MODELING OF INTEGRATED PLASMA PROCESSING: PLASMA PHYSICS, PLASMA CHEMISTRY AND SURFACE KINETICS

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AGENDA

- Integration in Plasma Processing

- Modeling Requirements:
  - Plasma Physics
  - Plasma Chemistry
  - Surface Kinetics

- Integrated process modeling of etching and cleaning of porous silica; and metal deposition for interconnect wiring.

- Concluding Remarks
Partially ionized plasmas are gases containing neutral atoms and molecules, electrons, positive ions and negative ions. 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.
COLLISIONAL LOW TEMPERATURE PLASMAS

- Lighting
- Thrusters
- Spray Coatings
- Displays
- Materials Processing
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.

Ref: IBM Microelectronics

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PLASMAS IN MICROELECTRONICS FABRICATION

- Plasmas play a dual role in microelectronics fabrication.

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

- 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.

- Ion Assisted Etching
- Neutral Dominated Etching

• 0.25 µm Feature
(C. Cui, AMAT)
rf BIASED INDUCTIVELY COUPLED PLASMAS

- Inductively Coupled Plasmas (ICPs) with rf biasing are used here.
- $< 10\text{s mTorr, } 10\text{s MHz, } 100\text{s W – kW,}$
electron densities of $10^{11}-10^{12} \text{ cm}^{-3}$.
GOAL FOR PROCESS MODELING: INTEGRATION

- Plasma processing involves an integrated sequence of steps, each of which depends on the quality of the previous steps.
GOAL FOR PROCESS MODELING: INTEGRATION

To address these complexities, modeling platforms must integrate:

- *Plasma Physics*
- *Plasma Chemistry*
- *Surface Kinetics*
HYBRID PLASMA EQUIPMENT MODEL

- **MAGNETOSTATICS MODULE**
- **MATCH BOX-COIL CIRCUIT MODEL**
- **ELECTROMECHANICS FREQUENCY DOMAIN**
- **ELECTROMAGNETICS FDTD**
- **BOLTZMANN MODULE**
- **ELECTRON ENERGY EQUATION**
- **NON-COLLISIONAL HEATING**
- **ON-THE-FLY FREQUENCY DOMAIN**
- **ELECTRON MONTE CARLO SIMULATION**
- **ELECTRON BEAM MODULE**
- **CONTINUITY**
- **MOMENTUM**
- **ENERGY**
- **LONG MEAN FREE PATH (MONTE CARLO)**
- **SPUTTER MODULE**
- **POISSON ELECTROSTATICS**
- **AMBIGULAR ELECTROSTATICS**
- **SIMPLE CIRCUIT MODULE**
- **SHEATH MODULE**
- **SIMPLE CIRCUIT MODULE**
- **E(r, θ, z, φ)**
- **B(r, θ, z, φ)**
- **E(r, θ, z, φ)**
- **B(r, θ, z, φ)**
- **S(r, z, φ)**
- **T_e(r, z, φ)**
- **µ(r, z, φ)**
- **σ(r, z)**
- **J(r, z, φ)**
- **lD(coils)**
- **E_s(r, z, φ)**
- **N(r, z)**
- **Φ(r, z, φ)**
- **S(r, z)**
- **V(rf), V(dc)**
- **VPEM: SENSORS, CONTROLLERS, ACTUATORS**

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

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

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

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

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

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

\[\alpha = \frac{(i \omega + \nu_m)}{q / m}, \quad \sigma_o = \frac{q^2 n_e}{m \nu_m}\]
ELECTROMAGNETICS MODEL (cont.)

- The electrostatic term in the wave equation is addressed using a perturbation to the electron density (2D).

\[
\nabla \cdot \overline{E} = \frac{\rho}{\varepsilon} = \frac{q\Delta n_e}{\varepsilon}, \quad \Delta n_e = -\nabla \cdot \left( \frac{\overline{\sigma} \cdot \overline{E}}{q} \right) / \left( \frac{1}{\tau} + i\omega \right)
\]

- Conduction currents can be kinetically derived from the Electron Monte Carlo Simulation to account for non-collisional effects (2D).

\[
J_e(\vec{r}, t) = J_o(\vec{r}) \exp(i(\omega t + \phi_v(\vec{r}))) = -qn_e(\vec{r})\vec{v}_e(\vec{r}) \exp(i(\omega t + \phi_v(\vec{r})))
\]
ELECTRON ENERGY TRANSPORT

• **Continuum (2D,3D):**

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

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 \( f(\varepsilon, \bar{r}, t) \)
  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).

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

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

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

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

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

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

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The inductively coupled electromagnetic fields have a skin depth of 3-4 cm.

Absorption of the fields produces power deposition in the plasma.

Electric Field (max = 6.3 V/cm)
- Ar/Cl₂ = 80/20
- 20 mTorr
- 1000 W ICP 2 MHz
- 250 V bias, 2 MHz (260 W)
Ar/Cl₂ ICP: POWER AND ELECTRON TEMPERATURE

- ICP Power heats electrons, capacitively coupled power dominantly accelerates ions.

- Power Deposition (max = 0.9 W/cm³)

- Electron Temperature (max = 5 eV)

- Ar/Cl₂ = 80/20, 20 mTorr, 1000 W ICP 2 MHz, 250 V bias, 2 MHz (260 W)
Ar/Cl$_2$ ICP: IONIZATION

- Ionization is produced by bulk electrons and sheath accelerated secondary electrons.

- **Beam Ionization**
  \[ \text{(max} = 1.3 \times 10^{14} \text{ cm}^{-3}\text{s}^{-1}) \]

- **Bulk Ionization**
  \[ \text{(max} = 5.4 \times 10^{15} \text{ cm}^{-3}\text{s}^{-1}) \]

- Ar/Cl$_2$ = 80/20, 20 mTorr, 1000 W ICP 2 MHz, 250 V bias, 2 MHz (260 W)
Ar/Cl\textsubscript{2} ICP: POSITIVE ION DENSITY

- Diffusion from the remote plasma source produces uniform ion densities at the substrate.

- Positive Ion Density
  \[\text{max} = 1.8 \times 10^{11} \text{ cm}^{-3}\]

- \(\text{Ar/Cl}_2 = 80/20, 20 \text{ mTorr}, 1000 \text{ W ICP 2 MHz, 250 V bias, 2 MHz (260 W)}\)
• PLASMA PHYSICS
  (Are we getting it right?)
FORCES ON ELECTRONS IN ICPs

- Inductive electric field provides azimuthal acceleration; penetrates
  \[ \delta = \left(\frac{m_e}{e^2 \mu_0 n_e}\right)^{\frac{1}{2}} \]  
  (1-3 cm)

- Electrostatic (capacitive); penetrates
  \[ \lambda_s \approx 10 \lambda_D, \lambda_D = \left(\frac{kT_e}{8\pi n_e e^2}\right)^{\frac{1}{2}} \]  
  (100s \(\mu\)m to mm)

- Non-linear Lorentz Force
  \[ \vec{F} = v_\theta \times \vec{B}_{rf} \]
ANAMOLOUS SKIN EFFECT AND POWER DEPOSITION

- Collisional heating:
  \[ \lambda_{\text{mfp}} < \delta_{\text{skin}} \Rightarrow \mathbf{J}_e(\mathbf{r},t) = \sigma(\mathbf{r},t)\mathbf{E}(\mathbf{r},t) \]

- Anomalous skin effect:
  \[ \lambda_{\text{mfp}} > \delta_{\text{skin}} \]
  \[ \mathbf{J}_e(\mathbf{r},t) = \iint \sigma(\mathbf{r},\mathbf{r}',t,t')\mathbf{E}(\mathbf{r}',t')d\mathbf{r}'dt' \]
  \[ \mathbf{F} = \mathbf{v} \times \mathbf{B} \]

- Electrons receive (positive) and deliver (negative) power from/to the E-field.

- E-field is non-monotonic.

Ref: V. Godyak, “Electron Kinetics of Glow Discharges”
ICP CELL FOR VALIDATION

- Experiments by Godyak et al are used for validation.
- The experimental cell is an ICP reactor with a Faraday shield to minimize capacitive coupling.
ELECTRON DENSITY: Ar, 10 mTorr, 200 W, 7 MHz

- On axis peak in \([e]\) occurs inspite of off-axis power deposition.

- Model is about 30% below experiments. This likely has to do with details of the sheath model.

- Ref: V. Godyak, Private Comm.

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ELECTRON TEMPERATURE: Ar, 10 mTorr, 200 W, 7 MHz

- Ref: V. Godyak, Private Comm.

- The high thermal conductivity and redistribution of energy by e-e collisions produces nearly uniform temperatures.

- $T_e$ peaks under the coils where power deposition is largest.

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EEDs ALONG THE CENTERLINE OF THE REACTOR

- Godyak (1998), z=5.0 cm
- Model, z=0.5 cm
- Model, z=5.0 cm
- Model, z=10.0 cm

The electron energy distributions show a bi-Maxwellian form, which is typical for low-pressure inductively coupled plasmas.

- Ar, 10 mTorr, 6.78 MHz, 200 W
COLLISIONLESS TRANSPORT ELECTRIC FIELDS

- We couple electron transport to Maxwell’s equations by kinetically deriving electron current.

\[
\oint j(\vec{r})\exp(i\omega(t-t_o)) \cdot dA = \sum_k q_k \vec{v}_k(\vec{r})\exp(i\omega(t_k-t_o))
\]

- \(E_\theta\) during the rf cycle exhibits extrema and nodes resulting from this non-collisional transport.

- “Sheets” of electrons provide current sources interfering or reinforcing \(E_\theta\) for the next sheet.

- Axial transport results from \(\vec{v} \times \vec{B}_{rf}\) forces.

- Ar, 10 mTorr, 7 MHz, 100 W
POWER DEPOSITION: POSITIVE AND NEGATIVE

- The end result is regions of positive and negative power deposition.

- Ar, 10 mTorr, 7 MHz, 100 W
The shorter skin depth at high frequency produces more layers of negative power deposition of larger magnitude.

- **6.7 MHz**
  - $(5 \times 10^{-5} - 1.4 \text{ W/cm}^3)$
- **13.4 MHz**
  - $(8 \times 10^{-5} - 2.2 \text{ W/cm}^3)$

Ref: Godyak, PRL (1997)
TIME DEPENDENCE OF THE EED

- Time variation of the EED is mostly at higher energies where electrons are more collisional.
- Dynamics are dominantly in the electromagnetic skin depth where both collisional and non-linear Lorentz Forces peak.
- The second harmonic dominates these dynamics.

- Ar, 10 mTorr, 100 W, 7 MHz, r = 4 cm
TIME DEPENDENCE OF THE EED: 2\textsuperscript{nd} HARMONIC

- Electrons in skin depth quickly increase in energy and are “launched” into the bulk plasma.
- Undergoing collisions while traversing the reactor, they degrade in energy.
- Those surviving “climb” the opposite sheath, exchanging kinetic for potential energy.
- Several “pulses” are in transit simultaneously.

- Amplitude of 2\textsuperscript{nd} Harmonic

- Ar, 10 mTorr, 100 W, 7 MHz, \(r = 4\) cm
CONSEQUENCES OF ELECTRON DYNAMICS IN ICPs

- The consequences of electron dynamics were investigated for Ar/N\textsubscript{2} gas mixtures.

- \(e^- + \text{Ar} \rightarrow \text{Ar}^+ + e^- + e^-, \quad \Delta \varepsilon = 16 \text{ eV}\)
  High threshold reactions capture modulation in the tail of the EED.

- \(e^- + \text{N}_2 \rightarrow \text{N}_2 (\text{vib}) + e^-, \quad \Delta \varepsilon = 0.29 \text{ eV}\)
  Low threshold reactions capture modulation of the bulk of the EED.

- Base case conditions:
  - Pressure: 5 mTorr
  - Frequency: 13.56 MHz
  - Ar / N\textsubscript{2}: 90 / 10
  - Power: 650 W

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• Ionization of Ar has more modulation than vibrational excitation of N\textsubscript{2} due to modulation of the tail of the EED.

- Ionization of Ar
  \(6 \times 10^{14} - 3 \times 10^{16} \text{ cm}^{-3}\text{s}^{-1}\)

- Excitation of N\textsubscript{2}(v)
  \(1.4 \times 10^{14} - 8 \times 10^{15} \text{ cm}^{-3}\text{s}^{-1}\)
HARMONICS OF Ar IONIZATION: FREQUENCY

- At large $\omega$, non-linear Lorentz forces are small, and so harmonic content is also small.

- At small $\omega$, both non-linear Lorentz forces and harmonic excitation by the electric field are large.

- $\text{Ar/N}_2=90/10$, 5 mTorr

- Harmonic Amplitude/Time Average

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• PLASMA CHEMISTRY
(Are we getting this right?)
REACTION MECHANISMS FOR PLASMA ETCHING

- Recipes for plasma etching of dielectric materials (e.g., SiO$_2$, Si$_3$N$_4$) often contain mixtures of many gases such as:
  
  Ar, C$_4$F$_8$, O$_2$, N$_2$, CO

- The fluorocarbon donors are often highly dissociated, thereby requiring databases for both feedstocks and their fragments.

- For predictive modeling, reaction mechanisms must be developed for arbitrary mixtures and wide ranges of pressures.
The first step in developing a reaction mechanism is compilation of electron impact cross section sets.

Ref: V. McKoy and W. L. Morgan

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ICP CELL AND \([\text{CF}_2^+]\) FOR \(\text{C}_4\text{F}_8\), 10 mTorr

- An ICP reactor patterned after Oeherlein, et al. was used for validation.
- Reactor has a metal ring with magnets to confine plasma.
- \(\text{CF}_2^+\) is one of the dominant ions in \(\text{C}_4\text{F}_8\) plasmas due to large dissociation.
- The major path for the \(\text{CF}_2^+\) is:
  - \(\text{C}_4\text{F}_8 + e \rightarrow \text{C}_2\text{F}_4 + \text{C}_2\text{F}_4 + e\)
  - \(\text{C}_2\text{F}_4 + e \rightarrow \text{CF}_2 + \text{CF}_2 + e\)
  - \(\text{CF}_2 + e \rightarrow \text{CF}_2^+ + e + e\)

- \(\text{C}_4\text{F}_8\), 10 mTorr, 1.4 kW, 13.56 MHz
$[n_e]$ and $T_e$ FOR C$_4$F$_8$, 10 mTorr

- Electron density peaks at $\approx 10^{12}$ cm$^{-3}$.
- The peak in $T_e$ occurs in the skin layer due to collisionless electron heating by the large electric field.
- $T_e$ is rather uniform in the bulk plasma where electrons thermalize through e-e collisions.
$I_p$ (PROBE CURRENT) IN ICPs SUSTAINED IN Ar, O$_2$

- Ar, 10 mTorr
- O$_2$, 10 mTorr

Magnetic confinement is generally more effective in electronegative plasmas with a larger variety of ions.
The differences in $I_p$ with and without magnets increases with power due to increased non-linear Lorentz force.

$I_p$ increases with Ar addition in Ar/C$_4$F$_8$ compared to Ar/O$_2$ due to higher dissociation of C$_4$F$_8$ and lower electronegativity.

- 13.56 MHz, -100 V probe bias.

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ION COMPOSITION IN C$_4$F$_8$, Ar/C$_4$F$_8$

- Optimization of processing conditions, for example, power critically depends on the composition of the radical and ion fluxes.

- 10 mTorr, 13.56 MHz
EFFECT OF MAGNETS ON [CF+] 

- Without magnets [CF+] has a maximum at the edge of the classical skin depth where the electron impact ionization is the largest.

- The static magnetic fields broaden the production of [CF+] in the radial direction.

- Ar/C₄F₈=20/80, 3 mTorr, 13.56 MHz, 400 W.
MERIE REACTOR

- The model reactor is based on a TEL Design having a transverse magnetic field.

TEL-DRM: Ar / C₄F₈ / O₂

- With reaction mechanisms developed for Ar / C₄F₈ / O₂ and improved ability to model MERIE systems, parameterizations were performed for TEL-DRM like conditions.
- Ar / C₄F₈ / O₂ = 200/10/5 sccm, 40 mTorr, 1500 W.
TEL-DRM: Ar / C₄F₈ / O₂

- The large variety of ion masses produces vastly different IEADs.
- Ar / C₄F₈ / O₂ = 200/10/5 sccm, 40 mTorr, 1500 W.
• SURFACE CHEMISTRY
(The most ill defined but perhaps most important step.)
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 SiO$_2$.

• 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
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 (SiO$_2$ > Si)
- Polymer Thickness (SiO$_2$ < Si)

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

- Profiles depend on ratio of polymer forming fluxes to energy activating fluxes. Small ratios produce bowing, large ratios tapering.

- Controlling this ratio through gas mixture (e.g., Ar/C₂F₆) enables specification of profile topology.

![Graph showing profile topology changes with Ar/C₂F₆ ratio](image)

<table>
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<th>Ar/C₂F₆</th>
<th>Φₙ/Φₖₐₜₜ</th>
<th>Wₜ / Wₚ</th>
<th>Φₙ/Φₖₐₜₜ</th>
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<td>4.0</td>
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</tr>
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</table>
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
WHAT CHANGES WITH POROUS SiO₂?

- The “opening” of pores during etching of P-SiO₂ 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.
ETCHING OF POROUS SiO₂

- Etch rates of P-SiO₂ 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-SiO₂.

- CHF₃ 10 mTorr, 1400 W


ADVMET_1002_23
PORE-DEPENDENT ETCHING

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

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

\( p \) = porosity

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

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

- 10 nm pores \( \frac{L}{a} \leq 1 \): 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.
OXYGEN PLASMA CLEANING OF POLYMER

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

• \( \text{O}_2 \) 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.

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EFFECT OF PORE RADIUS ON CLEANING

- Larger pores are more difficult to clean due small view angle of ion fluxes.
- Lower fluxes of less energetic ions reduce activation and lengthen cleaning time.

![Graph showing fraction of residual polymer vs. time for different pore radii.](image)

- 4 nm
- 16 nm
TOWARDS INTEGRATED PROCESS MODELING
(The last step...metal deposition.)
IONIZED METAL PHYSICAL VAPOR DEPOSITION (IMVPD)

- IMPVD is a technique to deposit seed layers and barrier coatings, and fill trenches.
- A flux of both neutral and metal atoms more uniformly produce depositions without formation of voids.

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Cu IMVPD: REACTOR SCALE MODELING

- 40 mTorr Ar
- 1 kW ICP
- 0.3 kW Magnetron
- -25 V bias
EFFECT OF PORE RADIUS ON Cu DEPOSITION

- Surrogate study for seed layer deposition and barrier coating.
- Voids are created at the pore surface or initiated due to the presence of pores.
- Presence of voids are pronounced for bigger pores.
- MERIE Fluorocarbon plasma etching of porous SiO₂

- ICP O₂ plasma cleaning of PR and polymer.

- IMPVD of Cu seed layer
Due to high dilution and low fractional dissociation, dominant ions are \( \text{Ar}^+ \), \( \text{C}_2\text{F}_4^+ \)

- \( \text{Ar}/\text{O}_2/ \text{C}_4\text{F}_8 = 200/5/10 \) sccm
- 2000 W
- 40 mTorr
MERIE: POROUS SiO$_2$ ETCH

• More rapid etching with porous SiO$_2$ results in less mask erosion and better profile control, but more polymer filling of pores.
Longer cleaning times are required with more porous materials to remove polymer which is shaded from ion flux.
Thicker seed layers are required with large pores to cover over (or fill) gaps resulting from open structures.
CONCLUDING REMARKS

• Integrated plasma process modeling requires addressing a wide range of physical phenomena.

• The large variety of gas mixtures, reactor geometries, plasma sources and materials motivates development of generalized modeling platforms with few a priori assumptions.

• The fundamental modeling challenges are no different than in experimental integration:
  
  • If a single module (process) is validated (optimized) in isolation, will it still be valid (optimum) when integrated with other steps?
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