



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

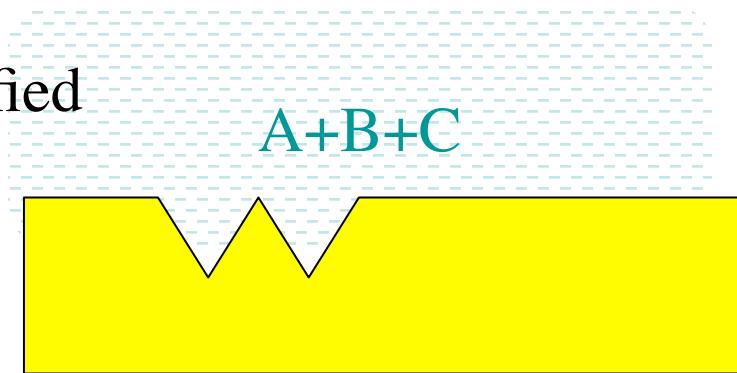
Typical etch, schematical, simplified

A: solvent, e.g. H_2O

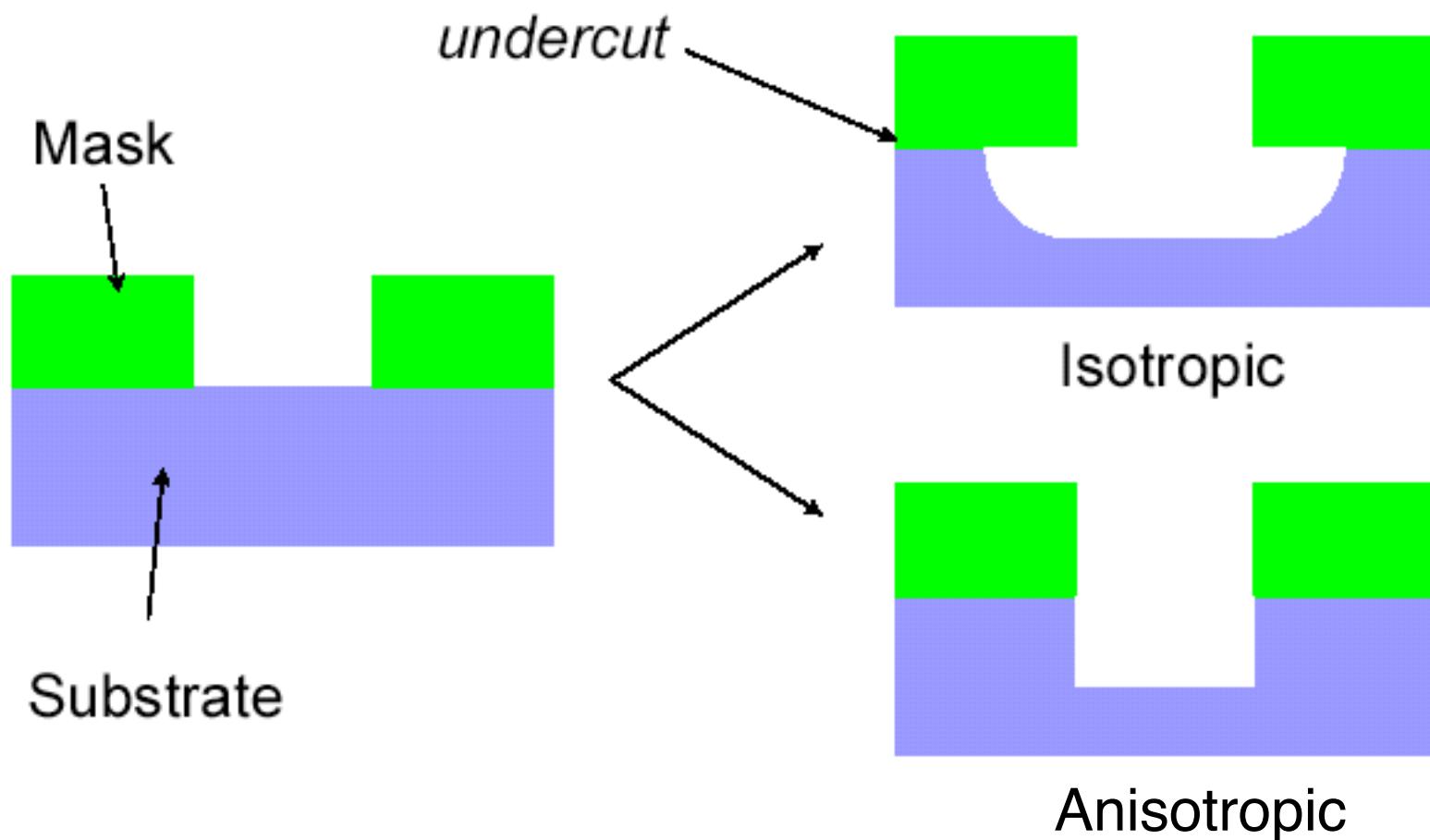
B: oxidizing agent

C: oxide dissolution, e.g. HF

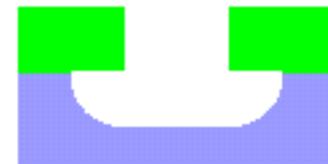
A+B+C



Etching: Isotropic vs. Anisotropic

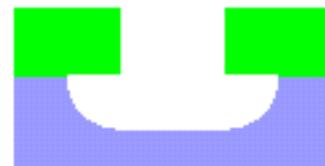


Isotropic Silicon Etching



- “HNA” Etch =
Hydrofluoric Acid+Nitric Acid+Acetic Acid
- HNO_3 oxidizes Si, HF etches oxide, HAc
stabilizes pH
 $(\text{HC}_2\text{H}_3\text{O}_2)$
- 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

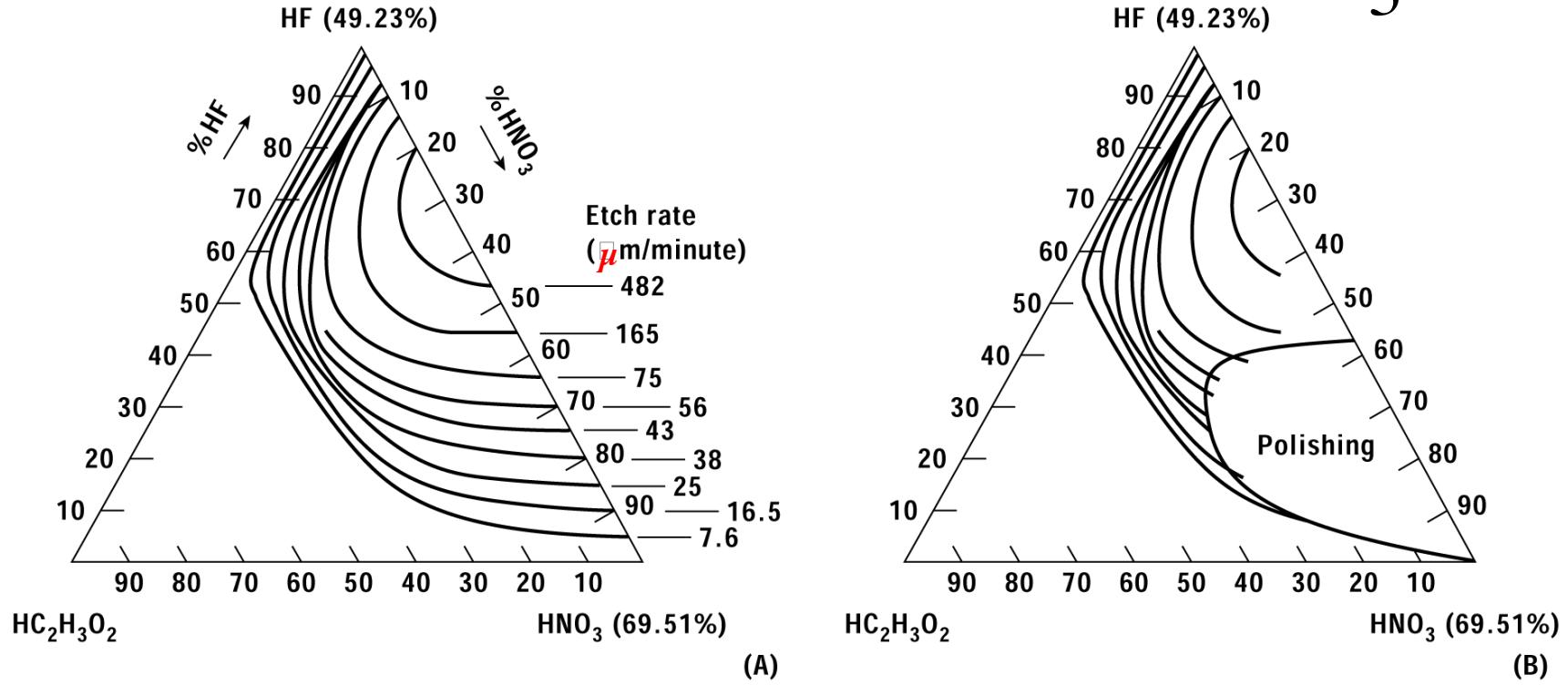


Figure 11.4 The etch rate of silicon in HF and HNO_3 (after Schwarz and Robbins, reprinted by permission of the publisher, The Electrochemical Society Inc.).

Etchrate GaAs in H_2SO_4

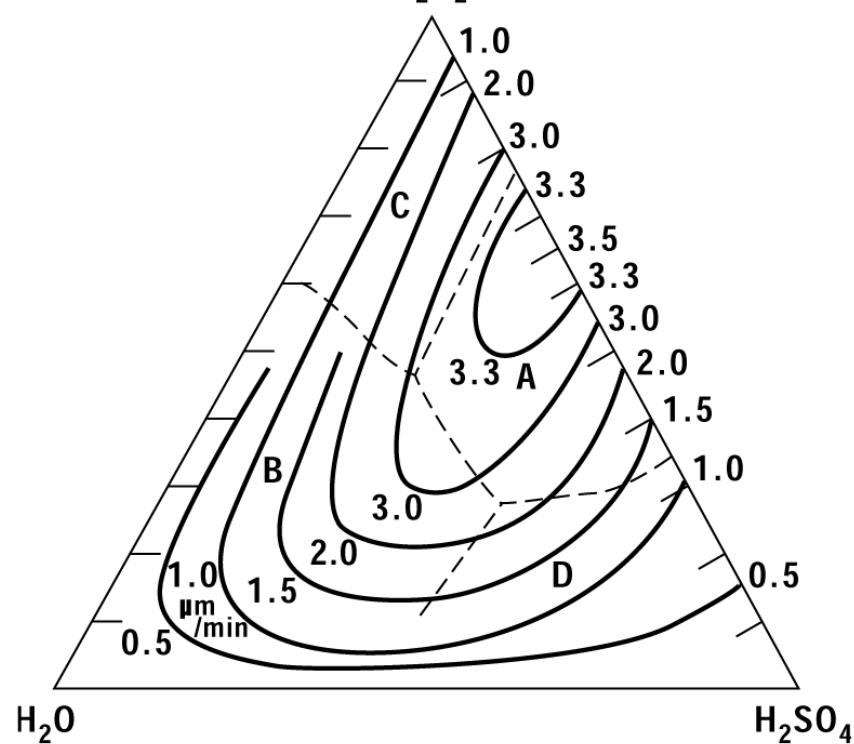


Figure 11.5 The etch rate of GaAs in H_2SO_4 , H_2O_2 , and H_2O . The bottom leg is the concentration of H_2SO_4 , the left leg is H_2O , and the right leg is H_2O_2 . All scales increase in the clockwise direction (*after Iida and Ito, reprinted by permission of the publisher, The Electrochemical Society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

Diffusion/reaction limited etching

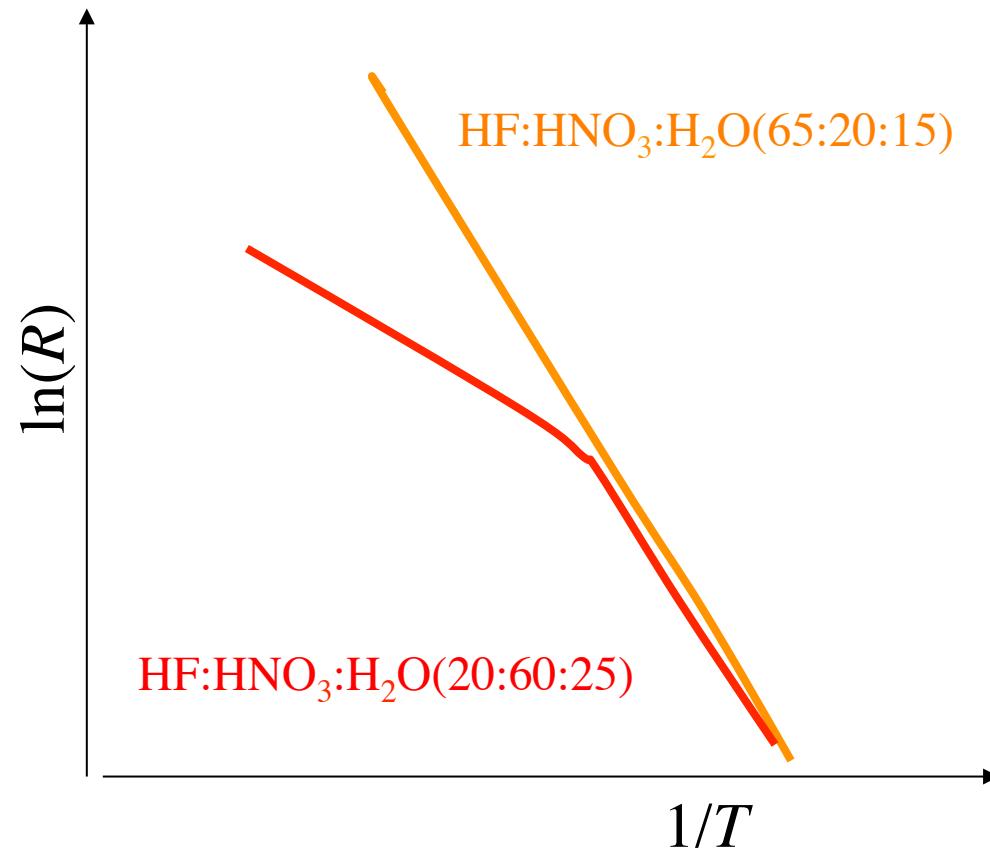
The attributes of **diffusion controlled** etch reactions are

- 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

Wet Etching -example diffusion/reaction limited



Wet Etching -xtal defects secondary identification

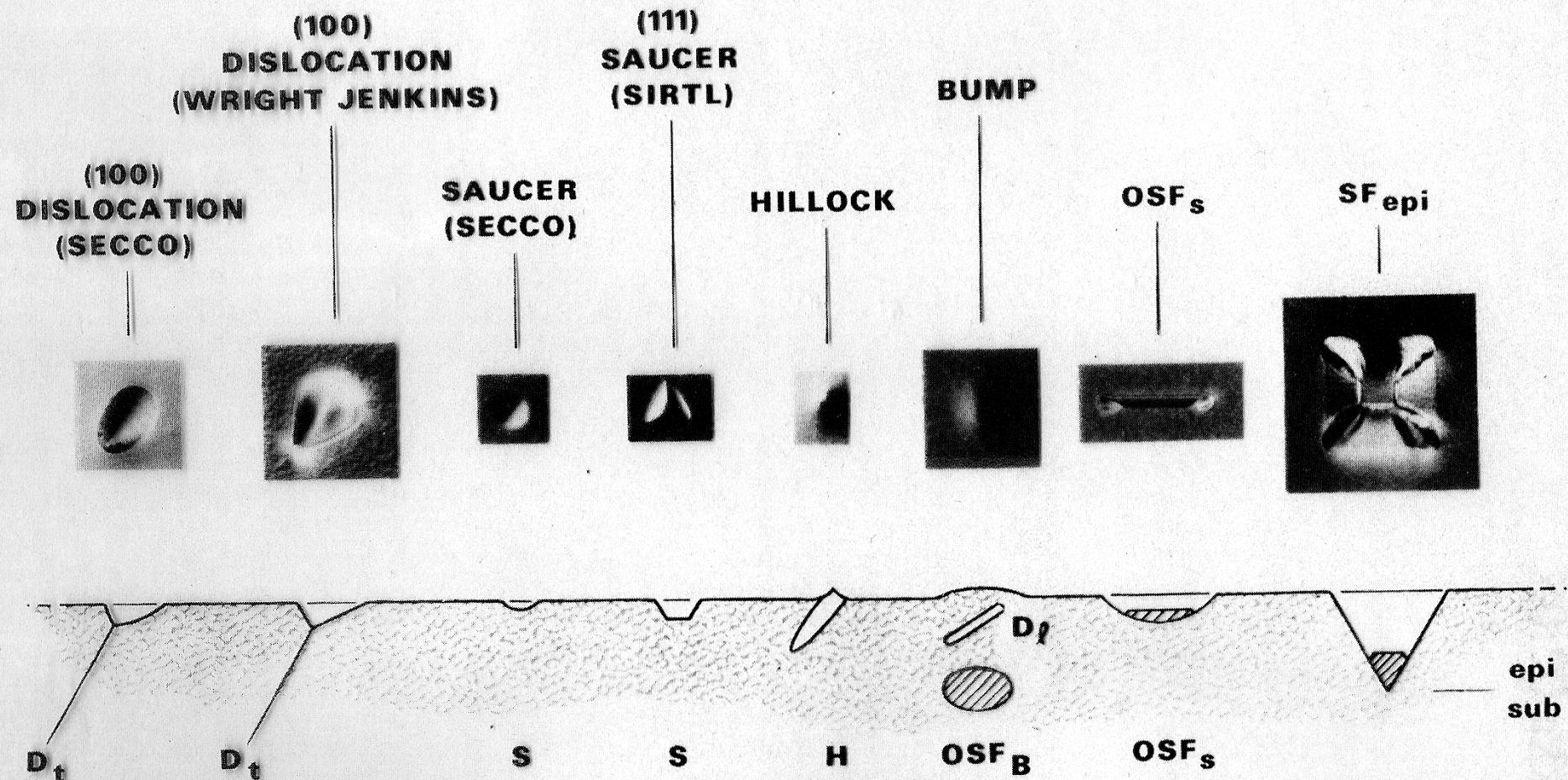
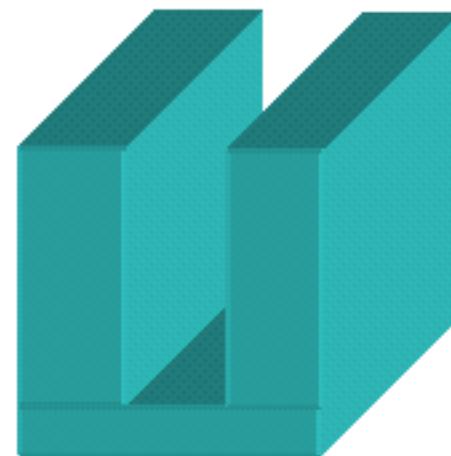


Fig. 4. A range of etch features found in silicon using the three etches listed in table 2.

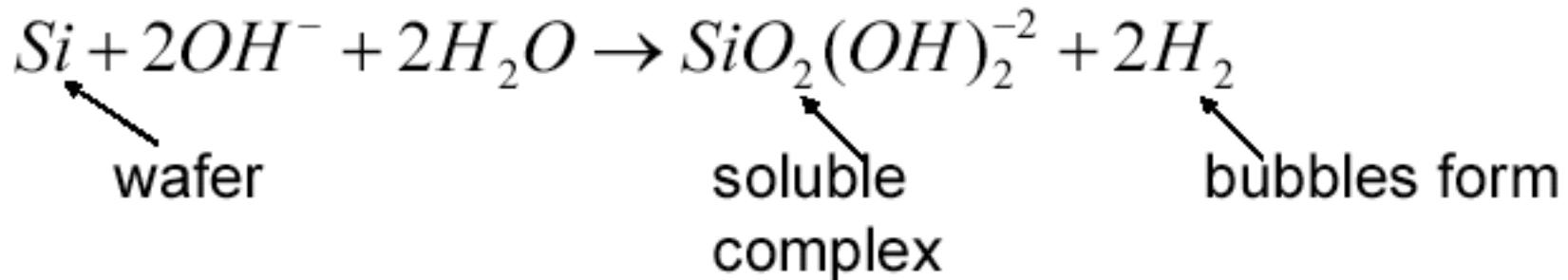
Anisotropic Wet Etching of Si

- Based on bases:

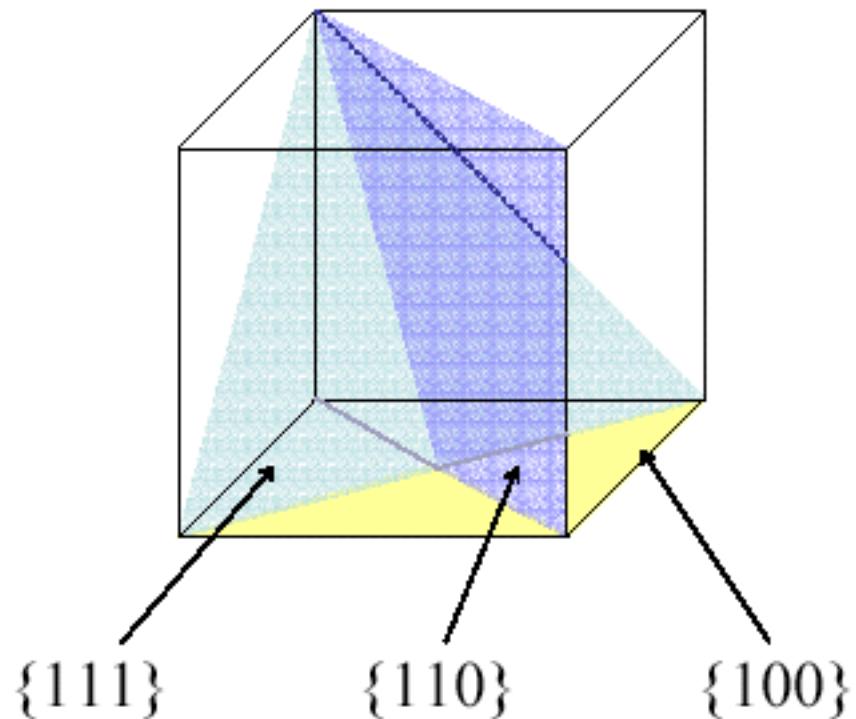
- KOH
 - NH₄OH
 - TMAH



- Etch mechanism (oxidation/reduction reaction)

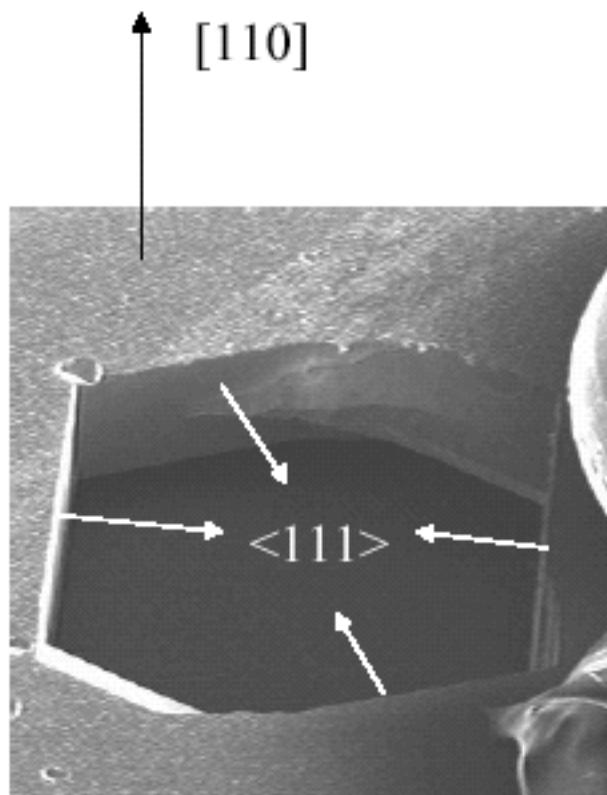
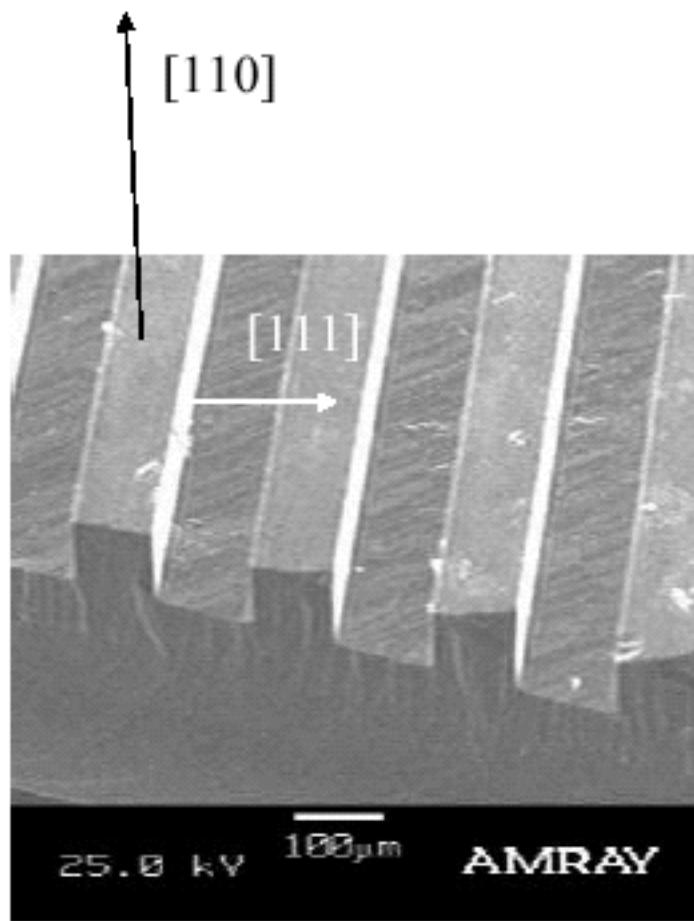


Relative Etch Rates in KOH

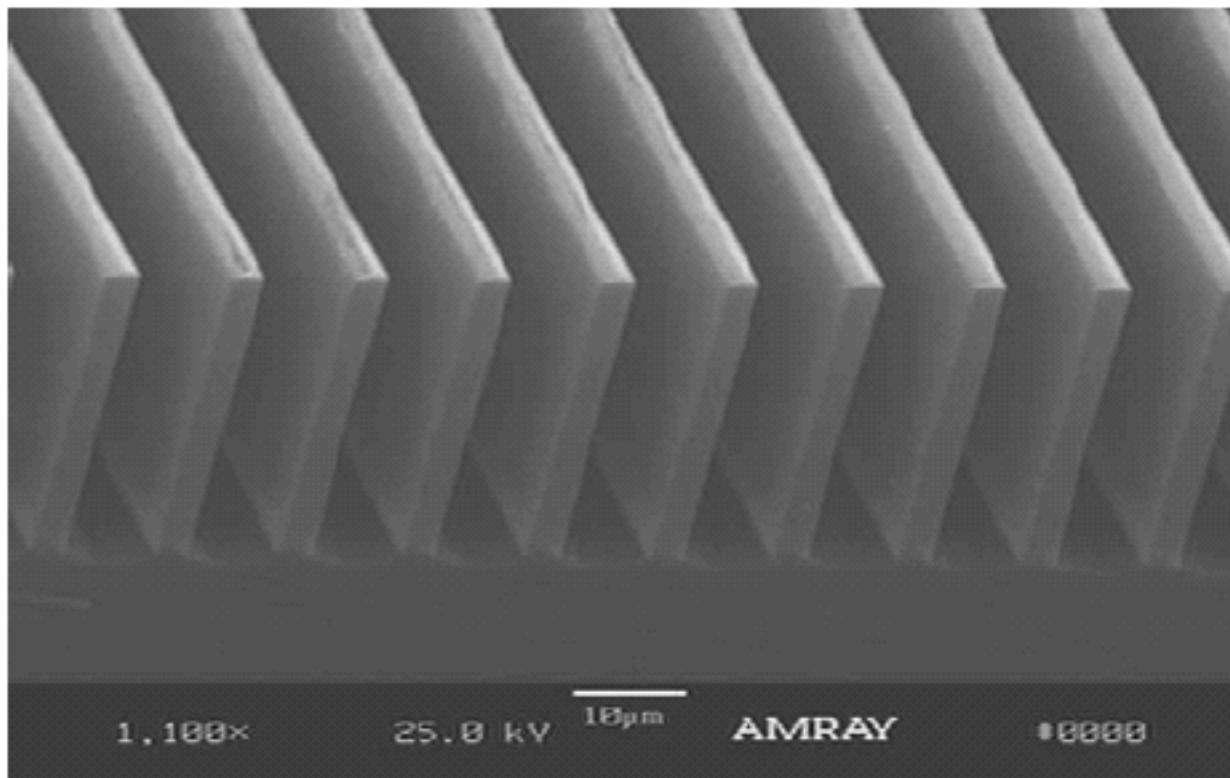


$ER_{(111)}:ER_{(100)}:ER_{(110)} \approx 1:300:600$

Shape of Etched Features



Wet Etcing -ex. MEMS shapes



Mask: 5 μm
lines and
spaces

Silicon (110),
oxide mask

Channels: 8 μm
 \times 24 μm

1,100 \times

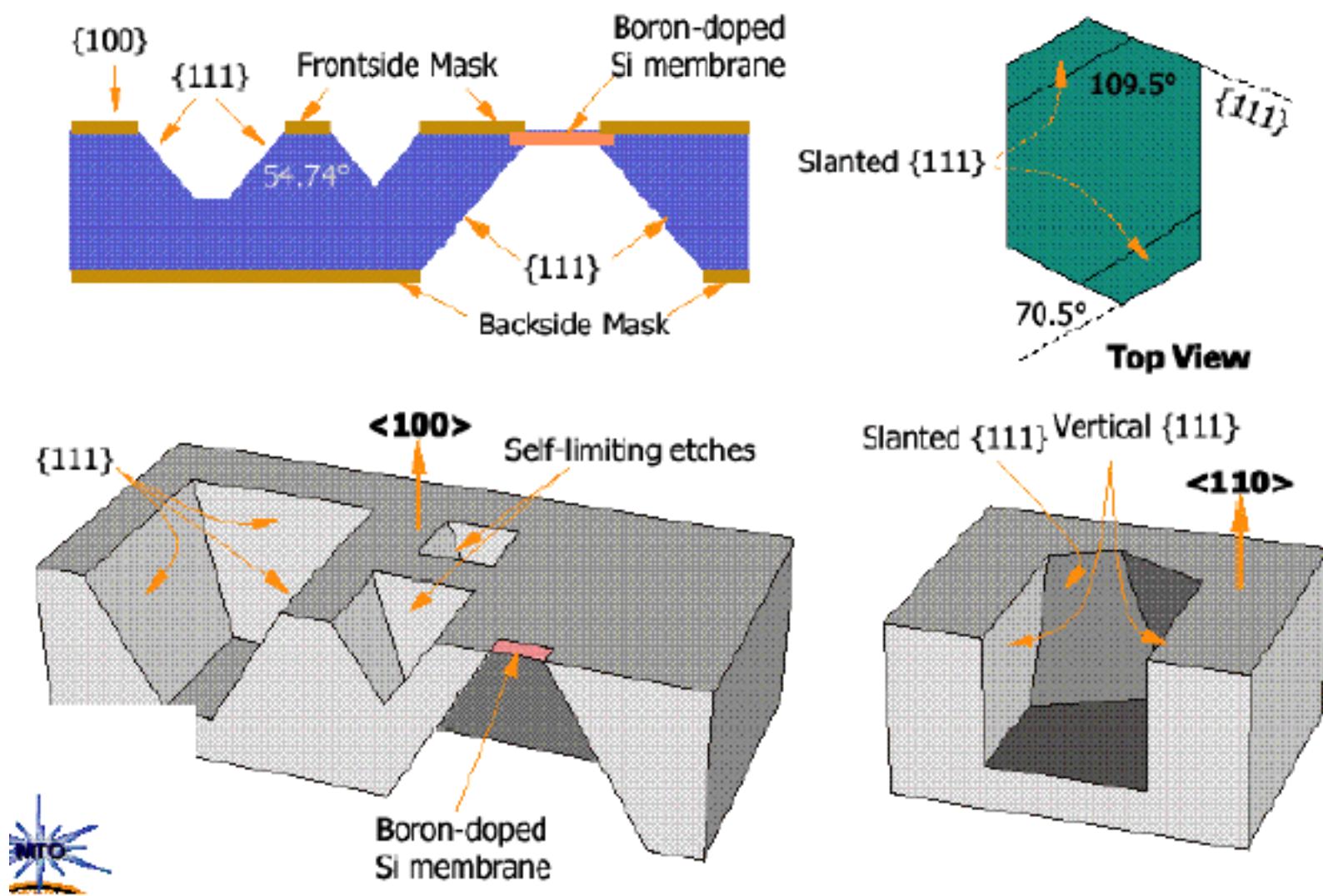
25.0 kV

10 μm

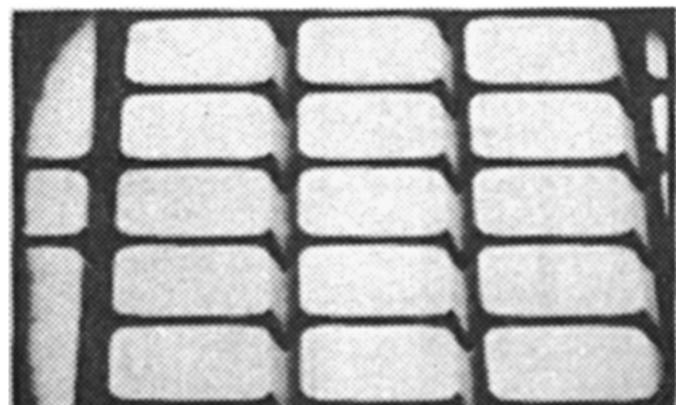
AMRAY

#0000

Bulk Micromachining: Anisotropic Wet Etching



KOH etch



SEM TOP VIEW (100) DI ETCH



SEM CROSSECTIONAL VIEW (100) DI ETCH

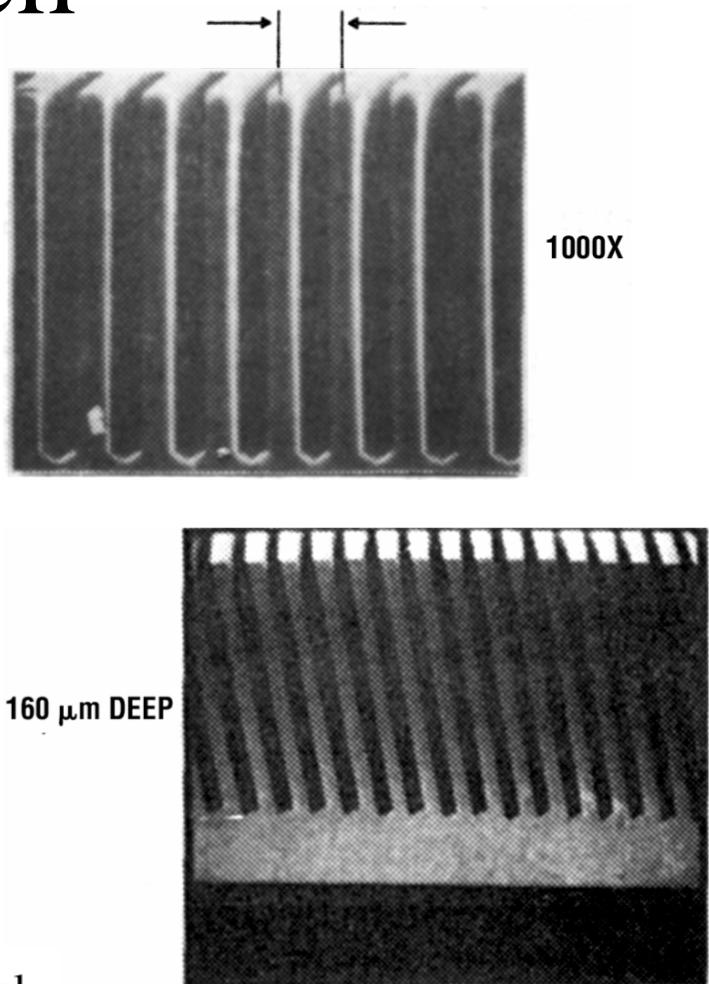
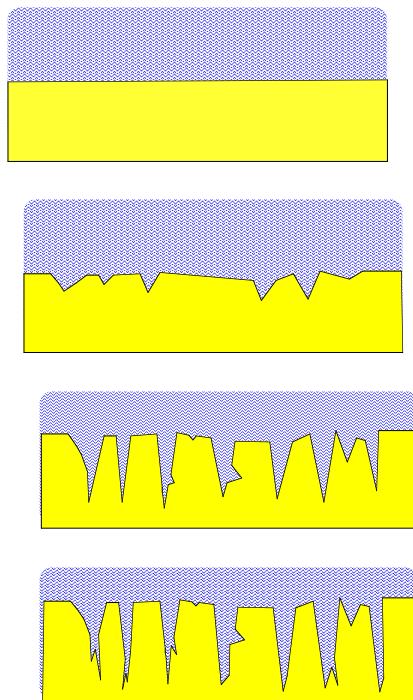


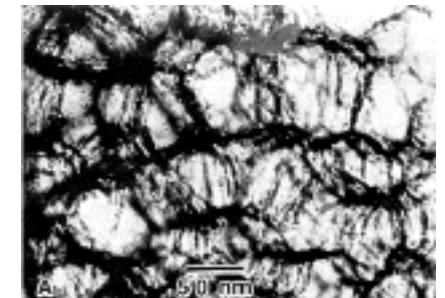
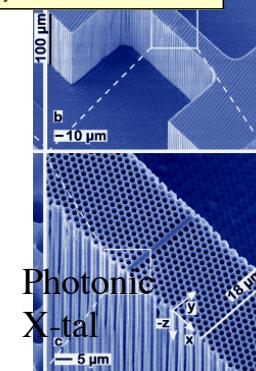
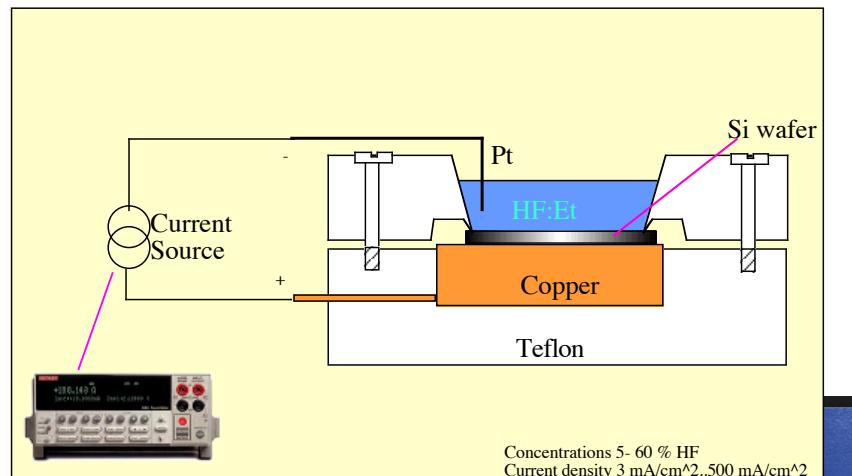
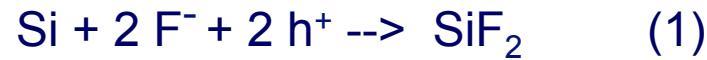
Figure 11.6 (100) silicon wafers after directional etching in KOH, isopropyl alcohol, and water. The upper photo shows a 50- μm -deep etch. The lower photographs are of 80- μm -deep trenches etched at 10 μm pitch on (110) and 107 off (110) (*after Bean, ©1978 IEEE*).

Wet Etching -porous 1/2-cond

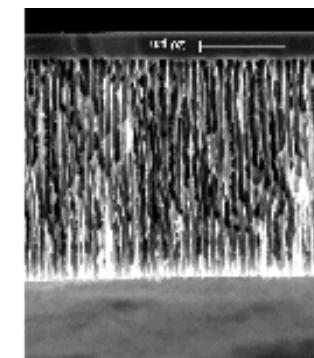
Interface-instability



Electrochemical reaction



nanowires



macropores

Etching -classification, Parameters

Etch rate R: 10nm $\text{-}\mu\text{m}/\text{min}$

Uniformity: % over wafer

Selectivity: i.e. $R_{\text{Si}}/R_{\text{SiO}_2}$

Anisotropy: $A=1-R_L/R_V$

Vertical

Lateral

Bias:

must be compensated for
in mask design

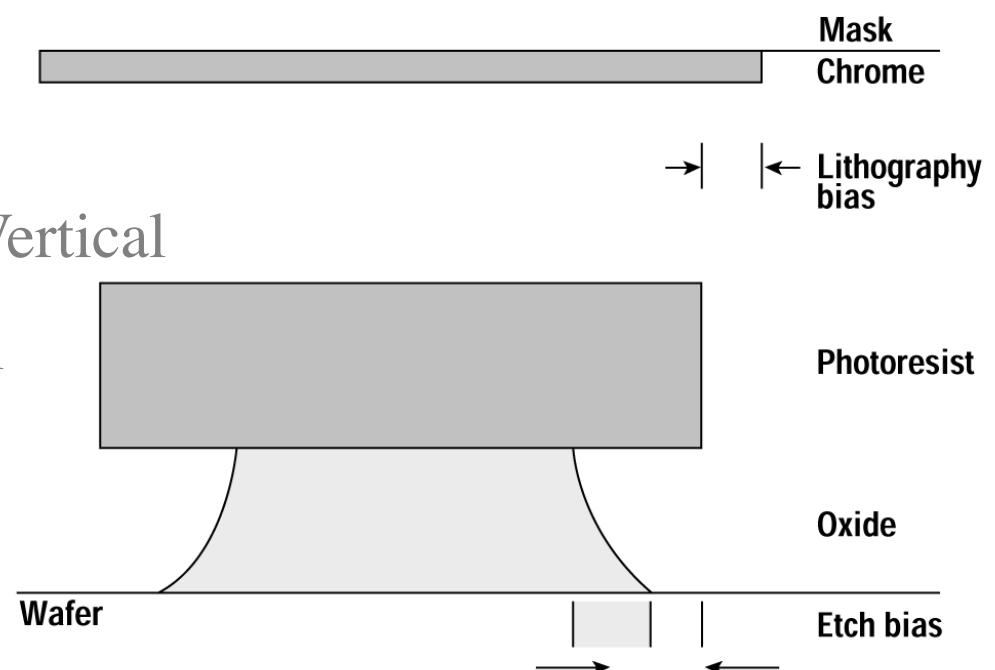
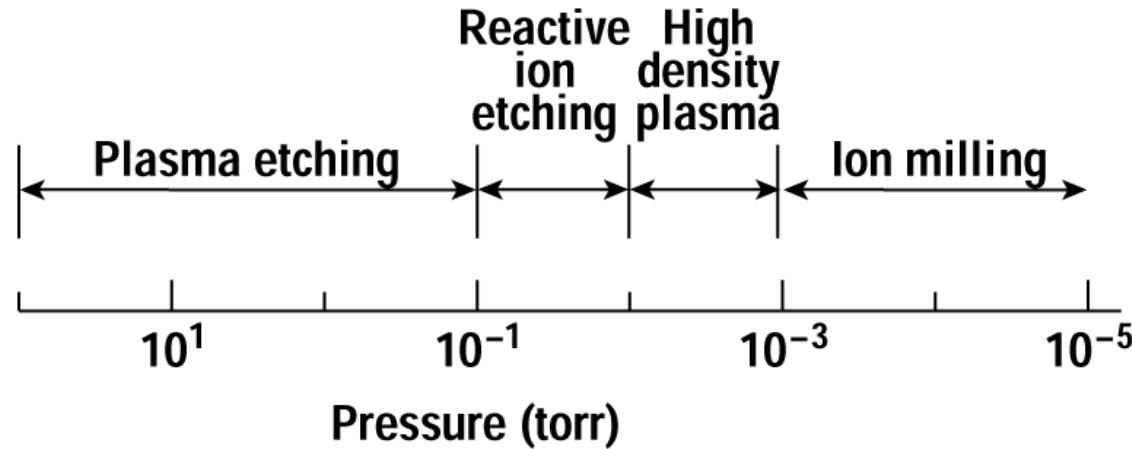


Figure 11.1 Typical isotropic etch process showing the etch bias.

Ideal for small devices: $A=1 \rightarrow$ motivation for dry etching

Dry etching and gas pressure

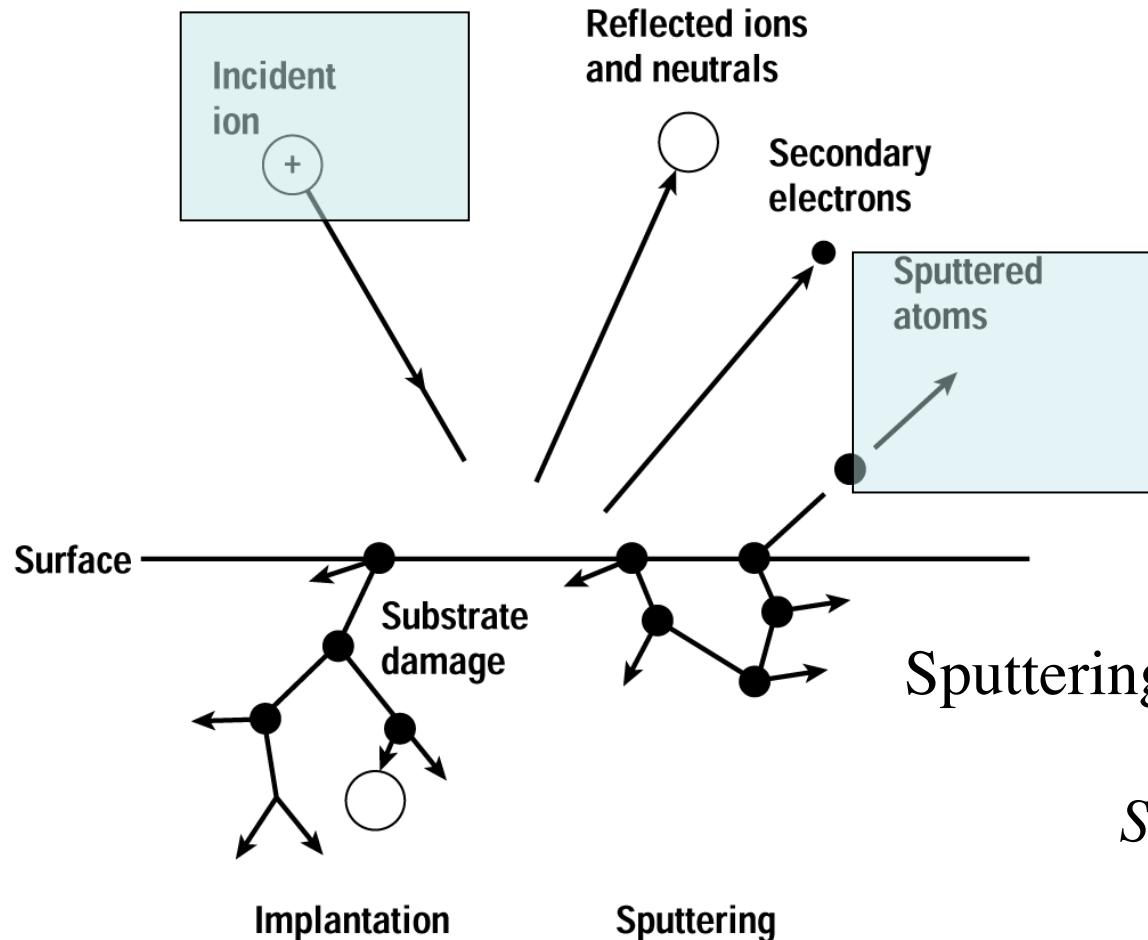


Dry etching mechanisms

Physical + chemical

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

Sputter process schematics



Physical PROCESS

- Dry etching
- (- Deposition
- Profiling AES,SIMS
- I²)

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

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

P. Sigmund Theory

λ : material parameter

U_0 surf. Bindings energy

$S_n(E)$ Nucl. Stopping power

α func. of M_1 / M_2

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

Sputtering rate versus energy

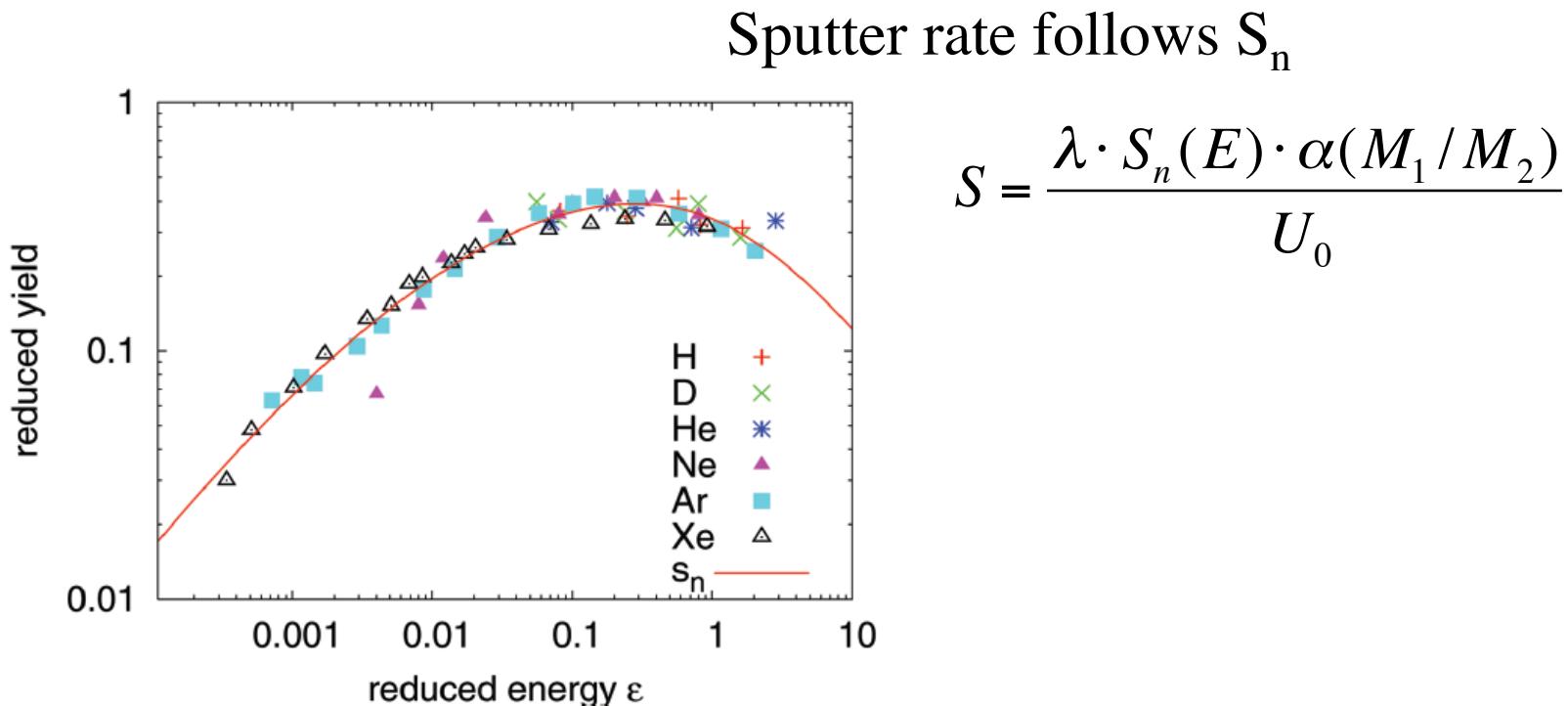


Figure 1. Compilation of experimentally determined sputter yields of Si with normally incident ions. The reduced sputter yields, $y = Y/C$, cf. Section 2.1, have been plotted *versus* the reduced energy ϵ and are seen to align well with the reduced nuclear stopping cross section s_n . Threshold effects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

Sputtering rate versus energy

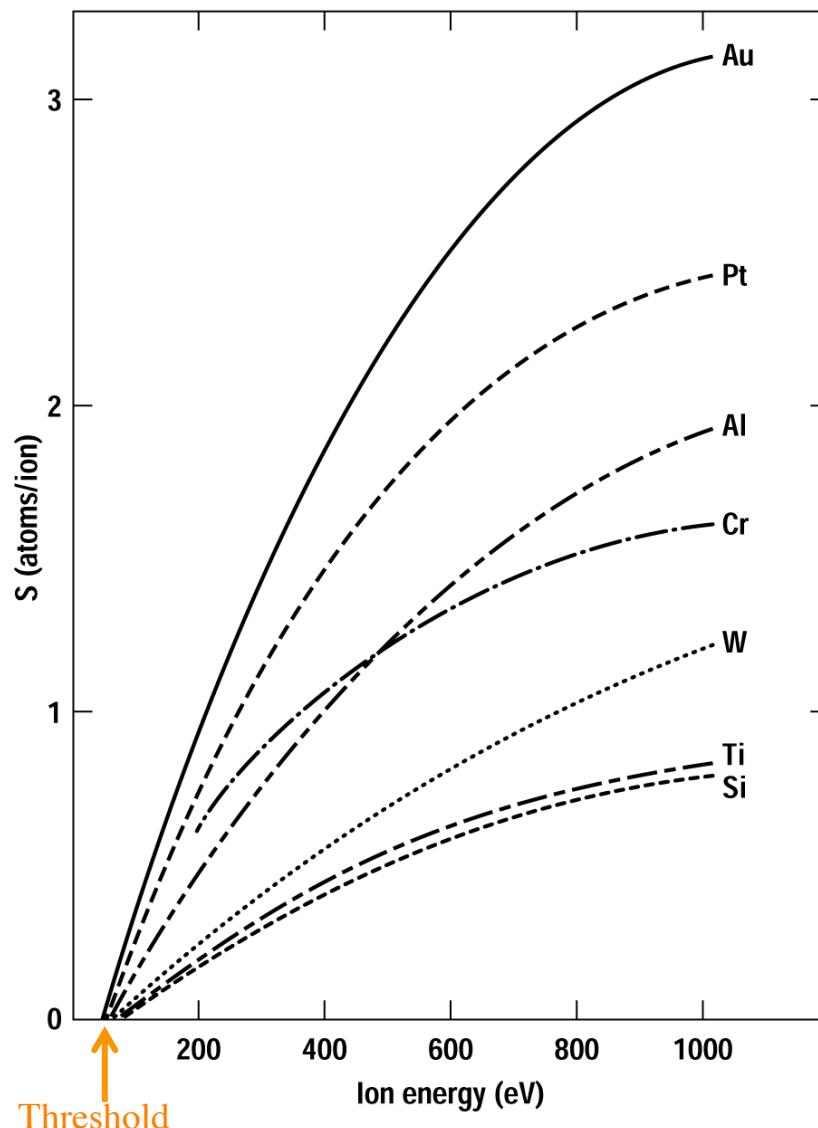


Figure 12.13 Sputter yield as a function of ion energy for normal incidence argon ions for a variety of materials (after Anderson and Bay, reprinted by permission).

Sputtering coef versus atomic number

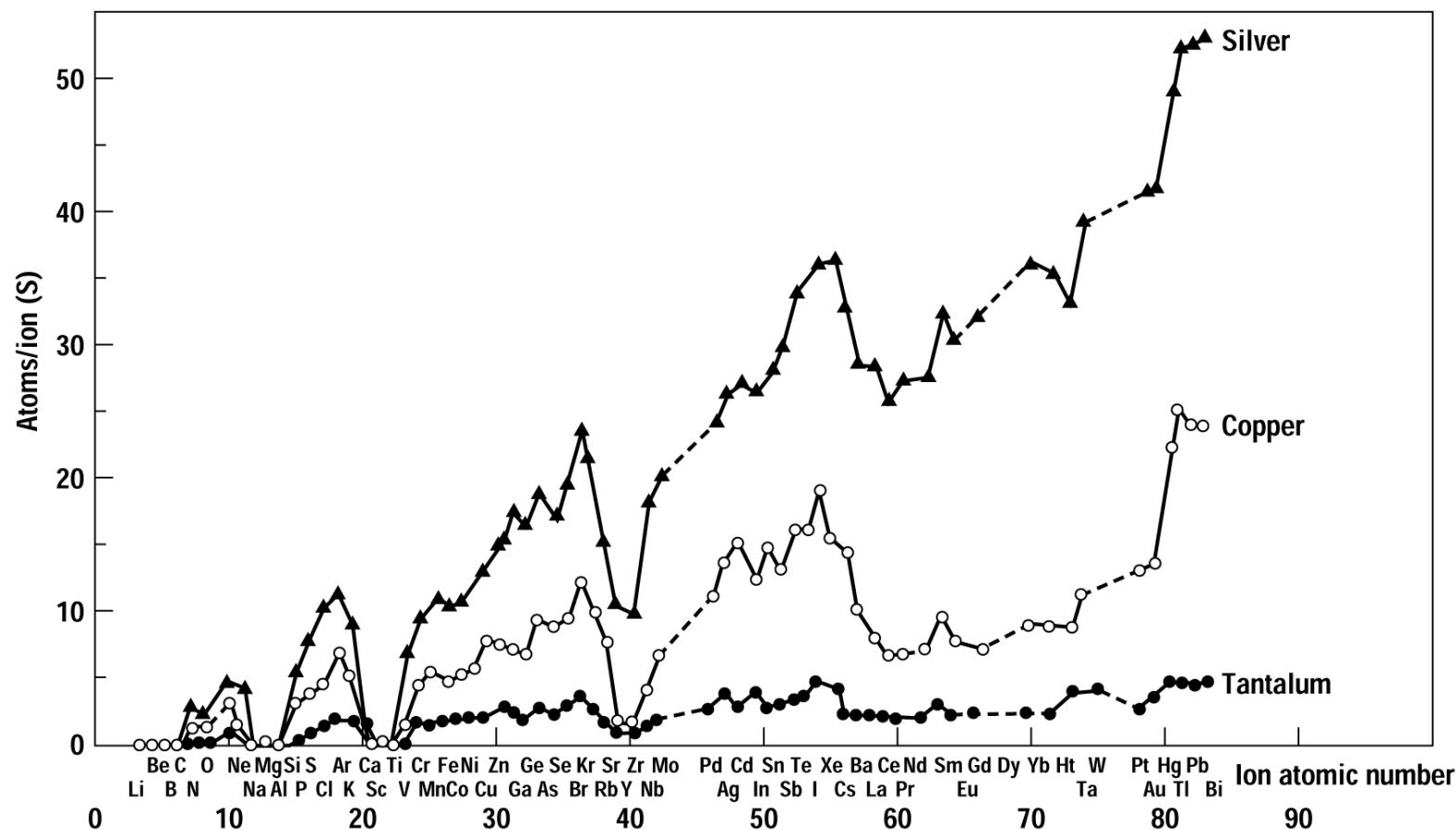
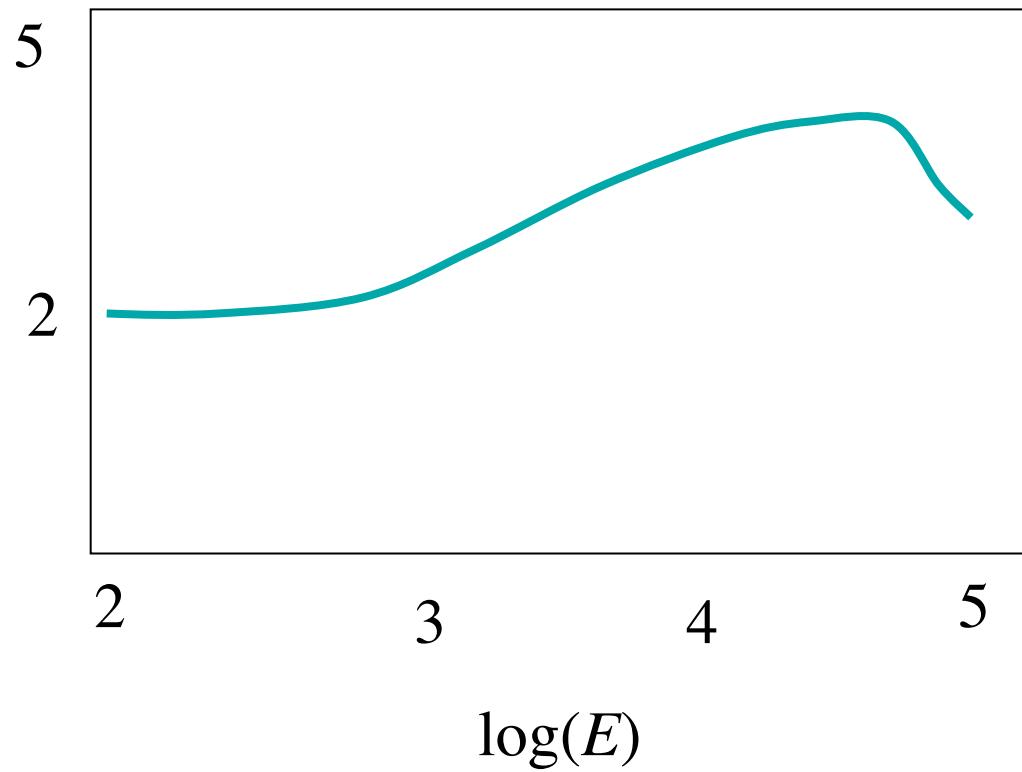


Figure 12.14 Sputter yield as a function of the bombarding ion atomic number for 45-keV ions incident on silver, copper, and tantalum targets (after Wehner, reprinted by permission, AIP).

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

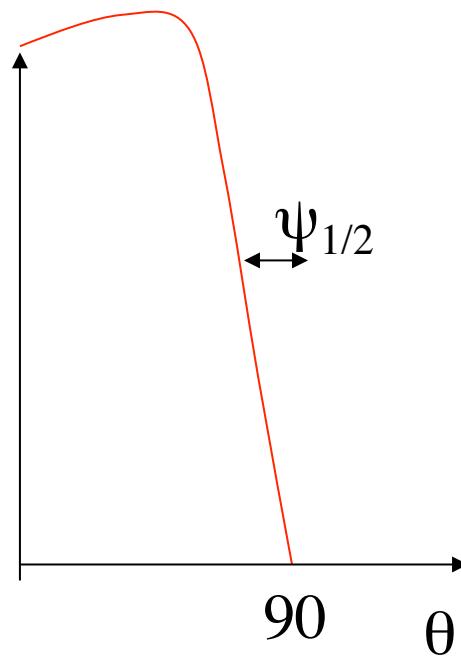
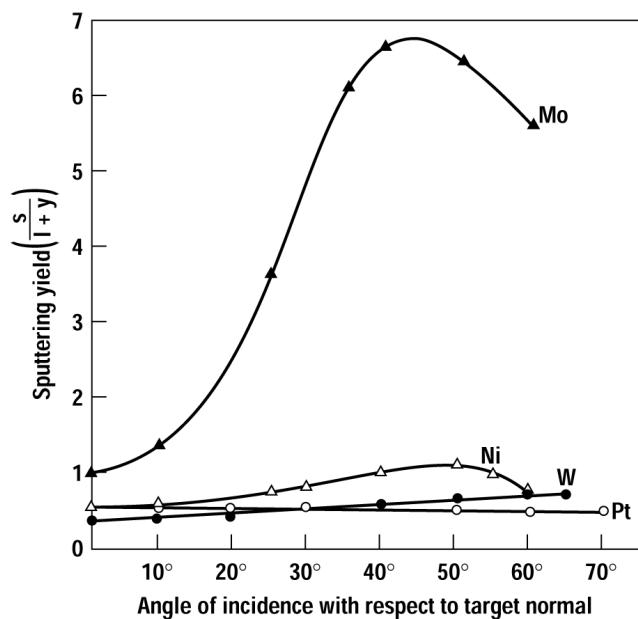
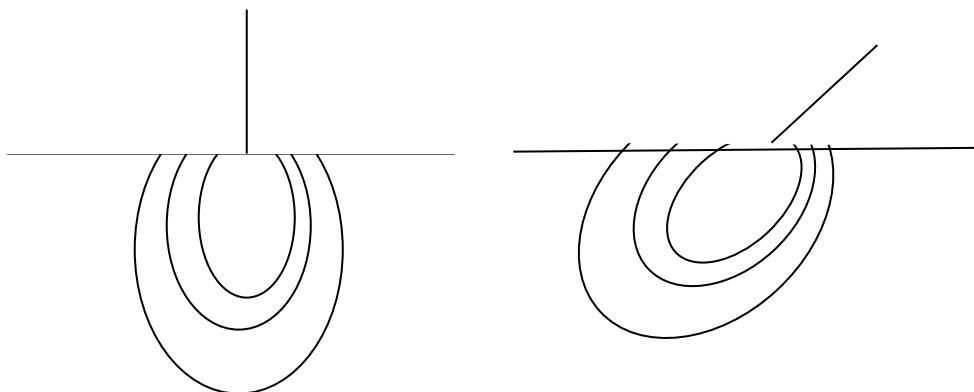


Figure 12.15 Typical angular dependence of the sputter yield for several different materials. The sputter profiles follow a cosine distribution (after Wehner, reprinted by permission, AIP).



Sputtering depends on angle of incidence n exit

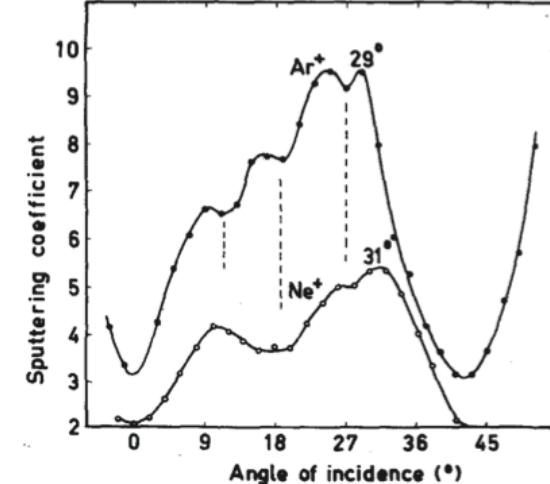
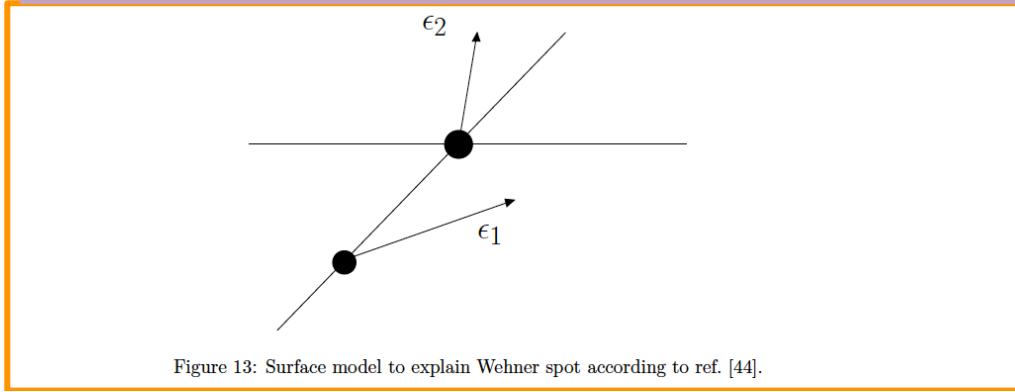
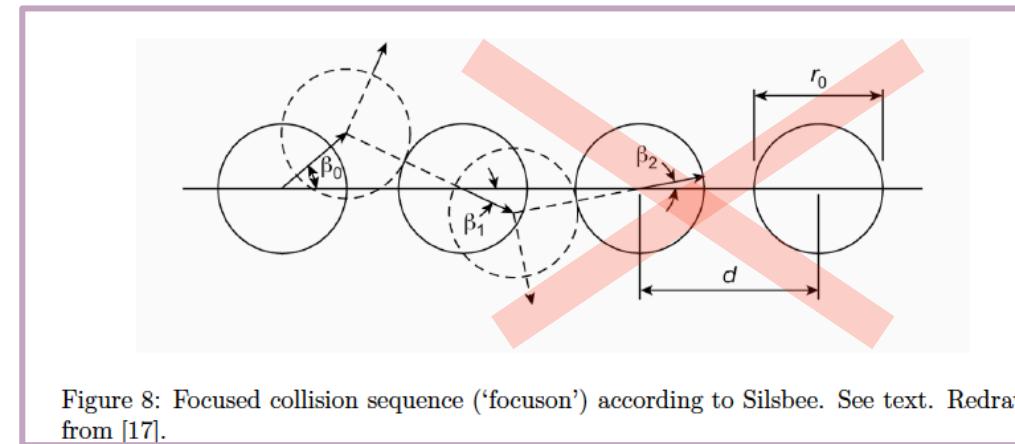
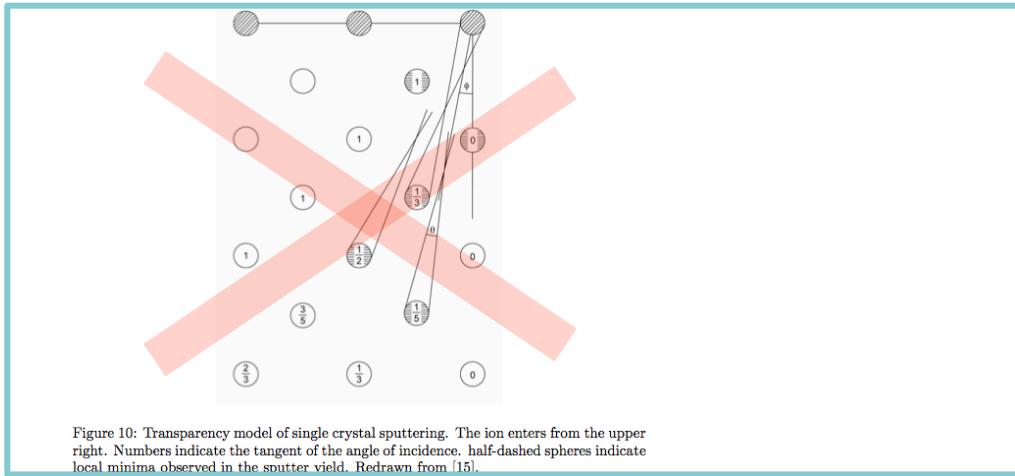


Figure 7: Sputter yield of a (100) copper crystal for 20 keV Ar and Ne ions as a function of the angle of incidence against the [100] surface normal. From [15].

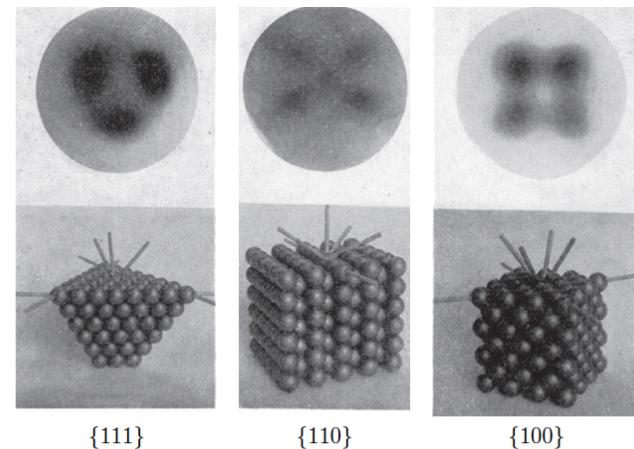
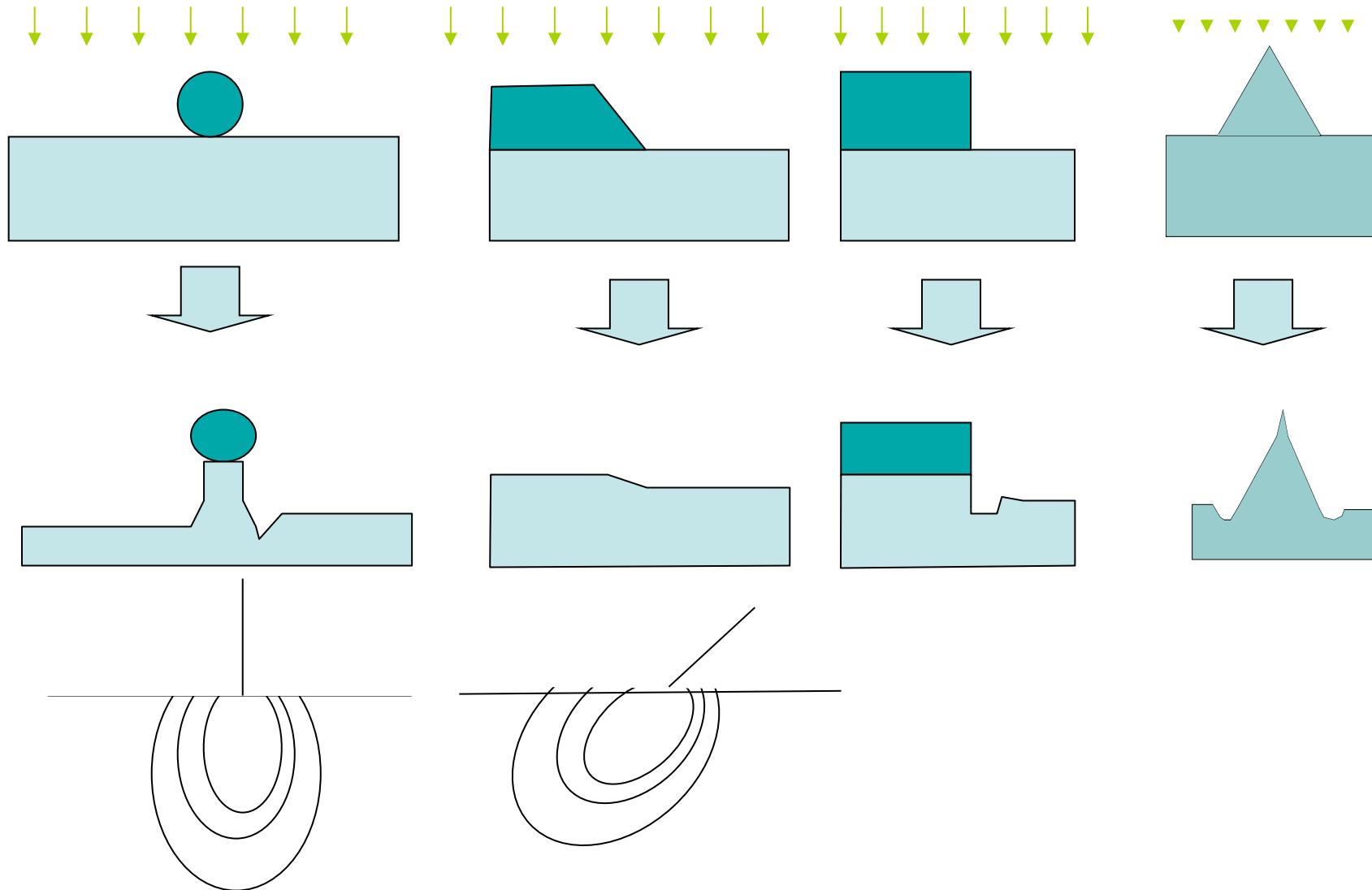


Figure 2: Angular distribution of gold atoms sputtered from single crystal surfaces by 100 (right and left) or 50 (center) eV Hg ions. From [6].

Development of topography with sputtering



Mask taper, redeposition, trenching

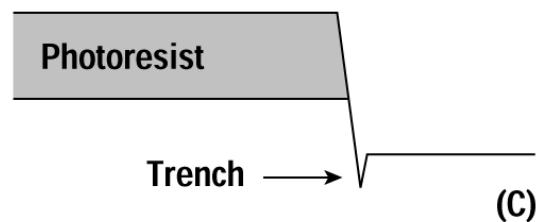
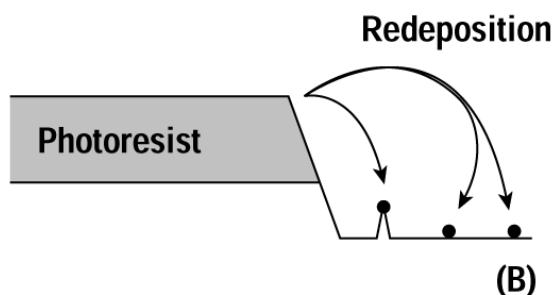
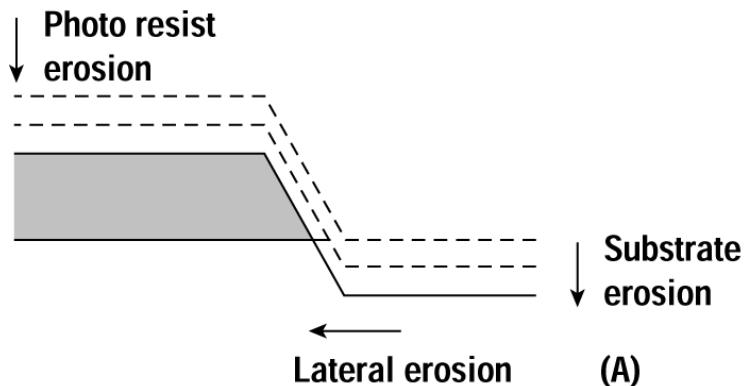
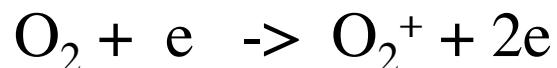


Figure 11.15 Problems that may occur during ion milling: (A) mask taper transfer, (B) redeposition from the mask, and (C) trenching.

Dry reactive ion -etching

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

Ionization



Fragmentation with ionization



Fragmentation with **ionization** og adhesion



Fragmentation without ionization



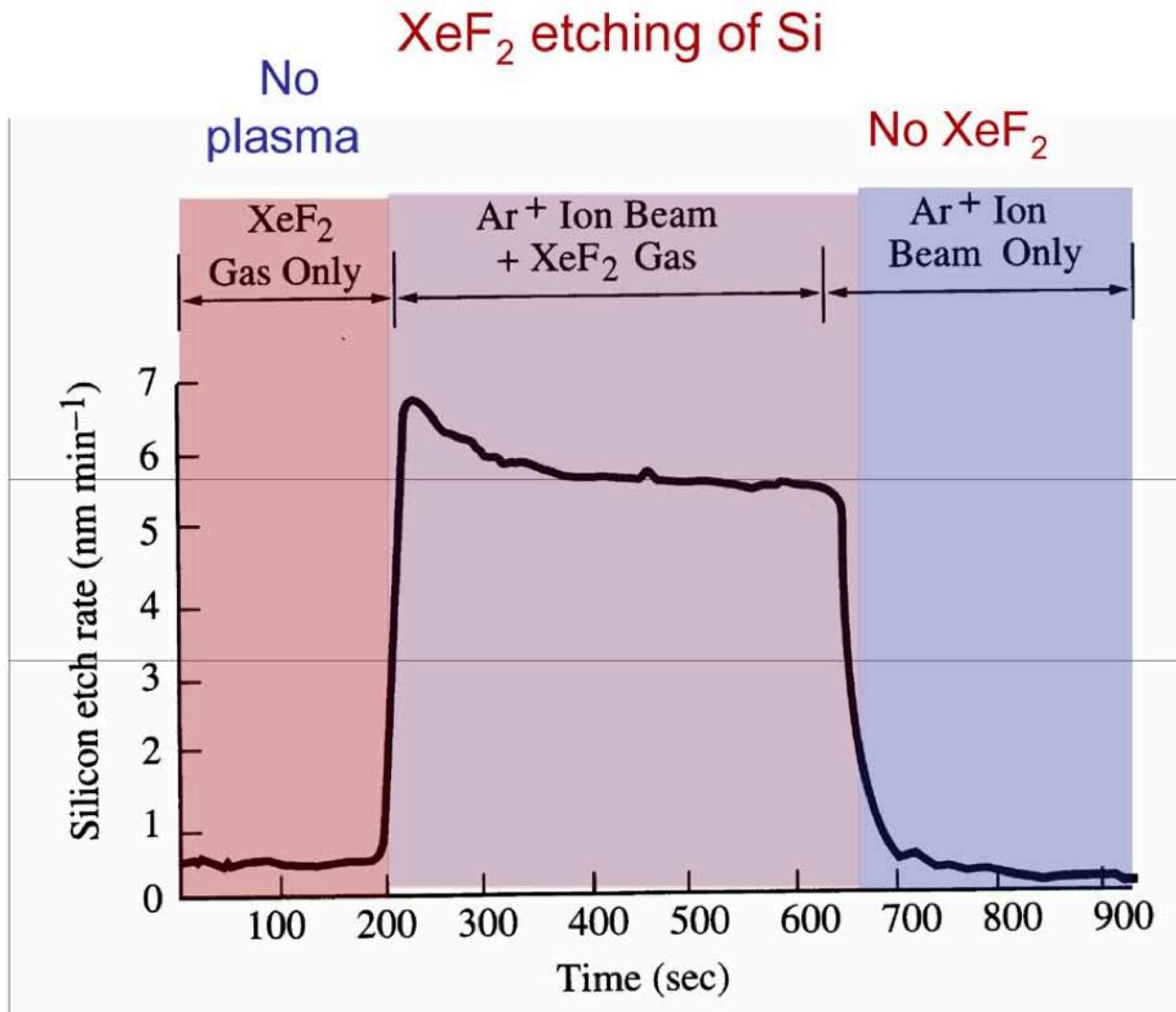
Point: Fragments and ions are more reactive than molecules

CF_4 doesn't react with Si at any temp below 1412 °C
F reacts spontaneously w. Si at RT, creates (vol) SiF_4

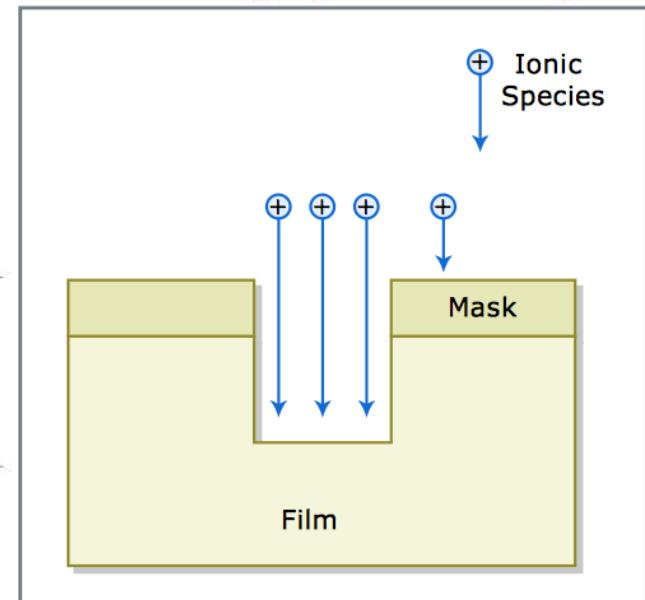
Ion-enhanced chemical etching

Physical and chemical processes not just independent of each other.

Ion beam can enhance chemical etching:



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



Wow! Figure by MIT OCW

The best of both
Aniso. + selective

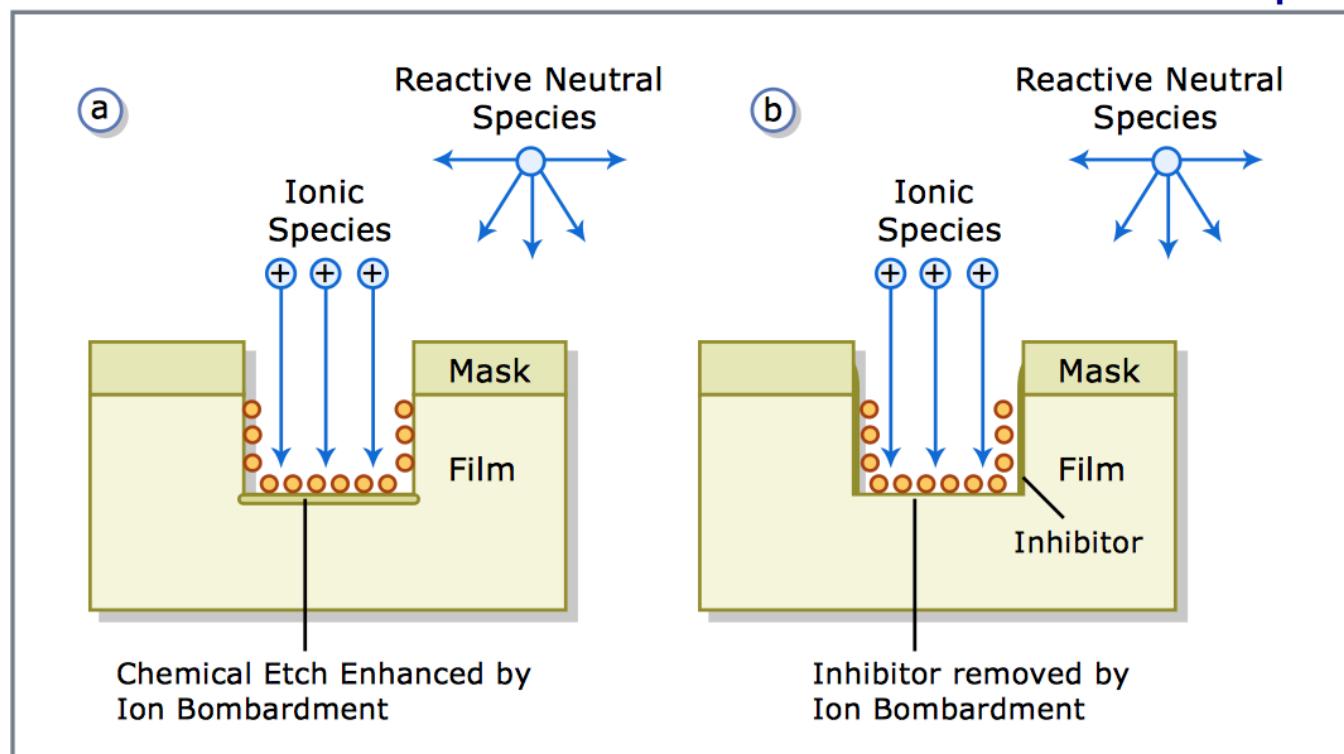
Ion-enhanced chemical etching

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 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 O₂, Si₃N₄ :
 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

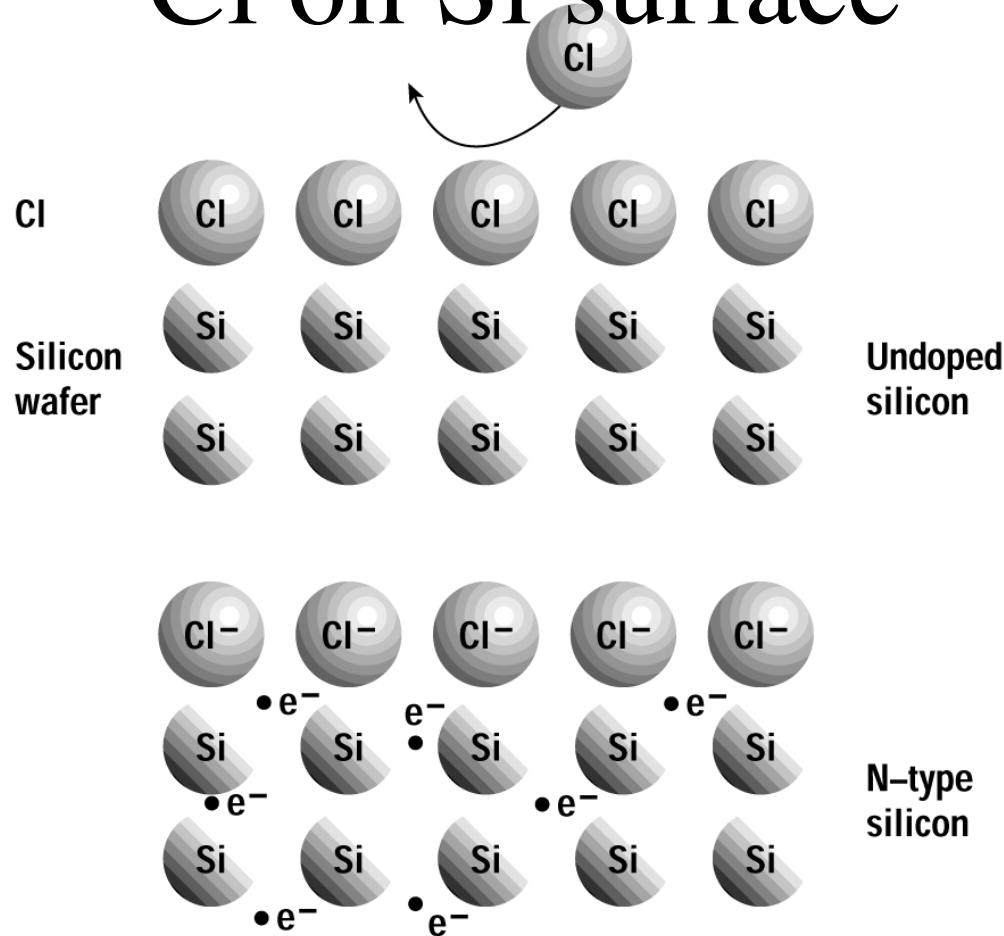


Figure 11.18 Once a monolayer of chlorine atoms builds on the surface, it impedes any chlorine addition.

Plasma etch in CF₄

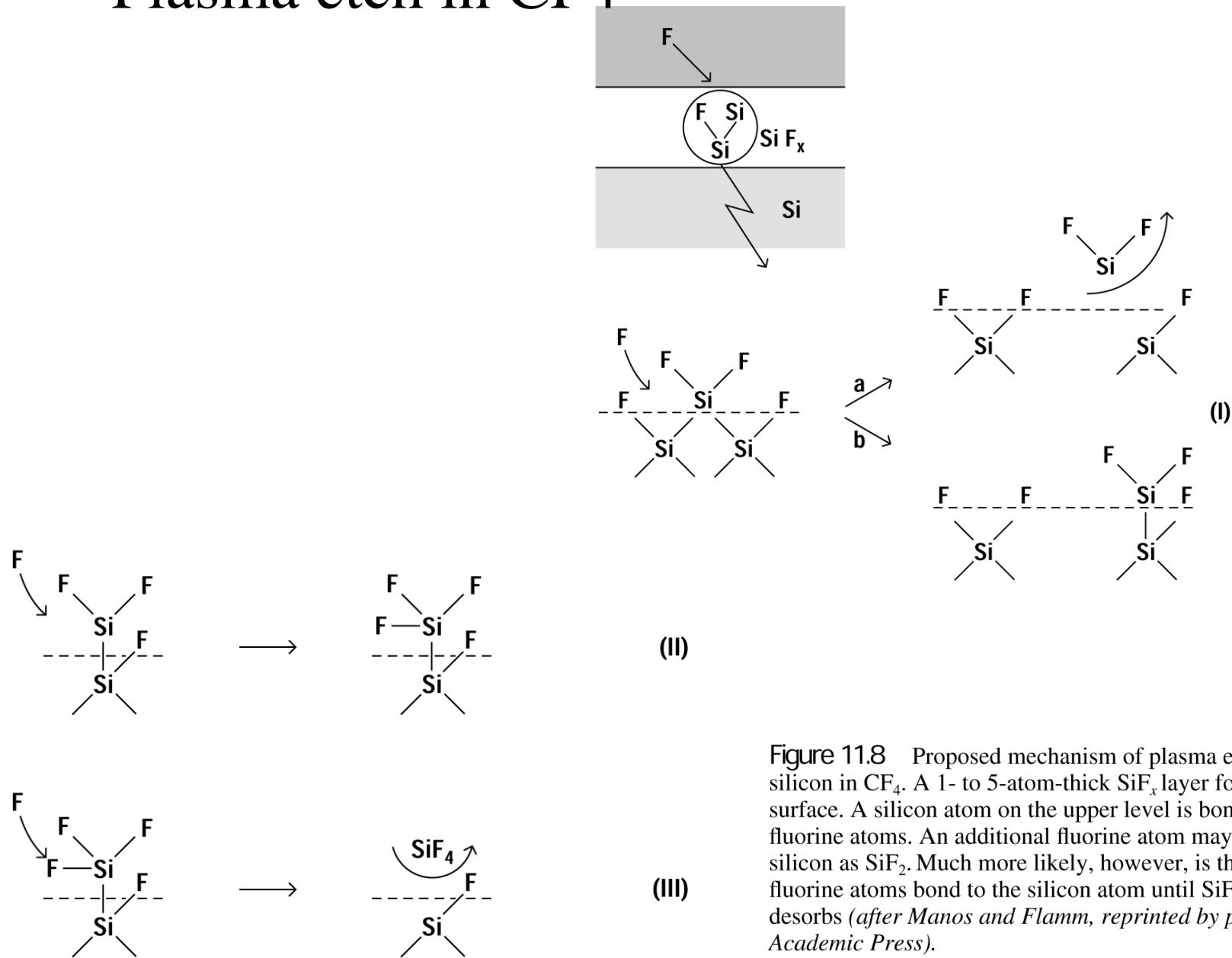


Figure 11.8 Proposed mechanism of plasma etching of silicon in CF₄. A 1- to 5-atom-thick SiFx layer forms on the surface. A silicon atom on the upper level is bonded to two fluorine atoms. An additional fluorine atom may remove the silicon as SiF₂. Much more likely, however, is that additional fluorine atoms bond to the silicon atom until SiF₄ forms and desorbs (*after Manos and Flamm, reprinted by permission, Academic Press*).

Sidewall passivation

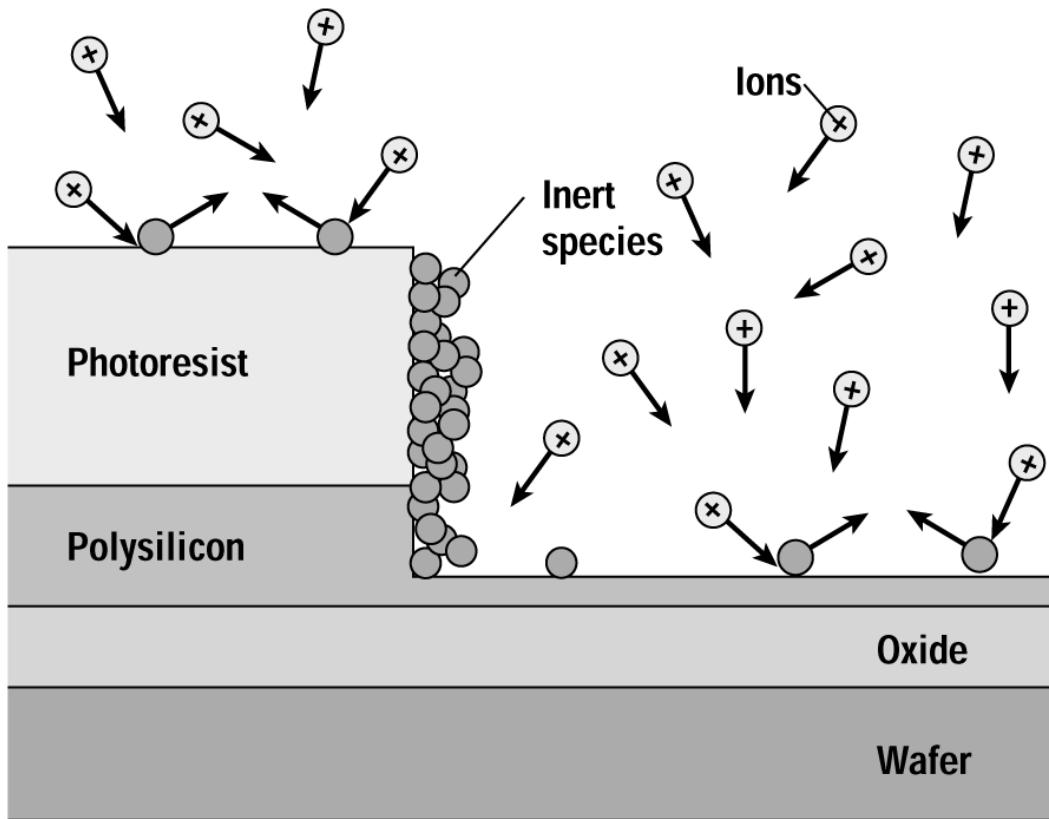
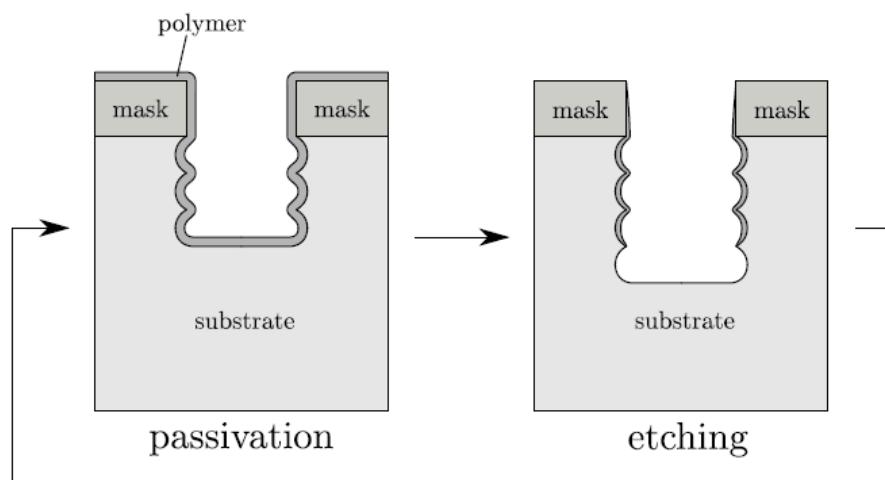
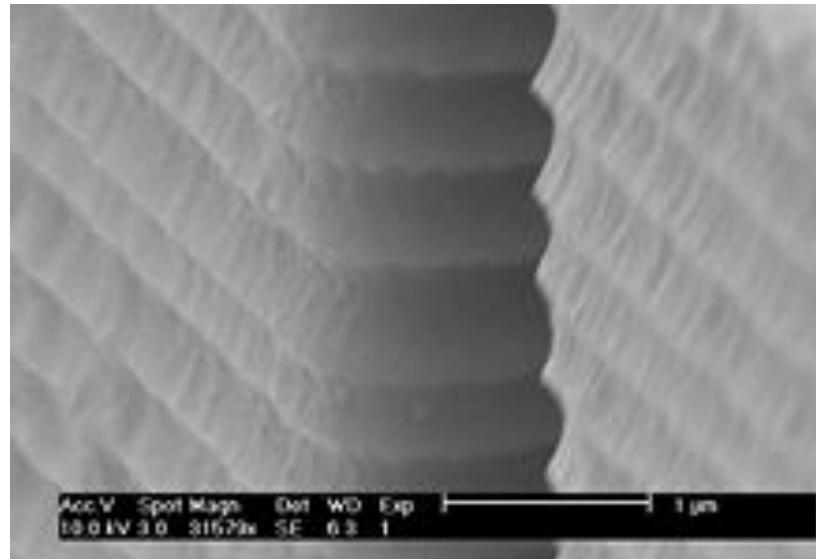
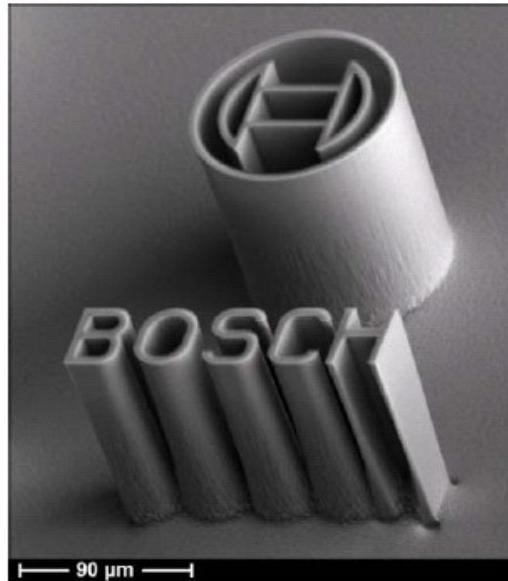


Figure 11.10 Schematic diagram of a high-pressure anisotropic etch showing the formation of sidewall passivating films.

Deep reactive Ion etching, Sidewall passivation, Bosch process



Plasma [SF₆] nearly isotropic etch

Deposition C₄F₈ (Octafluorocyclobutane)

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

Si/SiO₂ Etch rates

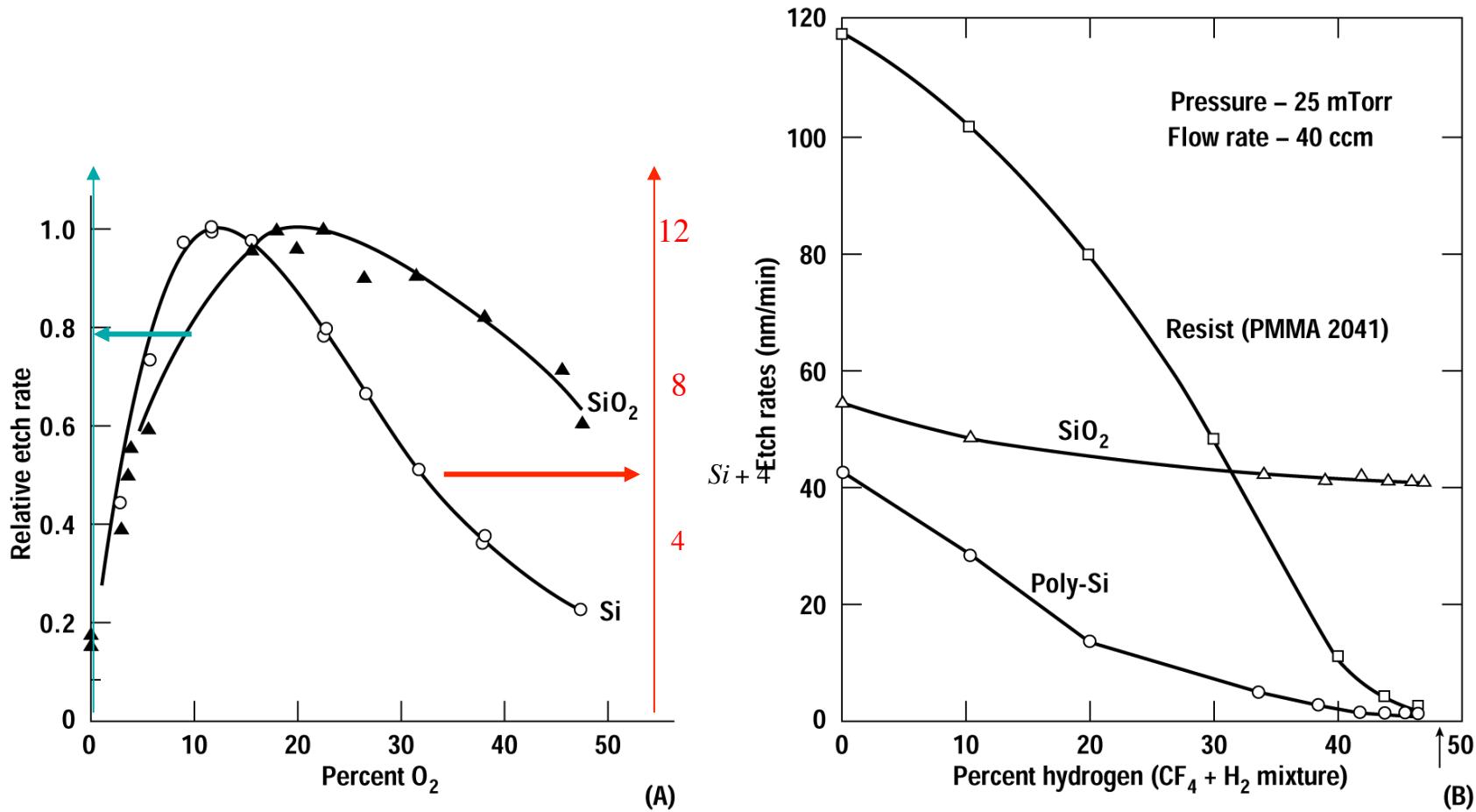
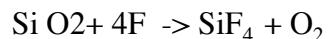
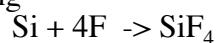


Figure 11.11 Etch rate of Si and SiO₂ in (A) CF₄/O₂ plasma (after Mogab *et al.*, reprinted by permission, AIP), and (B) CF₄/H₂ plasma (after Ephrath and Petrillo, reprinted by permission of the publisher, The Electrochemical Society Inc.).

Main etching

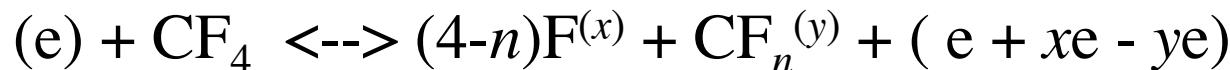


In plasma CF₄

Si/SiO₂ etch rate in CF + O₂

In gas

1
2



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

3



Add O₂ increases [F], deplete CF_n v. 2 ,
creates COF₂, CO, CO₂ so [F] increases

Measured max [F] at 23%

Si: O₂ chemisorb surface, blocks access to F, more the more O, more the more O₂,
so max below 23 %

SiO₂: O₂ always present on surface, so. max at 23 %

Concentrations in CF₄ plasma

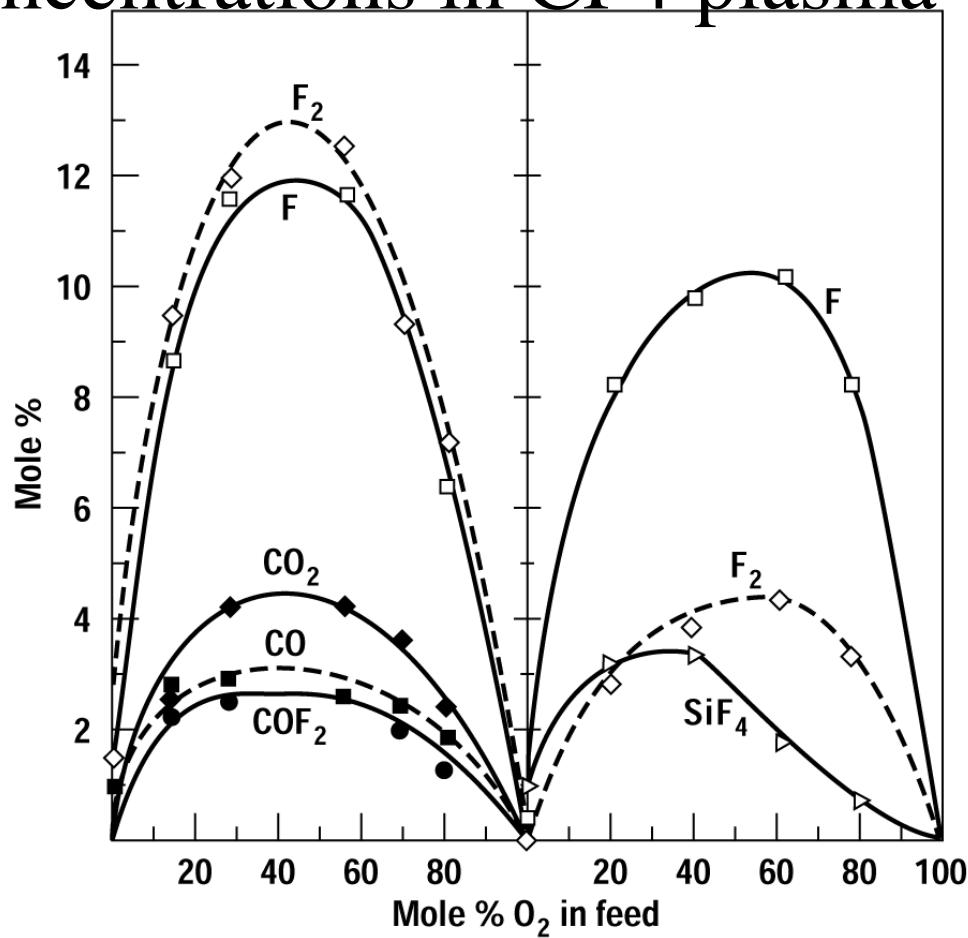


Figure 11.9 Species concentration in a CF₄ plasma as a function of the amount of oxygen in the feed gas (*after Smolinsky and Flamm, reprinted by permission, AIP*).

SiO_2 to Si X section

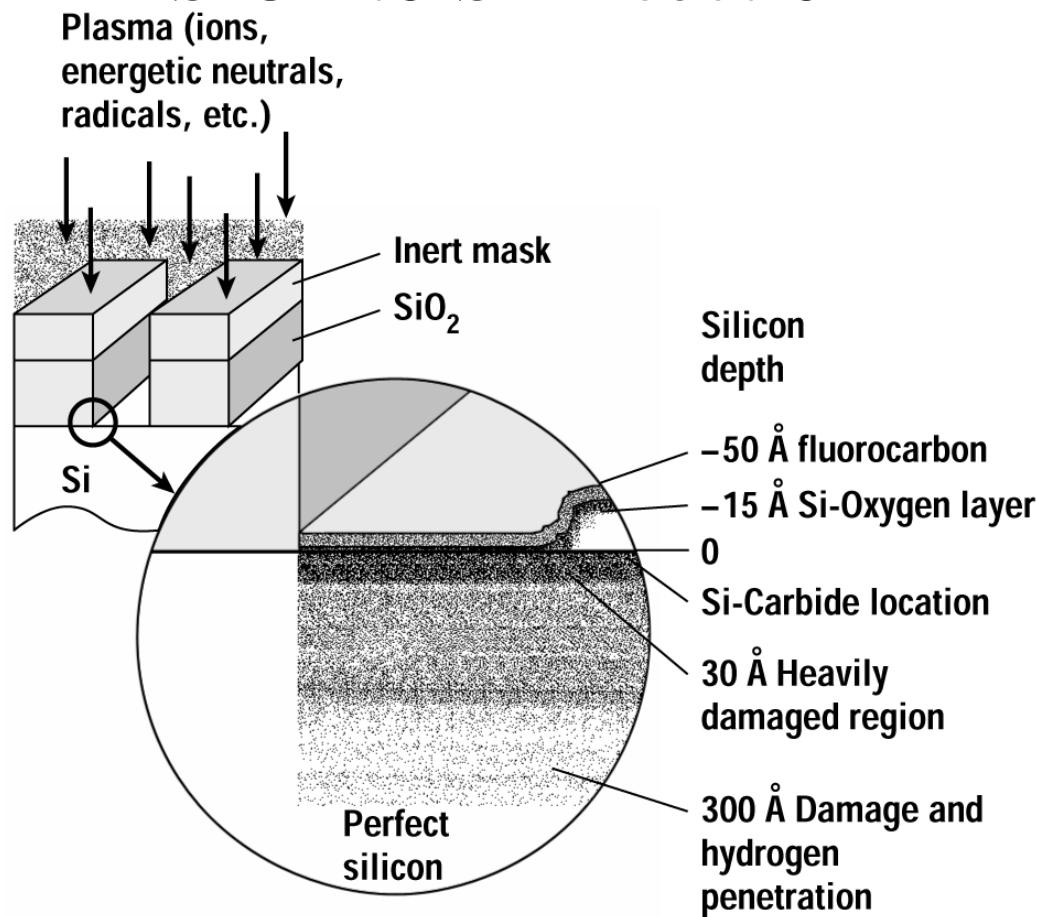


Figure 11.20 A cross section schematic of the results of a typical etch of SiO_2 down to Si using CF_4/H_2 (after Oehrlein, Rembetski, and Payne, reprinted by permission, AIP).

Kaufman ion Source

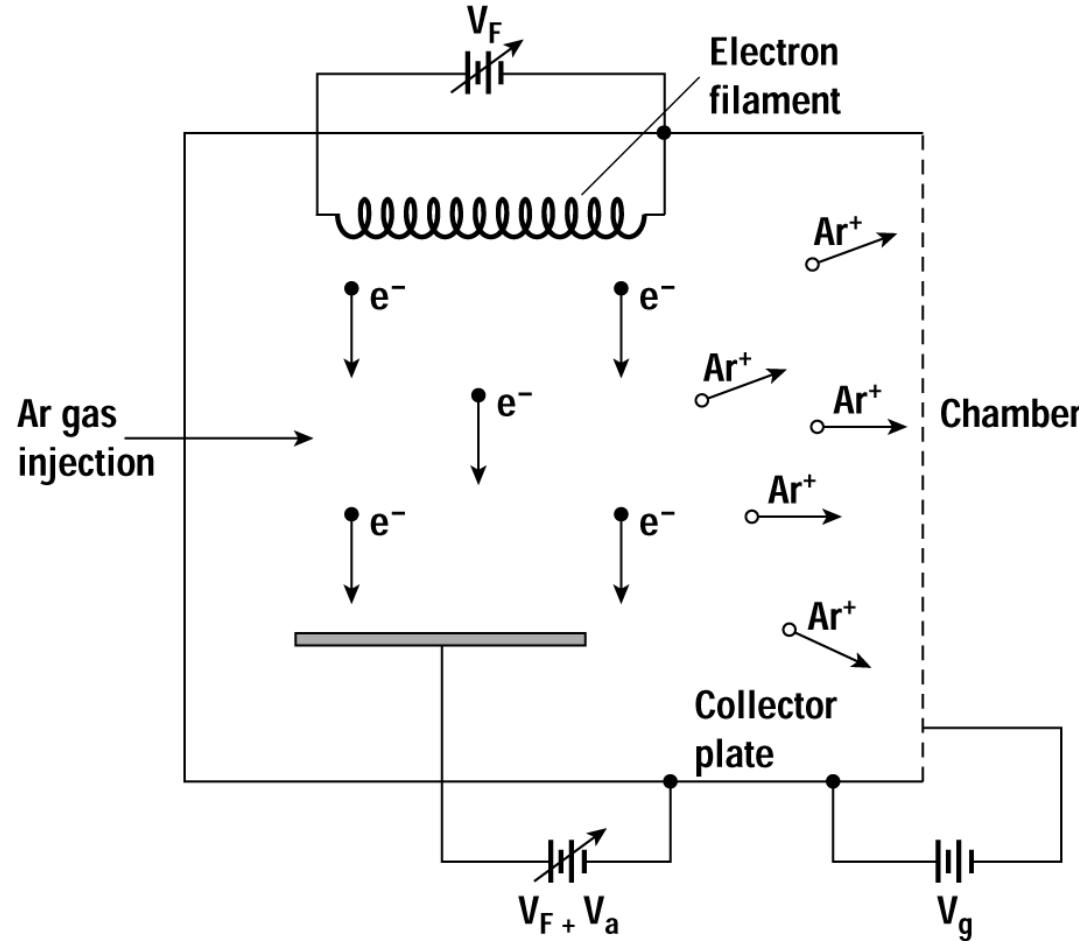


Figure 11.14 Cross section schematic of a Kaufman ion source.

Reactive bleed ion mill

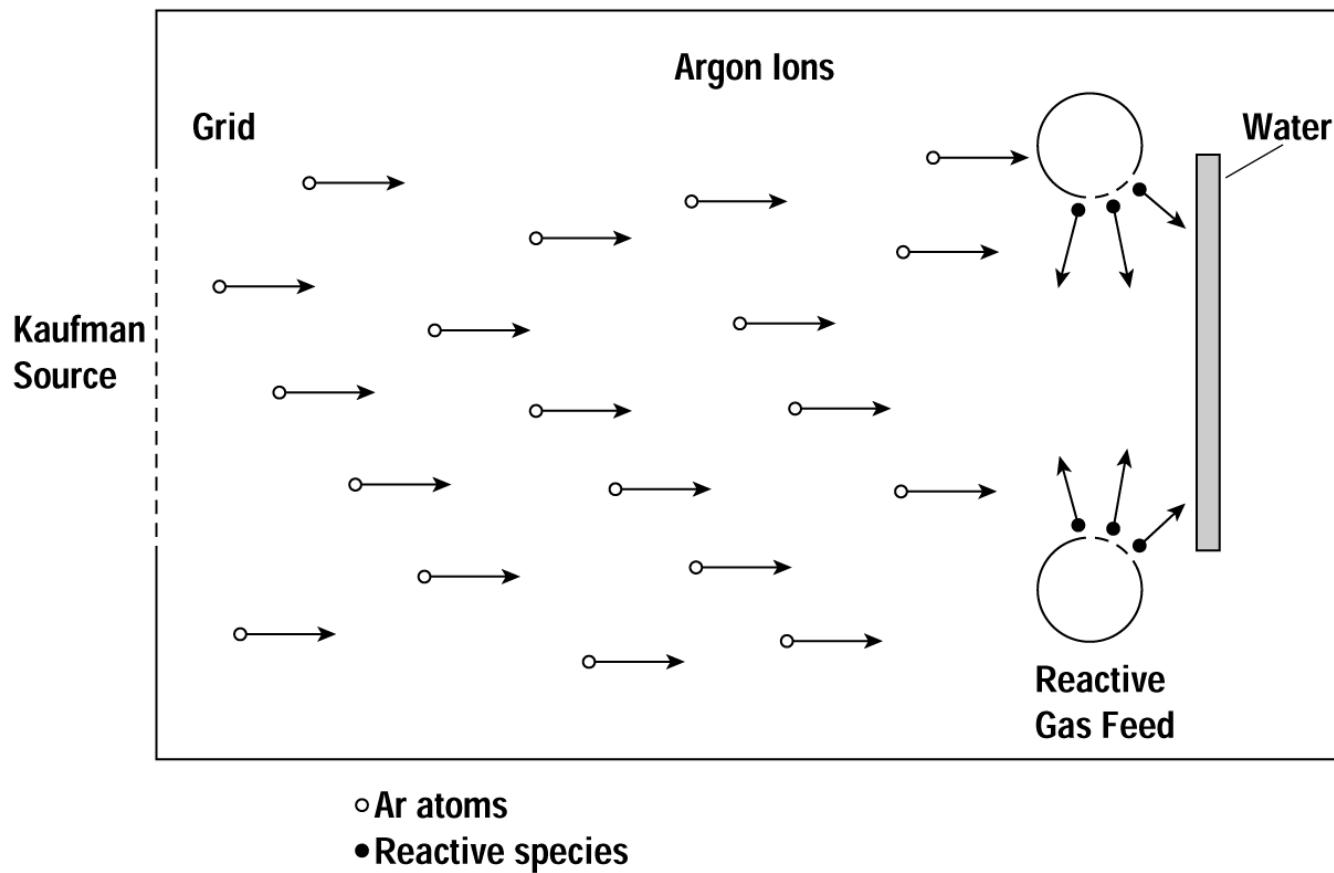


Figure 11.16 The use of a reactive bleed near the wafer surface in a conventional ion mill to introduce a chemical component to the etch process.

Batch RIE system

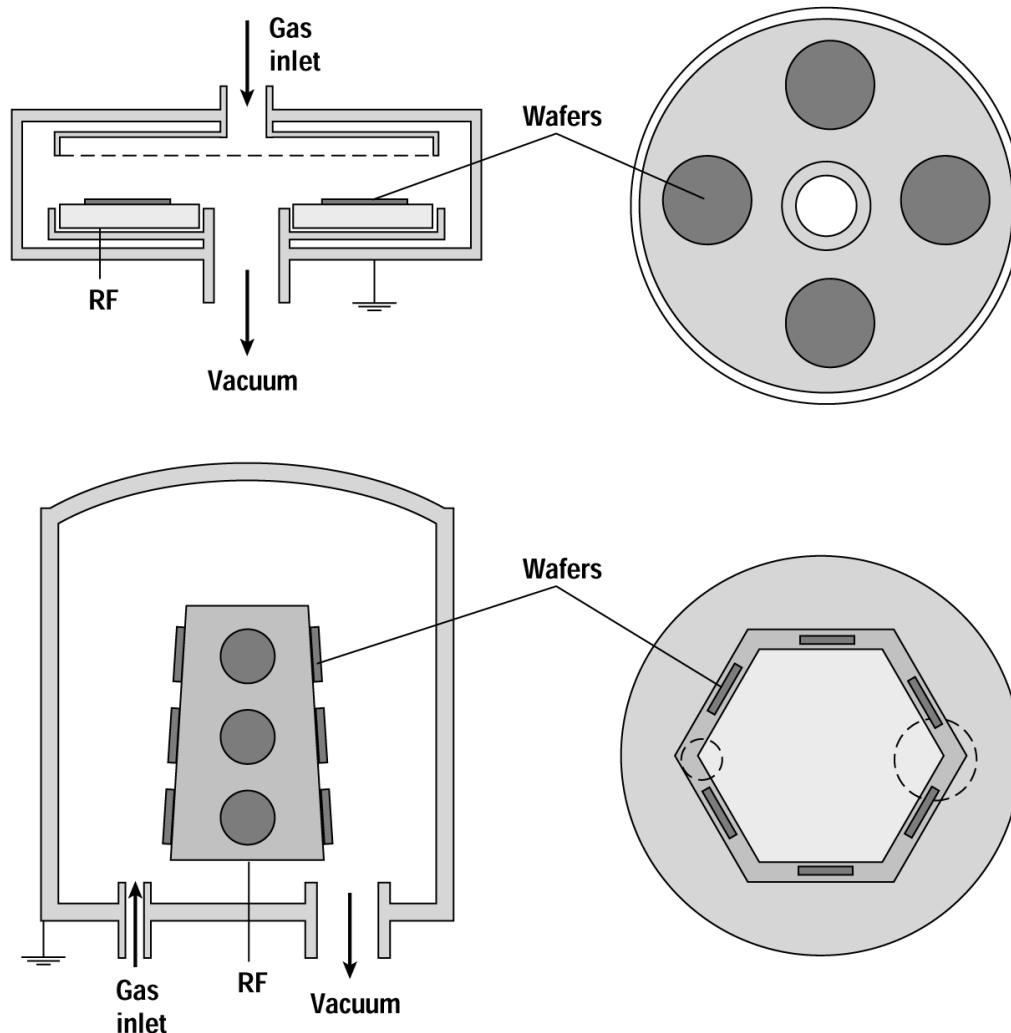


Figure 11.17 Top and side views of parallel-plate and hexode batch RIE systems. Typical conditions for either are 50 mtorr and 5 kW/m^2 . For larger wafers the exhaust in the upper figure is drawn from the periphery rather than the center.

Resist scumming

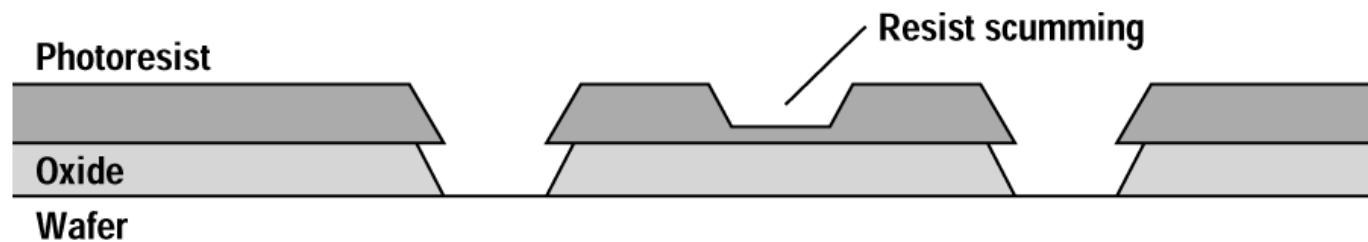


Figure 11.3 Resist scumming occurs when the photoresist is incompletely developed. The residual resist may serve as an etch mask to prevent a complete etch process.

Equipment plasma etcher



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

Sputtering system

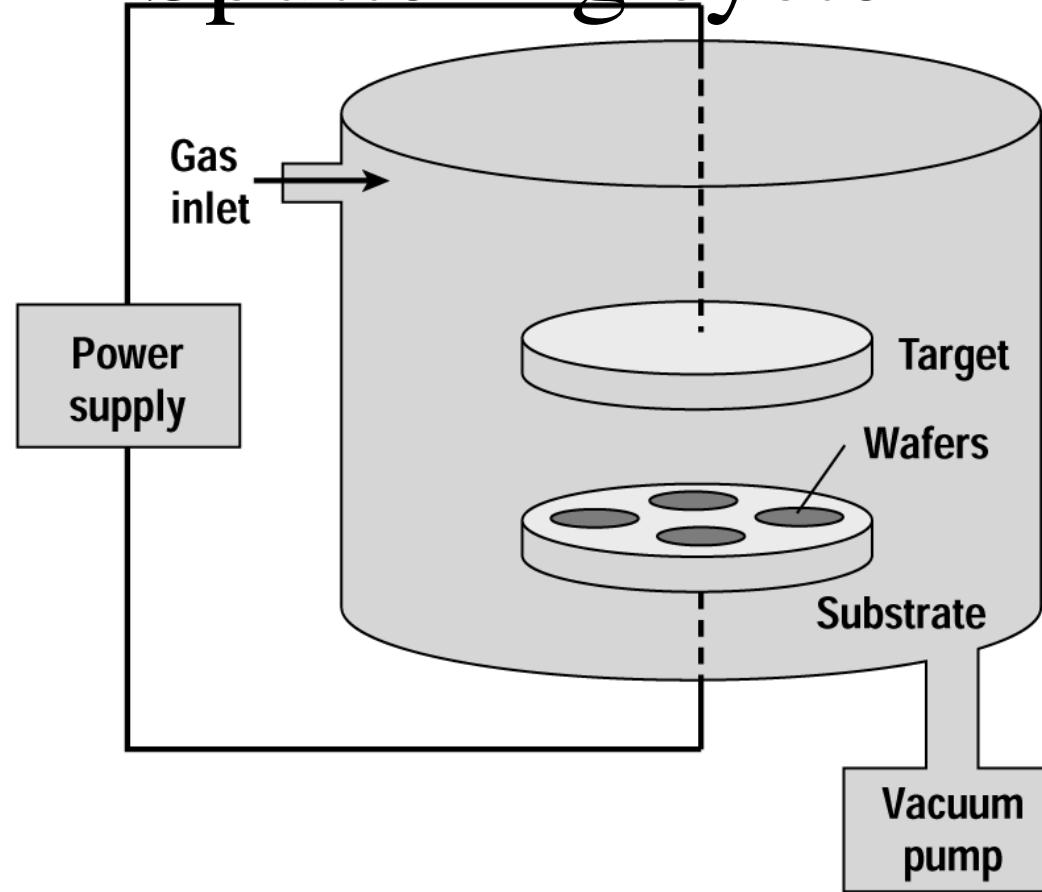


Figure 12.11 Chamber for a simple parallel-plate sputtering system.

Liftoff process

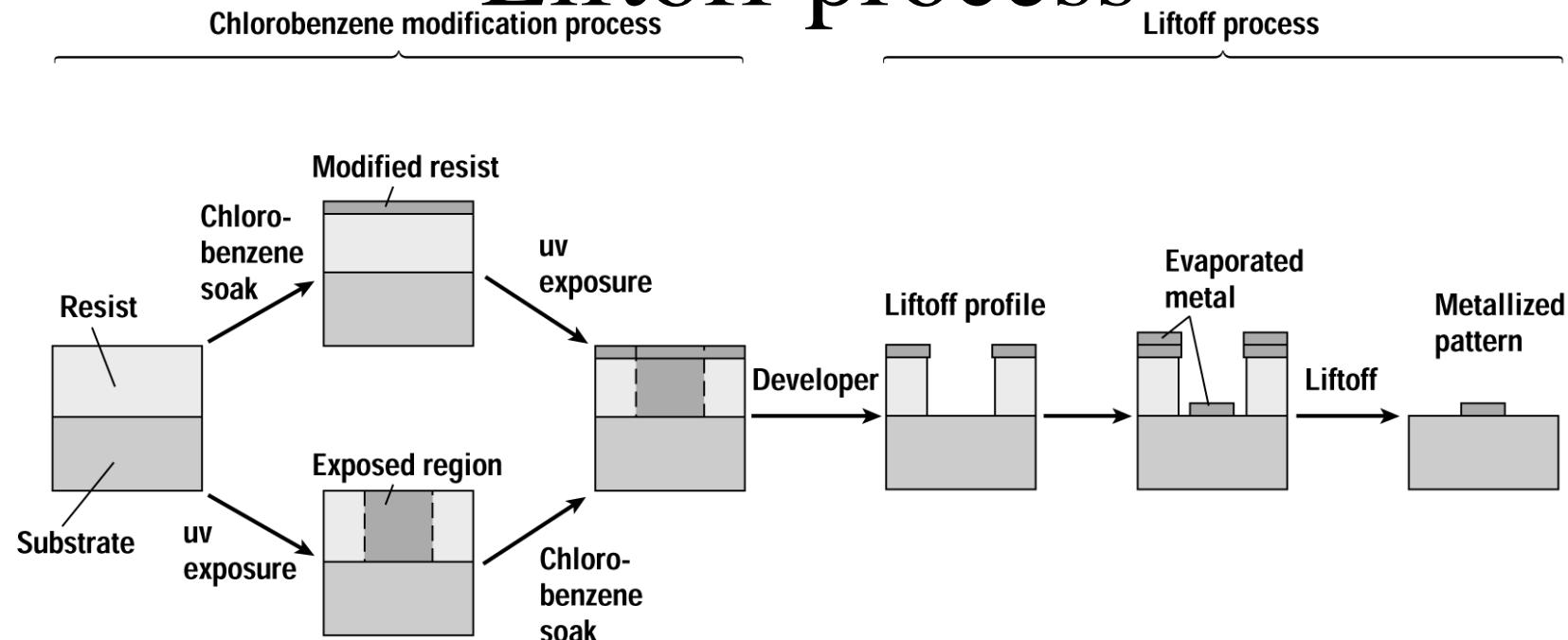


Figure 11.22 Process sequence for a liftoff operation (*after Hatzakis et al., © 1980 International Business Machines Corporation*).

The End