DEPOSITION AND COMPOSITION OF POLYMER FILMS IN FLUOROCARBON PLASMAS*

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AGENDA

- Fluorocarbon etching – resolution of polymer composition.
- Reaction mechanism.
- Global simulation of base case (pure C_4F_8).
- Parameterizations
    - Power
    - Self-Bias
- M/Ar/O_2 plasmas. (M = C_4F_8, C_2F_6)
- Pulsed operation.

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FLUOROCARBON PLASMA ETCHING

- The use of low-k dielectric materials for interconnect wiring presents new challenges to the semiconductor industry.
- Fluorocarbon plasma etching is still the foremost process for obtaining selectivity between dielectrics.
- Optimization of this process is critical as dielectrics thin and selectivity requirements become extreme.
- This selectivity is due to the deposition of a polymer layer, which is then consumed by oxidants in the underlying dielectric, leading to an etch.
- The thickness of this polymer also controls the ion energy hitting the dielectric surface.

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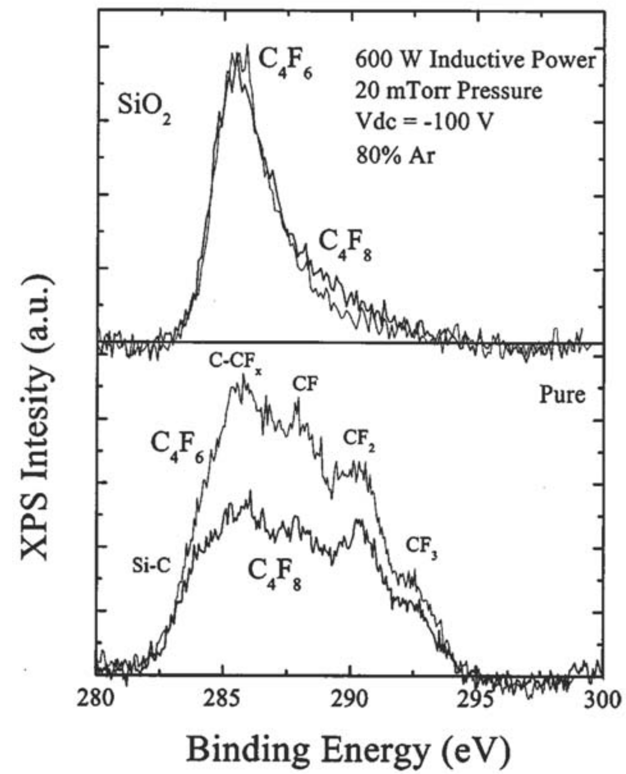
RESOLUTION OF POLYMER COVERAGE

- **To first order, etch rates are affected by ion energies only by the polymer thickness, and not by the composition of the film.**
- **The polymer deposition/sputtering rate, and the rate of reaction of the polymer with the dielectric depend on the composition of the polymer.**
- **To this end, a surface model has been developed to resolve the polymer on a mesoscale level.**
- **-C-, -CF-, $-CF_2-$, and $–CF_3-$ sites are differentiated, and the thickness of the polymer is the sum of the thicknesses of all of the above.**



- Li et al, JVSTA 20 (2002)

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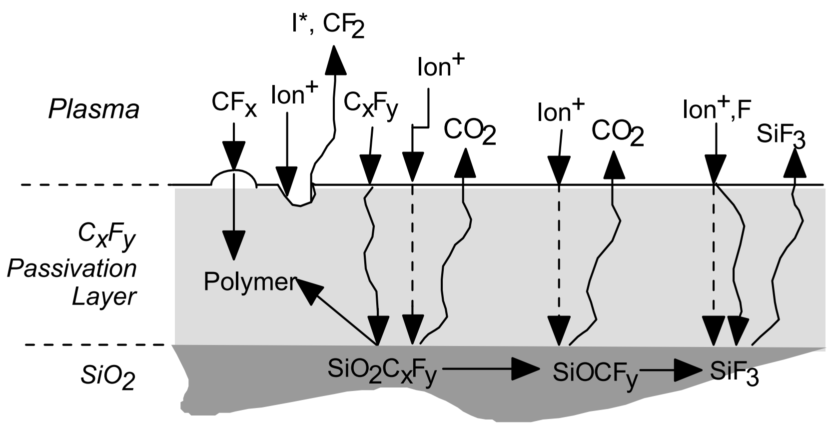
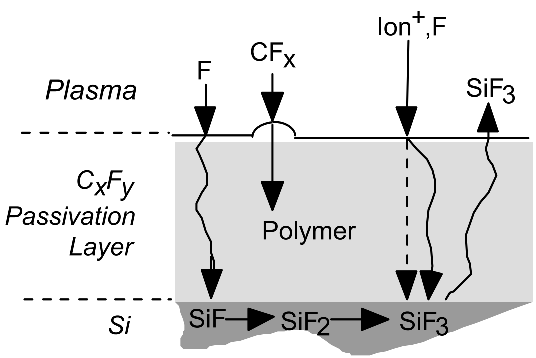
SURFACE REACTION MECHANISM: I

- CF_x and C_xF_y radicals are the precursors to the passivation layer which regulates delivery of precursors and activation energy.

- Chemisorption of CF_x produces a complex at the oxide-polymer interface.





- Low energy ion activation of the complex produces polymer.

$$k = k_0 \times \left(1 - \frac{E}{E_c}\right)$$

- E_c = maximum allowable energy
- k_0 = probability at E_c.

- C_xF_y radicals adds onto polymer to produce thicker polymer.

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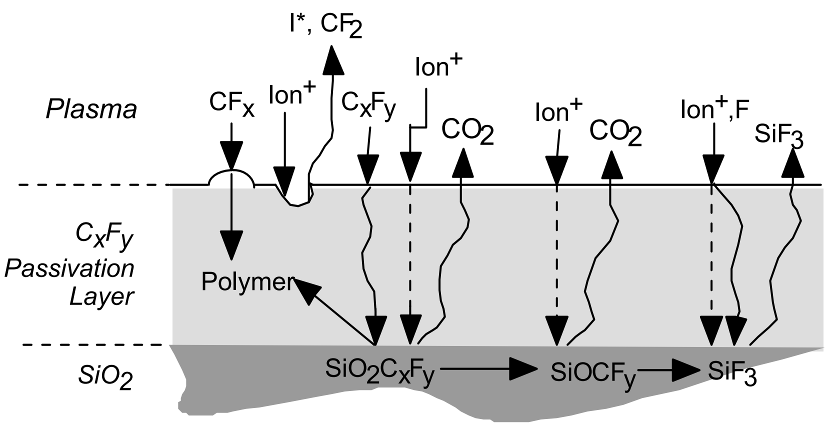
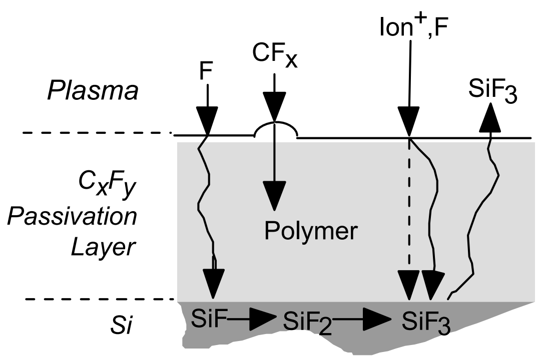
SURFACE REACTION MECHANISM: II

- **The polymer layer is sputtered by energetic ions**



$$p(E) = p_0 \frac{E^n - E_{th}^n}{E_r^n - E_{th}^n}$$

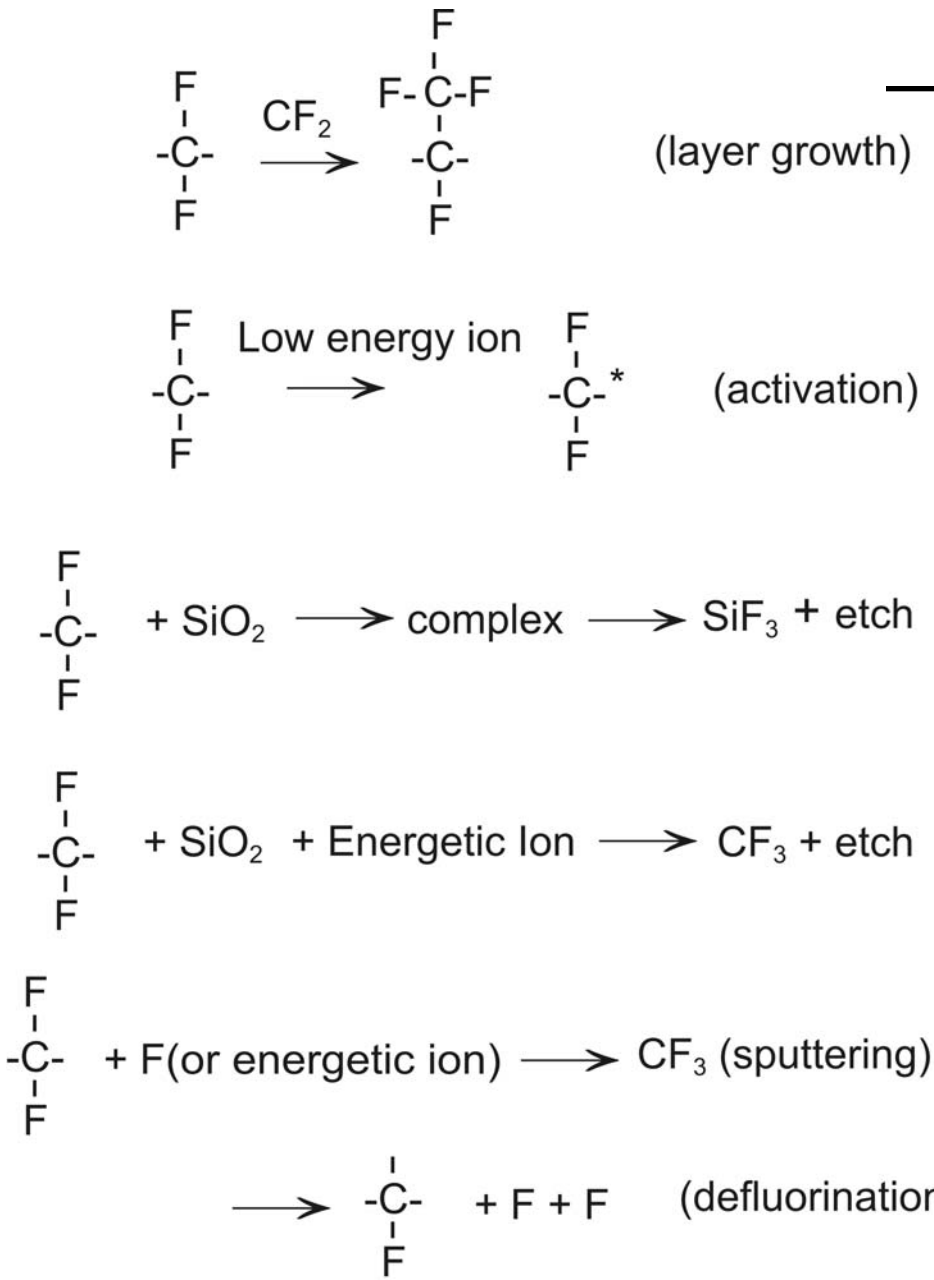
- **E_{th} = threshold energy**
- **E_r = reference energy**
- **p_0 = probability of sputtering at the reference energy.**

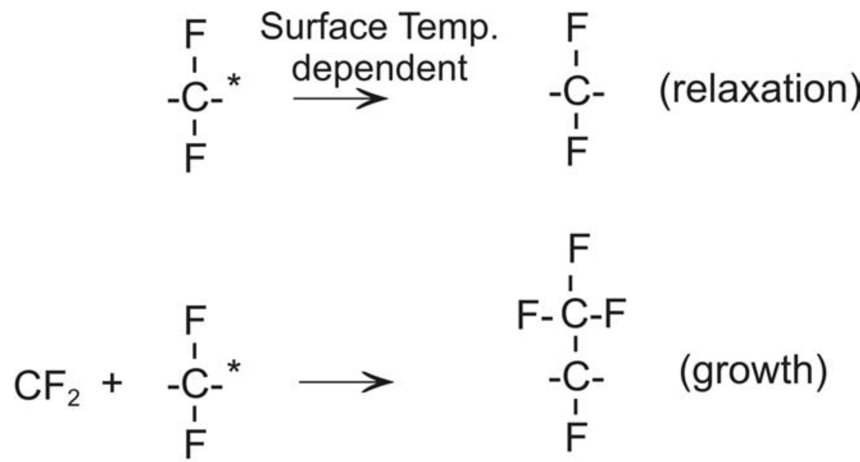


- **The complex formed at the oxide-polymer interface undergoes ion activated dissociation to form volatile etch products (SiF_3, CO_2).**

SURFACE REACTIONS

- **The fluorination state of "C-" is resolved (e.g. –C-, -C-F, etc.)**





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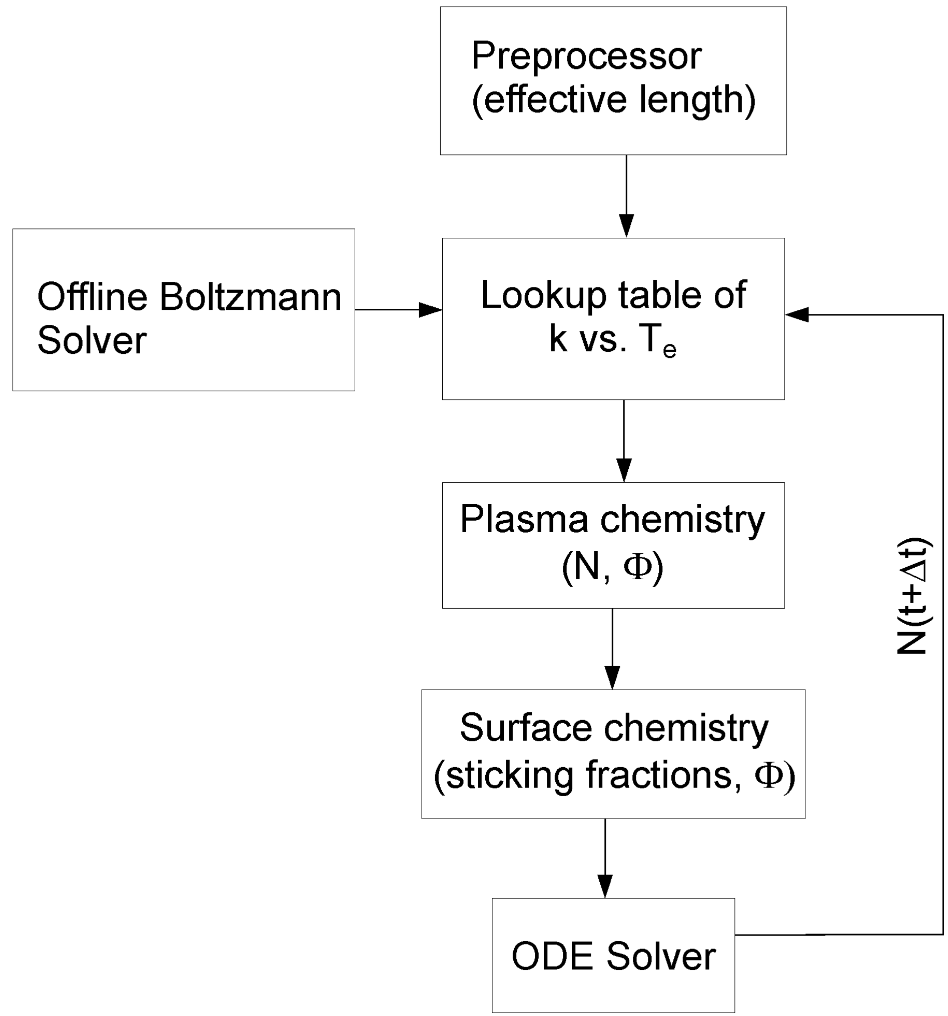
GLOBAL PLASMA MODEL

- **GLOBAL_KIN is a spatially homogeneous solver which periodically updates the gas and surface species.**
- **A preprocessor reads in a 2-D mesh to calculate an effective length scale, and fractional surface areas.**



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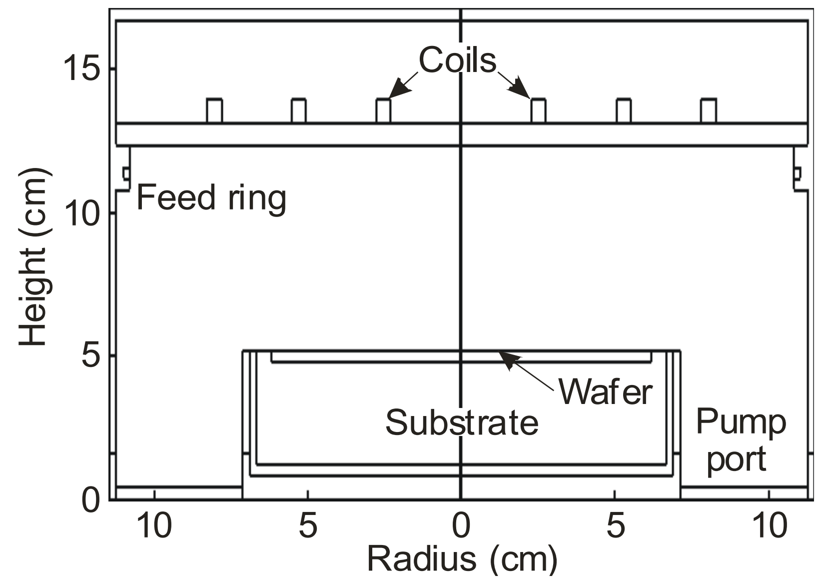
REACTOR GEOMETRY

- **The global model is used to efficiently develop surface chemistry reaction mechanisms. (2-D model – 5-6 hours, 0-D – 20 min)**

- **Geometry is based on the ICP reactor used by Oehrlein.**

- **Base operating conditions are**
  - **Pure C_4F_8**
  - **10 mTorr**
  - **50 sccm**
  - **1400 W ICP power**
  - **13.56 MHz**



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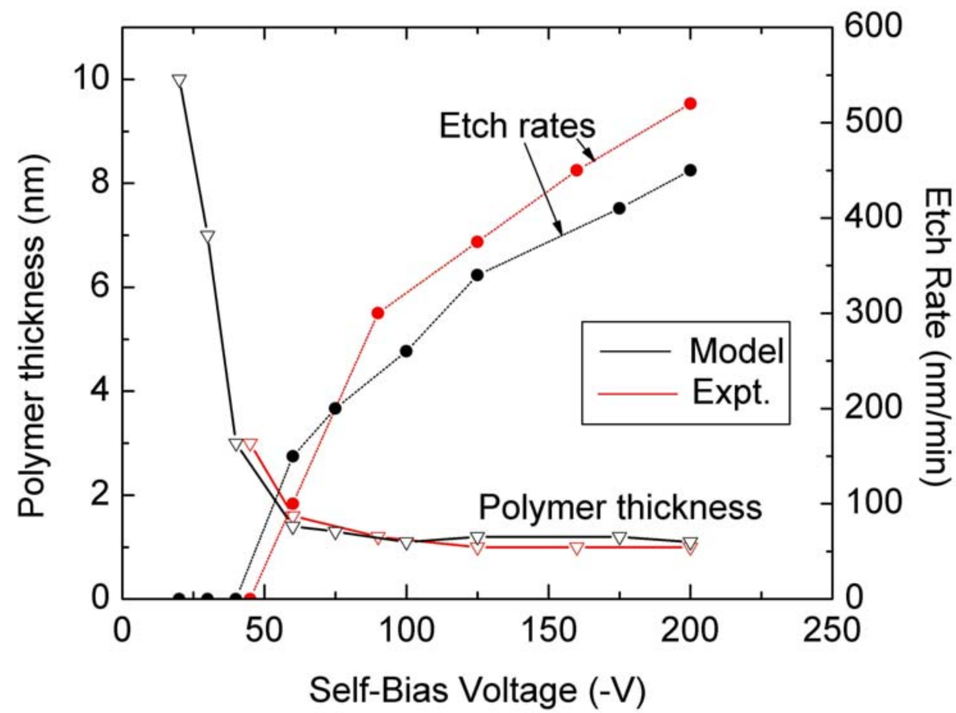
POLYMER THICKNESS AND SiO_2 ETCH RATE

- **The trends followed in etch rates are similar to those found by Oehrlein.***
- **Below a critical thickness (~ 1.5 nm), the ions directly etch the substrate.**
- **In these regimes, the thickness of the film is not the main parameter controlling etch rates.**



- 100% C_4F_8, 50 sccm, 1400 W

* Standaert et al, JVSTA 22 (2004)

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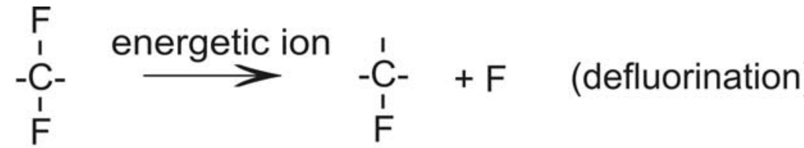
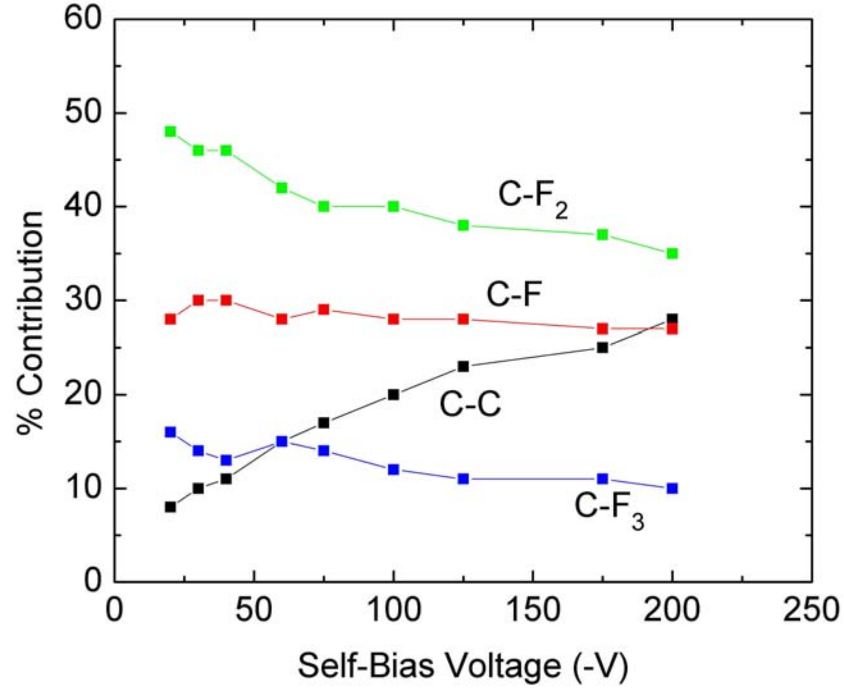
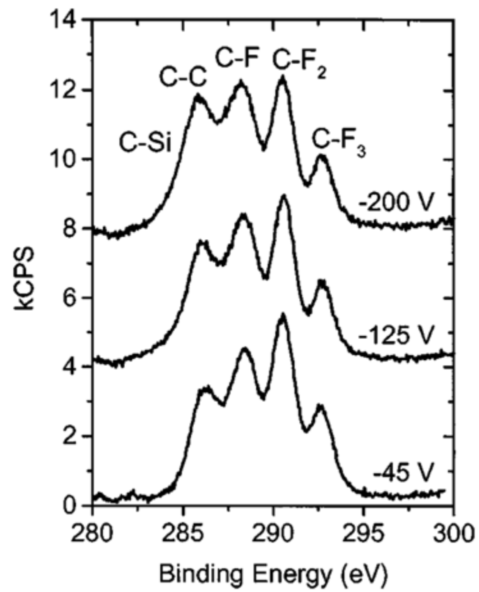
ION-INDUCED DEFLUORINATION

- **Ion-induced defluorination reactions have been proposed to explain etching through thicker (> 3 nm) films.***
- **As a result, the C-C contribution to the film increases with self-bias, due to C-F_2 being defluorinated.**







- 100% C_4F_8, 50 sccm, 1400 W

* Standaert et al, JVSTA 22 (2004)

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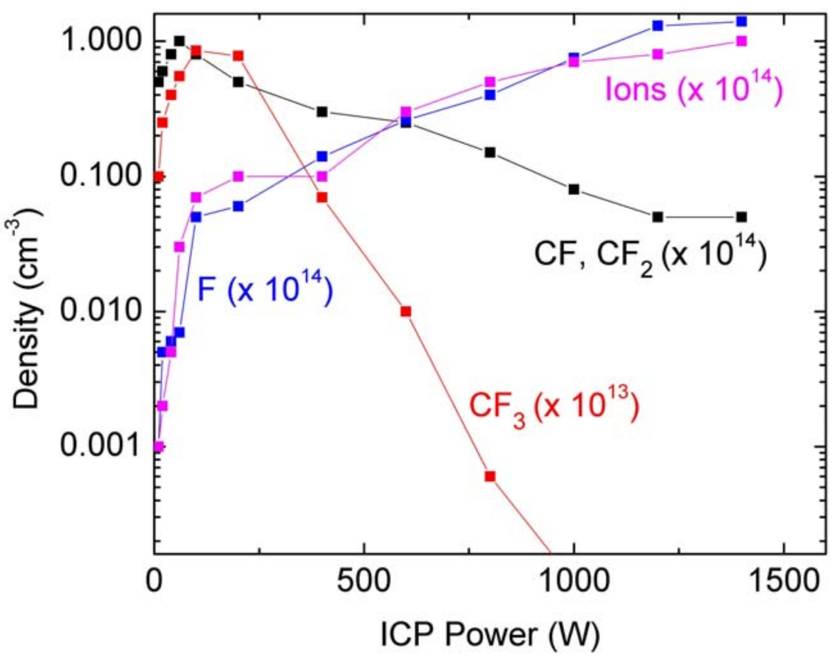
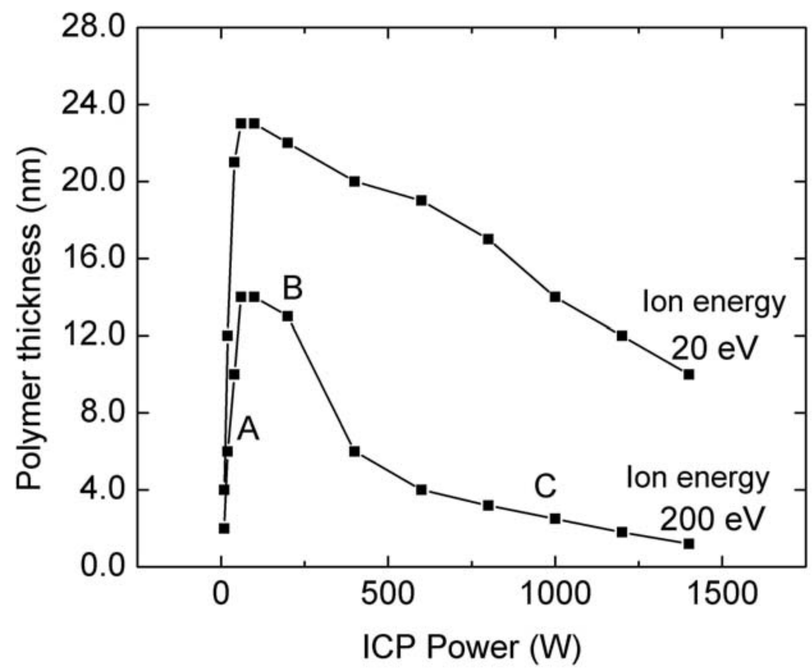
EFFECT OF POWER: FILM THICKNESS

- **A. The thickness of the film increases with increase in depositing radicals.**
- **B. The rate of deposition is then balanced out with ion sputtering**
- **C. Formation of volatile CF_4 due to increase in fluorine .**





- $100\%\ C_4F_8$, 50 sccm, 10 mTorr

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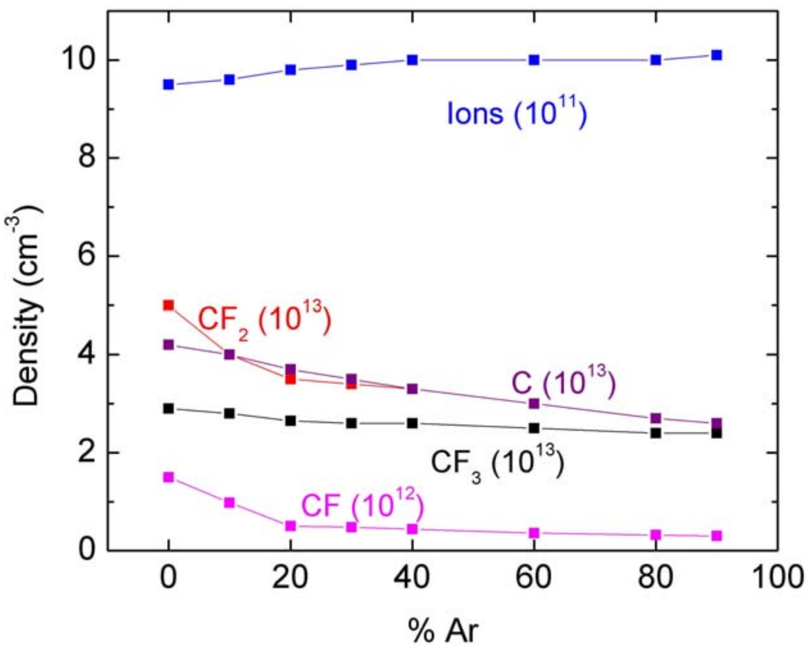
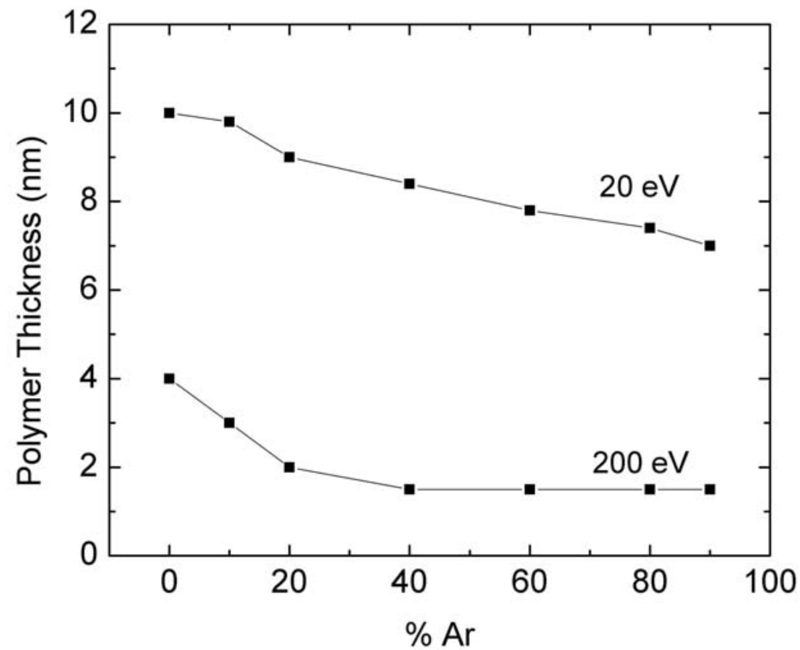
ADDITION OF ARGON: FILM THICKNESS

- **As Ar is added, thinner films are observed due to the reduction in density of depositing radicals and sputtering.**
- **At lower self-bias, the Ar^+ does not affect the sputtering, and the rate of reduction of film thickness is lower.**





- Gas Phase Densities
- 50 sccm, 1400 W, 10 mTorr

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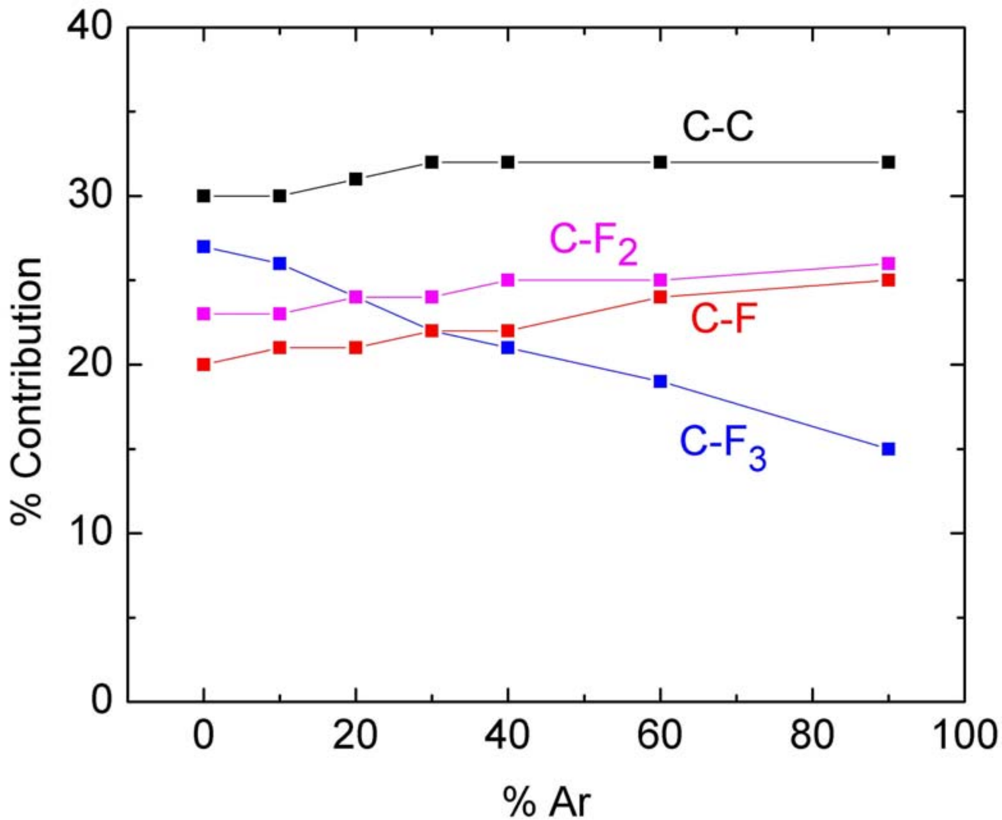
ADDITION OF ARGON: FILM COMPOSITION

- **As Ar is added, the percentage contribution of C-F_3 is reduced, because of increased sputtering by Ar ions.**



- 50 sccm, 1400 W, 10 mTorr

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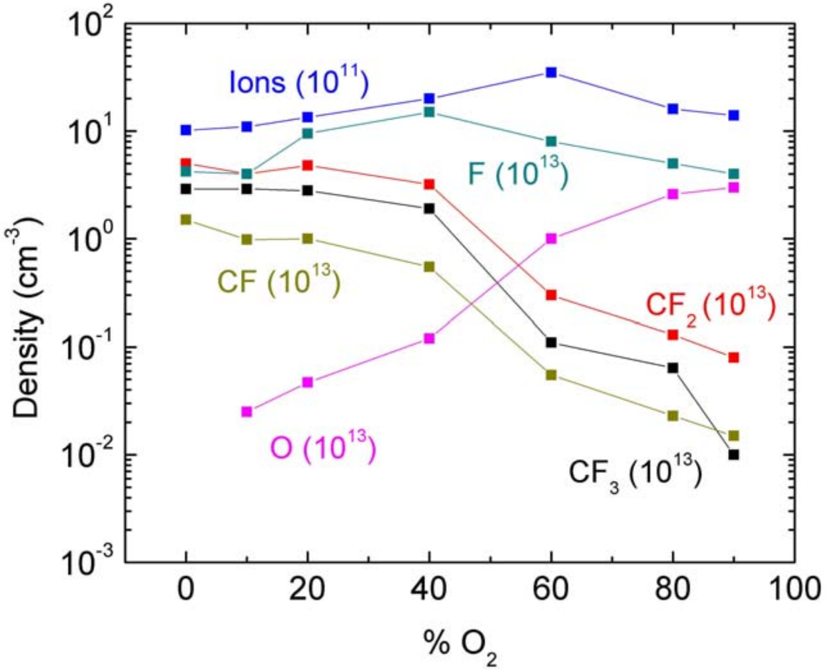
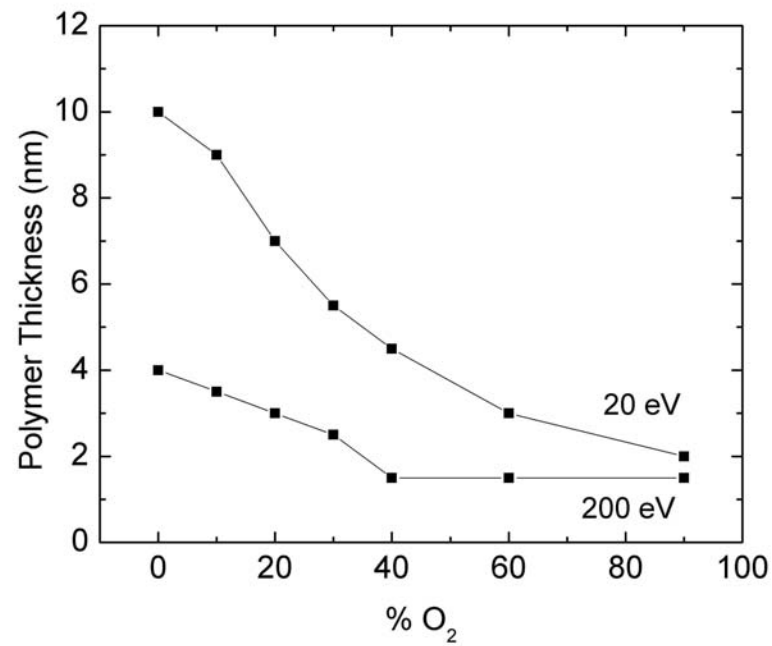
ADDITION OF OXYGEN: FILM THICKNESS

- With an increase in O_2, the depositing radical density falls.
- O radicals reactively etch the polymer film, reducing thickness.





- Gas Phase Densities

- 50 sccm, 10 mTorr

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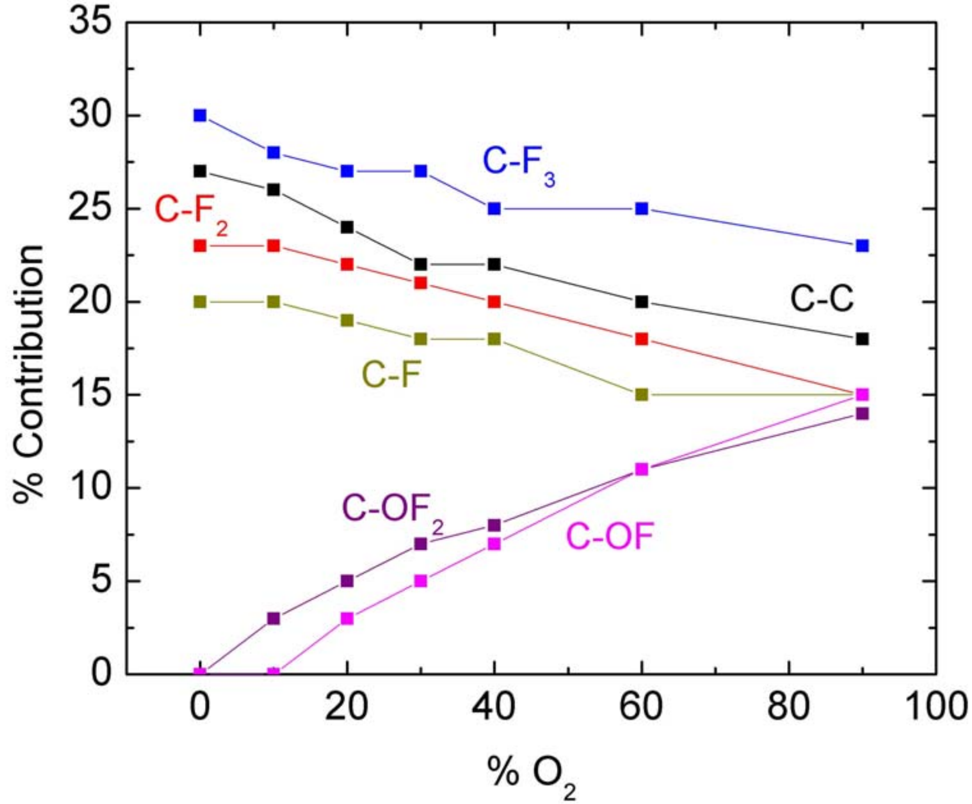
ADDITION OF OXYGEN: FILM COMPOSITION

- **Increased functionalization of surface sites is observed, while the contributions of C-Fx are reduced.**



- 50 sccm, 10 mTorr, 200 eV ions

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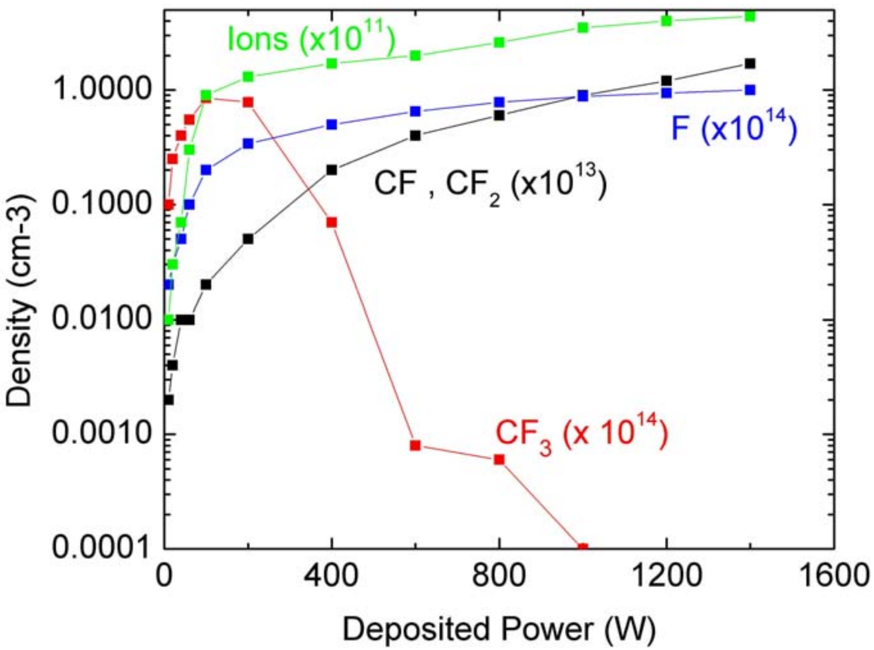
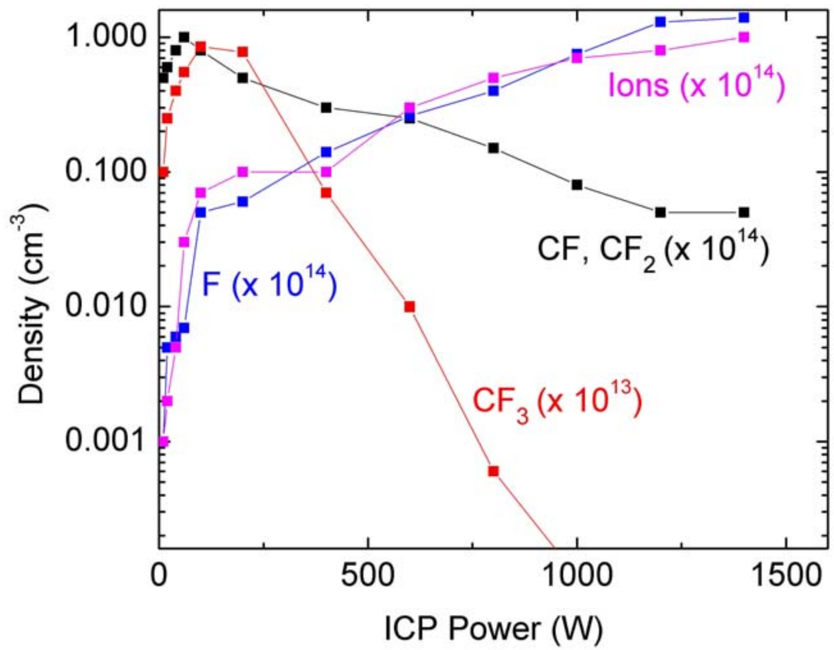
COMPARISON WITH C_2F_6 PLASMA: GAS PHASE

- In a C_2F_6 plasma, the branching ratio for CF_3 increases.
- As a result, the $–CF_3$ content in the film is significantly increased.



• 100% C_2F_6, 50 sccm, 10 mTorr



• 100% C_4F_8, 50 sccm, 10 mTorr

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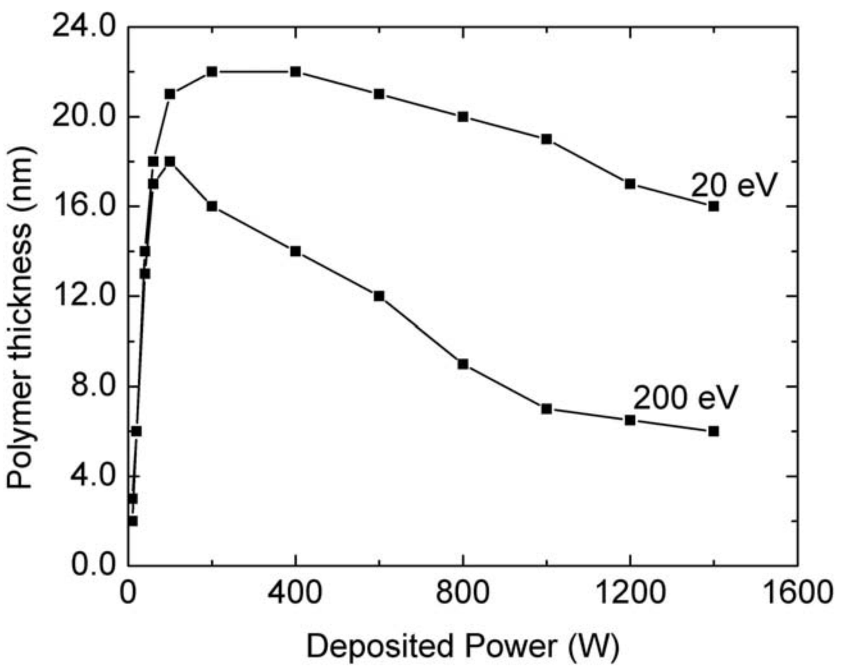
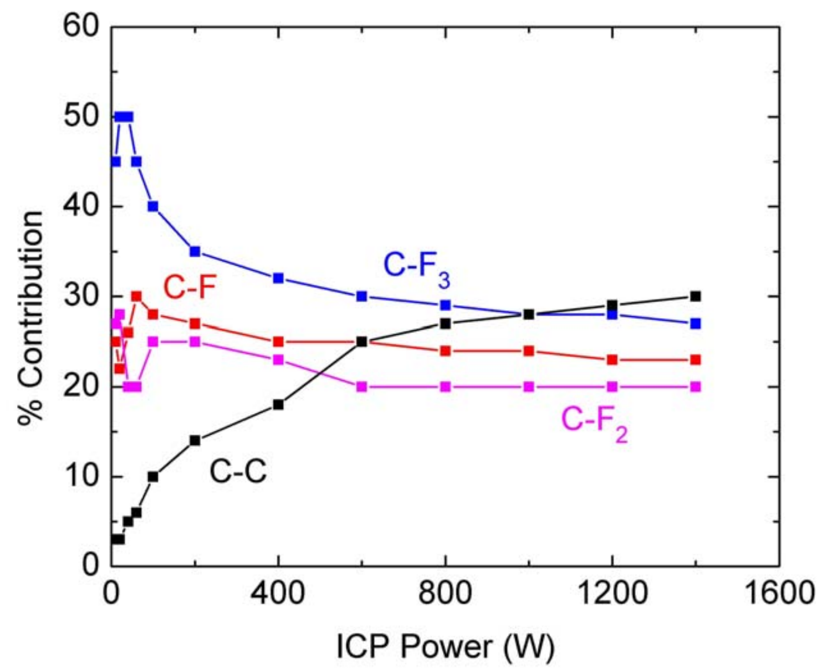
COMPARISON WITH C_2F_6 PLASMA: FILM PROPERTIES

- **At high ion energies, the $-CF_3$ is easily sputtered away, causing a sharp reduction in thickness.**
- **At lower ion energies, the high density of CF_3 leads to a balance of deposition of CFx and formation of volatile CF_4.**





- 100% C_2F_6, 50 sccm, 10 mTorr

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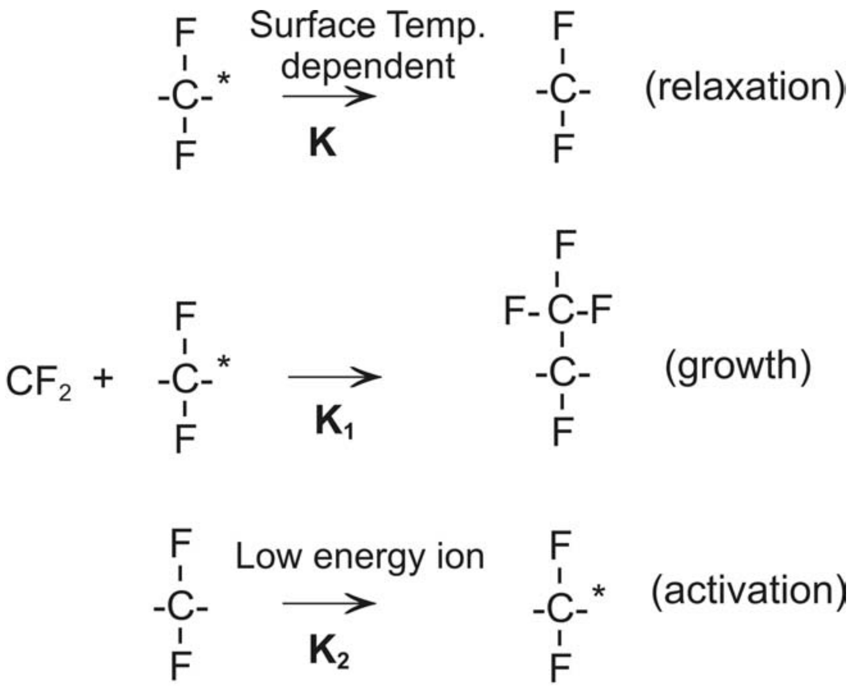
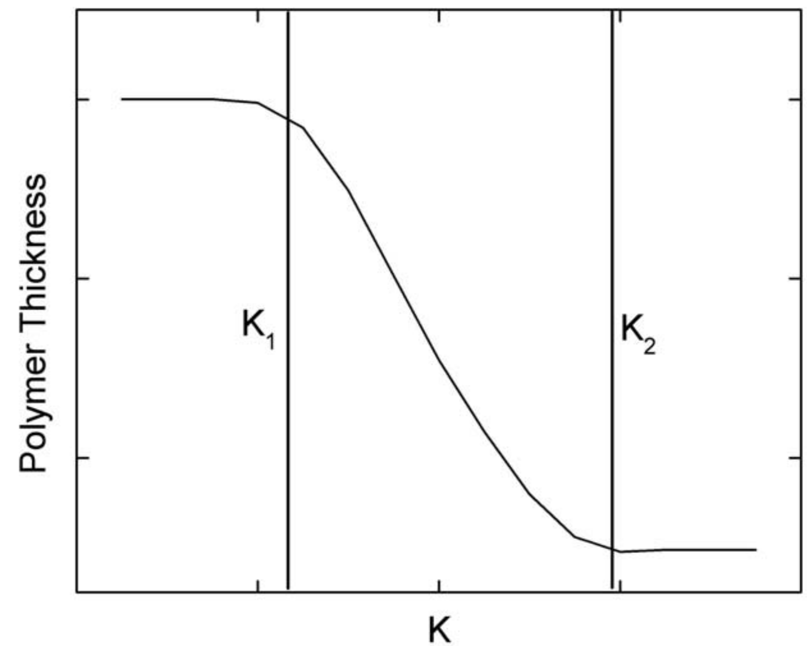
INFLUENCE OF SUBSTRATE TEMPERATURE

- Surface temperature changes the diffusion rate of surface sites.
- At low ion energies, most of the sites are activated, and the process can be modeled by each activated site having a lifetime dependent on substrate temperature.





MODULATED DISCHARGES

- PTFE-like ([CF_2]n) films have been shown to possess hydrophobic qualities.
- This makes these films attractive for applications like stain resistant clothes, nonfouling substrates, etc.
- In the past, CW discharges of tetrafluoroethylene (TFE) have been used to obtain cross-linked amorphous fluorocarbon films.
- Recently, modulated TFE discharges have been investigated for the formation of super-hydrophobic films which are ribbon-like in structure.*
- The reaction model developed in the previous study was applied to such discharges.

- * Cicala et al, Macromolecules (2002)

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REACTOR GEOMETRY

- The reactor is the same geometry as in the previous studies.
- The operating conditions are
  - Pure C_2F_4
  - 6 sccm
  - 300 mTorr
  - 30 W
- The period of the pulse is 100 ms, and the duty cycle is varied from 10 to 100%.

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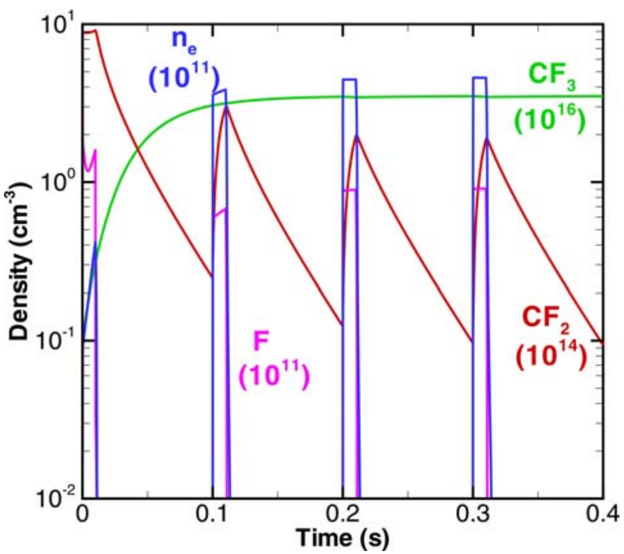
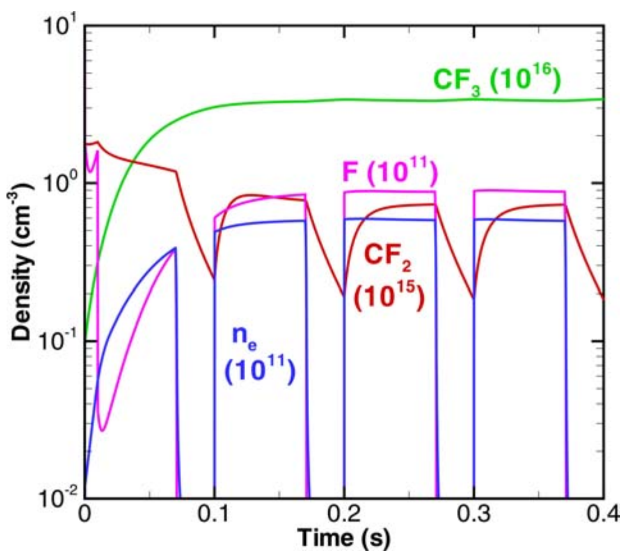
GAS PHASE DENSITIES – DUTY CYCLE

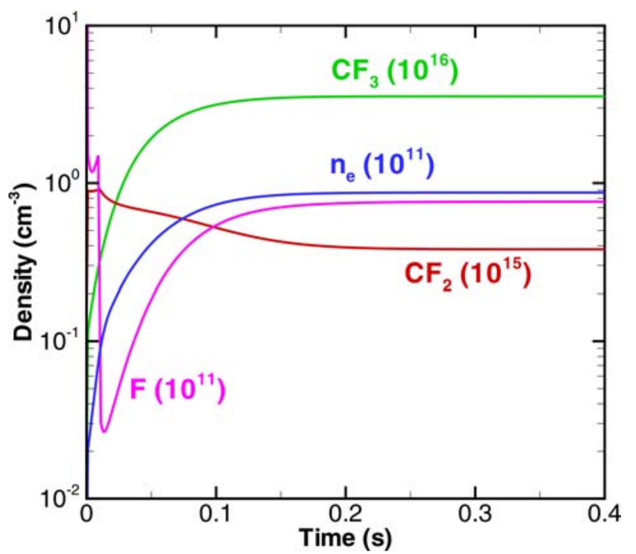
- **As duty cycle (DC) is increased, there is significant modulation of the CF_2 radicals.**
- **[F] tracks the pulse, leading to less removal of CF_x from the film via volatile products for lower DC.**



- 10% DC



- 70% DC



- 100% DC (CW)

- 6 sccm, 300 mTorr, C_2F_4

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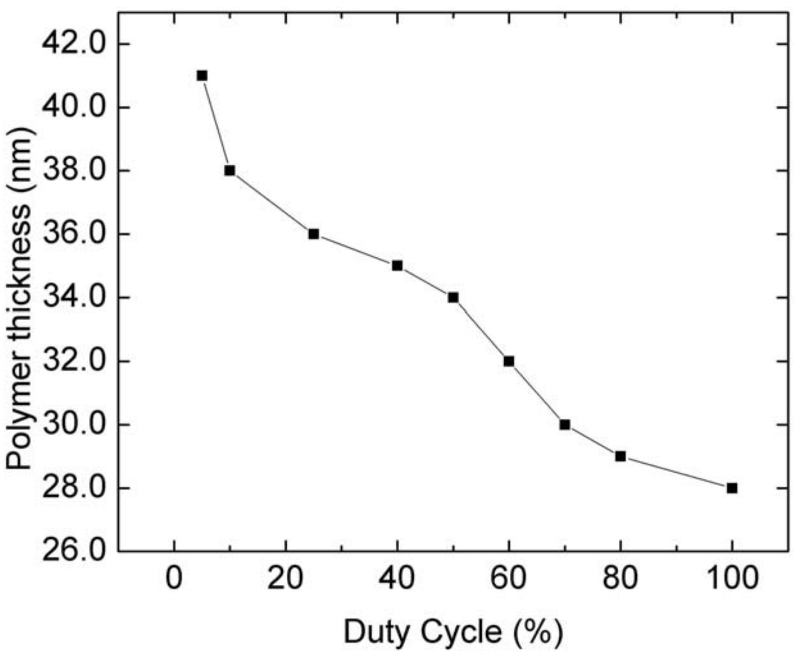
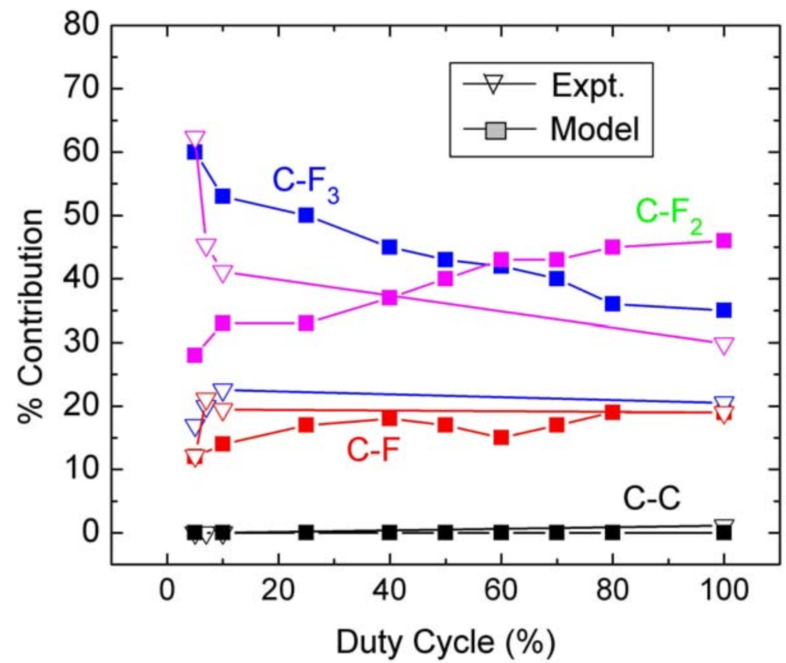
POLYMER THICKNESS AND COMPOSITION

- For lower DC, the films are thicker, and have a high percentage of $C\text{-}F_3$ compared to experiment.*
- As DC goes up, the percentage of $C\text{-}F_2$ rises due to the increase in CF_2 density, while the $C\text{-}F_3$ percentage is reduced due to the increase in [F] etching.





* Cicala et al, Macromolecules (2002)

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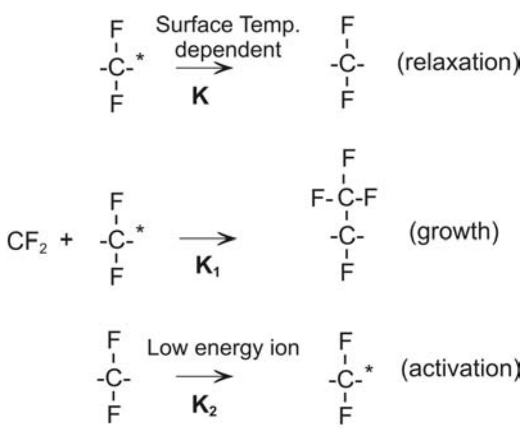
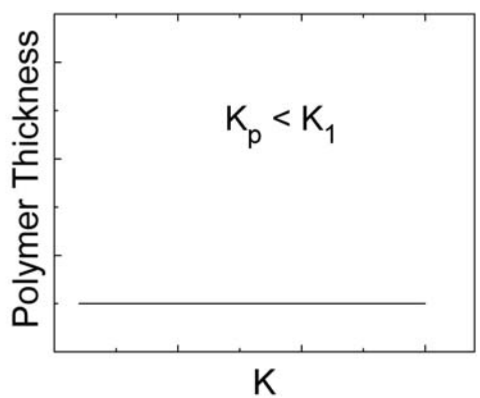
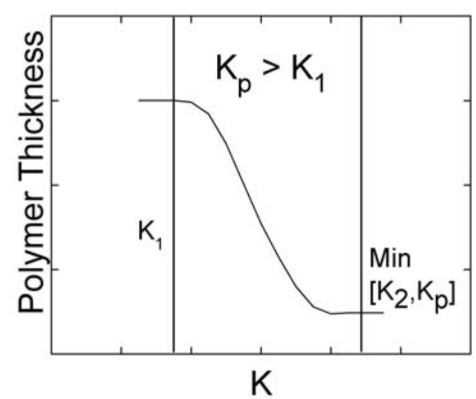
INFLUENCE OF SUBSTRATE TEMPERATURE

- The rate of activation K_p increases with duty cycle.
- At low K_p, the sites are de-activated before the radicals can attach. At higher K_p, the rates K_p and K_2 are the determining factors for polymer thickness.







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CONCLUDING REMARKS

- A surface reaction mechanism has been developed to resolve the composition of the fluorocarbon layer deposition.
- Ion-induced defluorination is important for etching processes for fluorocarbon thicknesses > 3 nm.
- With addition of Ar, there is a significant reduction in thickness.
- In a C_2F_6/Ar plasma, due to the increased CF_3 radicals, the surface composition is altered to more $–CF_3$.
- For modulated C_2F_4 discharges, the surface composition and thickness is a function of the duty cycle.
- Substrate temperature plays an important part in surface kinetics by affecting the lifetime of activated polymer sites.