ACHIEVING SELECTIVITY IN PLASMA PROCESSING: ADDRESSING THE PHYSICS WHILE STILL MAKING A PROFIT

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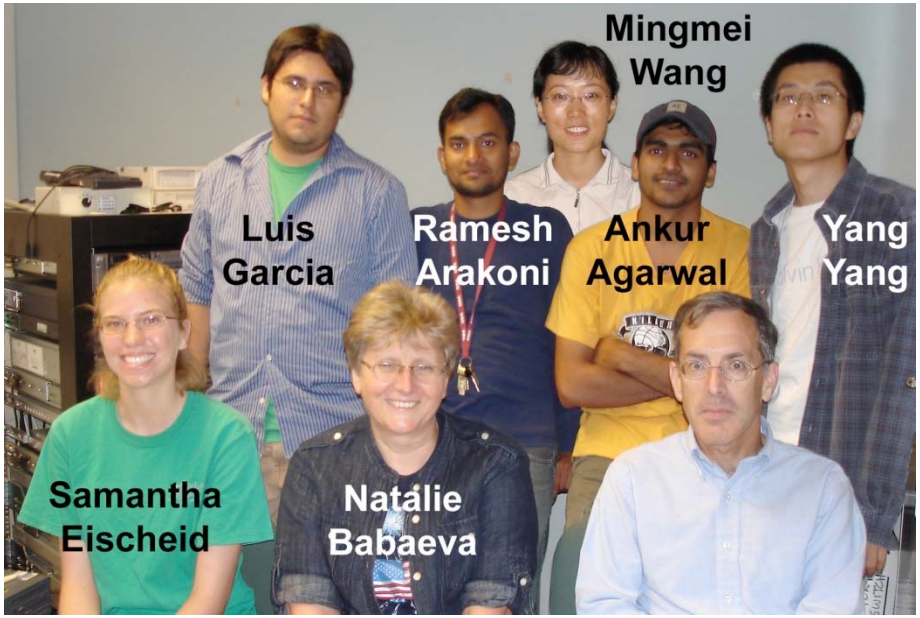

- Funding Agencies
  - 3M Corporation
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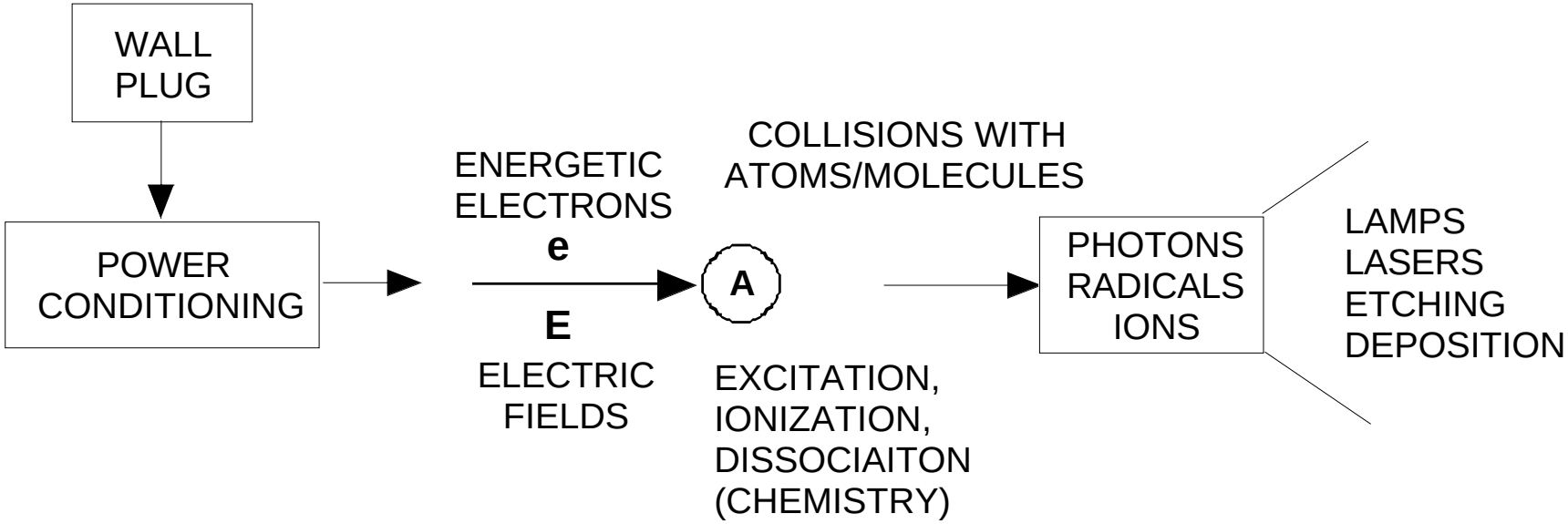
  - Micron, Inc.
  - Semiconductor Research Corporation
  - National Science Foundation
  - Air Force Office of Scientific Research

AGENDA

- Low Temperature Plasmas: A diversity of applications
- Economic Context
- Plasmas for Materials Processing
  - Microelectronics ($1000/cm^2)
  - Polymers ($0.05/m^2)
- Future Opportunities: Plasma 2010 Decadal Study…and chaos
- Concluding Remarks

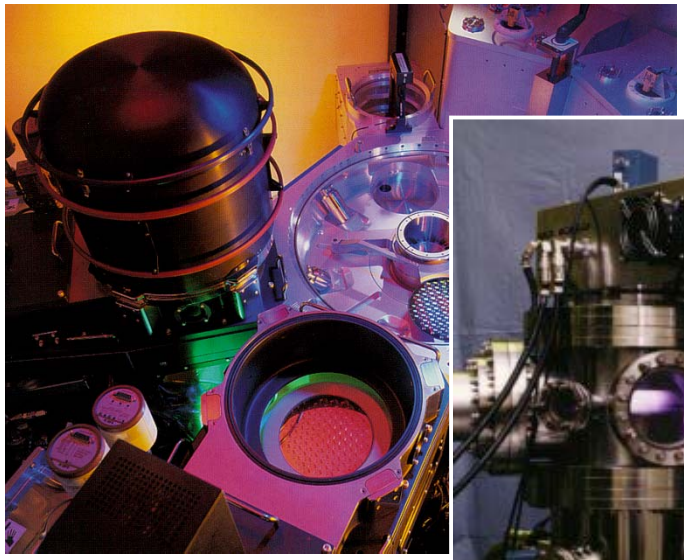
LOW TEMPERATURE PLASMAS: A POWER TRANSFER MEDIA

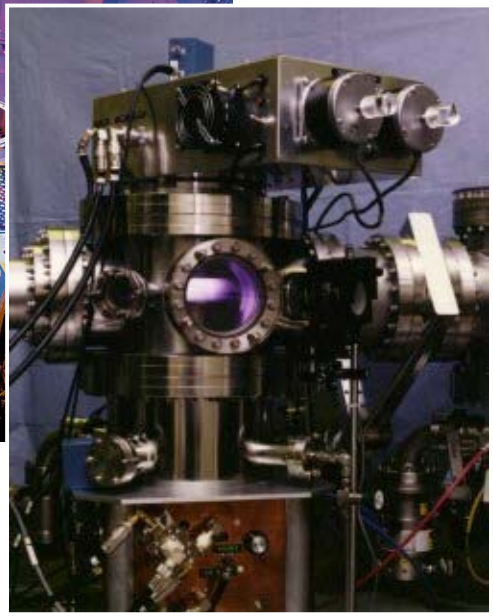


- **Electrons transfer power from the "wall plug" to internal modes of atoms / molecules to "make a product", very much like combustion.**
- **The electrons are "hot" (several eV or 10-30,000 K) while the gas and ions are cool, creating "non-equilibrium" plasmas.**

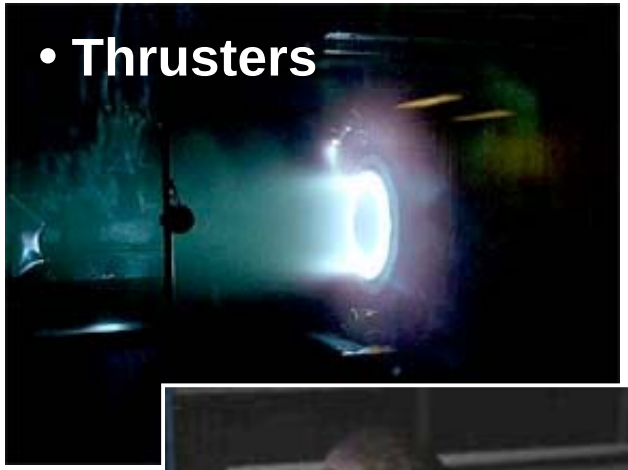
COLLISIONAL LOW TEMPERATURE PLASMAS

• Lighting





• Materials Processing



• Thrusters

• Spray Coatings

• Displays

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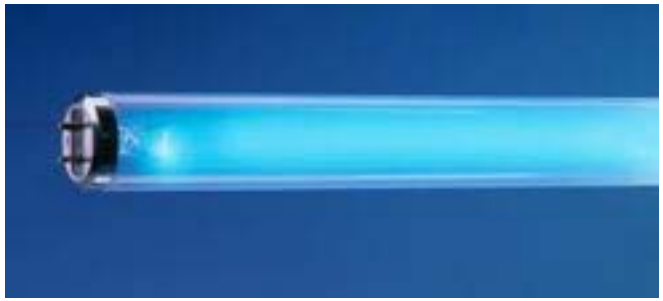
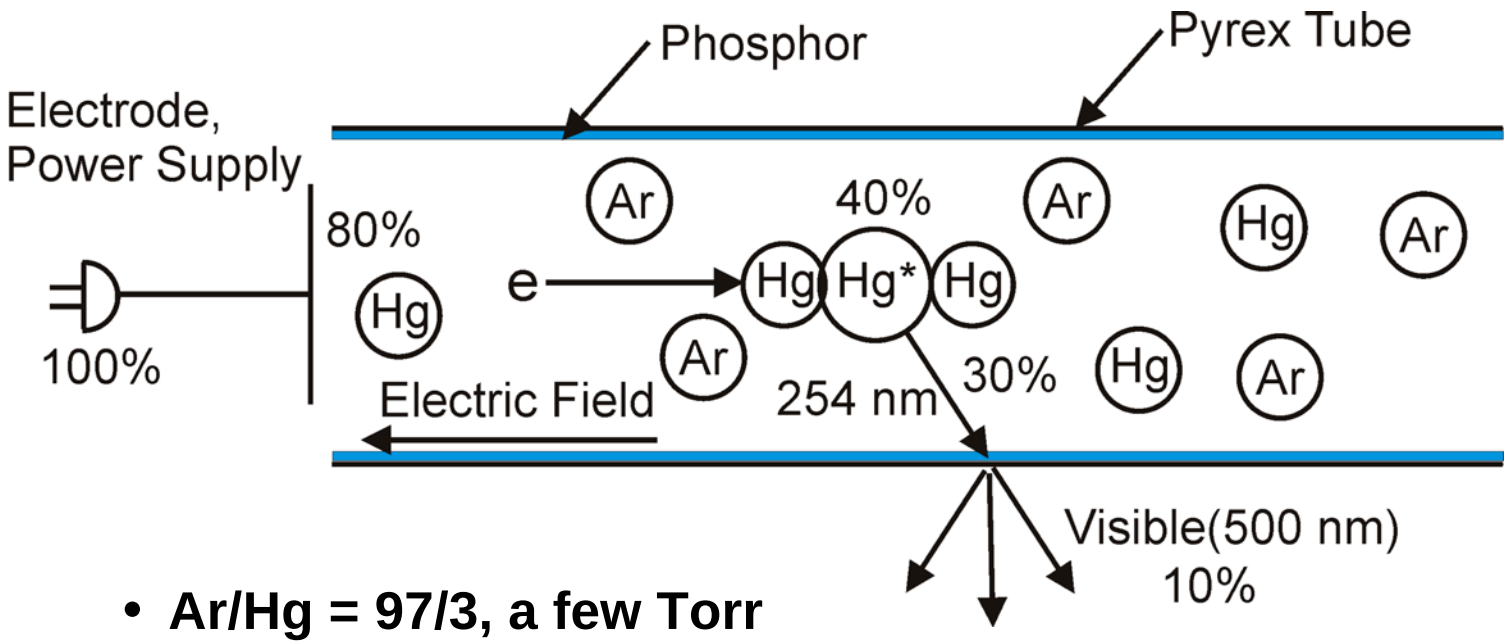
LOW TEMPERATURE PLASMAS: PHYSICS, A BUSINESS, A NATIONAL PRIORITY:

LIGHTING AS A CONTEXT

FLUORESCENT LIGHTING

- **Fluorescent lamps convert electricity to visible radiation with an efficiency of nearly 10%.**
- **Electron impact excitation of Hg produces UV light, converted to visible by phosphors.**

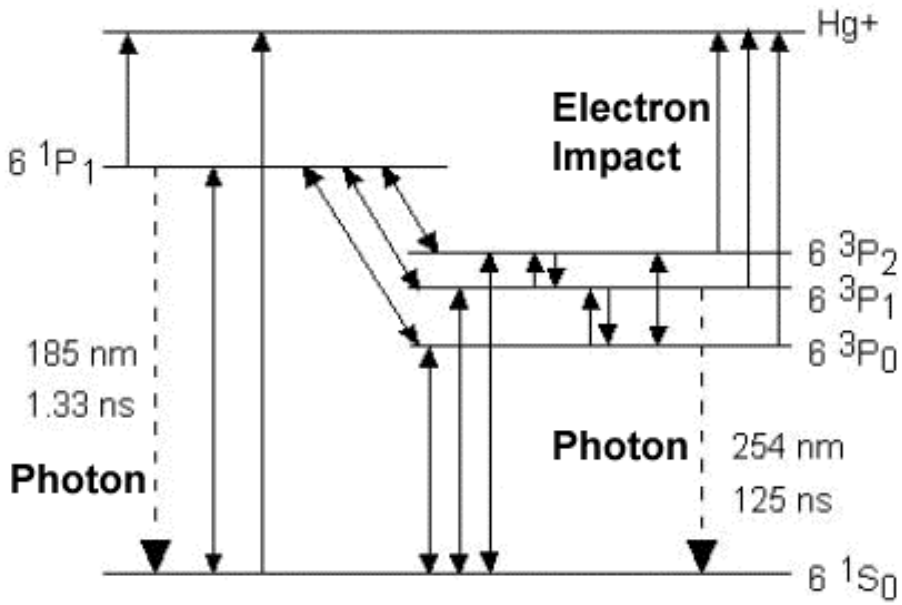


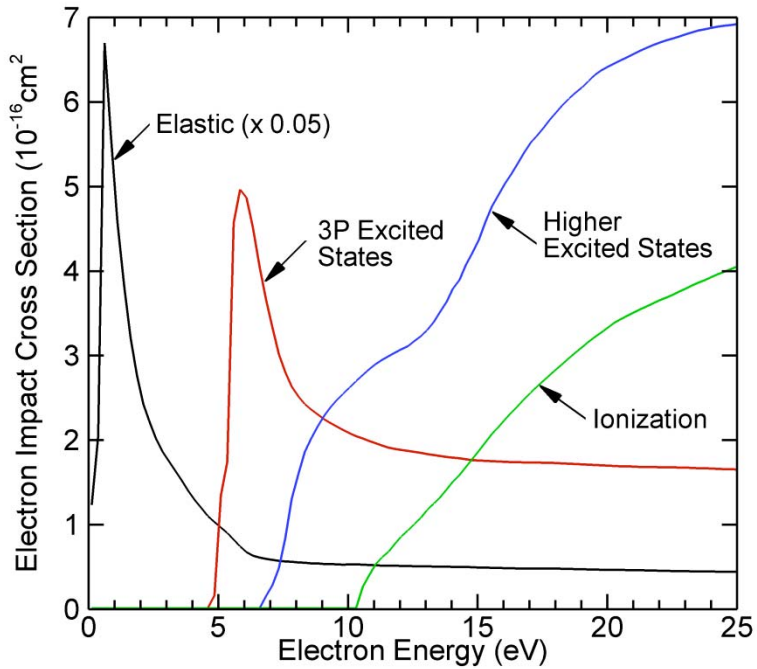


- **Ar/Hg = 97/3, a few Torr**

EXCITATION OF Hg ATOM

- **The desired states to excite in the Hg atom in a fluorescent lamp are in the Hg(^{3}P) multiplet.**

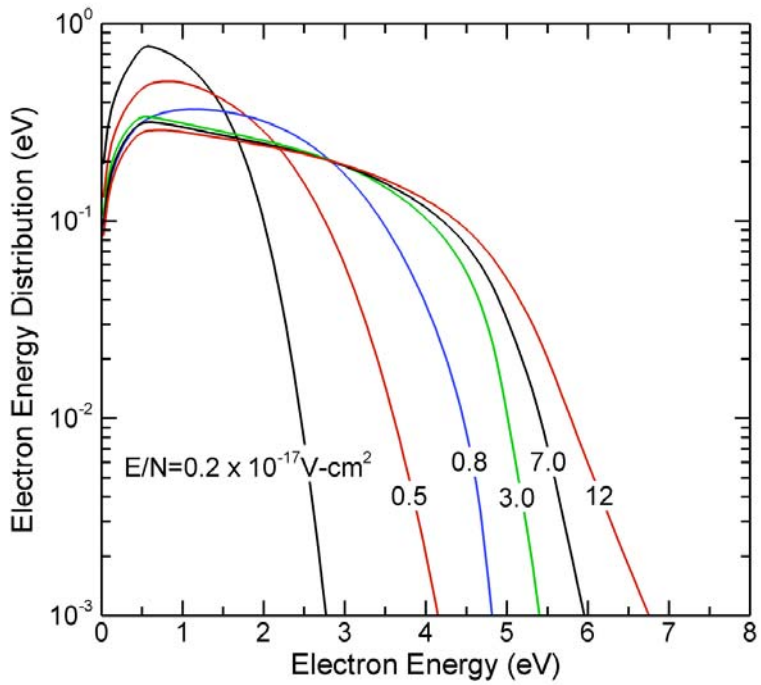


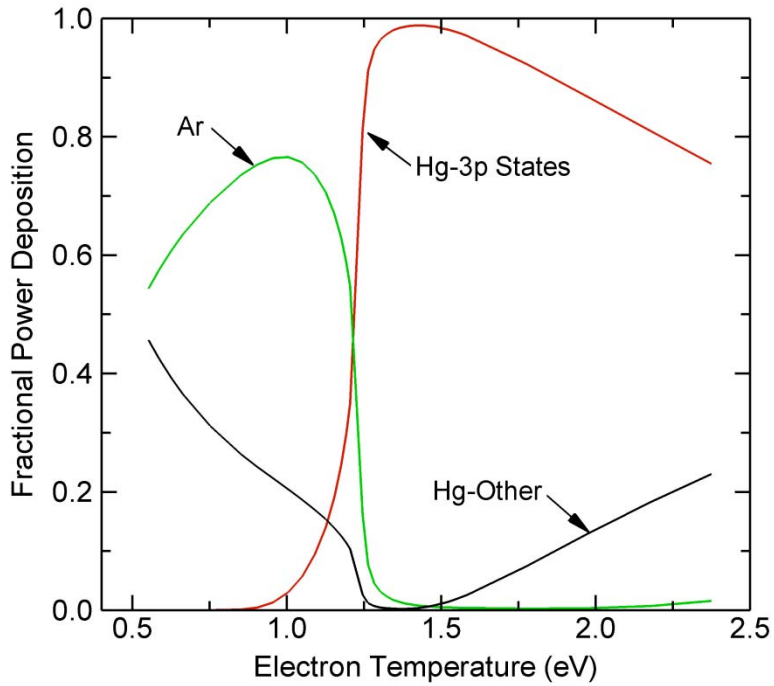


RATE OF EXCITATION AND POWER DISSIPATION

- **Rate of excitation is convolution of *f(ε)* and cross section *σ(ε)*.**

$$Excitation \sim \int f(\varepsilon)\varepsilon^{1/2}\sigma(\varepsilon)d\varepsilon$$



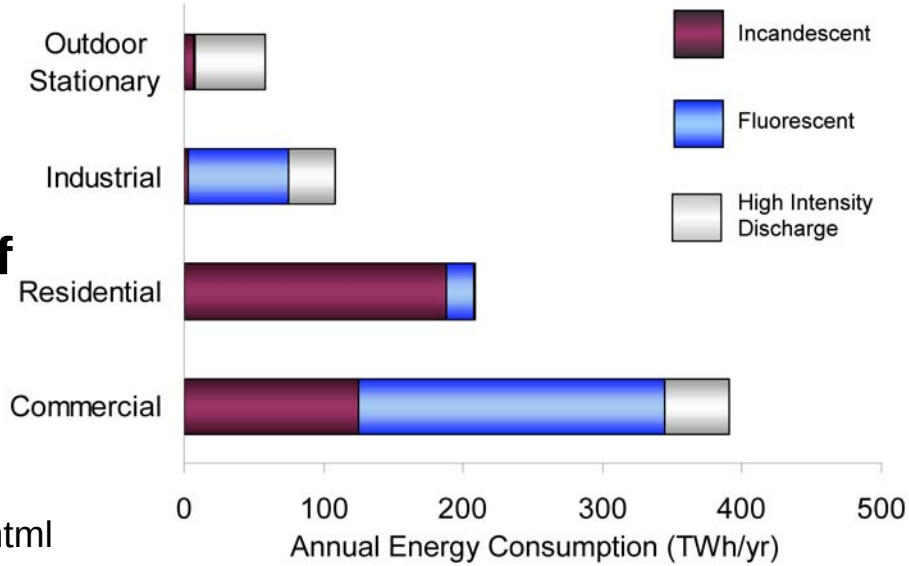


- **Tuning the electric field and T_e can maximize fraction of power expended in exciting Hg(^{3}P) states.**

- **Ar/Hg = 97/3**

CONTEXT: PLASMA LIGHTING

- **Annual US electrical power consumption: 3.5 x 10^{12} kW-Hr**
- **Electrical power expended in lighting: 22% (7.6 x 10^{11} kW-Hr)**
- **Fraction of expended in fluorescent lamps: 9% (3.1 x 10^{11} kW-Hr)**
- **The output of 35 1-GWe power plants excite a single multiplet of Hg in fluorescent lamps…a shift of 0.1 eV in *f(ε)* corresponds to 3 1-GWe plants.**

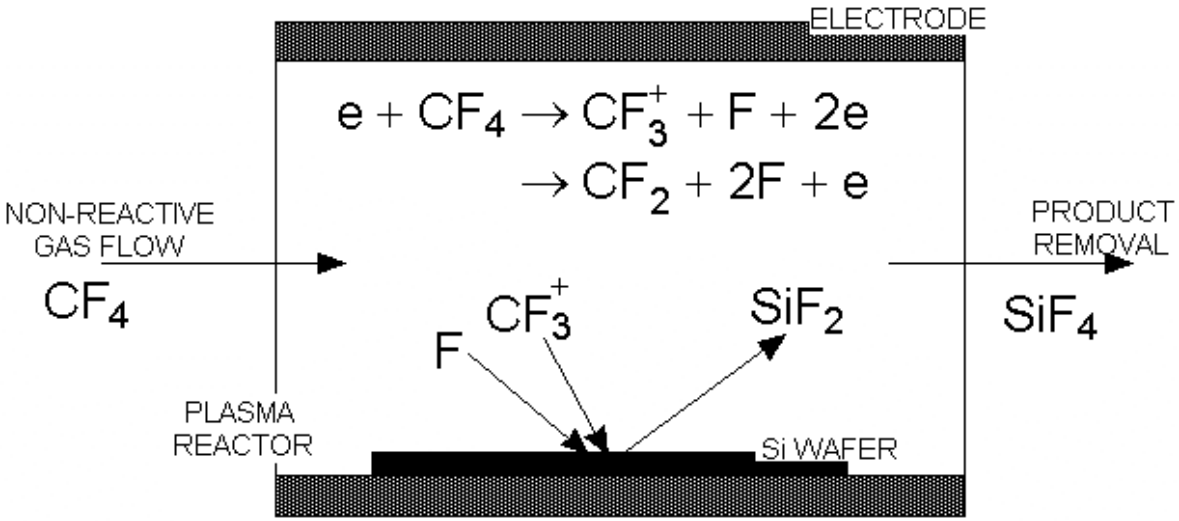


http://www.eia.doe.gov/cneaf/electricity/epa/epates.html
http://antwrp.gsfc.nasa.gov/apod/ap970830.html
http://www.eere.energy.gov/buildings/info/documents/pdfs/lmc_vol1_final.pdf

PLASMAS FOR MATERIALS PROCESSING

PLASMAS FOR MODIFICATION OF SURFACES

- **Plasmas are ideal for producing reactive species (radicals, ions) for modifying surface properties.**
  - **Selective production of fluxes of radicals and ions**
  - **Control of activation energy**
  - **Low material temperatures**
  - **Low environmental impact**



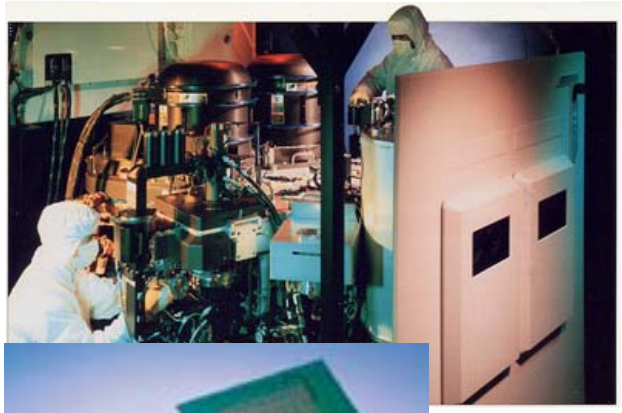
- **Extremely diverse industries rely on plasma modification of surfaces**

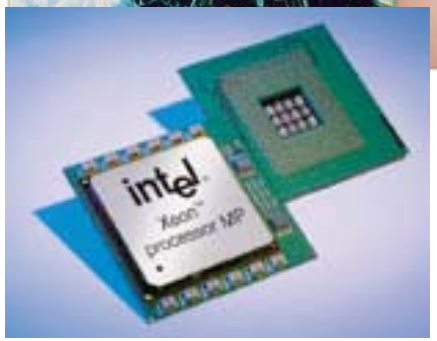
DIVERSE MATERIALS PROCESSING INDUSTRIES RELY ON PLASMAS

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/m^2 ← | → $1000/cm^2

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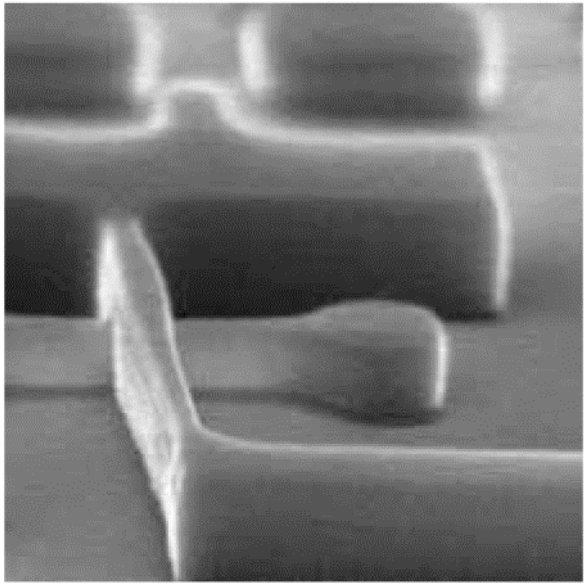
PLASMAS FOR MICROELECTRONICS FABRICATION

PLASMAS FOR MICROELECTRONICS FABRICATION

- **Plasmas are indispensable for etching, deposition and cleaning.**
- **Control of critical dimensions at 45 nm node require resolution of only a few nm.**
- **Required: Unprecedented control of reactant fluxes from the plasma onto the wafer:**
    - ***Uniformity*, *Composition*, *Distribution of Energies***



Intel 30 nm Tri-gate Transistor

- **Future technology nodes will have feature sizes where one monolayer deviation will significantly effect performance.**

- **http://www.intel.com/technology/silicon**

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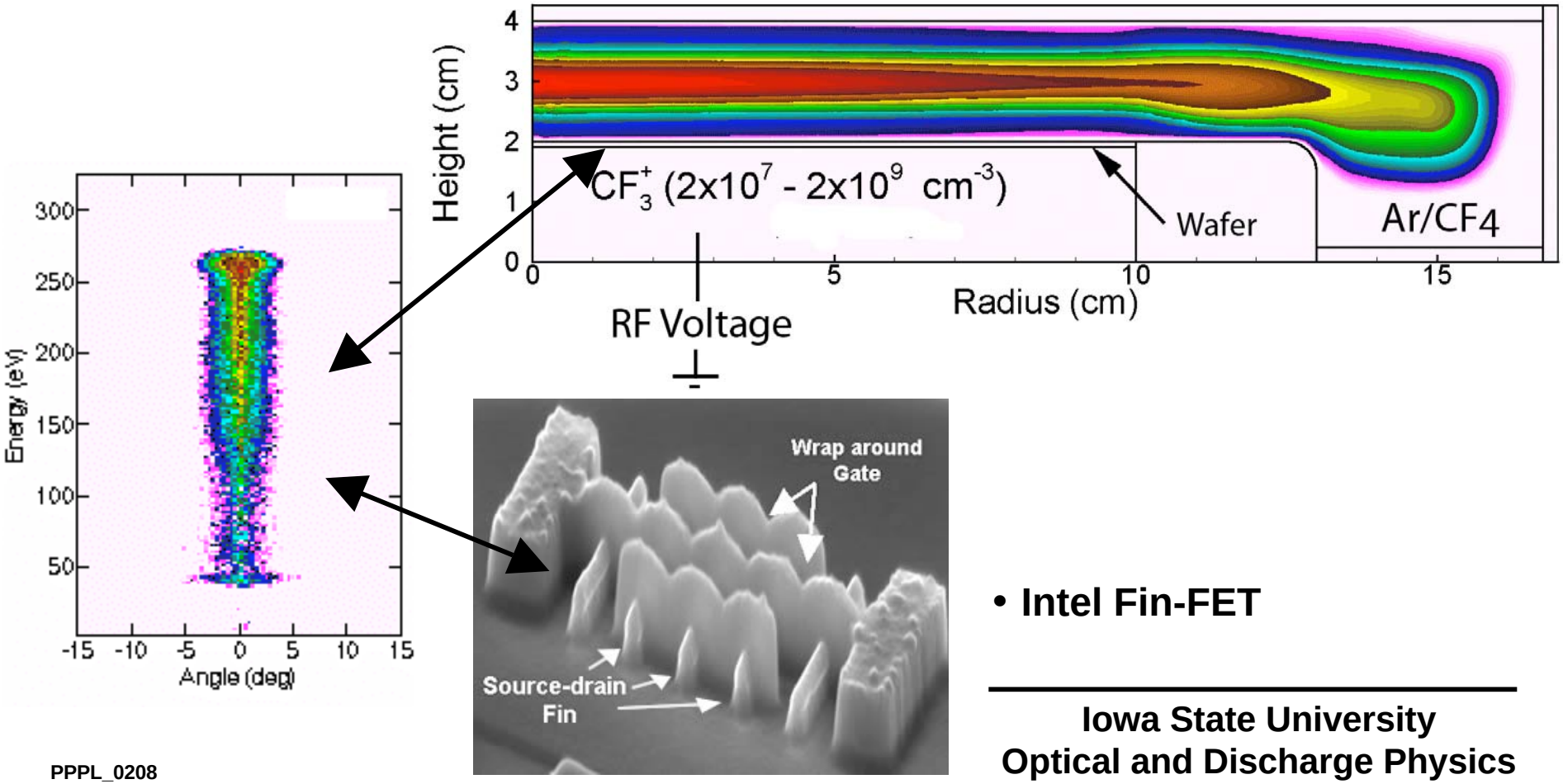
ACTIVATION ENERGY: SUB-eV, SUB-DEGREE CONTROL

- **Activation energy is largely delivered through ion bombardment.**
- **Distinguishing between materials will be determined by sub-eV and sub-degree control of ion energies.**



- **Intel Fin-FET**

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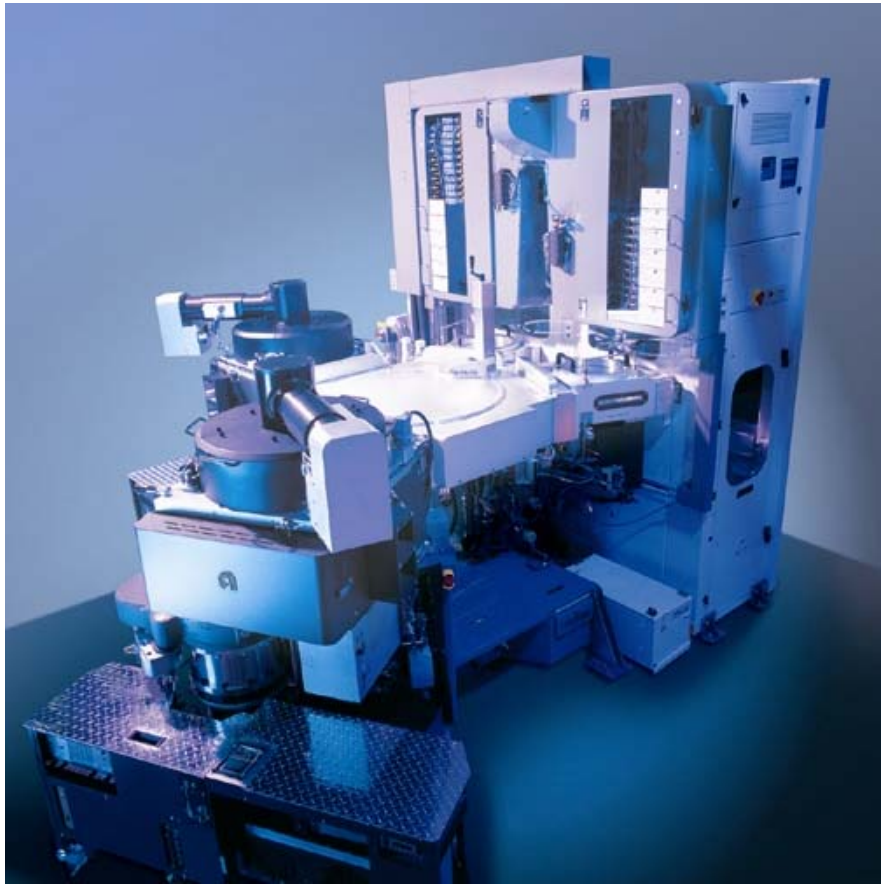
MULTI-FREQUENCY CAPACITIVELY COUPLED PLASMA ETCHER: APPLIED MATERIALS *CENTURA ENABLER*

- **Plasma etching of dielectric materials for logic contacts and interconnect – 300 mm wafers at the 45 nm node.**



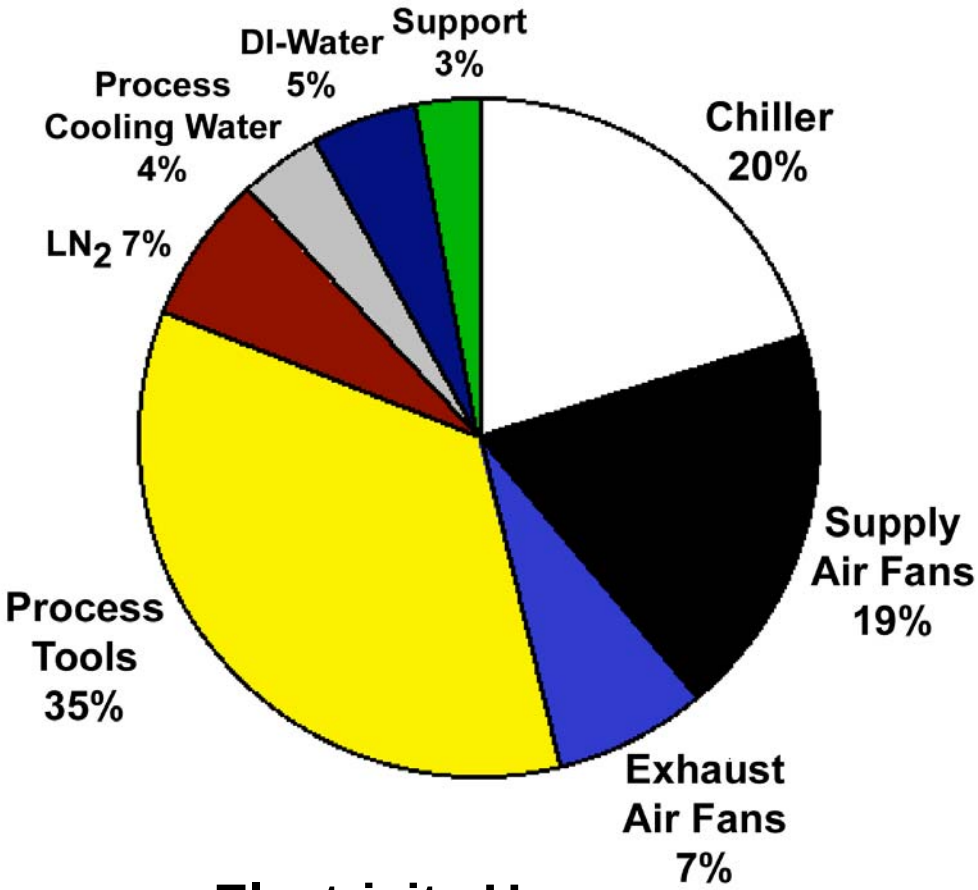
- **Ref: S. Rauf, AMAT**

POWER CONSUMPTION: PLASMA REACTORS

- You've got to make money doing this!...One consideration is simply power consumption.
- Plasma processing tools have multiple chambers, pumps, power supplies, heaters and scrubbers.
- Typical power is 25 kW/module, up to 100 kW for a multi-station platform.
- Plasma generation is 25-50% of power (other is pumps, heaters…).
- A few hundred such tools in a modern fab (plus cleanroom HVAC..)

- Ref: S. Rauf, AMAT, http://www.national.com

PLASMA TOOLS A LARGE FRACTION OF TOTAL



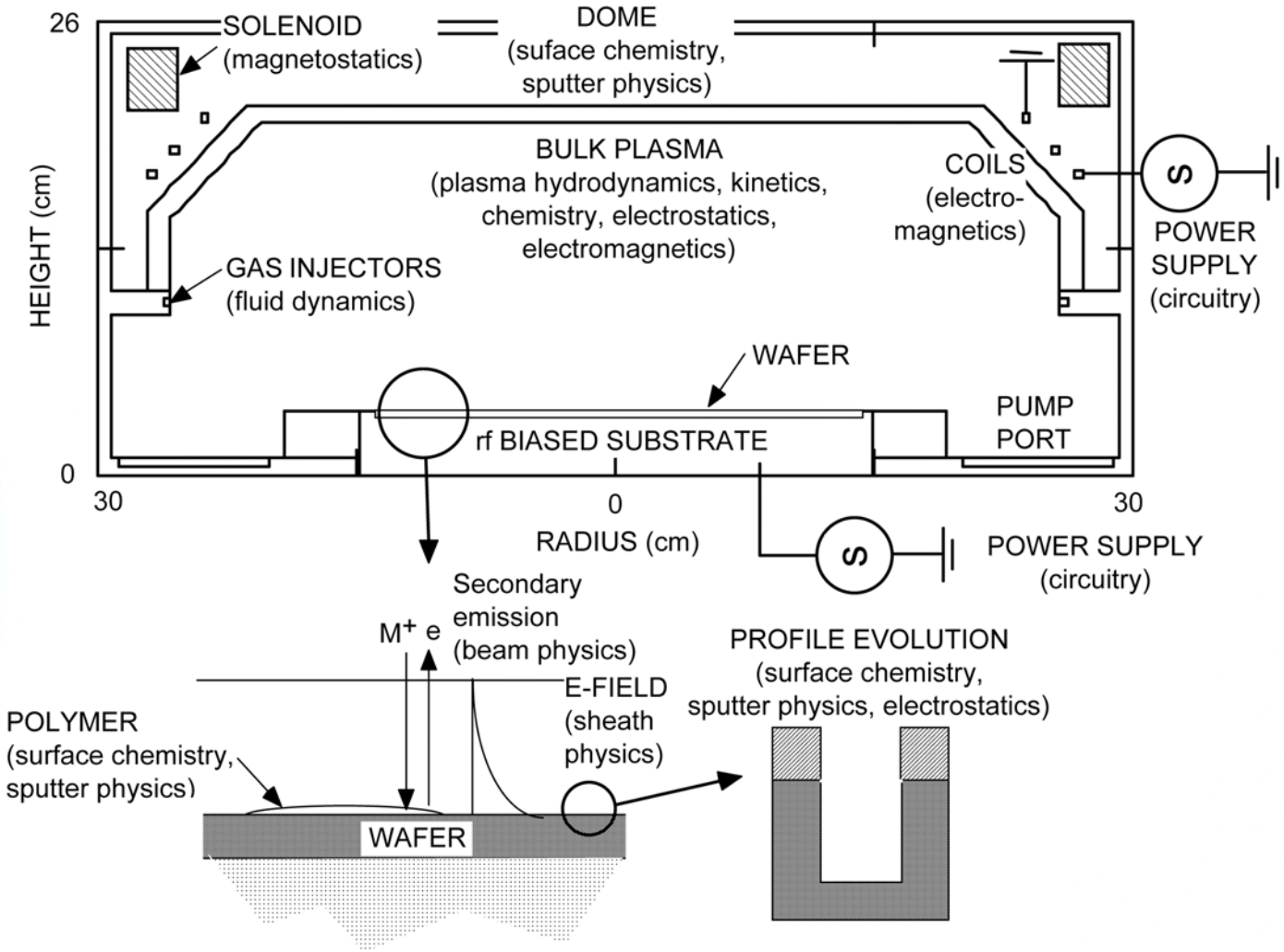
- **Electricity Usage**

- http://ateam.lbl.gov/cleanroom/Fact
- Hu and Chuah, Energy 28, 895 (2003)

- **Typical energy usage: 1 kW-hr/cm^2 of wafer**
- **Large fab: 30,000 300-mm wafer starts/month**
- **250 MkwH/year**
- **About 30-50 MW (ave)/fab**

- **About 1/3 of power is expended in process tools, most of them plasma tools.**

TYPICAL PLASMA ETCHING REACTOR



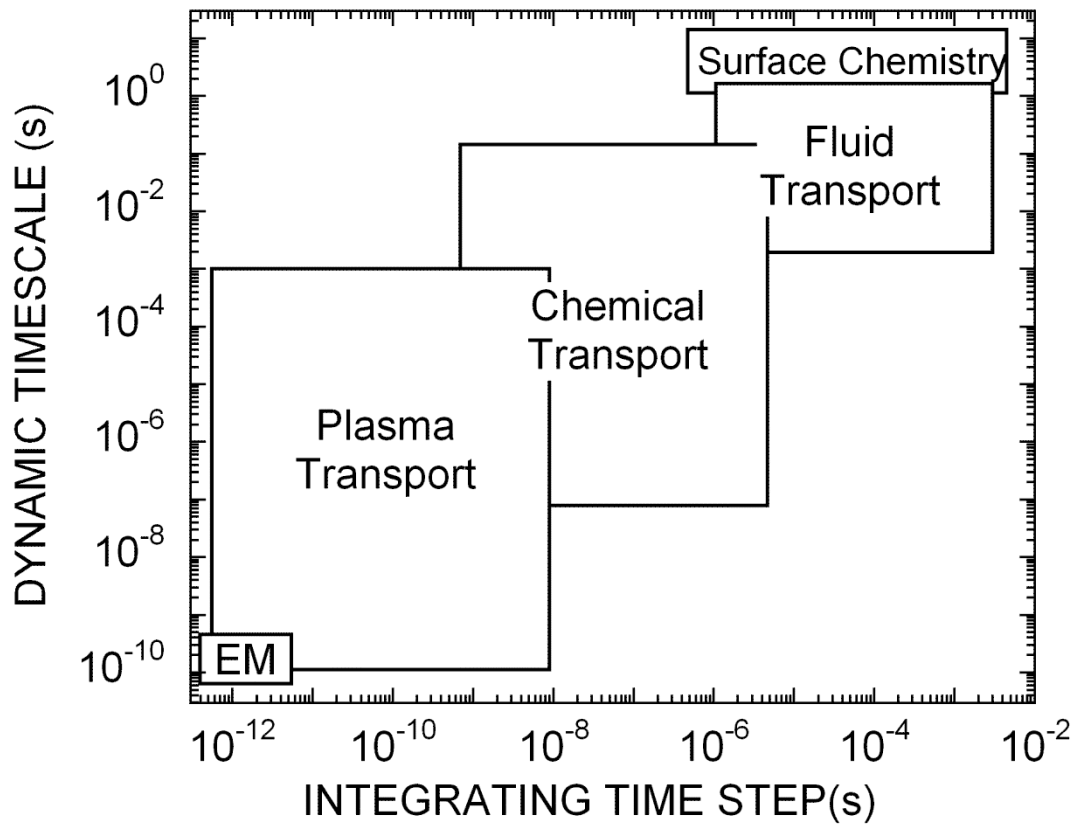
- **Hitachi XT ECR**

http://www.hitachi-hta.com

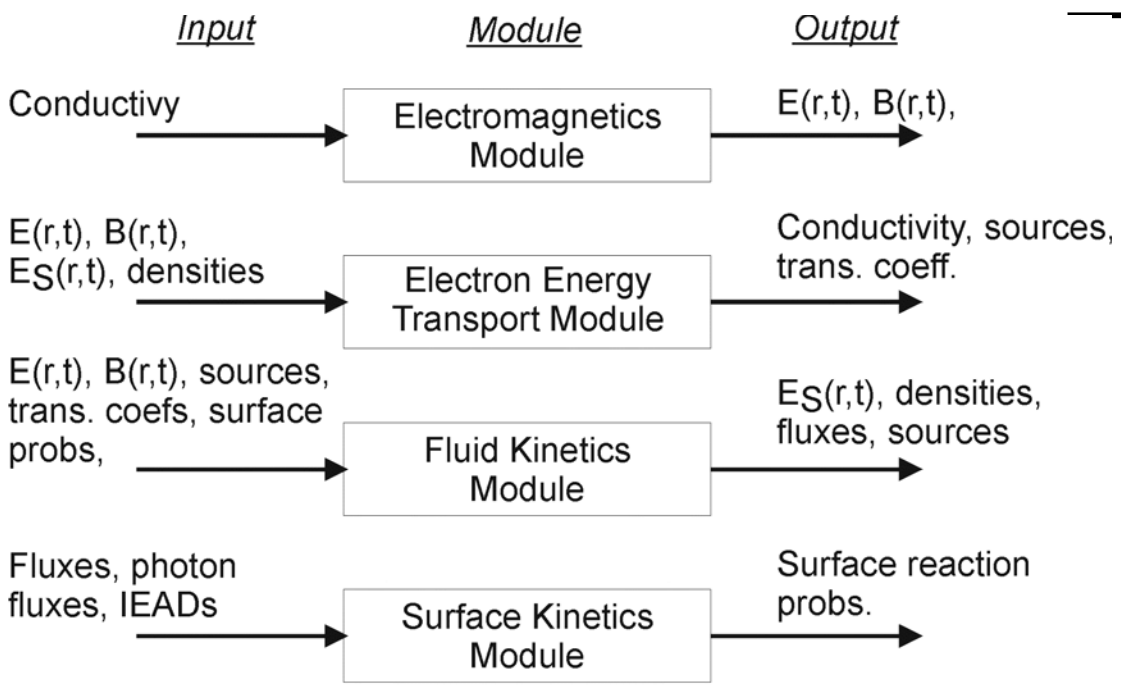
CHALLENGES TO MODELING: VERY MULTI-SCALE

- **Technological plasmas have vastly different timescales that must be addressed in models.**

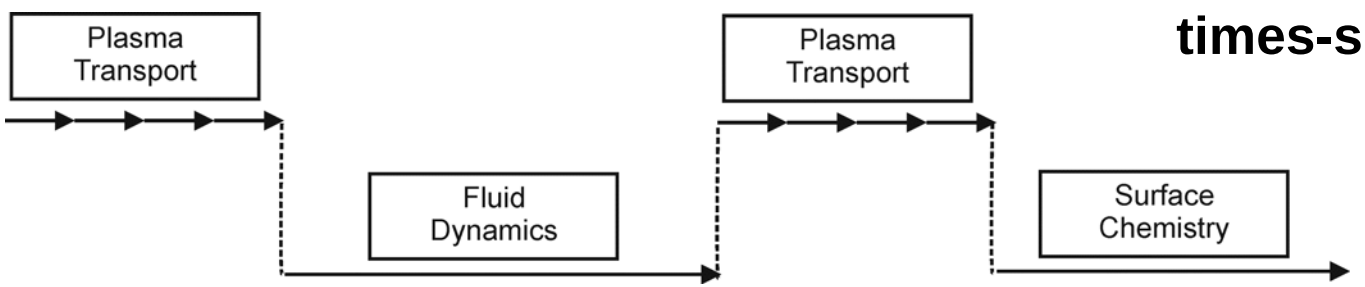
- **Integrating timestep (numerical stability): Δt**
- **Dynamic timescale (phenomena evolution): ΔT**
- **Plasma transport:**
  - **Dielectric relaxation $\Delta t = \varepsilon/\sigma \sim$ 1 ps – 10 ns**
  - **ΔT = ns - ms**
- **Surface chemistry:**
  - **$\Delta t = \mu s$, ΔT = 10 s**



HYBRID MODELING TECHNIQUES



- **Hybrid models resolve multi-physics over multi-scales.**
- **Compartmentalize physical processes into modules having minimum of overlap.**
- **Time slice on physics times-scales.**



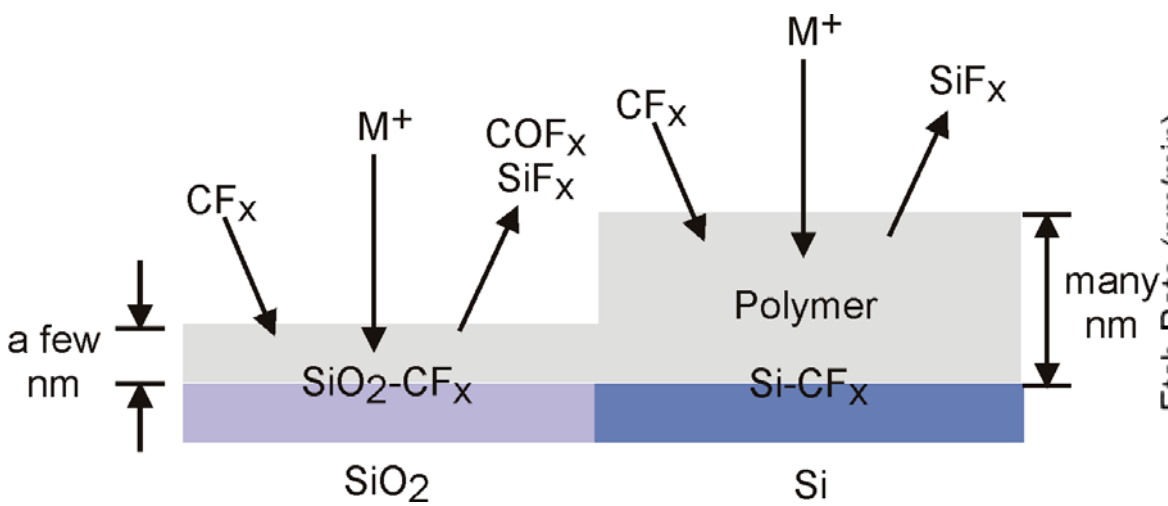
MODELING PLATFORMS: *HPEM, nonPDPSIM, MCFPM*

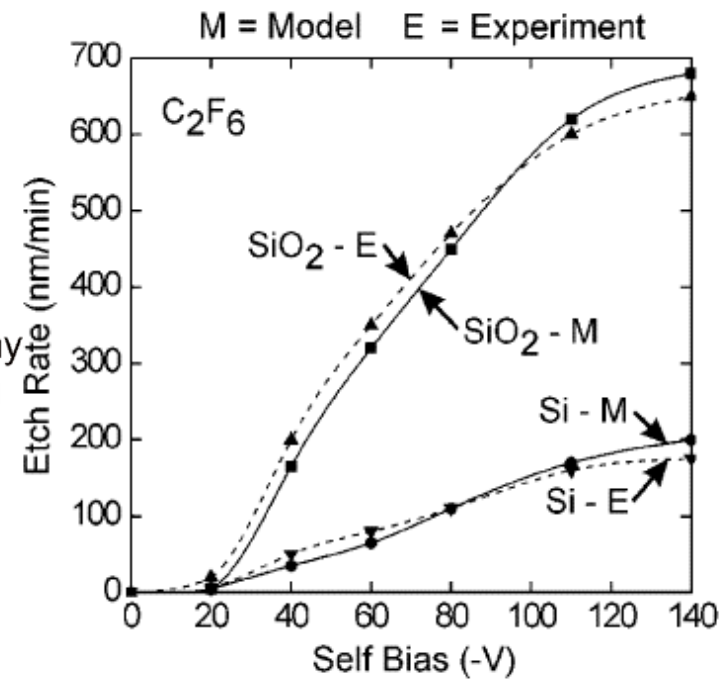
- **Examples will be discussed from hybrid modeling platforms.**
- ***HPEM (Hybrid Plasma Equipment Model)***
  - **More mature, more sophisticated physics**
  - **Lower pressures (sub-mTorr to 10s Torr)**
  - **Structured rectilinear meshes, generally semi-implicit**
- ***nonPDPSIM***
  - **Higher pressures (10s mTorr to multi-atmosphere)**
  - **Less mature but improving physics**
  - **Unstructured meshes, fully implicit**
- ***MCFPM (Monte Carlo Feature Profile Model)***
  - **Evolution of surface features**
  - **nm-to-atomic scale**
  - **Plasma and surface chemistry, charging**

CONTROLLING ACTIVATION ENERGY FOR ETCHING: NON-SINUSOIDAL WAVEFORMS

FLUOROCARBON PLASMA ETCHING OF Si/SiO_2

- **In fluorocarbon plasma etching of Si/SiO_2 CF_x radicals produce a polymer passivation layer which regulates activation energy.**
- **SiO_2 consumes the polymer in etching; thicker layers on Si result in slower etch rates, and the ability to achieve selectivity.**





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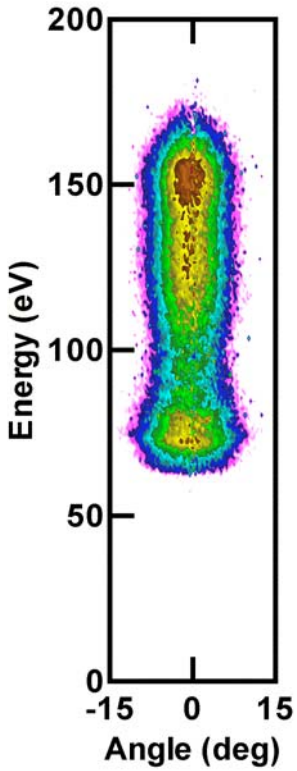
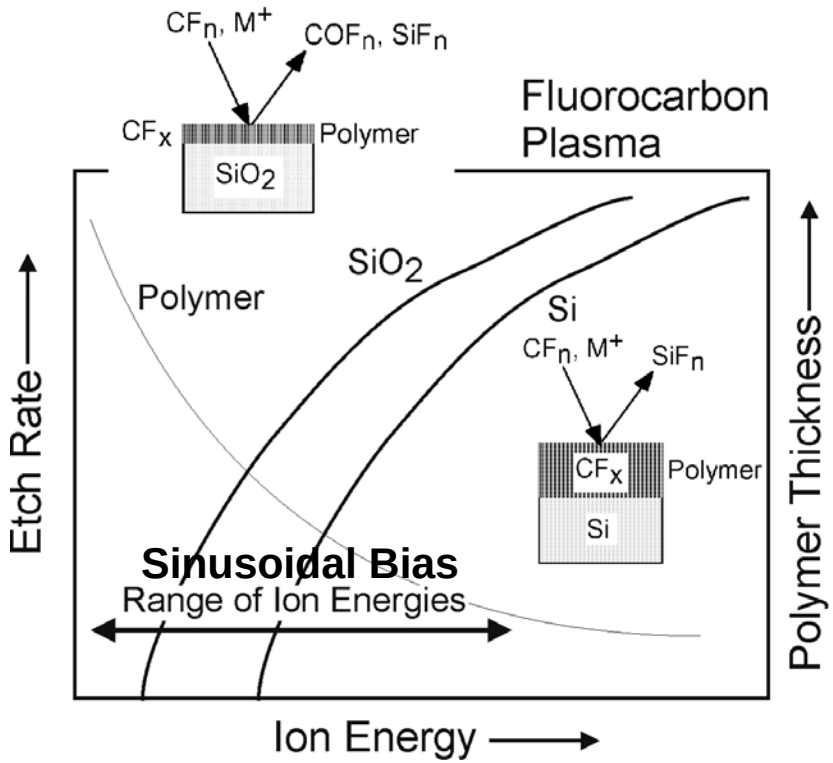
ACHIEVING HIGH SELECTIVITY



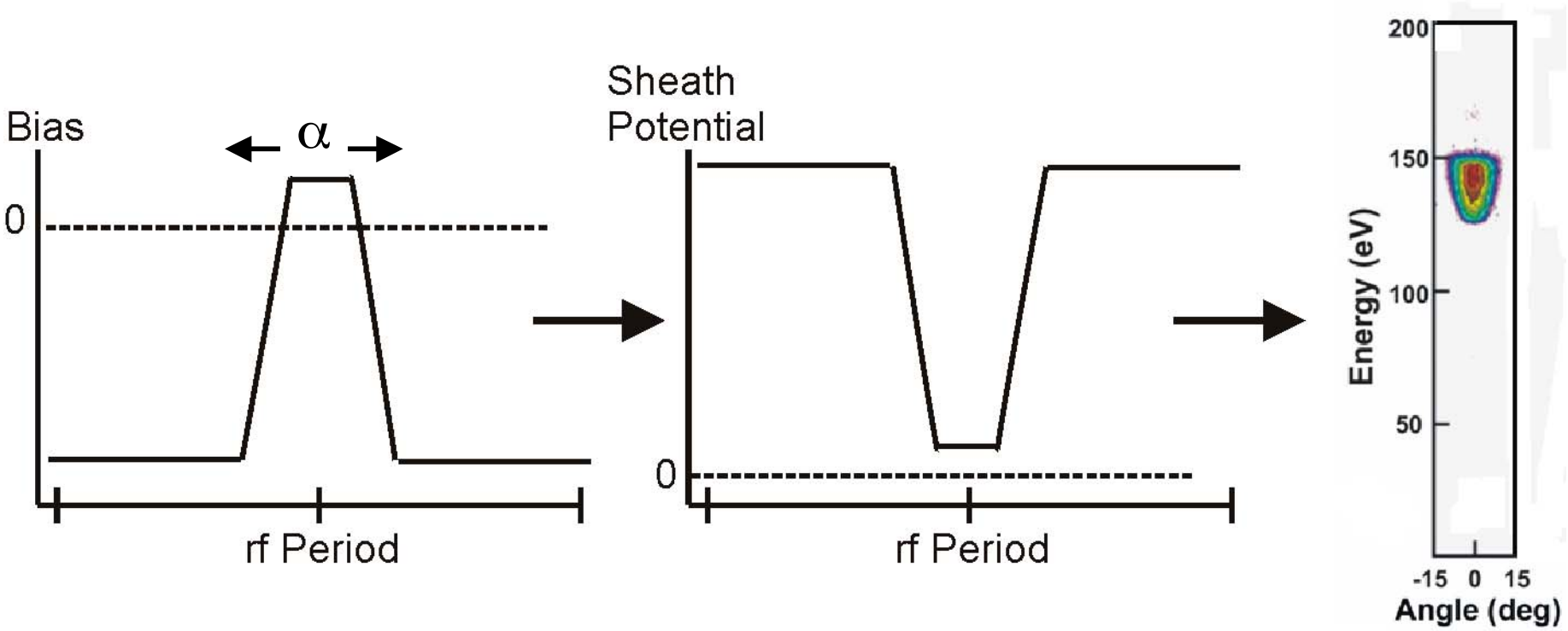


- **High selectivity achieved by controlling the ion energy distribution to wafer.**
- **Sinusoidal bias: Broad IEAD does not discriminate thresholds.**
- **Tailored bias: Produce a narrow IEAD which may discriminate between threshold energies.**

Ref: S.-B. Wang and A.E. Wendt, J. Vac. Sci. Technol. A, 19, 2425 (2001)

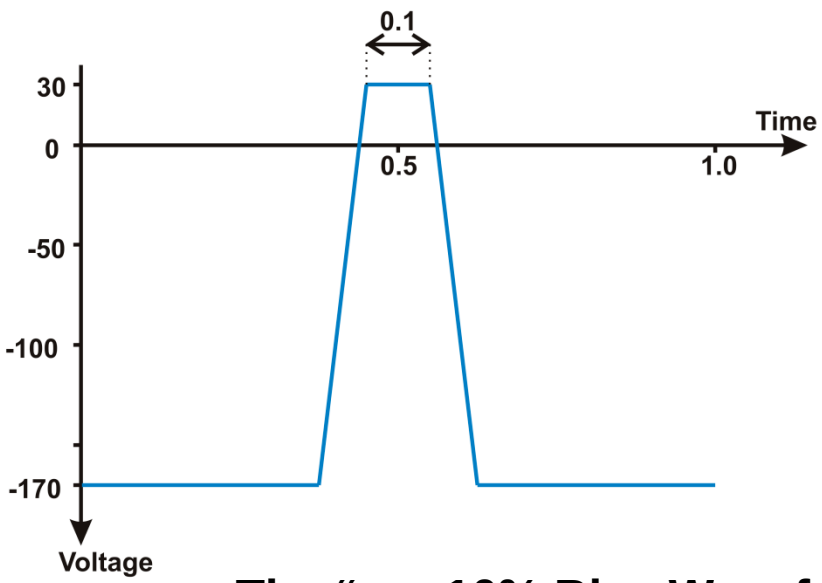
NON-SINUSOIDAL BIAS WAVEFORMS

- **Ions cross the sheath quickly compared to the rf period and arrive at wafer with nearly the instantaneous sheath voltage.**
- **By controlling the sheath potential with non-sinusoidal waveforms, one can control the IED.**

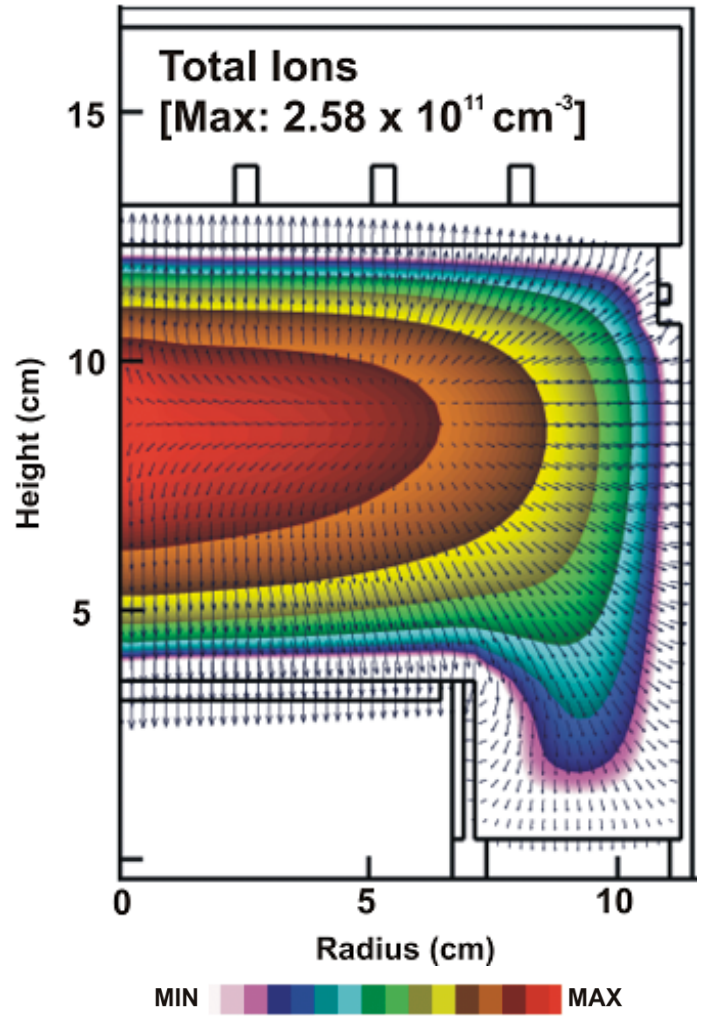


DEMONSTRATION SYSTEM: ICP, Ar/C_4F_8

- Investigate scalings using non-sinusoidal waveforms.
- ICP with rf bias.
  - Ar/C_4F_8 = 75/25, 100 sccm
  - 15 mTorr, 500 W
  - 200 V_{p-p}, 5 MHz



- The "α = 10% Bias Waveform



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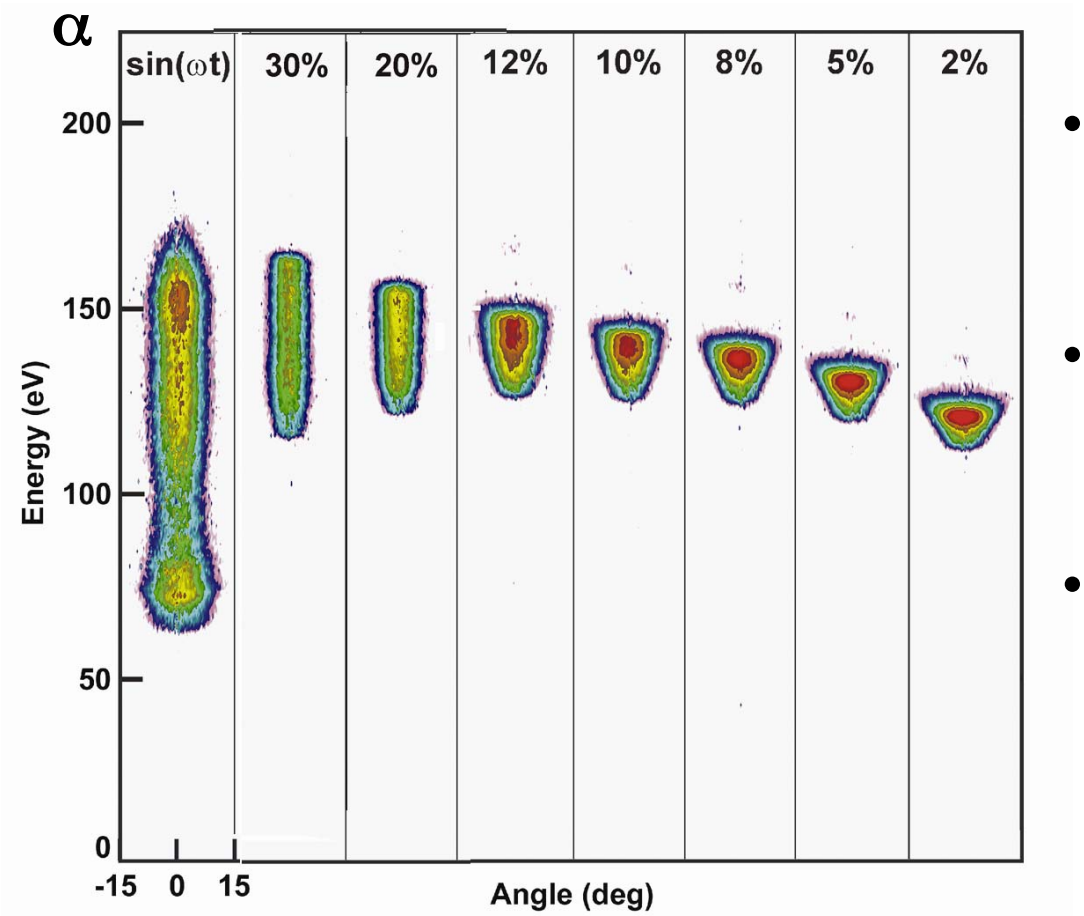
IEDs: DURATION OF POSITIVE SPIKE



V_{dc}: -73 -12 13 42 46 56 64 75

MIN MAX

- Custom bias produces constant sheath potential resulting in narrow IED.
- As α increases, IEDs broaden in energy and bias becomes less positive.
- 15 mTorr, 500 W, 5 MHz, 200 V_{p-p}, Ar/C_4F_8 = 75/25, 100 sccm

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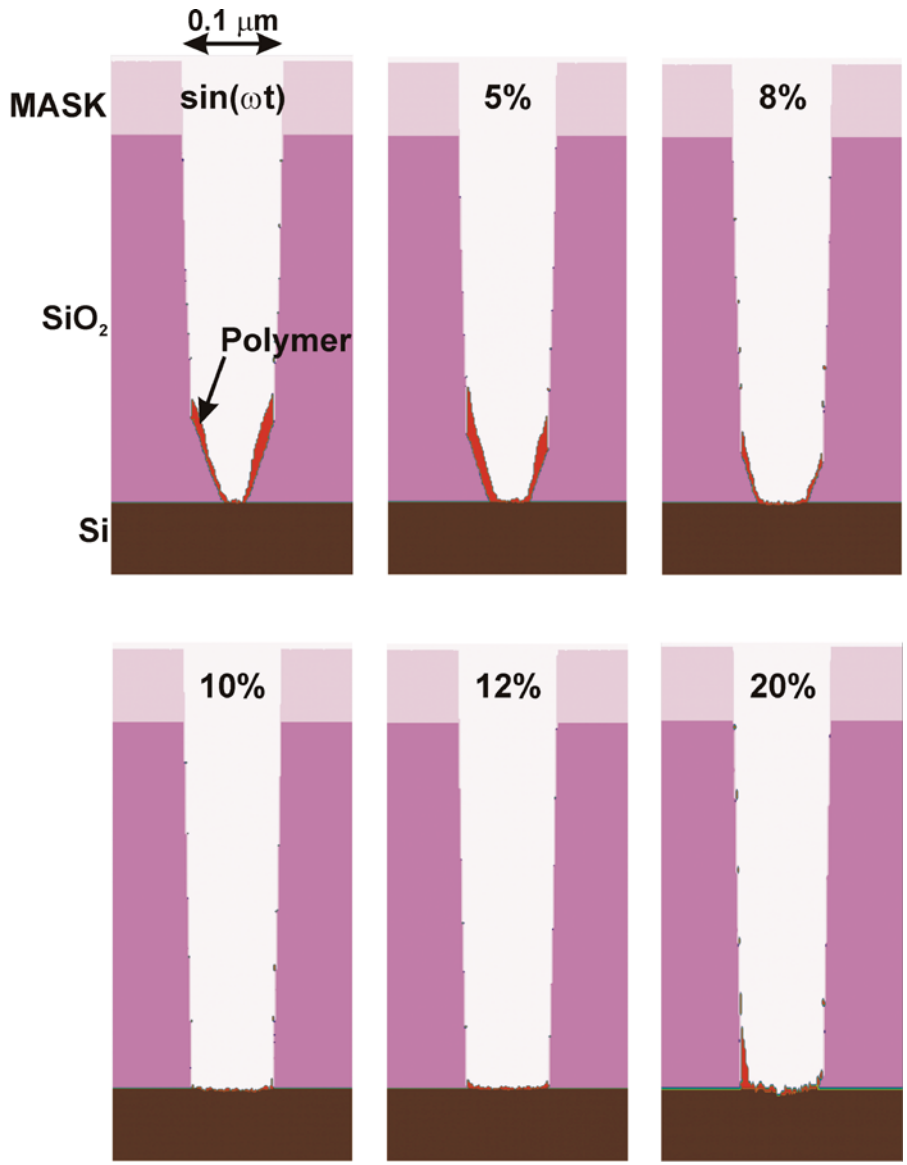
ETCH PROFILES vs α (POSITIVE EXCURSION)



- While keeping voltage constant, etch profile can be controlled by varying α.
- Small values of α produce an etch stop by promoting polymerization as does sinusoidal bias.
- Increasing α recoups critical dimension.
- 15 mTorr, 500 W, Ar/C_4F_8 = 75/25, 100 sccm

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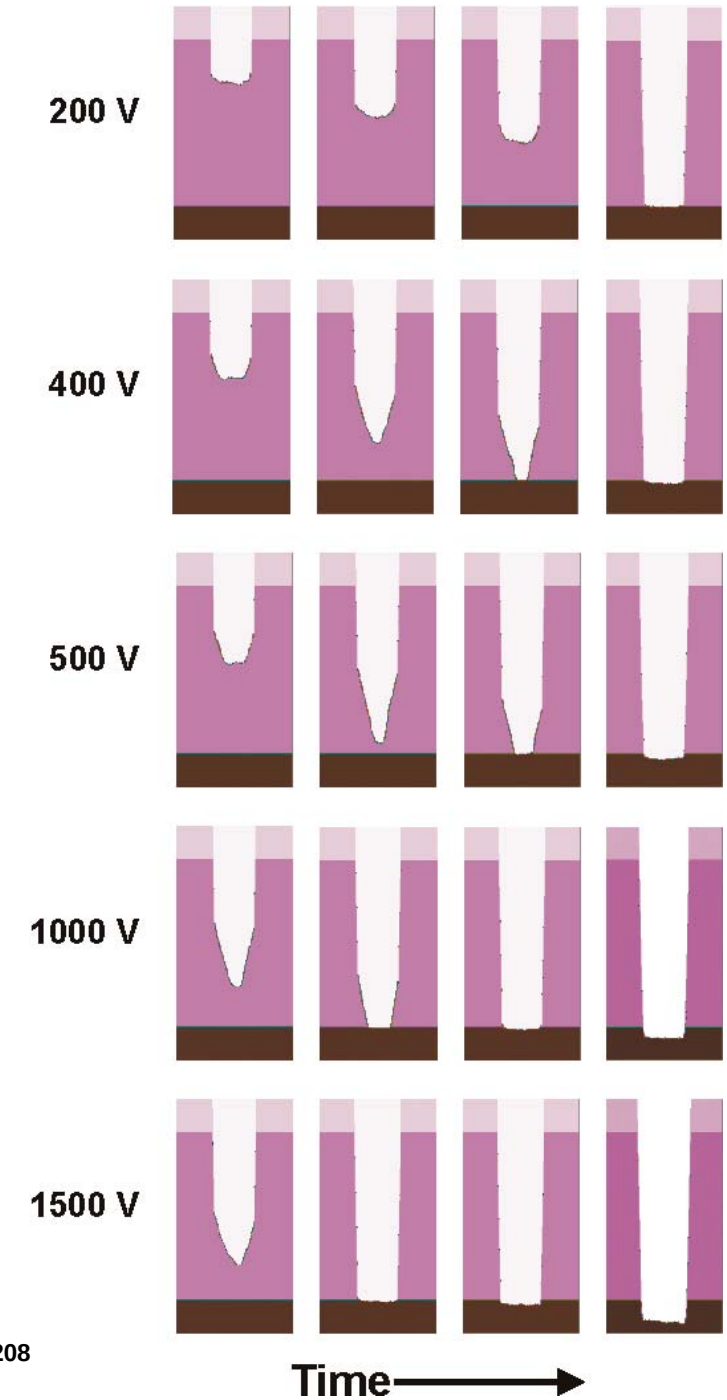

ETCH PROFILES vs VOLTAGE

- With α constant and varying voltage, etching proceeds with nearly mono-energetic ions.
- Transition between "selective" and "fast" is unambiguous.
- Low voltage: Slow rates with high selectivity.
- High voltage: High rates with no selectivity.
- 15 mTorr, 500 W, Ar/C_4F_8 = 75/25, 100 sccm

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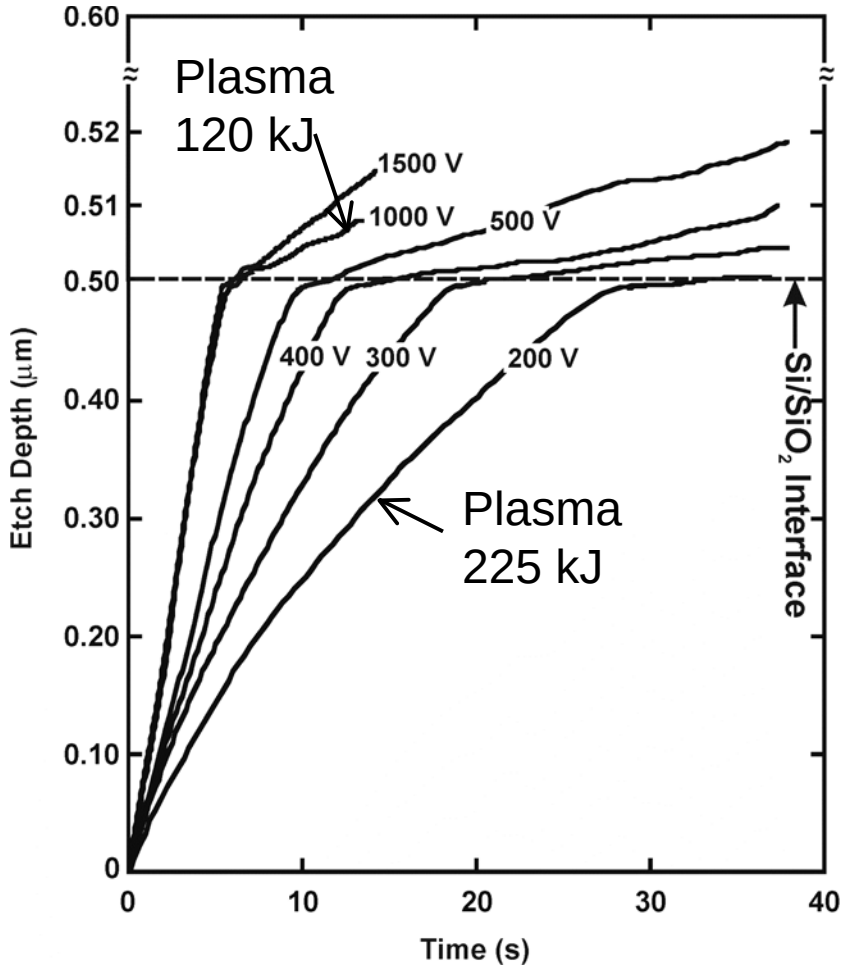
ETCH DEPTH vs VOLTAGE



- **Approaching the Si/SiO_2 interface with > 200 V bias compromises selectivity.**
- **Energy/wafer (plasma, pumps, heaters)**

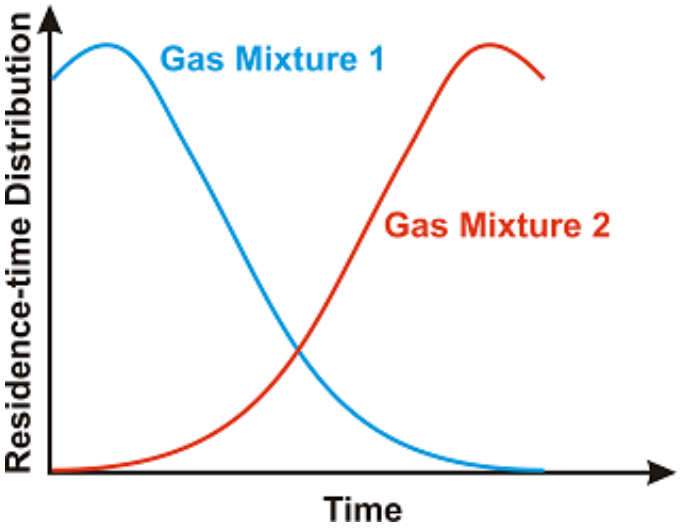
  1000 V Bias:
  240 kJ (fast-no selectivity)

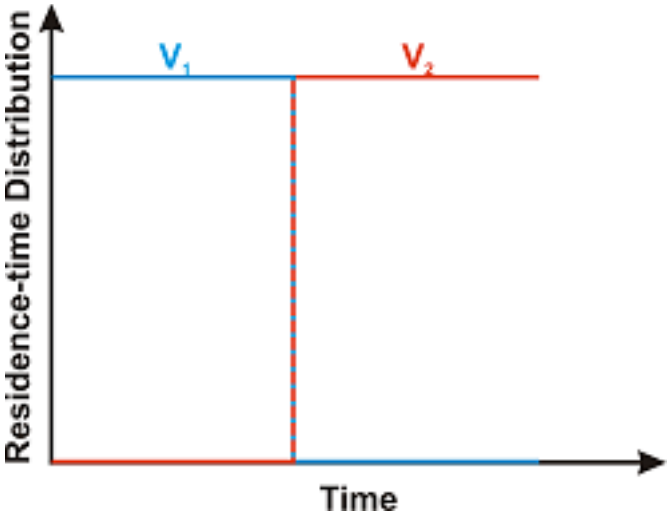
  200 V Bias:
  700 kJ (selective, energy intensive)

- **15 mTorr, 500 W, Ar/C_4F_8 = 75/25, 100 sccm**

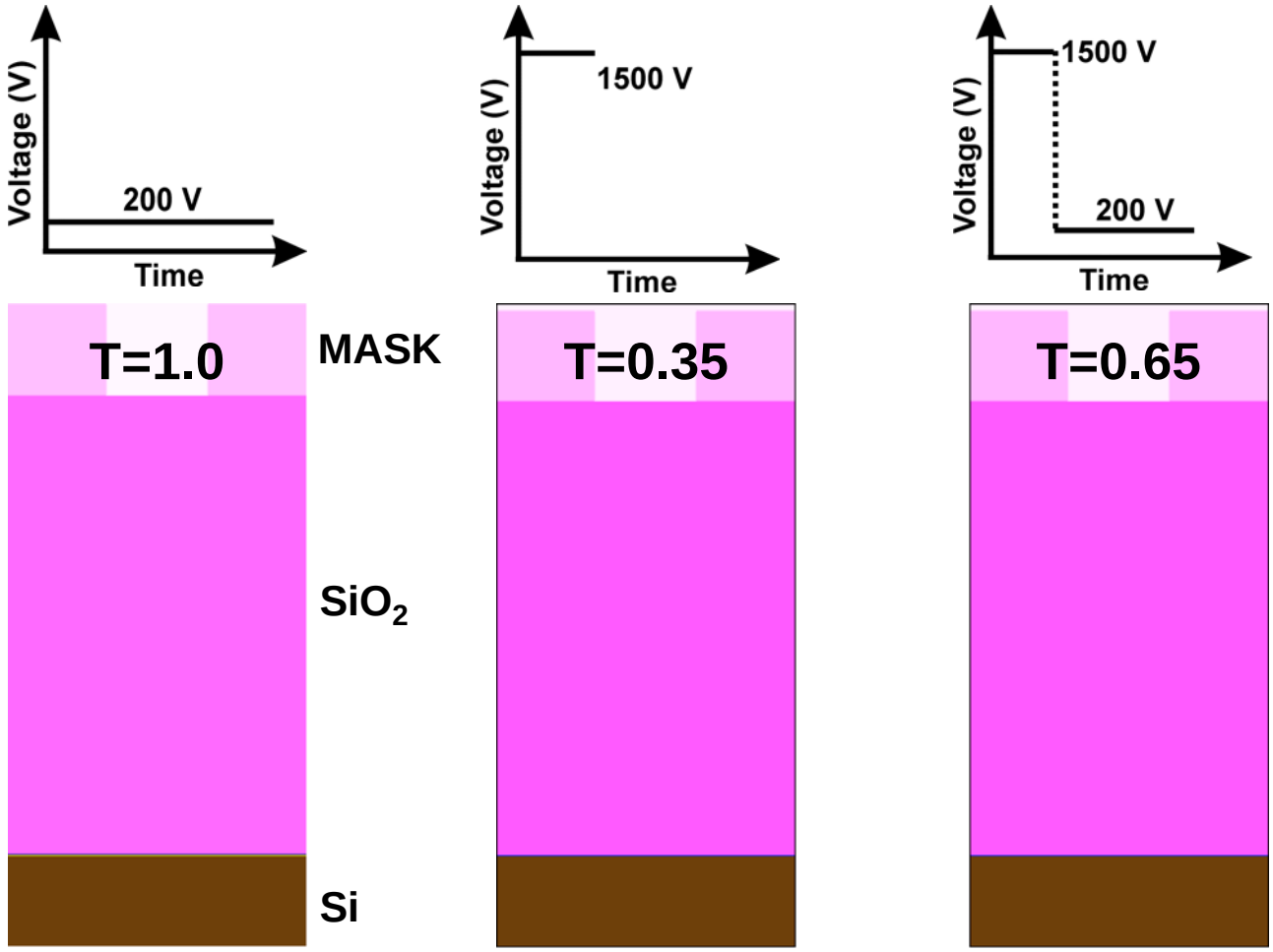
ETCHING RECIPES

- Etching usually occurs in 2 phases:
  - Main-etch: Fast but non-selective
  - Over-etch: Selective; Low bias
- Gas mixture is often changed to distinguish main and over-etch…slow due to gas exchange times.
- Custom tailored voltage waveform
  - Controlling physical component
  - Change amplitude – immediate control





ETCHING PROFILES – RECIPE

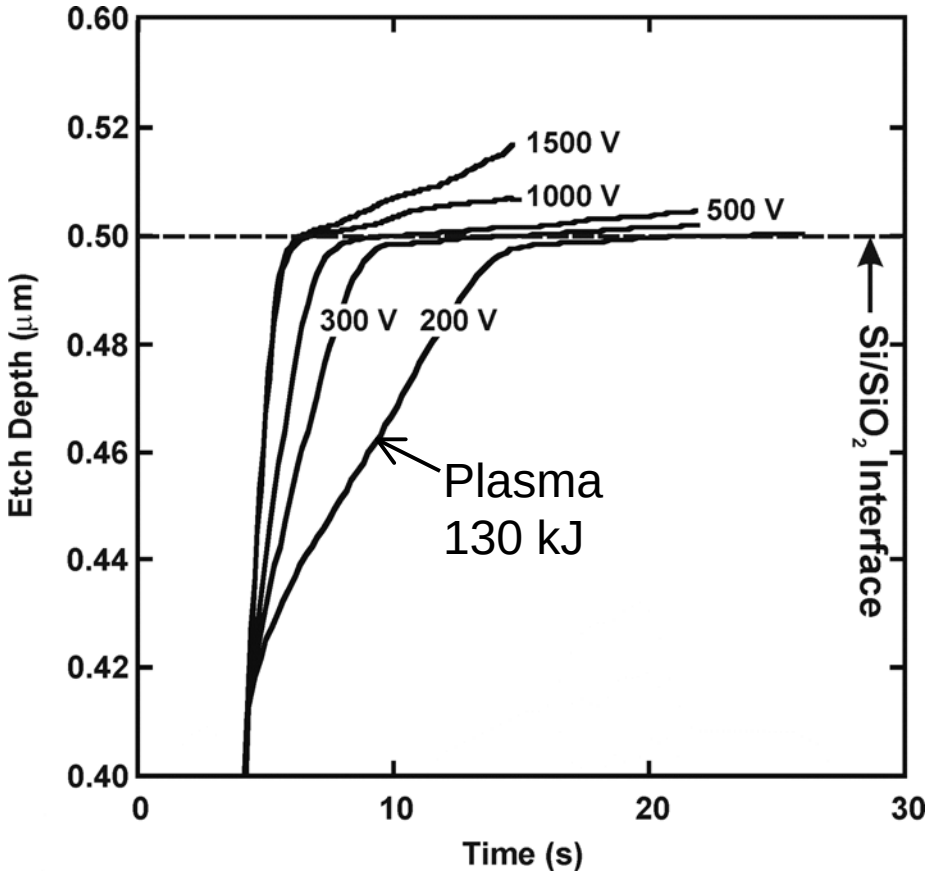


200 V
(Slow, selective)

1500 V
(Fast, non-selective)

1500/200 V
(Fast, selective)

ETCHING RECIPES: 1500 V MAIN ETCH



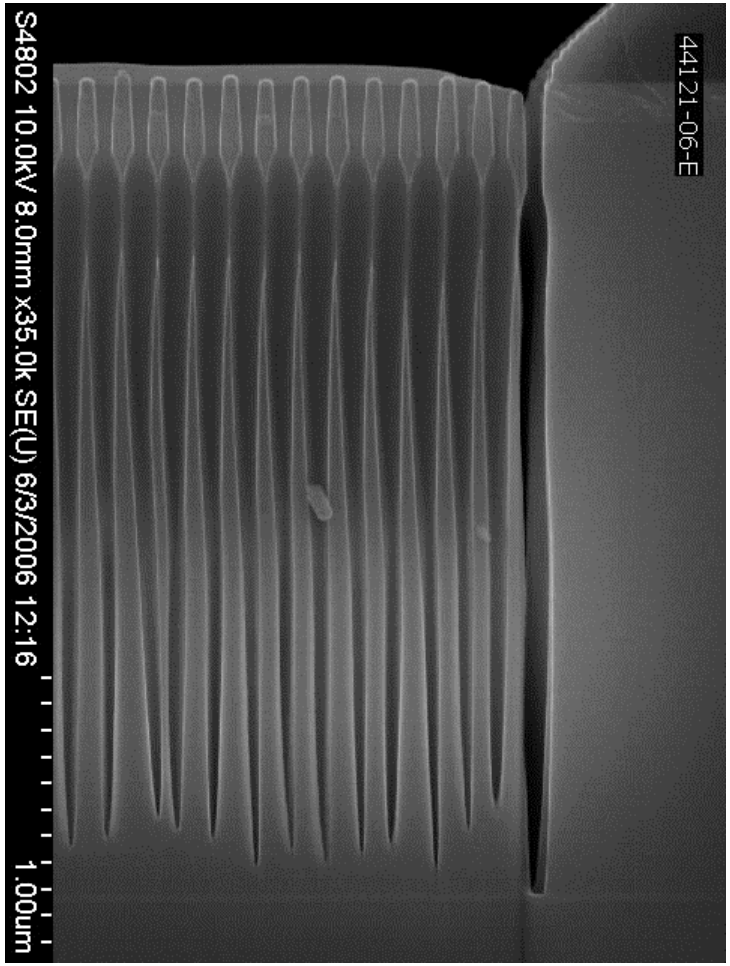
- **Etching proceeds rapidly with a 1500 V main etch.**
- **After 4.5 s, the voltage is reduced to maintain selectivity.**
- **"Soft landing"**
- **Energy/wafer (plasma only) for selective etches**

  200 V (cw) Bias: 700 kJ
  1500V / 200 V Bias: 370 kJ

- **15 mTorr, 500 W, Ar/C_4F_8 = 75/25, 100 sccm**

HIGH ASPECT RATIO CONTACT (HARC) ETCHING

- **Processes for HARC etching with aspect ratios > 50-100 are being developed for capacitors and through wafer vias.**



- **Very Challenging…**
- **Twisting or curvature of features is randomly observed.**
- **Features are so small that random fluctuations of fluxes of radicals, ions and electrons produces variations.**
- **Charging of features by electrons and ions produce random fields that deviate paths.**

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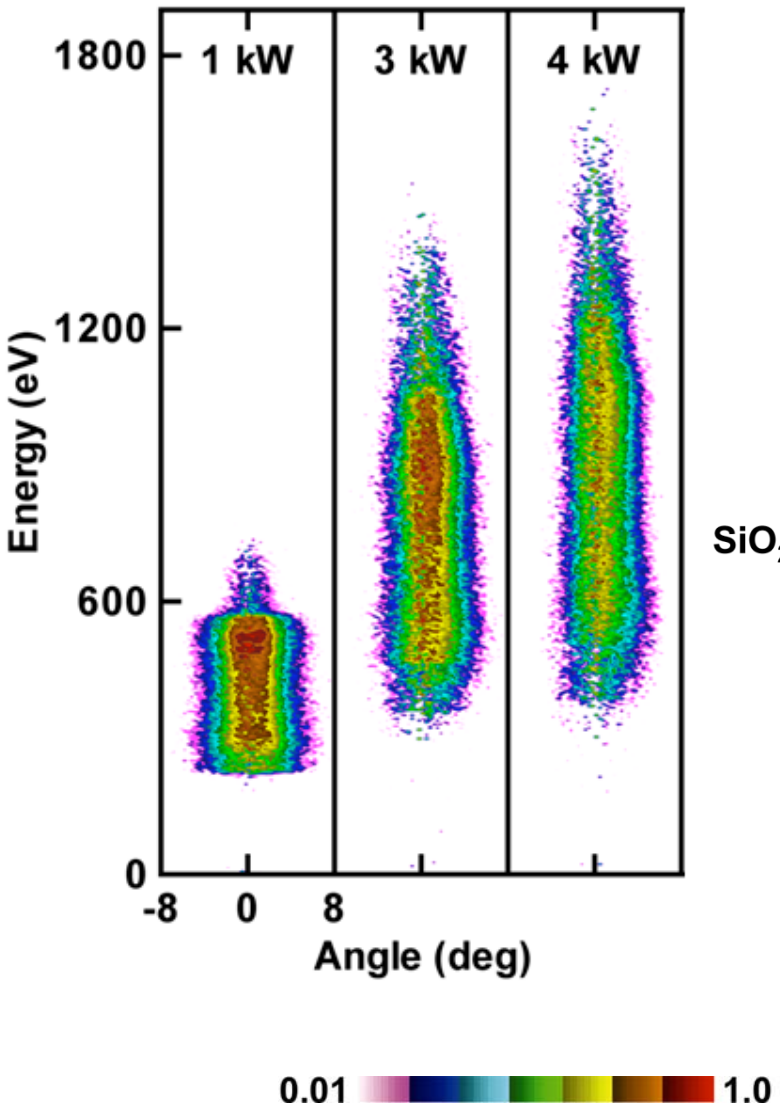
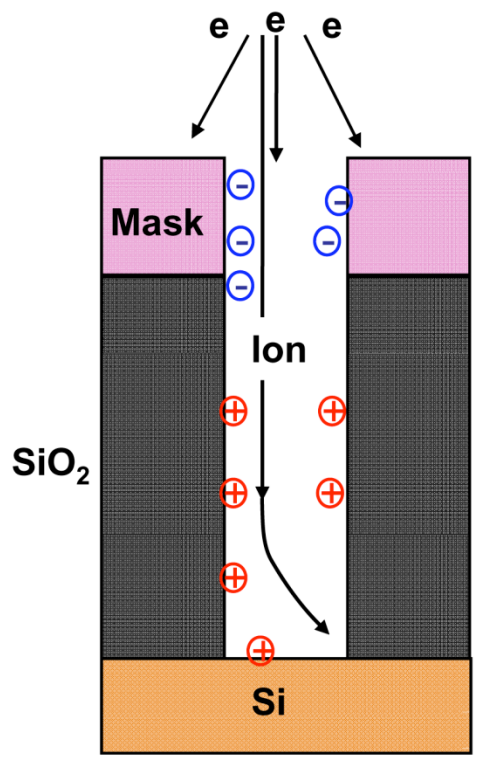
DUAL FREQUENCY CCP $Ar/C_4F_8/O_2$: CHARGING





- High energy ions are required for rapid etching.
- Electrons and ions deposit charge in the trench, producing E-fields that affect trajectories.
- Randomness of charging leads to erratic paths.
- 10 mTorr, $Ar/C_4F_8/O_2$ = 80/15/5, 10/40 MHz, 500 W.

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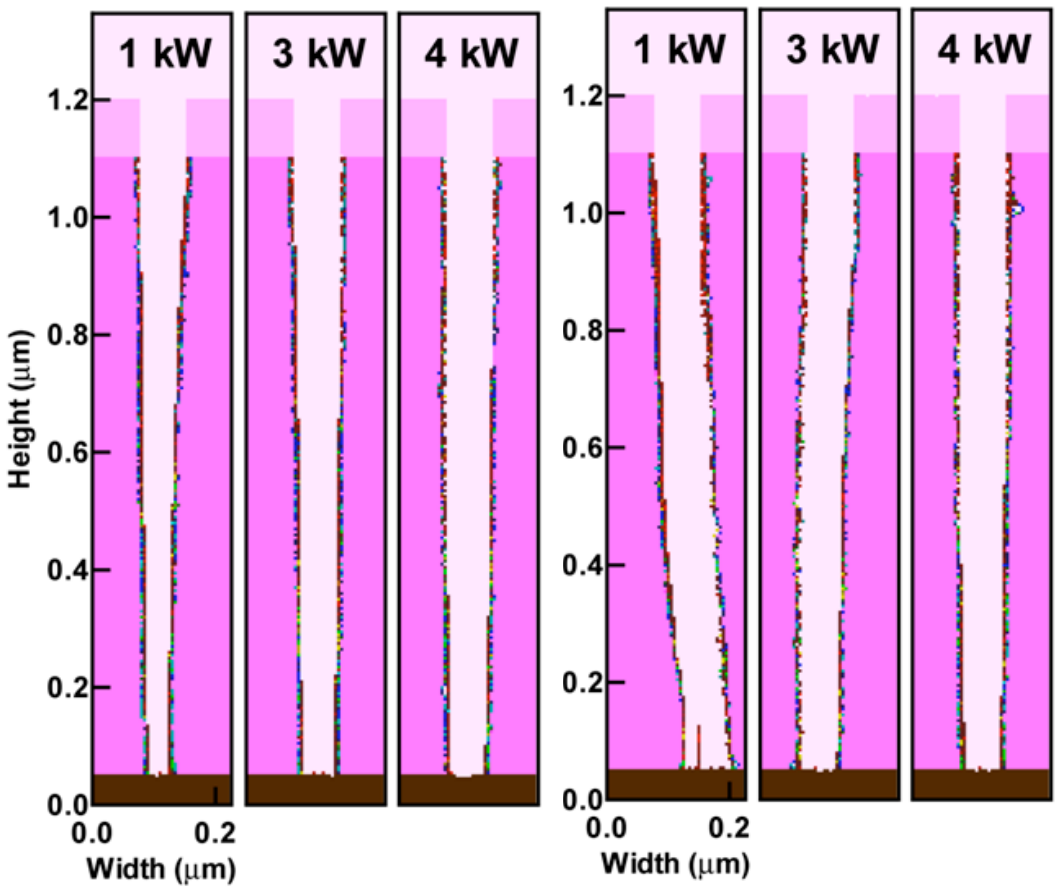
SiO_2 / Si HARC ETCH: EFFECTS OF CHARGING



- Without Charging
- With Charging

- Etch rate higher with increasing power.
- Without charging:
  - Generally straight profiles.
- With charging:
  - Ion trajectories perturbed.
  - Overcome with voltage.
- Some evidence of randomness due to small contact area.
- 10 mTorr, $Ar/C_4F_8/O_2$ = 80/15/5, 10/ 40 MHz, 500 W.

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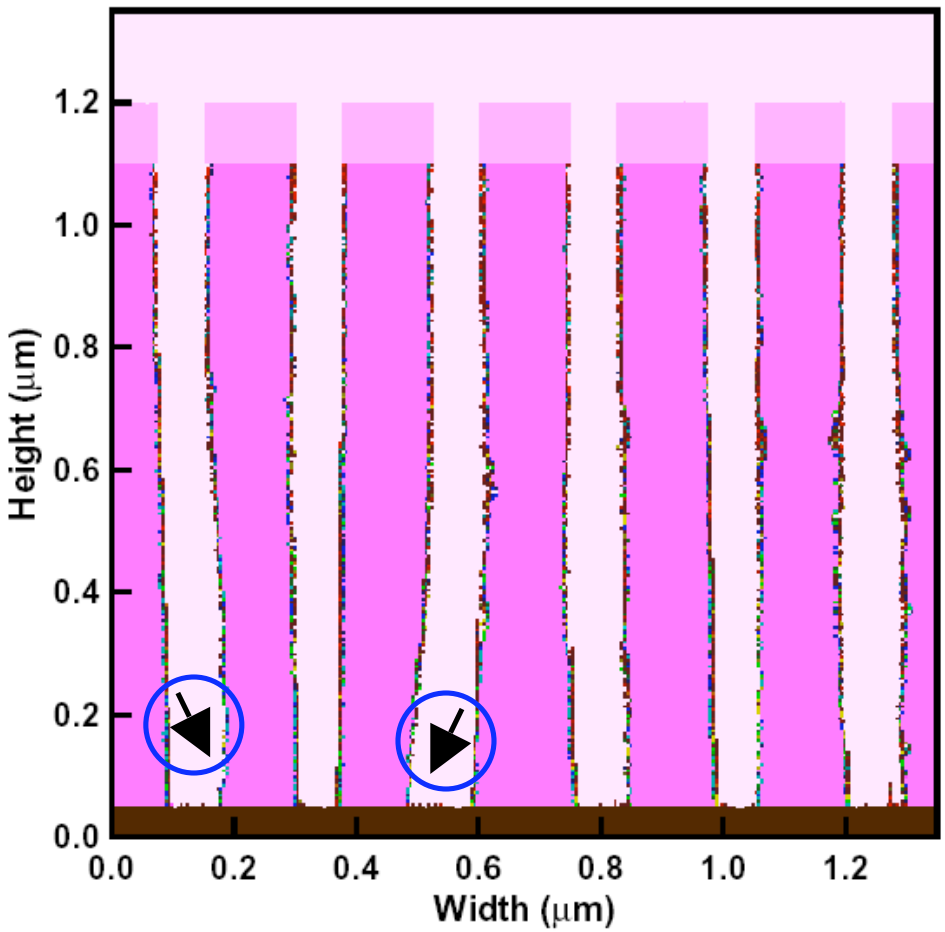
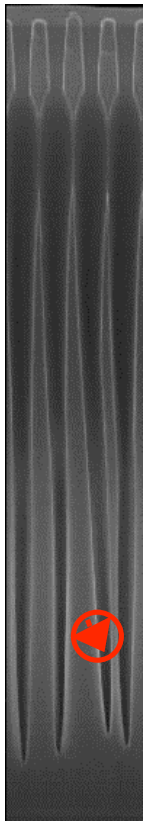
SiO_2/Si HARC ETCH: RANDOMNESS OF CHARGING?





- 6 Trenches receiving "same" fluxes.
- Stochastic nature of fluxes produces random twisting.
- Similar behavior observed experimentally.
- Effect is amplified by finite size of particles and mesh.
- 10 mTorr, $Ar/C_4F_8/O_2$ = 80/15/5, 300 sccm, LF 4 kW, HF 500 W.

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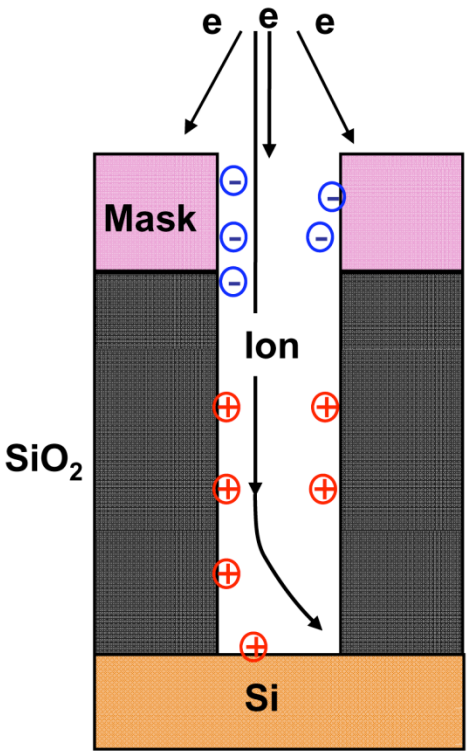
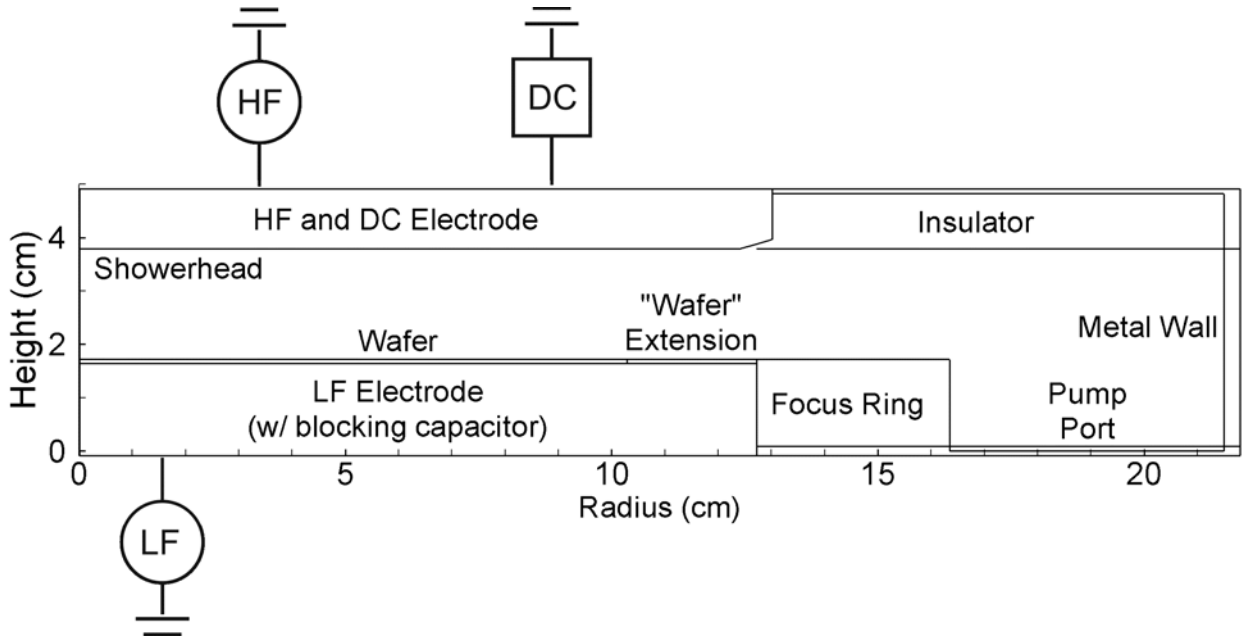
IS THERE A FIX? DC-AUGMENTED RF

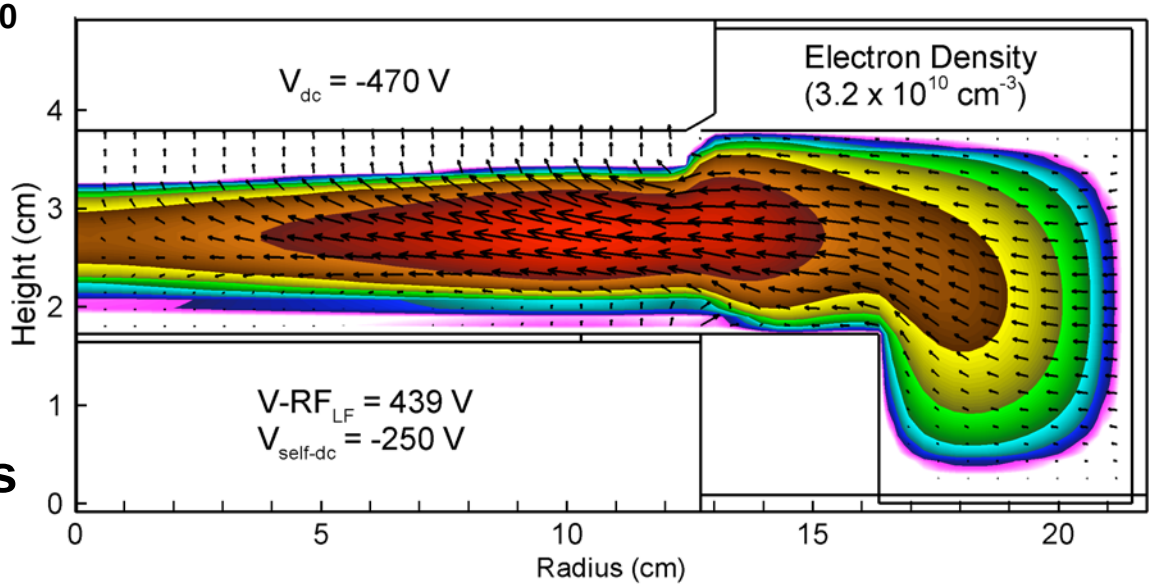




- **Single (or dual) frequency CCP…with negative dc bias on opposing electrode.**
- **DC ion current produces dc e-beam current incident onto wafer.**
- **Can dc e-beam be mono-energetic and narrow enough in angle to penetrate deep into features and neutralize positive charge?**

10 MHz LOWER, DC UPPER: [e] DENSITY, DC CURRENT

- Electron density 3 x 10^{10} cm^{-3}.
- Dc voltage on upper electrode requires dc current path to ground.
- LF electrode blocking capacitor and insulators require dc current returned to side wall.



- Dc current peaks near outer edge of electrode.
- Ar, 40 mTorr, LF: 10 MHz, 300 W, 440V/dc=-250V
- DC: 200 W, -470 V

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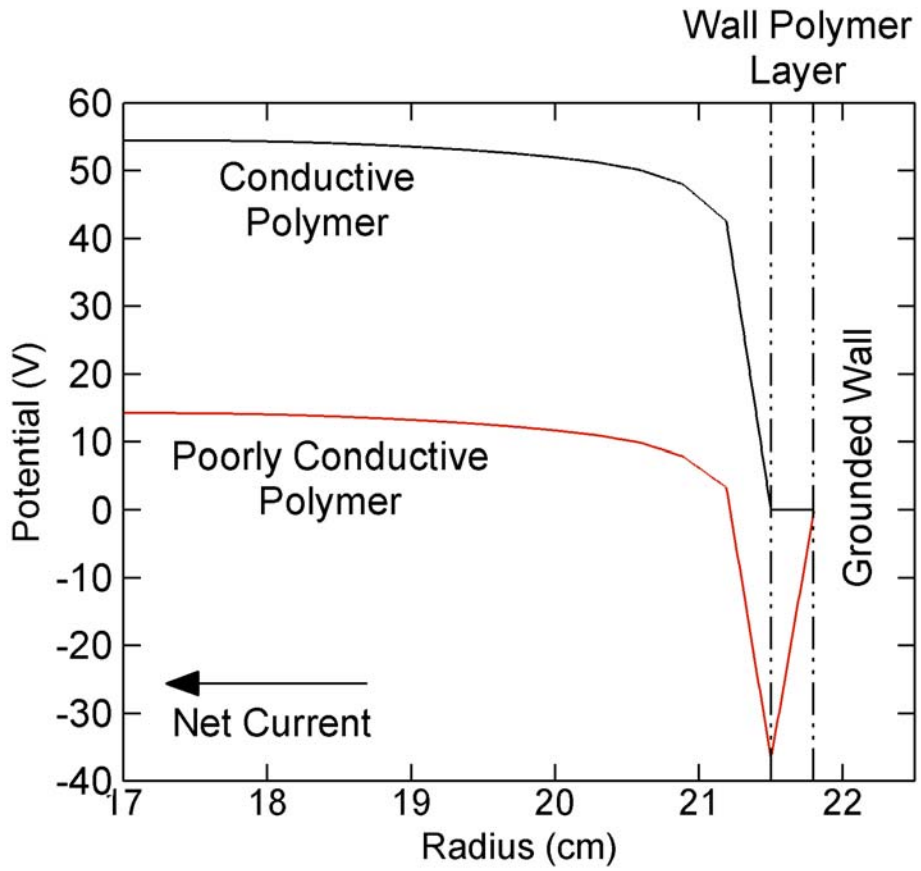
10 MHz LOWER, DC UPPER: POLYMERIZATION

- Polymerizing gas mixtures deposit insulating films on inside surfaces of reactor.
- Dc current must return to ground through polymer layers.
- Voltage drop increases across polymer layer to push through current.



- Ar, 40 mTorr, LF: 10 MHz, 300 W, 440V/dc=-250V
- DC: 200 W, -470 V

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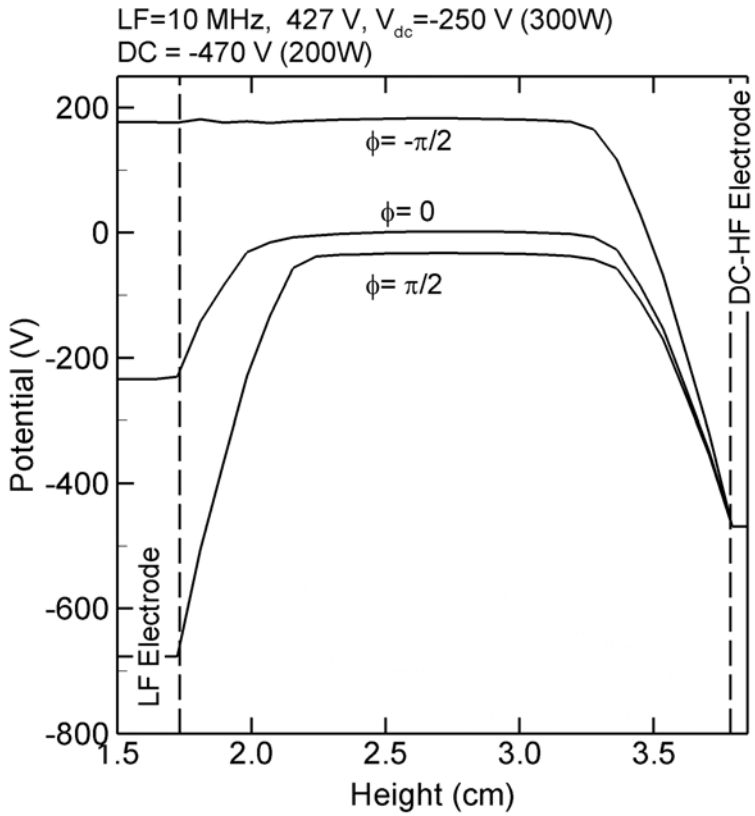
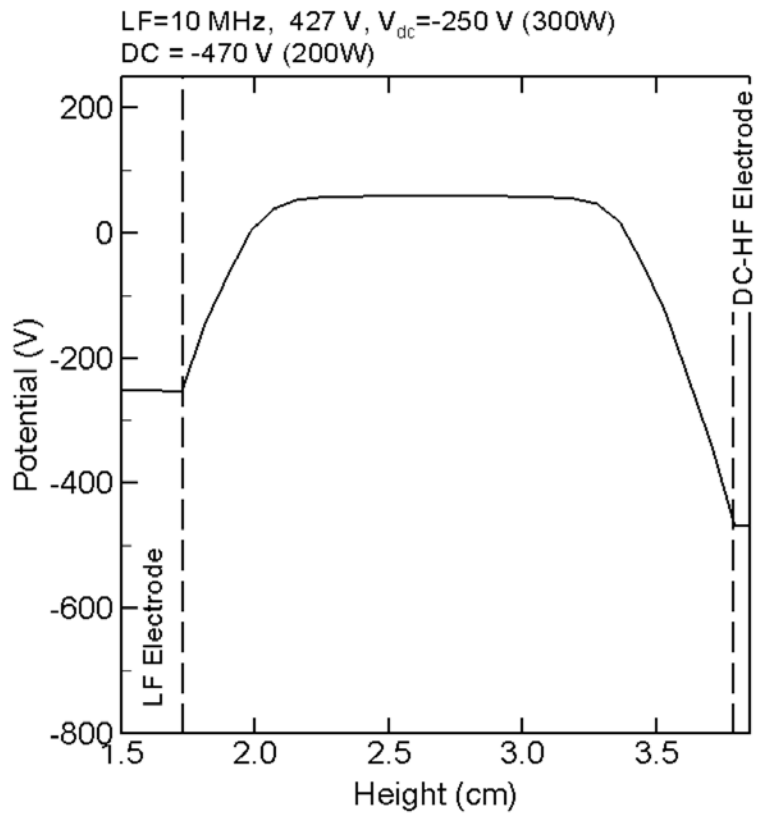
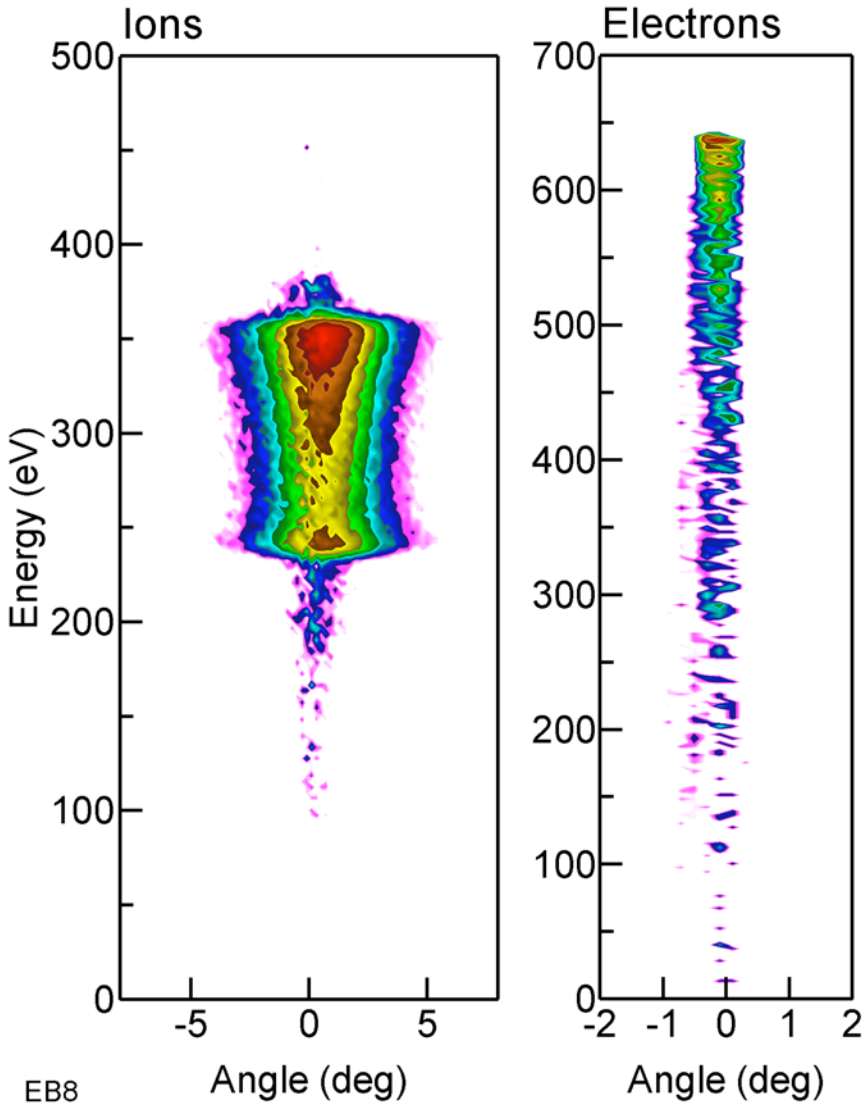
10 MHz LOWER, DC UPPER: PLASMA POTENTIAL





- **LF electrode passes rf current. DC electrode passes combination of rf and dc current with small modulation of sheath potential.**
- **Ar, 40 mTorr, LF: 10 MHz, 300 W, 440V/dc=-250V**
- **DC: 200 W, -470 V**

10 MHz LOWER, DC UPPER: [e], ION ENERGY DISTRIBUTIONS



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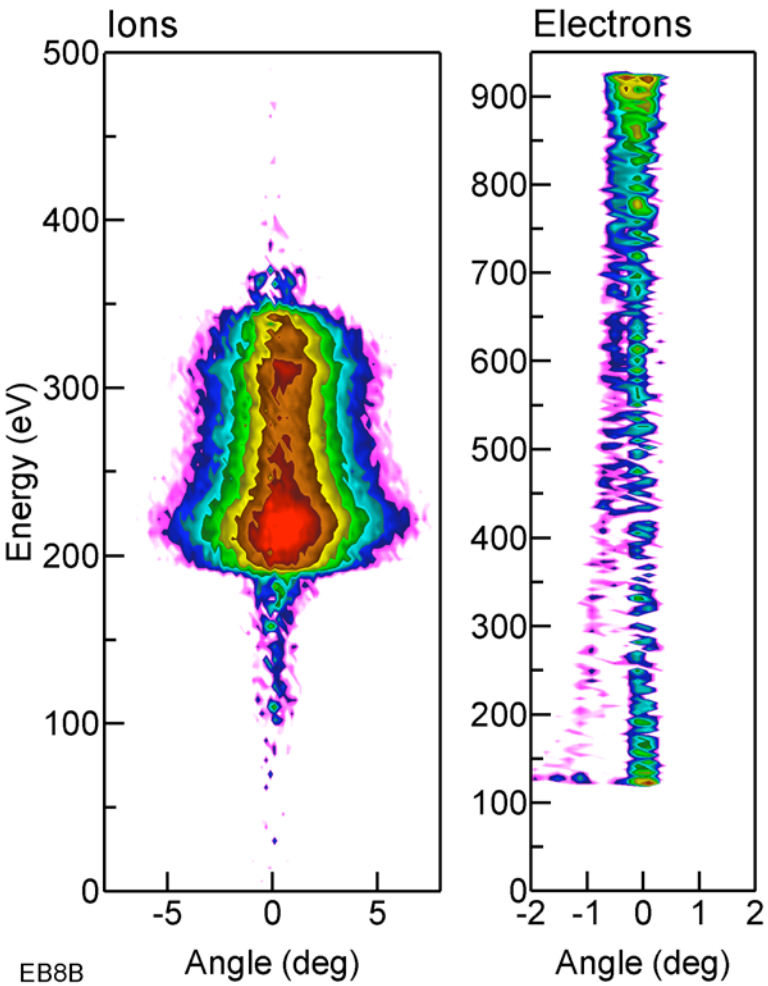
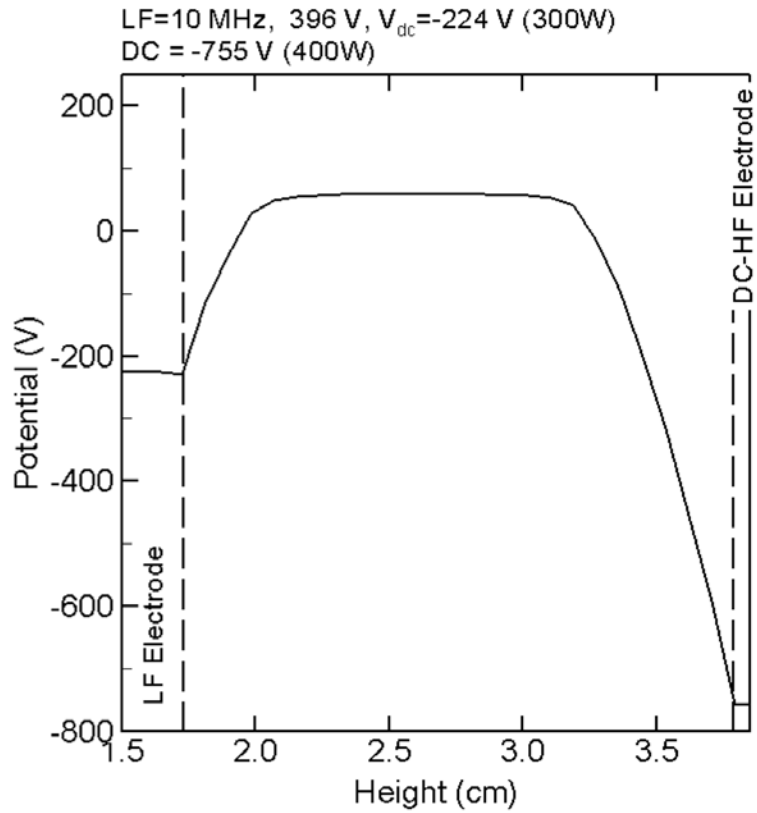
- Ion energy distribution to wafer is many degrees, 150 eV in width.
- Electron energy distributions onto wafer is narrower in angle and broader in energy.
- Reflects instantaneous potential difference between electrodes.
- Ar, 40 mTorr, LF: 10 MHz, 300 W, 440V/dc=-250V; DC: 200 W, -470 V

400 W DC: [e], ION ENERGY DISTRIBUTIONS





- **Increasing dc power extends range of electron energies incident on the wafer while also perturbing IEAD.**
- **Thicker sheath produces non-planar components that lead to angularly asymmetric electron fluxes.**
  - **Ar, 40 mTorr, 10 MHz, 300 W, 396V/dc=-224V; DC: 400 W, -755 V**

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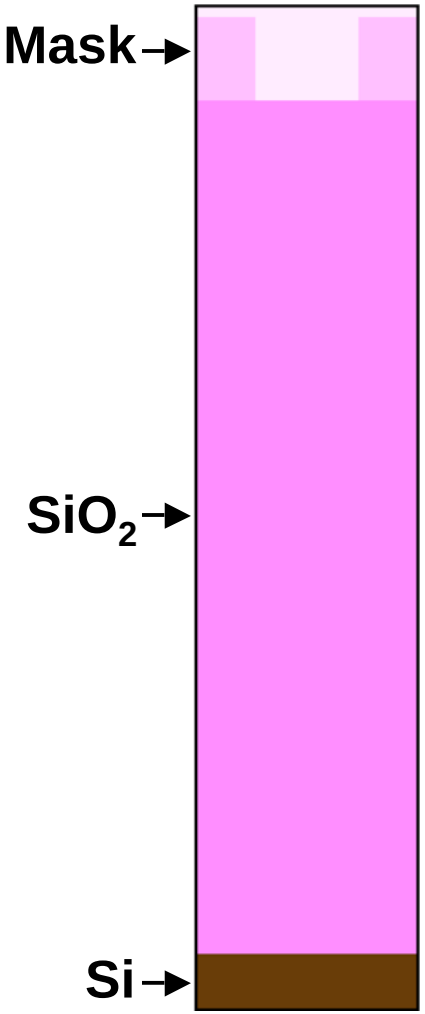
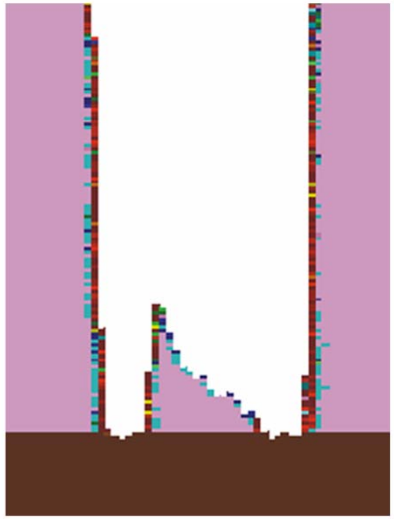
ANOTHER HARC CHALLENGE: MICRO-TRENCHING



Aspect Ratio = 1:10



Before
Over-etch

- As aspect ratio increases, more reflection of ions off side walls.
- Micro-trenching due to specular reflection.
- SiO_2 remains when underlying Si is exposed….over-etching is required.
- How do you maintain critical dimension?
- Ar/C_4F_8 = 75/25, 100 sccm, ICP, 15 mTorr, 500 W, 100 V at 5 MHz

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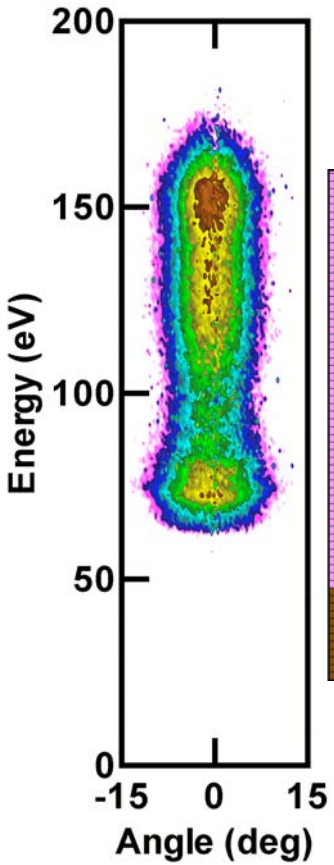
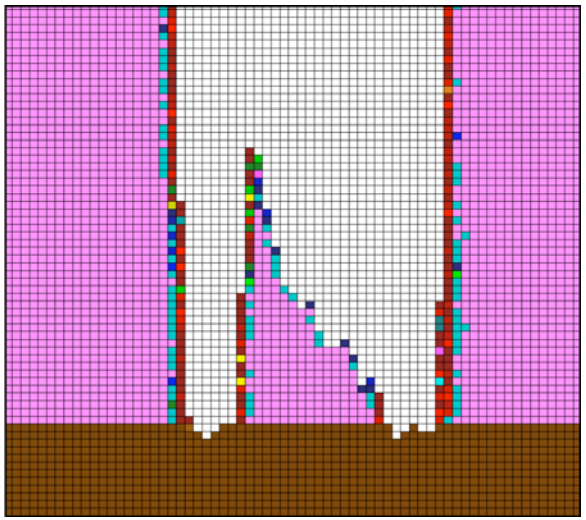
NON-SELECTIVE SINUSOIDAL BIAS





- Over-etch is used to clear out the remaining SiO_2.
- Conventional etching using a sinusoidal waveform does not have enough selectivity.
- Atomic layer resolution is required.
- Ar/C_4F_8 = 75/25, 100 sccm, ICP, 15 mTorr, 500 W, 100 V at 5 MHz

Aspect Ratio = 1:10

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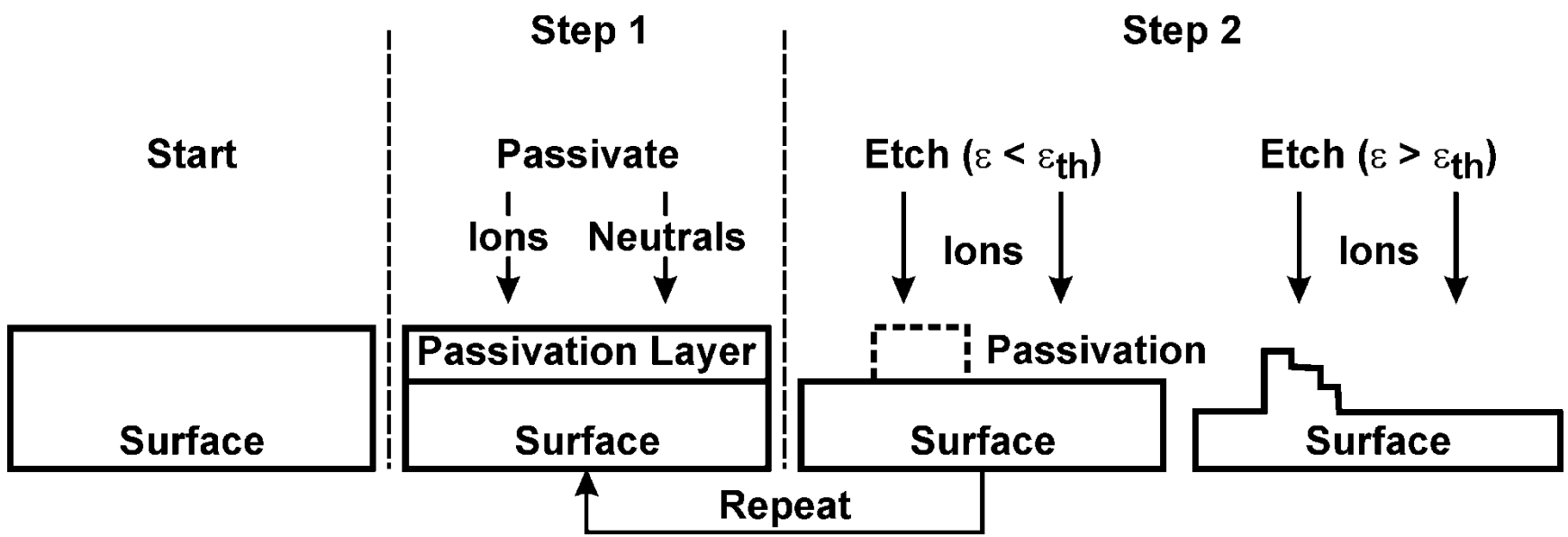
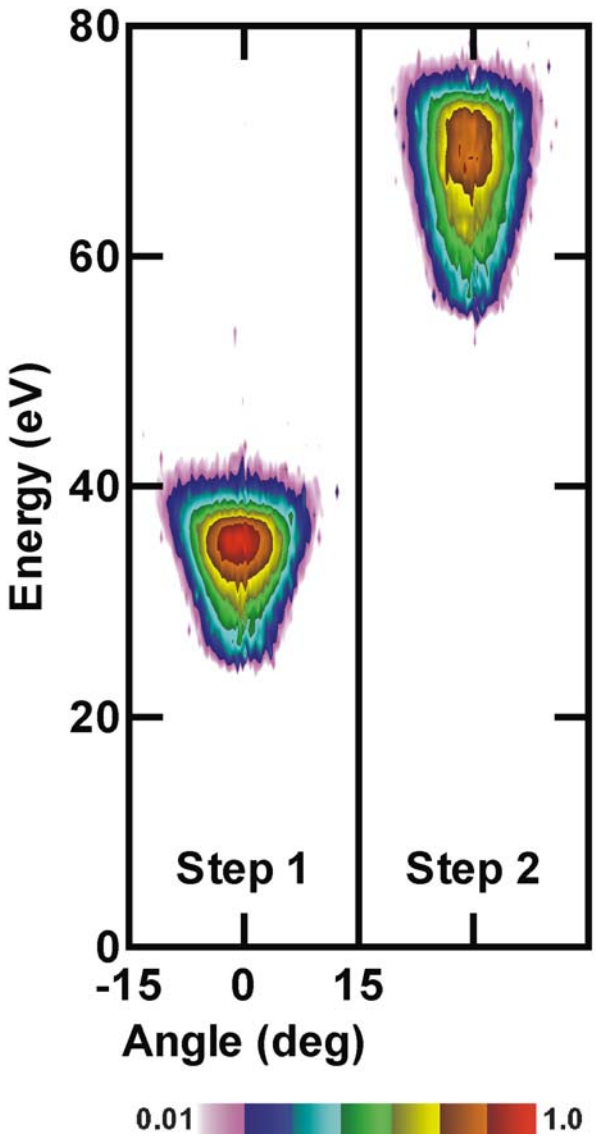
PLASMA ATOMIC LAYER ETCHING

- In Plasma Atomic Layer Etching (PALE), etching occurs monolayer by monolayer in a cyclic, self-limiting process.
  - Top monolayer is passivated in non-etching plasma in first step.
  - Second step removes top layer (self-limiting)
- Extreme control of energies to prevent erosion of the under-layer.



Ar/*c*-C_4F_8 TAILORED BIAS PALE: IEADs



- PALE of SiO_2 using ICP Ar/C_4F_8 with variable non-sinusoidal bias.
- Step 1
  - $V_{p\text{-}p}$ = 50 V
  - Passivate single layer with $SiO_2C_xF_y$
  - Low ion energies to reduce etching.
- Step 2
  - $V_{p\text{-}p}$ = 100 V
  - Etch/Sputter $SiO_2C_xF_y$ layer.
  - Above threshold ion energies.
- Narrow IEADs discriminate between threshold energies.
- Ar/C_4F_8 = 75/25, 100 sccm, 15 mTorr, 500 W

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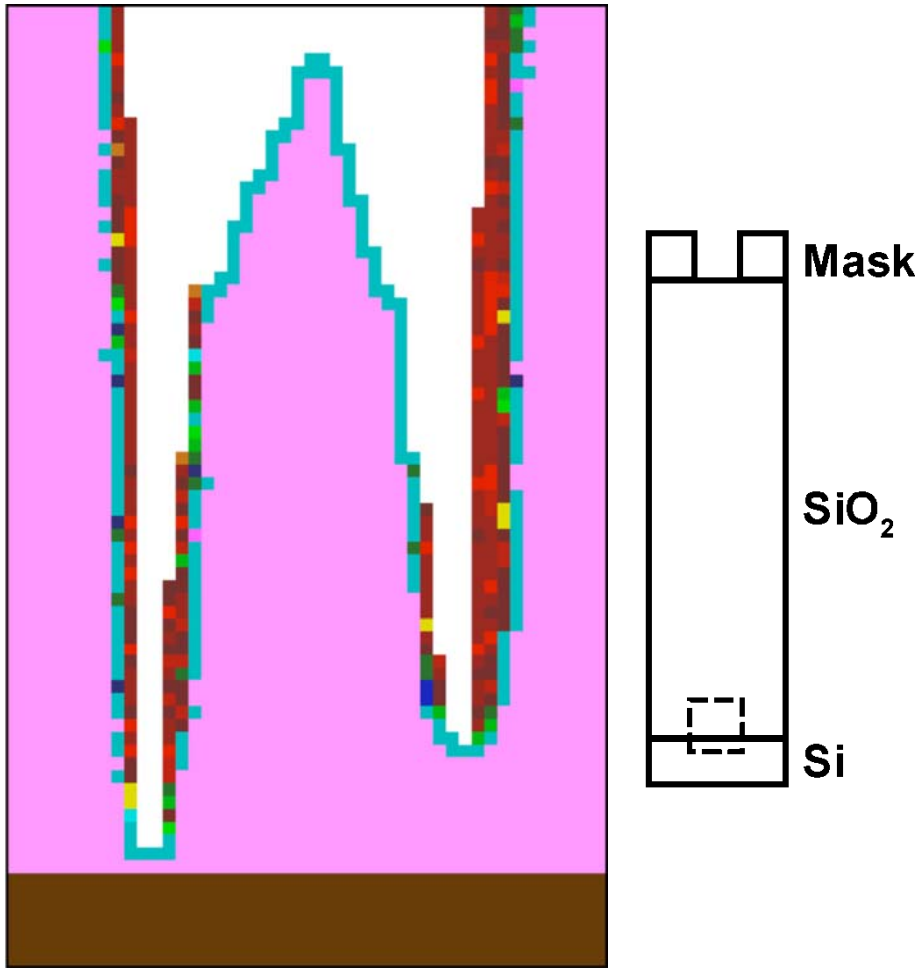
TAILORED BIAS PALE: EXTENDED OVER-ETCH

- PALE is used for over-etch.
- Extreme selectivity of PALE enables removal of SiO_2 without damage to underlying Si.
- 15 cycles of PALE over-etch clears the feature.
- More energy intensive per layer than conventional etching.
- Future technology nodes will be challenged to maintain lower J/cm^2 of wafer.



- 15 cycles of PALE

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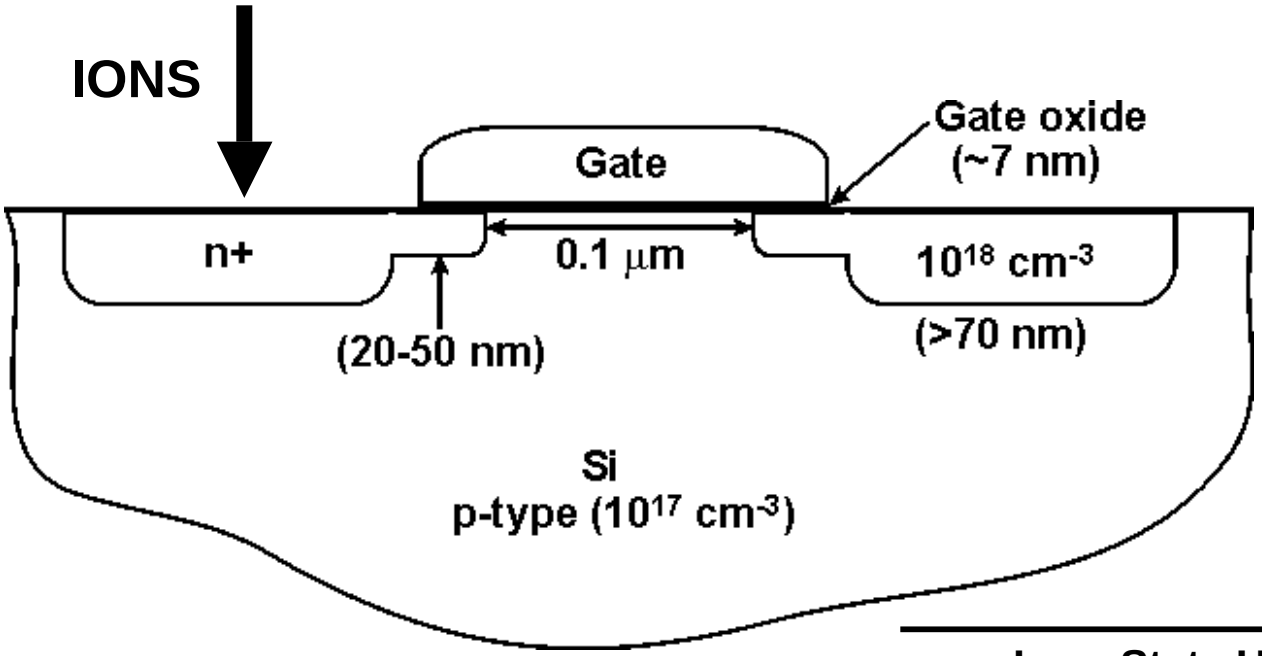
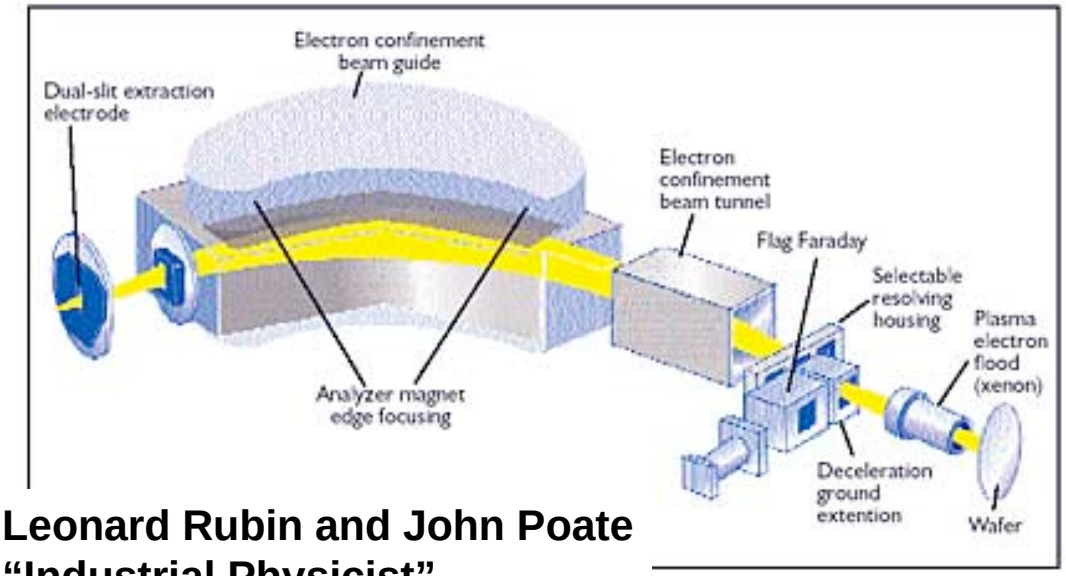
EQUIPMENT DESIGN MATTERS: CONTROLLING SHAPES OF IEADS FOR PLASMA ION IMPLANTATION

CMOS: COMPLEMENTARY METAL OXIDE SEMICONDUCTOR

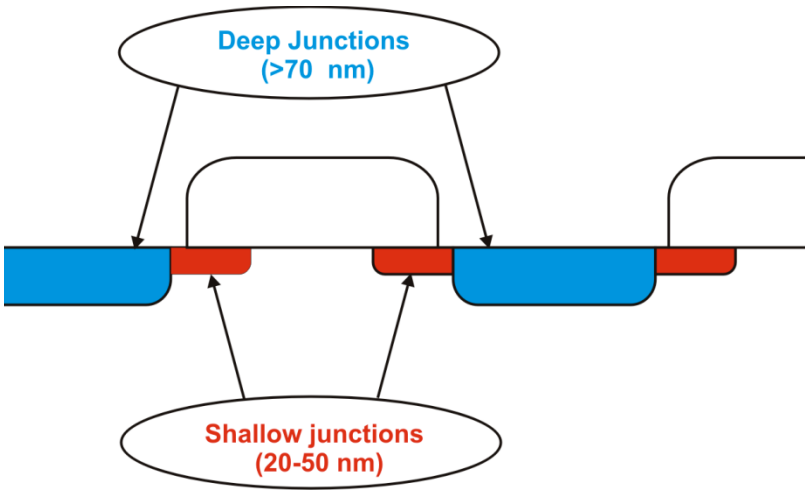
- **Highly doped n-type source and drain produced by ion implantation.**
- **n-type channel created in p-type substrate by "inversion" of substrate with bias on gate.**
- **To achieve small channel dimensions ion implantation to make source and drain must be shallow.**



ION IMPLANTATION

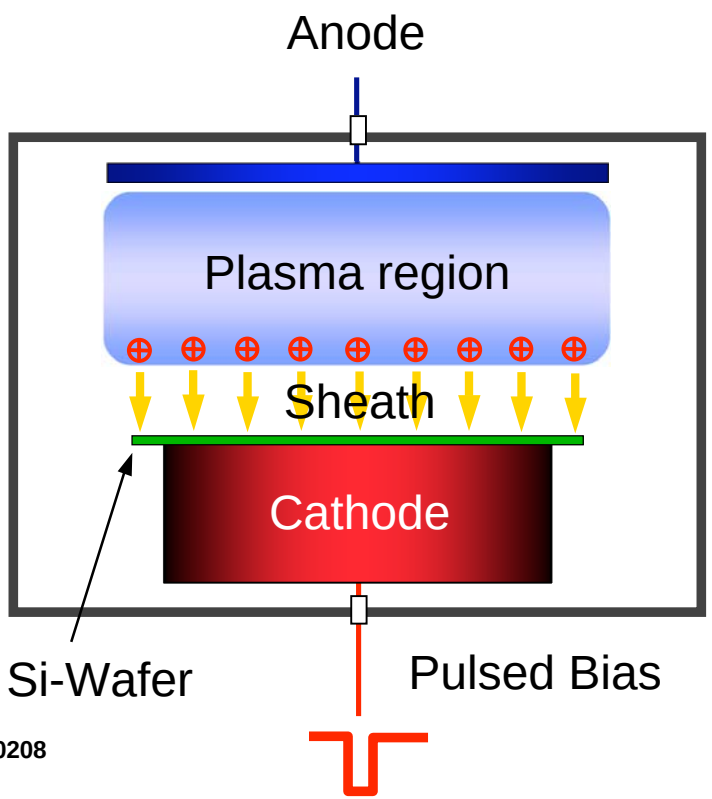


Leonard Rubin and John Poate
"Industrial Physicist"



- **Beam-line ion implantation (100s keV) techniques are used for depths > 100s nm.**
- **Ideally for ultra-shallow junctions (20-50 nm), dopant ions should have energies < 500 eV.**
- **Difficult to scale beam implantation to low energies and high currents.**
- **High power use (coils for magnets).**

PULSED PLASMA DOPING (PLAD)



- PLAD is a pulsed plasma technique for low energy ion implantation.
- The substrate is pulsed negative to the desired implant voltage.
- Ions are extracted from the plasma, accelerated across the sheath and implanted into the wafer.
- High throughput at low energies.
- Small footprint of tool…energy efficient…how to optimize?

Ref: VSEA ICOPS 2002

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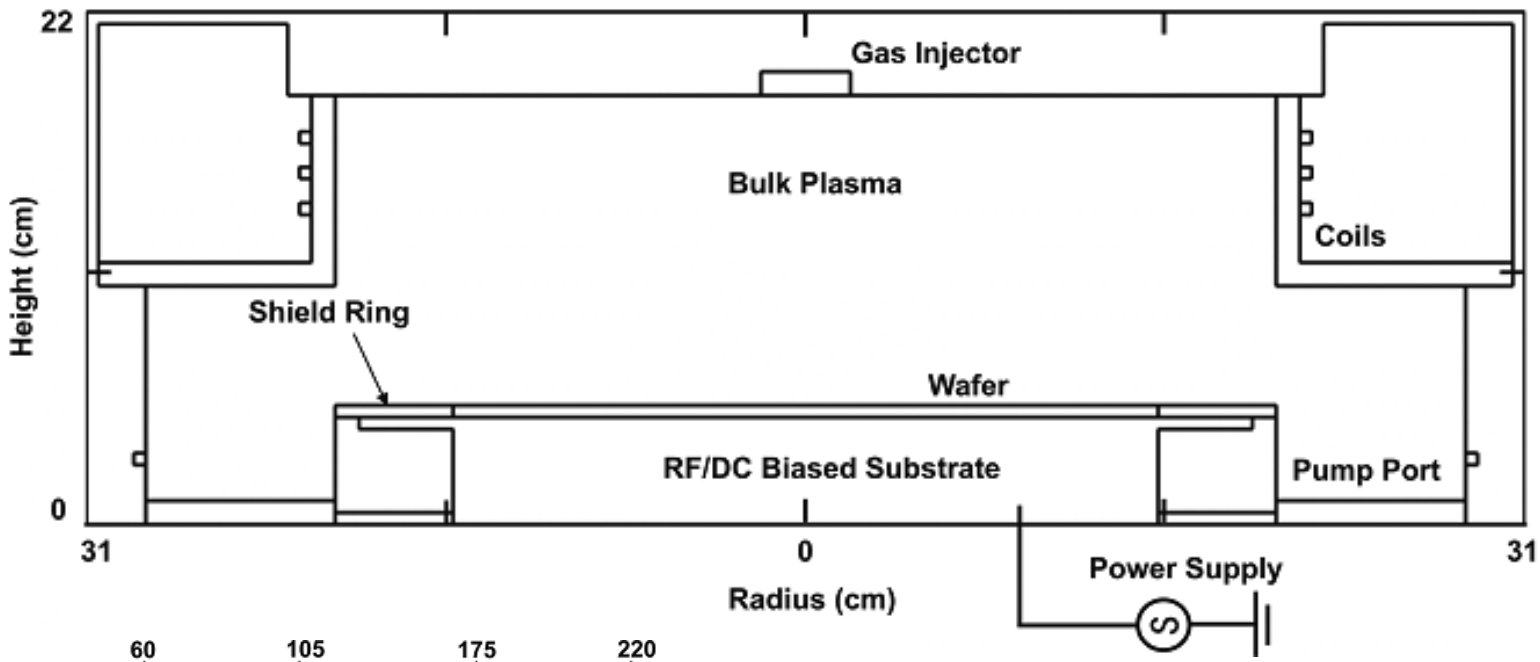
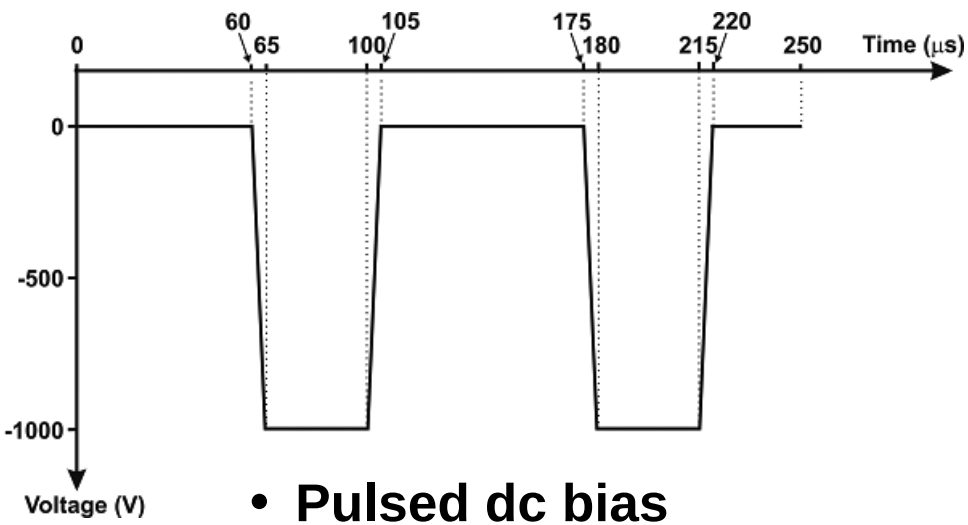
PLASMA ION IMPLANTATION REACTOR GEOMETRY





- Pulsed dc bias

- Inductively Coupled Plasma (ICP) with pulsed DC biasing.
- Ar/NF_3 (surrogate for Ar/BF_3)
- 10 mTorr, 500 W, 100 sccm, 100s-1000s V bias

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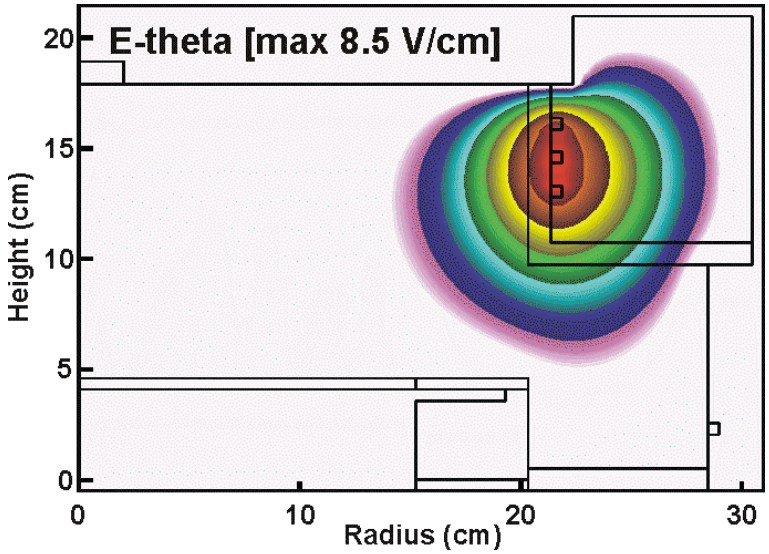
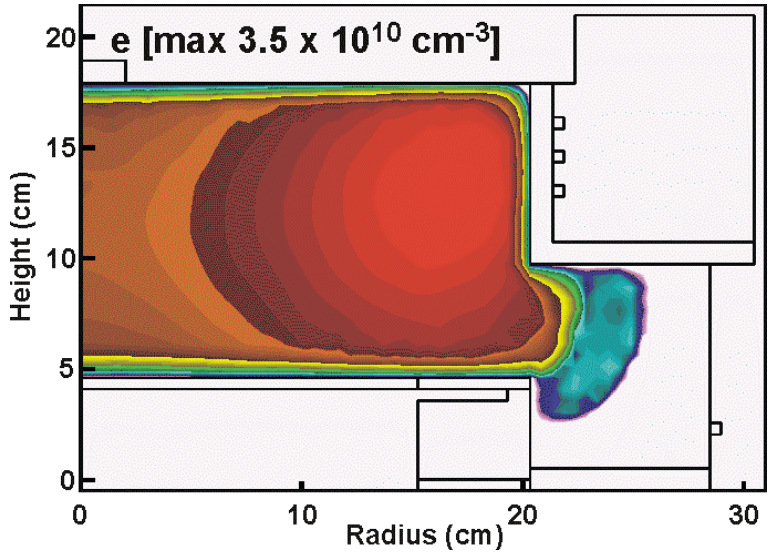
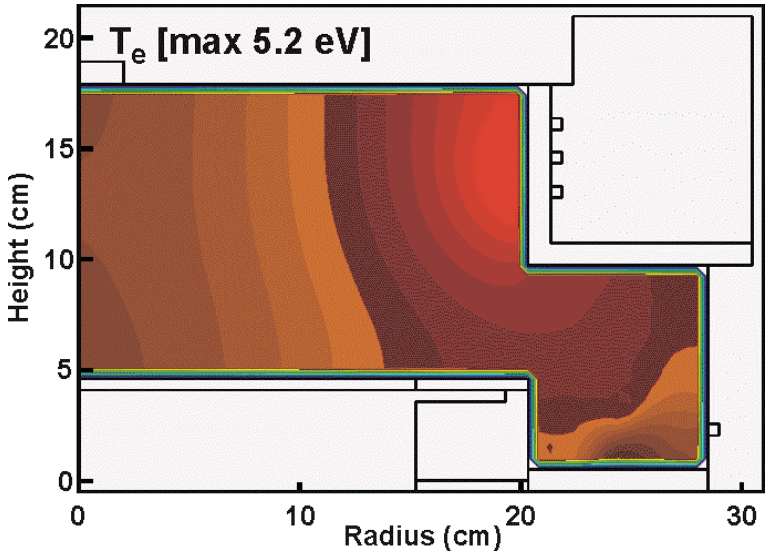
Ar/NF_3: ELECTRIC FIELD, T_e, [e]







- **Off axis power deposition produces non-uniform plasma.**
- **10 mTorr, 500 W, -1000 V pulse, 100 sccm, Ar/NF_3 = 0.8/0.2, t=250 μs**

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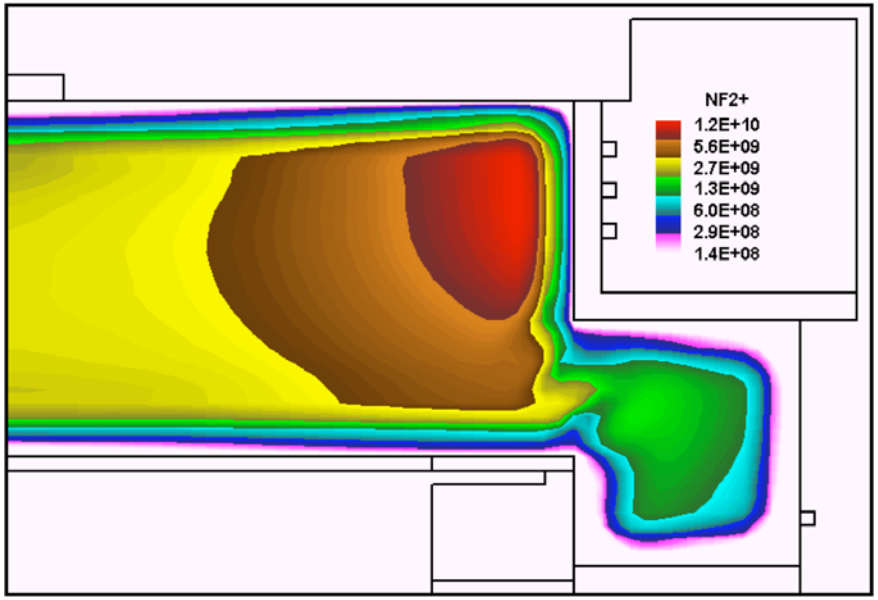
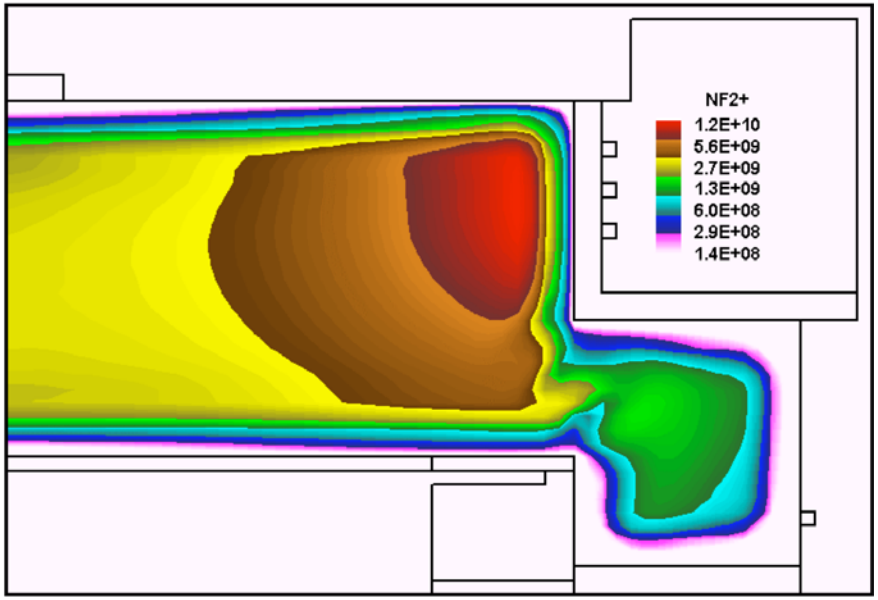
NF_2^+ DENSITY





- 1,000 V; Max: 1.4 x 10^{10} cm^{-3}
- 10,000 V; Max: 1.4 x 10^{10} cm^{-3}
- Plasma density peaks near the coils – sheath thinner on the outside of the substrate. Note pulsation due to negative ion-positive ion transport.
- 10 mTorr, 500 W, pulsed DC, 100 sccm, Ar/NF_3 = 0.8/0.2

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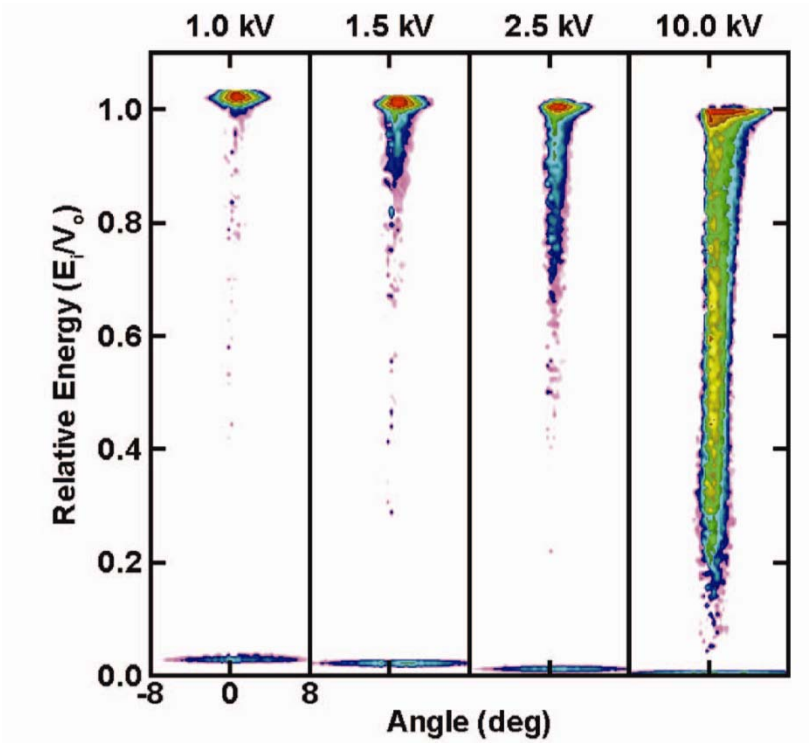
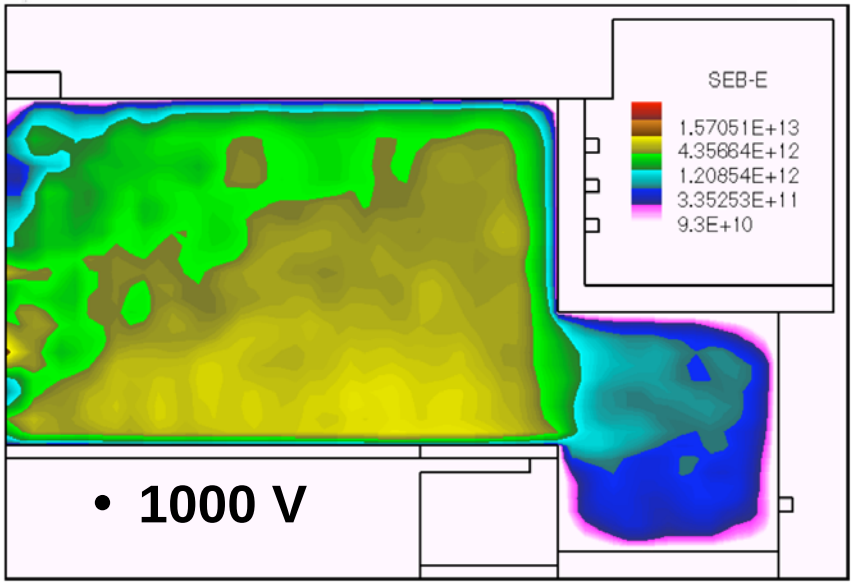
ION ENERGY ANGULAR DISTRIBUTION: PULSED DC BIAS





- 1000 V

- IEAD peaks near applied dc bias voltage.
- Angular distribution narrows with bias on; broad without bias.
- Longer "tail" with bias due to sheath thickening and electron impact ionization in sheath.
- *Asymmetry results from sheath structure.*

- Ionization by Beam Electrons

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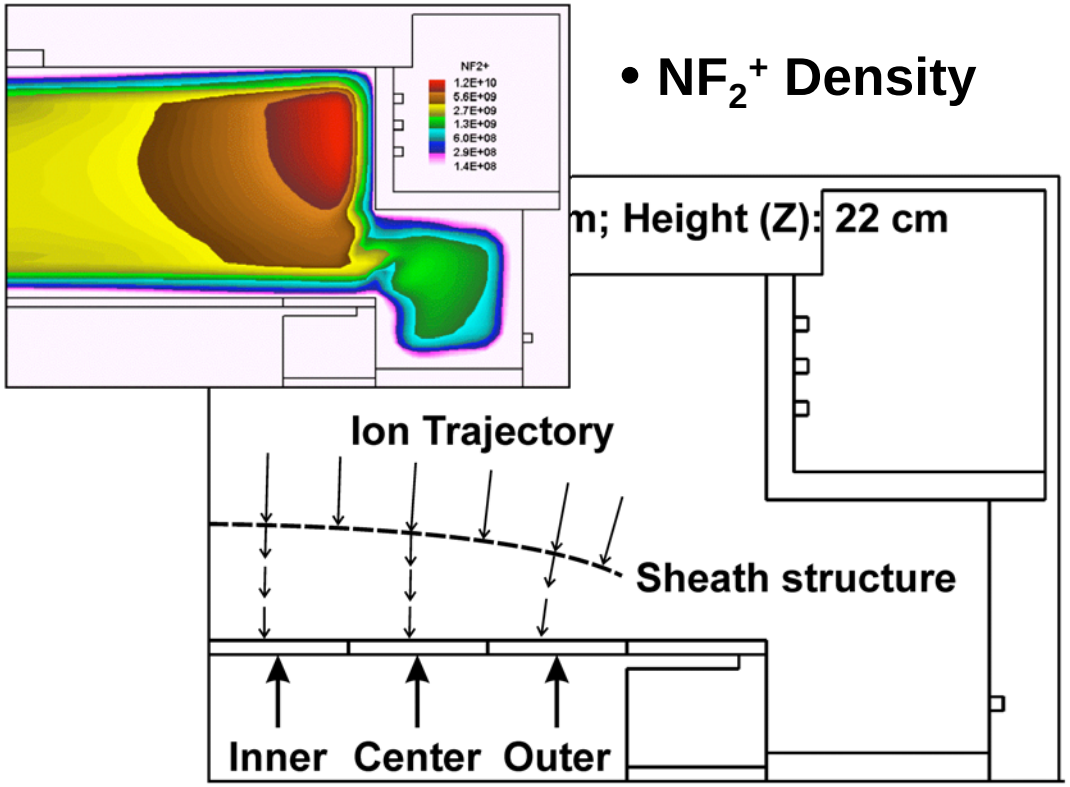
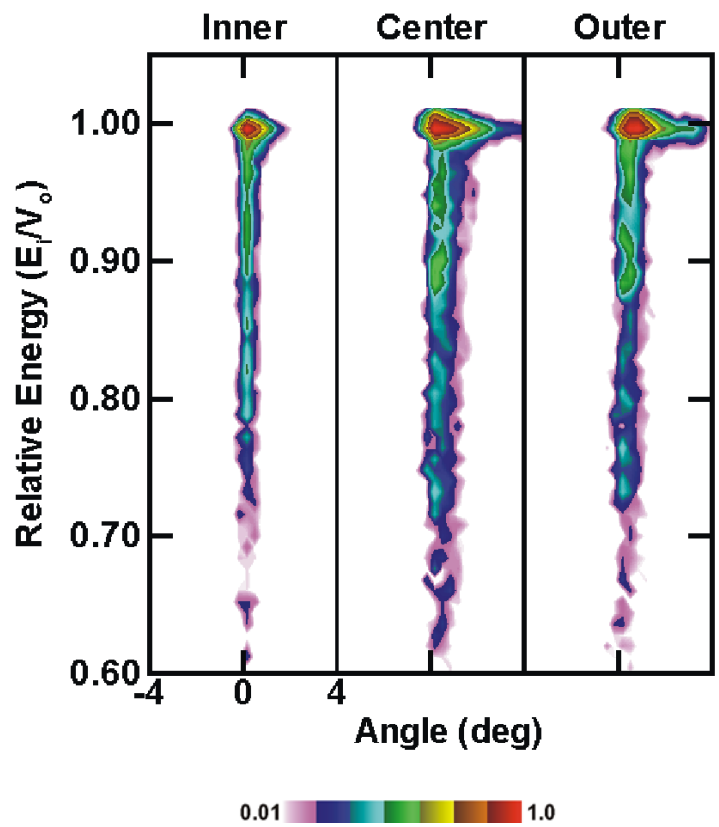
IEAD: STANDARD REACTOR DESIGN



- NF_2^+ Density



- **Off axis ion source and propagation of sheath into bulk plasma produces gradient to sheath and asymmetric IEAD.**

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- **10 mTorr, 500 W, -10,000 V pulsed DC, 100 sccm, Ar/NF_3=0.8/0.2**

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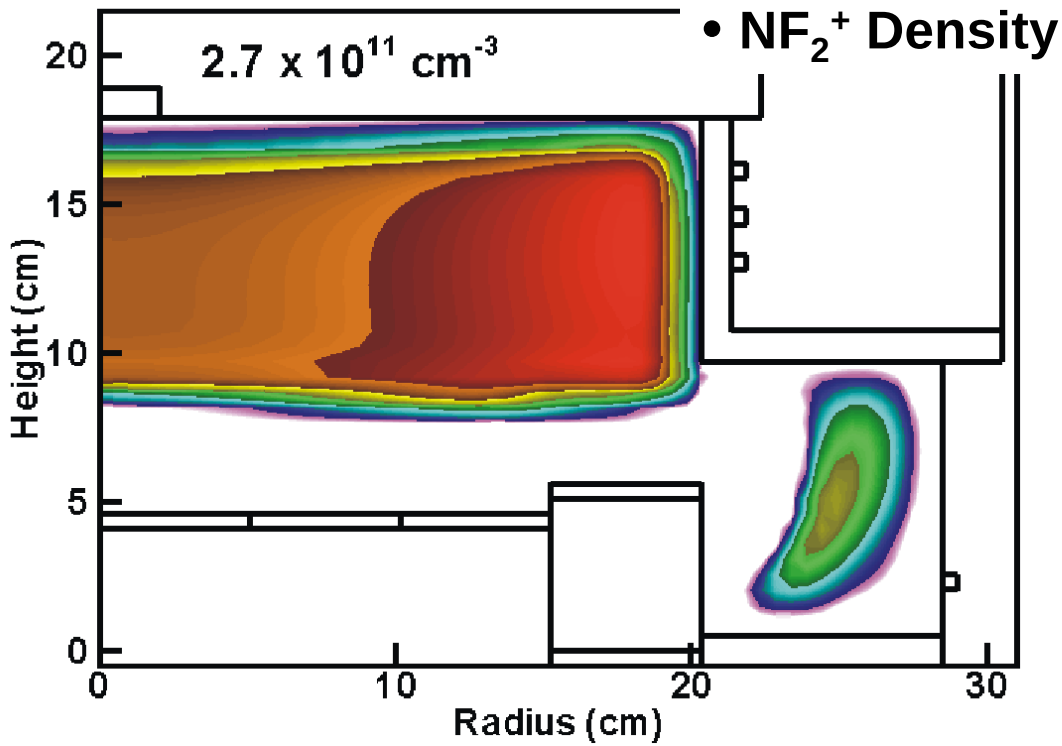
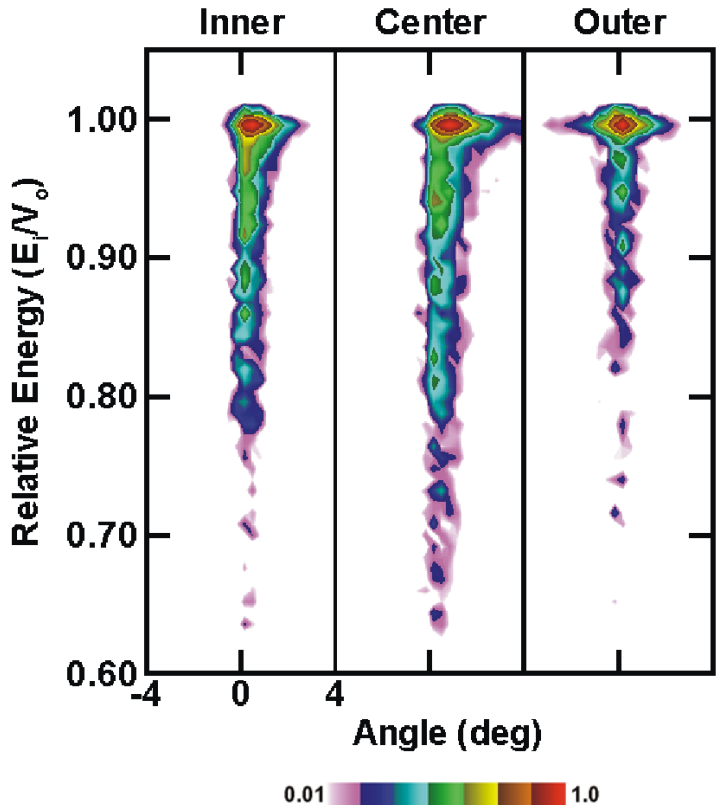
IEAD: REACTOR FOCUS RING





- **Raised focus ring raises sheath edge and lessens the gradient. IEADs become more symmetric.**

- **10 mTorr, 500 W, -10,000 V pulsed DC, 100 sccm, Ar/NF_3=0.8/0.2**

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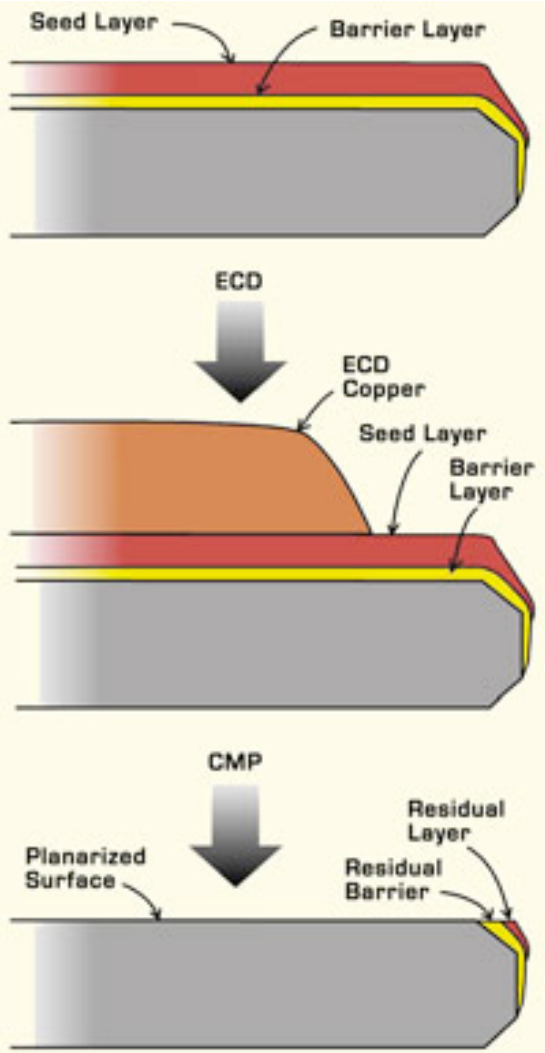
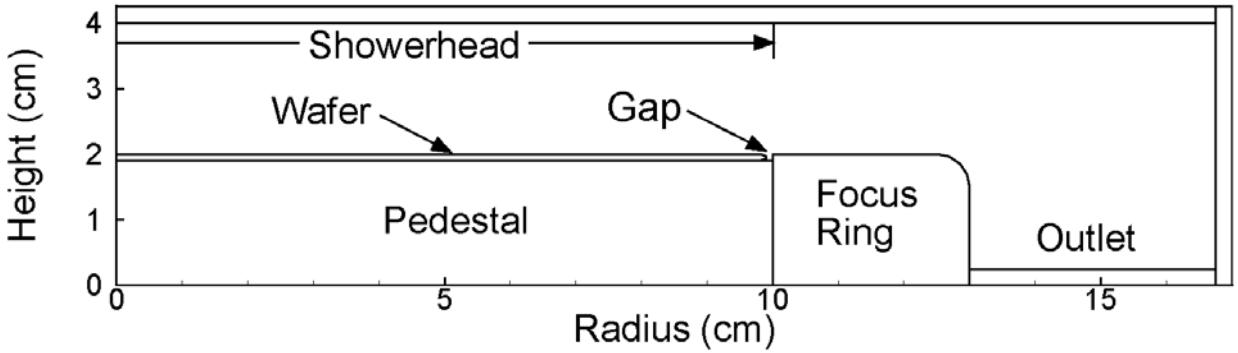
EQUIPMENT DESIGN MATTERS: PENETRATION OF PLASMA INTO SMALL GAPS

PLASMA PENETRATION INTO WAFER FOCUS RING GAP



- **PVD penetration persists after CMP**



- **Wafers are beveled at edge with small gap (< 500 μm) between wafer and focus ring for mechanical clearance.**
- **Penetration of plasma into gap produces particles and contaminating films.**
- **How large can gap be without having significant plasma penetration?**

http://www.micromagazine.com/archive/00/10/simpson.html

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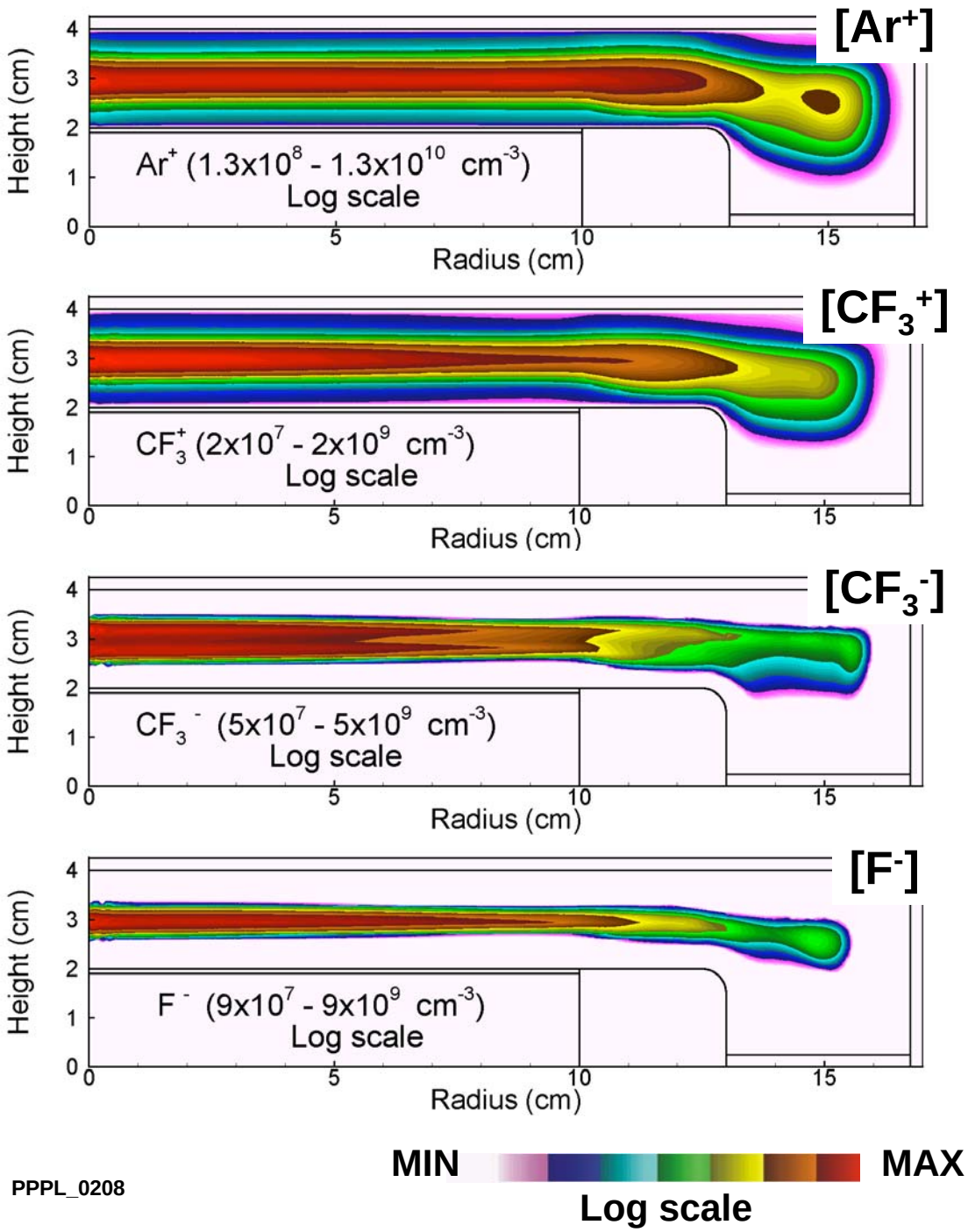
Ar/CF_4 CCP FOR SiO_2 Etching



- Dielectric etching performed in polymerizing capacitively coupled plasmas.
- Typical plasma densities are 10^{10}-10^{11} cm-3.
- Ar/CF_4 = 97/03, 10 MHZ, 90 mTorr, 300V, 300 sccm

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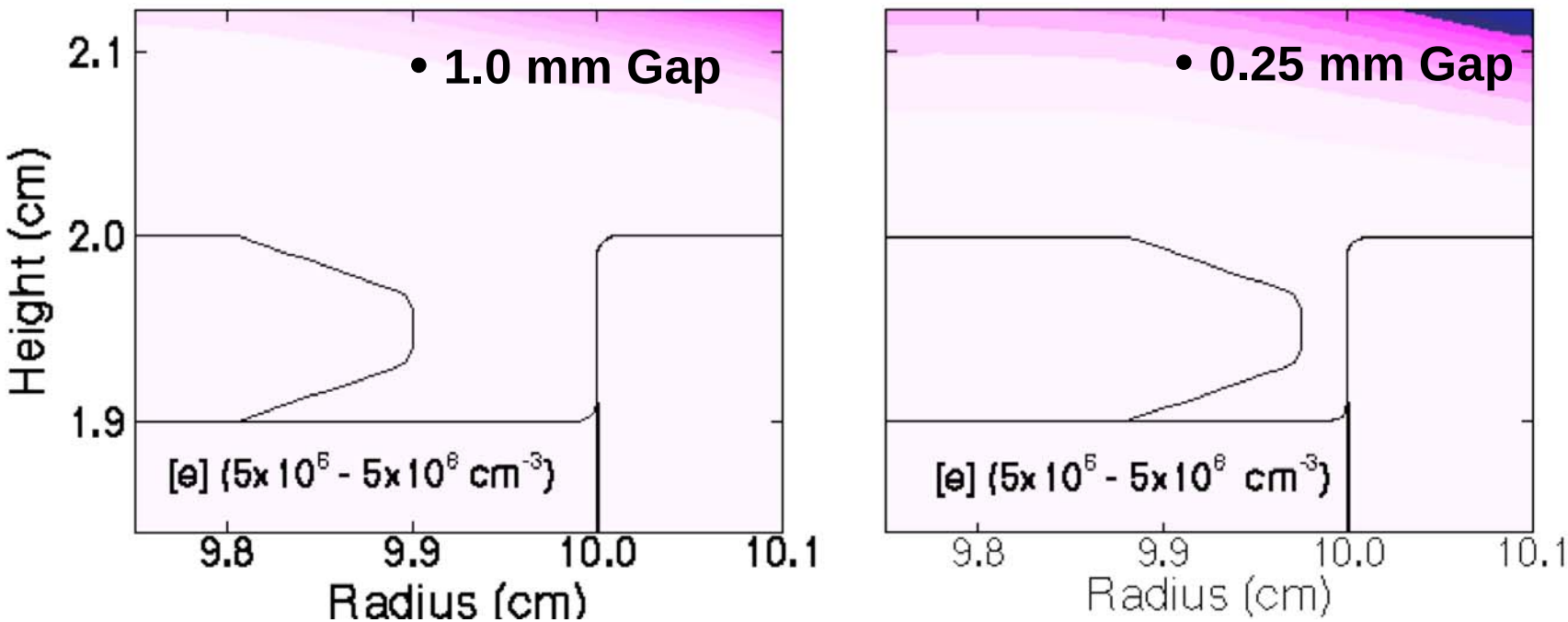
ELECTRON PENETRATION INTO GAP



- **Electron penetration into gaps in anode portion of cycle is nominal due to surface charging and sheath formation.**
- **Ar/CF_4 = 97/03, 10 MHz, 90 mTorr, 300 V, 300 sccm**

Animation Slide

MIN **MAX**

Log scale

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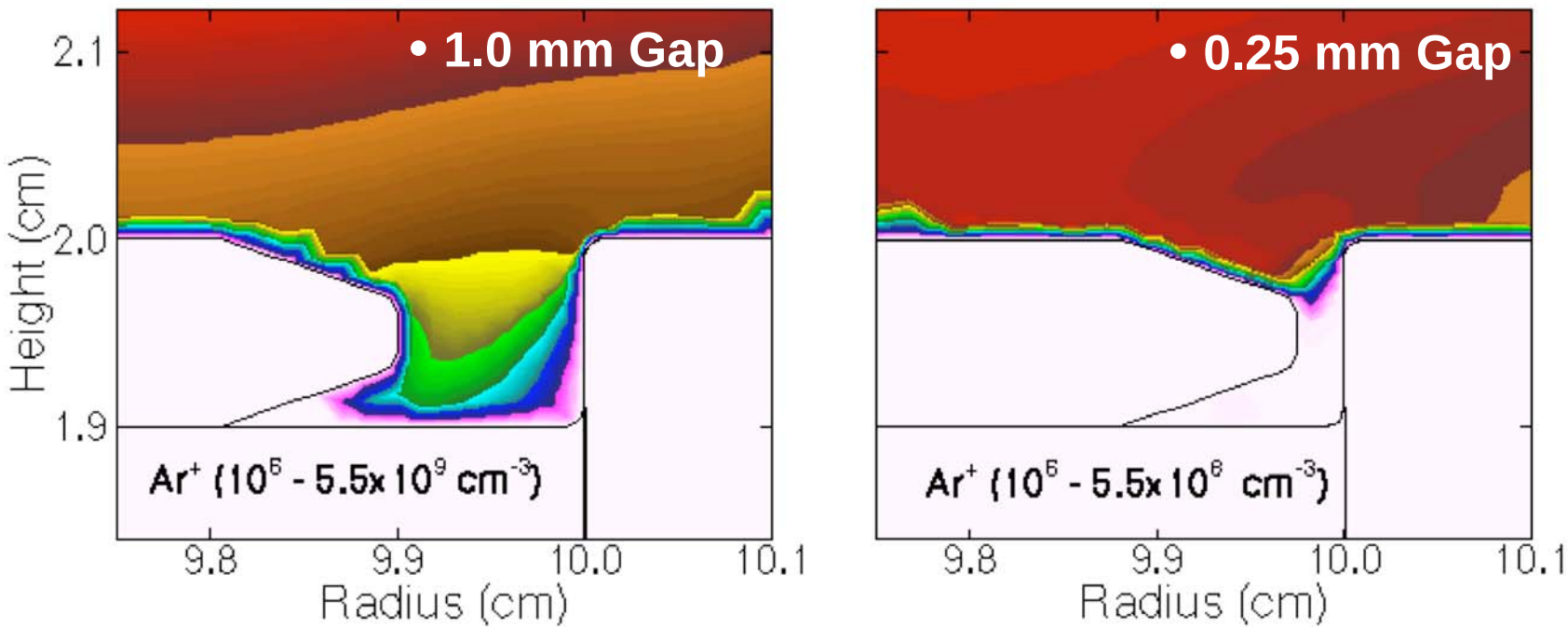
Ar^+ PENETRATION INTO GAP



- **Ions penetrate into larger gap throughout the rf cycle provided size is commensurate with sheath width. Smaller gap receives only nominal flux.**
- **Ar/CF_4 = 97/03, 10 MHz, 90 mTorr, 300 V, 300 sccm**

Animation Slide

MIN **MAX**

Log scale

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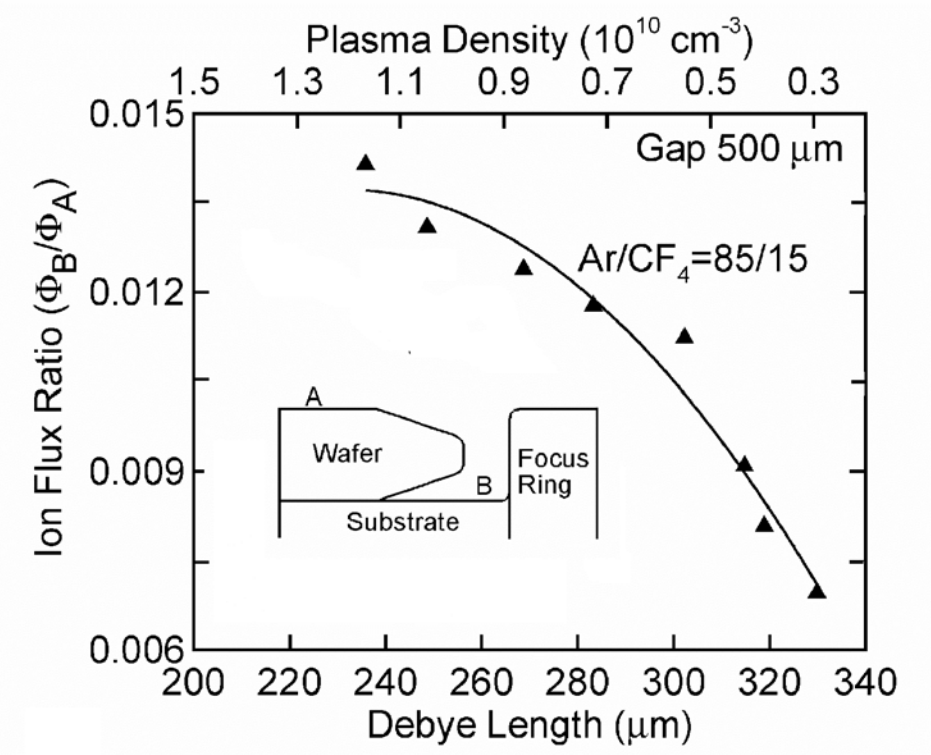
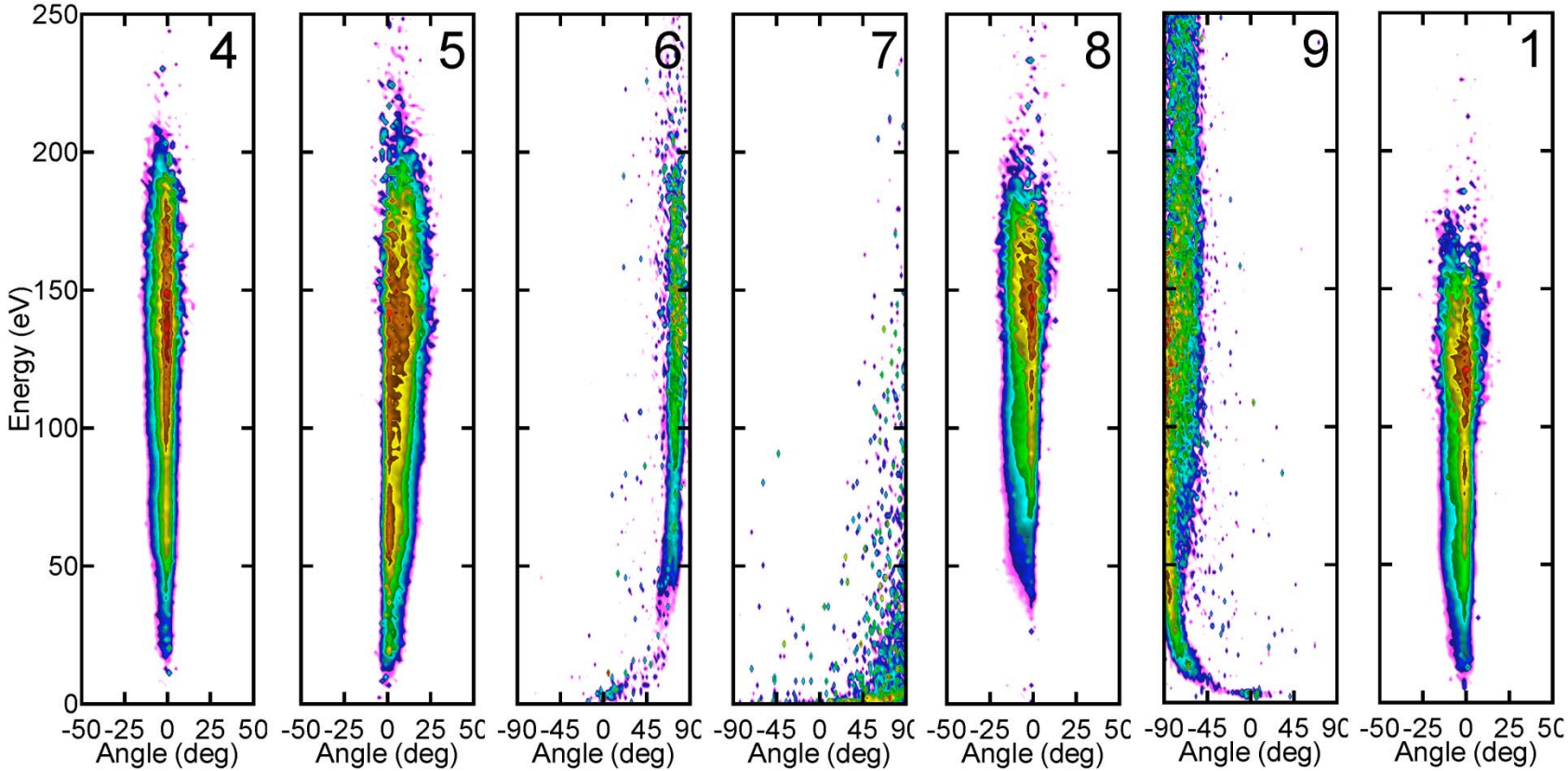
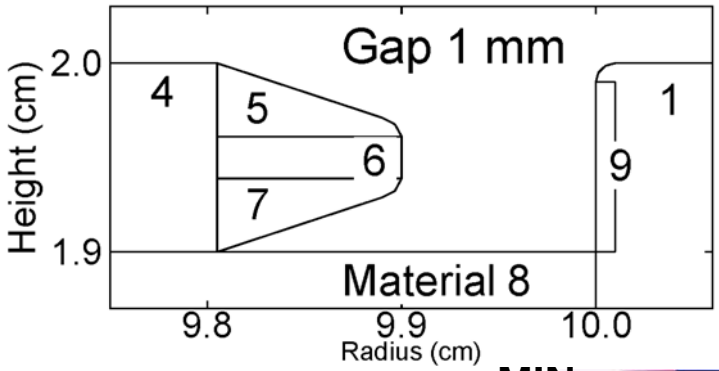
ION PENETRATION vs GAP SIZE vs DEBYE LENGTH



- **Ion penetration into gap depends on size of gap relative to sheath thickness.**
- **Gap ≥ sheath thickness allows penetration.**
- **High plasma density tools produce smaller sheaths and more penetration.**
- **Ar/CF$_4$ = 97/03, 10 MHz, 90 mTorr, 300 V, 300 sccm**

ION ENERGY AND ANGULAR DISTRIBUTIONS





- **IEADs differ significantly on different surfaces in gap.**

MIN **MAX**

Log scale

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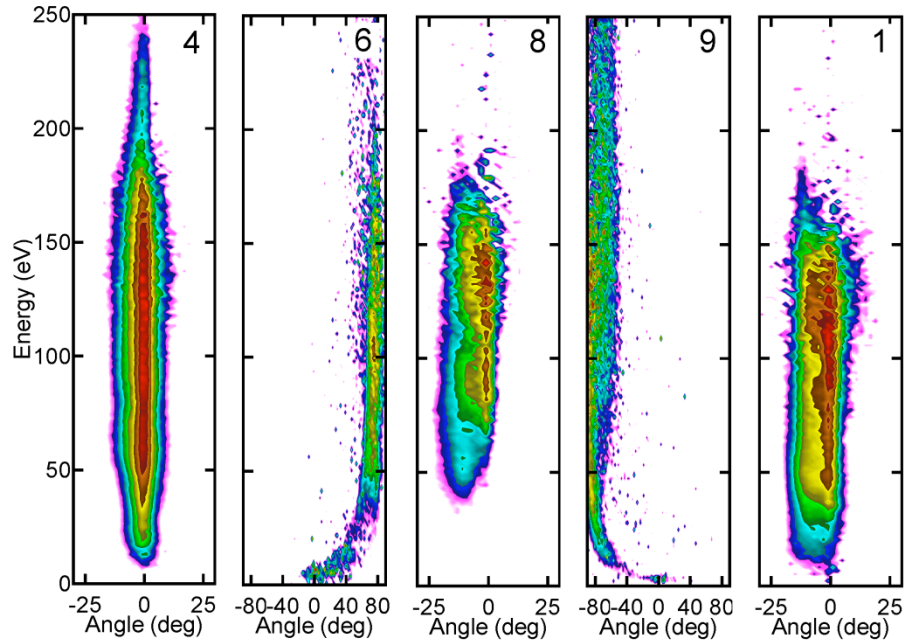
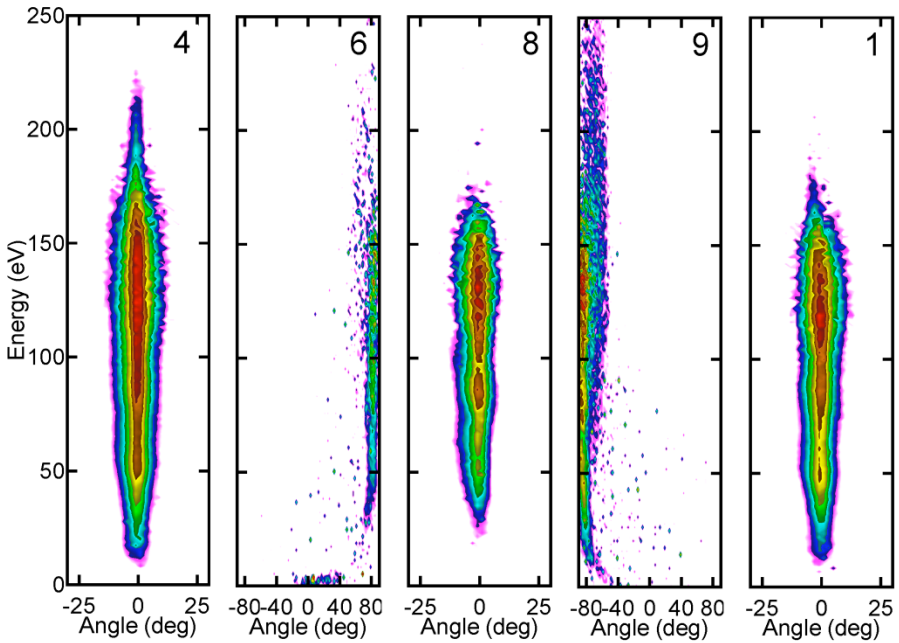
CAPACITANCE OF FOCUS RING: IEAD





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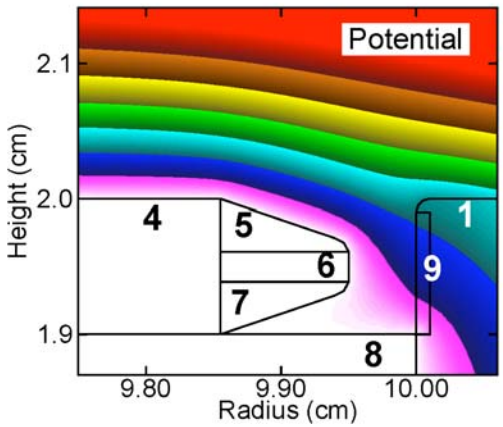
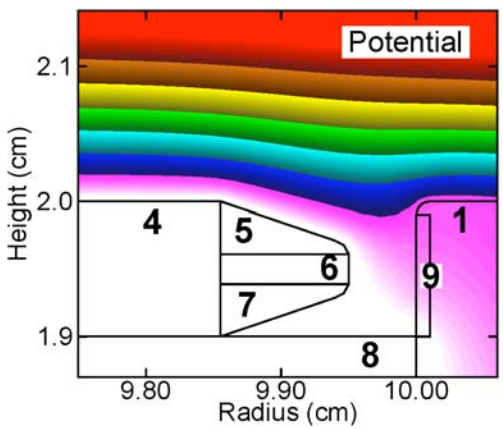
- $\varepsilon/\varepsilon_o = 4$



- $\varepsilon/\varepsilon_o = 20$



- Penetration of potential into focus ring with low capacitance produces lateral E-field.
- IEAD on substrate is asymmetric.

MIN MAX

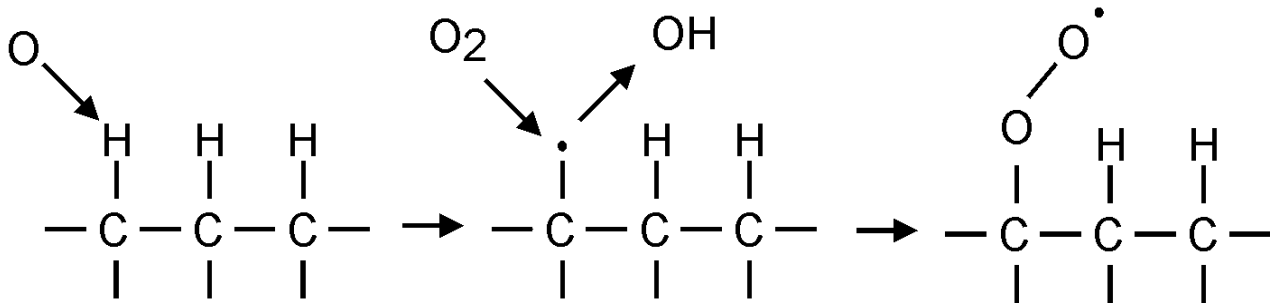
Log scale

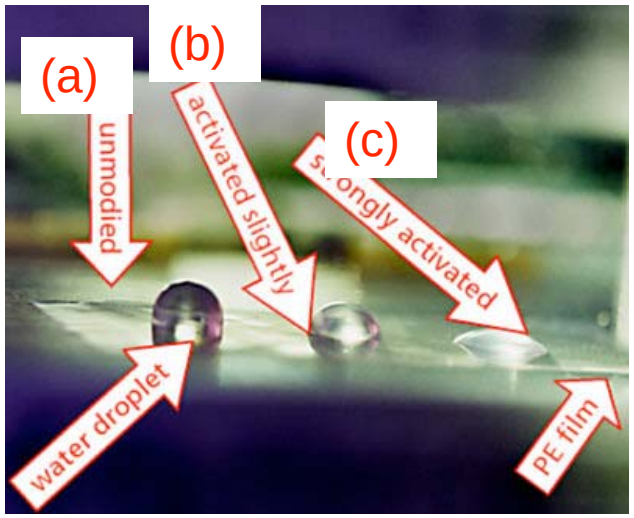
ATMOSPHERIC PRESSURE PLASMA FUNCTIONALIZATION OF POLYMERS

FUNCTIONALIZATION OF POLYMER SURFACES

- **Functionalization occurs by chemical interaction of plasma produced species - ions, radicals and photons with the surface.**

$$e + O_2 \rightarrow O + O + e$$

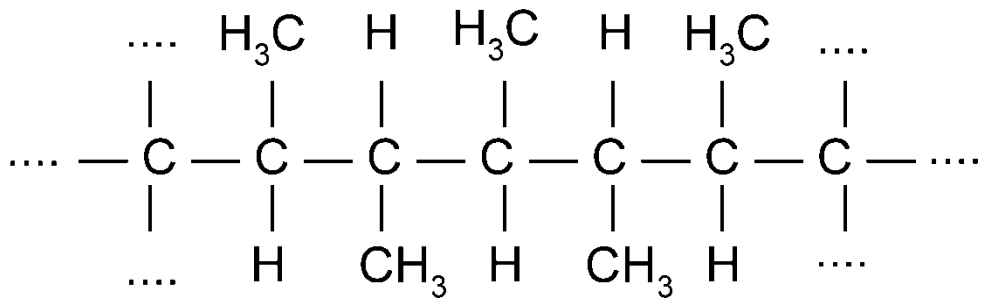




- **Example: H abstraction by O atom enables affixing O atoms as a peroxy site.**
- **Increase surface energy → increase wettability.**
- **Process treats the top few layers.**

Courtesy: http://www.polymer-surface.com

FUNCTIONAL GROUPS ON POLYPROPYLENE



Initiating

O + R-H	→	OH + R•	(Alkyl)
OH + R-H	→	H_2O + R•	(Alkyl)

Propogation

O_2 + R•	→	R-OO•	(Peroxy)
O + R•	→	R-O•	(Alkoxy)
O_3 + R•	→	R-O• + O_2	(Alkoxy)

Termination

OH + R•	→	R-OH	(Alcohol)
R-O• + R-H	→	R-OH + R•	(Alcohol)
R-O• + R-H	→	R=O + R-H	(Carbonyl)

- Ratio of O, OH, O_2 and O_3 fluxes determine surface composition.
- Magnitude of fluxes and residence time determines importance of surface-surface reactions.

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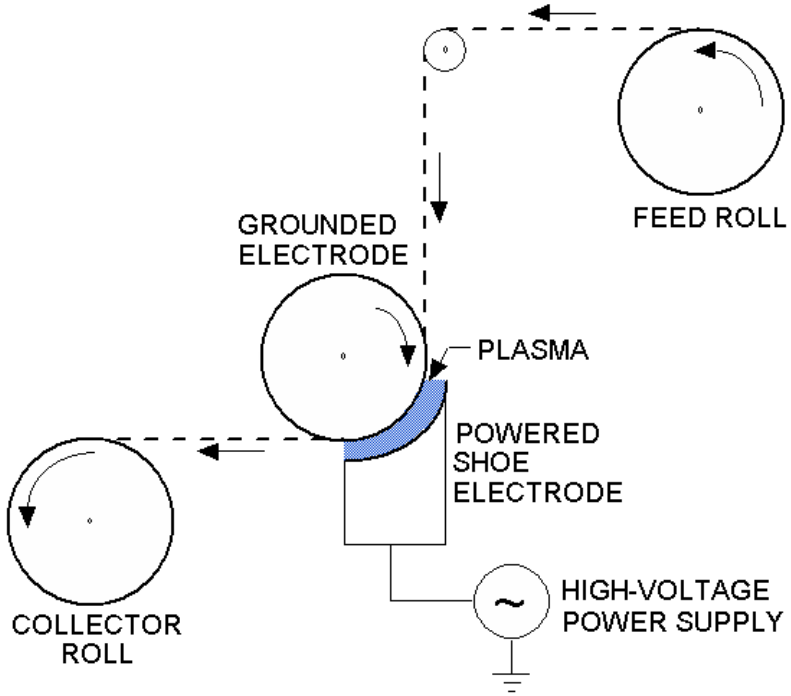
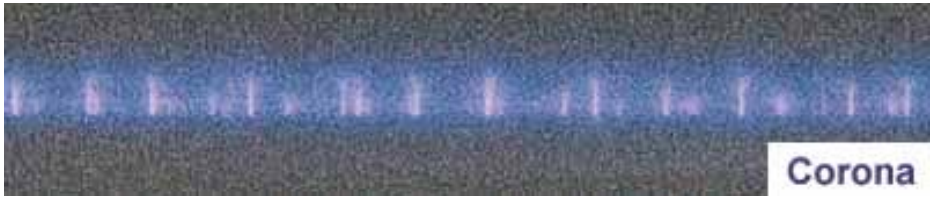
CORONA DISCHARGE TREATERS

- Tantec, Inc.

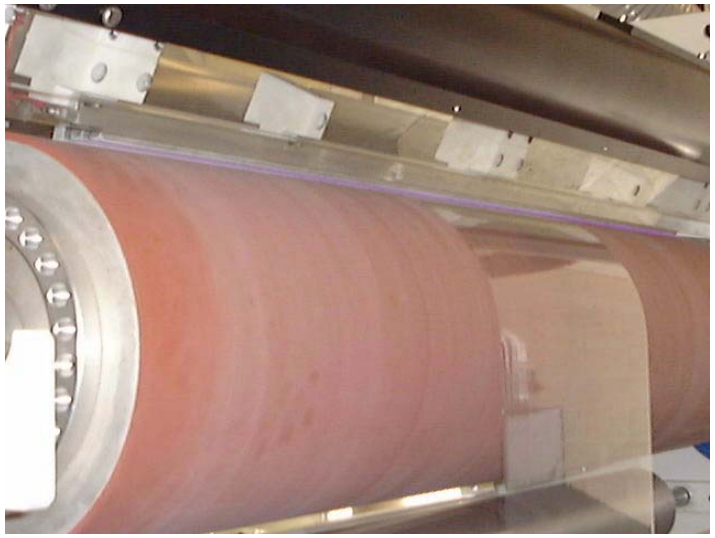
- Pulsed atmospheric corona discharges treat commodity polymers [e.g., poly-propylene (PP)]
- Low cost, high volume, low value…with potential for low cost, high volume, high value.

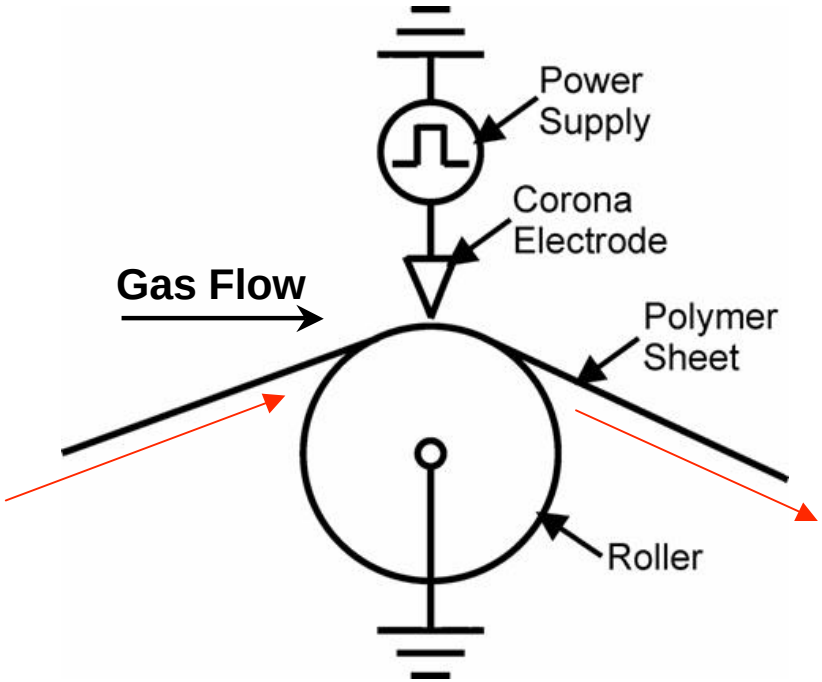




- Streamers 10s – 100s μm (Ref: Enercon)

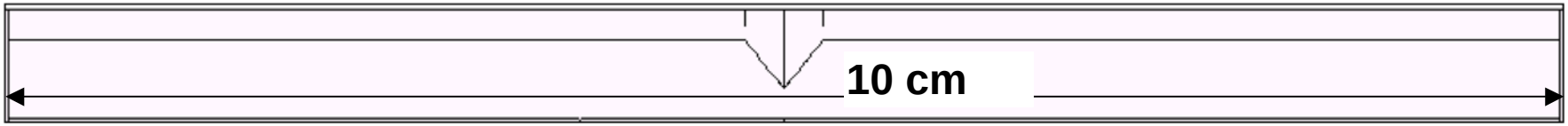
FORCED GAS FLOW AND WEB MOVEMENT

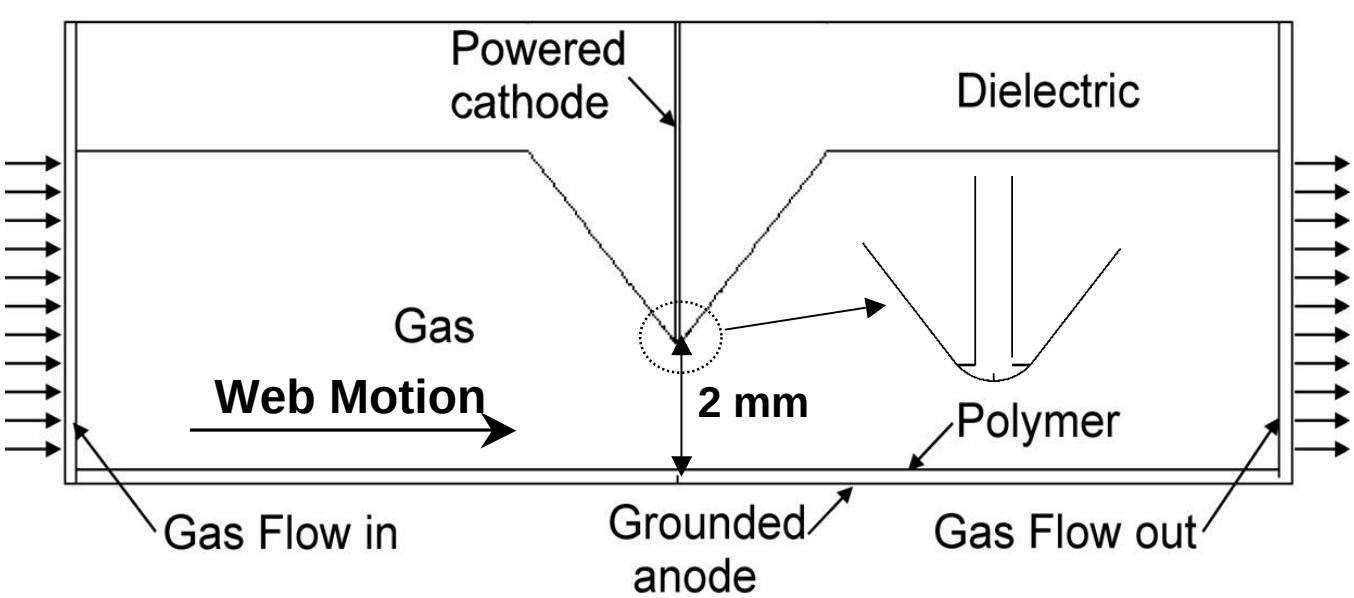




- **Polymer surfaces are continuously treated at web speeds of a few m/s with residence times in plasma of up to a few ms.**
- **Non-air gas mixtures are often "forced flowed" through gap to customize radicals to surface.**

FORCED GAS FLOW AND WEB MOVEMENT





- **Translate surface mesh points to account for web motion.**

- **- 5 kV, 1 atm, He/O_2/H_2O=89/10/1**
- **Inter-electrode gap: 2 mm**
- **Gas flow: 0 – 30 slpm (many m/s)**
- **Web speed: 0-8 m/s**

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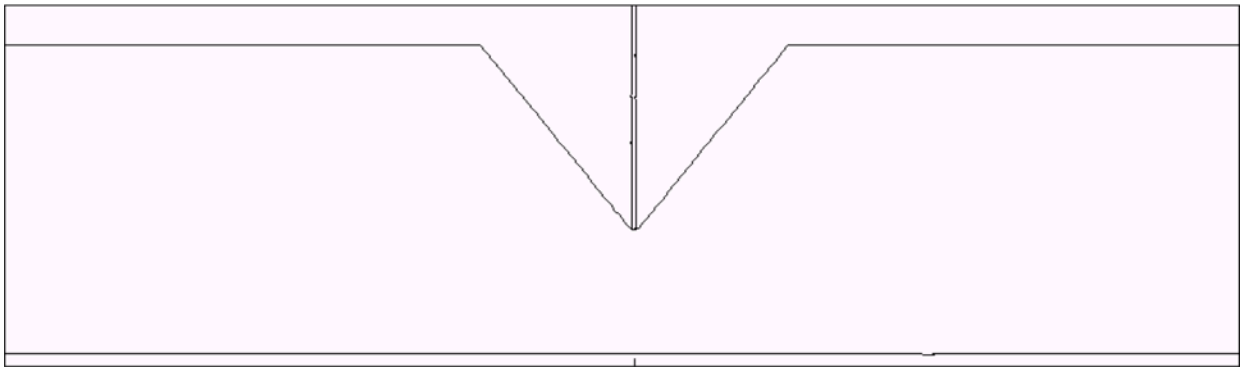
REPETITIVELY PULSED DISCHARGES – [e]



- 10^{14} cm^{-3}

- Electron avalanche from the powered electrode.
- The pulse duration a few ns
- Terminated by charging of dielectric.
- Peak [e] of a few 10^{14} cm^{-3}.

- $He/O_2/H_2O$=89/10/1, -5 kV, 10 kHz, 1 atm

Animation Slide-GIF

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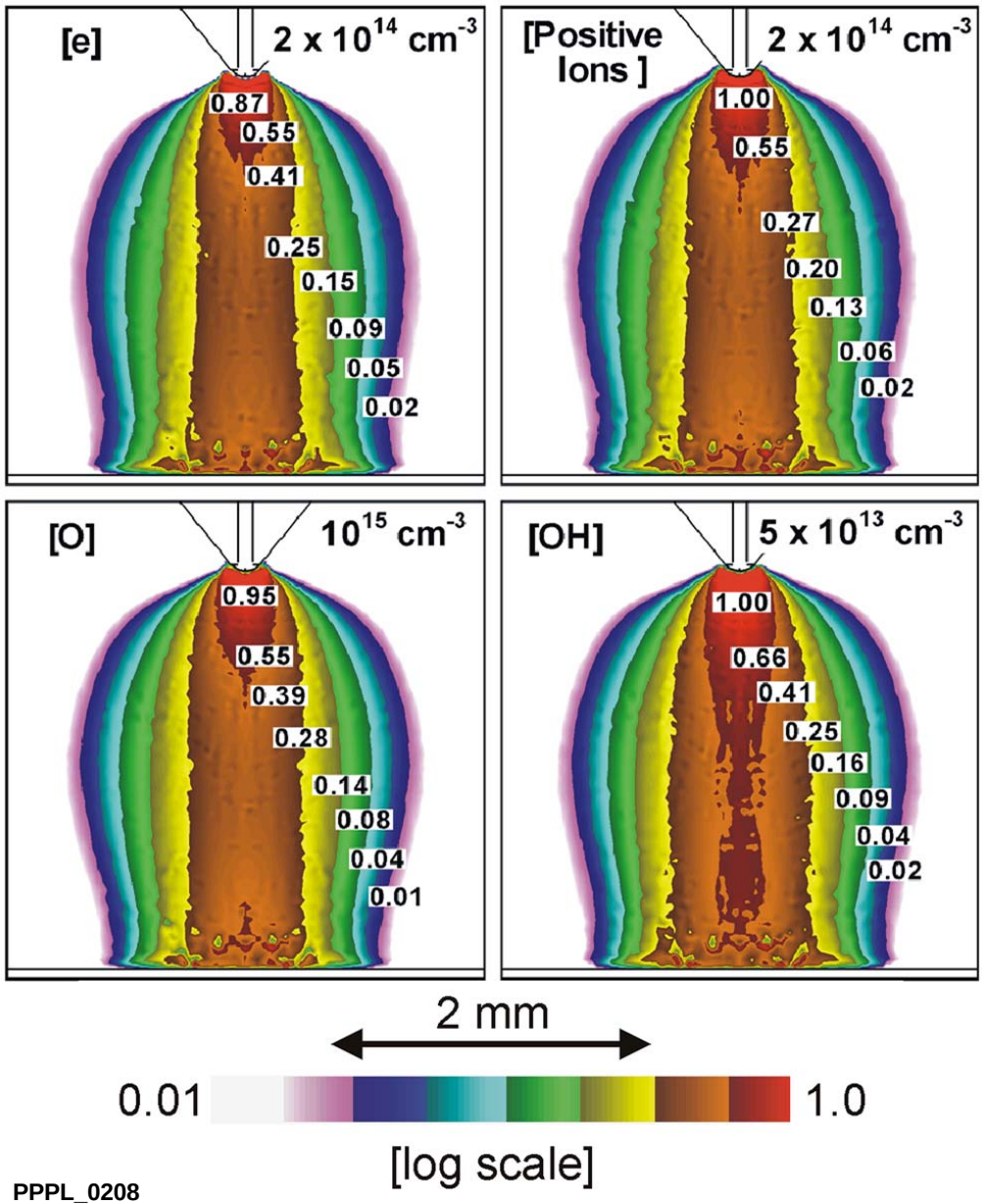
POST-PULSE REACTANT DENSITIES



- Important radicals are those containing O atoms.
- Post pulse radical densities:

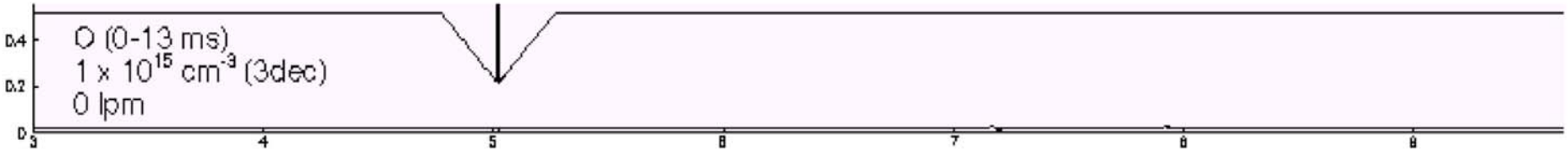
  [OH] 10^{14} cm^{-3}

  [O] 10^{15} cm^{-3}

  - $He/O_2/H_2O$=89/10/1, - 5 kV, 10 kHz, 1 atm

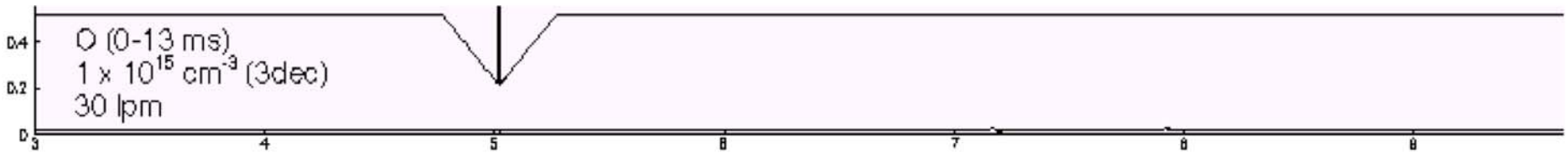
PPPL_0208

[O] – WITHOUT AND WITH FORCED GAS FLOW



- **Without forced flow**

- **[O] 10^{15} cm^{-3}**



- **With forced flow**

Flow →

- **O atoms are generated by electron impact with every pulse.**
- **Rapid reactions to form ozone ($O + O_2 + M \rightarrow O_3 + M$) deplete the O atoms within 10s μs of discharge pulse.**
- **Little change in O atom distribution with and without gas flow.**
- **$He/O_2/H_2O$=89/10/1**
- **10 kHz, 0 or 30 slpm, 1 atm.**

Animation Slide-GIF

0.001 **1**

log scale

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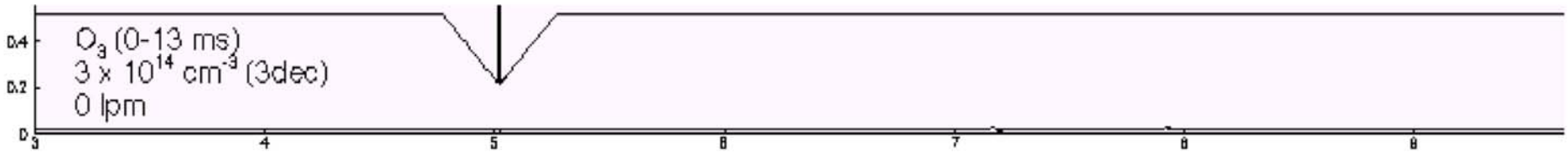
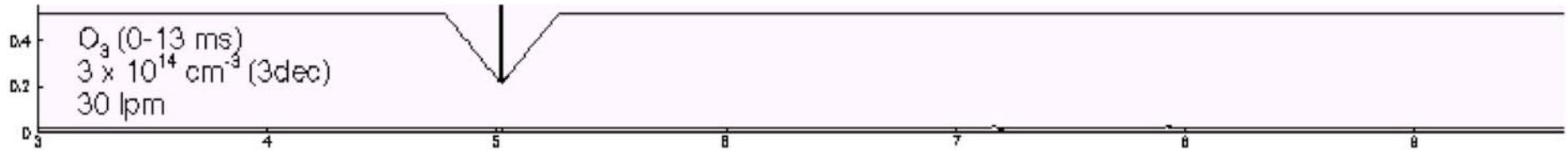
$[O_3]$ – WITHOUT AND WITH FORCED GAS FLOW



- **Without forced flow**
- **$[O_3]$ 3 x 10^{14} cm^{-3}**



- **With forced flow**

Flow →

- **O_3 is relatively unreactive and accumulates from pulse to pulse.**
- **Without forced flow, diffusion distributes O_3 up- and downstream.**
- **With forced flow, a plume of O_3 extends downstream.**
- **$He/O_2/H_2O$=89/10/1**
- **10 kHz, 0 or 30 slpm, 1 atm.**

Animation Slide-GIF

0.001 **1**

log scale

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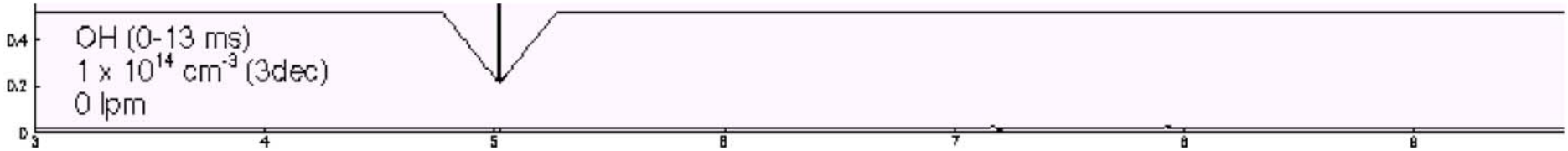
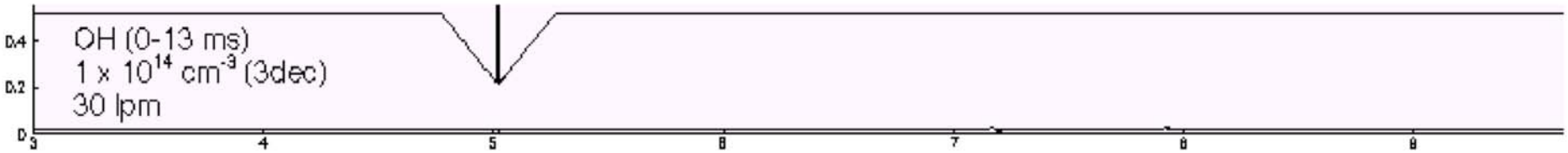
[OH] – WITHOUT AND WITH FORCED GAS FLOW



- Without forced flow
- [OH] 10^{14} cm^{-3}



- With forced flow

Flow →

- OH has an intermediate reactivity between O and O_3.
- Some modest accumulation occurs with a small plume downstream with forced flow.

- $He/O_2/H_2O$=89/10/1
- 10 kHz, 0 or 30 slpm, 1 atm.

Animation Slide-GIF

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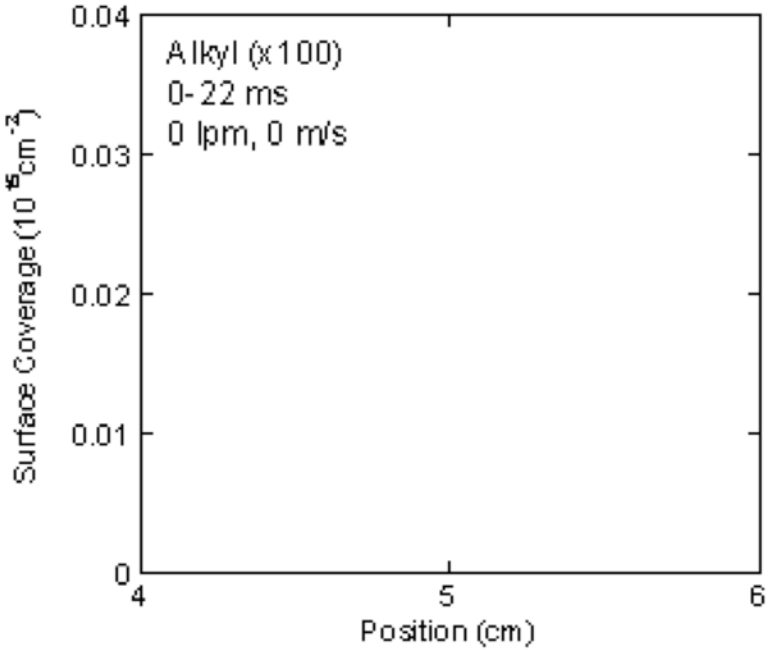
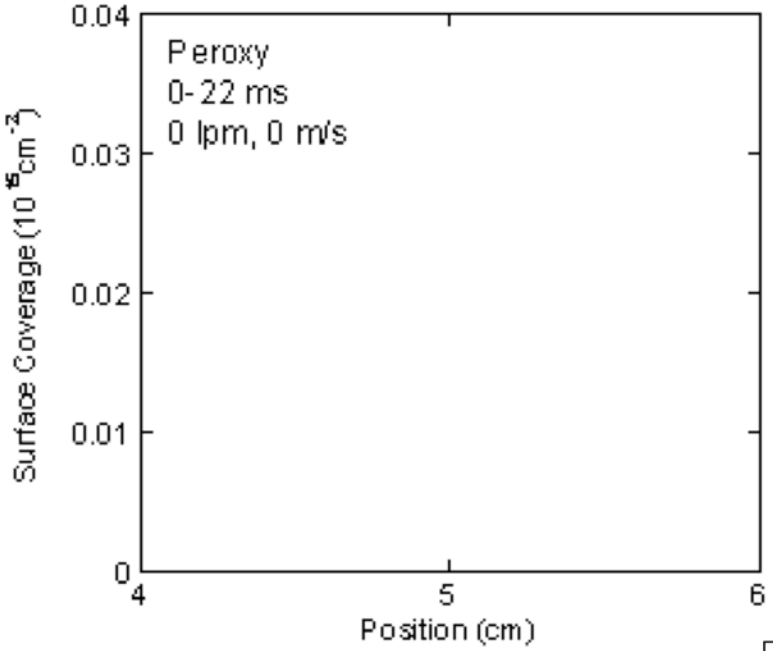
ALKYL, PEROXY COVERAGE (NO FLOW, NO MOTION)





- **Alkyl sites (R•) are produced by H abstraction by O and OH.**

$$RH + O \rightarrow R\bullet + OH$$

- **Alkyl sites are consumed by being passivated by O_2 to form peroxy sites (R-OO•)**

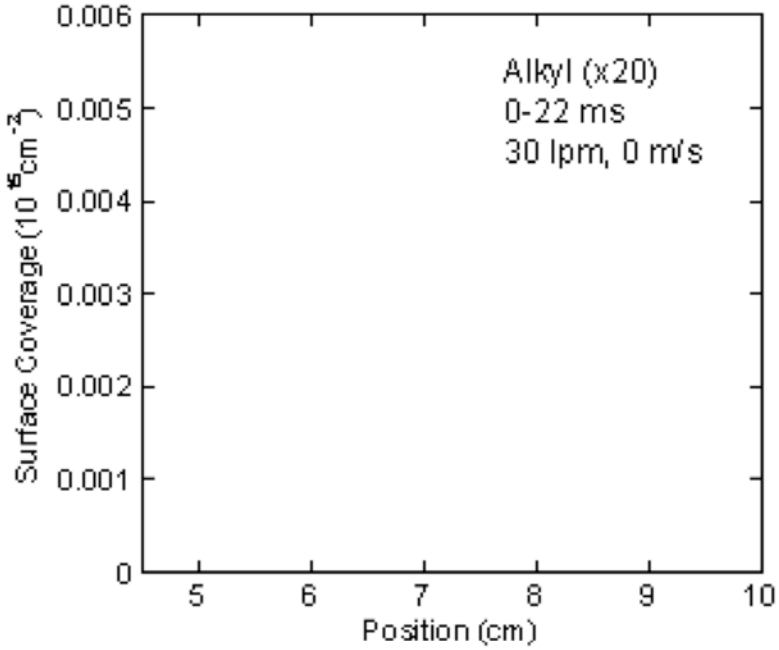
$$R\bullet + O_2 \rightarrow R\text{-}OO\bullet$$

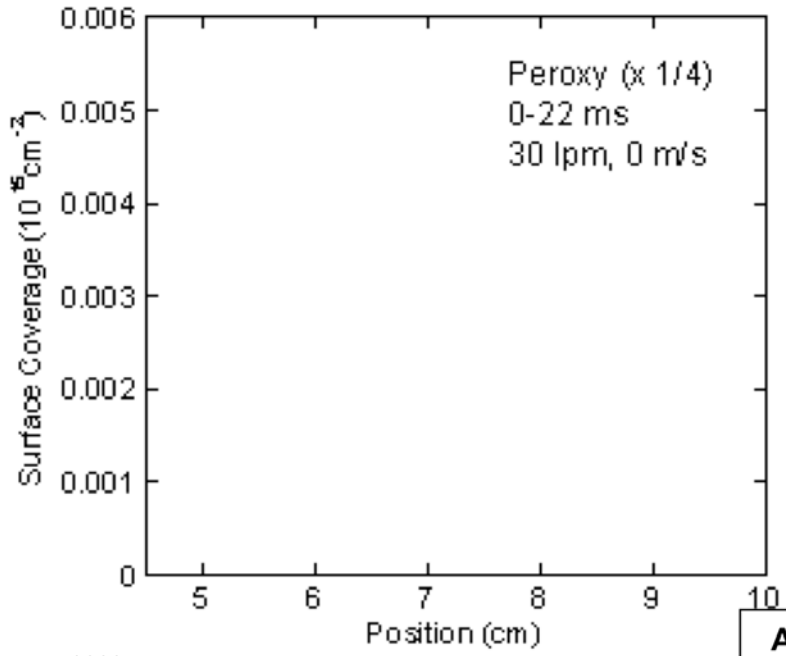
- **Peroxy groups are relatively unreactive and accumulate pulse to pulse.**
  - **- 5 kV, 1 atm, $He/O_2/H_2O$=89/10/1, 10 kHz, 0.022 s**

PPPL_0208

Animation Slide-GIF

ALKYL, PEROXY COVERAGE WITH FLOW





- **Alkyl (R•) sites are still rapidly produced and passivated with each pulse.**

$$(O, OH) + R\text{-}H \rightarrow R\bullet + (OH, H_2O)$$

- **The plume of OH radicals downstream produce a tail of R• sites.**
- **Peroxy sites accumulate downstream.**

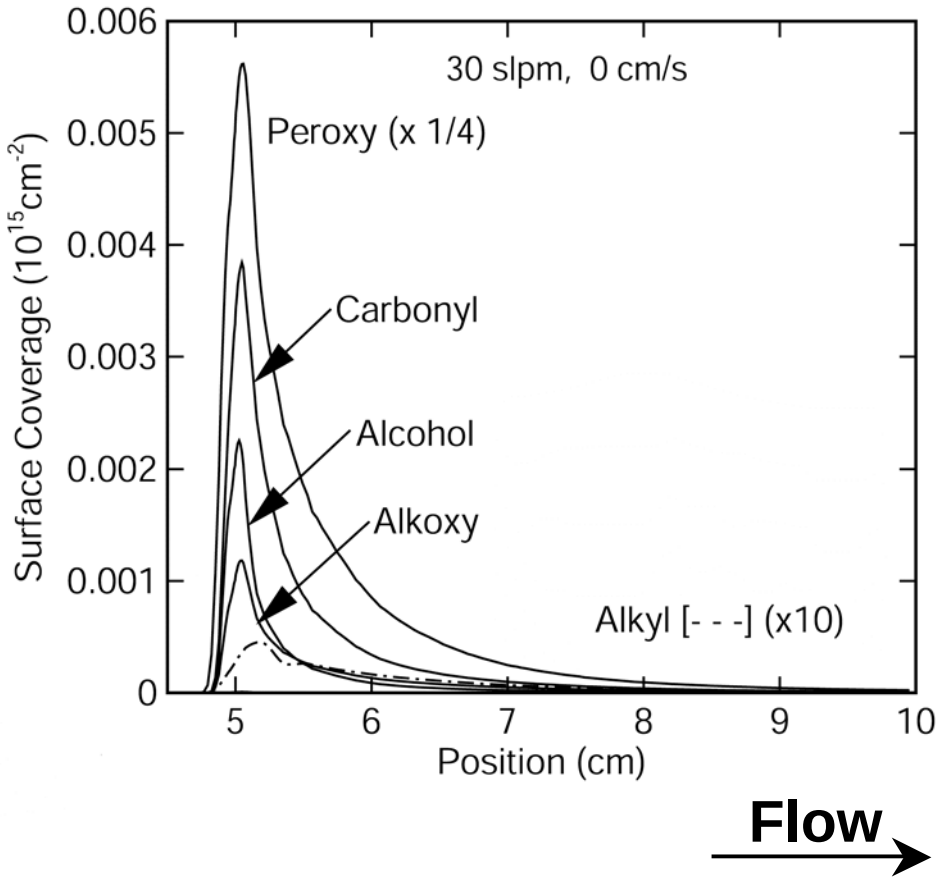
$$O_2 + R\bullet \rightarrow R\text{-}OO\bullet$$

- **1 atm, He/O_2/H_2O=89/10/1, 10 kHz, 0.022 s, 30 slpm**

Flow →

Animation Slide-GIF

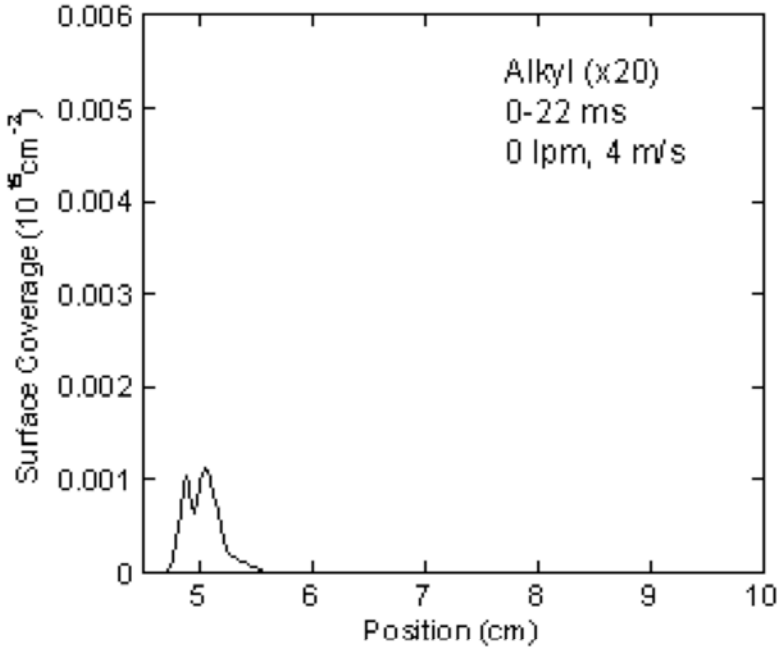
SURFACE COVERAGES WITH FLOW

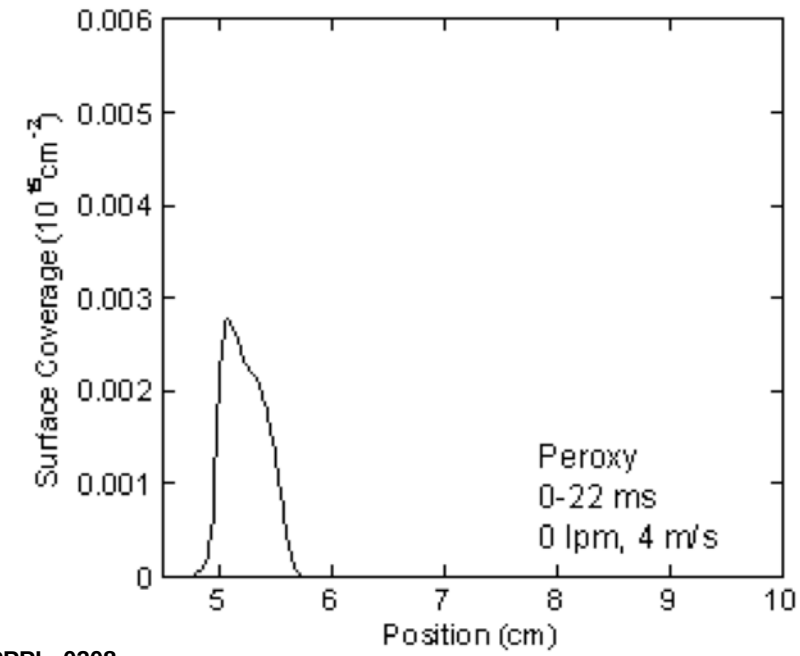


- **With stationary web, repetitive treatment of same sites produce large densities peroxy groups.**
- **Other groups are "etched away" by continual flux of O and OH radicals.**

- **1 atm, He/O_2/H_2O=89/10/1, 10 kHz, 0.022 s, 30 slpm**

ALKYL, PEROXY COVERAGE WITH WEB MOTION





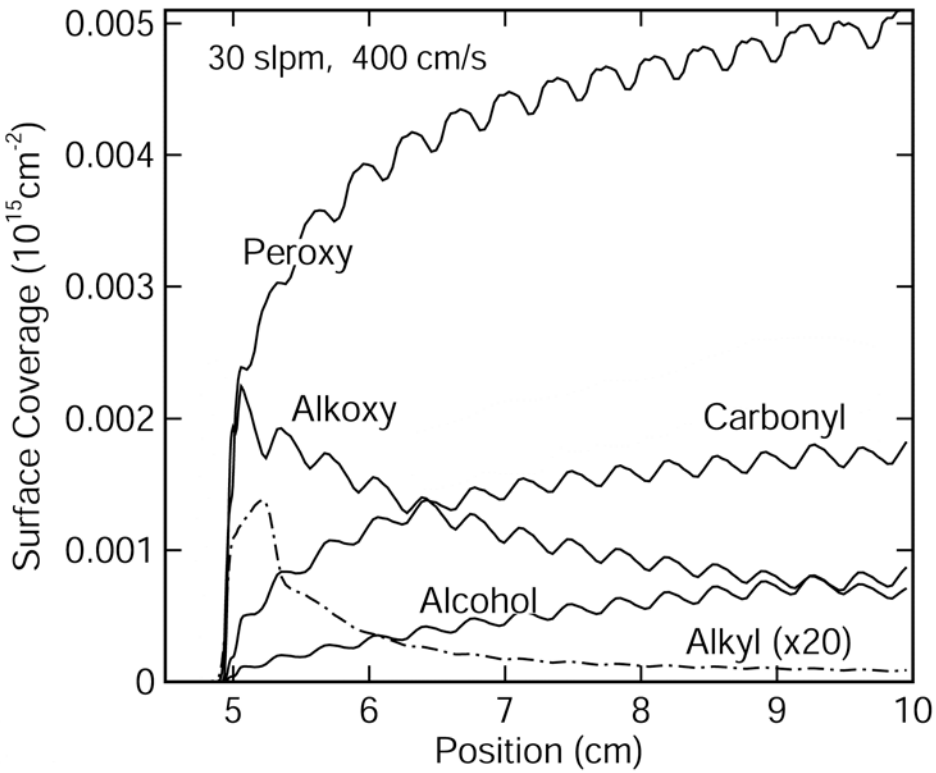
- **The rate of alkyl (R•) passivation is fast compared to web motion. Little R• moves downstream.**
- **Peroxy (R-OO•) sites being long lived, move with the web downstream.**
- **Web speed 4 m/s (no flow)**

- **1 atm, He/O_2/H_2O=89/10/1, 10 kHz, 0.022 s, 4 m/s**

Web →

Animation Slide-GIF

SURFACE COVERAGES WITH FLOW AND WEB MOTION



Flow → ← **Web**

- **1 atm, He/O_2/H_2O=89/10/1, 10 kHz, 0.022 s, 30 slpm**

- **With flow and motion in same direction, sites move "under plume" of radicals.**
- **Effectively larger fluence increases radical processes.**

Ratio of Peroxy/Carbonyl

Flow-no motion: 6

Motion-no flow: 1.7

Motion-flow 2.8

- **Flow, web-speed motion provides control over functional groups.**

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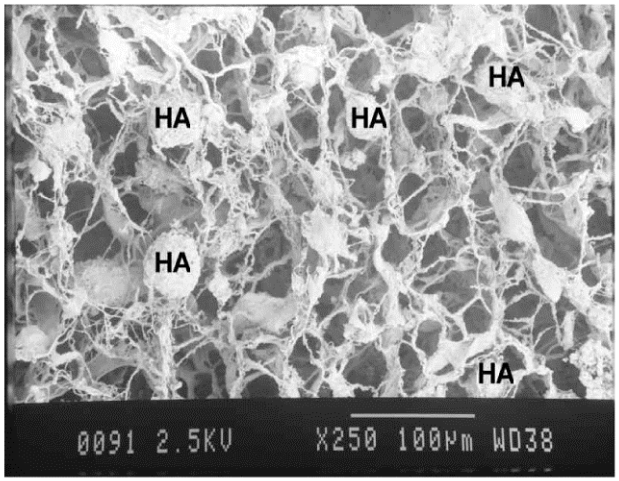
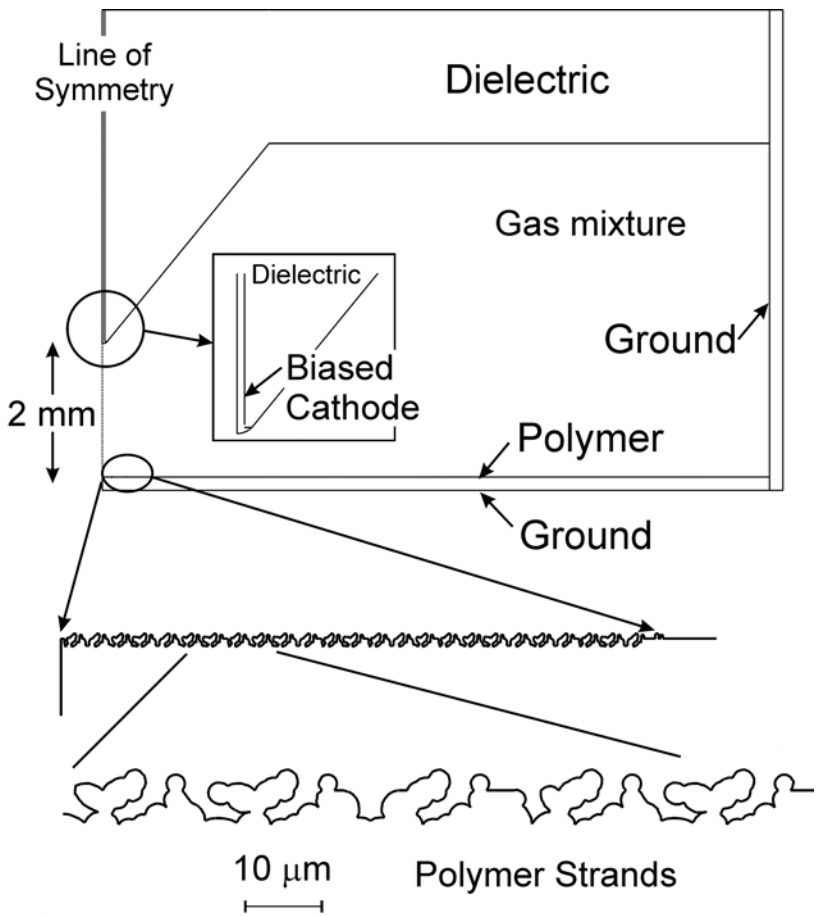
PLASMA FUNCTIONALIZATION OF TISSUE SCAFFOLDING



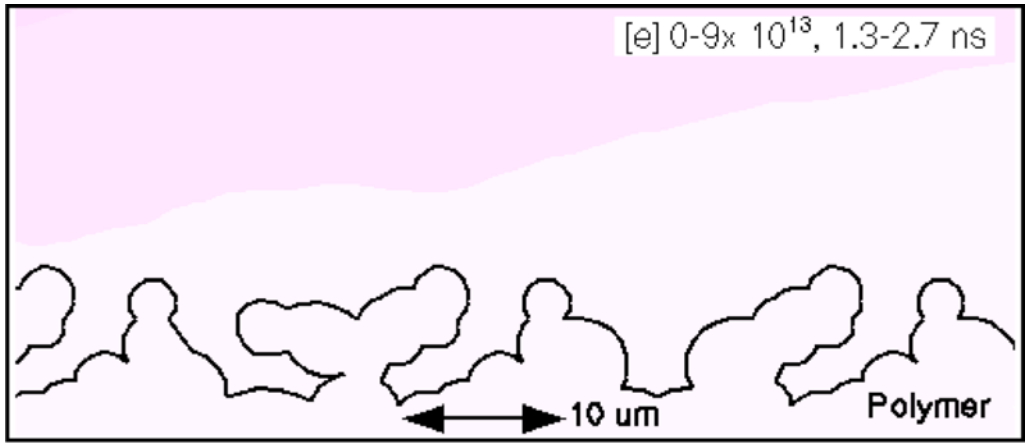


- **Tissue engineering requires "scaffolding" having nooks and crannies 10s -1000s μm in which cells adhere and grow.**
- **Scaffolding is functionalized to enhance cell adhesion or prevent unwanted cells from adhering.**
- **Can a now very expensive process be "cheapened" by using commodity plasma technologies?**

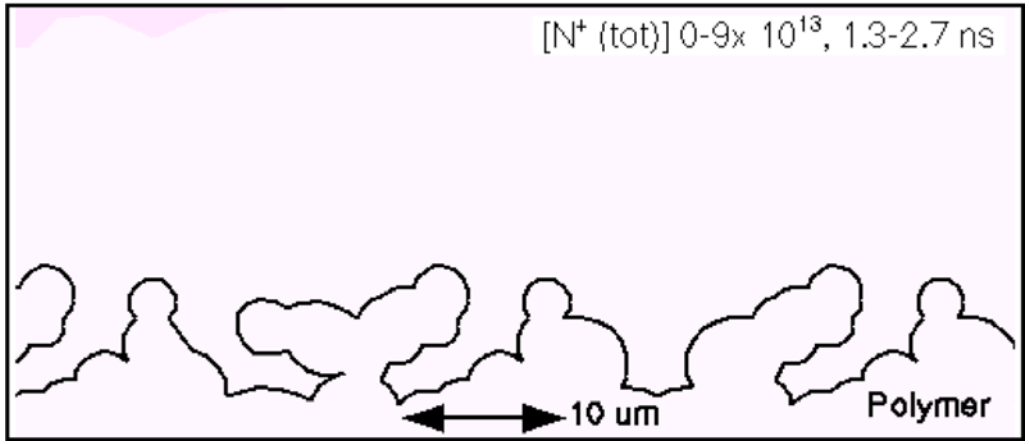
- *E. Sachlos,* European Cells and Materials v5, 29 (2003)

SURFACE INTERACTIONS: ELECTRON, IONS

Electrons



Positive Ions



- -15 kV, 760 Torr

min max

- As avalanche approaches surface, electrons penetrate into features.
- Charging of surface causes electrons to "bounce" off surface.
- Positive Ions penetrate only slowly into features.
- Ions peak at tips of features where charging produces cathode like conditions.

Animation Slide-GIF

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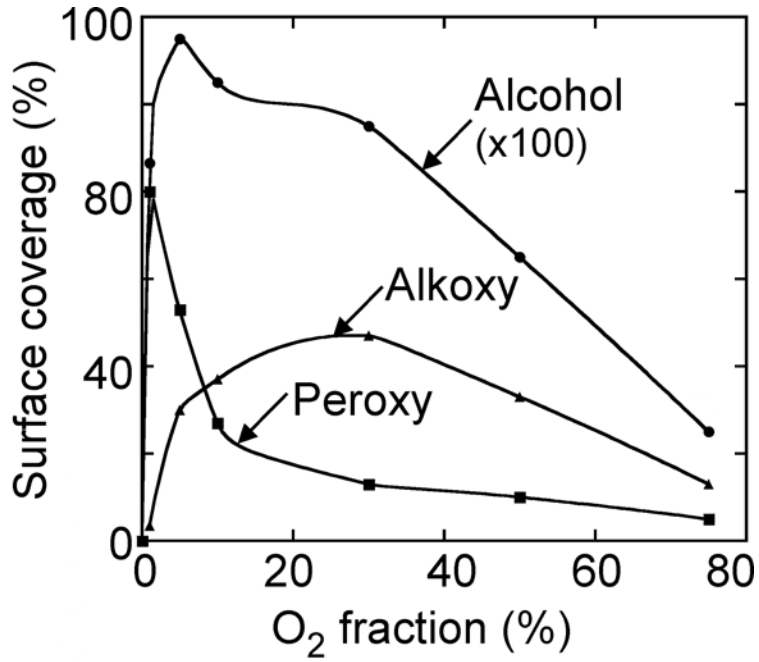

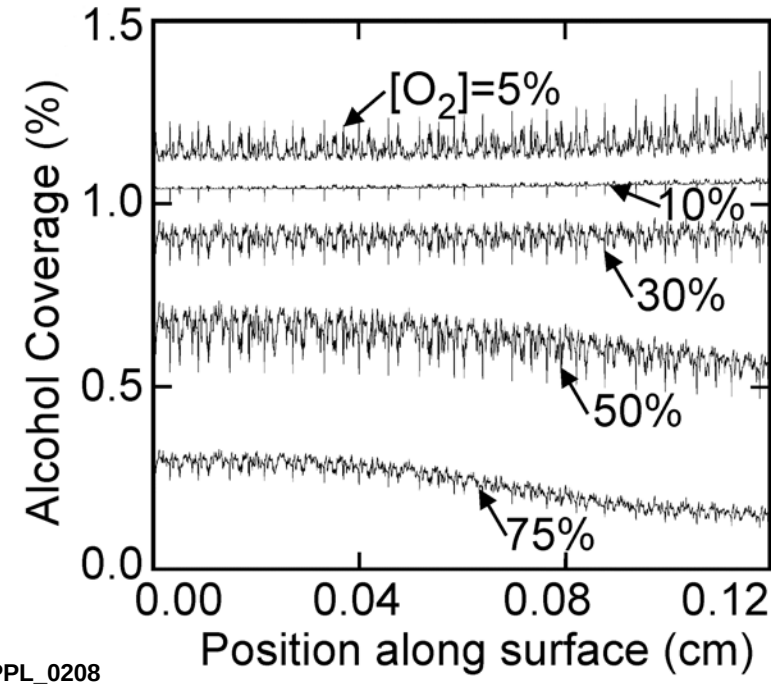

CONTROLLING FLUX OF OZONE TO SURFACE

- **Varying the amount O_2 in gas mixture enables control over functional groups.**
- **Ratio of O, OH and O_3 depend on O_2 fraction.**
- **By straddling reaction and transport limited regimes, uniform coverages can be obtained.**
- **$He/O_2/H_2O$ = 99-X /X/1**

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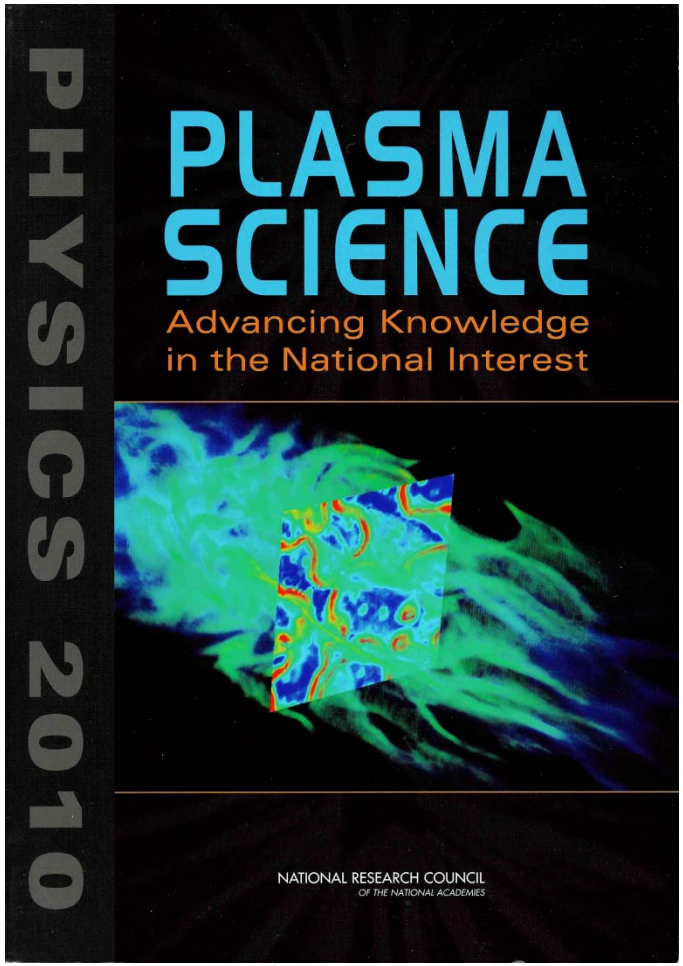
FUTURE SCIENCE CHALLENGES: PLASMA 2010

DECADAL STUDY: PLASMA 2010

- **In 2005, the National Academies convened the *Plasma 2010 Committee*.**
  - **Assess achievements of plasma science over past decade.**
  - **Identify opportunities and science challenges.**
  - **Offer guidance to address challenges and realize opportunities.**
- ***"Plasma Science: Advancing Knowledge in the National Interest"***
  National Academies Press
  http://www.nap.edu



SCIENTIFIC OPPORTUNITIES: ORGANICS

- ***Basic interactions of plasmas with organic materials and living tissue***

- **Now unclear which species and conditions are beneficial to biological and biologically compatible materials.**
- **Understand the behavior of biologically compatible materials and living tissue in contact with plasmas.**
- **Lessons can be learned from the development of plasmas for semiconductor processing.**
- **Example: Plasma wound sterilization**

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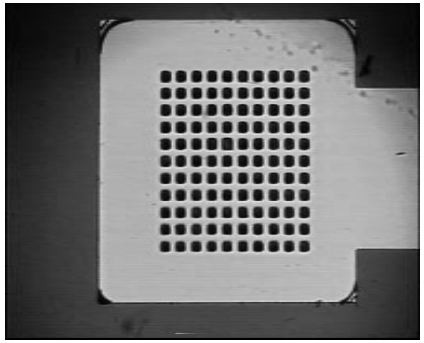
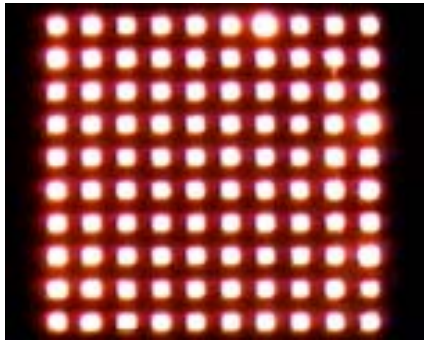
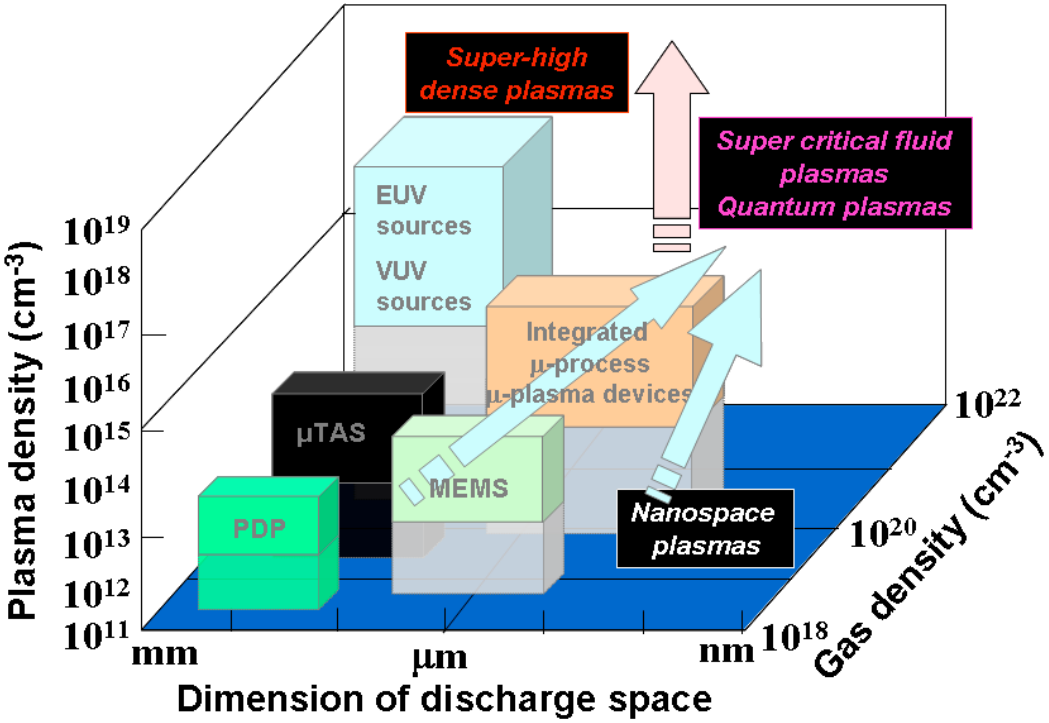
SCIENTIFIC OPPORTUNITIES: MICROPLASMAS



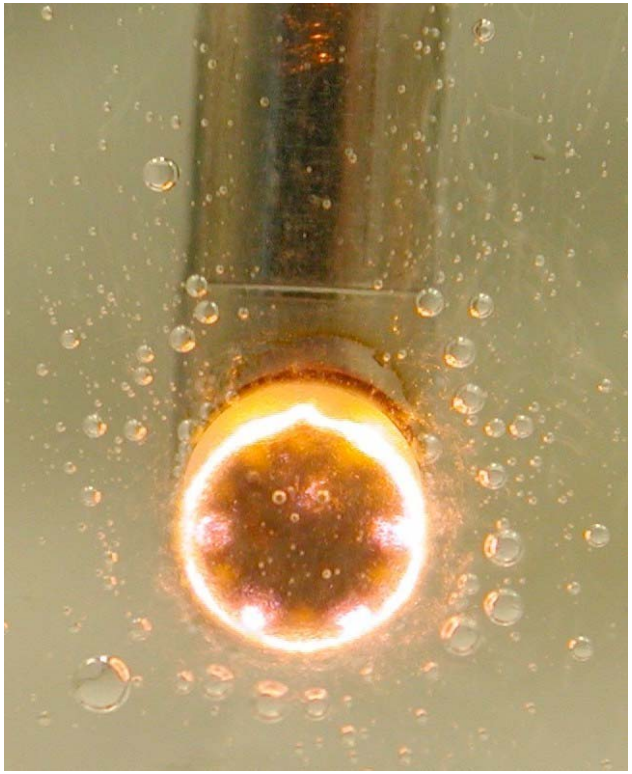




- ***Interaction of high-density (micro) plasmas with surfaces***
- **Microplasmas have very high charged particle densities.**
- **Electrons may merge with electrons in the confining materials.**
- **Solid-to-gas continuum... quantum effects may become important.**

SCIENTIFIC OPPORTUNITIES: CHAOTIC BEHAVIOR

- ***Methods to describe the behavior of plasmas that contain chaotic and stochastic processes.***



- **Low-temperature plasmas multi-scale.**
- **Many promising applications are inherently stochastic requiring unification of scales.**
- **Opportune time to develop general computational and diagnostic methods to treat complex, stochastic, multi-scale processes.**

- **Example: Plasma surgical instrument**

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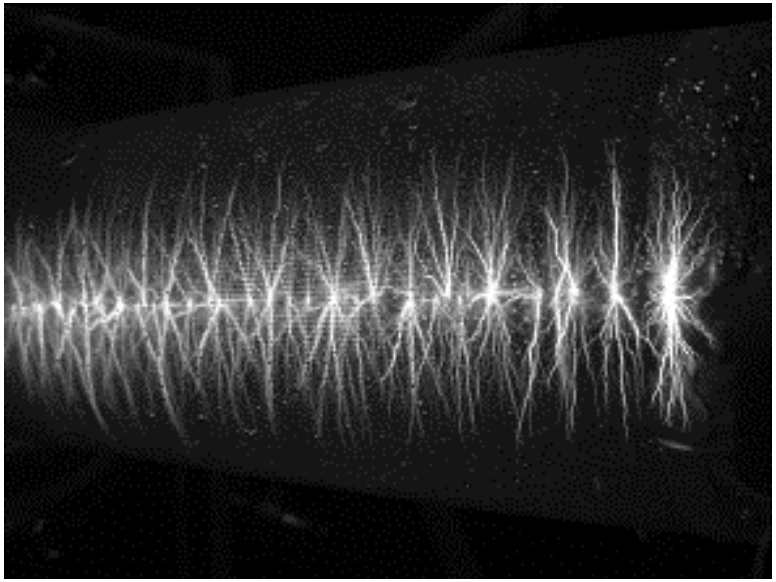
CHAOTIC BEHAVIOR IN HIGH PRESSURE DISCHARGES

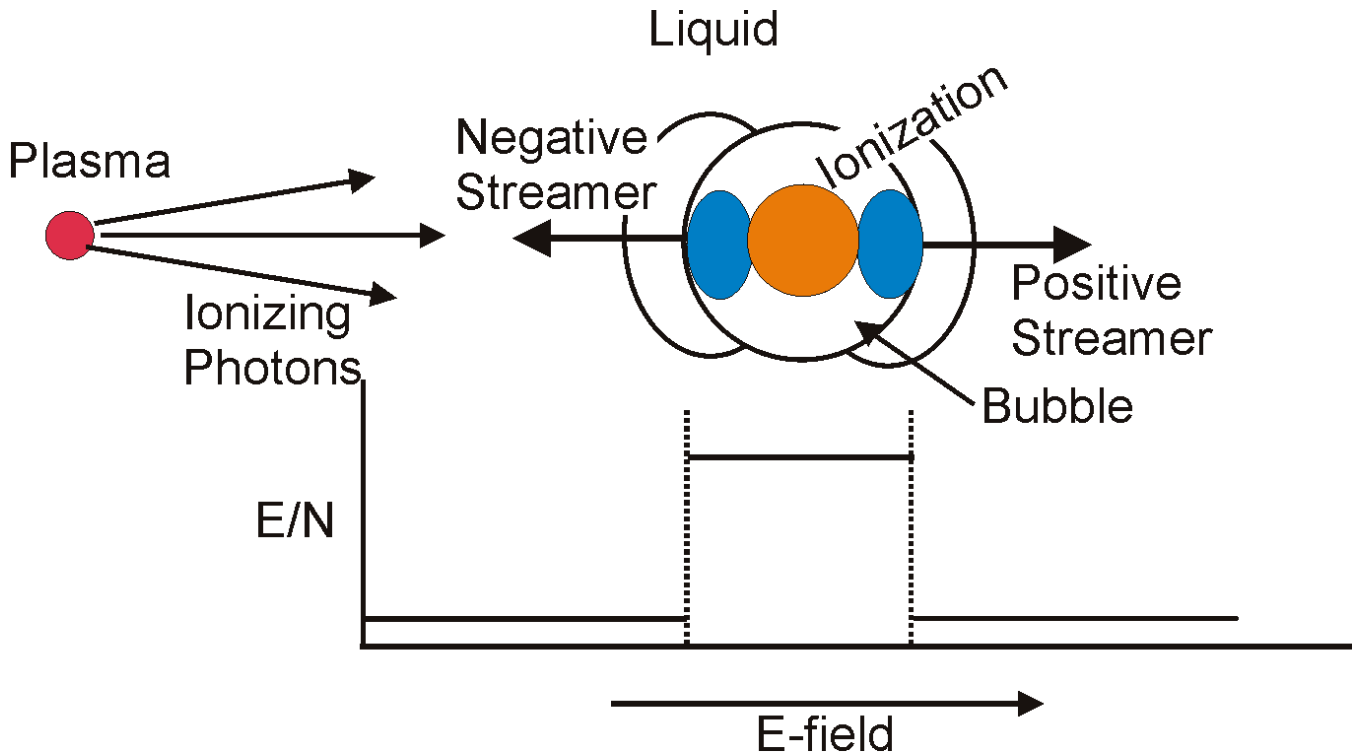
STREAMER BRANCHING AND CHAOS

- Origins of branching of streamers in high pressure gases and liquids are not understood.
- Branching is universal but chaotic- now unpredictable.
- Very large potential for science and technology advances
- Generally accepted that discharges in liquids propagate through a gas phase…initiated by bubbles?



- M. A. Malik, Y. TPS 33, 491 (2005)

BUBBLE THEORY OF PROPAGATION



- **Microscopic bubbles in liquid (naturally occurring).**
- **Ionizing radiation from plasma seeds electrons and ions inside bubble -- Large E/N inside bubble avalanches to streamer**
- **Vaporization of liquid by new streamers extend gas bubbles.**

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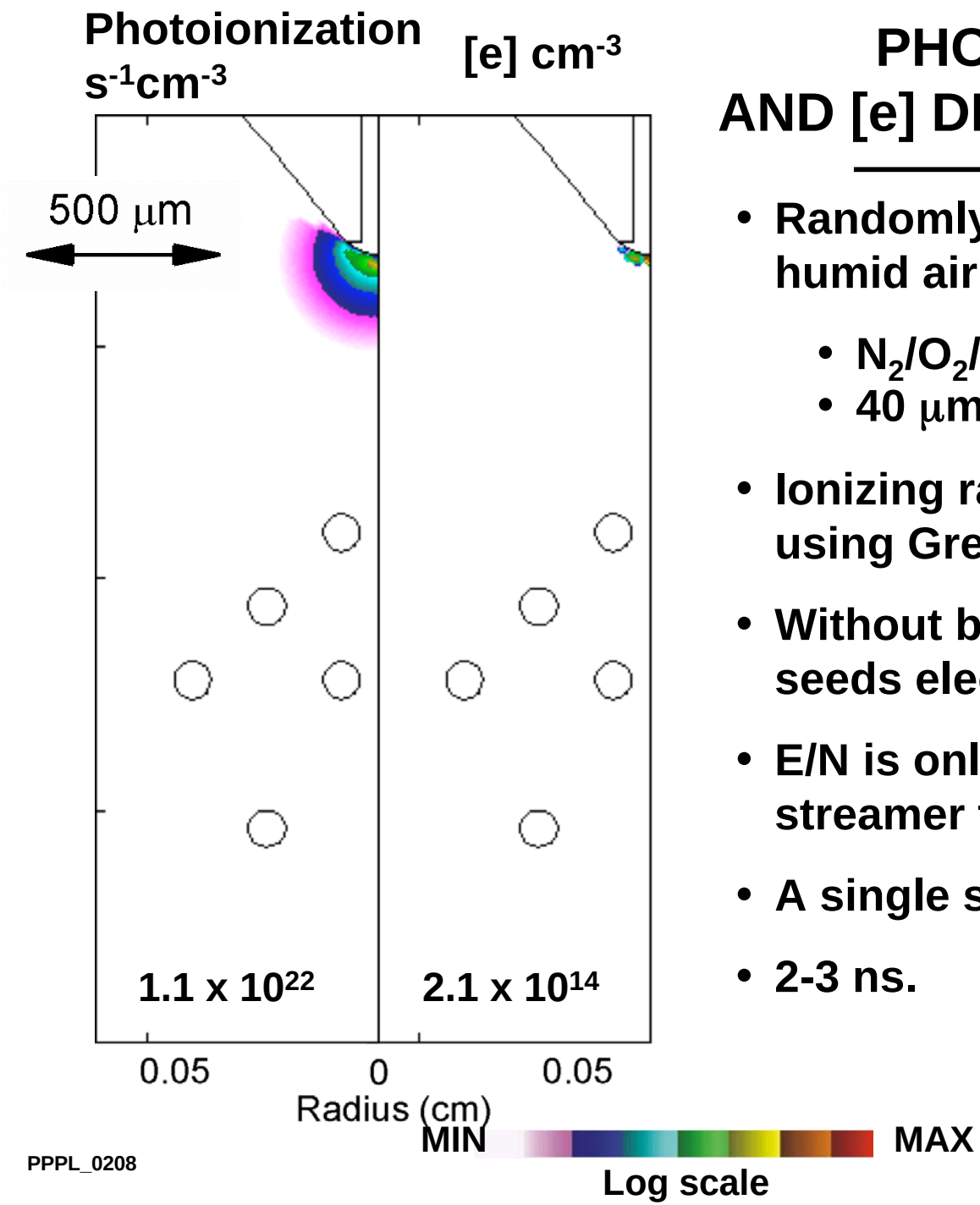
PHOTO-IONIZATION AND [e] DENSITY: NO BUBBLES



- Randomly placed "bubbles" in humid air positive corona.
  - $N_2/O_2/H_2O$ = 79.5/19.5/1, 760 Torr
  - 40 μm 150 Torr bubbles.
- Ionizing radiation from N_2* tracked using Greens function propagator.
- Without bubbles, photo-ionization seeds electrons ahead of streamer.
- E/N is only large enough at head of streamer to avalanche.
- A single streamer propagates.
- 2-3 ns.

Animation Slide

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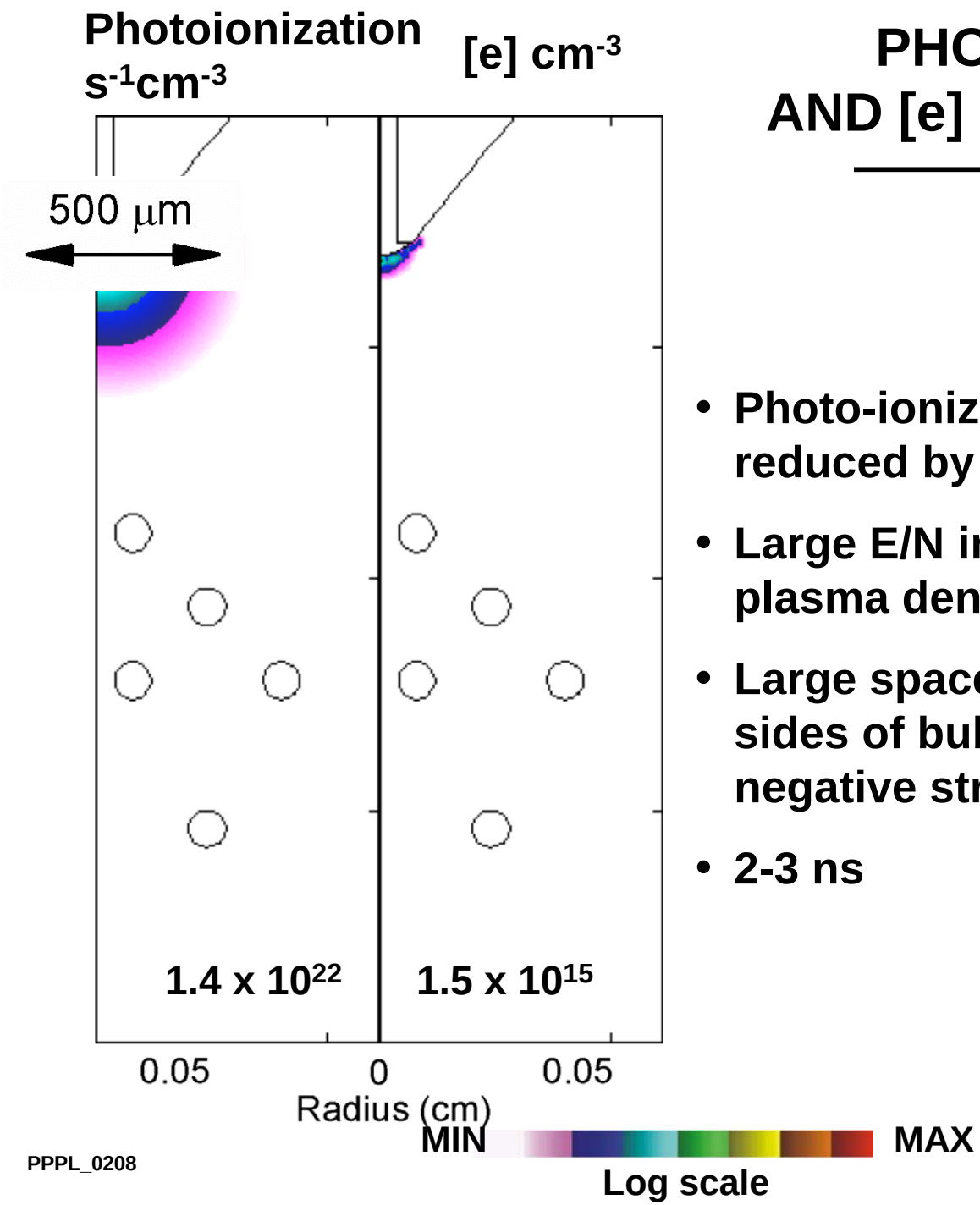
PHOTO-IONIZATION AND [e] DENSITY: BUBBLES



- Photo-ionization inside bubbles is reduced by pressure difference.
- Large E/N in bubbles avalanches plasma density.
- Large space charge at opposite sides of bubble launch positive and negative streamers.
- 2-3 ns

Animation Slide

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CONCLUDING REMARKS

- **Plasma materials processing has an extraordinary diverse range of applications.**
- **The unique ability to control the energy and variety of reactant fluxes enables customization of high value materials – or using commodity processes to create high value.**
- **The coming decade will see increasing use of plasmas for biological applications, from the treatment of biocompatible surfaces and living tissue, to surgical instruments.**
- **The close connectivity to commercial applications makes one pause to consider economics.**