FUNCTIONALIZATION OF ROUGH SURFACES AND POROUS MICRON-SIZED POLYMER BEADS USING ATMOSPHERIC PRESSURE PLASMAS*

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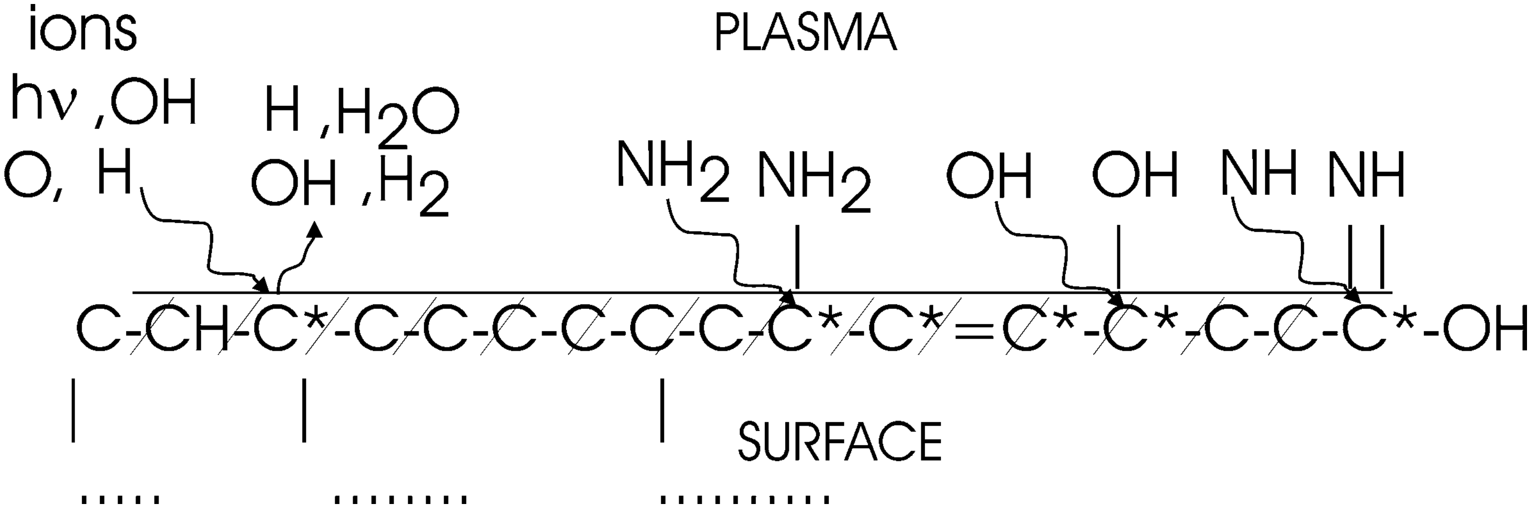
OUTLINE

- Introduction to plasma surface functionalization
- Description of the model
- Plasma dynamics in $He/NH_3/H_2O$ mixtures
- Functionalization of rough and porous surfaces
- Concluding remarks

FUNCTIONALIZATION OF SURFACES USING PLASMAS

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

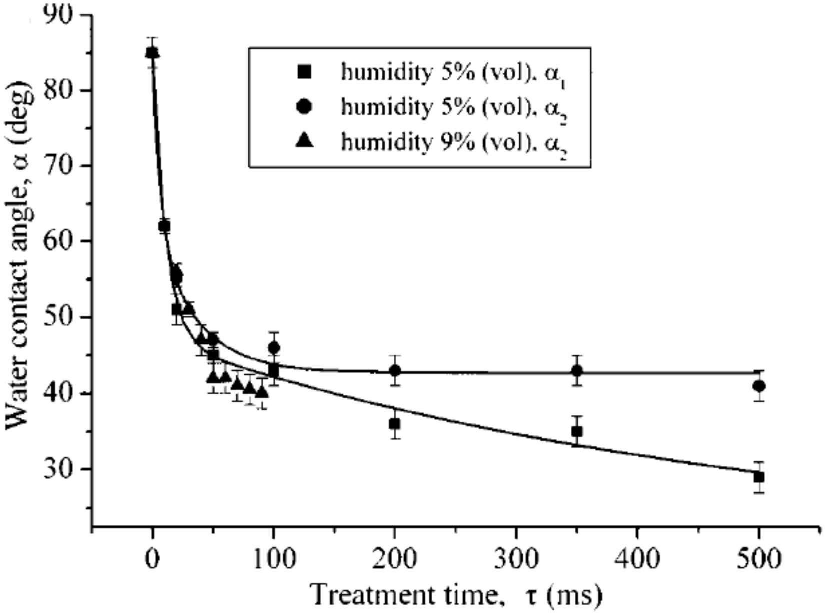


- **N-containing groups created using an ammonia plasma include**
  - **Amine –C-NH_2**
  - **Imine –C=NH**
  - **Nitrile –C ≡N**

SURFACE MODIFICATION OF POLYMERS

- **Pulsed atmospheric discharges (coronas) are widely used in industry to treat commodity polymers like polypropylene (PP).**

- **Tantec, Inc.**

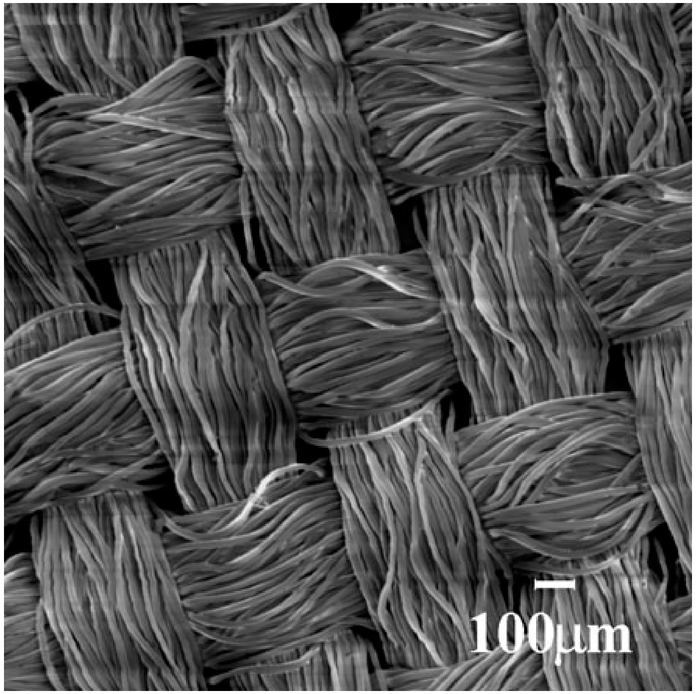


- **PE Film**

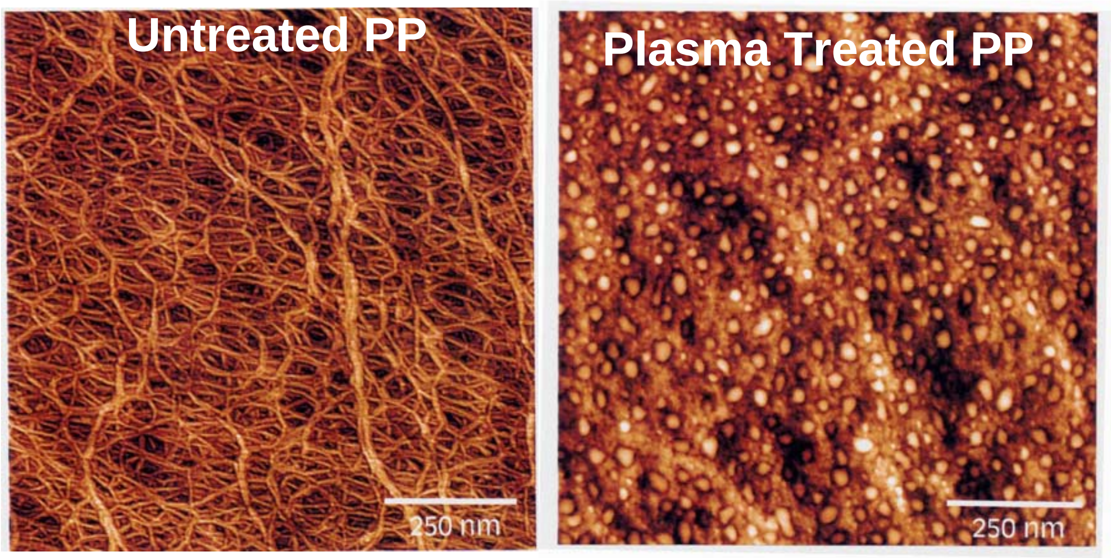
- **Functionalization increases surface energy and enhances wettability and adhesion.**

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

TREATMENT OF NON-PLANAR SURFACES



- **SEM of polyester fabric**
  (Borcia, *et al,* Plasma Sources Sci. Technol*, 12,* 235 (2003).

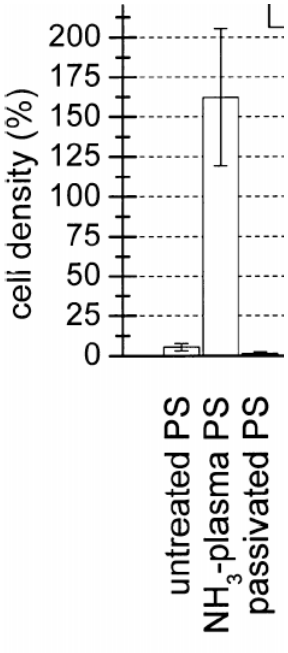


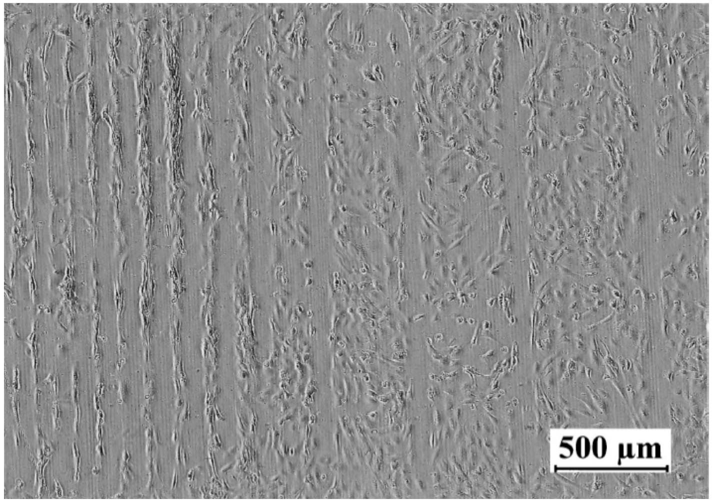
- **M. Strobel, 3M**

- **Roughness of surface to be treated may range from 100s nm to few µm.**

- **Penetration of plasma species into surface features determines the extent and uniformity of functionalization.**

FUNCTIONALIZATION FOR BIOCOMPATIBILITY





Micropatterned cell growth on NH_3 plasma treated PEEK[1]

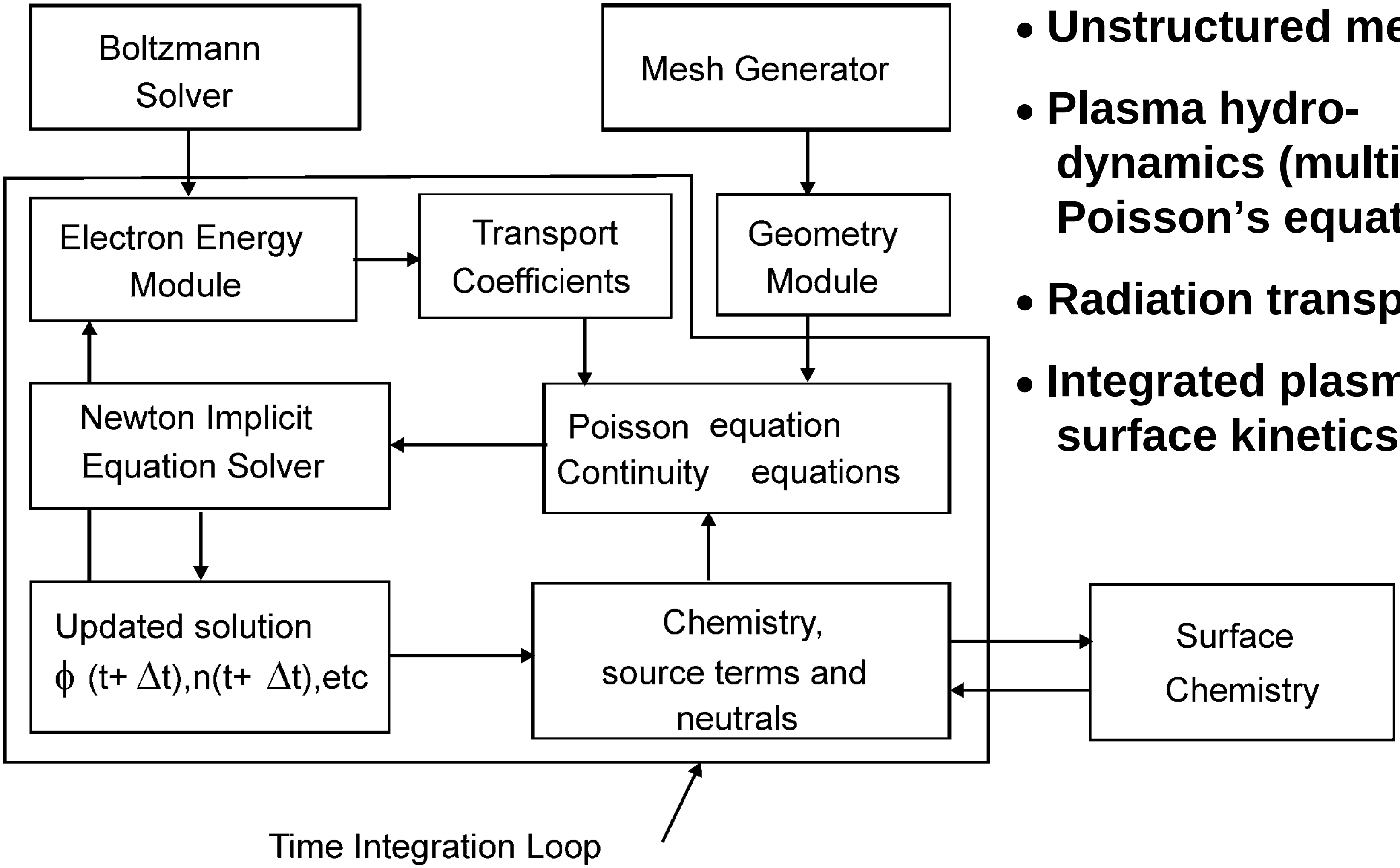
Textiles are used as scaffolds for tissue engineering[2], which could also be plasma treated

- 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]From K. Schroeder *et al*, Plasmas and Polymers, 7, 103, 2002)

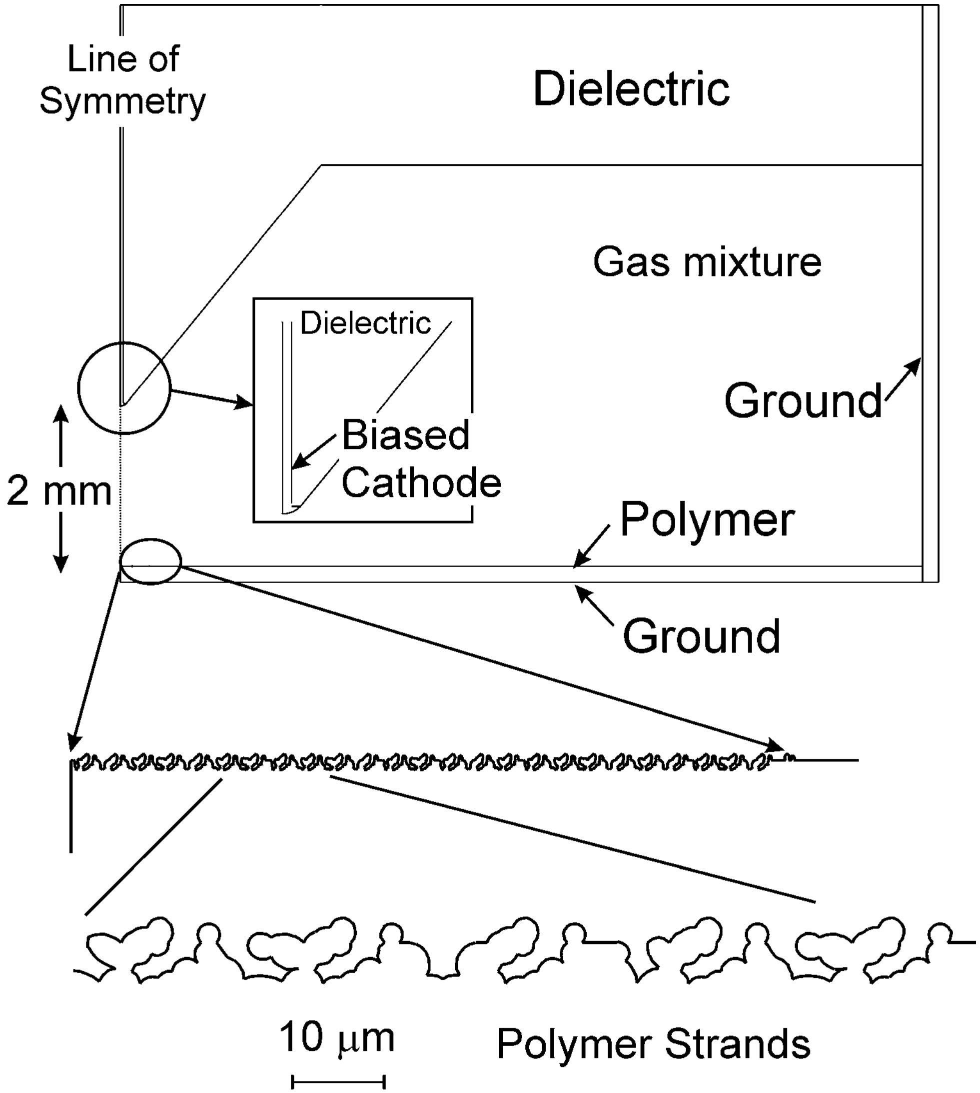
([2]From the website of the Biomedical Textile Research Center, Heriot Watt University, UK, http://www.hw.ac.uk/sbc/BTRC/BTRC/_private/Ouractivities.htm)

SCHEMATIC OF THE 2-D MODELING PLATFORM



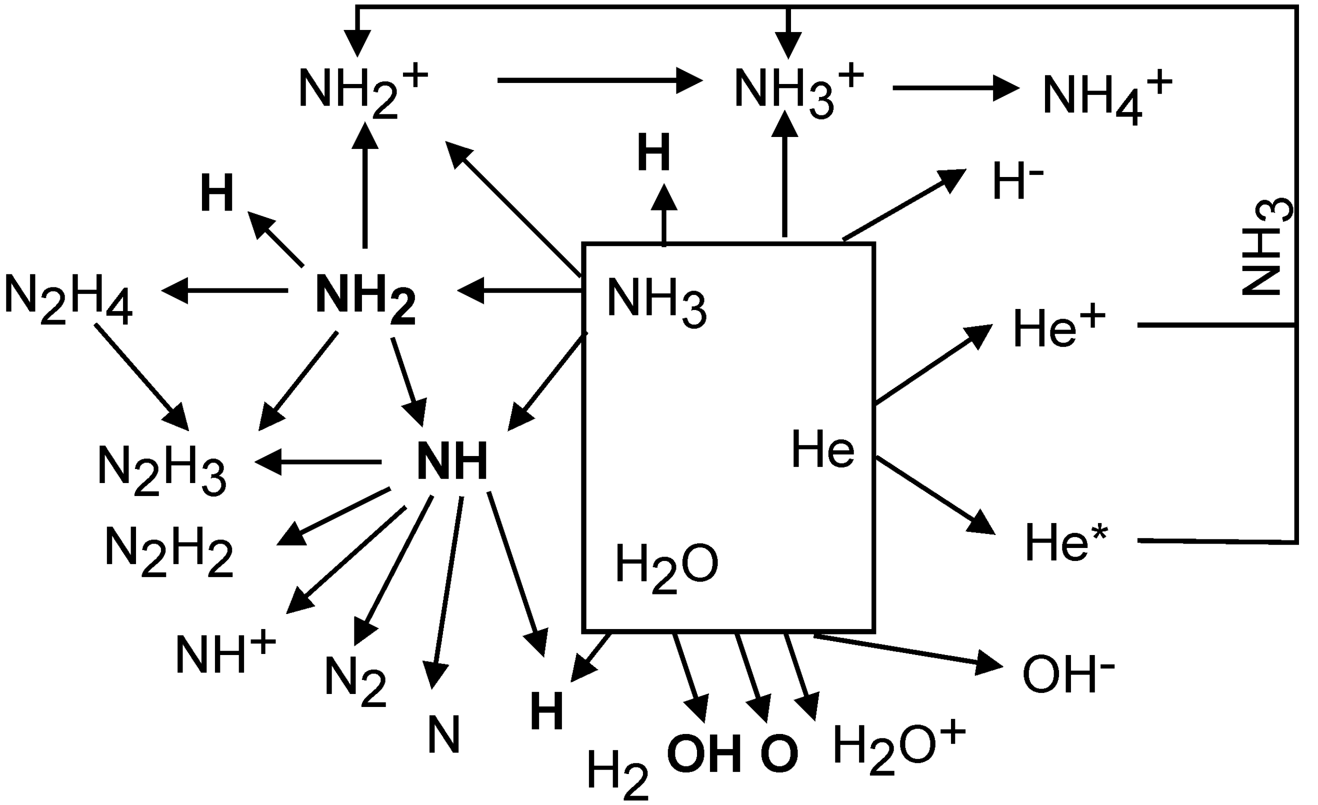
- **Unstructured mesh**
- **Plasma hydro-dynamics (multi-fluid, Poisson's equation)**
- **Radiation transport**
- **Integrated plasma-surface kinetics model**

DBD TREATMENT OF PP SURFACE WITH MICROSTRUCTURE



- Corona treating a polymer on the grounded electrode acts as a DBD.
- Gas mixture: $He/NH_3/H_2O$
- Features to represent surface roughness are modeled as shown.
- Interested in the variation in treatment uniformity of over different spatial scales.
- Polymer: polypropylene (PP)
- PRF – 10 kHz

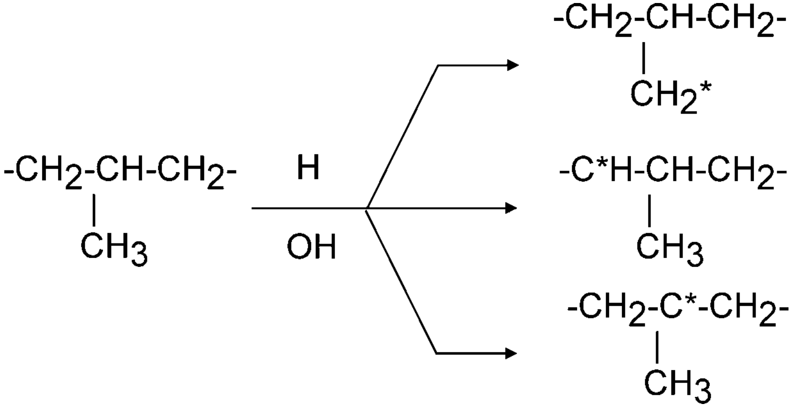
GAS PHASE CHEMISTRY - He/NH_3/H_2O MIXTURES

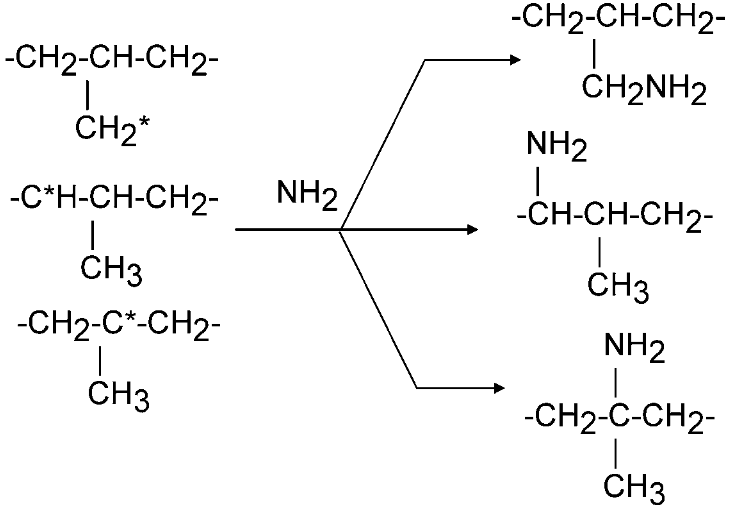


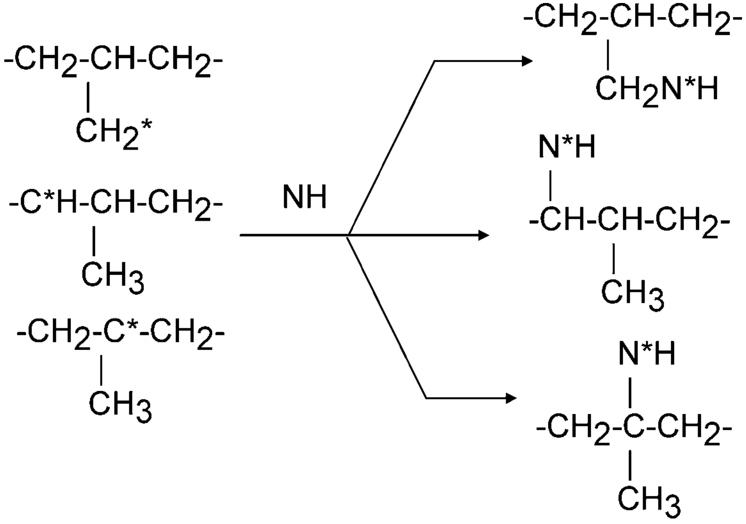
- Electron impact reactions initiate dissociation of larger molecules into fragments consisting of ions and radicals that react further.
- Radicals reacting with the surface include H, NH_2, NH, O and OH

SURFACE REACTION MECHANISM - I

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



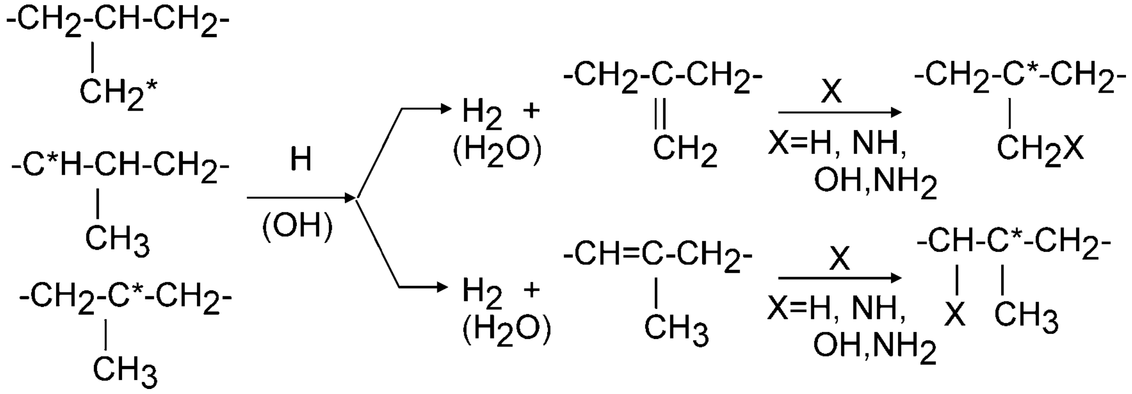




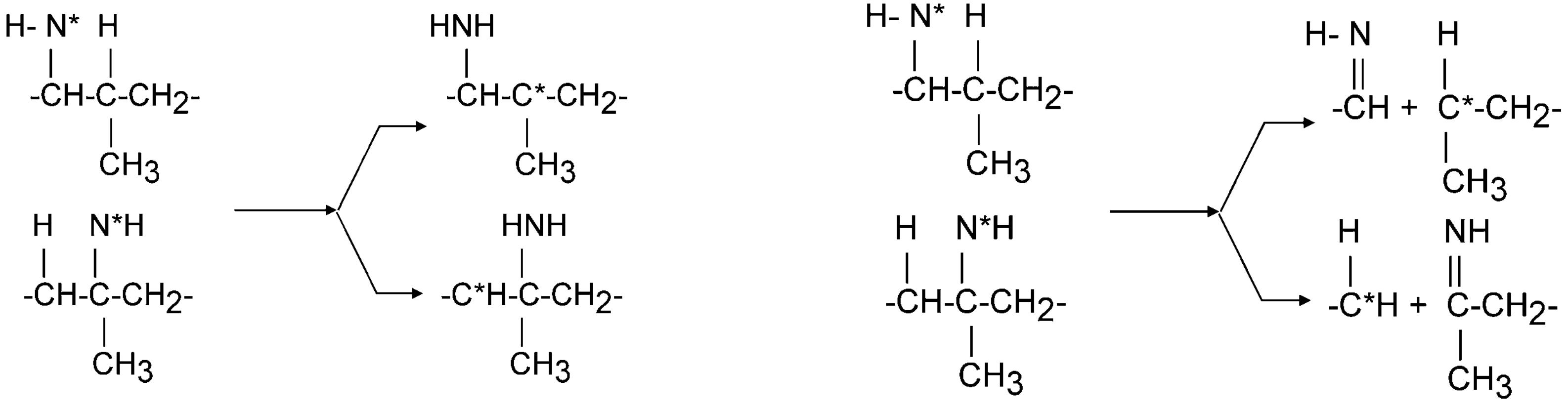
- **Alkyl radicals react with NH_2 and NH radicals creating amine groups and amino radical sites.**

SURFACE REACTION MECHANISM - II

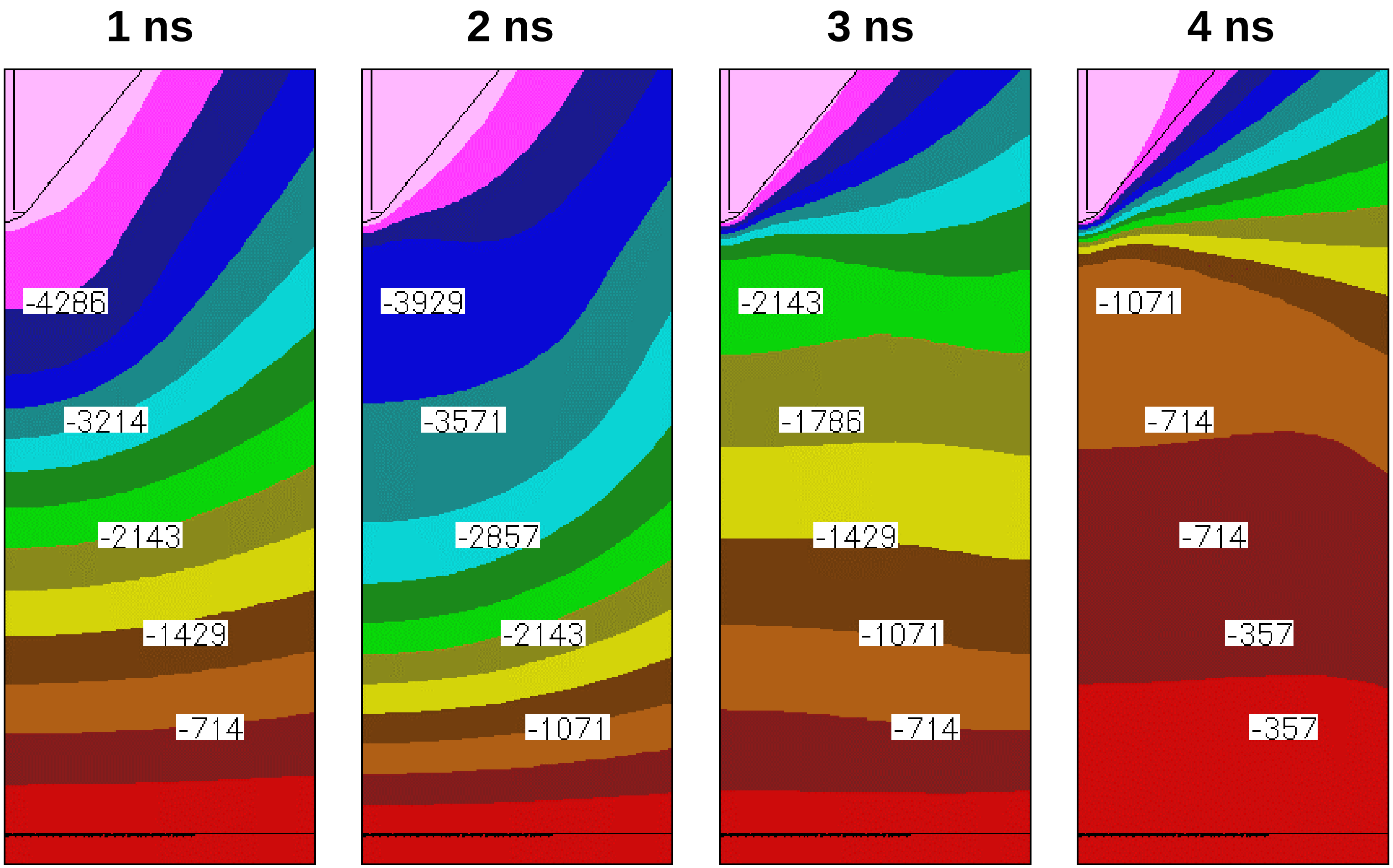
- **Abstraction of H or reaction between alkyl radicals may lead to intermediate alkene sites for addition and radicals are re-created.**



- **Intramolecular reactions around amino surface radicals could lead to amine or imine through chain scission.**



PLASMA DYNAMICS – PLASMA POTENTIAL



- - 5 kV, 760 Torr, He/NH_3/H_2O=98.9/1.0/0.1

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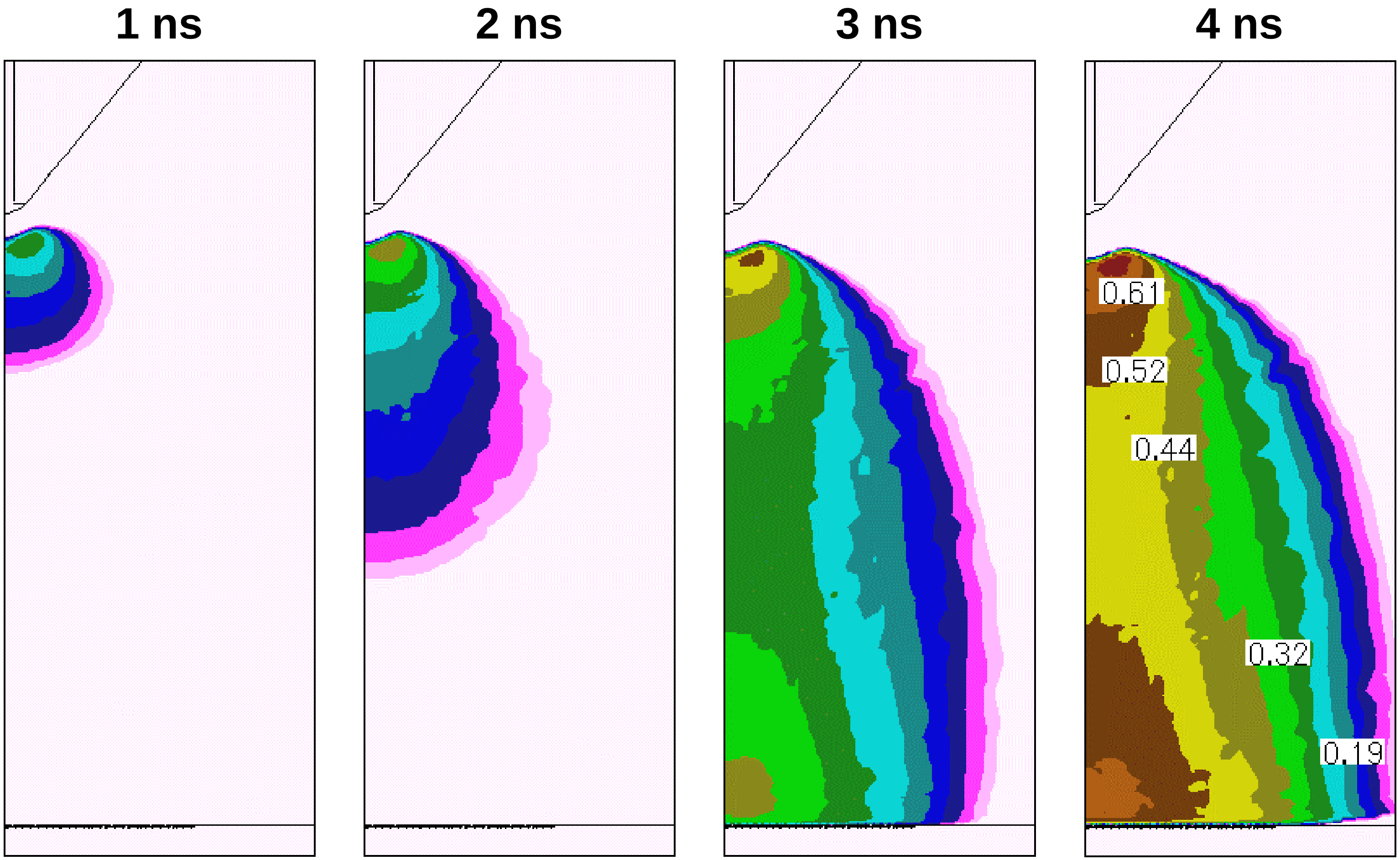
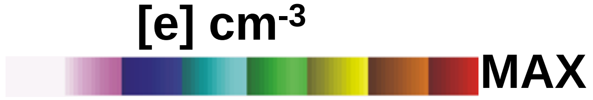
PLASMA DYNAMICS – ELECTRON DENSITY

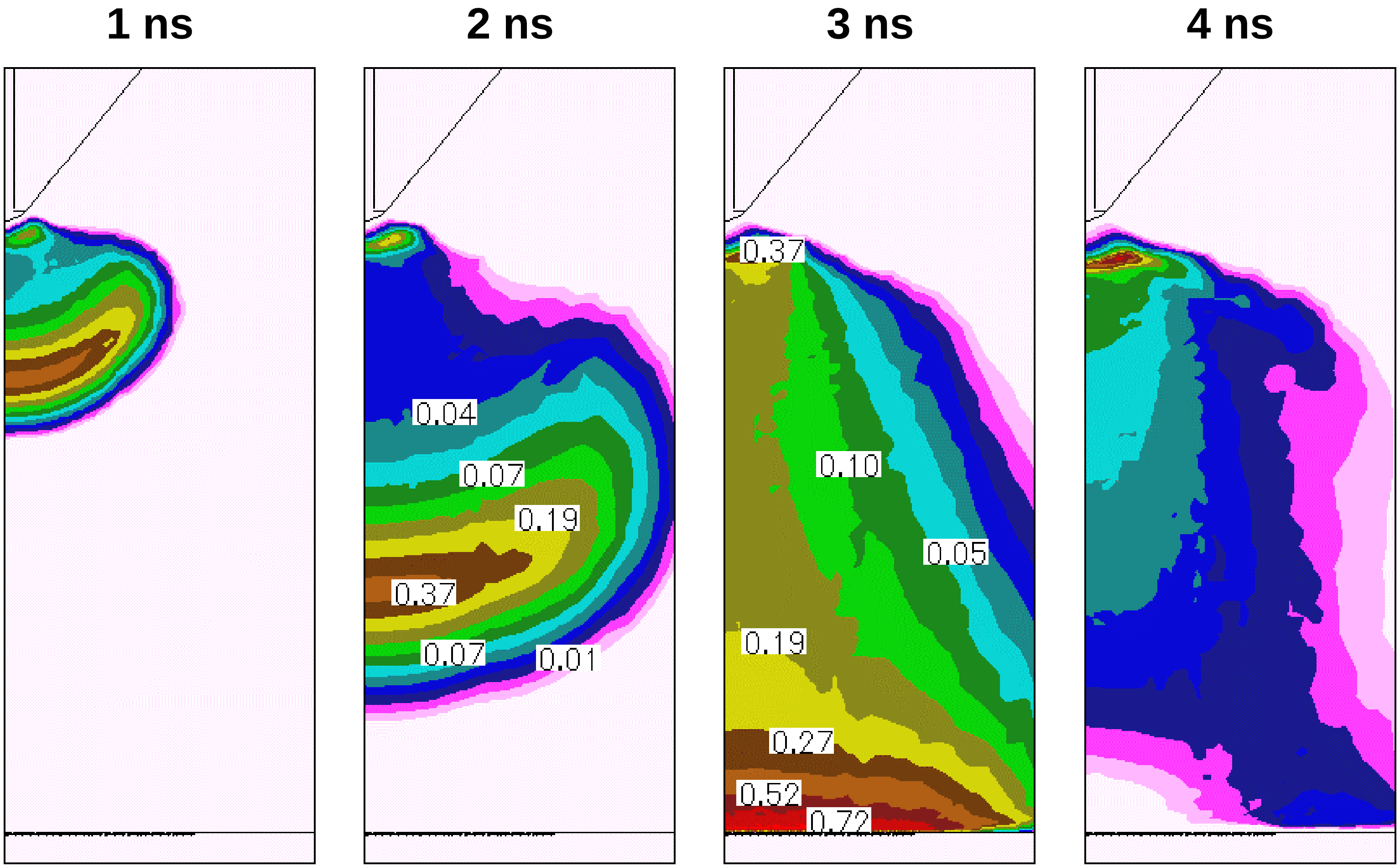


- - 5 kV, 760 Torr, $He/NH_3/H_2O$=98.9/1.0/0.1

MAX=2×10^{13}



PLASMA DYNAMICS – ELECTRON IMPACT SOURCES



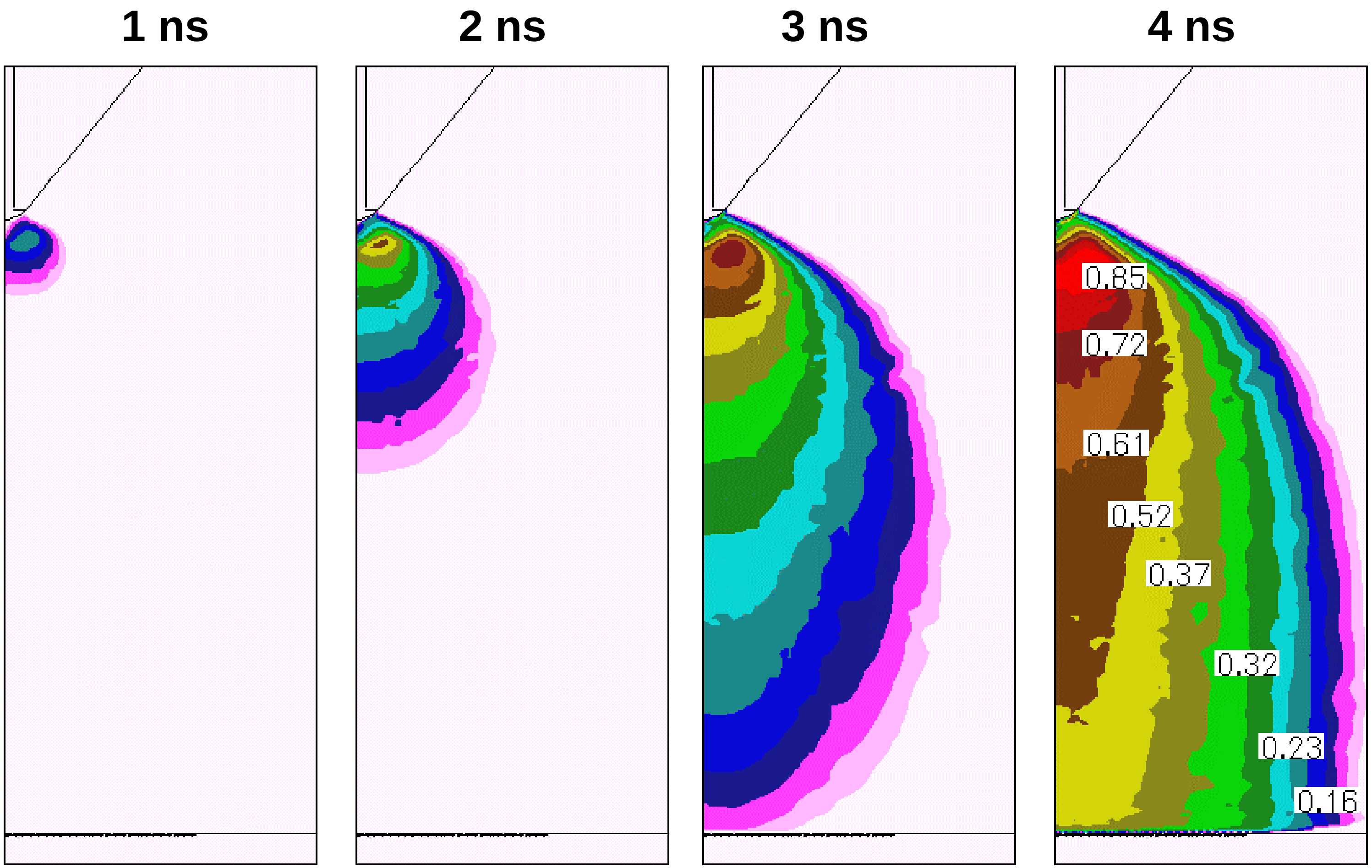
- - 5 kV, 760 Torr, He/NH_3/H_2O=98.9/1.0/0.1

MAX=$2\text{x}10^{22}$

[S-e] $cm^{-3}s^{-1}$

2-decade log scale

PLASMA DYNAMICS – NH_2 DENSITY



- -5 kV, 760 Torr, $He/NH_3/H_2O$=98.9/1.0/0.1

MAX=5×10^{13}

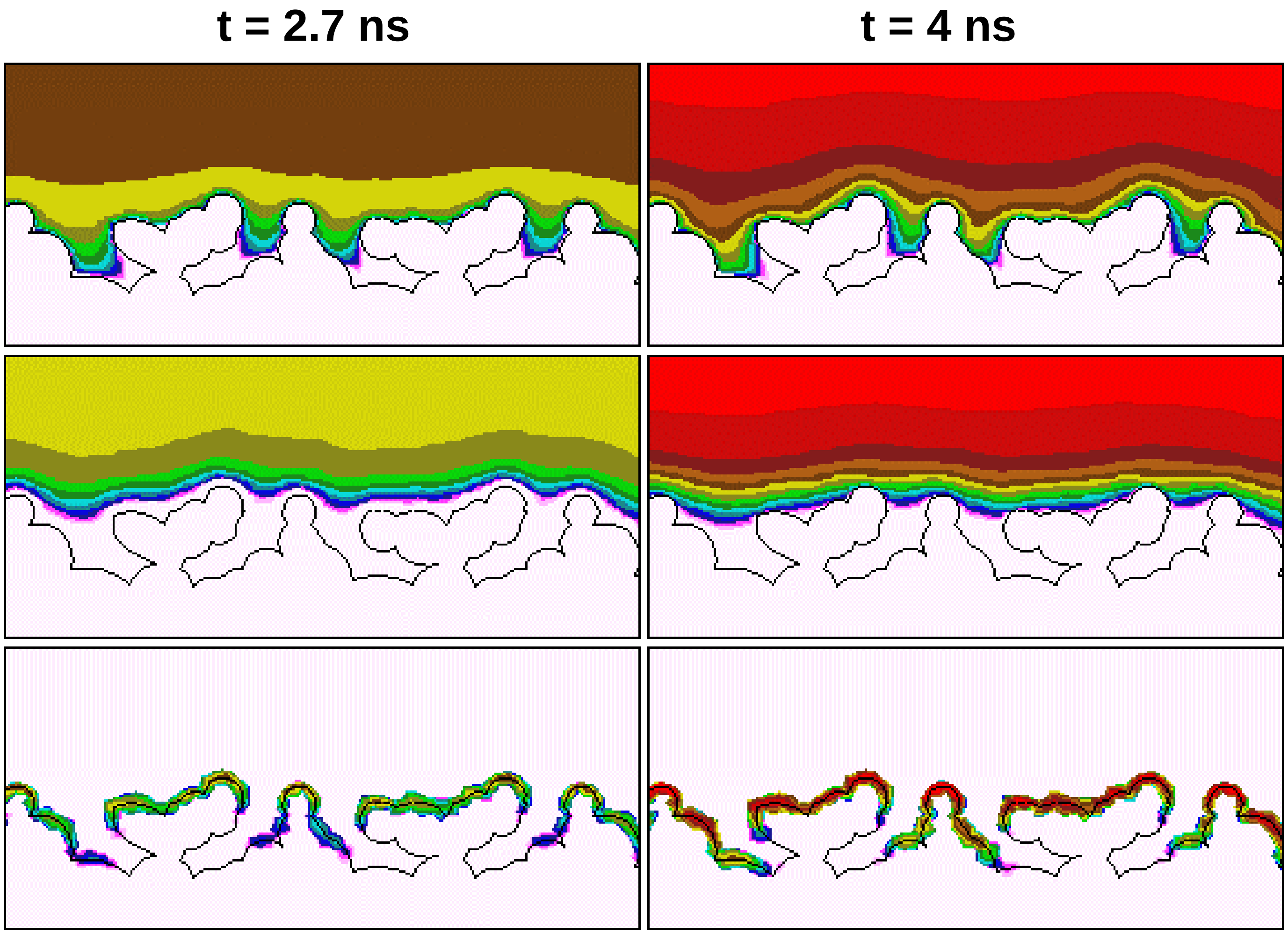
$[NH_2]$ cm^{-3}

MIN

MAX

1-decade log scale

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



[e] cm^{-3}

$10^{10} – 10^{13}$

[Positive ions] cm^{-3}

$10^{10} – 10^{13}$

[Surface (-ve) Charge] μC

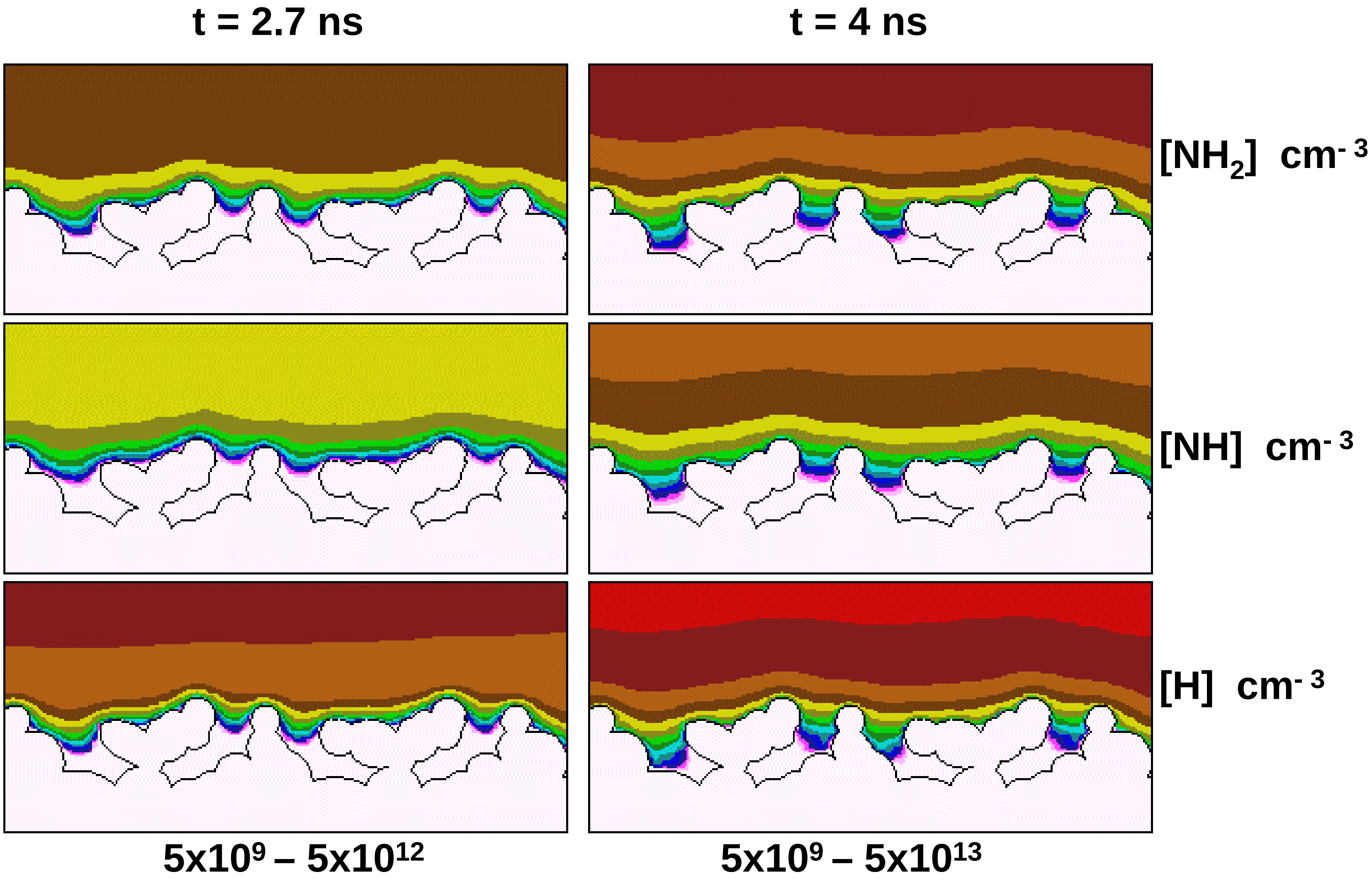
$10^{-1} – 10^{3}$

- - 5 kV, 760 Torr, He/NH_3/H_2O=98.9/1.0/0.1

MIN  MAX

log scale

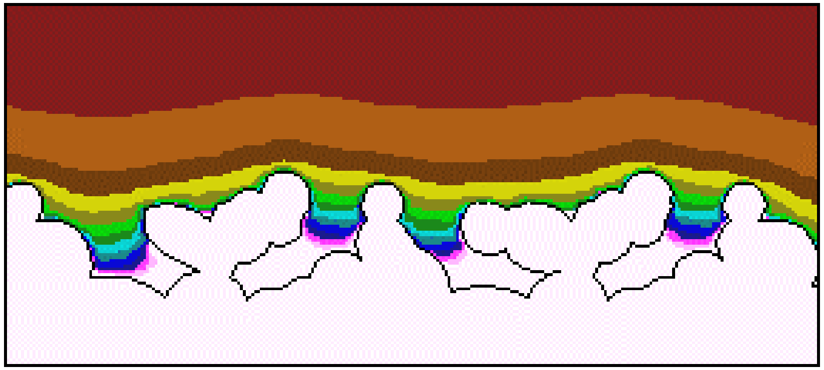
RADICAL DENSITIES DURING THE PULSE



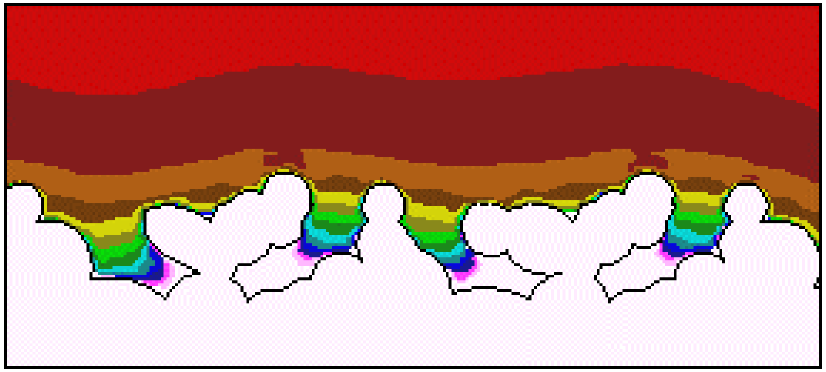
- \- 5 kV, 760 Torr, He/NH_3/H_2O=98.9/1.0/0.1

EFFECT OF VOLTAGE ON [NH_2] DURING THE PULSE

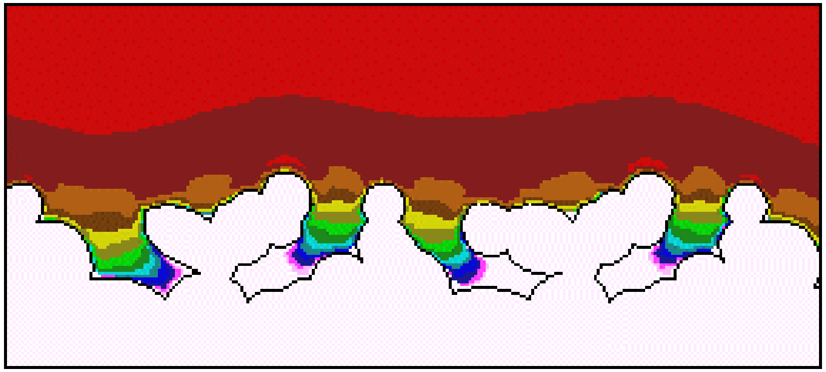
- 5 kV



- 10 kV



- 15 kV



- At higher voltages, increased dissociation of NH_3 results in higher [NH_2] near the surface during the pulse.

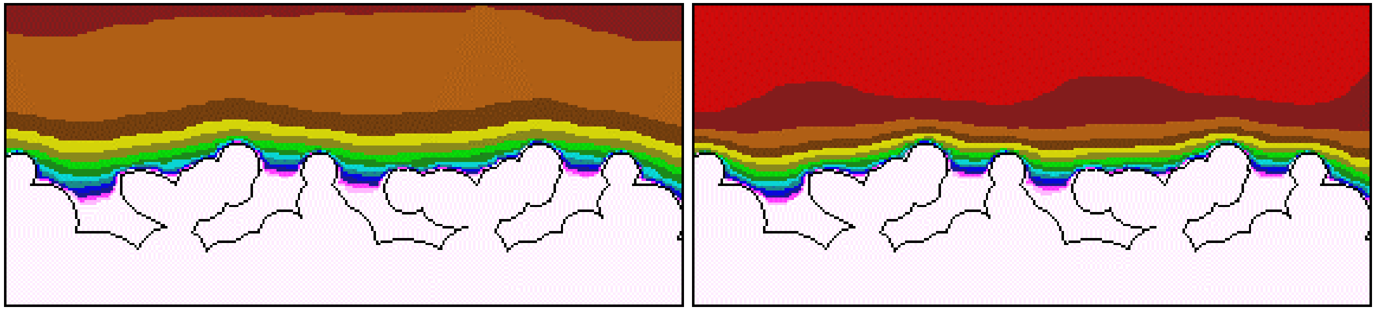
[NH_2] cm^{-3}

5×10^9  5×10^{13}

(log scale)

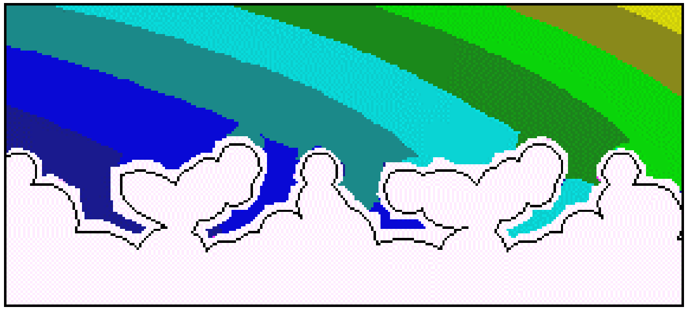
- 760 Torr, $He/NH_3/H_2O$=98.9/1.0/0.1, t = 4 ns

EFFECT OF NH_3 FRACTION ON $[NH_2]$


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

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

- **With higher NH_3 content, $[NH_2]$ during the pulse is higher.**


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

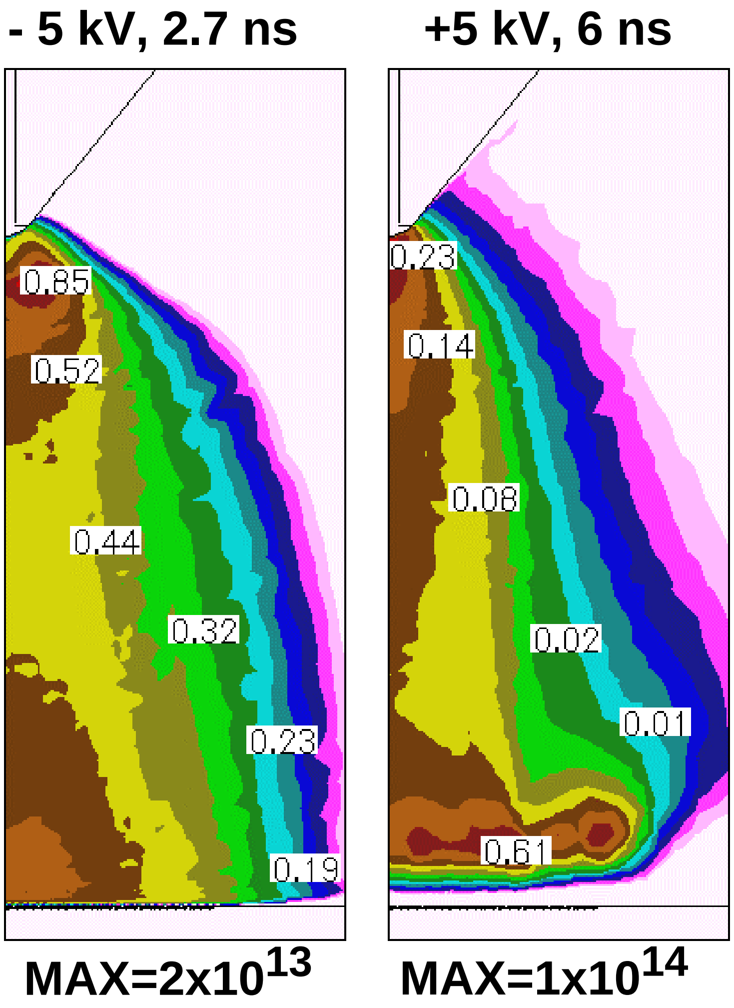

$2.25x10^{12}$ – $2.35x10^{12}$, t =90 µs

- **During the interpulse period $[NH_2]$ at the surface decreases because consumption reactions and diffusion dominate.**

- **- 5 kV, 760 Torr**

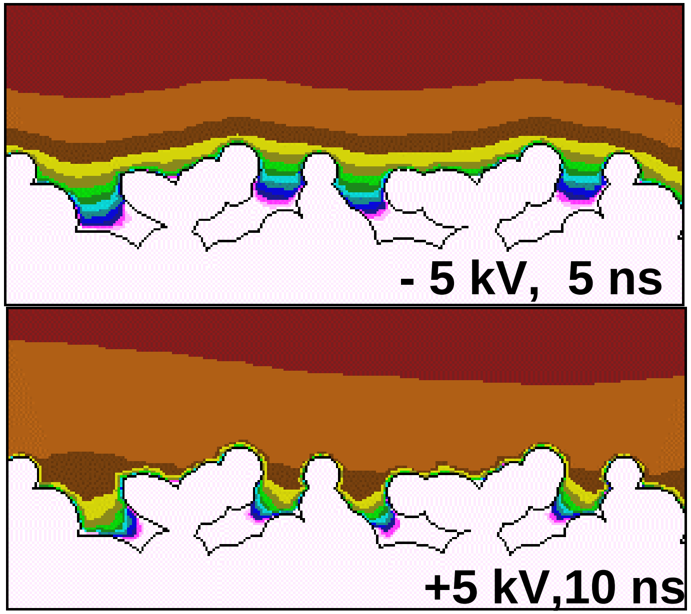
$[NH_2]$ cm^{-3}

EFFECT OF VOLTAGE POLARITY



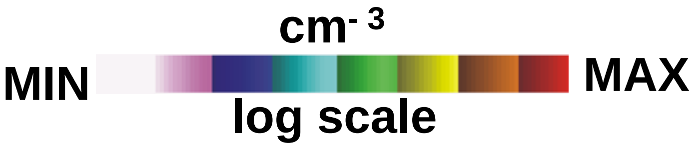
- [+ve IONS]

- [NH_2] during the pulse

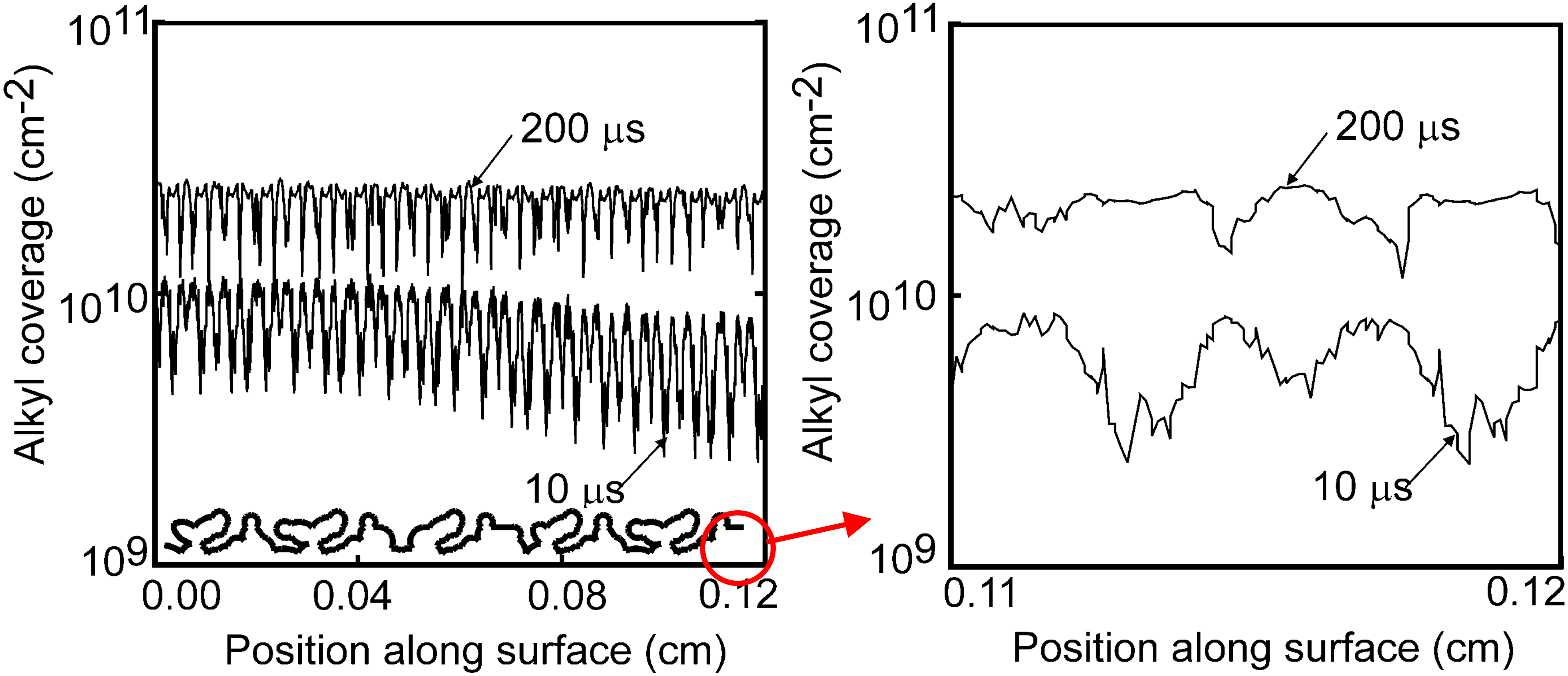


5×10^{10} - 5×10^{13}

- Positive discharge takes longer to close the gap and achieve similar radical densities near the surface.



SURFACE COVERAGE OF ALKYL RADICALS

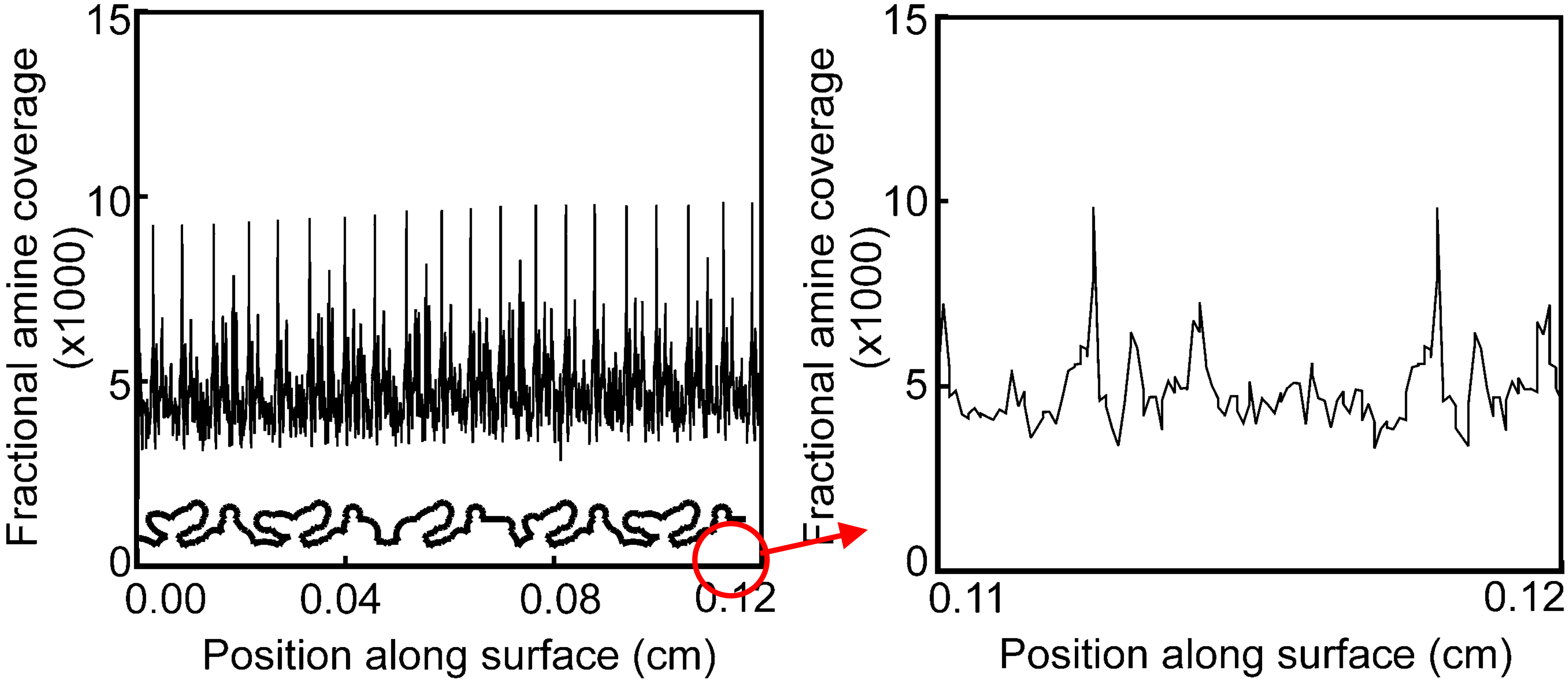


- **ALKYL (PP•) radicals are formed by the abstraction reactions**

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

- **- 5 kV, 760 Torr, 10 kHz, He/NH_3/H_2O=89.9/10.0/0.1**

SURFACE COVERAGE OF AMINE [C-NH$_2$] GROUPS

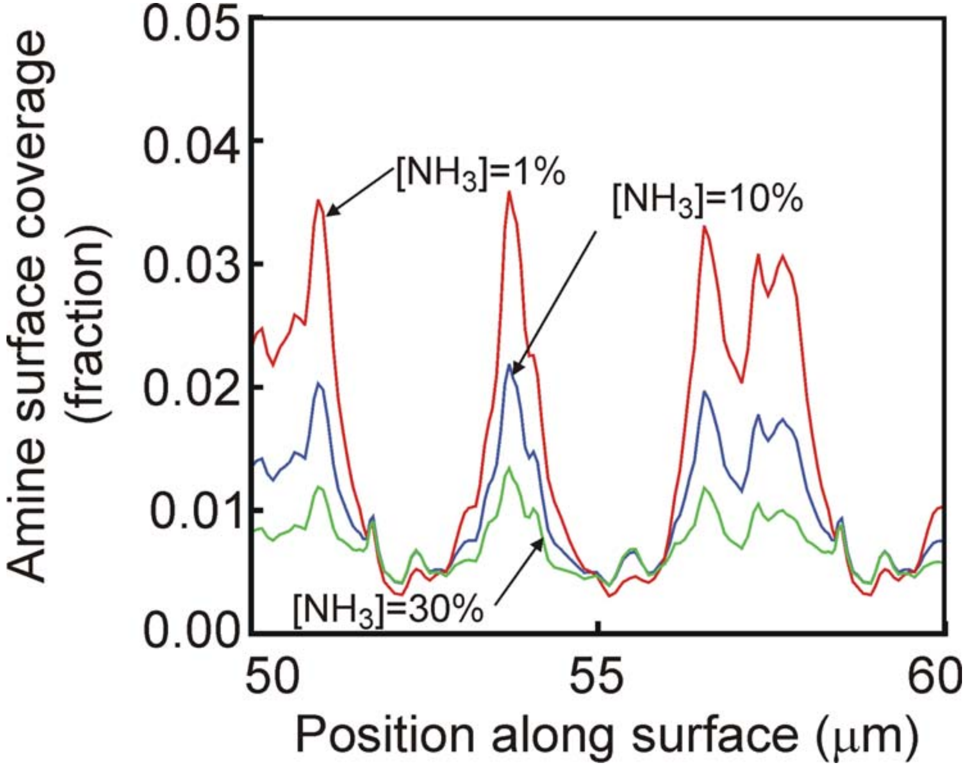


- **AMINE (C-NH$_2$) groups are created by addition of NH$_2$ to surface alkyl radicals**

NH$_2$ + PP• → PP-NH$_2$

- **- 5 kV, 760 Torr, 10 kHz, He/NH$_3$/H$_2$O=89.9/10.0/0.1, t = 0.1 s**

EFFECT OF NH_3 FRACTION ON TREATMENT

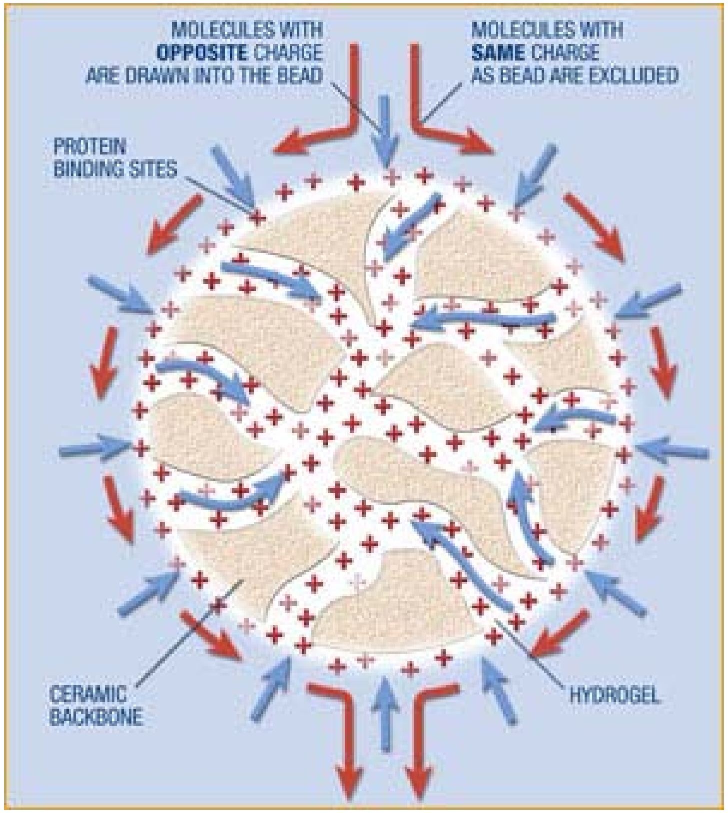


- Surface coverage of amine groups decreases as $[NH_3]$ increases.
- As $[NH_3]$ increases, less energy is expended into dissociating H_2O, decreasing OH fluxes.

- Since OH contributes significantly to initiating surface reactions by H abstraction, higher NH_3 leads to lower amine coverage.

- \- 5 kV, 760 Torr, $He/NH_3/H_2O=99-x/x/0.1$, 10 kHz, 1 s

TREATMENT OF POROUS POLYMER BEADS



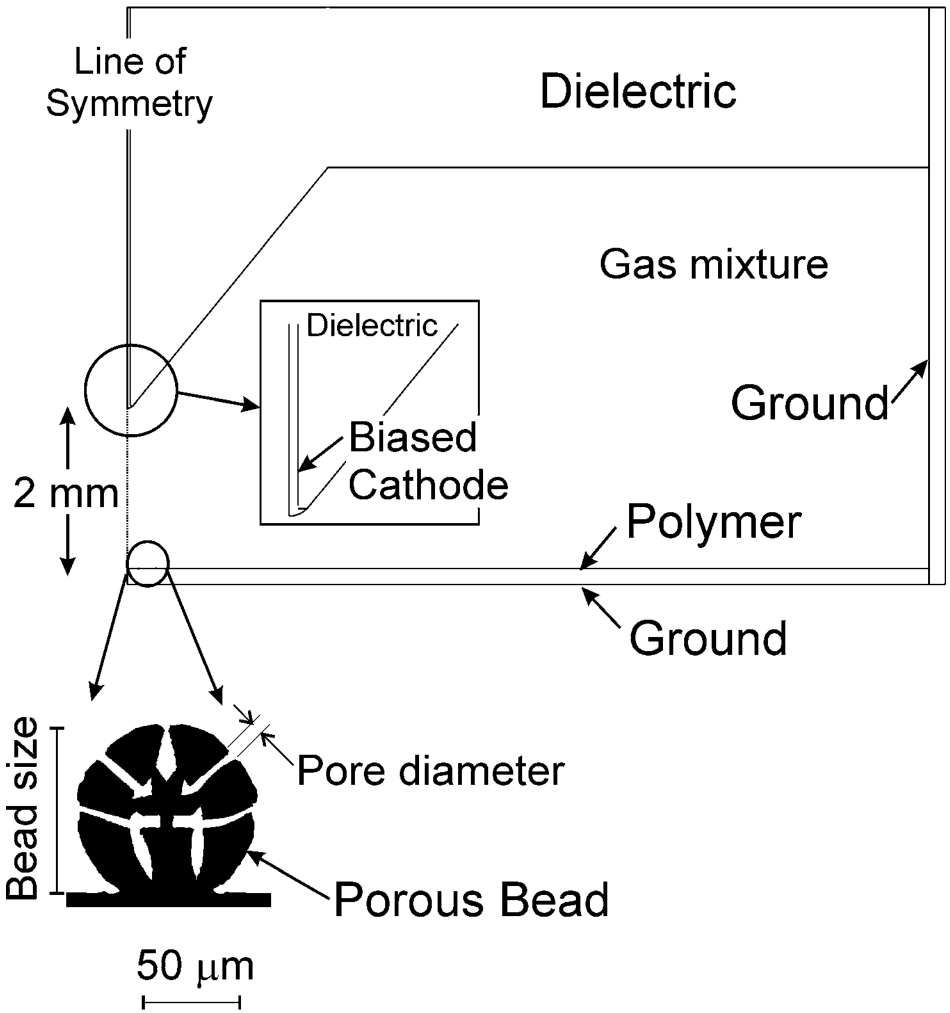
- Representation of Functionalized Porous Bead for Protein Binding sites, (from www.ciphergen.com)

- Macroporous beads are 10s μm in diameter with pore sizes < 10 μm.

- External bead surface and internal pore surfaces are functionalized for applications like polymer supported catalysts, protein immobilization.

- Penetration of reactive species into pores is critical to functionalization.

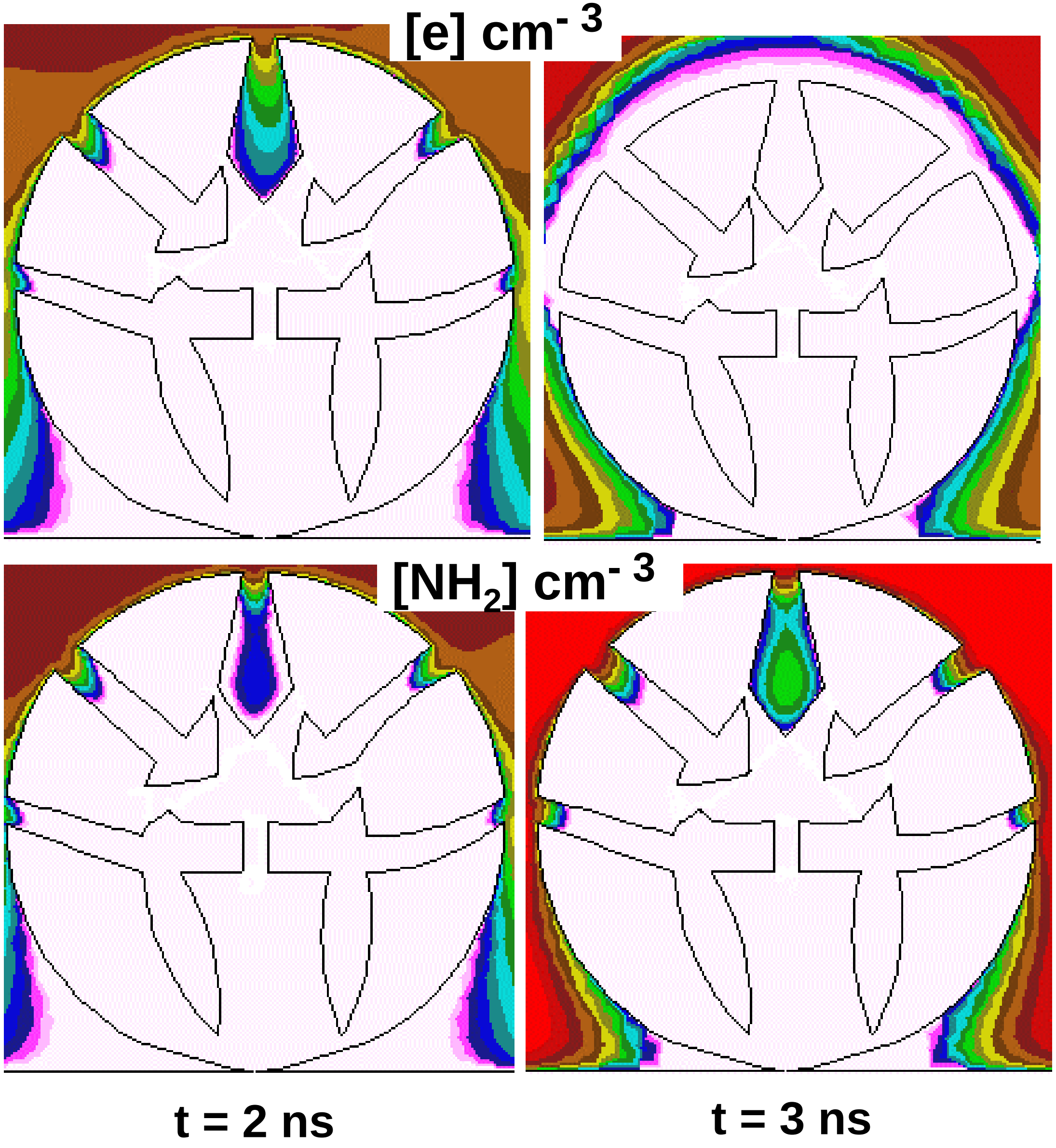
DBD TREATMENT OF POROUS POLYMER BEAD



- Corona treating a porous polymer bead placed on the lower dielectric.
- How well are the internal surfaces of porous polymer beads accessible to the plasma?
- What is the extent of functionalization on the internal surfaces?
- Non-interconnected pore architecture
- Bead size ~ 10s μm
  Pore dia ~ 2-10 μm

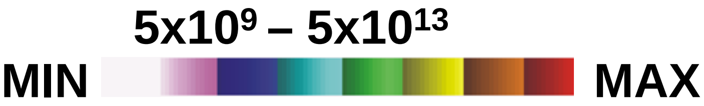
- - 5 kV, 760 Torr, $He/NH_3/H_2O$=89.9/10.0/0.1
- PRF – 10 kHz

PLASMA PENETRATION INTO INTERNAL SURFACES

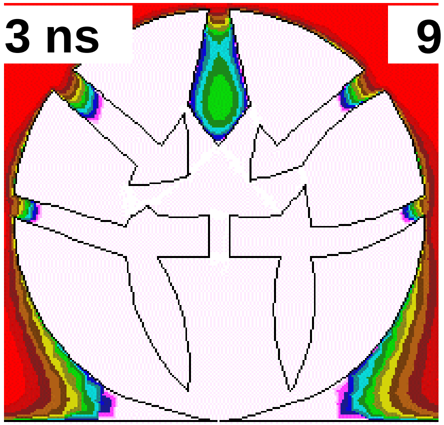


- Electron penetration into pores depends on the view-angle.
- Electrons recede due to surface charging effects.
- Radical production inside pores is high in those regions where plasma has penetrated.

- \- 5 kV, 760 Torr, $He/NH_3/H_2O=89.9/10.0/0.1$

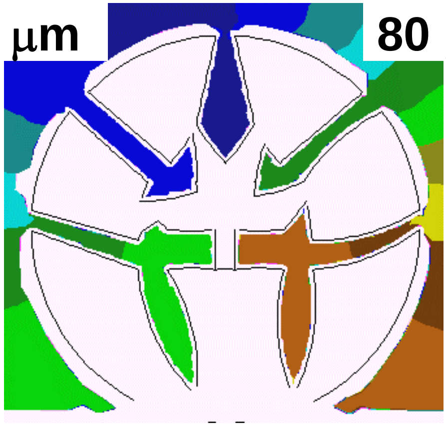


[NH_2] INSIDE PORES: EFFECT OF BEAD DIAMETER

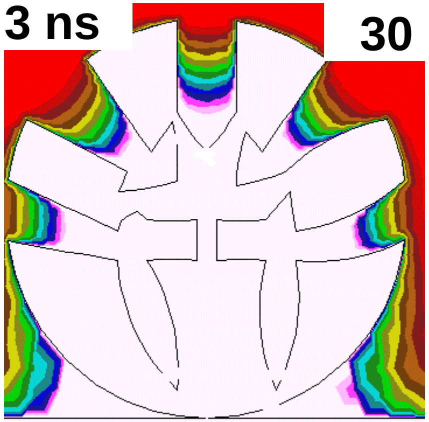


2x10^{10}- 2x10^{13}

90 μm

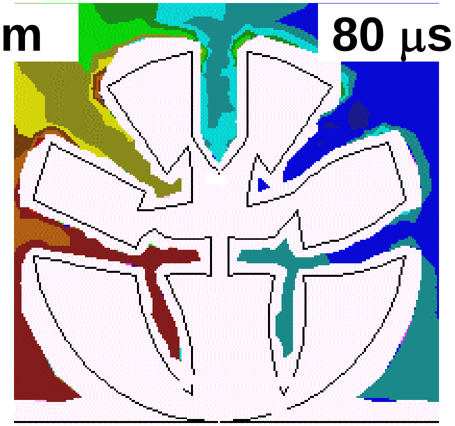


7.5x10^{12}- 8.5x10^{12}



2x10^{10}- 2x10^{13}

30 μm



9.1x10^{12}- 9.3x10^{12}

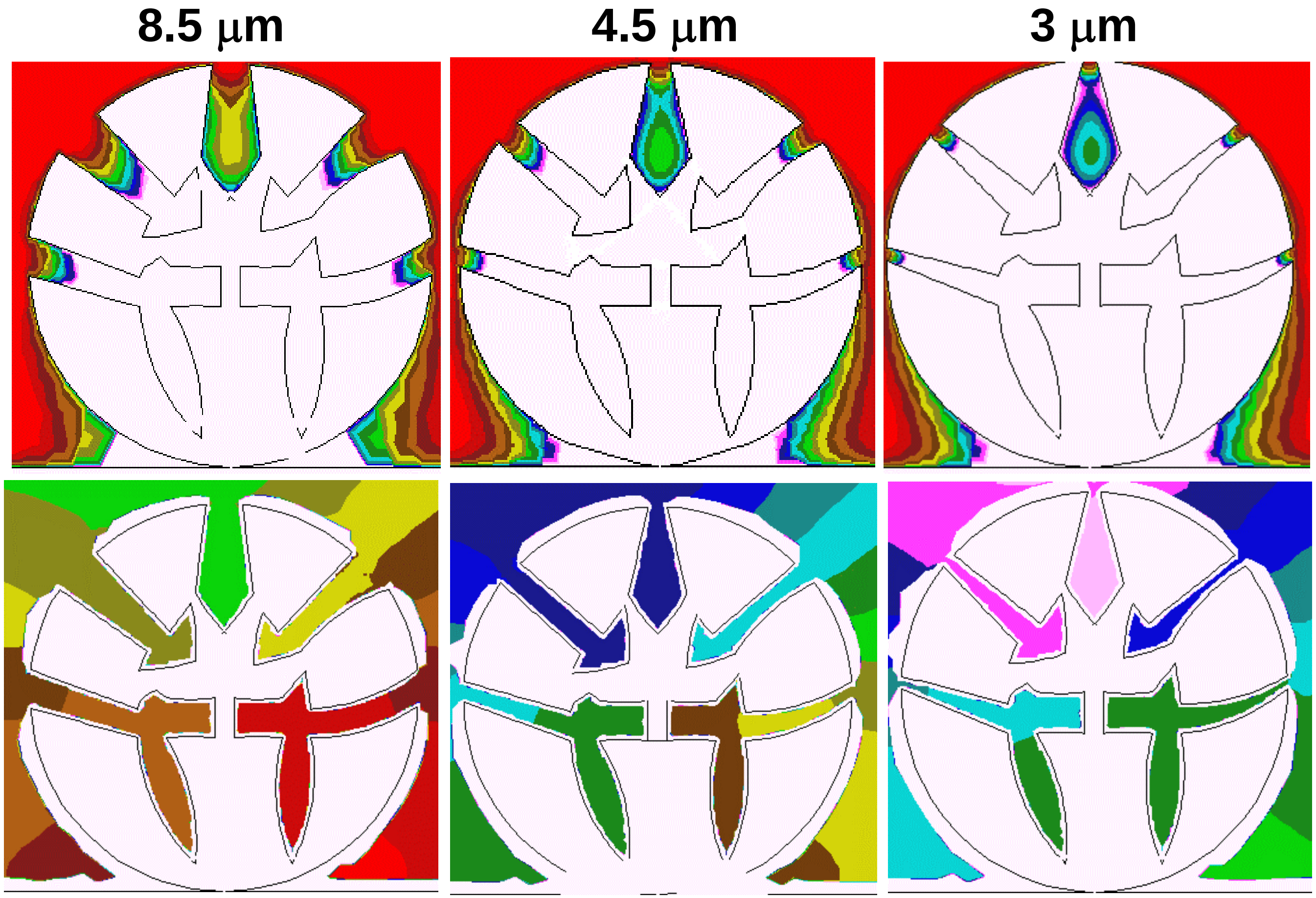
[NH_2] cm^{-3}

MIN  MAX

(log scale)

- During the pulse, [NH_2] increases slightly with bead size within pores.
- In the interpulse period, [NH_2] is higher within smaller beads.
- \- 5 kV, He/NH_3/H_2O=89.9/10.0/0.1, pore dia=4.5 μm, 760 Torr

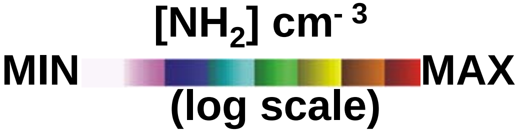
$[NH_2]$ INSIDE PORES : EFFECT OF PORE DIAMETER



- t = 3 ns
  2×10^{10}- 2×10^{13}

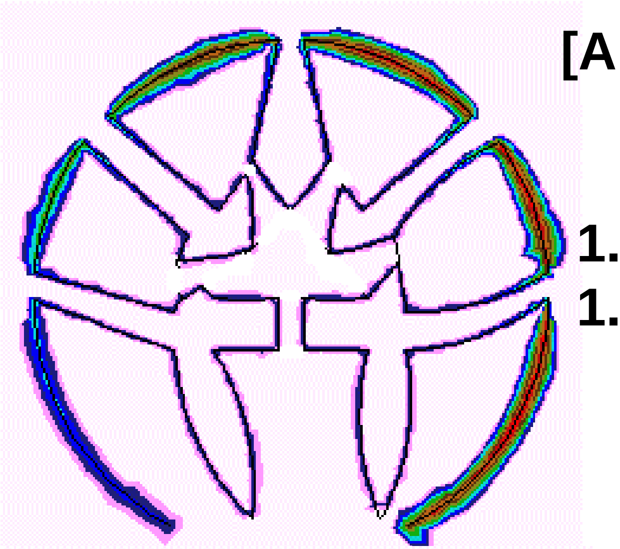
- t = 80 µs
  7.5×10^{12}- 8.65×10^{12}

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



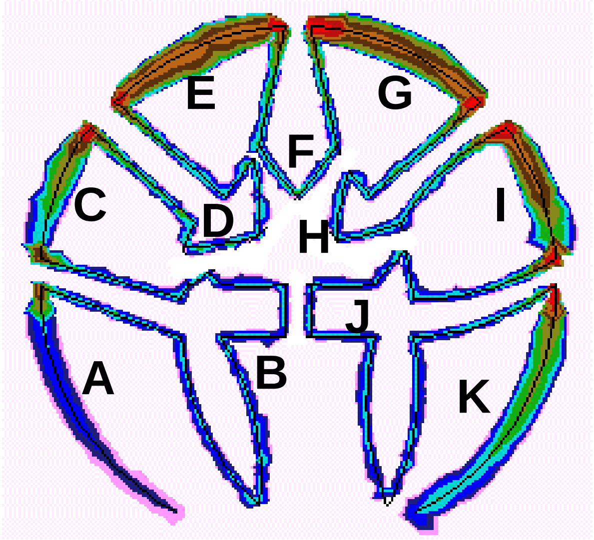
- - 5 kV, $He/NH_3/H_2O$=89.9/10.0/0.1, bead dia=90 µm, 760 Torr

FUNCTIONALIZATION OF POROUS BEAD SURFACES



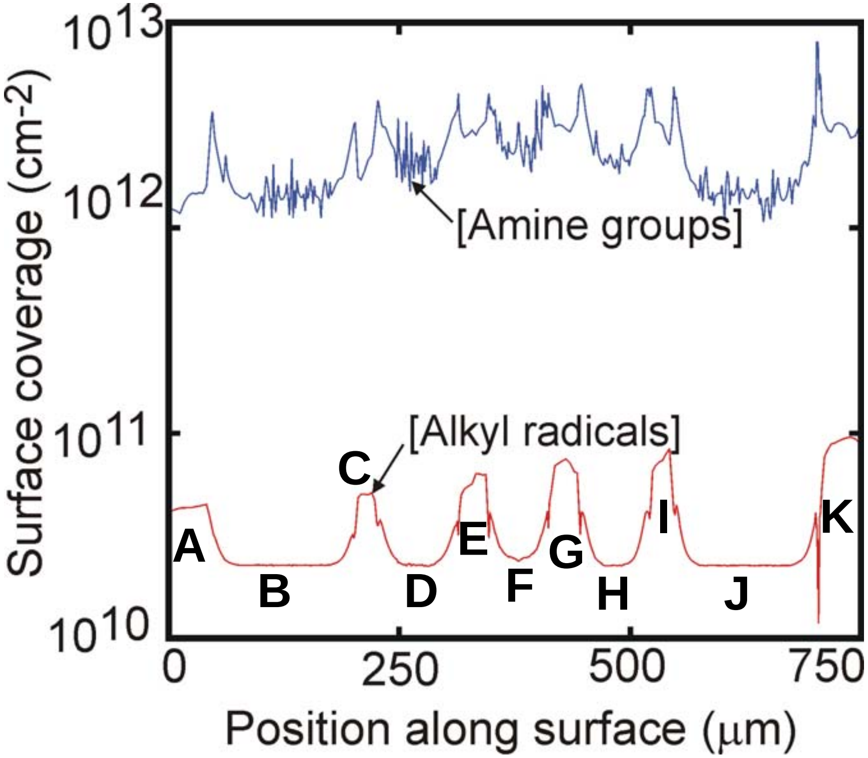
[ALKYL]

1.25×10^{10} – 1.25×10^{11}



[AMINE]

10^{12} – 10^{13}



- **- 5 kV, 760 Torr, 10 kHz, He/NH_3/H_2O=89.9/10.0/0.1, Bead size=90 µm, Pore dia= 4.5 µm, t=0.1 s**

Letters indicate position along the surface.

log scale, cm^{-2}

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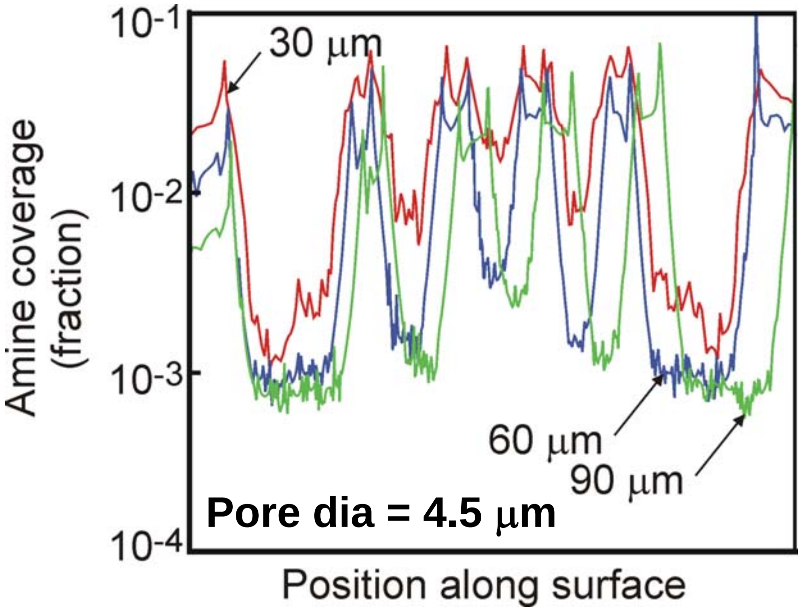
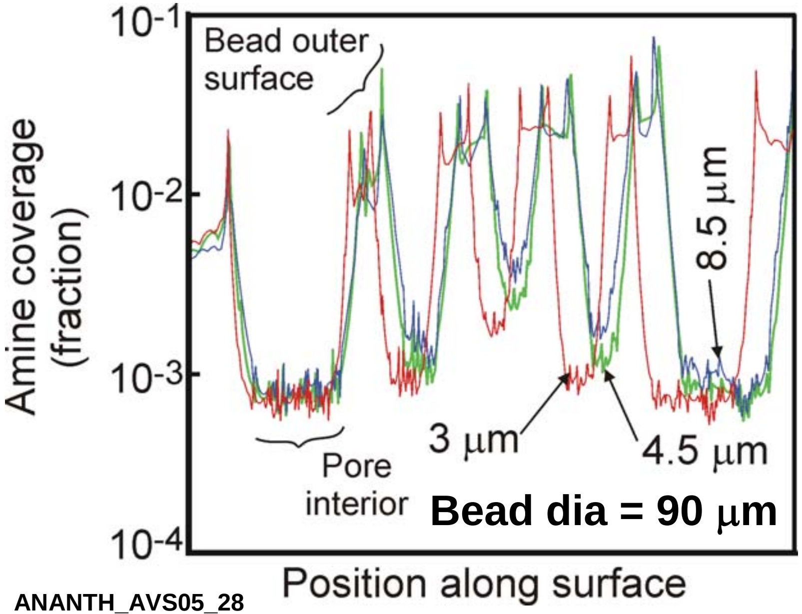
EFFECT OF BEAD, PORE DIAMETER ON TREATMENT





- **Outer bead surfaces have amine coverage significantly higher than interior pore surfaces in all cases.**
- **Interior pore surfaces of smaller beads have higher amine coverage due to higher average reactive radical fluxes.**
- **Similarly, interior pore surfaces of larger pore diameter bead have slightly higher amine coverage.**
- **- 5 kV, 760 Torr, 10 kHz, $He/NH_3/H_2O$=89.9/10.0/0.1, t=1 s**

CONCLUDING REMARKS

- Pulsed DBD-corona treatment of rough PP surfaces and porous μm-sized beads in $He/NH_3/H_2O$ mixtures was studied using an integrated multiscale plasma dynamics – surface kinetics model.
- Charged species have limited penetration due to surface charging while radicals can diffuse into surface features.
- Amine coverage of rough surfaces is significantly lower in the nooks and crannies as average fluxes of reactive species is lower.
- With higher NH_3 fraction, amine surface coverage reduces as less energy is expended in dissociating H_2O to produce OH radicals.
- The outer surfaces of porous beads have significantly higher amine coverage than the inner surfaces along the pores.
- Larger bead size and smaller pore diameter results in lower surface functionalization along inner surfaces due to greater diffusion barriers encountered by reactive species.