FUNCTIONALIZATION OF SURFACES BY PLASMAS AT LOW AND HIGH PRESSURE*

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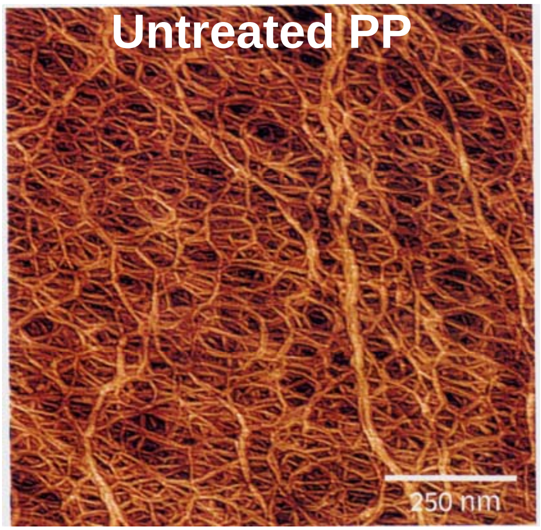
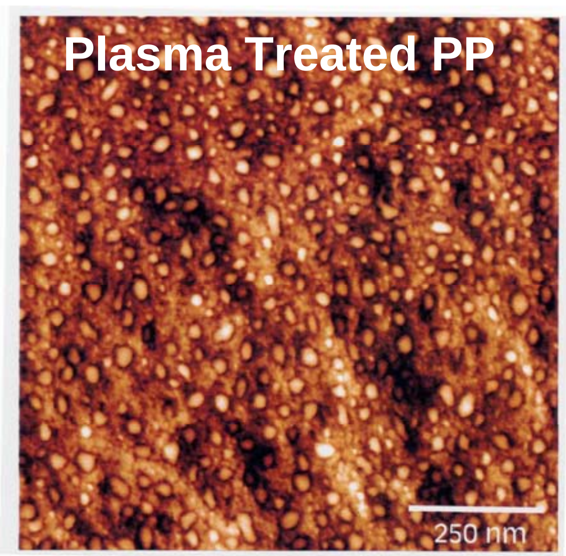
AGENDA

- Introduction to plasma surface functionalization
- Description of the model
- High Pressure:
  - Plasma dynamics in $He/NH_3/H_2O$ and humid air mixtures
  - Functionalization of rough and porous surfaces
- Low Pressure: Ions and Shadowing
- Concluding remarks

- Work supported by National Science Foundation, 3M Inc and Semiconductor Research Corp.

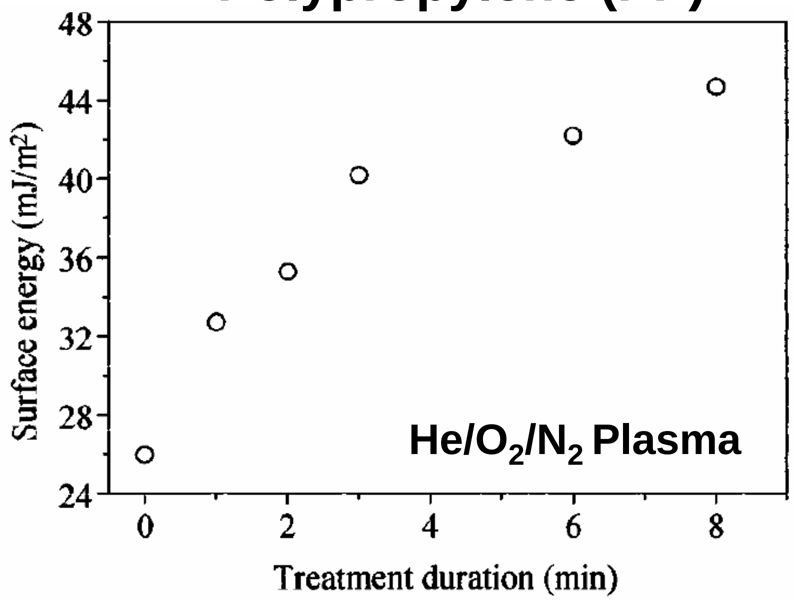
PLASMA FUNCTIONALIZATION SURFACES





- M. Strobel, 3M

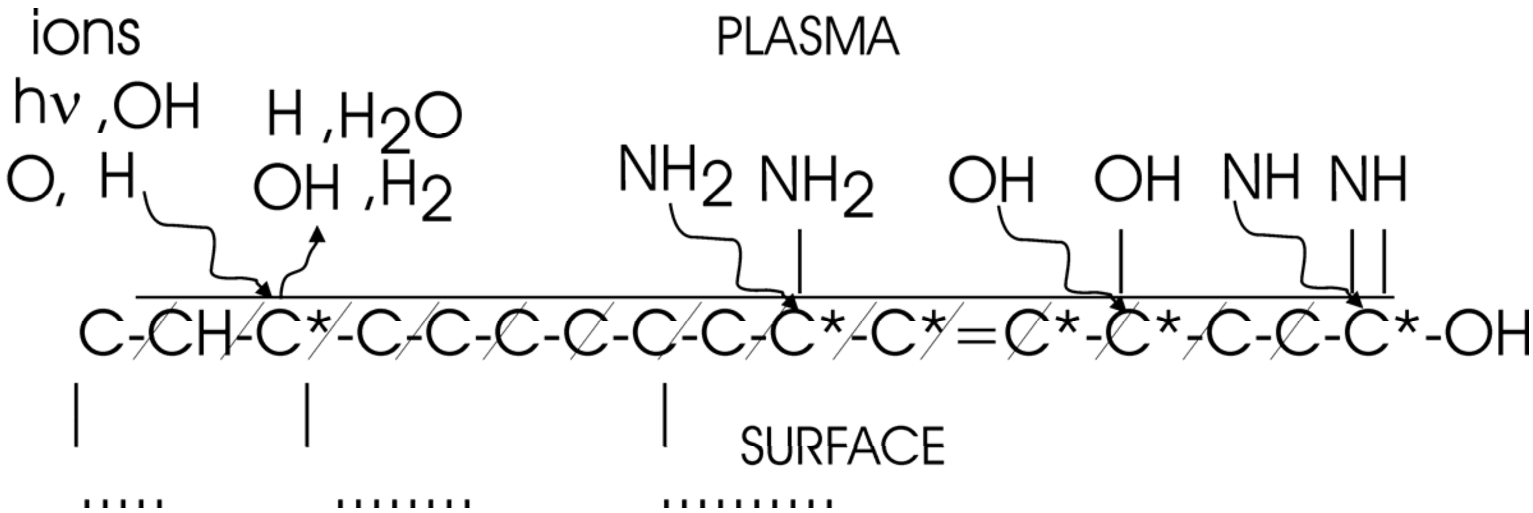
- To modify wetting, adhesion and reactivity of surfaces, such as polymers, plasmas are used to generate gas-phase radicals to functionalize their surfaces.
- Example: atm plasma treatment of PP
  - Polypropylene (PP)



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

FUNCTIONALIZATION OF POLYMERS USING PLASMAS

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



- **Example: An ammonia containing plasma fixes N-containing groups that are conducive to cell adhesion.**
  - **Amine –C-NH_2**
  - **Imine –C=NH**
  - **Nitrile –C ≡N**

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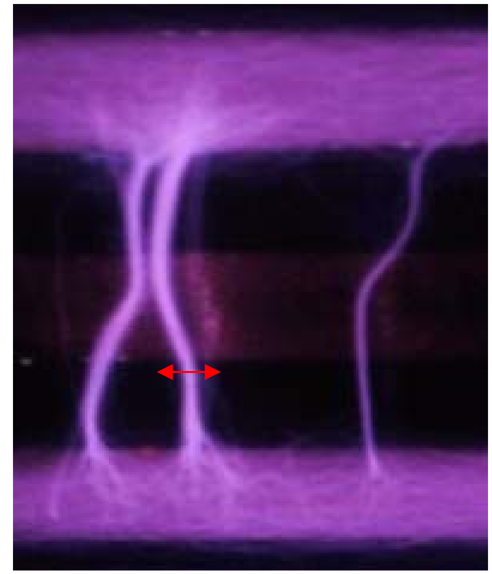
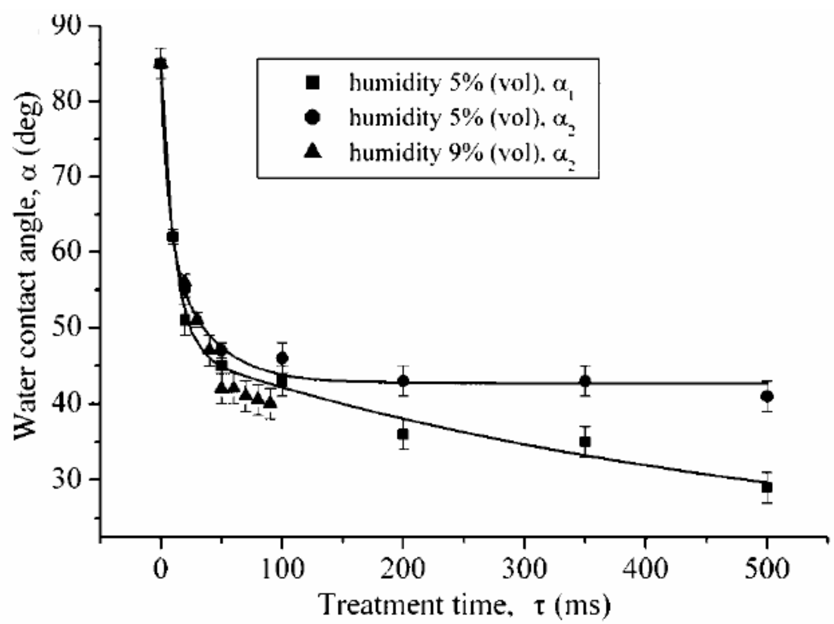
SURFACE MODIFICATION OF POLYMERS

- **Pulsed atmospheric filamentary discharges (coronas) are treat commodity polymers like poly-propylene (PP) and polyethylene (PE).**



- **Filamentary Plasma 10s – 200 μm**



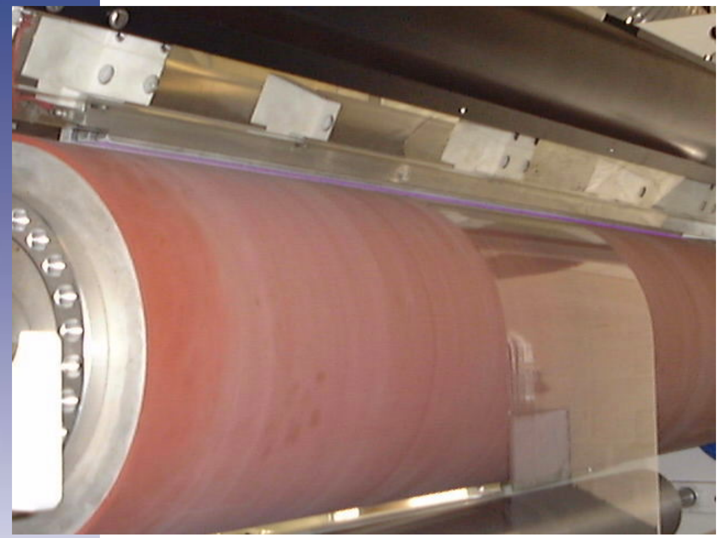
- **PE Film**

- **These processes are inexpensive, <\$0.05/m^2. Scaling to higher value material is attractive.**

- **Akishev, *et al*, Plasmas Polym., 7, 261 (2002).**

COMMERCIAL CORONA PLASMA EQUIPMENT

- Tantec, Inc.



- Sherman Treaters

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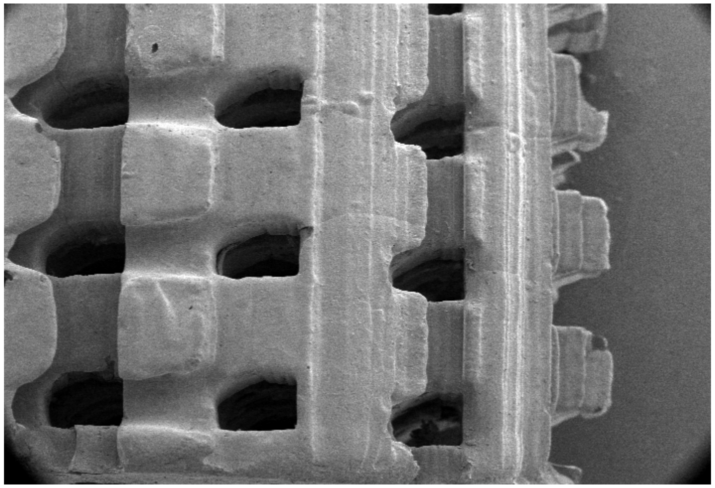
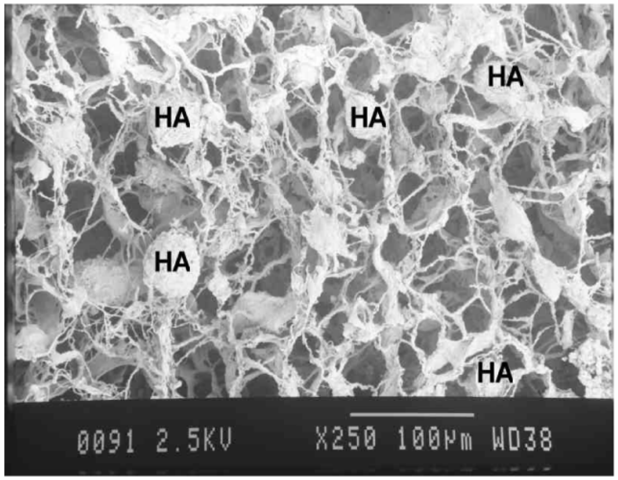
PLASMAS FOR MODIFICATION OF BIOCOMPATIBLE SURFACES: TISSUE ENGINEERING

- **Tissue engineering requires "scaffolding"; substrates with nooks and crannies 10s -1000s μm in which cells adhere and grow.**
- **Scaffolding is chemically treated (functionalized) to enhance cell adhesion or prevent unwanted cells from adhering.**



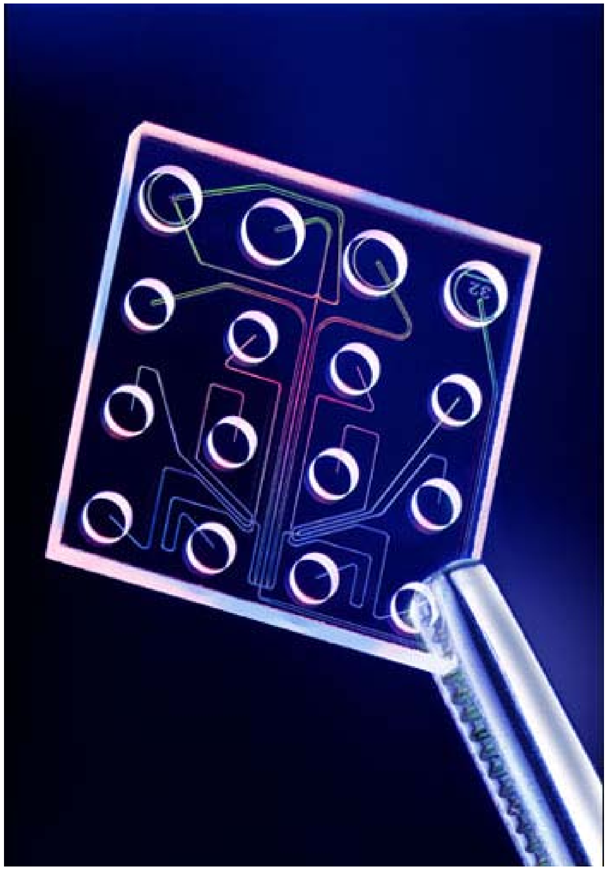
- ***Tien-Min Gabriel Chu***
  http://www.engr.iupui.edu/~tgchu



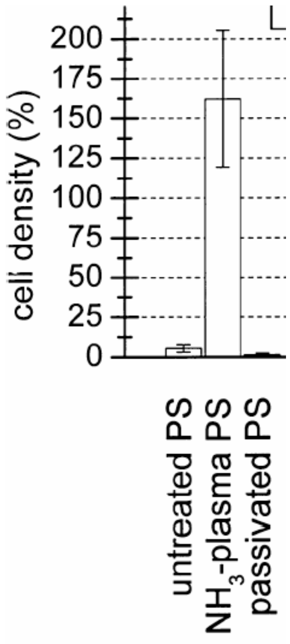
- *E. Sachlos,* European Cells and Materials v5, 29 (2003)

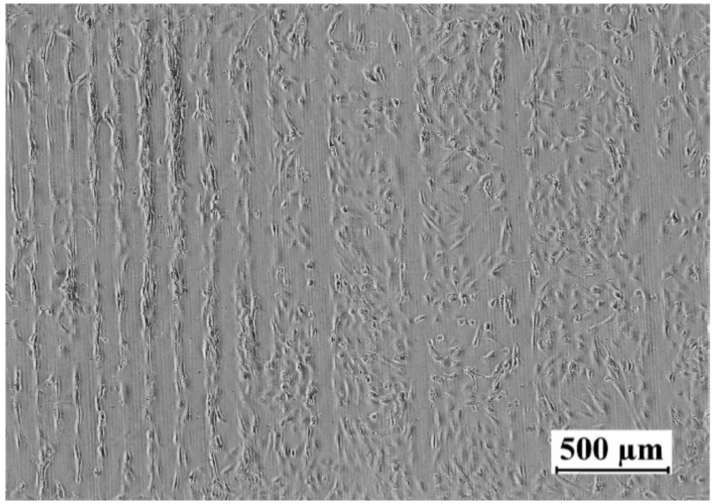
"LAB ON A CHIP"

- "Lab on a Chip" typically has microfluidic channels 10s -100s μm wide and reservoirs for testing or processing small amounts of fluid (e.g., blood)
- Internal surfaces of channels and reservoirs must be treated (i.e., functionalized) to control wetting and reactions.
- Desire for mass produced disposable units require cheap process.
- Ref: Calipers Life Sciences, Inc. http://www.caliperls.com

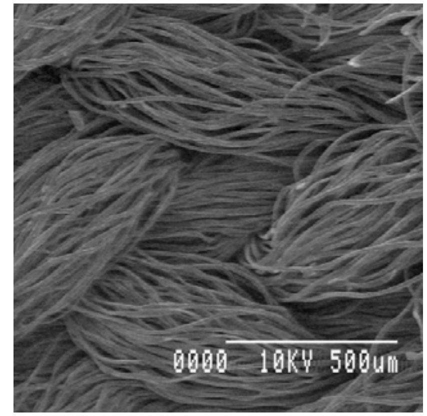


FUNCTIONALIZATION FOR BIOCOMPATIBILITY





Micropatterned cell growth on NH_3 plasma treated PEEK[1]



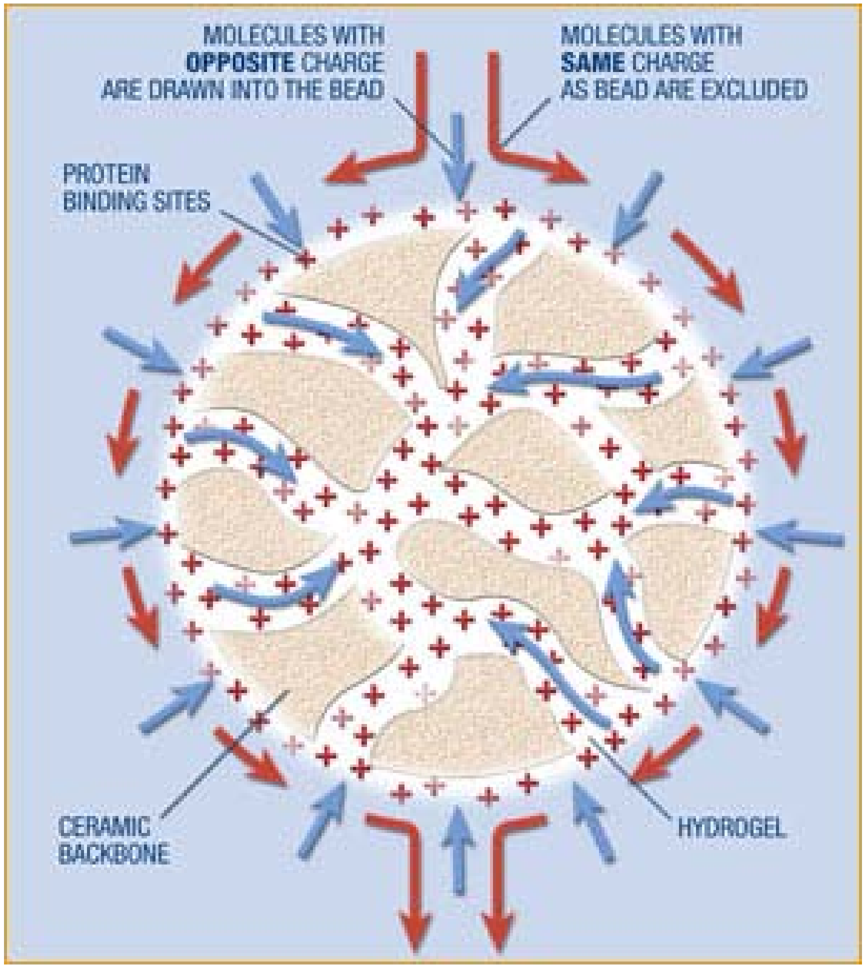
Textiles are used as scaffolds for tissue engineering[2], which could also be plasma treated

- **Ammonia plasma treatment creates amine ($C\text{-}NH_2$) groups on polymer[1] and textile[2] surfaces for applications such as cell adhesion, protein immobilization and tissue engineering.**

([1]K. Schroeder *et al*, Plasmas and Polymers, 7, 103, 2002)

([2]Biomedical Textile Research Center, Heriot Watt University, UK, http://www.hw.ac.uk/sbc/BTRC/BTRC/_private/Ouractivities.htm)

TREATMENT OF POROUS POLYMER BEADS



- **Macroporous beads are 10s µm in diameter with pore sizes < 10 µm.**
- **External and internal surfaces are functionalized for polymer supported catalysts and protein immobilization.**
- **Penetration of reactive species into pores is critical to functionalization.**

- **Functionalized Porous Bead for Protein Binding sites (www.ciphergen.com)**

FUNCTIONALIZING SMALL FEATURES

- Using atmospheric pressure plasmas (APPs) to functionalizing small features is ideal due to the low cost of the apparatus.
- Low pressures plasmas (LPPs), though more costly, likely provide higher degrees of uniformity.
  - Can APPs provide the needed uniformity and penetration capability into small features?
  - Are LPPs necessarily the plasma of choice for small feature functionalization.
- In this talk, the functionalization of small features using APPs and LPPs will be discussed using results from computer simulations.
  - NH_3 plasmas to fix $=NH_x$ functionality for cell adhesion.
  - O_2 plasmas to fix =O functionality for improved wettability.

DESCRIPTION OF nonPDPSIM: CHARGED PARTICLE, SOURCES

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

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

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

- **Electron energy equation:**

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

- **Photoionization:**

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

- **Surface chemistry model.**

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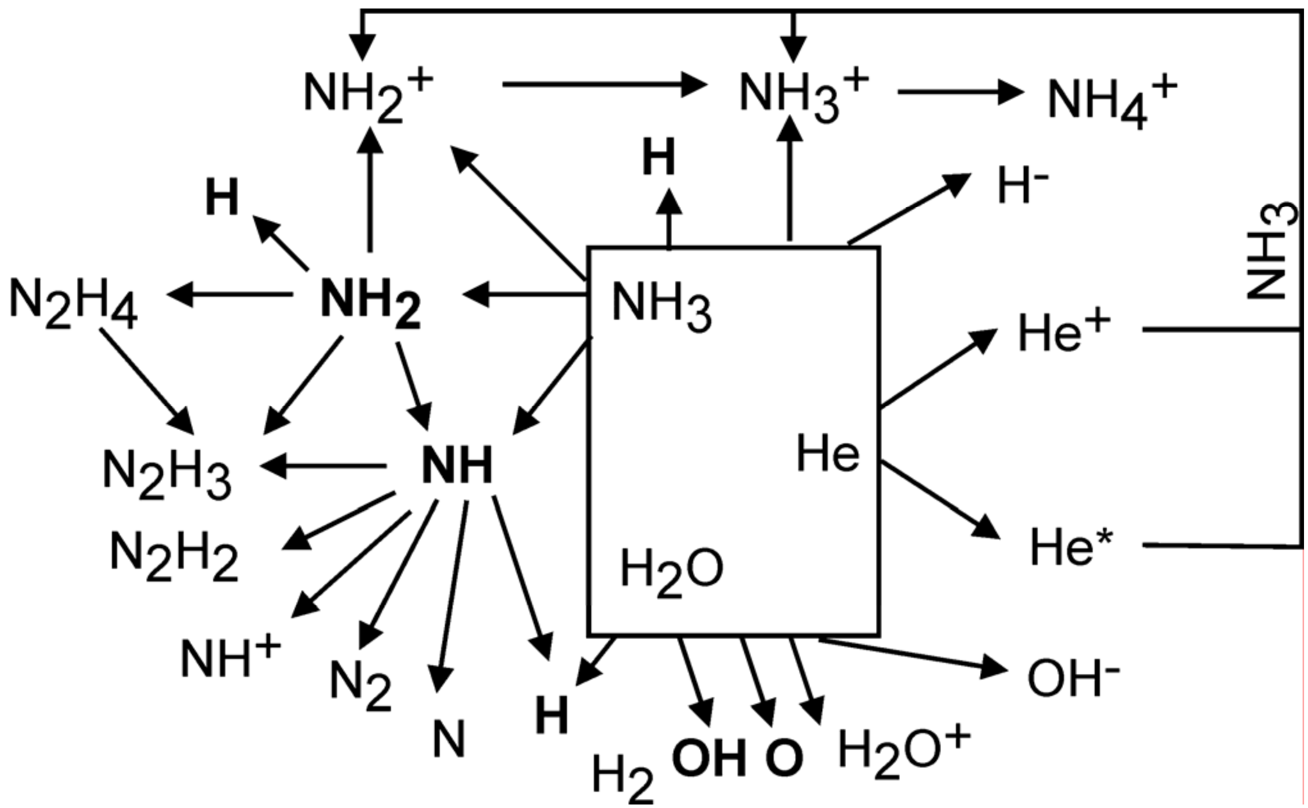
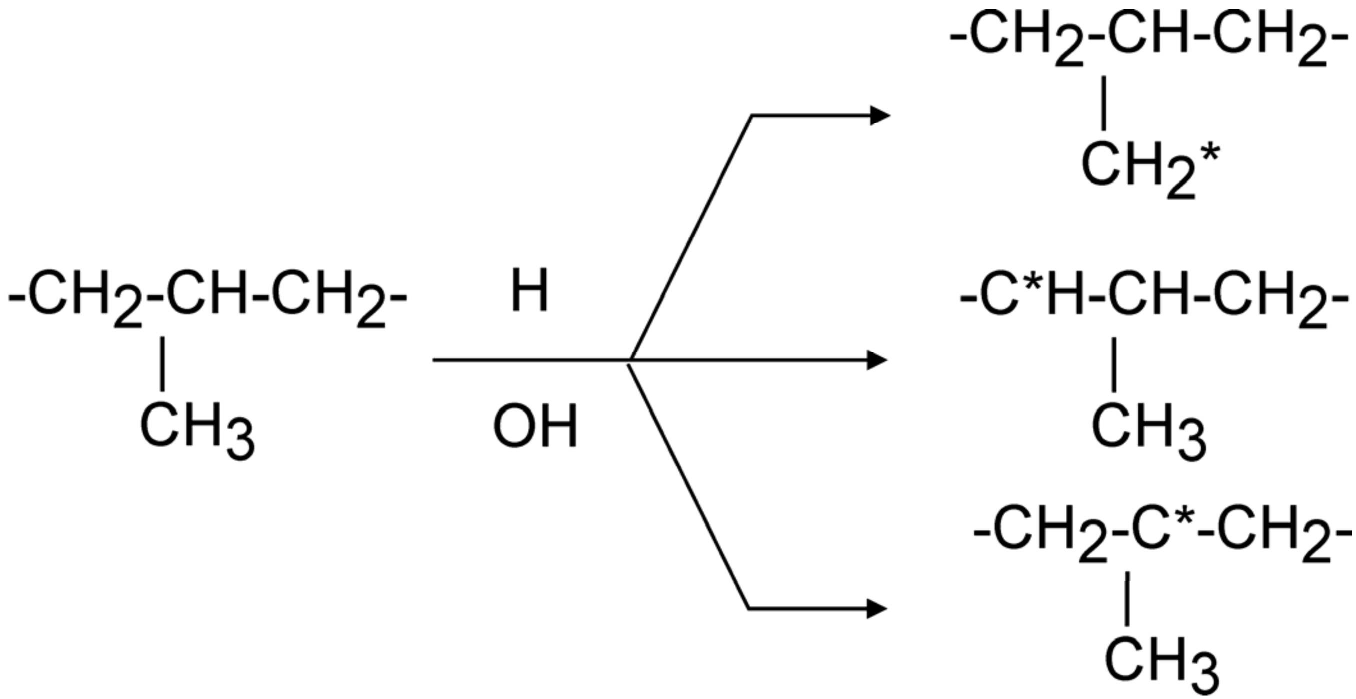
GAS PHASE CHEMISTRY - $He/NH_3/H_2O$ MIXTURES



- **Electron impact reactions initiate dissociate NH_3 and H_2O into radicals that functionalize surface.**
- **H, NH_2, NH, O and OH are major radicals for surface reactions.**

SURFACE REACTION MECHANISM

- Gas phase H, O and OH abstract H atoms from the PP surface producing reactive surface alkyl (R-•) radical sites.



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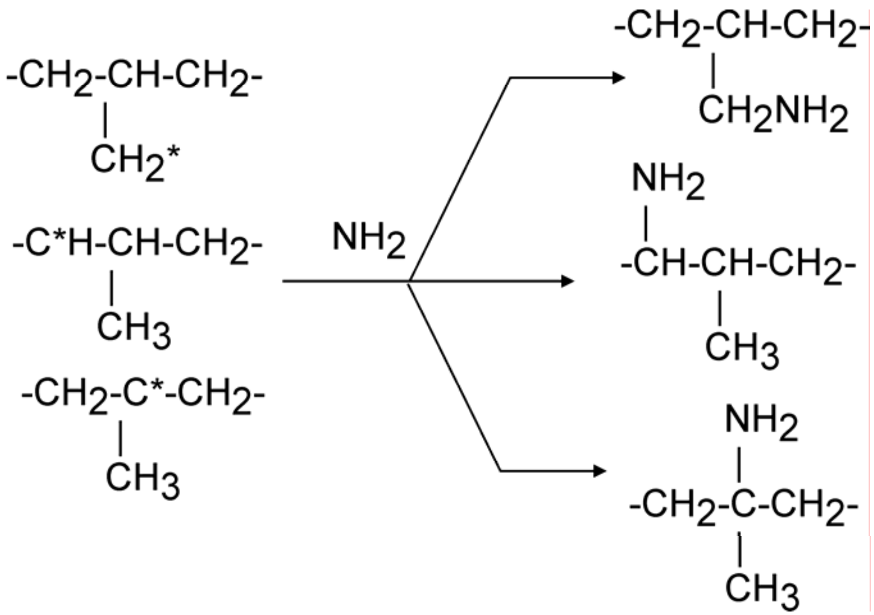
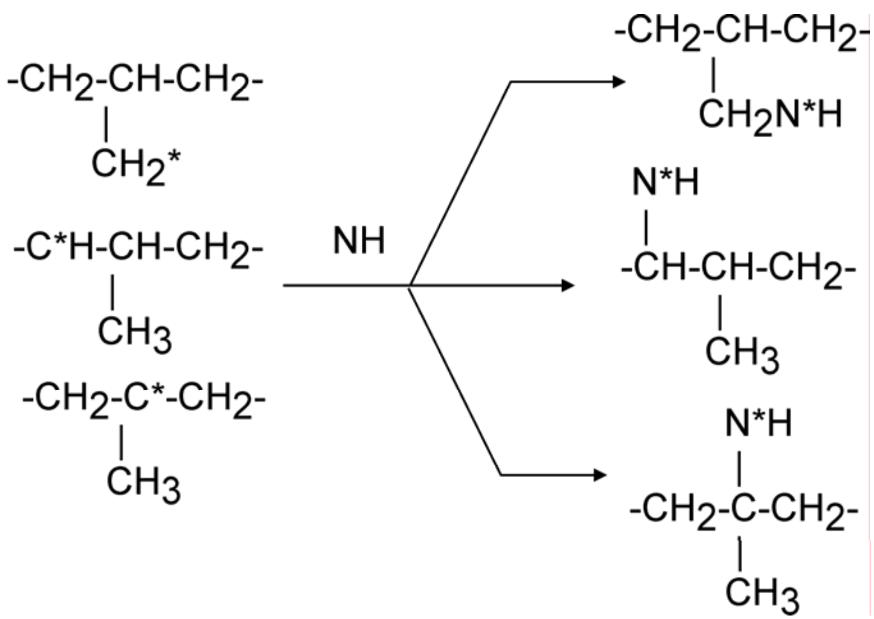
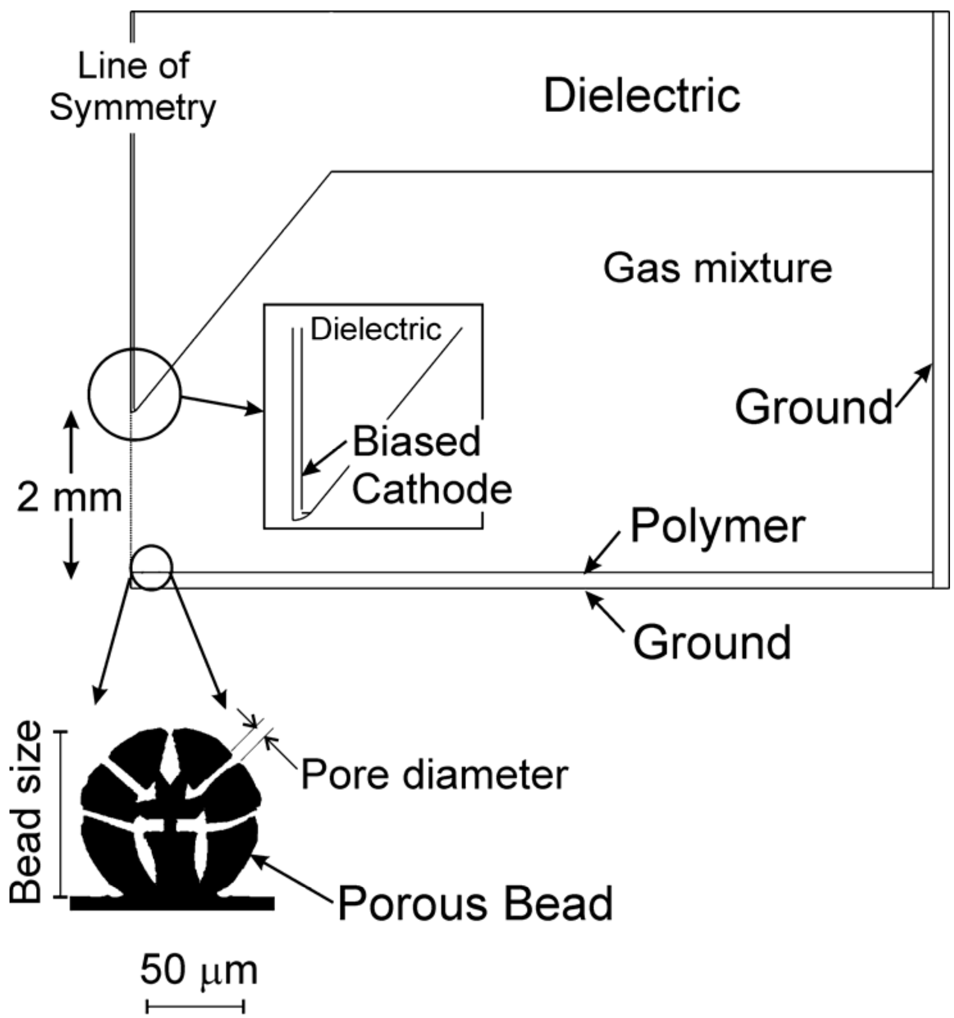
SURFACE REACTION MECHANISM





- **Gas phase NH_2 and NH radicals react with surface alkyl sites creating amine (R-NH_2) groups and amino (R-H•) sites.**

DBD TREATMENT OF POROUS POLYMER BEAD



- Corona treatment of porous polymer beads for drug delivery.
- How well are the internal surfaces of pores accessible to the plasma?
- What is the extent of functionalization on internal surfaces?
- Bead size ~ 10s μm
- Pore diameter ~ 2-10 μm

- - 5 kV, 1 atm, $He/NH_3/H_2O$=90/10/0.1
- PRF – 10 kHz

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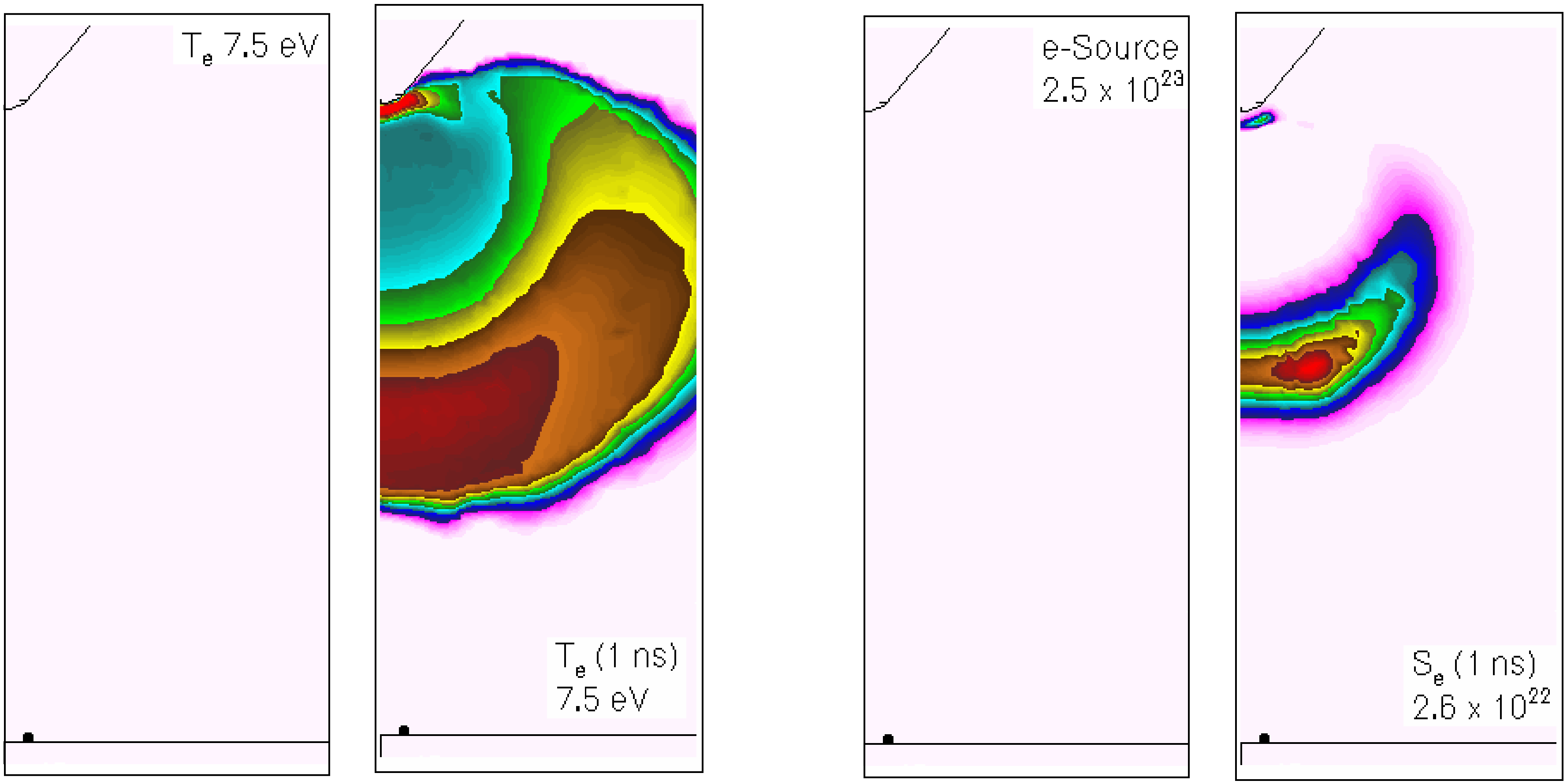
ELECTRON TEMPERATURE, SOURCE



- **Electron Temperature**
- **Electron Source**

Animation Slide-GIF

- **- 5 kV, 1 atm, He/NH_3/H_2O=90/10/0.1, 0-3.5 ns**

MIN **MAX**

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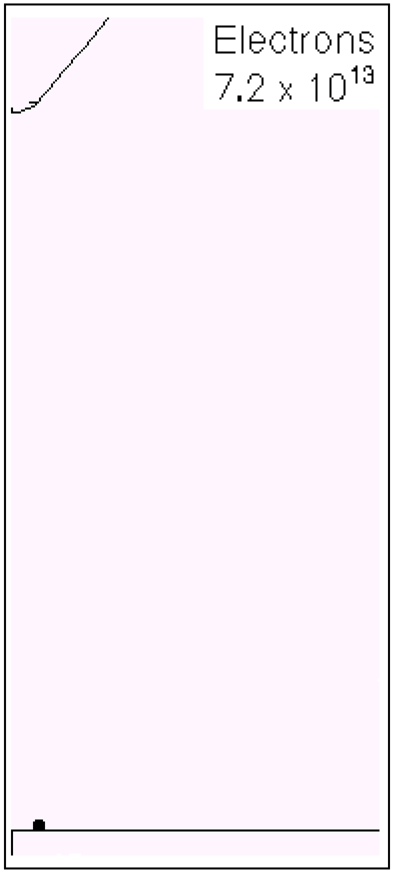
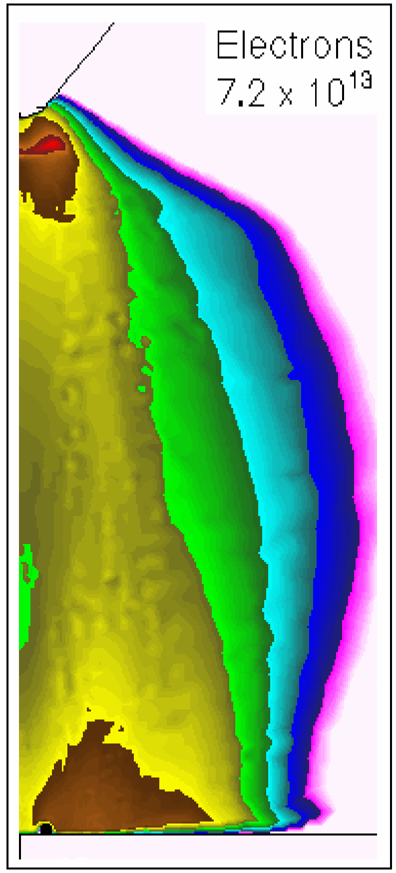
ELECTRON DENSITY





- **Electron density of 10^{13}-10^{14} cm^{-3} is produced.**
- **Electron impact dissociation generates radicals that functionalize surfaces.**

Animation Slide-GIF

- **- 5 kV, 1 atm, He/NH_3/H_2O=90/10/0.1, 0-3.5 ns**

MIN **MAX**

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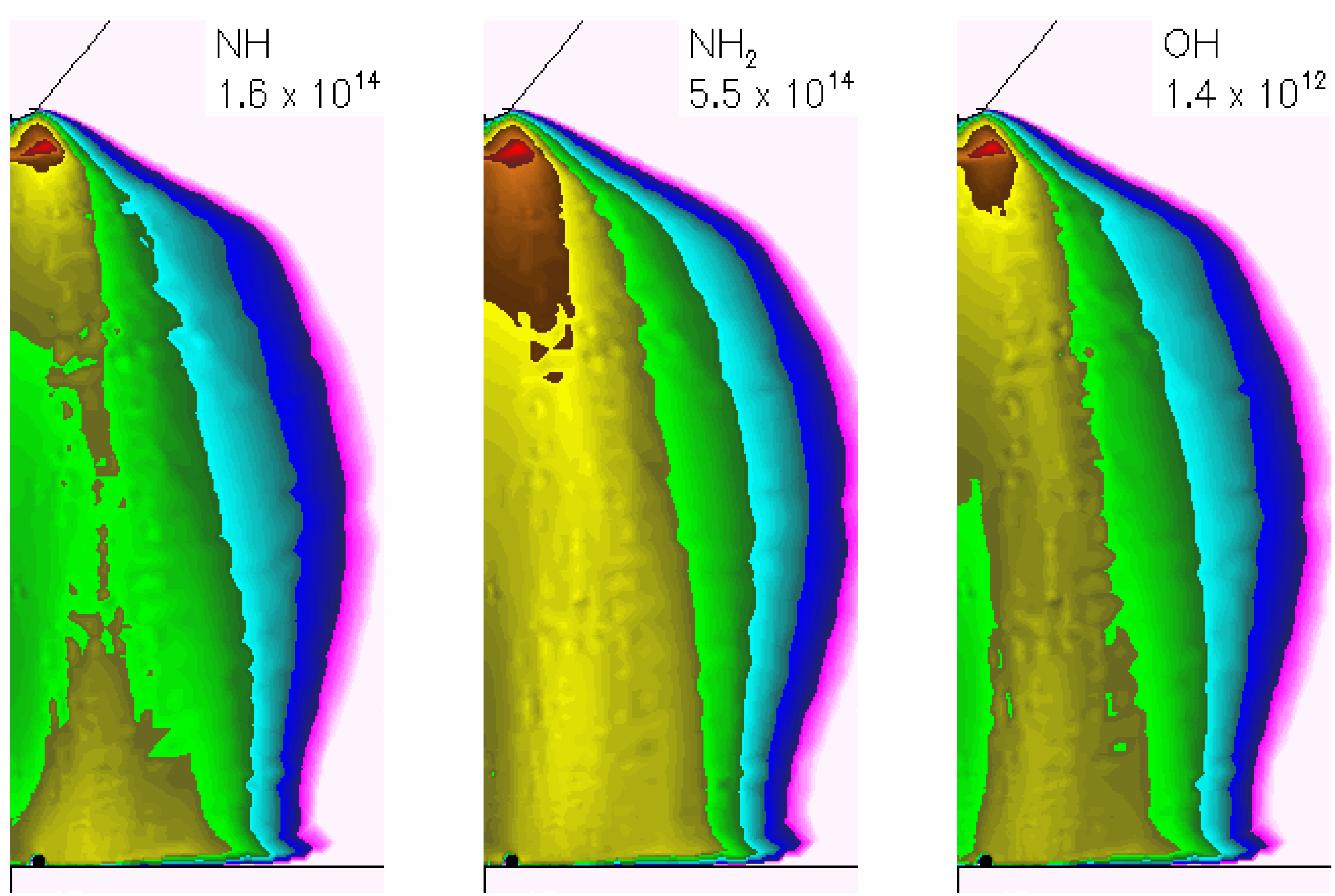
POST-PULSE RADICAL DENSITIES



- NH
- NH_2
- OH

- \- 5 kV, 1 atm, $He/NH_3/H_2O$=90/10/0.1

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MIN  MAX

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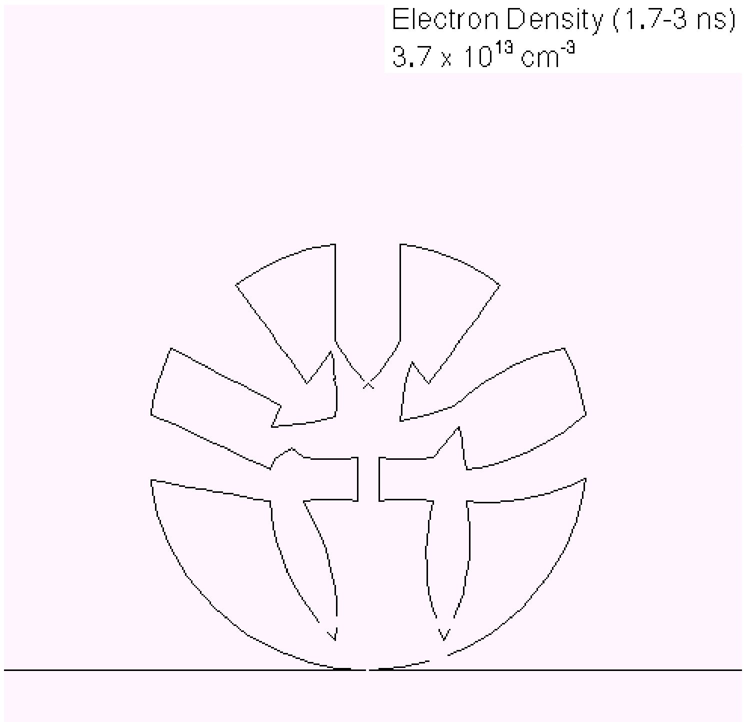
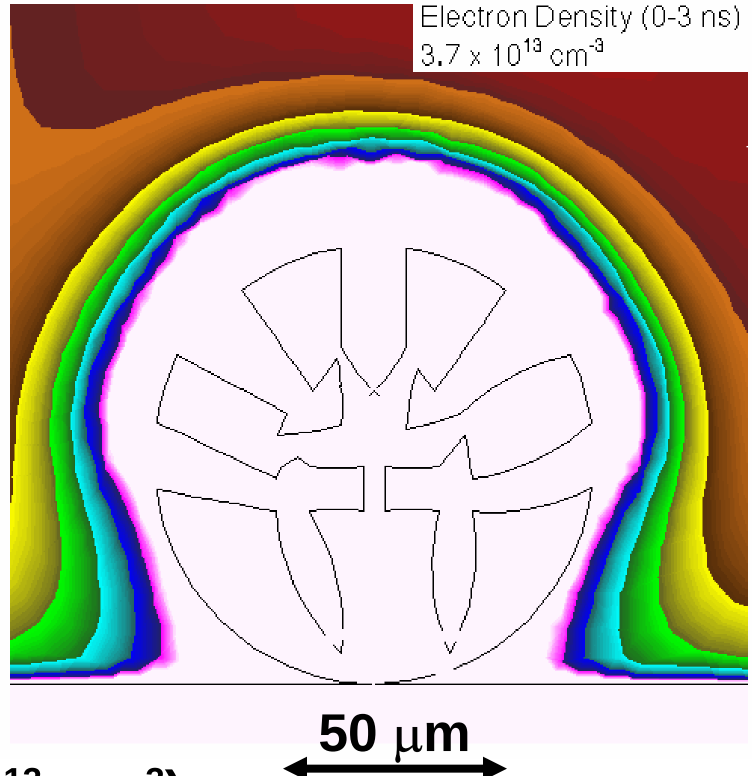
ELECTRON DENSITY IN AND AROUND BEAD





- **Electrons (3.7 x 10^{13} cm^{-3})**

- **In negative corona discharge, electrons lead the avalanche front and initially penetrate into pores. Charging of surfaces limit further electron penetration.**

Animation Slide-GIF

- **- 5 kV, 1 atm, He/NH_3/H_2O=90/10/0.1, 0-3 ns.**

MIN  **MAX**

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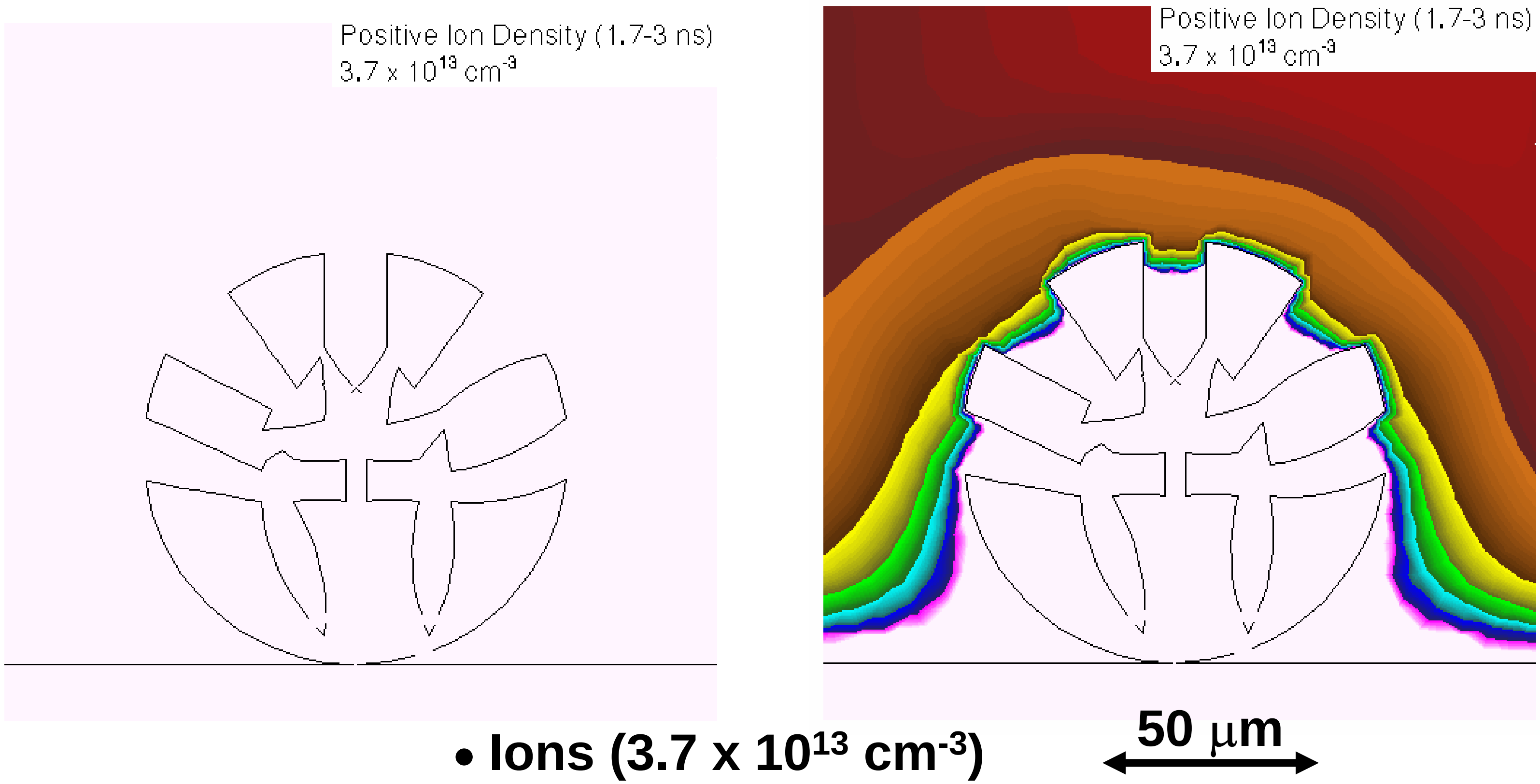
TOTAL POSITIVE ION DENSITY IN AND AROUND BEAD



- Ions (3.7×10^{13} cm^{-3})

- Ions lag electrons arriving at bead but persist at surfaces due to negative charging that makes the surfaces cathode like.

- Lower surface (anode) is ion repelling.

Animation Slide-GIF

- \- 5 kV, 1 atm, $He/NH_3/H_2O$=90/10/0.1, 0-3 ns

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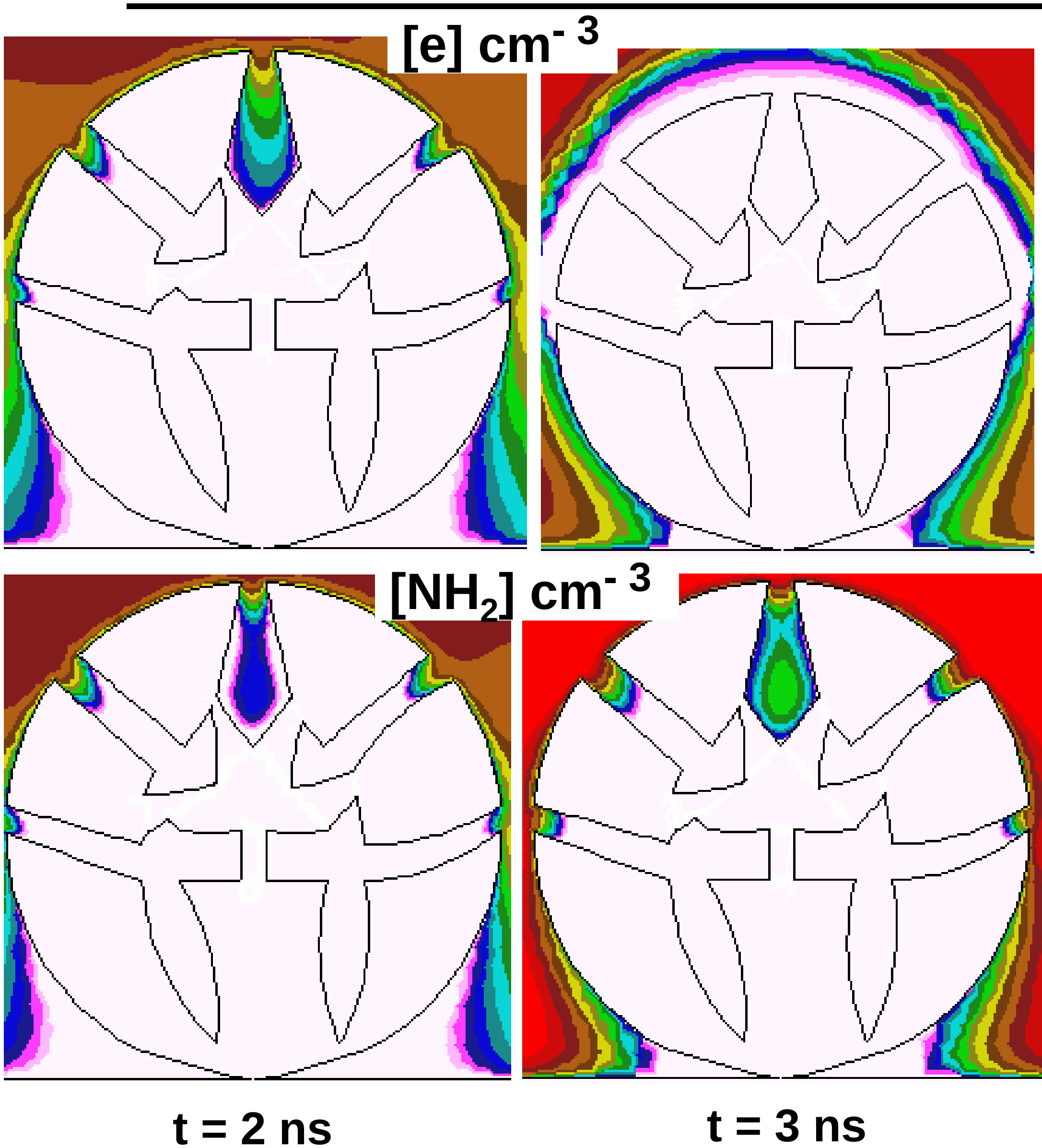
PLASMA PENETRATION INTO INTERNAL SURFACES



- Electron penetration into pores depends on the view-angle.
- Electrons recede due to surface charging effects.
- Radical production inside pores is high in those regions where plasma has penetrated.
- - 5 kV, 1 atm, $He/NH_3/H_2O$=90/10/0.1

$5\times10^{9} – 5\times10^{13}$

MIN MAX

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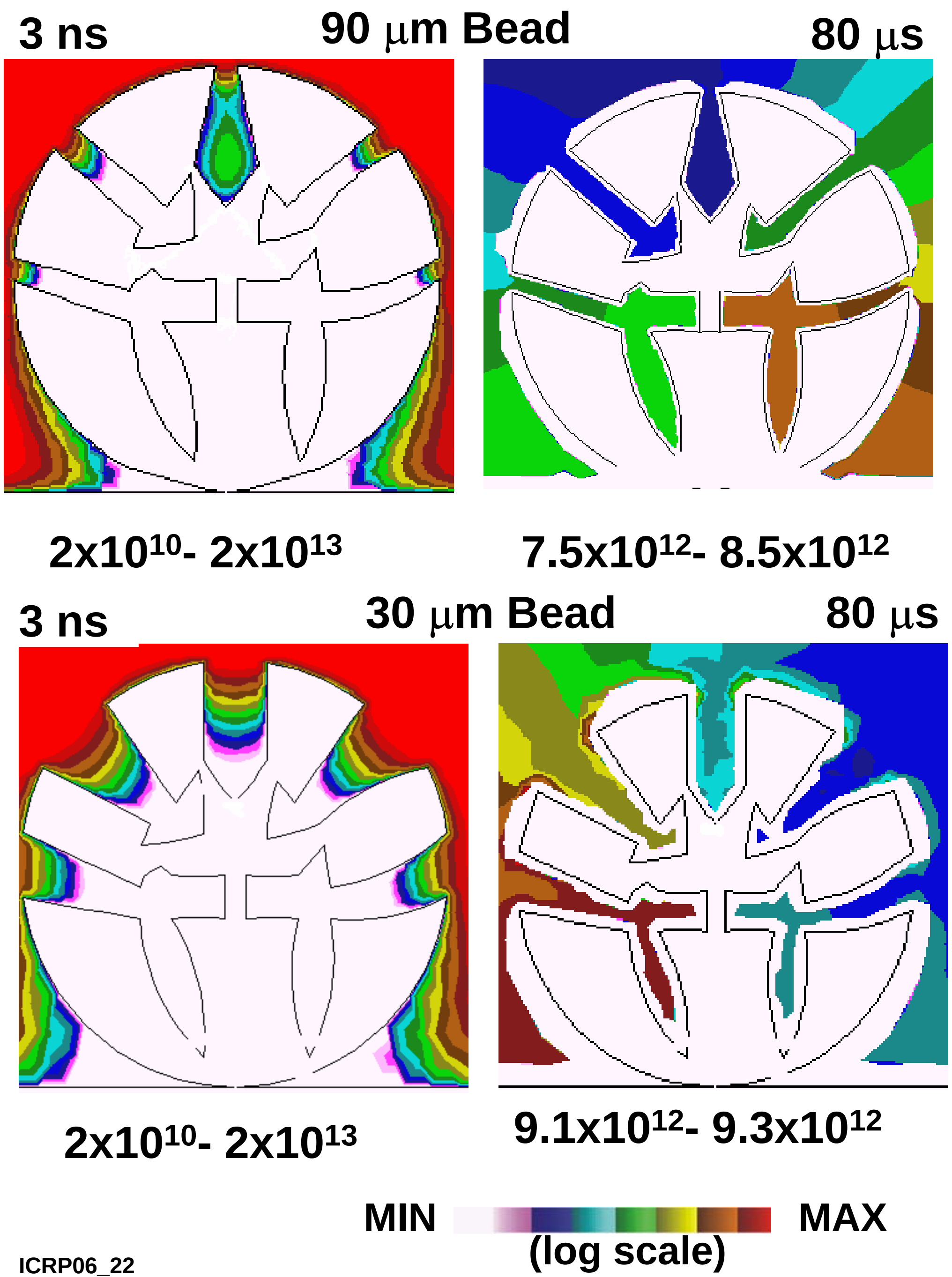

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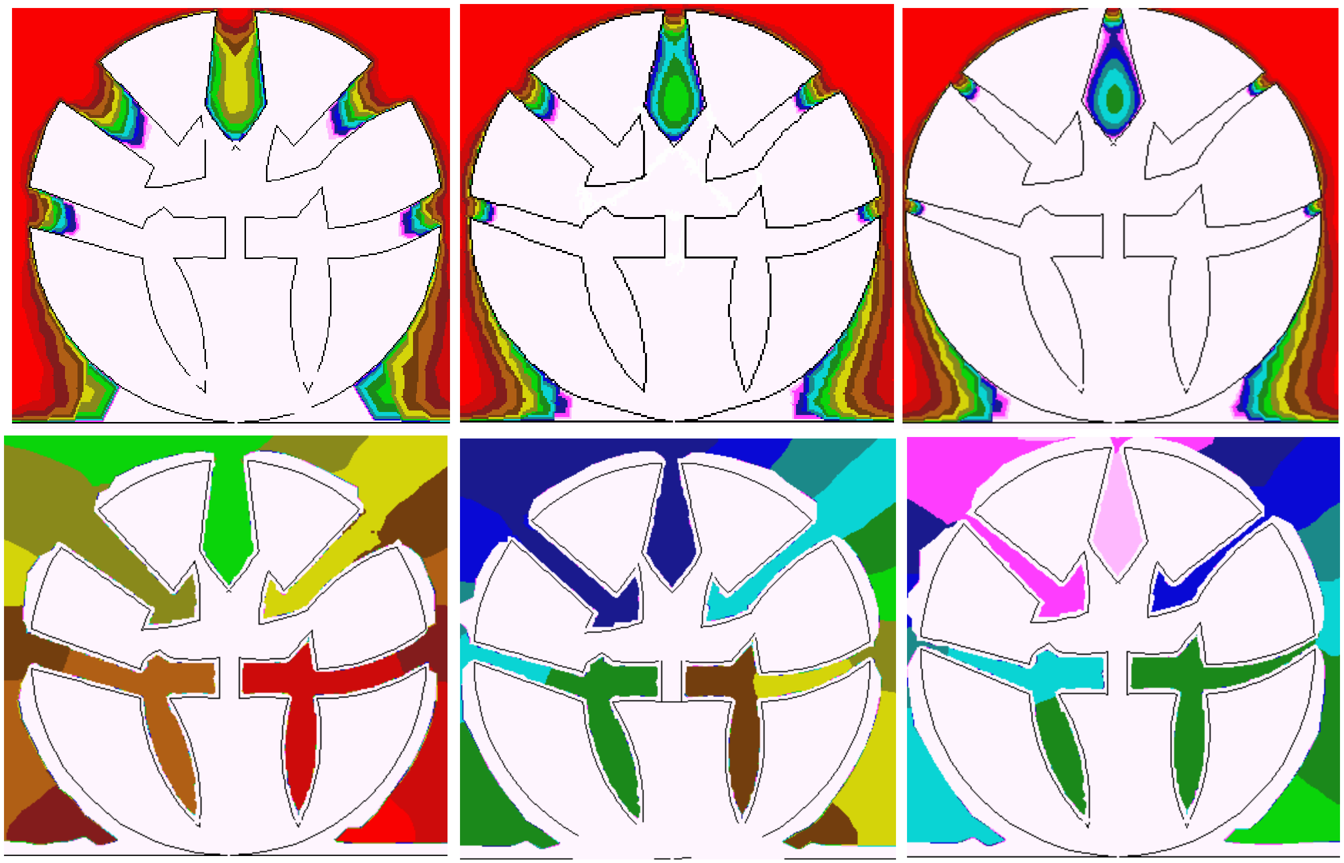
[NH_2] INSIDE PORES

- Since electrons poorly penetrate into most pores, little NH_2 is initially produced inside bead.
- NH_2 later diffuses into pores from outside.

- - 5 kV, $He/NH_3/H_2O$=90/10/0.1, pore dia=4.5 μm, 1 atm

[NH_2] INSIDE PORES : PORE DIAMETER



- t = 3 ns
  2×10^{10} - 2×10^{13}
- t = 80 μs
  7.5×10^{12}-8.7×10^{12}

- [NH_2] within pores increases with pore diameter during the pulse and in the interpulse period.

[NH_2] cm^{-3}

MIN  MAX

(log scale)

- - 5 kV, $He/NH_3/H_2O$=90/10/0.1, bead dia=90 μm, 1 atm

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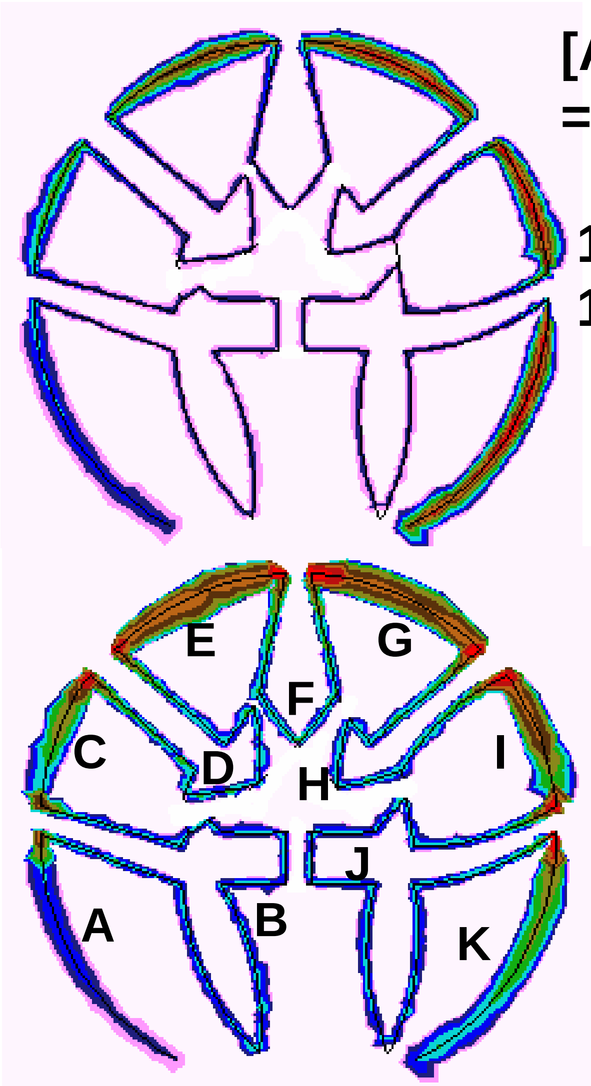
FUNCTIONALIZATION OF POROUS BEAD SURFACES

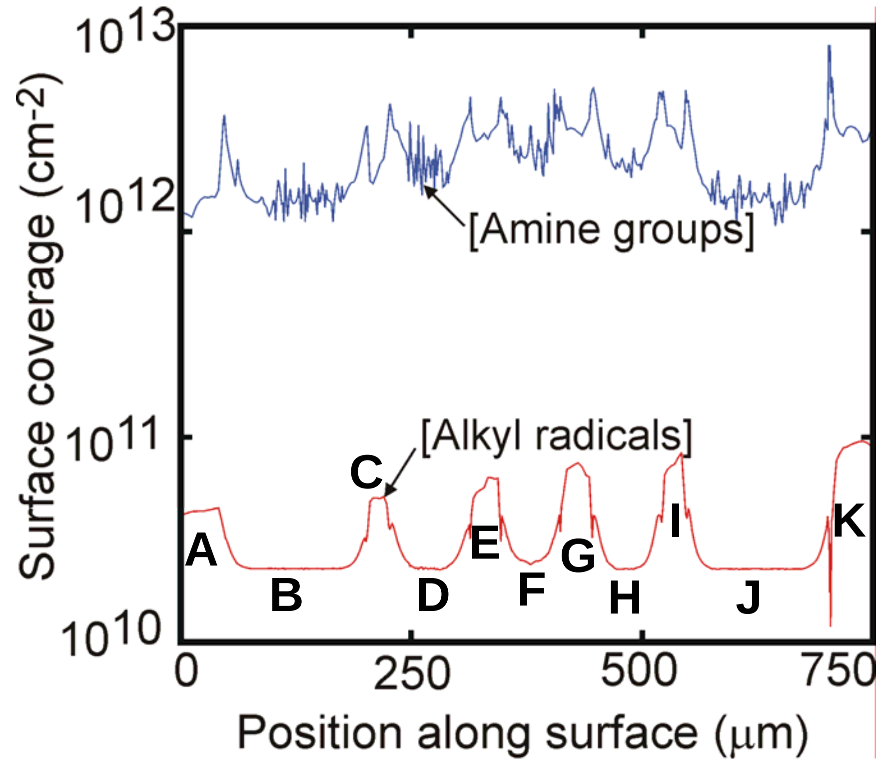


[ALKYL]
=C•

1.25×10^{10} – 1.25×10^{11}

[AMINE]
=C-NH_2

10^{12} – 10^{13}



Letters indicate position along the surface.

log scale, cm^{-2}

MIN MAX

- 5 kV, 1 atm, 10 kHz, $He/NH_3/H_2O$=90/10/0.1, Bead size=90 μm, Pore dia= 4.5 μm, t=0.1 s

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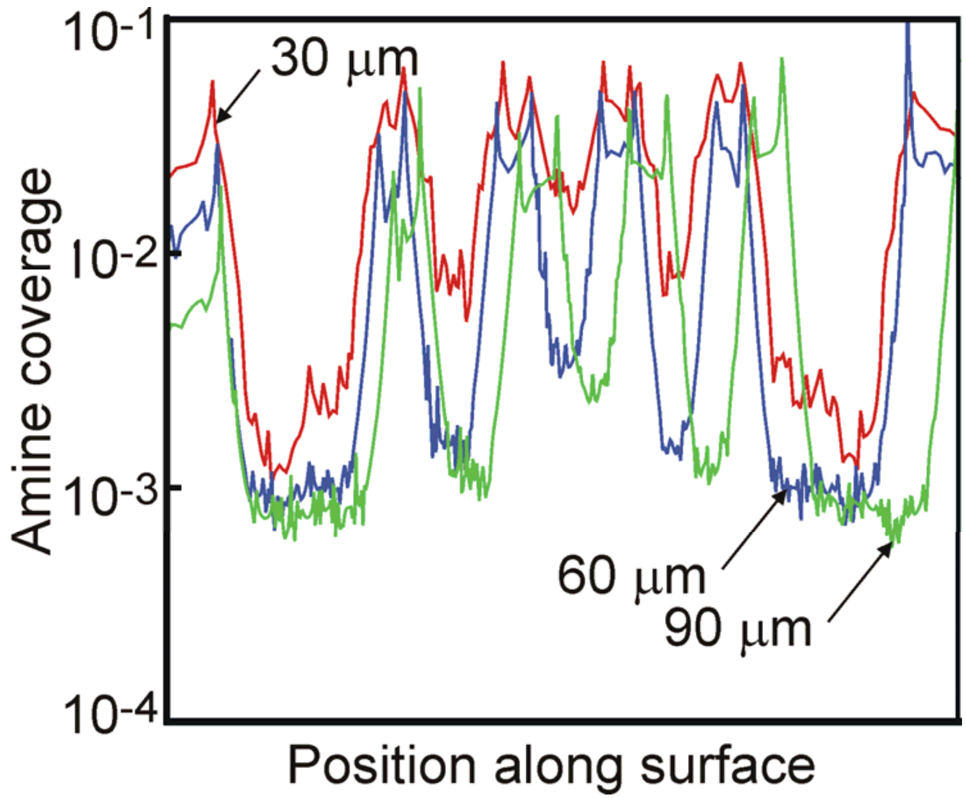
AMINE SURFACE COVERAGE: SIZE OF BEAD



Pore dia = 4.5 μm

- **- 5 kV, 1 atm, 10 kHz, $He/NH_3/H_2O$=90/10/0.1, t=1 s**

- **Outer surfaces have significantly higher amine coverage than interior pores.**
- **Smaller beads pores have more uniform coverage due to shorter diffusion length into pores.**
- **Beads sitting on electrode shadow portions of surface.**

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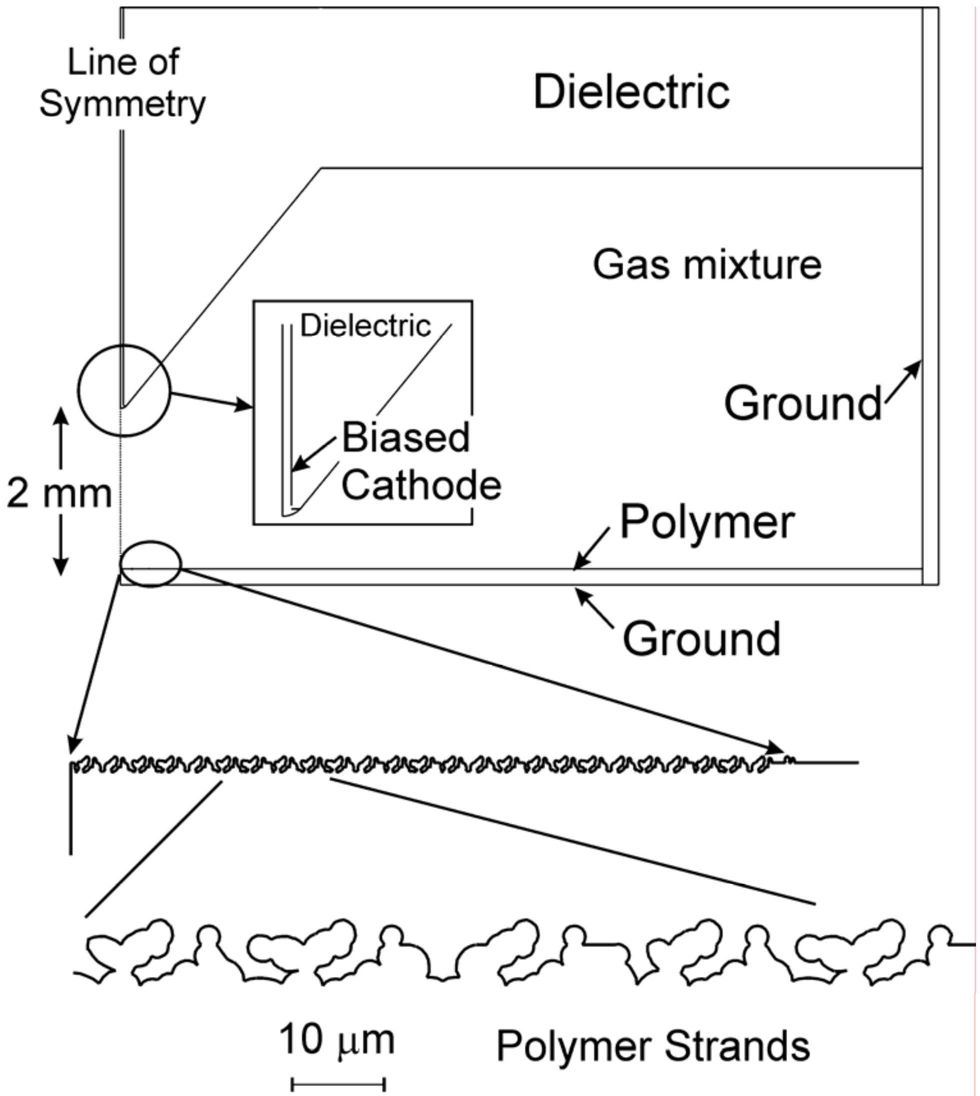
DBD TREATMENT OF PP SURFACE WITH MICROSTRUCTURE



- Corona functionalization of rough polymer.
- Scale length resembles tissue scaffold.
- 1 atm, $He/NH_3/H_2O$, 10 kHz
- Polypropylene.
- Small scale and large scale uniformity?

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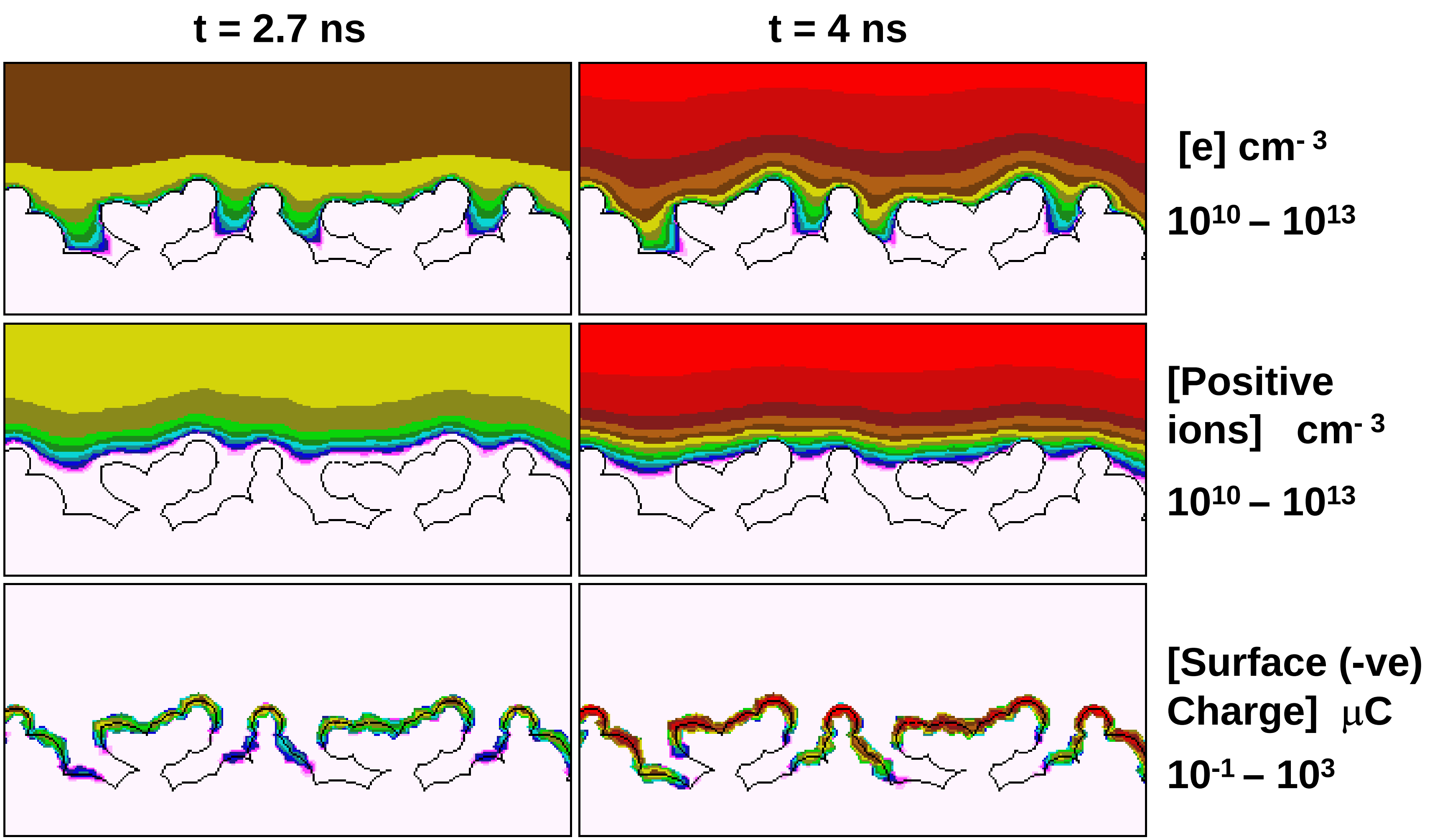
PENETRATION INTO SURFACE FEATURES – [e], [IONS]



- - 5 kV, 1 atm, $He/NH_3/H_2O$=98.9/1.0/0.1

MIN [color scale] MAX

log scale

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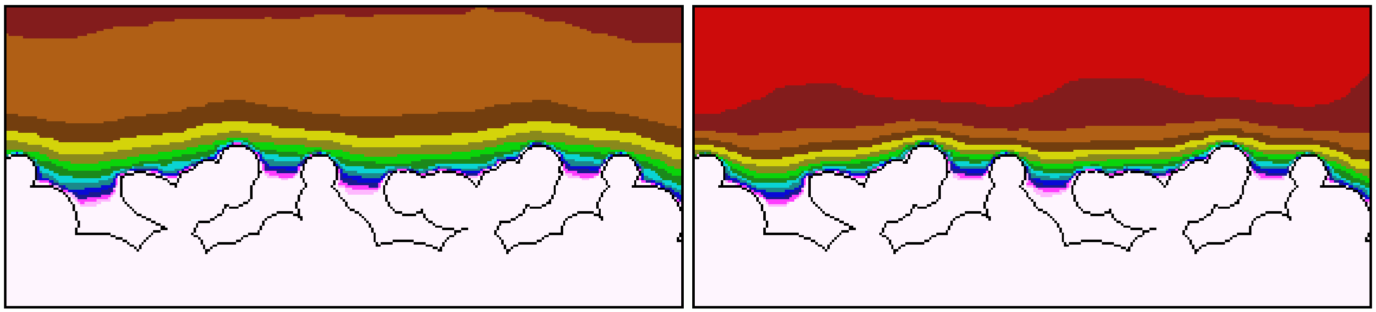
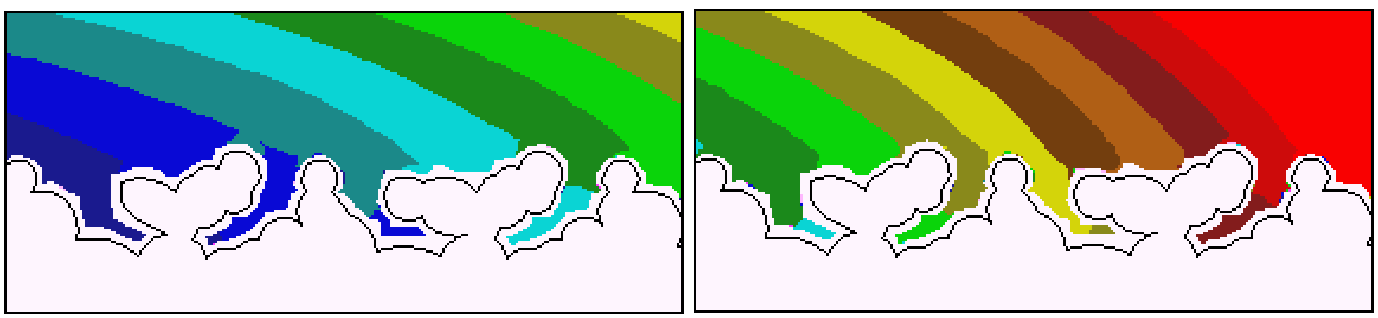
NH_2 DENSITY: EARLY AND LATE

[NH_3]=10% [NH_3]=30%



$3x10^{12}$ - $3x10^{14}$ t =3 ns



$1.8x10^{12}$ – $1.9x10^{12}$, t =90 μs $2.25x10^{12}$ – $2.35x10^{12}$, t =90 μs

- NH_2 is initially not produced inside the roughness, but later diffuses into the interior.

- \- 5 kV, 1 atm

[NH_2] cm^{-3}

MIN  MAX

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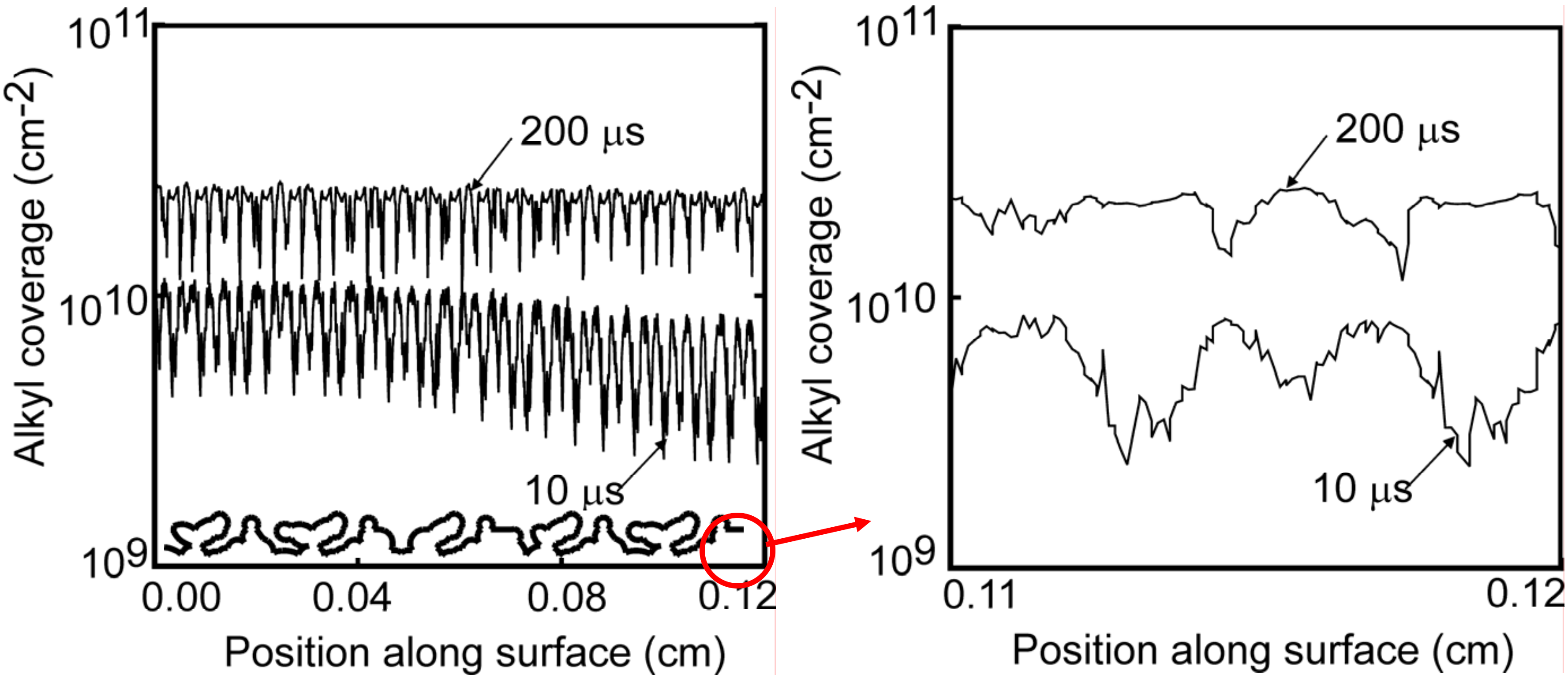
SURFACE COVERAGE OF ALKYL RADICALS (=C•)



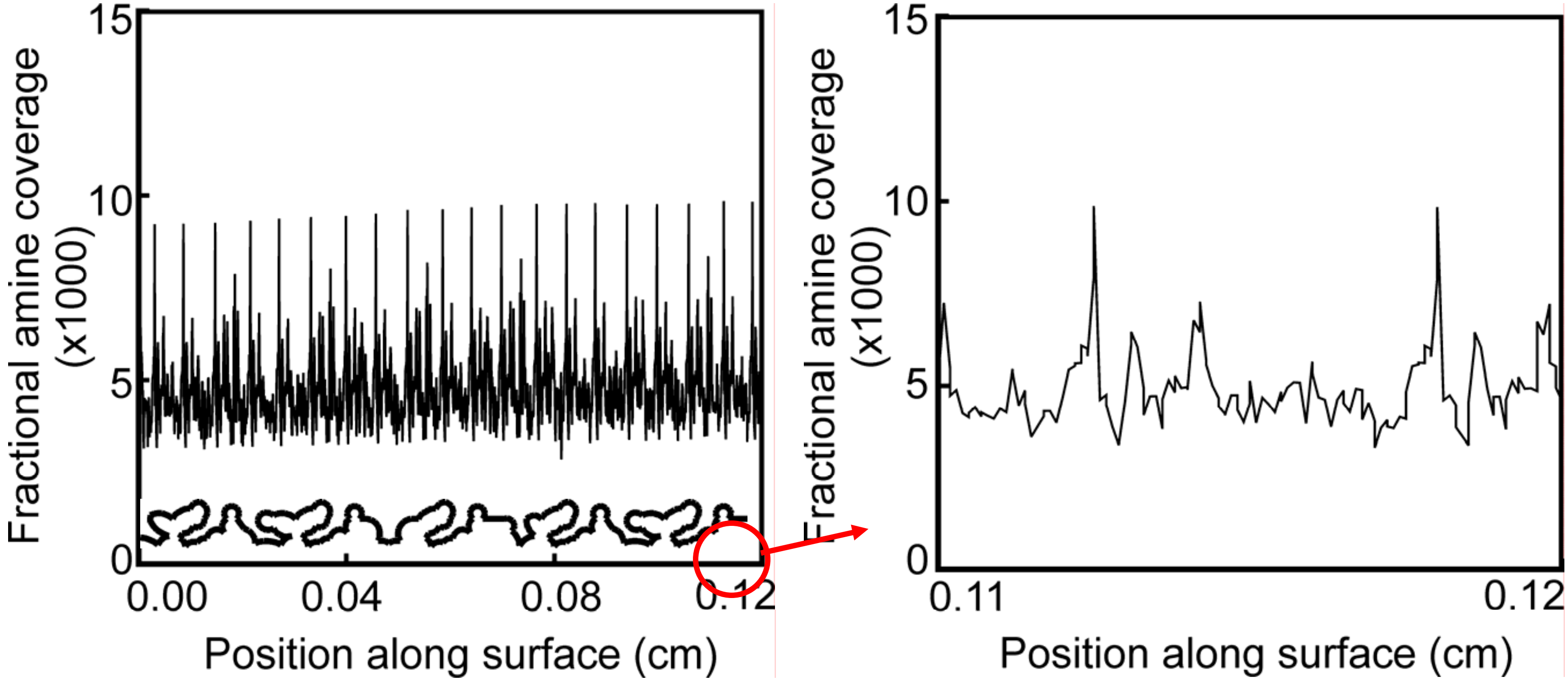
- **Alkyl sites are formed by the abstraction reactions**

OH + PP → PP• + H_2O **H + PP → PP• + H_2**

- **Large scale and small scale uniformity improves with treatment.**

- **- 5 kV, 1 atm, 10 kHz, $He/NH_3/H_2O$=90/10/0.1**

SURFACE COVERAGE OF AMINE GROUPS [=C-NH_2]



- **Amine groups are created by addition of NH_2 to alkyl sites.**

$$NH_2 + PP\bullet \rightarrow PP\text{-}NH_2$$

- **Points with large view angles are highly treated.**
  - **- 5 kV, 1 atm, 10 kHz, He/NH_3/H_2O=90/10/0.1, t = 0.1 s**

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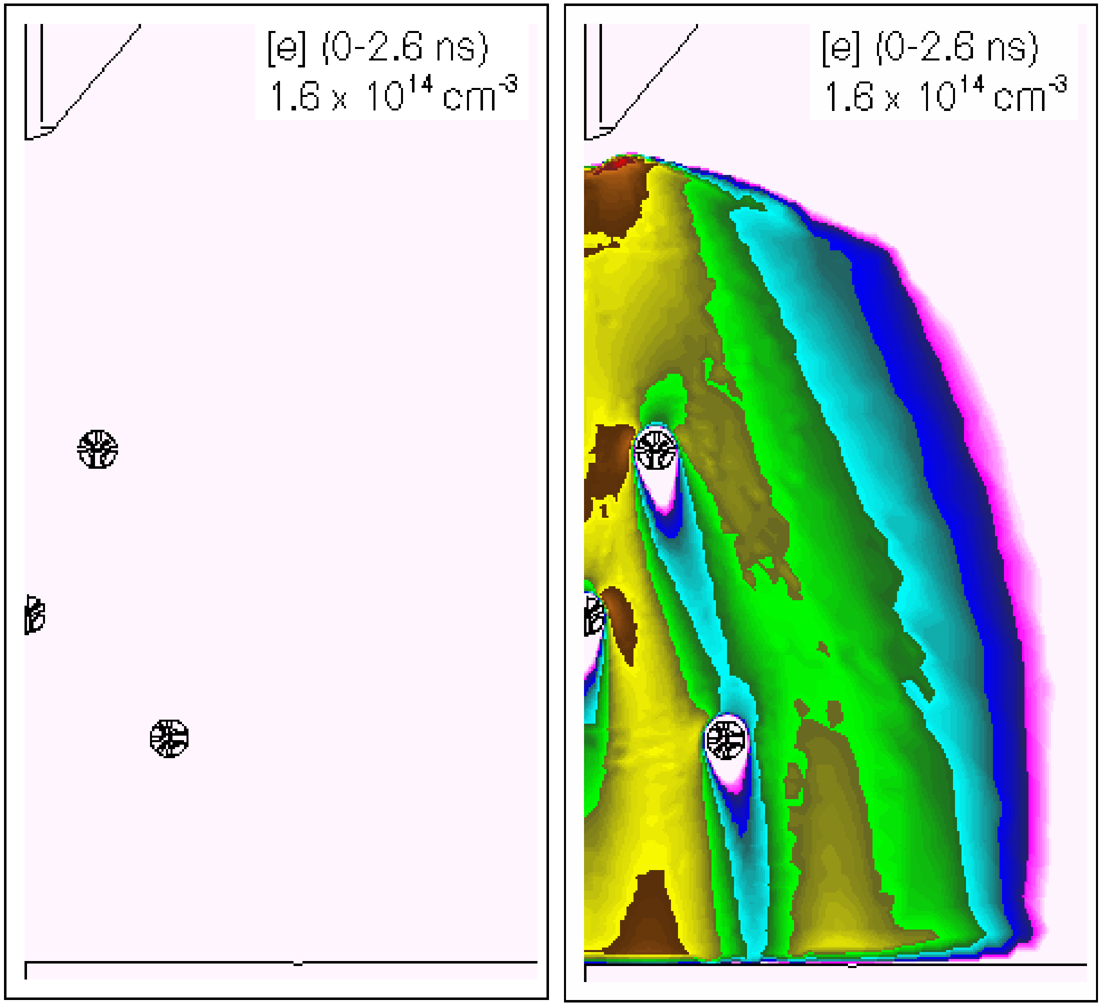
BEADS IN DISCHARGE: ELECTRON DENSITY



- Electron Density (1.6×10^{14} cm^{-3}), 0-2.5 ns

MIN  MAX

- Uniformity may be improved by dropping beads through discharge instead of placing on a surface.
- $He/O_2/H_2O$ = 89/10/1, 1 atm
- Electrons produce a wake beyond the particle.

Animation Slide-GIF

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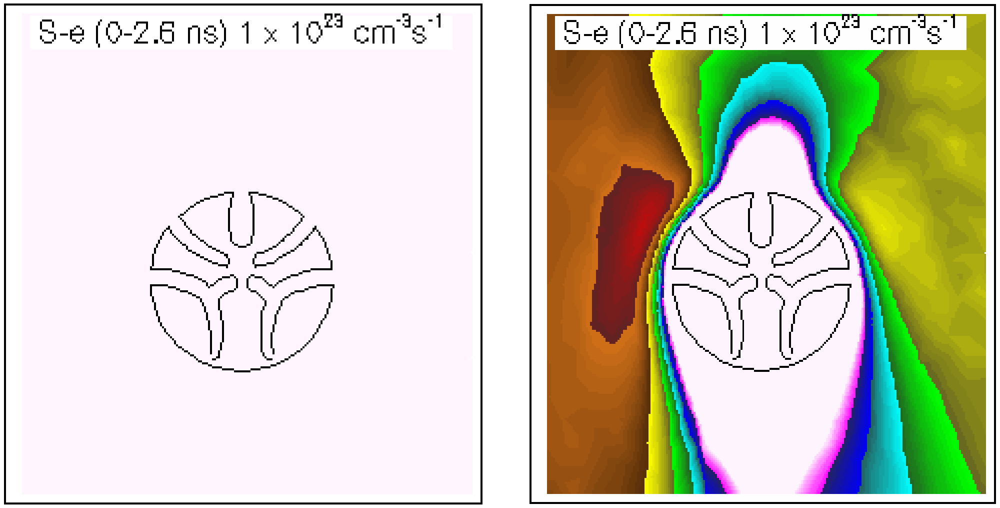
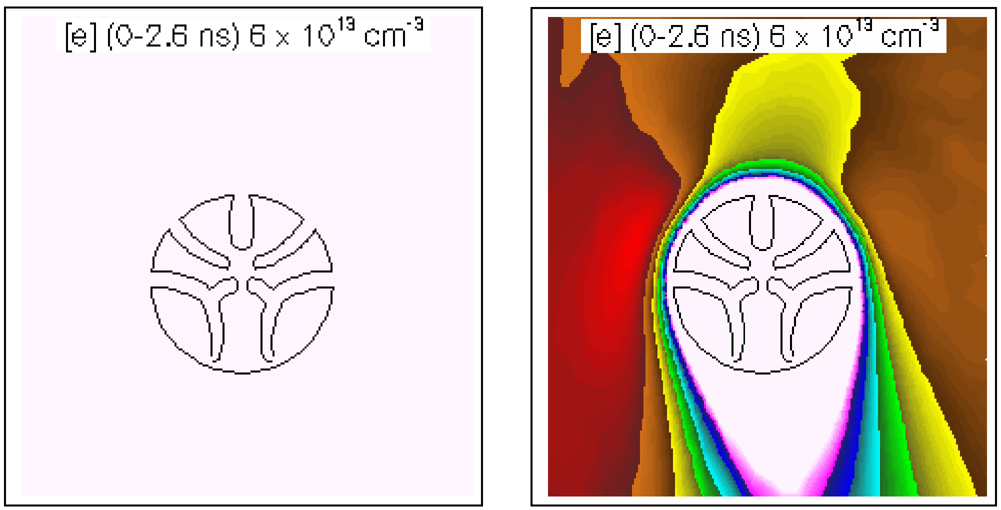
ELECTRON DENSITY AND SOURCE



- **Electron Source (10^{23} $cm^{-3}s^{-1}$)**



- **Electron Density (6×10^{13} cm^{-3})**

MIN **MAX**

- **Ionization occurs around particle during initial avalanche and restrike.**
- **Sheath forms above particle, wake forms below particle.**
- **$He/O_2/H_2O$ = 89/10/1, 1 atm**
- **0-2.6 ns**

Animation Slide-GIF

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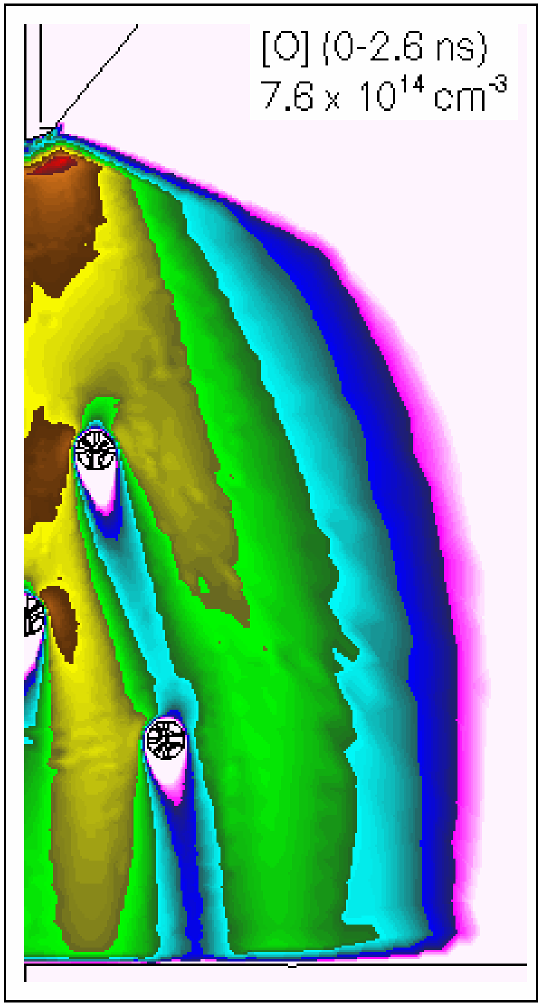
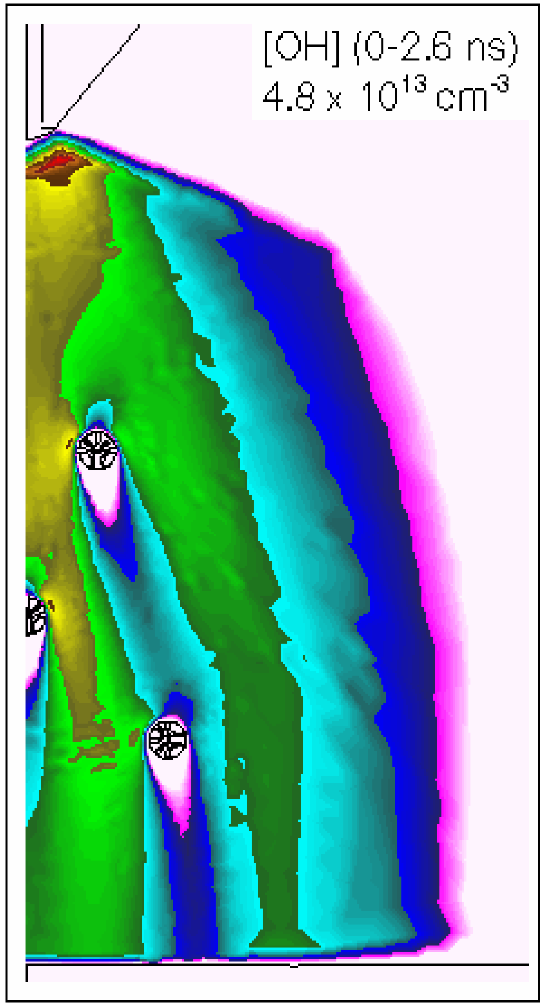
POST-PULSE O and OH DENSITIES





- [O] (8×10^{14} cm^{-3})
- [OH] (5×10^{13} cm^{-3})

- **Directly after the pulse, radicals have a similar wake below the particles.**
- **$He/O_2/H_2O$ = 89/10/1, 1 atm**
- **0-2.6 ns**

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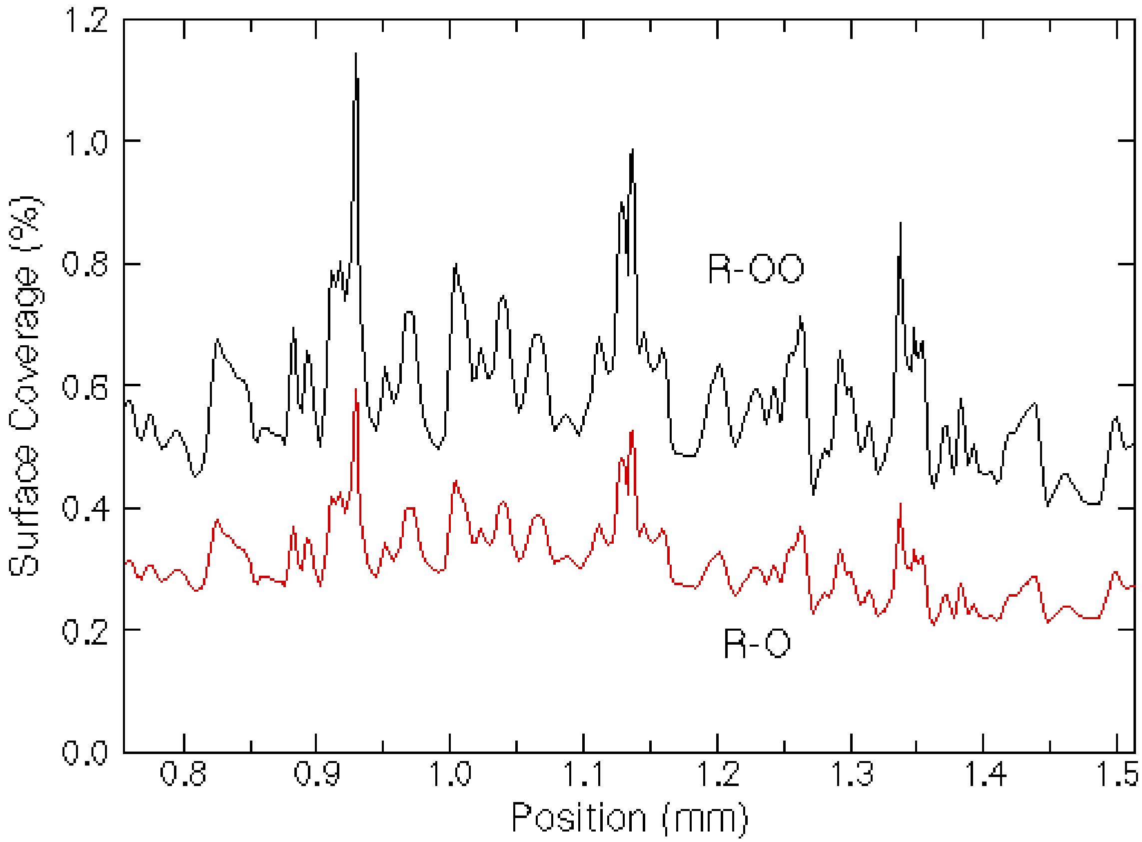
BEADS IN DISCHARGE: SURFACE COVERAGE

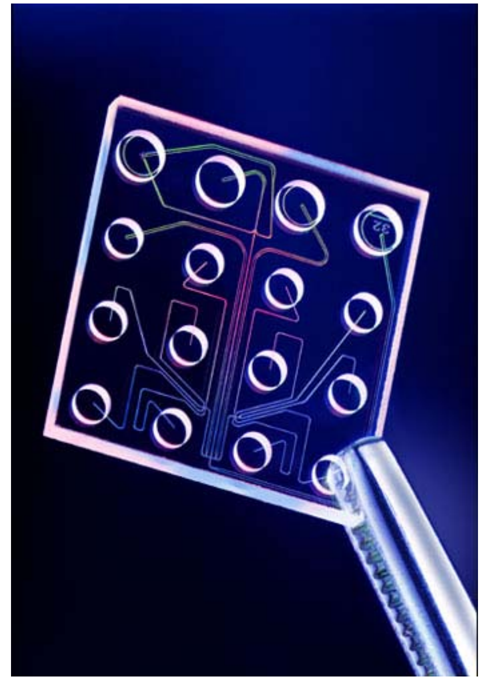


- Uniformity of functionalization, locally poor, is improved around the particle.
- $He/O_2/H_2O$ = X/Y/Z, 1 atm

- Alkoxy (=C-O) and Peroxy (=C-OO) Coverage

PROCESSING COMPLEX SHAPES

- www.bostonscientific.com



- www.caliperls.com

- **Functionalization of complex shapes requires plasma to penetrate deep into structure.**

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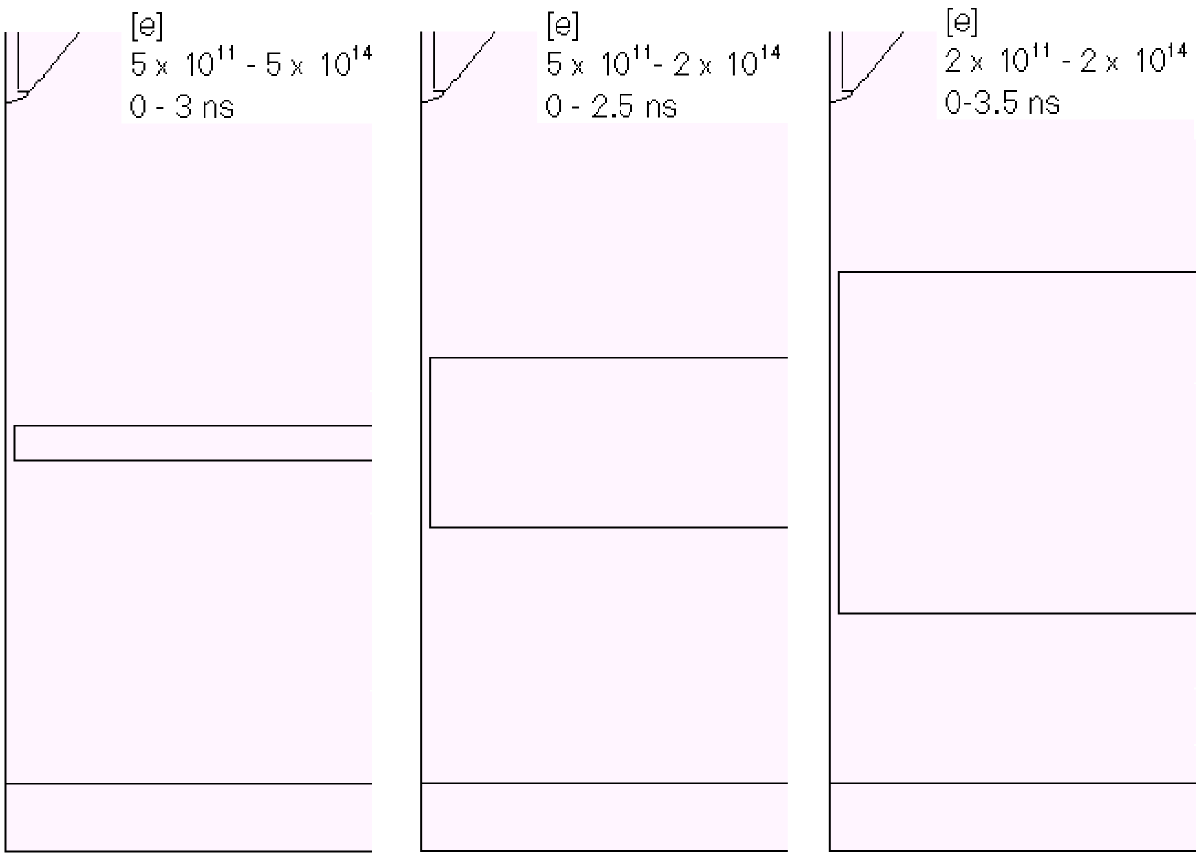
PLASMA PENETRATION INTO DEEP 50 μm SLOTS: ELECTRONS



- 100 μm
- 500 μm
- 1000 μm

2 mm

- Slow penetration through dielectric results from surface charging.
- Rapid "restrike" through conductive and precharged slot.

Animation Slide-GIF

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

MIN  MAX

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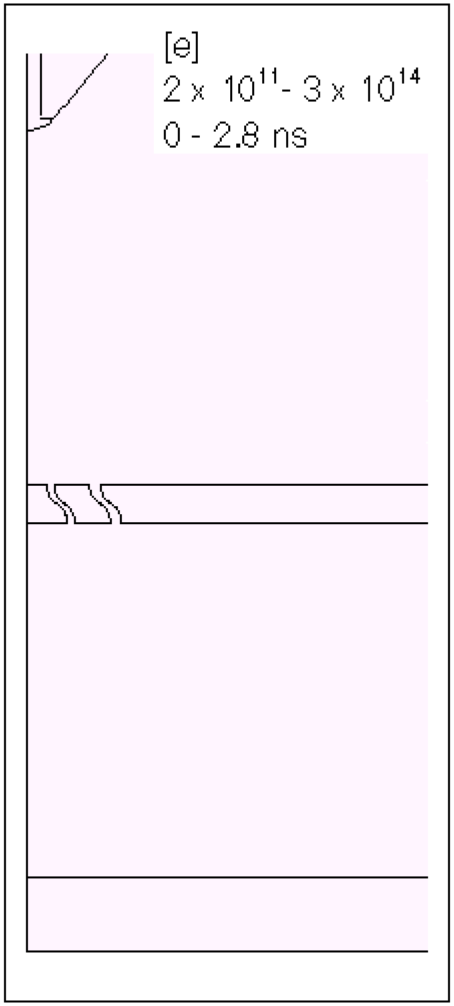
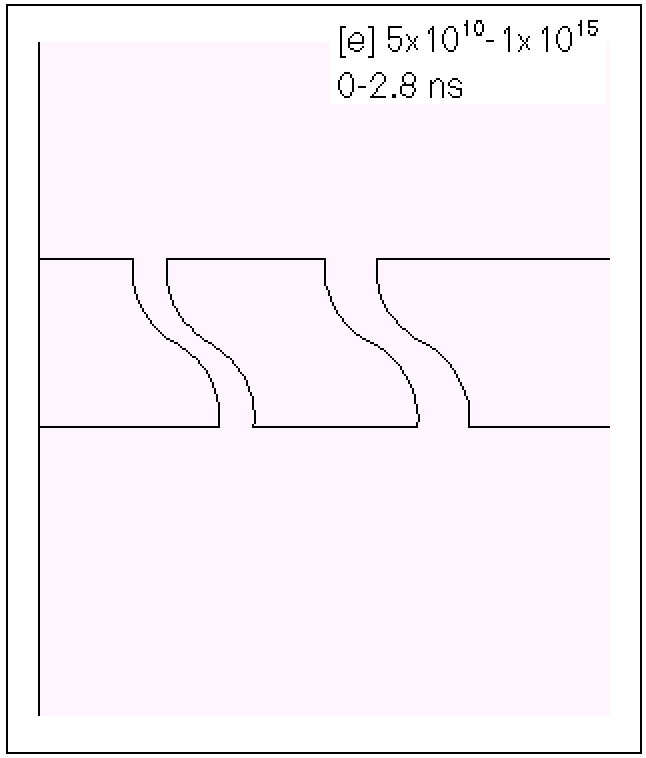
SHAPES OF SLOTS MATTER: ELECTRONS

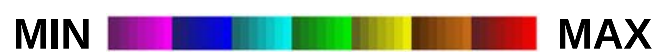




- 20 and 30 μm slots

Animation Slide-GIF

- Charging of internal surfaces of slots produce opposing electric fields that limit penetration.
- Restrike fills smaller slot with plasma.



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

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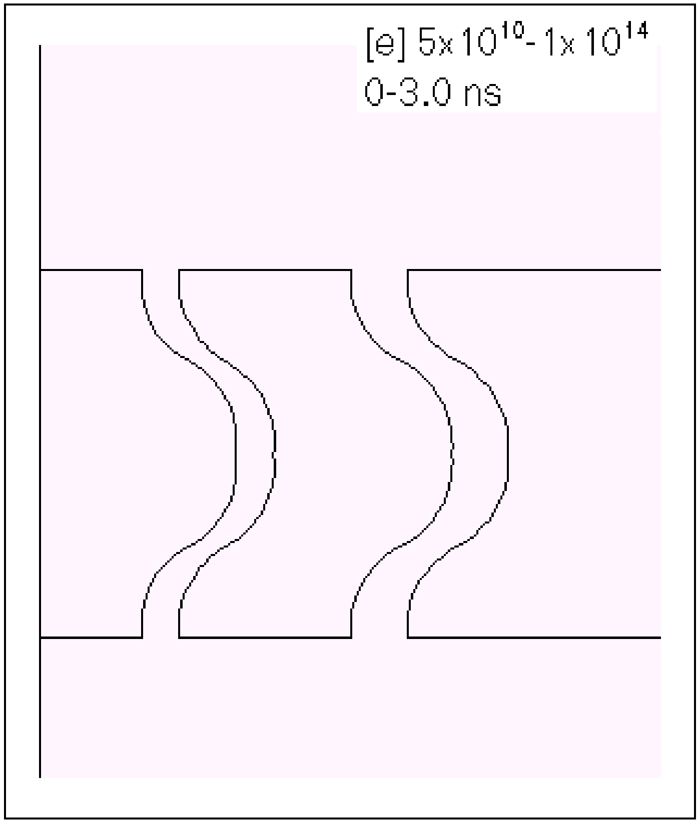
SHAPES OF SLOTS MATTER: ELECTRONS

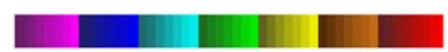


- Charging of surfaces and topology of slot determine plasma penetration.
- Here plasma is unable to penetrate through structure.
- Direction of applied electric field and charge induced fields are in the opposite direction of required penetration.

- 20 and 30 μm slots

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

Animation Slide-GIF

MIN  MAX

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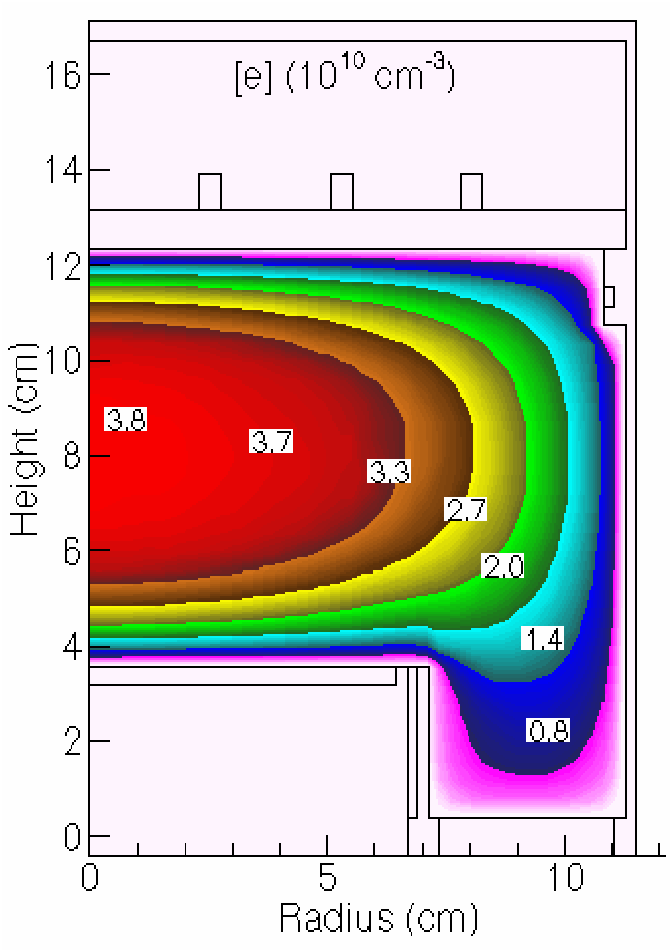
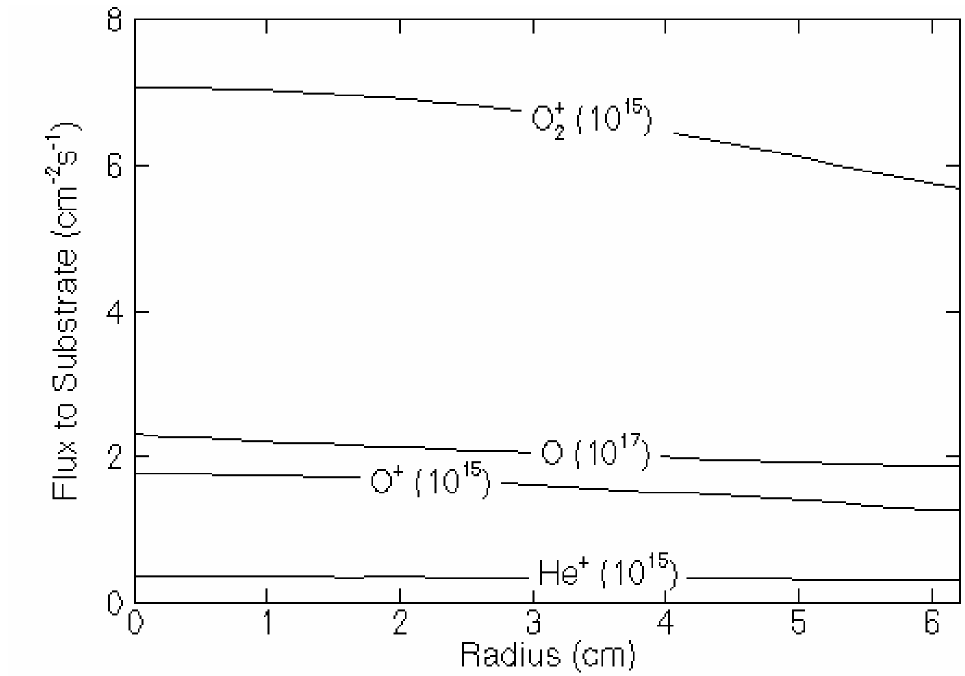
SHOULDN'T LOW PRESSURE BE BETTER?





- **Low pressure discharges with more uniform fluxes, longer mean free paths should be better for functionalization of small features.**
- **Results from HPEM.**

- **ICP without bias, He/O_2=75/25, 15 mTorr 300 W**

ACTIVATION OF SURFACE SITES AND SPUTTERING

- **Large fluxes of O atoms in low pressure systems increase likelihood of alkoxy formation (=C-O)**

$$O \; + \; =C-H \;\rightarrow\; =C\cdot + OH \qquad p = 0.001$$
$$O \; + \; =C\cdot \;\rightarrow\; =C-O \qquad p = 0.1$$
$$O_2 + \; =C\cdot \;\rightarrow\; =C-OO \qquad p = 0.001$$

- **Low energy ion activation of surface sites increases rate of reaction direct peroxy (=C-OO formation)**

$$M^+ \; + \; =C\cdot \;\rightarrow\; [=C\cdot]^* + M$$
$$O_2 + \; [=C\cdot]^* \;\rightarrow\; =C-OO \qquad p = 0.1$$

- **High energy ions sputter the polymer.**

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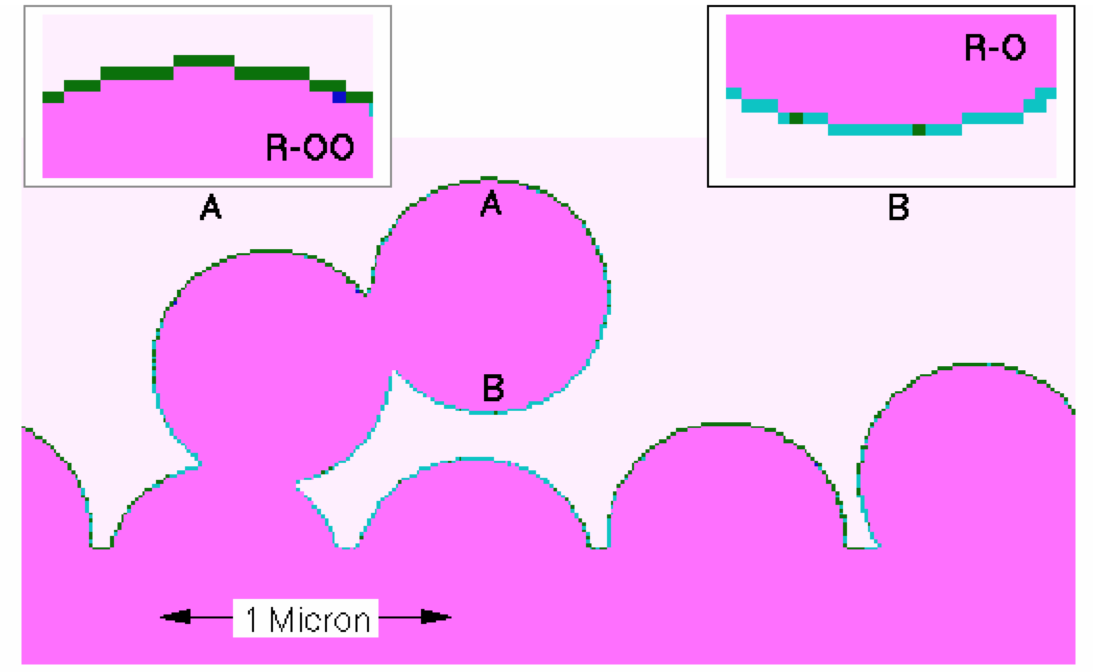
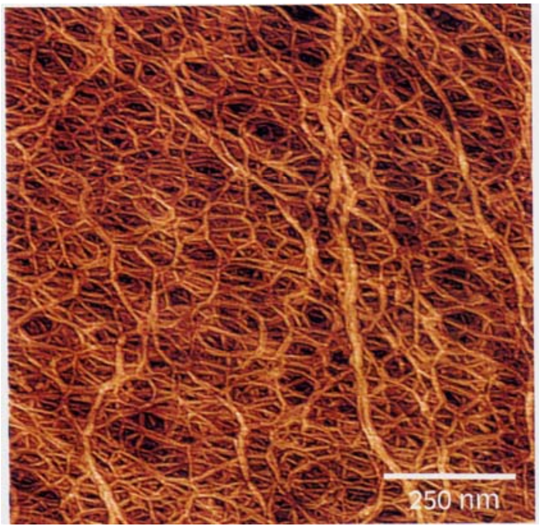
DIRECTIONALITY OF ION FLUXES IS A PROBLEM





- **Polypropylene M. Strobel, 3M**

- **Strands flex with age. Bottom surfaces may eventually be exposed.**
- **Top surfaces subject to low energy ion fluxes have activated sites and larger peroxy coverage.**
- **Results from Monte Carlo Feature Profile Model (MCFPM).**

- **ICP without bias, He/O_2=75/25, 15 mTorr 300 W**

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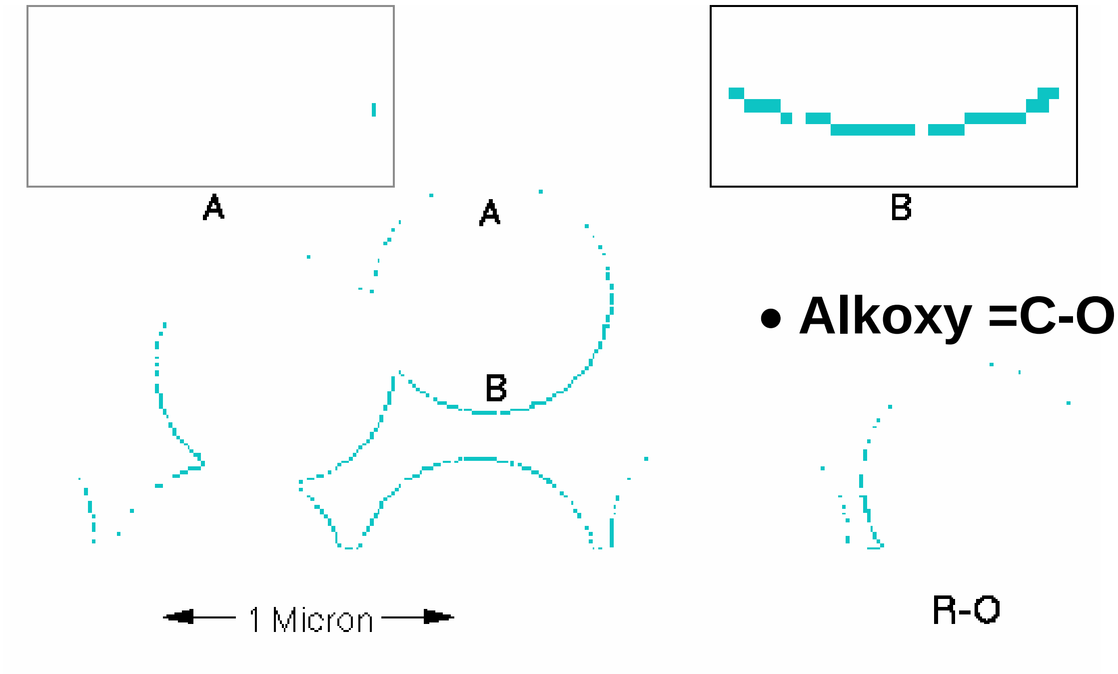

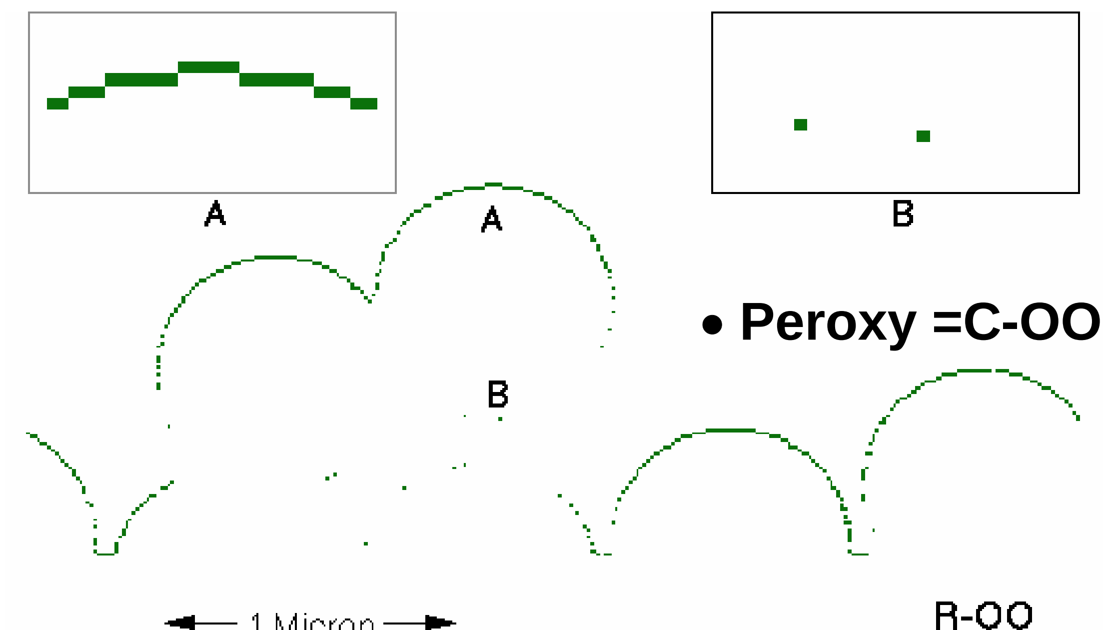

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FUNCTIONALIZATION: TOP vs BOTTOM OF STRANDS

- **Undersides of strands are mostly alkoxy.**
- **Topsides, which receive low energy ion activation, are mostly peroxy.**
- **ICP without bias**
- **He/O_2=75/25, 15 mTorr 300 W**

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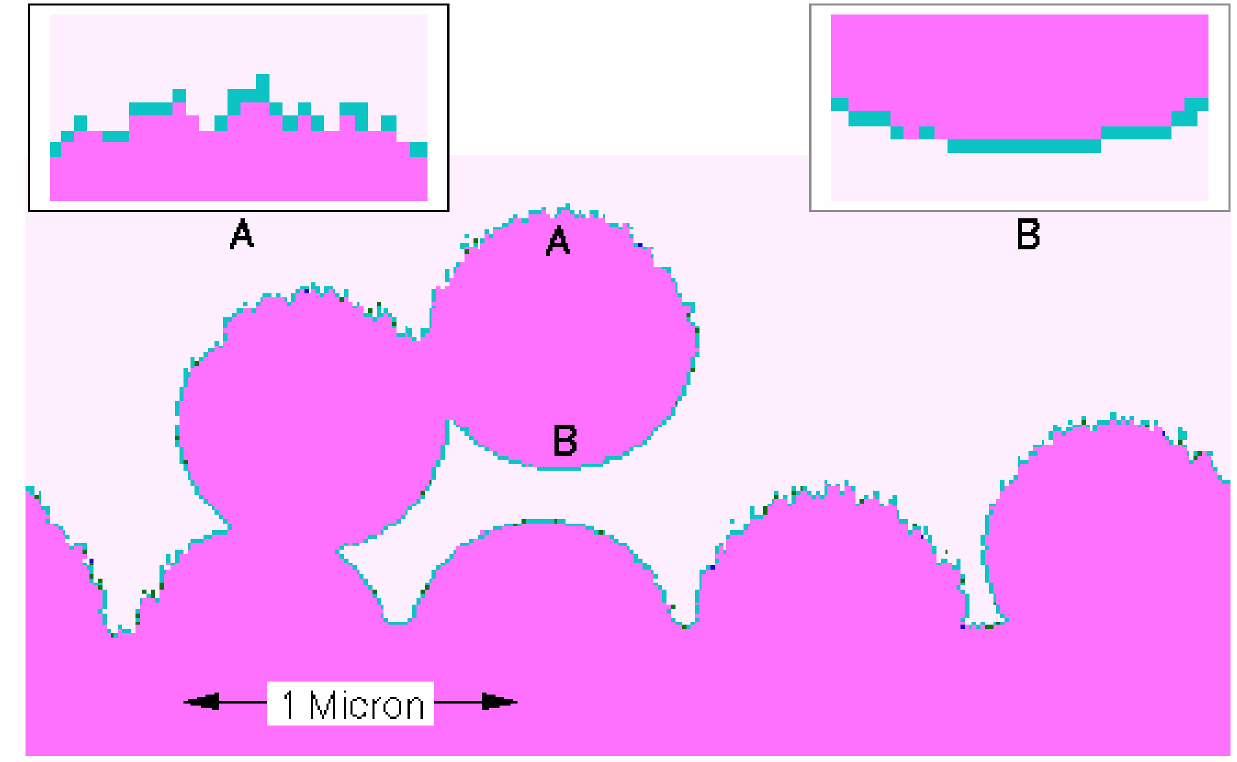
MODERATE BIAS: SPUTTERING, LOW ACTIVATION



- **Even with moderate 35V bias, sputter begins and activation is lessened. Surfaces are almost exclusively alkoxy (=C-O).**

- **ICP, 35v rf bias, He/O_2=75/25, 15 mTorr 300 W**

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CONCLUDING REMARKS

- Functionalization of complex surfaces will have challenges at both high and low pressure.
- High Pressure:
  - Penetration of plasma into small spaces is problematic.
  - Must rely on slower diffusion of neutral radicals.
  - 3-body reactions deplete radicals
- Low Pressure:
  - Directionality of activation energy, an advantage in microelectronics processing, leads to uneven functionalization.
  - Difficult to treat soft materials.
- Developing high pressure processes will result in much reduced cost.