SIMULATION OF POROUS LOW-*k* DIELECTRIC SEALING BY COMBINED He AND NH_3 PLASMA TREATMENT*

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AGENDA

- Low-*k* Dielectrics
- Modeling Platforms
- Modeling of Porous Low-*k* Sealing
    - Goals and Premises for Sealing Mechanism
- Sealing Mechanism
    - Surface Site Activation by He plasma pre-treatment
    - Sealing by Ar/NH_3 Treatment
- Sealing Efficiency Dependence
    - Porosity and Interconnectivity
    - Treatment time and Pore Radius
- Concluding Remarks

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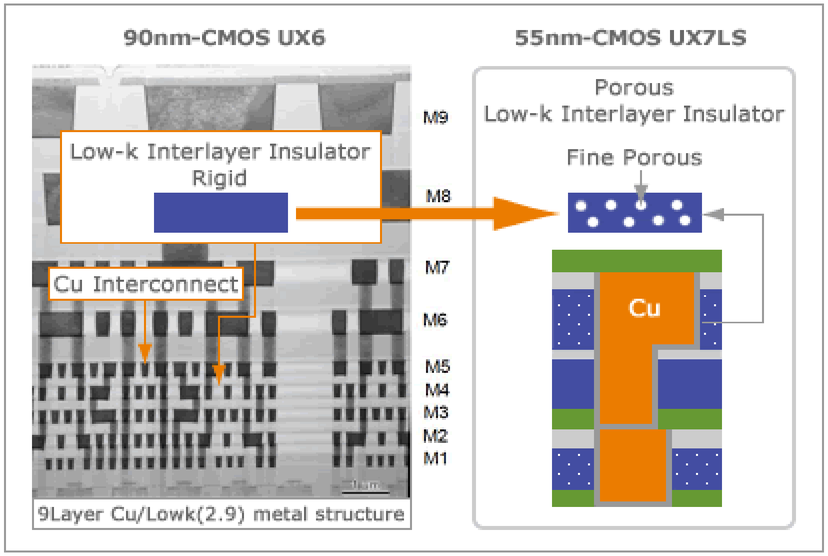
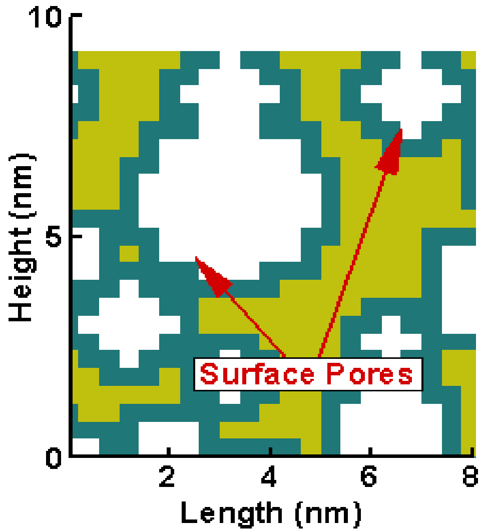
POROUS LOW-*k* DIELECTRIC

- **Metal interconnect lines in ICs run through dielectric insulators.**
- **The capacitance of the insulator contributes to *RC* delays.**
- **Porous oxides, such as C doped SiO_2 (with CH_n lining pores) have a low dielectric constant which reduces the RC delay.**
- **Porosity is ≤ 0.5. Inter-connected pores open to surface offer pathways to degrade *k*-value by reactions.**



Ref: http://www.necel.com/process/en/images/porous_low-k_e.gif



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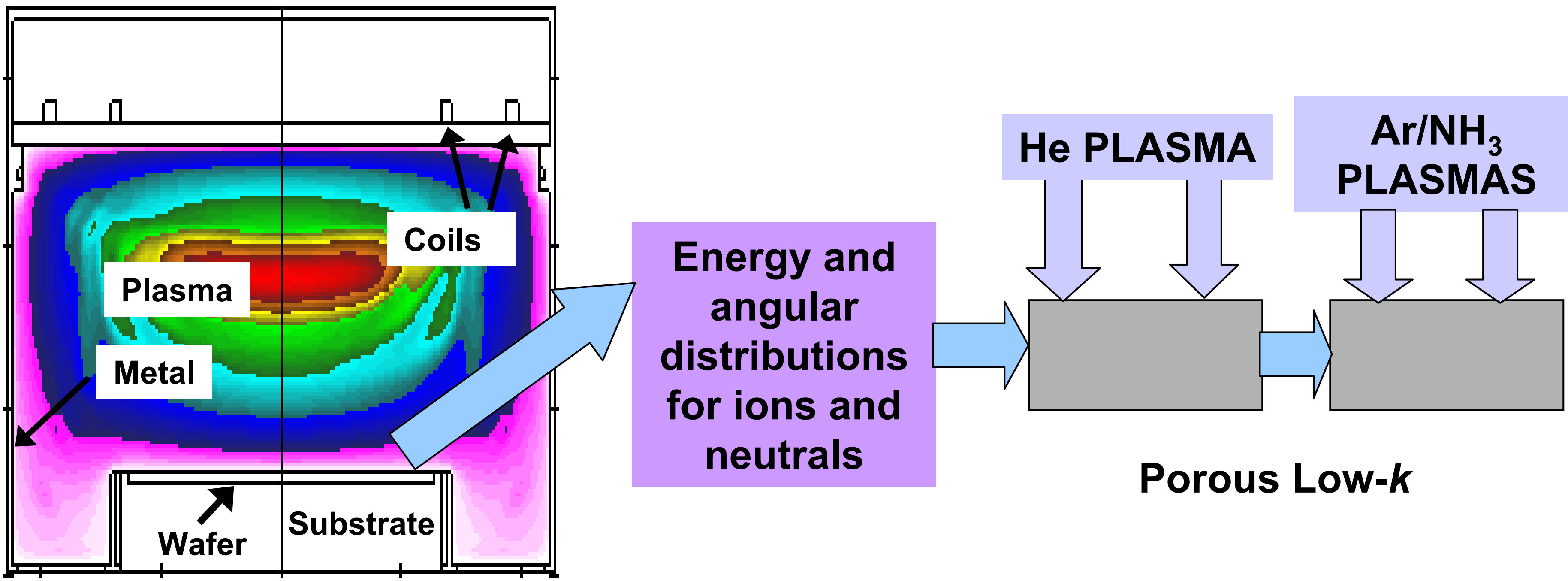
GOALS AND PREMISES OF SEALING MECHANISM

- **To prevent the degradation of low-k materials pores open to the surface has to be sealed.**
- **He followed by NH_3 plasma treatment has been shown to seal the pores.**
  - **He^+ and photons break Si-O bonds while knocking off H atom from CH_n.**
  - **Subsequent NH_3 exposure seals the pores by adsorption reactions forming C-N and Si-N bonds.**
- **Experimental results from the literature were used to build the sealing mechanism.**

Plasma	Treatment Time (s)	Function
He	20	Surface Activation
NH_3	20 (Post-He)	Sealing

Ref: A. M. Urbanowicz, M. R. Baklanov, J. Heijlen, Y. Travaly, and A. Cockburn, Electrochem. Solid-State Lett. 10, G76 (2007).

MODELING : LOW-*k* PORE SEALING



- Hybrid Plasma Equipment Model (HPEM)
- Plasma Chemistry Monte Carlo Module (PCMCM)
- Monte Carlo Feature Profile Model (MCFPM)

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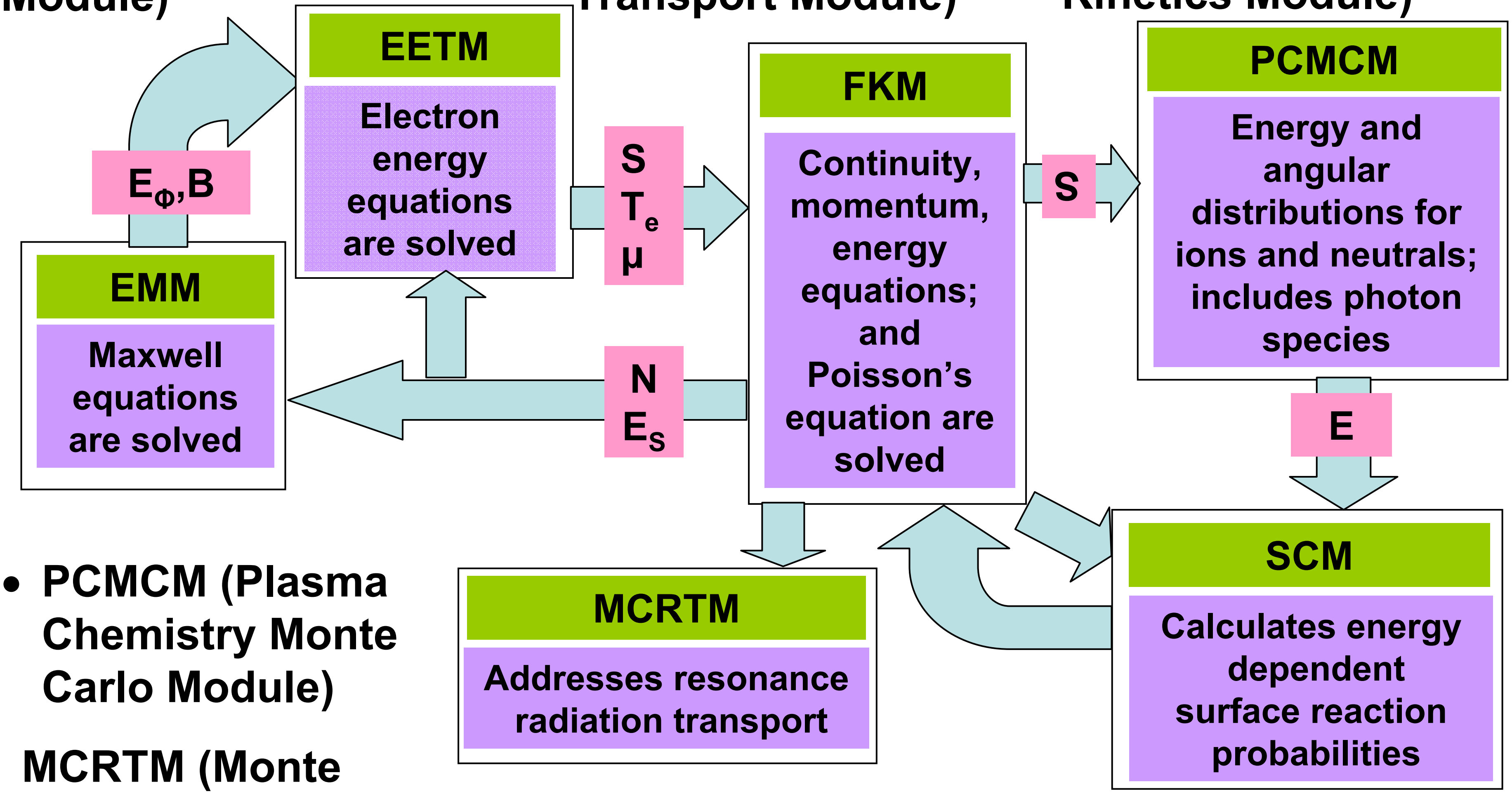
HYBRID PLASMA EQUIPMENT MODEL (HPEM)

- EEM (Electromagnetics Module)
- EETM (Electron Transport Module)
- FKM (Fluid Kinetics Module)



- PCMCM (Plasma Chemistry Monte Carlo Module)
- MCRTM (Monte Carlo Radiation Transport Module)
- SCM (Surface Chemistry Module)

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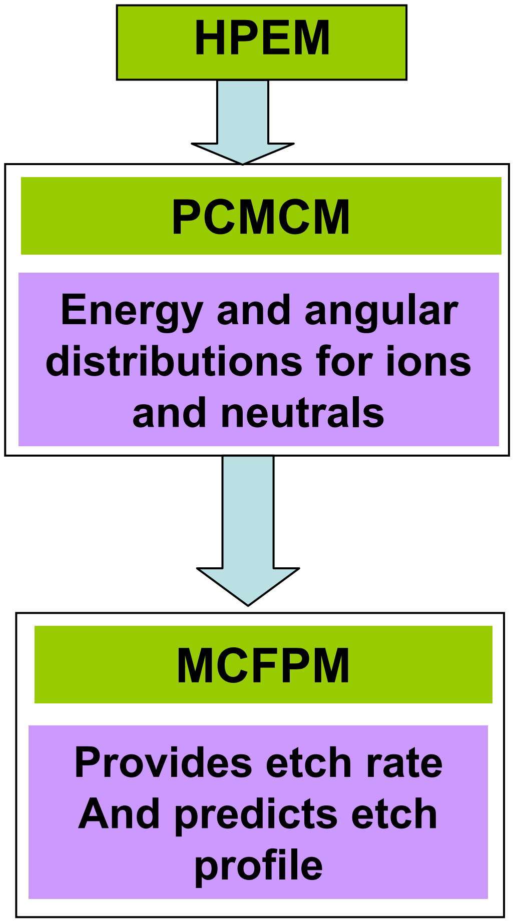
MONTE CARLO FEATURE PROFILE MODEL (MCFPM)



- The MCFPM resolves the surface topology on a 2D Cartesian mesh to predict etch profiles.
- Each cell in the mesh has a material identity. (Cells are 4 x 4 A).
- Gas phase species are represented by Monte Carlo pseudoparticles.
- Pseudoparticles are launched towards the wafer with energies and angles sampled from the distributions obtained from the PCMCM.
- Cells identities changed, removed, added for reactions, etching deposition.

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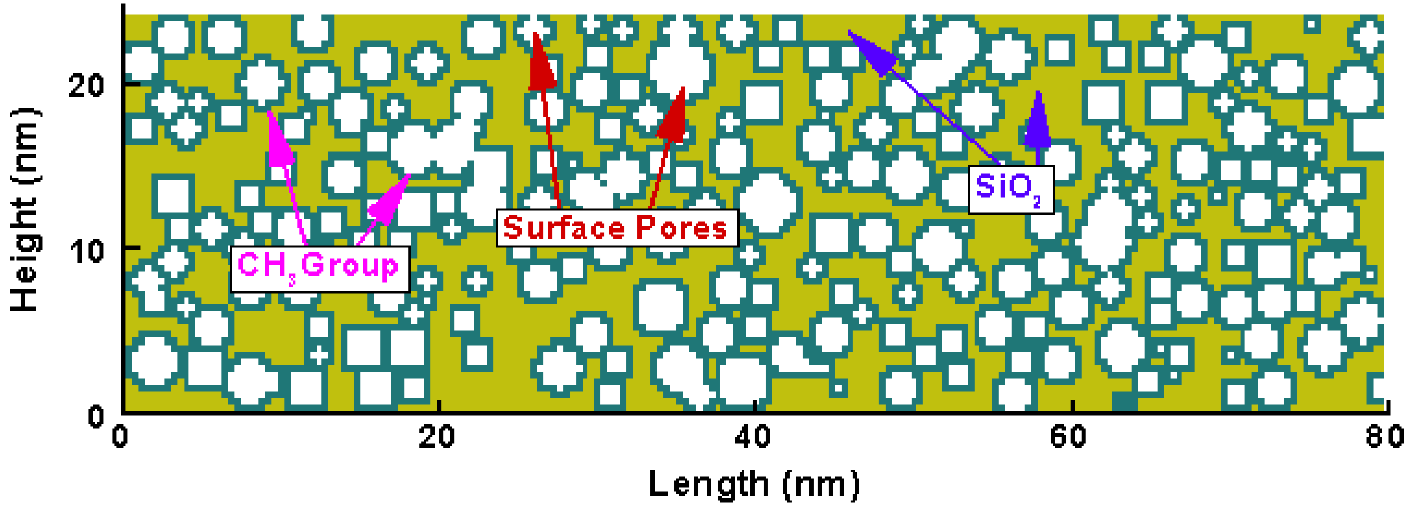
INITIAL LOW-*k* PROFILE FOR SIMULATION



- **80 nm wide and 30 nm thick porous SiO_2**
- **CH_3 groups line the pores**
- **Average pore radius: 0.8-1.4 nm**
- **Pores open to surface need to be sealed**
- **Will be exposed to successive He and NH_3 plasmas.**

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SURFACE ACTIVATION IN He PLASMA

- He^+ and photons break Si-O bonds and removes H from CH_3 groups.

- Bond Breaking

$$He^+(g) + SiO_2(s) \rightarrow SiO(s) + O(s) + He(g)$$

$$He^+(g) + SiO(s) \rightarrow Si(s) + O(s) + He(g)$$

$$h\nu + SiO_2(s) \rightarrow SiO(s) + O(s)$$

$$h\nu + SiO(s) \rightarrow Si(s) + O(s)$$

- Activation

$$He^+(g) + CH_n(s) \rightarrow CH_{n-1}(s) + H(g) + He(g)$$

$$h\nu + CH_{n-1}(s) \rightarrow CH_{n-2}(s) + H(g)$$

$$He^+(g) + CH_n(s) \rightarrow CH_{n-1}(s) + H(g) + He(g)$$

$$h\nu + CH_{n-1}(s) \rightarrow CH_{n-2}(s) + H(g)$$

- Reactive sites assist sealing in the subsequent Ar/NH_3 treatment.

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SEALING MECHANISM IN Ar/NH_3 PLASMA

- N/NH_x species are adsorbed by activated sites forming Si-N and C-N bonds to seal pores.
- Further Bond Breaking

$$M^+(g) + SiO_2(s) \rightarrow SiO(s) + O(s) + M(g)$$

$$M^+(g) + SiO(s) \rightarrow Si(s) + O(s) + M(g)$$

- N/NH_x Adsorption

$$NH_x(g) + SiO_n(s) \rightarrow SiO_nNH_x(s)$$

$$NH_x(g) + Si(s) \rightarrow SiNH_x(s)$$

$$NH_x(g) + CH_n(s) \rightarrow CH_nNH_x(s)$$

$$NH_x(g) + C(s) \rightarrow CNH_x(s)$$

- $SiNH_x$-NH_y/CNH_x-NH_y compounds help seal the pores where end nitrogens are bonded to either Si or C atom by Si-C/Si-N bond

$$NH_y(g) + SiNH_x(s) \rightarrow SiNH_x\text{-}NH_y(s)$$

$$NH_y(g) + CNH_x(s) \rightarrow CNH_x\text{-}NH_y(s)$$

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He AND Ar/NH_3 PLASMAS

- He^+ and photons in He plasma break Si-O bonds and activate CH_n groups.
- He Plasma Species:

  He He^* He^+ *hv e*

- Ar/NH_3 = 25/75 treatment seals the surface pores.
- Ar/NH_3 Plasma Species:

  Ar Ar^* Ar^+ e
  NH_3 NH_2 NH   H   N
  NH_3^+ NH_2^+ NH_4^+ NH^+

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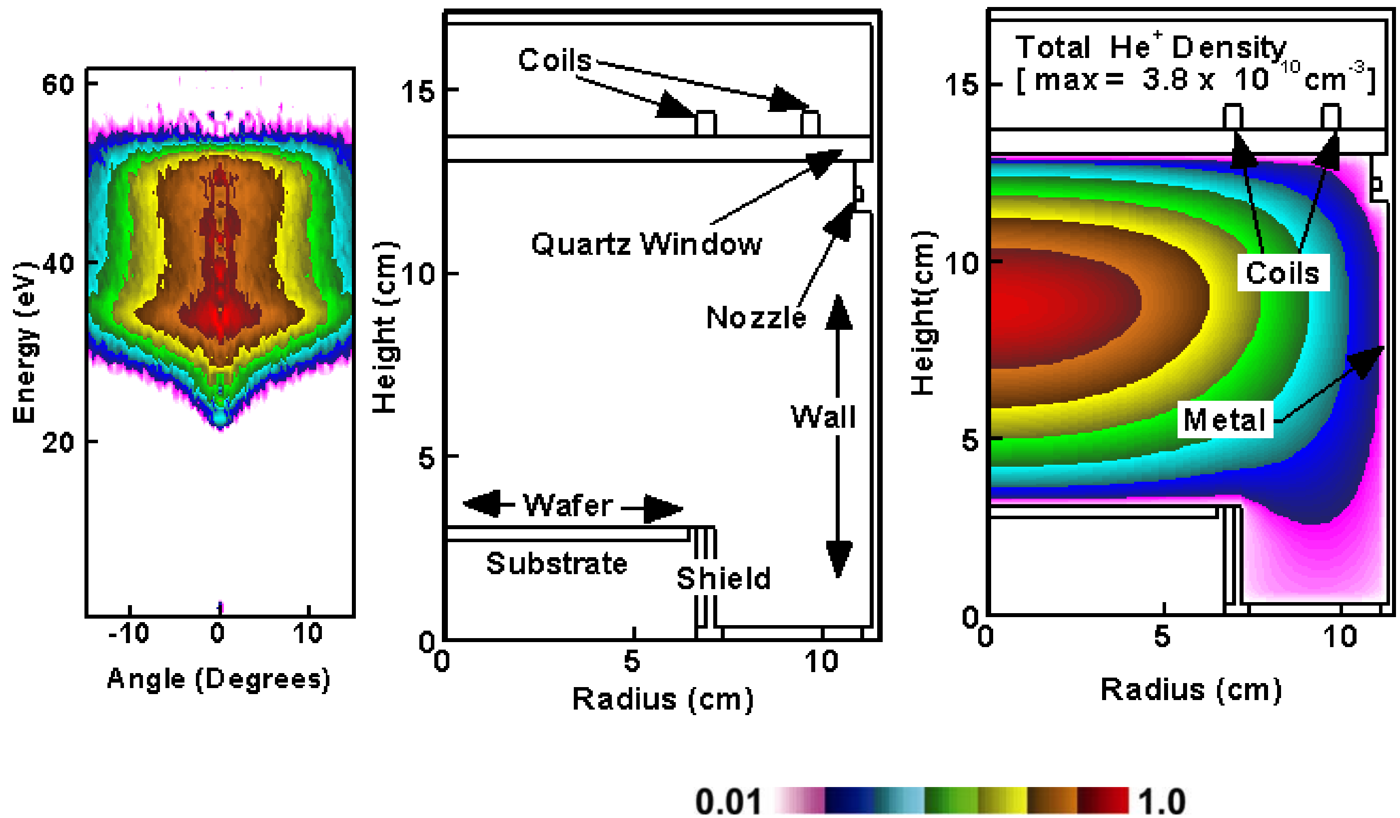
He PLASMA PRE-TREATMENT

- Ion density: 3.8×10^{10} cm^{-3}.
- Porous low-*k* was exposed for 30s to the plasma.
- 20V substrate bias assisted ablating H and Si-O bond breaking.
- Conditions: He, 10 mTorr, 300 W ICP, 20V Bias



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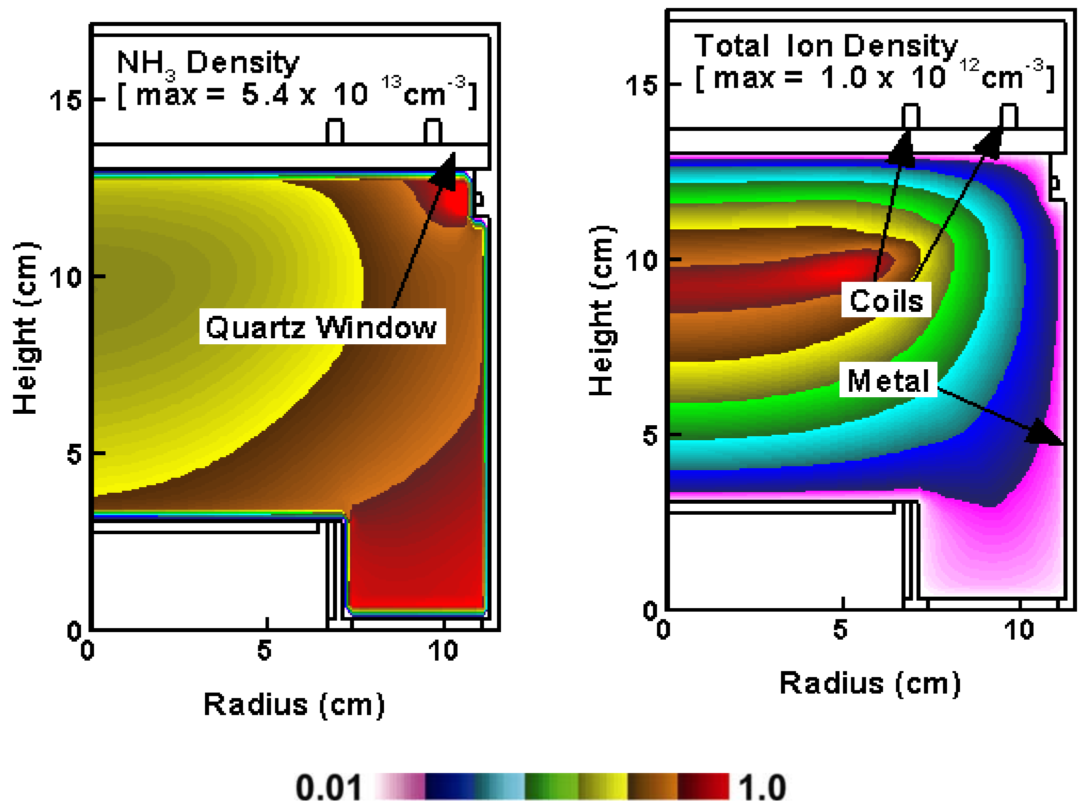
Ar/NH_3 PLASMAS

- **Total ion density:**
  1.0x 10^{11} cm^{-3}
- **Ion densities (cm^{-3}):**
  NH_3^+ 2.6 x 10^{10}
  NH_4^+ 2.9 x 10^{10}
  NH_2^+ 1.0 x 10^{10}
  NH^+ 1.4 x 10^{09}
  H^+ 1.6 x 10^{10}
- **Neutral densities (cm^{-3}):**
  NH_3 5.30 x 10^{13}
  NH_2 2.40 x 10^{13}
  NH 1.6 x 10^{12}
  N 2.4 x 10^{12}
  Ar 6.0 x 10^{12}



- **Conditions: Ar/NH_3 = 25/75, 10 mTorr, 300 W ICP**

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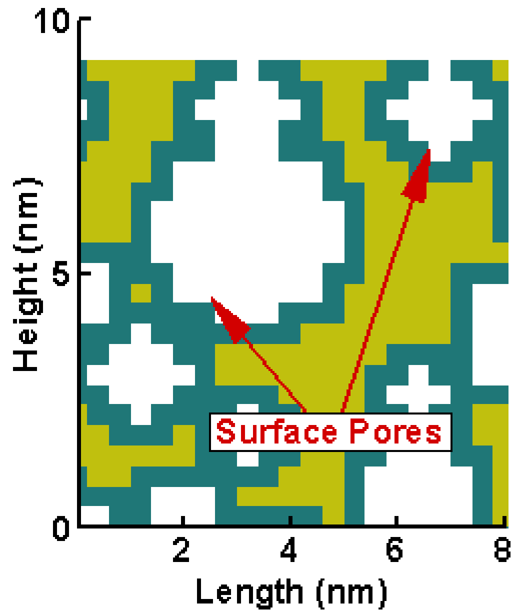
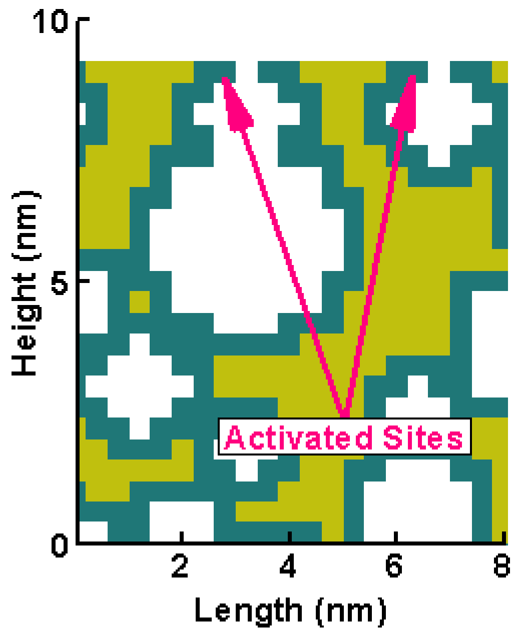
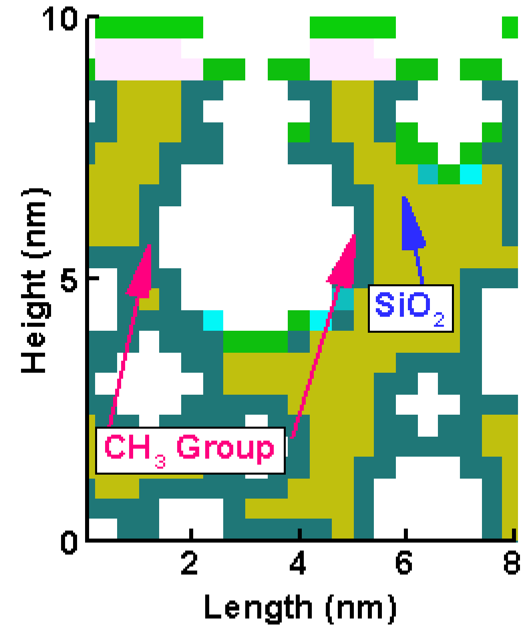
PORE-SEALING BY SUCCESSIVE He AND NH_3/Ar TREATMENT



•Initial Surface Pores



•Site Activation Employing He Plasma



•Sealing Employing Ar/NH_3 Plasmas

- Surface pore sites are activated by 30s He plasma treatment.
- Successive 20s NH_3 treatment seals the pores forming Si-N and Si-C bonds.

Animation Slide-GIF

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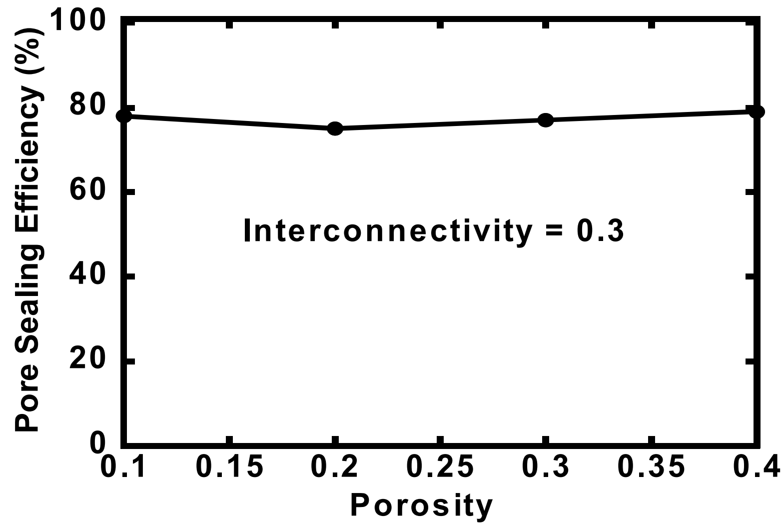
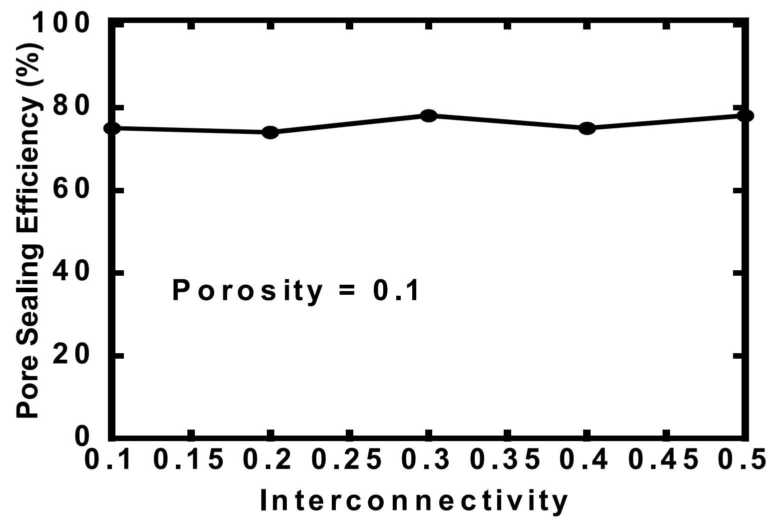
SEALING: POROSITY AND INTERCONNECTIVITY

- **Sealing efficiency is independent of porosity and interconnectivity, optimizing at 75-80%**
- **With higher porosity, the number of open pores to the surface increases.**
- **If pore radius remains the same, sealing efficiency is constant.**
- **With higher porosity but a fixed pore radius, number of surface pores increases.**
- **The fixed probabilities of C-N, Si-N and N-N bond formation result in a constant sealing efficiency.**





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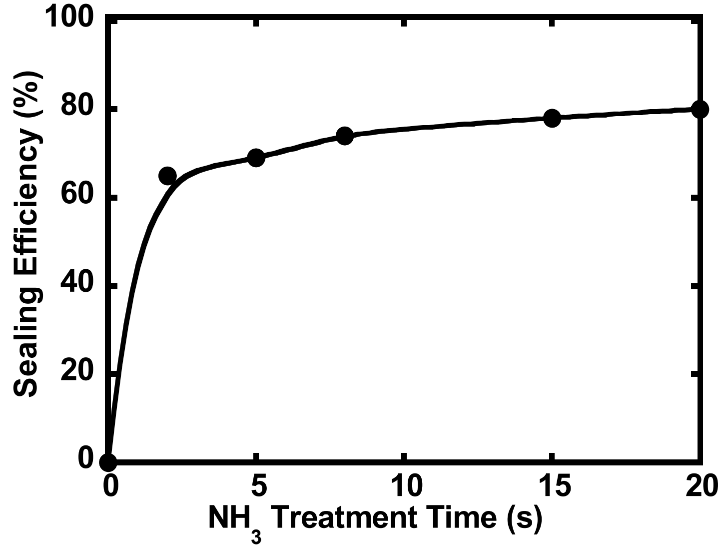
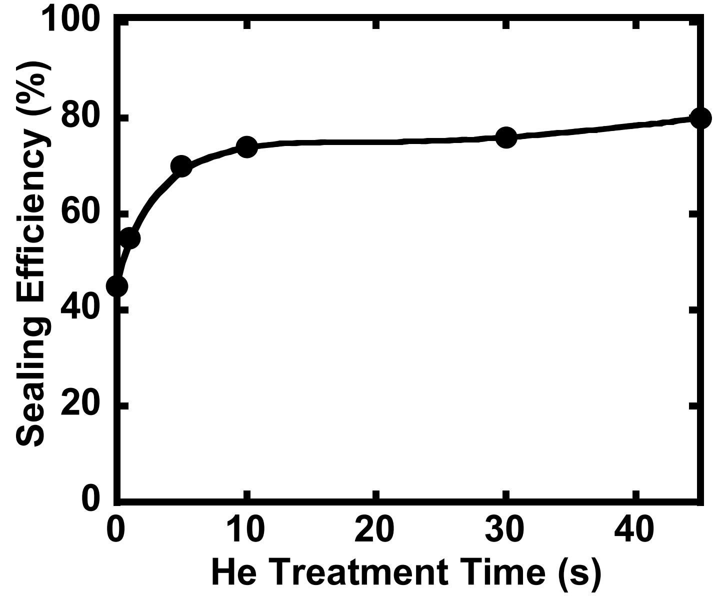
SEALING: TREATMENT TIME DEPENDENCE

- Without He plasma treatment, Ar/NH_3 plasmas seal only 45% of pores.
- NH_x ions are unable to activate all the surface sites to complete the sealing.
- Sealing efficiency increases with He treatment time for 30s, then saturates.
- 30s treatment breaks all surface Si-O bonds and activates all surface CH_3 groups.
- Sealing efficiency of pores increases for 20s of Ar/NH_3 treatment, then saturates – all dangling bonds on the surface are passivated.





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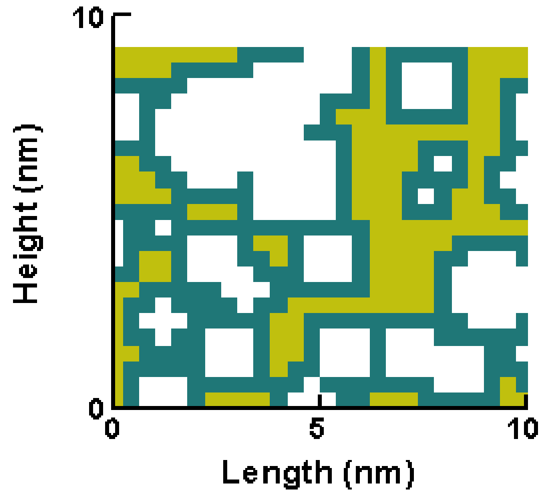
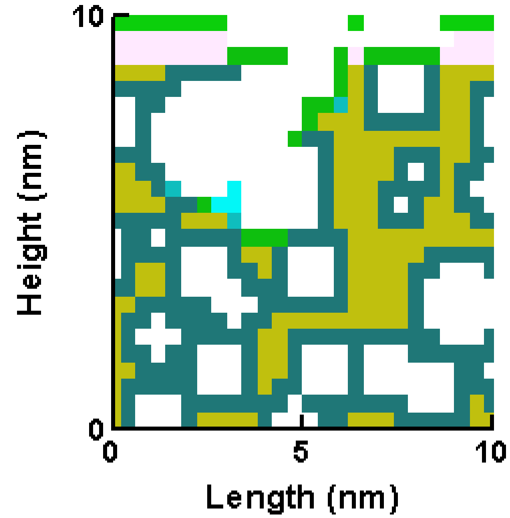
SEALING: He TREATMENT TIME DEPENDENCE

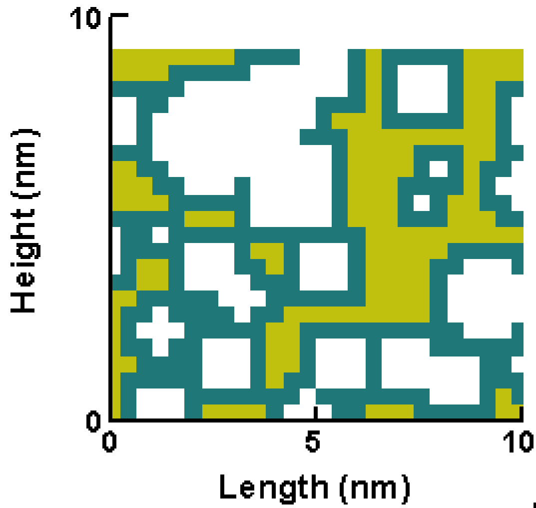
- He plasma is responsible for Si-O bond breaking and removing H from CH_3 groups to create reactive sites.
- Increasing He plasma treatment time increases sealing efficiency until all of the surface sites are activated.

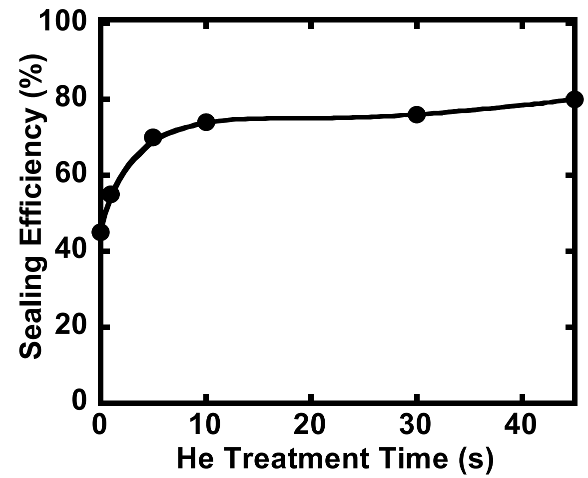


•Ar/NH_3 Treatment Without He Pre-treatment



•Ar/NH_3 Treatment With He Pre-treatment





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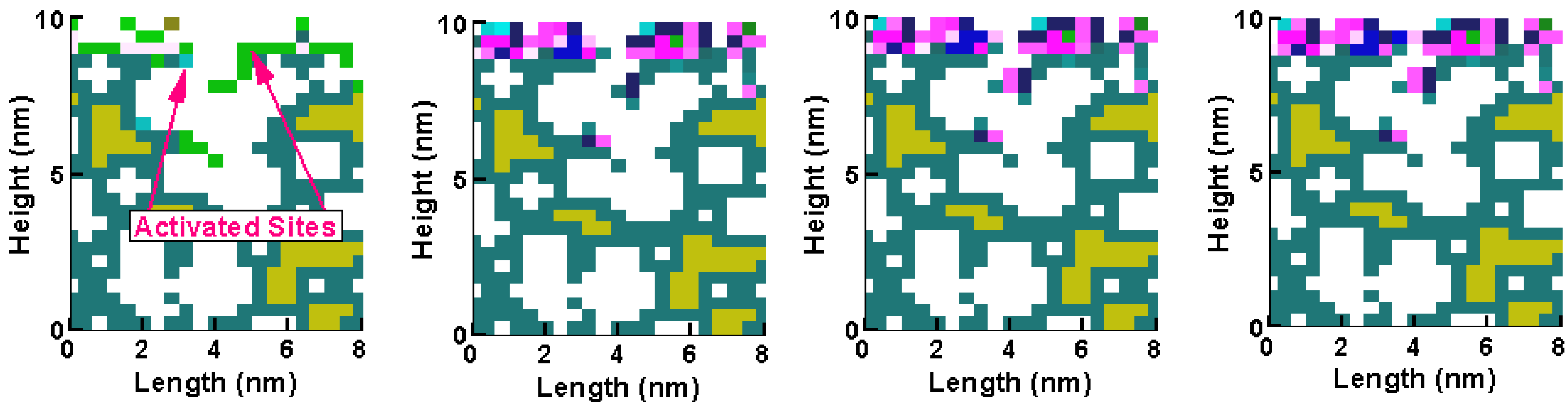
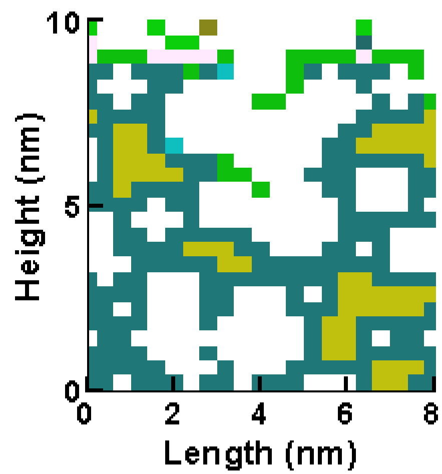
SEALING: Ar/NH_3 TREATMENT TIME DEPENDENCE

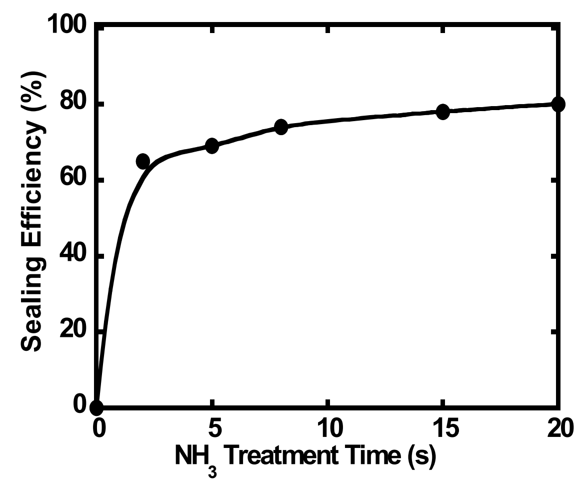


0s　　2s　　5s　　10s

- NH_x species are adsorbed by reactive sites produced by He plasma to form Si-C and Si-N bonds.
- 80% of surface pores are sealed within 20s…all surface activated sites are passivated by C-N/Si-N bonds.



•Pore Sealing by Ar/NH_3 Plasmas



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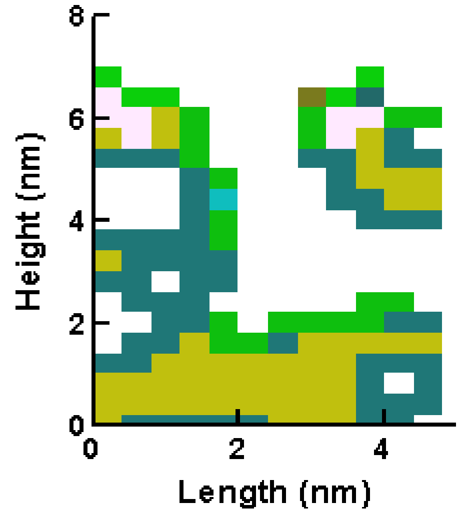
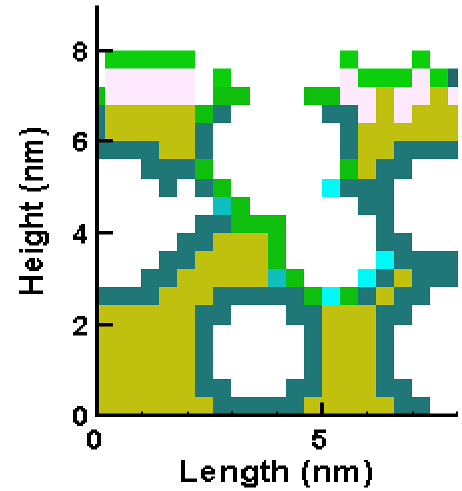
SEALING EFFICIENCY: PORE RADIUS

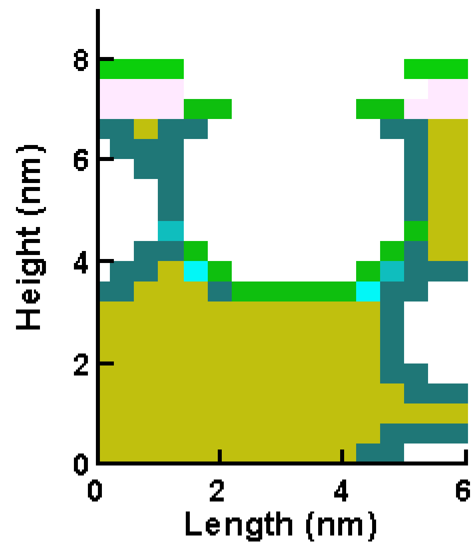
- Sealing efficiency decreases with increasing pore size.
- Sealing efficiency drops below 70% as for pore radius > 1.0 nm.
- C-N and Si-N are “first bonds.”
- Sealing requires N-N bonding, which has limited extent.
- Too large a gap prevents sealing.



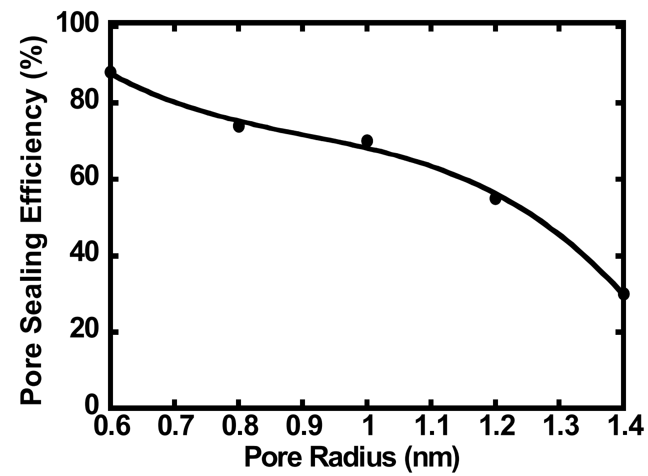
8A Pore



10A Pore



14A Pore



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CONCLUDING REMARKS

- **Simulation of porous low-*k* material sealing was investigated employing successive He and NH_3 plasma treatment.**
- **Si-N and C-N bonds formed by adsorption on active sites followed by one N-N bond linking C or Si atoms from opposite pore walls.**
- **Pore sealing efficiency is independent of porosity and interconnectivity, while dependent on both He and NH_3 plasma treatment time.**
- **The sealing efficiency degrades when the pore radius is greater than 1 nm.**
- **Sealing efficiency will improve if the pore radius standard deviation can be maintained low.**