PLASMA PROCESSING AND POLYMERS: FRITO BAGS TO MICROELECTRONICS FABRICATION

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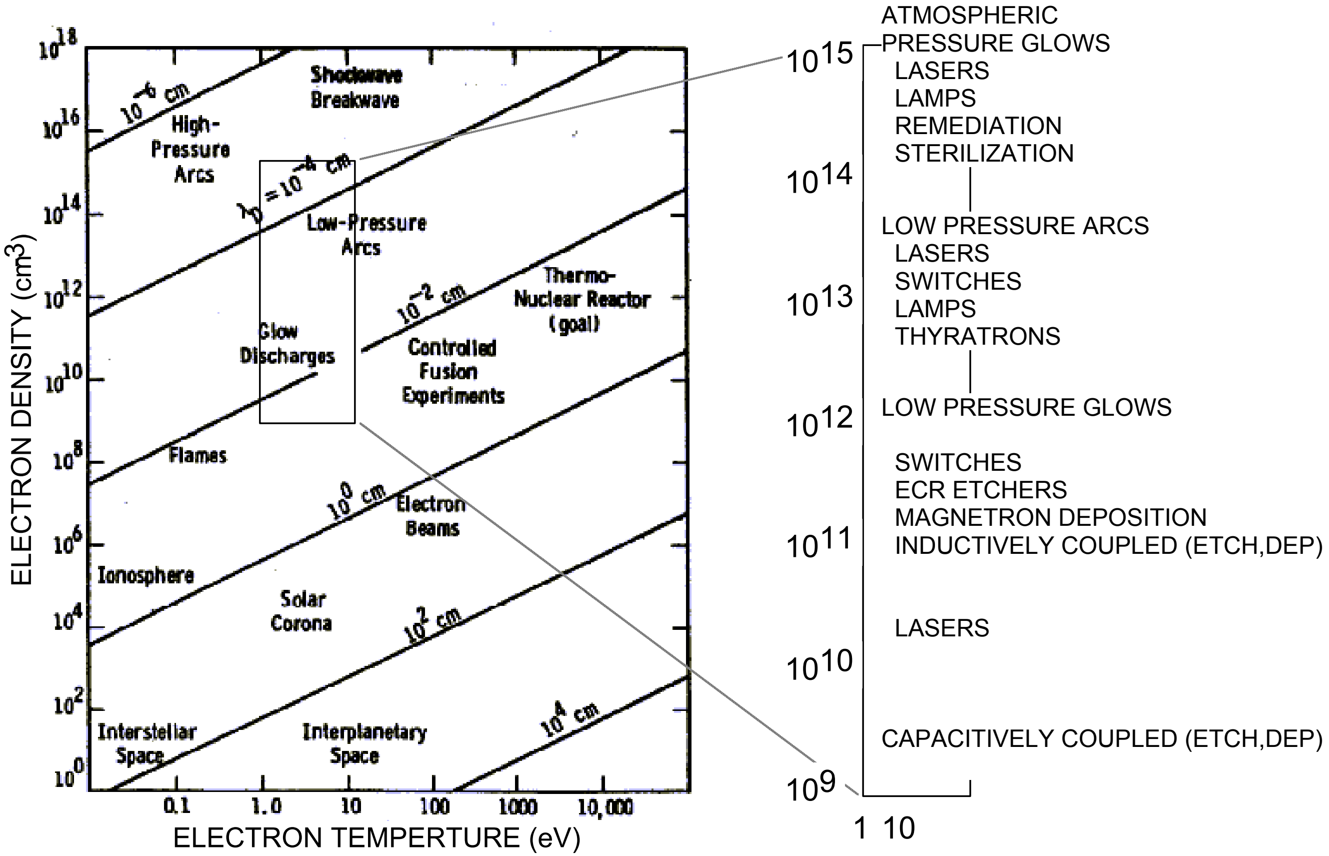
November 2002

AGENDA

- Plasmas: Tools for eV physics and chemistry
- Plasmas and Polymers: Extremes in Physics and Applications
- Plasmas for functionalization of polymers
- Polymers for selectivity in plasma etching
- Concluding Remarks

PARTIALLY IONIZED PLASMAS

- **Partially ionized plasmas are gases containing neutral atoms and molecules, electrons, positive ions and negative ions.**
- **An air plasma: N_2, O_2, N_2^+, O_2^+, O^-, e where [e] << Neutrals**



ATMOSPHERIC PRESSURE GLOWS
LASERS
LAMPS
REMEDIATION
STERILIZATION

LOW PRESSURE ARCS
LASERS
SWITCHES
LAMPS
THYRATRONS

LOW PRESSURE GLOWS

SWITCHES
ECR ETCHERS
MAGNETRON DEPOSITION
INDUCTIVELY COUPLED (ETCH,DEP)

LASERS

CAPACITIVELY COUPLED (ETCH,DEP)

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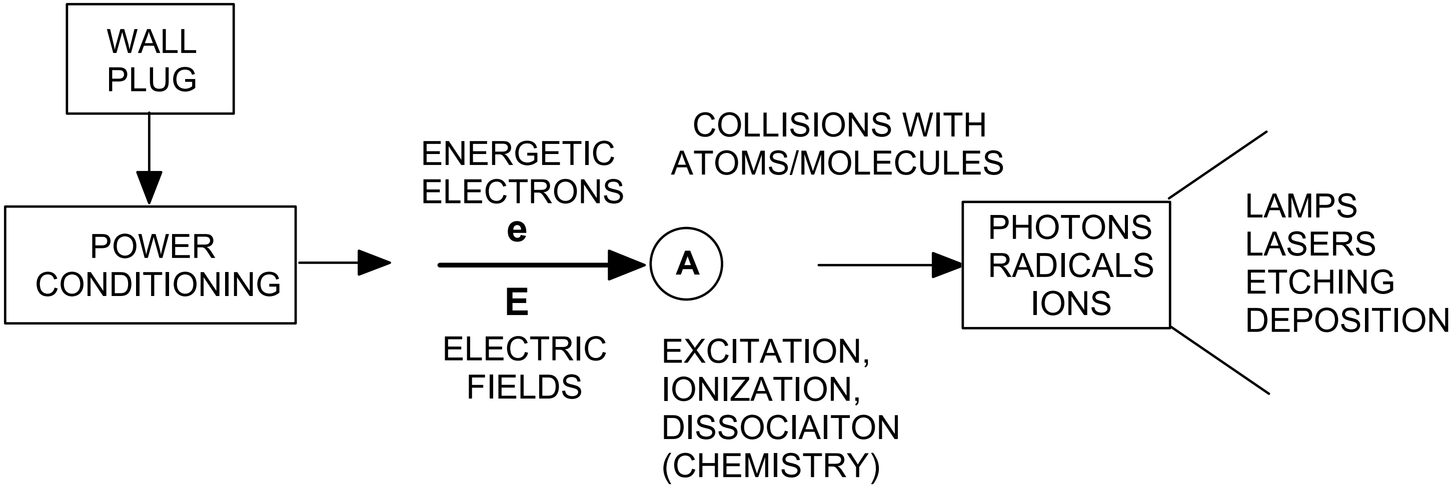
COLLISIONAL LOW TEMPERATURE PLASMAS

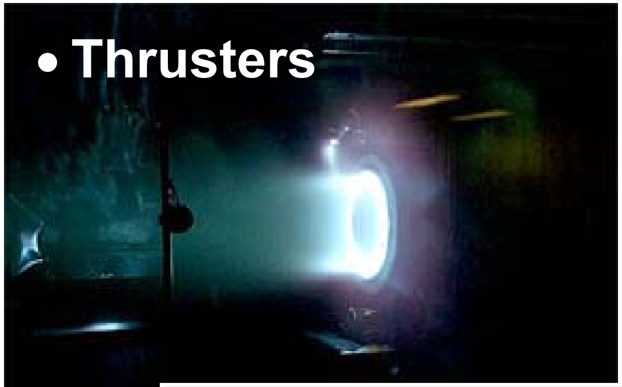
- **These systems are the plasmas of every day technology.**



- **Electrons transfer power from the "wall plug" to internal modes of atoms / molecules to "make a product”, very much like combustion.**
- **The electrons are “hot” (several eV or 10-30,000 K) while the gas and ions are cool, creating“non-equilibrium” plasmas**

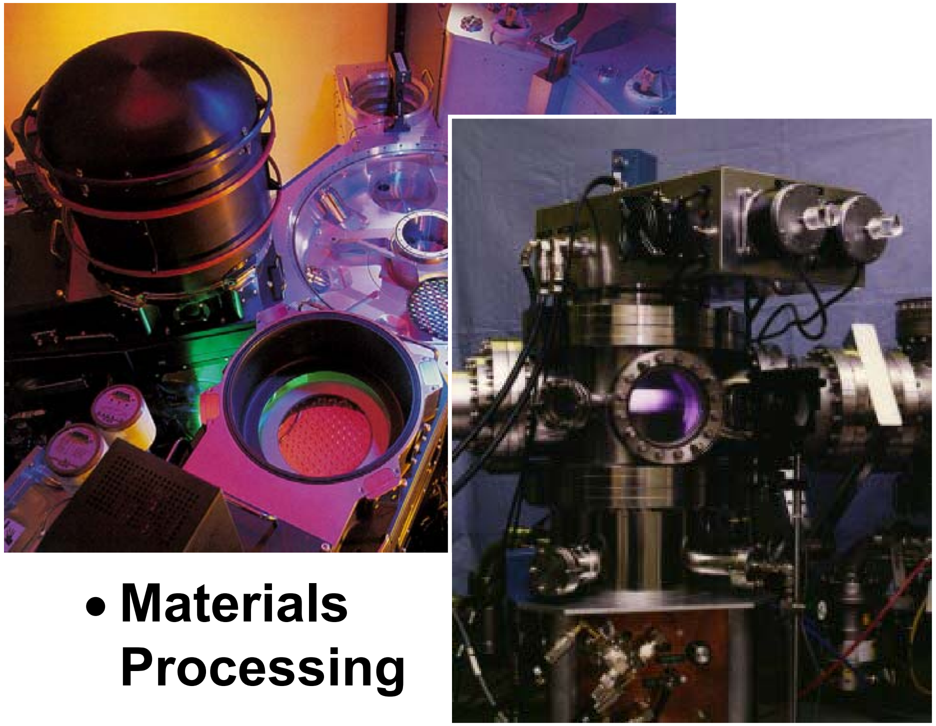
COLLISIONAL LOW TEMPERATURE PLASMAS

- Lighting



- Thrusters

- Spray Coatings

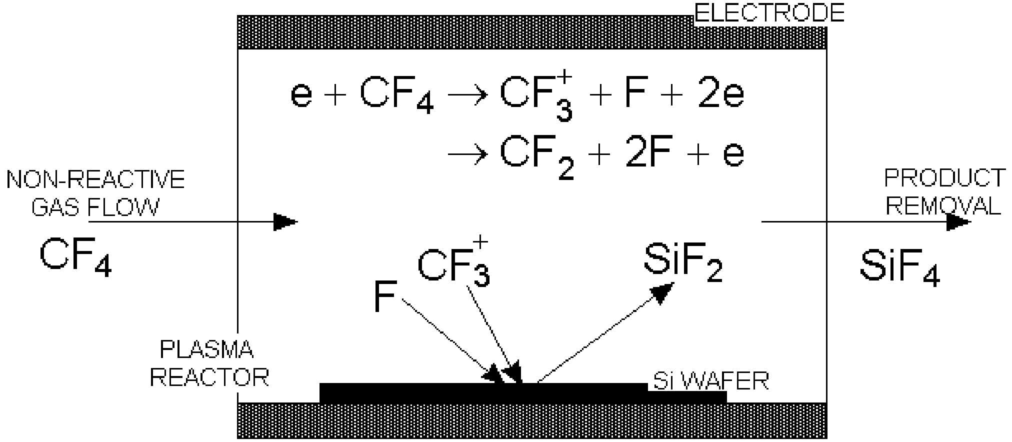


- Materials Processing

- Displays

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:**

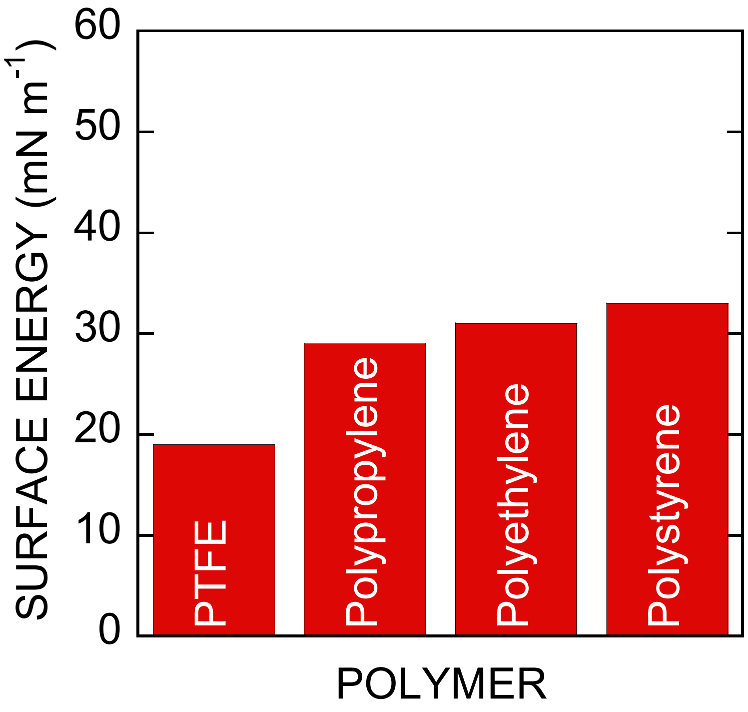


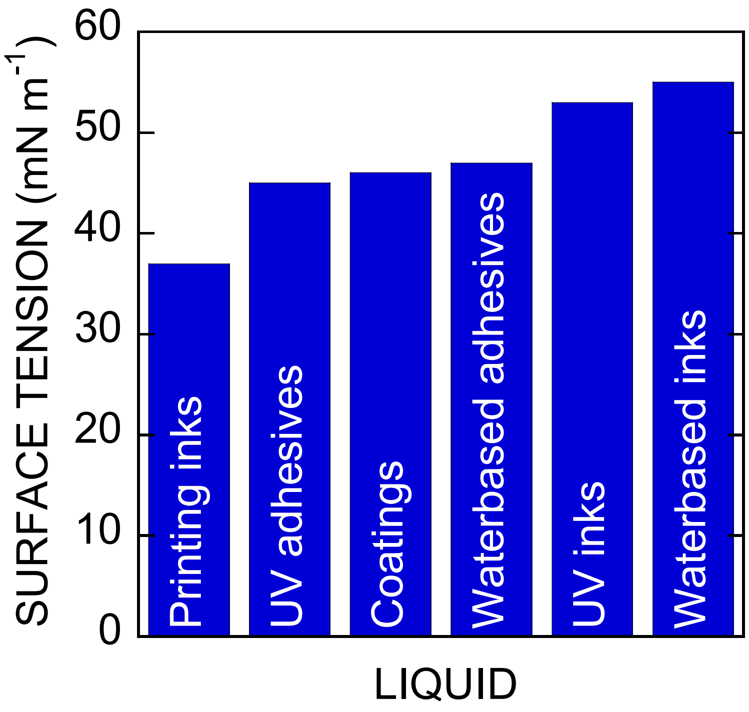
- **Functionalization of surfaces (high pressure)**
- **Etching for microelectronics fabrication (low pressure)**

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

SURFACE ENERGY AND FUNCTIONALITY OF POLYMERS

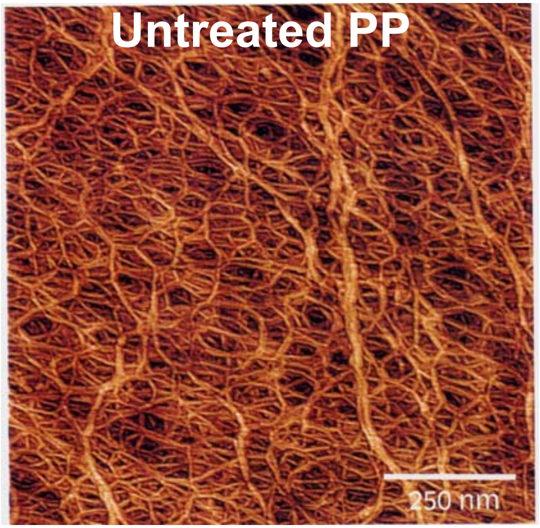
- **Most polymers, having low surface energy, are hydrophobic.**
- **For good adhesion and wettability, the surface energy of the polymer should exceed of the overlayer by ≈2-10 mN m^{-1}.**

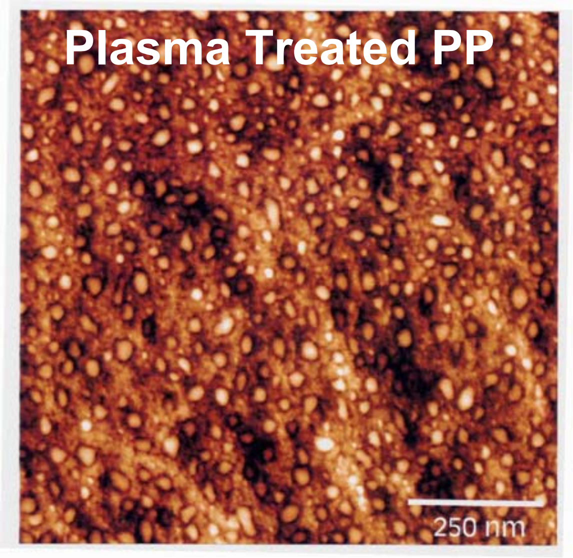




PLASMA SURFACE MODIFICATION OF POLYMERS

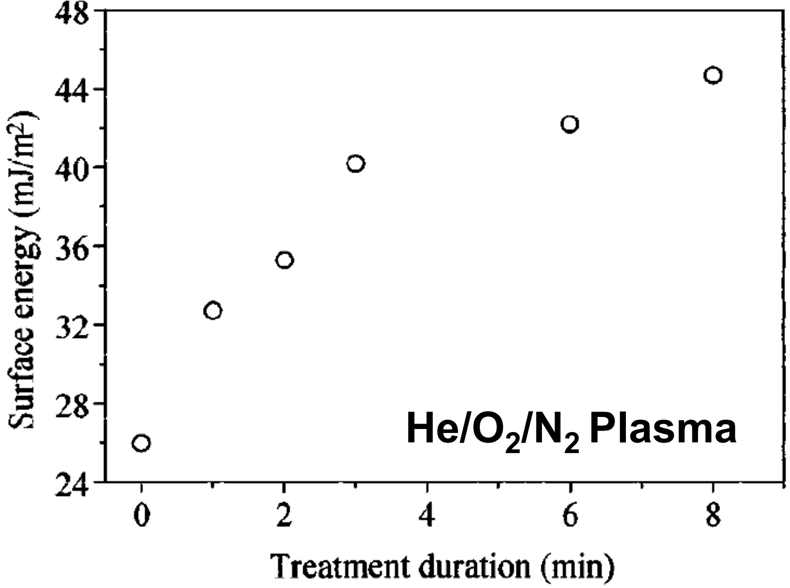
- **To improve wetting and adhesion of polymers atmospheric plasmas are used to generate gas-phase radicals to functionalize their surfaces.**





- **M. Strobel, 3M**

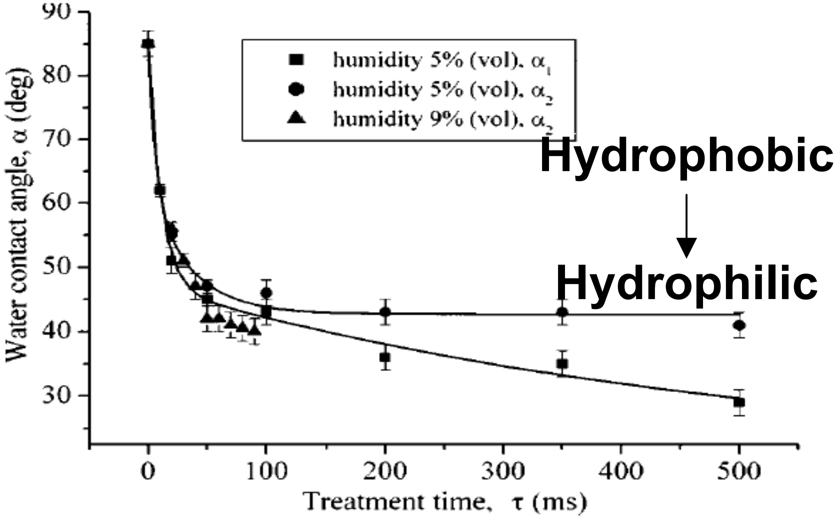
- **Polypropylene (PP)**



- **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).

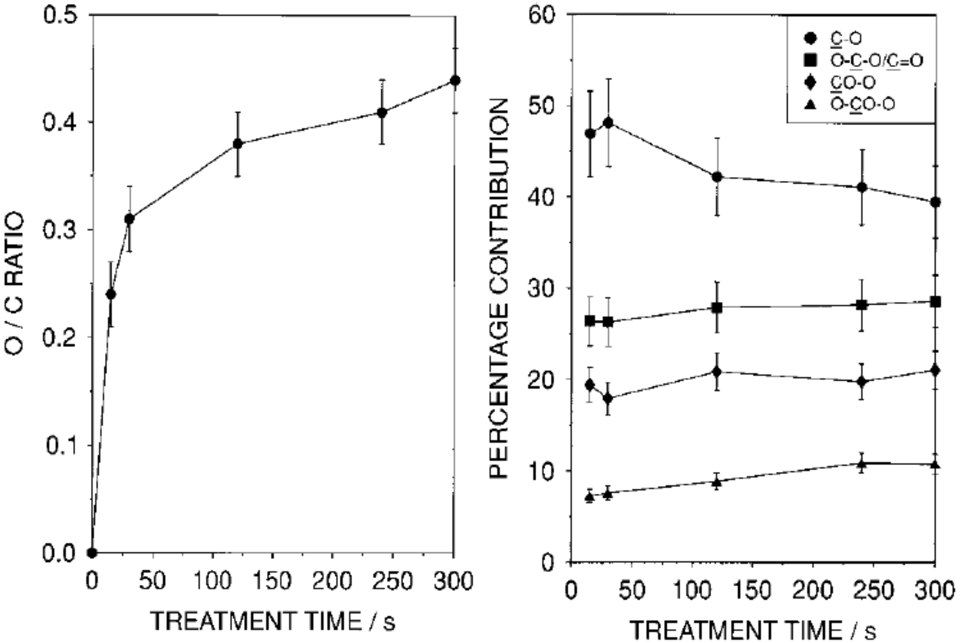


Hydrophobic

↓

Hydrophilic

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



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

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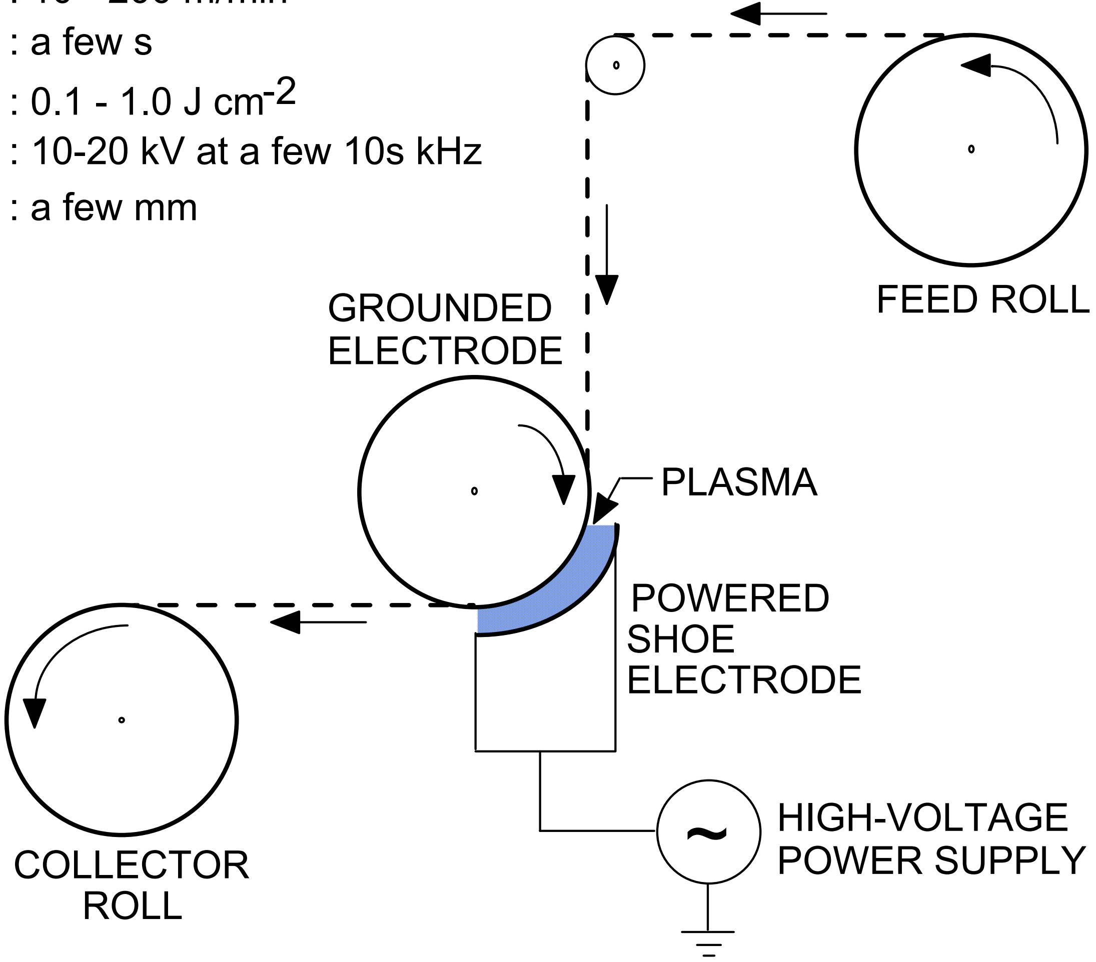
POLYMER TREATMENT APPARATUS

- 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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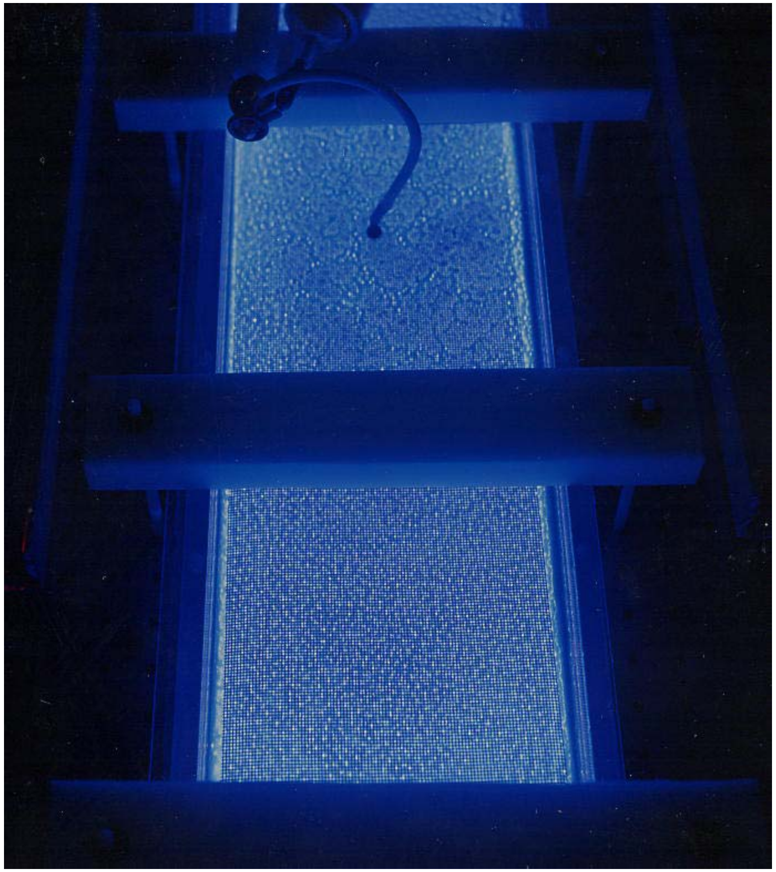
COMMERCIAL CORONA PLASMA EQUIPMENT


Tantec Inc.

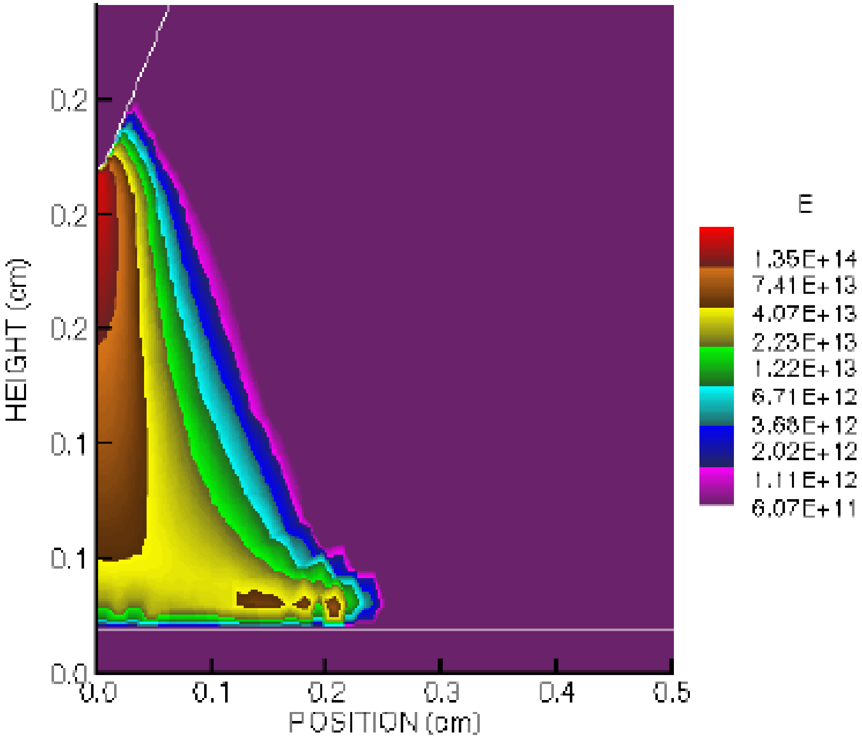
CORONA/DIELECTRIC BARRIER PLASMAS

- Corona and dielectric barrier discharge plasmas operate in a filamentary mode.



- Laboratory Dielectric Barrier Discharge

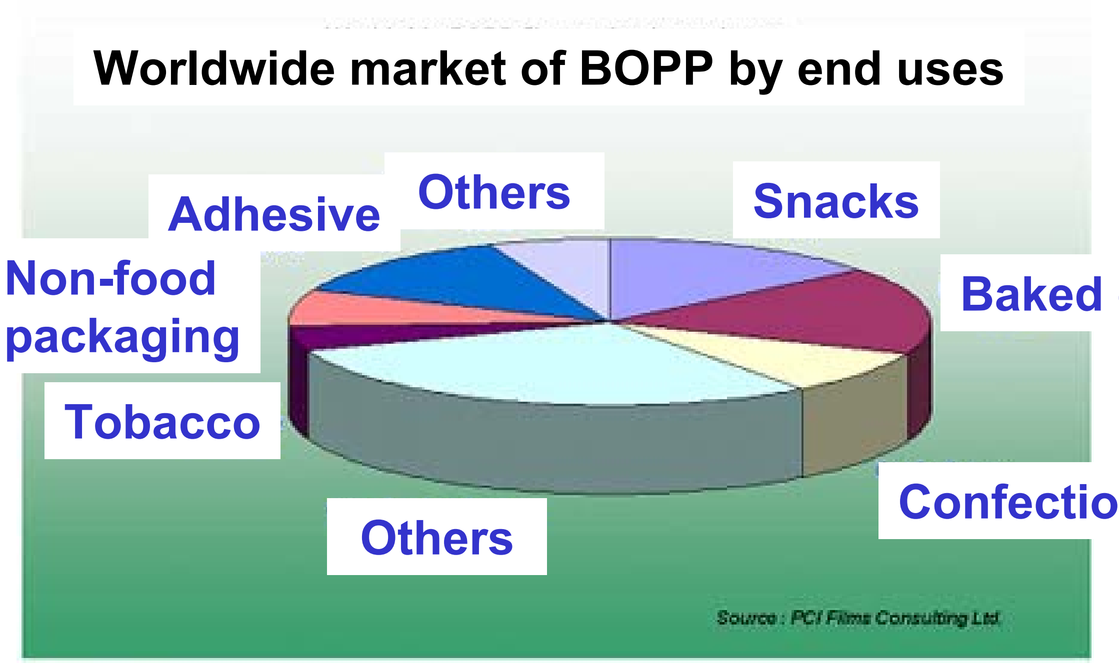
- Electron Density (2-d Model)



- 1 atm, Dry Air, -15 kV, 30 ns

POLYPROPYLENE

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



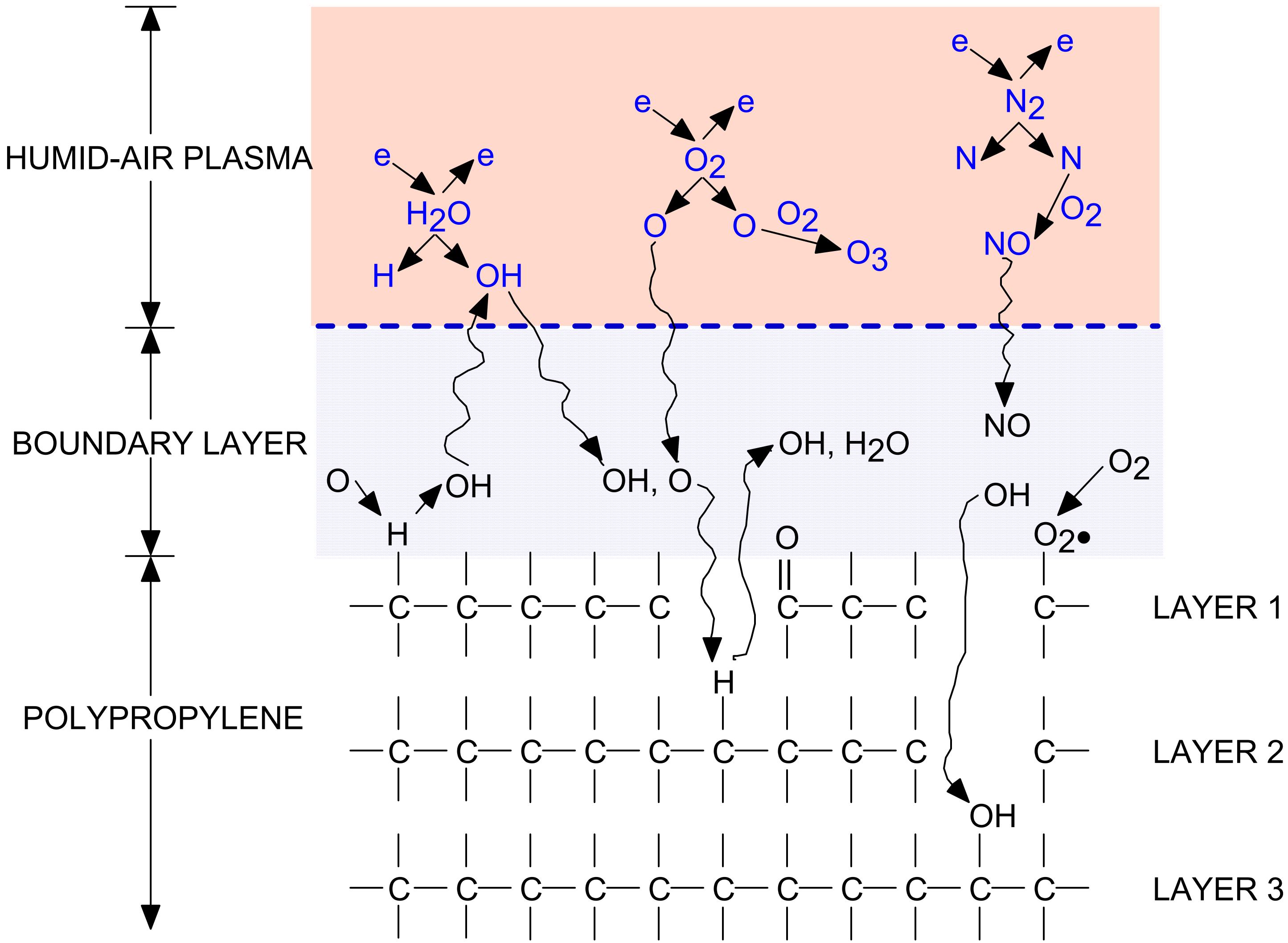
Worldwide market of BOPP by end uses

Source : PCI Films Consulting Ltd

FUNCTIONALIZATION OF THE PP SURFACE

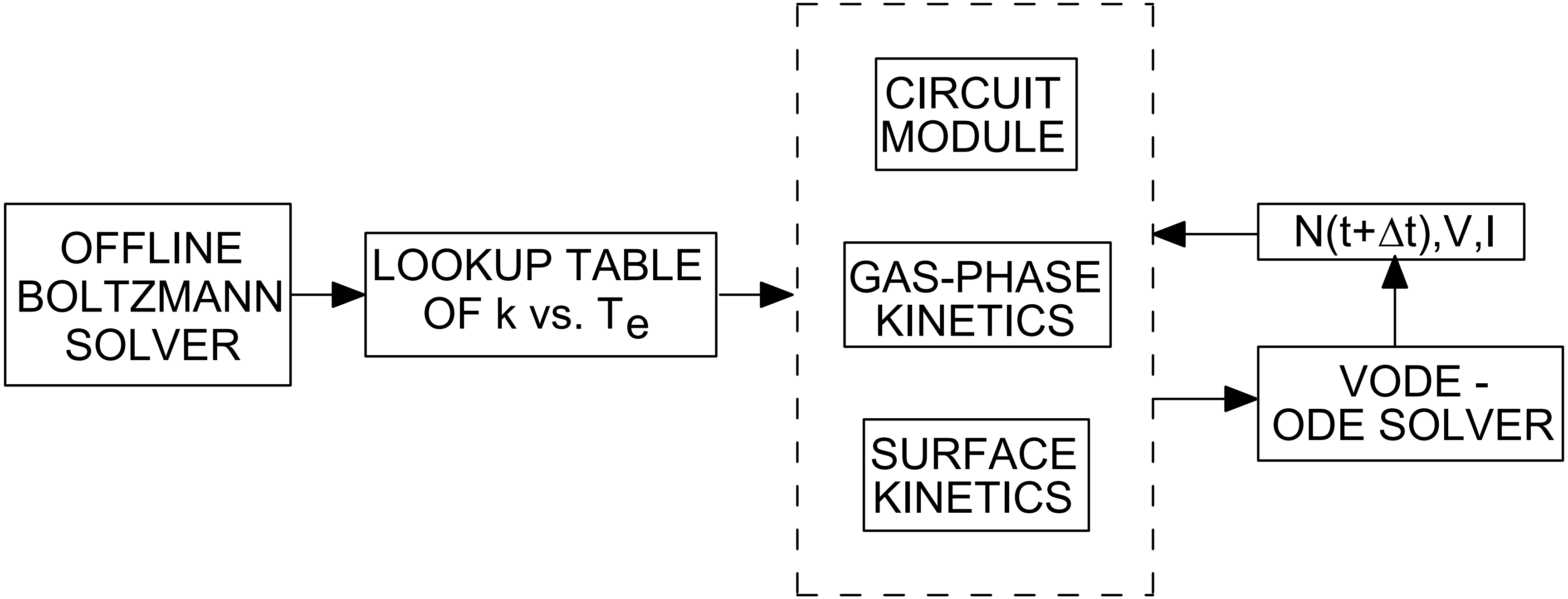
- Untreated PP is hydrophobic.
- Increases in surface energy by plasma treatment are attributed to the functionalization of the surface with hydrophilic groups.
  - Carbonyl (-C=O)
  - Alcohols (C-OH)
  - Peroxy (-C-O-O)
  - Acids ((OH)C=O)
- The degree of functionalization depends on process parameters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

REACTION PATHWAY



DESCRIPTION OF THE MODEL: GLOBAL_KIN

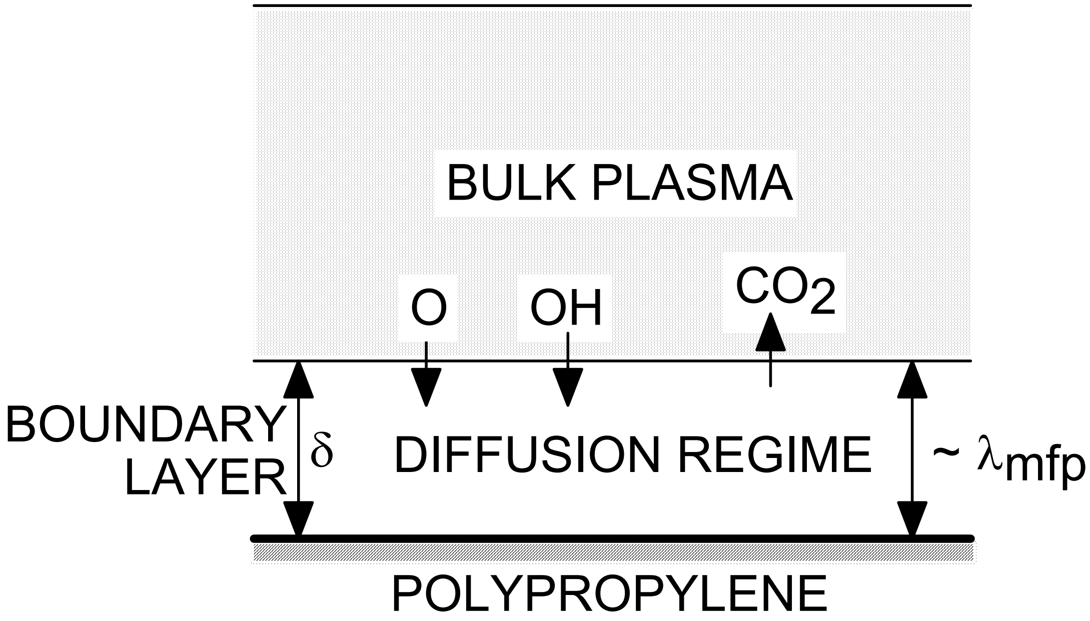
- **Modules in GLOBAL_KIN:**
  - **Circuit model**
  - **Homogeneous plasma chemistry**
  - **Species transport to PP surface**
  - **Heterogeneous surface chemistry**



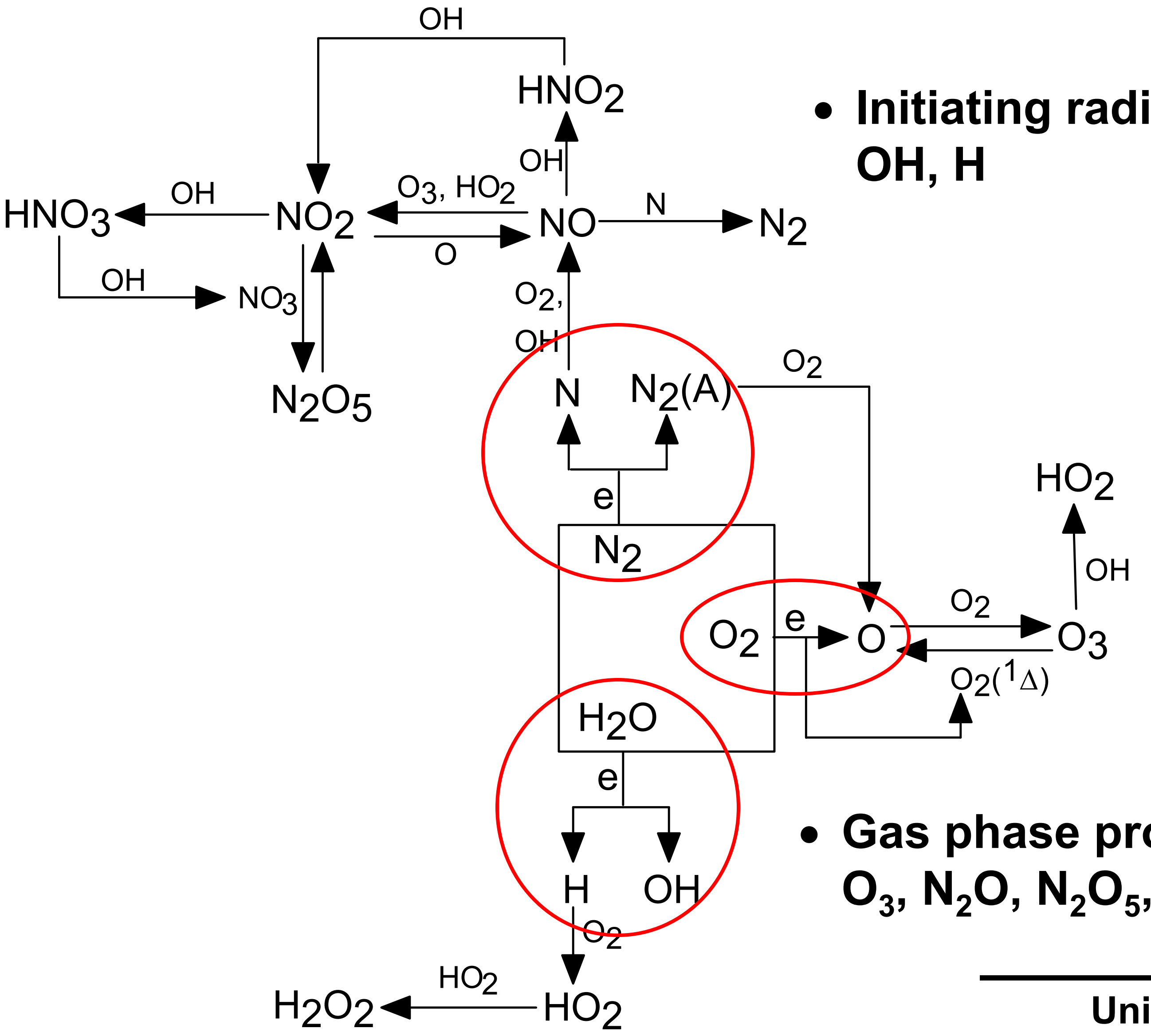
SPECIES TRANSPORT TO THE POLYMER SURFACE

- **Species in the bulk plasma diffuse to the PP surface through a boundary layer (d ~ a few $\lambda_{mfp} \approx \mu m$).**

- **Radicals react on the PP based on a variable density, multiple layer surface site balance model.**



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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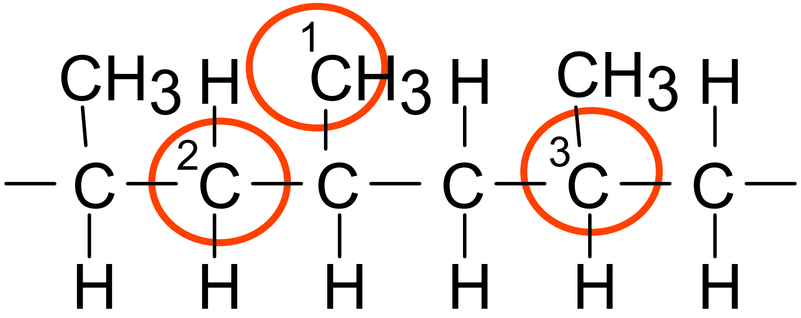
POLYPROPYLENE (PP) POLYMER STRUCTURE



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:**

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

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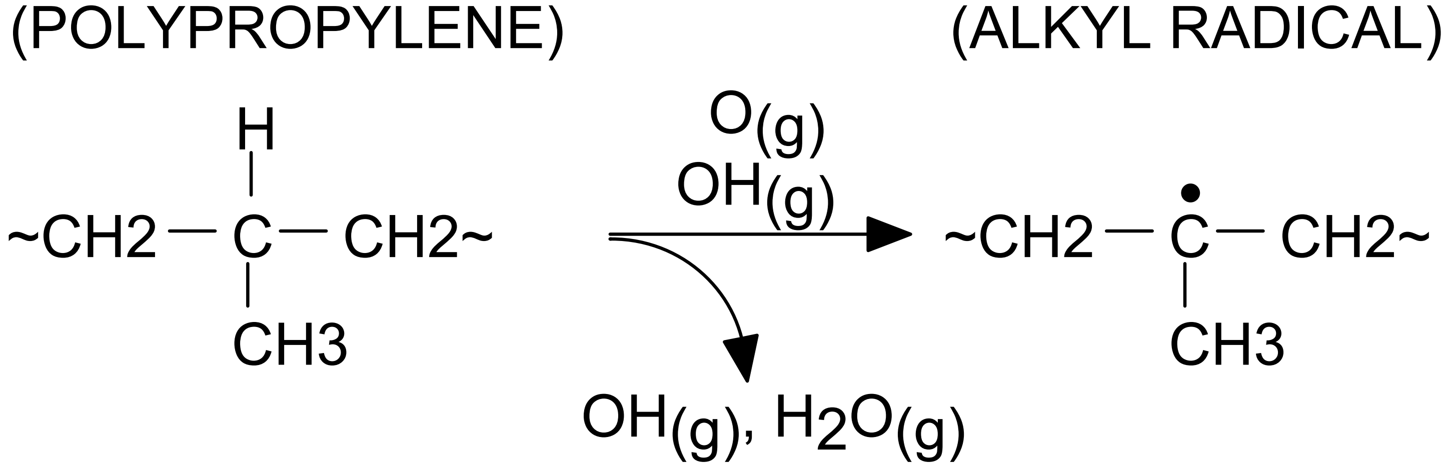
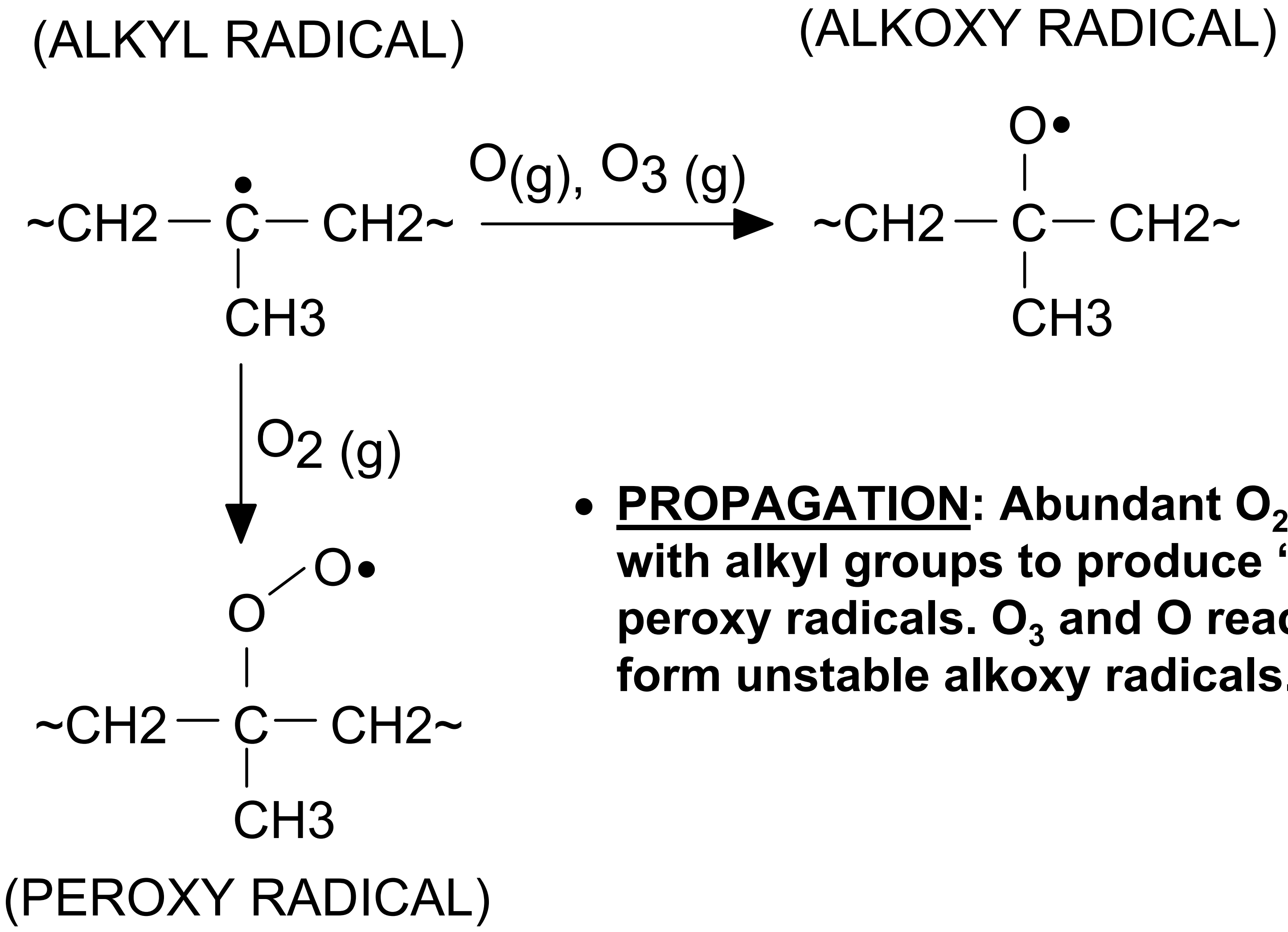
PP SURFACE REACTION MECHANISM: INITIATION

- **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.**



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.**

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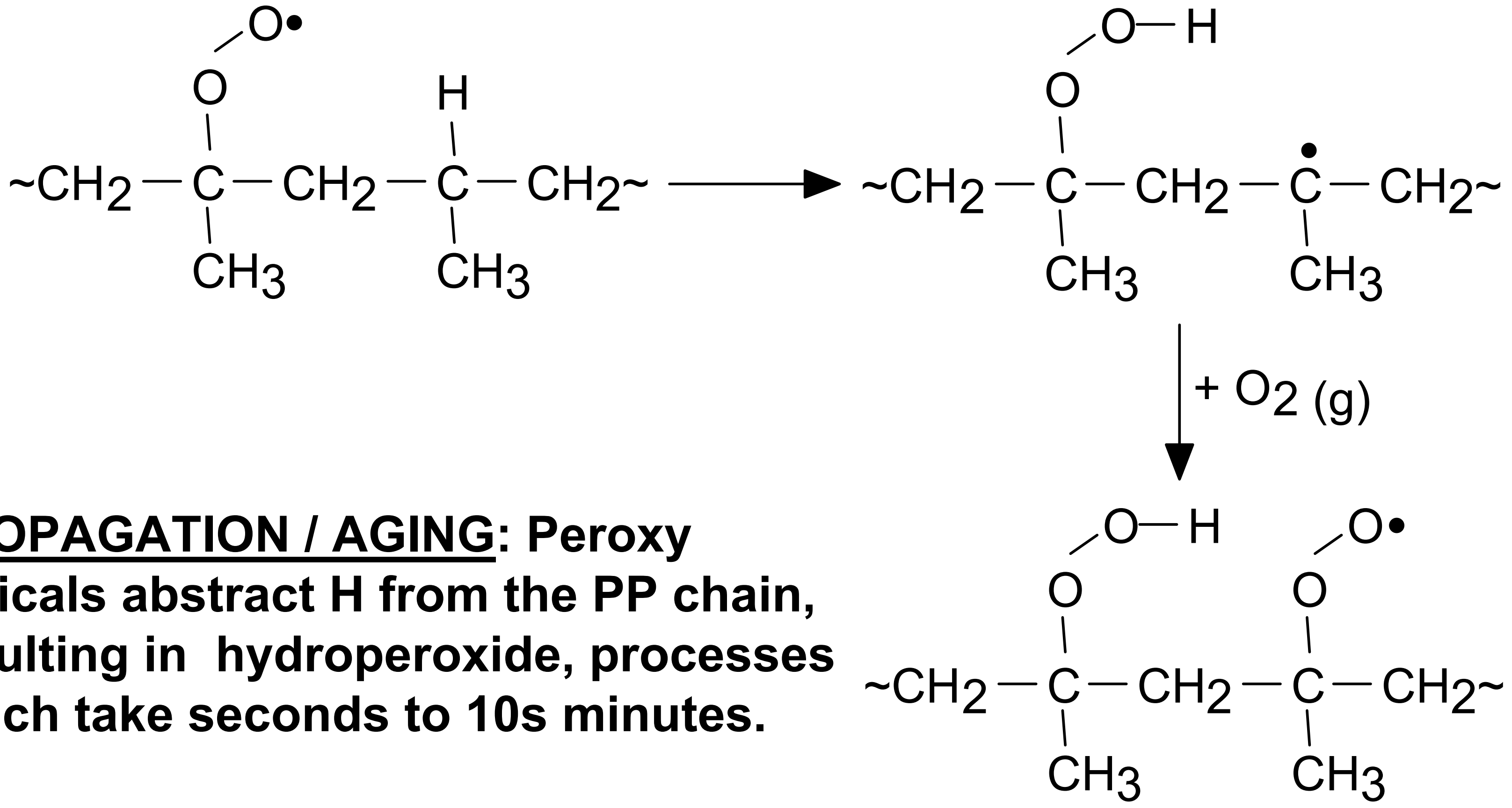
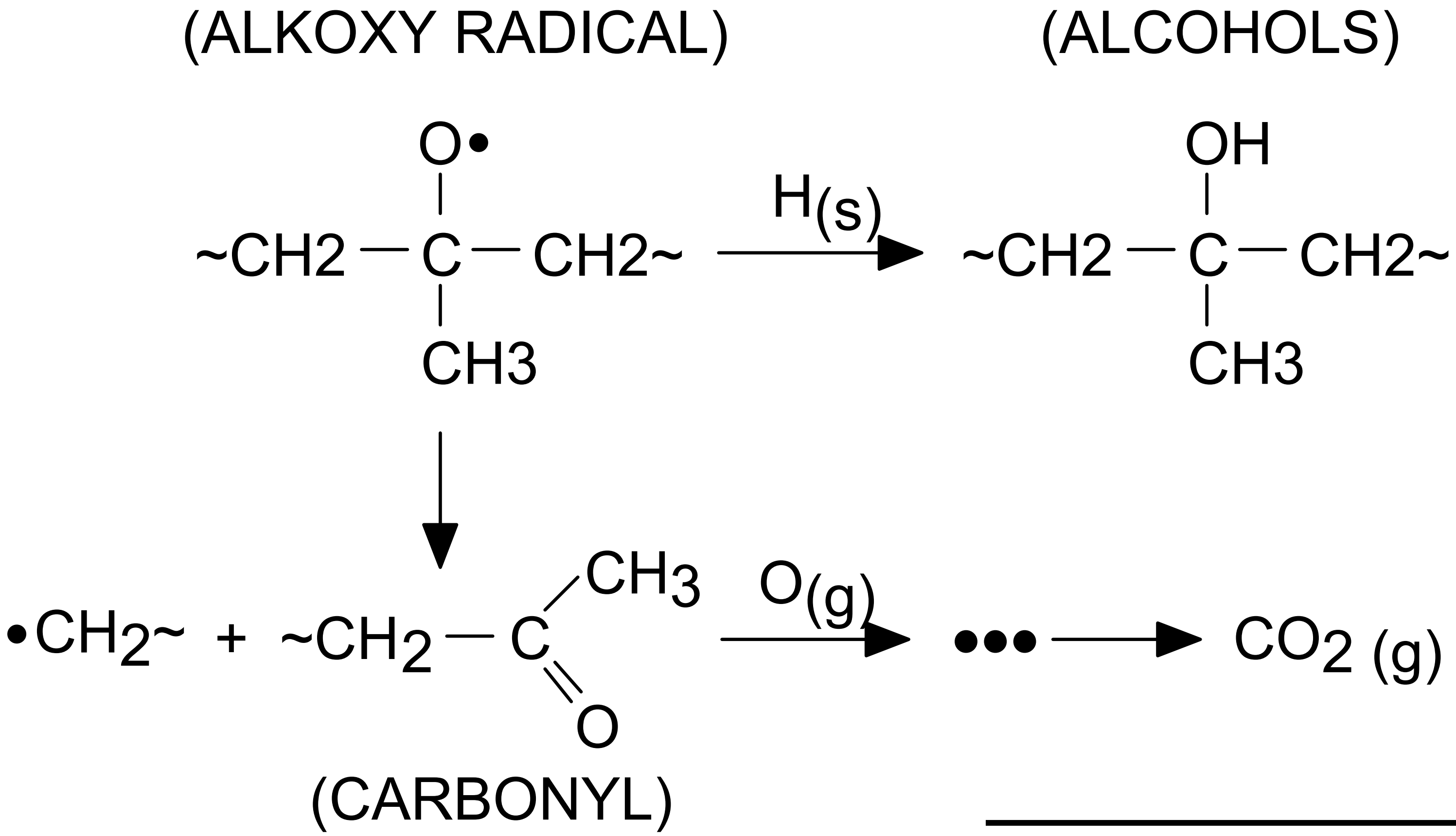
PP SURFACE REACTIONS: PROPAGATION / AGING

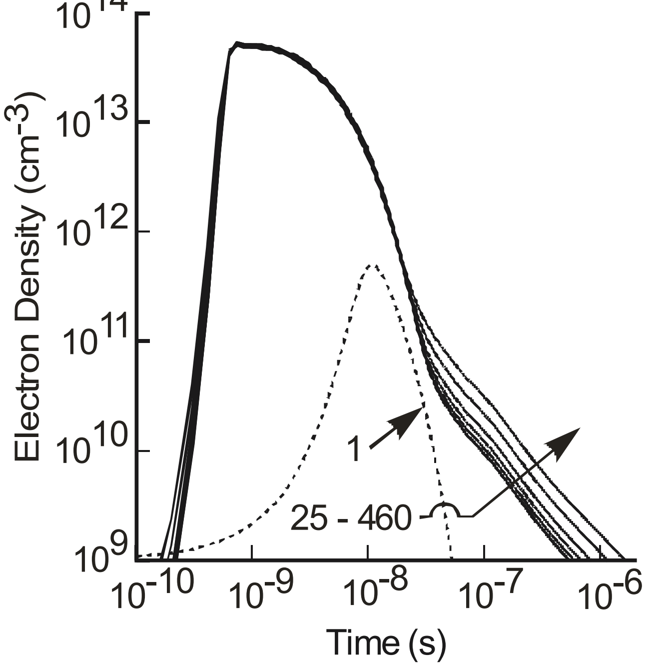


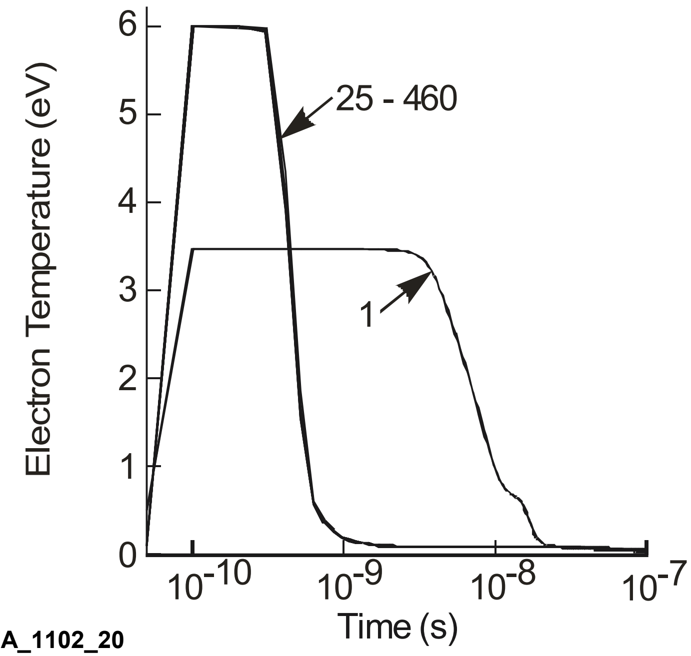
- **PROPAGATION / AGING: Peroxy radicals abstract H from the PP chain, resulting in hydroperoxide, processes which take seconds to 10s minutes.**

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.**





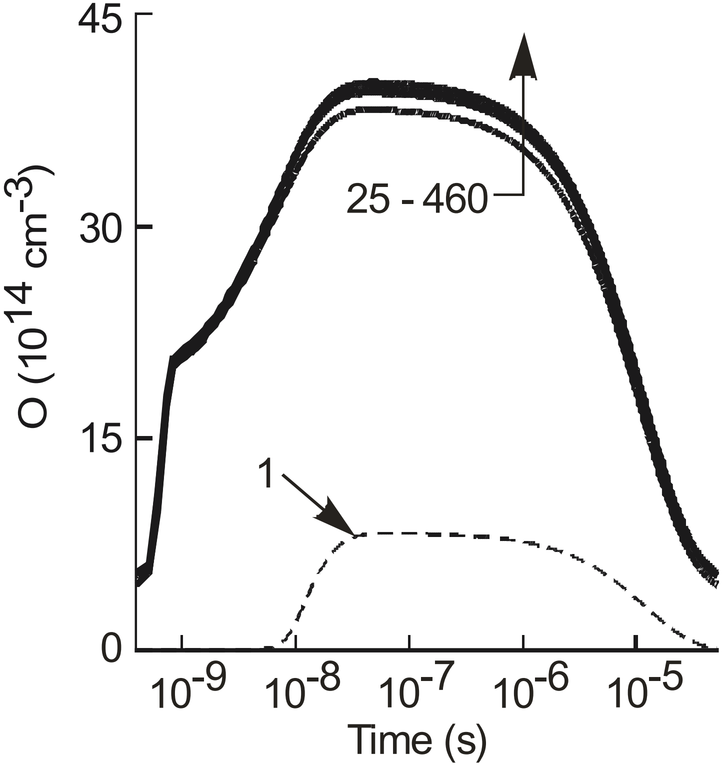


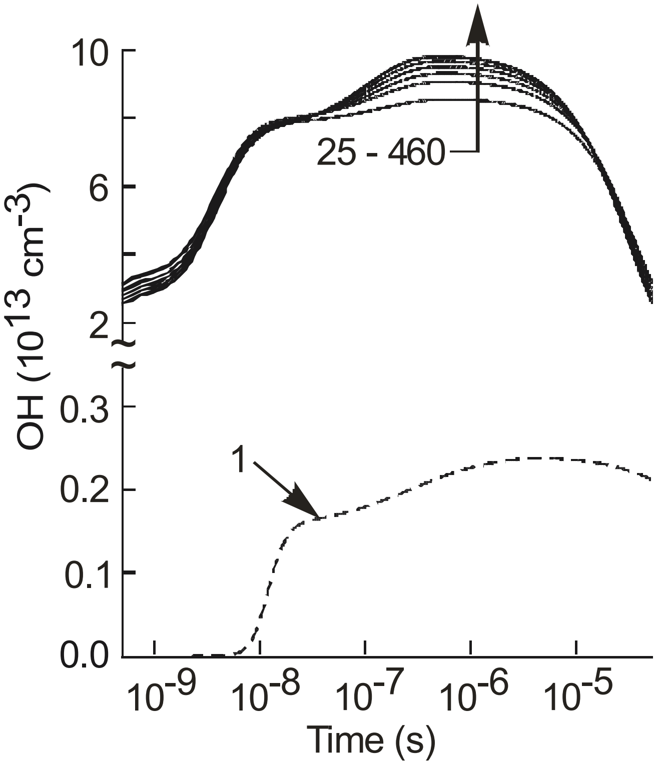
BASE CASE: n_e, T_e

- 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 voltage.s
- $N_2/O_2/H_2O$ = 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

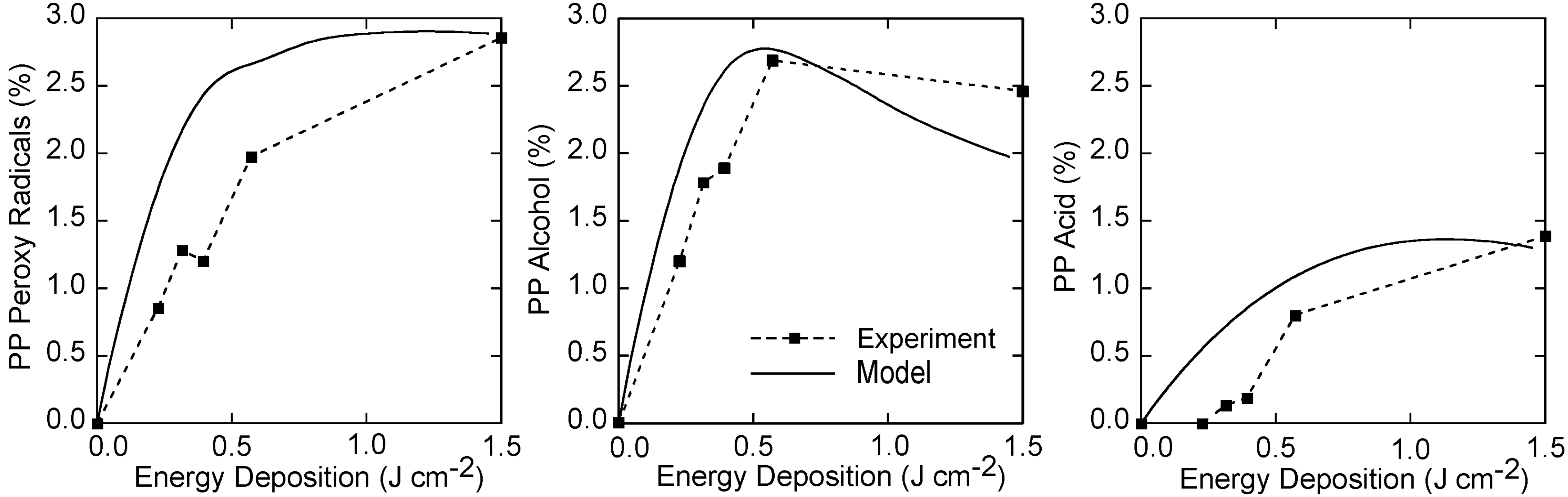
- **Electron impact dissociation of O_2 and H_2O produces O and OH. O is consumed in the primarily to form O_3,**
- **After 100s of pulses, radicals attain a periodic steady state.**





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).

GAS-PHASE PRODUCTS: O_3, N_XO_Y, HNO_X

- **O_3 is produced by the reaction of O with O_2,**

$$O + O_2 + M \rightarrow O_3 + M.$$

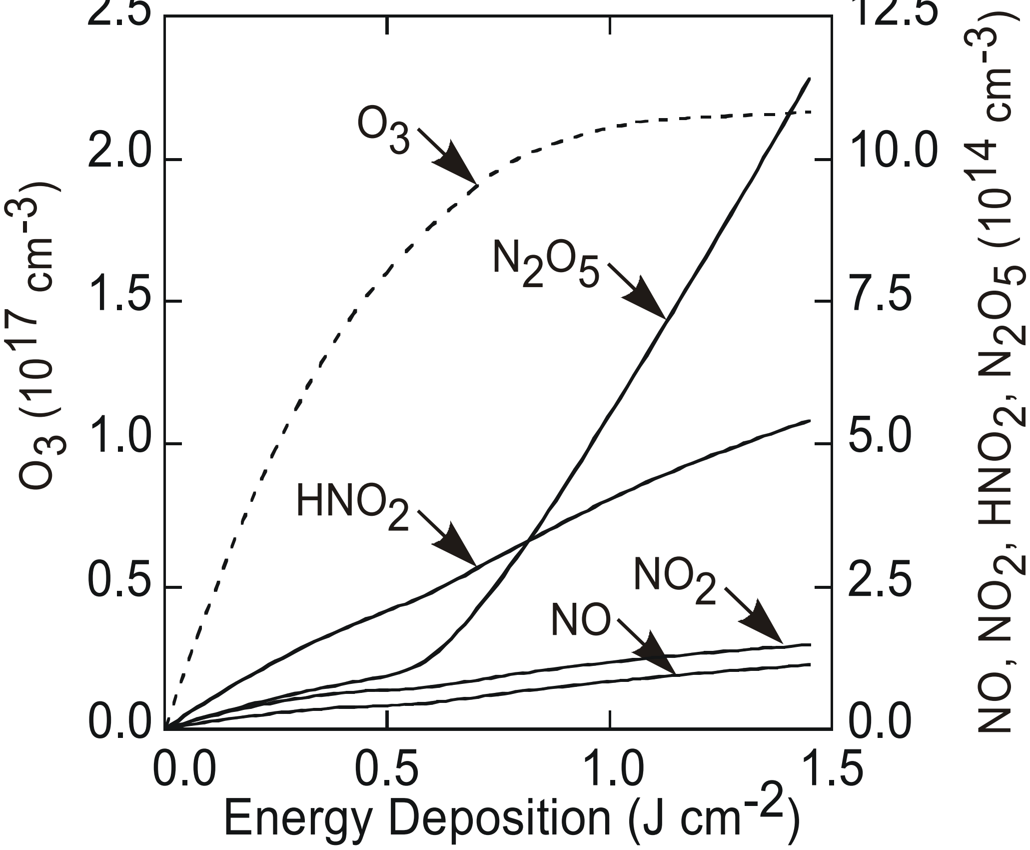
- **N containing products include NO, NO_2, HNO_2 andN_2O_5,**

$$N_2 + O \rightarrow NO + N,$$

$$NO + O + M \rightarrow NO_2 + M,$$

$$NO + OH + M \rightarrow HNO_2 + M$$

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$$



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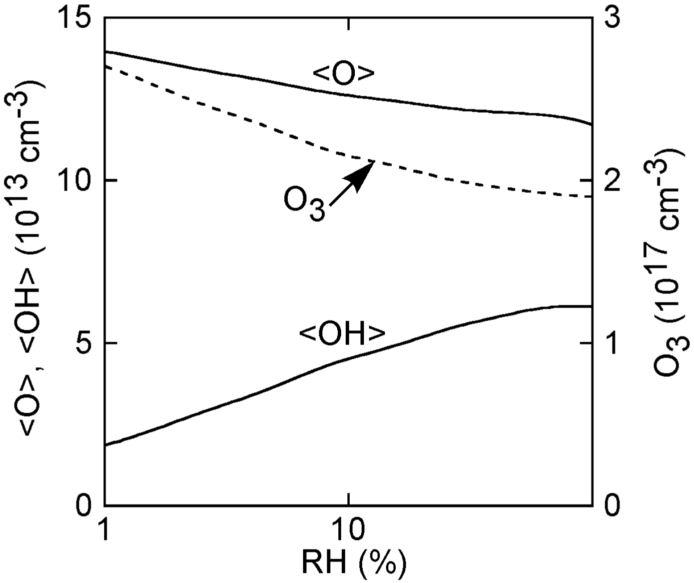
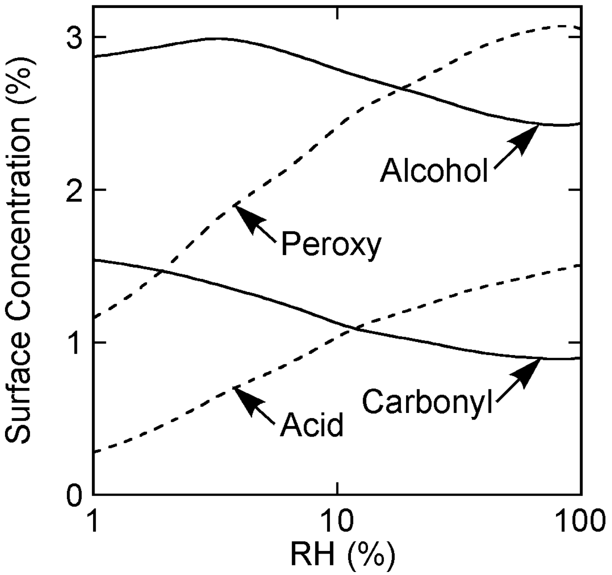
HUMIDITY: PP FUNCTIONALIZATION BY OH

- **Increasing RH produces more OH. Reactions with PP generate more alkyl radicals, rapidly converted to peroxy radicals by O_2.**

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





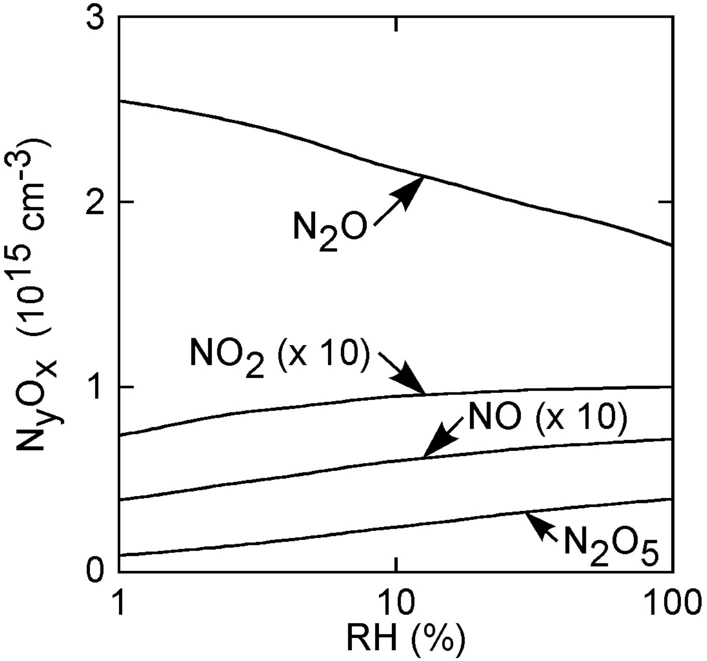
- **Alcohol and carbonyl densities decrease due to increased consumption by OH to form alkoxy radicals and acids.**

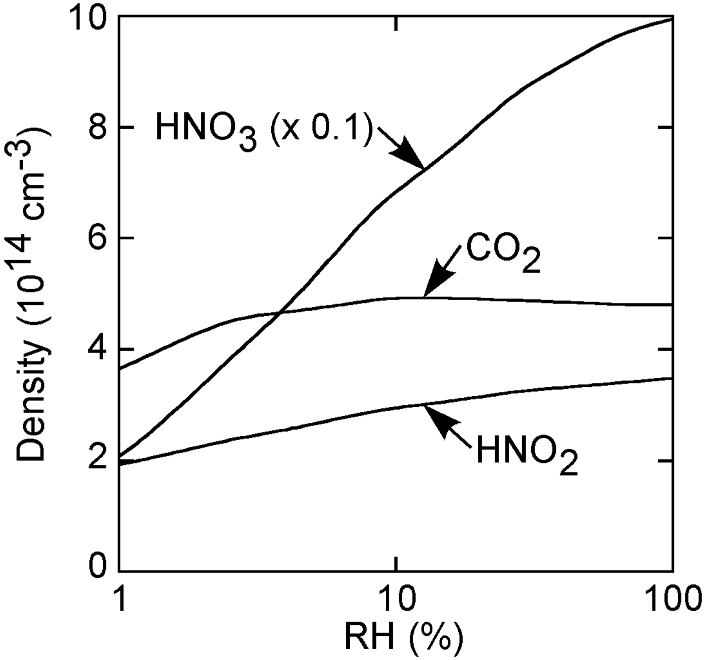
$PP\text{-}OH + OH_{(g)} \rightarrow PP\text{-}O\bullet + H_2O_{(g)}$, $\quad$ $PP{=}O\bullet + OH_{(g)} \rightarrow (OH)PP{=}O$

EFFECT OF RH: GAS-PHASE PRODUCTS

- **Higher RH results in decreasing O and increasing OH.**
- **Production of O_3 decreases while larger densities of HNO_x are generated.**

$$N + OH \rightarrow NO + H, \quad NO + OH \rightarrow HNO_2, \quad NO_2 + OH \rightarrow HNO_3.$$





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EFFECT OF T_{Gas}: PP FUNCTIONALIZATION

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

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

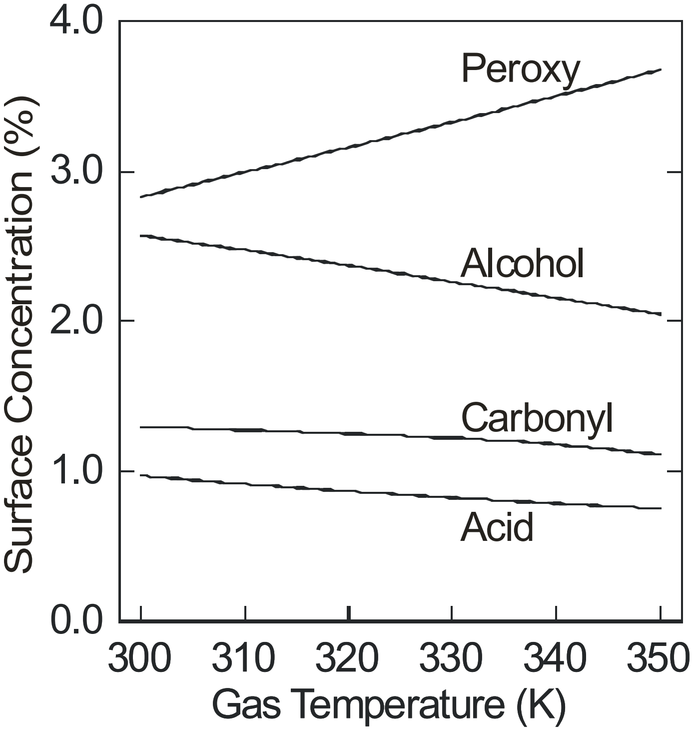
- **… and lower production of alcohols, carbonyl, and acids.**

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

$PP\text{-}O\bullet \rightarrow PP{=}O$

$PP{=}O \rightarrow PP{=}O\bullet$

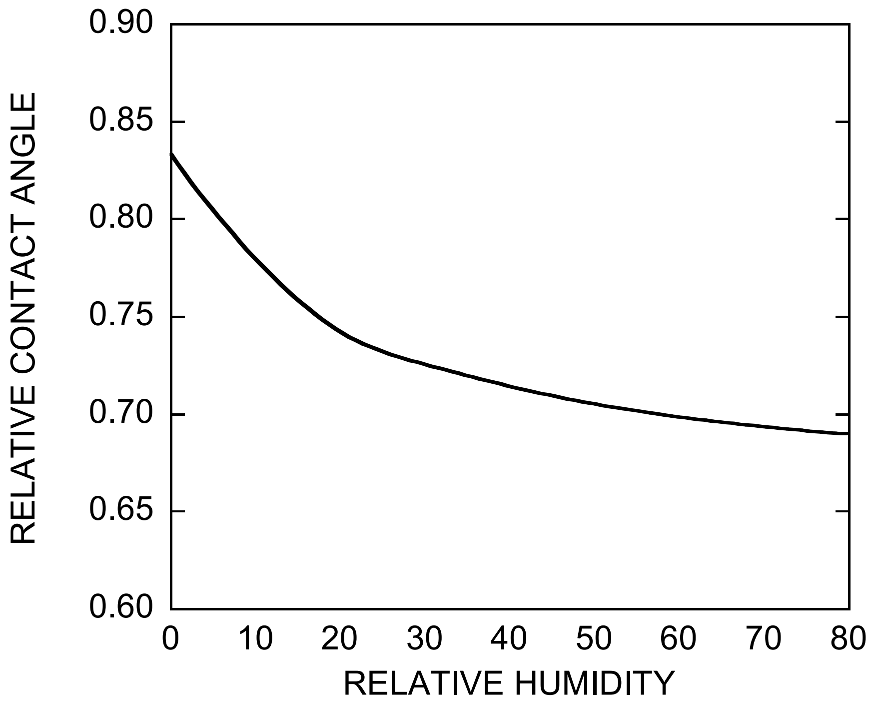
$PP{=}O\bullet + OH \rightarrow (OH)PP{=}O\bullet$



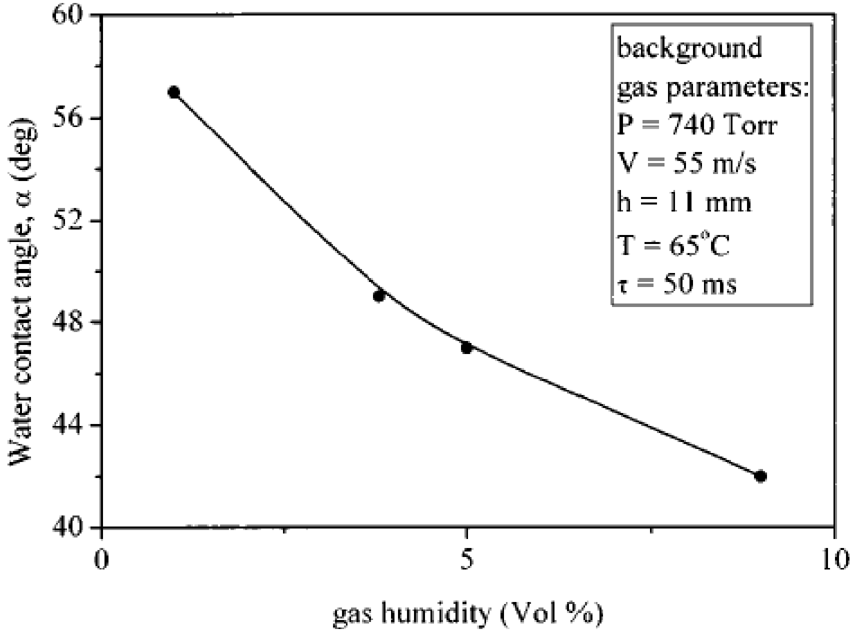
- **Lower consumption of alkyl radicals by O_3 enables reactions with O_2 to dominate, increasing densities of peroxy.**

RH: PREDICTED CONTACT ANGLE

- Relation for wettability / contact angle vs concentration of functional groups is non-linear and poorly known.
- Assume wettability is mainly due to O on PP.



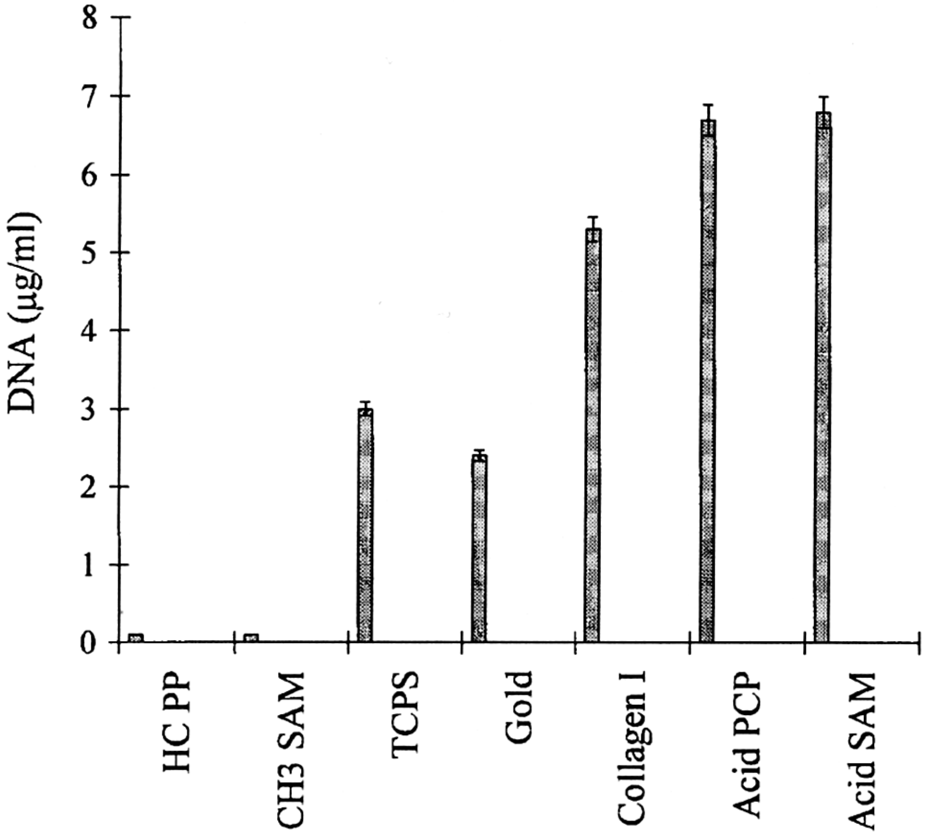
- Model PP, Humid-air



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

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*.**

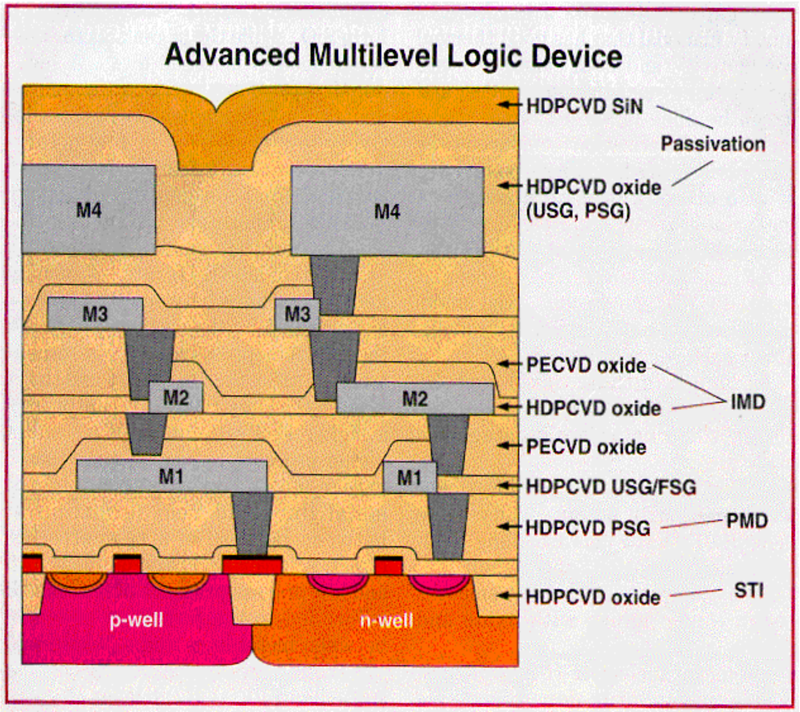


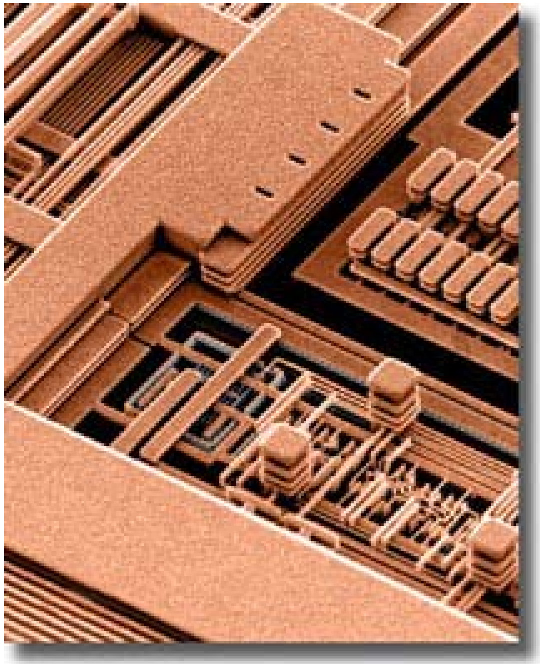
- **Keratinocyte cells adhere to hydrocarbon polymers containing carboxylic acid groups (PCP, SAM).**

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

PLASMAS AND MICROELECTRONICS FABRICATION

- The striking improvement in the functionality of microelectronics devices results from shrinking of individual components and increasing complexity of the circuitry





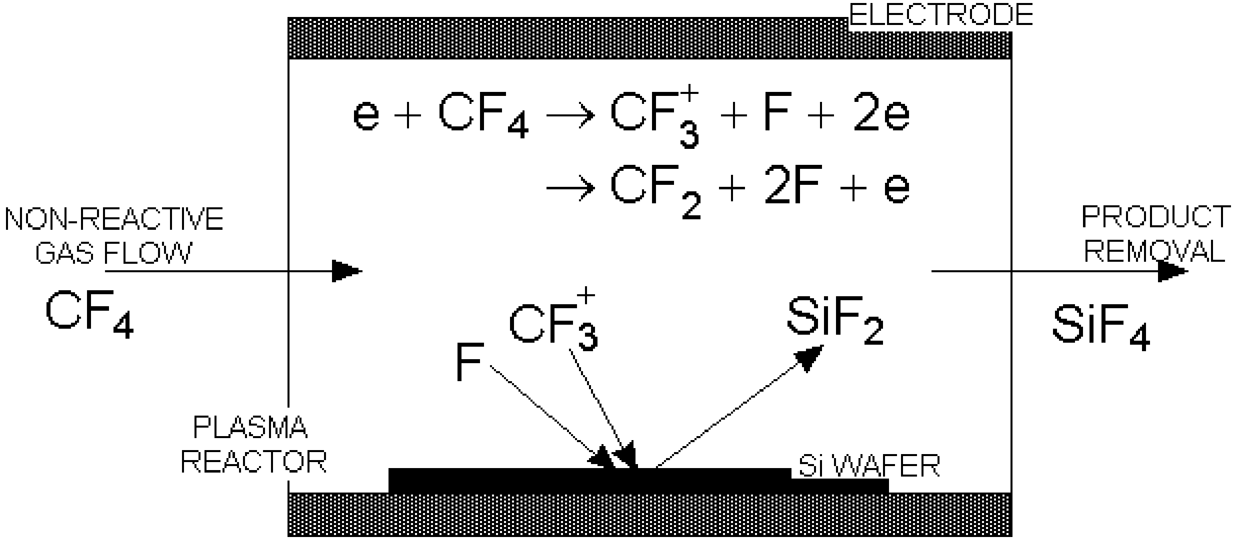
Ref: IBM Microelectronics

- Plasmas are absolutely essential to the fabrication of microelectronics.

PLASMAS IN MICROELECTRONICS FABRICATION

- **Plasmas play a dual role in microelectronics fabrication.**

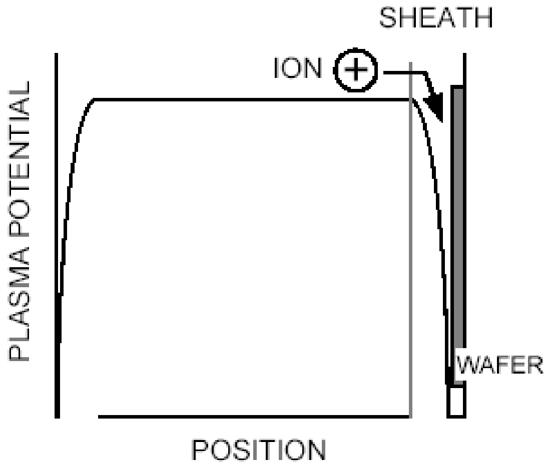
- **First, electron impact on otherwise unreactive gases produces neutral radicals and ions.**

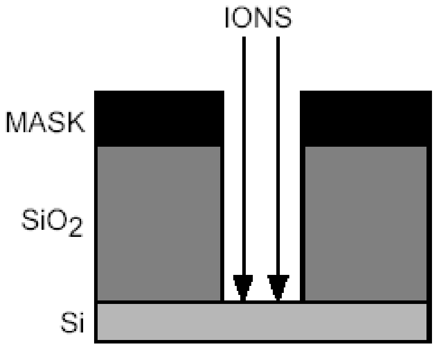


- **These species then drift or diffuse to surfaces where they add, remove or modify materials.**

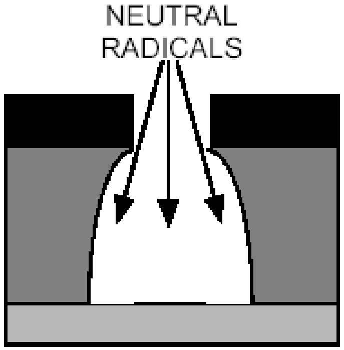
PLASMAS IN MICROELECTRONICS FABRICATION

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

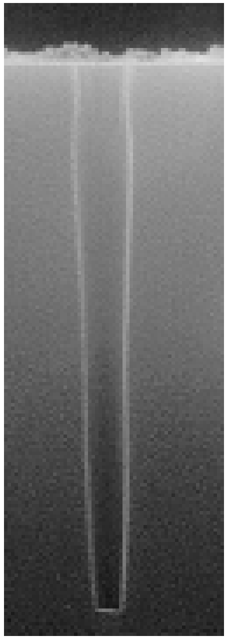




- Ion Assisted Etching

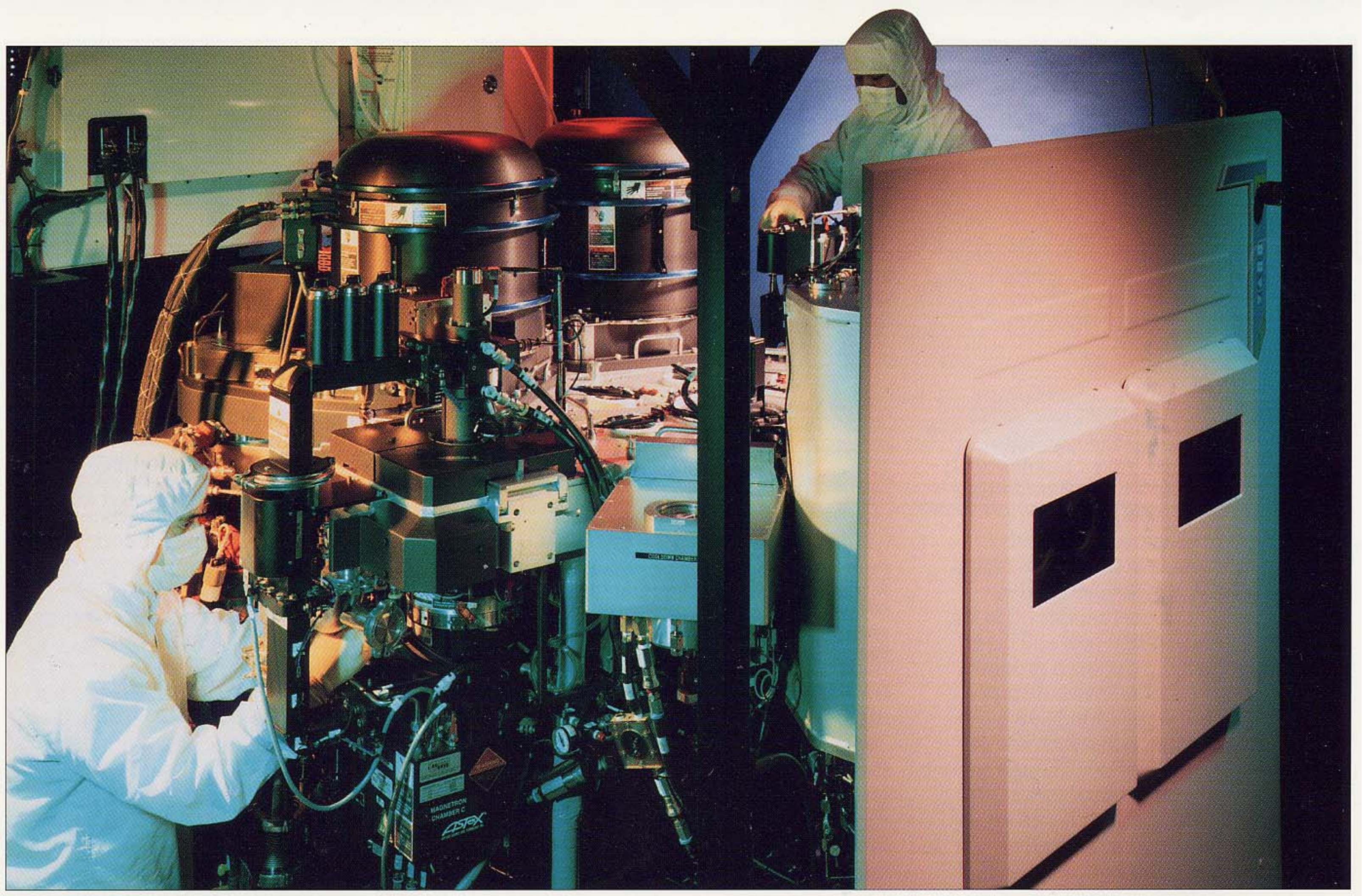


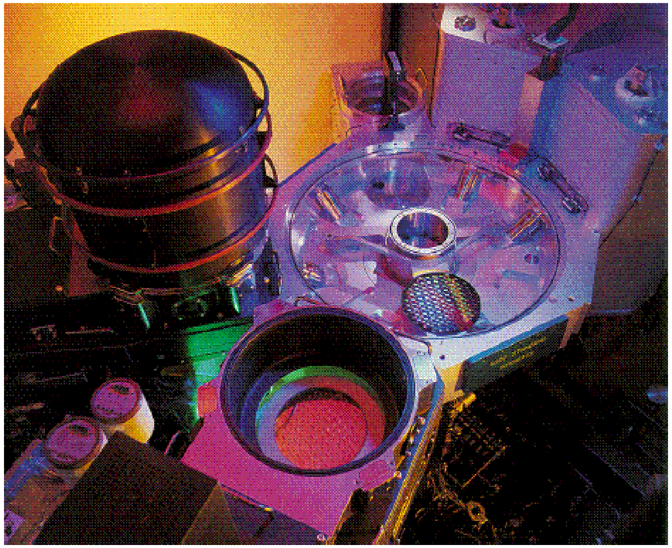
- Neutral Dominated Etching



- **0.25 μm Feature (C. Cui, AMAT)**

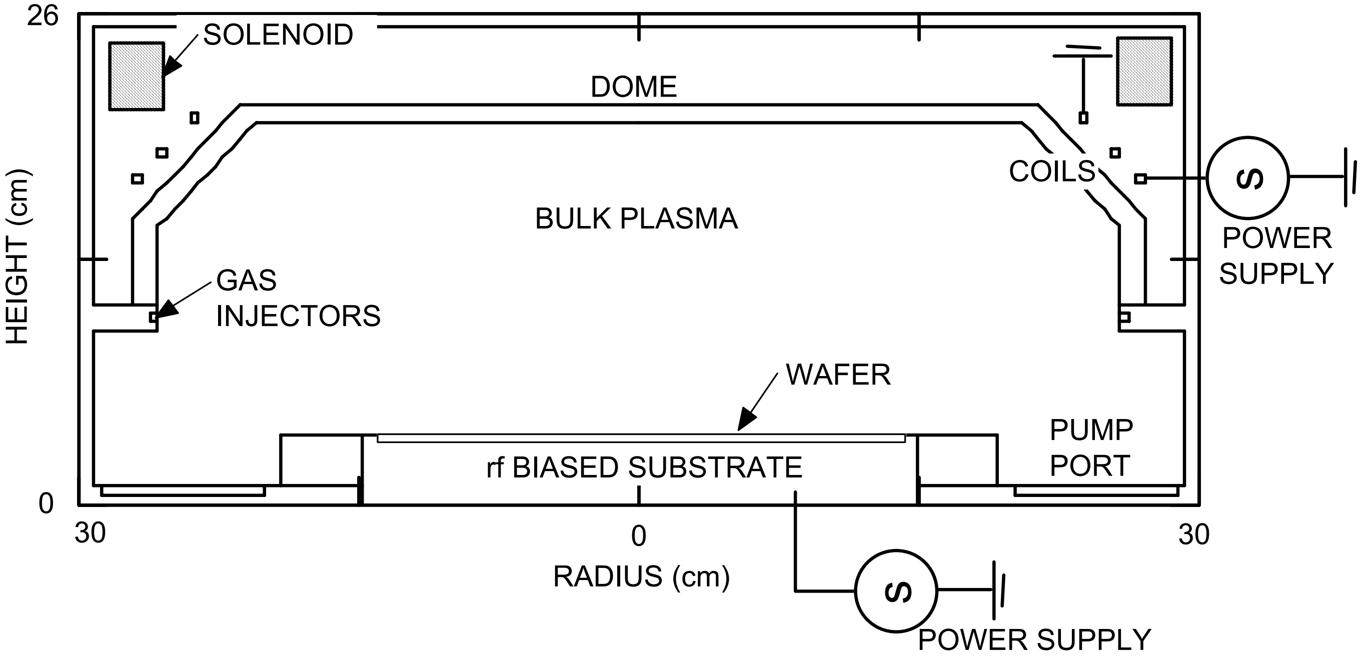
APPLIED MATERIALS DECOUPLED PLASMA SOURCES (DPS)





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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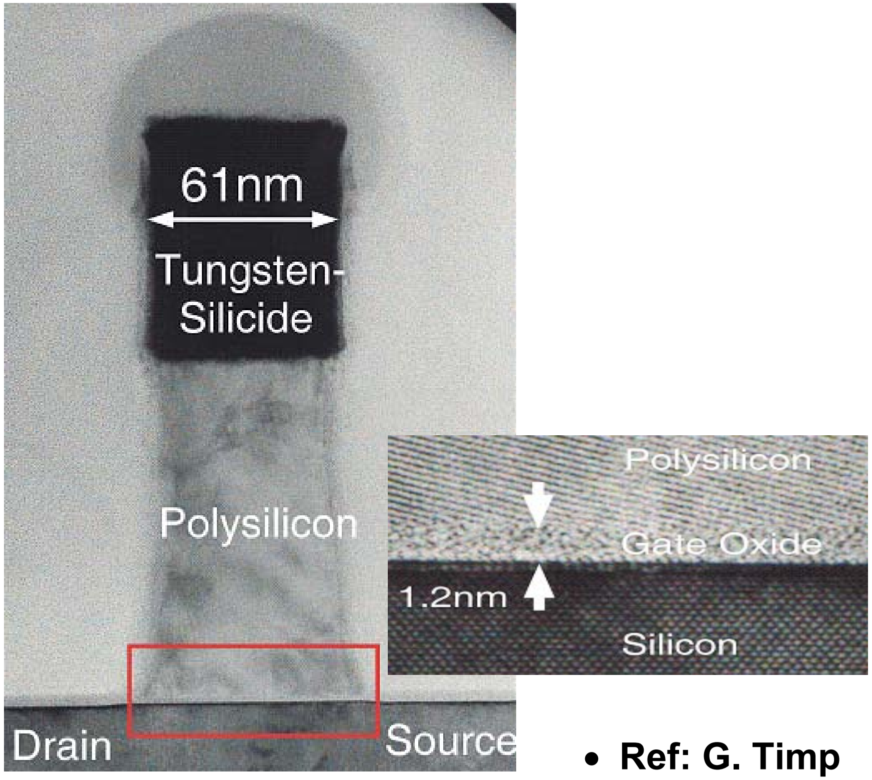
SELECTIVITY IN MICROELECTRONICS FABRICATION: PLASMAS AND POLYMERS

- 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.

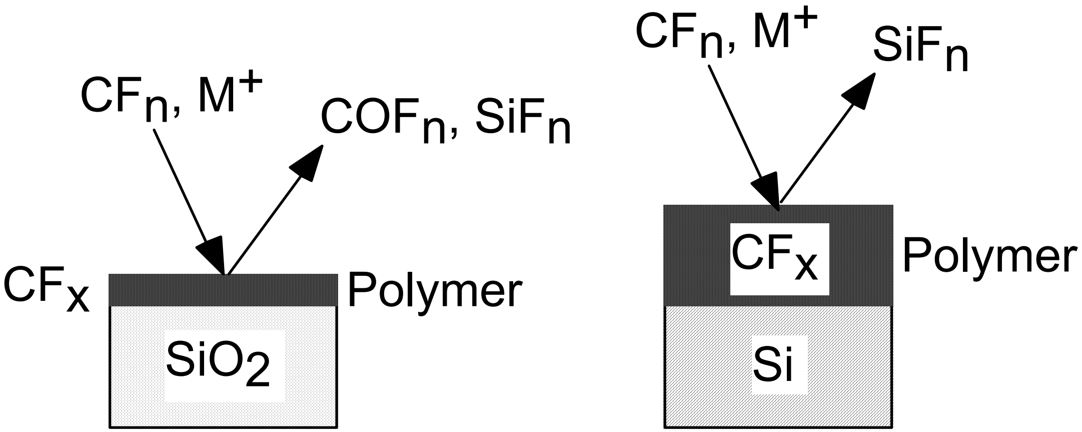


- Ref: G. Timp

FLUORCARBON PLASMA ETCHING: SELECTIVITY

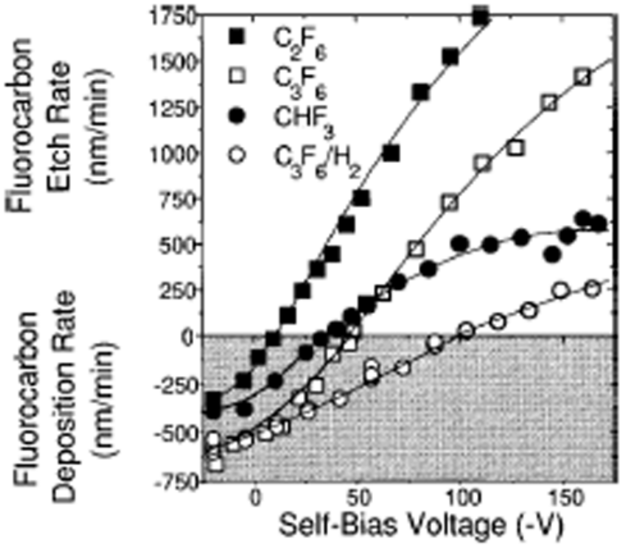
- **Selectivity in fluorocarbon etching relies on polymer deposition.**
- **Electron impact dissociation of feedstock fluorocarbons produce polymerizing radicals and ions, resulting in polymer deposition.**

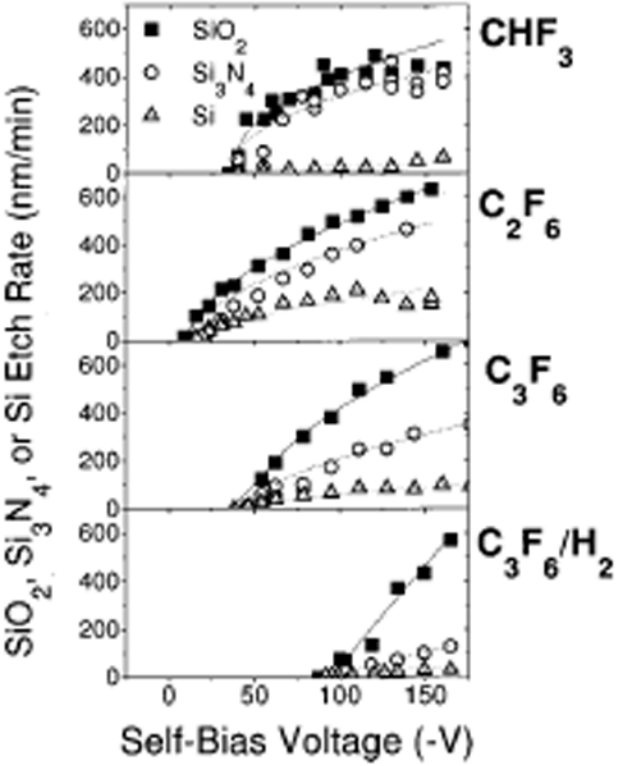
$$e + Ar/C_4F_8 \longrightarrow CF_n, M^+$$

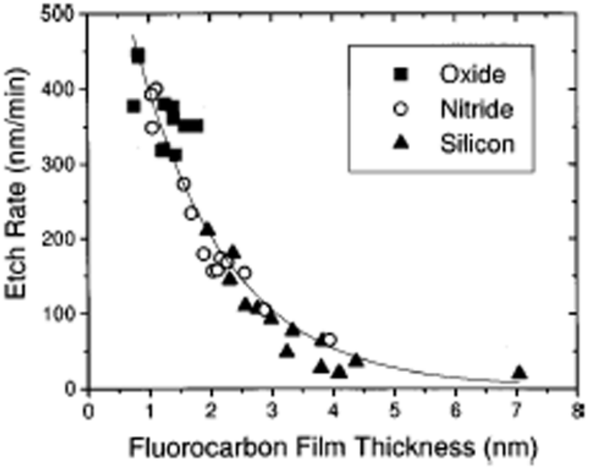


- **Compound dielectrics contain oxidants which consume the polymer, producing thinner polymer layers.**
- **Thicker polymer on non-dielectrics restrict delivery of ion energy (lower etching rates).**

FLUORCARBON PLASMA ETCHING: SELECTIVITY







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

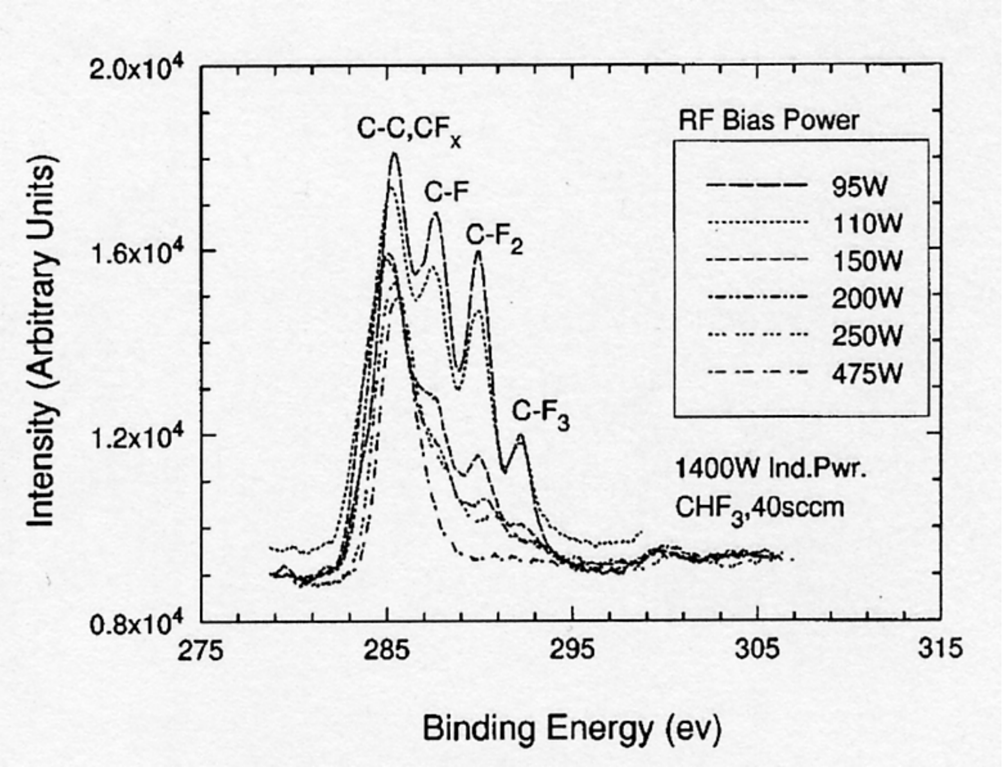
- **Etch Rate (SiO_2 > Si)**

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

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

FLUORCARBON PLASMA ETCHING: POLYMER

- The polymer composition deposited in fluorocarbon plasmas depends on feedstock, pressure, power, bias power.



- Rueger et al., JVST A 15, 1881 (1997)

- For discussion PTFE (poly)tetrafluoroethylene $[C_2F_4]_n$ is a good approximation for most layers.

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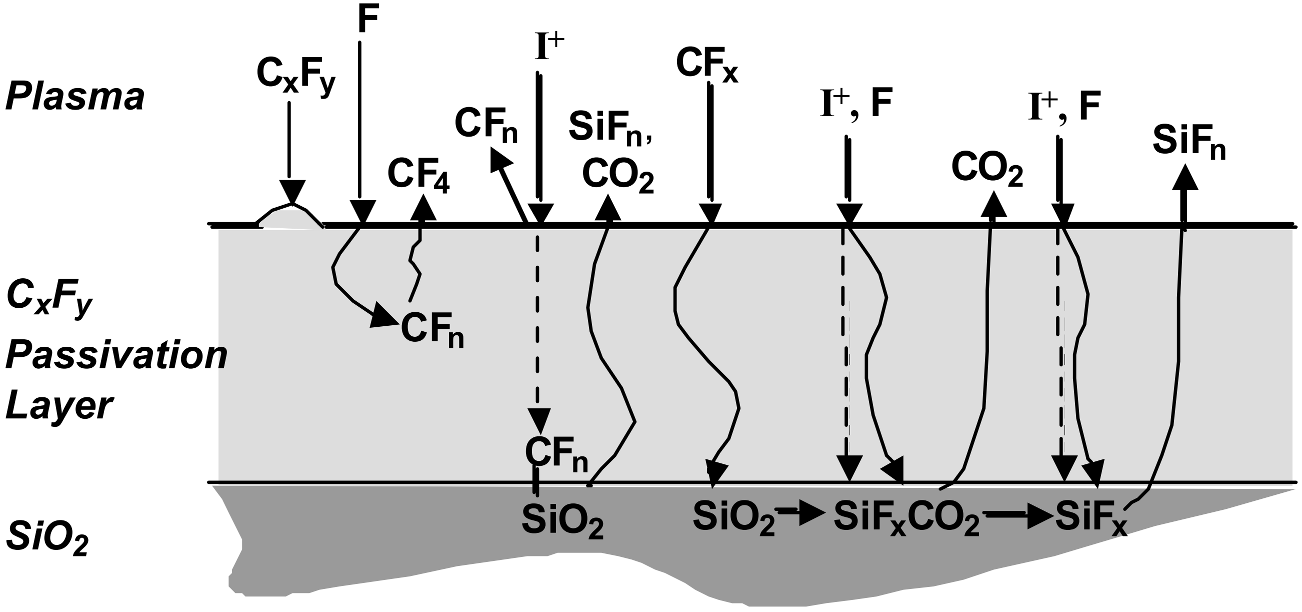
SURFACE KINETICS: FLUOROCARBON PLASMA ETCHING Si/SiO_2

- 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.

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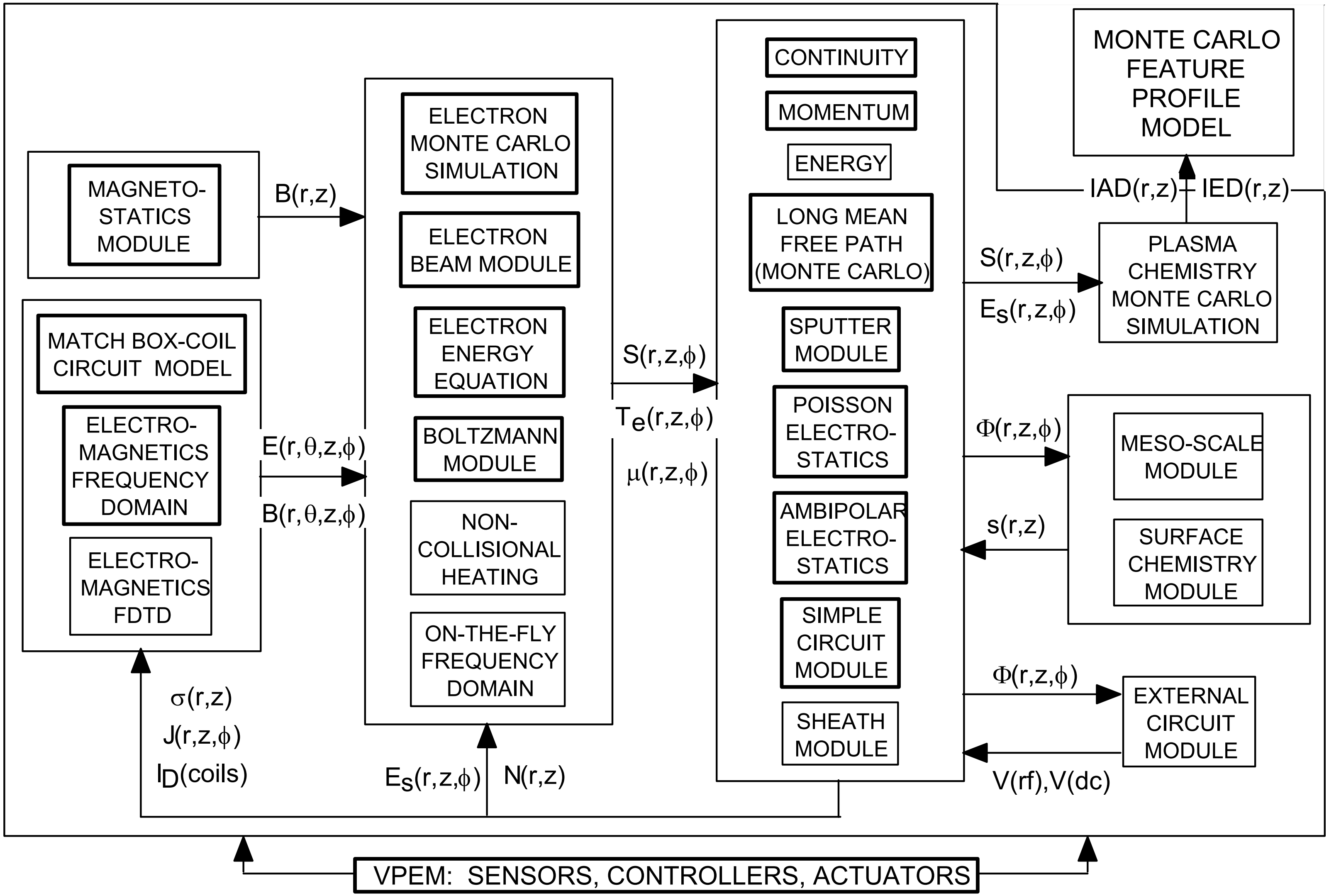
MODELING OF FLUOROCARBON PLASMA ETCHING

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

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

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

HYBRID PLASMA EQUIPMENT MODEL



MAGNETO-STATICS MODULE

MATCH BOX-COIL CIRCUIT MODEL

ELECTRO-MAGNETICS FREQUENCY DOMAIN

ELECTRO-MAGNETICS FDTD

$B(r,z)$

$E(r,\theta,z,\phi)$

$B(r,\theta,z,\phi)$

ELECTRON MONTE CARLO SIMULATION

ELECTRON BEAM MODULE

ELECTRON ENERGY EQUATION

BOLTZMANN MODULE

NON-COLLISIONAL HEATING

ON-THE-FLY FREQUENCY DOMAIN

$S(r,z,\phi)$

$T_e(r,z,\phi)$

$\mu(r,z,\phi)$

CONTINUITY

MOMENTUM

ENERGY

LONG MEAN FREE PATH (MONTE CARLO)

SPUTTER MODULE

POISSON ELECTRO-STATICS

AMBIPOLAR ELECTRO-STATICS

SIMPLE CIRCUIT MODULE

SHEATH MODULE

$\sigma(r,z)$

$J(r,z,\phi)$

I_D(coils)

$E_s(r,z,\phi)$ $N(r,z)$

MONTE CARLO FEATURE PROFILE MODEL

IAD(r,z) IED(r,z)

$S(r,z,\phi)$

$E_s(r,z,\phi)$

PLASMA CHEMISTRY MONTE CARLO SIMULATION

$\Phi(r,z,\phi)$

MESO-SCALE MODULE

$s(r,z)$

SURFACE CHEMISTRY MODULE

$\Phi(r,z,\phi)$

EXTERNAL CIRCUIT MODULE

V(rf),V(dc)

VPEM: SENSORS, CONTROLLERS, ACTUATORS

ELECTROMAGNETICS MODULE

- **The wave equation is solved in the frequency domain using sparse matrix techniques (2D,3D):**

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

$$\vec{E}(\vec{r},t)=\vec{E}'(\vec{r})\exp(-i(\omega t+\varphi(\vec{r})))$$

- **Conductivities are tensor quantities (2D,3D):**

$$\overline{\overline{\sigma}}=\sigma_o\frac{m\nu_m}{q\alpha}\frac{1}{\left(\alpha^2+\left|\vec{B}\right|^2\right)}\begin{pmatrix}\alpha^2+B_r^2 & \alpha B_z+B_rB_\theta & -\alpha B_\theta+B_rB_z\\ -\alpha B_z+B_rB_\theta & \alpha^2+B_\theta^2 & \alpha B_r+B_\theta B_z\\ -\alpha B_\theta+B_rB_z & -\alpha B_r+B_\theta B_z & \alpha^2+B_z^2\end{pmatrix}$$

$$\vec{j}=\overline{\overline{\sigma}}\cdot\vec{E}\qquad\qquad\alpha=\frac{\left(i\omega+\nu_m\right)}{q/m},\quad\sigma_o=\frac{q^2n_e}{m\nu_m}$$

ELECTRON ENERGY TRANSPORT

- **<u>Continuum (2D,3D):</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

- **Power deposition has contributions from wave and electrostatic heating.**

- **<u>Kinetic (2D,3D)</u>: A Monte Carlo Simulation is used to derive $f\left(\varepsilon,\vec{r},t\right)$ including electron-electron collisions using electromagnetic fields from the EMM and electrostatic fields from the FKM.**

PLASMA CHEMISTRY, TRANSPORT AND ELECTROSTATICS

- **Continuity, momentum and energy equations are solved for each species (with jump conditions at boundaries) (2D,3D).**

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

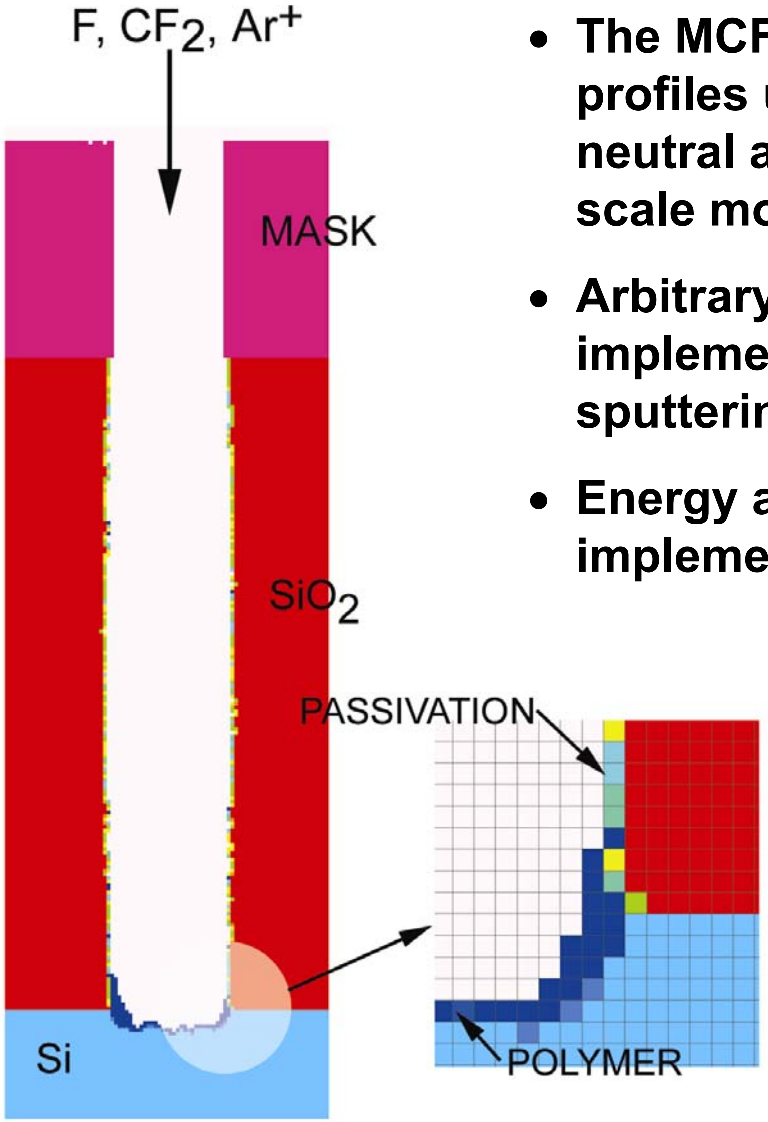
$$\frac{\partial\left(N_i \vec{v}_i\right)}{\partial t} = \frac{1}{m_i} \nabla\left(k N_i T_i\right) - \nabla \cdot \left(N_i \vec{v}_i \vec{v}_i\right) + \frac{q_i N_i}{m_i}\left(\vec{E} + \vec{v}_i \times \vec{B}\right) - \nabla \cdot \overline{\mu}_i - \sum_j \frac{m_j}{m_i + m_j} N_i N_j \left(\vec{v}_i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

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

- **Implicit solution of Poisson's equation (2D,3D):**

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

MONTE CARLO FEATURE PROFILE MODEL (MCFPM)



- **The MCFPM predicts time and spatially dependent profiles using energy and angularly resolved neutral and ion fluxes obtained from equipment scale models.**
- **Arbitrary chemical reaction mechanisms may be implemented, including thermal and ion assisted, sputtering, deposition and surface diffusion.**
- **Energy and angular dependent processes are implemented using parametric forms.**
- **Mesh centered identify of materials allows “burial”, overlayers and transmission of energy through materials.**

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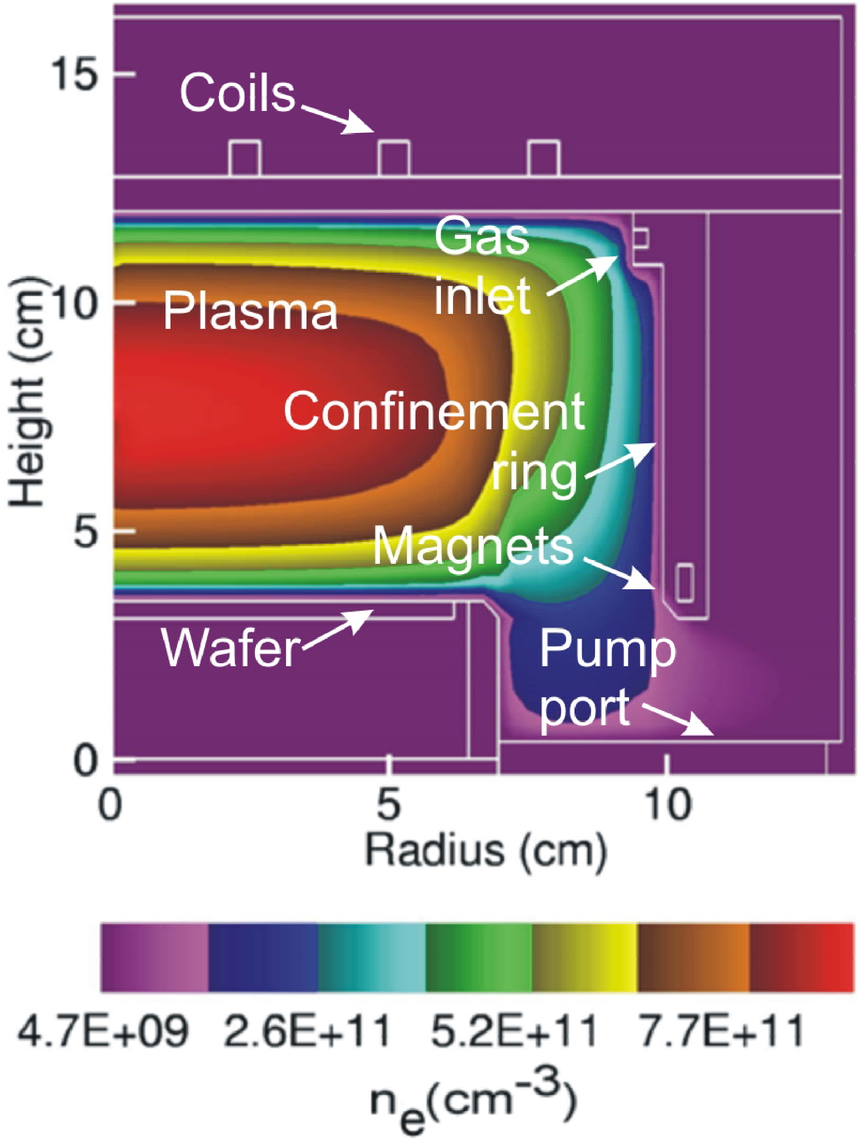
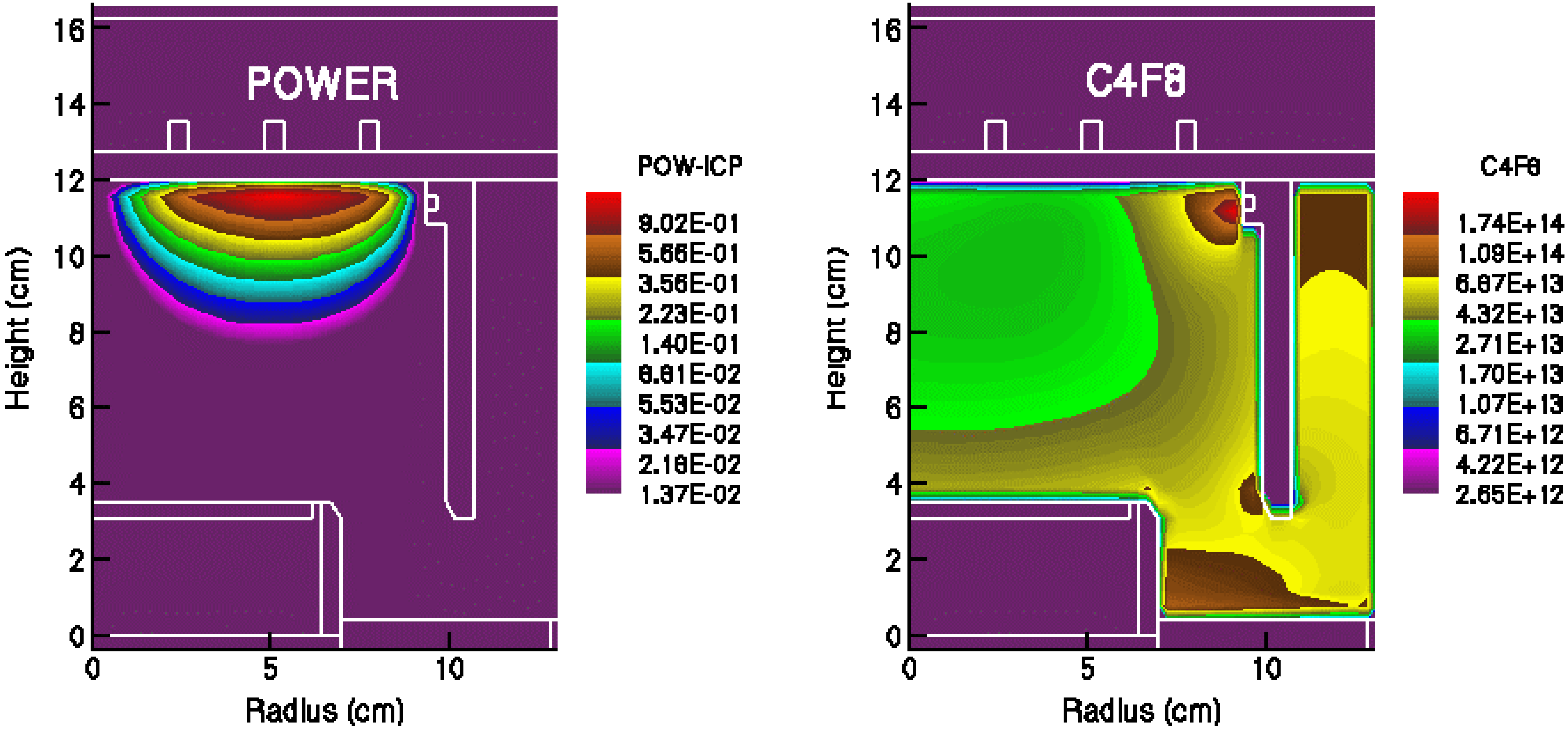
TYPICAL ICP CONDITIONS: [e] FOR C_4F_8, 10 mTORR



- An ICP reactor patterned after Oeherlein, et al. was used for validation.
- Reactor uses 3-turn coil (13.56 MHz) with rf biased substrate (3 MHz)
- Electron densities are 10^{11}-10^{12} cm^{-3} for 1.4 kW.

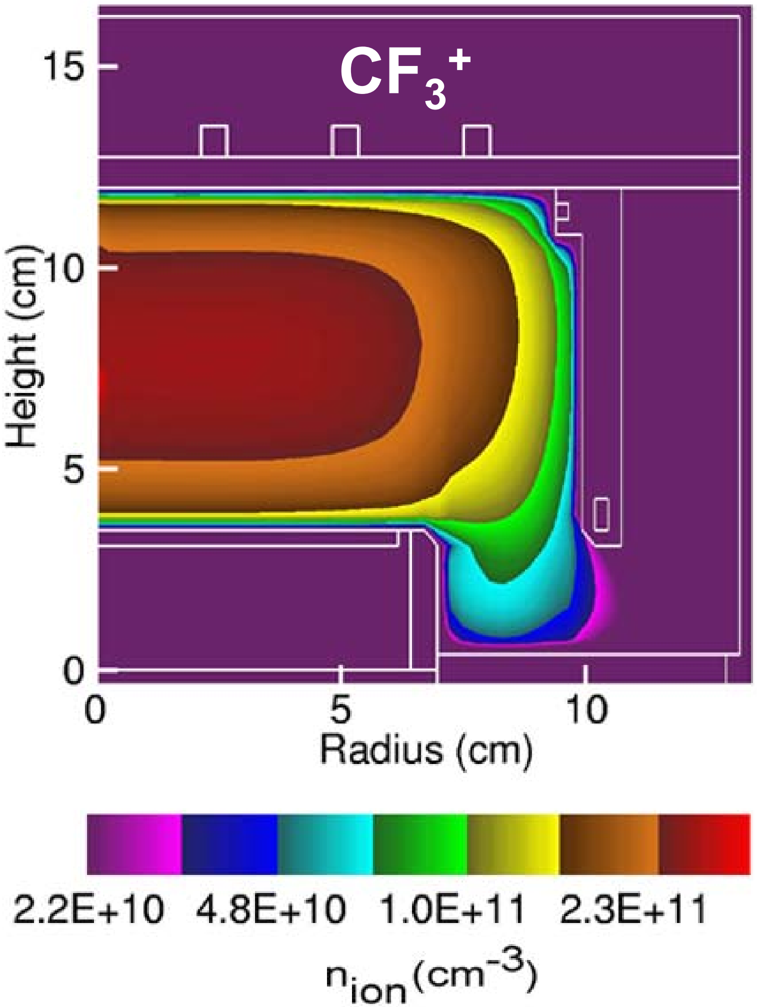
POWER, C_4F_8 DENSITY



- **Large power deposition typically results in near total dissociation of feedstock gases.**

- **C_4F_8, 10 mTorr, 1.4 kW, 13.56 MHz**

MAJOR POSITIVE IONS



- CF_3^+, CF_2^+, and CF^+ are dominant ions due to dissociation of C_4F_8.

- C_4F_8, 10 mTorr, 1.4 kW, 13.56 MHz

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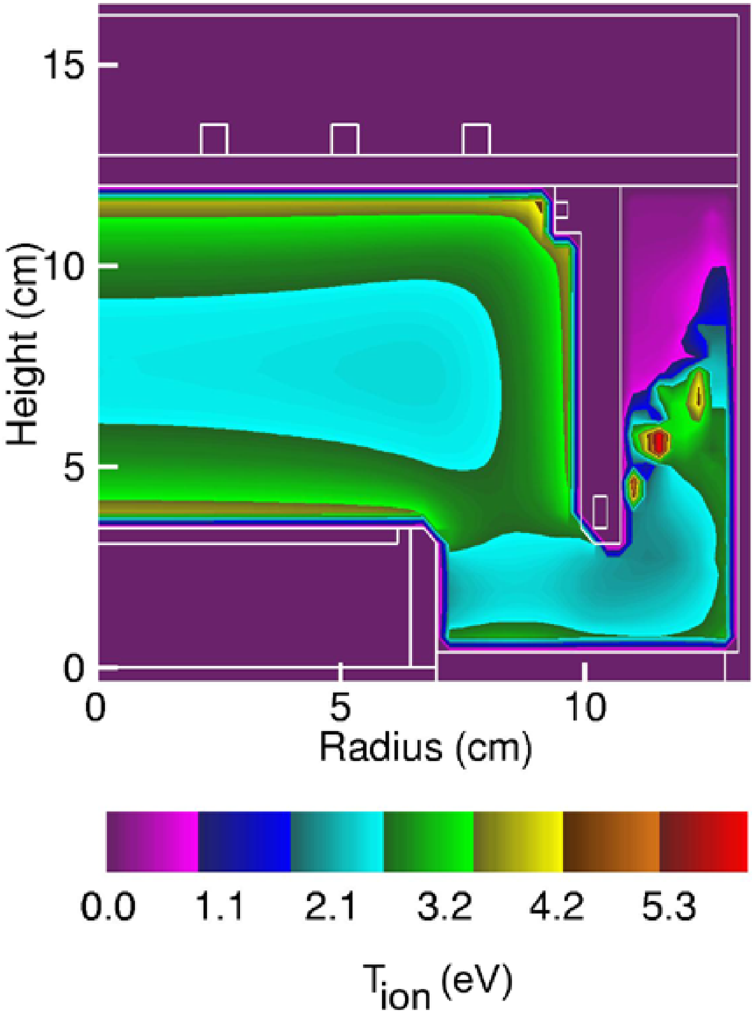
CF_3^+ TEMPERATURE

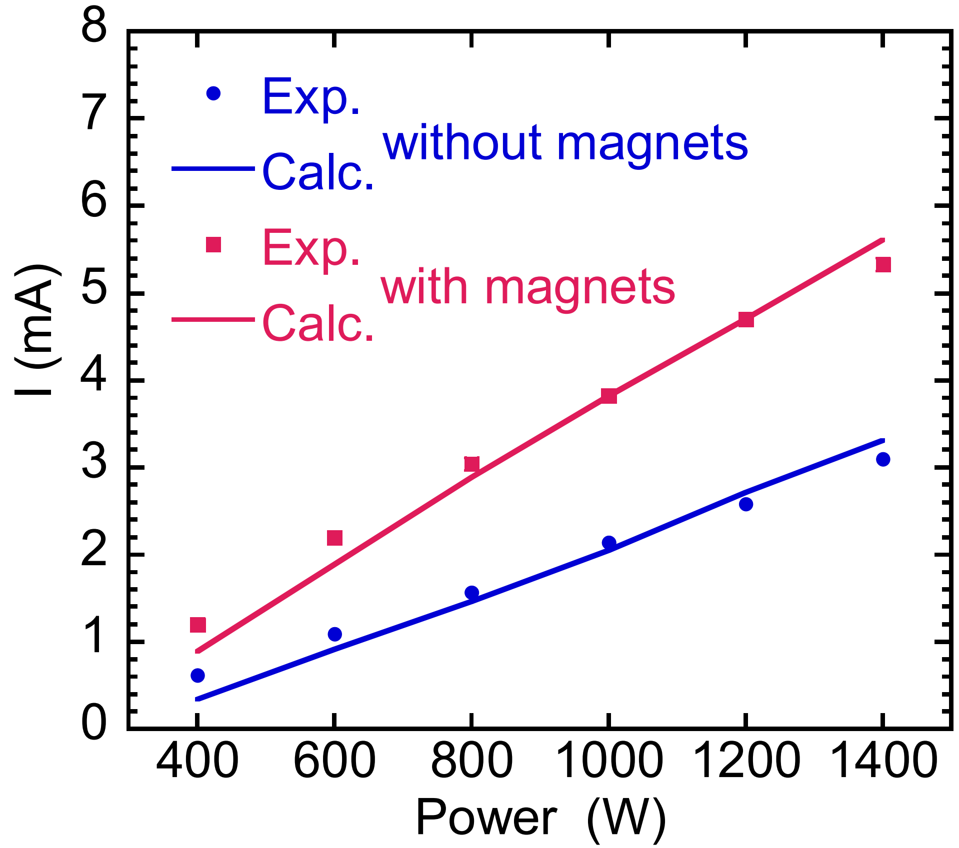


- **The ion temperature is peaked near the walls where ions gain energy during acceleration in the presheath.**

- **C_4F_8, 10 mTorr, 1.4 kW, 13.56 MHz**

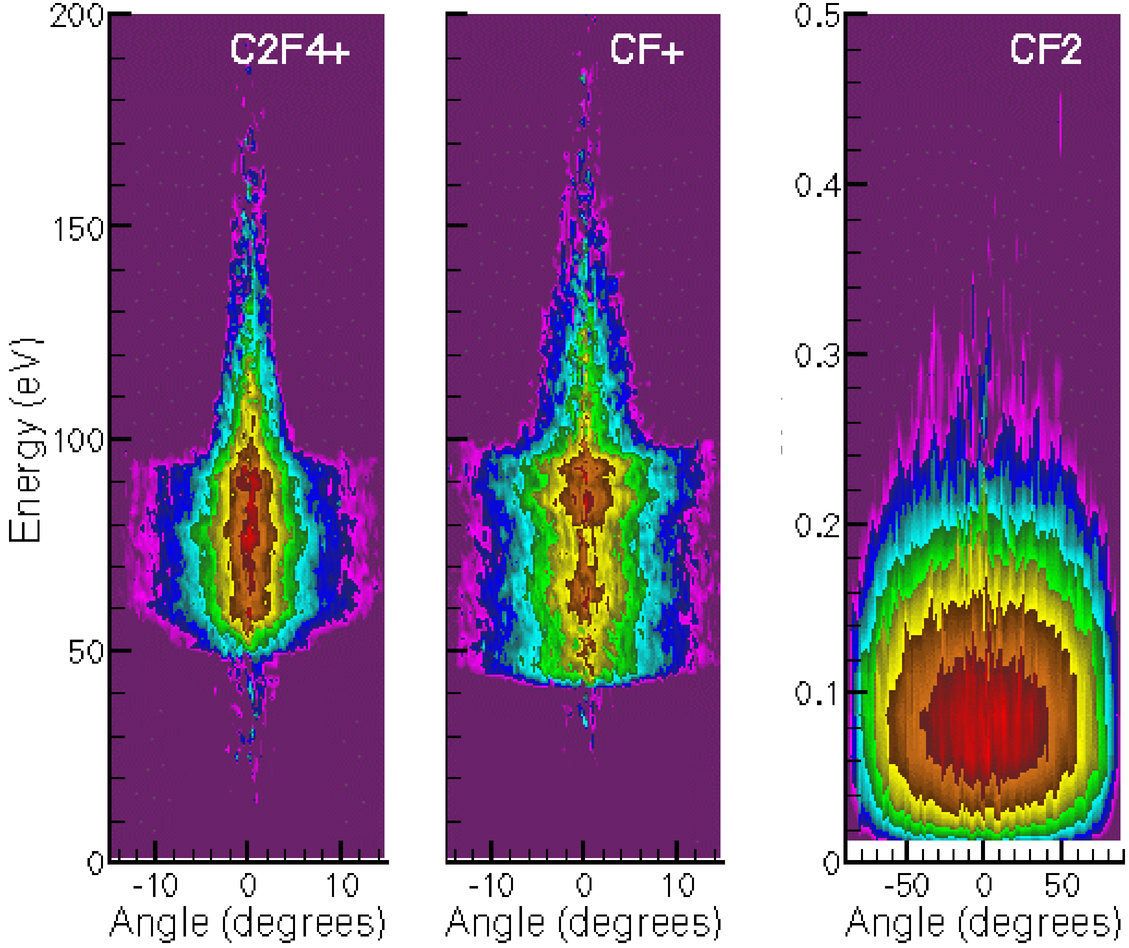
I_P VERSUS ICP POWER for C_4F_8

- **Extensive validation of the plasma models are performed with available data for densities, temperatures and fluxes.**
- **Ion saturation current derived from the model are compared to experiments: Ion densities are larger with moderate static magnetic fields.**



- **C_4F_8, 10 mTorr, 13.56 MHz, 100 V probe bias**
- **Experiments: G. Oehrlein, Private Comm.**

ION/NEUTRAL ENERGY/ANGULAR DISTRIBUTIONS



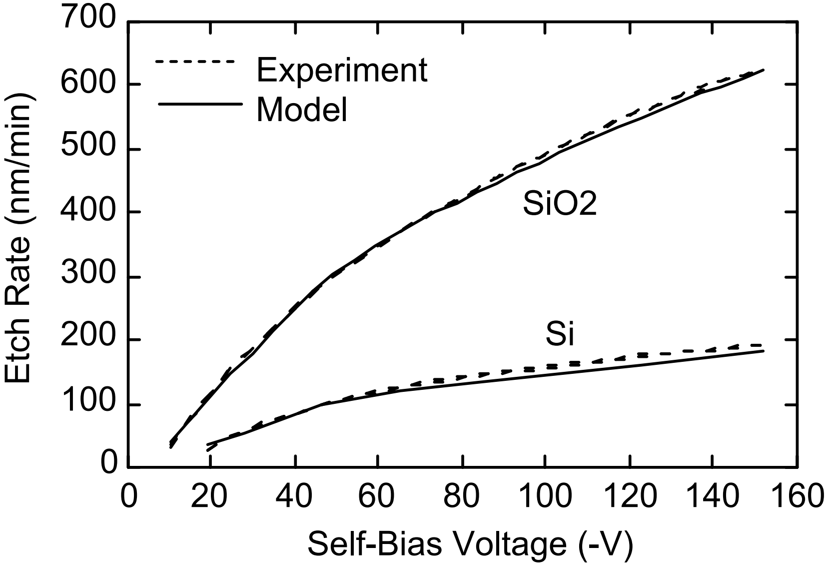
- **The end products of reactor scale modeling are energy and ion angular distributions to the surface.**
- **In complex gas mixtures the IEADs can significantly vary from species to species.**

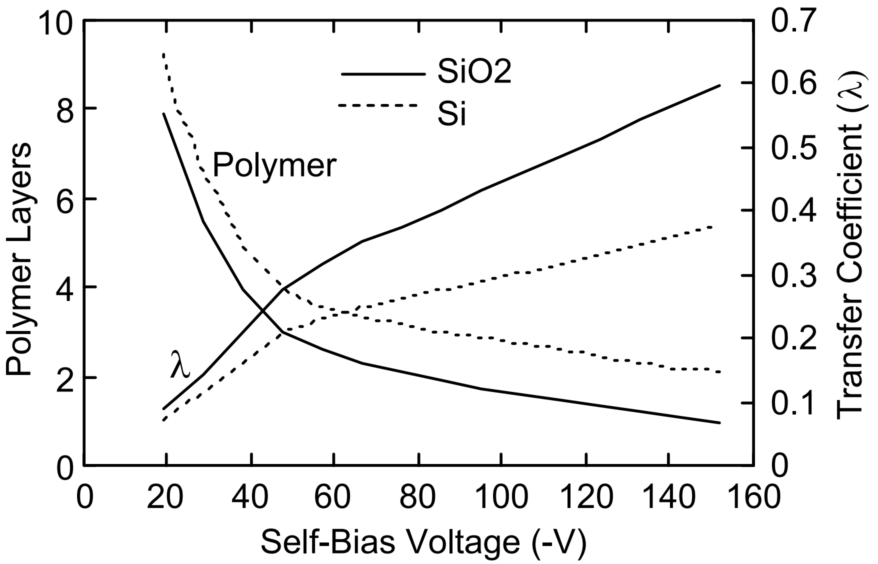
- **Ar/C_4F_8, 40 mTorr, 10b MHz, MERIE**

ADVMET_1002_28

ETCH RATES AND POLYMER THICKNESS

- **Etch rates for Si and SiO_2 increase with increasing bias due, in part, to a decrease in polymer thickness.**
- **The polymer is thinner with SiO_2 due to its consumption during etching, allowing for more efficient energy transfer through the layer and more rapid etching.**

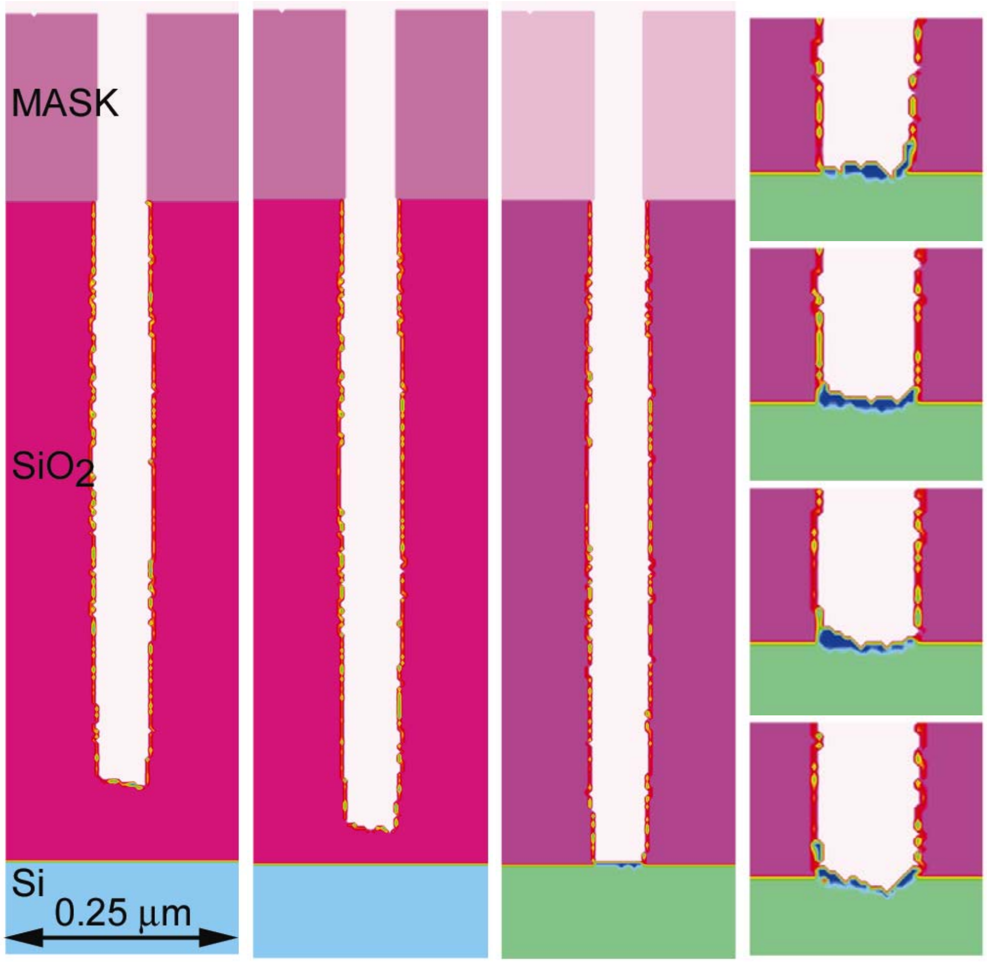


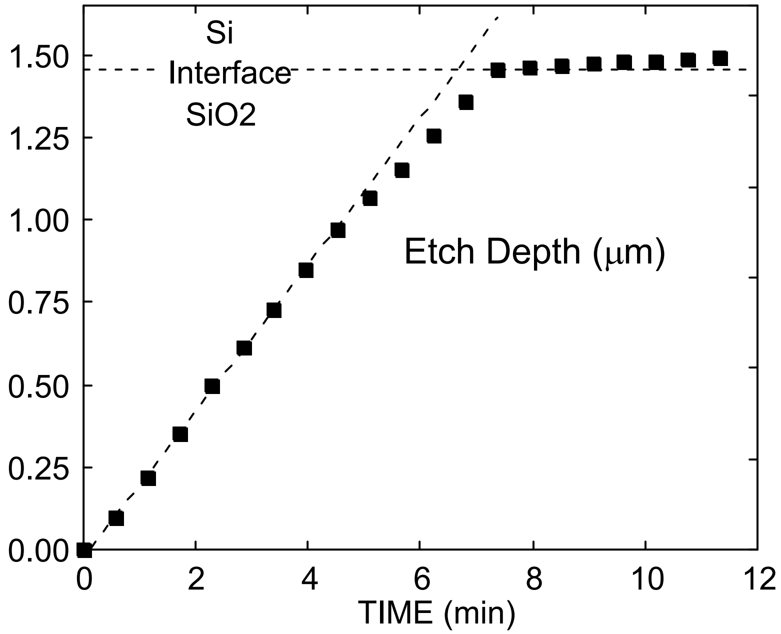


- **C_2F_6, 6 mTorr, 1400 W ICP, 40 sccm**
- **Exp. Ref: T. Standaert, et al.
  J. Vac. Sci. Technol. A 16, 239 (1998).**

POLYMERIZATION AIDS SELECTIVITY

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





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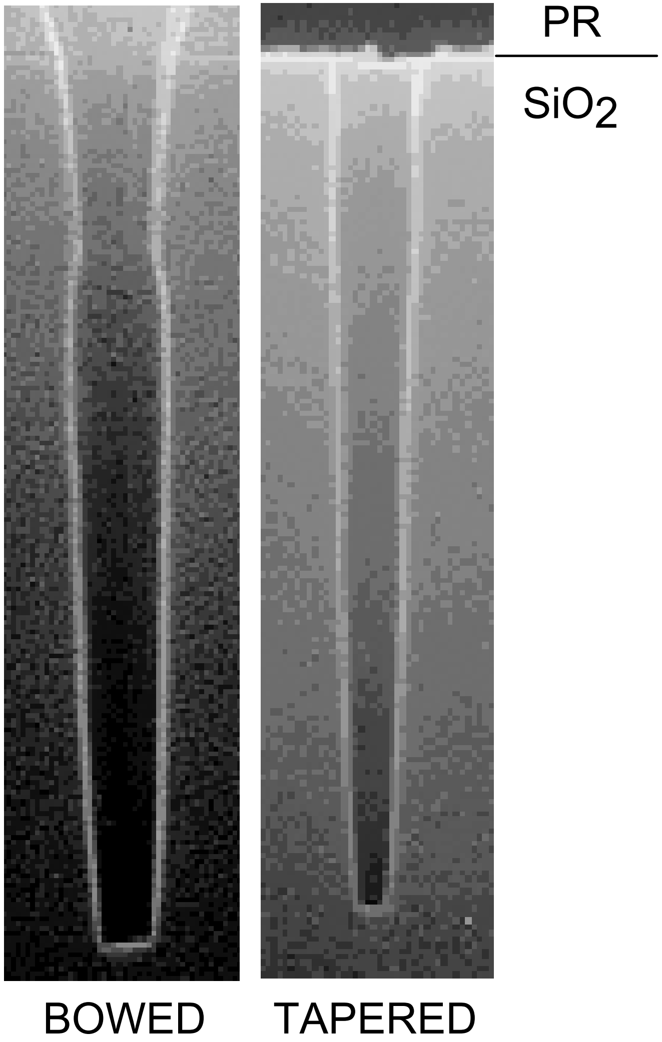
TAPERED AND BOWED PROFILES

- **In high aspect ratio (HAR) etching of SiO_2 the sidewall of trenches are passivated by neutrals (CF_x, $x \leq 2$) due to the broad angular distributions of neutral fluxes.**

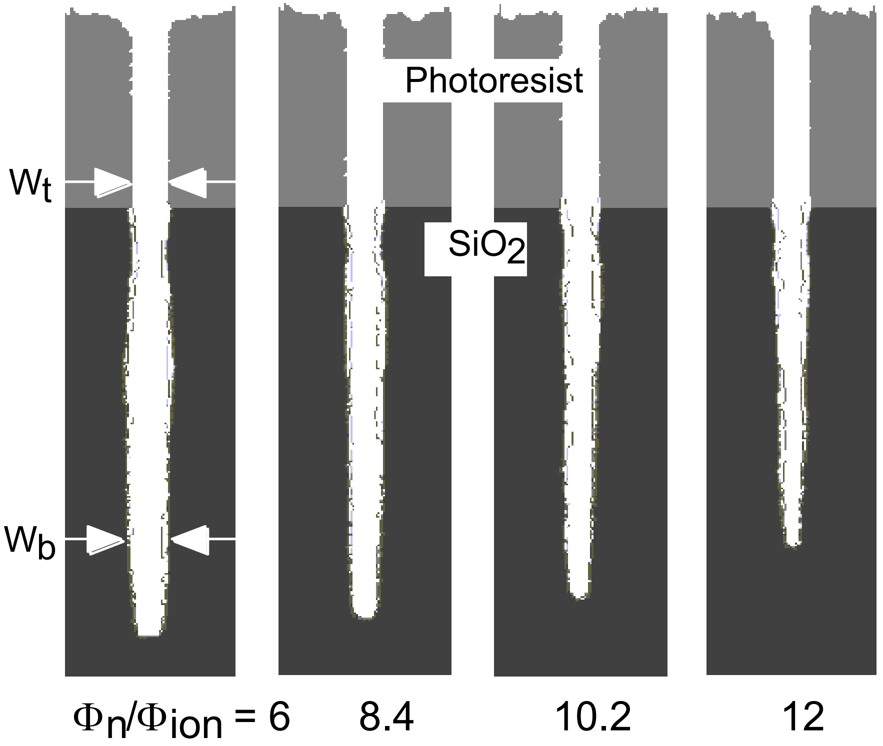
- **Either tapered or bowed profiles can result from a non-optimum combination of processing parameters including:**

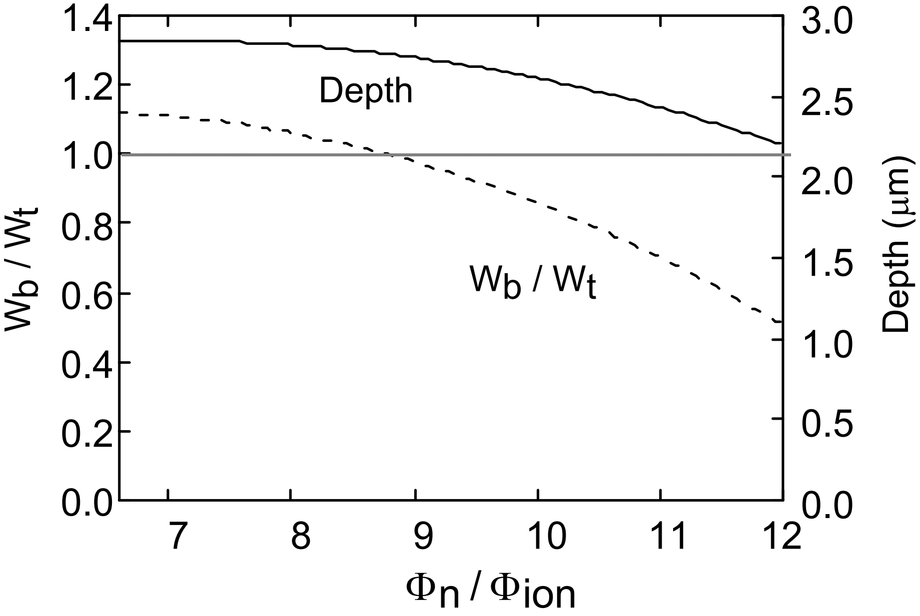
    - **Degree of passivation**
    - **Ion energy distribution**
    - **Radical/ion flux composition.**



PROFILE TOPOLOGY: NEUTRAL TO ION FLUX RATIO

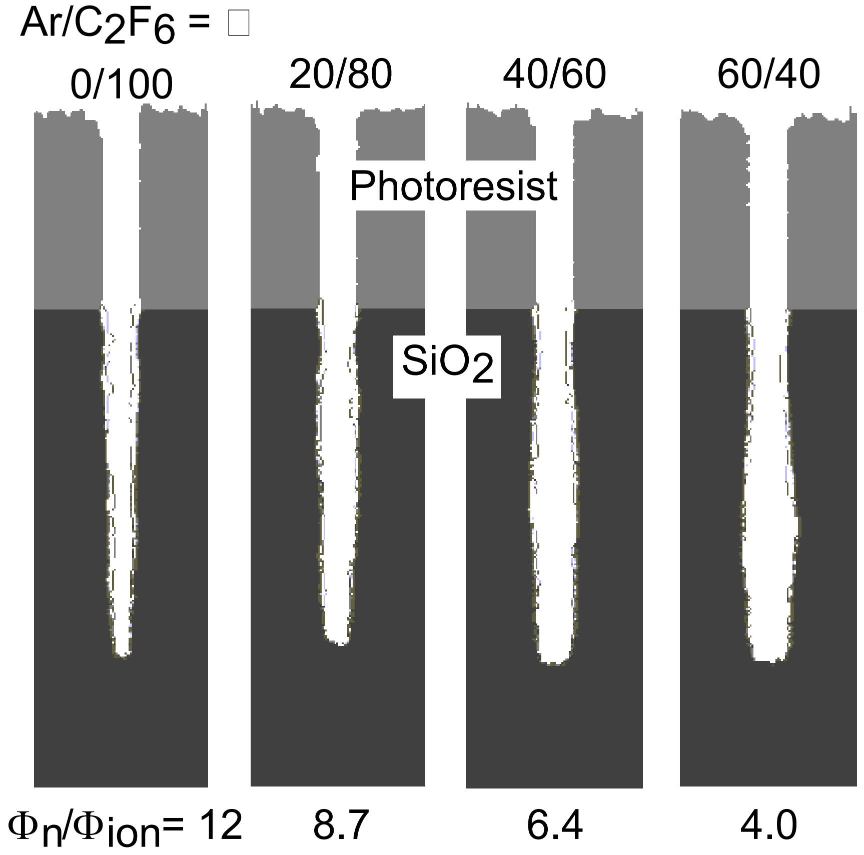
- **The etch profile is sensitive to the ratio of polymer forming fluxes to energy activating fluxes. Small ratios result in bowing, large ratios tapering.**

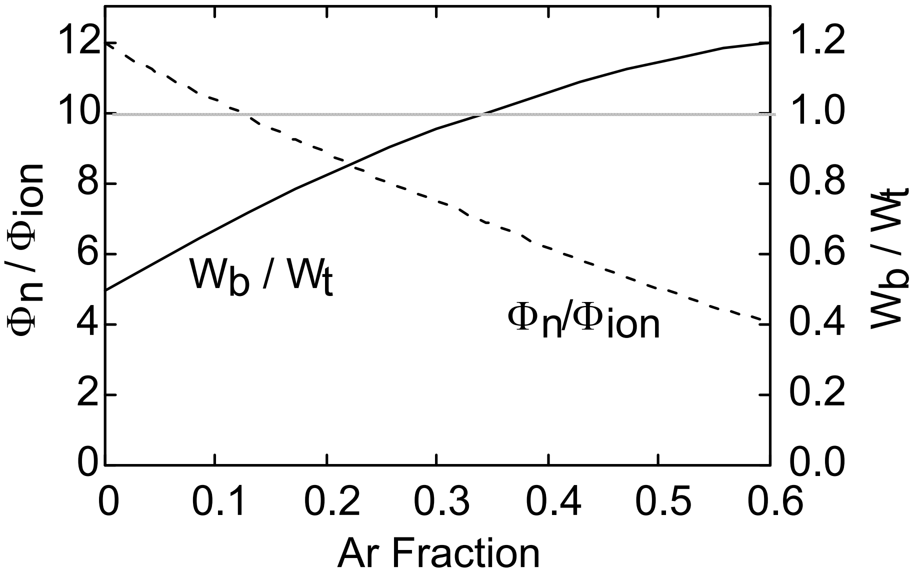




PROFILE TOPOLOGY: ENGINEERING SOLUTIONS

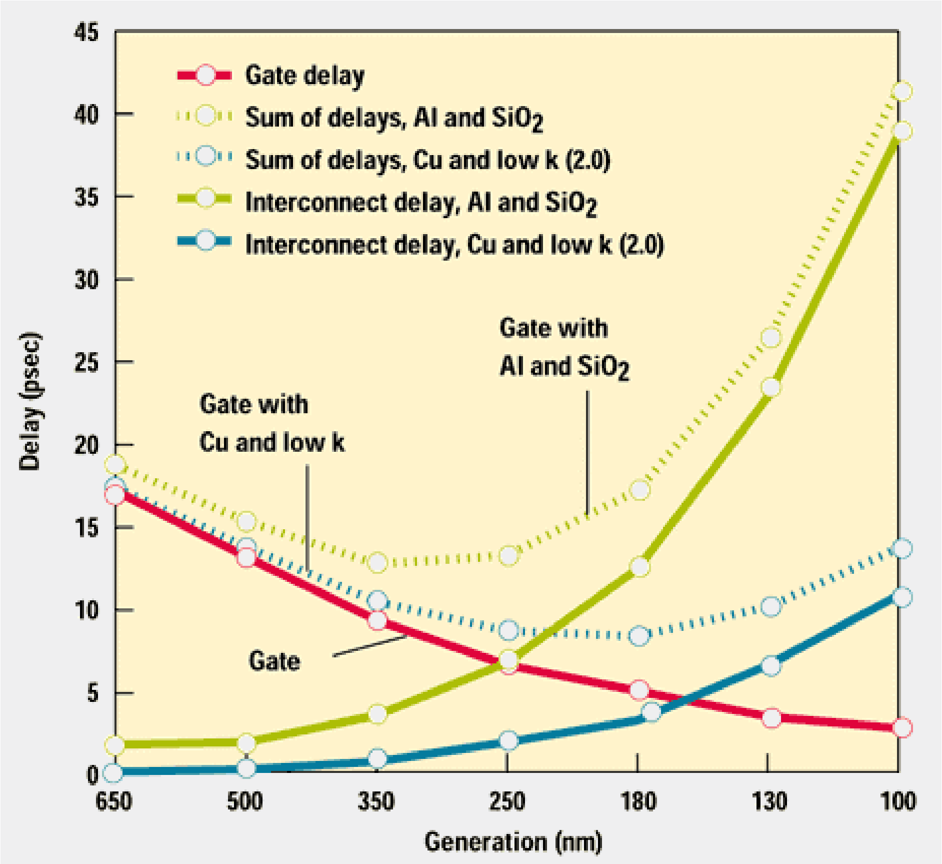
- **Knowledge of the fundamental scaling parameter for controlling sidewall slop enables engineering solutions and real-time-control options.**
- **Example: Ar/C_2F_6 ratio controls polymerizing/ion flux ratio, and hence profile topology.**





LOW-K DIELECTRICS

- As feature sizes decrease and device count increases, the diameter of interconnect wires shrinks and path length increases.



- Large RC-delay limits processor performance.
- To reduce RC-delay, low dielectric constant (low-k) materials are being investigated.

- L. Peters, *Semi. Intl.*, 9/1/1998

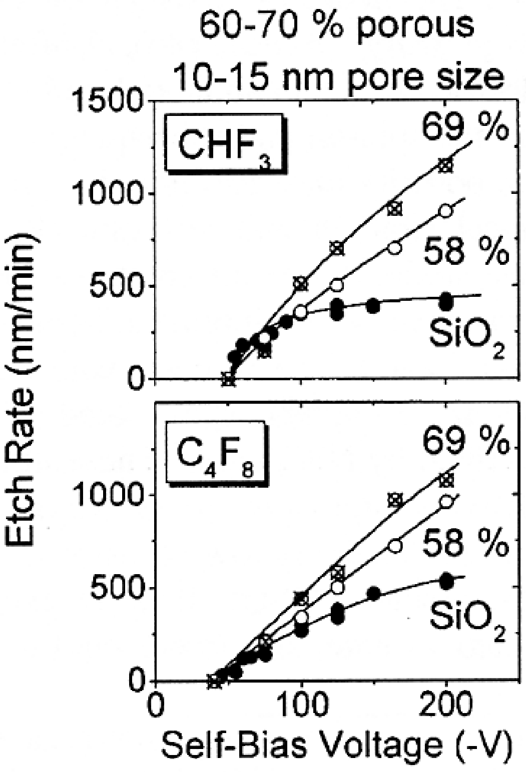
POROUS SILICON DIOXIDE

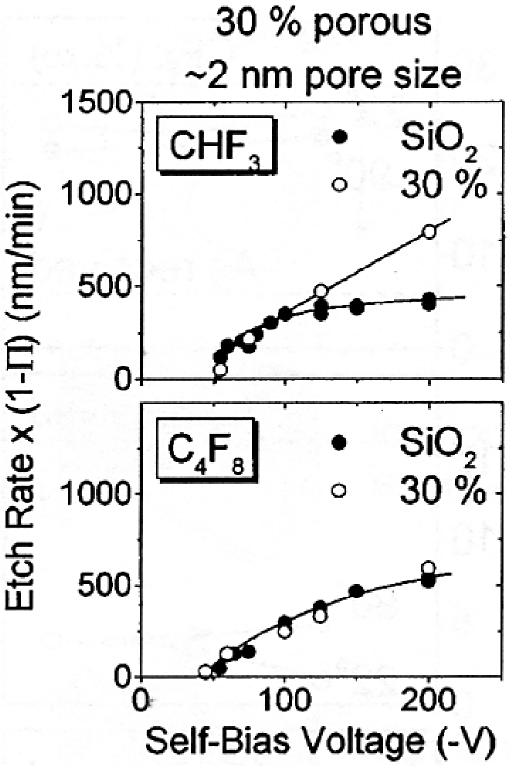
- Porous SiO_2 (xerogels) have low-k properties due to their lower mass density resulting from (vacuum) pores.
  - Typical porosities: 30-70%
  - Typical pore sizes: 2-20 nm

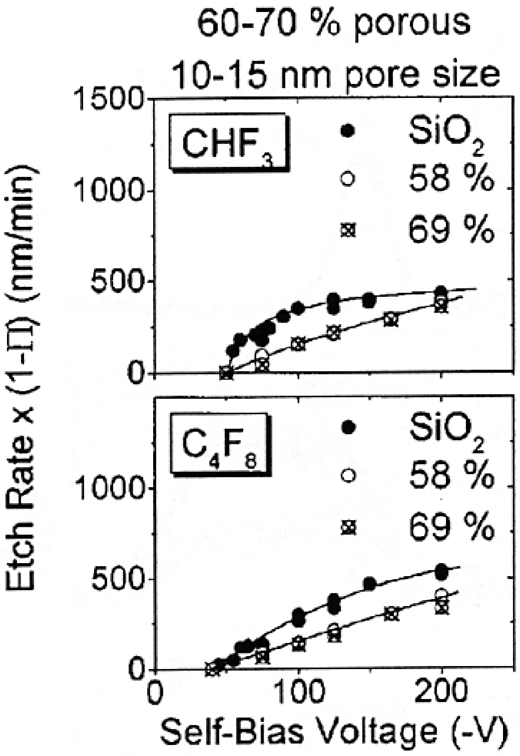
- Porous SiO_2 (P-SiO_2) is, from a process development viewpoint, an ideal low-k dielectric.
  - Extensive knowledge base for fluorocarbon etching of conventional non-porous (NP-SiO_2).
  - No new materials (though most P-SiO_2 contains some residual organics)
  - Few new integration requirements

ETCHING OF P-SiO_2: GENERAL TRENDS

- **Etching of Porous SiO_2 typically proceeds at a higher rate than NP-SiO_2 for the same conditions due to the lower mass density.**





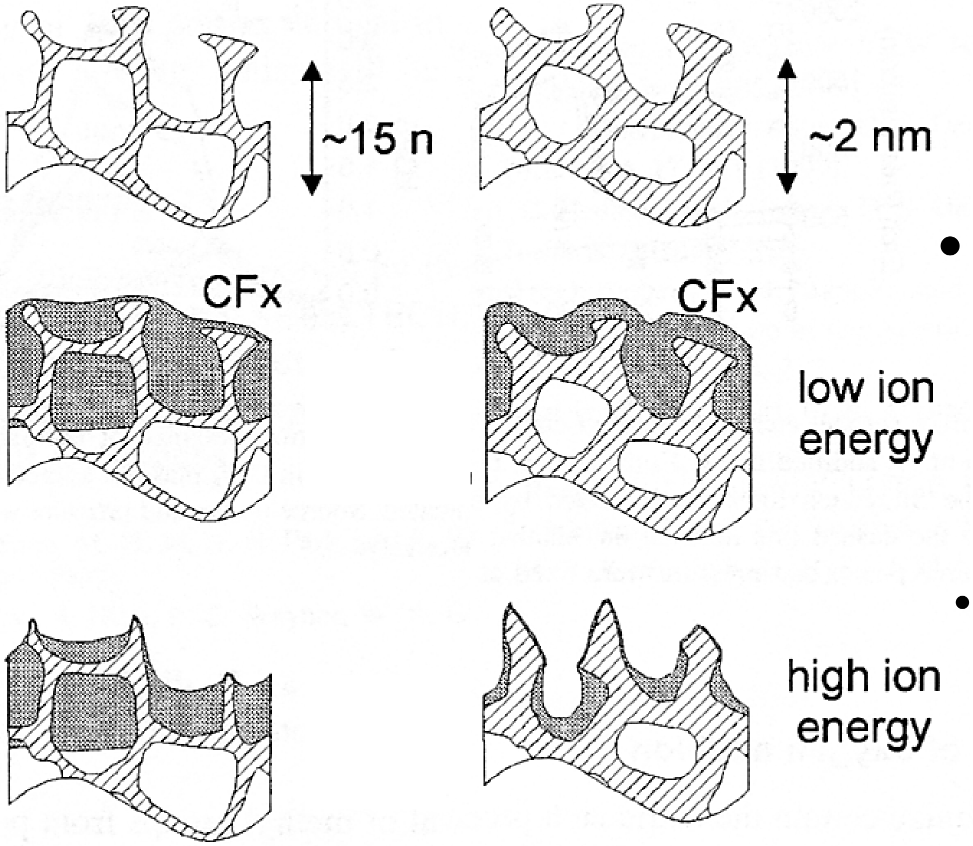


- **When correcting for mass, etch rates are either larger or smaller than NP- SiO_2, depending on porosity, pore size, polymerization.**

  - **Standaert et al, JVSTA 18, 2742 (2000).**

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)**

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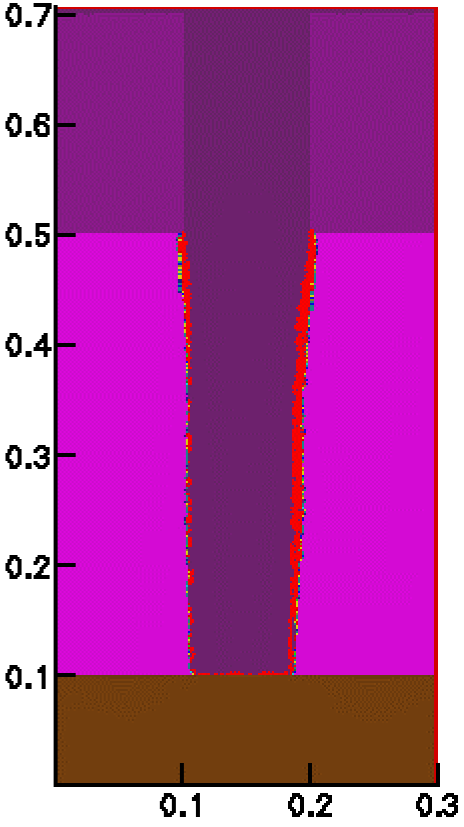
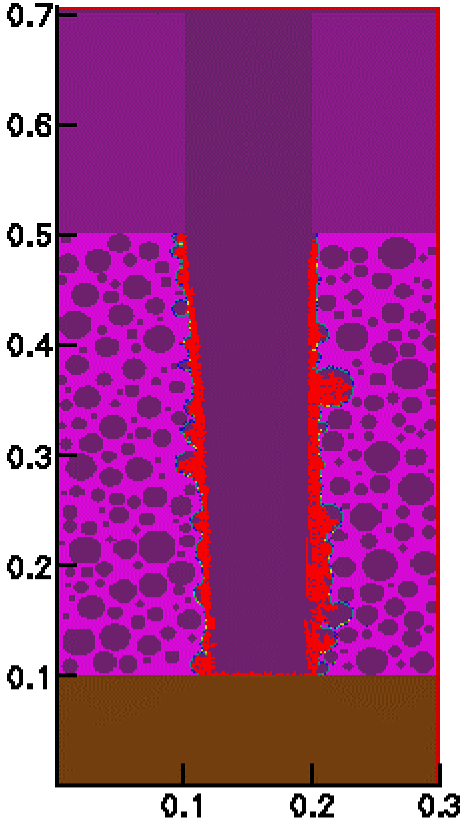
ETCH PROFILES IN SOLID AND POROUS SiO_2



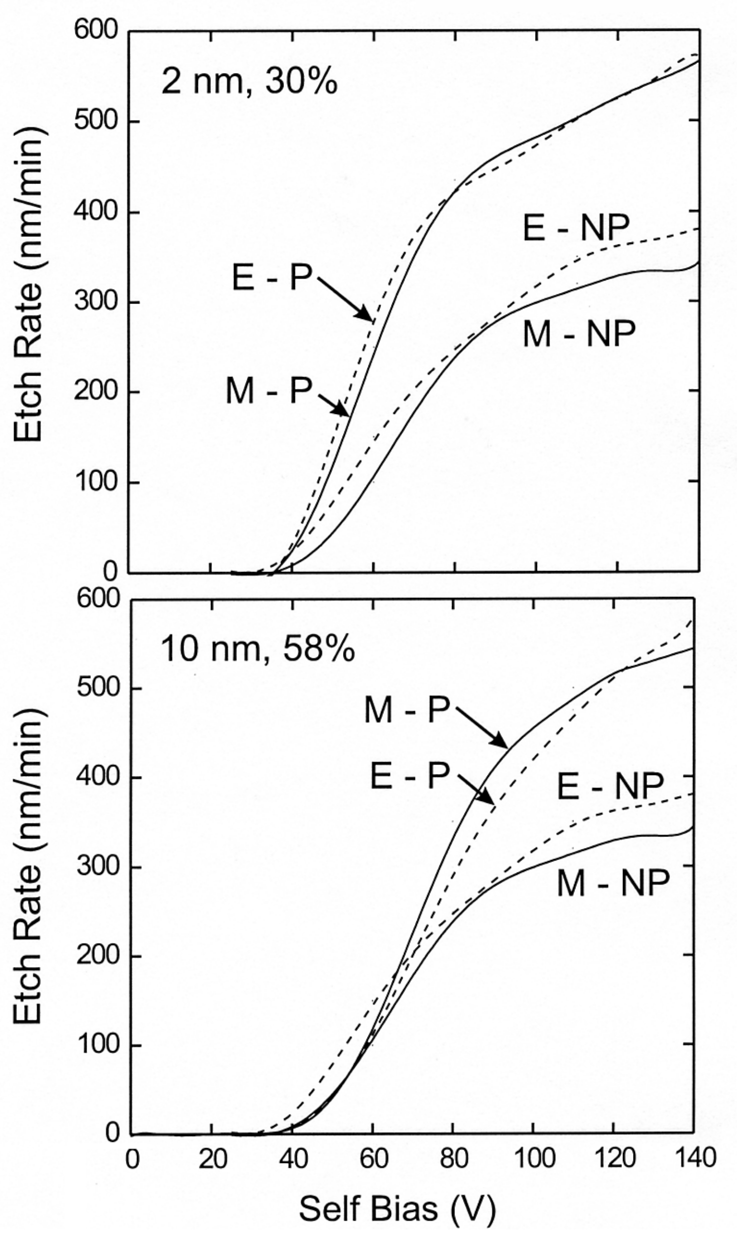
- **Solid**



- **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.**

ETCHING OF POROUS SiO_2



- Etch rates of P-SiO_2 are generally higher than for non-porous (NP).
- Examples:
  - 2 nm pore, 30% porosity
  - 10 nm pore, 58% porosity
- Higher etch rates are attributed to lower mass density of P-SiO_2.
- CHF_3 10 mTorr, 1400 W

P - Porous
NP - Non porous
E - Experimental
M - Model

Exp: Oehrlein et al. Vac. Sci.Technol. A **18**, 2742 (2000)

PORE-DEPENDENT ETCHING

- **To isolate the effect of pores on etch rate, corrected etch rate is defined as**

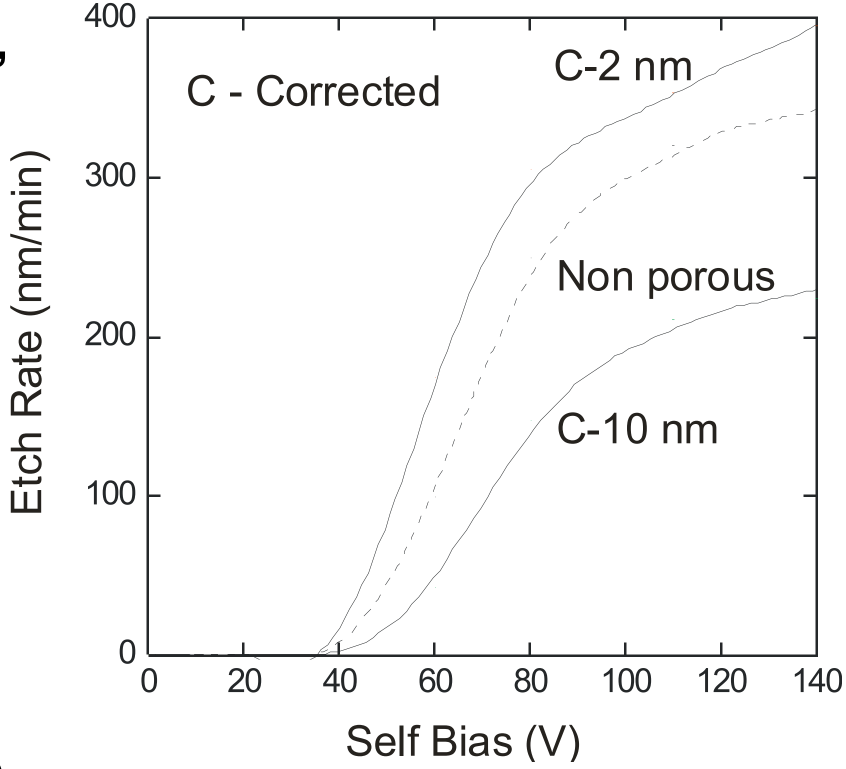
$$\text{Etch Rate (ER)}_{\text{corrected}} = \text{ER}_{\text{regular}} \times (1-p),$$

$$p = \text{porosity}$$

- **If etching depended only on mass density, corrected etch rates would equal that of NP- SiO_2.**

- **2 nm pores $L/a \geq 1$: C-ER > ER(SiO_2). Favorable yields due to non-normal incidence may increase rate.**

- **10 nm pores $L/a \leq 1$: C-ER < ER(SiO_2). Filling of pores with polymer decrease rates.**



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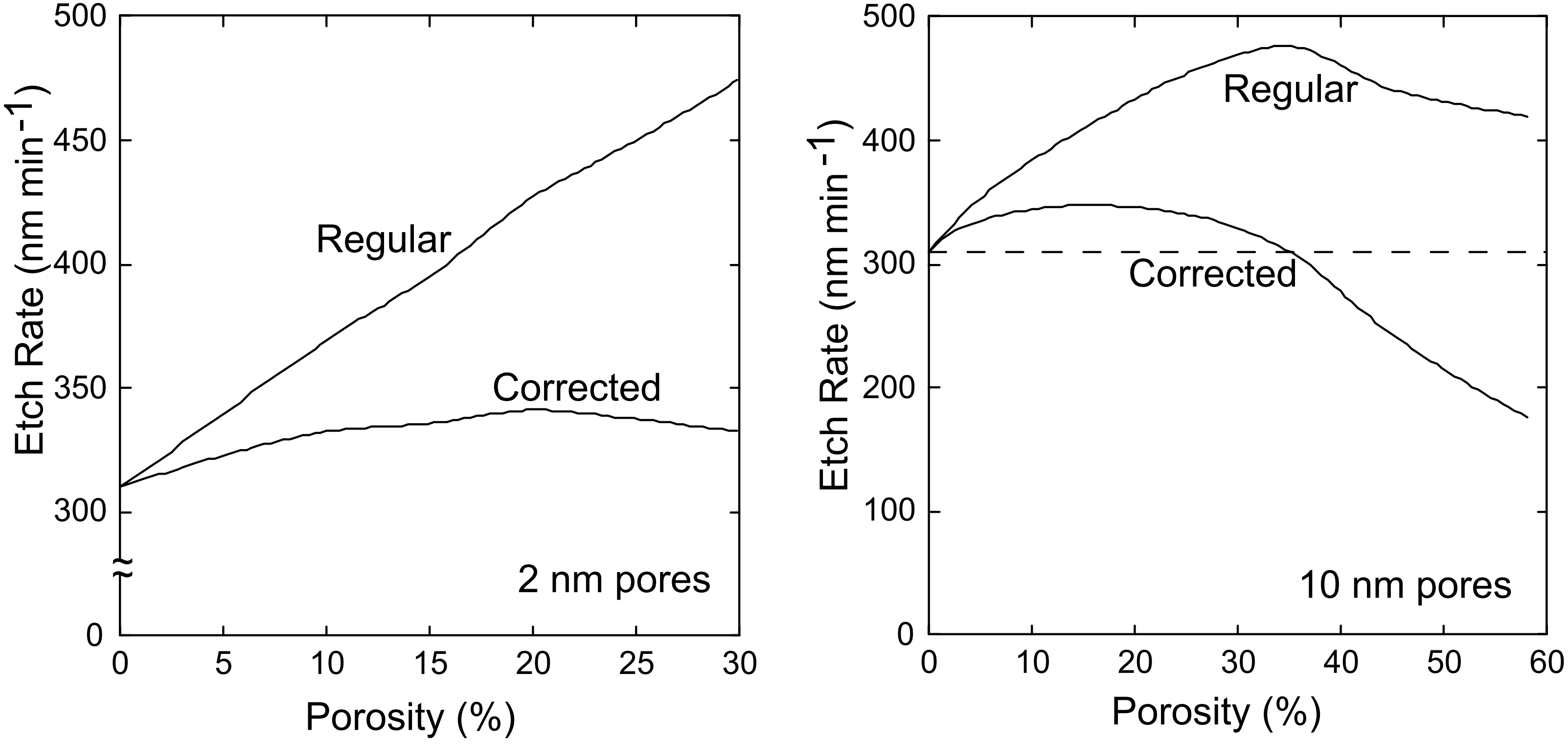
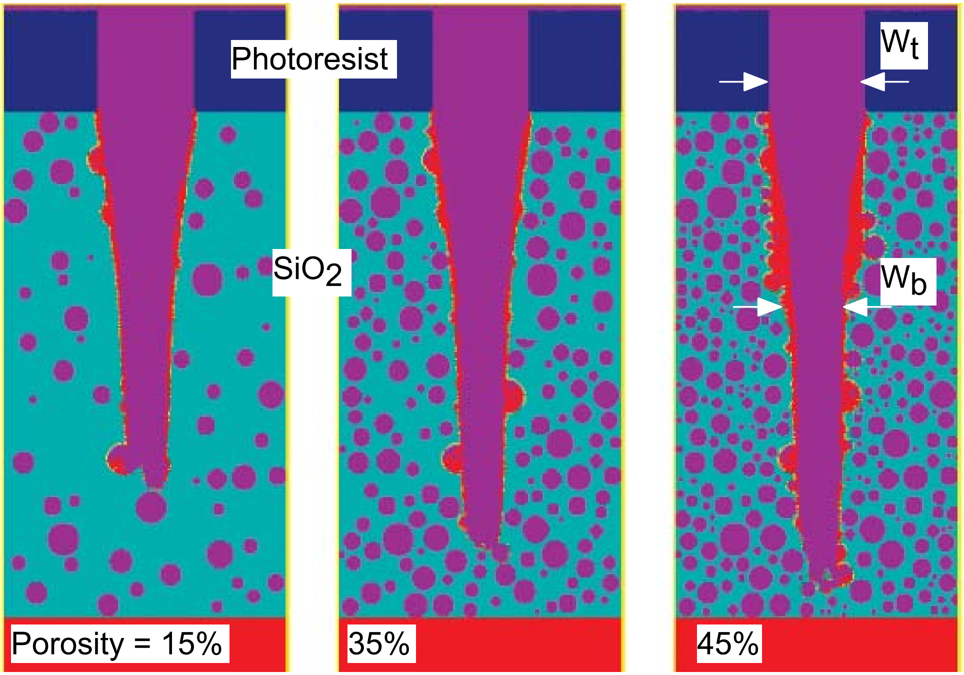
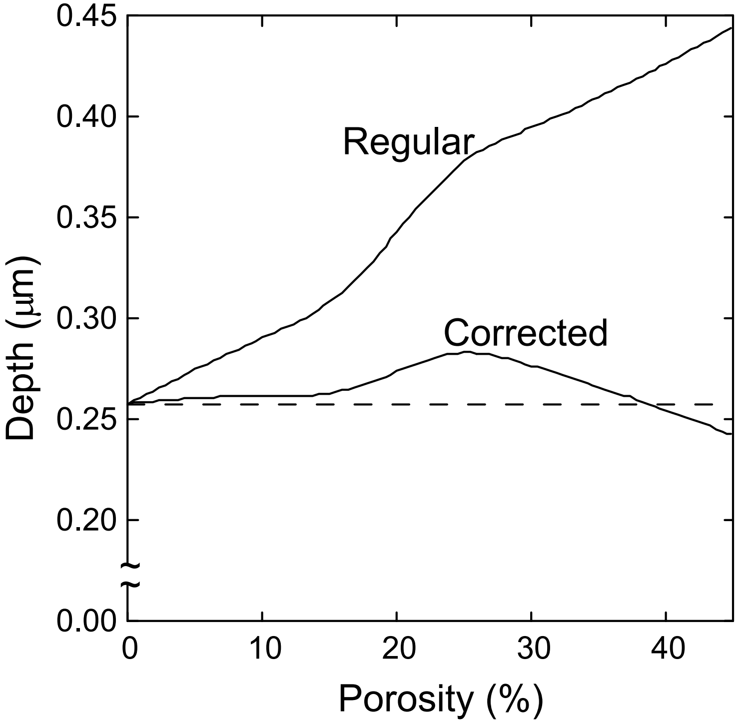
EFFECT OF POROSITY ON BLANKET ETCH RATES



- **2 nm pores: Etch rate increases with porosity.**
- **10 nm pores: Polymer filling of pores reduces etch rate at large porosities.**

EFFECT OF POROSITY ON HAR TRENCHES

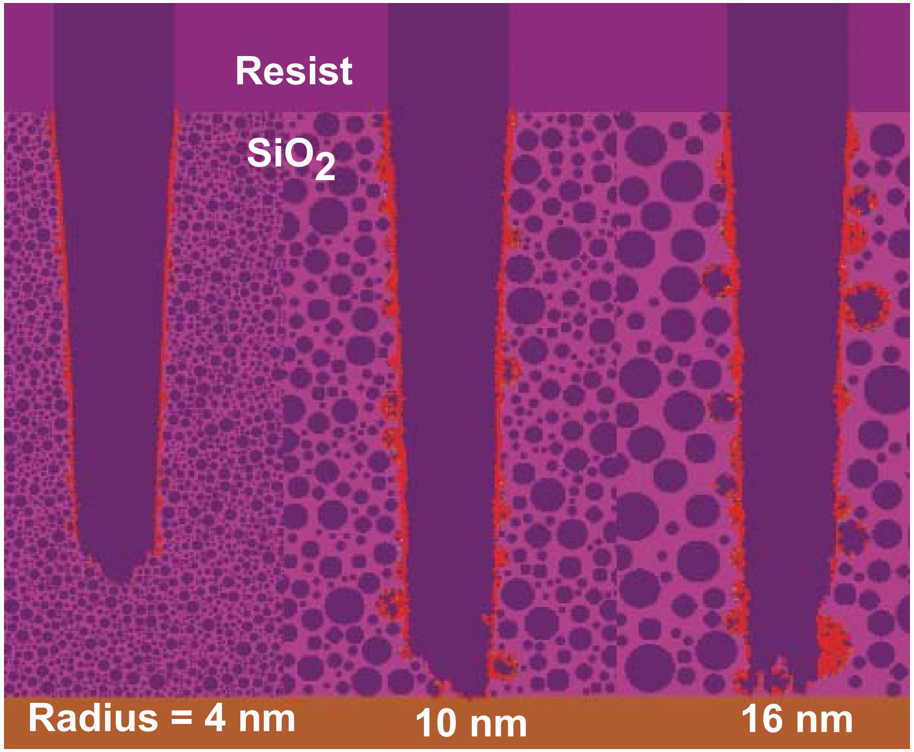


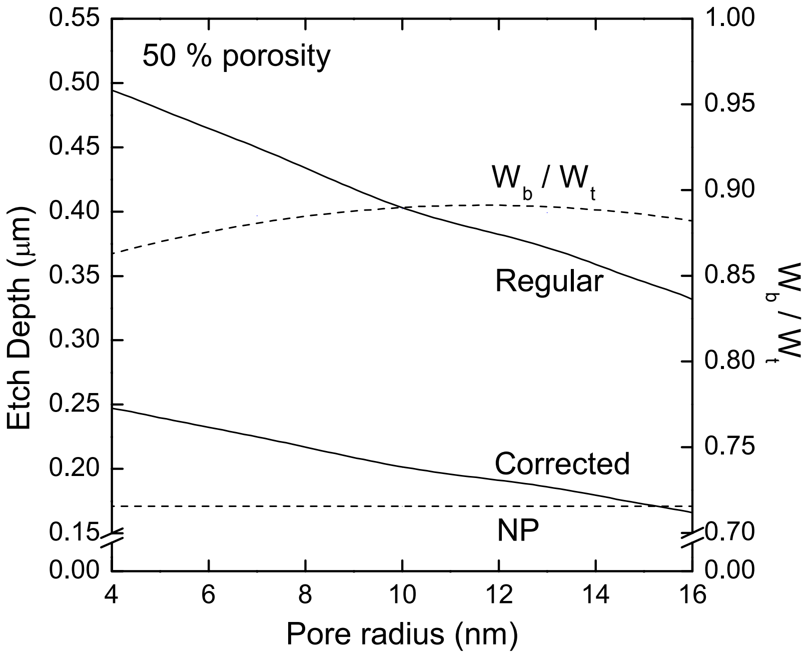


- **10 nm pores. W_t = 0.1 µm**

- **At higher porosities, more opportunity for pore filling produces thicker average polymer layers and lower etch rates.**
- **Corrected etch rates fall below SiO_2 rates when critically thick polymer layers are formed.**

EFFECT OF PORE RADIUS ON HAR TRENCHES





- With increase in pore radius, L/a decreases, enabling pore filling and a decrease in etch rates.
- Thick polymer layers eventually leads to etch rates falling below NP. There is little variation in the taper.

OXYGEN ETCHING OF PTFE

- After etching, the polymer must be removed from the feature.

- O_2 plasmas are typically used for polymer stripping, usually during photoresist mask removal.

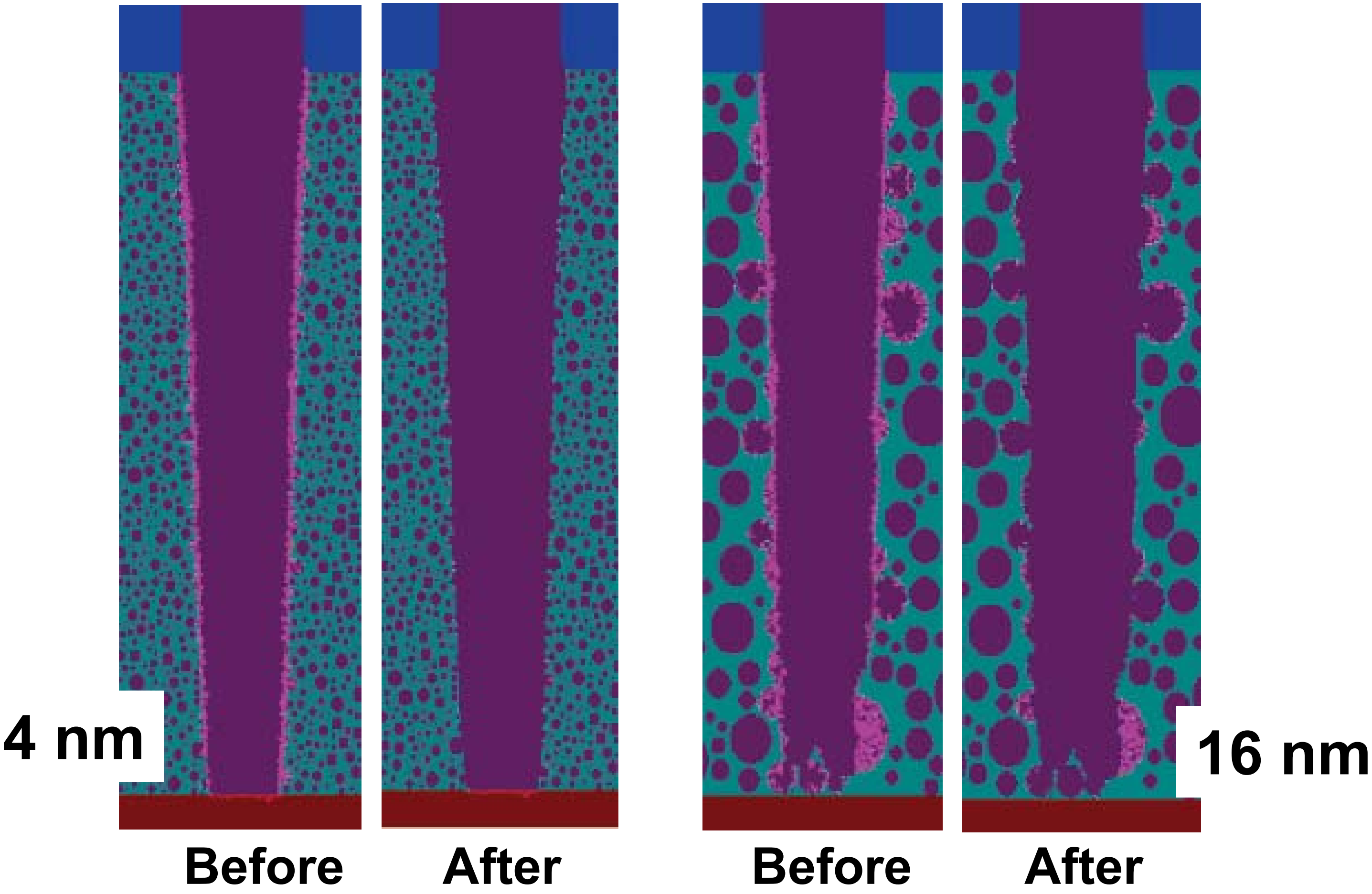
- Unlike hydrocarbon polymers which spontanesouly react with O, fluorocarbon polymers require ion activation for etching.

  - Polymer + Energetic Ion → Activated Polymer Site (P*)
  - P* + O → Volatile Products

- Removal of polymer from porous materials is difficult due to shadowing of ion fluxes caused by the pore morphology.

EFFECT OF PORE RADIUS ON CLEANING

- **Larger pores are more difficult to clean due small view angle of ion fluxes producing lower fluxes of less energetic ions.**



CONCLUDING REMARKS

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

- The ability for plasmas to produce reactive species and polymers to “accept” those species at ambient temperatures have enabled a wide range of technological applications.

- Inspite of years of use, lack of fundamental understanding of many of the basic plasma-surface processes has largely limited the technology to empirical development.

- As these processes become better characterized, new technologies will come to the forefront; from biocompatible surfaces to flexible display panels.

ACKNOWLEDGEMENTS

- Dr. Alex V. Vasenkov
- Mr. Rajesh Dorai
- Mr. Arvind Sankaran
- Mr. Pramod Subramonium

- Funding Agencies:
  - 3M Corporation
  - Ford Motor Corporation
  - Semiconductor Research Corporation
  - National Science Foundation
  - SEMATECH