Plasma Etching

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Background

• As integrated circuit device dimensions continue to be scaled down to <0.1 μm, strict requirements are being imposed on plasma etching technology.

• Especially, the precise or nanometer-scale control is indispensable for etched profiles and critical dimensions, together with higher selectivity, higher microscopic uniformity, and less damage.

• Moreover, new materials such as metals and low- and high-κ* dielectrics are being employed for <0.1 μm devices, and so the etching of such new materials are also required in integrating them into device fabrication. *κ: dielectric constant

• This lecture presents the current status of plasma etching technology based on the physical and chemical mechanisms underlying the processing, along with the future prospect towards nano-scale processes.
1. Introduction

- Si-ULSI Devices
- Requirements for Plasma Etching
Si- ULSI Devices

Logic Technology Families

Power Saving (Low Standby)
Mobile Phone
PDA, “x-man”
LP SRAM

High Speed/ Performance (Low Voltage)
Hi-End Graphics
MPU
Networking
HS SRAM

Integration Solution (General Purpose)
DVD
FPGA
Set-Top
PC Graphics
HDTV
Networking
Hard Drive
MPEG2 CODEC

CL015LP
CL013LP
CL015LV/HS
CL013LV/HS
CL015G
CL013G

Si- ULSI Devices (continued)

Silicide Layer
Silicon Gate Electrode
1.2 nm SiO₂ Gate Oxide
Strained Silicon

50nm

http://www.tsmc.com
http://www.intel.com/research/silicon
Trends of Si-ULSI Devices (1)

Transistor Physical Gate Length

Technology Node

Year

Microns

0.5μm
0.35μm
0.25μm
0.18μm
0.13μm
90nm
65nm
45nm
30nm
20nm
15nm

Planar CMOS Transistor Scaling

Today

Future

50 nm
30 nm
20 nm
15 nm

http://www.intel.com/research/silicon
As integrated circuit device dimensions continue to be scaled down, increasingly strict requirements are being imposed on plasma processing technology, including the etching and deposition of new materials as well as the more precise control of etching of conventional materials.

Great attention has recently been placed on integrating high and low dielectric constant \((k)\) materials into the fabrication of gate stacks and multi-level interconnections, respectively, for advanced sub-100 nm microelectronic devices.

The technological challenge continues for growing ultra-thin SiO\(_2\) film of high quality, to maintain the gate capacitance without increasing the leakage current and reducing the oxide reliability; however, the ultimate solution would rely on high-\(k\) materials such as HfO\(_2\) and ZrO\(_2\), and their silicates and aluminates.

Moreover, for gate stacks with high-\(k\) dielectrics, gate electrodes of conventional Poly-Si are required ultimately to be replaced by metal gates of TiN, TaN, Ru/RuO\(_2\), Pt and Ir.

Plasma processing is indispensable for the fabrication or etching of gate electrodes, and also for the removal or etching of high-\(k\) dielectric.
Multi-level Interconnects and Low-k Inter-layer Dielectric

Low-k inter-layer dielectrics (ILD) are required for reducing the resistance-capacitance time delay, which is getting more conspicuous as the shrinkage of the spacing between metal lines in high-density multi-level interconnections.

Plasma processing is indispensable for chemical vapor deposition (CVD) of ILD, and also for the fabrication or etching of high-aspect-ratio contact (HARC) and via holes through ILD.

Requirements for Plasma Etching

For ULSI fabrication

(1) Etch anisotropy and selectivity (↑)
   – Profile control, Critical dimension (CD) control
   – Selectivity over mask and underlying layers

(2) Plasma damage (↓)
   – Charging damage
   – Physical damage (ion-bombardment, impurity permeation)
   – Radiation damage

(3) Microscopic uniformity (on a chip and cell scale) (↑)
   – Etch rate, Profile, Selectivity, Damage, etc.
   – Dependence on aspect ratio (AR), feature size, and pattern density

(4) Macroscopic uniformity (on a wafer scale) (↑)
   – Etch rate, Profile, Selectivity, Damage, etc.

(5) Etching of new materials and device structures
   – Low-k, High-k, Metal, Dual gate, etc.

The ULSI devices are substantially planar (2D), usually 5-10 μm thick, owing to limitations of the traditional fabrication processes for ULSI.
In addition to (1) ~ (5) for ULSI, (6) High etch rate (or Etching of deep structures) (7) Etching of 3D microstructures

MEMS devices are manufactured using processes based on USLI fabrication technologies, and also using emerging technologies to fabricate 3D, deep (up to 1 mm) microstructures with higher throughputs and lower costs.

Microfabrication using Etching

DRAM cell 0.2 μm
Photonic crystal 1 μm
Micro cantilever 0.2 mm
Micro turbine 2 mm
2. Fundamentals of Plasma Etching Technology

- Etching Characteristics
- Core Technology of Plasma Etching
  Plasma reactor
  Feed gas
  Process control

Plasma Etching Technology

- Etching Characteristics:
  - Etch anisotropy and selectivity
  - Microscopic uniformity
  - Plasma damage

- Plasma etching (or processing) technology consists of three core technologies: (1) Plasma reactor, (2) Reactive Gas, and (3) Process control.

- Plasma plays two roles in plasma processing:
  1. To generate ions and reactive neutrals from feed gases through electron impact events, which are then transported onto substrate surfaces.
  2. To form the sheath above substrate surfaces, which accelerates the ions onto substrate surfaces.
### Plasma Etching

**ICP Cl2 Plasma**

**ICP (Inductively Coupled Plasma)**

- **RF Coil**
- **RF Power Source** (13.56 MHz)
- **Dielectric Plate**
- **Feed Gas**
- **Plasma**
- **Substrate**
- **Cooling Water**
- **To Pump**

**Etched Profile (Poly-Si)**

- **CCP* mode** (100 W)

*CCP: Capacitively Coupled Plasma

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### Etch Anisotropy and Selectivity

**Etching Process**

- **Start**
- **After Lithography**
  - **Underetch** (50% Etching)
  - **Just Etch** (100% Etching)
  - **Overetch** (50% Overetch) (150% Etching)

**Anisotropy:**

\[ A = 1 - \frac{ER_{lateral}}{ER_{vertical}} \]

**CD Loss / Gain:**

\[ \Delta W = W_0 - W_1 \]

**Selectivity:**

\[ S = \frac{ER_{film}}{ER_{mask or under layer}} \]

**Isotropic**

**Anisotropic**
Profile Irregularities

*The nonuniform surface coverage of neutrals results from the difference in anisotropy between incoming ions and neutral reactants.

**The nonvertical ion incidence originates from the thermal motion of ions, scattering of ions through collision with neutrals in the sheath, and deflection of ion trajectories due to charging of mask dielectrics.

***The charging results from the difference in anisotropy between incoming ions and electrons.

**Nonuniformity Surface Coverage of Neutrals in Microstructural Features combined with Nonvertical Ion Incidence**

**Differential Charging of Microstructural Features and the Consequent Deflection of Ion Trajectories**

**Nonvertical Incidence of Ions**

**Ion Reflection from Feature Sidewalls**

**Charging of Mask Dielectrics and the Consequent Deflection of Ion Trajectories**

Selectivity over underlying films is required during overetch.

Selectivity over mask is required during main and overetch.
**Microscopic Uniformity**

- **Etch Rate**
  - (a) (Neutral) Reactants
  - Large aspect-ratio features etch slower than smaller ones.
  - [Shadowing for Incoming (Neutral) Reactants]
  - Large aspect-ratio features etch slower than smaller ones.

- **Etched Profile**
  - (b) Inverse RIE Lag
  - Large aspect-ratio features etch faster than smaller ones.
  - [Shadowing for Incoming Surface Inhibitors]
  - Large aspect-ratio features exhibit more significant trenching than smaller ones.
  - (c) Surface Inhibitors
  - Large aspect-ratio features etch more tapered than smaller ones.
  - [Charging of Mask Dielectrics and the consequent Deflection of Ion Trajectories]
  - Large aspect-ratio features exhibit more significant trenching than smaller ones.

- **Plasma Damage**
  - (i) Charging Damage
    - “plasma current”: $J_i, J_e$ ($\sim$ mA/cm$^2$)
  - (ii) Physical Damage
    - ion with high energy ($E_i \sim 100$ eV)
  - (iii) Radiation Damage
    - high energy photon ($h\nu \sim 10$ eV)
Plasma Etching Reactors

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<td>16 K</td>
<td>64 K</td>
<td>256 K</td>
<td>1 M</td>
<td>4 M</td>
<td>16 M</td>
<td>64 M</td>
<td>256 M</td>
<td>1 G</td>
<td>(4 G)</td>
<td>(16 G)</td>
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<td>Feature Size</td>
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<td>3 μm</td>
<td>2 μm</td>
<td>1.3 μm</td>
<td>0.8 μm</td>
<td>0.5 μm</td>
<td>0.35 μm</td>
<td>0.25 μm</td>
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<td>6”</td>
<td>8”</td>
<td>8”/12”</td>
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</table>

- **Barrel type**
  - DC Self-bias
  - RIE (batch type)
  - RIE (single type)

- **Low-Pressure, High-Density**
- **Independent Ion Energy Control**

- **External Magnetic Fields**
  - MERIE
  - Dipole Ring Magnet

- **Two RF/Microwave Sources**: for Plasma Source and for RF Biasing
  - Narrow Gap, Triode, Two-frequency
  - Pulse Modulation
  - Pulse Biasing
  - Frequency Control
  - High Flow Rate
  - Wall Temperature Control
  - Wafer Temperature Control

- **Low-Pressure, High-Density Plasmas**
- **External Magnetic Fields**
- **No Magnetic Fields**

Plasma Sources (1)

**CCP (Capacitively Coupled Plasma)**

- Barrel type (Multi Wafer Type)

**Downstream Plasma**

- CDE (Chemical Dry Etching)

**Two-Frequency CCP**

- Anode Coupling
  - RF Power Source (40 MHz)
- Cathode Coupling
  - RF Power Source (13.56 MHz)
Plasma Sources (2)  | Middle and High Density
---|---
**MERIE (Magnetically Enhanced RIE)**
- Grounded Plate
- Magnetic Field Coil
- RF Coil
- Plasma Substrate
- Wafer Stage
- Feed Gas
- RF Power Source (13.56 MHz)

**ICP (Inductively Coupled Plasma)**
- RF Power Source (2.0 MHz)
- Plasma Substrate
- Wafer Stage
- Feed Gas
- Cooling Water
- RF Bias Source (4 MHz)

**SWP (Surface Wave-excited Plasma)**
- Teflon Plate
- Quartz Plate
- Aluminum Plate
- Waveguide
- Microwaves (2.45 GHz)
- Plasma
- Wafer Stage
- Feed Gas
- Cooling Water
- RF Bias (50 MHz)

**ECR (Electron Cyclotron Resonance)**
- ECR Resonance Region
- Plasma
- Wafer Stage
- Feed Gas
- RF Bias (803 MHz)

**HWP (Helicon Wave-excited Plasma)**
- Dielectric Belljar
- Permanent Magnets
- Magnetic Field Coil
- Antenna
- Plasma
- Wafer Stage
- Feed Gas
- RF Bias Source (70.56 MHz)

Trends of Plasma Etching Reactors

- **Ion Energy (eV)**
  - ECR
  - Helicon
  - ICP
  - MERIE
  - Barrel

- **Gas Pressure (Torr)**
  - 10^{-4} to 10^{1}

Plasma Properties
- Ion Transport through Collisionless Sheath
- Low Flux of Neutral Reactants
- High Flux of Ions
- Low Ion Incident Energy

Processing
- High Anisotropy
- Little Lateral Etching
- High Selectivity
- Low Damage
Halogen-containing gases are primarily employed for plasma etching.

N₂, O₂, and CH₄ gases are also employed in some cases; e.g., N₂/H₂ for organic low-κ films, O₂/Cl₂ for Ru, and CH₄/H₂ for ITO.

Rare gases such as He and Ar are often employed as diluent gases. (Kr and Xe are also employed in some cases.)

* Presently not used owing to toxicity problems.

Feed gases are preferred for etching to give reactive atoms which can break the bond of materials and form etch or reaction products.

**Reactive Gases for Plasma Etching**

*From CRC Handbook of Physics and Chemistry*

**Bond Strength of Diatomic molecules**

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<th>Molecule</th>
<th>Bond Strength</th>
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Reactive Gases for Plasma Etching

Boiling temperature of Materials (at a vapor pressure of 1 atm)

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<th>Material</th>
<th>Temp (°C)</th>
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<th>Temp (°C)</th>
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- Feed gases are preferred for etching to give reaction or etch products having lower boiling temperatures (or higher vapor pressures).

From CRC Handbook of Physics and Chemistry

Process Control in Plasma Processing

- Equipment Functions (Externally Controllable Parameters)
- Plasma Excitation Source: frequency, power, time modulation
- RF Bias Source: frequency, power, time modulation
- Feedstock Gas: species, flow rate, pumping speed, pressure, temperature
- Reactor and Electrode: geometry / structure, material, temperature, external fields
- Wafer / Substrate Stage: geometry / structure, material, temperature

- Plasma Characteristics
  - (Plasma Parameters and Structures)
  - Electrons: density, velocity distribution
  - Ions and Neutrals: chemical composition, concentration, velocity distribution
  - Plasma Structures: plasma and surface potentials, sheath voltage and thickness

- Incident Characteristics on Substrates
  - Ions, Neutrals, and Electrons: flux, chemical composition, velocity distribution (incident energy and angular distribution)

- Processing Characteristics (Etching and Deposition Characteristics)
  - Rate, Profile, Selectivity, Step Coverage, Electrical and Mechanical Properties, Damage, Macroscopic Uniformity, Microscopic Uniformity
3. Role of Plasma in Plasma Etching Technology

- Gas-phase Reactions (to generate ions and neutrals)
- Ion Acceleration through the Sheath (DC self-bias voltage)

Reaction Processes in Plasma Reactor

1) Gas-Phase Reactions
   - Electron-impact events
   - Ion reactions
   - Neutral reactions

2) Plasma-Wall Interactions
   - Adsorption / deposition on walls
   - Charge neutralization on walls
   - Wall recombination, Wall erosion

3) Plasma-Surface Interactions
   - Adsorption, Desorption, Purely chemical reactions,
   - Physical sputtering, Ion-assisted reactions,
   - Deposition, Passivation layer formation

4) Plasma-Surface Interactions in Microstructural Features
   - Shadowing, Surface charging, Surface reemission / reflection, Surface reactions
Gas-Phase Reactions

Cl/Cl₂ Reaction Processes in Chlorine Plasmas

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Process</th>
<th>$E_a$ (eV)</th>
<th>Cross section (cm$^2$)</th>
<th>Rate coefficient$^a$ (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron-impact reactions:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular ionization</td>
<td>$e + Cl_2 \rightarrow Cl^+_2 + e + e$</td>
<td>11.48</td>
<td>$\sigma_1$</td>
<td>$k_1$</td>
</tr>
<tr>
<td>Dissociative ionization</td>
<td>$e + Cl_2 \rightarrow Cl^+ + Cl + e$</td>
<td>15.48</td>
<td>$\sigma_2$</td>
<td>$k_2$</td>
</tr>
<tr>
<td>Ion-pair formation</td>
<td>$e + Cl \rightarrow Cl_e^+ + e$</td>
<td>11.87</td>
<td>$\sigma_3$</td>
<td>$k_3$</td>
</tr>
<tr>
<td>Dissociative attachment</td>
<td>$e + Cl \rightarrow (Cl_e^+) \rightarrow Cl + Cl^*$</td>
<td>0</td>
<td>$\sigma_4$</td>
<td>$k_4$</td>
</tr>
<tr>
<td>Dissociative excitation</td>
<td>$e + Cl_2 \rightarrow Cl^+_2 + e \rightarrow Cl + Cl^* + e$</td>
<td>3.12</td>
<td>$\sigma_5$</td>
<td>$k_5$</td>
</tr>
<tr>
<td>Atomic ionization</td>
<td>$e + Cl \rightarrow Cl^+ + e$</td>
<td>13.01</td>
<td>$\sigma_6$</td>
<td>$k_6$</td>
</tr>
<tr>
<td>Electron detachment</td>
<td>$e + Cl \rightarrow Cl + e$</td>
<td>23.80</td>
<td>$\sigma_7$</td>
<td>$k_7$</td>
</tr>
<tr>
<td>Dissociative recombination</td>
<td>$Cl^+_2 + e \rightarrow Cl = Cl^*$</td>
<td>3.62</td>
<td>$\sigma_8$</td>
<td>$k_8$</td>
</tr>
<tr>
<td>Atomic recombination</td>
<td>$Cl^+ + e \rightarrow Cl$</td>
<td>0</td>
<td>$\sigma_9$</td>
<td>$k_9$</td>
</tr>
<tr>
<td>$Cl^+ + e \rightarrow Cl + e$</td>
<td>$-13.01$</td>
<td>$\sigma_{10}$</td>
<td>$k_{10}$</td>
<td></td>
</tr>
<tr>
<td>$Cl^+ + e \rightarrow Cl^* + e$</td>
<td>$0$</td>
<td>$\sigma_{11}$</td>
<td>$k_{11}$</td>
<td></td>
</tr>
<tr>
<td>$Cl^+ + Cl \rightarrow Cl^2 + Cl$</td>
<td>$-3.12$</td>
<td>$\sigma_{12}$</td>
<td>$k_{12}$</td>
<td></td>
</tr>
</tbody>
</table>

Ion reactions:
- Ion-atom reaction: $Cl_e^+ + Cl \rightarrow Cl_e + Cl$
- Charge exchange: $Cl^+ + e \rightarrow Cl$

Neutral reactions:
- Volume recombination: $Cl + Cl \rightarrow Cl + Cl$
- Wall recombination: $Cl + Cl \rightarrow Cl + Cl$
- Surface recombination: $Cl + wafer \rightarrow (0.25)SiCl_4 + wafer$

$^a$ In $k_9$, the electron temperature $T_e$ is in eV. Rate coefficients $k_i$ are values at $T_e=300$ K. Coefficients $\gamma_1$ and $\gamma_2$ are reactive sticking probabilities.

* For anodized aluminum $\gamma=0.65$ for stainless steel or $\gamma=0.007$.

Total Ionization Cross Section: $Q_i = \sigma_1 + \sigma_2 + \sigma_3$

Rate coefficients $k_i$ are values at $T_e=300$ K. Coefficients $\gamma_1$ and $\gamma_2$ are reactive sticking probabilities.

Total Cross section for Negative Ion Formation: $Q_n = \sigma_4$

$^*$ For anodized aluminum $\gamma=0.65$ for stainless steel or $\gamma=0.007$.

Gas-Phase Reactions (continued)

Electron-Impact Reactions for Cl/Cl₂

Collision Cross Section

$$k = \langle \sigma v_e \rangle = \int dv_e f_e(v_e) \sigma(v_e) v_e$$

Rate Coefficient

$$k = \langle \sigma v_e \rangle = \int dv_e f_e(v_e) \sigma(v_e) v_e$$
Reactants and Products

0-dimensional Calculation – Cl₂ Plasma –

\[
\frac{dy}{dt} = (k_2 + k_4 + 2k_5)n_2n_x - k_1n_x[Cl] \\
+ (k_x[Cl] + k_9[Cl] + k_{10}[Cl^+] + k_{11}n_x[Cl^+])n_x - (k_{12} + k_{13}n_x)n_x[Cl] \\
+ (k_{14}[Cl] + 2k_{15}[Cl^+] + (k_{16}[Cl^+] + 2k_{17}[Cl^+]n_x = \frac{[Cl]}{t_x} - \frac{[Cl]}{t_x}
\]

Plasma Diagnostics
(including diagnostics of the fluxes and energies of ions and neutrals incident on the surface).

Reactants and Products (continued)

Flux of Ions and Neutrals Incident on Substrate Surfaces

Neutral Flux :

\[ \Gamma_n \approx (n \ln 4) \left( \frac{8 k T_n}{\pi m n} \right)^{1/2} \]

Ion Flux :

\[ \Gamma_i \approx 0.6 n_i \left( \frac{k T_i}{m_i} \right)^{1/2} \]

- The neutral-to-ion flux ratio \( \Gamma_{Cl} / \Gamma_i \) is of the order of 10 at 10 mTorr, decreases with decreasing pressure.
- The neutral-to-ion flux ratio \( \Gamma_{Cl_2} / \Gamma_i \) is about one order of magnitude higher than \( \Gamma_{Cl} / \Gamma_i \).
Reactants and Products (continued)

**Plasma and Surface Diagnostics**
(by using FTIR absorption spectroscopy)

- Silicon tetrachloride SiCl$_4$ was the only IR-absorbing etch product species detected in the gas phase, while unsaturated SiCl$_x$ ($x=1$–3) as well as SiCl$_4$ were observed on the surface.
- [SiCl$_4$] $\sim 1 \times 10^{13}$ cm$^{-3}$ $\sim$ [Cl$_2$] in the gas phase.
- A broad absorption feature due to Si–O vibrations or silicon oxides was found to occur both in the gas phase and on the surface, where oxygen came from the dielectric windows and chamber walls.

---

**Electron-Impact Reactions and Neutral reactions for Product Species**

**Electron-Impact Reactions**

\[
\begin{align*}
\text{e}^- + \text{SiCl}_4 & \rightarrow \text{Cl}^- + \text{SiCl}_3 \\
\text{e}^- + \text{SiCl}_4 & \rightarrow \text{Cl}^- + \text{SiCl}_2 + \text{Cl} \\
\text{e}^- + \text{SiCl}_4 & \rightarrow \text{Cl}^- + \text{SiCl} + \text{Cl}_2 \\
\text{e}^- + \text{SiCl}_4 & \rightarrow \text{Cl}_2^- + \text{SiCl}_2 \\
\text{e}^- + \text{SiCl}_4 & \rightarrow \text{Cl}_2^- + \text{SiCl} + \text{Cl}
\end{align*}
\]

At $E_e < 10$ eV, $k_1 \sim 10^{-7}$, $k_2 \sim 10^{-7}$, $k_3 \sim 10^{-9}$, $k_4 \sim 10^{-9}$, and $k_5 \sim 10^{-10}$ cm$^3$/s

**Neutral Reactions**

\[
\begin{align*}
\text{SiCl} + \text{O}_2 & \rightarrow \text{SiO} + \text{ClO} \\
\text{SiCl}_2 + \text{O}_2 & \rightarrow \text{SiO} + \text{ClO} + \text{Cl} \\
\text{SiCl}_3 + \text{O}_2 & \rightarrow \text{SiO} + \text{ClO} + \text{Cl}_2 \\
\text{SiCl}_4 + \text{O}_2 & \rightarrow \text{SiO} + \text{ClO} + \text{Cl}_2 + \text{Cl}
\end{align*}
\]

At $T \sim 300$ K, $k_6 \sim 10^{-12}$, $k_7 \sim 10^{-15}$, $k_8 \sim 10^{-12}$, and $k_9 \sim 10^{-17}$ cm$^3$/s
Si etching in Cl₂ Plasma

(a) Two-dimensional Fluid Simulation - Cl₂ Plasma (10 mTorr) -

(b)

Neutral Flux (10¹⁸ cm⁻² s⁻¹/g₁₆)

Ion Flux (10¹⁶ cm⁻² s⁻¹/g₁₆)

[SiCl₂] (10¹⁵ cm⁻³)

[Cl⁺] (10¹¹ cm⁻³)

Reactive Species in Real Etching Environments

During Si etching in Cl₂ plasmas a)

<table>
<thead>
<tr>
<th>Source</th>
<th>Feed Gas</th>
<th>Reaction Product</th>
<th>Impurity from Walls and Windows</th>
<th>Mask Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral Reactant</td>
<td>Cl₂, Cl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ion</td>
<td>Cl₂⁺, Cl⁺</td>
<td>O₂⁺, O⁺</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface Inhibitors</td>
<td>Depositing Species</td>
<td>SiClₓ, SiOₓClᵧ b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactive species</td>
<td></td>
<td></td>
<td>CₓHᵧ c)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O₂, O</td>
<td></td>
</tr>
</tbody>
</table>

a) The situation is similar to Si etching in Cl₂/O₂ plasmas.
b) Silicon oxides SiOₓ would also occur.
c) In case of photoresist mask.
In case of hard mask (or SiO₂ mask), Si and/or O would occur.

In real etching environments, reactive species responsible for etching surface reactions come not only from feed gases but also reaction products, impurities from walls and/or windows, and mask materials.
Plasma Reactor

Plasma Reactor

Feed Gas

Substrate

Electrode

Sheath

To Pump

Blocking Capacitor

RF Source

DC Self-bias Voltage

Two-dimensional Particle-in-cell/Monte Carlo (PIC/MC) Simulation
– Ar Plasma (200 mTorr) –

Total current : $I = I_i + I_e + I_d$

$I_i$: Ion current
$I_e$: Electron current
$I_d$: Displacement current

$1/2 \frac{V_{pp}}{\Phi_p + \Phi_d}$
Incident Ions and Electrons

\[ E_i \approx \Phi_p + V_{dc} \]

(a) Ar\(^+\)

(b) e\(^-\)

(c) Ar\(^+\)

(d) e\(^-\)

Energy Distribution of Incident Ions

* Incident ion energy (or IEDF) depends on rf frequency, voltage, sheath width, ion mass, and pressure.
Incident angular distribution of ion fluxes (or IADF) depends on sheath voltage, sheath width, ion mass, and pressure.

4. Surface Reaction Processes in Plasma Etching
(Plasma-Surface Interactions)

- Surface Reactions
- Transport of Ions and Neutrals in Microstructural Features
- Feature Profile Evolution
- Microscopic Uniformity
- Surface Charging
Etching Surface Reactions

- Etching occurs through surface reactions with ions and neutrals incident on surfaces from the plasma, where the positive ions are incident on surfaces after been accelerated through the sheath, while the neutrals are incident isotropically on surfaces.

  (High-energy electrons are also incident on surfaces after being decelerated through the sheath, playing an important role in differential charging of feature surfaces.)

- Etching characteristics achieved depends primarily on the chemical constituent of ions and neutrals incident on surfaces, flux and energy and angular distributions of incident ions and neutrals, and surface temperature.

- Moreover, the etching of patterned features (or the feature profile evolution during etching) are determined also by the transport of ions and neutrals in microstructural features, because the etching reactions occur in feature surfaces in microstructures.

Study of Etching Surface Reactions

- Surface reactions responsible for etching have been investigated by using: Beam experiments (including surface diagnostics)
  Plasma experiments (including plasma and surface diagnostics, plasma simulation*)
  *Particle model and Fluid model
  Process simulation (semi-empirical profile simulation, molecular dynamics (MD) simulation)


- The etch rate is enhanced by about an order of magnitude by simultaneous exposure of ions and reactive neutrals.
### Etching Mechanisms

<table>
<thead>
<tr>
<th>Etching Mechanism</th>
<th>Purely Chemical</th>
<th>Physical / Chemical Sputtering</th>
<th>Ion-Assisted</th>
<th>Inhibitor Deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reactive Neutral</td>
<td>Energetic Ion</td>
<td>Energetic Ion (reactive)</td>
<td>Energetic Ion</td>
</tr>
<tr>
<td>Adskorption (+ mixing)</td>
<td>![Diagram]</td>
<td>![Diagram]</td>
<td>![Diagram]</td>
<td>![Diagram]</td>
</tr>
<tr>
<td>Reaction</td>
<td>![Diagram]</td>
<td>![Diagram]</td>
<td>![Diagram]</td>
<td>![Diagram]</td>
</tr>
<tr>
<td>Desorption</td>
<td>![Diagram]</td>
<td>![Diagram]</td>
<td>![Diagram]</td>
<td>![Diagram]</td>
</tr>
</tbody>
</table>

### Etching Mechanism vs. Characteristics

<table>
<thead>
<tr>
<th>Etching Mechanism</th>
<th>Anisotropy</th>
<th>Selectivity</th>
<th>Damage</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical</td>
<td>×</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F+Si→SiF4↑</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sputtering</td>
<td></td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>A⁺+Si→Si↑</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A⁺+Si→ASi↑)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ion-Assisted</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl⁺+Si→SiClx</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B⁺+SiClx→SiCl4↑</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Ion-Assisted) Inhibitor Deposition</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The etch anisotropy relies primarily on the ion-assisted reaction at the bottom of the feature and the passivation layer formation on feature sidewalls.

There are two mechanisms for the formation of passivation layers on feature surfaces:
(i) Inhibitor deposition.
(ii) Inhibitor adsorption or surface oxidation.

There are two mechanisms for ion-assisted (or ion-enhanced) reaction:
(i) Chemical sputtering (or Physically enhanced chemical sputtering), where energetic ions enhance the step of Reaction.
(ii) Chemically enhanced physical sputtering (or Physical sputtering), where energetic ions enhance the step of Desorption.

Ion-Assisted Reaction

Beam Experiments  Etch Yield $Y(E_i, \theta)$ vs. Incident Ion Energy $E_i$

- The etch yield depends on ion energy as $Y(E_i) = A(E_i^{1/2} - E_{th}^{1/2})$ at $E_i < 1$ keV, where $A$ is a constant, in physical sputtering as well as ion-assisted etching reaction.
- In ion-assisted etching, the etch yield depends also on neutral-to-ion flux ratio.

Ion-Assisted Reaction

Beam Experiments

Etch Yield $Y(E_i, \theta)$ vs. Ion Incidence Angle $\theta$

- The etch yield peaks at normal incidence ($\theta = 0^\circ$) in ion-assisted etching reaction, while it peaks at around $\theta = 65^\circ$ in physical sputtering.


Ion-Assisted Reaction

(continued)

Reaction Products

- The amount of lower chlorinated SiCl$_x$ species increases with increasing ion energy.
- The velocity distribution of etch product species desorbed from surfaces changes from MB to CC, as the ion energy is increased.


*MB: Maxwell-Boltzmann  *CC: Collision Cascade
Ion-Assisted Reaction (continued)

Si etching in Cl₂ plasmas

Surface Reaction Layer (Chlorinated Surface Layer (SiClₓ Layer)


- The chlorinated surface layer consists of SiClₓ (x=1-3)
- The thickness of SiClₓ layer increases with increasing ion incident energy.

Surface Reaction Processes

Model of Surface Chemistry in Real Etching Environments
(Si etching in Cl₂, Cl₂/O₂ Plasmas)

Decomposition / Reaction
→ Deposition : \( \Gamma_p \)
Redeposition : \( \Gamma_q \)

Infinitiesimal Reaction Surface

SiClₓ Chlorinated Surface \( \theta_n \) Si Clean Surface \( 1-\theta_n-\theta_o-\theta_p \) SiOₓ Oxidized Surface \( \theta_o \) SiOₓClₓ Deposited Surface \( \theta_p \)
Surface Reaction Processes

Langmuir Adsorption Kinetics Model (monolayer adsorption)

Temporal Change of the Coverage of Infinitesimal Reaction Surfaces:

\[
\frac{\partial \Theta_n}{\partial t} = S_{n0} \Gamma_n \left(1 - \Theta_n - \Theta_o - \Theta_p\right) - (xY_{sn} + Y_n) \Gamma \Theta_n - S_{o0} \Gamma_o \Theta_o - \left(S_{p0} \Gamma_p + S_{q0} \Gamma_q\right) \Theta_n
\]

\[
\frac{\partial \Theta_o}{\partial t} = S_{o0} \Gamma_o \left(1 - \Theta_o - \Theta_p\right) - Y_{so} \Gamma_i \Theta_o - \left(S_{p0} \Gamma_p + S_{q0} \Gamma_q\right) \Theta_o
\]

\[
\frac{\partial \Theta_p}{\partial t} = \left(S_{p0} \Gamma_p + S_{q0} \Gamma_q\right) \left(1 - \Theta_p\right) - Y_{p} \Gamma_i \Theta_p
\]

Etch and Deposition Rates:

\[
ER = \frac{1}{\rho_s} \left[Y_{sn} \Theta_n + Y_o \Theta_o + Y_s \left(1 - \Theta_n - \Theta_o - \Theta_p\right)\right]
\]

\[
DR = \frac{1}{\rho_p} \left[\left(S_{p0} \Gamma_p + S_{q0} \Gamma_q\right) - Y_{p} \Gamma_i \Theta_p\right]
\]

Interface Evolution Rate:

\[
v = ER - DR
\]

Surface Reaction Processes

Parameters for Surface Reaction Processes (Si etching in Cl2, Cl2/O2 Plasmas)

- Ion-Enhanced Etch Yield of Si: \( Y_{sn} = 0.4 \) (\( E_i = 50 \) eV, maximum at \( \theta = 0^\circ \))
  from a Cl+/Cl2+ ion beam study [M. Balooch et al., JVST A14, 229 (1996)].

- Total Removal Yield of Cl Adsorbed: \( (xY_{sn} + Y_n) = 3 \) (\( E_i = 50 \) eV, maximum at \( \theta = 0^\circ \))
  determined by comparing an ion-neutral synergy model with aspect-ratio dependence data on etch rate obtained in ECR Ar/Cl2 plasmas [A.D. Bailey III et al., JVST B13, 2133 (1995)].

- Sputter Yields of Si and SiOy: \( Y_s (\theta=0^\circ) = 0.06 \) (maximum at \( \theta = 60^\circ \))
  \( Y_{so} (\theta=0^\circ) = 0.02 \) (maximum at \( \theta = 60^\circ \))
  from Cl+/Cl2+ ion beam study [D.J. Oostra et al., Appl. Phys. Lett. 50, 1506 (1987)].
  [S. Tachi et al., JVST A9, 796 (1991)].

- Sputter Yield of Surface Inhibitors SiuClvOw: \( Y_p (\theta=0^\circ) = Y_{sn} \) (maximum at \( \theta = 60^\circ \))
  assumed.

- Sticking Coefficient of Neutral Reactants on Si: \( S_{n0} = 0.55 \)
  from beam study of Cl on Si [D.J.D.Sullivan et al., J. Phys. Chem. 97, 12051 (1993)].
  \( * \sim 0.001 \) for Cl on Si.

- Sticking Coefficient of O on Si and SiClx: \( S_{o0} = 1 \)
  \( * \sim 0.001 \) for O2 on Si from beam study [J.R. Engstrom et al., Phys. Rev. B41, 1038 (1990)].

- Sticking Coefficient of Etch Products on Si, SiClx, and SiOy: \( S_{p0}, S_{q0} = 0.1 \sim 0.5 \) (assumed)
  \( * \sim 0.002 \) for SiCl4 on Si from beam study [L.J. Whitman et al., Surf. Sci. 232, 297 (1990)].
  \( * \sim 0.1 \sim 0.5 \) for SiClx+ \( (x=1,2; E_i=30 \) eV) from beam study [T. Sakai et al., 32, 3089 (1993)].
  \( * \sim 1 \) for products on themselves.
Transport of Ions and Neutrals in microstructures

Ions and neutrals coming from the plasma onto substrate surfaces are further transported onto sidewalls and bottom surfaces in microstructural features. Here, neutrals include reactants, etch products and by-products, surface inhibitors, and oxygen.

Ion Flux Incident on Feature Surfaces:

\[ \Gamma_i(P) = \int_{0}^{\theta_2} G_i(\theta) \cos(\theta - \psi) \, d\theta \]

(a) Direct incidence (Neutral shadowing)

Neutral Flux Incident on Feature Surfaces:

\[ \Gamma_n(P) = \int_{0}^{\theta_2} \left( \frac{1}{2} \right) \cos(\theta - \psi) \, d\theta \]

(b) Direct incidence (Ion shadowing)

\[ + \int_{\text{Profile}} \left( \frac{1}{2r} \right) Y_n \Gamma_i(Q) \Omega_n(Q) \]

(c) Incidence through desorption from feature surfaces

\[ + \left[ 1 - S_n(Q) \right] \Gamma_n(Q) \cos \phi_i \cos \phi_Q \, d\theta \]

(d) Incidence through surface reemission

Transport of Ions and Neutrals (continued)
Transport of Ions and Neutrals

Geometrical Shadowing of Ions and Neutrals

Rectangular Trench

Geometrical Shadowing
- Ion shadowing
- Neutral shadowing with surface reemission

Feature Profile Evolution

Etched profiles are simulated through modeling the transport of ions and neutrals in microstructures along with surface reaction kinetics thereat.

String Model

- 

Si etching in Cl2/O2 plasmas

- RIE lag occurs in (a) and (b), being suppressed in (c) with increasing oxygen flux from the plasma.
- Inverse RIE lag occurs in (d) at high oxygen flux.
- Sidewall tapering occurs in (b), (c), and (d) where surface inhibitors come from the plasma.
Microscopic Uniformity (continued)

<Example 1>

Si etching in SF₆/Ar plasmas

↑ RIE lag (reactive-ion-etching lag):
- Large aspect-ratio features etch slower than smaller ones.
  (Narrow space features etch slower than wider ones.)

Inverse RIE lag:
- Large aspect-ratio features etch faster than smaller ones.
  (Narrow space features etch faster than wider ones.)
- The degree of inverse RIE lag increases with increasing O₂ concentration in Cl₂/O₂ plasmas.

<Example 2>

Outwardly tapered sidewall:
- Large aspect-ratio features etch less tapered than smaller ones.
  (Narrow space features etch less tapered than wider ones.)
- The degree of sidewall tapering increases with increasing pressure in Cl₂ plasmas.

Poly-Si etching in Cl₂/O₂ plasmas
Microscopic Uniformity

<Example 3> Poly-Si etching in Cl2/O2 plasmas

<table>
<thead>
<tr>
<th>Micropillar:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micropillars often occur in wide space features (or small aspect-ratio features).</td>
</tr>
</tbody>
</table>

† Microscopic uniformity during overetch:
- The thinning and breaking of thin gate oxides during overetch step occurs preferentially in large open spaces in pure Cl2 plasmas, while in dense areas at high level O2 addition in Cl2/O2 plasmas.

Microscopic Uniformity

<Example 4> Poly-Si etching in Cl2O2 plasmas

Linewidth Shift: $\Delta W = W_{after} - W_{before}$

† Microscopic uniformity (etch rate, sidewall profile) is achieved at ~10% O2 addition in Cl2/O2 plasmas.
Passivation Layer Formation

Si etching in Cl2/O2 plasmas

† XPS Analysis

Etched Profile and Profile Simulation → Atomic-scale Cellular Model

• Passivation layers are formed on feature surfaces through deposition of surface inhibitors (primarily etch products and by-products) and/or surface oxidation.
• The thickness of passivation layers is significantly large on feature sidewalls.

Ion Reflection

Si etching in Cl2/O2 plasmas

Without ion reflection on feature sidewalls

With ion reflection on feature sidewalls

Etched Profile Simulation † Atomic-scale Cellular Model

• Ion reflection on feature sidewalls is responsible for profile anomalies such as microtrenching and footing on sidewalls near the feature bottom and thereat, which are also affected by deposition of etch products and by-products and surface oxidation.
Notch is a sharp undercut that occurs on feature sidewalls near the bottom of the feature.

In etching of conducting films on dielectrics (e.g., poly-Si gate etch), notching occurs during overetch step, at the inner sidewall foot of the outermost feature of a L&S structure neighboring an open area.

The notch is caused by the deflection of ion trajectories in microstructural features due to the localized charging of feature surfaces, which in turn originates intrinsically from the difference of the velocity distribution between ions and electrons incident on substrate surfaces.

Such a phenomena is known as “electron shading effect”, which causes charging damage as well as profile anomalies.

Profile Simulation

-String Model-

Charging (1): Conductor feature surfaces (during overetch)

Charging (2): Dielectric feature surfaces
**Al etch**

Reactive species in Al etching with BCl3/Cl2 and BCl3/Cl2/O2 plasmas

<table>
<thead>
<tr>
<th>Role in Surface Reactions</th>
<th>Source</th>
<th>Feed Gas</th>
<th>Reaction Product</th>
<th>Impurity from Walls and Windows</th>
<th>Mask Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral Reactant</td>
<td></td>
<td>Cl2, Cl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ion</td>
<td></td>
<td>Cl2+, Cl-</td>
<td>BCl+</td>
<td>O2+, O+</td>
<td></td>
</tr>
<tr>
<td>Surface Inhibitors</td>
<td>Depositing</td>
<td>BxClx, BxOy</td>
<td>AlClx, AlOxClx, CxHy</td>
<td>O2, O</td>
<td></td>
</tr>
<tr>
<td>Reactive</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a) Al is etched pure-chemically in Cl2, showing no ion-assisted reaction characteristics. Thus, surface inhibitor deposition is indispensable on sidewalls to obtain anisotropic profiles of Al. Selectivity is required over photoresist mask. b) (BOCl)x is volatile. c) Compounds of AlClx and CxHy are usually primary surface inhibitors during Al etching.*

---

**SiO2 etch**

Reactive species in SiO2 etching with fluorocarbon plasmas

<table>
<thead>
<tr>
<th>Role in Surface Reactions</th>
<th>Source</th>
<th>Feed Gas</th>
<th>Reaction Product</th>
<th>Impurity from Walls and Windows</th>
<th>Mask Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral Reactant</td>
<td></td>
<td>F2, F</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ion</td>
<td></td>
<td>F2+, F+, CFx+</td>
<td>O2+, O+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface Inhibitors</td>
<td>Depositing</td>
<td>CxFy, (CF)x</td>
<td>SiFy, SiOxFy, CxHy</td>
<td>O2, O</td>
<td></td>
</tr>
<tr>
<td>Reactive</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a) SiO2 is etched in fluorocarbon (CFx, CxFy, etc.) plasmas with relatively high rf bias voltage; thus the etched profiles are usually anisotropic. C is indispensable in SiO2 etching through breaking strong Si–O bonds and/or oxygen removal in the form of volatile compounds such as CO. In addition, F is also indispensable for Si removal through the formation of volatile SiFy [e.g., SiO2 + 2CF + 2F → SiCl4 + 2CO]. b) Selectivity is required over Si, where fluorocarbon radicals CxFy play an important role; in some cases, Hx is added to scavenge F and thus to release or increase surface inhibitors CxFy. c) Surface reaction layer contains SiCxFyOy. d) Hard mask (e.g., poly-Si) is also often employed.*
5. Current Issues of Plasma Etching Technology

- Current issues
- Poly-Si gate etch
- High-\(k\) gate etch
  (HfO\(_2\), Dual metal gate)
- Metal etch (Pt, Ru)
- Deep RIE of Si

Current Issues

- **Etching of Conventional Materials** :
  - Etch anisotropy and selectivity
    * Profile and CD control on atomic scale
    * Selectivity over underlying ultra thin films
    * Surface roughness on atomic scale (LER\(^+\), etc.)
  - Microscopic uniformity
  - Plasma damage

- **Etching of New Materials** :
  - Substrate : SiGe, Ge
  - Gate : High-\(k\)\(^*\) dielectrics (HfO\(_2\), ZrO\(_2\), etc.)
    / Metal electrodes (TaN, Mo, Ru, W, etc.)
  - Capacitor : High-\(k\)\(^*\) dielectrics (Ta2O5, BST)
    / Metal electrodes (Pt, Ir, Ru)
  - Inter layer dielectrics (ILD) :
    Low-\(k\) dielectrics (SiOC, MSQ\(^**\), Organic)

\(^*\) \(k\): dielectric constant
\(^**\) MSQ: methylsilsesquioxane

* LER: line edge roughness

These issues are also to be resolved in etching of new materials
(1) Profile (Mainly gate electrode)
- Feature: feature size, critical dimension
  Minimum feature size L < 0.1 μm
  CD loss/gain ΔL < 0.01 μm (=10 nm)
- Profile irregularities: notch, microtrench, (owing to bending of ion trajectory)
*In case of hard etching materials
  More sidewall deposition → CD gain, Needs for removing of residues on sidewalls

(2) Selectivity
- Gate Electrode (poly-Si, metal)
  Mask ---- Hard mask (SiO₂)
  Underlying Layer ------ Gate Dielectrics
- Gate Dielectric (SiO₂, SiON, High-κ dielectric)
  Mask ---- Gate Electrode (+ Mask)
  Underlying Layer------ Si

(3) Plasma Damage
- Charging Damage
  Gate Dielectrics (Dielectric Breakdown)
  Transistor (deterioration)
- Gate Dielectrics: deterioration of dielectric
- Gate Dielectrics: penetrate

(4) Microscopic Uniformity
- Pattern sensitivity* of feature or profile irregularities
- Pattern sensitivity of etch rate or selectivity
  RIE lag, inverse RIE lag
- Pattern sensitivity of damage
  *feature size, aspect ratio, pattern density

(5) Macroscopic Uniformity
- Wafer Uniformity

A thin passivation layer of feature sidewalls plays a key role in achieving the nanometer-scale control of the profile and CD during main etch and overetch processes.
In the plasma etching of 10-nm-scale microstructures, the ion-enhanced etching at the bottom of the feature and the passivation layer formation on feature sidewalls are still key mechanisms to be precisely controlled.

---

**High-\(k\) Gate Etch**

- As integrated circuit device dimensions continue to be scaled down, recent efforts have been made to replace gate silicon-oxides with silicon-oxynitrides of slightly higher dielectric constant (\(k\)), and nowadays, new high-\(k\) (>20) dielectrics or metal oxides such as Al2O3, HfO2, and ZrO2 are being developed to replace SiO2.

- In integrating these high-\(k\) dielectric materials into device fabrication, selective etching over the underlying Si is required for their removal prior to forming the source and drain contacts.

- Moreover, the etching of high-\(k\) dielectrics at higher etch rates with low ion energies and/or less ions is indispensable in mass production, for chamber cleaning of the chemical vapor deposition (CVD) and atomic layer deposition (ALD) apparatuses to prepare high-\(k\) thin films.

- The etching of HfO2 films in BCl3-containing plasmas without rf biasing or under low ion-energy conditions, together with a wafer temperature control, would be promising candidate for the process concerned.
Etching of High-\(k\) Materials

High-\(k\) dielectrics are generally difficult materials for etching, owing to strong metal-oxygen bonds and non-volatile etch products or halogen compounds.

<table>
<thead>
<tr>
<th>Element</th>
<th>Halogen compound</th>
<th>Melting Point (°C)</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (Z=13)</td>
<td>AlF3</td>
<td>2250</td>
<td>1276</td>
</tr>
<tr>
<td></td>
<td>AlCl3</td>
<td>192.6</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>AlBr3</td>
<td>97.5</td>
<td>255</td>
</tr>
<tr>
<td>Si (Z=14)</td>
<td>SiF4</td>
<td>–</td>
<td>90.2</td>
</tr>
<tr>
<td></td>
<td>SiCl4</td>
<td>68.85</td>
<td>57.65</td>
</tr>
<tr>
<td></td>
<td>SiBr4</td>
<td>5.2</td>
<td>154</td>
</tr>
<tr>
<td>Zr (Z=40)</td>
<td>ZrF4</td>
<td>–</td>
<td>912 *sp</td>
</tr>
<tr>
<td></td>
<td>ZrCl4</td>
<td>–</td>
<td>331 *sp</td>
</tr>
<tr>
<td></td>
<td>ZrBr4</td>
<td>–</td>
<td>360 *sp</td>
</tr>
<tr>
<td>Hf (Z=72)</td>
<td>HfF4</td>
<td>–</td>
<td>970 *sp</td>
</tr>
<tr>
<td></td>
<td>HfCl4</td>
<td>–</td>
<td>317 *sp</td>
</tr>
<tr>
<td></td>
<td>HfBr4</td>
<td>–</td>
<td>323 *sp</td>
</tr>
</tbody>
</table>

*sp: sublimation point

Bond strengths for diatomic species:

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Strength (eV)</th>
<th>Bond</th>
<th>Bond Strength (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-O</td>
<td>8.38</td>
<td>Si-O</td>
<td>8.29</td>
</tr>
<tr>
<td>B-F</td>
<td>7.85</td>
<td>Si-F</td>
<td>5.73</td>
</tr>
<tr>
<td>B-Cl</td>
<td>5.30</td>
<td>Si-Cl</td>
<td>4.21</td>
</tr>
<tr>
<td>B-Br</td>
<td>4.11</td>
<td>Si-Br</td>
<td>3.81</td>
</tr>
<tr>
<td>C-O</td>
<td>11.15</td>
<td>Zr-O</td>
<td>8.03</td>
</tr>
<tr>
<td>C-F</td>
<td>5.72</td>
<td>Zr-F</td>
<td>6.38</td>
</tr>
<tr>
<td>C-Cl</td>
<td>4.11</td>
<td>Zr-Cl</td>
<td>5.11</td>
</tr>
<tr>
<td>C-Br</td>
<td>2.90</td>
<td>Zr-Br</td>
<td>–</td>
</tr>
<tr>
<td>Al-O</td>
<td>5.30</td>
<td>Hf-O</td>
<td>8.30</td>
</tr>
<tr>
<td>Al-F</td>
<td>6.88</td>
<td>Hf-F</td>
<td>6.73</td>
</tr>
<tr>
<td>Al-Cl</td>
<td>5.30</td>
<td>Hf-Cl</td>
<td>5.16</td>
</tr>
<tr>
<td>Al-Br</td>
<td>4.45</td>
<td>Hf-Br</td>
<td>–</td>
</tr>
</tbody>
</table>

The etching of HfO\(_2\) occurred at >20% Cl\(_2\) addition. The HfO\(_2\) etch rate was maximum at ~60% Cl\(_2\), being ~100 nm/min with a selectivity of ~10 over Si and of ~2 over SiO\(_2\).

Note that a high etch selectivity >50 for HfO\(_2\)/Si was obtained at 40-50% Cl\(_2\) addition, with a HfO\(_2\) etch rate of ~50 nm/min and HfO\(_2\)/SiO\(_2\) selectivity of 1.5-2, where the deposition was still dominant over the etching on Si.

In BCl\(_3\)/Cl\(_2\)/O\(_2\) plasmas, the HfO\(_2\) etch rate was enhanced with O\(_2\) addition, being ~150 nm/min at ~5% O\(_2\) with a selectivity of ~4 over Si and of ~1.2 over SiO\(_2\). At high O\(_2\) addition >10%, the heavy deposition occurred to inhibit etching on all sample surfaces.
### Metals for high-\(k\) gate stack

<table>
<thead>
<tr>
<th>FET</th>
<th>Metals</th>
<th>Nitrides, Carbides</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-MOSFET</td>
<td>Ti, Ta</td>
<td>TaN, TaC</td>
</tr>
<tr>
<td>P-MOSFET</td>
<td>Pt, Ir, Mo, Ru</td>
<td></td>
</tr>
<tr>
<td>Midgap</td>
<td>W</td>
<td>TiN</td>
</tr>
</tbody>
</table>

关于高-\(k\)/金属门极堆叠，一种方法是采用单种金属门极材料并使用中间工作函数的门极，适用于 \(n\)-和 \(p\)-MOSFETs。

### Physical properties of potential etch product species

<table>
<thead>
<tr>
<th>Element</th>
<th>Halogen compound</th>
<th>Melting point (°C)</th>
<th>Boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti ((Z=22))</td>
<td>TiF4</td>
<td>284</td>
<td>136.45</td>
</tr>
<tr>
<td></td>
<td>TiCl4</td>
<td>-25</td>
<td>230</td>
</tr>
<tr>
<td></td>
<td>TiBr4</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Ru ((Z=44))</td>
<td>RuO4</td>
<td>25.4</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>RuO2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>RuF5</td>
<td>86.5</td>
<td>227</td>
</tr>
<tr>
<td></td>
<td>RuF3</td>
<td>&gt; 600 *dec</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>RuCl3</td>
<td>&gt; 500 *dec</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>RuBr3</td>
<td>&gt; 400 *dec</td>
<td>-</td>
</tr>
<tr>
<td>Ta ((Z=73))</td>
<td>TaF5</td>
<td>95.1</td>
<td>229.2</td>
</tr>
<tr>
<td></td>
<td>TaCl5</td>
<td>216</td>
<td>239.35</td>
</tr>
<tr>
<td></td>
<td>TaBr5</td>
<td>265</td>
<td>349</td>
</tr>
<tr>
<td>Ir ((Z=77))</td>
<td>IrF6</td>
<td>44</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>IrF3</td>
<td>250</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>IrCl3</td>
<td>763</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>IrBr3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pt ((Z=78))</td>
<td>PtF6</td>
<td>61.3</td>
<td>69.1</td>
</tr>
<tr>
<td></td>
<td>PtF4</td>
<td>600</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>PtCl4</td>
<td>327</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>PtBr4</td>
<td>180</td>
<td>-</td>
</tr>
</tbody>
</table>

*dec: decomposes  (from CRC Handbook of Physics and Chemistry, 1998)

### Etching of Metals

- Etching of Pt relies intrinsically on physical sputtering, because halogen and other compounds of Pt are not volatile; thus, the Pt sidewalls are largely tapered owing to redeposition of Pt sputtered on feature sidewalls during etching.
- Etching of Ru is caused by ion-assisted reaction in O\(_2\)-containing plasmas, because RuO\(_4\) is volatile to be relatively easily desorbed from surfaces; thus, vertical sidewalls are obtained for Ru.
Metal Etch (continued)

Dual metal gate

High-k
/P-metal deposition, PR formation

P-metal etch

N-metal / Poly-Si deposition, HM formation

High-k etch (removal)

P-metal etch (patterning)

Deep RIE

– Bosch process (for MEMS) –

To fabricate 3D, deep structures with higher throughputs and lower costs

Deep RIE* (Bosch process)  *RIE: reactive ion etching
Cyclic process consisting of
  isotropic etching with SF$_6$ plasmas
  → sidewall passivation with C$_x$F$_y$ plasmas
  → anisotropic etching with SF$_6$ plasmas
  → isotropic etching with SF$_6$ plasmas
achieves an etch rate of > 10 μm/min for Si.

Minimum gap: 6 μm
Height: 120 μm
Deep RIE (continued)

C₄F₈/Ar Plasma

Mask

Si substrate

C₄F₈

Passivation layer formation on sidewalls (and on bottom surfaces)

SF₆/Ar Plasma

Ar⁺ SF₅⁺

F* F* F*

Removal of passivation layers on bottom surfaces

SF₆/Ar Plasma

Ar⁺ SF₅⁺

F* F*

Si etching (at bottom surfaces)

Anisotropic Etch (with low pressure, high bias)

Isotropic Etch (with high pressure, low bias)

*Higher etch rates and the suppress of scallops on sidewalls are issues to be further improved.

6. Summary

– Future Prospects
Nanofabrication Technology

— Top-down approach, Bottom-up approach —

<table>
<thead>
<tr>
<th>Scale</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 nm (1 μm)</td>
<td>Bulk materials and/or thin films</td>
</tr>
<tr>
<td>100 nm</td>
<td>Fabrication of microstructures</td>
</tr>
<tr>
<td>10 nm</td>
<td>Self-assembly/re-organization of atoms</td>
</tr>
<tr>
<td>1 nm</td>
<td>Nanomaterials and devices</td>
</tr>
<tr>
<td>0.1 nm (1 Å)</td>
<td>Nanomaterials and devices</td>
</tr>
</tbody>
</table>

Top-down approach — fabrication from bulk materials and/or thin films of the material to obtain microstructures (devices)

Bottom-up approach — manipulation/rearrangement of atoms and self-assembly/re-organization of atoms to obtain nanostructures (materials, devices)

VLSI ULSI

Nanoelectronics

Fabrication of Nanoelectrode Arrays

— Bottom-up approach — (CNT Nanoelectrode Array / CNT Interconnects)

J. Li, Q. Ye, A. Cassell, H. T. Ng, R. Stevens, J. Han, M. Meyyappan, Appl. Phys. Lett., 82 (15), 2491 (2003).
Summary

• Plasma etching is now an indispensable technology for micro- and nano-fabrication of ULSI and MEMS devices.
• To meet the requirements for near-future and future devices, the precise control of etching characteristics is further required, based on the precise control of the etching mechanisms concerned.

*Current issues / requirements for plasma etching technology have been summarized in this lecture.

• In turn, a better understanding of the physical and chemical mechanisms underlying the processing continues to be required in the gas-phase and on the surfaces,

*Ion-assisted reaction and passivation layer formation continue to be key mechanisms to be precisely controlled on surfaces.

• A combination of top-down (plasma etching) and bottom-up approaches would be important for nanofabrication technology of <10 nm scale.

For further reading

• Books

• Journals :
*Journal of Vacuum Science and Technology A, B (AVS/AIP)
*Journal of Physics D : Applied Physics (IOP) *Plasma Sources Science and Technology (IOP)
*Japanese Journal of Applied Physics (JSAP)