PLASMA PROCESSING AND POLYMERS: FRITO BAGS TO MICROELECTRONICS FABRICATION

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AGENDA

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

- Partially ionized plasmas are gases containing neutral atoms and molecules, electrons, positive ions and negative ions.

- An air plasma: \( \text{N}_2, \text{O}_2, \text{N}_2^+, \text{O}_2^+, \text{O}^-, \text{e} \) where \([\text{e}] \ll \text{Neutrals}\)
These systems are the plasmas of every day technology.

Electrons transfer power from the "wall plug" to internal modes of atoms / molecules to "make a product", very much like combustion.

The electrons are “hot” (several eV or 10-30,000 K) while the gas and ions are cool, creating “non-equilibrium” plasmas.

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COLLISIONAL LOW TEMPERATURE PLASMAS

- Lighting
- Thrusters
- Spray Coatings
- Displays

- Materials Processing
**PLASMAS FOR MODIFICATION OF SURFACES**

- Plasmas are ideal for producing reactive species (radicals, ions) for modifying surface properties.
- Two of the most technologically (and commercially) important uses of plasmas involve polymers:
  - Functionalization of surfaces (high pressure)
  - Etching for microelectronics fabrication (low pressure)

- Both applications utilize unique properties of low temperature plasmas to selectively produce structures.
SURFACE ENERGY AND FUNCTIONALITY OF POLYMERS

- Most polymers, having low surface energy, are hydrophobic.
- For good adhesion and wettability, the surface energy of the polymer should exceed that of the overlayer by \( \approx 2-10 \text{ mN m}^{-1} \).
PLASMA SURFACE MODIFICATION OF POLYMERS

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

- Polypropylene (PP)


M. Strobel, 3M
PLASMA PRODUCED WETTABLEITY

- Increases in wettability with plasma treatment result from formation of surface hydrophilic groups such as C-O-O (peroxy), C=O (carbonyl).

- Polyethylene, Humid-air

- Polypropylene, Air corona
POLYMER TREATMENT APPARATUS

- TYPICAL PROCESS CONDITIONS:
  - Web speed: 10 - 200 m/min
  - Residence time: a few s
  - Energy deposition: 0.1 - 1.0 J cm⁻²
  - Applied voltage: 10-20 kV at a few 10s kHz
  - Gas gap: a few mm

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COMMERCIAL CORONA PLASMA EQUIPMENT

Tantec Inc.

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CORONA/DIELECTRIC BARRIER PLASMAS

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

- Laboratory Dielectric Barrier Discharge

- Electron Density (2-d Model)

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

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

Worldwide market of BOPP by end uses

- Snacks
- Baked goods
- Confectionary
- Tobacco
- Non-food packaging
- Adhesive
- Others

Source: PCI Films Consulting Ltd.
FUNCTIONALIZATION OF THE PP SURFACE

- Untreated PP is hydrophobic.

- Increases in surface energy by plasma treatment are attributed to the functionalization of the surface with hydrophilic groups.
  
  - Carbonyl (-C=O)
  - Alcohols (C-OH)
  - Peroxy (-C-O-O)
  - Acids ((OH)C=O)

- The degree of functionalization depends on process parameters such as gas mix, energy deposition and relative humidity (RH).

- At sufficiently high energy deposition, erosion of the polymer occurs.
DESCRIPTION OF THE MODEL: GLOBAL_KIN

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

![Diagram of the model](attachment:diagram.png)
SPECIES TRANSPORT TO THE POLYMER SURFACE

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

- Radicals react on the PP based on a variable density, multiple layer surface site balance model.
REACTION MECHANISM FOR HUMID-AIR PLASMA

- Initiating radicals are O, N, OH, H

- Gas phase products include O₃, N₂O, N₂O₅, HNO₂, HNO₃.
POLYPROPYLENE (PP) POLYMER STRUCTURE

Three types of carbon atoms in a PP chain:
- Primary – bonded to 1 C atom
- Secondary – bonded to 2 C atoms
- Tertiary – bonded to 3 C atoms

The reactivity of an H-atom depends on the type of C bonding. Reactivity scales as:

\[ H_{\text{TERTIARY}} > H_{\text{SECONDARY}} > H_{\text{PRIMARY}} \]
The surface reaction mechanism has *initiation*, *propagation* and *termination* reactions.

**INITIATION**: O and OH abstract H from PP to produce alkyl radicals; and gas phase OH and H$_2$O.

\[
\text{(POLYPROPYLENE)} \quad \text{(ALKYL RADICAL)}
\]

\[
\begin{array}{c}
\text{H} \\
\sim \text{CH}_2 \quad \text{C} \quad \text{CH}_2 \sim \\
\text{CH}_3 \\
\end{array}
\quad \begin{array}{c}
\text{O(g)} \\
\text{OH(g)} \\
\text{OH(g), H}_2\text{O(g)} \\
\end{array}
\quad \begin{array}{c}
\sim \text{CH}_2 \quad \text{C} \quad \text{CH}_2 \sim \\
\text{CH}_3 \\
\end{array}
\]
**PP SURFACE REACTION MECHANISM: PROPAGATION**

(ALKYL RADICAL)

\[ \text{~CH}_2\text{C~CH}_2\text{~} \]

\( \text{CH}_3 \)

\[ \text{O}_2 \text{~(g)} \]

(ALKOXY RADICAL)

\[ \text{~CH}_2\text{C~CH}_2\text{~} \]

\( \text{CH}_3 \)

\[ \text{O}^\cdot \]

\( \text{O}_3 \text{~(g)} \)

(PEROXY RADICAL)

\[ \text{~CH}_2\text{C~CH}_2\text{~} \]

\( \text{CH}_3 \)

\[ \text{O}^\cdot \]

\[ \text{O}_2 \text{~(g)} \]

- **PROPAGATION**: Abundant O\(_2\) reacts with alkyl groups to produce “stable” peroxy radicals. O\(_3\) and O react to form unstable alkoxy radicals.
• **PROPAGATION / AGING:** Peroxy radicals abstract H from the PP chain, resulting in hydroperoxide, processes which take seconds to 10s minutes.
PP SURFACE REACTION MECHANISM: TERMINATION

- **TERMINATION**: Alkoxy radicals react with the PP backbone to produce alcohols and carbonyls. Further reactions with O eventually erodes the film.

```
(ALKOXY RADICAL)                  (ALCOHOLS)

O•                                  OH
~CH2~CH2~→ H(s) ~CH2~CH2~
CH3                                  CH3

•CH2~ + ~CH2~C
CH3

(CARBONYL)                        CO2 (g)

O(g) → •••
```

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BASE CASE: $n_e, T_e$

- Ionization is dominantly of $N_2$ and $O_2$,
  
  \[
  e + N_2 \rightarrow N_2^+ + e + e,
  \]
  
  \[
  e + O_2 \rightarrow O_2^+ + e + e.
  \]

- After a few ns current pulse, electrons decay by attachment (primarily to $O_2$).

- Dynamics of charging of the dielectrics produce later pulses with effectively larger voltages.

- $N_2/O_2/H_2O = 79/20/1$, 300 K
- 15 kV, 9.6 kHz, 0.8 J-cm$^{-2}$
- Web speed = 250 cm/s (460 pulses)
GAS-PHASE RADICALS: O, OH

- Electron impact dissociation of O$_2$ and H$_2$O produces O and OH. O is consumed in the primarily to form O$_3$,

- After 100s of pulses, radicals attain a periodic steady state.
PP SURFACE GROUPS vs ENERGY DEPOSITION

- Surface concentrations of alcohols, peroxy radicals are near steady state with a few J-cm\(^{-2}\).

- Alcohol densities decrease at higher J-cm\(^{-2}\) energy due to decomposition by O and OH to regenerate alkoxy radicals.

- Air, 300 K, 1 atm, 30% RH

GAS-PHASE PRODUCTS: $O_3$, $N_xO_y$, HNO$_x$

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

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

- $N$ containing products include NO, NO$_2$, HNO$_2$ and N$_2$O$_5$,

$$N_2 + O \rightarrow NO + N,$$
$$NO + O + M \rightarrow NO_2 + M,$$
$$NO + OH + M \rightarrow HNO_2 + M$$
$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$$
HUMIDITY: PP FUNCTIONALIZATION BY OH

- Increasing RH produces more OH. Reactions with PP generate more alkyl radicals, rapidly converted to peroxy radicals by O₂.

\[
PP-H + OH_{(g)} \rightarrow PP\cdot + H_2O_{(g)} \quad PP\cdot + O_2(g) \rightarrow PP-O_2\cdot
\]

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

\[
PP-OH + OH_{(g)} \rightarrow PP-O\cdot + H_2O_{(g)} , \quad PP=O\cdot + OH_{(g)} \rightarrow (OH)PP=O
\]
EFFECT OF RH: GAS-PHASE PRODUCTS

- Higher RH results in decreasing O and increasing OH.
- Production of O₃ decreases while larger densities of HNOₓ are generated.

\[ N + OH \rightarrow NO + H, \quad NO + OH \rightarrow HNO₂, \quad NO₂ + OH \rightarrow HNO₃. \]
EFFECT OF T$_\text{Gas}$: PP FUNCTIONALIZATION

- Increasing T$_\text{gas}$ decreases O$_3$ leading to lower alkoxy production.
  
  \[ \text{PP} \cdot + O_3(g) \rightarrow \text{PP}-O\cdot + O_2(g). \]

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

  \[
  \begin{align*}
  \text{PP}-O\cdot + \text{PP}-H & \rightarrow \text{PP}-OH + \text{PP}\cdot \\
  \text{PP}-O\cdot & \rightarrow \text{PP}=O \\
  \text{PP}=O & \rightarrow \text{PP}=O\cdot \\
  \text{PP}=O\cdot + \text{OH} & \rightarrow (\text{OH})\text{PP}=O\cdot 
  \end{align*}
  \]

- Lower consumption of alkyl radicals by O$_3$ enables reactions with O$_2$ to dominate, increasing densities of peroxy.
RH: PREDICTED CONTACT ANGLE

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

- Polyethylene, Humid-air

Model PP, Humid-air
WHAT’S THE UPSIDE: BETTER FRITO BAGS OR ENGINEERED BIOCOMPATIBLE COATINGS?

• The ability to control functional groups on polymers through fundamental understanding of plasma-solid interactions opens the realm of engineered large area specialty surfaces.

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

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

Plasmas are absolutely essential to the fabrication of microelectronics.
PLASMAS IN MICROELECTRONICS FABRICATION

- Plasmas play a dual role in microelectronics fabrication.

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

  \[
  e + CF_4 \rightarrow CF_3^+ + F + 2e \\
  \rightarrow CF_2 + 2F + e
  \]

- These species then drift or diffuse to surfaces where they add, remove or modify materials.
PLASMAS IN MICROELECTRONICS FABRICATION

• Second, ions deliver directed activation energy to surfaces fabricating fine having extreme and reproducible tolerances.

- 0.25 μm Feature
  (C. Cui, AMAT)
APPLIED MATERIALS DECOUPLED PLASMA SOURCES (DPS)
rf BIASED INDUCTIVELY COUPLED PLASMAS

- Inductively Coupled Plasmas (ICPs) with rf biasing are used here.
- < 10s mTorr, 10s MHz, 100s W – kW, electron densities of \(10^{11}-10^{12}\) cm\(^{-3}\).
SELECTIVITY IN MICROELECTRONICS FABRICATION: PLASMAS AND POLYMERS

- Fabricating complex microelectronic structures made of different materials requires extreme selectivity in, for example, etching Si with respect to SiO₂.

- Monolayer selectivity is required in advanced etching processes.

- These goals are met by the unique plasma-polymer interactions enabled in fluorocarbon chemistries.

- Ref: G. Timp
FLUOROCARBON PLASMA ETCHING: SELECTIVITY

- Selectivity in fluorocarbon etching relies on polymer deposition.

- Electron impact dissociation of feedstock fluorocarbons produce polymerizing radicals and ions, resulting in polymer deposition.

\[ e + \text{Ar/C}_4\text{F}_8 \rightarrow \text{CF}_n, \text{M}^+ \]

- Compound dielectrics contain oxidants which consume the polymer, producing thinner polymer layers.

- Thicker polymer on non-dielectrics restrict delivery of ion energy (lower etching rates).
FLUOROCARBON PLASMA ETCHING: SELECTIVITY

- Low bias: Deposition
- High bias: etching
- Etch Rate \((\text{SiO}_2 > \text{Si})\)
- Polymer Thickness \((\text{SiO}_2 < \text{Si})\)

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

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

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

Rueger et al., JVST A 15, 1881 (1997)
SURFACE KINETICS: FLUOROCARBON PLASMA ETCHING Si/SiO₂

- $C_xF_y$ passivation regulates delivery of precursors and activation energy.
- Chemisorption of $CF_x$ produces a complex at the oxide-polymer interface.
- 2-step ion activated (through polymer layer) etching of the complex consumes the polymer. Activation scales inversely with polymer thickness.
- Etch precursors and products diffuse through the polymer layer.

In Si etching, $CF_x$ is not consumed, resulting in thicker polymer layers.
MODELING OF FLUOROCARBON PLASMA ETCHING

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

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

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

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

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

\[\vec{E}(\vec{r}, t) = \vec{E}'(\vec{r}) \exp(-i(\omega t + \phi(\vec{r})))\]

• Conductivities are tensor quantities (2D,3D):

\[\vec{\sigma} = \sigma_o \left(\frac{m v_m}{q \alpha}\right) \left(\frac{1}{\alpha^2 + |\vec{B}|^2}\right)\]

\[\begin{pmatrix}
\alpha^2 + B_r^2 & \alpha B_z + B_r B_\theta & -\alpha B_\theta + B_r B_z \\
-\alpha B_z + B_r B_\theta & \alpha^2 + B_\theta^2 & \alpha B_r + B_\theta B_z \\
-\alpha B_\theta + B_r B_z & -\alpha B_r + B_\theta B_z & \alpha^2 + B_z^2
\end{pmatrix}\]

\[\vec{j} = \vec{\sigma} \cdot \vec{E}\]

\[\alpha = \frac{(i \omega + v_m)}{q / m}, \quad \sigma_o = \frac{q^2 n_e}{m v_m}\]
ELECTRON ENERGY TRANSPORT

- **Continuum (2D,3D):**

\[
\frac{\partial}{\partial t} \left( \frac{3}{2} n_e k T_e \right) = S(T_e) - L(T_e) - \nabla \cdot \left( \frac{5}{2} \Phi k T_e - \overline{\kappa}(T_e) \cdot \nabla T_e \right) + S_{EB}
\]

where
- \( S(T_e) \) = Power deposition from electric fields
- \( L(T_e) \) = Electron power loss due to collisions
- \( \Phi \) = Electron flux
- \( \kappa(T_e) \) = Electron thermal conductivity tensor
- \( S_{EB} \) = Power source source from beam electrons

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

- **Kinetic (2D,3D):** A Monte Carlo Simulation is used to derive \( f(\varepsilon, \vec{r}, t) \) including electron-electron collisions using electromagnetic fields from the EMM and electrostatic fields from the FKM.
PLASMA CHEMISTRY, TRANSPORT AND ELECTROSTATICS

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

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

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

\[
\frac{\partial (N_i \varepsilon_i)}{\partial t} + \nabla \cdot Q_i + P_i \nabla \cdot U_i + \nabla \cdot (N_i U_i \varepsilon_i) = \frac{N_i q_i^2 \nu_i}{m_i (\nu_i^2 + \omega^2)} E^2 + \frac{N_i q_i^2}{m_i \nu_i} E_s^2 + \sum_j 3 \frac{m_j}{m_i + m_j} N_i N_j R_{ij} k_B (T_j - T_i) \pm \sum_j 3 N_i N_j R_{ij} k_B T_j
\]

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

\[
\nabla \cdot \varepsilon \nabla \Phi(t + \Delta t) = -\left( \rho_s + \sum_i q_i N_i - \Delta t \cdot \sum_i (q_i \nabla \cdot \vec{\phi}_i) \right)
\]
MONTE CARLO FEATURE PROFILE MODEL (MCFPM)

• The MCFPM predicts time and spatially dependent profiles using energy and angularly resolved neutral and ion fluxes obtained from equipment scale models.

• Arbitrary chemical reaction mechanisms may be implemented, including thermal and ion assisted, sputtering, deposition and surface diffusion.

• Energy and angular dependent processes are implemented using parametric forms.

• Mesh centered identify of materials allows “burial”, overlayers and transmission of energy through materials.
TYPICAL ICP CONDITIONS: \([e] \) FOR \(\text{C}_4\text{F}_8, 10 \text{ mTorr}\)

- An ICP reactor patterned after Oehlerlein, et al. was used for validation.
- Reactor uses 3-turn coil (13.56 MHz) with rf biased substrate (3 MHz)
- Electron densities are \(10^{11}-10^{12} \text{ cm}^{-3}\) for 1.4 kW.
Large power deposition typically results in near total dissociation of feedstock gases.

- \( \text{C}_4\text{F}_8 \), 10 mTorr, 1.4 kW, 13.56 MHz
MAJOR POSITIVE IONS

- $\text{CF}_3^+$, $\text{CF}_2^+$, and $\text{CF}^+$ are dominant ions due to dissociation of $\text{C}_4\text{F}_8$.

- $\text{C}_4\text{F}_8$, 10 mTorr, 1.4 kW, 13.56 MHz
The ion temperature is peaked near the walls where ions gain energy during acceleration in the presheath.

- CF$_3^+$, 10 mTorr, 1.4 kW, 13.56 MHz
I_p VERSUS ICP POWER for C_4F_8

- Extensive validation of the plasma models are performed with available data for densities, temperatures and fluxes.

- Ion saturation current derived from the model are compared to experiments: Ion densities are larger with moderate static magnetic fields.

- C_4F_8, 10 mTorr, 13.56 MHz, 100 V probe bias

- Experiments: G. Oehrlein, Private Comm.

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The end products of reactor scale modeling are energy and ion angular distributions to the surface.

In complex gas mixtures, the IEADs can significantly vary from species to species.

- Ar/C\textsubscript{4}F\textsubscript{8}, 40 mTorr, 10b MHz, MERIE
**ETCH RATES AND POLYMER THICKNESS**

- Etch rates for Si and SiO₂ increase with increasing bias due, in part, to a decrease in polymer thickness.
- The polymer is thinner with SiO₂ due to its consumption during etching, allowing for more efficient energy transfer through the layer and more rapid etching.

- **C₂F₆**, 6 mTorr, 1400 W ICP, 40 sccm

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POLYMERIZATION AIDS SELECTIVITY

- Less consumption of polymer on Si relative to SiO₂ slows and, in some cases, terminates etching, providing high selectivity.
TAPERED AND BOWED PROFILES

- In high aspect ratio (HAR) etching of SiO₂ the sidewall of trenches are passivated by neutrals (CFₓ, x ≤ 2) due to the broad angular distributions of neutral fluxes.

- Either tapered or bowed profiles can result from a non-optimum combination of processing parameters including:
  - Degree of passivation
  - Ion energy distribution
  - Radical/ion flux composition.
PROFILE TOPOLOGY: NEUTRAL TO ION FLUX RATIO

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

![Diagram showing etch profiles and a graph with depth values and Wb/Wt ratios against Phi_n/Phi_ion]

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PROFILE TOPOLOGY: ENGINEERING SOLUTIONS

- Knowledge of the fundamental scaling parameter for controlling sidewall slope enables engineering solutions and real-time-control options.

- Example: $\text{Ar/C}_2\text{F}_6$ ratio controls polymerizing/ion flux ratio, and hence profile topology.

\[ \text{Ar/C}_2\text{F}_6 = \]

<table>
<thead>
<tr>
<th>Ar/C2F6</th>
<th>$\Phi_n/\Phi_{ion}$</th>
<th>$W_b/W_t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0/100</td>
<td>12</td>
<td>1.2</td>
</tr>
<tr>
<td>20/80</td>
<td>8.7</td>
<td></td>
</tr>
<tr>
<td>40/60</td>
<td>6.4</td>
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<td>60/40</td>
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</tr>
</tbody>
</table>

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LOW-K DIELECTRICS

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

- Large RC-delay limits processor performance.

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

POROUS SILICON DIOXIDE

• Porous SiO$_2$ (xerogels) have low-k properties due to their lower mass density resulting from (vacuum) pores.

  • Typical porosities: 30-70%
  • Typical pore sizes: 2-20 nm

• Porous SiO$_2$ (P-SiO$_2$) is, from a process development viewpoint, an ideal low-k dielectric.

  • Extensive knowledge base for fluorocarbon etching of conventional non-porous (NP-SiO$_2$).

  • No new materials (though most P-SiO$_2$ contains some residual organics)

  • Few new integration requirements
ETCHING OF P-SiO$_2$: GENERAL TRENDS

- Etching of Porous SiO$_2$ typically proceeds at a higher rate than NP-SiO$_2$ for the same conditions due to the lower mass density.

- When correcting for mass, etch rates are either larger or smaller than NP-SiO$_2$, depending on porosity, pore size, polymerization.

- Standaert et al, JVSTA 18, 2742 (2000).
WHAT CHANGES WITH POROUS SiO$_2$?

- The “opening” of pores during etching of P-SiO$_2$ results in the filling of the voids with polymer, creating thicker layers.
- Ions which would have otherwise hit at grazing or normal angle now intersect with more optimum angle.

- An important parameter is L/a (polymer thickness / pore radius).

- Adapted: Standaert, JVSTA 18, 2742 (2000)
ETCH PROFILES IN SOLID AND POROUS SiO$_2$

- Porous SiO$_2$ is being investigated for low-permittivity dielectrics for interconnect wiring.

- In polymerizing environments with heavy sidewall passivation, etch profiles differ little between solid and porous silica.

- The “open” sidewall pores quickly fill with polymer.

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**Solid**

- Position ($\mu$m)

**Porous SiO$_2$**

- Porosity = 45%
- Pore radius = 10 nm

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ETCHING OF POROUS SiO$_2$

- Etch rates of P-SiO$_2$ are generally higher than for non-porous (NP).

- Examples:
  - 2 nm pore, 30% porosity
  - 10 nm pore, 58% porosity

- Higher etch rates are attributed to lower mass density of P-SiO$_2$.

- CHF$_3$ 10 mTorr, 1400 W

PORE-DEPENDENT ETCHING

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

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

\( p = \text{porosity} \)

If etching depended only on mass density, corrected etch rates would equal that of NP- SiO\(_2\).

- \(2\) nm pores \( L/a \geq 1 : \) C-ER > ER(SiO\(_2\)). Favorable yields due to non-normal incidence may increase rate.

- \(10\) nm pores \( L/a \leq 1 : \) C-ER < ER(SiO\(_2\)). Filling of pores with polymer decrease rates.
• 2 nm pores: Etch rate increases with porosity.

• 10 nm pores: Polymer filling of pores reduces etch rate at large porosities.
EFFECT OF POROSITY ON HAR TRENCHES

- At higher porosities, more opportunity for pore filling produces thicker average polymer layers and lower etch rates.

- Corrected etch rates fall below SiO₂ rates when critically thick polymer layers are formed.

10 nm pores. $W_t = 0.1 \ \mu m$

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With increase in pore radius, L/a decreases, enabling pore filling and a decrease in etch rates.

Thick polymer layers eventually leads to etch rates falling below NP. There is little variation in the taper.
OXYGEN ETCHING OF PTFE

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

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

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

  - Polymer + Energetic Ion $\rightarrow$ Activated Polymer Site (P*)
  - $P^* + O \rightarrow$ Volatile Products

- Removal of polymer from porous materials is difficult due to shadowing of ion fluxes caused by the pore morphology.
EFFECT OF PORE RADIUS ON CLEANING

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

Before | After | Before | After
--- | --- | --- | ---
4 nm | | 16 nm |
CONCLUDING REMARKS

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

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

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

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