Lecture 7

Etching
Figures of merit

- Etch rate: sufficiently high but not too high, usually 100-1000 Å/min
- Etch rate uniformity: percentage variation of etch rate
- Etch selectivity: etch rate of various materials
- Etch anisotropy (lateral vs. vertical)
  \[ A = 1 - \frac{R_L}{R_V} \]
- Material damage produced by etching
- Safety to health and environment
Wet etching

Advantages
• highly selective
• doesn’t introduce damage

Drawbacks
• lack of anisotropy
• poor process control
• excessive particle contamination
Wet etching of SiO$_2$.  

- Wet etching in dilute solutions of HF: 6:1; 10:1 and 20:1 (HF:H$_2$O)

  Typical etch rate for thermal oxide (6:1): 1200 Å/min

  $$\text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2 + \text{SiF}_6 + 2\text{H}_2\text{O}$$

  To avoid pH and concentration change, buffered HF (BHF) is used

  $$\text{NH}_4\text{F} \rightleftharpoons \text{NH}_3 + \text{HF}$$

  Etching rates:
  - BHF 20:1: thermal oxide  300 Å/min
  - Si$_3$N$_4$ 10 Å/min
Wet etching of SiO$_2$.

- Etched groove (with and without steering)
Other wet etching recipes

- **Silicon Nitride** (if oxidized at high T, oxide should be removed first)
  - $\text{H}_3\text{PO}_4$ at 140 – 200 °C
  - 3:10 mixture of 49%HF and 70%HNO$_3$ at 70 °C.

- **Aluminium etch** (alloys might be difficult!)
  - 20% v/v acetic acid, 77% H$_3$PO$_4$, 3% HNO$_3$. 
Isotropic etching of Silicon

- Silicon etching \((\text{oxidation} + \text{HF})\)

\[
Si + HNO_3 \leftrightarrow H_2SiF_6 + HNO_2 + H_2 + H_2O
\]

Acetic acid is commonly used as a diluent.
Wet etching of Si

\[ Si + 2OH^- \rightarrow Si(OH)_2^{2+} + 4e^- \]
\[ 4H_2O + 4e^- \rightarrow 4OH^- + H_2 \]
\[ Si(OH)_2^{2+} + 4OH^- \rightarrow SiO_2(OH)_2^{2-} + 2H_2O \]

Types of etchants:
- Alkali hydroxide etchants: KOH, NaOH, CsOH, RbOH
- Ammonium hydroxide etchants: \( \text{NH}_4\text{OH} \), tertramethyl ammonium hydroxide (TMAH) \((\text{CH}_3)_4\text{NOH}\)
- Other etchants: hydrazine/water, amine gallate etc.

Etch rate depends on the crystallographic orientation. Highly packed planes are the slowest to etch.
Anisotropic etching of Silicon

- Crystallographic orientations (Miller indices)
Anisotropic etching of Silicon

- Crystalline structure of Silicon
  - Diamond like structure
- Marking orientation on Silicon wafers
Anisotropic etching of Silicon

- Wet etching of (100) Silicon
Anisotropic etching of Silicon
Anisotropic etching of Silicon

• Etching rate for many alkaline solutions is slow in (111) direction, so anisotropic etch with high aspect ratio can be achieved

• Mixture: (KOH:Isopropyl Alcohol: Water) (23.4 : 13.5 : 63) gives etching rate ratio (100)/(111) 100/1.

• Special purpose wet etch
  – doping selective etch:
    HF/HNO₃/CH₃COOH 1:3:8 – 15 times higher etch rate for heavily doped silicon (>10¹⁹ cm⁻³)
    ethylene-diamine-pyrocatehol-water etches lightly doped silicon without attacking heavily doped
  – Defect selective etch rate ratio (100)/(111) 100/1.
### Anisotropic etching of Silicon

- Characteristics of different etchants

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>KOH</th>
<th>NH₄OH</th>
<th>TMAH</th>
<th>EDP</th>
<th>Hydrazine</th>
<th>Amine Gallate</th>
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<tr>
<td>References</td>
<td>[10–16]</td>
<td>[17, 18]</td>
<td>[19–23]</td>
<td>[24]</td>
<td>[25, 26]</td>
<td>[27]</td>
</tr>
<tr>
<td>Concentration (weight %)</td>
<td>40 – 50</td>
<td>1 – 18</td>
<td>10 – 40</td>
<td>See*</td>
<td>See b</td>
<td>See c</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>80</td>
<td>75 – 90</td>
<td>90</td>
<td>70 – 97</td>
<td>100</td>
<td>118</td>
</tr>
<tr>
<td>{111} etch rate (nm/min)</td>
<td>2.5 – 5</td>
<td>-</td>
<td>20 – 60</td>
<td>5.7 – 17</td>
<td>2</td>
<td>17 – 34</td>
</tr>
<tr>
<td>{100} etch rate (μm/min)</td>
<td>1 – 2</td>
<td>0.1 – 0.5</td>
<td>0.5 – 1.5</td>
<td>0.2 – 0.6</td>
<td>2</td>
<td>1.7 – 2.3</td>
</tr>
<tr>
<td>{110} etch rate (μm/min)</td>
<td>1.5 – 3</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Si₃N₄ etch rate (nm/min)</td>
<td>0.23</td>
<td>-</td>
<td>1 – 10</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SiO₂ etch rate (nm/min)</td>
<td>1 – 10</td>
<td>-</td>
<td>0.05 – 0.25</td>
<td>0.2</td>
<td>0.17</td>
<td>Slow</td>
</tr>
<tr>
<td>Al attack</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>-</td>
<td>Yes</td>
</tr>
</tbody>
</table>

a. 1 L ethylene diamine NH₂-CH₂-CH₂-NH₂, 160 g pyrocatechol C₆H₆(OH)₂, 6 g pyrazine C₆H₄N₄, 133 mL H₂O
b. 100 mL N₂H₄, 100 mL H₂O (explosive, very dangerous!)
c. 100g gallic acid, 305 mL ethanolamine, 140 mL H₂O, 1.3 g pyrazine, 0.26 mL FC-129 surfactant
Wet etching of other orientation of Silicon
Chemical Mechanical Polishing (CMP)

- used to achieve global planarization: globally flat surface, free of scratches and contamination

containing 12-30% of SiO$_2$ particles, KOH and NH$_4$OH, pH~10 to keep silica negatively charged

Resulting smoothness:

$$R_s = \frac{3}{4} \phi P / (2K_p E)$$

<table>
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<tr>
<th>Table 11.2</th>
<th>Typical CMP process parameters and results for oxide planarization</th>
</tr>
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<tr>
<td>Thermal oxide removal rate</td>
<td>(Å/min)</td>
</tr>
<tr>
<td>Deposited oxide removal rate</td>
<td>(Å/min)</td>
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<tr>
<td>Polishing time</td>
<td>(min)</td>
</tr>
<tr>
<td>Pad pressure</td>
<td>(psi)</td>
</tr>
<tr>
<td>Pad rotation</td>
<td>(rpm)</td>
</tr>
<tr>
<td>Wafer rotation</td>
<td>(rpm)</td>
</tr>
</tbody>
</table>
Advantages:

- easy start and stop
- less sensitive to small changes in temperature
- large variety of chemistry, anisotropic etch with tunable anisotropy and selectivity can be achieved
Plasma etching

- DC plasma (glow discharge)
Plasma etching

- RF plasma
High-Pressure Plasma Etching

- Historically, the first plasma systems
- high pressure, typically 500mTorr
- mean free path shorter than the chamber size, low ion energy
- etch process depends primarily on the chemistry

Example: CF$_4$ plasma

\[ C \vee F + Si \vee Si = Si - F + 17 \text{kJ/mol} \]

105 kJ/mol  42 kJ/mol  130 kJ/mol

net positive energy (from collision with high-energy electrons) is required for the reaction
High-Pressure Plasma Etching

- Mechanisms for Si etching in CF$_4$ plasma:

- Rate can be estimated by flux of reactive species (F$_2$, CF$_x$, x=1,2,3)

\[
J_n = \sqrt{\frac{n^2RT}{2\pi M}}
\]
High-Pressure Plasma Etching

SiO$_2$ etching:

$$F + F + Si + O = Si - F + -5Kcal / mol$$

- SiO$_2$ etching is more aggressive; selectivity Si/SiO$_2$ is 50:1 at room T, 100:1 at -30 ºC
- high concentration fluorine is preferable for high Si/SiO$_2$ selectivity
- preferred species CF$_4$, C$_2$F$_6$, SF$_6$
- small addition of oxygen improve both etch rates, large addition removes selectivity
High-Pressure Plasma Etching

• Anisotropic etch

Formation of hydrocarbon film can be encouraged by addition of hydrogen (H₂, CHF₃ etc.)
High-Pressure Plasma Etching

- Anisotropic etch
High-Pressure Plasma Etching

- Loading effect: etch rate in may plasma etches decreases with increase in the area of exposed film

\[ R = \frac{R_0}{1 + kA} \]

- End-point detection:
  - laser interferometry
  - mass spectrometry analysis of the gas composition
Ion Milling

- Accelerated ions of noble gases are used
- purely mechanical etching
- high directionality
- applicable to wide range of materials

Kaufman source

- independent control over ion and ion energy
- beam divergences 5° - 7°
- large ion currents over large area

$$j_{\text{max}} \approx K \sqrt{\frac{q V_t^{3/2}}{m I_g^2}}$$
Ion Milling

- typical problem during ion milling
Ion Milling

- Chemically assisted Ion-beam milling (CAIBE): reactive species are added to the beam (e.g. O$_2$)
- Ion-assisted chemical etch
Reactive Ion Etching (RIE)

- in RIE the wafer rests on the powered electrode that increases bombardment energy.
- the pressure is lower to improve plasma contact with the wafer

Typically
50mTorr
5kW/cm².
Reactive Ion Etching (RIE)

- Si etching in Cl plasma
Reactive Ion Etching (RIE)

- Sidewall passivation in HCl/O$_2$/BCl$_3$ plasma
Reactive Ion Etching (RIE)

• Problem during RIE
  – residual damage in the substrate after etch due to ion bombardment.
  – chemical contamination (due to polymerization; metallic impurities due to sputtering of chamber, electrodes etc., )

O₂ plasma cleaning followed by wet acid cleaning and H₂ plasma treatment
Reactive Ion Etching (RIE)

• Problem during RIE
  – residual damage in the substrate after etch due to ion bombardment.
  – chemical contamination (due to polymerization; metallic impurities due to sputtering of chamber, electrodes etc, )

  carbon can penetrate as deep as 300Å (forming Si-C bonds), hydrogen as deep as several microns.
  Solution: Cleaning + Annealing

  O₂ plasma cleaning followed by wet acid cleaning and H₂ plasma treatment
Summary dry etching

< 100 MILLITORR

PHYSICAL SPUTTERING
(and Ion Beam Milling)

- Physical momentum transfer
- Directional etch (anisotropic) possible
- Poor selectivity
- Radiation damage possible

100 MILLITORR RANGE

RIE (Halocarbon Gas)

- Physical (ion) and chemical
- Directional
- More selective than sputtering

HIGHER PRESSURE

PLASMA ETCHING

- Chemical, thus faster by 10-1000X
- Isotropic
- More selective
- Less prone to radiation damage

HIGHER EXCITATION ENERGY
Lift Off

- Process sequence
Lift Off

- resist profiles after different treatment
Problem:

- You have to machine an orifice 10 x 10 um through a Si wafer (520um thick). What should be the size of the mask on the back side? How long will it take? You are going to use KOH solution with etching rates 5nm/min in \{111\} planes and 2um/min for \{100\} planes.
- 11.2
- 11.3