Inductively-coupled plasmas in Cl\textsubscript{2} and O\textsubscript{2}: Comparing HPEM with advanced diagnostic measurements

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Motivation

Most academic studies..

Diatomic gas plasmas

Rare gas plasmas: Ar

Diatomic gas plasmas

Mixtures of polyatomic gases:
- $C_4F_8/O_2/Ar$
- $SiH_4/H_2$
- $Cl_2/HBr/O_2$

Diatomic gases show most of the mechanisms occurring in polyatomics:
- Dissociation, surface recombination
- Electronegativity
- Vibrational + rotational excitation

But fewer particles, easier to measure

Most applications..
What we can measure and how

- Atoms \( \rightarrow \) TALIF
- Molecules (n,T) \( \rightarrow \) UV Absorption Spectroscopy
- Electrons \( \rightarrow \) Microwave Hairpin probe
- Negative ions \( \rightarrow \) Laser photodetachment + HP

Measurements in:
- Pure O\(_2\)
- Pure Cl\(_2\)
- (Cl\(_2\)/O\(_2\) mixtures)

Comprehensive data set
- Validate/improve models of molecular gas plasmas:
  - Global models,
  - HPEM (2D Hybrid fluid model)
The Inductively coupled plasma reactor at LPP:

- Industrial Scale Reactor dimension for 300mm wafers
- Industrial gases (Cl₂, HBr)

Pressure: 5-100 mTorr
Power: up to 500W

- All surfaces Al₂O₃ (no substrate)

Chamber: Anodized aluminium Ø 55cm height 10cm

13.56 MHz power supply
4 turn spiral antenna
Al₂O₃ window
Atom densities: Two-Photon Absorption Laser-Induced Fluorescence (TALIF)

- High spatial and temporal resolution measurements
- Relative densities of ground-state Cl and O atoms
- Absolute densities: use calibration techniques

Niemi et al.: PSST 14 (2005) 375-386
Absorption spectroscopy: high-sensitivity ultra-broad-band

Baseline noise $\approx 10^{-5}$, 250nm spectrum simultaneously
Electron density: Hairpin probe

$\frac{1}{4}$ wave resonator: $\sim 3$ GHz:
- measure plasma permittivity from frequency shift with plasma
- deduce electron density from permittivity

Avoids many of the problems of Langmuir probes:
- Probe contamination
- Return current path (insulating reactor walls!)
- RF compensation

Negative ions: detect electron pulse from laser photodetachment
Pure Cl\textsubscript{2}:
Electron densities

Very marked maximum at \( \sim 10 \) mTorr

Electron density \( (10^{10} \text{ cm}^{-3}) \)
Pressure (mTorr)

Pure Cl\textsubscript{2}
Simulations: Cl\textsubscript{2} 20 mTorr 500W

Difficulty of comparison Model/Experiment:

- **Experiment**: measure trends of one variable at one point as external conditions varied
- **Model**: one set of external conditions
- outputs all variables at all positions;
- Trends slow to simulate
Electron density at 200W: Expt vs model

Experiment shows sharp drop at low pressure (<10 mTorr)

- not seen in model?

⇒ Capacitive coupling?
Effect of capacitive coupling: 200W

Capacitive coupling causes gradual decrease in electron density at low pressure, but does not explain the discrepancy.

Power coupling efficiency?
- Coil resistive losses vary less than 10% over this range
Electron density radial profile:
Cl\textsubscript{2}, mid-plane 500W

Up to 10 mTorr: Centre maximum
Electron density radial profile:
Cl$_2$, mid-plane 500W

Above 10 mTorr:
Maximum moves away from centre:
“Doughnut” shape under the spiral antenna

Centre density drops at higher pressure
Simulations show electron density moving off-axis at high pressure.
Pure Cl$_2$:
Atom density

With RF power: increases but saturates
– full dissociation?
Pure Cl₂: Atom density

Normalised to initial Cl₂ density:

\[ \frac{n_\text{Cl}}{n_\text{Cl}_2^0} \]

Dissociation maximal at lowest pressure
25% at 2 mTorr
> 10% at pressure > 5%!

Gas Temperature?
Cl atom density: 200 W

Good agreement for atom densities
Gas temperature:
From Ar\textsuperscript{m} IRLAS (line integrated)

Temperature reaches 1200K (expt)
2000K (model)

Trend at low pressure?
Spatial variation?
Gas temperature:

simulation 20 mTorr

simulation 100 mTorr

Pressure trend at 500W

NEW Technique: Doppler resolution TALIF
- Directly measure atom translation temperature
- Point measurement
Absorption spectra in pure Cl₂

No plasma

Absorbance ($10^{-3}$)

Wavelength (nm)

60 mTorr
Pure Cl$_2$

Increasing power

Cl$_2$ depletion saturates at about 50%

dissociation or gas heating?

-cold, undissociated gas persists close to walls

Little evidence of vibrational excitation
Pure Cl$_2$ : Summary

Atom density saturates at less than $\approx$10% of initial gas density due to:
- gas heating/expansion
- rapid recombination at chamber walls

Translation temperature up to 1200K
Pure O$_2$:
Electron density

Broad maximum @ 40 mTorr
Electron density :O2 200 W

Better agreement than for Cl₂: Predicts maximum at the correct pressure

Electron density moves off-axis
Pure O$_2$ : UV absorption

Cold O$_2$ does not absorb above $\approx$200nm....
Pure O₂: UV absorption

Cold O₂ does not absorb above ≈200nm....
O\textsubscript{2} Potential energy curves

B← X Schumann-Runge bands:

High vibrational levels of X ground state overlap with low (bound) levels of B state
Pure $O_2$:
UV absorption

Levels up to $v'' \approx 18$
Half-way to dissociation!

![Graph showing absorbance levels up to $v'' \approx 18$]
Pure O\textsubscript{2}:
Vibrational temperature

Fit the vibrational bands

\[ T_{\text{vib}} = 10,000K \ (v' = 12-16) \]

Not currently included in HPEM
Pure O₂ : UV absorption

What about rotational (∼ translational) temperature?

Look at one band in higher resolution: Change grating from 300l/mm to 2400l/mm:
Pure O$_2$: UV absorption

Increase resolution: Change grating from 300 l/mm to 2400 l/mm:

![Graph showing UV absorption spectra of Pure O$_2$.]
Pure $\text{O}_2$: Rotational temperature

Fit to simulated spectra to determine $T_{\text{rot}}$: up to 850K!

At these pressures $T_{\text{trans}} \approx T_{\text{rot}} \ll T_{\text{vib}}$

Gas temperature up to 900K
Gas temperature:
Pure O2 200 W

Excellent agreement!
Pure $O_2$: Atom density

O density increases:
- with pressure
- with RF power: but saturates

→ Is this full dissociation?
Pure O₂: "Dissociation degree"

Divide atom density by nominal gas density (assuming room temperature gas):

Maximal at 10 mTorr  
(nₑ maximum at 40 mTorr)

Dissociation saturates @ 20-30%  
Saturation not due to full dissociation!

→ due to gas heating
Pure O$_2$ : Summary

Atom density saturates at $\approx$20% of initial gas density due to combination of gas heating/expansion and rapid recombination at chamber walls.

O$_2$ rotation/translation temperature up to 850K
O$_2$ vibrational temperature : tail at 10,000K
Comparing sophisticated models with comprehensive diagnostics
  - only way to clarify the dominant mechanisms

Difficulties in comparing model to experiments:
  - Pressure/power trends vs 2D full data for one set of conditions
  - Strong non-uniformities:
    - Centre values? Line averaged values? Maximal values

Gas temperature defines gas density
  - very important to model properly
  - multiple gas heating mechanisms possible

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