Plasma Etching: Atomic Scale Surface Fidelity and 2D Materials

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Goal of IC manufacturing is to produce structures with highest possible degree of matching to the intent of the design engineers.

Def. fidelity: the degree to which something matches or copies something else (Merriam-Webster).

Fidelity goes beyond statistical criteria such as accuracy and precision and has customer end goal in mind.

For instance, selectivity is fidelity in the vertical direction, CD is fidelity in horizontal direction.

New approach is needed to achieve atomic scale fidelity in etch.
Atomic Layer Deposition (ALD)
Deposition with Atomic Scale Fidelity

ALD is characterized by sequential, self-limiting surface reactions; the fundamental benefits of ALD are conformality and uniformity.
Atomic Layer Etching (ALE): Use Time Domain to Simplify

Si ALE example:

Surface Modification

Chlorination

Purge

Removal

Purge

Neutral-limited \( \sim J_N \)

\[ \sim (1 - e^{-J_N}) \]

Surface coverage

Stops when surface saturates

Chlorine dose

Ions give directionality

Ion-limited \( \sim J_i \)

Etch Amount

Stops when reactants consumed

Ion dose
# Atomic Layer Etch (ALE)

*Analogous to ALD*

<table>
<thead>
<tr>
<th>ETCH</th>
<th>Start</th>
<th>Reaction A</th>
<th>Switch Steps</th>
<th>Reaction B</th>
<th>End/Repeat</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Generic ALE:</td>
<td></td>
<td>Modification</td>
<td>Self-Limiting</td>
<td></td>
<td>Film Removed</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b) Example Si ALE:</td>
<td>Si Surface</td>
<td>Cl₂</td>
<td>Chlorination</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ion Bombardment</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Removal step instead of adsorption step**

<table>
<thead>
<tr>
<th>DEPOSITION</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>c) Example SiO₂ ALD:</td>
<td>O Radical</td>
<td>Adsorption</td>
<td>Si Source</td>
<td>SiO₂ Added</td>
</tr>
</tbody>
</table>

As in Coburn and Winters 1970’s experiment, ALE also has synergy

- ALE is characterized by perfect synergy as a result of saturation

Each individual step alone ideally does not etch, etch occurs only when steps are combined into series

Synergy Test
Silicon Example

Goal: minimize secondary reactions

- $\text{Cl}_2$ plasma
- Ar+ removal

- Separated steps as self-limiting as possible for reducing flux-dependence
- For higher productivity, ALE can remove more than monolayer per cycle
Removal step has defined ion energy “window” with saturation achieved.

Modification step also has operating window that depends on kinetic energy of reactants or surface temperature.

Similar operating window known in ALD.
Atomic Layer Etching Offers Fundamental Advantages

- **Surface:**
  - Uniform
  - Separated and self-limiting reactions are key to ALE benefits

- **Aspect Ratio Independence:**
  - Smooth and stoichiometric
  - Same etch depth
  - 100 nm

- **Uniformity:**
  - Uniform
  - Full removal
  - 300 mm

**Modification** ➔ **Partial removal** ➔ **Full removal**
Silicon ALE on Lam’s Kiyo® Reactor

**Uniform Across Wafer**
- Before ±1.4 nm 3σ
- ALE ±1.5 nm 3σ

**Self-Limiting in Time**
- % Saturation vs. Ar Plasma Step Time (s)

**Self-Limiting in Energy**
- Etch per Cycle vs. Ar Bias Voltage (V)
  - 35-65 V ALE window

**Aspect Ratio Independent**
- Relative Etch Rate vs. Aspect Ratio

**Atomically Smooth Surfaces**
- After 50 nm Si etched:
  - 2 nm
High ALE Selectivity Predicted by Simulation

**Experiment**

Before etch

![Before etch image](image-url)

Gate oxide thickness: \(2.3 \pm 0.2\) nm

After ALE (30 nm over etch)

![After ALE image](image-url)

No gate oxide loss: \(2.3 \pm 0.2\) nm

**Simulation**

![Simulation image](image-url)

Gate oxide

Penetration limited to first monolayer


**ALE: Critical Contact Etching**

**Application:** Logic Contact ≤10 nm Node

- **Deposit thin fluorocarbon film,** then activate with Ar⁺ and remove

- **Selectivity advantage:** nitride less reactive with fluorocarbon film so etch stops

**Challenges:**
- Corner nitride spacer loss
- Etch stop in <10 nm space

**ALE achieves high selectivity even in aspect ratios >10:1**

- **DEMONSTRATED ON LAM FLEX™ TOOL:**

  - Oxide etches
  - Nitride: low reactivity

**Time →**


Hudson et al., AVS Symp. (2014)
ALE of 2D Materials


“Atomic layer etching of graphene for full graphene device Fabrication”; Lim et al.; Carbon 50, 429 (2012):
The surface of graphene is changed from sp2 to sp3 bonding via oxygen radical chemisorption. 30 eV Ar bombardment removes CO but leaves the sp2 bonded underlayer intact.

Atomic layer etching is a promising approach to thin and pattern graphene and other 2D materials