Rethinking the Art of Plasma Etch

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MIPSE
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The Art of Etching: Rembrandt in the 1600s

- Covered a plate (4x7 inch) with resin
- Scratched design through resin with soft needle
- Immersed plate in dilute HCl acid bath
- Made gradations in lines by multiple etching (~12)
- Sometimes took several years to finish

Etchings of Self
Brief History of the Art of Etching

Nature

Hieroglyphics

Etched in stone

Woodblock printing and chokin engravings in Asia

Metal acid-etch in Middle Ages in Europe

Semiconductor industry

Feature size (m)

<0 A.D.  500 A.D.  1500 A.D.  1970s to today

1,000,000 x smaller

Physical
Chemical
Physical + Chemical

Source: Intel
How Chips Are Made

- Wafer
- Deposition
- Lithography
- Etch
- Strip
- Clean

300 mm wafer

Photoresist

Residue/Particle
# Enabling Benefits of Plasma Etching

<table>
<thead>
<tr>
<th>Enablement</th>
<th>Mechanism</th>
<th>Challenge</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anisotropy:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isotropic</td>
<td>Vs. Anisotropic</td>
<td>&gt;50:1 aspect ratio, &lt;10 nm features</td>
</tr>
<tr>
<td><strong>Smoothness:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lithography (Top-down)</td>
<td>Post-etch</td>
<td>EUV, smoothness to &lt;0.5 nm</td>
</tr>
<tr>
<td>Chop corners fill crevices</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Shrinks</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lithography (Top-down)</td>
<td>Post-etch</td>
<td>Small CD, CD-independent</td>
</tr>
<tr>
<td>45 nm</td>
<td>19 nm</td>
<td></td>
</tr>
<tr>
<td><strong>Selectivity:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Area selective etch</td>
<td></td>
<td>No loss, sharp corners, similar materials</td>
</tr>
</tbody>
</table>

Image source: Intel, ECS 4 (6) 2015
**What is Etching?**

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**Overcoming the Surface Binding Energy ($E_0$)**

$E_0 = \text{Surface binding energy}$

**Si example:**

$E_0 = 4.7 \text{ eV}$

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<table>
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<tr>
<th>Mechanical</th>
<th>Chemical</th>
<th>Thermal</th>
<th>Physical</th>
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<tbody>
<tr>
<td><img src="image1.png" alt="Mechanical" /></td>
<td><img src="image2.png" alt="Chemical" /></td>
<td><img src="image3.png" alt="Thermal" /></td>
<td><img src="image4.png" alt="Physical" /></td>
</tr>
</tbody>
</table>

- **Mechanical**
- **Chemical**
- **Thermal**
- **Physical (anisotropic)**
How Does Plasma Etching Work?

**Ion-Neutral Synergy**

\[
\text{Etch Rate} \approx \frac{1}{U_0} \frac{1}{(E_i^{1/2} - E_{ih}^{1/2}) J_i + \nu S_0 J_N}
\]

Equation assumes no sputtering and spontaneous etch; Gottscho, et. al, J. Vac. Sci. Technol. B 10, 1992

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**Neutrals only**

**Radicals + Ions**

**Ions only**

Spontaneous isotropic

Sputtering

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**Chang, et.al, JVST, 1997**

**Ratio of Cl to Ar+ flux**

**Ratio of Neutrals to Ions**

Ion-limited

\[\text{ER} \sim J_i\]

Neutral-limited

\[\text{ER} \sim J_N\]

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Coburn & Winters, J. Appl. Phys, May 1979
Conventional Etching Couples Ion and Neutral Generation and Delivery

Plasma produces ions & radicals

Wafer bias voltage controls ion energy

**Dissociation:** $e^- + AB \rightarrow A + B + e^-$

**Ionization:** $e^- + Ar \rightarrow Ar^+ + 2e^-$

Conventional operation: continuous and simultaneous

- **Coupled ionization and dissociation** limits process window
- **Cumulative surface damage** leads to increased device leakage current
- **Transport limitations** lead to device variability
Simultaneous and Continuous - Not Self-Limiting... Just Limiting

Etching rate decreases with increasing aspect ratio, regardless of whether neutral or ion flux is limiting: shadowing, Knudsen transport, differential charging all scale with aspect ratio.

Non-uniform chemical and electrical potentials create concentration gradients across wafer. In either limiting regime, etching will be non-uniform because neutral and ion fluxes and their ratio all vary radially.
The New Art of Etching is Based on Academic Research and Simulation

Dielectric ALE predicted by simulation in 2006

Dielectric ALE verified in laboratory by 2013

Today: ALE in high volume manufacturing

LAM RESEARCH INTRODUCES DIELECTRIC ATOMIC LAYER ETCHING CAPABILITY FOR ADVANCED LOGIC

Source: Plasma ALE, Agarwal & Kushner, 33rd IEEE ICOPS, 2006

Fluorocarbon assisted atomic layer etching of SiO2 using cyclic Ar/C4F8 plasma

Citation: Journal of Vacuum Science & Technology A 32, 023013 (2014) doi: 10.1116/1.4843575

View online: http://dx.doi.org/10.1116/1.4843575

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Published by the AVS: Science & Technology of Materials, Interfaces, and Processing
Rethinking the Art of Etching: Self-Limiting Cycles of Adsorption and Desorption

Ref: JVST A 33, 020802 (2015)
## Benefits of Atomic Layer Processing

<table>
<thead>
<tr>
<th>Surface</th>
<th>ALD</th>
<th>ALE</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Atomically smooth</td>
<td></td>
</tr>
<tr>
<td>Feature</td>
<td>2.04 nm</td>
<td>2.07 nm</td>
</tr>
<tr>
<td></td>
<td>2.00 nm</td>
<td>50 nm</td>
</tr>
<tr>
<td>Uniform across wafer</td>
<td>1.16 nm 1.16 nm 1.16 nm</td>
<td>±0.15% range on 1,200 Å film</td>
</tr>
<tr>
<td>Data from Lam 2014</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radial Distance (mm)</td>
<td>±1.5 nm 3σ</td>
<td></td>
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ALE is Inherently Smoother

As shown in the images:

**After “RIE” (Cl₂/Ar at 50 eV)**
- AFM 1x1 μm
- RMS = 2.3 nm
- Micro-trenching

**After ALE (Cl₂-Ar at 50 eV)**
- RMS = 0.4 nm
- Flat etch front

Blanket epi-Si wafers etched 50 nm on Lam Kiyo:
- Cr coating

Compare to simulation of 5 nm etch (adapted from Agarwal and Kushner, 2007):
Same Chemistry, Same Energy... So What Is the Difference?

With Cl

50 eV

Cl\-

Weak Cl-Cl bond

4 eV bond

strong Si-Cl bond

Cl-bond induces roughness

Source: Fiel et al, JAP, 74, 1997

Only Ar

50 eV

Ar\+

Ballistic movement

Ar ion enables flattening

Source: Fiel et al, JAP, 74, 1997

And Humbrid and Graves, 2004
### Monte-Carlo, Sputter-Based Simulation of ALE Smoothing

<table>
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<tr>
<th>Lateral movement</th>
<th>Geometrical reactivity</th>
<th>Angle-dependent yield</th>
<th>Erosion of peaks</th>
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<td>Ballistic and/or thermally-induced surface diffusion</td>
<td>More reactant/nm² on convex surface</td>
<td>Faster etching at higher angles</td>
<td>Sputtered material redeposits in valleys</td>
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- **Lateral movement**
  - Ballistic and/or thermally-induced surface diffusion

- **Geometrical reactivity**
  - More reactant/nm² on convex surface

- **Angle-dependent yield**
  - Faster etching at higher angles

- **Erosion of peaks**
  - Sputtered material redeposits in valleys

- **Angle of incidence (θ)**
  - Sputter trajectories
  - $60° - 70°$
  - $θ_{max}$, $π/2$

- **Sputter yield**
Simulation Captures Time Evolution of Smoothing

Smoothing evolution

- Data on blanket W ALE
- Simulation w RMS scaled

Limit appears to be atomic scale

Monte Carlo simulation
W ALE @ 65 eV ions

Simulations converge to atomic limit
- 0.2 nm (i.e. ±1 atom)
Practical Limits of Atomic Layer Etching

ALE Synergy %
\[
\text{ALE Synergy \%} = \frac{\text{EPC} - (\alpha + \beta)}{\text{EPC}} \times 100\%
\]

- \(\text{EPC} = \text{total etch per cycle}\)
- \(\alpha = \text{etch from dose step alone}\)
- \(\beta = \text{etch from ion step alone}\)

Synergy metric useful to characterize degree of ALE ideality

- Background etching during dose step from photon energy
- Sputtering after reactant depletion
- Cross-contamination between steps (e.g., from chamber wall outgassing)
- Incoming surface imperfections
Etching Energetics and the Concept of an ALE Ion Energy Window

Relative energy barriers:

- Surface binding energy, $E_O$
- Desorption barrier, $E_{des}$
- Adsorption barrier, $E_{ads}$

$E_{ads} < E_{des} < E_O$

Si ALE values:

- $E_{O} = 4.7 \text{ eV}$
- $E_{des} = 2.3 \text{ eV}$ [1]
- $E_{ads} < 0.3 \text{ eV}$ [2]
- $\Delta E_{ads} = 3.5 \text{ eV}$

ALE Window Widens with Increasing $E_0$

![Image of periodic table and graphs]


Table: Surface binding energy $E_0$

- Under 2 eV
- 2-3 eV
- 3-4 eV
- 4-5 eV
- 5-6 eV
- 6-7 eV
- 7+ eV

Graphs showing EPC (nm/cycle) vs. Ar ion energy (V) for different materials and conditions.
ALE Trends Scale with Surface Binding Energy

$E^*_{\text{ads}} < \varepsilon_A < E^*_{\text{des}} < \varepsilon_B < E_0$

Ref: Kanarik et al, JVST 35 (5) 2017
For Ar exposure time ~5 sec, synergy and EPC measured in center of window
Let’s Examine the Concept of an ALE Window Further…

- Concept came from Atomic Layer Deposition: “the temperature range where an ALD process fulfills the requirement of self-terminating reactions” (Puurunen, 2005)

- In directional ALE we use “ion energy” instead of T to activate the reactions. Until recently, everyone though the ALE window was always <100 eV.

Window is determined for a fixed ion dose
The ALE Window Widens Dramatically for Shorter Exposure Times

There isn’t just “one” window....

Universal scaling relationship for ALE

\[ \text{Si} - \text{SiCl}_x(s) + \text{Ar}^+ \rightarrow \text{Si}(s) + \text{SiCl}_x(g), \]

where \( Y(\varepsilon_i) \sim \sqrt{\varepsilon_i} - \sqrt{\varepsilon_{th}} \) (Steinbruchel, 1989)

For 97% removal time: \( t_{97\%} \sim \frac{1}{\sqrt{\varepsilon_i}} \)

References:
Universal scaling relationship: JVST A 39, 010401 (2021)
Atomic Layer Etching is the “New Art Form”
- Simpler to design and control - coupling between neutrals and ions is eliminated
- Process window scales with surface binding energy
- Critically important to use inert gas ions
- Benefits are smoothing, aspect ratio independence, and macroscopic uniformity - to atomic dimensions
- Throughput and management of non-synergistic effects remain big challenges

Smoothing an inherent benefit of ALE
- Inert gas ion bombardment sufficient for smoothing to occur
- Requires high synergy
- More cycles, more smoothing… to an atomic limit
- ALE being used for LWR smoothing to lower dose requirements in EUV lithography

Universal scaling relationship for ALE
- Inverse relationship between root ion energy and exposure time for achieving ALE
- Single ALE window for a given material system
Re-Thinking the Art of Etch

Weathering of sandstone

Etch of metal vase

ALE of EUV film

EUV 25 nm
(~150 atoms)
The Artists

References: (1) JVST A 33, 020802 (2015); and (2) J. Phys. Chem. Lett., 2018, 9 (16), pp 4814-4821

Keren Kanarik
Samantha Tan
Wenbing Yang
Tamal Mukherjee
Alex Kabansky
Skip Berry
Thorsten Lill
Taeseung Kim
Jengyi Yu
Rich Wise
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Trusted **Productivity**
Fast **Solutions**