Lecture 7 Dry Etching Techniques

- **Introduction**
  1. Pattern transfer by dry etching:
     Using either a reactive gas or plasma (atoms or radical species) to react with surface to form volatile compounds, or energetic ions to bombard out atoms from surface. The process is in dry state.

  2. Five basic types of dry etching
     a. Gas Phase etching (Non-plasma base)
     b. Sputtering etching (plasma base)
     c. Plasma etching (plasma base)
     d. Ion-enhanced Energetic (plasma base)
     e. Ion-enhanced inhibitor (plasma base)

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Fig. 8-2 Processes taking place during plasma etching (from [2], reprinted with permission from *Plasma Etching*, p. 93, 1989).
3. The mechanisms of the etching processes can be classified into chemical and physical etching. a. and c. are fully chemical etching process, b. is fully physical etching, while d. and e. are the combination of chemical and physical processes.

4. Chemical etching is typically isotropic, of high etching rate, of high selectivity, and of low substrate damage.

5. Sputtering, a physical process, is caused by surface bombardment with high-energy ions, providing anisotropic etching, but with poor selectivity, high surface damage, and low etching rate.

6. Advantages of dry etching:
   a. Control of under cut and pattern size is feasible.
   b. Photoresist adhesion is not a sever problem as in wet etching processes.
   c. An-isotropic and high aspect ratio patterns are possible.
   d. Better uniformity
   e. Less waste

7. Plasma based etching
   a. Plasma consists of ions, electrons, and free radicals
   b. Reactive species are produced by feeding etchant gas into a glow discharge at pressures from 0.001-10 torr.
   c. The important electron-gas and gas-gas reactions:

   **Excitation:** \( \text{A}_2 + \text{e}^- \rightarrow \text{A}_2^* + \text{e}^- \)

   **Dissociation:** \( \text{A}_2 + \text{e}^- \rightarrow 2\text{A} + \text{e}^- \)

   **Electron Attachment:** \( \text{A}_2 + \text{e}^- \rightarrow \text{A}_2^- \)

   **Dissociative Attachment:** \( \text{A}_2 + \text{e}^- \rightarrow \text{A} + \text{A}^- \)

   **Ionization:** \( \text{A}_2 + \text{e}^- \rightarrow \text{A}_2^+ + 2\text{e}^- \)
Photoemission: \( A_2^* \rightarrow A_2 + h\nu \)

Abstraction: \( A + B_2 \rightarrow AB + B \)

d. Many species are metastable and have short lifetime. Usually free radicals are a major reactant species in dry etching processes.

e. Most commonly used species, in descending order of reactivity: O~F>C>Cl>Br

f. If the lifetime is sufficiently large, the species can diffuse to the substrate where it adsorbs and react with the surface. Process will proceed if the product is volatile and can be pump away, otherwise will stop.

g. Three important steps: (1) generation of active species (2) transport to the substrate (3) removal of reaction products from the surface.

8. The degree of isotropic etching:

\[ D_{ie} = \frac{l_u}{d_e} \]

\( l_u \): amount of undercut
\( d_e \): thickness of etched layer

Fig. 8-1 Types of plasma etching: (a) isotropic etch; (b) sloped wall via etch; (c) vertical wall (anisotropic etch).
Gas phase etching

Gas phase etcher

1. XeF₂ etching

\[ 2\text{XeF}_2 + \text{Si} \rightarrow 2\text{Xe} + \text{SiF}_4 \]

- a. Crystal sublimate into gas which etches silicon surface.
- b. Isotropic etching, controlled by temperature and pressure
- c. High etching rate: 3-10 µm/min for silicon at around 1 torr.
- d. High selectivity to SiO₂, Si₃N₄, Al, PR…
- e. Very sensitivity to moisture, forming HF which attack many materials.
- f. Good for post CMOS process
- g. Produce a rough surface ~couple µms. Pulsing can improve a little.

2. Inter-halogen (BrF₃, ClF₃) etching:
   a. Isotropic etching
   b. High etching rate (similar to XeF₂) for silicon.
   c. High selectivity to SiO₂, Si₃N₄, Al, PR…
   d. Smooth surface (~50 nm)
   e. Corrosive gas
Sputtering etching

1. Carried in a self-sustained glow discharge which is created by the breakdown of a heavy inert gas such as argon.
2. Multiplied electrons reach the anode and $\text{Ar}^+$ ions bombard the cathode, and hence the substrate atoms are sputtered by momentum transfer.
3. d.c. sputtering suitable for only conductors, but r.f. sputtering can be used for both conductors and insulators.
4. To have larger voltage drop on cathode during r.f. sputtering, cathode can be made smaller than anode.
5. r.f. discharge is more efficient in promoting and sustaining the plasma discharge, thus can be operated at lower pressure.

\[
\frac{V_c}{V_A} = \left(\frac{A_A}{A_C}\right)^n
\]

, usually $n \sim 1-4$, $A$: area, $V$: voltage

Fig. 8.2 Sputtering in a d.c.-excited glow discharge.
Plasma etching

1. Fundamentals
   a. Performed under low ion bombardment and caused mainly by chemical reactions with plasma species.
   b. Physical etching is negligible and process is isotropic.
   c. Performed at high pressure: larger than 0.1-1 torr.
   d. Substrates are placed on ground electrode with low potential and with weak ion bombardment.
   e. Three type reactors: barrel, parallel plate, downstream type:

![Diagram of a barrel reactor.]

![Plasma etching in a parallel plate reactor.]

Fig. 4-4 Diagram of a barrel reactor.

Fig. 8-3 Plasma etching in a parallel plate reactor.
2. Mechanisms

Three steps:

(1) Active species are formed in the plasma from non-reactive gases

(2) Active species formed in the plasma adsorb on and react with the surface to form volatile products.

(3) Volatile products are pumped out. (temperature usually less than 100 °C)

Reactions in CF₄ Plasma:

\[ 2e + 2\text{CF}_4 \rightarrow \text{CF}_3 + \text{CF}_2 + 3\text{F} + 2e \]  \hspace{2cm} (1)

(e+halocarbon \(\rightarrow\) saturated species+unsaturated species+atoms)

\[ \text{F} + \text{CF}_2 \rightarrow \text{CF}_3 \]  \hspace{2cm} (2)

(reactive atoms, molecules+unsaturated species \(\rightarrow\) saturated species)
4F+Si → SiF$_4$ \hspace{1cm} (3)

(atoms + surface → chemisorbed layer + volatile products)

nCF$_2$ + surface → (CF$_2$)$_n$ \hspace{1cm} (4)

(unsaturated species + surfaces → films)

If (3) dominates → etching occurs,
If (4) dominates → passivation occurs

3. Loading effects
   a. Most isotropic etching exhibits a loading effect: high consumption rate of the etchant by the etched film causing the depletion of the active etchant.
   b. If the depletion is by surface reactions, then small increases in flow rates will cause large increases in etching rate. ==> reaction limited, small features etched faster than the large ones. (compare 10 µm window to a 1mm window)
   c. At end point, the etching rate increase drastically, posing large lateral etching.
   d. If etching area is very large, the etching rate is inversely proportional to wafer areas.
   e. Transportation limitations (such as diffusion controlled reactions), lead to localized depletion of etchant (local loading), causing etching non-uniformity => diffusion limited, very small features will be etched slower than the normal ones (compare 1 µm window to a 10 µm window).
   f. The loading effect can be reduced by choosing correct pressure and flow rate. High flow rate can reduce the problem but not change much etching rate.

* Reactive ion etching
1. Fundamentals
   a. Most used dry etching technique, based on the combination of chemical activity of reactive species generated in the plasma with physical effects caused by ion bombardment.
   b. Negative DC bias is generated on the sample electrode, by applying RF power to the electrode.
   c. High-energy ion bombardment (300-700 V) by large negative potentials established on the power electrodes (wafers) than the ground electrodes.
   d. Lower operation pressure: 10-200 mtorr (usually lower than 0.1 torr).

![Diagram of reactive ion etching.](image)

Fig. 8-5 Diagram of reactive ion etching.

2. Mechanisms of RIE
   a. Model for Ion enhanced etching:
      (1) Chemically enhanced physical sputtering model:
         higher sputtering yield produced by chemical modification of surface
      (2) Damage model: lattice damage by ion bombardment enhances the reaction rate of the etchant species with the substrate.
(3) Chemical sputtering model: collision cascade energy induced by ion bombardment increases the mobility of molecules which form volatile products and desorb from the substrate.

b. First model is widely accepted for fluorine silicon system

c. Most of the VLSI materials react with halogen (卤素) atoms to form volatile compounds: Si, SiO\textsubscript{2}, Si\textsubscript{3}N\textsubscript{4}, GaAs, polyimide, photoresist, Al, W, Mo, and Ti can be dried etched in a plasma.
4. Anisotropy

a. Etch directionality is generally achieved by input of direct energy on the surface exposed to a chemical etchant, supplied by ion, electron, and photo bombardment. Heavy ion CR$_3^+$ is usually used in RIE.

b. The etching slope is defined:

\[
\frac{X}{Z} = \frac{V_x}{V_z}
\]

$V_x$: etching rate at zero bias, $V_z$: etching rate at applied negative bias.

c. SF$_6$ plasma provides high rates of isotropic etching, while Cl$_2$ plasma yields lower etching rate but better profile control.

d. By adjusting etching parameters, etching can be change between isotropic or anisotropic.

![Diagram showing etched profile](image-url)
5. Side wall passivation

a. Etching rate: n type silicon > silicon > p-type silicon
b. Silicon can be etched by chlorine or bromine plasmas only under ion bombardment.

c. Sidewall passivation (blocking): adding oxygen to chlorine plasma, a film, mainly stoichiometric SiO₂, can grow on the sidewall. While features bottom is bombarded by ions.
d. If the fed gas is halogen deficient, carbon-containing species polymerize can form a protective film that stops the etching of the substrate almost complete, while the bottom is ion-bombarded to prevent the formation of polymer films.
e. Addition cleaning step is required to remove the sidewall film for further process.

Fig. 8-7 A model for sidewall film formation in a HCl/O₂/BCl₃ RIE (from [20], reprinted with permission).
6. selectivity

a. Different rates of the processes taking place on the different materials.

b. CF$_4$+H$_2$ or CHF$_3$ plasma can have selectivity between Si and SiO$_2$

c. Fluorine-contained plasmas can be changed from etching to polymerization, depending on the F/C ratio.

d. Adding Oxygen in CF$_4$, which from CO, CO$_2$, COF, and COF$_2$, increases the F/C ratio, increases the etching rate of silicon.

e. Adding hydrogen in CF$_4$, scavenging fluorine atoms, thus block silicon surface with fluorocarbon. But SiO$_2$ has oxygen to provide for CO or CO$_2$ formation, thus can still remained etched. => used for the selective etching of silicon dioxide over silicon.

f. Etching rate for RIE usually less than 1µm/min,

Comparison of different etching techniques:
TABLE 8-1 Comparison of Different Etching Techniques (from [25], reprinted with permission)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>ICP</th>
<th>ECR</th>
<th>Helium</th>
<th>SPRP</th>
<th>MERIE</th>
<th>RIE</th>
<th>PE</th>
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<tbody>
<tr>
<td>Frequency</td>
<td>13.56 MHz</td>
<td>2.45 GHz</td>
<td>13.56 MHz</td>
<td>400 kHz</td>
<td>13.56 MHz</td>
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<td>Gas pressure (torr)*</td>
<td>~ 1 (^{-3})</td>
<td>~ 4 (^{-4})</td>
<td>~ 1 (^{-3})</td>
<td>~ 1 (^{-1})</td>
<td>~ 1 (^{-2})</td>
<td>~ 7 (^{-2})</td>
<td>~ 1 (^{-1})</td>
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<tr>
<td>Electron temperature (eV)</td>
<td>~ 4</td>
<td>~ 4</td>
<td>~ 4</td>
<td>~ 10</td>
<td>~ 5</td>
<td>~ 8</td>
<td>~ 8</td>
</tr>
<tr>
<td>Plasma density (cm(^3) ) *</td>
<td>~ 5 (^{11})</td>
<td>~ 3 (^{11})</td>
<td>~ 5 (^{11})</td>
<td>~ 8 (^{10})</td>
<td>~ 5 (^{10})</td>
<td>~ 1 (^{10})</td>
<td>~ 3 (^{8})</td>
</tr>
<tr>
<td>Ion current density (mA/cm(^2))</td>
<td>~ 10</td>
<td>~ 10</td>
<td>~ 10</td>
<td>~ 2</td>
<td>~ 1</td>
<td>~ 0.1</td>
<td>~ 0.1</td>
</tr>
<tr>
<td>Ion energy (eV)</td>
<td>Controllable</td>
<td>Controllable</td>
<td>Controllable</td>
<td>30–150</td>
<td>~ 200</td>
<td>200–1000</td>
<td>~ 20</td>
</tr>
</tbody>
</table>

ICP – inductively coupled plasma
ECR – electron cyclotron resonance
SPRP – split power reverse phase/rainbow 4500
MERIE – magnetically enhanced RIE
RIE – reactive ion etching
PE – plasma etching

* indicates ~ \times 10^n

* Etching of specific materials

Plasma gases used for etching of different materials

TABLE 8-2 Plasma Gases Used for Etching of Different Materials (from [26])

<table>
<thead>
<tr>
<th>Material</th>
<th>Gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>CF(_4)/O(_2), CF(_2)Cl(_2), CF(_3)Cl, SF(_6)/O(_2)/Cl(_2), Cl(_2)/H(_2)/C(_2)F(_4)/CCl(_4), C(_2)ClF(_2)/O(_2), SiF(_4)/O(_2), NF(_3), ClF(_3), CCl(_4), Cl(_2)/H(_2)/C(_2)F(_4)/O(_2), C(_2)ClF(_2)/O(_2), SiF(_4)/O(_2), CF(_2)Cl/Br(_2), CF(_3)Cl/Br(_2)</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>CF(_4)/H(_2), C(_2)F(_6), C(_2)F(_8), CHF(_3)/O(_2)</td>
</tr>
<tr>
<td>Si(_3)N(_4)</td>
<td>CF(_4)/O(_2)/H(_2), C(_2)F(_6), C(_2)F(_8), CHF(_3)</td>
</tr>
<tr>
<td>Organics</td>
<td>O(_2), CF(_4)/O(_2), SF(_6)/O(_2), CHF(_3)</td>
</tr>
<tr>
<td>Silicides</td>
<td>CF(_4)/O(_2), NF(_3), SF(_6)/Cl(_2), CF(_4)/Cl(_2)</td>
</tr>
<tr>
<td>Al</td>
<td>BCl(_3), BCl(_3)/Cl(_2), CCl(_4)/Cl(_2)/BCl(_3), SiCl(_4)/Cl(_2)</td>
</tr>
<tr>
<td>Cr</td>
<td>Cl(_2), CCl(_4)/Cl(_2)</td>
</tr>
<tr>
<td>Mo, Nb, Ta, Ti, W</td>
<td>CF(_4)/O(_2), SF(_6)/O(_2), NF(_3)/H(_2)</td>
</tr>
<tr>
<td>Au</td>
<td>C(_2)Cl(_2)/C(_2)Cl(_4), Cl(_2), CCl(_3)</td>
</tr>
<tr>
<td>GaAs</td>
<td>BCl(_3)/Ar, Cl(_2)/O(_2)/H(_2), CCl(_4)/Cl(_2)/O(_2)/Ar/He, CCl(_4)</td>
</tr>
<tr>
<td>InP</td>
<td>CH(_4)/H(_2), C(_2)H(_6)/H(_2), Cl(_2)/Ar</td>
</tr>
</tbody>
</table>
1. Silicon and Polysilicon Etching
   a. CF$_4$ and SF$_6$ are usually used for etchant. But may cause residue. Adding oxygen to reduce residue.
   b. NF$_3$ and ClF$_3$ do not form residue.
   c. Chlorine and Bromine atoms are used in RIE for anisotropic etching of silicon, because these gases can not etch silicon at room temperature without the assistance of ion bombardment.

2. Silicon dioxide and silicon nitride
   a. selective silicon dioxide etching: using CF$_4$+H$_2$, C$_2$H$_4$ or CH$_4$.

3. Metals
   a. Al, W, Mo and Ti can be etched.
   b. Require a first step to remove metal oxide-using ion bombardment.
   c. Prevent water vapor and oxygen in chamber to form metal oxide again.
   d. Al, Cr using chlorine based etchant.

References: