OPTIMIZING PLASMA PROCESSING FROM $0.05/m^2 to $1000/cm^2

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  - 3M Corporation
  - Semiconductor Research Corporation
  - National Science Foundation
  - SEMATECH
  - CFDRC Inc.

WHOSE DOLLAR?

- **It will soon be free for Australians to visit the US…..**

Australian Dollars to 1 USD (invert,data)

	latest (Jan 23)	**lowest** (Jan 22)	**highest** (Aug 28)
120 days	1.29634	1.28353	1.56495

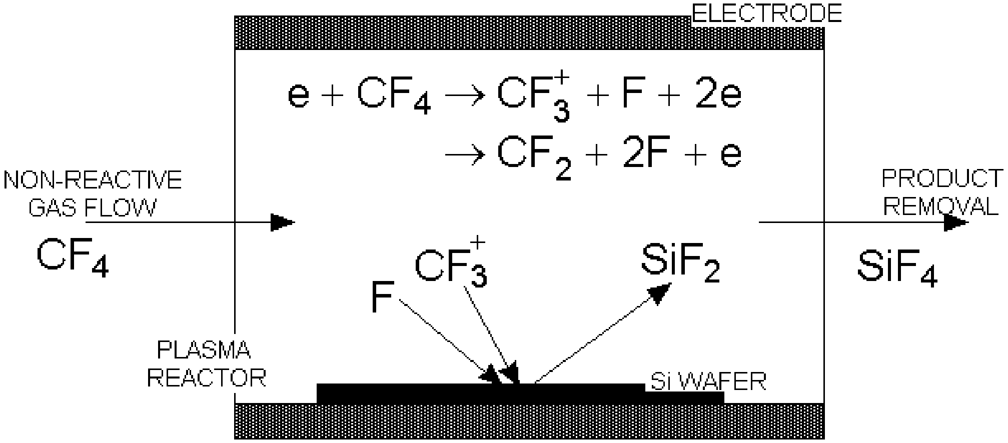
- **Ref: http://www.x-rates.com**

AGENDA

- Plasmas and Polymers: Extremes in Physics and Applications
- Plasmas for functionalization of polymers ($0.05/m^2)
- Polymers for selectivity in plasma etching ($1000/cm^2)
- Challenges for adapting commodity processes for high value materials.
- Concluding Remarks

PLASMAS FOR MODIFICATION OF SURFACES

- **Plasmas are ideal for producing reactive species (radicals, ions) for modifying surface properties.**
- **Two of the most technologically (and commercially) important uses of plasmas involve polymers:**



- **Functionalization of surfaces (high pressure)**
- **Etching for microelectronics fabrication (low pressure)**

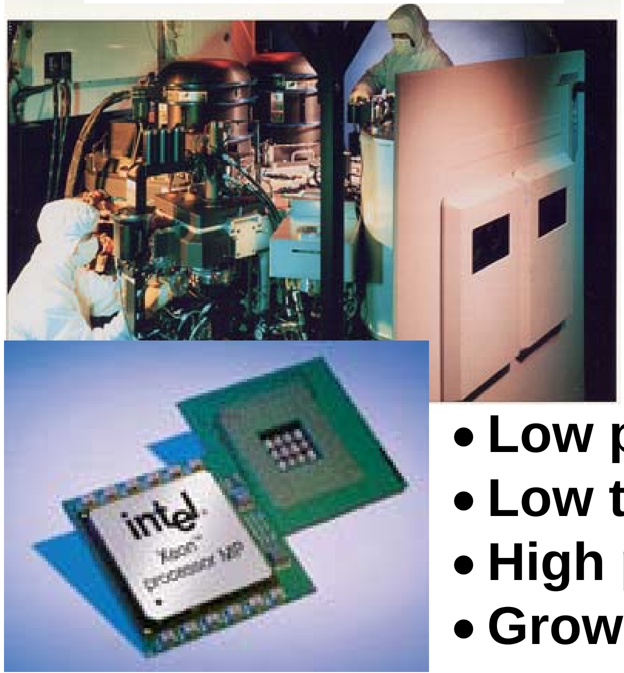
- **Both applications utilize unique properties of low temperature plasmas to selectively produce structures.**

EXTREMES IN CONDITIONS, VALUES, APPLICATIONS

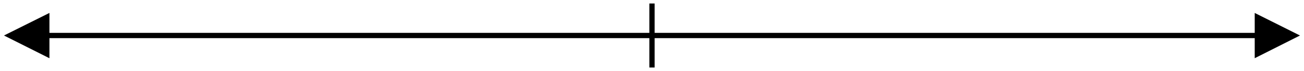
Web Treatment of Films

- High pressure
- High throughput
- Low precision
- Modify cheap materials
- Commodity

Microelectronics



- Low pressure
- Low throughput
- High precision
- Grow expensive materials
- High tech

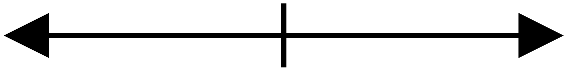


$0.05/m²

$1000/cm²

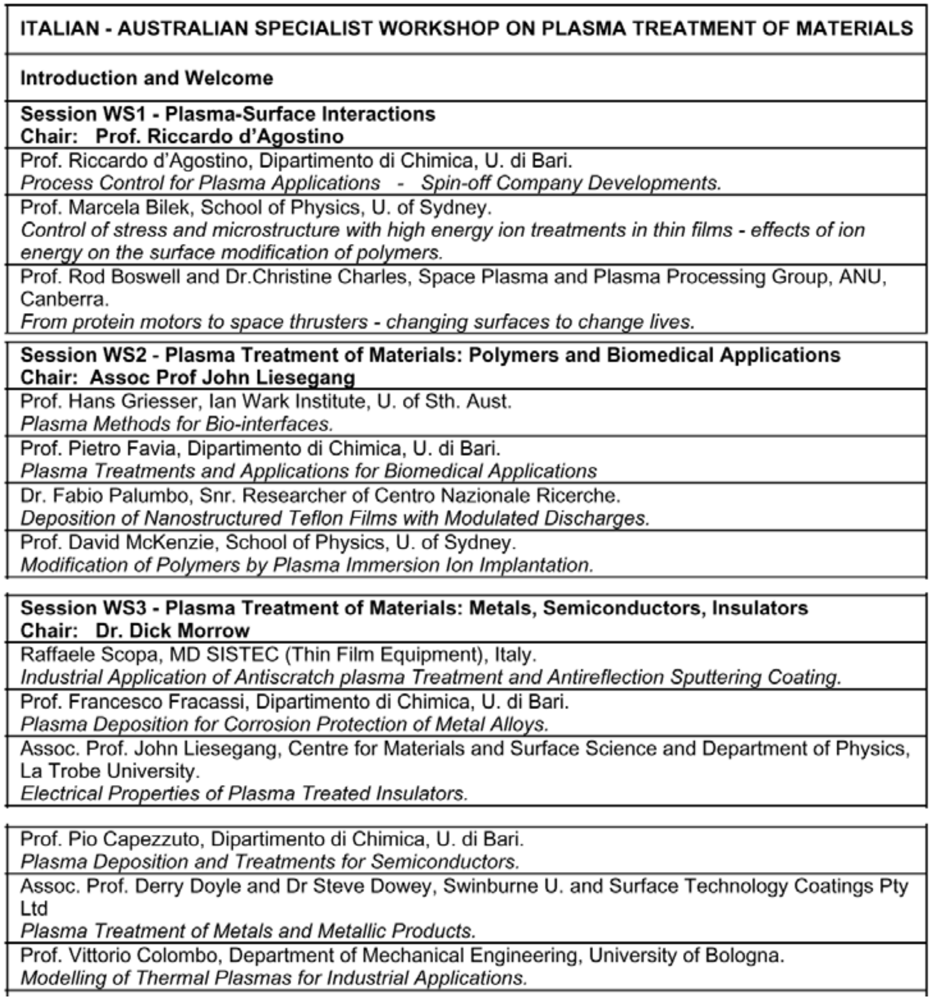
MOTIVATION: CAN WE LEVERAGE OUR LEARNING?

- **Can commodity processes be used to fabricate high value materials?**



$0.05/m^2 ? $1000/cm^2

- **Where will, ultimately, biocompatible polymeric films fit on this scale? Artificial skin for $0.05/cm^2 or $1000/cm^2?**



ITALIAN - AUSTRALIAN SPECIALIST WORKSHOP ON PLASMA TREATMENT OF MATERIALS

Introduction and Welcome

Session WS1 - Plasma-Surface Interactions
Chair: Prof. Riccardo d'Agostino

Prof. Riccardo d'Agostino, Dipartimento di Chimica, U. di Bari.
Process Control for Plasma Applications - Spin-off Company Developments.

Prof. Marcela Bilek, School of Physics, U. of Sydney.
Control of stress and microstructure with high energy ion treatments in thin films - effects of ion energy on the surface modification of polymers.

Prof. Rod Boswell and Dr.Christine Charles, Space Plasma and Plasma Processing Group, ANU, Canberra.
From protein motors to space thrusters - changing surfaces to change lives.

Session WS2 - Plasma Treatment of Materials: Polymers and Biomedical Applications
Chair: Assoc Prof John Liesegang

Prof. Hans Griesser, Ian Wark Institute, U. of Sth. Aust.
Plasma Methods for Bio-interfaces.

Prof. Pietro Favia, Dipartimento di Chimica, U. di Bari.
Plasma Treatments and Applications for Biomedical Applications

Dr. Fabio Palumbo, Snr. Researcher of Centro Nazionale Ricerche.
Deposition of Nanostructured Teflon Films with Modulated Discharges.

Prof. David McKenzie, School of Physics, U. of Sydney.
Modification of Polymers by Plasma Immersion Ion Implantation.

Session WS3 - Plasma Treatment of Materials: Metals, Semiconductors, Insulators
Chair: Dr. Dick Morrow

Raffaele Scopa, MD SISTEC (Thin Film Equipment), Italy.
Industrial Application of Antiscratch plasma Treatment and Antireflection Sputtering Coating.

Prof. Francesco Fracassi, Dipartimento di Chimica, U. di Bari.
Plasma Deposition for Corrosion Protection of Metal Alloys.

Assoc. Prof. John Liesegang, Centre for Materials and Surface Science and Department of Physics, La Trobe University.
Electrical Properties of Plasma Treated Insulators.

Prof. Pio Capezzuto, Dipartimento di Chimica, U. di Bari.
Plasma Deposition and Treatments for Semiconductors.

Assoc. Prof. Derry Doyle and Dr Steve Dowey, Swinburne U. and Surface Technology Coatings Pty Ltd
Plasma Treatment of Metals and Metallic Products.

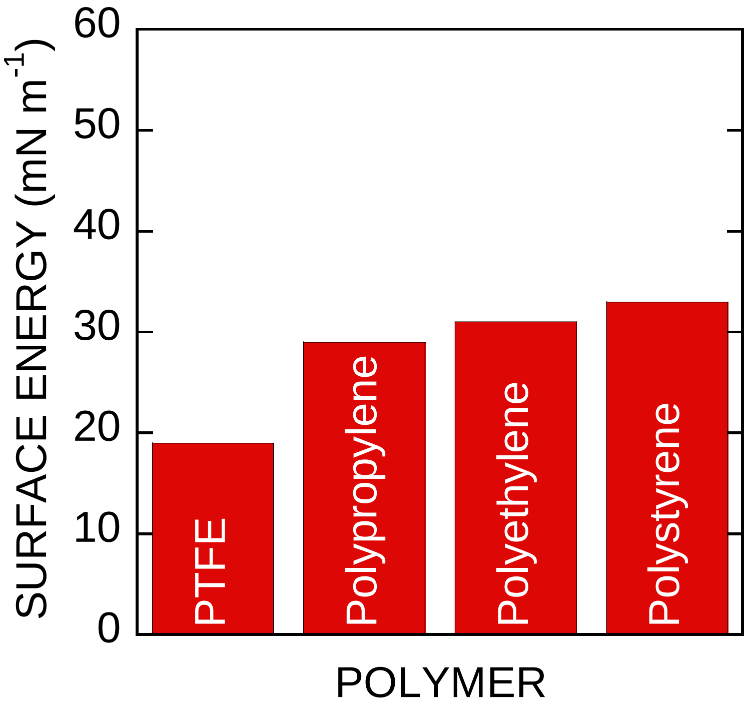
Prof. Vittorio Colombo, Department of Mechanical Engineering, University of Bologna.
Modelling of Thermal Plasmas for Industrial Applications.

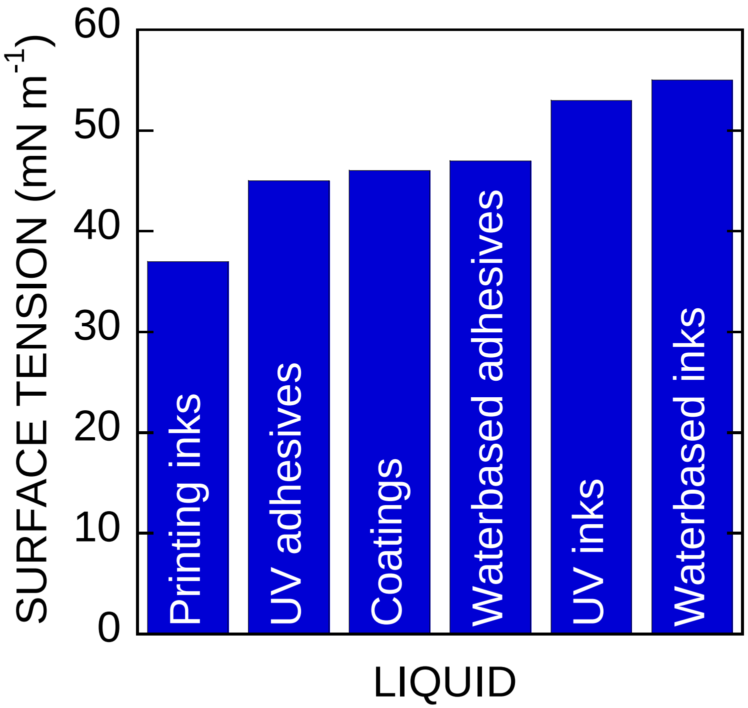
- **Tomorrow's Workshop…..**

LOW COST, COMMODITY FUNCTIONALIZATION OF POLYMER

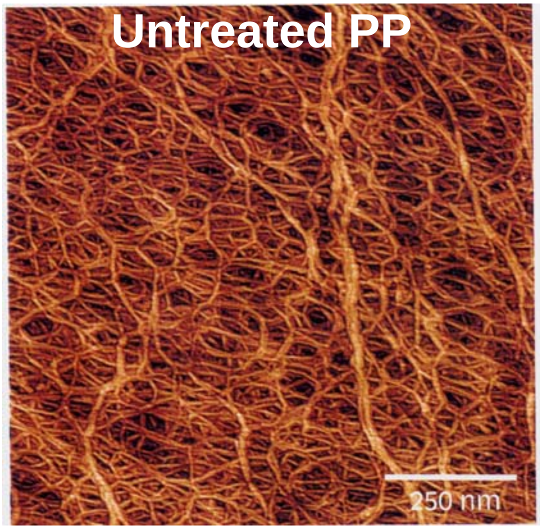
SURFACE ENERGY AND FUNCTIONALITY OF POLYMERS

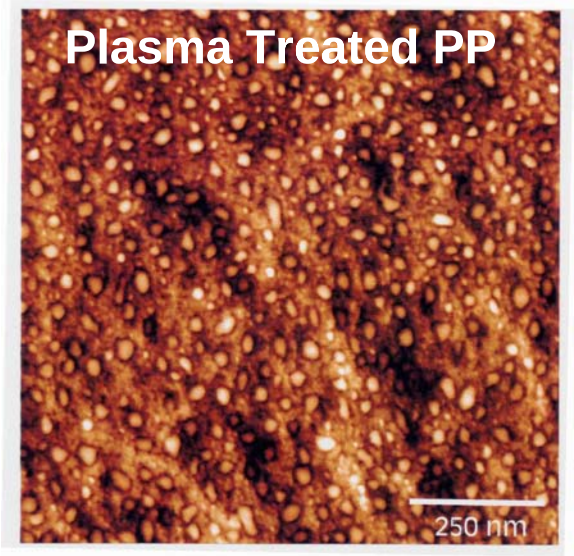
- **Most polymers, having low surface energy, are hydrophobic.**
- **For good adhesion and wettability, the surface energy of the polymer should exceed of the overlayer by ≈2-10 mN m^{-1}.**





PLASMA SURFACE MODIFICATION OF POLYMERS

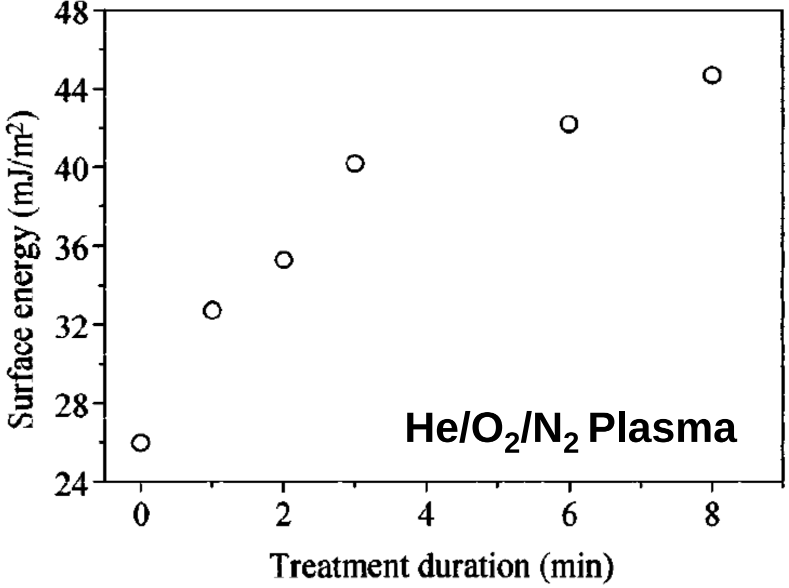




- M. Strobel, 3M

- To improve wetting and adhesion of polymers atmospheric plasmas are used to generate gas-phase radicals to functionalize their surfaces.

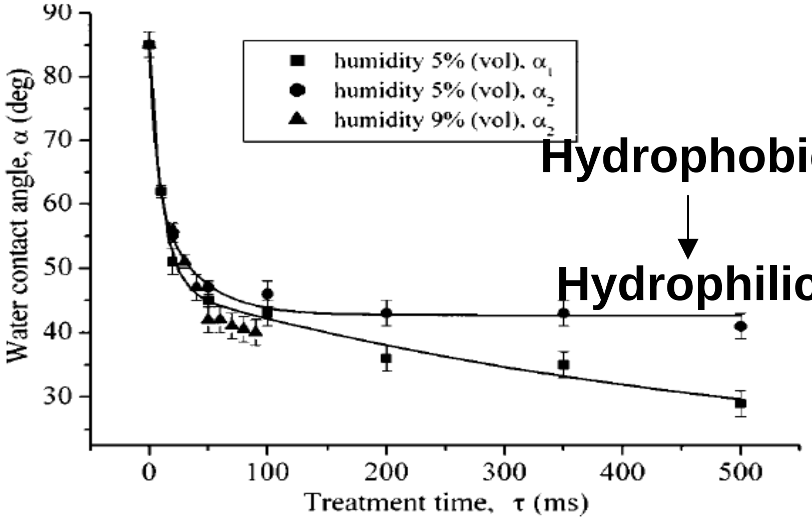
- Polypropylene (PP)



- Massines *et al.* J. Phys. D 31, 3411 (1998).

PLASMA PRODUCED WETTABILITY

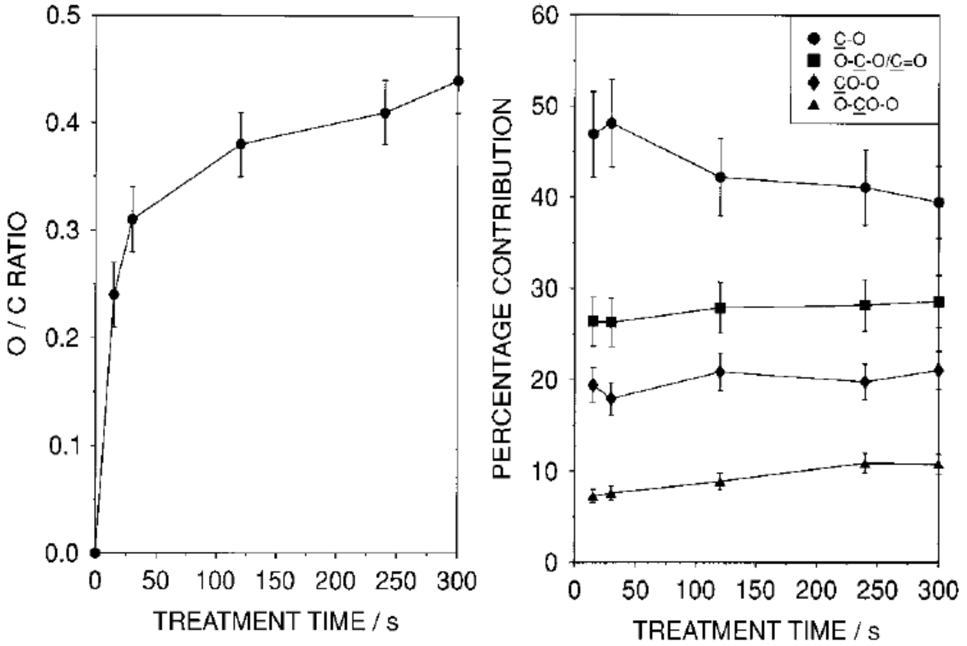
- Increases in wettability with plasma treatment result from formation of surface hydrophilic groups such as C-O-O (peroxy), C=O (carbonyl).



Hydrophobic

↓

Hydrophilic



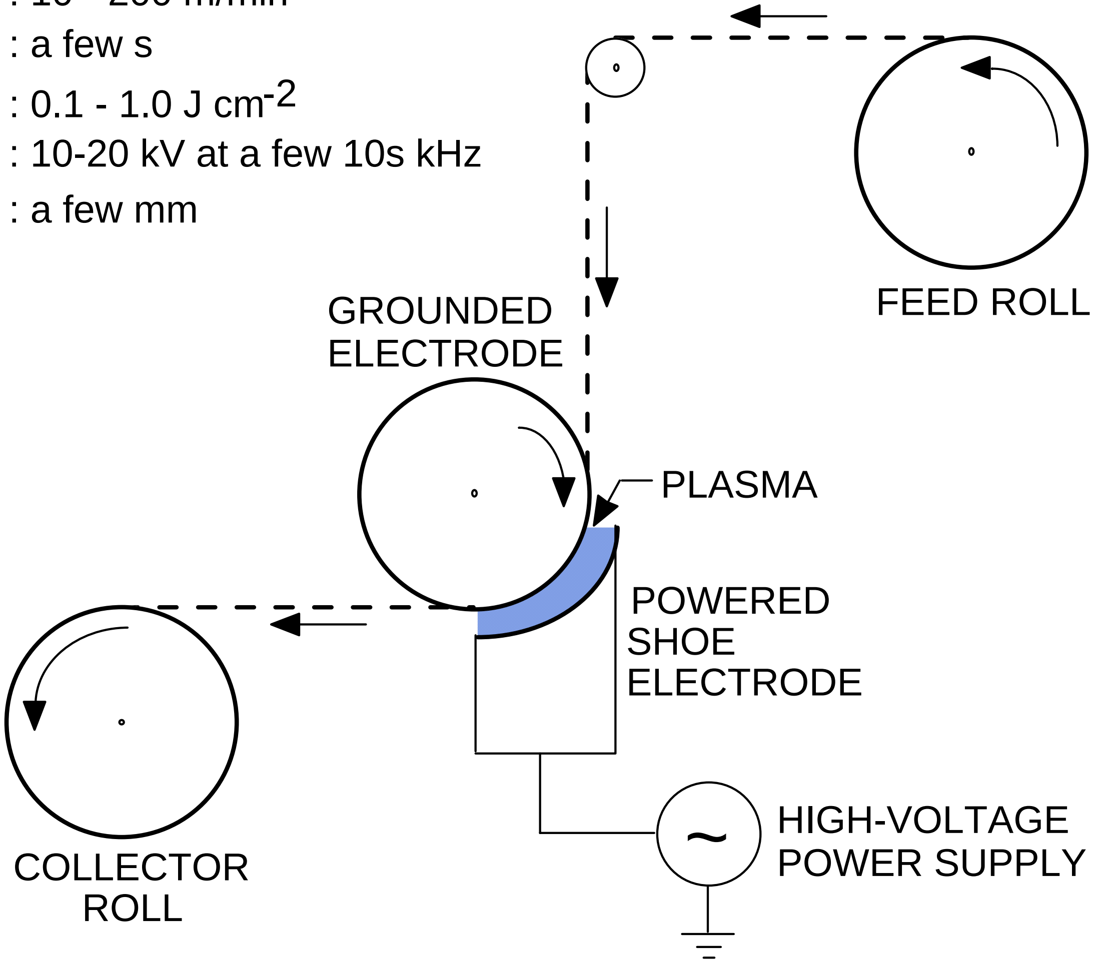
- **Polyethylene, Humid-air**
- **Akishev, Plasmas Polym. 7, 261 (2002).**

- **Polypropylene, Air corona**
- **Boyd, Macromol., 30, 5429 (1997).**

POLYMER TREATMENT APPARATUS

- TYPICAL PROCESS CONDITIONS:

Web speed	: 10 - 200 m/min
Residence time	: a few s
Energy deposition	: 0.1 - 1.0 J cm^{-2}
Applied voltage	: 10-20 kV at a few 10s kHz
Gas gap	: a few mm



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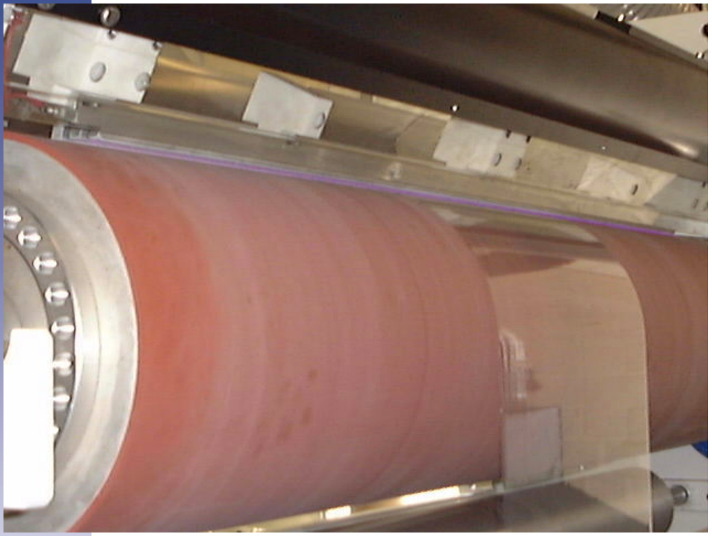
COMMERCIAL CORONA PLASMA EQUIPMENT

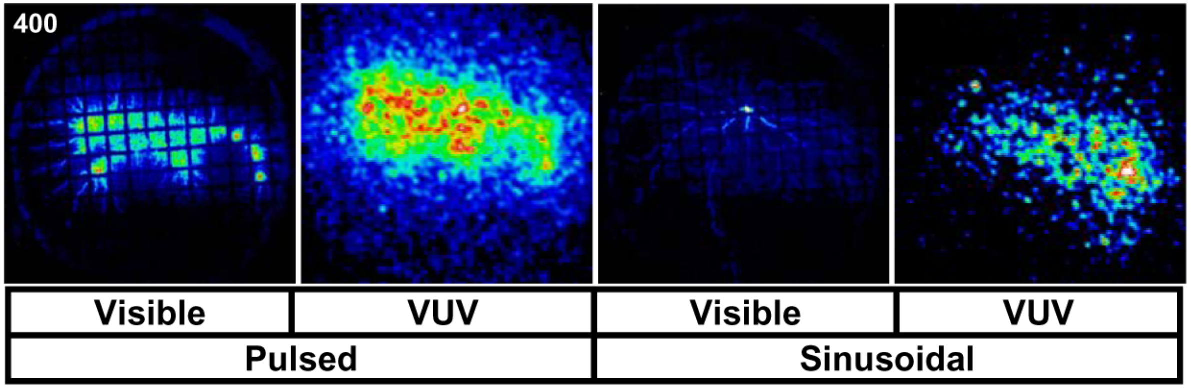


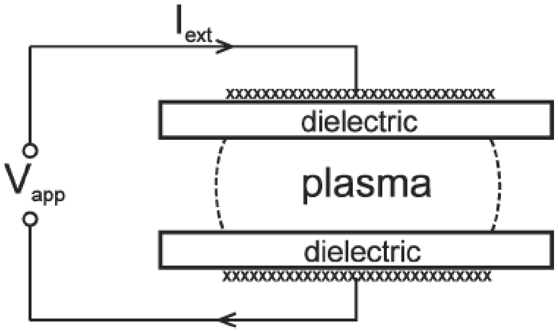
- **Sherman Treaters**

- **Tantec, Inc.**

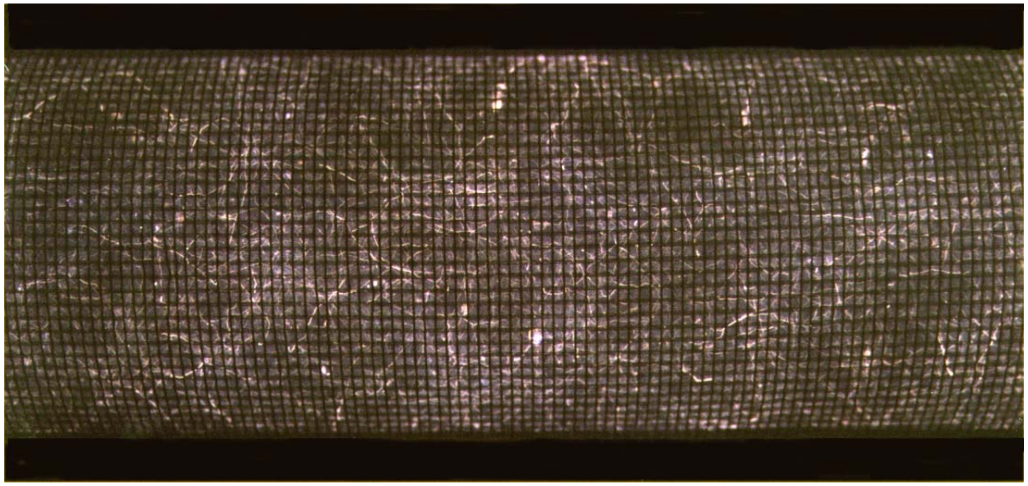
CORONA/DIELECTRIC BARRIER PLASMAS

- **Corona dielectric barrier discharge plasmas operate filamentary mode.**





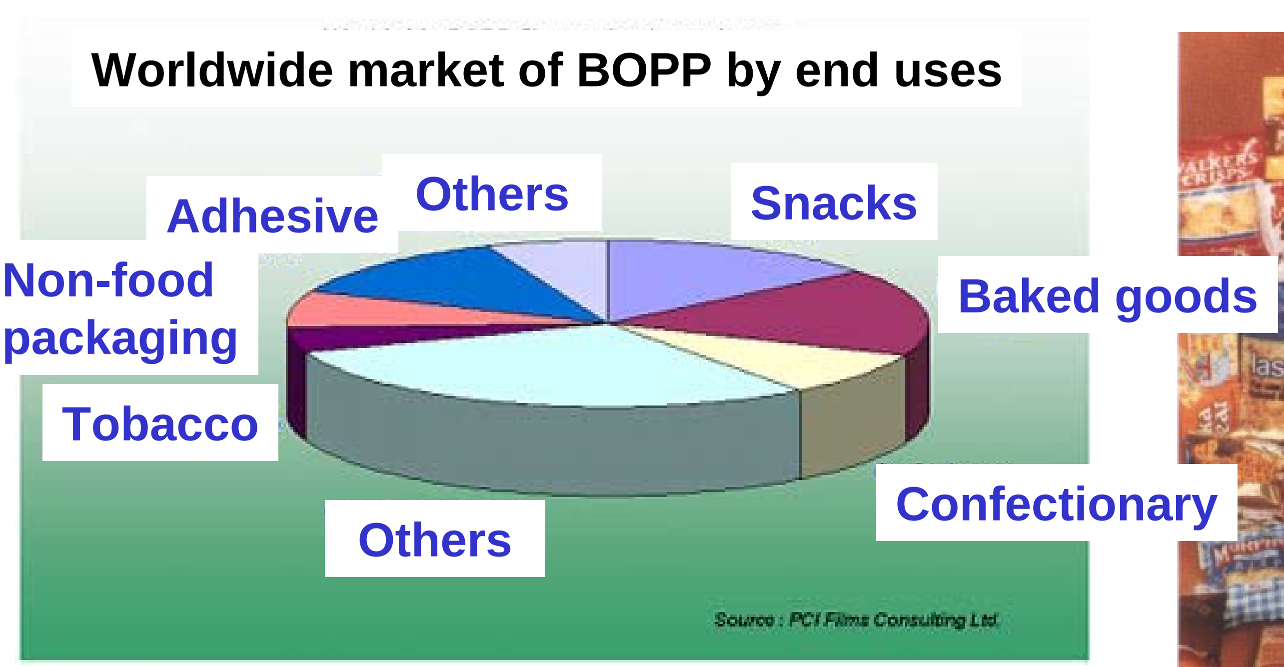
- **Xe DBD (400 Torr, 3 mm, 8 kV) [Mildren, Carman Falconer, TPS 30, 192 (2002)]**



- **Glass sphere 1 atm O_2 DBD (10 mm gap, 2 mm spheres, 17.5 kV) [Murphy and Morrow, TPS 30, 180 (2002)]**

POLYPROPYLENE

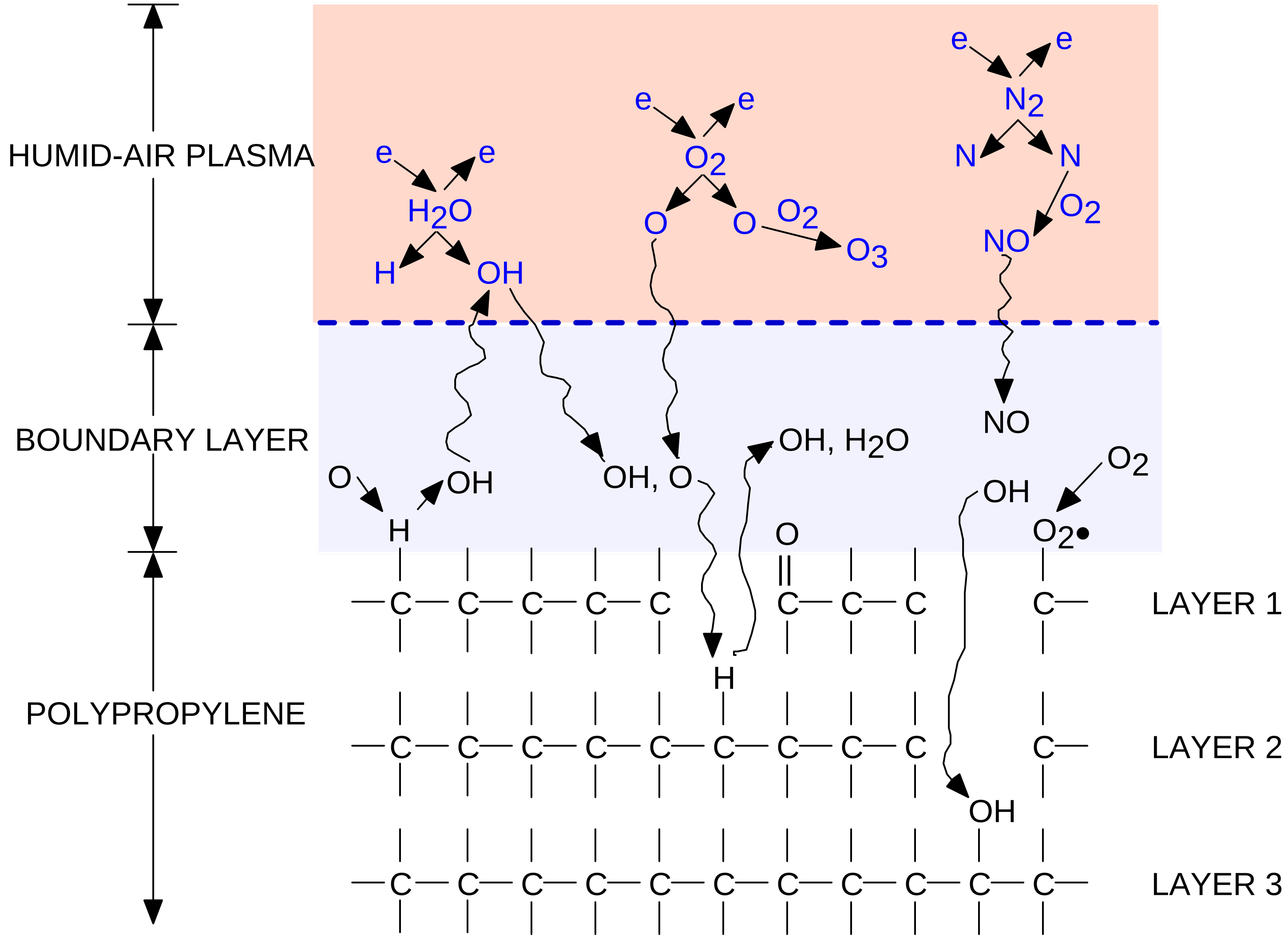
- **PP is a hard but flexible plastic. 5 million metric tons of PP film are used yearly, much of it functionalized with plasmas.**



FUNCTIONALIZATION OF THE PP SURFACE

- **Untreated PP is hydrophobic.**
- **Increases in surface energy by plasma treatment are attributed to the functionalization of the surface with hydrophilic groups.**
  - **Carbonyl (-C=O)**
  - **Alcohols (C-OH)**
  - **Peroxy (-C-O-O)**
  - **Acids ((OH)C=O)**
- **The degree of functionalization depends on process parameters such as gas mix, energy deposition and relative humidity (RH).**
- **At sufficiently high energy deposition, erosion of the polymer occurs.**

REACTION PATHWAY



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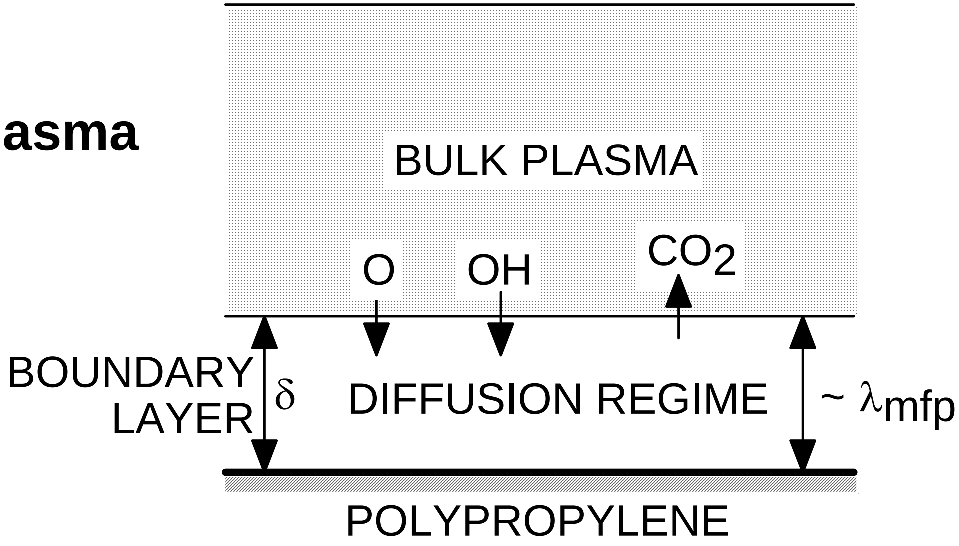
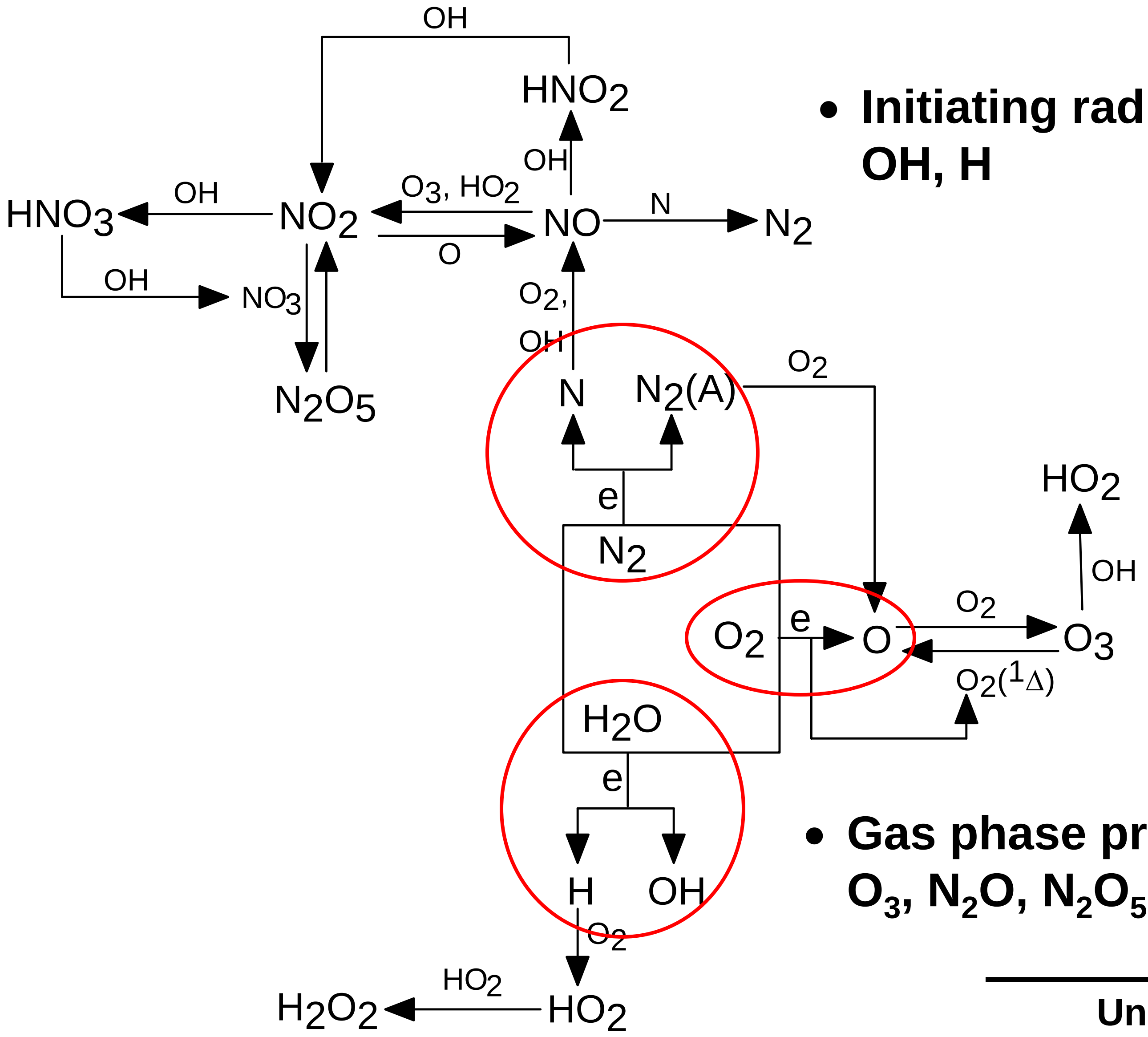
GLOBAL_KIN AND SURFACE KINETICS

- **Reaction mechanisms in pulsed atmospheric air plasma treatment of polymers have been investigated with global kinetics and surface models.**

- **GLOBAL_KIN**
  - **2-Zone homogeneous plasma chemistry (bulk plasma, boundary layer)**
  - **Plug flow**
  - **Multilayer surface site balance model**
  - **Circuit module**
  - **Boltzmann derived *f*(ε)**



REACTION MECHANISM FOR HUMID-AIR PLASMA



- **Initiating radicals are O, N, OH, H**

- **Gas phase products include O_3, N_2O, N_2O_5, HNO_2, HNO_3.**

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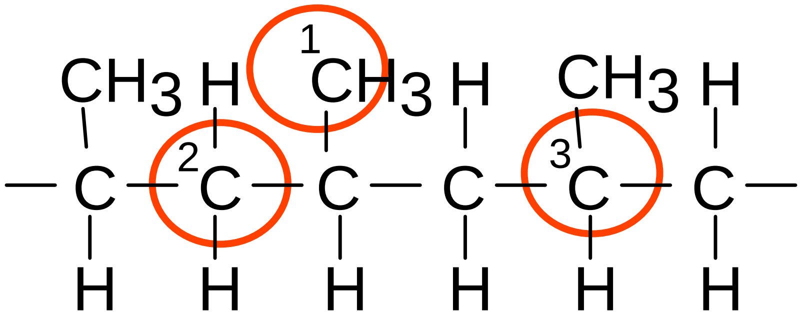
POLYPROPYLENE (PP) POLYMER STRUCTURE



1 - Primary C

2 - Secondary C

3 - Tertiary C

- **Three types of carbon atoms in a PP chain:**
  - **Primary – bonded to 1 C atom**
  - **Secondary – bonded to 2 C atoms**
  - **Tertiary – bonded to 3 C atoms**

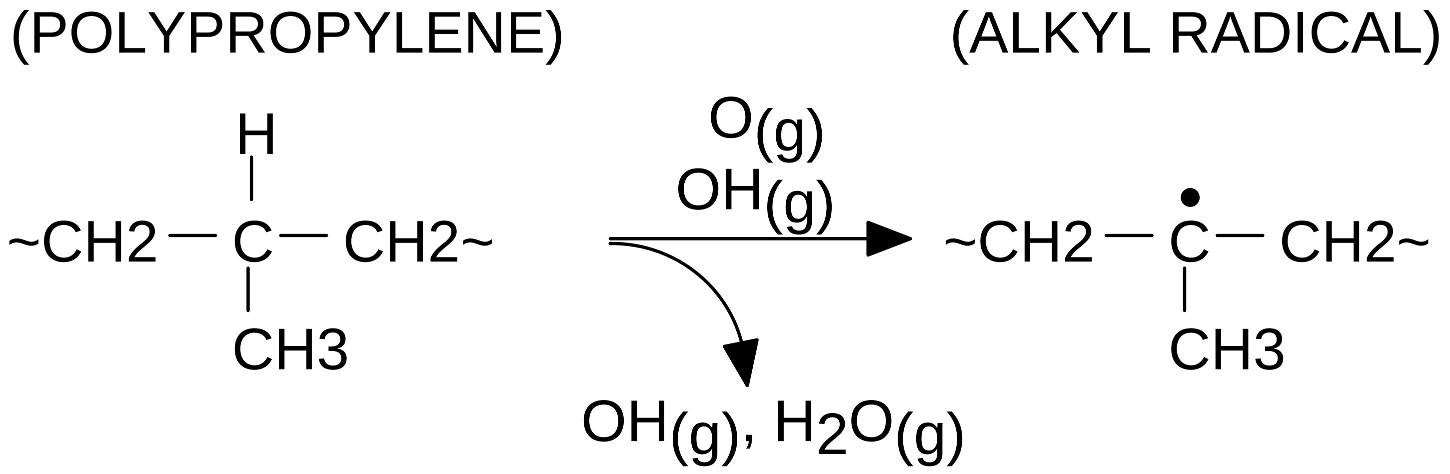
- **The reactivity of an H-atom depends on the type of C bonding. Reactivity scales as:**

$$H_{TERTIARY} > H_{SECONDARY} > H_{PRIMARY}$$

PP SURFACE REACTION MECHANISM: INITIATION

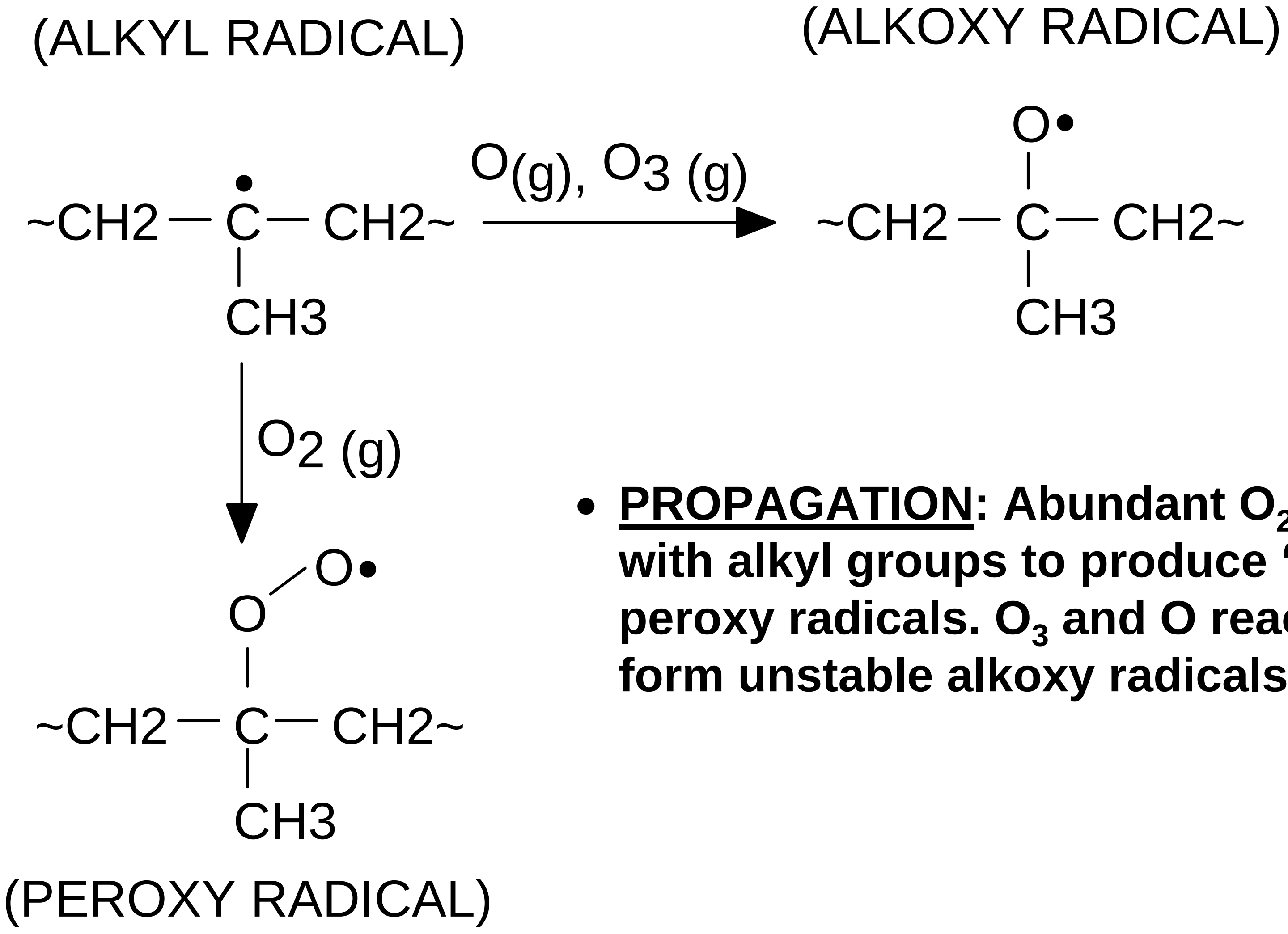
- The surface reaction mechanism has ***initiation, propagation*** **and** ***termination*** **reactions.**

- **<u>INITIATION</u>: O and OH abstract H from PP to produce alkyl radicals; and gas phase OH and H_2O.**



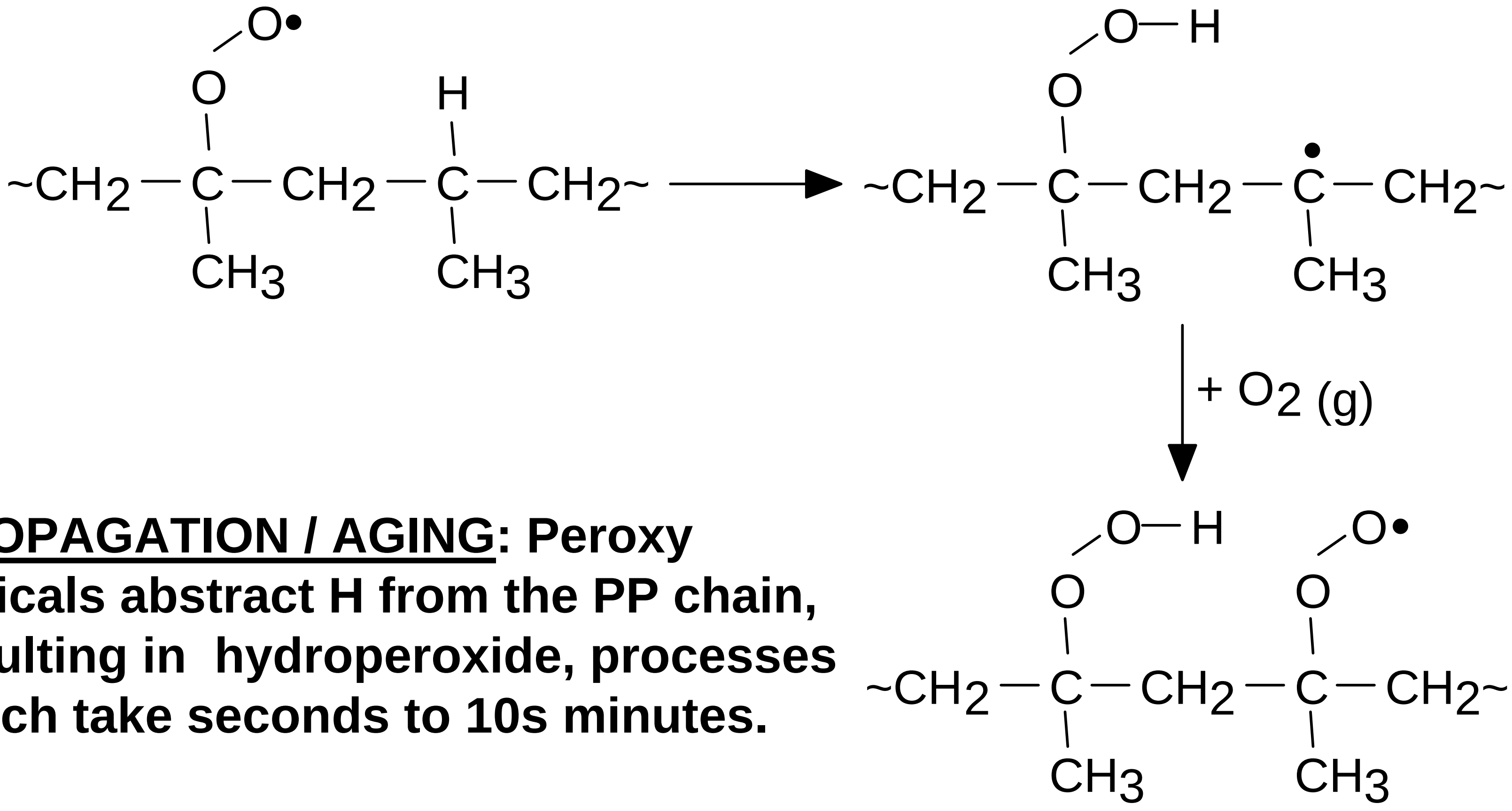
$$\sim CH2 - \overset{\overset{H}{|}}{\underset{\underset{CH3}{|}}{C}} - CH2\sim \xrightarrow[\text{OH}_{(g)},\ \text{H}_2\text{O}_{(g)}]{\text{O}_{(g)}\ \text{OH}_{(g)}} \sim CH2 - \overset{\bullet}{\underset{\underset{CH3}{|}}{C}} - CH2\sim$$

PP SURFACE REACTION MECHANISM: PROPAGATION



- **<u>PROPAGATION</u>: Abundant O_2 reacts with alkyl groups to produce “stable” peroxy radicals. O_3 and O react to form unstable alkoxy radicals.**

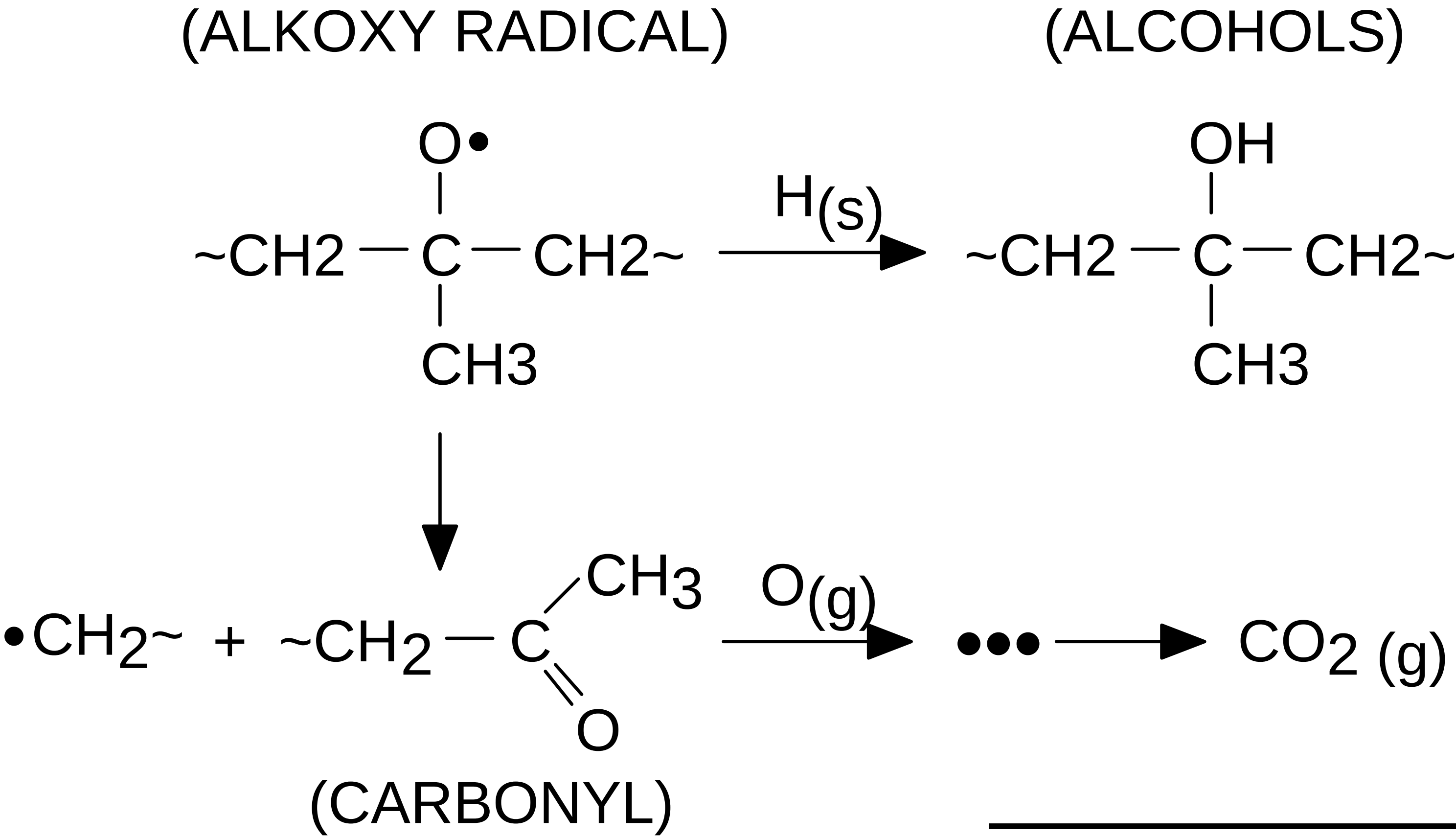
PP SURFACE REACTIONS: PROPAGATION / AGING

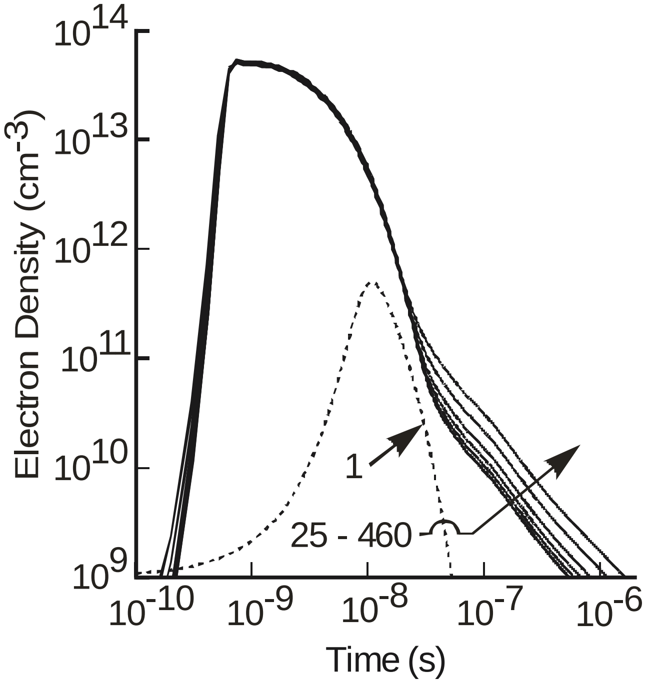


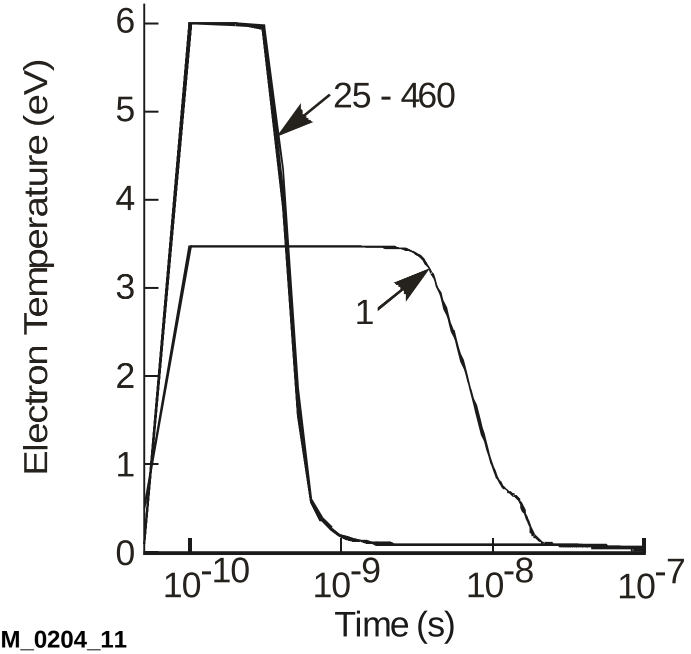
- **<u>PROPAGATION / AGING</u>: Peroxy radicals abstract H from the PP chain, resulting in hydroperoxide, processes which take seconds to 10s minutes.**

PP SURFACE REACTION MECHANISM: TERMINATION

- **TERMINATION: Alkoxy radicals react with the PP backbone to produce alcohols and carbonyls. Further reactions with O eventually erodes the film.**







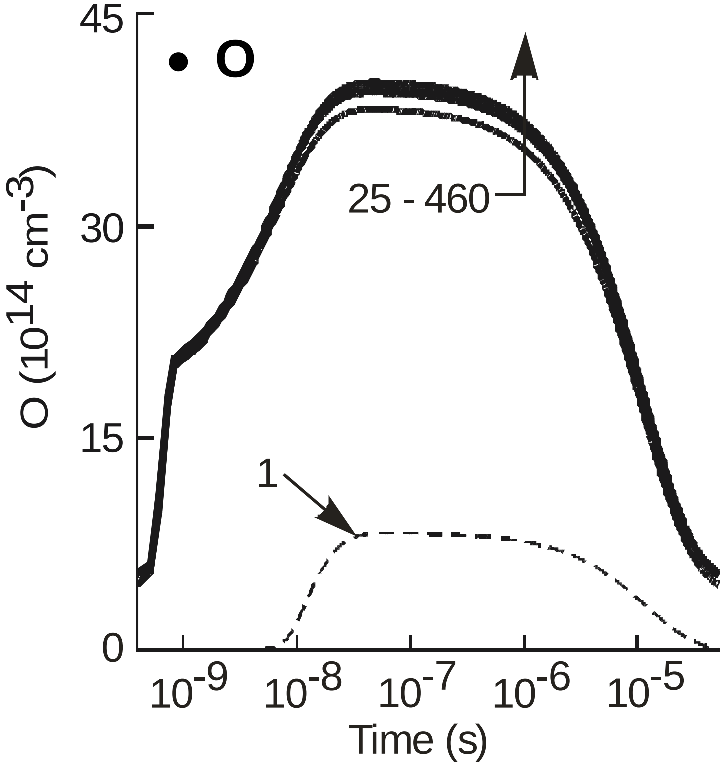
GEM_0204_11

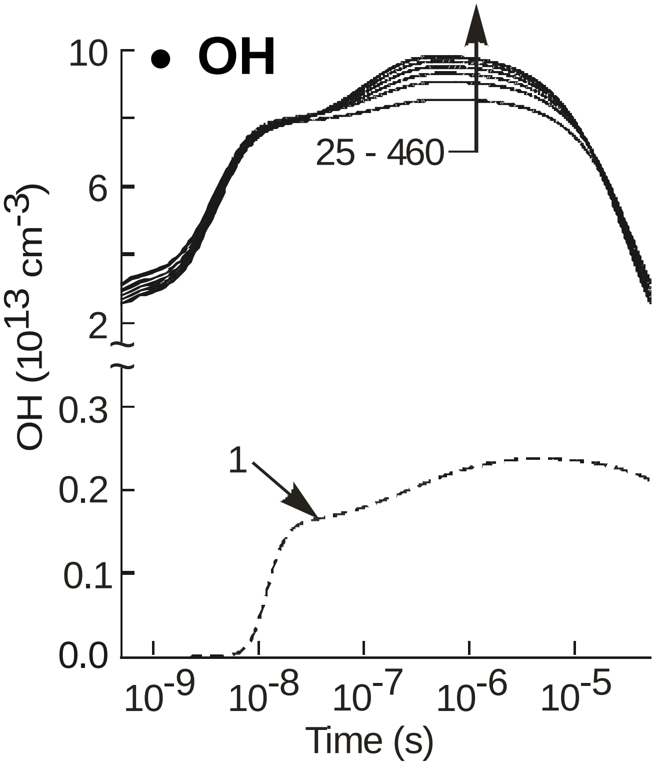
BASE CASE: n_e, T_e

- Ionization is dominantly of N_2 and O_2,
  - $e + N_2 \rightarrow N_2^+ + e + e$,
  - $e + O_2 \rightarrow O_2^+ + e + e$.
- After a few ns current pulse, electrons decay by attachment (primarily to O_2).
- Dynamics of charging of the dielectrics produce later pulses with effectively larger voltages; residual preionization and metastables also persist.
- $N_2/O_2/H_2O$ = 79/20/1, 300 K
- 15 kV, 9.6 kHz, 0.8 J-cm^{-2}
- Web speed = 250 cm/s (460 pulses)

GAS-PHASE RADICALS: O, OH

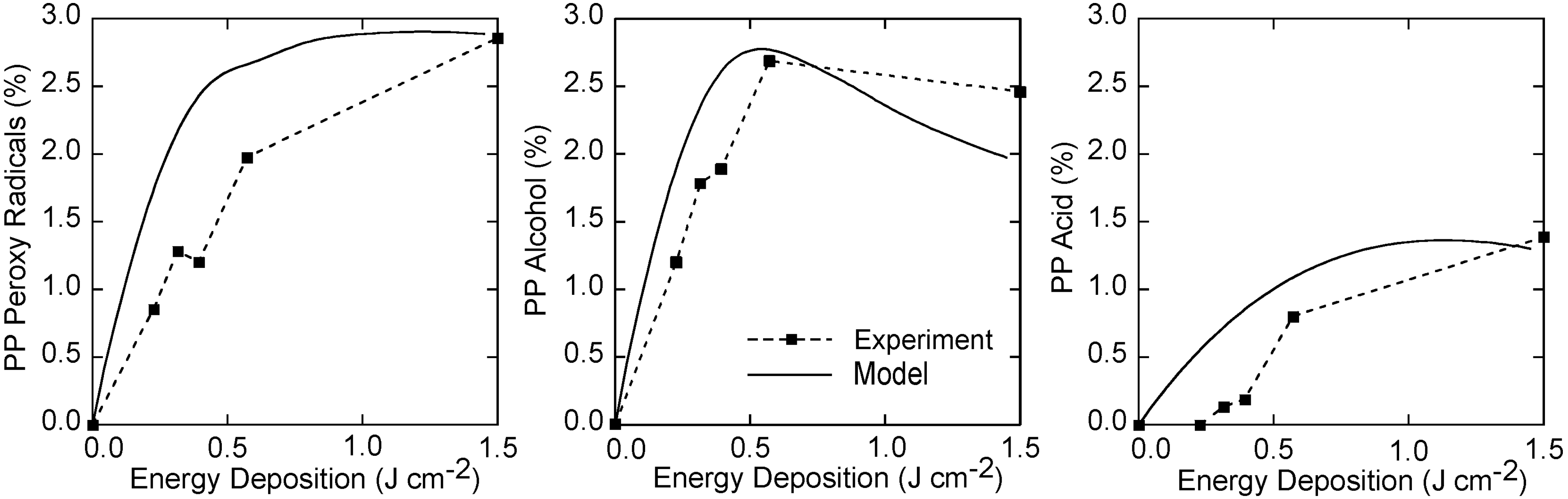
- Electron impact dissociation of O_2 and H_2O produces O and OH. O is consumed primarily to form O_3; OH is consumed by both bulk and surface processes.
- After 100s of pulses, radicals attain a periodic steady state.





PP SURFACE GROUPS vs ENERGY DEPOSITION

- Surface concentrations of alcohols, peroxy radicals are near steady state with a few J-cm^{-2}.
- Alcohol densities decrease at higher J-cm^{-2} energy due to decomposition by O and OH to regenerate alkoxy radicals.



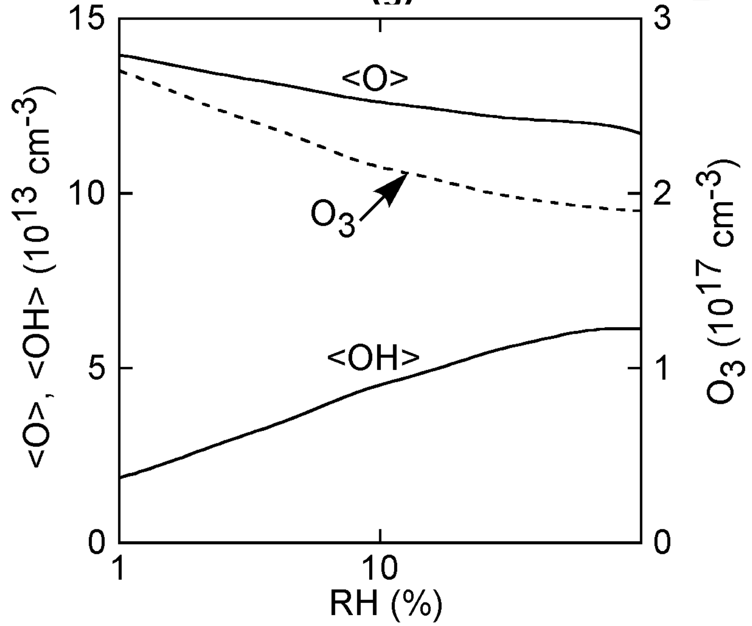
- Air, 300 K, 1 atm, 30% RH

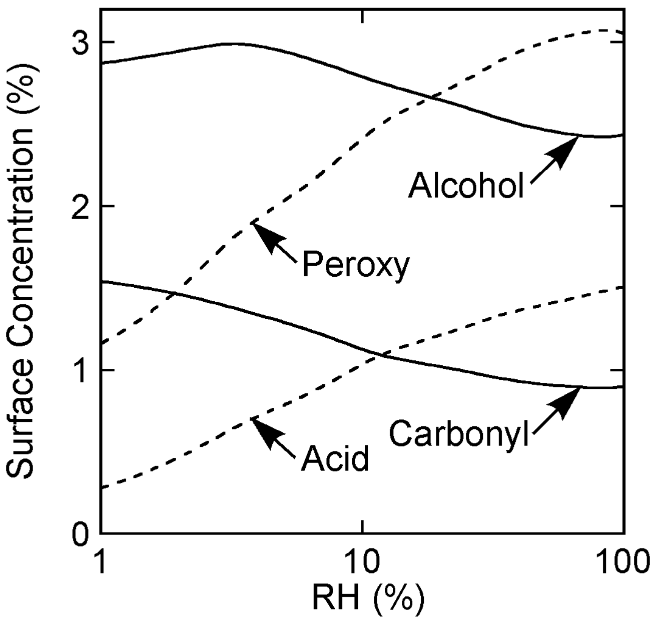
- Ref: L-A. Ohare *et al.*, Surf. Interface Anal. 33, 335 (2002).

HUMIDITY: PP FUNCTIONALIZATION BY OH

- Increasing RH produces OH which react with PP to form alkyl radicals, which are rapidly converted to peroxy radicals by O_2.

$PP\text{-}H + OH_{(g)} \rightarrow PP\bullet + H_2O_{(g)}$ $PP\bullet + O_{2(g)} \rightarrow PP\text{-}O_2\bullet$





- Alcohol and carbonyl densities decrease due to increased consumption by OH to form alkoxy radicals and acids.

$PP\text{-}OH + OH_{(g)} \rightarrow PP\text{-}O\bullet + H_2O_{(g)}$, $PP{=}O\bullet + OH_{(g)} \rightarrow (OH)PP{=}O$

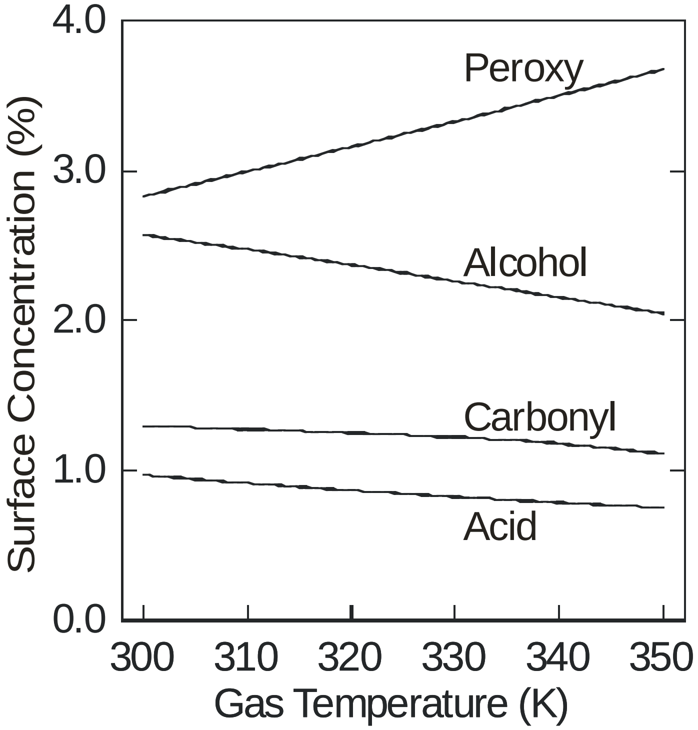
EFFECT OF T_{Gas}: PP FUNCTIONALIZATION

- **Increasing T_{gas} decreases O_3 leading to lower alkoxy production.**

  - **$PP\bullet + O_{3(g)} \rightarrow PP\text{-}O\bullet + O_{2(g)}$.**

- **… and lower production of alcohols, carbonyl, and acids.**

$$PP\text{-}O\bullet + PP\text{-}H \rightarrow PP\text{-}OH + PP\bullet$$
$$PP\text{-}O\bullet \rightarrow PP{=}O$$
$$PP{=}O \rightarrow PP{=}O\bullet$$
$$PP{=}O\bullet + OH \rightarrow (OH)PP{=}O\bullet$$



- **Lower consumption of alkyl radicals by O_3 enables reactions with O_2 to dominate, increasing densities of peroxy.**

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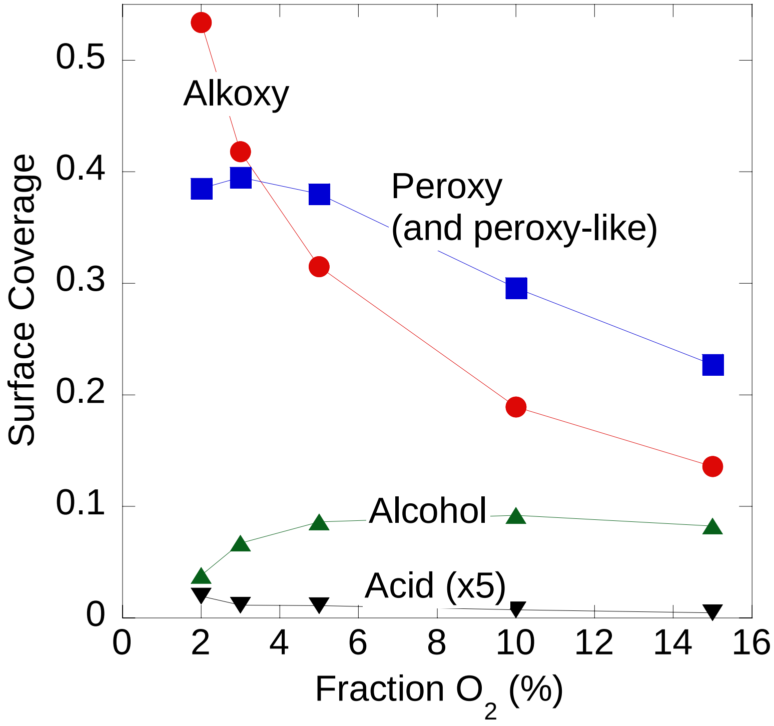
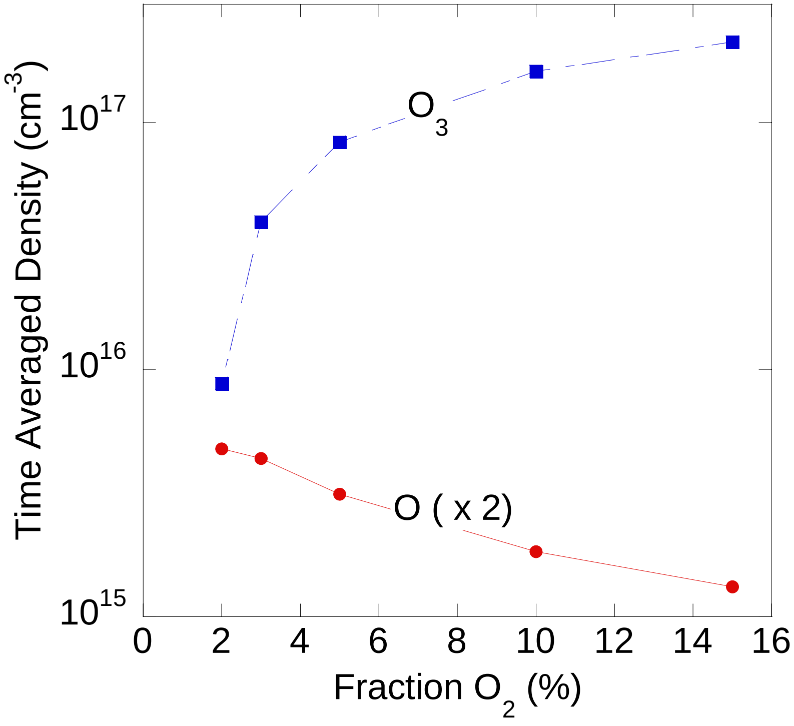
COMMODITY TO HIGH VALUE

- **As the material value increases (cents to dollars /cm^2?) higher process refinement is justified to customize functionalization.**

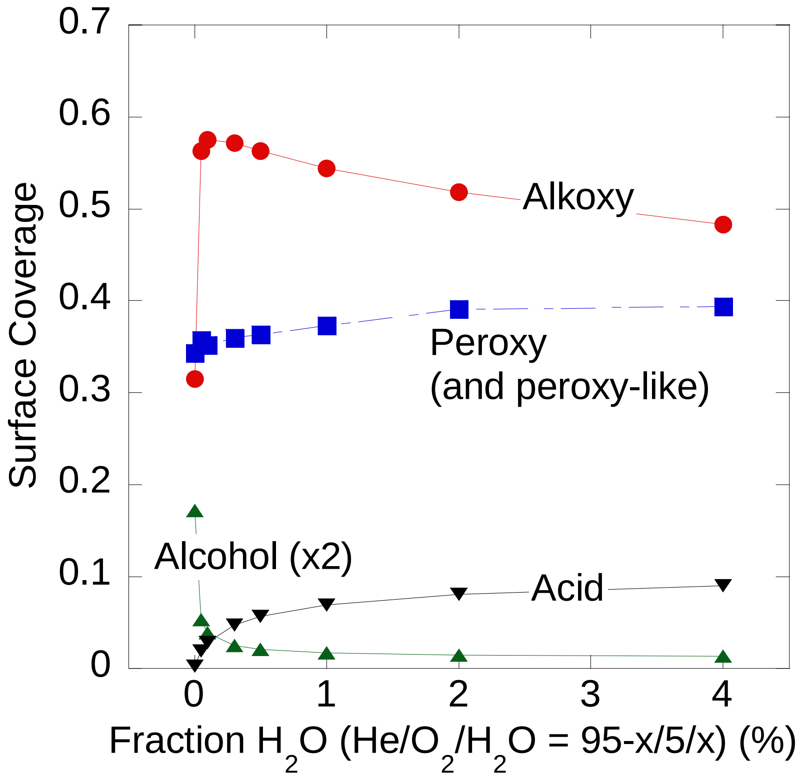




- **Control of O to O_3 ratio using He/O_2 mixtures can be used to customize surface functionalization.**
- **1 atm, He/O_2, 15 kV, 3 mm, 9.6 kHz, 920 pulses.**

COMMODITY TO HIGH VALUE

- **Additional "tuning" of functionalization can be achieved with sub-mTorr control of water content.**



- **Small water addition "tuning" of functionalization can be achieved with sub-mTorr control of water content.**
- **H and OH reduce O_3 while promoting acid formation.**

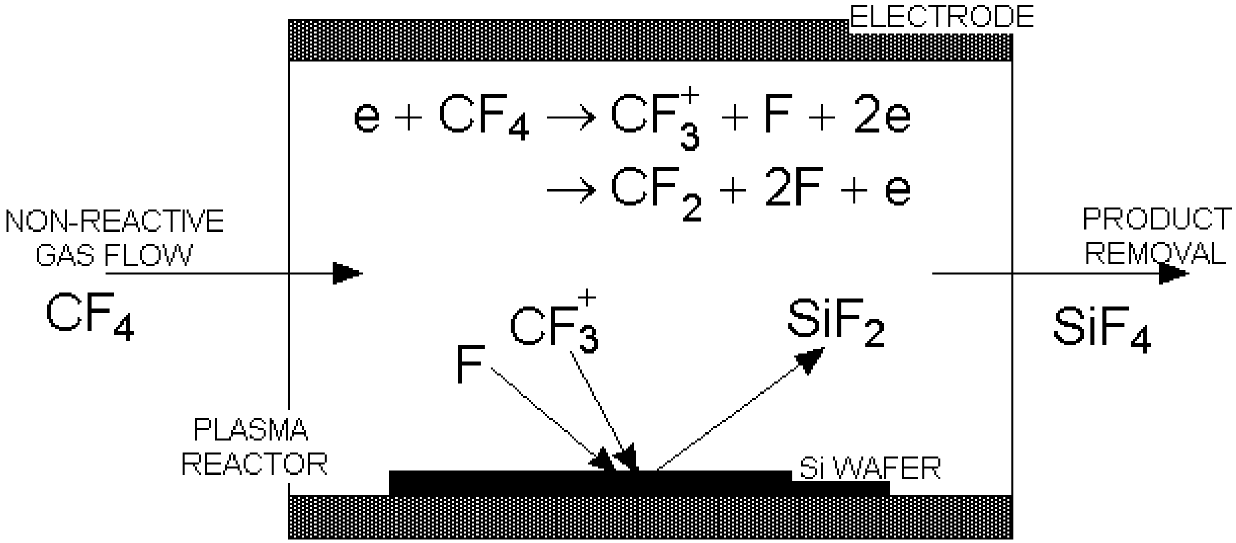
- **1 atm, He/O_2/ H_2O, 15 kV, 3 mm, 9.6 kHz, 920 pulses.**

HIGH COST, UTILIZATION OF POLYMERS IN MICROELECTRONICS FABRICATION

PLASMAS IN MICROELECTRONICS FABRICATION

- Plasmas play a dual role in microelectronics fabrication.

- First, electron impact on otherwise unreactive gases produces neutral radicals and ions.



$$\begin{aligned} e + CF_4 &\rightarrow CF_3^+ + F + 2e \\ &\rightarrow CF_2 + 2F + e \end{aligned}$$

- These species then drift or diffuse to surfaces where they add, remove or modify materials.

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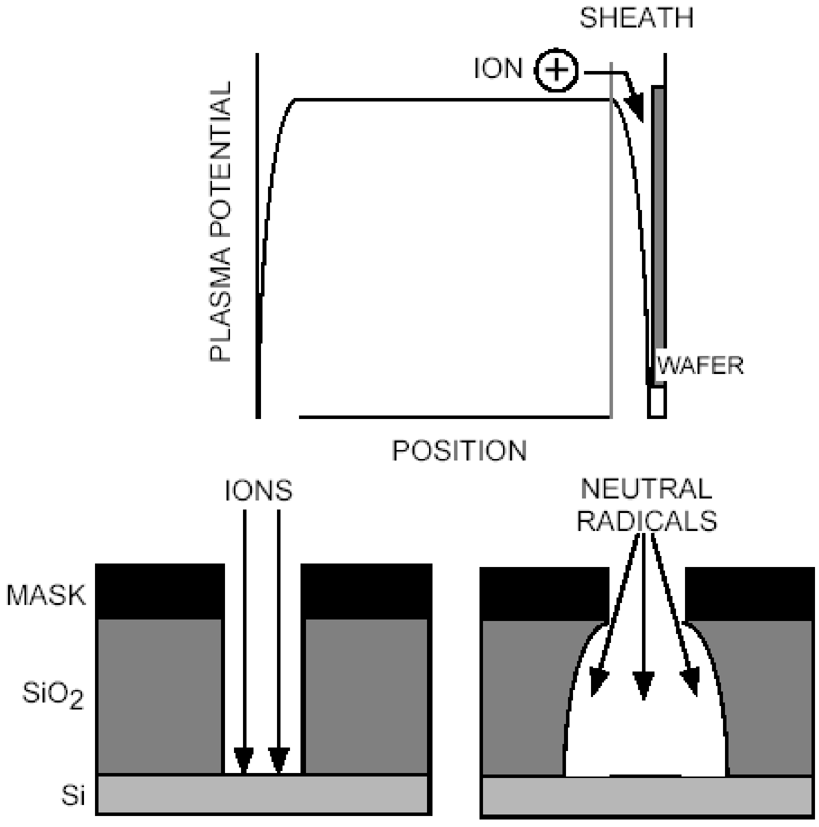
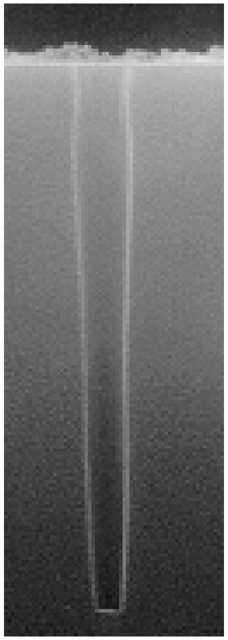
PLASMAS IN MICROELECTRONICS FABRICATION

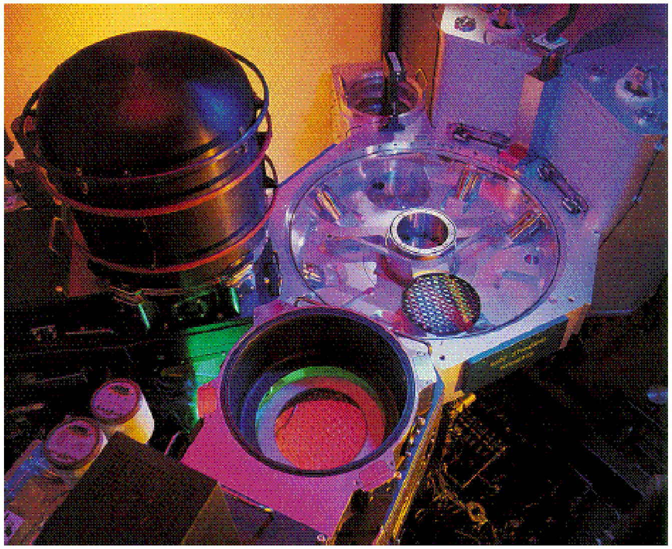
- **Second, ions deliver directed activation energy to surfaces fabricating fine having extreme and reproducable tolerances.**



- Ion Assisted Etching
- Neutral Dominated Etching

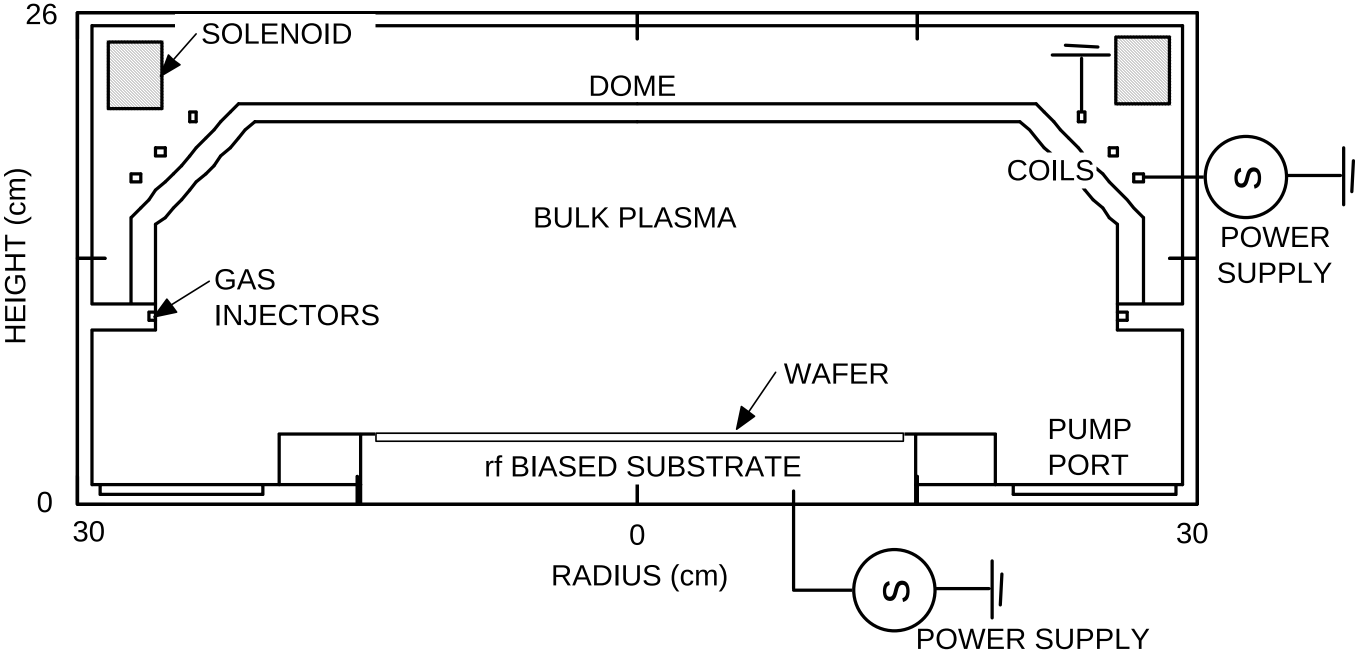


- **0.25 μm Feature (C. Cui, AMAT)**



rf BIASED INDUCTIVELY COUPLED PLASMAS

- **Inductively Coupled Plasmas (ICPs) with rf biasing are used here.**
- **< 10s mTorr, 10s MHz, 100s W – kW, electron densities of 10^{11}-10^{12} cm^{-3}.**



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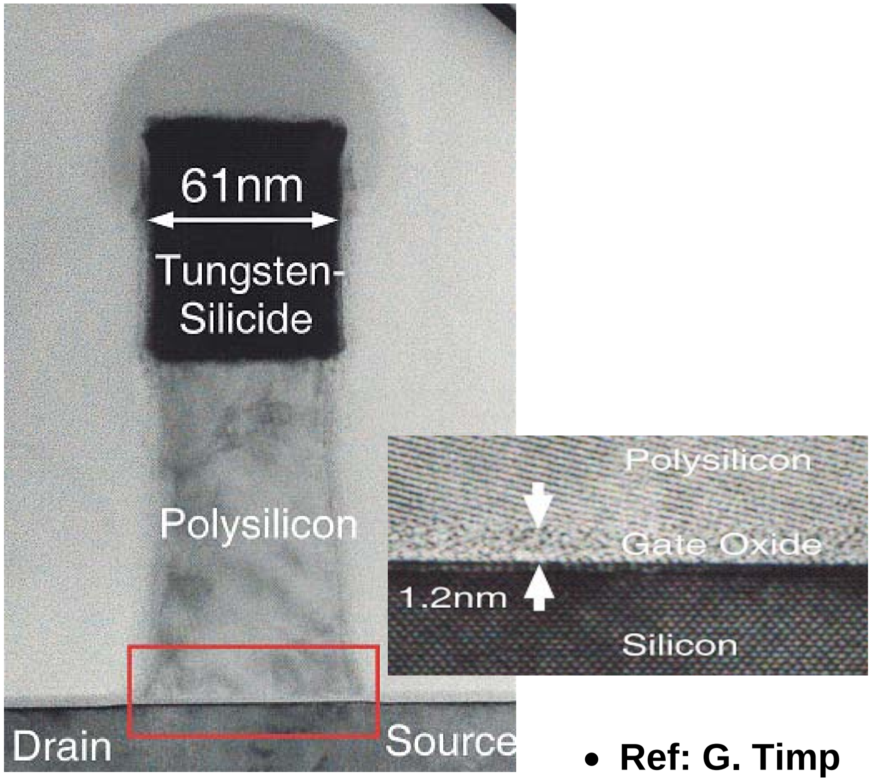
SELECTIVITY IN MICROELECTRONICS FABRICATION: PLASMAS AND POLYMERS

- **Fabricating complex microelectronic structures made of different materials requires extreme *selectivity* in, for example, etching Si with respect to SiO_2.**

- **Monolayer selectivity is required in advanced etching processes.**

- **These goals are met by the unique plasma-polymer interactions enabled in fluorocarbon chemistries.**

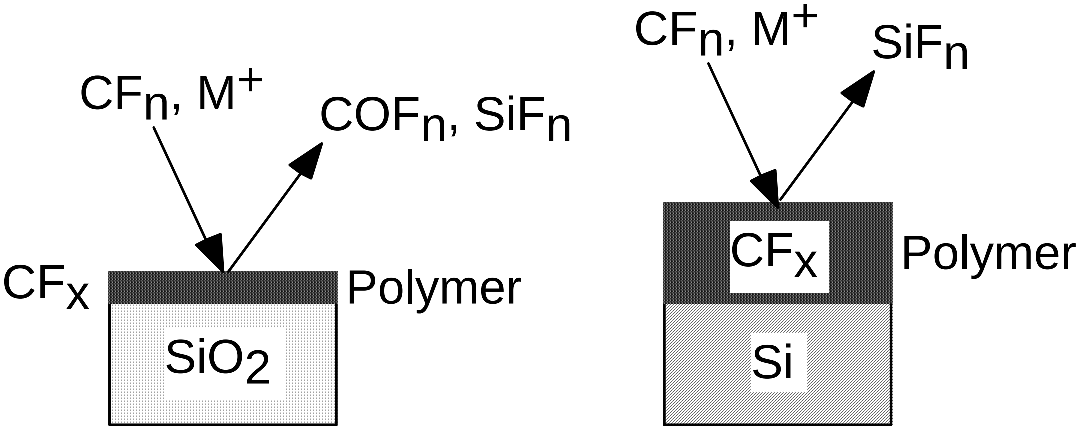


- **Ref: G. Timp**

FLUORCARBON PLASMA ETCHING: SELECTIVITY

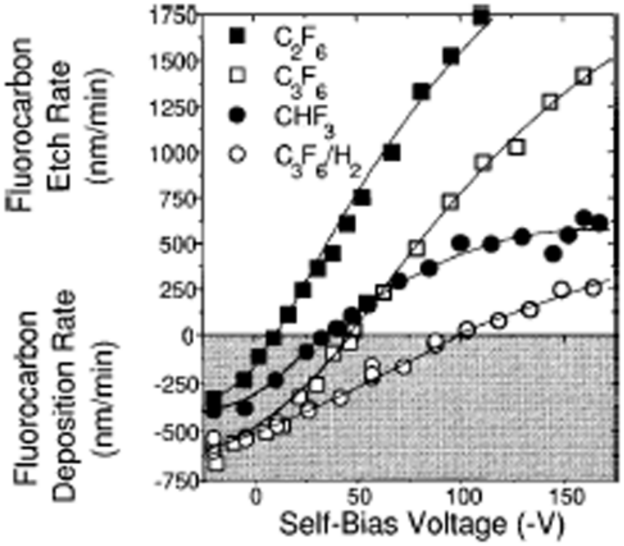
- **Selectivity in fluorocarbon etching relies on polymer deposition.**
- **Electron impact dissociation of feedstock fluorocarbons produce polymerizing radicals and ions, resulting in polymer deposition.**

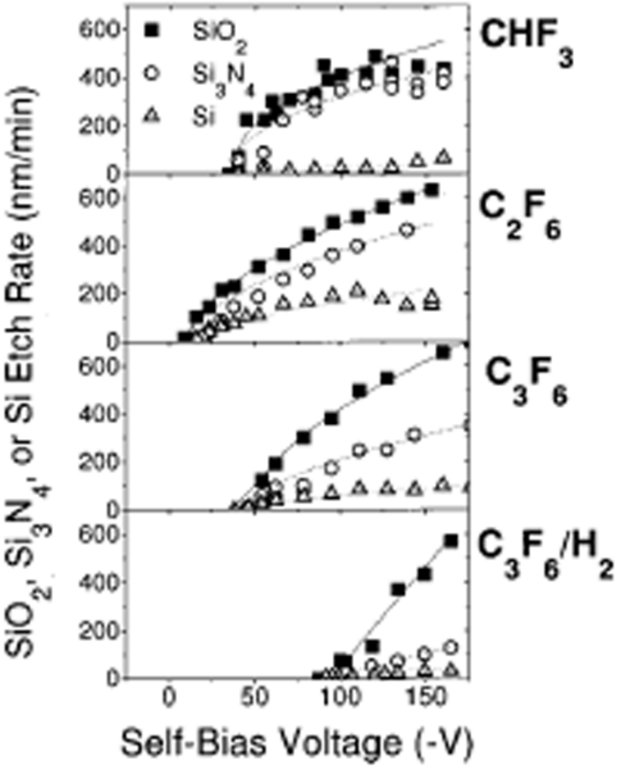
$$e + Ar/C_4F_8 \longrightarrow CF_n, M^+$$

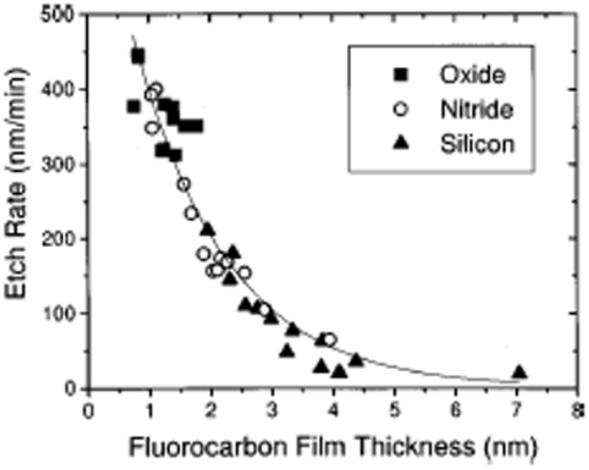


- **Compound dielectrics contain oxidants which consume the polymer, producing thinner polymer layers.**
- **Thicker polymer on non-dielectrics restrict delivery of ion energy (lower etching rates).**

FLUORCARBON PLASMA ETCHING: SELECTIVITY







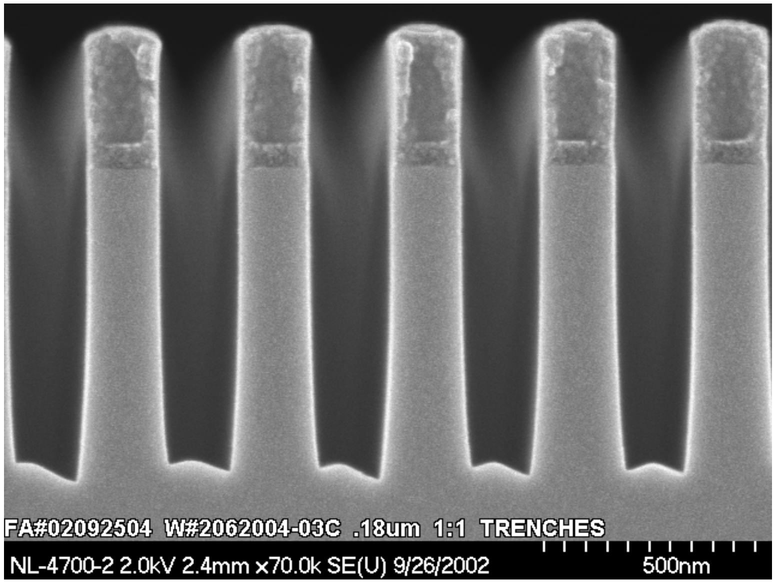
- **Low bias: Deposition**
- **High bias: etching**

- **Etch Rate (SiO_2 > Si)**

- **Polymer Thickness (SiO_2 < Si)**

- **G. Oerhlein, et al., JVSTA 17, 26 (1999)**

FLUOROCARBON ETCHING: GAS CHEMISTRY



- MERIE
- 1500 W, 40 mTorr
- $Ar/O_2/C_4F_8$: 200/5/10 sccm
- Ref: SEMATECH

- Additives (Ar, CO and O_2) regulate the polymer thickness and delivery of activation energy.

- Ar controls the ratio of polymerizing flux to ion flux. O_2 controls polymer thickness by O atom etching.

- Optimization of these processes is critical as dielectrics thin, selectivity requirements become extreme and new materials such as low-k dielectrics are considered.

MODELING OF FLUOROCARBON PLASMA ETCHING

- Our research group has developed an integrated reactor and feature scale modeling hierarchy to model plasma processing systems.

  - **HPEM (Hybrid Plasma Equipment Model)**
    - Reactor scale
    - 2- and 3-dimensional
    - ICP, CCP, MERIE, ECR
    - Surface chemistry
    - First principles

  - **MCFPM (Monte Carlo Feature Profile Model)**
    - Feature scale
    - 2- and 3-dimensional
    - Fluxes from HPEM
    - First principles

ELECTROMAGNETICS AND ELECTRON KINETICS

- **The wave equation is solved in the frequency domain using tensor conductivities and sparse matrix techniques:**

$$-\nabla\left(\frac{1}{\mu}\nabla\cdot\overline{E}\right)+\nabla\cdot\left(\frac{1}{\mu}\nabla\overline{E}\right)=\frac{\partial^2\left(\varepsilon\overline{E}\right)}{\partial t^2}+\frac{\partial\left(\overline{\overline{\sigma}}\cdot\overline{E}+\overline{J}\right)}{\partial t}$$

- **<u>Electron energy transport: Continuum and Kinetics</u>**

$$\partial\left(\frac{3}{2}n_e kT_e\right)/\partial t=S\left(T_e\right)-L\left(T_e\right)-\nabla\cdot\left(\frac{5}{2}\Phi kT_e-\overline{\overline{\kappa}}\left(T_e\right)\cdot\nabla T_e\right)+S_{EB}$$

where $S(T_e)$ = Power deposition from electric fields
$L(T_e)$ = Electron power loss due to collisions
Φ = Electron flux
$\kappa(T_e)$ = Electron thermal conductivity tensor
S_{EB} = Power source source from beam electrons

- **<u>Kinetic</u>: MCS is used to derive $f\left(\varepsilon,\vec{r},t\right)$ including e-e collisions using electromagnetic and electrostatic fields .**

PLASMA CHEMISTRY, TRANSPORT AND ELECTROSTATICS

- **Continuity, momentum and energy equations are solved for each species (with jump conditions at boundaries).**

$$\frac{\partial N_i}{\partial t} = -\nabla \cdot (N_i \vec{\mathrm{v}}_i) + S_i$$

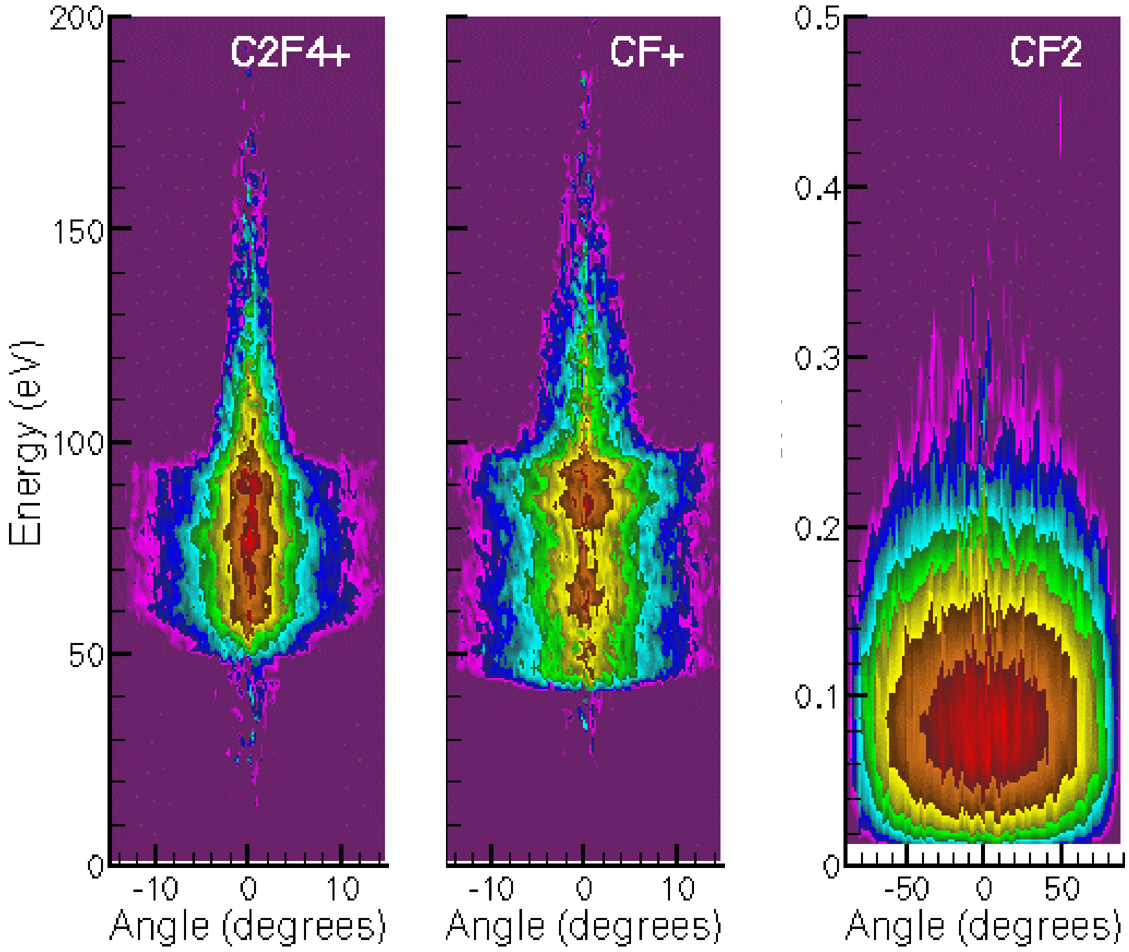
$$\frac{\partial \left(N_i \vec{v}_i\right)}{\partial t} = \frac{1}{m_i} \nabla \left(k N_i T_i\right) - \nabla \cdot \left(N_i \vec{v}_i \vec{v}_i\right) + \frac{q_i N_i}{m_i} \left(\vec{E} + \vec{v}_i \times \vec{B}\right) - \nabla \cdot \bar{\mu}_i - \sum_j \frac{m_j}{m_i + m_j} N_i N_j \left(\vec{v}_i - \vec{v}_j\right) \nu_{ij}$$

$$\frac{\partial \left(N_i \varepsilon_i\right)}{\partial t} + \nabla \cdot \mathrm{Q}_i + P_i \nabla \cdot \mathrm{U}_i + \nabla \cdot (N_i \mathrm{U}_i \varepsilon_i) = \frac{N_i q_i^2 \nu_i}{m_i (\nu_i^2 + \omega^2)} E^2 + \frac{N_i q_i^2}{m_i \nu_i} E_s^2 + \sum_j 3 \frac{m_{ij}}{m_i + m_j} N_i N_j R_{ij} k_B (T_j - T_i) \pm \sum_j 3 N_i N_j R_{ij} k_B T_j$$

- **Implicit solution of Poisson's equation:**

$$\nabla \cdot \varepsilon \nabla \Phi\left(t + \Delta t\right) = -\left(\rho_s + \sum_i q_i N_i - \Delta \mathrm{t} \cdot \sum_{\mathrm{i}} \left(\mathrm{q}_{\mathrm{i}} \nabla \cdot \vec{\phi}_i\right)\right)$$

ION/NEUTRAL ENERGY/ANGULAR DISTRIBUTIONS



- **MC methods are used to obtain energy and angular distributions of particles striking surfaces.**

- **Ar/C_4F_8, 40 mTorr, 10b MHz, MERIE**

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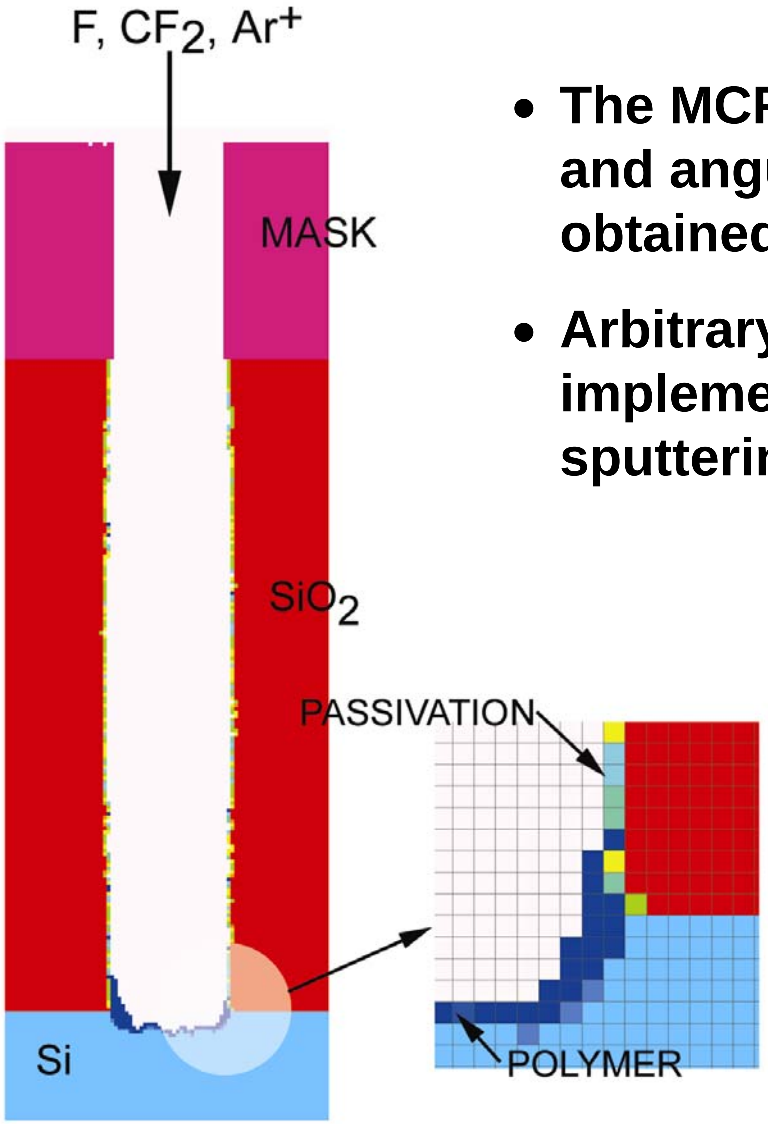
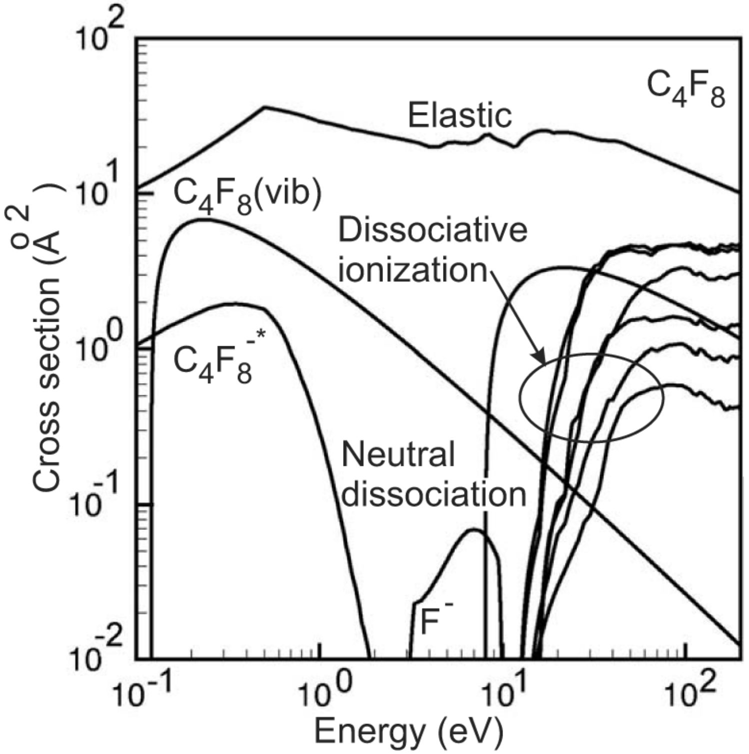
MONTE CARLO FEATURE PROFILE MODEL (MCFPM)



- **The MCFPM predicts profiles using energy and angularly resolved neutral and ion fluxes obtained from equipment scale models.**
- **Arbitrary reaction mechanisms may be implemented (thermal and ion assisted, sputtering, deposition and surface diffusion).**
- **Mesh centered identify of materials allows “burial”, overlayers and transmission of energy through materials.**

REACTION MECHANISM: Ar/c-C_4F_8/O_2/CO

- **Reaction mechanisms were developed for plasmas sustained in arbitrary mole fractions of Ar/c-C_4F_8/O_2/CO.**



Refs:

- **G. I. Font et al, J. Appl. Phys 91, 3530 (2002).**
- **C. Q. Jiao et al, Chem. Phys. Lett. 297, 121 (1998).**

- **c-C_4F_8 dissociative excitation is dominated by branching to C_2F_4.**

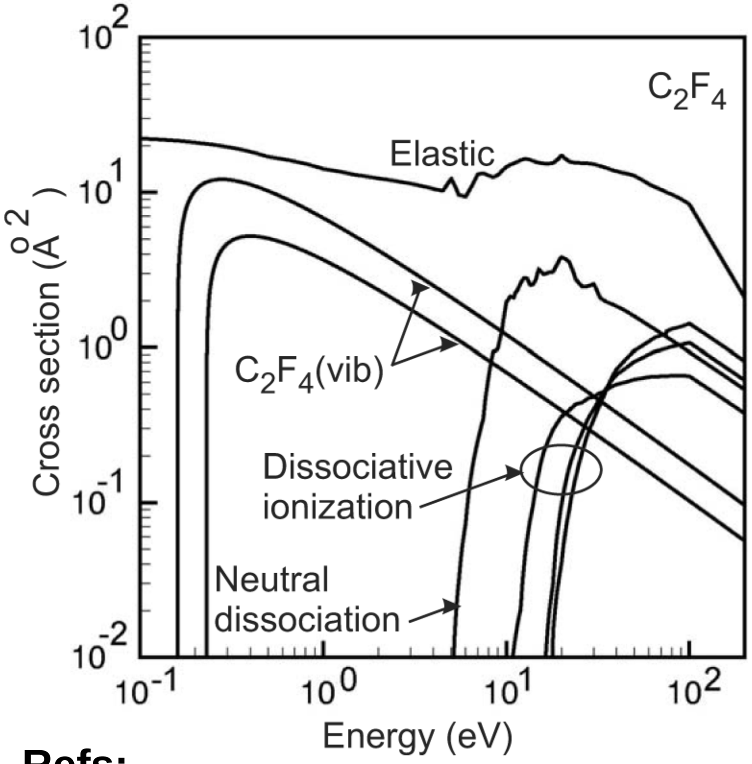
- **Dissociative ionization has dominate branchings to: $C_2F_4^+$, $C_3F_5^+$, CF^+, CF_3^+**

- **Importance of attachment depends on disposition of $(C_4F_8\text{-})^*$ ($\tau \leq 1\ \mu$s).**

$$e + C_4F_8 \underset{e}{\overset{\tau}{\leftrightarrow}} \left(C_4F_8^-\right)^* \xrightarrow{M} C_4F_8^-$$

REACTION MECHANISM: Ar/c-C_4F_8/O_2/CO

- C_2F_4 dissociative excitation branching is likely dominated by CF_2.

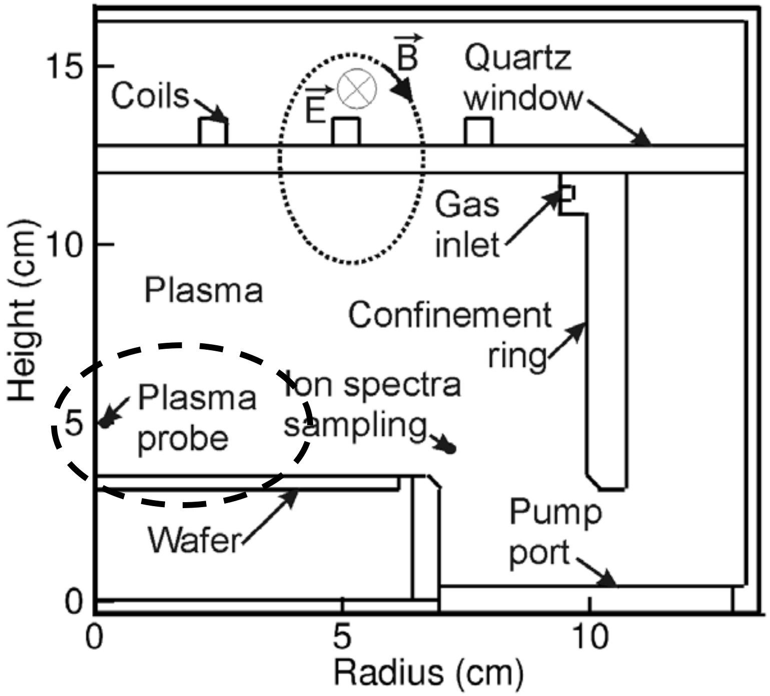


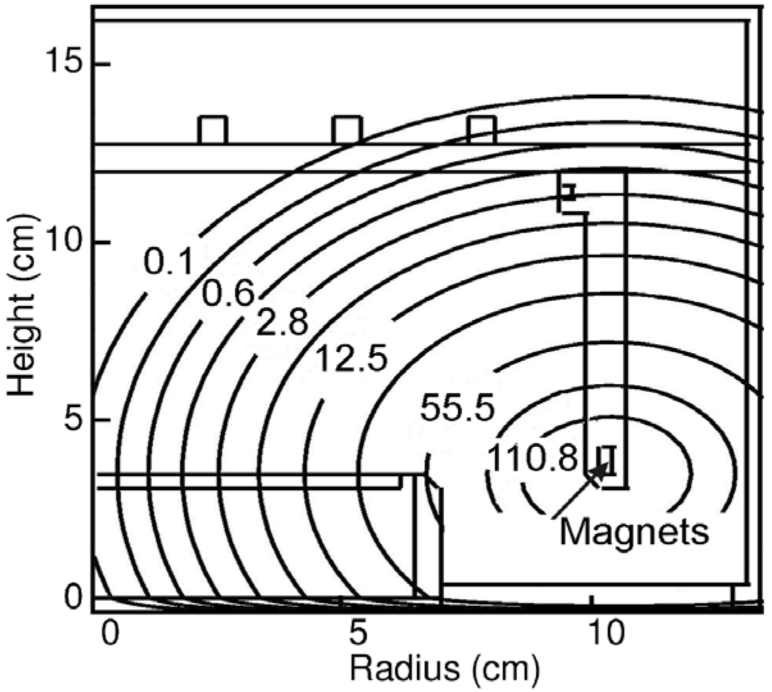
Refs:

- K. Yoshida et al., J. Appl. Phys. 91, 2637 (2002).
- C. Winstead and V. McKoy, J. Chem. Phys. 116, 1380 (2002).

- Dissociative ionization has dominate channels to: $C_2F_4^+$, $C_2F_3^+$, CF^+
- Attachment is negligible.
- Large fractions of CF_n^+ reslut from ionization of dissociation products and charge exchange from Ar^+, CO^+, O_n^+.

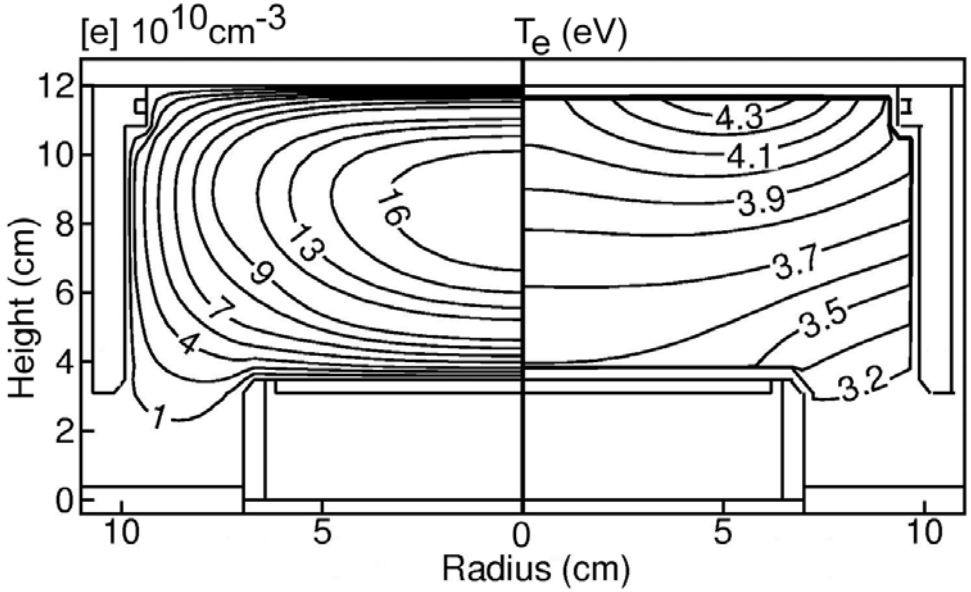
ICP CELL FOR VALIDATION AND INVESTIGATION

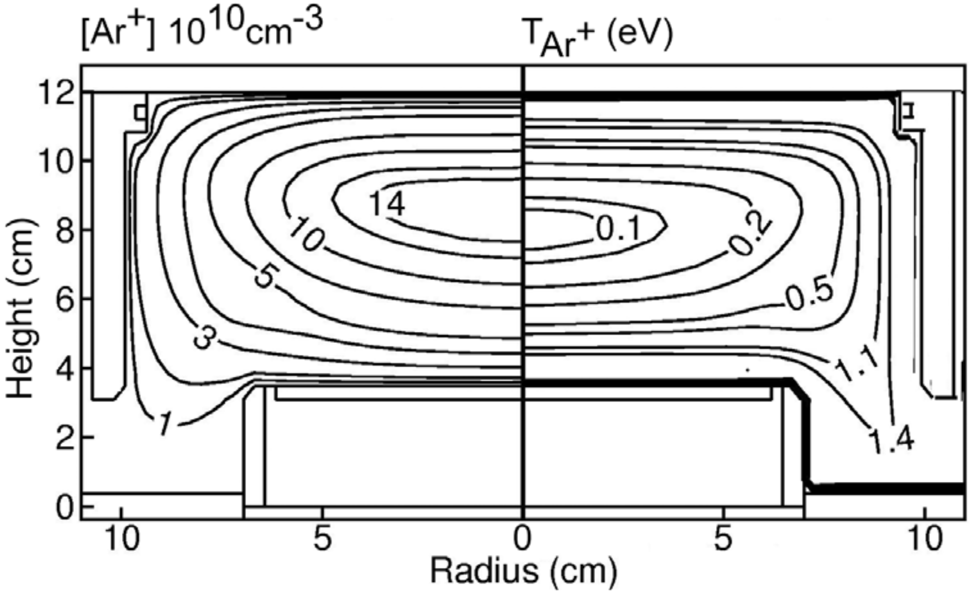




- **An ICP reactor patterned after Oeherlein et. al. (J. Vac. Sci. Technol. A, 1998) was used for validation and basis for study.**
- **Permanent magnets on ring provide confinement by reduction in cross field electron mobility.**

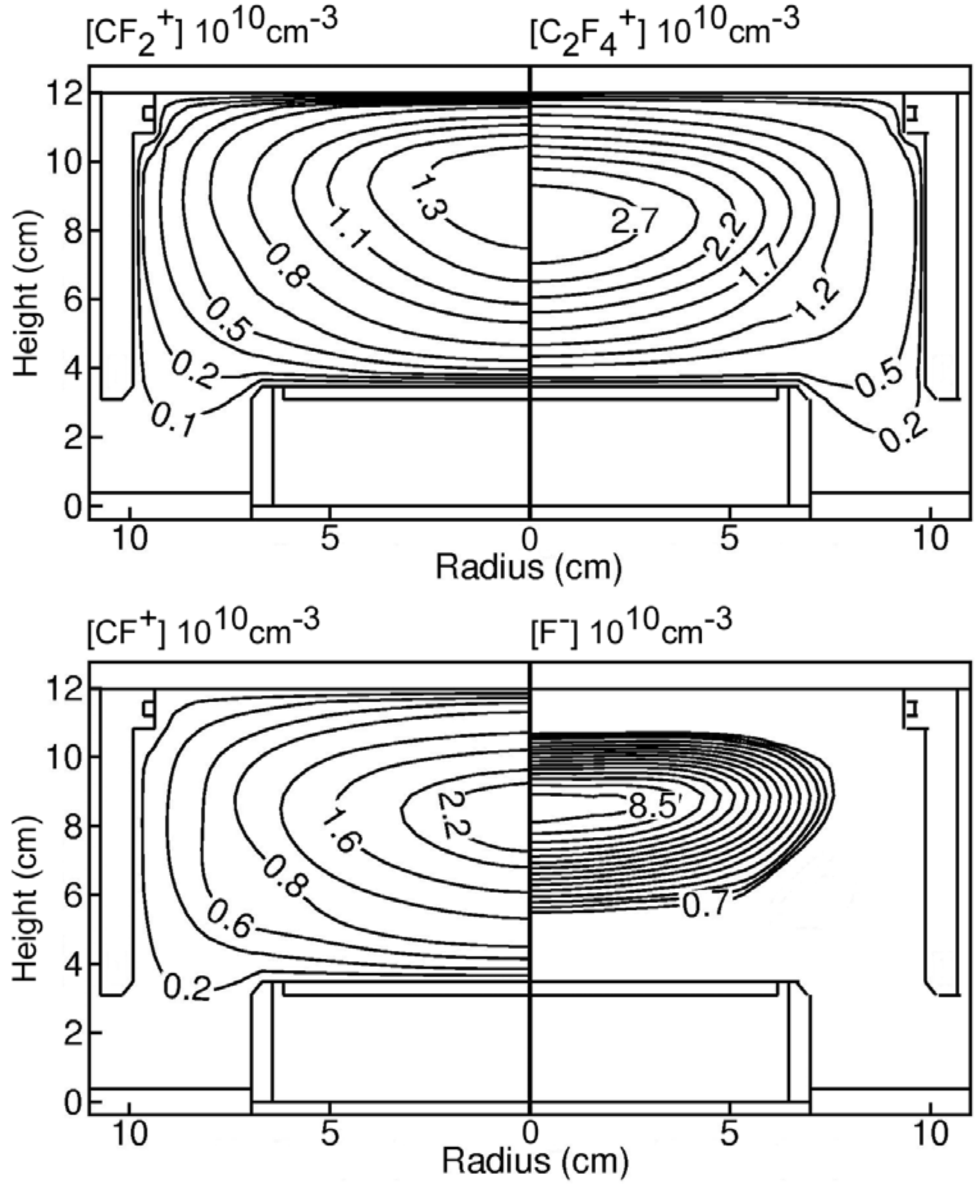
PLASMA PROPERTIES: ICPs IN $Ar/c\text{-}C_4F_8/CO/O_2$



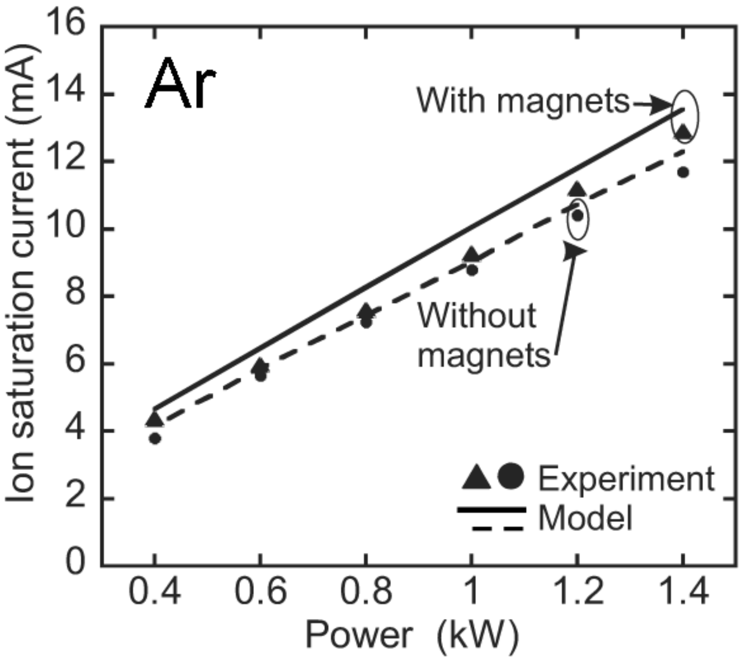


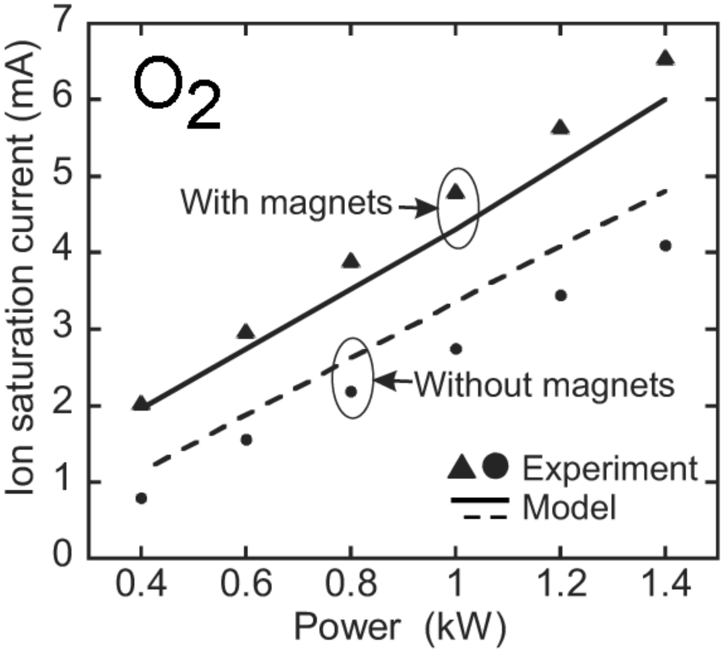
- In mixtures typically used for dielectric etch $c\text{-}C_4F_8$ has a low mole fraction.
- Ions are dominated by Ar^+ having temperatures near 1 eV in presheaths.
- T_e has large gradients due to collisional nature of plasma.
  - $Ar/c\text{-}C_4F_8/CO/O_2$ = 60/5/25/10, 10 mTorr, 600 W, 13.56 MHz, 20 sccm.

PLASMA PROPERTIES: ICPs IN Ar/c-C_4F_8/CO/O_2



- **M- are dominated by F- due to charge exchange with CF_n- .**
- **Fractions of M- critically depend on F →walls→F_2 (large rates of attachment; to F_2) and disposition of $(C_4F_8\text{-})^*$.**
- **Densities of $C_mF_n^+$ are commensurate with CF_n^{+}.**
- **Ratios critically depend on power, wall reactions and charge exchange with Ar^+.**
  - **Ar/c-C_4F_8/CO/O_2 = 60/5/25/10, 10 mTorr, 600 W, 13.56 MHz, 20 sccm.**

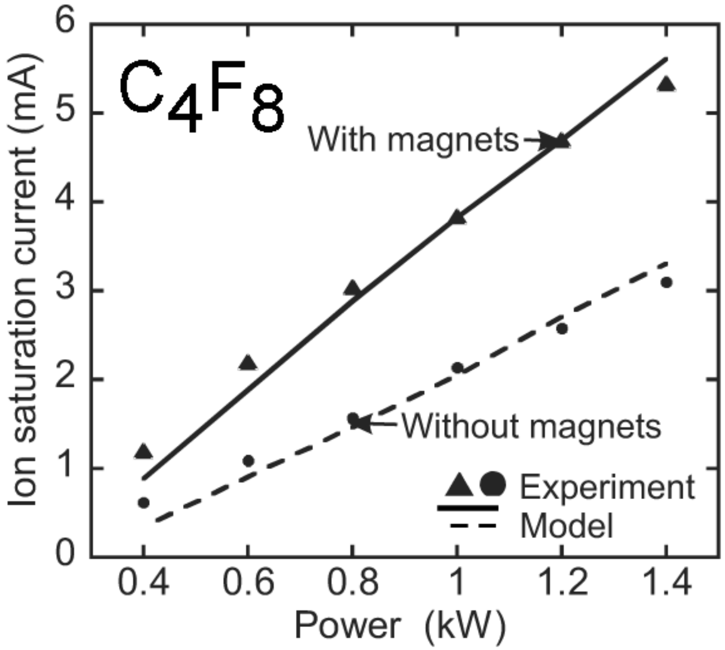




I_{sat} in Ar, O_2 WITH / WITHOUT MAGNETS

- I_{sat} is nearly linearly proportional to power, indicating little change in ionization mechanism.
- I_{sat} increases with magnetic confinement.
- B-fields are only large at outer radius. Losses to top/bottom are little affected; and increase in I_{sat} is not large.
- I_{sat} increases with electronegativity.
    - 10 mTorr and 40 sccm.

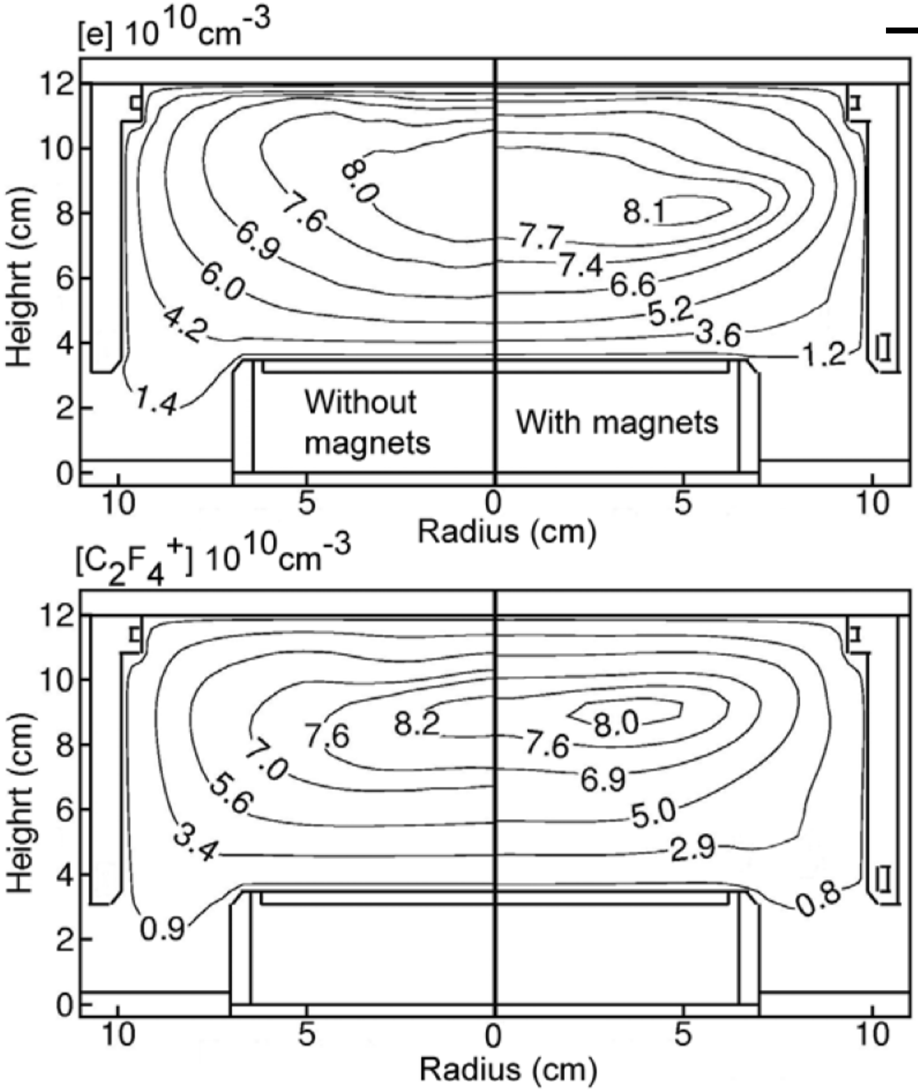
I_{sat} in c-C_4F_8 WITH / WITHOUT MAGNETS



- 10 mTorr and 40 sccm.

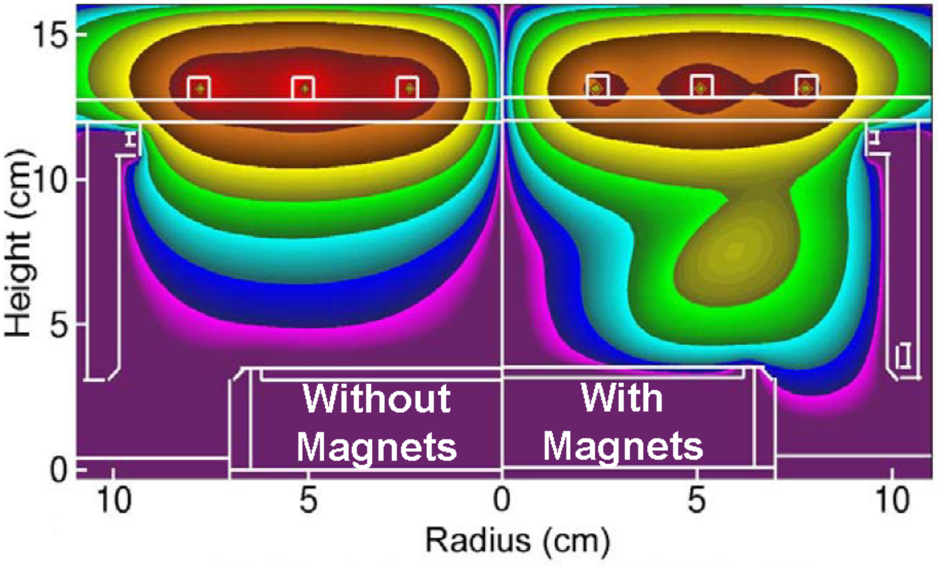
- Trend of larger proportional increases in I_{sat} with confinement and electro negativity continue with c-C_4F_8.
- Systematic results suggest transport (as opposed to kinetics) as dominating for changes in B-field.

EFFECT OF MAGNETS: c-C_4F_8

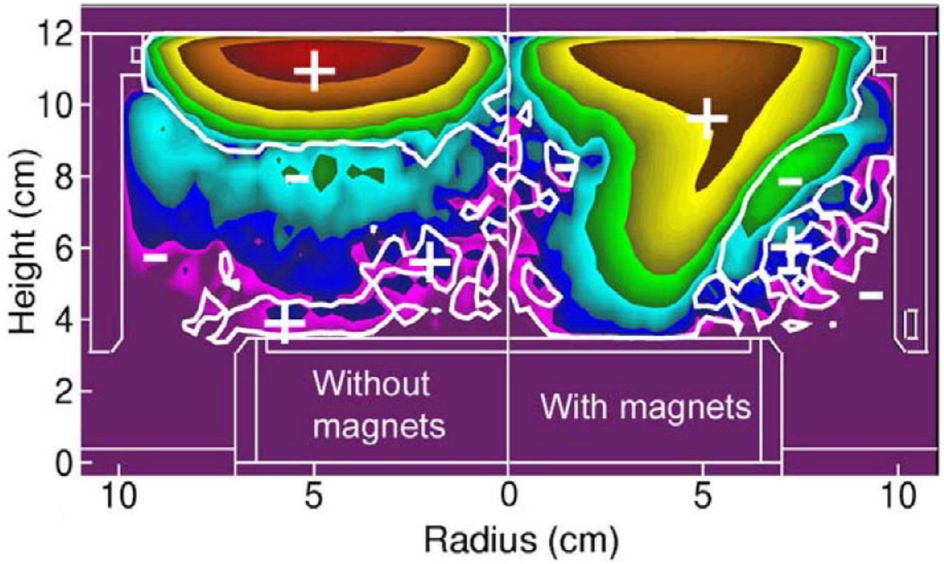


- c-C_4F_8, 6 mTorr, 600 W, 13.56 MHz, and 40 sccm.

- Change in peak plasma density is not large.
- Major effect of B-Field is redistribution of plasma.
- Ion-drift is not directly affected by B-field (R_{Larmor} a few cm).
- Electrons decreased cross field mobility shifts plasma potential and lower ambipolar fields.
- End result is increased density of lighter ions.



- $E(\theta)$ [0.05 – 10 V/cm]



- Power [10^{-3} – 4 W/cm ^{3}]

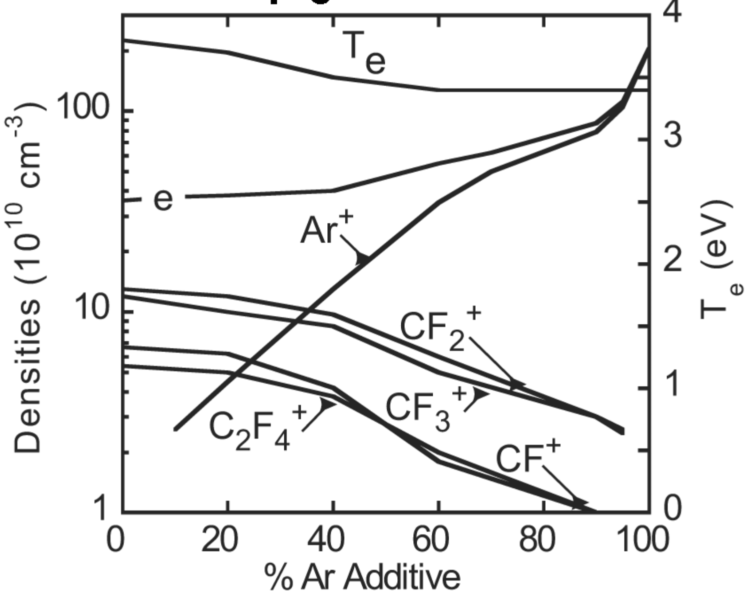
GEM_0204_20

EFFECT OF MAGNETS ON E-FIELD and POWER

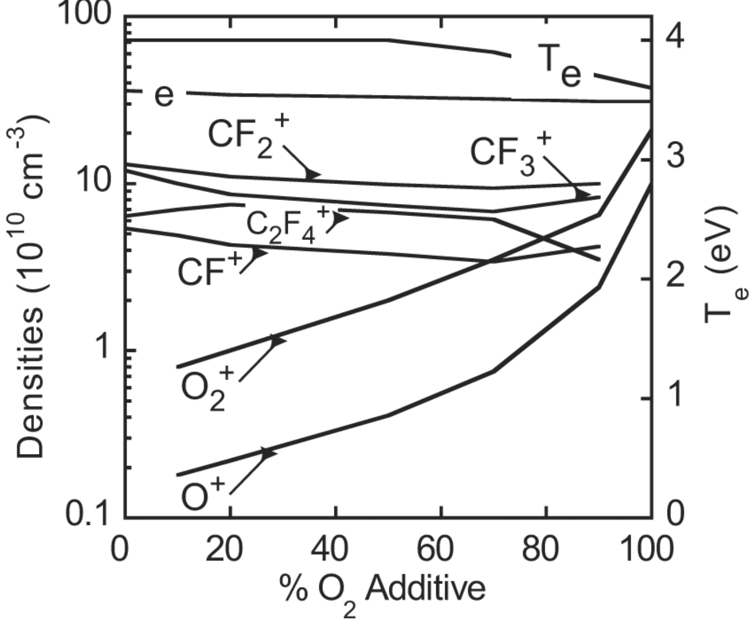
- **B-field produces tensor conductivity and reduces electron azimuthal mobility.**
- **The skin depth is increased producing larger E_θ in the bulk plasma.**
- **Positive power extends deeper into the plasma, redistributing and increasing [e] near the substrate.**
  - **Ar/c-C_4F_8 = 90/10, 6 mTorr, 600 W, 13.56 MHz, 40 sccm**

MIXTURES: Ar/c-C_4F_8, O_2/c-C_4F_8

Ar/c-C_4F_8

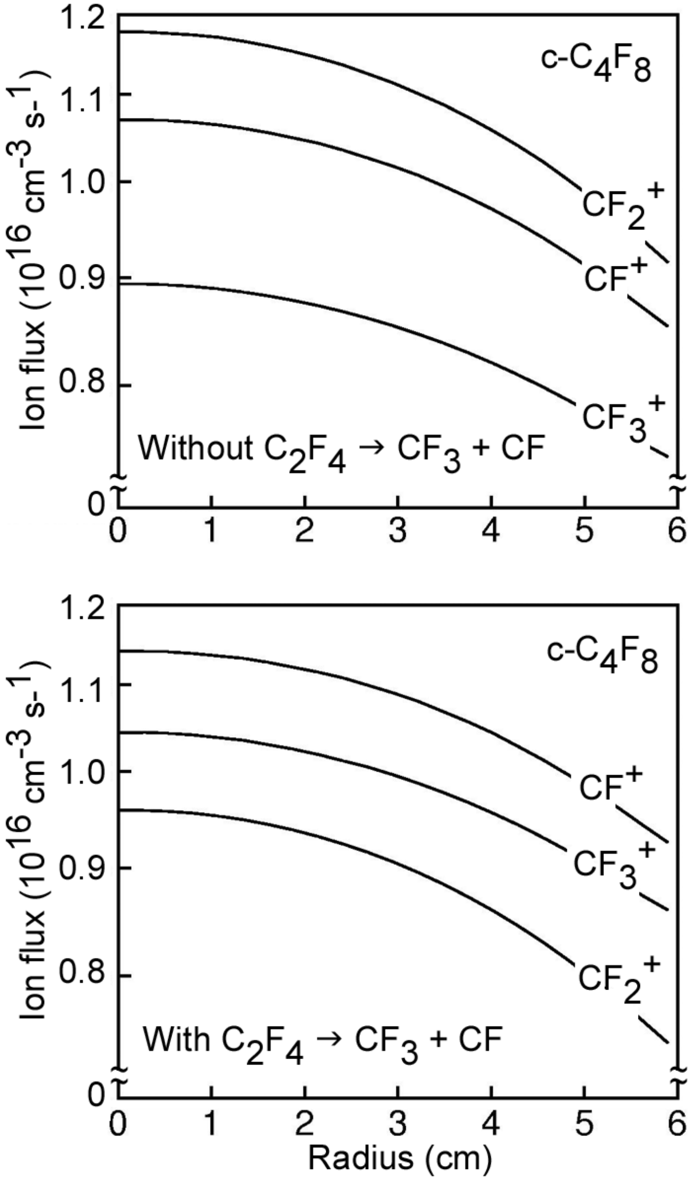


O_2/c-C_4F_8



- [e] Increases rapidly with Ar due to increased rates of ionization, particularly from excited states.
- [e] is not terribly sensitive to O_2 addition due to similar rates of power dissipation.
- $C_mF_n^+$ retain densities to larger O_2 mole fractions, due to lower dissociation and favorable charge exchange rates.
- T_e decreases with Ar and O_2 as ionization is more efficient.
- 10 mTorr, 600 W, 13.56 MHz, 40 sccm.

SENSITIVITY: DISSOCIATION OF C_2F_4 AND ION FLUXES



- **The branchings for dissociative excitation of C_2F_4 are critical to the mechanism.**
- **With $C_2F_4 \rightarrow CF_2 + CF_2$, CF_2^+ has the largest flux to the substrate.**
- **With equal branchings**

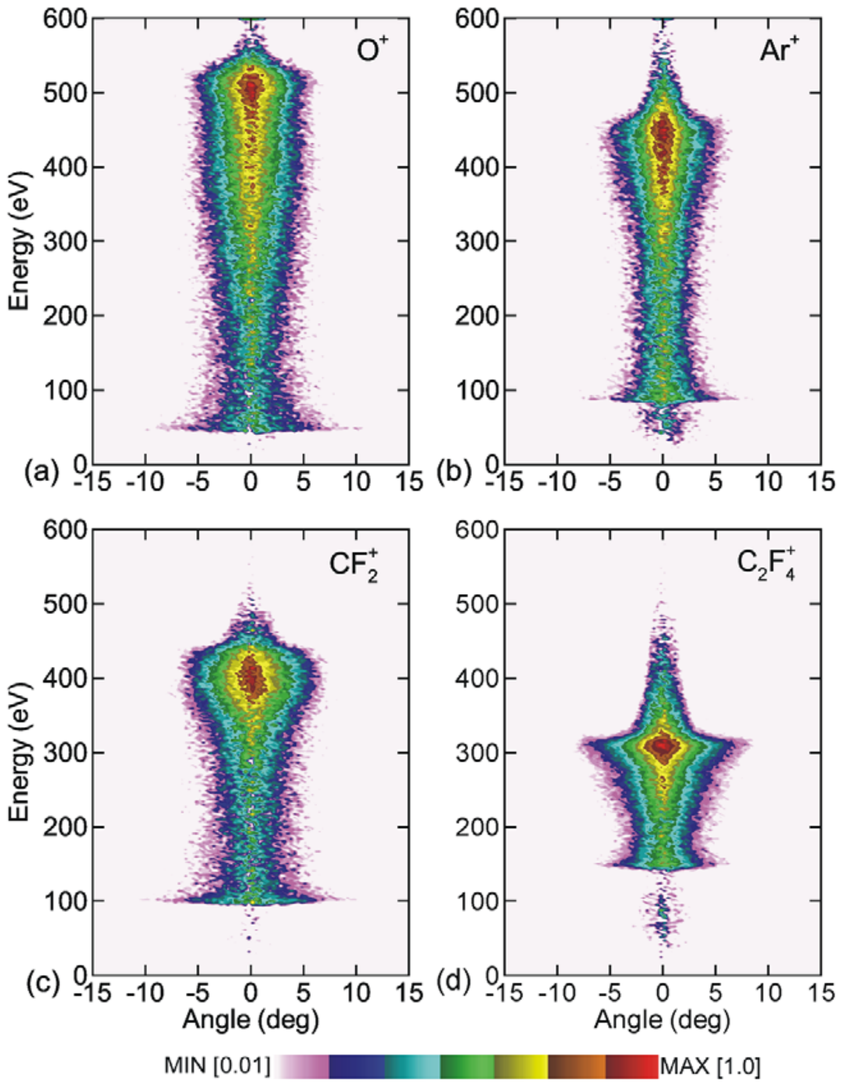
  $C_2F_4 \rightarrow CF_2 + CF_2$

  $\rightarrow CF + CF_3$,

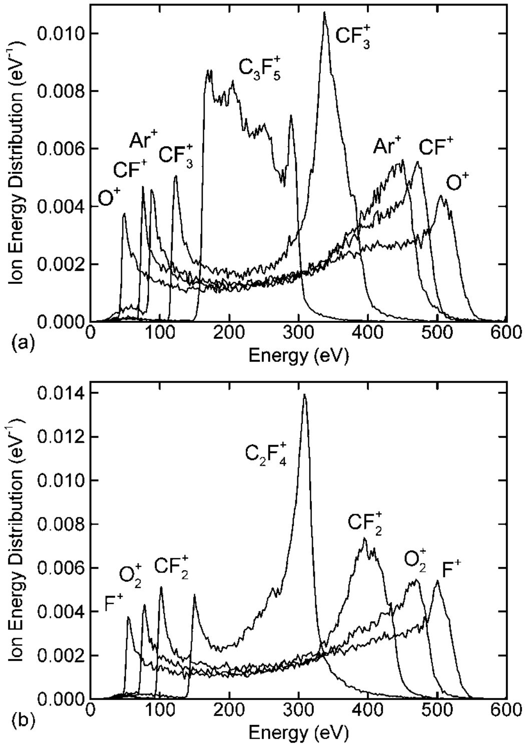
  CF_3^+ and CF^+ fluxes dominate.
- **Also sensitive to wall sticking coefficients.**
- **c-C_4F_8, 10 mTorr, 600 W, 13.56 MHz, 40 sccm.**

TEL-DRM Ar / C_4F_8 / O_2 IEADs FOR 2000 W

- **Complex gas mixtures have similar trends for IEADs. Heavier ions are more sensitive to sheath reversal.**



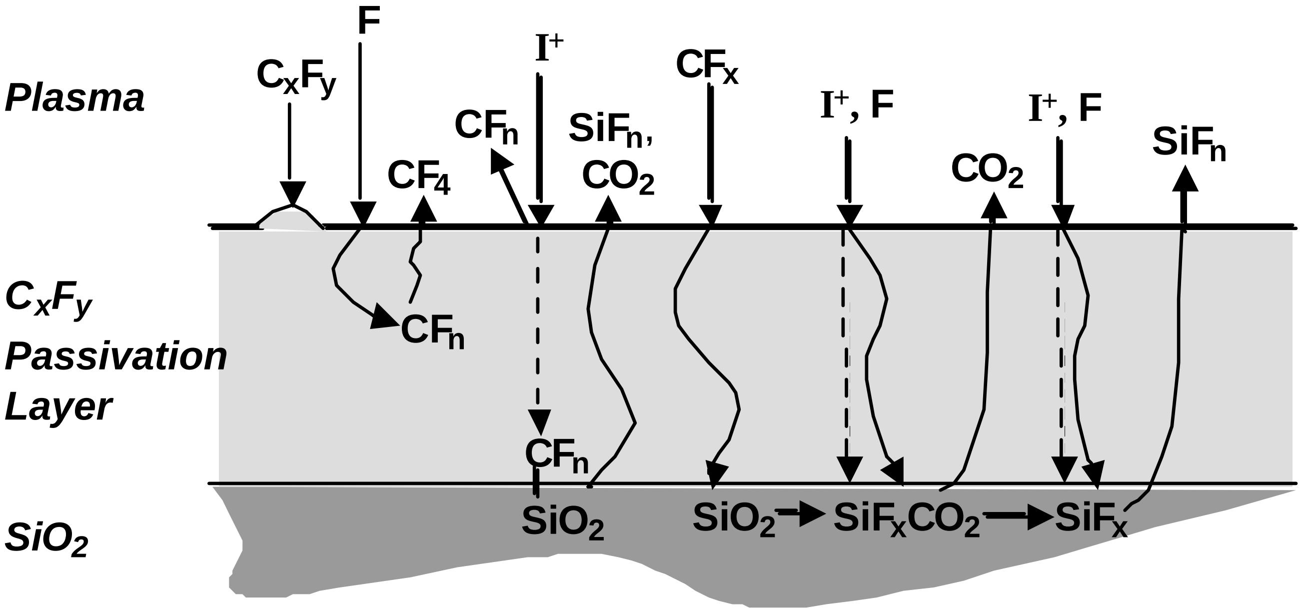
IEAD - 2000 W



- **$Ar/C_4F_8/O_2$ = 200/10/5 sccm, 40 mTorr, 2000 W, 100 G**

SURFACE KINETICS: FLUOROCARBON PLASMA ETCHING Si/SiO_2

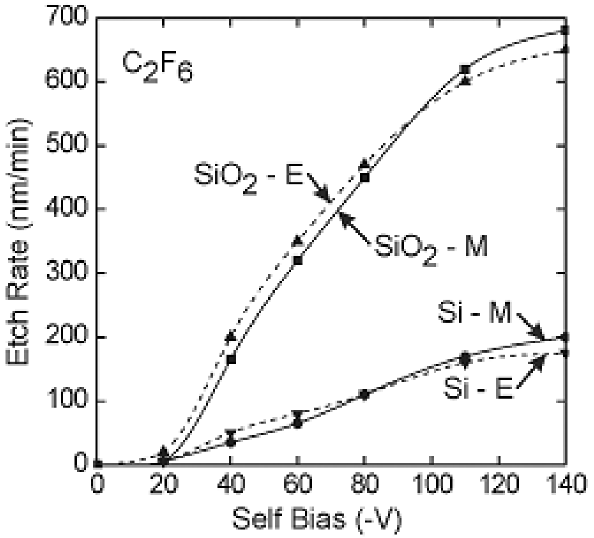
- **C_xF_y passivation regulates delivery of precursors and activation energy.**
- **Chemisorption of CF_x produces a complex at the oxide-polymer interface.**
- **2-step ion activated (through polymer layer) etching of the complex consumes the polymer. Activation scales inversely with polymer thickness.**
- **Etch precursors and products diffuse through the polymer layer.**

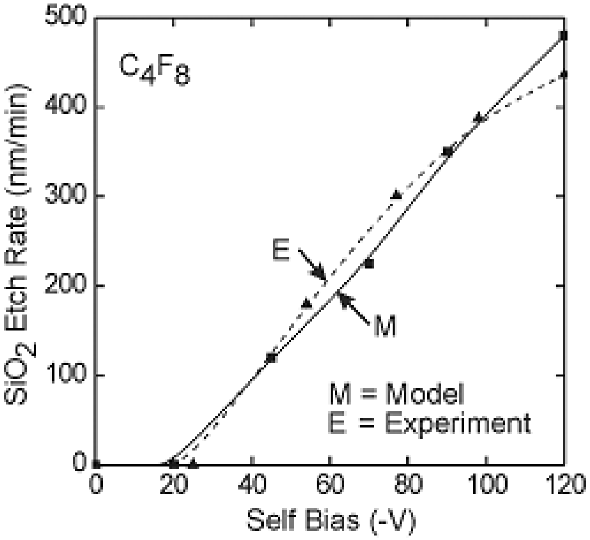


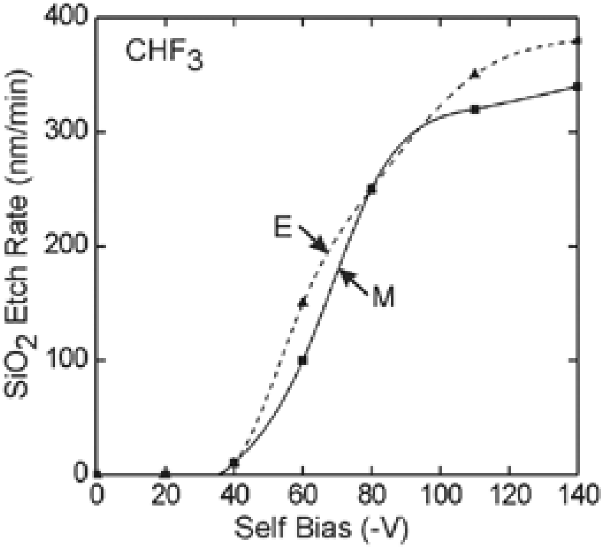
- **In Si etching, CF_x is not consumed, resulting in thicker polymer layers.**

VALIDATION: C_2F_6, C_4F_8, CHF_3

- **Mechanism was validated over multiple chemistries. Lower etch rates by chemistry are attributable to thicker polymer layers and different composition in H containing plasmas.**



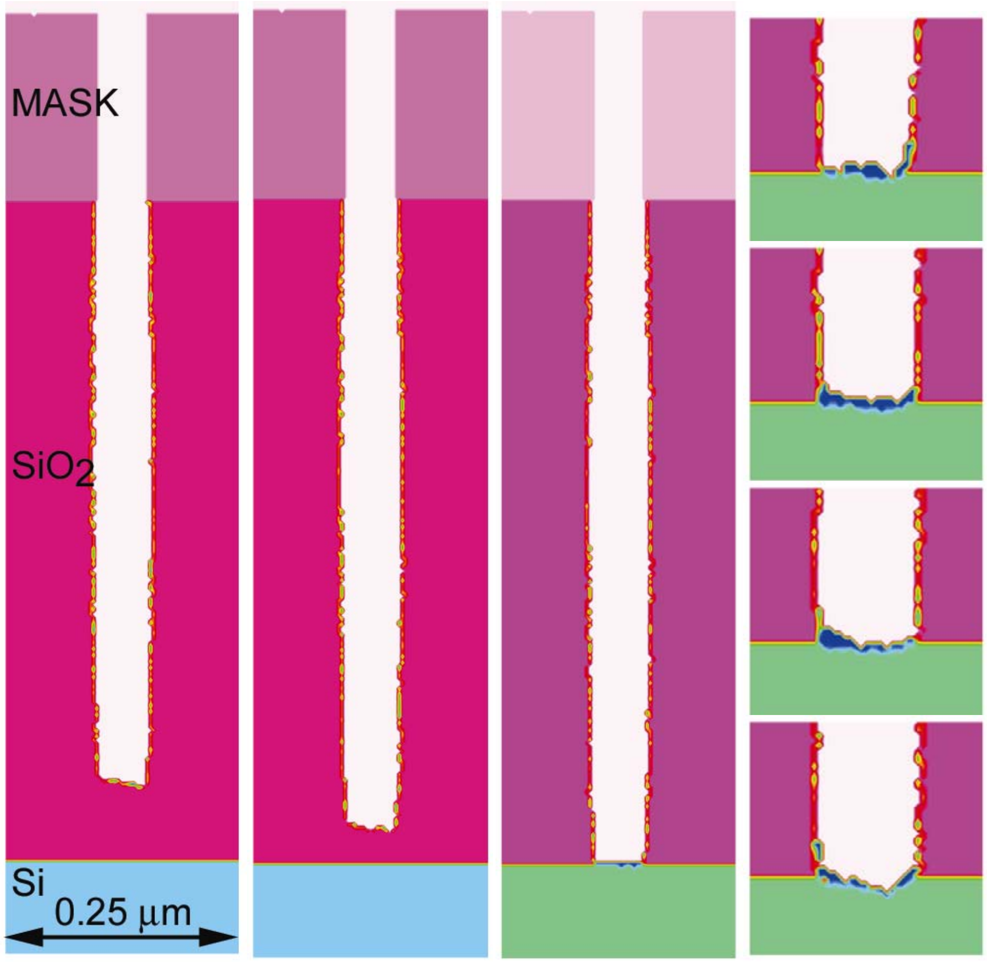


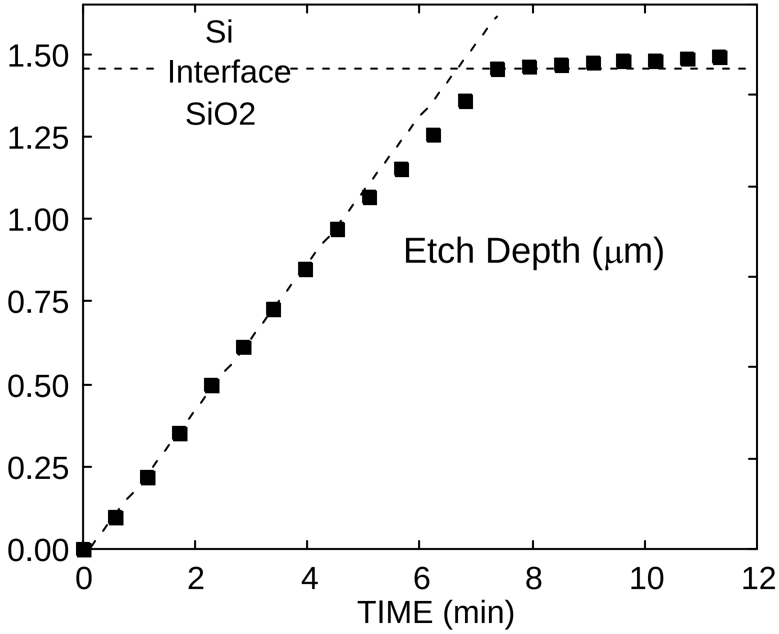


- **Experiments: Schaepkens *et al* J. Vac. Sci. Technol. A 17, 26 (1999): Oehrlein *et al* private communications**

POLYMERIZATION AIDS SELECTIVITY

- **Less consumption of polymer on Si relative to SiO_2 slows and, in some cases, terminates etching, providing high selectivity.**



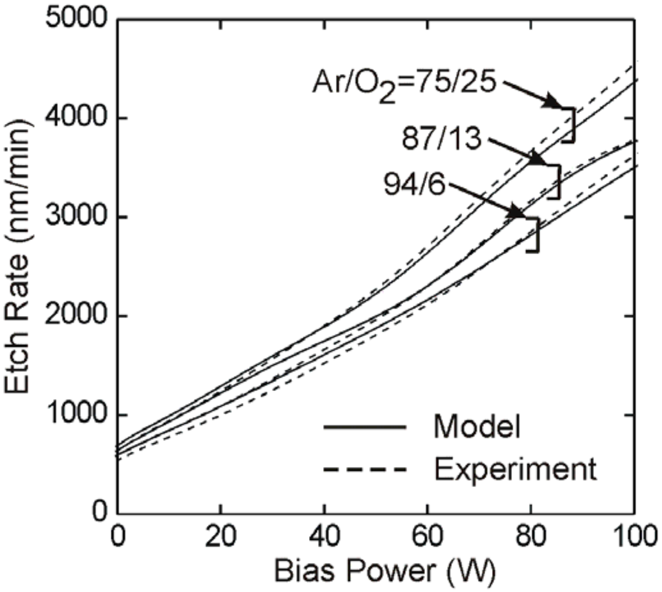


SURFACE REACTION MECHANISMS - STRIP

- Little polymer removal is observed in the absence of ion bombardment suggests an ion activated intermediate.

$$P(s) + O(g) \rightarrow P^*(s)$$

$$P^*(s) + I(g) \rightarrow COF_x(g)$$



- Mechanism was validated with etching of polytetrafluoroethylene in Ar/O_2 plasmas.[1]
- Etch rates increase with bias and O_2.
- Fluorocarbon polymer deposited during SiO_2 etching and photoresist are treated similarly.

- ICP: 4 mTorr 600 W (13.56 MHz)
- Bias power at 3.4 MHz

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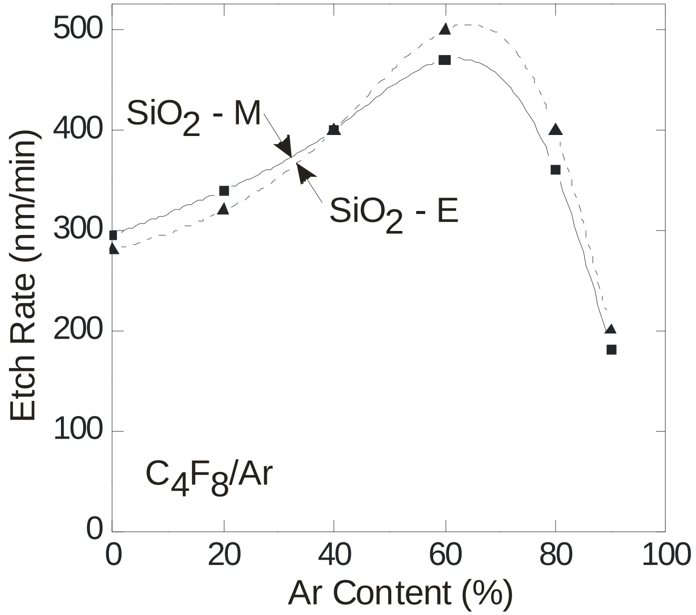
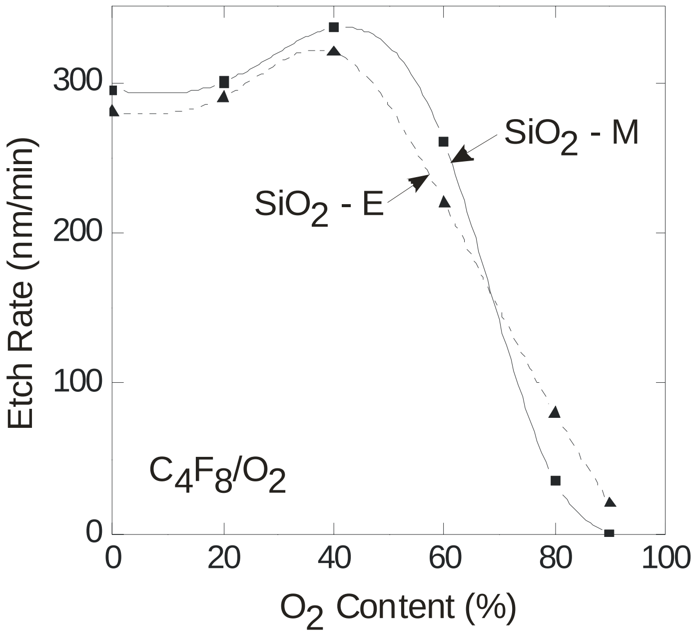
[1] Standaert *et al* J. Vac. Sci. Technol. A 19, 435 (2001)

VALIDATION: C_4F_8/Ar and C_4F_8/O_2



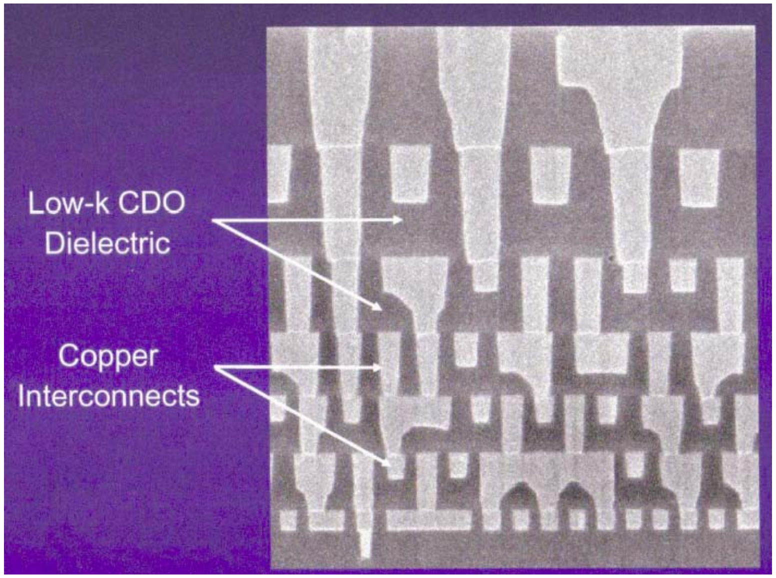


- **Larger ionization rates result in larger ion fluxes in Ar/C_4F_8 mixtures which reduces polymer thickness.**
- **With high Ar, the polymer thins to sub-monolayer (less deposition, more sputtering). Etch rates decrease.**
- **O_2 etches polymer and reduces its thickness. Rate has a maximum with O_2, similar to Ar addition.**
  - **40 sccm, 600 W ICP, 20 mTorr, -125 V self-bias**

Li *et al*, J. Vac. Sci. Technol. A **20,** 2052, 2002.

POROUS Si FOR LOW-K DIELECTRIC

- **As feature sizes decrease and device count increases, the diameter of interconnect wires shrinks and path length increases.**
- **Larger RC-delay limits performance.**

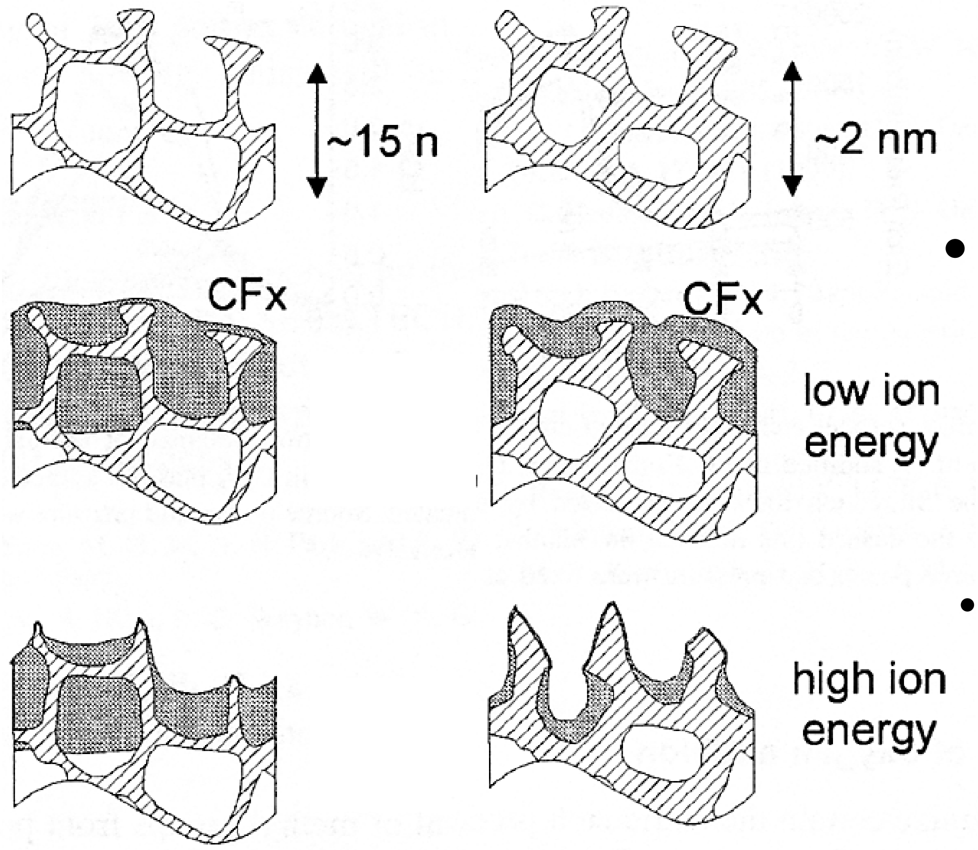


- **Ref: S. Rossnagel, IBM**

- **Low-K materials reduce RC.**
- **Porous SiO_2 (xerogels) have low-k properties due to their lower mass density resulting from (vacuum) pores.**
  - **Porosities: 30-70%**
  - **Pore sizes: 2-20 nm**

WHAT CHANGES WITH POROUS SiO_2?

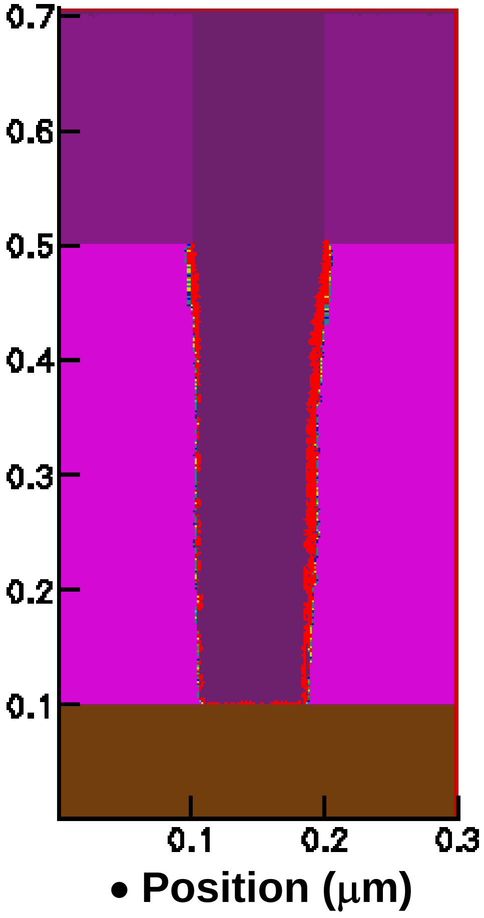
- The "opening" of pores during etching of P-SiO_2 results in the filling of the voids with polymer, creating thicker layers.
- Ions which would have otherwise hit at grazing or normal angle now intersect with more optimum angle.



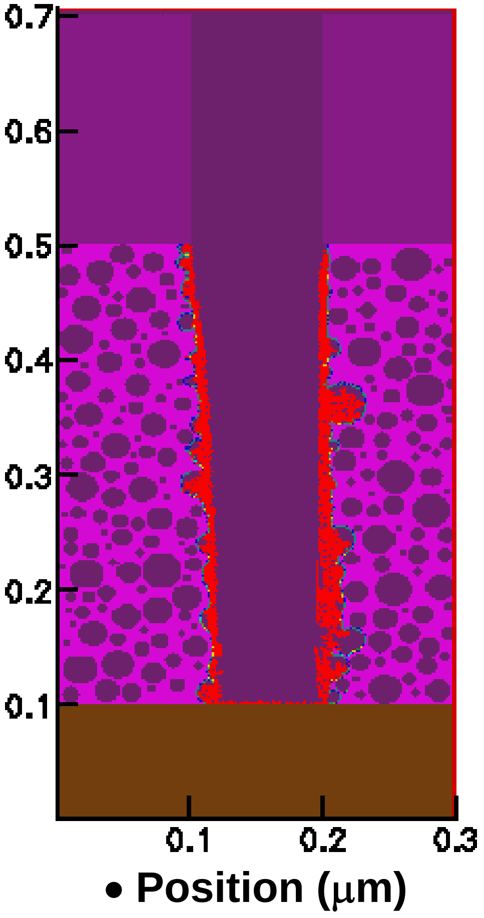
- An important parameter is L/a (polymer thickness / pore radius).

- Adapted: Standaert, JVSTA 18, 2742 (2000)

ETCH PROFILES IN SOLID AND POROUS SiO_2



- Solid

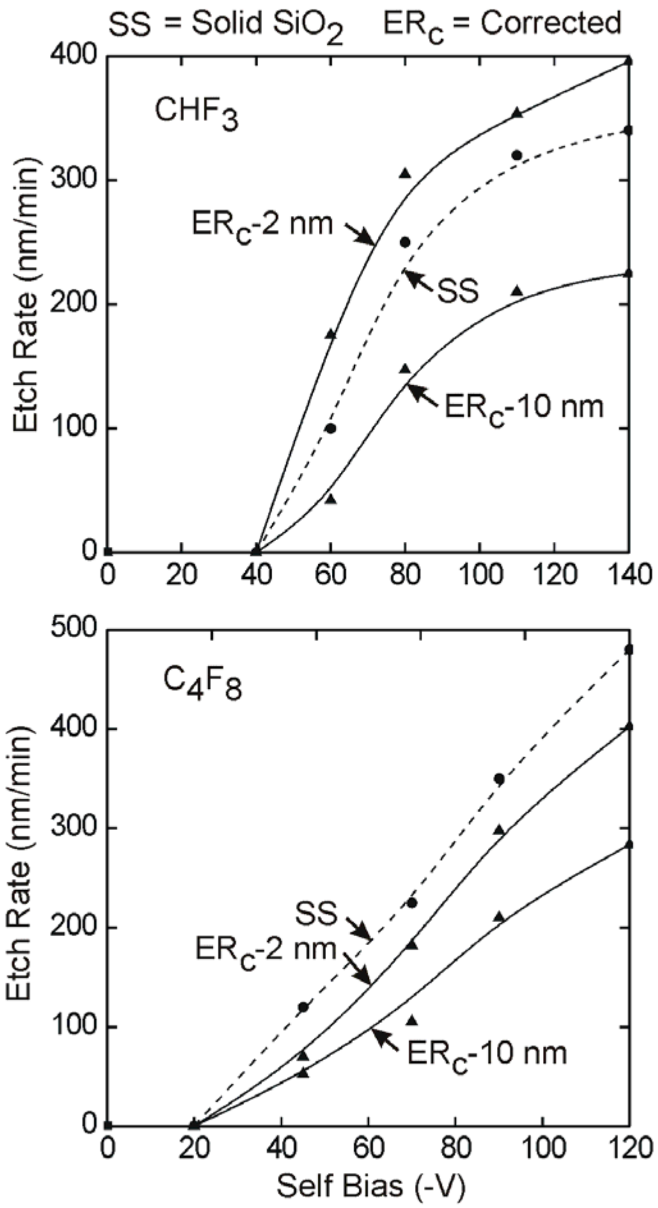


- Porosity = 45 %
  Pore radius = 10 nm

- Porous SiO_2 is being investigated for low-permittivity dielectrics for interconnect wiring.
- In polymerizing environments with heavy sidewall passivation, etch profiles differ little between solid and porous silica.
- The “open” sidewall pores quickly fill with polymer.

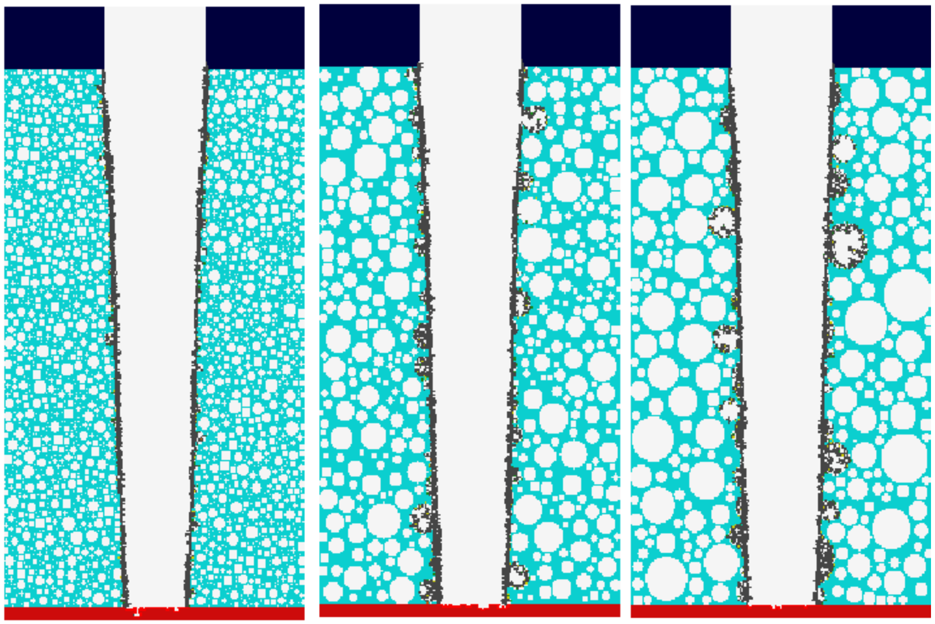
ANIMATION SLIDE

PORE DEPENDENT ETCH RATES

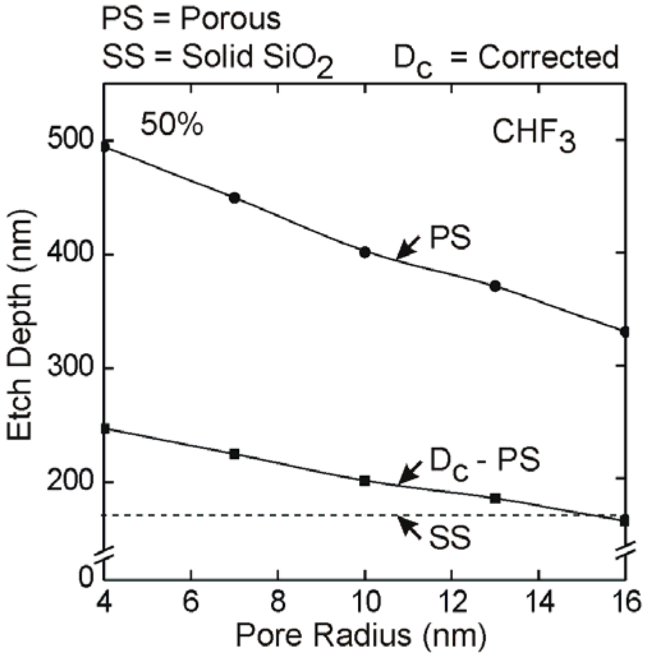


- $ER_c = ER\ (1\text{-porosity})$
- If etching depended only on mass density, ER_c of PS would = ER of SS.
- For CHF_3, 2 nm pores $L/a \geq 1$: $ER_c >$ ER of SS. Favorable yields due to non-normal incidence increases rate.
- For C_4F_8, 2 nm pores $L/a \leq 1$: $ER_c <$ ER of SS. Small L (large a) increases polymer thickness by filling pores.
- 10 nm pores $L/a \leq 1$: $ER_c <$ ER of SS. Filling of pores with polymer decreases rates.

EFFECT OF PORE RADIUS ON HAR TRENCHES

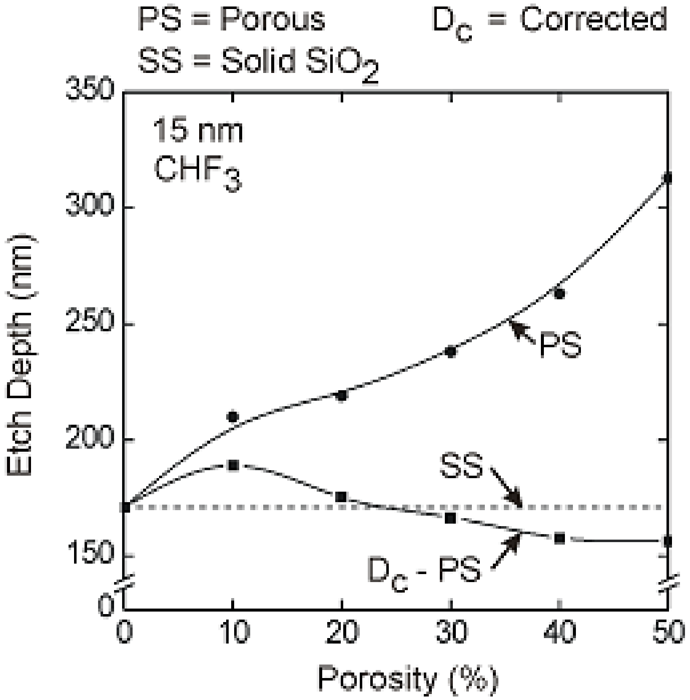


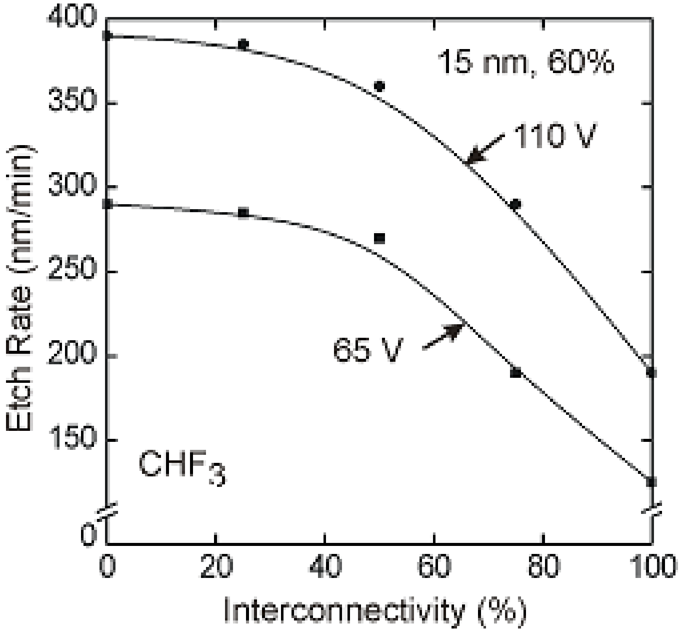
4 nm 10 nm 16 nm



- **With increase in pore radius, L/a decreases causing a decrease in etch rates.**
- **Thicker polymer layers eventually lead to mass corrected etch rates falling below SS. There is little variation in the taper.**

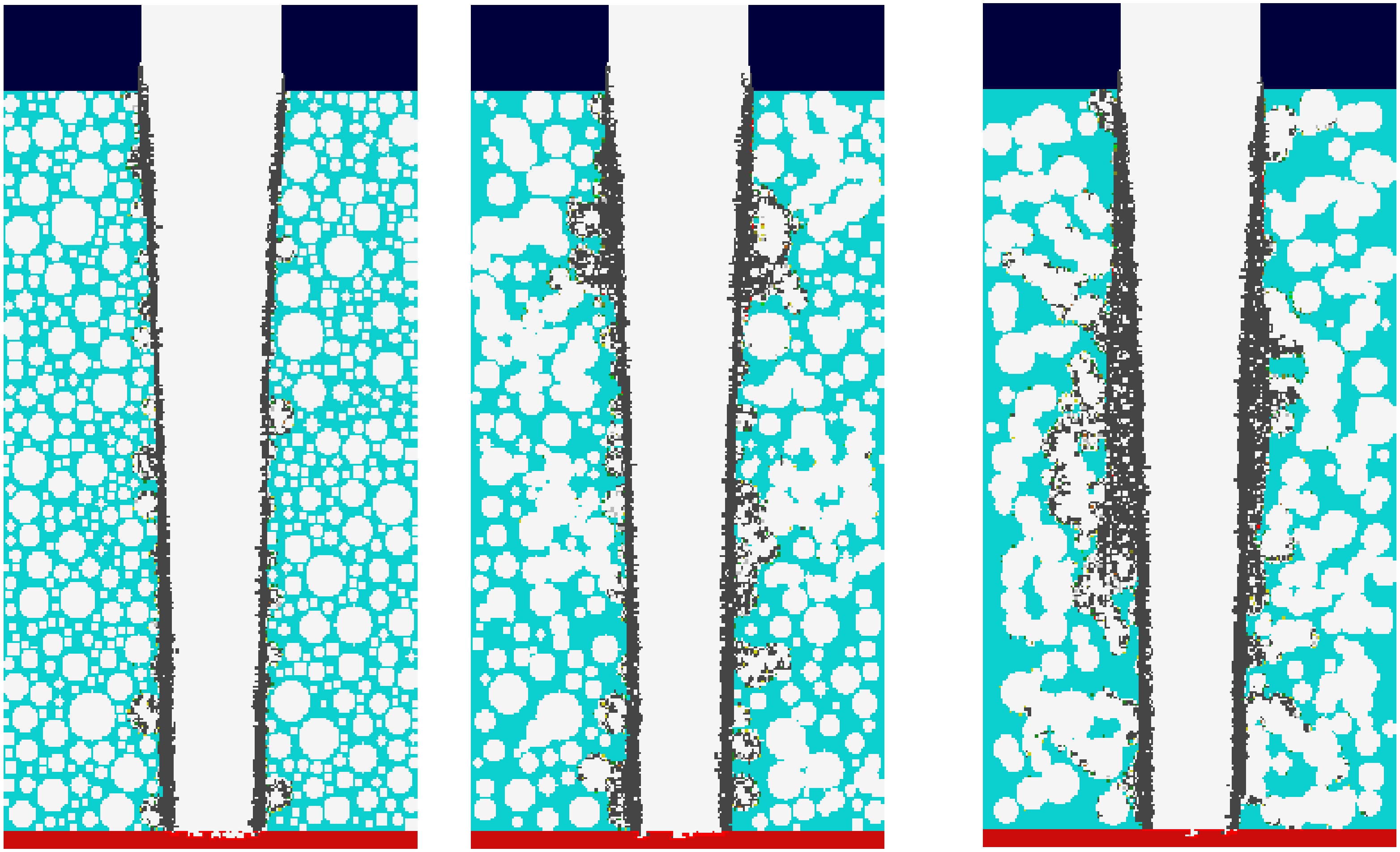
EFFECT OF POROSITY, INTERCONNECTIVITY





- **At higher porosities, larger pores and higher interconnectivity, filling of pores produces thicker polymer layers and lower etch rates.**
- **Corrected etch rates fall below SS rates when critically thick polymer layers are formed.**

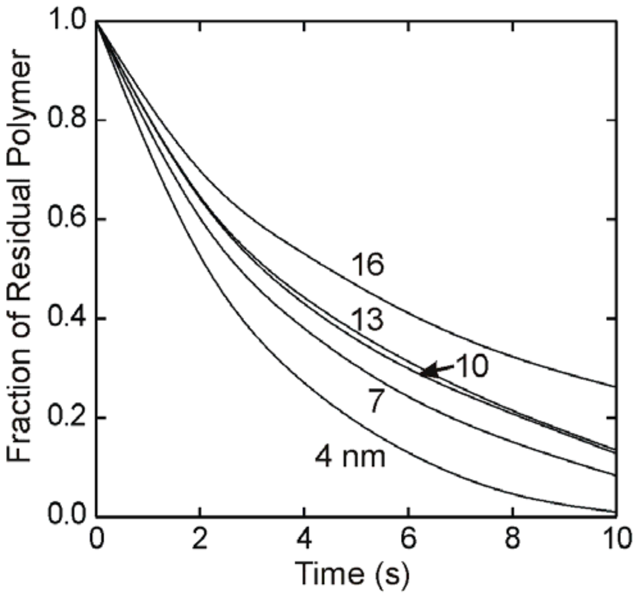
HAR PROFILES: INTERCONNECTED PORES

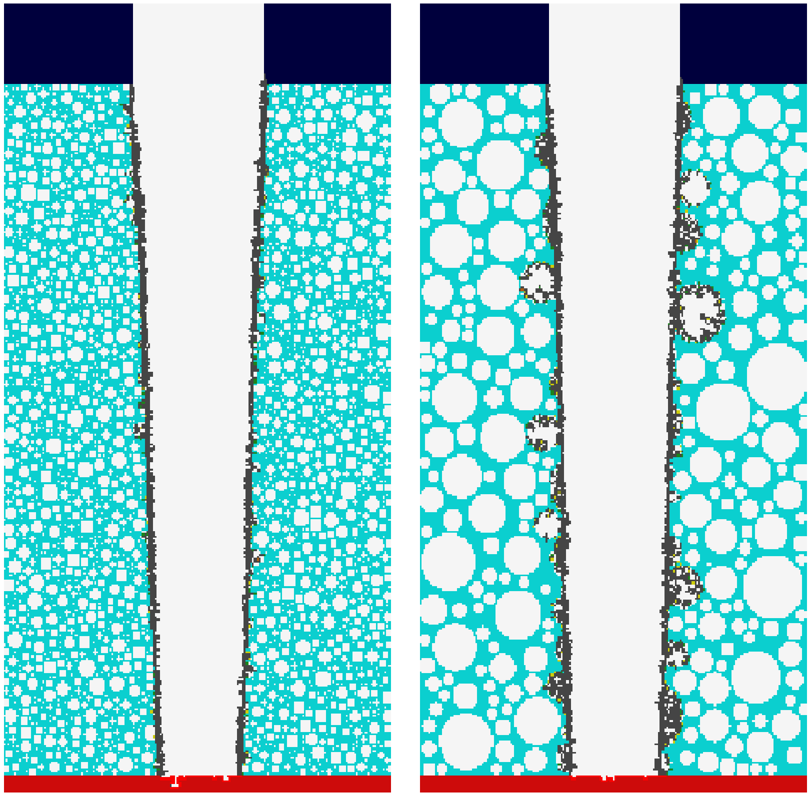


0% **60%** **100%**

Interconnectivity

EFFECT OF PORE RADIUS ON CLEANING





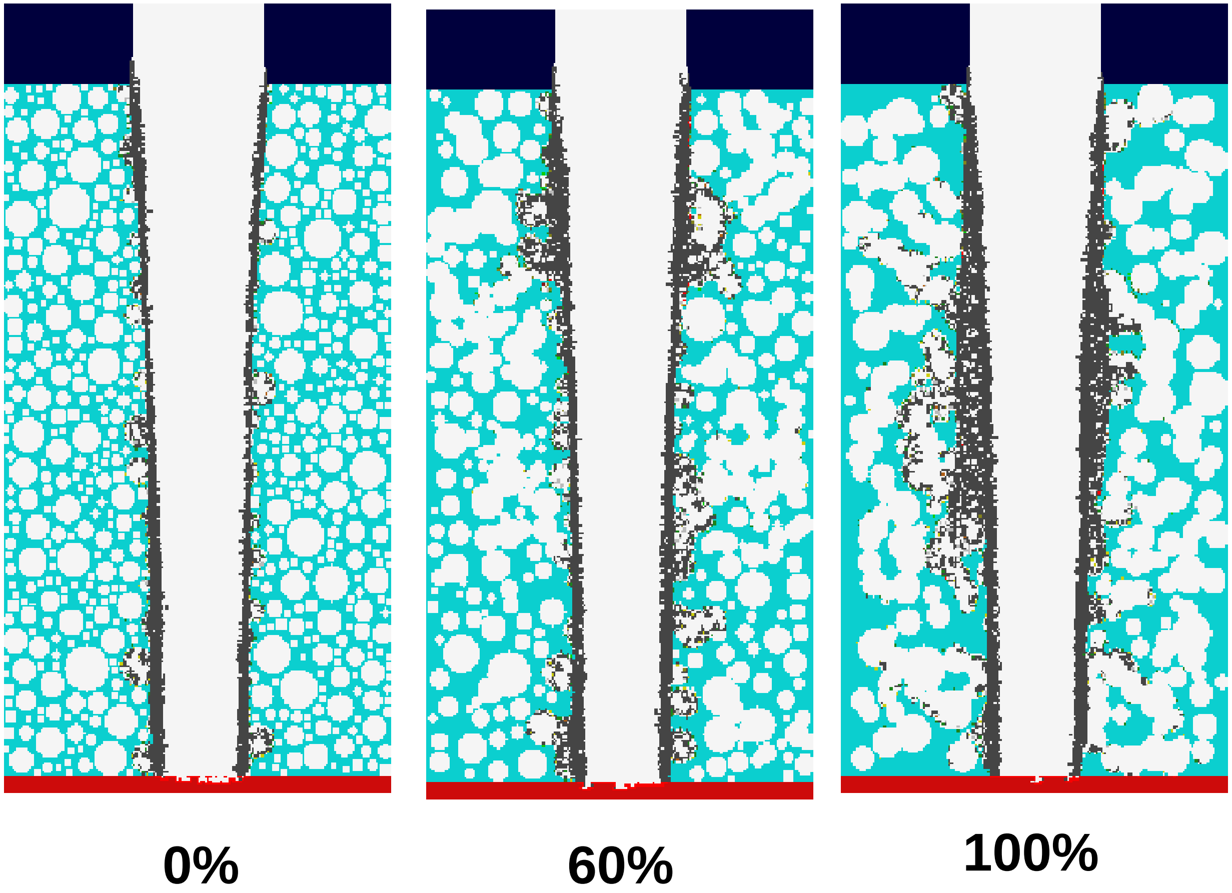
4 nm **16 nm**

- **Larger pores have poor view angles to ions and thicker polymer layers.**
- **Lower rate of cleaning results.**

- **Ar/O_2=99/1, 40 sccm, 600 W, 4 mTorr**

ANIMATION SLIDE

CLEANING INTERCONNECTED PORES



- **Cleaning is inefficient with interconnected pores.**
- **Higher interconnectivity leads to larger shadowing of ions.**

- **Interconnectivity**

- **Ar/O_2=99/1, 40 sccm, 600 W, 4 mTorr**

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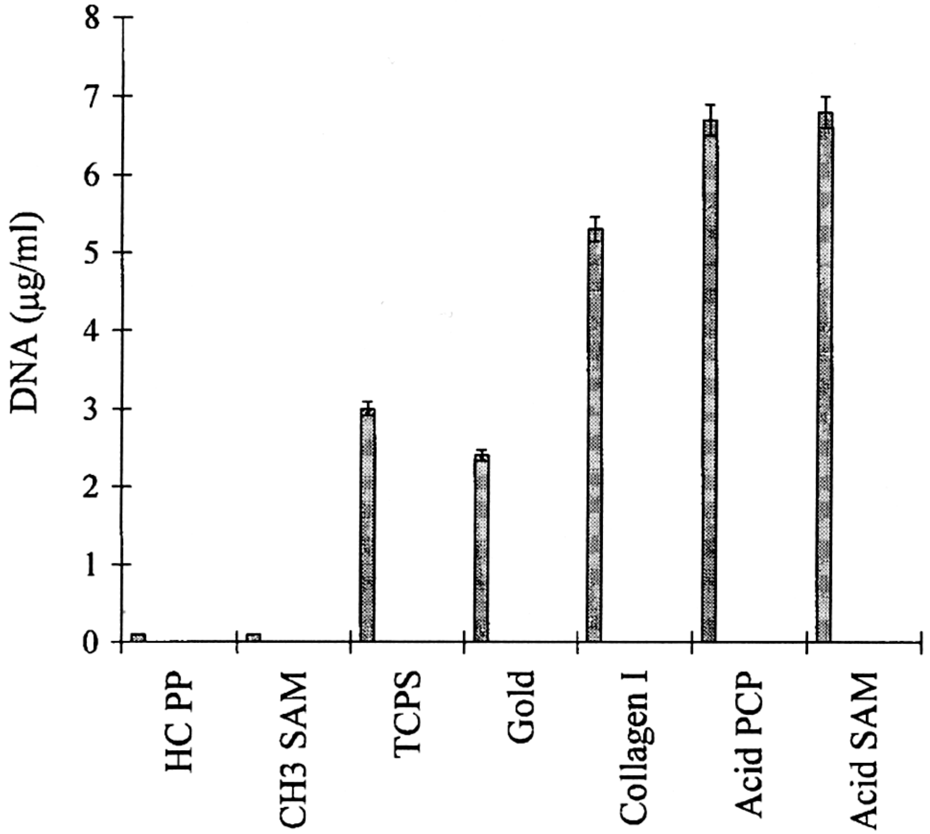
ANIMATION SLIDE

THE CHALLENGE: COMMODITY PROCESSING FOR HIGH VALUE MATERIALS

WHAT'S THE UPSIDE: BETTER FRITO BAGS OR ENGINEERED BIOCOMPATIBLE COATINGS?

- ***The ability to control functional groups on polymers through fundamental understanding of plasma-solid interactions opens the realm of engineered large area specialty surfaces*.**

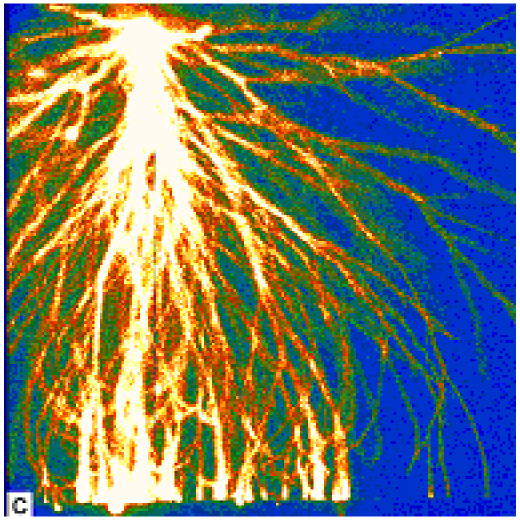


- **Keratinocyte cells adhere to hydrocarbon polymers containing carboxylic acid groups (PCP, SAM).**
- **Can we leverage our knowledge of commodity processing to these precious materials?**

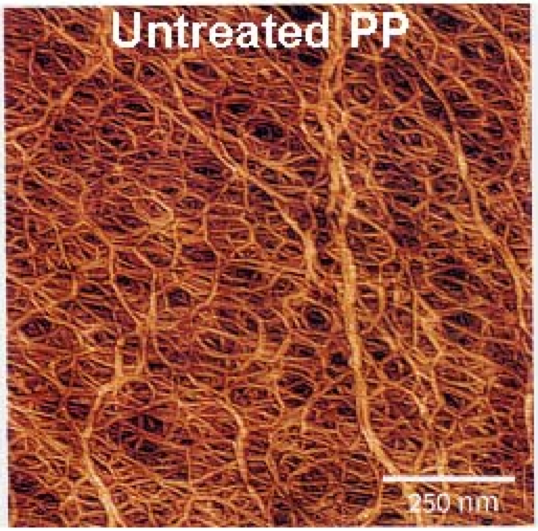
- **Haddow et al., J. Biomed. Mat. Res. 47, 379 (1999)**

POLYMER PROCESSING BY CORONA DBDs

- The surface modification of polymers (such as PP) by corona DBDs is a geometrically complex process.
  - The plasma is filamentary non-uniformly producing reactants
  - The surface is at best rough and at worst a mesh of strands



E. M. van Veldhuizen [TPS 30, 162 (2002)] Air, 2.5 cm gap, 25 kV



- M. Strobel, 3M

- Can multidimensional plasma-surface integrated models shed light on these processes?

DESCRIPTION OF MODEL: CHARGED PARTICLE, SOURCES

- **Continuity (sources from electron and heavy particle collisions, surface chemistry, photo-ionization, secondary emission), fluxes by modified Sharfetter-Gummel with advective flow field.**

$$\frac{\partial N_i}{\partial t} = -\vec{\nabla} \cdot \vec{\phi} + S_i$$

- **Poisson's Equation for Electric Potential:** $-\nabla \cdot \varepsilon \nabla \Phi = \rho_V + \rho_S$

- **Photoionization, electric field and secondary emission:**

$$S_{Pi}(\vec{r}) = \int \frac{N_i(\vec{r})\sigma_{ij} N_j(\vec{r}\,') \exp\left(\frac{-\left|\vec{r}\,' - \vec{r}\right|}{\lambda}\right) d^3\vec{r}\,'}{4\pi \left|\vec{r}\,' - \vec{r}\right|^2}$$

$$S_{Si} = -\nabla \cdot j, \quad j_E = AT^2 \exp\left(\frac{-\left(\Phi_W - \left(q^3 \mathrm{E}/\varepsilon_0\right)^{1/2}\right)}{kT_S}\right), \quad j_S = \sum_j \gamma_{ij} \phi_j$$

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DESCRIPTION OF MODEL: CHARGED PARTICLE, SOURCES

- **Fluid averaged values of mass density, mass momentum and thermal energy density obtained in using unsteady algorithms.**

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \vec{v}) + (inlets, pumps)$$

$$\frac{\partial (\rho \vec{v})}{\partial t} = \nabla (NkT) - \nabla \cdot (\rho \vec{v} \vec{v}) - \nabla \cdot \overline{\mu} + \sum_i q_i N_i \vec{E}_i$$

$$\frac{\partial (\rho c_p T)}{\partial t} = -\nabla \left(-\kappa \nabla T + \rho \vec{v} c_p T\right) + P_i \nabla \cdot v_f - \sum_i R_i \Delta H_i + \sum_i \vec{j}_i \cdot \vec{E}$$

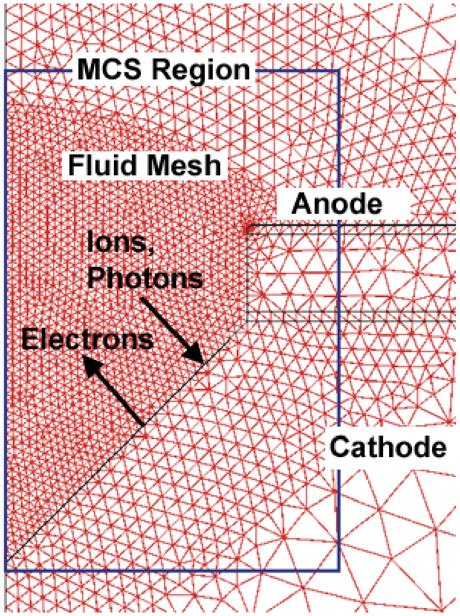
- **Individual fluid species diffuse in the bulk fluid.**

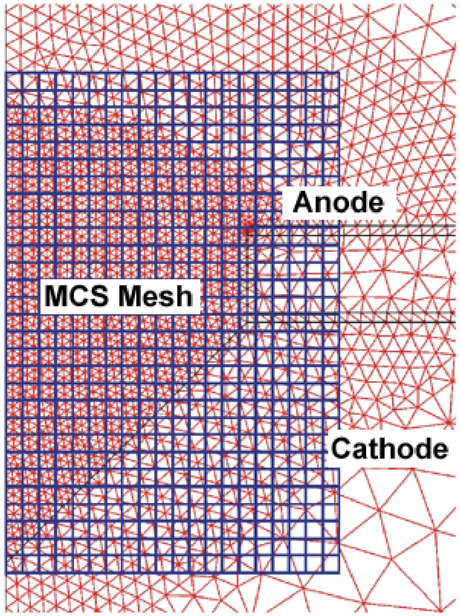
$$N_i(t+\Delta t) = N_i(t) - \nabla \cdot \left(\vec{v}_f - D_i N_T \nabla \left(\frac{N_i(t+\Delta t)}{N_T} \right) \right) + S_V + S_S$$

ELECTRON TRANSPORT: BULK AND BEAM

- **Bulk electron energy equation with Boltzmann's equation derived transport coefficients.**

$$\frac{\partial(n_e\varepsilon)}{\partial t} = \vec{j}\cdot\vec{E} - n_e\sum_i N_i\kappa_i - \nabla\cdot\left(\frac{5}{2}\varepsilon\varphi - \lambda\nabla T_e\right), \quad \vec{j} = q\vec{\phi}_e$$

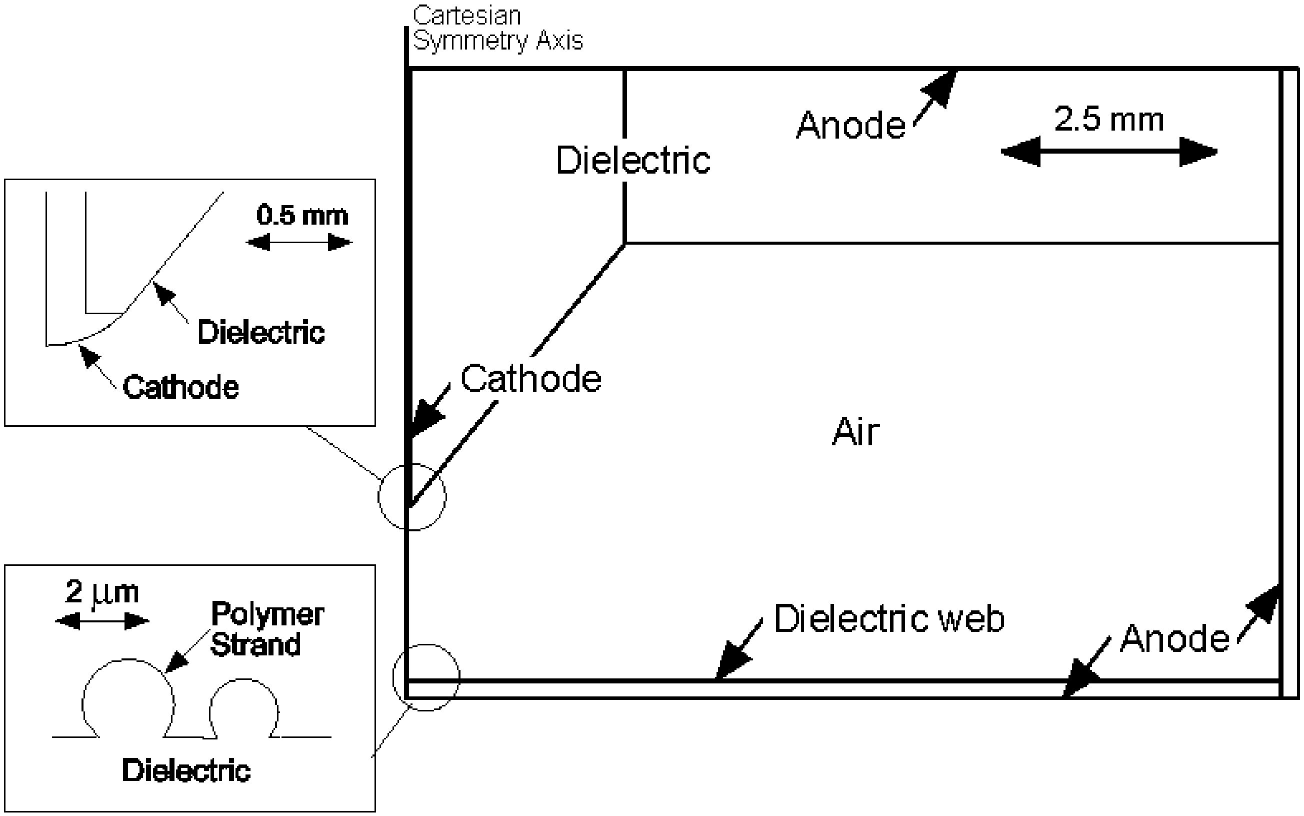


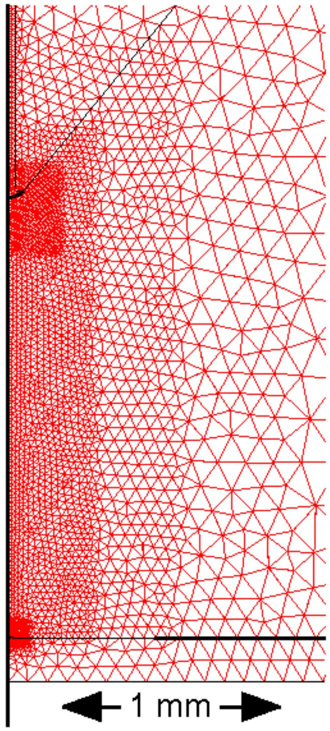


- **Transport of energetic secondary electrons is addressed with a Monte Carlo Simulation.**
- **Electrons and their progeny are followed until slowing into bulk plasma or leaving MCS volume.**

DEMONSTRATION GEOMETRY

- **Demonstration case is a corona-rod, 2 mm gap, 15 kV pulse.**
- **Gas Mixture: $N_2/O_2/H_2O$ =79.5 / 19.5 / 1, 1 atm**

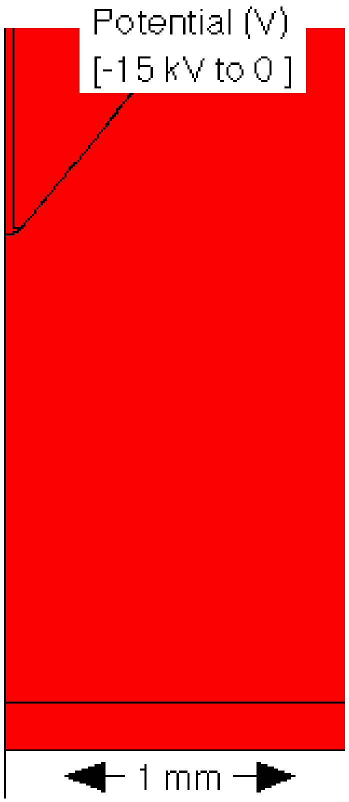




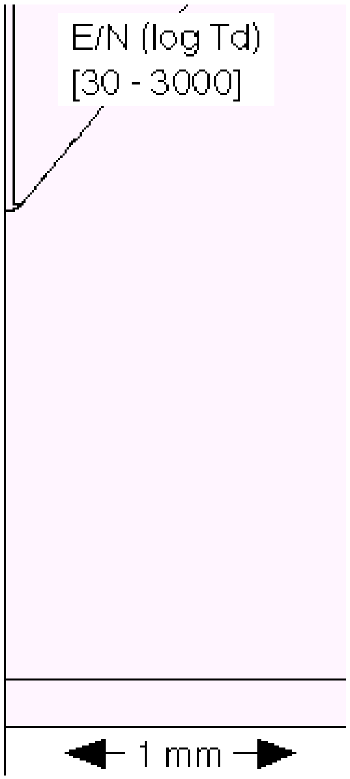
POTENTIAL, ELECTRIC FIELD, CHARGE

Animation Slide

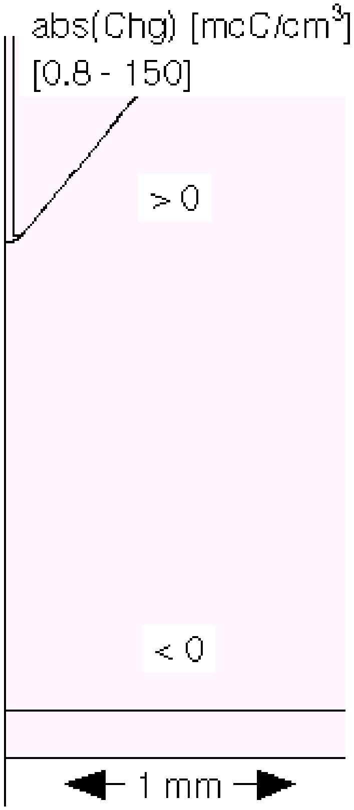
- **Pulse is initiated with electron emission from tip of cathode.**
- **Development of plasma streamer deforms potential producing large electric field. Pulse is terminated with dielectric charging.**



- **Potential**



- **E/N**



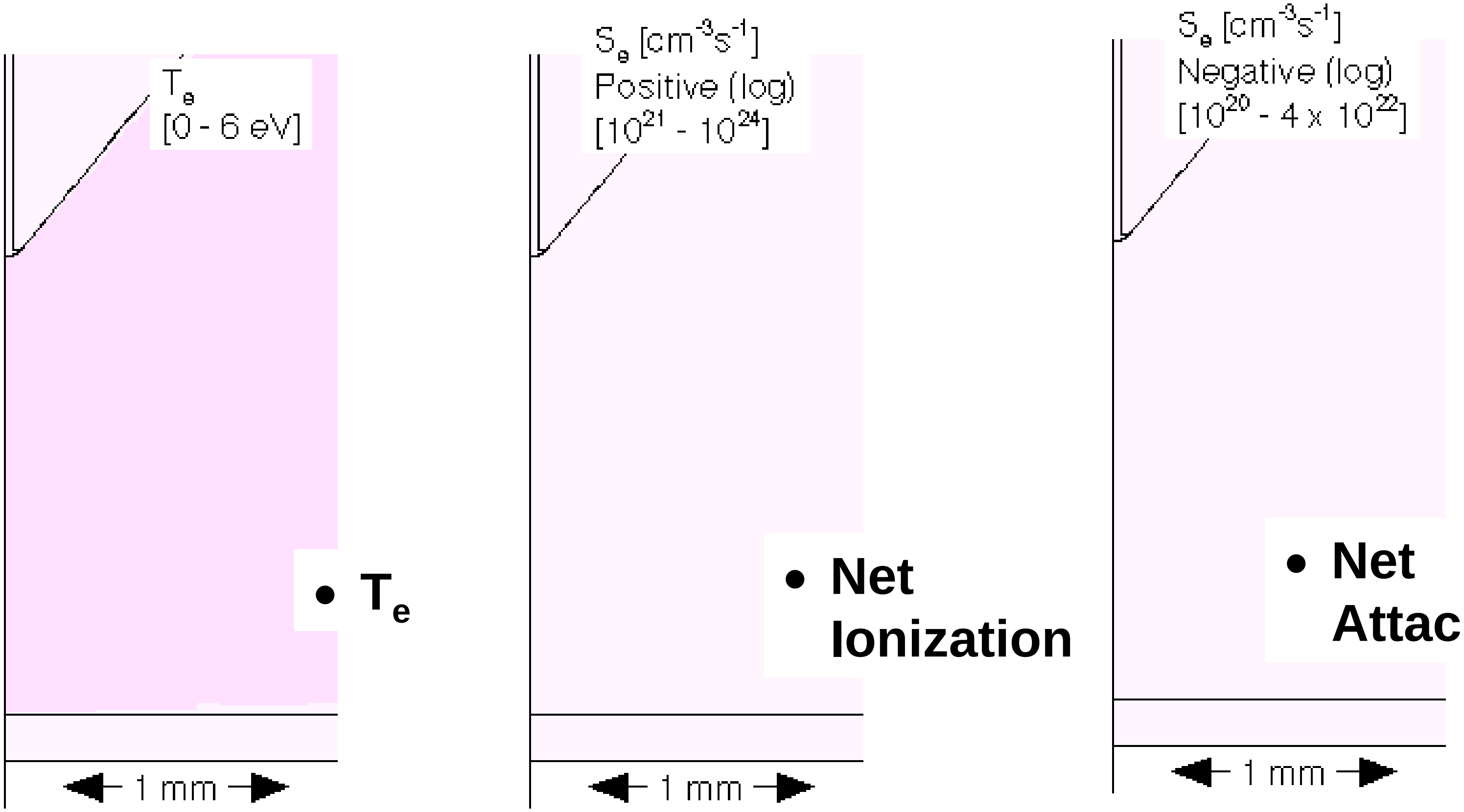
- **Charge**

- **$N_2/O_2/H_2O$ =79.5 / 19.5 / 1, 1 atm, 15 kV, 0-15 ns**

ELECTRON TEMPERATURE, SOURCES

Animation Slide

- Electric field at head of streamer elevates electron temperature, producing a transitory wave of ionization. 2-body attachment occurs in high T_e regions; 3-body attachment in low T_e.



- T_e
- Net Ionization
- Net Attachment

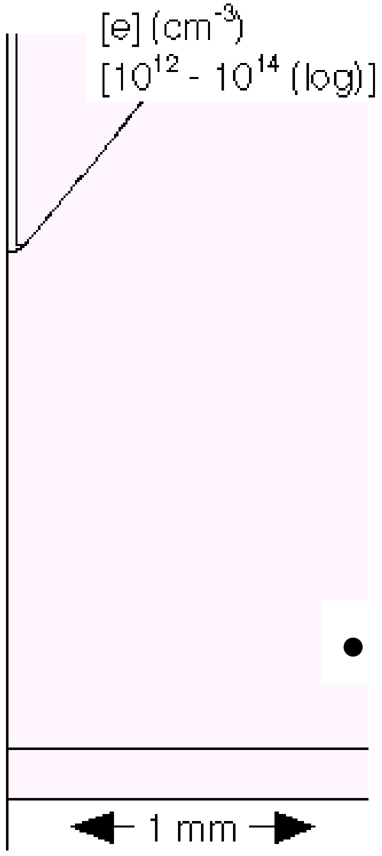
- $N_2/O_2/H_2O$ =79.5 / 19.5 / 1, 1 atm, 15 kV, 0-15 ns

MIN MAX

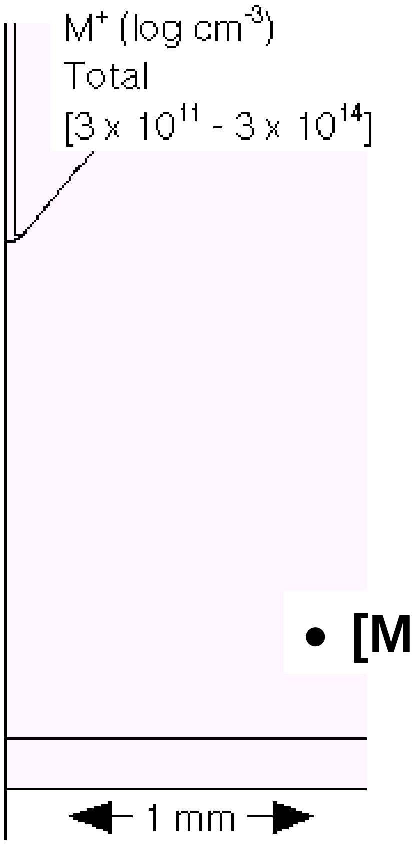
ELECTRON AND ION DENSITIES

Animation Slide

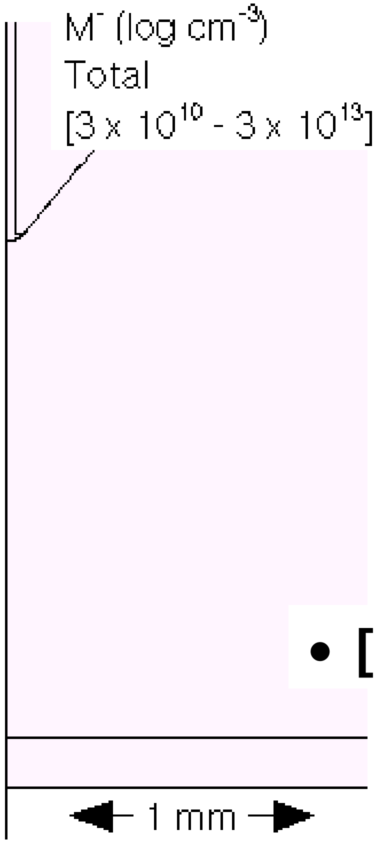
- **Electrons are consumed by 3-body attachment at the end of the pulse.**



- **[e]**



- **[M+]**



- **[M-]**

- **$N_2/O_2/H_2O$ =79.5 / 19.5 / 1, 1 atm,**
  15 kV, 0-15 ns

MIN 🟪🟦🟩🟨🟫🟥 **MAX**

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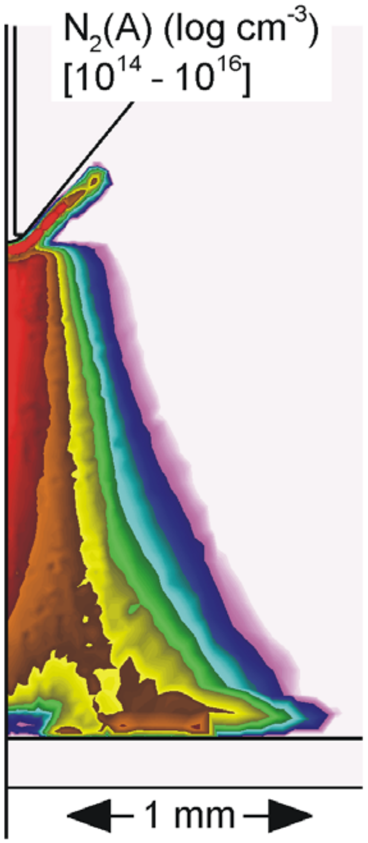
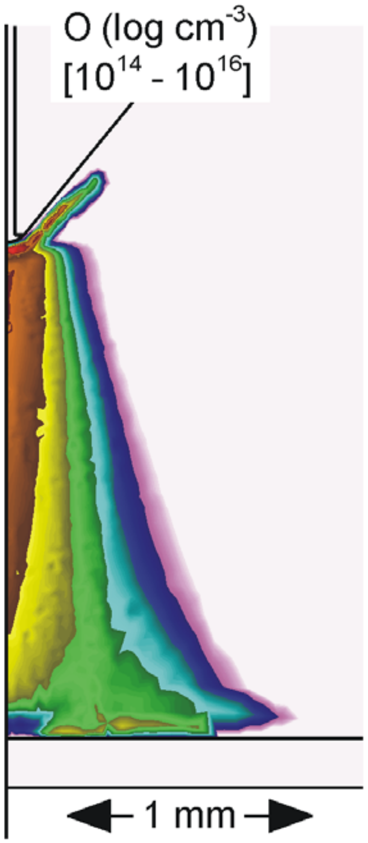
POST PULSE RADICAL DENSITIES

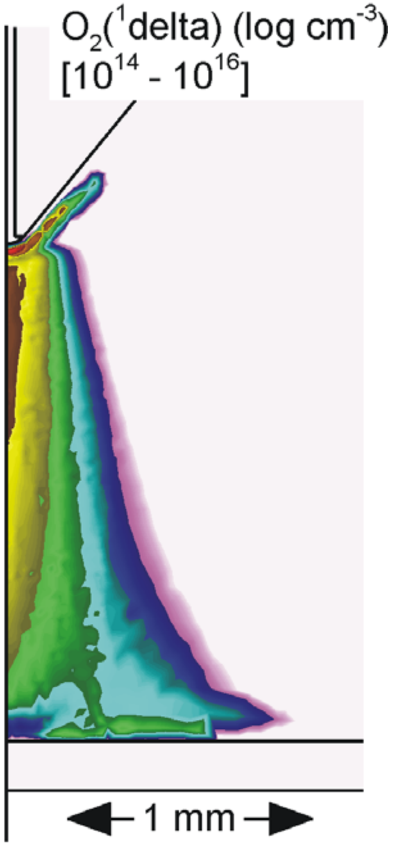
- **Radical and ion densities at end of pulse are as high as 10s ppm. Temperature rise is nominal due to short pulse duration.**



- **$N_2(A)$**



- **O**



- **$O_2(^1\Delta)$**

- **$N_2/O_2/H_2O$ =79.5 / 19.5 / 1, 1 atm, 15 kV, 0-15 ns**

MIN 🟪🟦🟩🟨🟫🟥 **MAX**

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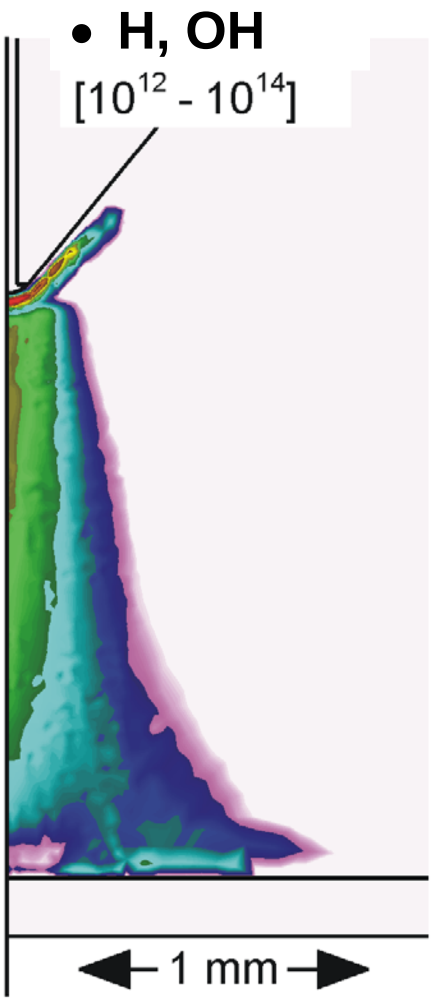
H, OH POST PULSE DENSITIES



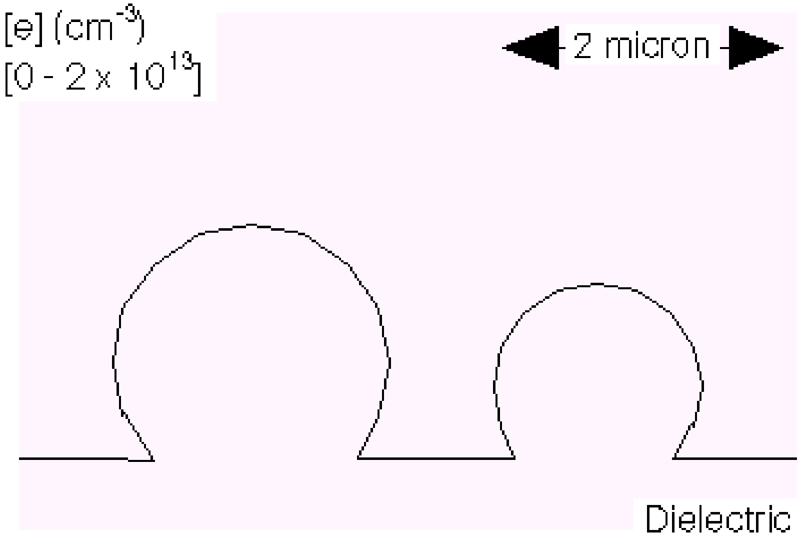
- H and OH densities (from H_2O dissociation) are essentially the same after the short current pulse.

- $N_2/O_2/H_2O$ =79.5 / 19.5 / 1, 1 atm, 15 kV, 0-15 ns

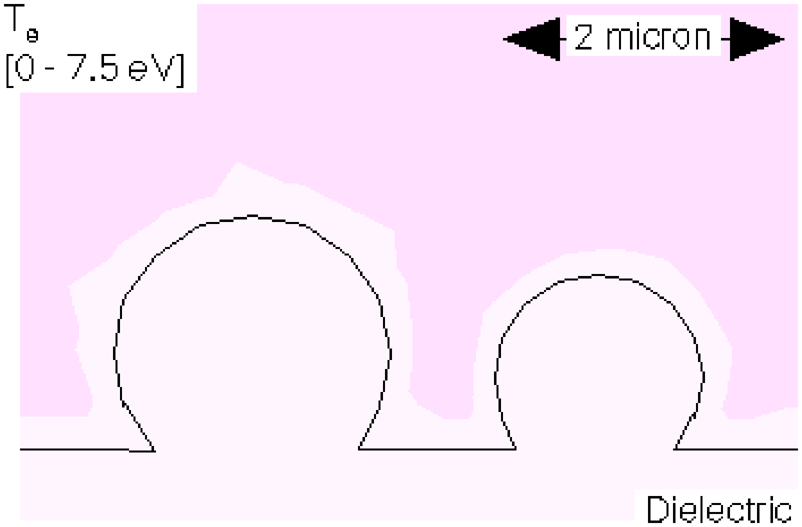
POLYMER SURFACE STRUCTURES

Animation Slide

- **The avalanche exposes the tubules to a burst of hot electrons, unevenly charging surfaces. Ion fluxes are also uneven.**



- **Electron density**



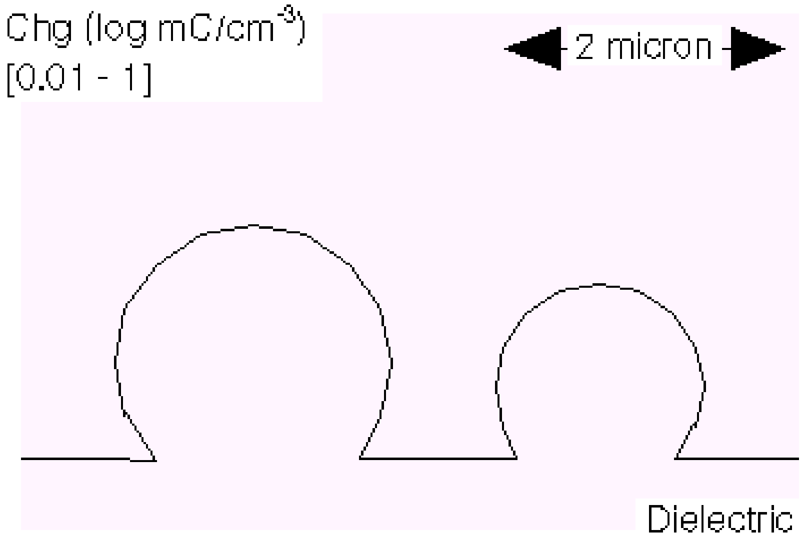
- **Electron Temperature**

- **$N_2/O_2/H_2O$ =79.5 / 19.5 / 1, 1 atm, 15 kV, 2.5 ns**

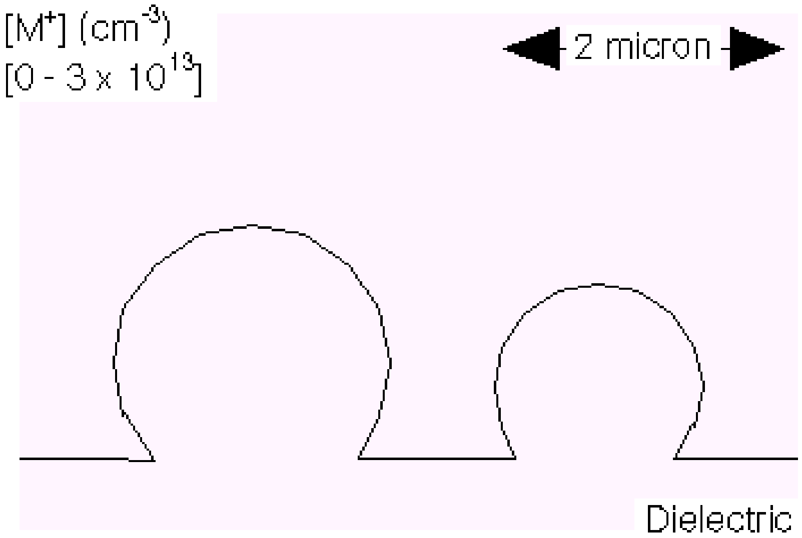
MIN **MAX**

RESOLVING POLYMER SURFACE STRUCTURES

- The avalanche exposes the tubules to a burst of hot electrons, unevenly charging surfaces. Ion fluxes are also uneven.



- Charge density



- M+ density

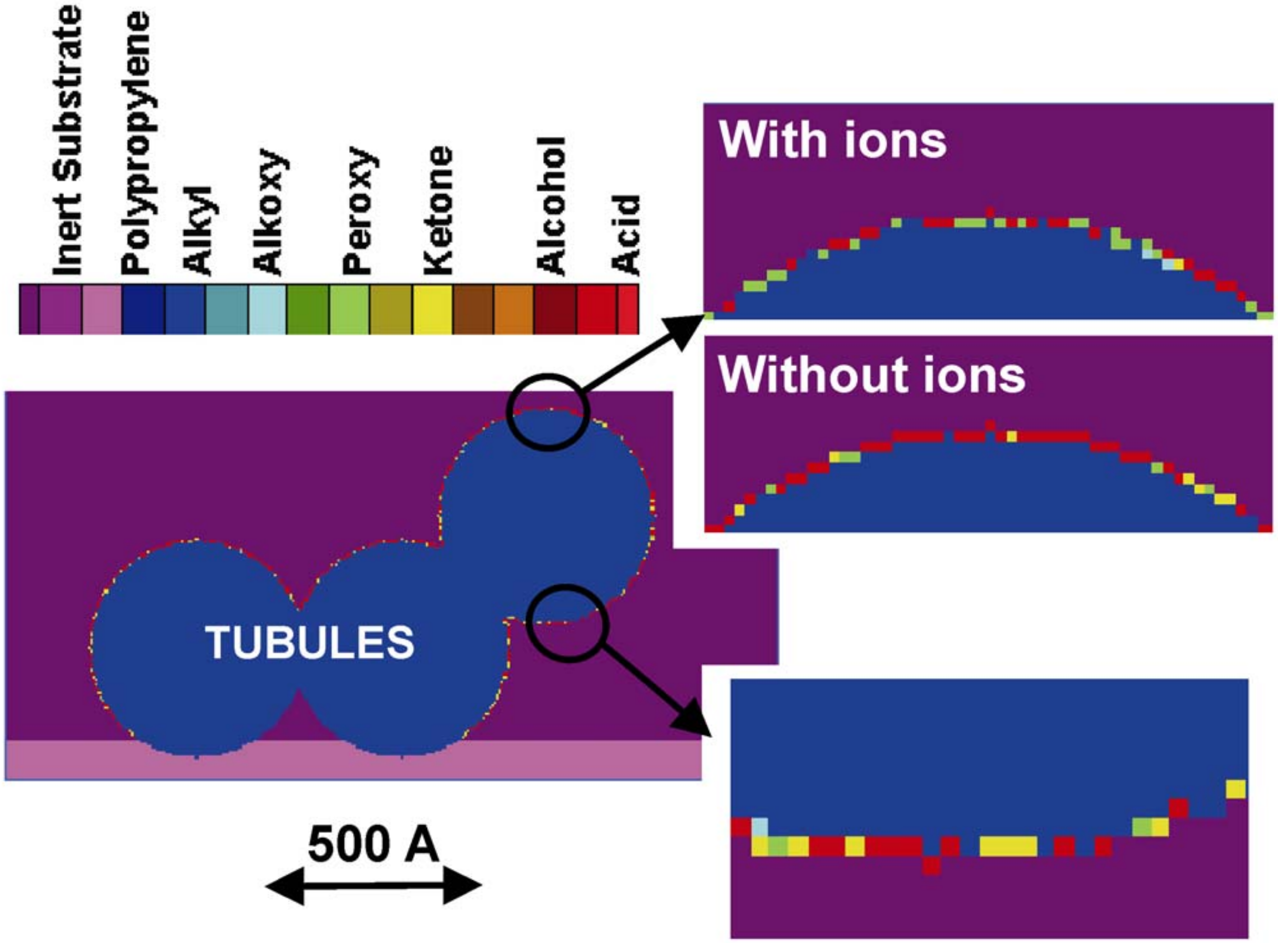
Animation Slide

- $N_2/O_2/H_2O$ =79.5 / 19.5 / 1, 1 atm, 15 kV, 2.5 ns

MIN ▨ MAX

EXAMPLE: RESOLVING POLYMER SURFACE STRUCTURES

- “Commodity” knowledge bases leveraged with high tech surface evolution techniques resolves modification of polymer tubules.



- With ion reactions which remove O (from peroxy, alkyls) and H- (from alcohol) the top surface has more peroxy sites.

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CONCLUDING REMARKS

- Plasmas and polymers enjoy a unique relationship in the realm of gas-surface interactions.

- Commodity processes based on plasma functionalization of polymers is perhaps the major use of plasmas (after lighting).

- Processes based on plasma polymerization enable manufacture of high value components.

- We are now well positioned to adapt commodity processes towards the processing of new materials (e.g., biocompatible, flexible display panels) with attractive costs.