FLUOROCARBON ETCHING OF POROUS SILICON DIOXIDE: PLASMA CHEMISTRY AND SURFACE KINETICS

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October 2002
AGENDA AND ACKNOWLEDGEMENTS

• Fluorocarbon plasma etching of dielectrics
• Description of modeling hierarchy
• Scaling laws for solid and porous dielectric etching
• Concluding Remarks
• Acknowledgements:
  • Prof. Gottlieb Oehrlein
  • Semiconductor Research Corporation, National Science Foundation, Sematech, Applied Materials
**FLUOROCARBON PLASMA ETCHING: DIELECTRICS**

- Fluorocarbon plasma etching of dielectrics, and selectivity with respect to conductors, is one of the first plasma processing technologies.

- Earliest works of Coburn and Winters addressed CF₄ etching of Si and SiO₂.

- In spite of longevity, fluorocarbon plasma etching is still the foremost process for obtaining selectivity between dielectrics (e.g., SiO₂, Si₃N₄) and underlying conductors (e.g., Si, p-Si).

- Optimization of these processes is critical as dielectrics thin and selectivity requirements become extreme.

- The use of low-k dielectrics for interconnect wiring with new materials has brought new challenges.
FLUORCARBON 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.

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

- 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).
FLUORCARBON PLASMA ETCHING: SELECTIVITY

- Low bias: Deposition
- High bias: etching
- Etch Rate (SiO₂ > Si)

- Polymer Thickness (SiO₂ < Si)

- G. Oerhlein, et al., JVSTA 17, 26 (1999)
PLASMA ETCHING OF LOW-K DIELECTRICS

- Low dielectric constant (low-k) dielectrics are generally classified as inorganic, organic or hybrid.

<table>
<thead>
<tr>
<th>Inorganic</th>
<th>Organic</th>
<th>Hybrid</th>
</tr>
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<tbody>
<tr>
<td>SiO₂</td>
<td>Parylene-N</td>
<td>Benzocyclobutene (BCB)</td>
</tr>
<tr>
<td>SiO₂₋₈Fγ</td>
<td>Parylene-F</td>
<td>Methyl silsesquioxane (MSQ)</td>
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<tr>
<td>Hydrogen silsesquioxane (HSQ)</td>
<td>Polyarylene ether (PAE-2)</td>
<td>Porous MSQ</td>
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<tr>
<td>Porous HSQ</td>
<td>Polytetrafluoroethylene (PTFE)</td>
<td>Organosilicate glasses (OSG)</td>
</tr>
<tr>
<td>Xerogels*</td>
<td>SiLK/porous SiLK</td>
<td></td>
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<tr>
<td></td>
<td>Fluorinated polyimide (FPI)</td>
<td></td>
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<td></td>
<td>FLARE/Porous FLARE</td>
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</tbody>
</table>

- Fluorocarbon etching chemistry | Oxygen etching chemistry             | Fluorocarbon and/or oxygen chemistry       |

- Resist mask                     | SiO₂ or Si₃N₄ mask                   | SiO₂ or Si₃N₄ mask                         |

*contain residual organic groups and could therefore also be listed under hybrid materials

- Inorganics are etched using fluorocarbon chemistries; organics are etched using oxygen chemistries.

Solid State Technology, May 2000

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**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-SiO₂: GENERAL TRENDS

- Etching of Porous SiO₂ typically proceeds at a higher rate than NP-SiO₂ for the same conditions due to the lower mass density.

- When correcting for mass, etch rates are either larger or smaller than NP-SiO₂, depending on porosity, pore size, polymerization.

- Standaert et al, JVSTA 18, 2742 (2000).
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
The wave equation is solved in the frequency domain using sparse matrix techniques (2D,3D):

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

$$\vec{E}(\vec{r}, t) = \vec{E}'(\vec{r}) \exp(-i(\omega t + \varphi(\vec{r})))$$

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

$$\overline{\sigma} = \sigma_o \frac{m v_m}{q \alpha} \frac{1}{\left( \alpha^2 + |\vec{B}|^2 \right)} \begin{pmatrix} \alpha^2 + B_r^2 & \alpha B_z + B_r B_\theta & -\alpha B_\theta + B_r B_z \\ -\alpha B_z + B_r B_\theta & \alpha^2 + B_\theta^2 & \alpha B_r + B_\theta B_z \\ -\alpha B_\theta + B_r B_z & -\alpha B_r + B_\theta B_z & \alpha^2 + B_z^2 \end{pmatrix}$$

$$\vec{j} = \overline{\sigma} \cdot \vec{E}$$

$$\alpha = \frac{(i \omega + v_m)}{q / m}, \quad \sigma_o = \frac{q^2 n_e}{m v_m}$$
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).

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

\[
\frac{\partial (N_i \vec{v}_i)}{\partial t} = \frac{1}{m_i} \nabla (k N_i T_i) - \nabla \cdot (N_i \vec{v}_i \vec{v}_i) + \frac{q_i N_i}{m_i} \left( \vec{E} + \vec{v}_i \times \vec{B} \right) - \nabla \cdot \vec{\mu}_i
\]

\[
\frac{\partial (N_i \varepsilon_i)}{\partial t} + \nabla \cdot \vec{Q}_i + P_i \nabla \cdot \vec{U}_i + \nabla \cdot (N_i \vec{U}_i \varepsilon_i) = \frac{N_i q_i^2 \nu_i}{m_i (\nu_i^2 + \omega_i^2)} \frac{E^2}{m_i \nu_i}
\]

\[
+ \frac{N_i q_i^2}{m_i \nu_i} E_s^2 + \sum_j 3 \frac{m_{ij}}{m_i + m_j} N_i N_j R_{ij} k_B (T_j - T_i) \pm \sum_j 3 N_i N_j R_{ij} k_B T_j
\]

- 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”, overlays and transmission of energy through materials.
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$^{-3}$. 
TYPICAL ICP CONDITIONS: [e] FOR C₄F₈, 10 mTorr

- An ICP reactor patterned after Oeherlein, et al. was used for validation.
- Reactor uses 3-turn coil (13.56 MHz) with rf biased substrate (3 MHz)
- Electron densities are $10^{11}$-$10^{12}$ 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: C₄F₈, 10 mTORR

- CF₃⁺, CF₂⁺, and CF⁺ are dominant ions due to dissociation of C₄F₈.

- C₄F₈, 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$_3^+$ TEMPERATURE**

- **C$_4$F$_8$, 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.
ION/NEUTRAL ENERGY/ANGULAR DISTRIBUTIONS

• 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$_4$F$_8$, 40 mTorr, 10b MHz, MERIE

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SURFACE KINETICS DURING Si/SiO\textsubscript{2} ETCHING

- Fluorocarbon etching of SiO\textsubscript{2} relies on a polymerization and chemically enhanced sputtering.
- C\textsubscript{x}F\textsubscript{y} passivation regulates delivery of precursors and activation energy.
- Chemisorption of CF\textsubscript{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\textsubscript{x} is not consumed, resulting in thicker polymer layers.
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

POLYMERIZATION AIDS SELECTIVITY

- Less consumption of polymer on Si relative to SiO$_2$ slows and, in some cases, terminates etching, providing high selectivity.
TAPERED AND BOWED PROFILES

- In high aspect ratio (HAR) etching of SiO$_2$ the sidewall of trenches are passivated by neutrals ($\text{CF}_x$, $x \leq 2$) 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 profile with different ratios of \( \Phi_n/\Phi_{ion} \) and corresponding changes in depth and \( W_b / W_t \).]
PROFILE TOPOLOGY: ENGINEERING SOLUTIONS

- Knowledge of the fundamental scaling parameter for controlling sidewall slop 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.

\[
\begin{align*}
\text{Ar/C}_2\text{F}_6 &= \quad 0/100 \quad 20/80 \quad 40/60 \quad 60/40 \\
\Phi_n/\Phi_{ion} &= \quad 12 \quad 8.7 \quad 6.4 \quad 4.0
\end{align*}
\]
Lack of fundamental parameters often requires calibration of models using design of experiment methodologies. In turn, the dominant, rate limiting processes are determined.

Parameterization of $\text{CF}_2$ sticking probability

$\text{Ar/C}_2\text{F}_6 = 20/80$, 1000 W ICP, 150 V bias
ASIDE ON REACTION MECHANISMS

• A reaction mechanism is simply a set of reactions with fundamental coefficients and probabilities which should not depend on the chemistry (e.g., CHF$_3$ vs C$_2$F$_6$ vs C$_4$F$_8$)

• The chemistry merely determines the magnitude of the fluxes but not the reaction pathways.

• An etch mechanism valid for C$_2$F$_6$ plasmas should, with no change, also be valid for C$_4$F$_8$ plasmas.

• Development of reaction mechanisms across different chemistries should result in more reliable mechanisms.
CALIBRATION OF REACTION MECHANISM: I

• The mechanism was validated by comparison to experiments by Oehrlein et al using C₂F₆ gas chemistry.¹

• Threshold for SiO₂ etching was well captured at self-bias ≈ 20 V. For Si the etch rates were lower due to thicker polymer.

CALIBRATION OF REACTION MECHANISM: II

- Threshold for SiO₂ and Si etching were well captured at for CHF₃.

- Differences between model and experiments for SiO₂ are attributed to H radicals forming hydrocarbon polymer chains.

- This is accounted for in the model by modifying sputtering rates to account for mass differences.

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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 SiO₂

- Porous SiO₂ 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.

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

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PORE-DEPENDENT ETCHING

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

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

\( p \) = porosity

• If etching depended only on mass density, corrected etch rates would equal that of NP- SiO₂.

• 2 nm pores \( L/a \geq 1 \) : C-ER > ER(SiO₂). Favorable yields due to non-normal incidence may increase rate.

• 10 nm pores \( L/a \leq 1 \) : C-ER < ER(SiO₂). Filling of pores with polymer decrease rates.

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EFFECT OF POROSITY ON BLANKET ETCH RATES

- **2 nm pores**: Etch rate increases with porosity.
- **10 nm pores**: Polymer filling of pores reduces etch rate at large porosities.

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EFFECT OF POROSITY ON HAR TRENCHES

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

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

- Corrected etch rates fall below SiO$_2$ rates when critically thick polymer layers are formed.
EFFECT OF $\phi_n/\phi_{ion}$ ON HAR TRENCHES

- $\phi_n =$ total neutral flux
- $\phi_{ion} =$ total ion flux
- Small values of $\phi_n/\phi_{ion}$ may be polymer starved, producing lower etch rates.
- Medium and large $\phi_n/\phi_{ion}$ produces thicker polymer, lower etch rates.
- Increasing $\phi_n/\phi_{ion}$ produces increasing taper.
EFFECT OF $\phi_n/\phi_{ion}$ ON POROUS HAR TRENCHES

- 2 nm pores.
- P- SiO$_2$ is more sensitive to the consequences of varying $\phi_n/\phi_{ion}$ compared to NP-SiO$_2$.
- For large values of $\phi_n/\phi_{ion}$ previously enhanced etch rates (for small pores) become depressed until etching finally stops.
- Once tapering begins the L/a increases disproportionately quickly.
EFFECT OF PORE RADIUS ON HAR TRENCHES

- Porosity 25%. For sufficiently low porosity is little change in the etch rate or taper with pore radius.
CONCLUDING REMARKS

- Etching of porous silicon-dioxide obeys many of the same scaling laws as solid materials.

- Net enhancements are seen with low porosity; net slowing of the etch rate occurs with large porosity (or pore size).

- The ratio of polymer thickness-to-pore size appears to determine much of this behavior. Thin polymer layers which fill pores appear to be thicker.

- Increased sensitivity to small changes in neutral-to-ion ratios could make maintaining CDs more problematic.