## Unraveling the Complex Processes in a Fluorocarbon Plasma

Matthew Goeckner

University of Texas at Dallas

This program was funded by a grant from NSF/DOE, contract number CTS-0078669



# OUTLINE

- Plasma Chemistry in a nut shell
- Approaches to solving this complex problem
- Our approach mGEC
- Results
- Implications
- Acknowledgements

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## **Plasma Chemistry in a nutshell**





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# **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

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## So how does one solve this complex problem?



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## **Studies of Interactions in a Plasma**



M.J. Kushner, et al., J. Appl. Phys. 80, 1337 (1996).

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## 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<sub>2</sub> on SiO<sub>2</sub>
  - 300 K surface
  - From  $C_2F_6$  Plasma
  - LIF signal for the CF<sub>2</sub> (0,11,0) state
     a) without surface, b) with, c)
     difference
  - C.I. Butoi, (Fisher), et al., JVSTA 18 2685 (2000)





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(c)

## Experimental work from Fisher, et al.

- Fisher finds that scattering depends on material
  - E.R. Fisher, Plasma Process. Polym 1, 13 (2004)

This result is important to our

•

conclusions



% Crosslinking

## 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<sup>+</sup>
  - Shows initial and final positions of initial surface (top) and initial bulk (bottom) atoms
  - D.B. Graves and D. Humbird , Appl. Surf. Sci. **192**, 72 (2002)



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## Molecular Dynamics models by Graves, et al.

Depth (Å)- Species density (arb) Chemistry is found to play a role in this process Example results Elemental profiles and structure depend on incoming flux - CF<sub>2</sub> F Increasing and Ar<sup>+</sup> (a) F/CF<sub>2</sub> » a = 9, 0, 1 flux ratio » b = 8, 1, 1 » c = 7, 2, 1 Si D. Humbird and D.B. Graves, JAP 96, 65 (2004) The shift in species density • seen here is important to our conclusions (C) **Plasma Science and Applications Laboratories** Matthew J. Goeckner

## 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
  - MJ Kushner, JAP **53**, 2923 (1982)



$$e + CF_{4} \xrightarrow{F,F_{2}} CF_{3}^{+} CF_{3}^{-} CF_{2}^{+} CF^{+} F_{1}^{+} F_{1}^{-} e^{-} e^{-} F_{1}^{+} F_{1}^{+} F_{1}^{-} e^{-} e^{-} F_{1}^{-} e^{-} F_{1}^{-} F_{1}^{-} F_{2}^{-} F_{1}^{-} F_{1}^{-} F_{1}^{-} F_{2}^{-} F_{1}^{-} F_{1}^{-} F_{2}^{-} F_{1}^{-} F_{1}^{-} F_{2}^{-} F_{1}^{-} F_{1}^{-} F_{1}^{-} F_{2}^{-} F_{1}^{-} F_$$

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## 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  $C_x F_y$  densities
    - » A.V. Vasenkov, Li, Oehrlein, Kushner, JVSTA 22, 511 (2004)
- 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."
    - » A.V. Vasenkov, Li, Oehrlein, Kushner, JVSTA 22, 511 (2004)



# TYPICAL INTERACTIONS IN A PLASMA SYSTEM



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# **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,  $Al_2O_3$ , Si, etc)
  - Heated uniformly to 200 $\pm$ 1 °C
- Use a well understood plasma source
  - Similar to GEC ICP reference cell source
- Use a simple Fluorocarbon gas
  - CF<sub>4</sub> (All data in talk)
  - C<sub>4</sub>F<sub>8</sub> (Runs just starting)







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## 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

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## **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

Wall diameter (cm)	Gap (cm)
20.32	10.16
20.32	15.24
66.04	10.16
66.04	15.24

F	CF	CF2	CF3	
0%	0	0	0	
0%	0	0	1%	
0%	0	1%	0	
0%	0	1%	1%	
0%	1%	0	0	
0%	1%	0	1%	
0%	1%	1%	0	
0%	1%	1%	1%	
1%	0	0	0	
1%	0	0	1%	
1%	0	1%	0	
1%	0	1%	1%	
1%	1%	0	0	
1%	1% 0		1%	
1%	1% 1%		0	
1%	1%	1%	1%	

# **Initial HPEM Study of sticking coefficient**



# Approach to study

- Use both experimental and modeling to understand complete system
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#### • mGEC studies

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# • Will start with standard results (etch rate) and compare to wall and gas results





• 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?

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- 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?

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## **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?

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## **Ion Density**



- Ion Density increases by an order of magnitude as the gap is decreased
- Ion energy increases by  $\approx 10 \text{ eV}$  with Gap
  - Ion assisted deposition is only explanation for increased deposition
    - Wall plays role How?

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- Etch of substrate (Si or SiO<sub>2</sub>) => deposition on walls
- Deposition on substrate => cleaning  $CF_x$  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





## **Gas-phase chemistry studies**

- Gas phase chemistry depends on a number of items
  - Si vs SiO<sub>2</sub> 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:**

CF<sub>4</sub> - 10 SCCM, 5 mTorr, 400 W source, 70 W bias 5 cm gap, 20.3 cm Al wall

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# Gas-phase data vs wall conditions, etch rates

#### Same conditions



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

NOTE: In both cases the etch surface temperature is constant!





- Decreased SiF<sub>4</sub> density ('confirms' Si etch data)
- ~ Constant  $COF_2$  density ('confirms' SiO<sub>2</sub> etch data)

**NOTE:** Gas temperature likely below 'wall temperature' - Other surfaces at 'room' temperature

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#### Gas-phase data vs wall conditions, CF<sub>4</sub> Same conditions

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

## CF<sub>4</sub> breaks up a little more -or-CF<sub>4</sub> 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<sub>2</sub> and CF<sub>3</sub> production from the walls

#### OR

Suggests decrease in  $CF_2$  and  $CF_3$  loss to the walls



#### **Gas-phase data vs wall conditions** Same conditions

- The major radicals in a  $CF_4$  plasma are, CF,  $CF_2, CF_3$
- CF is not observed in any configuration • studied (=>  $n_{CF} < 5 \times 10^{11} \text{ cm}^{-3}$ )
- Under etch conditions:
- $n_{CF2} \text{ and } n_{CF3} \text{ are functions of wall}$  temperature and wall conditions  $\text{ As } T_{wall} \text{ both } n_{CF2} \text{ and } n_{CF3} \text{ up to a point}$  Dirty walls are source of radical up to ~450 K  $CF_x \text{ film provides more } CF_2, CF_3 \text{ to gas } 0$

```
Or
```

Less CF<sub>2</sub>, CF<sub>3</sub> radicals lost to CF<sub>x</sub> film Either way, we should be able to see by growing film on HOT substrates



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## **Initial interpretation of Temperature Data**

- At first blush
  - Looks like trends seen with  $H_2O$ 
    - » 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











• Desorption curve is similar in shape as high temperature part **but not at fast** 



## Gas-phase data vs wall conditions, CF<sub>4</sub>

• The simplest mathematical model is:

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

• This gives rise to fitting of

Gap	A	В	С		Ēd
ст	nm/min	nm/min	nm/min	kJ.mot <sup>-1</sup> eV	kJ.mol <sup>-1</sup> eV
4	8 10 <sup>-6</sup>	$5.65 \ 10^5$	95	-39.5 -0.41	33.6 0.35
5	1.75 10 <sup>-6</sup>	9.5 10 <sup>5</sup>	75	-42 -0.44	33.4 0.35
5.75	$4.95 \ 10^{-7}$	$4.2 \ 10^5$	41.5	-44.9-0.47	31.2 0.32
Vacuum		$1.73 \ 10^3$		N/A	33.4 0.35
CF <sub>4</sub>		$1.73 \ 10^3$		N/A	33.4 0.35

- E<sub>a</sub> is an adsorption process and represents an adsorption energy These adsorption energies are the ~same! => energy physisorption Matches reported CF<sub>2</sub> adsorption energy - 39 kJ/mol => likely CF<sub>2</sub>
  - o Cruden, Gleason and Sawin, Ultraviolet absorption measurement of CF2 in the parallel plate pyrolytic chemical vapour deposition process, J Phys. D 35 2002, 480
- E<sub>d</sub> 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<sub>4</sub>

• The simplest mathematical model is:

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

• This gives rise to fitting of

Gap	A	В	C	Ea	L	Ed	l
ст	nm/min	nm/min	nm/min	kJ.mol <sup>-1</sup>	eV	kJ.mol <sup>-1</sup>	eV
4	8 10 <sup>-6</sup>	5.65 10 <sup>5</sup>	95	-39.5	-0.41	33.6	0.35
5	1.75 10 <sup>-6</sup>	9.5 10 <sup>5</sup>	75	-42	-0.44	33.4	0.35
5.75	4.95 10 <sup>-7</sup>	4.2 10 <sup>5</sup>	41.5	-44.9	-0.47	31.2	0.32
Vacuum		1.73 10 <sup>3</sup>		N/A		33.4	0.35
CF <sub>4</sub>		1.73 10 <sup>3</sup>		N/A		33.4	0.35

- The 'constants' A, B, C may be functions of other parameters e.g. A=A(n<sub>F</sub>, n<sub>CF</sub>, n<sub>CF2</sub>, n<sub>CF3</sub>, n<sub>CF</sub>, ion)
- For example, the ion current (or flux <sub>ion</sub>) ratio is 1 : 0.83 : 0.72 Lets compare this to A, B, C

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• <u>Type of Fluorine content</u> in CF<sub>x</sub> film seems to governed by source height

- Likely n<sub>F</sub> / n<sub>CFx</sub> increases with gap (We are trying to confirm this!)
- A and B might be functions  $n_{CFx} / n_F$  where  $CF_2$  is probably the primary fluorocarbon

## So what do we know?

• Deposition rate follows

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

• **C** ion 
$$(C \sim 0.02$$
 ion)

- A B ? From E<sub>a</sub> probably n<sub>CF2</sub>
- If A B n<sub>CF2</sub> Then why the drop with Gap?
   Other radicals?
  - » n<sub>CF</sub> very low
  - »  $n_{CF2}$ ,  $n_{CF3}$  and  $n_{CF4} \sim constants$  with gap
  - » BUT XPS data indicates  $n_F$  and gap (Still checking)

Perhaps A B n<sub>CF2</sub> / n<sub>F</sub>

## 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:

Bond	Energy		
	kJ.mol <sup>-1</sup>	eV	
С-С	370	3.8	
<i>C</i> - <i>F</i>	448	4.6	

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<sub>x</sub> fills broken bond
    - »  $CF_x$  molecules need to be readily available => physisorbed radicals more likely to bond

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- » 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<sub>2</sub> 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<sub>2</sub> 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

$$DR \ 0.02 \ _{ion} \ A \ n_{CF_x} / n_F, \ _{ion} \ e^{E_a / RT} \ B \ n_{CF_x} / n_F, \ _{ion} \ e^{E_d / RT}$$

- 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

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• Probably explains CF<sub>x</sub> 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 
$$Ae^{E_a/RT} Be^{E_d/RT}$$
  
 $0.02$  ion  $An_{CF_x}/n_F$ , ion  $e^{E_a/RT} Bn_{CF_x}/n_F$ , ion  $e^{E_d/RT}$ 

- 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 C<sub>4</sub>F<sub>8</sub> right now. Cl<sub>2</sub> chemistries to be added soon.)

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# ACKNOWLEDGEMENTS

- We wish to thank Prof. Kushner for helpful discussions and the use of his HPEM code.
- We thank Profs. Fisher, Graves, Kushner and Sawin for the use of their data in this talk
- Also thanks to: my colleague Prof. Lawrence Overzet

and our students Dr. Baosuo Zhou (Now at Micron) Dr. Eric Joseph (Now at IBM) Sanket Sant (PhD late spring 06)

- This program was funded by UTD and a grant from NSF/DOE, contract number CTS-0078669.
- Industrial donations have come from Varian Semiconductor, Novellus, Matheson Tri-Gas, and Texas Instruments.

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