Unraveling the Complex Processes in a Fluorocarbon Plasma

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OUTLINE

• Plasma Chemistry in a nut shell

• Approaches to solving this complex problem

• Our approach - mGEC

• Results

• Implications

• Acknowledgements
Plasma Chemistry in a nutshell

- Parent Gas
- Sticking Coefficient
- Gas-phase reactions
- F Density
- F\(^+\) Density
- CO\(_2\) Density
- CO Density
- SiF\(_4\) Density
- COF\(_2\) Density
- CF\(_4\) Density
- CF\(_3\) Density
- CF\(_2\) Density

- Plasma-gas reactions
- Surface-phase reactions
- Surface-phase reactions
- CF\(_2\) Density
- e\(^-\) Density
- CF\(_3\) Density
- CF\(_4\) Density
- F\(_2\) Density
- F Density
TYPICAL INTERACTIONS IN A PLASMA SYSTEM

• PLASMA PHYSICS SUBSYSTEM
  – Gas collision processes
  – Surface collision processes

• GAS PHASE CHEMISTRY SUBSYSTEM
  – Feed gas
  – Collisions with plasma (electrons)
  – Collisions with other gases
  – Collisions with surfaces

• SURFACE CHEMISTRY/PHYSICS SUBSYSTEM
  – Surface reactions
  – Liberation of gas-phase chemicals
So how does one solve this complex problem?
Often experiments are setup to study individual aspects of the process.

- Examples include (but are not limited to):
  - Coburn and Winters
  - Fisher (interaction of plasma generated radical beams with surfaces)
  - Aydil (surface coverage and chemistry in plasma processing tools)
  - Oehrlein (polymerization and surface chemistry in processing plasmas)
  - Lawler (gas phase densities in lighting and other environments)
  - Schoenbach (micro-hollow cathode light sources)
  - Graves (prepared radical and ion beam interactions with surfaces)

Models can control all aspect of the process.

- Examples include (but are not limited to):
  - Kushner (numerical simulations of plasma processes and chemistry)
  - Graves (MD simulations)
  - Economou (numerical simulations of plasma flow and chemistry)


Coburn and Winters, J. Appl. Phys. 50, (1979)
or In “Glow Discharge Processes” by Chapman (Wiley, 1980) p317
Experimental work from Fisher, *et al.*

- Imaging Radicals Interacting with Surfaces (IRIS) system
  - Radicals produced in remote plasma
  - Passed as molecular beam to sample chamber
  - Material sample moved into and out of beam
  - Use Laser induced Fluorescence used to compare
  - P.R. McCurdy, (Fisher), *et al.*, RSI 68 1684 (1997)

- Example results from CF$_2$ on SiO$_2$
  - 300 K surface
  - From C$_2$F$_6$ Plasma
  - LIF signal for the CF$_2$ (0,11,0) state
    a) without surface, b) with, c) difference
Experimental work from Fisher, *et al.*

- Fisher finds that scattering depends on material

- This result is important to our conclusions
Molecular Dynamics models by Graves, et al.

- Molecular Dynamics follows the movement of 1000’s of particles
  - Interaction with incoming particles
  - Include as many chemical and physical processes as possible

- Example
  - a-Si bombarded by 2 monolayers (ML) of 200 eV Ar⁺
  - Shows initial and final positions of initial surface (top) and initial bulk (bottom) atoms
Molecular Dynamics models by Graves, et al.

- Chemistry is found to play a role in this process
  - Example results
  - Elemental profiles and structure depend on incoming flux - CF$_2$ F and Ar$^+$
    - a = 9, 0, 1
    - b = 8, 1, 1
    - c = 7, 2, 1

- The shift in species density seen here is important to our conclusions

Increasing F/CF$_2$ flux ratio
Plasma models by Kushner, *et al.*

- Full model of complete system
  - Use a hybrid (fluid and Monte Carlo) to predict
    - plasma (ions and electrons)
    - Neutrals (all radicals)
  - Requires ‘knowing’ all reaction rates
  - This is the well known “Hybrid Plasma Equipment Model” - HPEM
Plasma models by Kushner, et al.

- HPEM now used to routinely predict gas phase densities
  - 2-D and 3-D versions
  - Example:
    » ICP reactor,
    » Ar/c-C_4F_8/O_2/CO feed gas
    » Predicted C_xF_y densities

- To further improve HPEM need to understand surface process
  - “We acknowledge that the dispositions of surface reactions are critical to the development of a successful reaction mechanism for the low-pressure plasmas of interest.”
TYPICAL INTERACTIONS IN A PLASMA SYSTEM

- **PLASMA PHYSICS SUBSYSTEM**
  - gas collision processes
  - surface collision processes

- **GAS PHASE CHEMISTRY SUBSYSTEM**
  - Feed gas
  - Collisions with plasma (electrons)
  - Collisions with other gases
  - Collisions with surfaces

- **SURFACE CHEMISTRY/PHYSICS SUBSYSTEM**
  - Surface reactions
  - Liberation of gas-phase chemicals
DESIGN CRITERION: Plasma and Gas Source

- Set out to build a system in which “ALL” free parameters on surfaces can be systematically controlled
  - Multiple diameters
  - Multiple source to chuck gaps
  - Multiple surface materials (Al, Al₂O₃, Si, etc)
  - Heated uniformly to 200±1 °C

- Use a well understood plasma source
  - Similar to GEC ICP reference cell source

- Use a simple Fluorocarbon gas
  - CF₄ (All data in talk)
  - C₄F₈ (Runs just starting)
Experimental Setup

Tools

- In situ Spectroscopic ellipsometer
  - Typical 240 to 800 nm
  - 633 nm for time resolved
  - Fixed angle (~ 72°)

- In situ Multi-Pass FTIR
  - 4 – 40 pass White- type cell with MCT cooled detector
  - Typical 16 passes, 512 scan averaging, 650 - 4000 cm\(^{-1}\)
Approach to study

- Use both experimental and modeling (HPEM) to understand complete system
  - With initial studies from standard GEC reactor (for comparison)

- mGEC studies
  - Modeling studies using HPEM include
    » Examined sticking coefficients
    » Chamber geometry
  - Experimental studies include
    » Etch/deposition rates (via ellipsometer)
    » Langmuir probe measurements (CF$_4$, Ar O$_2$)
    » Gas phase chemistry (FTIR, OES/acinominty)
    » Surface chemistry (via XPS, ATR-FTIR, FTIR)

- Want to understand how processes on substrate are influenced by
  - Walls (surface phase chemistry)
  - Gas
Initial HPEM Study of sticking coefficient

- Full DOE
  - 2 chamber diameters
  - 2 source-chuck gaps
  - 2 sticking coefficients (each specie)
    » 0% (no sticking)
    » 1%

» Sticking coefficient (SC) is the percentage of radicals impacting a wall that sticks
Initial HPEM Study of sticking coefficient

- Plasma parameters
  - Unaffected by sticking coefficients
  - Affected by chamber geometry

- Gas phase chemistry
  - CF, CF₂, CF₃ only affect themselves
  - F affects itself and other species

Effective sticking coefficients can be estimated by setting SC for F then adjusting the others to get the correct result

- Remember: This does not contain reactions on the walls

Still really need to understand what happens on the walls!
Approach to study

• Use both experimental and modeling to understand complete system
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• Want to understand how processes on substrate are influenced by
  – Walls (surface phase chemistry)
  – Gas

• Will start with standard results (etch rate) and compare to wall and gas results
SiO$_2$ etch rates studies vs reactor geometry

**Source-chuck gap**

- Increase in source height lowers deposition and etch rates as well as shifting the threshold
  - Decreased Neutral Flux and/or Ion Density? Different etch yield?

- Significantly larger decrease in dep, etch and threshold with presence of wall
  - Neutral flux limited by 20 cm wall? Ion density effected by gap?
SiO₂ etch rates studies vs reactor geometry

Wall Diameter

- Wall diameter non-influential at 4 cm source height.
- Wall diameter is influential at 6 cm source height
  - Wall causes a decrease in etch rate maximum and CFx deposition rates
  - Greater fractional loss of neutrals to the wall at 6 cm source height?
  - GAP DOES matter - why?
Influence of GAP
As a Function of Source Height

* Net power transmission decreased due to increased reflected power in matching network.

- Deposition occurs with decreasing Gap
  - Transition occurs at < 6 cm with wall; < 5 cm without wall
- Does the surface history matter?
Influence of GAP - History matters!

As a Function of Source Height

- Ion assisted deposition shows hysterisis
  - Dependent on pre-existing CFx film / ion assisted deposited film
  - Dependent on chemisorption sites?
  - Do ion energy or flux matter?
Ion Density
As a Function of Source Height
20 sccm CF₄ 400W, 38 mTorr

- Ion Density increases by an order of magnitude as the gap is decreased
- Ion energy increases by ~ 10 eV with Gap
  - Ion assisted deposition is only explanation for increased deposition
  - Wall plays role - How?
Surface (wall) deposition
FTIR data

- Etch of substrate (Si or SiO₂) => deposition on walls
- Deposition on substrate => cleaning CFₓ film from walls

Either etch or deposition can give handle on wall substrate interactions
The link is likely via the gas-phase chemistry
Will start with etch
IR Spectrum during CF$_4$ plasma
Data from Si substrate etch => deposition on walls

Typical IR spectrum from Si etch
Gas-phase chemistry studies

- Gas phase chemistry depends on a number of items
  - Si vs SiO₂ substrate
  - Etch vs deposition
  - Wall temperature
  - Wall diameter
  - Wall material
    » Clean
    » Seasoned
    » Others?? (Measurements starting)

We will be examining these to understand the etch/deposition processes

Conditions for next few slides:
- CF₄ - 10 SCCM, 5 mTorr,
- 400 W source, 70 W bias
- 5 cm gap, 20.3 cm Al wall
**Gas-phase data vs wall conditions, etch rates**

**Same conditions**

- **SiO\textsubscript{2}** etch is **not** dependent on
  - wall temperature
  - clean/seasoned

- **Si** etch is **dependent** on
  - wall temperature
  - clean/seasoned

**NOTE:** In both cases the etch surface temperature is constant!
Gas-phase data vs wall conditions, etch products

Same conditions

- Decreased SiF$_4$ density (‘confirms’ Si etch data)
- ~ Constant COF$_2$ density (‘confirms’ SiO$_2$ etch data)

NOTE: Gas temperature likely below ‘wall temperature’ - Other surfaces at ‘room’ temperature
Gas-phase data vs wall conditions, CF$_4$

Same conditions

- In comparison the feed gas density decreases drastically
  - Density drops slightly more than ideal gas law

  CF$_4$ breaks up a little more - or -
  CF$_4$ production on walls drops

- Breakup should be due to plasma
  - Plasma density and temperature approx independent of wall temperature
  - Increased breakup should not be significant

If less CF$_4$ produced at the walls
  Suggests increase in CF$_2$ and CF$_3$
  production from the walls
  OR
  Suggests decrease in CF$_2$ and CF$_3$ loss to the walls

![Graph showing CF$_4$ density vs wall temperature for clean and seasoned walls. Ideal gas law line is also shown.](c)
The major radicals in a CF₄ plasma are, CF, CF₂, CF₃.

CF is not observed in any configuration studied (=> n_{CF} \ll 5 \times 10^{11} \text{ cm}^{-3})

Under etch conditions:

- n_{CF₂} and n_{CF₃} are functions of wall temperature and wall conditions
  - As T_{wall} increases, both n_{CF₂} and n_{CF₃} up to a point
  - Dirty walls are source of radical up to \sim 450 \text{ K}

CFₙ film provides more CF₂, CF₃ to gas

Or

Less CF₂, CF₃ radicals lost to CFₙ film

Either way, we should be able to see by growing film on HOT substrates
Deposition rate vs substrate temperature and gap

No Bias - ‘cold’ walls

- Surface temperature measured on face of Si substrate.
- Deposition measured via ellipsometer
  - Each curve represents multiple runs on multiple days.
- Gap was varied from 4 to 5.75 cm
  - 5 mTorr CF4, 400 W power, chuck floating

- What do the curves tell us?

Region 1: exp drop
  - likely chem or physisorb

Region 2: linear drop
  - likely direct ion deposition

Region 3: exp drop
  - likely temperature driven desorption

Region 4: flat
  - likely limit set by ion bombardment rate
Initial interpretation of Temperature Data

• At first blush
  - Looks like trends seen with H₂O
    » Colder surfaces (0 °C) - Adsorption
    » Intermediate (~25 °C) - Balance
    » Hotter surfaces (100 °C) - Desorption

• If this holds then
  - Simple heating will result in desorption
    - Simple experiment can test this
      » Thick Film deposited
      » Plasma turned off
      » Feed Gas off
      » Heat the film and watch
Deposition (etch) rate vs substrate temperature and gap

- Desorption curve is similar in shape as high temperature part **but not at fast**
Gas-phase data vs wall conditions, CF$_4$

- The simplest mathematical model is:

$$DR \ C \ Ae^{E_a/RT} \ Be^{E_d/RT}$$

- This gives rise to fitting of

<table>
<thead>
<tr>
<th>Gap</th>
<th>$A$</th>
<th>$B$</th>
<th>$C$</th>
<th>$E_a$</th>
<th>$E_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm</td>
<td>nm/min</td>
<td>nm/min</td>
<td>nm/min</td>
<td>kJ/mol</td>
<td>eV</td>
</tr>
<tr>
<td>4</td>
<td>$8 \times 10^{-6}$</td>
<td>$5.65 \times 10^5$</td>
<td>95</td>
<td>-39.5</td>
<td>-0.41</td>
</tr>
<tr>
<td>5</td>
<td>$1.75 \times 10^{-6}$</td>
<td>$9.5 \times 10^5$</td>
<td>75</td>
<td>-42</td>
<td>-0.44</td>
</tr>
<tr>
<td>5.75</td>
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<td>41.5</td>
<td>-44.9</td>
<td>-0.47</td>
</tr>
<tr>
<td>Vacuum</td>
<td>$1.73 \times 10^3$</td>
<td>N/A</td>
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<td>33.4</td>
<td>0.35</td>
</tr>
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<td>CF$_4$</td>
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<td>N/A</td>
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<td>33.4</td>
<td>0.35</td>
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- $E_a$ is an adsorption process and represents an adsorption energy
  *These adsorption energies are the ~same! => energy physisorption*
  *Matches reported CF$_2$ adsorption energy - 39 kJ/mol => likely CF$_2$
  - Cruden, Gleason and Sawin, Ultraviolet absorption measurement of CF$_2$ in the parallel plate pyrolytic chemical vapour deposition process, J Phys. D 35 2002, 480*

- $E_d$ is an desorption process and represents an desorption energy
  *These desorption energies are the ~same! => energy non chemical*
Gas-phase data vs wall conditions, CF$_4$

- The simplest mathematical model is:

\[
DR \cdot C \cdot Ae^{E_a/RT} \cdot Be^{E_d/RT}
\]

- This gives rise to fitting of

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- The ‘constants’ A, B, C may be functions of other parameters
e.g. $A = A(n_F, n_{CF}, n_{CF2}, n_{CF3}, n_{CF}, \text{ion})$

- For example, the ion current (or flux $\text{ion}$) ratio is 1 : 0.83 : 0.72
  Lets compare this to A, B, C
Deposition model vs wall conditions

- Data suggests that C is linked to $I_{\text{ion}}$ and independent of $I_{\text{substrate}}$.
- We know that $n_{\text{CF}_2}$, $n_{\text{CF}_3}$, and $n_{\text{CF}_4}$ are constant.
- We also know that $E_a$ is linked to $\text{CF}_2$.
- We also know that $n_{\text{CF}_2}$, $n_{\text{CF}_3}$, and $n_{\text{CF}_4}$ are constant.

$C = \text{const}_{\text{ion}}$ in this regime.

This const (i.e. sticking coefficient) is $\sim 0.05$ or 5% if Teflon (~2% if porous).
One more bit of data

**XPS data of deposited films**

- **Type of Fluorine content in CF<sub>x</sub> film seems to governed by source height**
  - Likely n<sub>F</sub> / n<sub>CF<sub>x</sub></sub> increases with gap (We are trying to confirm this!)
  - A and B might be functions n<sub>CF<sub>x</sub></sub> / n<sub>F</sub> - where CF<sub>2</sub> is probably the primary fluorocarbon
So what do we know?

- Deposition rate follows

\[ DR \propto C \cdot Ae^{E_a/RT} \cdot Be^{E_d/RT} \]

- \( C_{\text{ion}} \) (\( C \approx 0.02 \))

- \( A \) and \( B \) - From \( E_a \) probably \( n_{\text{CF2}} \)

- If \( A \) and \( B \) \( n_{\text{CF2}} \) - Then why the drop with Gap?
  - Other radicals?
    - \( n_{\text{CF}} \) very low
    - \( n_{\text{CF2}}, n_{\text{CF3}} \) and \( n_{\text{CF4}} \) \( \sim \) constants with gap
    - BUT XPS data indicates \( n_F \) and gap (Still checking)

Perhaps \( A \) and \( B \) \( n_{\text{CF2}} / n_F \)
So what do we know?

- Assume that the deposited film is Teflon like
  (In reality it is probably very porous and highly cross linked!)

- The energy of the bonds are:

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ.mol(^{-1})</td>
</tr>
<tr>
<td>C-C</td>
<td>370</td>
</tr>
<tr>
<td>C-F</td>
<td>448</td>
</tr>
</tbody>
</table>

Incident ions probably break these bonds at similar rates

If so, we can create a simple model of the growth.
Simple picture of ion assisted growth

- Direct ion adsorption
- Ion induced adsorption/desorption
  - Ion impact can break C–F or C–C bonds
  - Growth can happen if C-F bond broken
    » CF_x fills broken bond
    » CF_x molecules need to be readily available => physisorbed radicals more likely to bond
    » Would cause very porous, highly cross linked films
  - Removal can happen if C–C bond broken
    » Form gaseous species by F addition (e.g. CF_4)
    » Light CF_x species can thermally desorb from the surface
Simple picture of ion induced growth

- This simple picture seems to explain a lot of the published results
  Examples:
  - Fisher’s work shows that the CF$_2$ scattering coefficient depends on the C-C cross linking
  - Graves’ work would suggest heavy cross linking (e.g. porous films) necessary for etch
  - Several authors CF$_2$ being produced at wall
  - ETC
Conclusions

• Deposition determined by
  – Chamber geometry
  – Surface temperature
  – Surface material

This is probably why results vary so much

• From experiments
  \[
  DR = 0.02_{\text{ion}} A \frac{n_{\text{CF}_x}}{n_F},_{\text{ion}} e^{\frac{E_a}{RT}} B \frac{n_{\text{CF}_x}}{n_F},_{\text{ion}} e^{\frac{E_d}{RT}}
  \]

• Ions seem to cause deposition through two processes
  – Direct ion incorporation - with \( \sim 2\% \) sticking coefficient
  – Ion induced chemisorption and desorption
    » Deposition two step - Physisorb -> Chemical bond
    » Desorption two step - Bond destruction via ion impact -> thermal desorption

• Probably explains \( \text{CF}_x \) layer in etch
Conclusions

- Still need to confirm functionality of A and B

- Still need to confirm ‘Sticking coefficient’ of ions
  - Likely ion species/energy dependent
  - Still need to examine

\[ DR \ Const_{ion} A e^{E_a/RT} B e^{E_d/RT} \]

0.02 \( A n_{CF_x} / n_F \), \( e^{E_a/RT} B n_{CF_x} / n_F \), \( e^{E_d/RT} \)

- Future studies will need to account for
  - Deposition Surface temperature
  - Etch surface temperature (?)
  - Ion flux
  - Ion energy (?)
  - ALL radical specie fluxes to surface
  - Surface type (?)
  - Chemistries (Working with C4F8 right now. Cl2 chemistries to be added soon.)
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