FYS4310

Pattern transfer, Etching

Wet-etching

Dry-etching   ion-etching   sputtering

Chapt 11, 12.6. 12.7

Etching -uses for 1/2 conductors

1. Surface polish (chemical mechanical polishing)
2. Rinse/clean surface (wet, dry)
3. Passivate/terminate surface (wet, gas)
4. Make patterns in dielectrics, metals and so forth
5. 3-D structure making, micro machining (wet, dry)
6. Identification/study X-tal defects
7. Decorate p-n junction (stain etching)
8. Identify Ga/As (111) (polar)surface, xtal orientation
9. etc

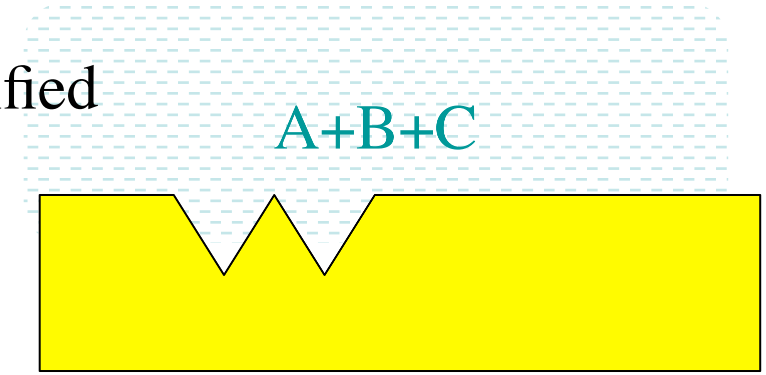
Wet Etching -classification

Anisotropic Preferential Reaction limited

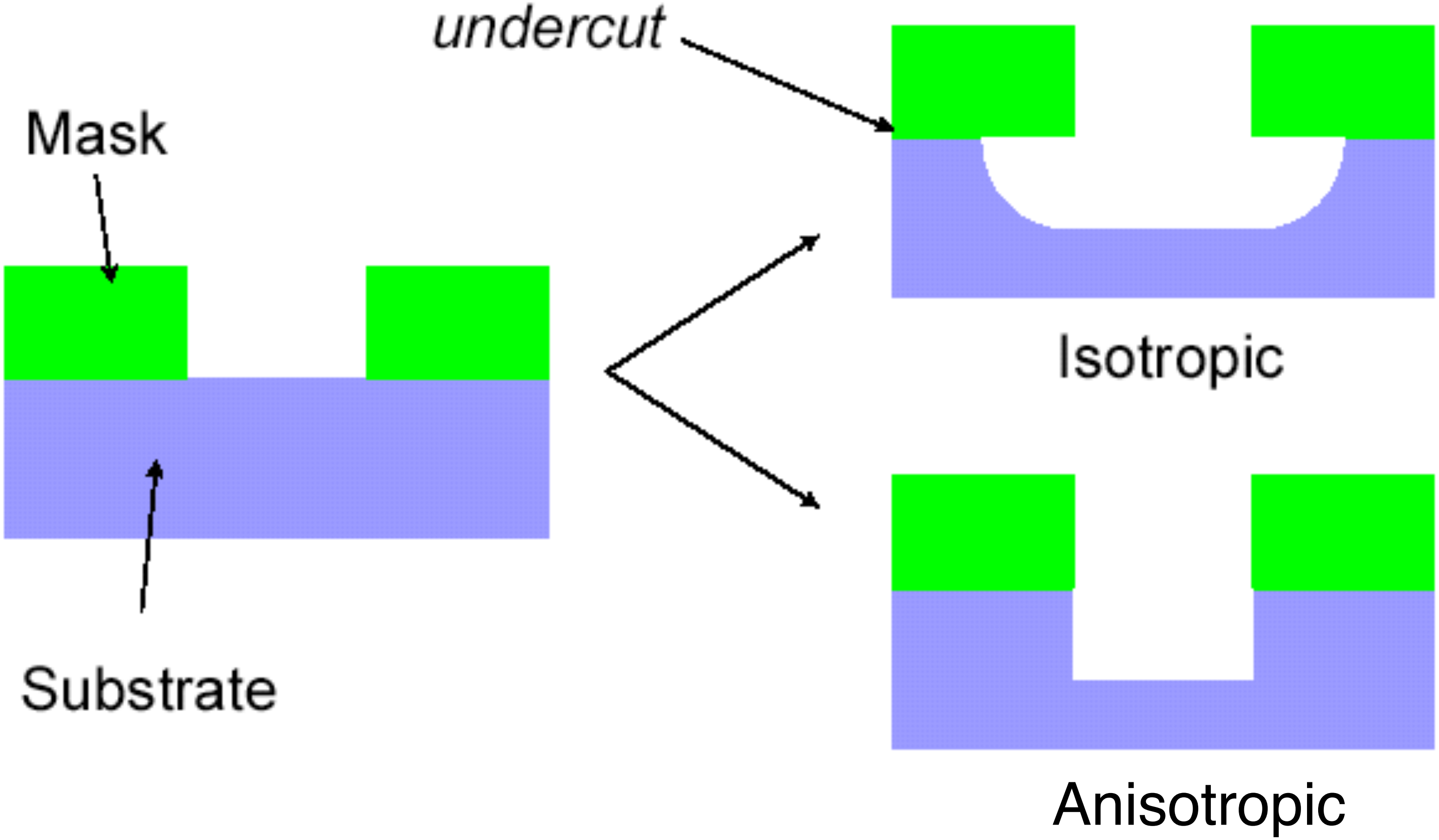
Isotropic Polishing Diffusion limited

Typical etch, schematical, simplified

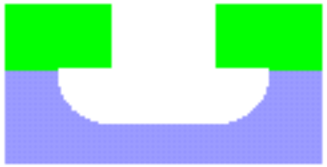
A: solvent, e.g. H_20
B: oxidizing agent
C: oxide disolution, e.g. HF



Etching: Isotropic vs. Anisotropic

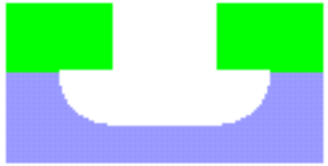


Isotropic Silicon Etching



- "HNA" Etch =
  *H*ydrofluoric Acid+*N*itric Acid+*A*cetic Acid
- HNO_3 oxidizes Si, HF etches oxide, HAc $(HC_2H_3O_2)$ stabilizes pH
- Etch rate is doping dependent-useful with etch stop
- Also attacks SiO_2 at fairly high rates (30-70 nm/min)

HNA Recipes



HF	HNO_3	HAc	Etch Rate (μm/min)
1	3	8	0.7-3.0
1	2	2	4
1	7.5	3	7

(From Kovacs, p. 33)

Etchrate Si in HF and HNO_3

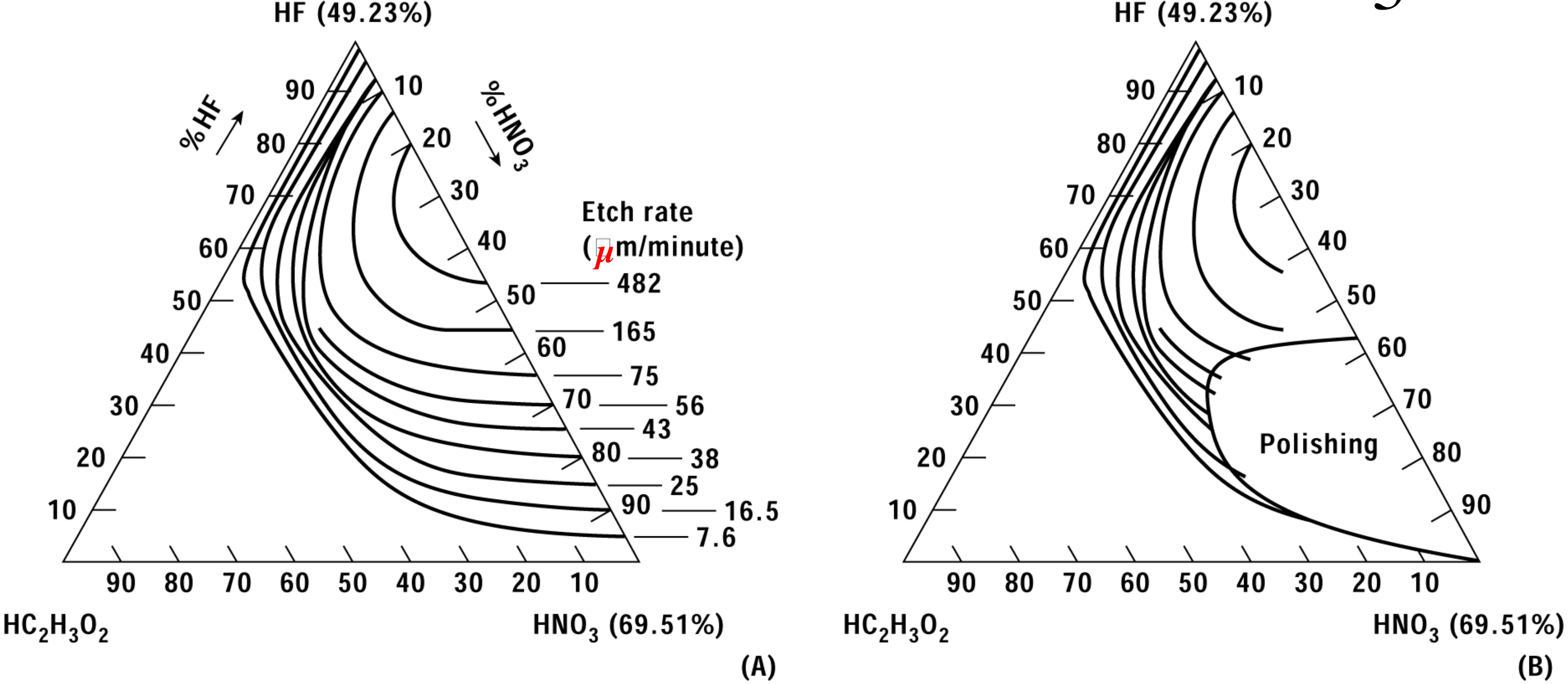


Figure 11.4 The etch rate of silicon in HF and H~~F~~NO_3 *(after Schwarz and Robbins, reprinted by permission of the publisher, The Electrochemical Society Inc.).*

Etchrate GaAs in H_2SO_4

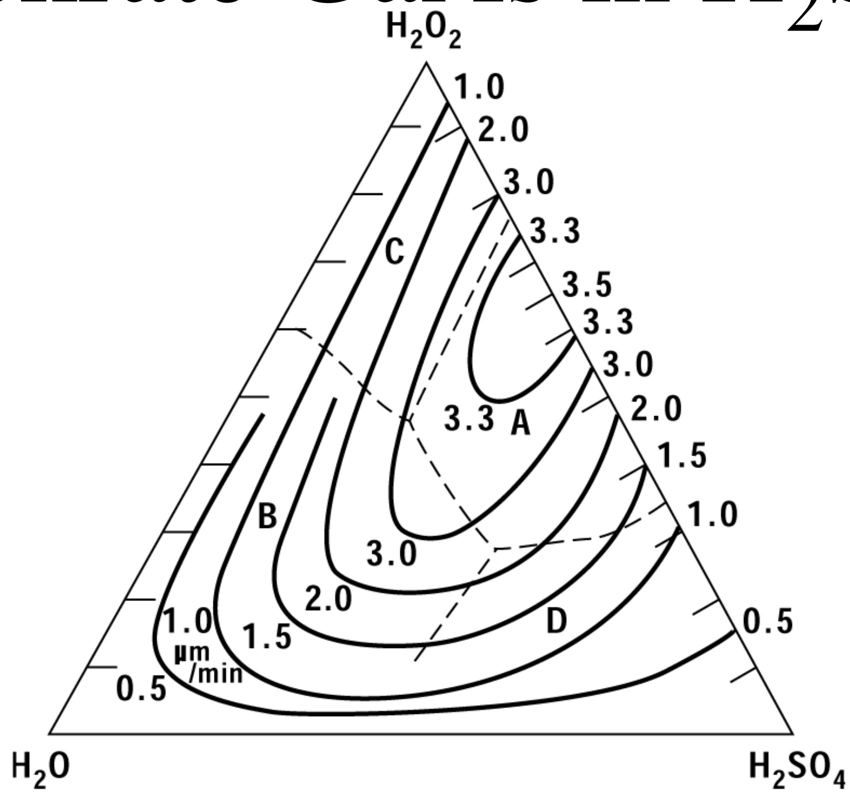


Figure 11.5 The etch rate of GaAs in H_2SO_4, H_2O_2, and H_2O. The bottom leg is the concentration of H_2SO_4, the left leg is H_2O, and the right leg is H_2O_2. All scales increase in the clockwise direction *(after Iida and Ito, reprinted by permission of the publisher, The Electrochemical Society Inc.).*

Diffusion/reaction limited etching

The attributes of **diffusion controlled** etch reactions are

1) The activation energy is viscosity controlled, 1-6 kcal/mol *i.e. diffusion in liquid*

2) The reaction rate increases with agitation

3) All substances and crystal orientations etch at the same rate

4) The activation energy increases with stirring ? *Maybe 007 was wrong?*

5) The etch ~~depth is proportional to the square root of etch time~~ ?

The etch rate decreases with time

The attributes of **reaction-rate controlled** etch reactions are

1) The rate changes with etchant concentration

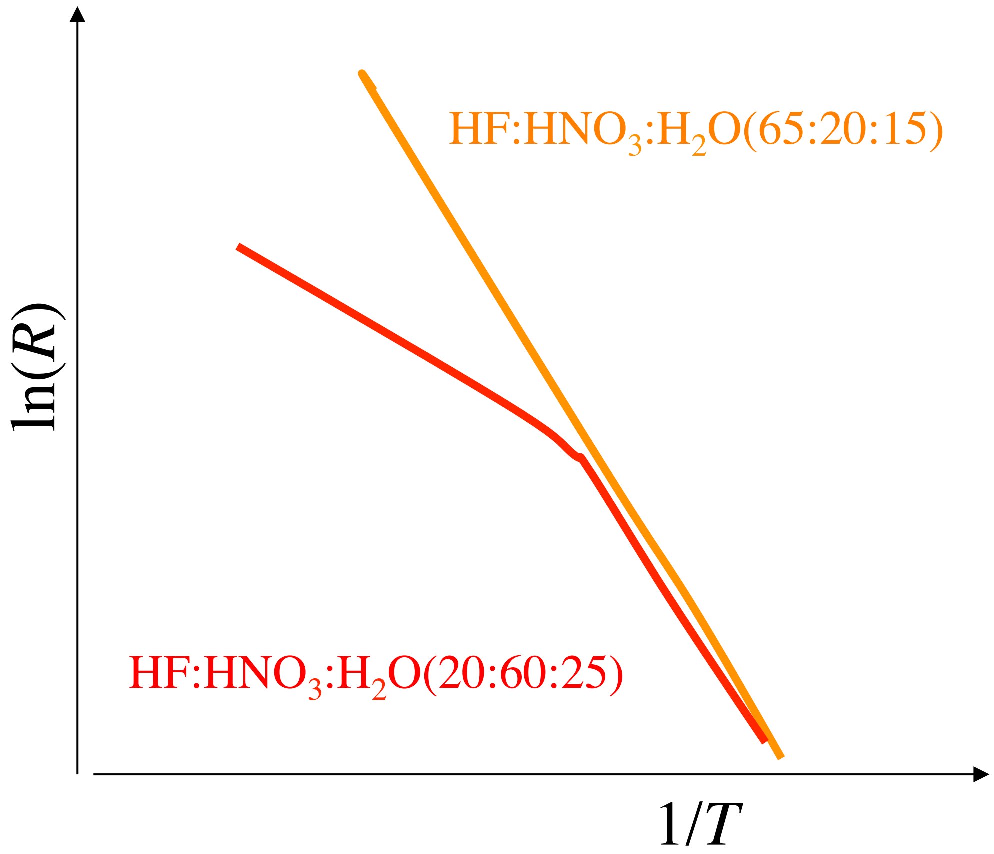
2) The rate is not sensitive to agitation

3) The activation energy is typically 8-20 kcal/mol

4) The etch depth is linearly dependent on etch time

David Hayes MSc thesis U Florida 1999

Wet Etching -example diffusion/reaction limited



Wet Etching -xtal defects secondary identification

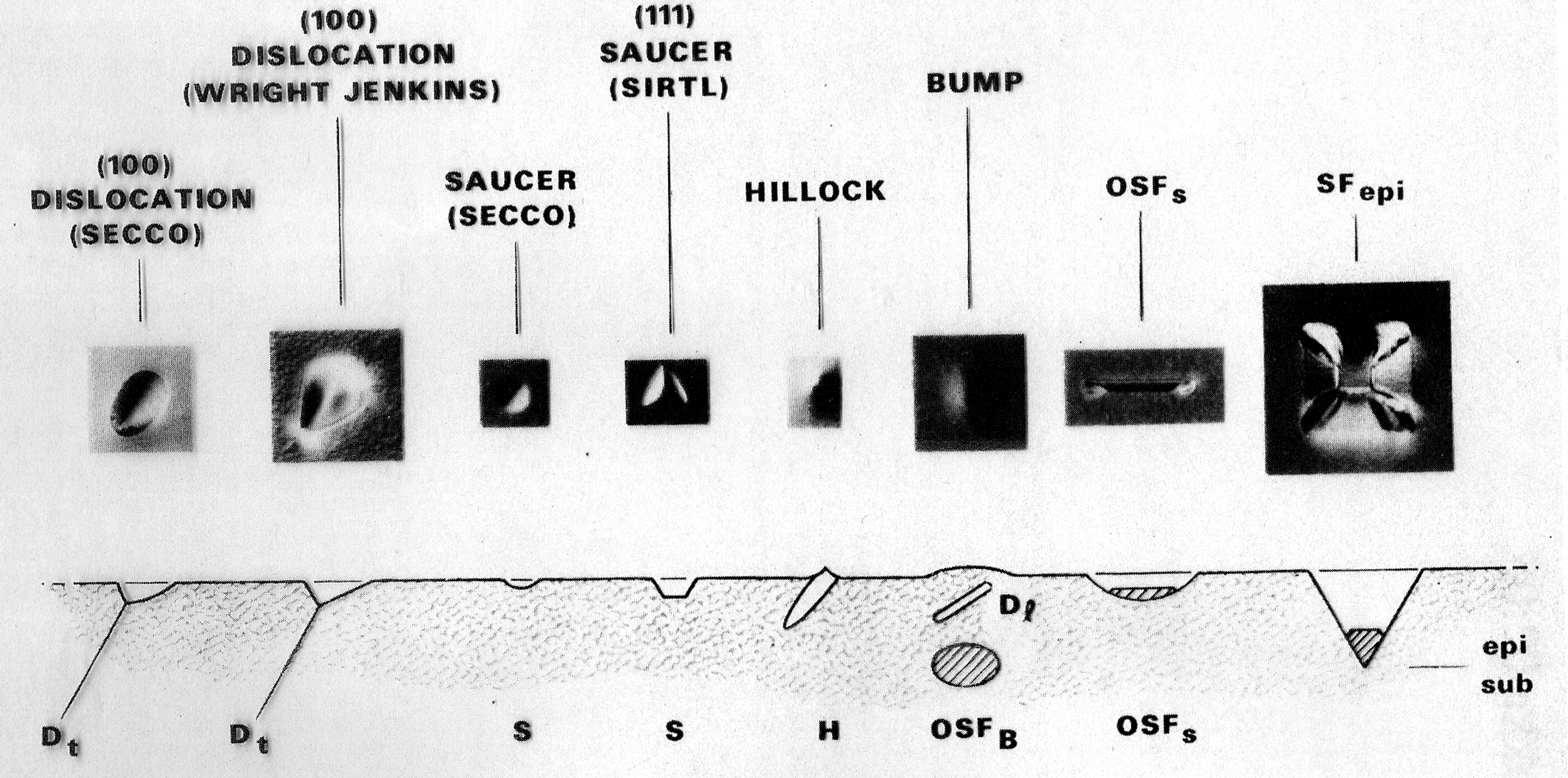


Fig. 4. A range of etch features found in silicon using the three etches listed in table 2.

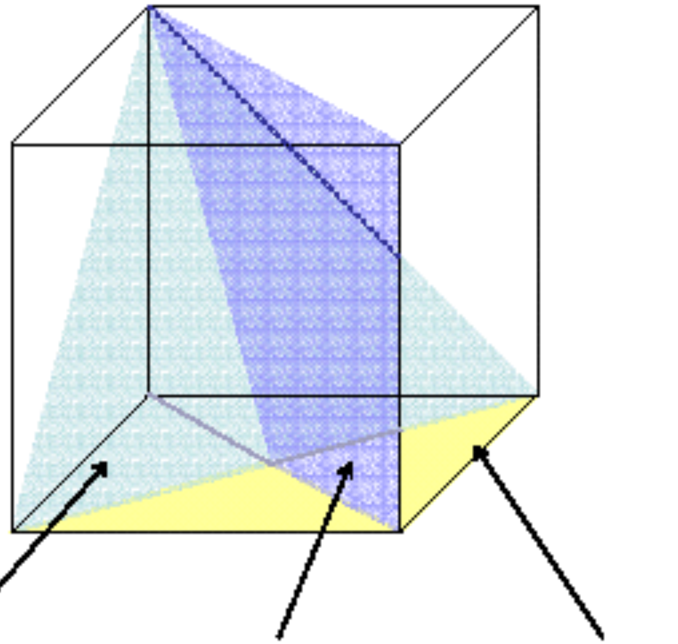
Anisotropic Wet Etching of Si

- Based on bases:
  - KOH
  - NH_4OH
  - TMAH

- Etch mechanism (oxidation/reduction reaction)

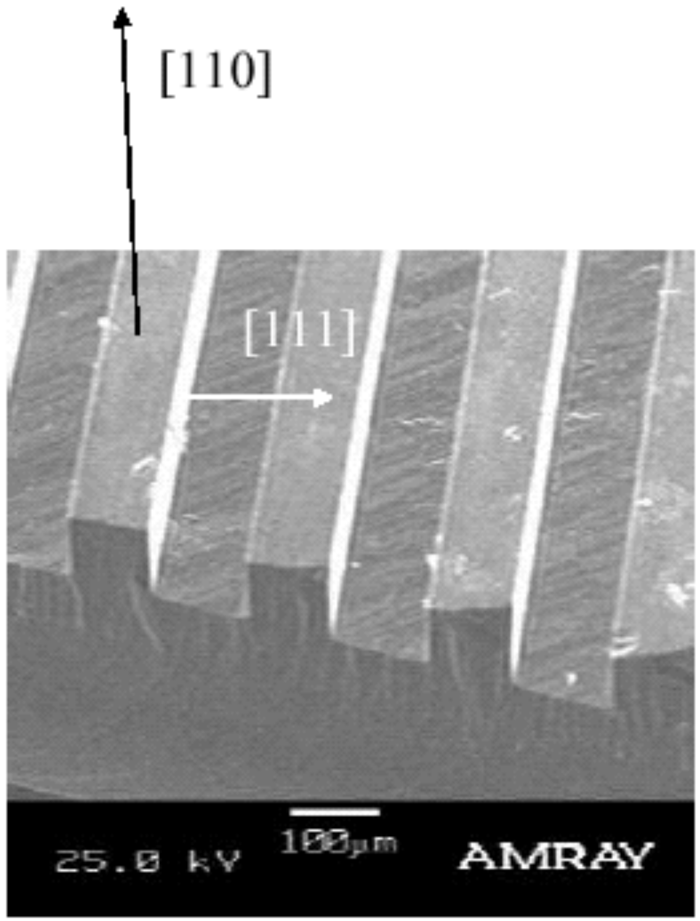
$$\underset{\text{wafer}}{Si} + 2OH^- + 2H_2O \rightarrow \underset{\text{soluble complex}}{SiO_2(OH)_2^{-2}} + \underset{\text{bubbles form}}{2H_2}$$

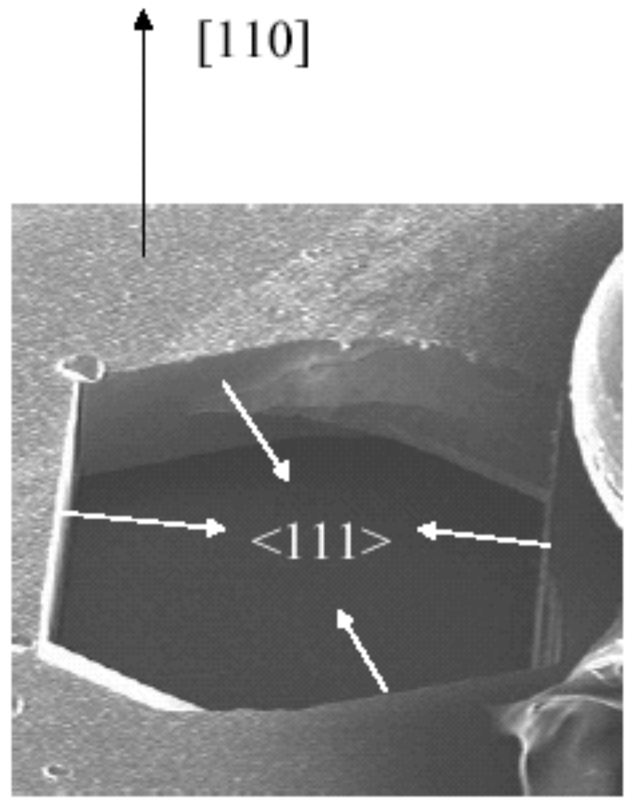
Relative Etch Rates in KOH



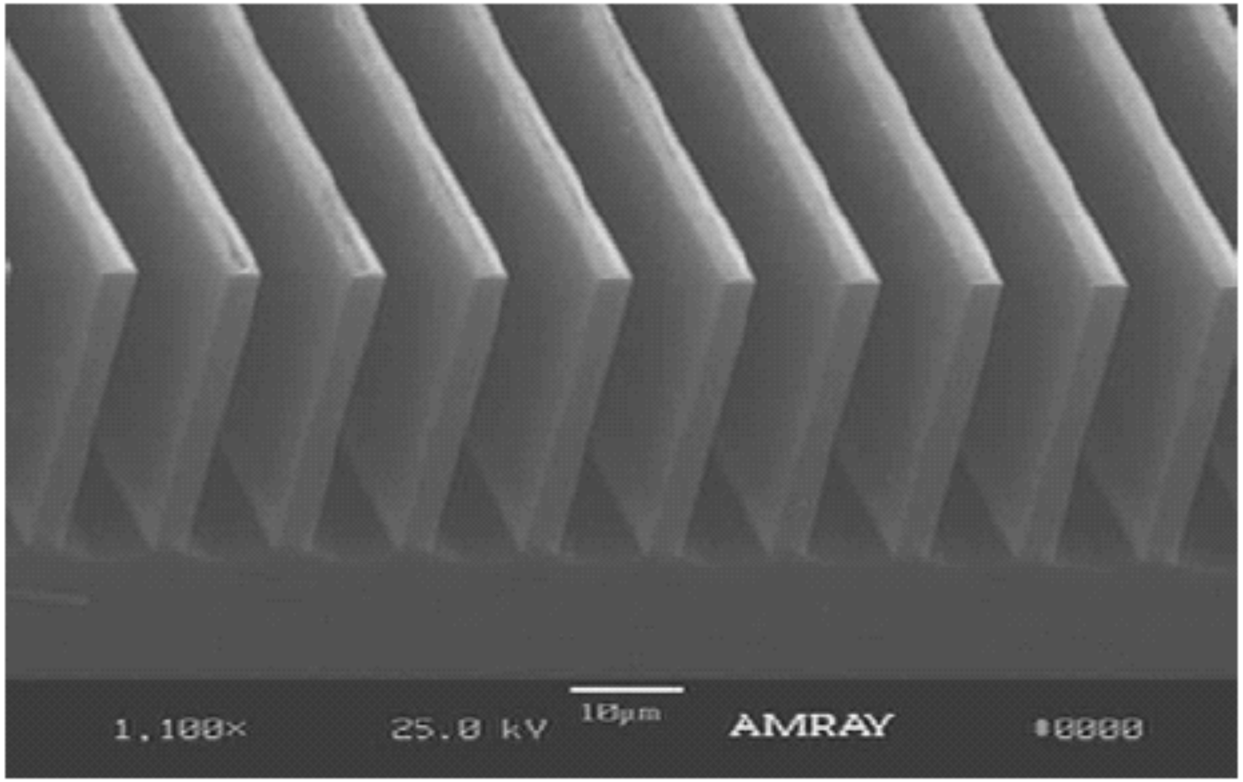
$$\boxed{ER_{(111)}:ER_{(100)}:ER_{(110)} \approx 1:300:600}$$

Shape of Etched Features





Wet Etcing -ex. MEMS shapes

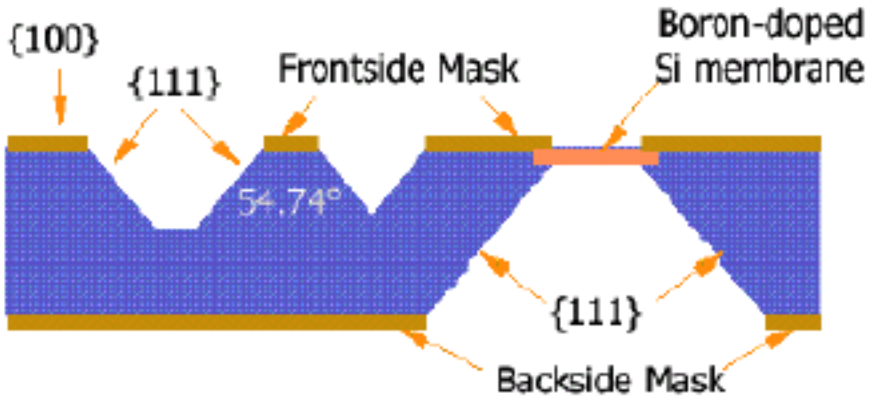


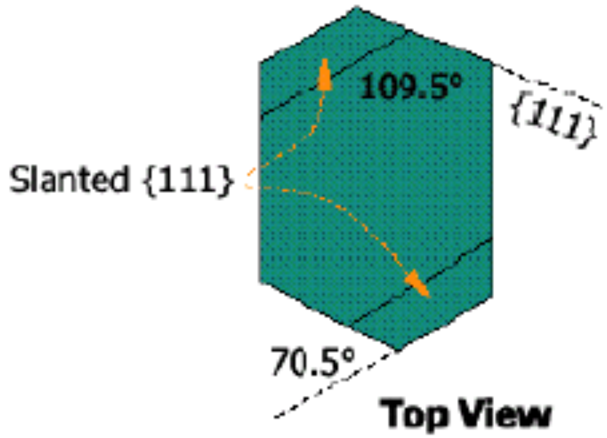
Mask: 5 μm lines and spaces

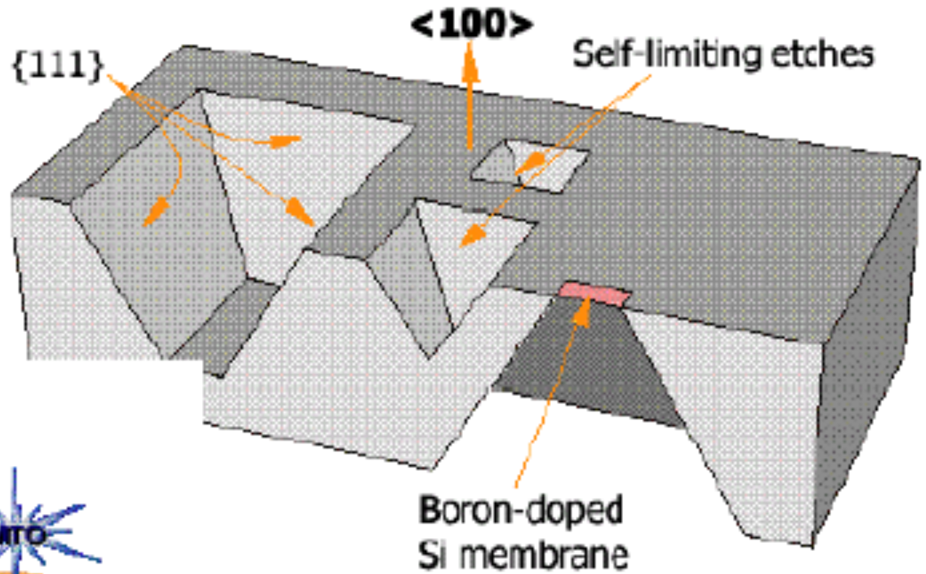
Silicon (110), oxide mask

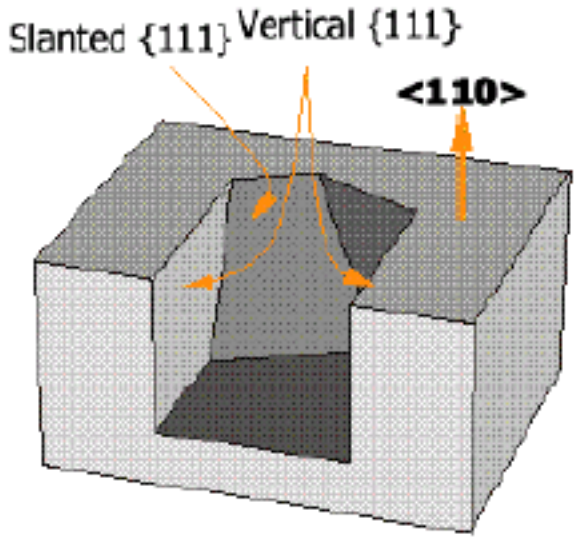
Channels: 8 μm X 24 μm

Bulk Micromachining: Anisotropic Wet Etching



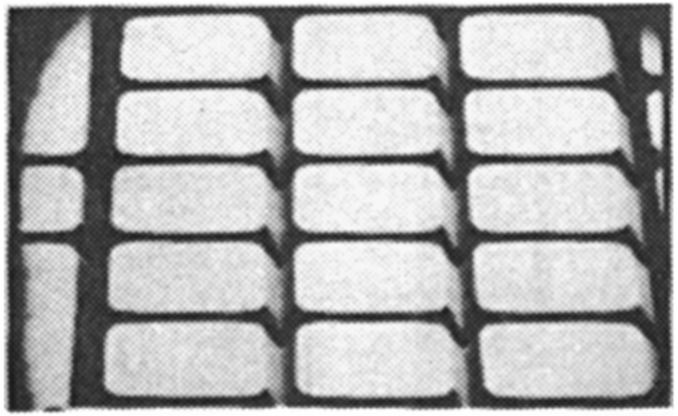






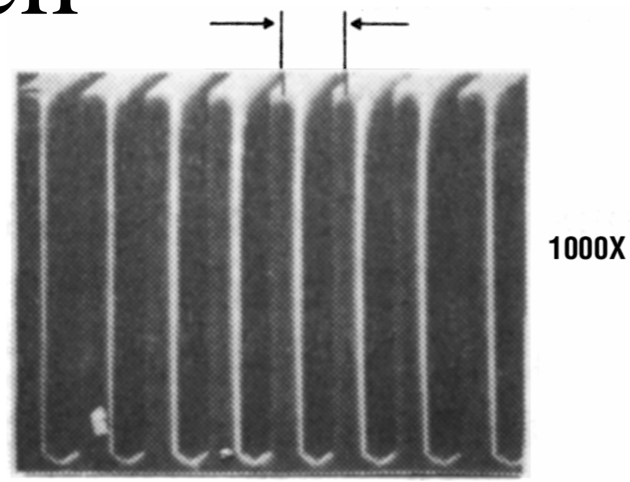
W.Tang DARPA

KOH etch



SEM TOP VIEW (100) DI ETCH

SEM CROSSECTIONAL VIEW (100) DI ETCH



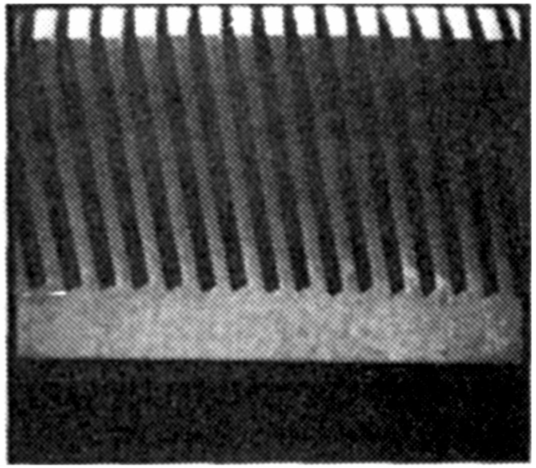
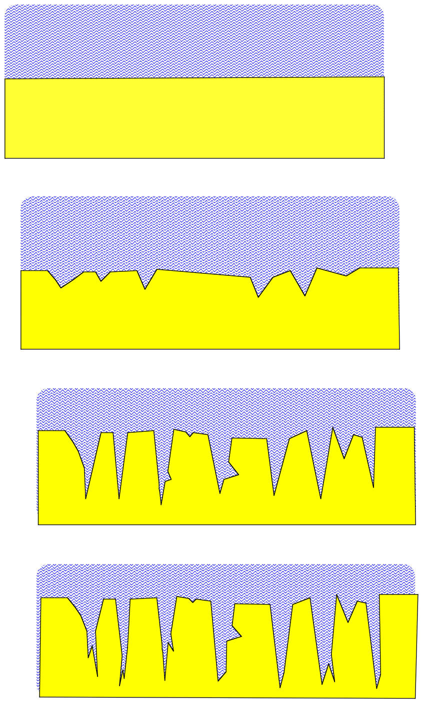


Figure 11.6 (100) silicon wafers after directional etching in KOH, isopropyl alcohol, and water. The upper photo shows a 50-μm-deep etch. The lower photographs are of 80-μm-deep trenches etched at 10 μm pitch on (110) and 107off (110) *(after Bean, ©1978 IEEE).*

Wet Etching -porous 1/2-cond

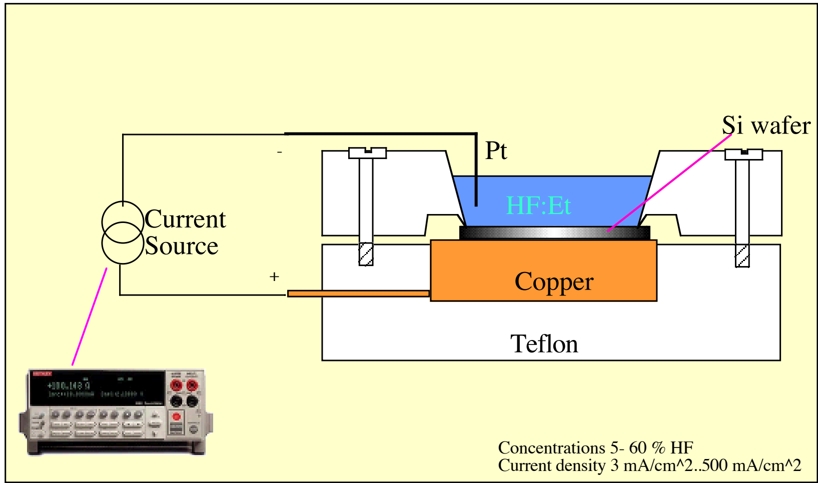
Interface-instability

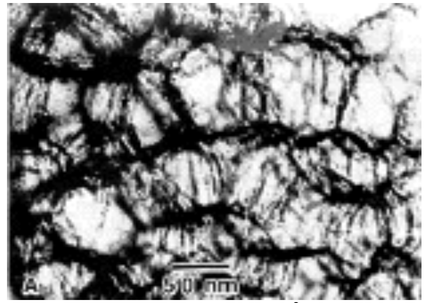


Electrochemical reaction

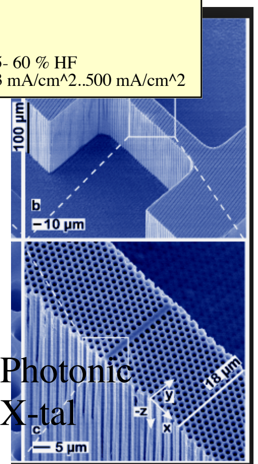
$$Si + 2\,F^{-} + 2\,h^{+} \rightarrow SiF_2 \qquad (1)$$

$$SiF_2 + 2HF \rightarrow SiF_4 + H_2 \qquad (2)$$

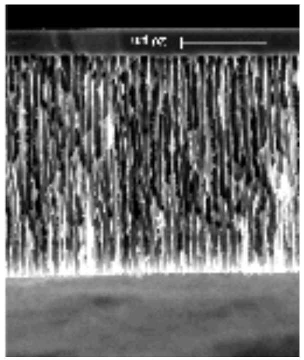




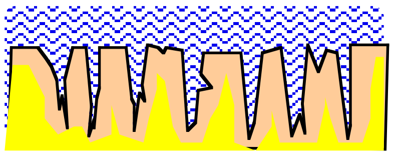
nanowires



Photonic X-tal



macropores



Etching -classification, Parameters

Etch rate R: 10nm -μm/min

Uniformity: % over wafer

Selectivity: i.e. R_{Si}/R_{SiO_2}

Anisotropy: $A=1-R_L/R_V$ Vertical Lateral

Bias:
must be compensated for
in mask design

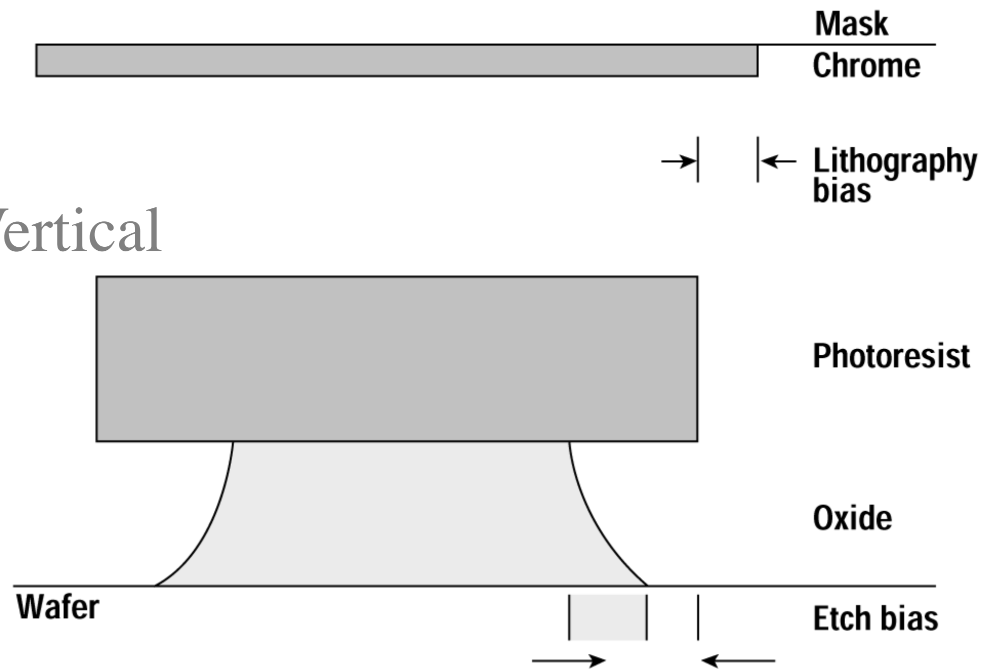
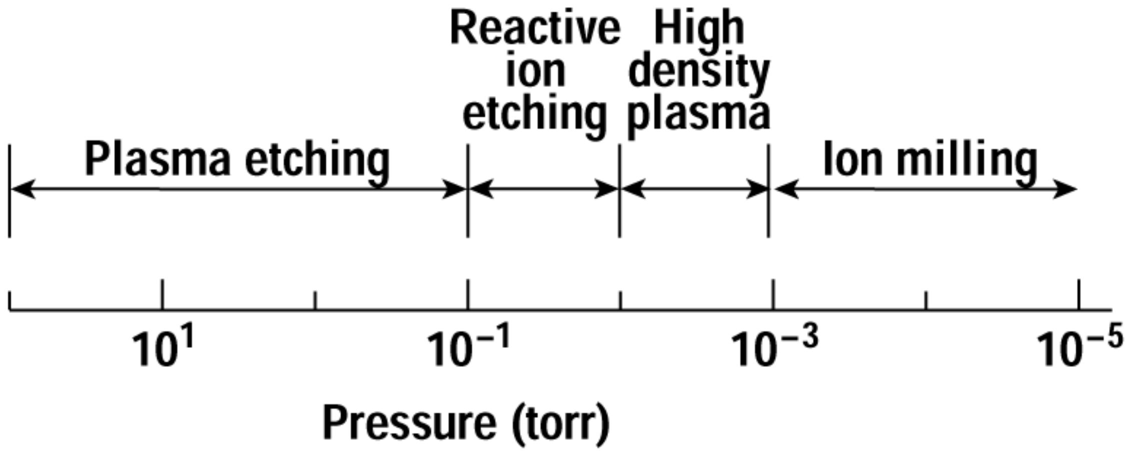


Figure 11.1 Typical isotropic etch process showing the etch bias.

Ideal for small devices: A=1 --> motivation for dry etching

Dry etching and gas pressure



Dry etching mechanisms

Physical + chemical

e.g. Ion beam etch with inert gas = pure physical, pure sputtering

Sputter process schematics

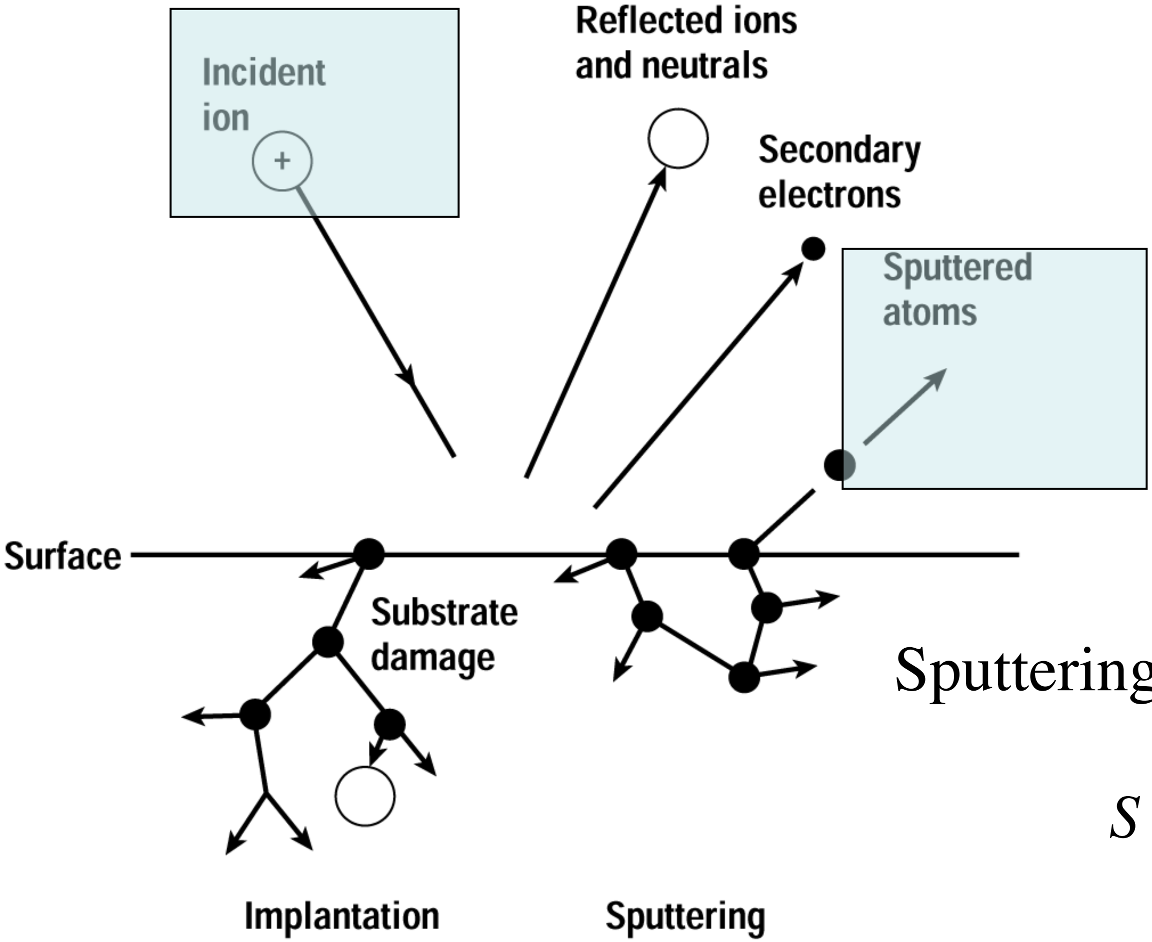


Figure 12.12 Possible outcomes for an ion incident on the surface of a wafer.

Physical PROCESS
-Dry etching
(- Deposition
- Profiling AES,SIMS
- I^2)

Sputtering coefficient $S = N_{sput}/N_{in}$

$$S = \frac{\lambda \cdot S_n(E) \cdot \alpha(M_1/M_2)}{U_0}$$

P. Sigmund Theory

λ: material parameter
U_0 surf. Bindings energy
$S_n(E)$ Nucl. Stopping power
α func. of M_1/M_2

Sputtering rate versus energy

Sputter rate follows S_n

$$S = \frac{\lambda \cdot S_n(E) \cdot \alpha(M_1 / M_2)}{U_0}$$

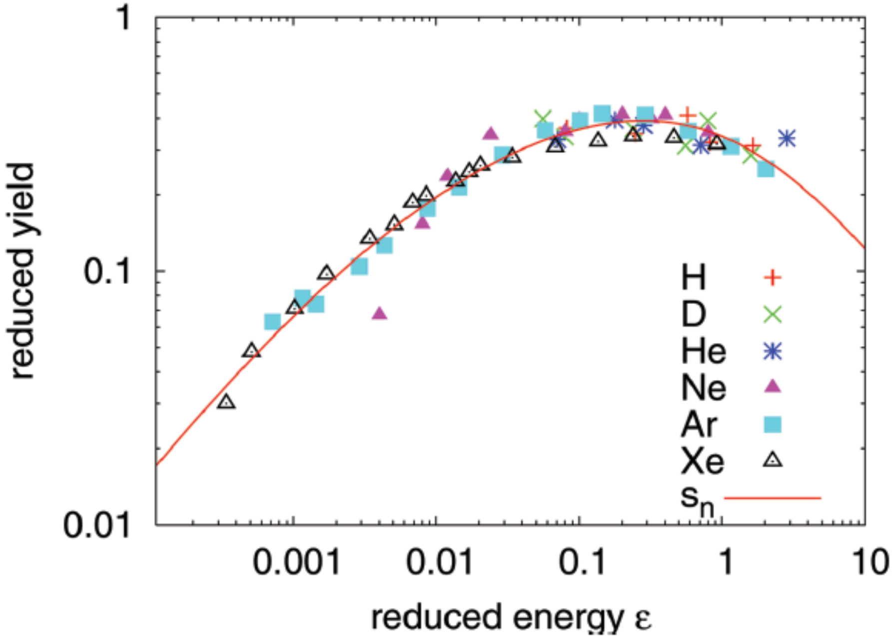


Figure 1. Compilation of experimentally determined sputter yields of Si with normally incident ions. The reduced sputter yields, $y = Y/C$, cf. Section 2.1, have been plotted *versus* the reduced energy ϵ and are seen to align well with the reduced nuclear stopping cross section s_n. Threshold effects have been taken into account via the factor η, Equation (4). Compilation and analysis due to Wittmaack (2003).

Sputtering rate versus energy

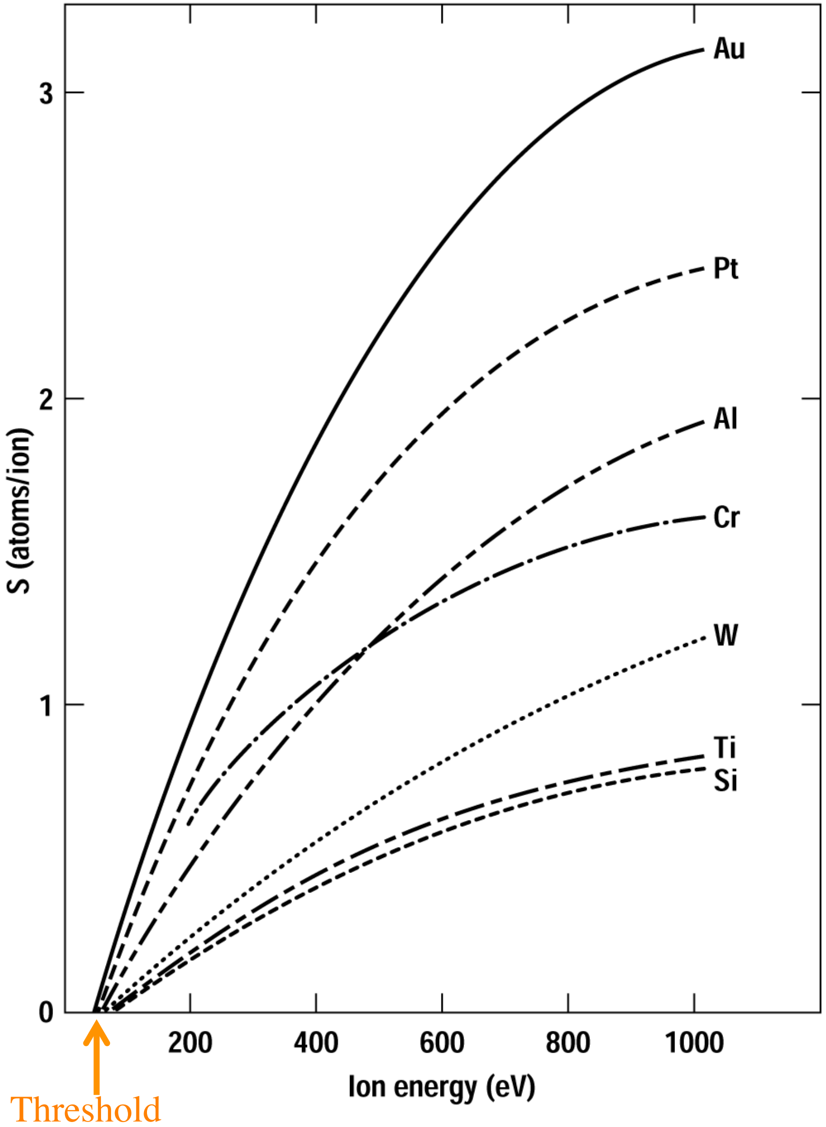


Figure 12.13 Sputter yield as a function of ion energy for normal incidence argon ions for a variety of materials *(after Anderson and Bay, reprinted by permission)*.

Sputtering coef versus atomic number

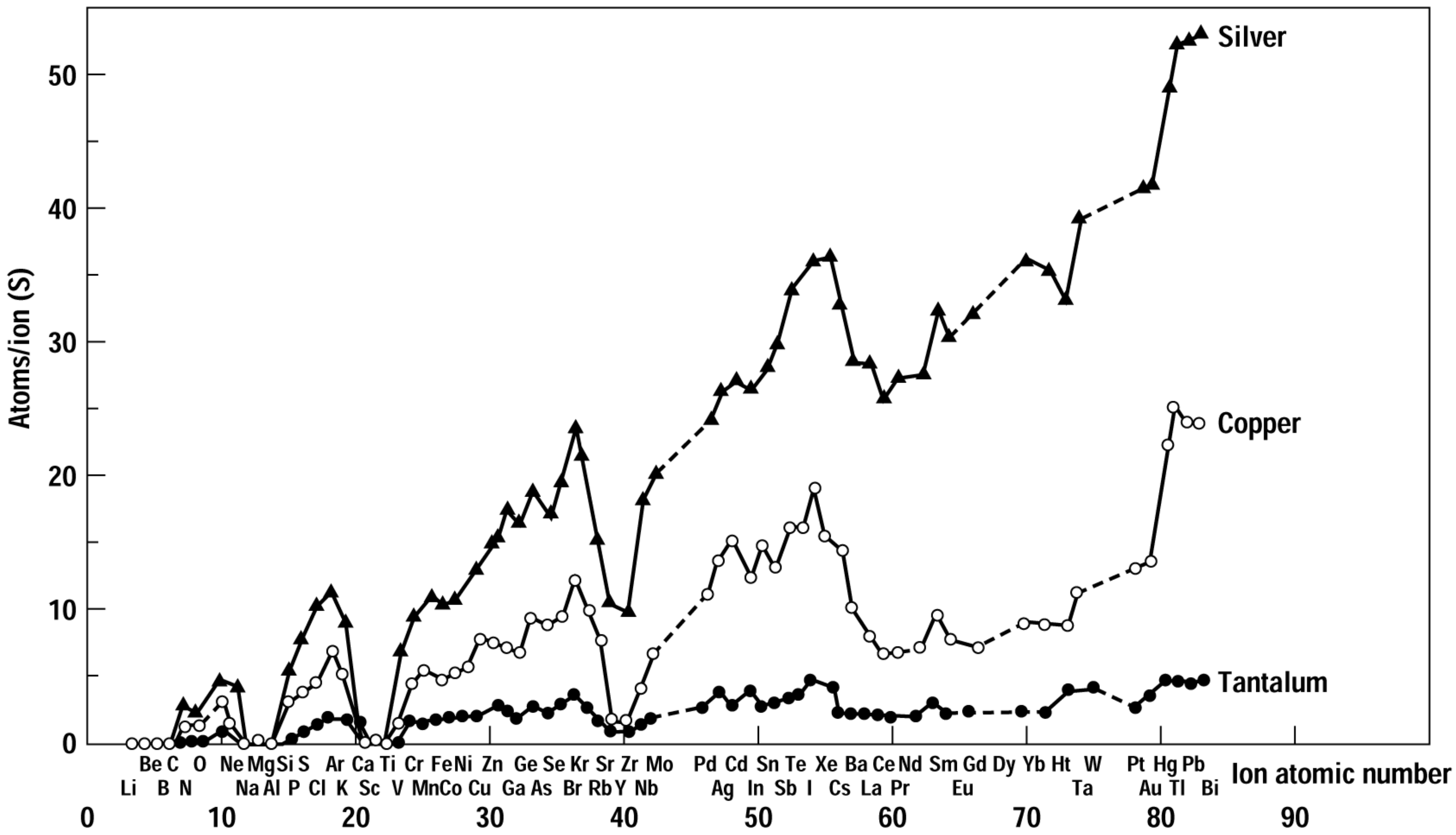
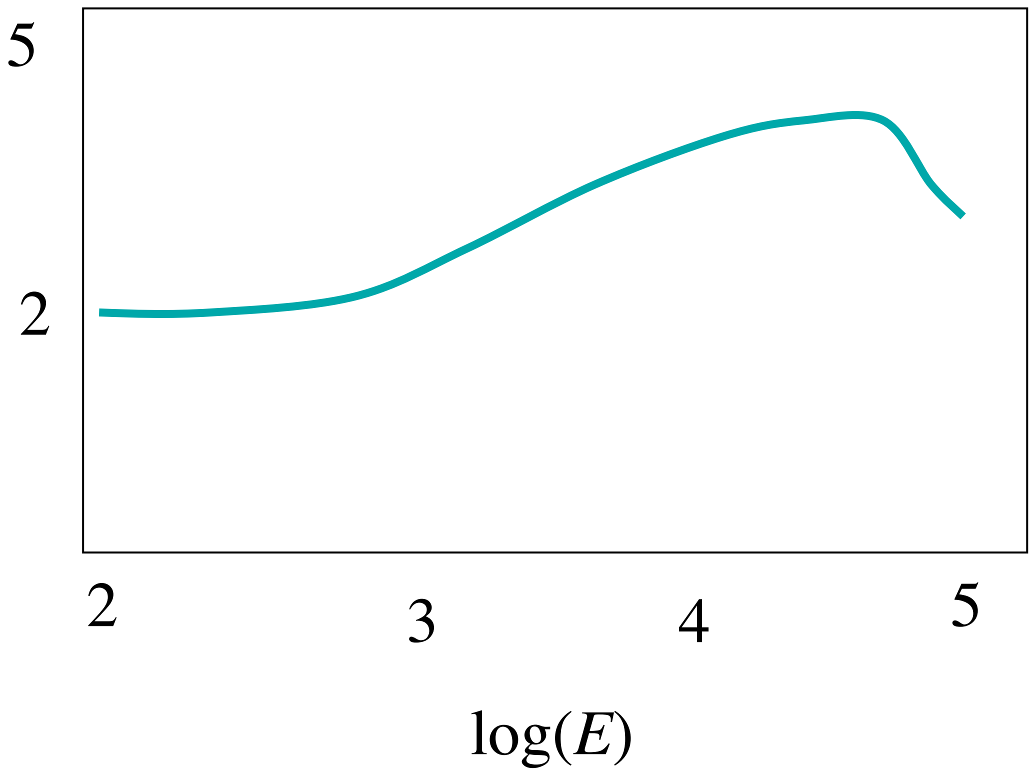


Figure 12.14 Sputter yield as a function of the bombarding ion atomic number for 45-keV ions incident on silver, copper, and tantalum targets *(after Wehner, reprinted by permission, AIP).*

Sputtering rate versus energy



For E= 500 eV, Ar
S=0.5-1.5 for all materials
, so poor selectivity

Sputtering coeff. depends on angle of incidence

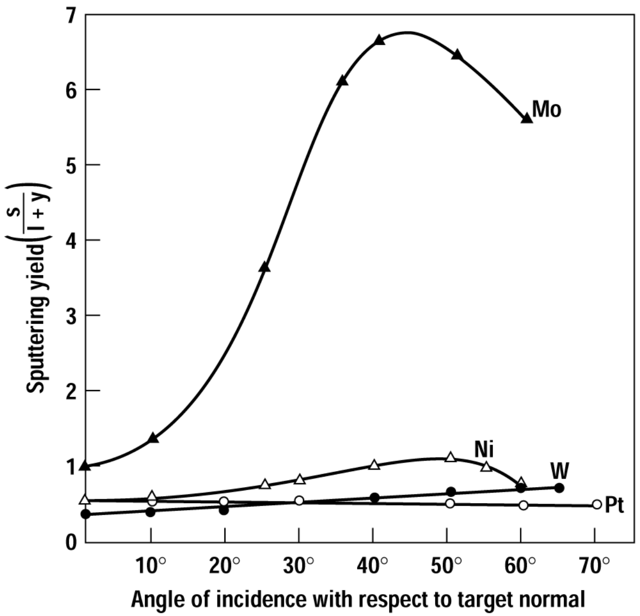
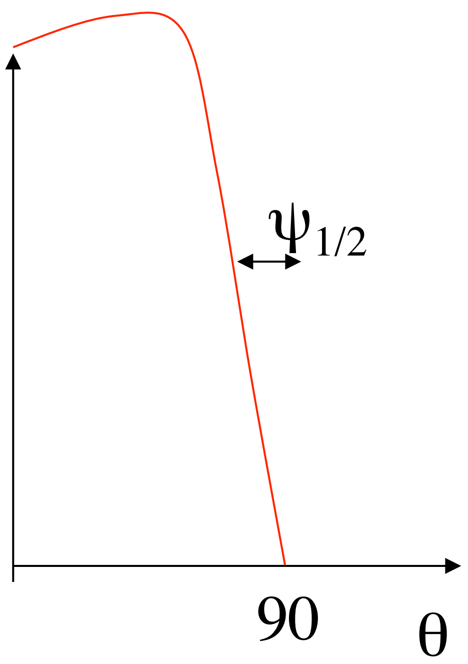
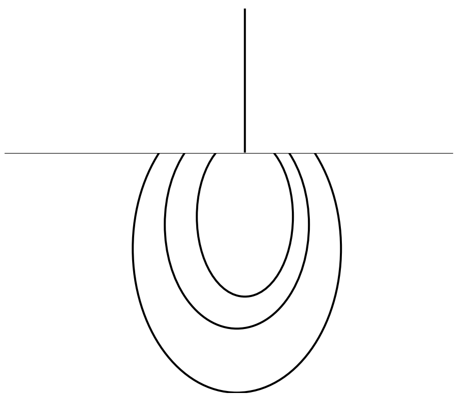
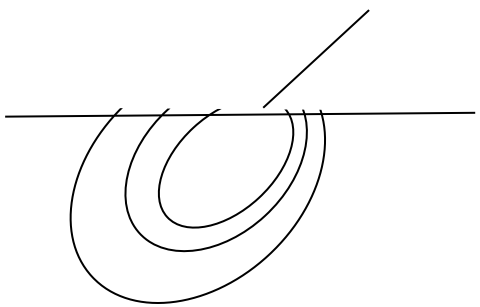


Figure 12.15 Typical angular dependence of the sputter yield for several different materials. The sputter profiles follow a cosine distribution *(after Wehner, reprinted by permission, AIP).*







Sputtering depends on angle of incidence n exit

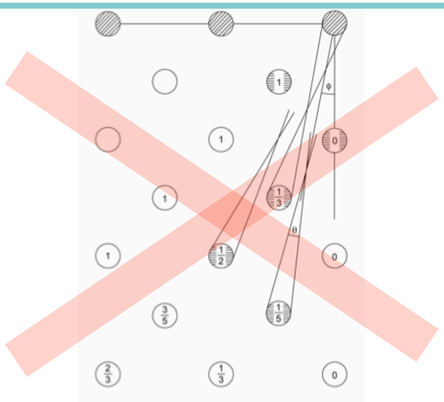


Figure 10: Transparency model of single crystal sputtering. The ion enters from the upper right. Numbers indicate the tangent of the angle of incidence. half-dashed spheres indicate local minima observed in the sputter yield. Redrawn from [15].

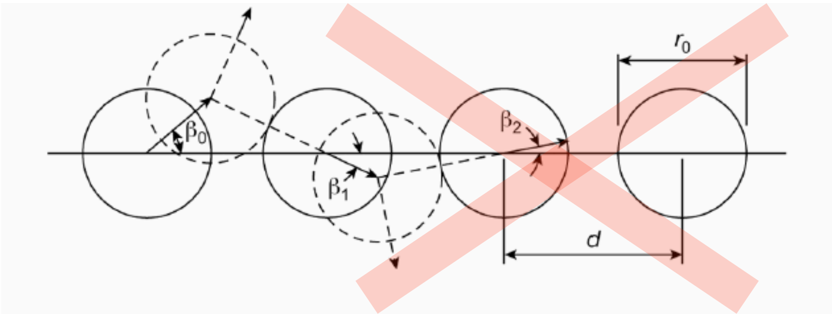


Figure 8: Focused collision sequence ('focuson') according to Silsbee. See text. Redrawn from [17].

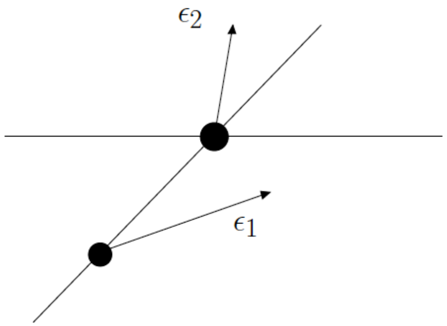


Figure 13: Surface model to explain Wehner spot according to ref. [44].

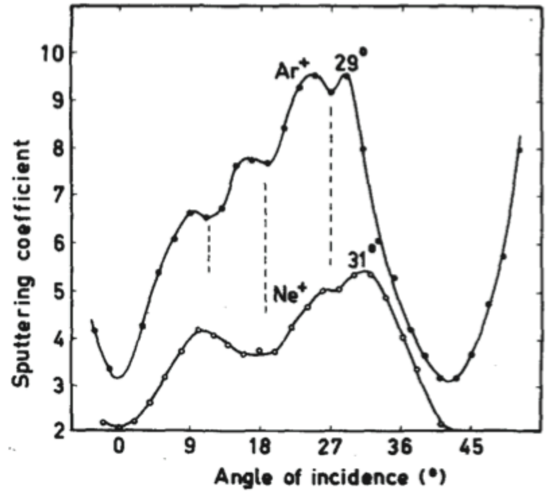
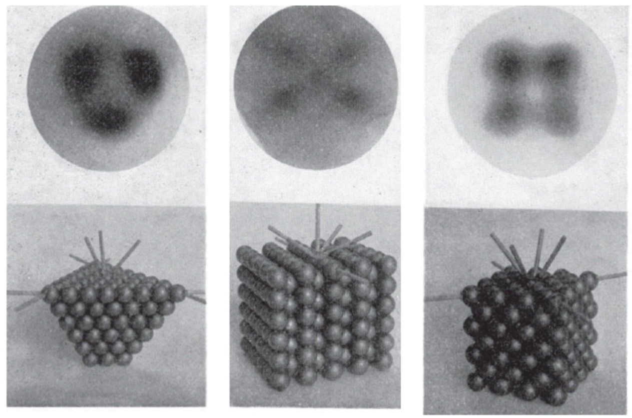


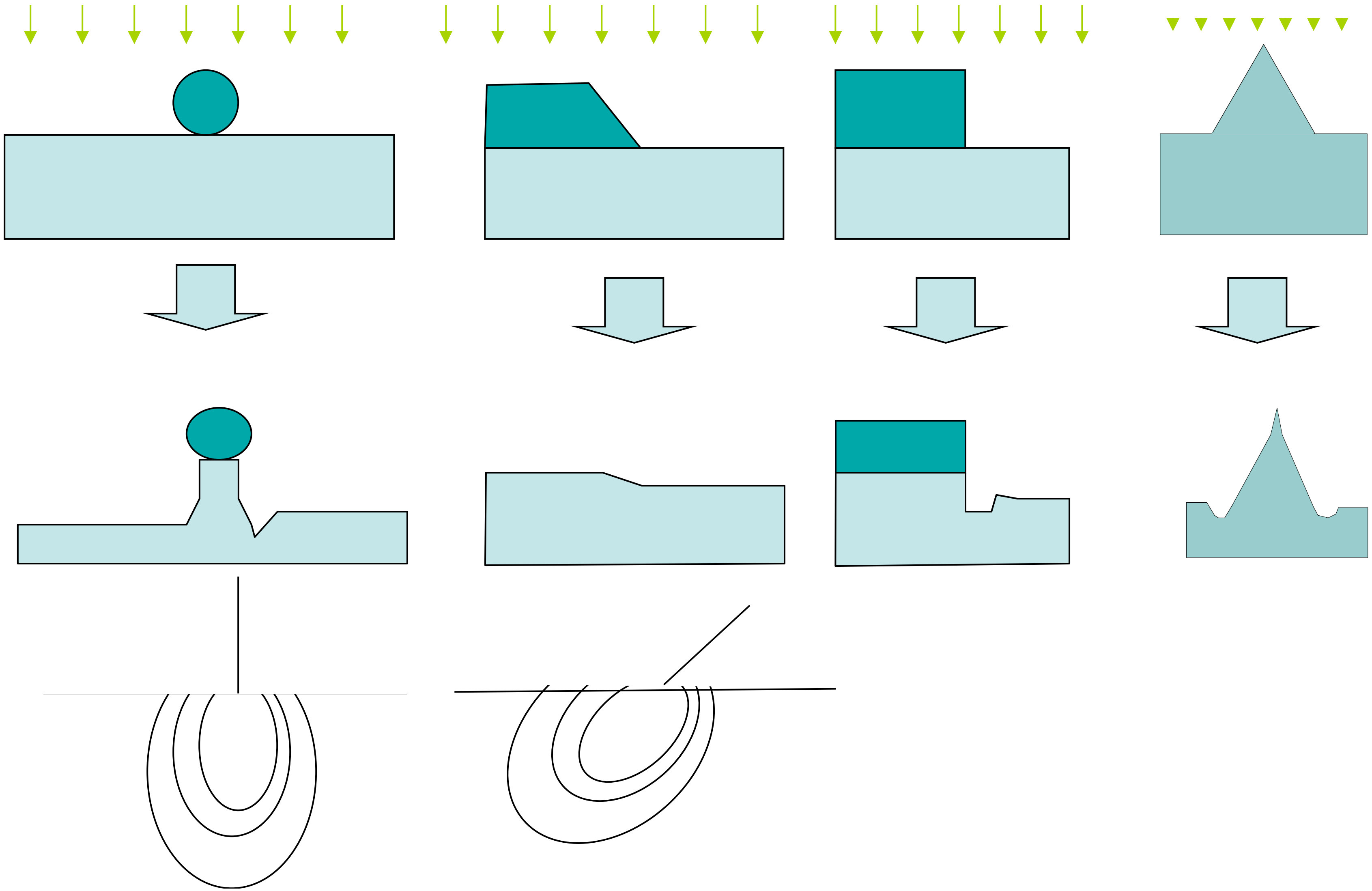
Figure 7: Sputter yield of a (100) copper crystal for 20 keV Ar and Ne ions as a function of the angle of incidence against the [100] surface normal. From [15].



{111} {110} {100}

Figure 2: Angular distribution of gold atoms sputtered from single crystal surfaces by 100 (right and left) or 50 (center) eV Hg ions. From [6].

Development of topography with sputtering



Mask taper, redeposition, trenching

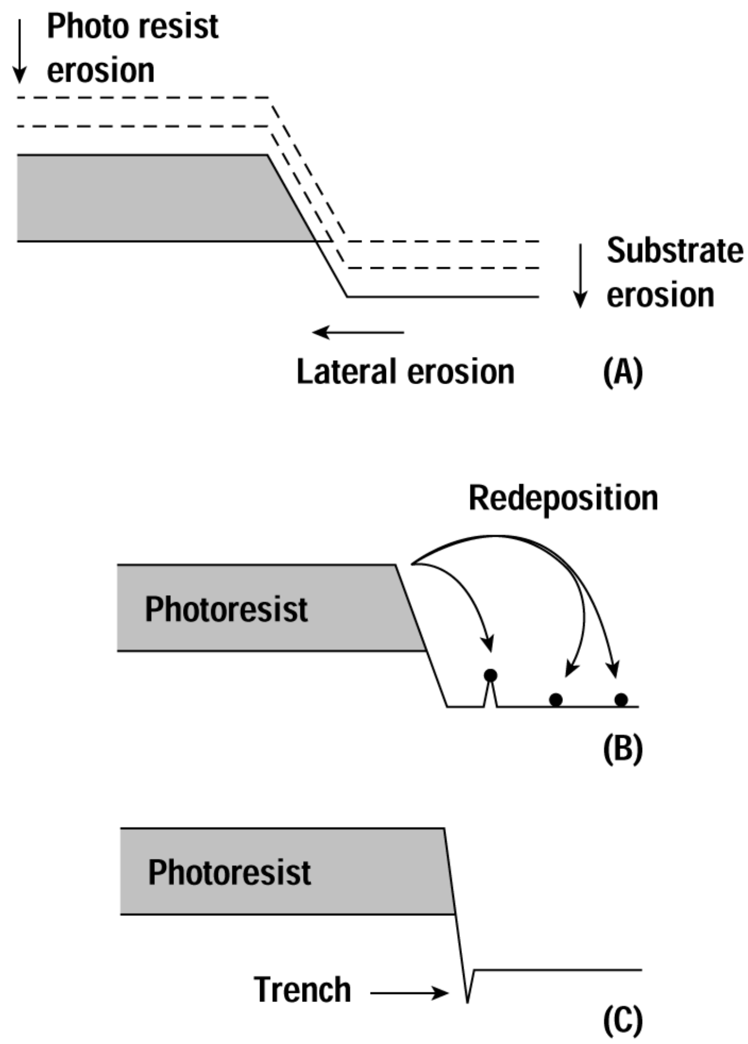


Figure 11.15 Problems that may occur during ion milling: (A) mask taper transfer, (B) redeposition from the mask, and (C) trenching.

Dry reactive ion -etching

Under **ion bombardment** , e.g. in a **plasma** these processes occur

Ionization

eks $Ne + e \rightarrow Ne^{+} + 2e$

$O_2 + e \rightarrow O_2^{+} + 2e$

Fragmentation with ionization

eks $CF_4 + e \rightarrow CF_3^{+} + F + 2e$

Fragmention with ionization og adhesion

eks $CF_4 + e \rightarrow CF_3^{+} + F^{-} + e$

Fragmentation without ionization

eks $O_2 + e \rightarrow 2O + e$

$CF_3Cl + e \rightarrow CF_3 + Cl + e$

$C_2F_6 + e \rightarrow 2CF_3 + e$

Point: Fragments and ions are more reactive than molecules

CF_4 doesn't react with Si at any temp below1412 °C
F reacts spontaneously w. Si at RT, creates (vol)SiF_4

Ion-enhanced chemical etching

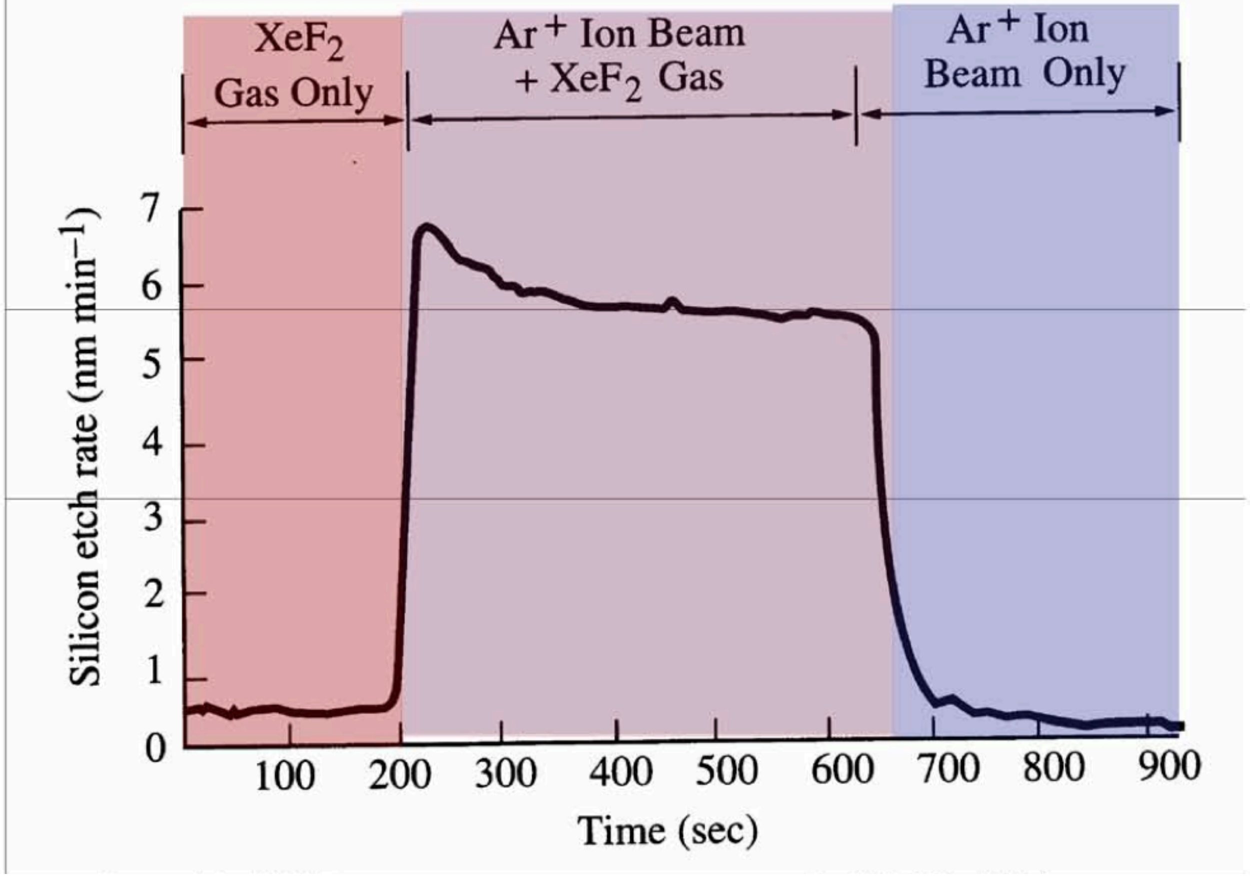
Physical and chemical processes not just independent of each other.

Ion beam can enhance chemical etching:

XeF_2 etching of Si

No plasma

No XeF_2



Further, the profile is not linear combo, but highly anisotropic

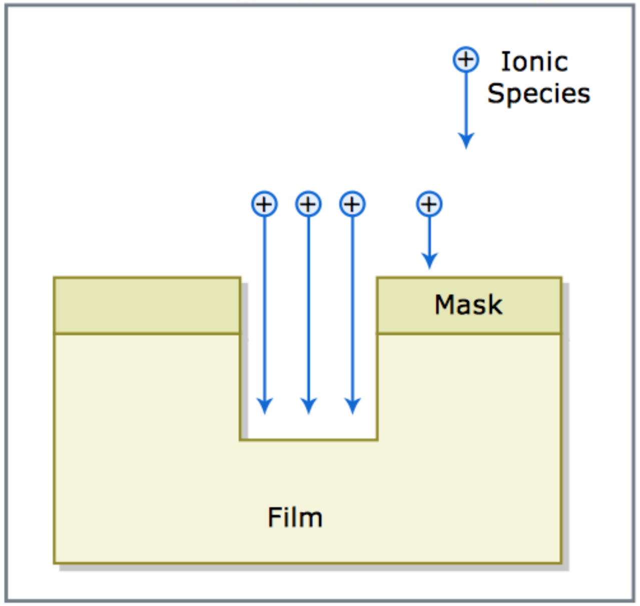


Figure by MIT OCW

Wow!

The best of both

Aniso. + selctive

Ion-enhanced chemical etching

Why does rate of one process depend on the other being present?

Tailor mix of gas as well as ion energy & rate to select desired wall profile.

Possible mechanisms:

1. Ions break bonds, render XeF_2 more reactive
2. Ions increase formation of of volatile byproducts
3. Ion beam may sputter away byproducts

See also next slide

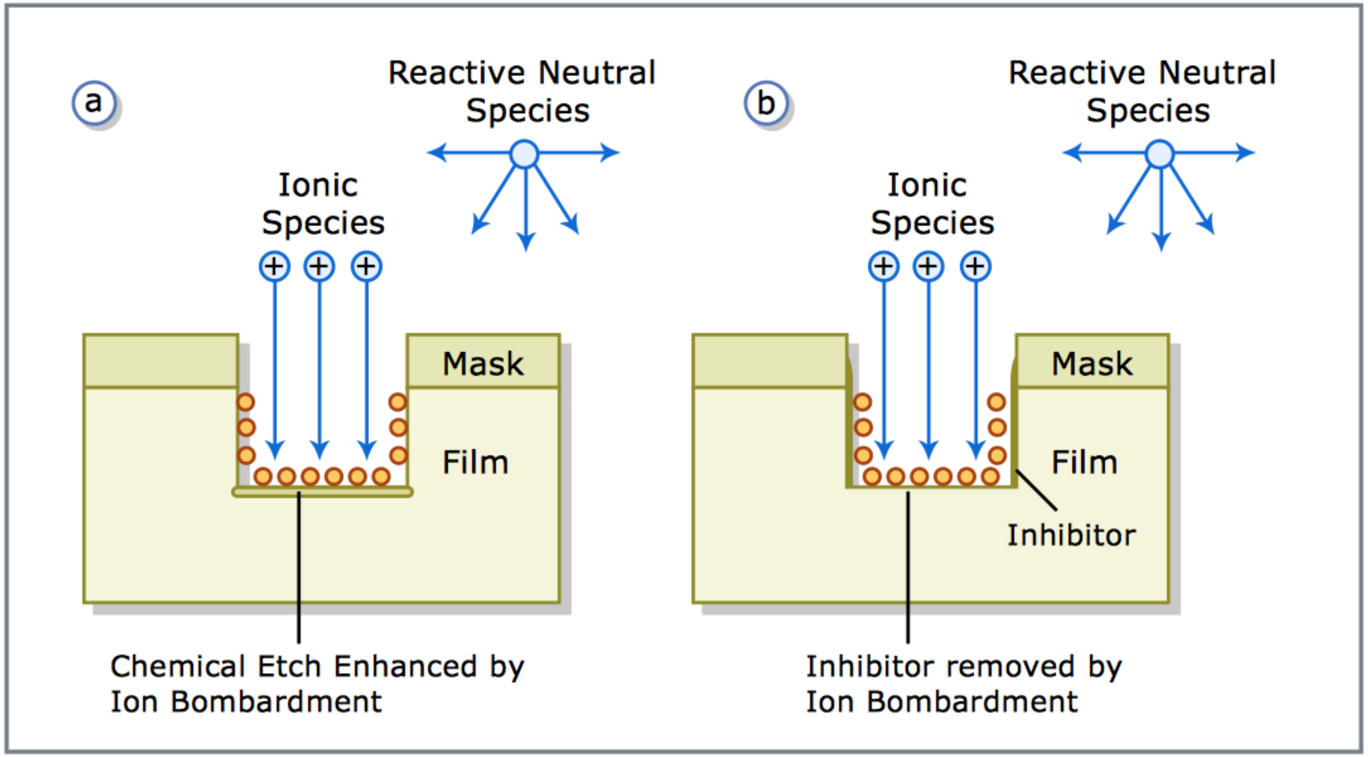


Figure by MIT OCW.

Dry etch mechanisms, examples

O_2 does not attack photoresist
O og O- reacts to CO, CO_2 og H_2O

Rate for fragmentation or ionization depend on
process parameters: pressure, power, frequency, flowrate

Normally direct physical sputtering not important
For the typical case
More important is the effect of bombarding ion on chem. reactions
i.e. Ion assisted reaction between neutral atoms and surface

Mechanisms

1. Radiation -> dangling bond, kink site-> adsorption
2. Dissociation of adsorbed molecules, e.g. Cl_2 , XeF_2
3. Removal, sputtering of non volatile etch products

Dry etch, common gasses

Halogens

Si: CF_4, CF_4+O_2, SF_6, SF_6+O_2, NF_3,
Cl_2, CCl_4, CCl_3F

Si O_2, Si_3N_4 :
CF_4, CF_4+H_2, C_2F_6, C_3F_8, CHF_3,

Al, AlSi :
CCl_4, BCl_3

Al-Cu :
BCl_3+Cl_2

Cl on Si surface

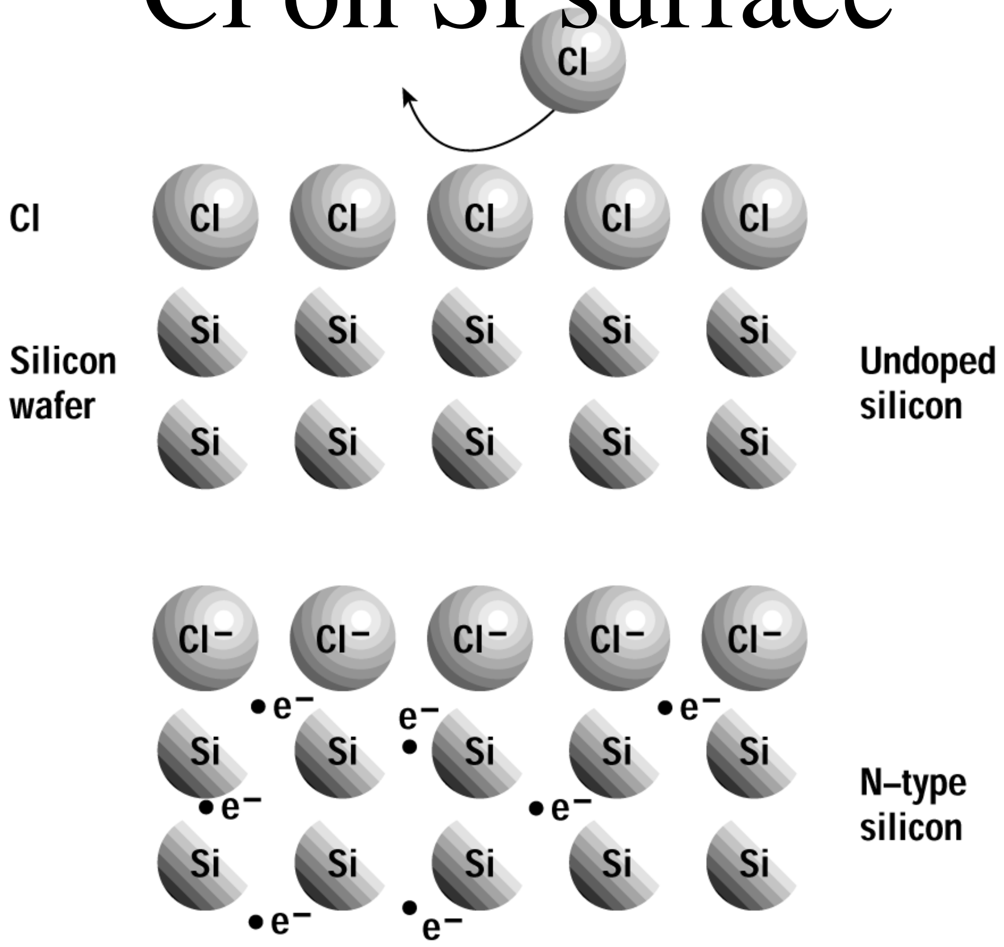
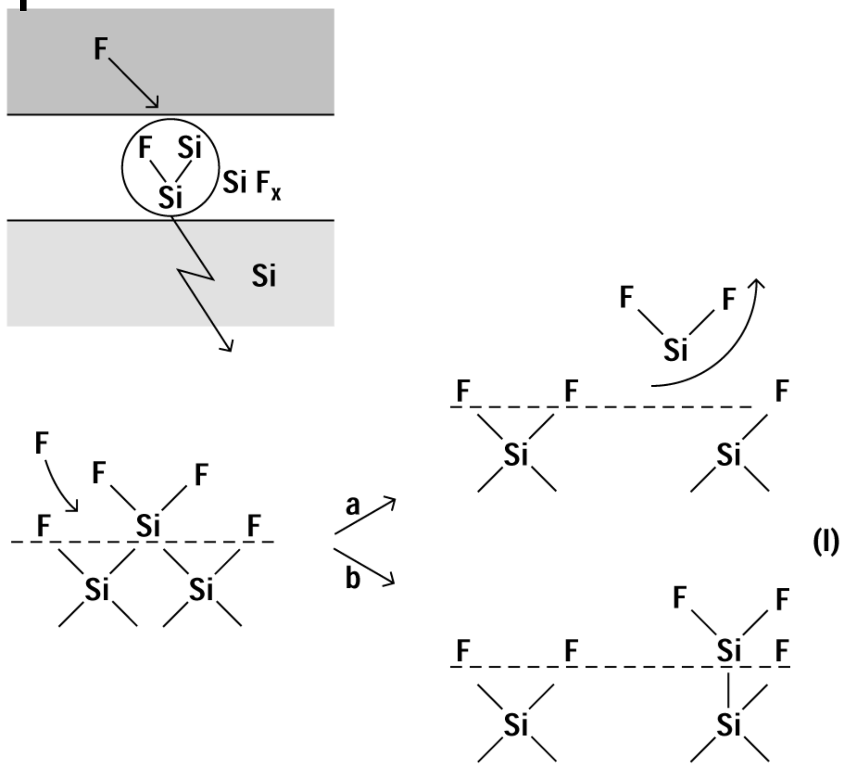


Figure 11.18 Once a monolayer of chlorine atoms builds on the surface, it impedes any chlorine addition.

Plasma etch in CF4



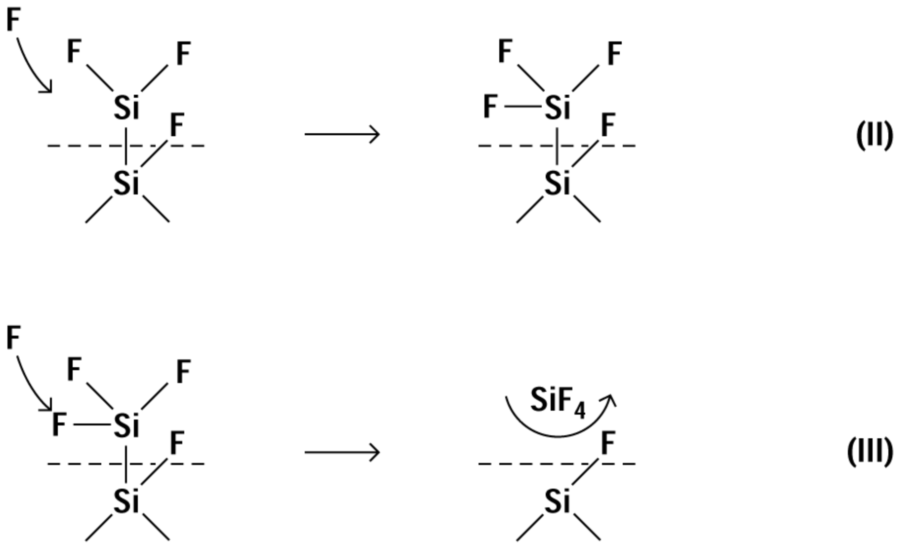


Figure 11.8 Proposed mechanism of plasma etching of silicon in CF_4. A 1- to 5-atom-thick SiF_x layer forms on the surface. A silicon atom on the upper level is bonded to two fluorine atoms. An additional fluorine atom may remove the silicon as SiF_2. Much more likely, however, is that additional fluorine atoms bond to the silicon atom until SiF_4 forms and desorbs *(after Manos and Flamm, reprinted by permission, Academic Press).*

Sidewall passivation

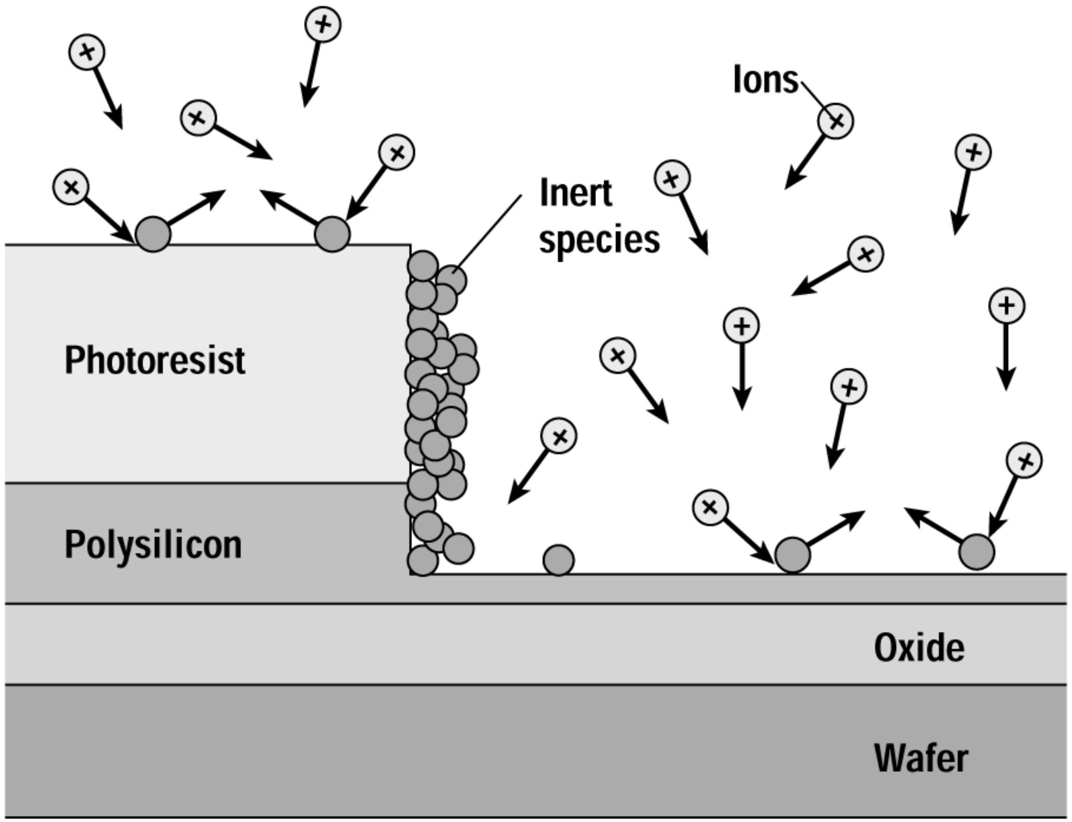
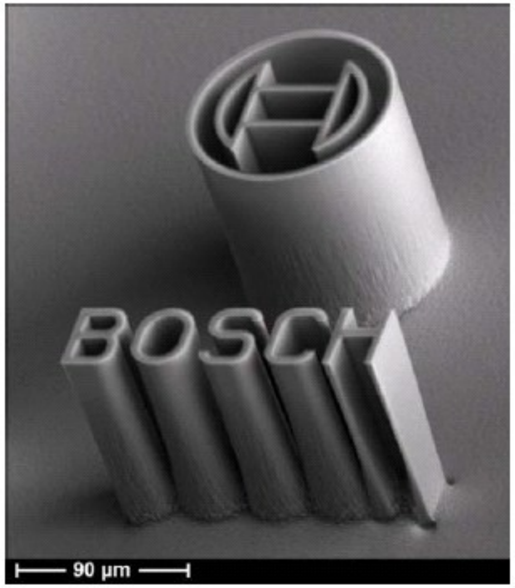
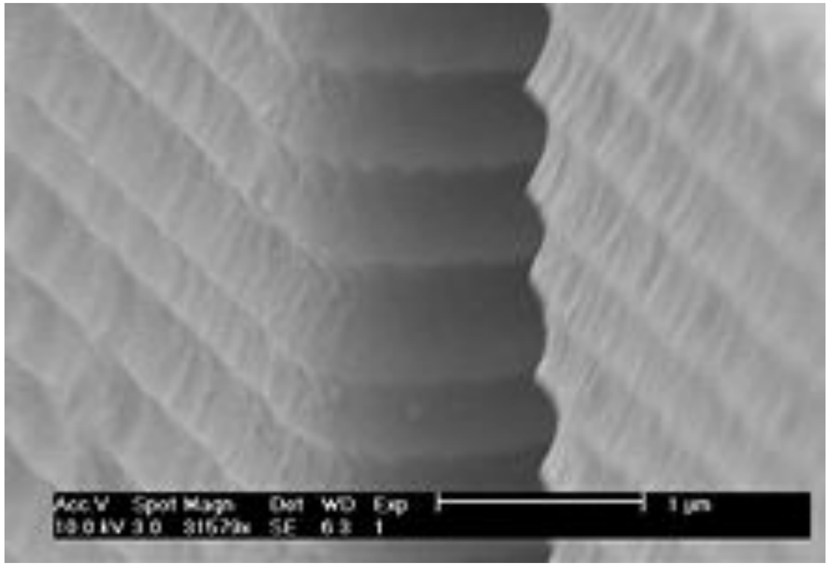


Figure 11.10 Schematic diagram of a high-pressure anisotropic etch showing the formation of sidewall passivating films.

Deep reactive Ion etching, Sidewall passivation, Bosch process





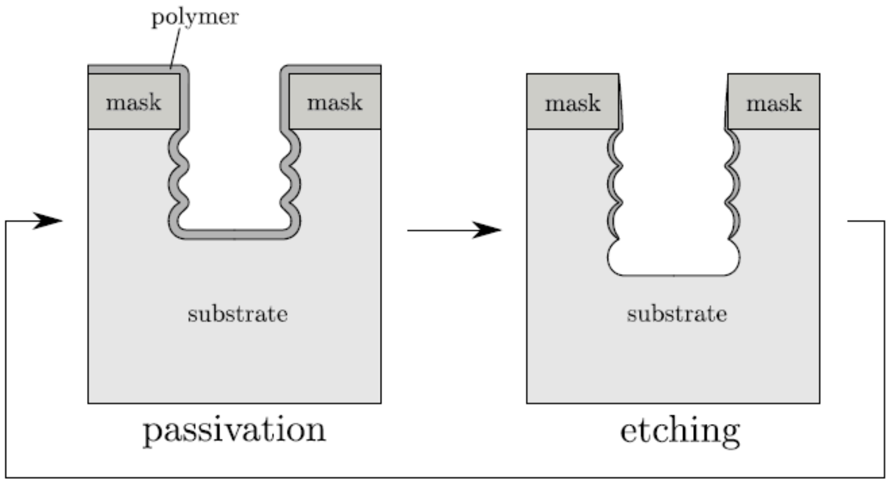


Figure 4.15: A schematic illustration of the Bosch process. The deposition of a passivation layer protects the sidewalls during the subsequent etching cycle.

Plasma [SF6] nearly isotropic etch

Deposition C_4F_8 (Octafluorocyclobutane)

Si/SiO2 Etch rates

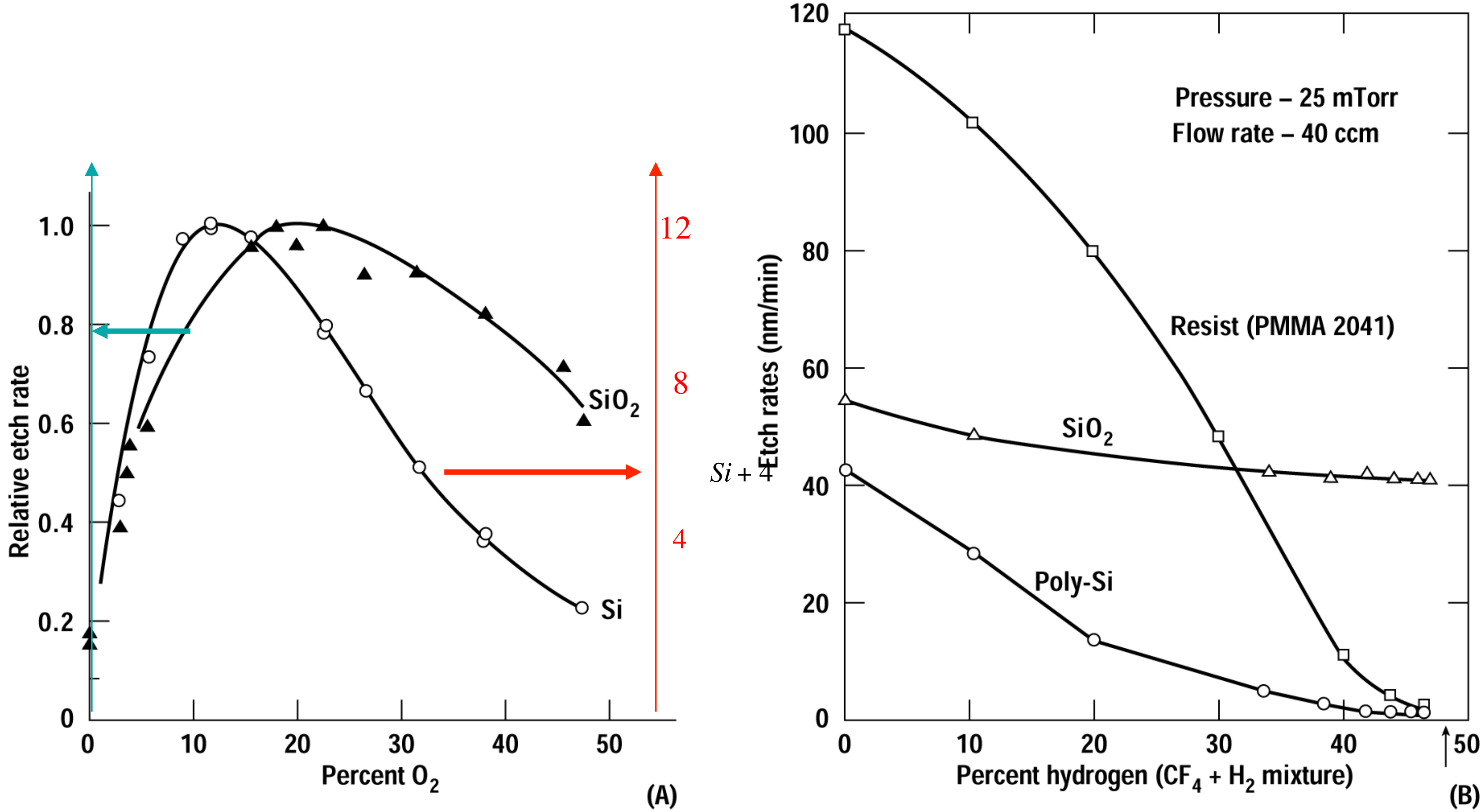


Figure 11.11 Etch rate of Si and SiO_2 in (A) CF_4/O_2 plasma *(after Mogab et al., reprinted by permission, AIP)*, and (B) CF_4/H_2 plasma *(after Ephrath and Petrillo, reprinted by permission of the publisher, The Electrochemical Society Inc.)*.

Main etching

$Si + 4F \rightarrow SiF_4$

$Si\,O2 + 4F \rightarrow SiF_4 + O_2$

In plasma CF_4

Si/SiO_2 etch rate in CF $+O_2$

In gas

1. $(e) + CF_4 \;\text{<-->}\; (4-n)F^{(x)} + CF_n^{(y)} + (\,e + xe - ye)$

2. $CF_n \;\text{<-->}\; F^- + CF_{n-1}$

1 og 2 gives that F concentration is low, F etches by

3. $Si + 4F \;\text{->}\; SiF_4(g)$

Add O_2 increases [F], deplete CFn v. 2 ,
creates COF_2, CO, CO_2 so [F] increases

Measured max [F] at 23%

Si: O_2chemisorb surface, blocks access to F, more the more O, more the more O_2,
so max below 23 %

SiO_2: O2 always present on surface, so. max at 23 %

Concentrations in CF4 plasma

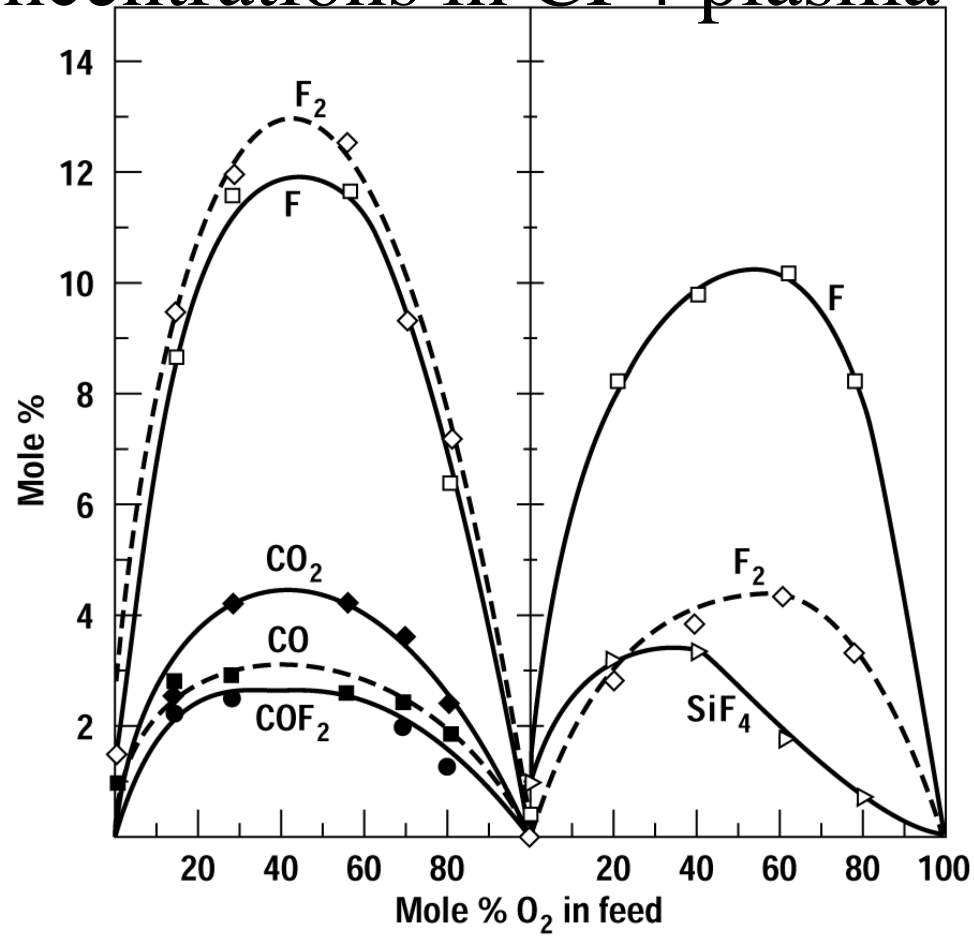


Figure 11.9 Species cocentration in a CF_4 plasma as a function of the amount of oxygen in the feed gas *(after Smolinsky and Flamm, reprinted by permission, AIP).*

SiO2 to Si X section

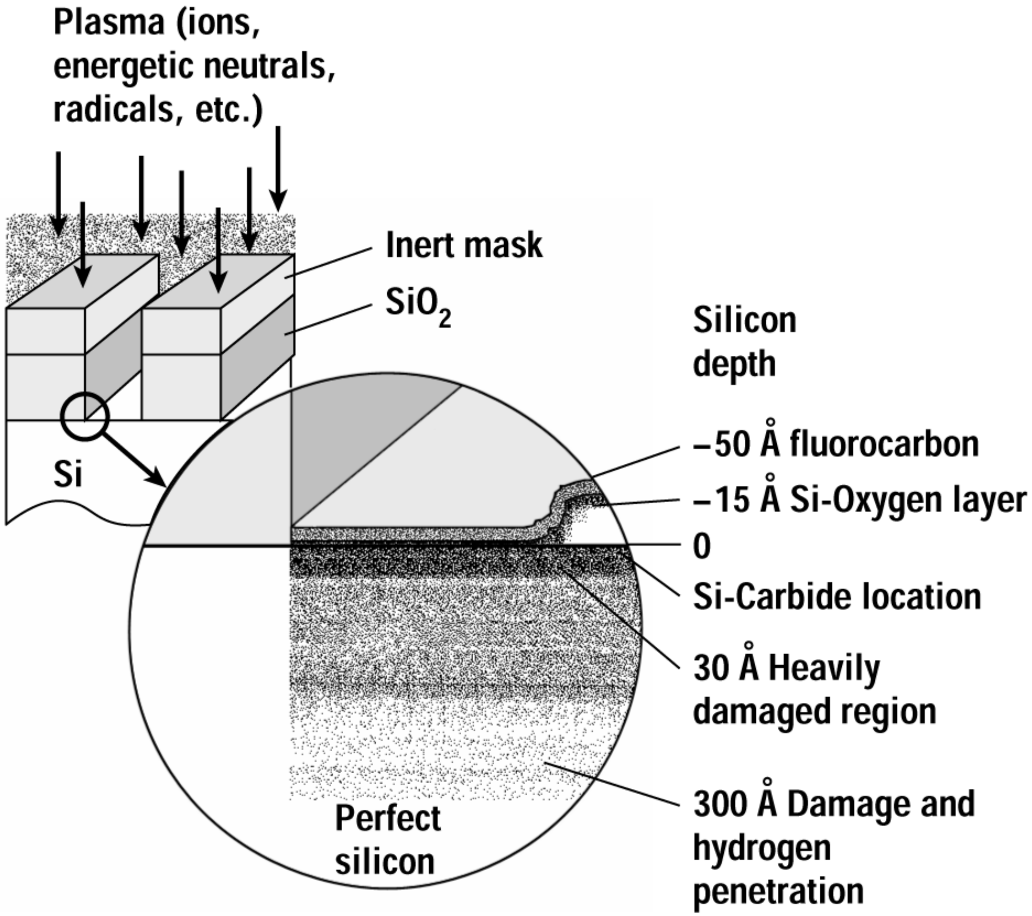


Figure 11.20 A cross section schematic of the results of a typical etch of SiO_2 down to Si using CF_4/H_2 *(after Oehrlein, Rembetski, and Payne, reprinted by permission, AIP).*

Kaufman ion Source

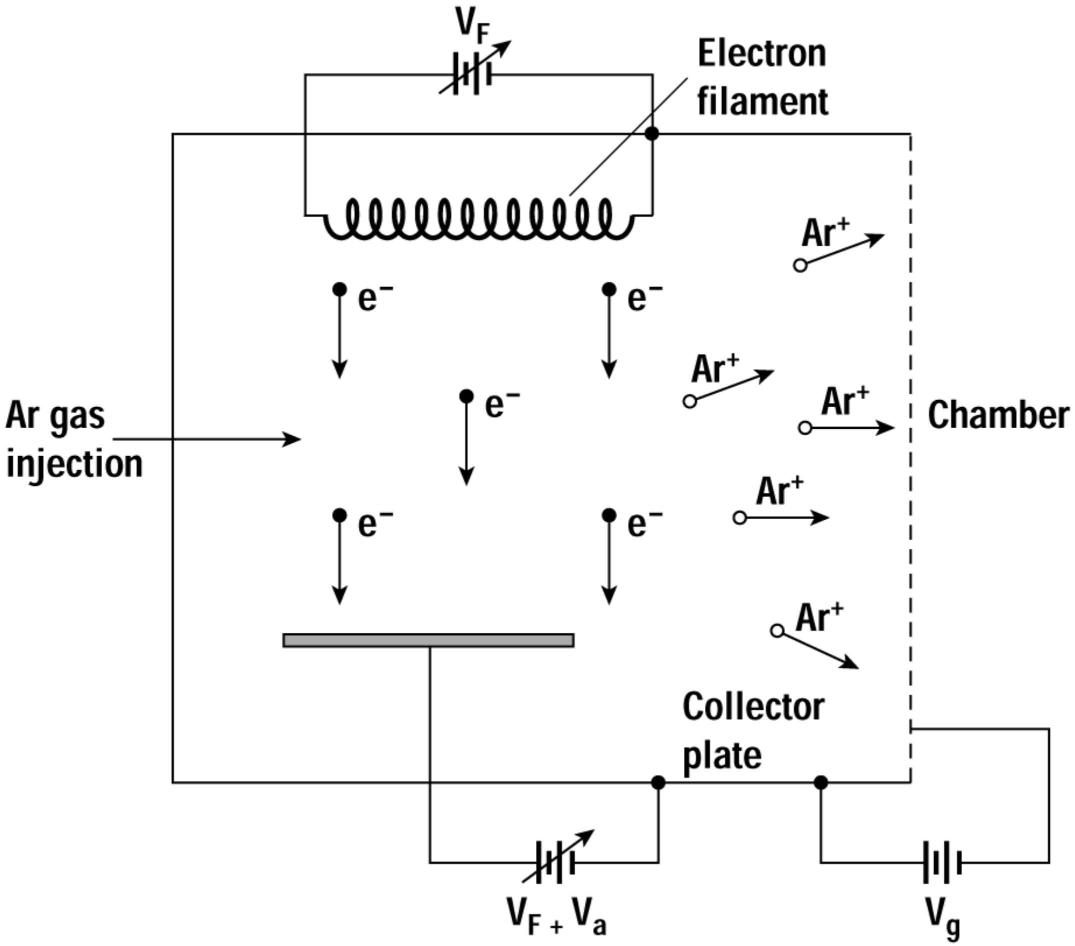


Figure 11.14 Cross section schematic of a Kaufman ion source.

Reactive bleed ion mill

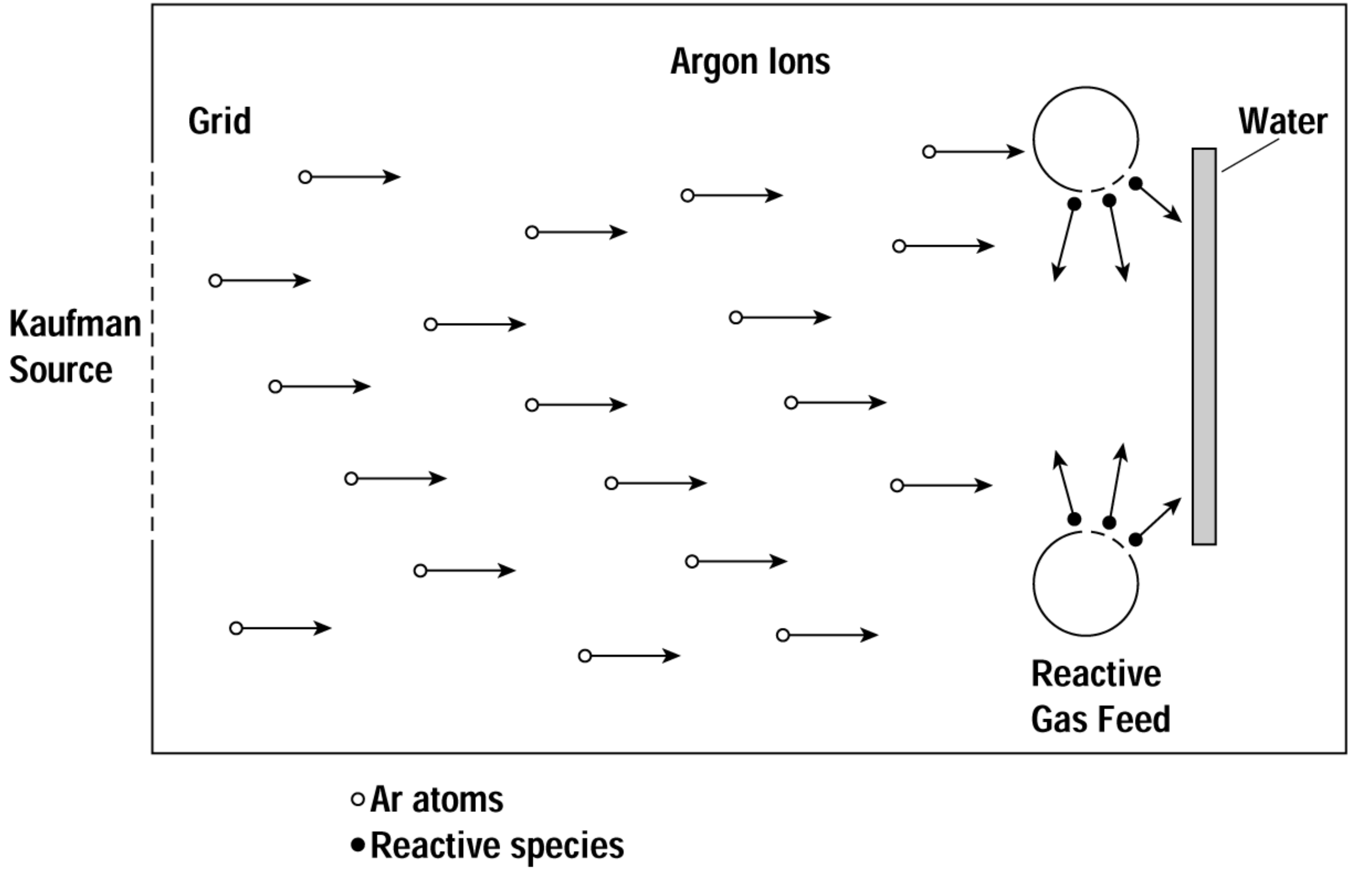


Figure 11.16 The use of a reactive bleed near the wafer surface in a conventional ion mill to introduce a chemical component to the etch process.

Batch RIE system

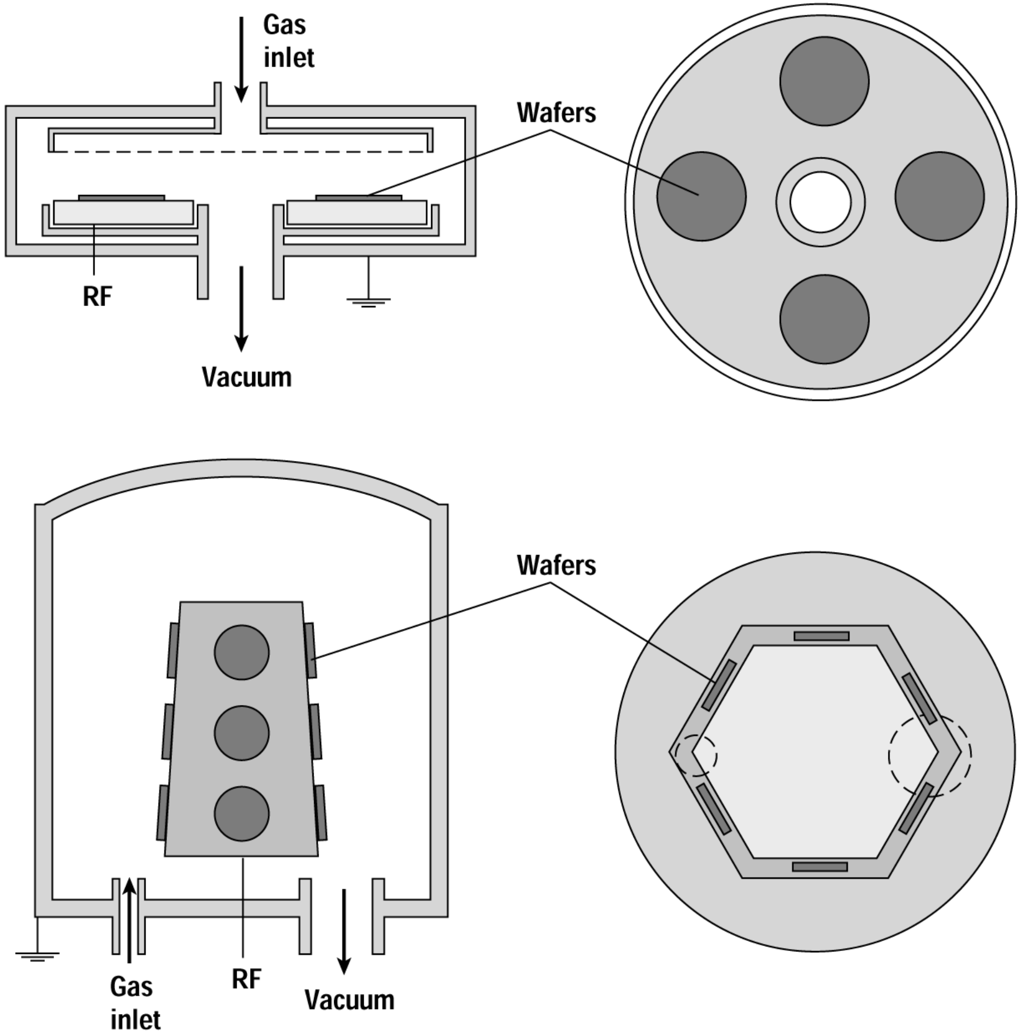


Figure 11.17 Top and side views of parallel-plate and hexode batch RIE systems. Typical conditions for either are 50 mtorr and 5 kW/m^2. For larger wafers the exhaust in the upper figure is drawn from the periphery rather than the center.

Resist scumming

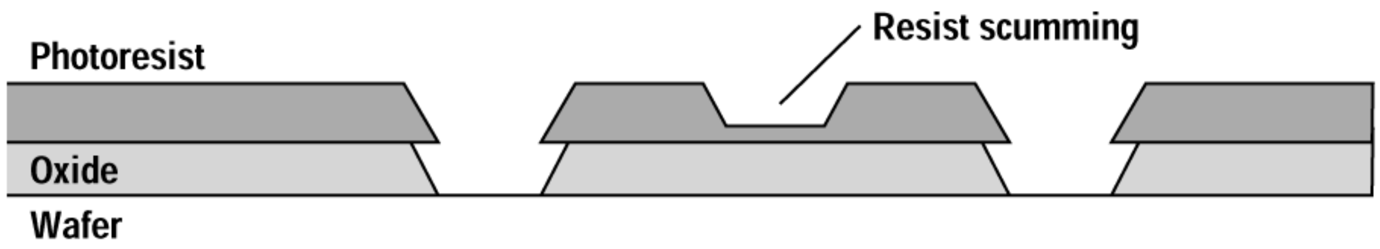


Figure 11.3 Resist scumming occurs when the photoresist is incompletely developed. The residual resist may serve as an etch mask to prevent a complete etch process.

Equipment plasma etcher

Figure 11.21 Applied Materials high-density plasma silicon etch system *(photo courtesy Applied Materials).*

Sputtering system

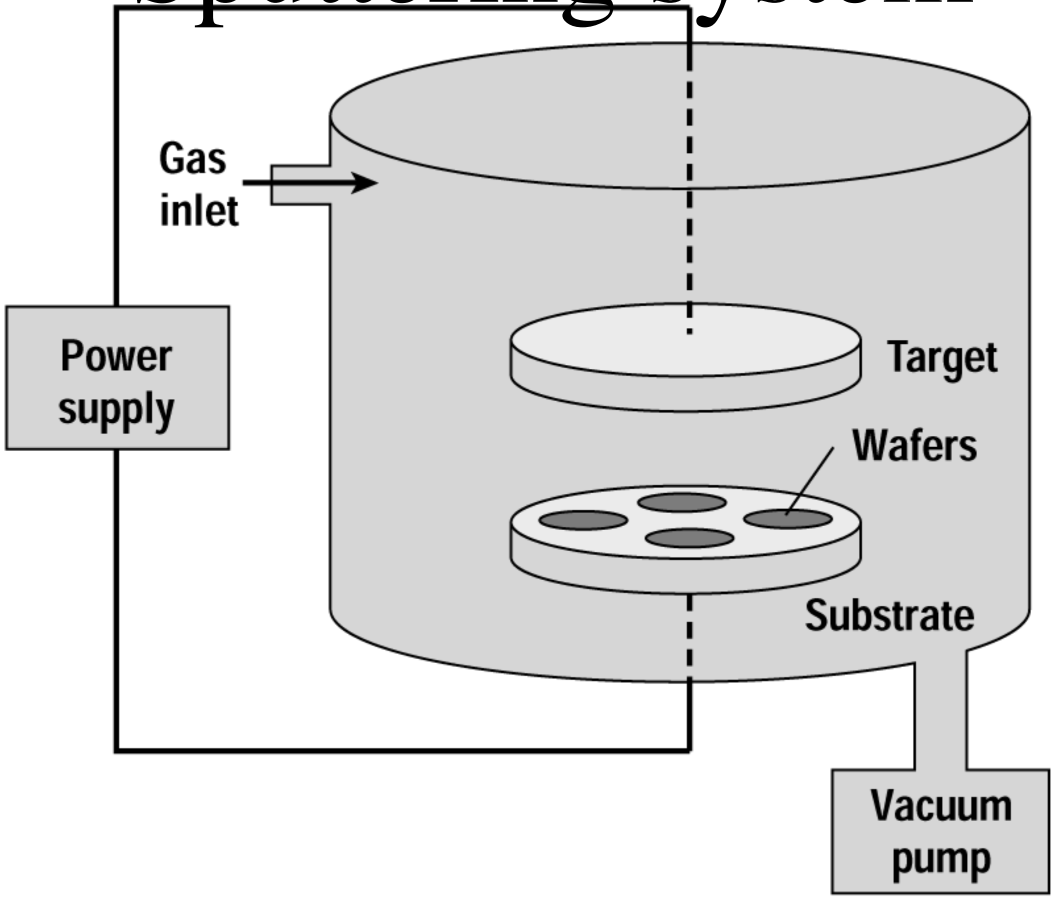


Figure 12.11 Chamber for a simple parallel-plate sputtering system.

Liftoff process

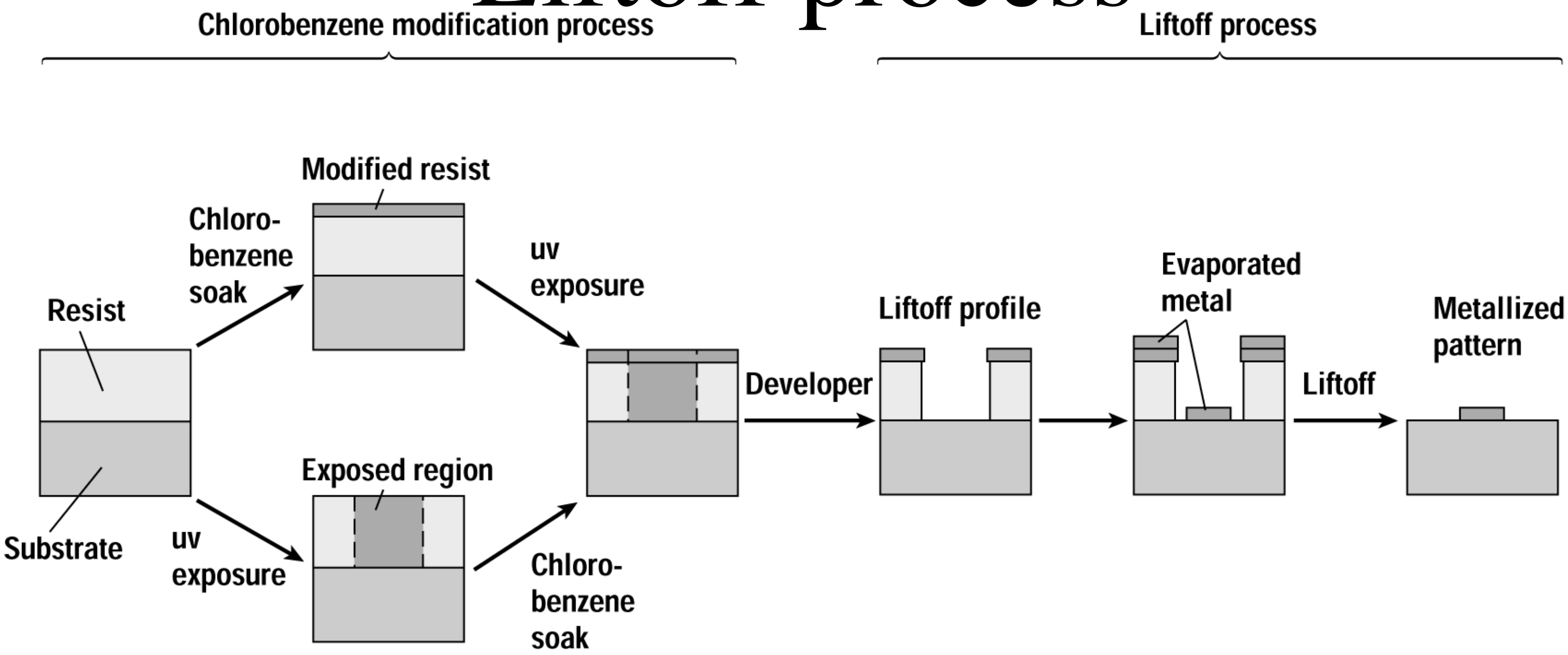


Figure 11.22 Process sequence for a liftoff operation *(after Hatzakis et al., © 1980 International Business Machines Corporation).*

The End