Lecture 7

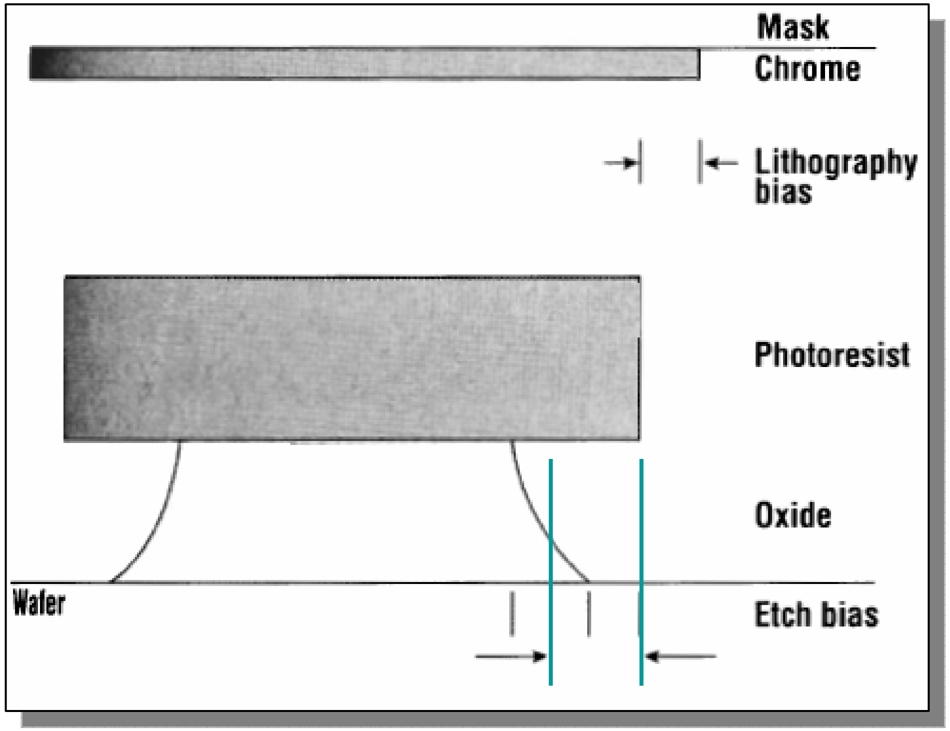
Etching

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



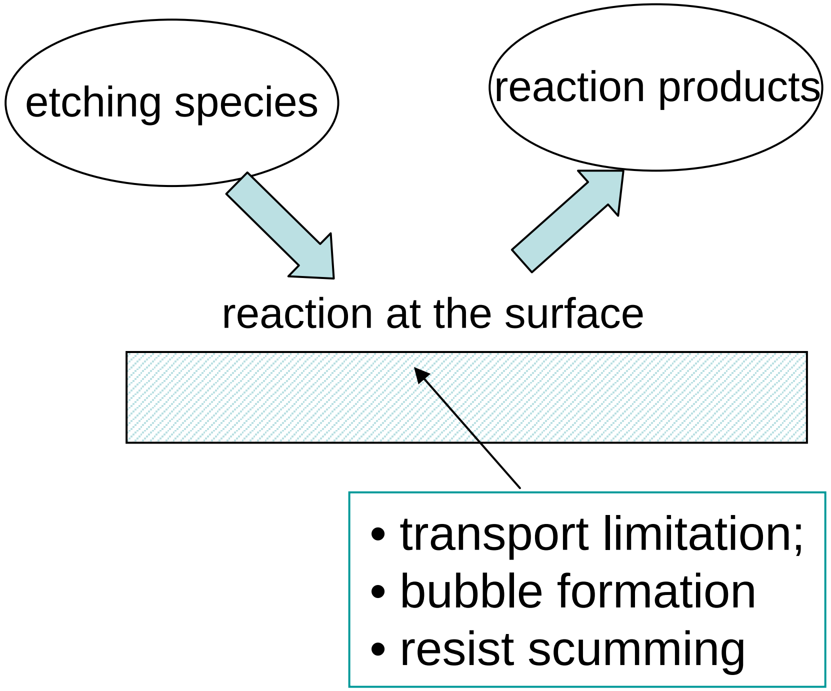
Wet etching

Advantages

- highly selective
- doesn't introduce damage

Drawbacks

- lack of anisotropy
- poor process control
- excessive particle contamination

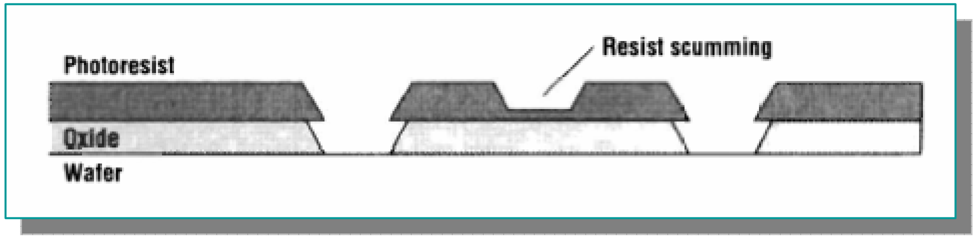


etching species

reaction products

reaction at the surface

- transport limitation;
- bubble formation
- resist scumming



Wet etching of SiO_2.

- Wet etching in dilute solutions of HF:
  6:1; 10:1 and 20:1 ($HF:H_2O$)

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

$$SiO_2 + 6HF \rightarrow H_2 + SiF_6 + 2H_2O$$

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

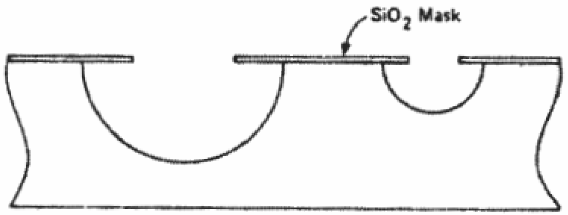
$$NH_4F \rightleftharpoons NH_3 + HF$$

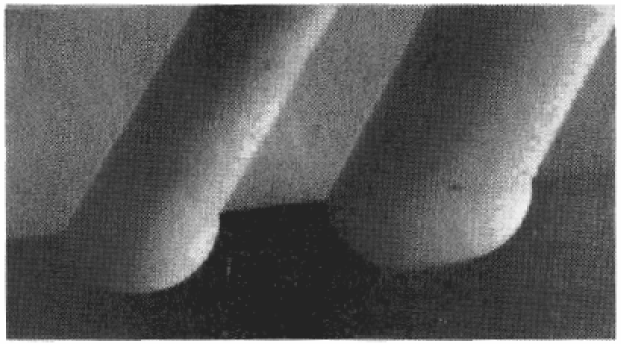
Etching rates:

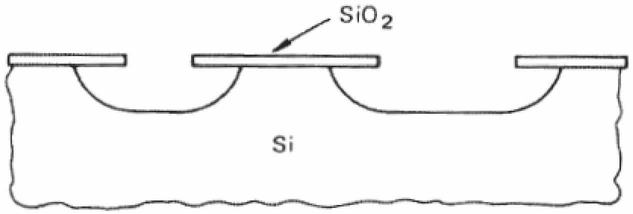
BHF 20:1:	thermal oxide	300 Å/min
	Si_3N_4	10 Å/min

Wet etching of SiO_2.

- Etched groove (with and without steering)







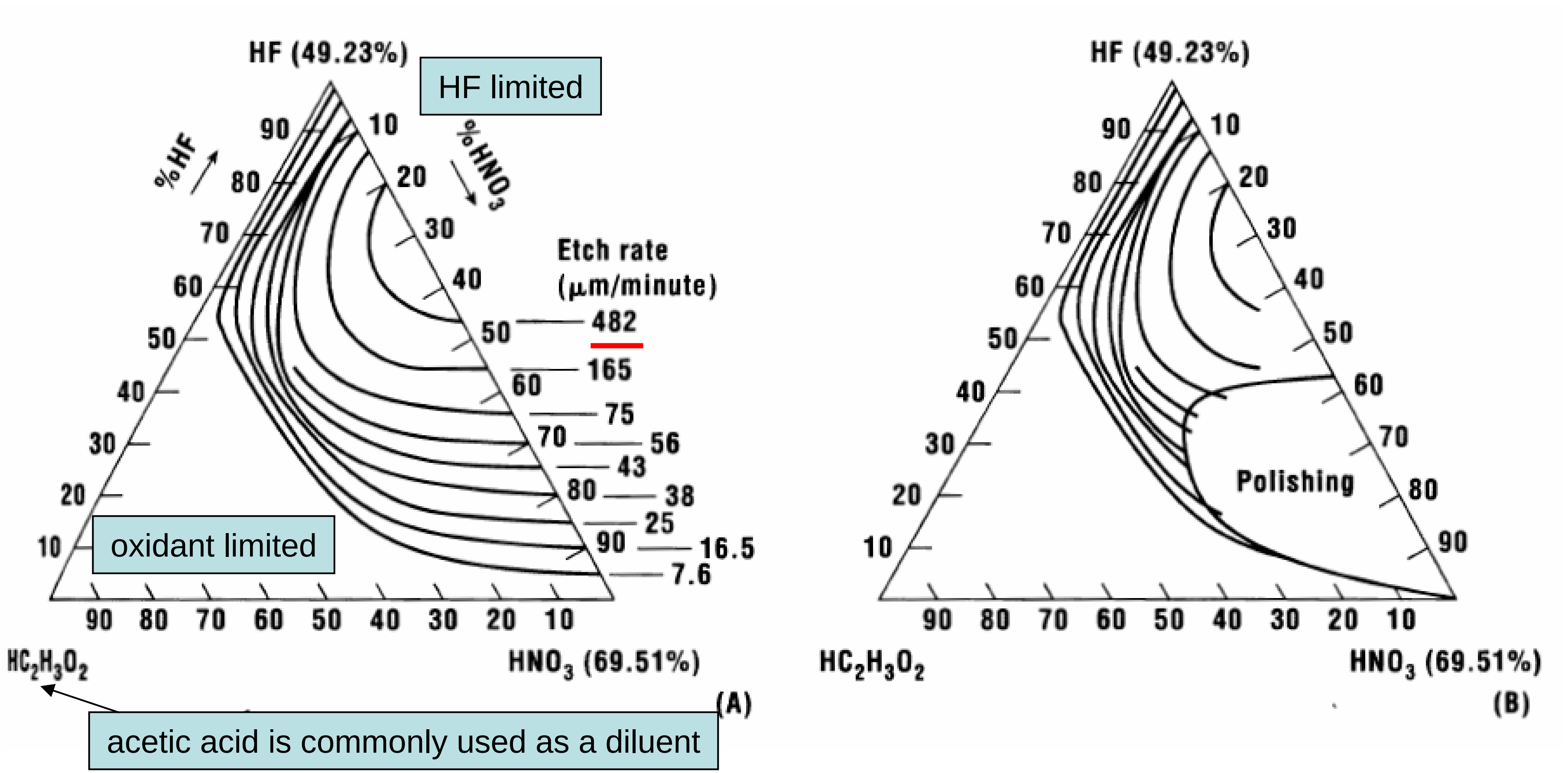
Other wet etching recipes

- Silicon Nitride (if oxidized at high T, oxide should be removed first)
  - H_3PO_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_3PO_4, 3% HNO_3.

Isotropic etching of Silicon

- Silicon etching (oxidation + HF)

$$Si + HNO_3 \rightleftharpoons H_2SiF_6 + HNO_2 + H_2 + H_2O$$



HF limited

oxidant limited

acetic acid is commonly used as a diluent

Wet etching of Si

$$Si + 2OH^- \rightarrow Si(OH)_2^{2+} + 4e^-$$

$$4H_2O + 4e^- \rightarrow 4OH^- + H_2$$

$$Si(OH)_2^{2+} + 4OH^- \rightarrow SiO_2(OH)_2^{2-} + 2H_2O$$

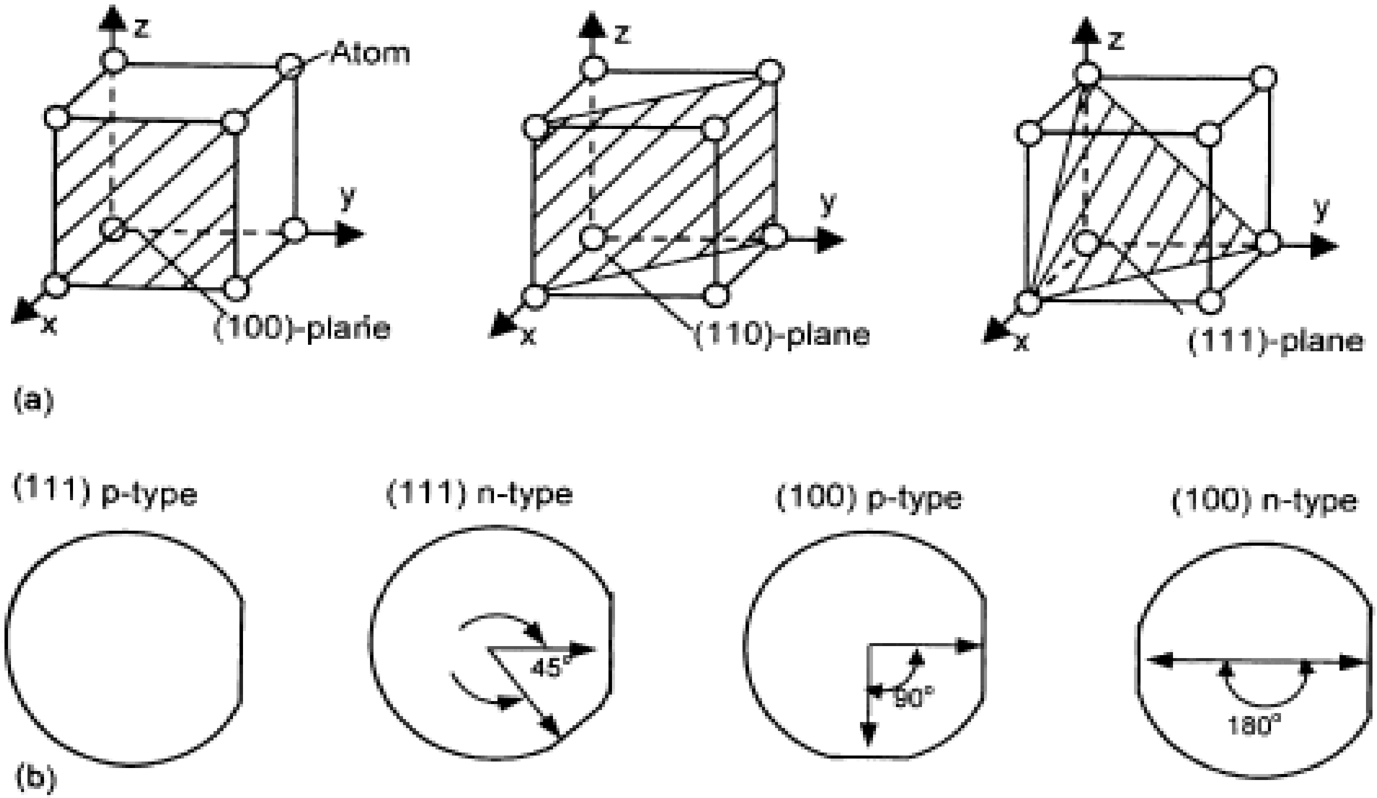
Types of etchants:

- Alkali hydroxide etchants: KOH, NaOH, CsOH, RbOH
- Ammonium hydroxide etchants: Nh_4OH, tertramethyl ammonium hydroxide (TMAH) $(CH_3)_4NOH$
- Other etchants: hydrazine/water, amine gallate etc.

Etch rate depends on the crystallographic orientation. Highly packed planes are the slowest to etch

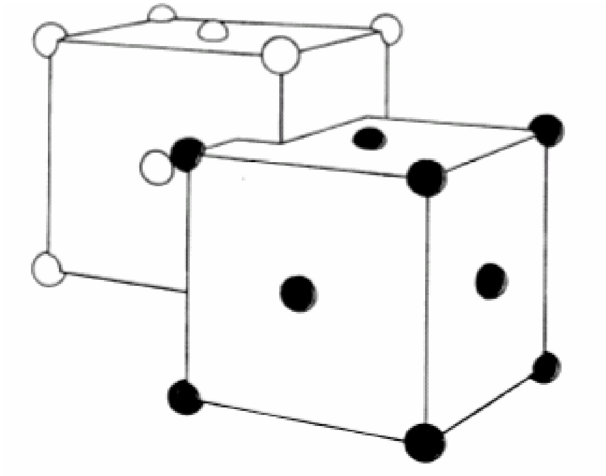
Anisotropic etching of Silicon

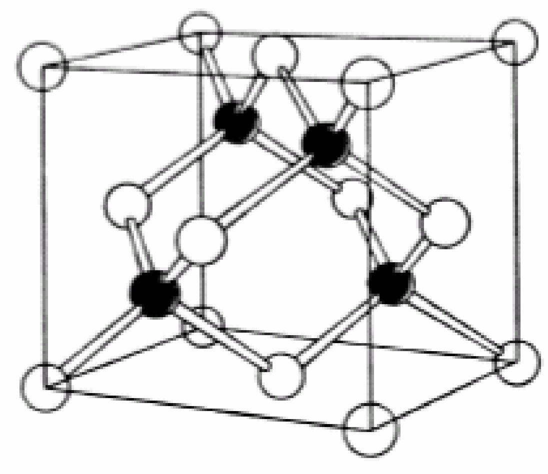
- Crystallographic orientations (Miller indices)



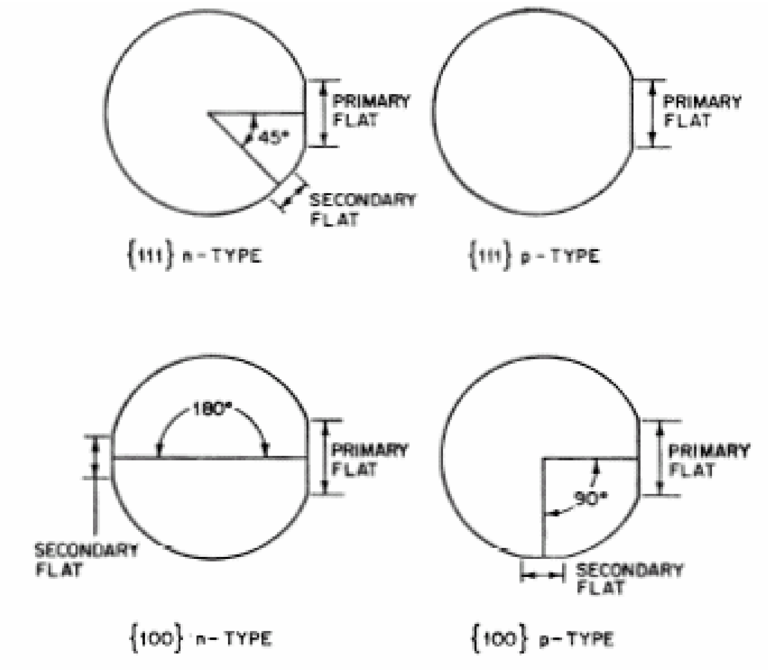
Anisotropic etching of Silicon

- Crystalline structure of Silicon
  - **Diamond like structure**



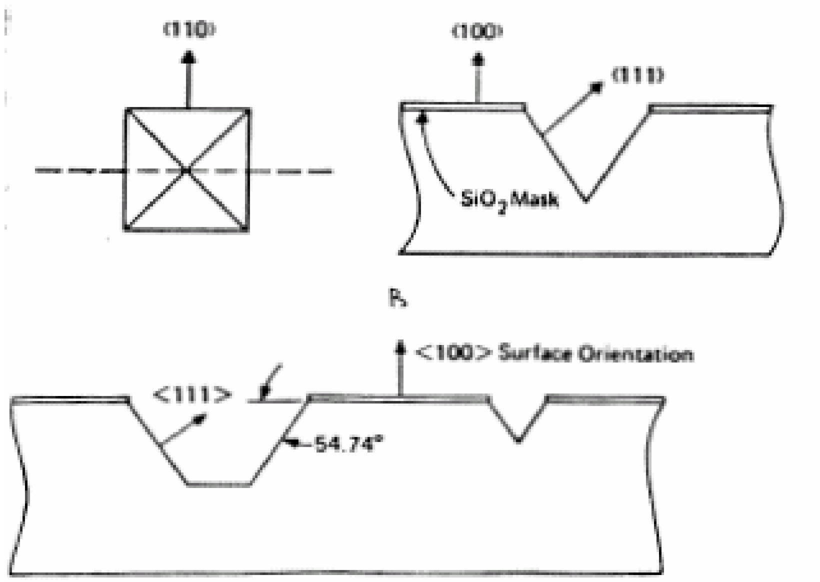


  - **Marking orientation on Silicon wafers**

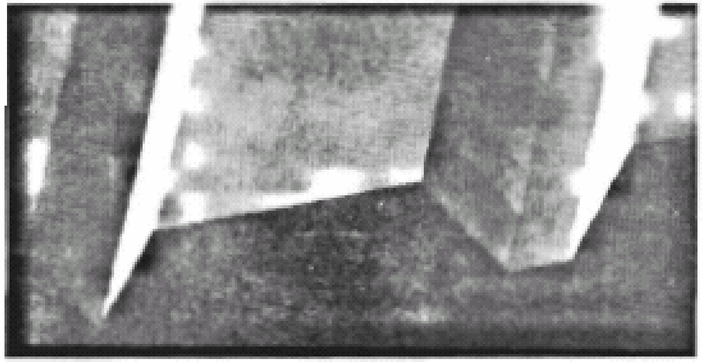


Anisotropic etching of Silicon

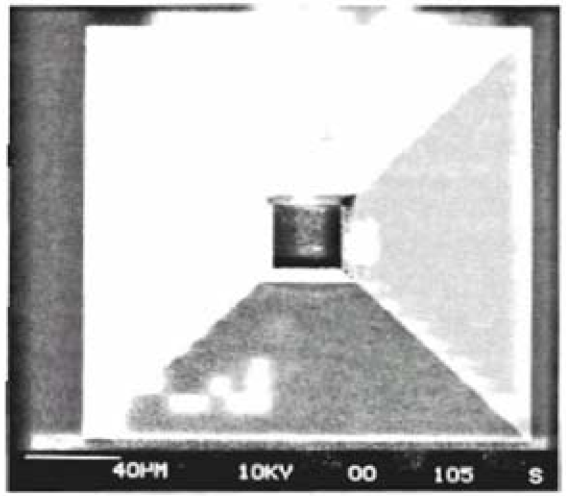
- Wet etching of (100) Silicon

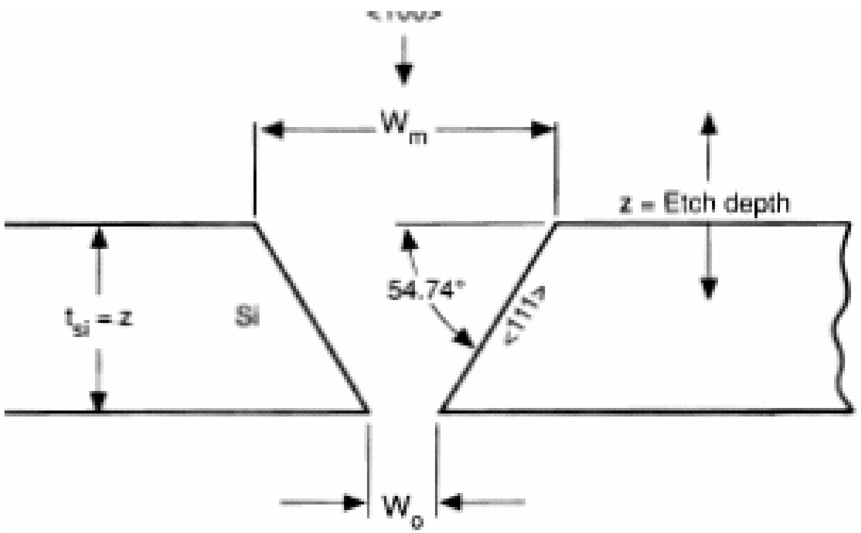


A



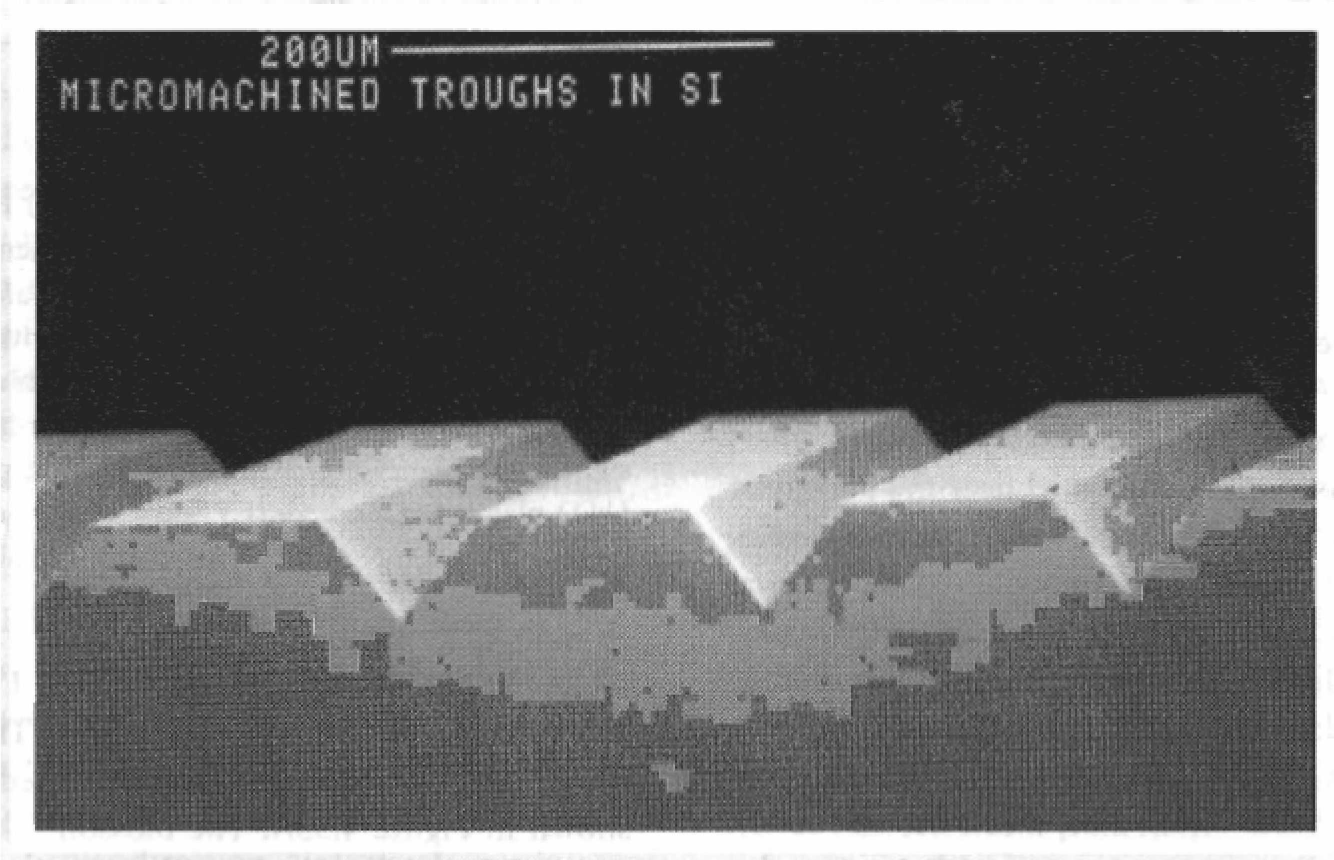
Orifice (A via through Si wafer)





Anisotropic Etching of (100) Silicon

Anisotropic etching of Silicon



Anisotropic etching of Silicon

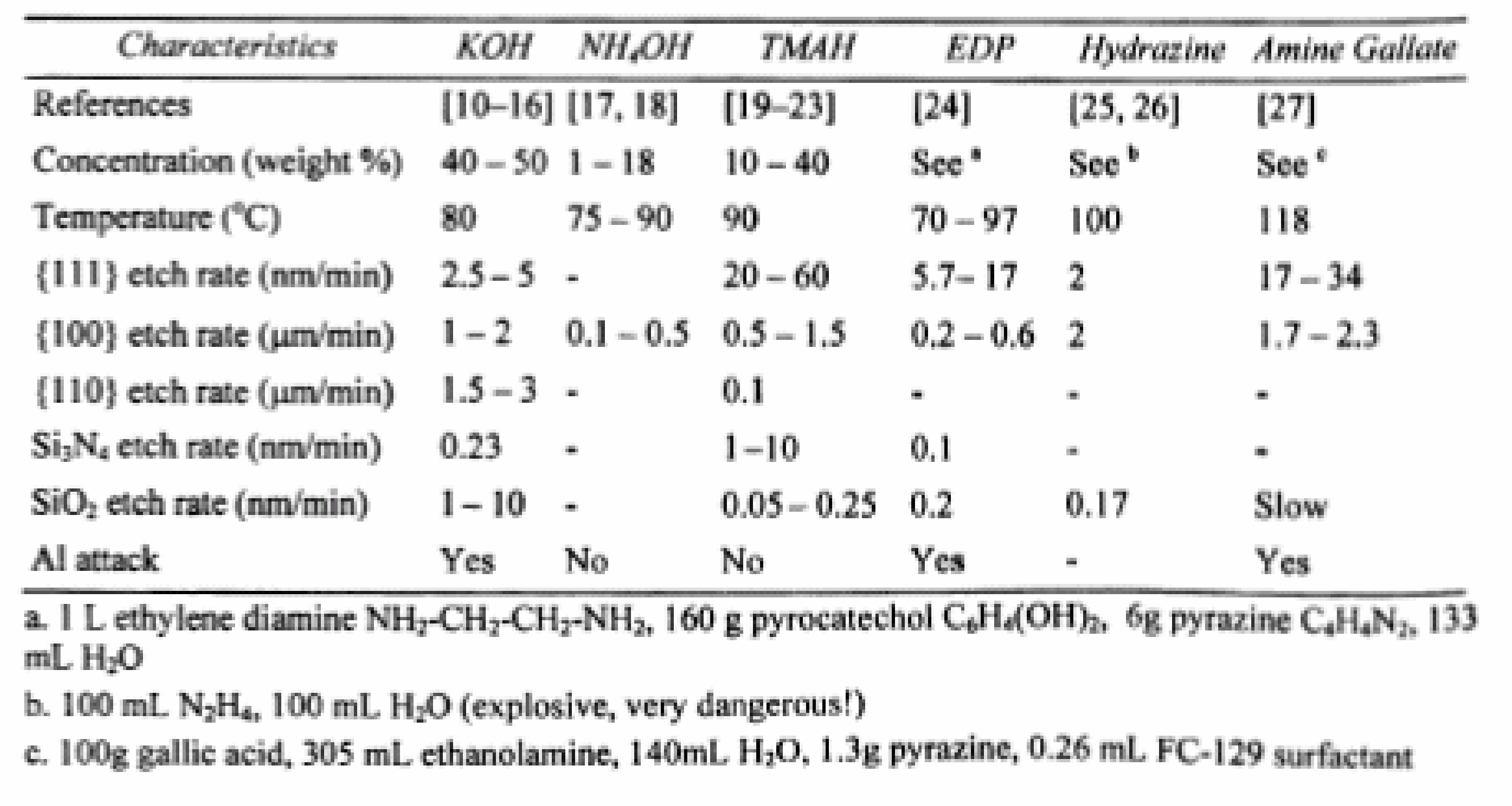
- Etching rate for many alkaline solutions is slow in (111) direction, so anisotropic etch with high aspect ratio can be achieved

- 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:
    $HF/HNO_3/CH_3COOH$ 1:3:8 – 15 times higher etch rate for heavily doped silicon (>10^{19} cm^{-3})
    ethylene-diamine-pyrocatehol-water etches lightly doped silicon without attacking heavily doped
  - Defect selective etchrate ratio (100)/(111) 100/1.

Anisotropic etching of Silicon

- Chracteristics of different etchants



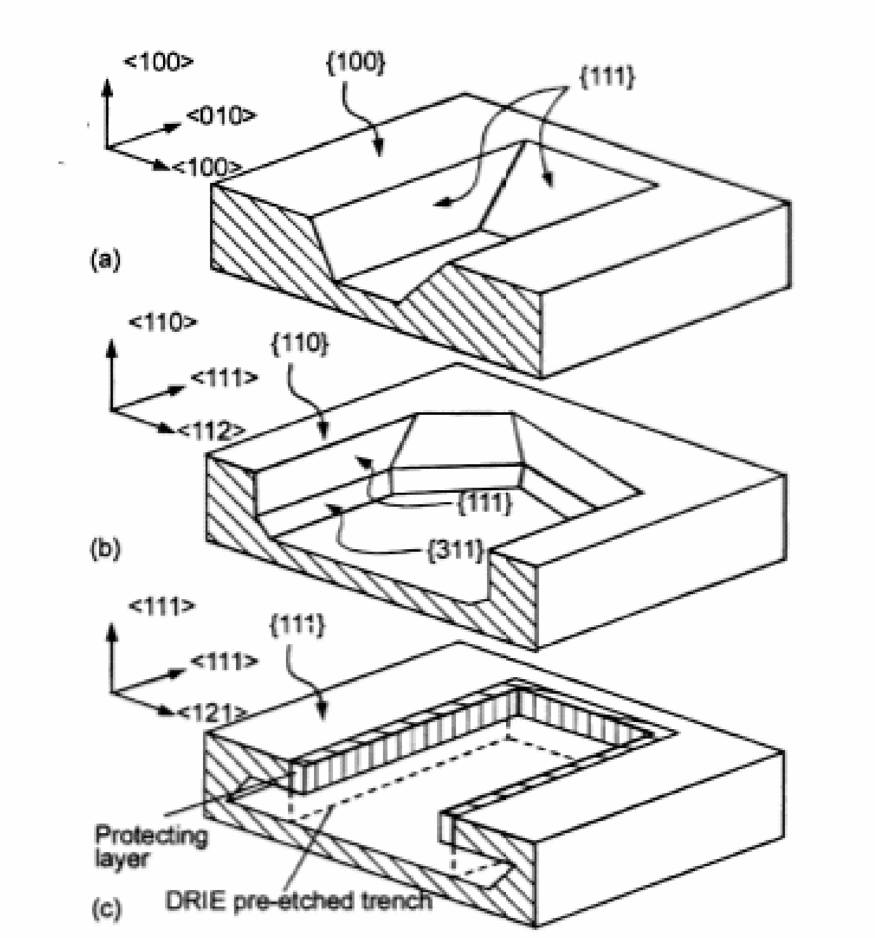
Characteristics	*KOH*	*NH_4OH*	*TMAH*	*EDP*	*Hydrazine*	*Amine Gallate*
References	[10–16]	[17, 18]	[19–23]	[24]	[25, 26]	[27]
Concentration (weight %)	40 – 50	1 – 18	10 – 40	See [a]	See [b]	See [c]
Temperature (°C)	80	75 – 90	90	70 – 97	100	118
{111} etch rate (nm/min)	2.5 – 5	-	20 – 60	5.7 – 17	2	17 – 34
{100} etch rate (μm/min)	1 – 2	0.1 – 0.5	0.5 – 1.5	0.2 – 0.6	2	1.7 – 2.3
{110} etch rate (μm/min)	1.5 – 3	-	0.1	-	-	-
Si_3N_4 etch rate (nm/min)	0.23	-	1 – 10	0.1	-	-
SiO_2 etch rate (nm/min)	1 – 10	-	0.05 – 0.25	0.2	0.17	Slow
Al attack	Yes	No	No	Yes	-	Yes

a. 1 L ethylene diamine NH_2-CH_2-CH_2-NH_2, 160 g pyrocatechol $C_6H_4(OH)_2$, 6g pyrazine $C_4H_4N_2$, 133 mL H_2O

b. 100 mL N_2H_4, 100 mL H_2O (explosive, very dangerous!)

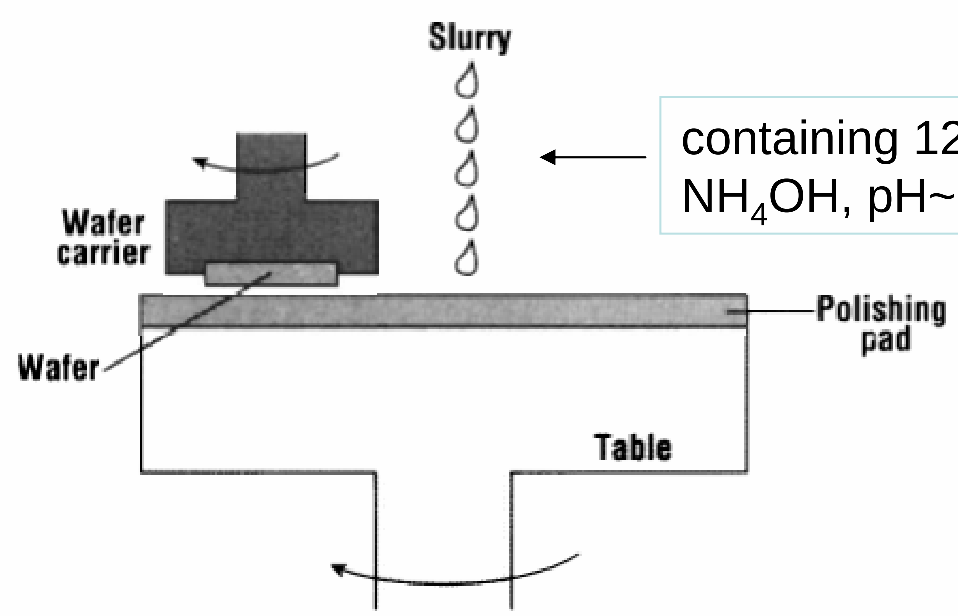
c. 100g gallic acid, 305 mL ethanolamine, 140mL H_2O, 1.3g pyrazine, 0.26 mL FC-129 surfactant

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_4OH, pH~10 to keep silica negatively charged

Resulting smoothness:

$$R_S = {}^3\!/_4\,\phi P/(2K_pE)$$

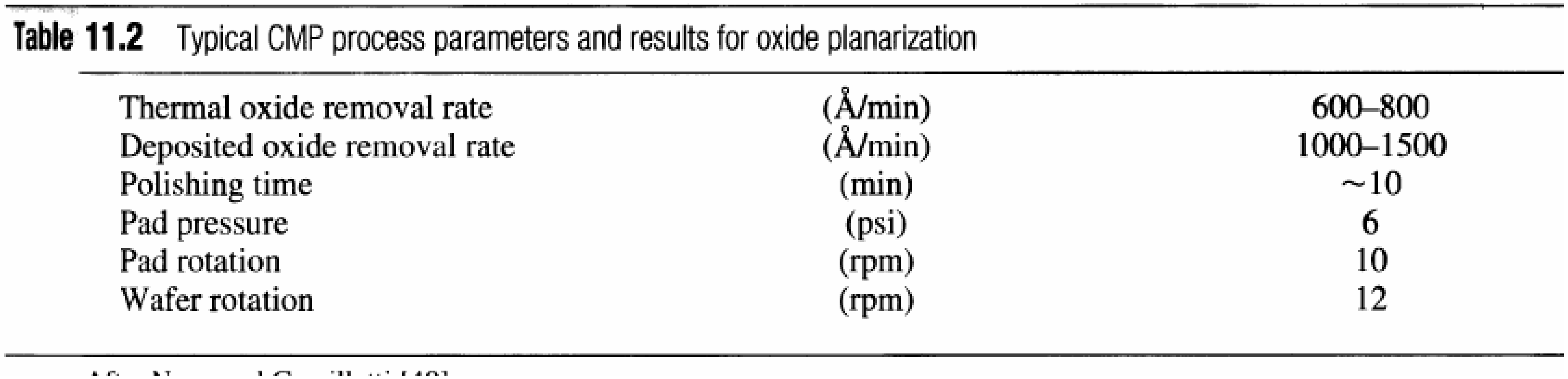
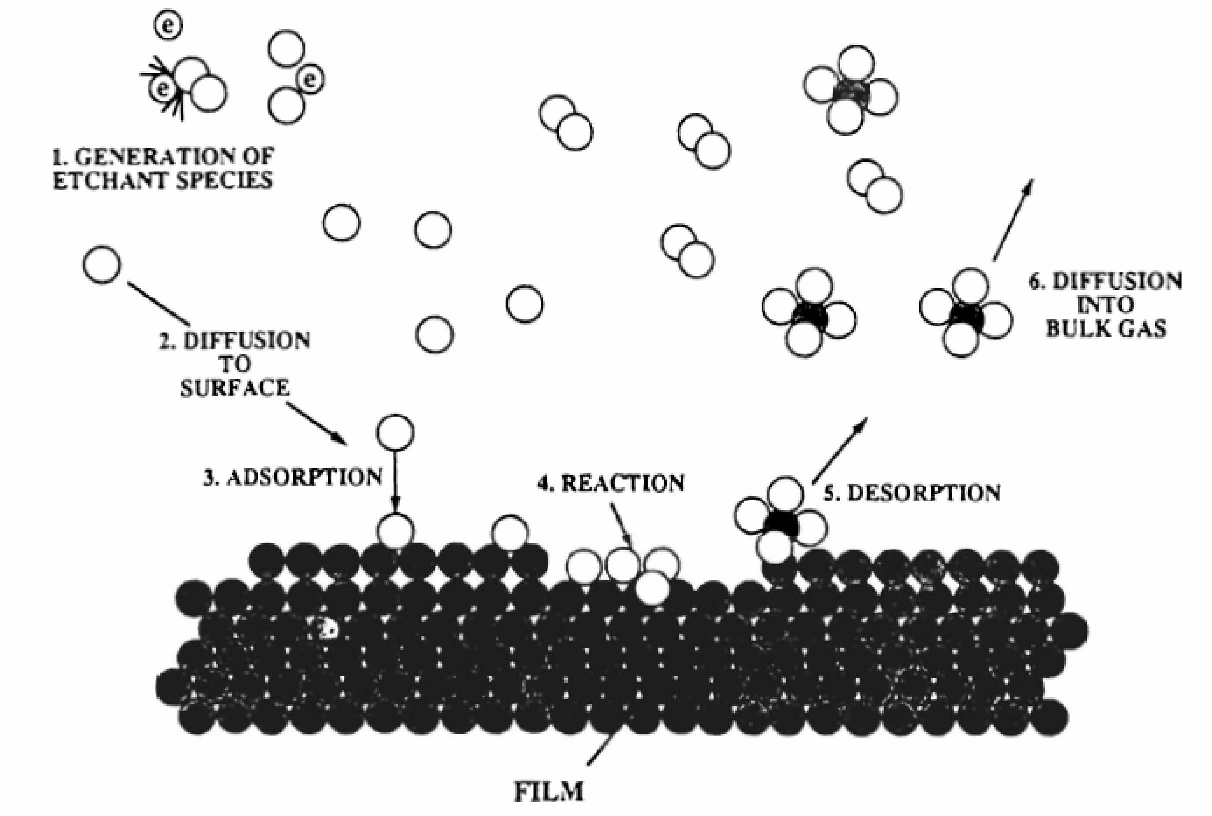


Table 11.2 Typical CMP process parameters and results for oxide planarization

Thermal oxide removal rate	(Å/min)	600–800
Deposited oxide removal rate	(Å/min)	1000–1500
Polishing time	(min)	~10
Pad pressure	(psi)	6
Pad rotation	(rpm)	10
Wafer rotation	(rpm)	12

Plasma etching

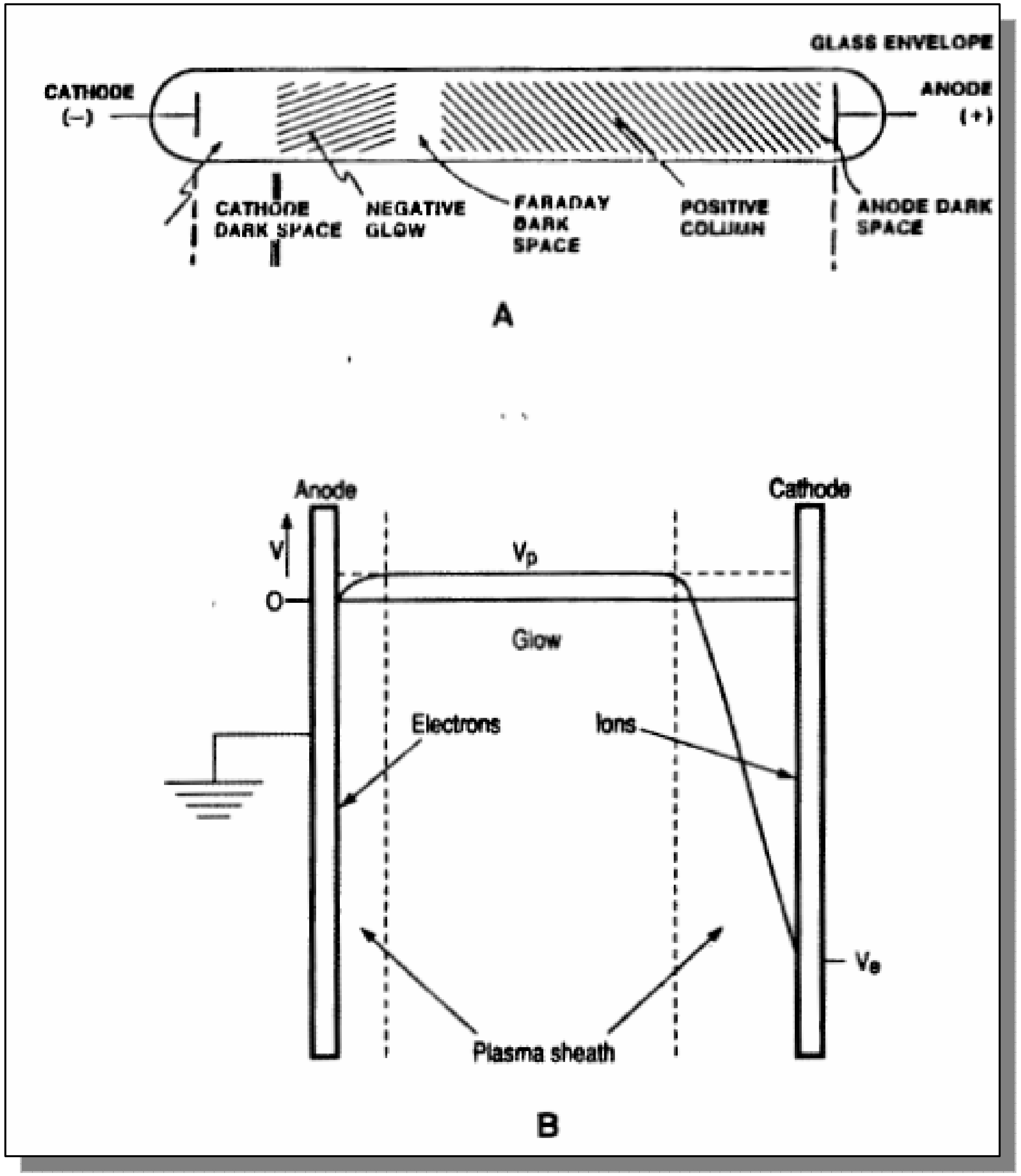


Advantages:

- 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

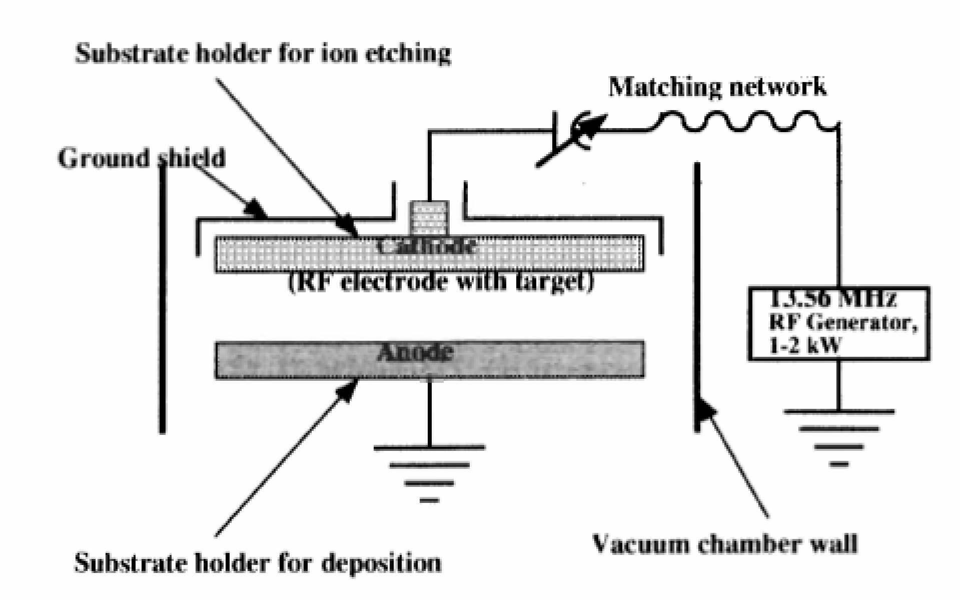
Plasma etching

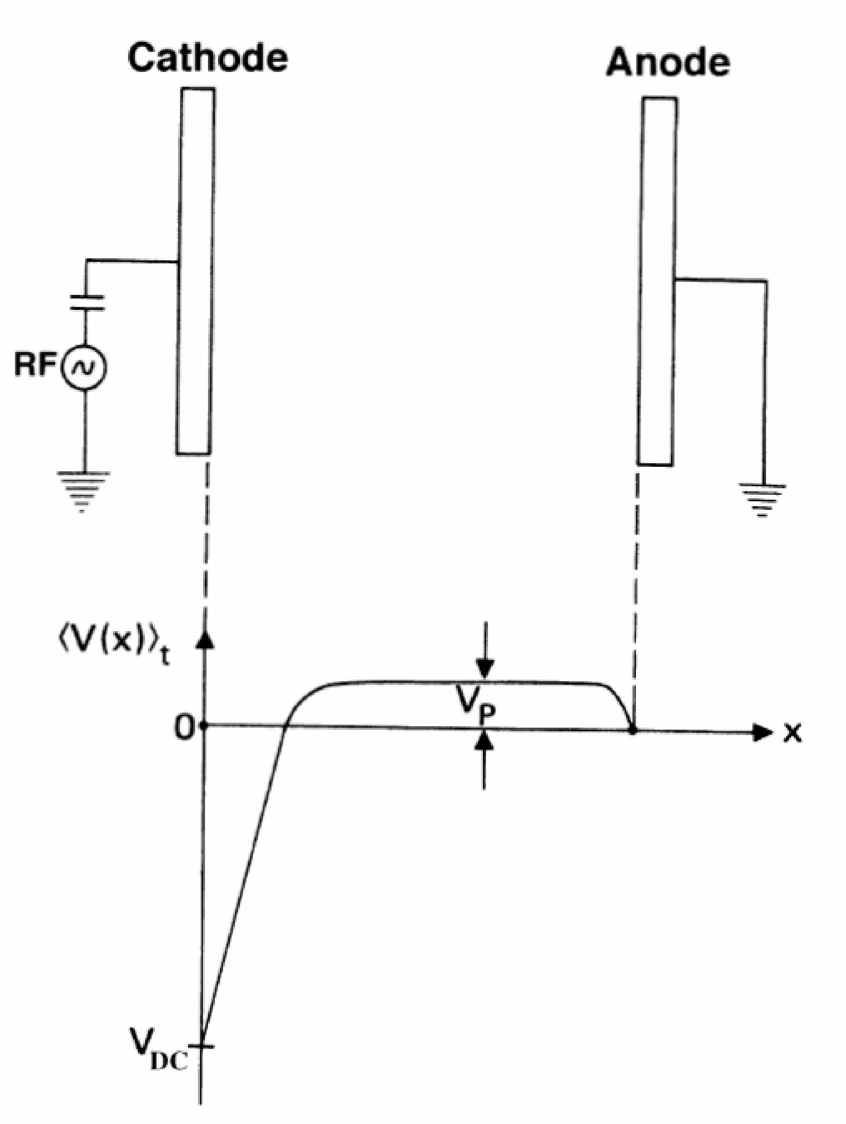
- DC plasma
  (glow discharge)



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

$$C \underline{\vee} F + Si \underline{\vee} Si = Si - F + 17kJ/mol$$

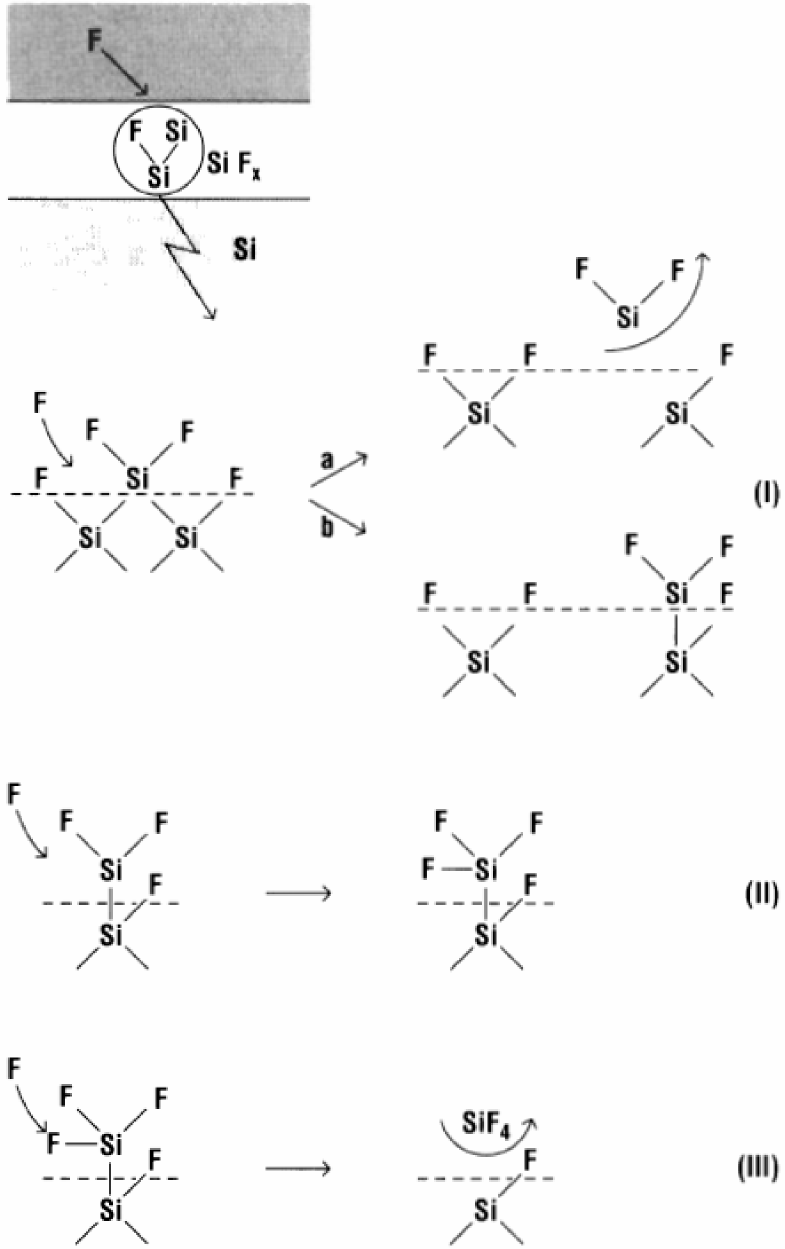
105 kJ/mol **42 kJ/mol** **130 kJ/mol**

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)

$$J_n = \sqrt{\frac{n^2 RT}{2\pi M}}$$

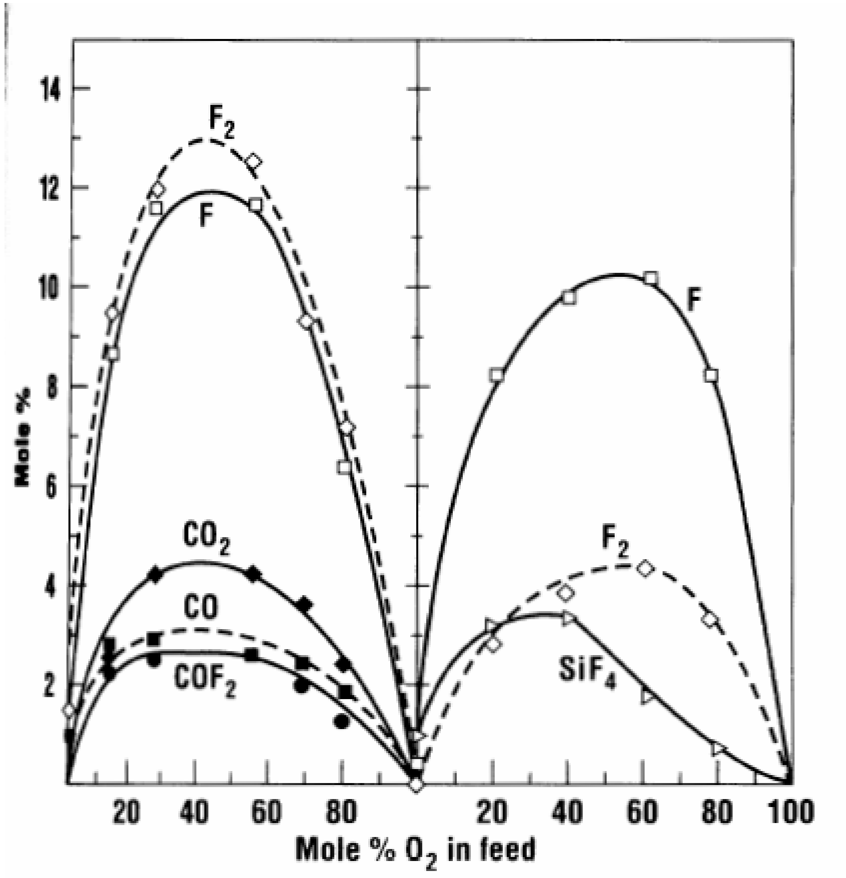


High-Pressure Plasma Etching

SiO_2 etching:

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

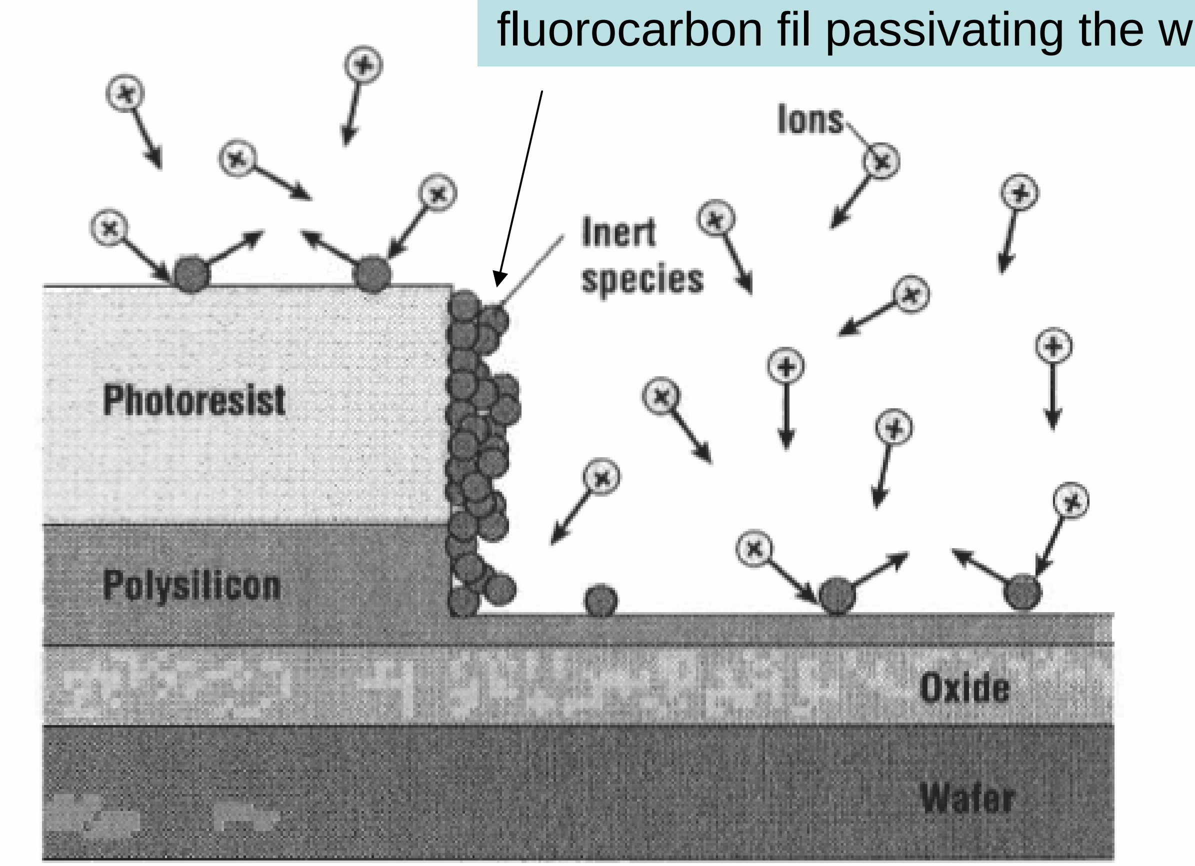
- SiO2 etching is more aggressive; selectivity Si/SiO2 is 50:1 at room T, 100:1 at -30 ºC
- high concentration fluorine is preferable for high Si/SiO2 selectivity
- preferred species CF4, C2F6, SF6
- small addition of oxygen improve both etch rates, large addition removes selectivity



High-Pressure Plasma Etching

- Anisotropic etch

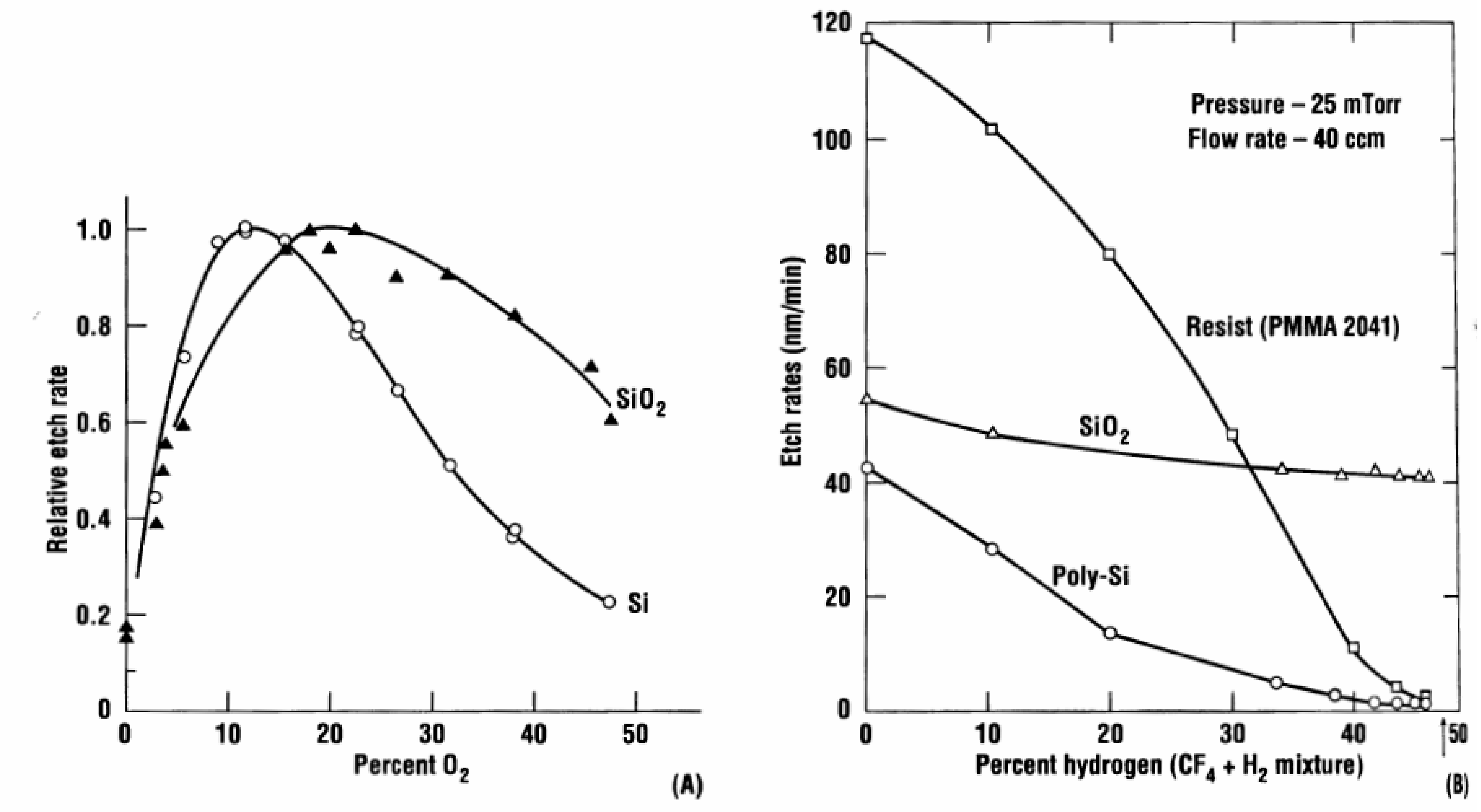
fluorocarbon fil passivating the wall



Formation of hydrocarbon film can be encouraged by addition of hydrogen (H_2, CHF_3 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

etching rate for an empty chamber

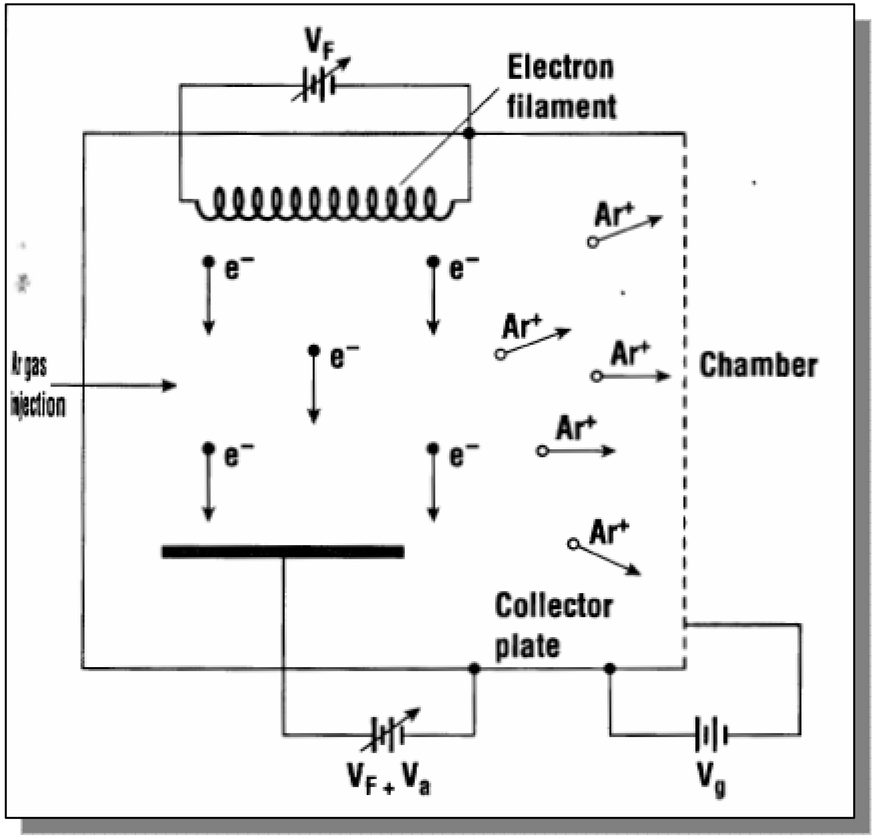
$$R = \frac{R_0}{1 + kA}$$

area of the exposed film

- 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



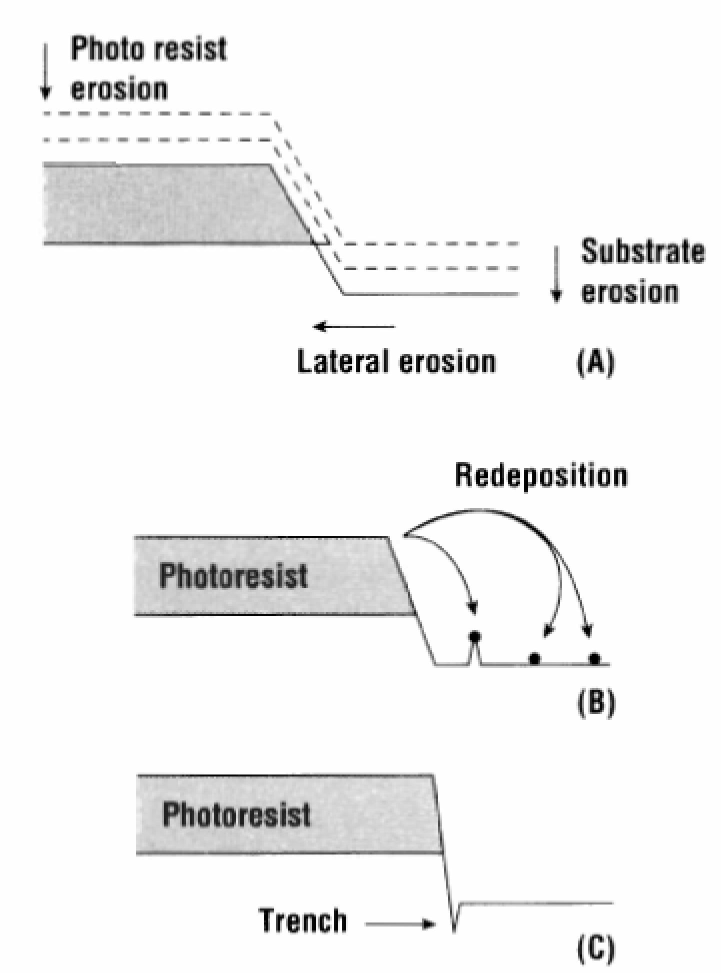
Kaufman source

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

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

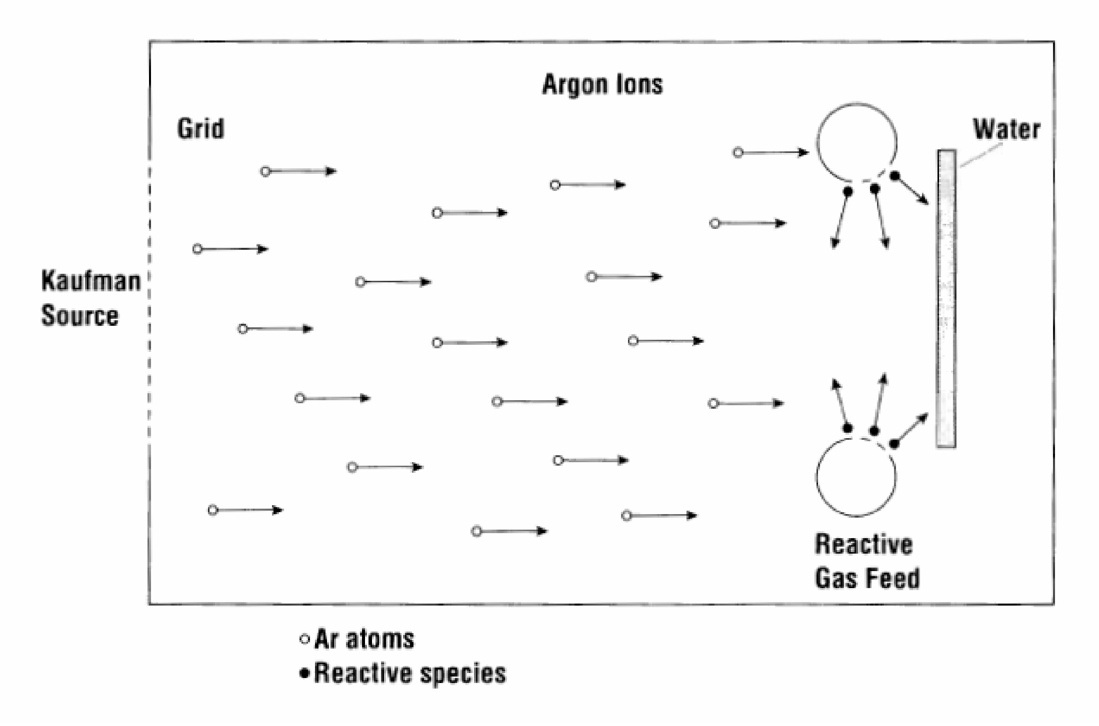
Ion Milling

- 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



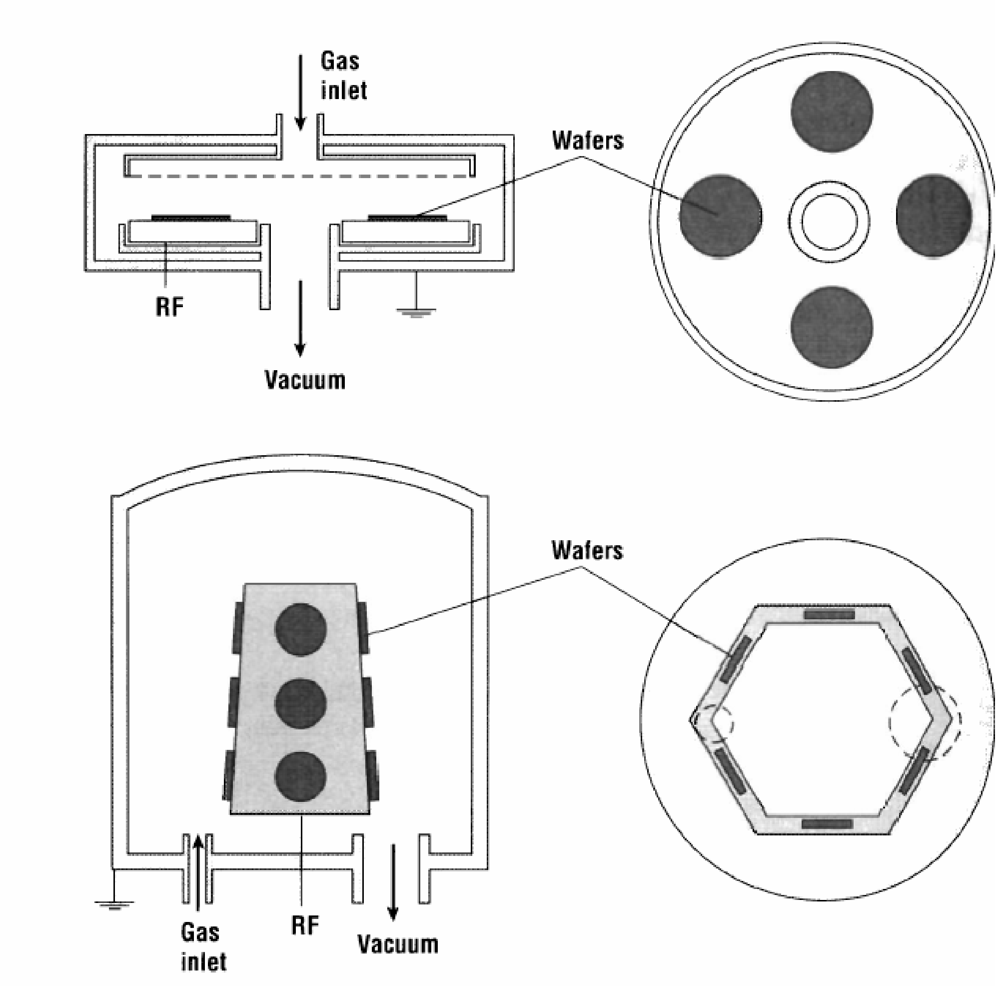
Reactive Ion Etching (RIE)

- 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

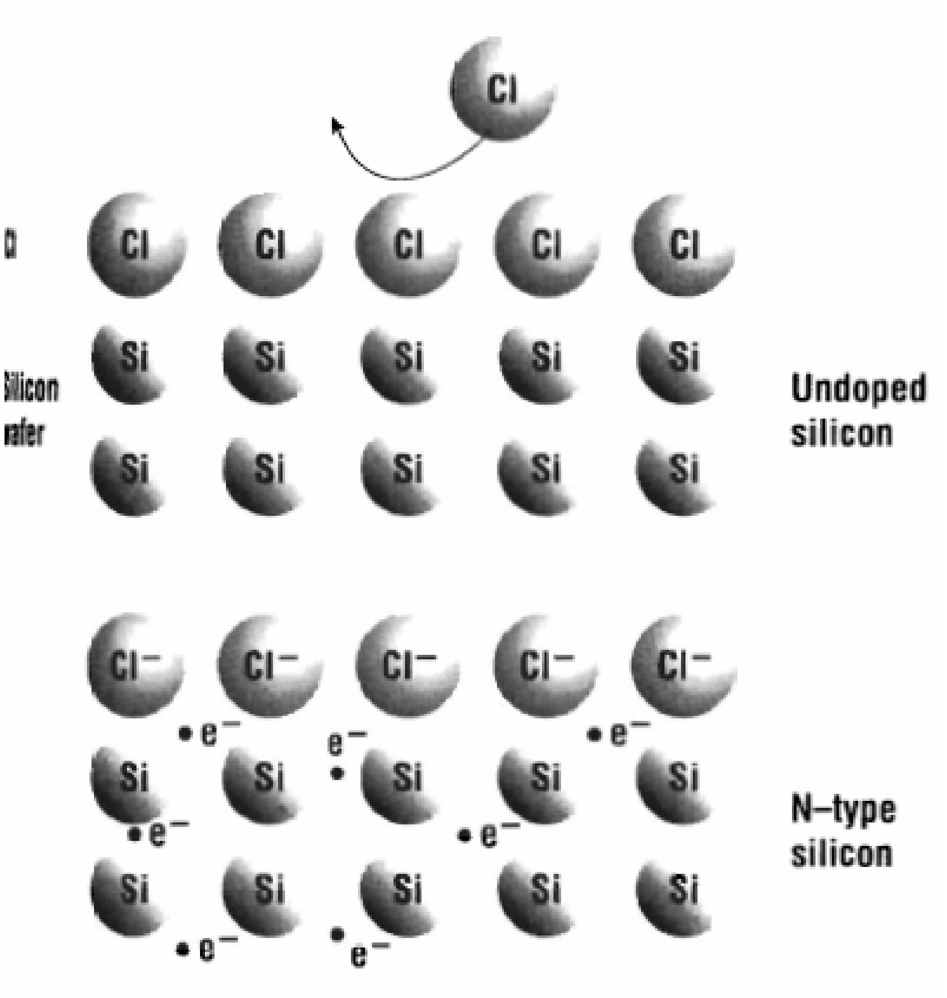
50mTorr

5kW/cm^2.



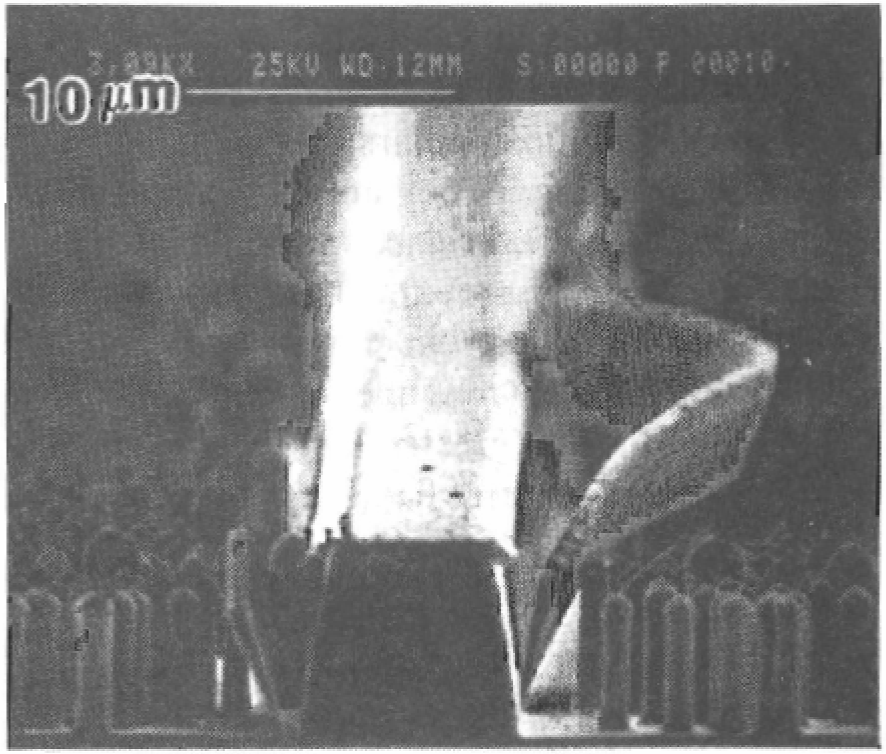
Reactive Ion Etching (RIE)

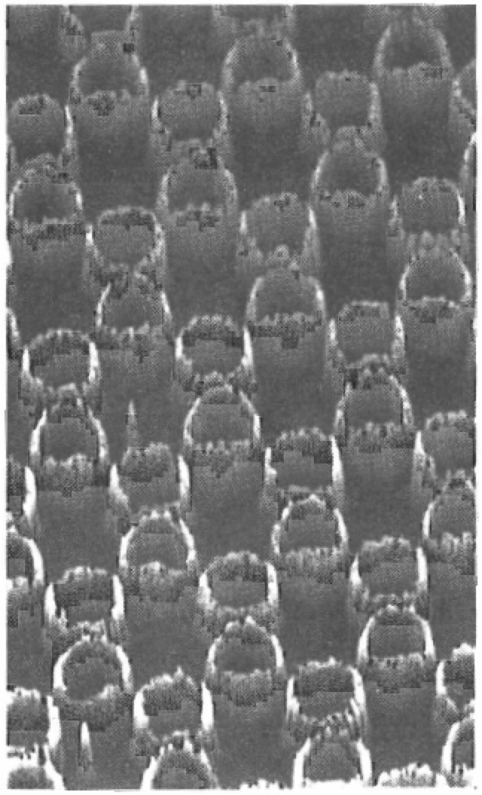
- Si etching in Cl plasma



Reactive Ion Etching (RIE)

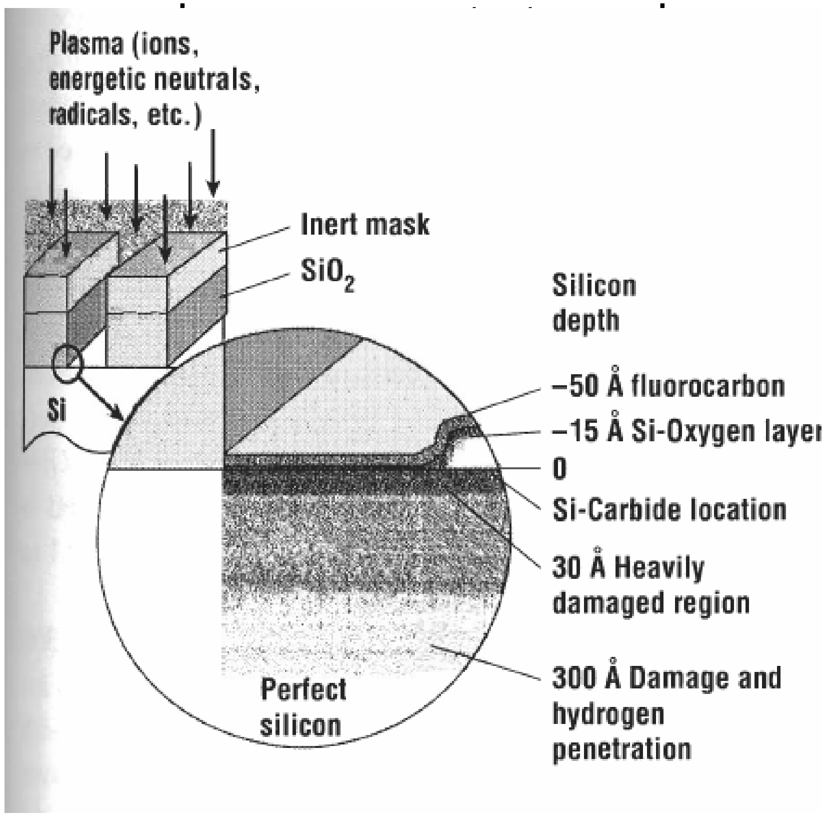
- Sidewall passivation in $HCl/O_2/BCl_3$ plasma





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,)



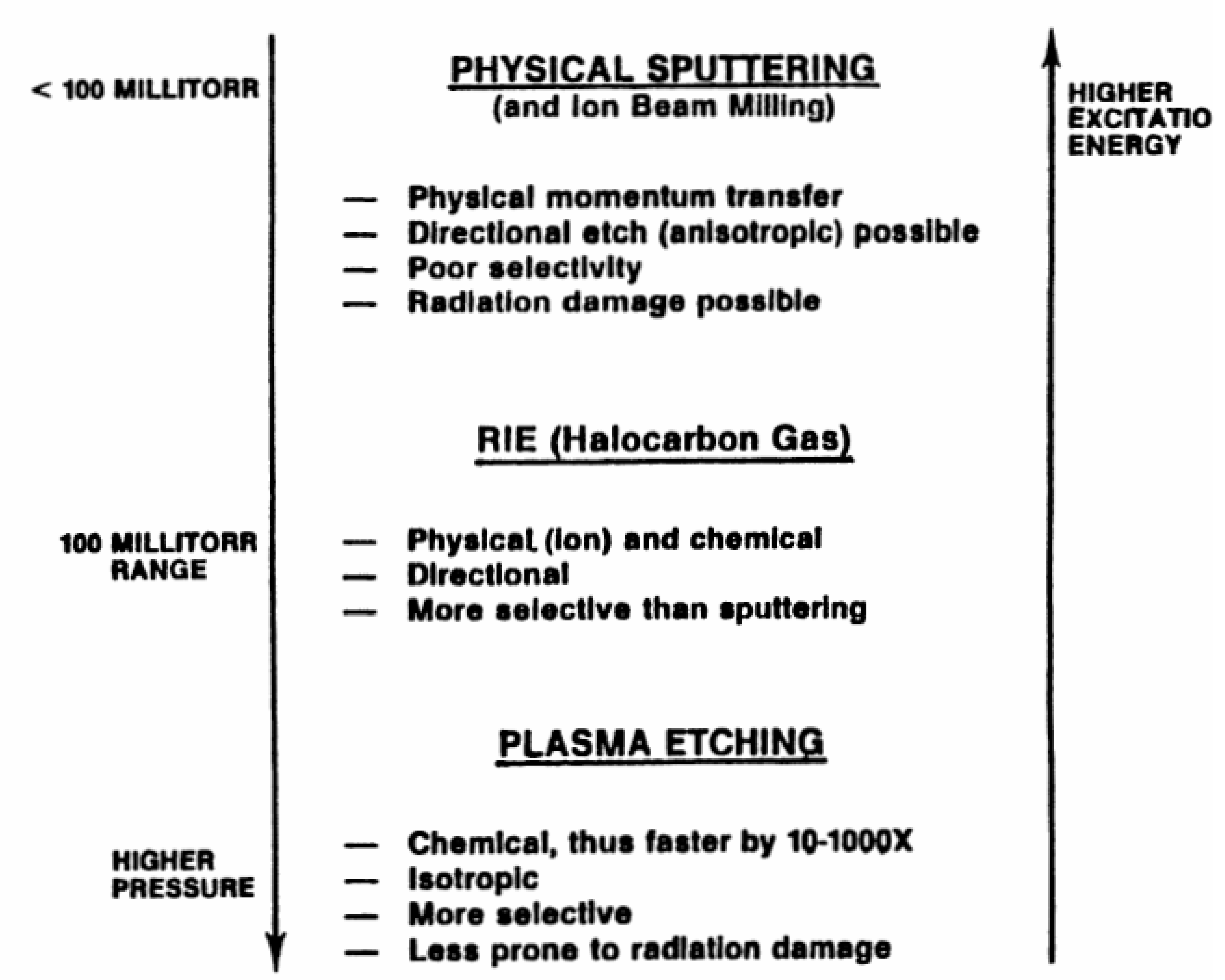
Reactive Ion Etching (RIE)

- 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

O_2 plasma cleaning followed by wet acid cleaning and H_2 plasma treatment

Summary dry etching



< 100 MILLITORR

PHYSICAL SPUTTERING
(and Ion Beam Milling)

HIGHER
EXCITATIO
ENERGY

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

RIE (Halocarbon Gas)

100 MILLITORR
RANGE

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

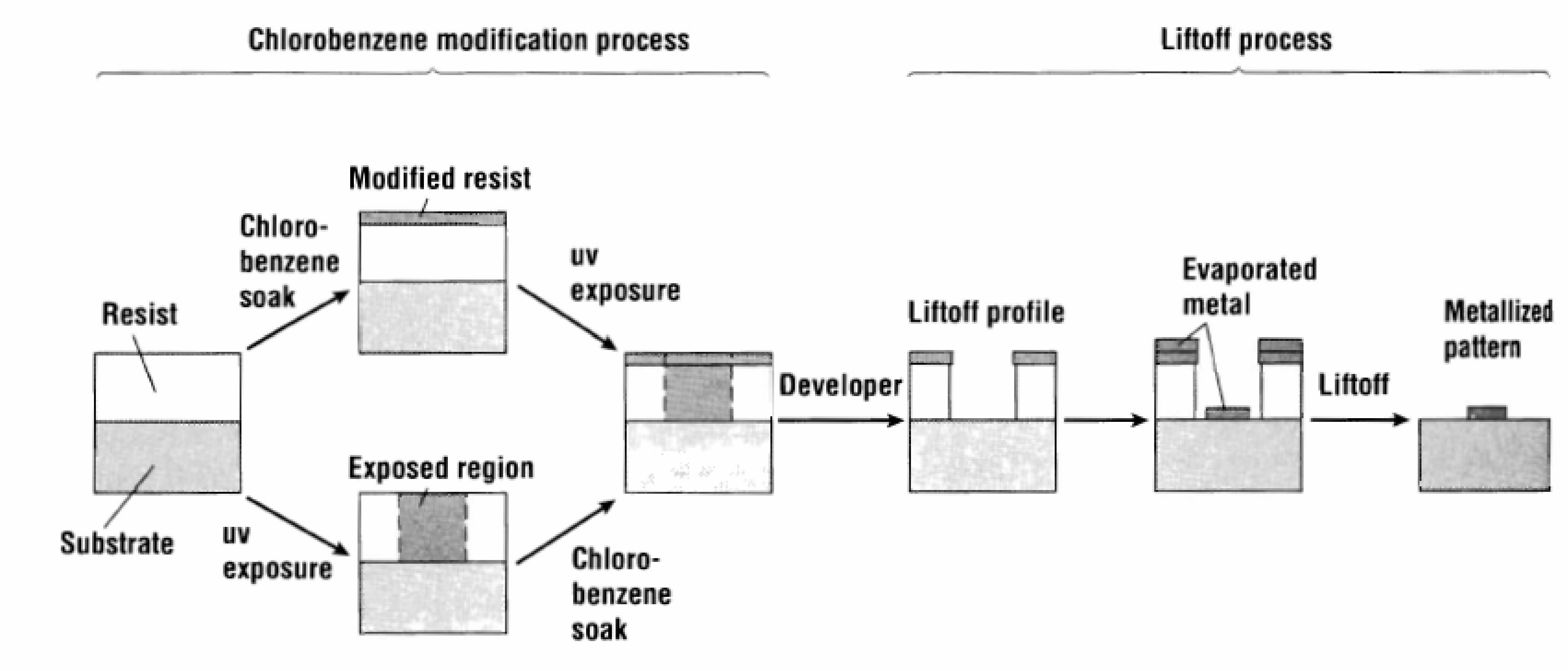
PLASMA ETCHING

HIGHER
PRESSURE

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

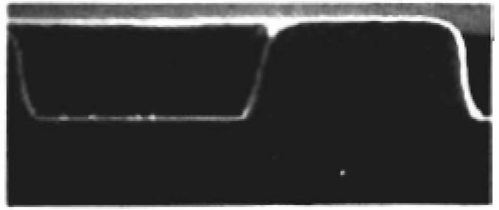
Lift Off

- Process sequence

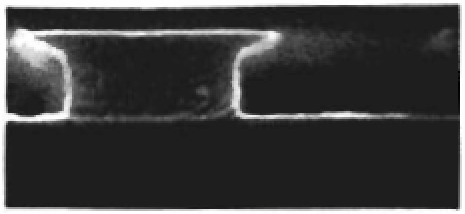


Lift Off

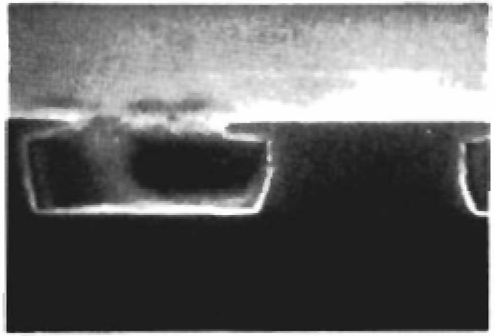
- resist profiles after different treatment



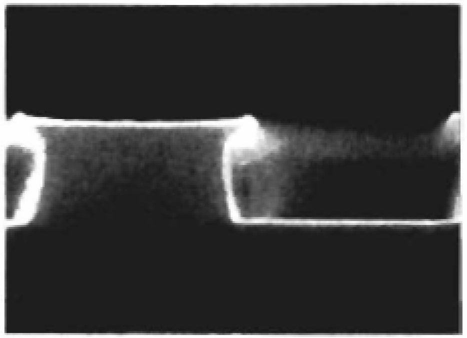
No soaking



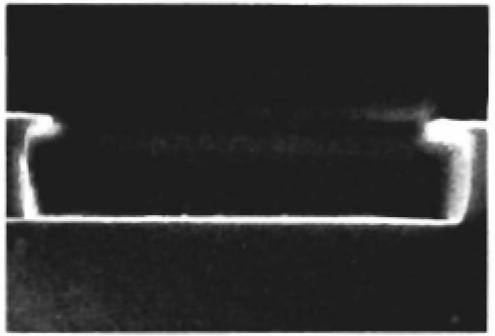
Bromobenzene



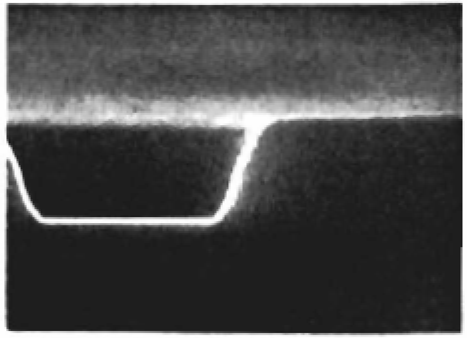
Chorobenzene



Toluene



Fluorobenzene



Kerosene

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