successfully applied to low-pressure ICP - what about higher pressure?