Etching and Thin Film Deposition

Prof. Steven Soper
What Happens After We Do Photolithography?

- **Energy**
  - Mask + Aligner
  - Modified Photoresist
  - Un-Modified Photoresist
  - Wafer

- **Wet Etching** (anisotropic)

- **Wet Etching** (isotropic)

- **Dry Etching**

"How to Make It and How to Use It", The University of Kansas, Lawrence, KS  August 2019
Etching

- Pattern transfer by chemical/physical removal of material from substrate where pattern is defined by a protective layer (photoresist, oxide, metal)
- Subtractive/Top-down process in which bulk material is removed to create smaller structures
Etching Metrics

Etch Rate
- Etched depth per unit time
- If it’s too high, difficult to control

Uniformity – Percentage variation of etch across the wafer

Selectivity
- Ratio of etching rate between different materials, usually the higher the better
- Generally, chemical etching has higher selectivity, physical etching (sputtering, ion milling) has low selectivity

Etch selectivity = \frac{\text{Etch rate of material we want to remove (} V_m \text{)}}{\text{Etch rate of masking material (} V_r \text{)}}
Wet Etching and Dry Etching

Wet etching
• Substrate is placed in chemical solution and material is removed via chemical reaction
• Benchtop process

Dry etching
• Substrate is placed in chamber (typically gas in vacuum).
• Etch species are accelerated towards surface to remove material via chemical and physical mechanisms
• More complex/expensive machinery than wet etching
Types of Etching Processes

• **Anisotropic:**
  - Uniform etch rates in all directions (orientation dependent) \( A=1 \)
  - Dry etching profiles are anisotropic
  - Best for making small gaps and vertical sidewalls
  - Typically more costly

• **Isotropic:**
  - Different etch rates in vertical and lateral directions (orientation independent) i.e \( A=0 \)
  - Wet etching profiles are isotropic except for etching crystalline material.
  - Best to use with large geometries, when sidewall slope does not matter, and to **undercut** the mask
  - Quick, easy, cheap

\[
Anistrophy, A = 1 - \frac{R_L}{R_V}
\]

\( R_L \) – Lateral etch rate
\( R_V \) – Vertical etch rate

(a) Completely anisotropic (b) Partially anisotropic (c) Isotropic
Wet Etching in Microfluidics - Silicon

Wet Etching of Silicon can be isotropic or anisotropic (orientation dependent) depending on the etchant used.

Isotropic

- Wet etching of Si recommended when dry process is not available
- Performed with HNA: HNO₃, HF, and acetic acid (up to 50 µm/min)
- HNO₃: oxidizes Si, HF: dissolves the generated oxide layer, acetic acid is diluent
- Best masking material for HNA: Si₃N₄ or SiO₂

Anisotropic

- Etch rate depends on crystalline orientation
- Typical solution is KOH > 20% at elevated temperature (80-90 C)
- Relative etch rates: (110) > (100) > (111)
- Etch ratio of (100): (111) crystallographic planes is ~400:1
- Also common is 40% tetramethylammonium hydroxide (TMAH) and ethylenediamine pyrocatechol (EDP)
- Can create an etch stop by doping with boron

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Wet Etching in Microfluidics - Glass

- Purely isotropic etch profiles
- Etched with solutions of hydrofluoric acid (HF) (up to 8 μm/min)
- Glass is a mixture of oxides (CaO, MgO, Al₂O₃) whose composition affects etching behavior
- HCl or H₃PO₄ can be added to remove insoluble products and improve etch quality (rate, morphology)
- Choice of masking layer is important to avoid pinholes and delamination. Options include:
  - Photoresist
  - Amorphous Si
  - Cr/Au
  - Cr/photoresist
# Glass and Si WET Etchants for Microfluidics

<table>
<thead>
<tr>
<th>Etched material</th>
<th>Process</th>
<th>Suitable etchants</th>
<th>Suitable masking layers</th>
<th>Etch rate</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>Wet</td>
<td>HF/HCl (10:1) HF</td>
<td>Cr/Au/Photoresist* Amorphous Si*</td>
<td>Up to 7–8 ( \mu m/min ) (for Corning 7740)</td>
<td>The process is strongly dependent on glass composition</td>
</tr>
<tr>
<td></td>
<td>Wet</td>
<td>HF/NH(_4)F</td>
<td>SiC/Photoresist</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass</td>
<td>Dry</td>
<td>SF(_6), C(_4)F(_8), CF(_4), CHF(_3) Bosch</td>
<td>Ni plated* Thick amorphous Si* SU8 resist</td>
<td>Up to 0.5–0.8 ( \mu m/min )</td>
<td>The process is strongly dependent on glass composition</td>
</tr>
<tr>
<td>Glass</td>
<td>Dry</td>
<td>Cryogenic</td>
<td>SiO(_2) (wet or PECVD) • Metal</td>
<td>Up to 7 ( \mu m/min )</td>
<td>Smooth walls</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HNA (HNO(_3)+HF+CH(_3)COOH)</td>
<td>Si(_3)N(_4) (LPCVD)</td>
<td>4–90 ( \mu m/min )</td>
<td>Isotropic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>KOH</td>
<td>Si(_3)N(_4) (LPCVD, PECVD) • SiO(_2) (thermal/wet) • SiC (PECVD)</td>
<td>1.4 ( \mu m/min ) in (100) direction</td>
<td>Anisotropic</td>
</tr>
<tr>
<td>Silicon</td>
<td>Wet</td>
<td>EDP</td>
<td>SiO(_2), Si(_3)N(_4), Ta, Au, Cr, Ag, Cu</td>
<td>1.25 ( \mu m/min ) in (100) direction</td>
<td>Anisotropic</td>
</tr>
<tr>
<td>Silicon</td>
<td>Wet</td>
<td>TMAH</td>
<td>SiO(_2), Si(_3)N(_4)</td>
<td>1 ( \mu m/min ) in (100) direction</td>
<td>Anisotropic</td>
</tr>
</tbody>
</table>


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Dry Etching Process

- In dry etching, the etch reactants come from a gas or vapor-phase source and are typically ionized
  - atoms or ions from the gas are the reactive species that etch the exposed film
- Solid surface is etched in gas/vapor phase by physical methods (sputtering, ion beam milling) or chemical reaction (using reactive gases or plasma) or with combination of both chemical and physical bombardment (reactive ion etching)
# Types of Dry Etching

<table>
<thead>
<tr>
<th>Type of Etching</th>
<th>Excitation Energy</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma Etching</td>
<td>10’s to 100’s of Watts</td>
<td>Medium (&gt;100 torr)</td>
</tr>
<tr>
<td></td>
<td><em>isotropic, chemical, selective</em></td>
<td></td>
</tr>
<tr>
<td>Reactive Ion Etching</td>
<td>100’s of Watts</td>
<td>Low (10-100 mtorr)</td>
</tr>
<tr>
<td></td>
<td><em>directional, physical &amp; chemical, fairly selective</em></td>
<td></td>
</tr>
<tr>
<td>Sputter Etching</td>
<td>100’s to 1000’s of Watts</td>
<td>Low (~10 mtorr)</td>
</tr>
<tr>
<td></td>
<td><em>directional, physical, low selectivity</em></td>
<td></td>
</tr>
</tbody>
</table>

Dry etching spectrum

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Physical dry etching

- Etching occurs as a result of a physical effect, namely momentum transfer between energetic Ar+ ions and the substrate surface.
- No chemical reaction involved.
- Example: Sputtering and ion beam milling.
- Plasma source can be dc or RF discharge.

Plasma etching

- Only role of plasma is to supply gaseous, reactive etchant species.
- Neutral chemical species responsible for most of reactive etching (not ions).
- Ions rarely act as reactant species.
- Volatile products removed by vacuum system.
- Non-reactive species may decrease reaction rate by blocking surface sites.

Dry Etching

Reactive Ion etching

- Combines physical etching with chemical reactions.
- Plasma etching with ion bombardment.
- Ion-surface interactions promote dry etching by disrupting unreactive substrate and causes damage (dangling bonds, dislocations) resulting in substrate that is more reactive to etchant.
- Dry etchants for Si – CF₄, SF₆ & BCl₂+Cl₂ with etch rate of ~50nm/min.
Reactive Ion Etching (Dry Etching)

1. Wafer is grounded
2. Another electrode is connected to the RF power source
3. Oscillating (RF) electric field applied to ionize gas (~13 MHz)
4. Gas enters top of chamber and exits bottom of chamber using pump
5. Type of gas and pressure depend on etch material and structure demands (SF$_6$ used for Si)
6. Gas ions (+) form in the chamber, e- bombard the wafer, create (-) surface
7. Voltage difference causes gas ions to sputter material from wafer
Dry etching - Deep Reactive Ion Etching (DRIE)

- Dry etching technique used for creating high aspect ratio structures in Si, SiO₂, quartz, and some metals
- High density plasma enables etch rates much higher than standard RIE
- High aspect ratio features are achieved using the Bosch process (cryogenic DRIE also capable of high aspect ratios)
- Preferred method of etching Si compared to wet etching

**Bosch Process**

- Etching occurs when fluorine radials react with the Si surface to form the volatile reaction product SiF₄ and is pumped away.
- A negative voltage bias on the wafer is used to control the flux of positive ions from the plasma to the wafer surface.
- Etching is enhanced when SFₓ⁺ ions bombard the Si surface, making it more reactive.

- A fluorocarbon (nCF₂) passivation layer is deposited to prevent etching of side-walls.

- By quickly cycling between passivation and etching steps, very high aspect ratio features (etch depth/feature width) can be created.
- An inherent characteristic of the Bosch process due to alternating passivation/etch steps is side-wall scalloping.
# Wet vs. Dry Etching

<table>
<thead>
<tr>
<th>Wet Etching</th>
<th>Dry Etching</th>
</tr>
</thead>
<tbody>
<tr>
<td>High selectivity (up to 100:1)</td>
<td>Relatively low selectivity (1:1 but much higher with metals)</td>
</tr>
<tr>
<td>High etch rate (many microns/minute)</td>
<td>Relatively slow etch rates (&lt; 1um/min but can be much higher)</td>
</tr>
<tr>
<td>Low cost</td>
<td>Expensive</td>
</tr>
<tr>
<td>Batch system with high throughput</td>
<td>High aspect ratio features due to high anisotropy (&gt; 20:1)</td>
</tr>
<tr>
<td>Limited resolution (inadequate for &lt;1 um)</td>
<td>Capable of defining submicron features</td>
</tr>
<tr>
<td>Generally isotropic (anisotropic possible for single crystalline materials)</td>
<td>Vertical profiles can be produced in crystalline, polycrystalline, and amorphous materials</td>
</tr>
<tr>
<td>Generates a lot of waste</td>
<td>Clean process</td>
</tr>
<tr>
<td>Hard to control (not reproducible)</td>
<td>Potential heat/radiation damage</td>
</tr>
</tbody>
</table>
Wet vs. Dry Etching - Example

Wet etched Cr

Dry etched (RIE) Cr
1. **Etching processes:**

Spin photoresist (PR)  
Photolithography  
Etch using PR as mask  
Remove PR

Preparation of optical masks, patterning metals, oxides, etc., patterning microfluidic channels in glass, silicon

2. **Lift off processes**

Spin (PR)  
Photolithography  
Evaporate metal  
Lift Off excess metal with PR

Patterning of difficult to etch metals (Pt)
Atomic Layer Deposition (ALD)

Advantages

- Precise control of layer thickness
- Films are highly conformal – uniform coating on films, particles, and porous samples
- Stoichiometric control
- Low temperature process (as low as RT)
- Excellent adhesion due to chemical bonds at first layer

But, very slow! Many hours for 10’s of nms

Li$_x$TiO$_y$ deposited by ALD in 300:1 AAO nanotemplates

Al$_2$O$_3$ – ZrO$_2$ nanolaminates

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Atomic Layer Deposition

ALD Films

- ALD films deposited with digital control of thickness; “built layer-by-layer”
- Each film has a characteristic growth rate for a particular temperature

ALD Deposition Rates at 250°C

Common ALD Materials

- Oxides: Al₂O₃, HfO₂, La₂O₃, SiO₂, TiO₂, ZnO, ZrO₂, Ta₂O₅, In₂O₃, SnO₂, ITO, FeOₓ, NiO₂, MnOₓ, Nb₂O₅, MgO, NiO, Er₂O₃
- Nitrides: WN, Hf₃N₄, Zr₃N₄, AlN, TiN, TaN, NbNₓ
- Metals: Ru, Pt, W, Ni, Co
- Sulphides: ZnS

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Physical Vapor Deposition (PVD)

- PVD: Deposition technique in which some form of energy is used to transfer material from a target to the substrate, where it condenses

a) Thermal evaporation
- Heated filament used to boil off material
- Depositing alloys is difficult
- Poor adhesion
- Poor step coverage
- Not possible for refractory metals (limited choice of materials)

b) Electron beam evaporation
- High intensity electron beam focused on target material causes evaporation
- Deposition rates (10’s nm/min)
- Wider choice of materials
- Higher purity films
- Can cause x-ray and/or ion damage to substrate

c) Pulsed laser deposition
- Like e-beam evaporation, but laser is used instead for removing target material
- Wide choice of target materials
- High purity
- Slow dep. rates

d) Sputter deposition
- Plasma creates ions that are accelerated toward target. Momentum transfer from ions to target causes target material to be ejected toward surface (sputtering), where it condenses
- High purity films over large area are possible
- Just about any material can be sputtered – including compounds, but used mainly for metal deposition
- Better step coverage than evaporated films, but not always as smooth
- Deposition rate: 10’s nm/min
Sputter Deposition

- Voltage is applied across a rarified gas
- Breakdown of the gas forms a plasma
- Positive ions from plasma strike the negative electrode (cathode and target)
- Energy from the ions is transferred to the target atoms
- Some target atoms escape from target surface (they are sputtered)
- The sputtered atoms condense on the substrate
- Deposition of compounds (oxides, nitrides) possible with introduction of reactive gases

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• Just about any material can be sputtered (including compounds and refractory metals)

• Metal oxides and nitrides can be deposited via reactive sputtering
  • Reactive sputtering: metal sputtering in the presence of a reactive gas

• Better step coverage than evaporated films, but not always as smooth

• Deposition rate: 10’s nm/min

• Not good for shadow masks due to angular distribution of ion trajectory
Electron Beam Evaporation

- Electrons are generated by electron gun (cathode)
- Emitted electrons are accelerated towards crucible (anode) by high voltage potential
- Localized heating of target material (evaporation)
- Deposition with reactive species to create metal oxide/nitrides is possible
- High purity films compared to PVD
- Can be used with shadow masks
SEMs of Thermally and E-beam Evaporated Al Films