Lecture 7 Dry Etching Techniques

- **Introduction**

1. Pattern transfer by dry etching:
Using <u>either</u> a reactive gas or plasma (atoms or radical species) to react with surface to form volatile compounds, <u>or</u> 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)

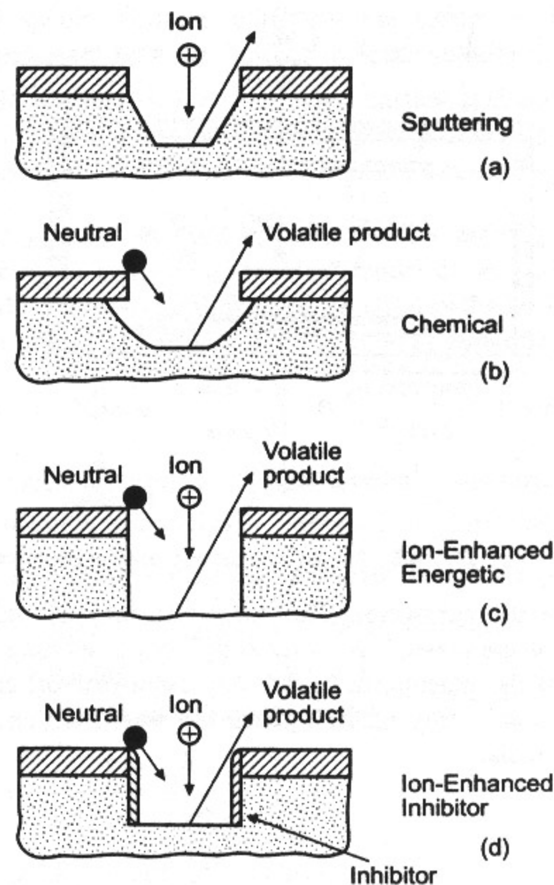


Fig. 8-2 Processes taking place during plasma etching (from [2], reprinted with permission from *Plasma Etching*, p. 93, 1989).

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:**

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>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

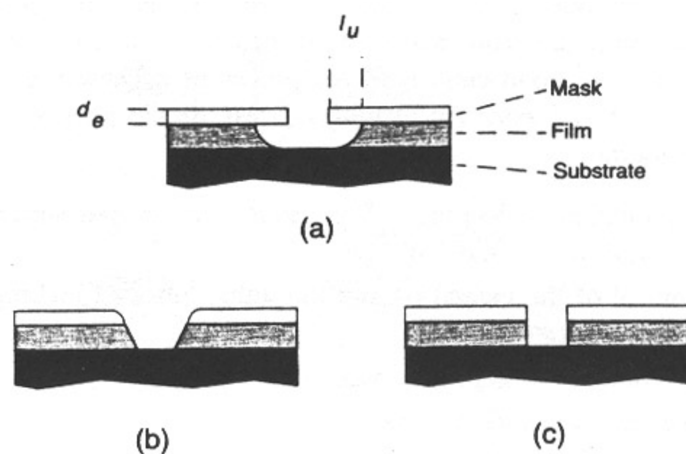
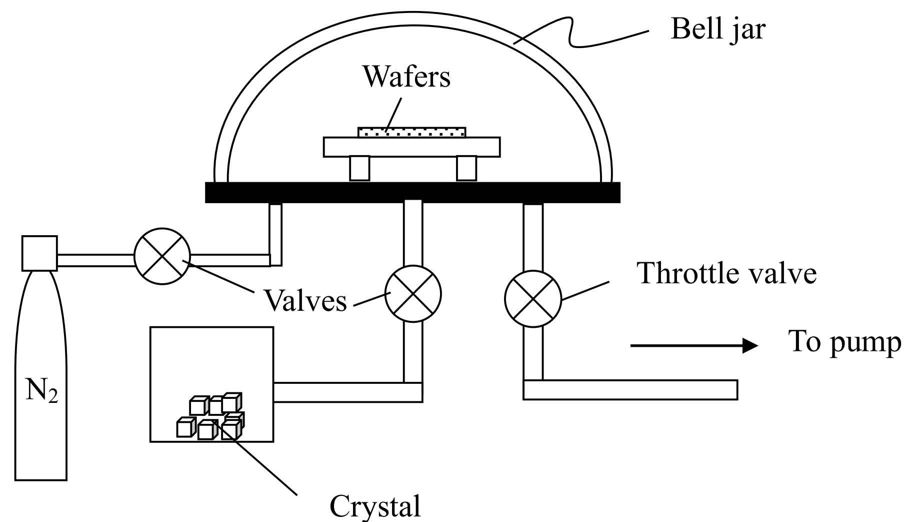


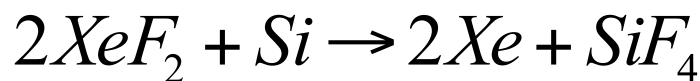
Fig. 8-1 Types of plasma etching: (a) isotropic etch; (b) sloped wall via etch; (c) vertical wall (anisotropic etch).

- **Gas phase etching**

Gas phase etcher



1. XeF_2 etching



$$2XeF_2 + Si \rightarrow 2Xe + SiF_4$$

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 SiO_2, Si_3N_4, 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 (BrF_3, ClF_3) etching:
a. Isotropic etching
b. High etching rate (similar to XeF_2) for silicon.
c. High selectivity to SiO_2, Si_3N_4, 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 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~1-4, A: area, V: voltage**

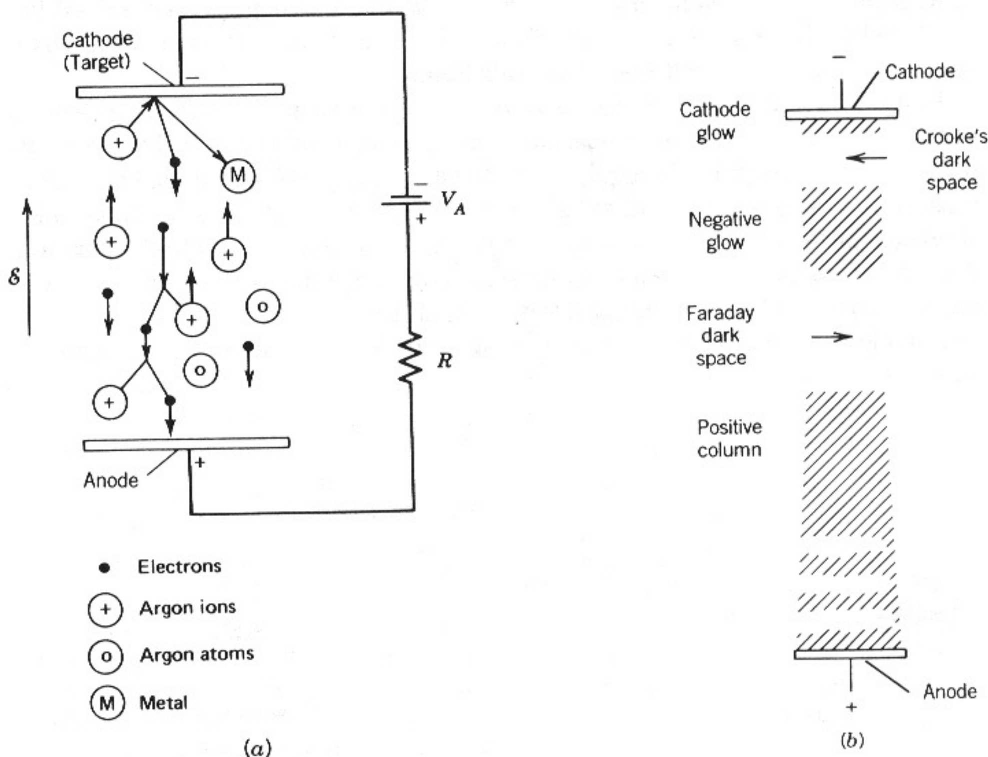


Fig. 8.2 Sputtering in a d.c.-excited glow discharge.

- **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:**

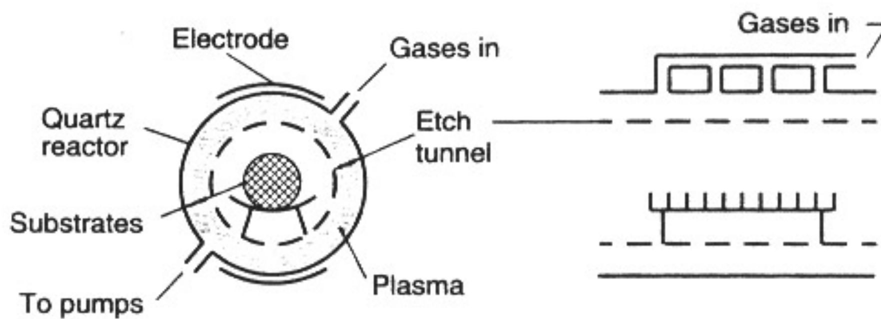


Fig. 4-4 Diagram of a barrel reactor.

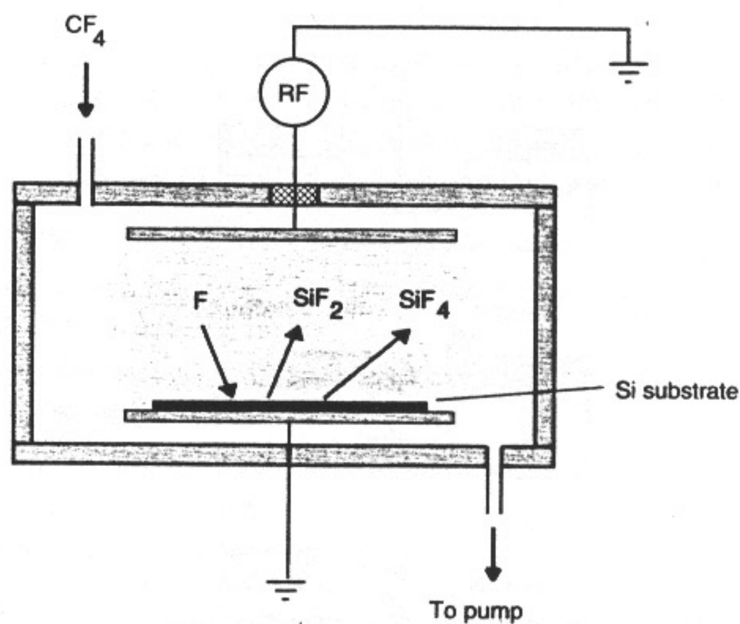


Fig. 8-3 Plasma etching in a parallel plate reactor.

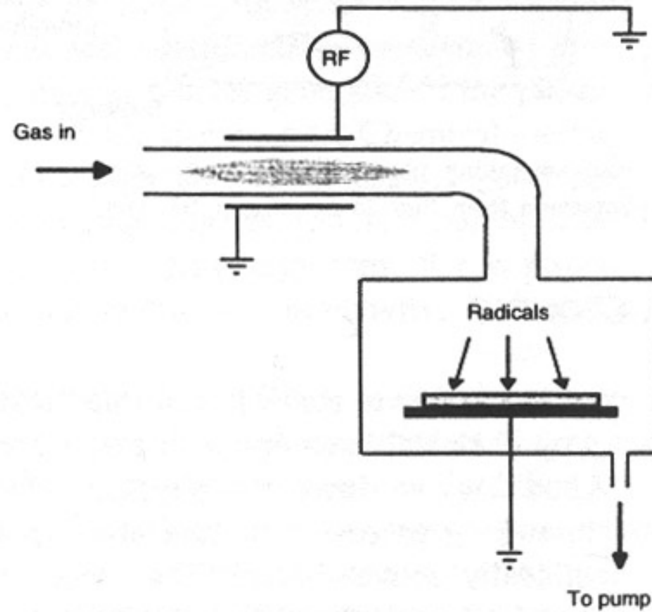


Fig. 8-4 Plasma etching in a downstream configuration

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 CF_4 Plasma:

$$2e+2CF_4 \rightarrow CF_3+CF_2+3F+2e \qquad (1)$$

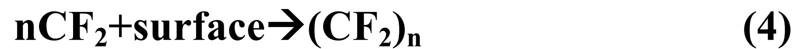
(e+halocarbon→saturaed species+unsaturated species+atoms)

$$F+CF_2 \rightarrow CF_3 \qquad (2)$$

(reactive atoms, molecules+unsaturated species→saturated species)

$$4F + Si \rightarrow SiF_4 \quad (3)$$

(atoms+surface→chemisorbed layer+volatile products)



$$nCF_2 + surface \rightarrow (CF_2)_n \quad (4)$$

(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).

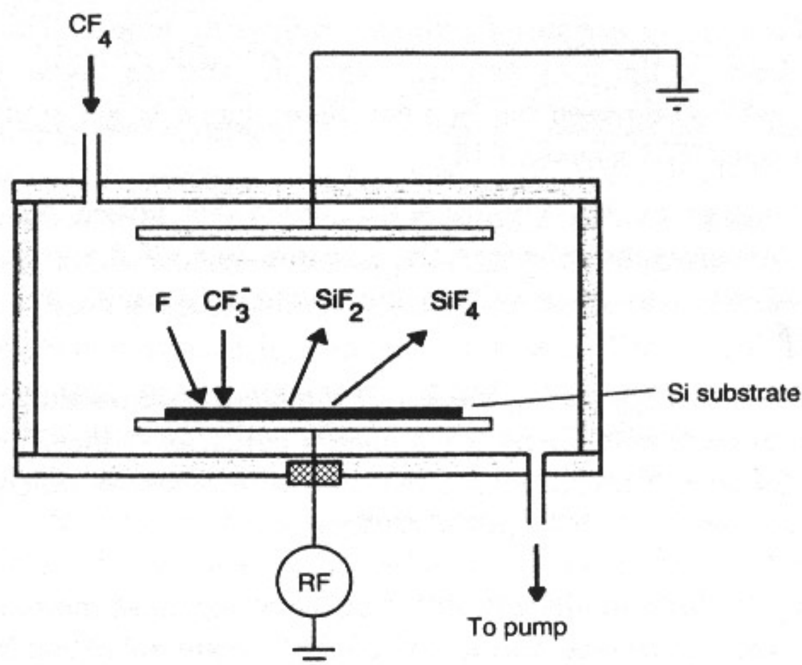


Fig. 8-5 Diagram of reactive ion etching.

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 (鹵素) atoms

to form volatile compounds: Si, SiO_2, Si_3N4, 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 ansisotropic.**

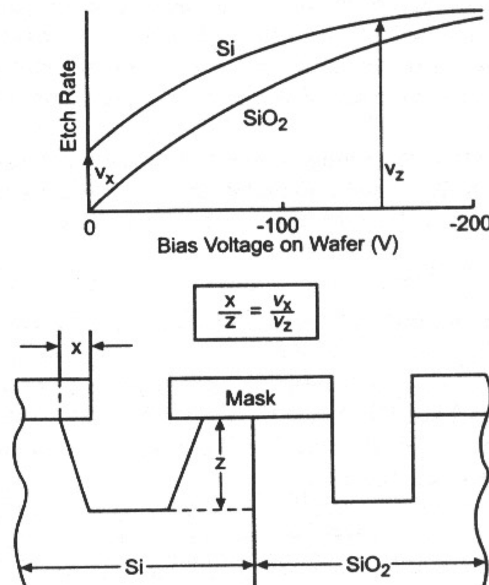


Fig. 8-6 Shape of etched profile as a function of etching rate dependence on substrate bias (from [16], reprinted with permission from S. Veprek and M. Venugopalan, eds., *Topics in Current Chemistry, Plasma Chemistry III*, Berlin: Springer-Verlag, 1980).

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 SiO_2, 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.**

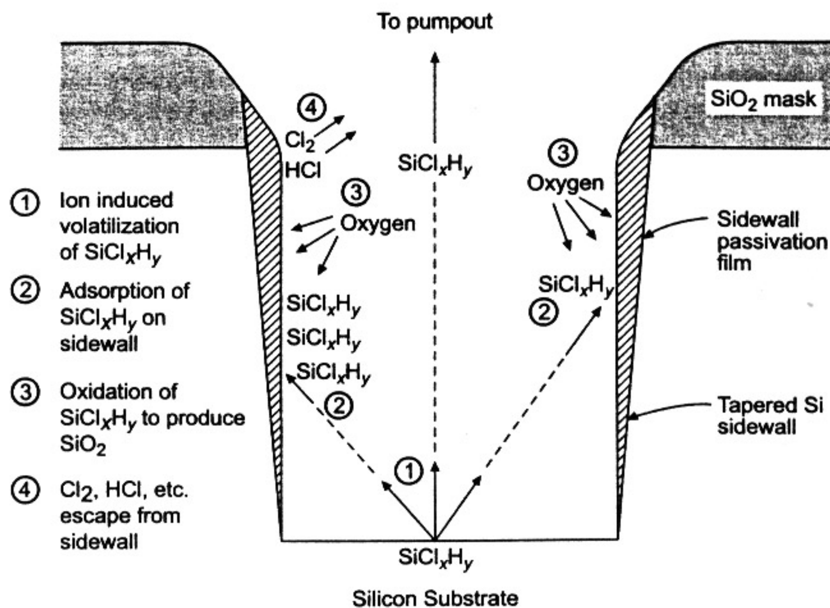


Fig. 8-7 A model for sidewall film formation in a $HCl/O_2/BCl_3$ RIE (from [20], reprinted with permission).

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.**

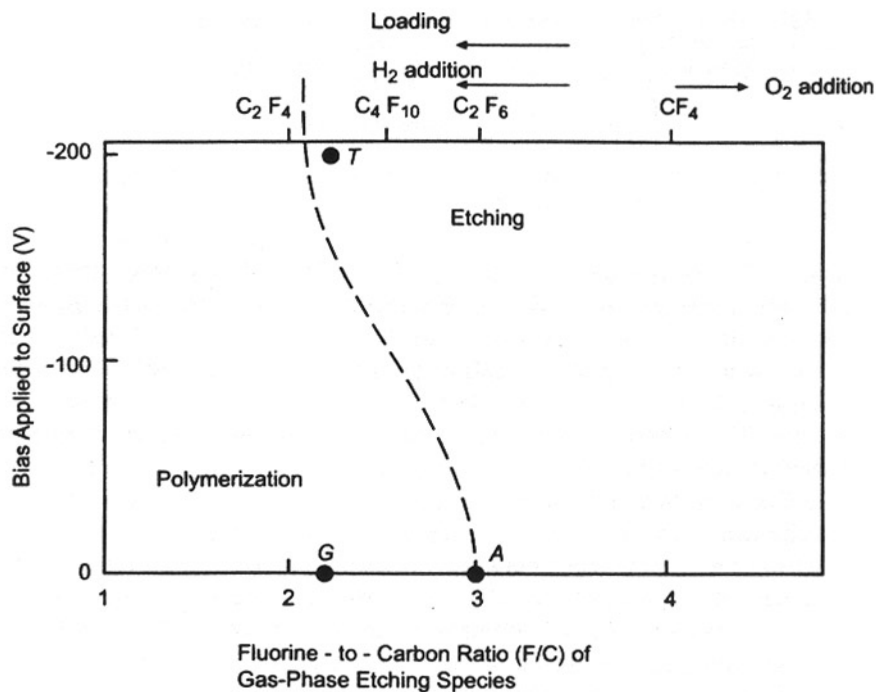


Fig. 8-8 Effect of plasma composition and bias on the etching/polymerization boundary (from [21], reprinted with permission).

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)

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

ICP – inductively coupled plasma
ECR – electron cyclotron resonance
SPRP – split power reverse phase/rainbow 4500
* indicates ~ $\times 10^x$
MERIE – magnetically enhanced RIE
RIE – reactive ion etching
PE – plasma etching

- **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])

Material	Gases
Silicon	CF_4/O_2, CF_2Cl_2, CF_3Cl, $SF_6/O_2/Cl_2$, $Cl_2/H_2/C_2F_6/CCl_4$, C_2ClF_5/O_2, SiF_4/O_2, NF_3, ClF_3, CCl_4, CCl_3F_5, C_2ClF_5/SF_6, C_2F_6/CF_3Cl, Br_2, CF_3Cl/Br_2
SiO_2	CF_4/H_2, C_2F_6, C_3F_8, CHF_3/O_2
Si_3N_4	$CF_4/O_2/H_2$, C_2F_6, C_3F_8, CHF_3
Organics	O_2, CF_4/O_2, SF_6/O_2
Silicides	CF_4/O_2, NF_3, SF_6/Cl_2, CF_4/Cl_2
Al	BCl_3, BCl_3/Cl_2, $CCl_4/Cl_2/BCl_3$, $SiCl_4/Cl_2$
Cr	Cl_2, CCl_4/Cl_2
Mo, Nb, Ta, Ti, W	CF_4/O_2, SF_6/O_2, NF_3/H_2
Au	$C_2Cl_2F_4$, Cl_2, $CClF_3$
GaAs	BCl_3/Ar, $Cl_2/O_2/H_2$, $CCl_2F_2/O_2/Ar/He$, CCl_4
InP	CH_4/H_2, C_2H_6/H_2, Cl_2/Ar

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_2H_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:

[1] Alfred Grill, "Cold Plasma in Materials Fabrication-from fundamentals to applications", IEEE press, New York, 1993.

[2] Sorab K. Ghandhi, "VLSI Fabrication Principles-silicon and gallium arsenide", John Wiley $ Sons, Inc, New York, 1994.