PLASMA in INDUSTRY

MICROELECTRONICS (etching, PE-CVD, etc)

SiOx ctngs in many applications

STERILIZATION in hospital

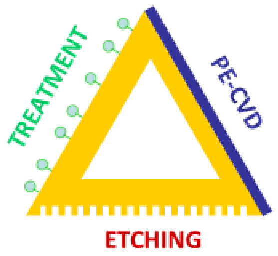
PLASMA SOURCES in Plasma Medicine

…

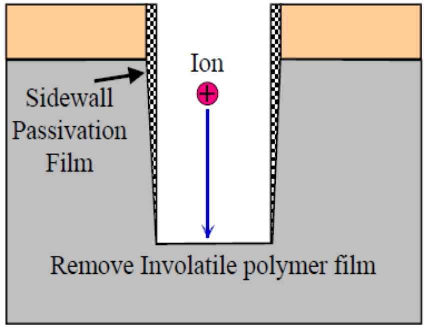
INDUSTRIAL AREAS of COLD PLASMAS

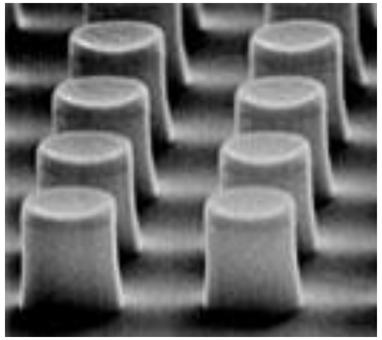
MICROELECTRONICS
SEMICONDUCTORS
SOLAR CELLS
LIGHT SOURCES
OZONE PRODUCTION
AUTOMOBILE
FOOD PACKAGING
TEXTILE
BIOMATERIALS
MICROFLUIDICS
MEMS
CLEANING
STERILIZATION
BIOLOGY
ENVIRONMENT

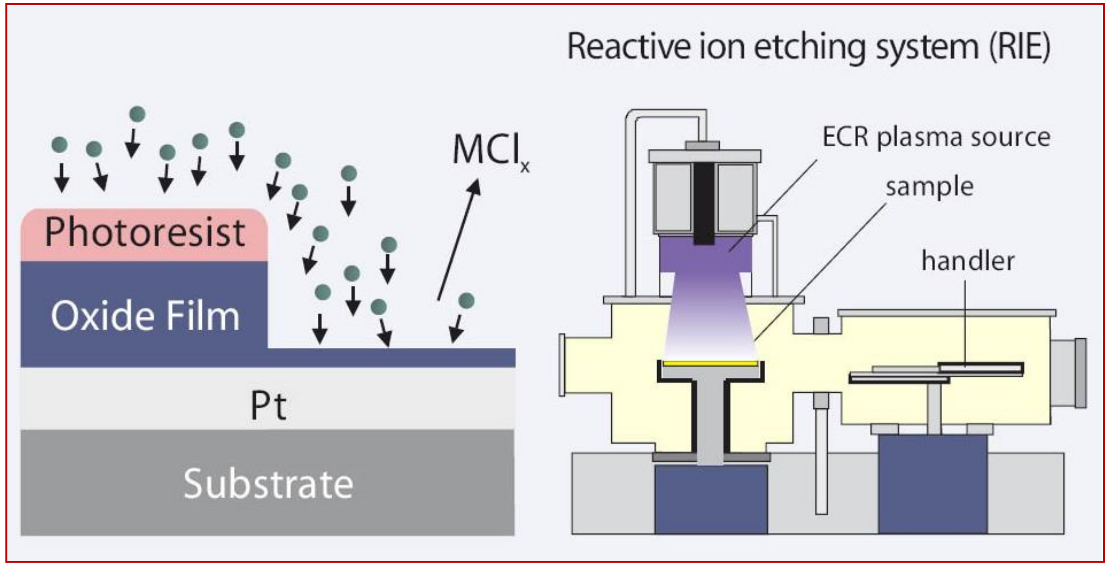
CATALYSIS
MEDICINE
POLYMERS
PAPER
WETTABILITY
ADHESION
METALLIZATION
PRINTING, DYEING
CORROSION PROTECTION
CULTURAL HERITAGE
COMPOSITES
SENSORS
OPTICS
BUILDINGS

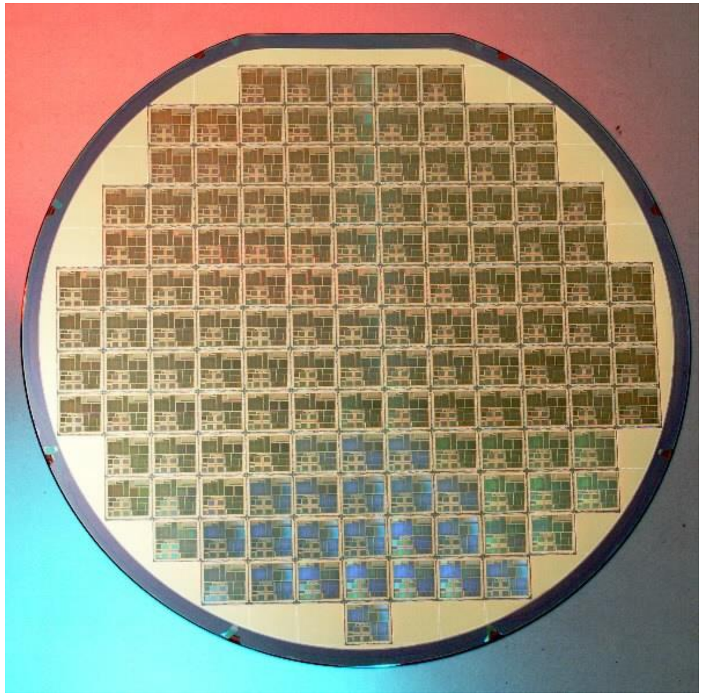


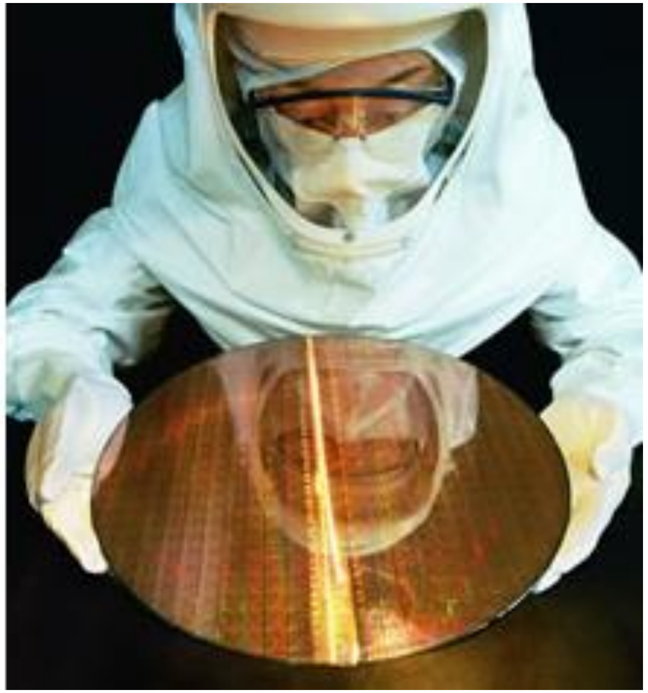
MICROELECTRONICS
etching, PE-CVD, etc






Reactive ion etching system (RIE)

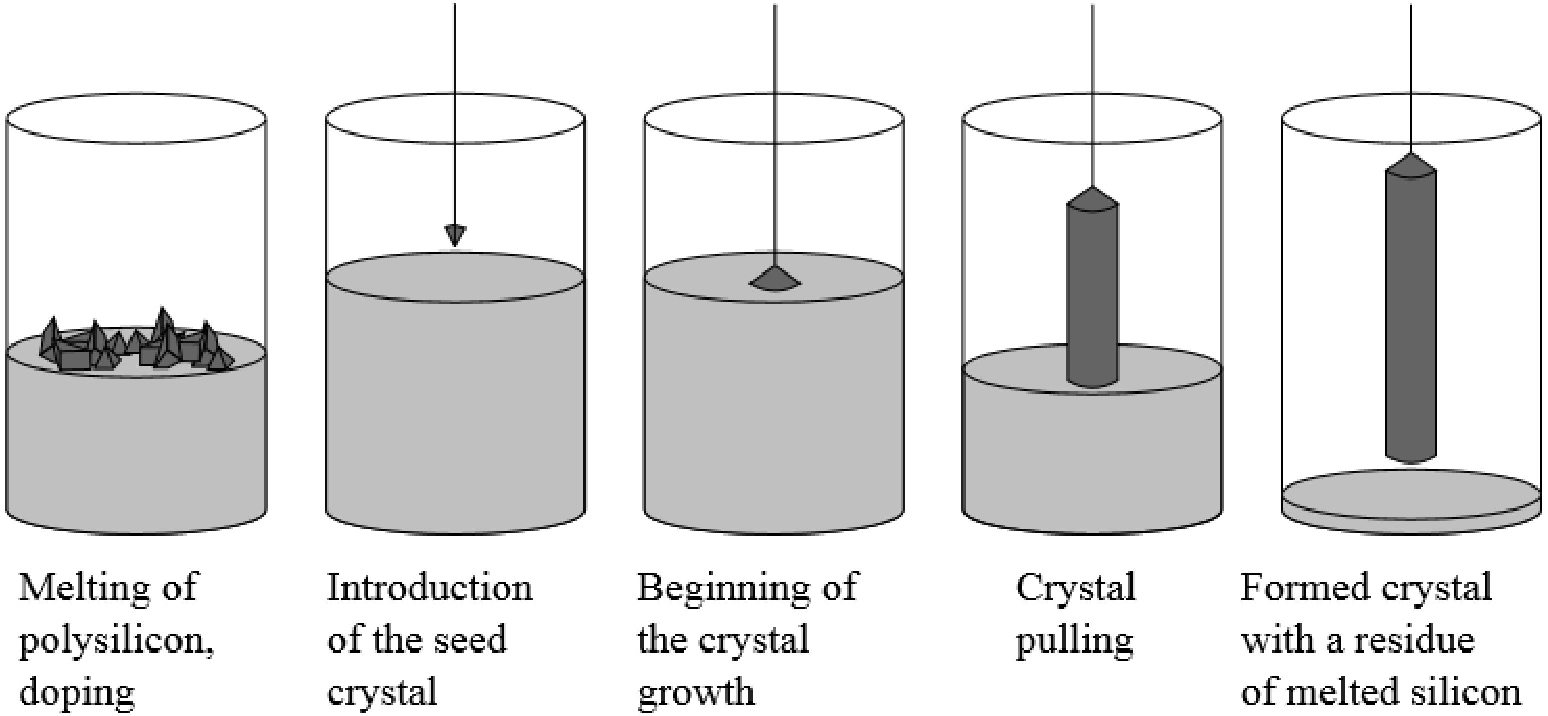




Solar grade silicon cannot be used for microelectronics.

To properly control the quantum mechanical properties of silicon, bulk Si wafers used in the IC making process must first be refined to 99.9999999 % ("9N", "9 nines“), which requires repeated refining.

Most Si crystals for device production are produced with the **Czochralski process**, (Cz-Si). Single crystals grown in this way contain impurities dissolved from the crucible, and need to be refined with the **melting zone technique**.

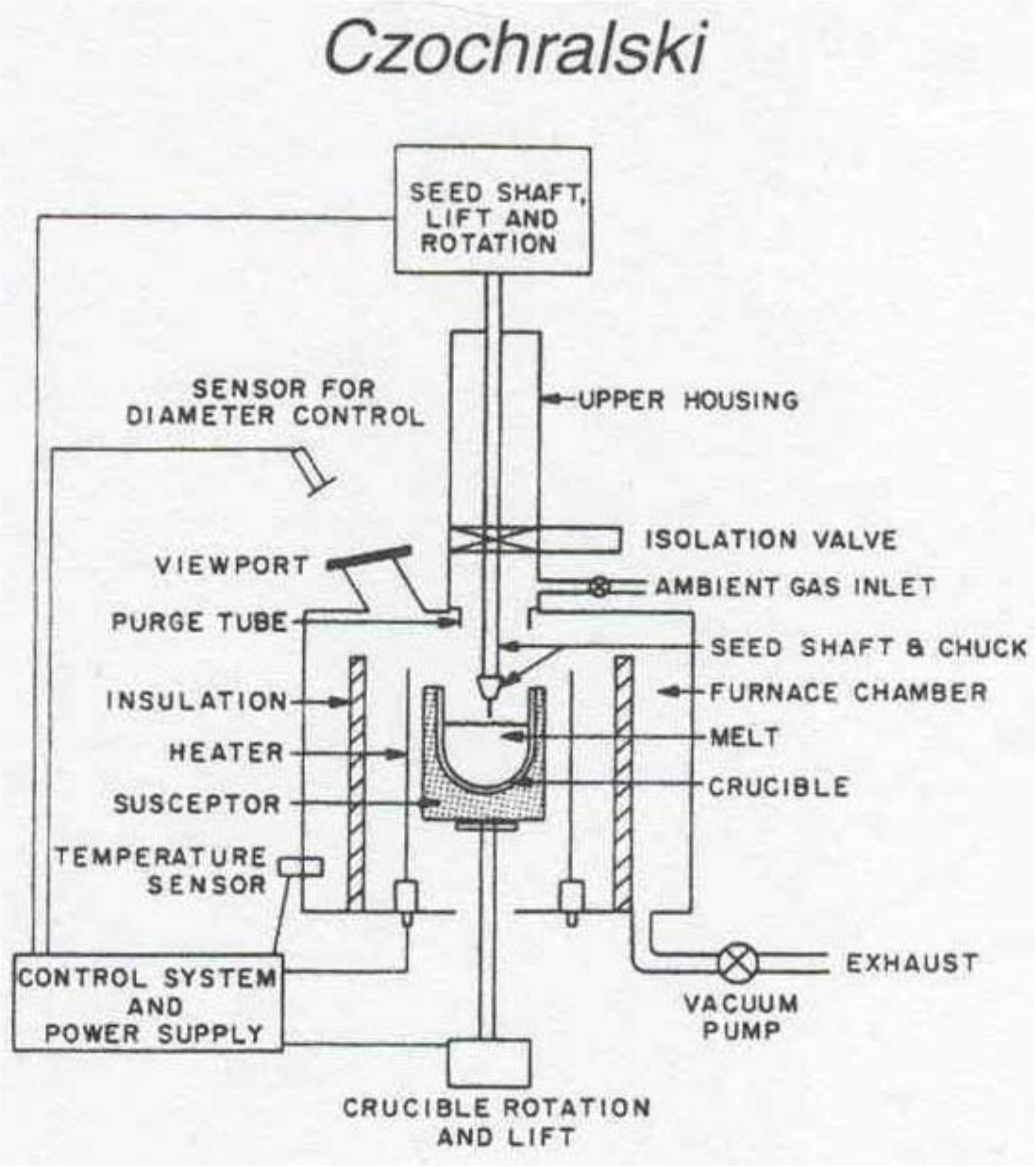


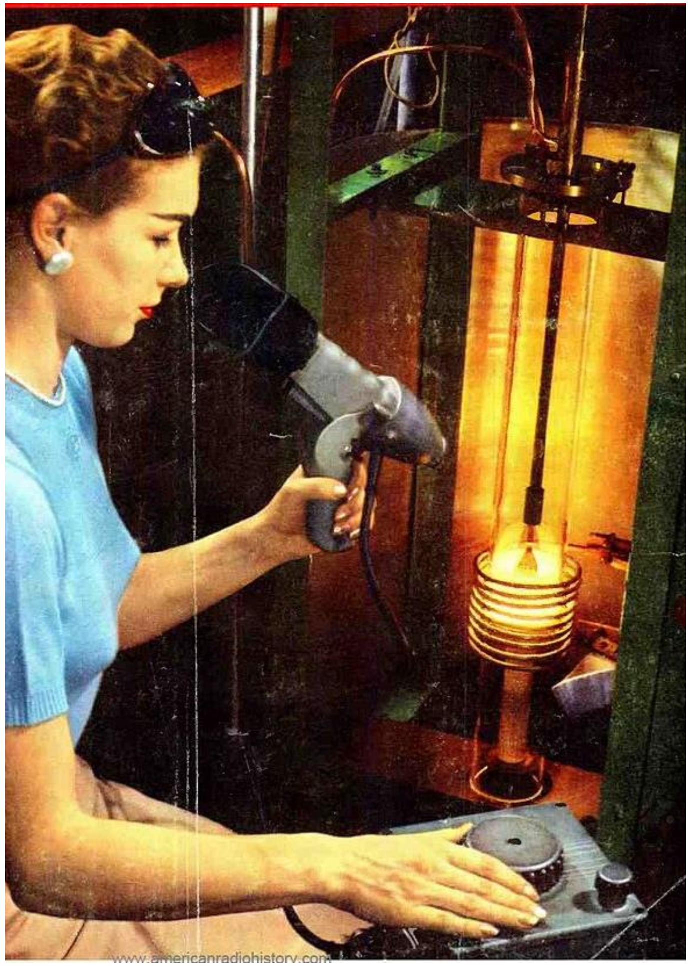
SC and IC industry use wafers with standard dimensions, a few inches wide in early days, **200 and 300 mm dia** today. The width is controlled by precise control of temperature, rotation speeds and withdrawn rate of the seed holder. The crystal ingots from which wafers are sliced can be 2 m long, hundreds Kg heavy.

Si wafers, introduced in the 1940’s, are **0.2 – 0.75 mm thick**, polished to great flatness for IC, or textured for solar cells. Larger wafers improve the manufacturing efficiency, with more chips fabricated per wafer. Wafers **up to 450 mm dia are used**.

When Si is fully melted, at about 1500°C, a small seed crystal mounted at the end of a rotating shaft is slowly lowered until it just dips below the surface of molten Si. The atmosphere of the chamber has to be inert. The shaft rotates counterclockwise and the crucible clockwise. The rotating rod is then drawn upwards very slowly, forming a rough cylinder, 1-2 m long, depending on the amount of Si in the crucible.

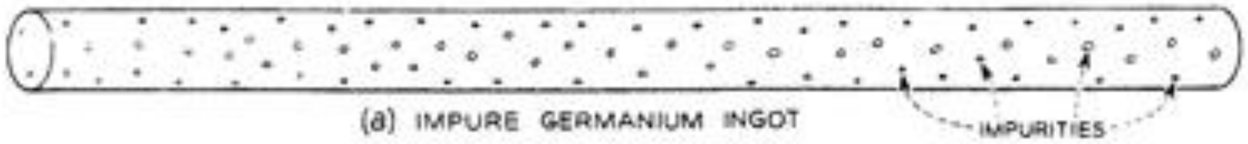
The electrical characteristics of Si are controlled by adding **P or B dopants**, a method also used with GaAs and other SCs. Si ingots are refined and purified to the electronic grade with the **melting zone technique**.



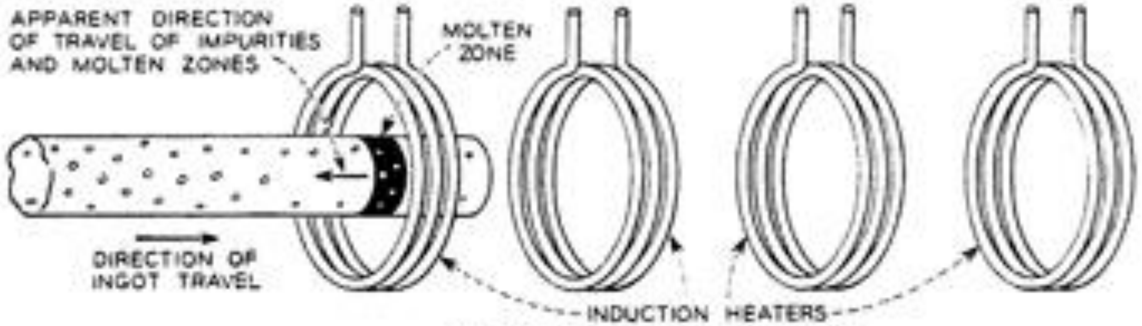


Si crystal grown by Czochralski process at Raytheon, 1956.
The induction heating coil is visible, and the end of the crystal just emerging from the melt. The technician is measuring the temperature with an optical pyrometer. In the earliest Si plants, crystals produced by this early apparatus were only one inch wide.

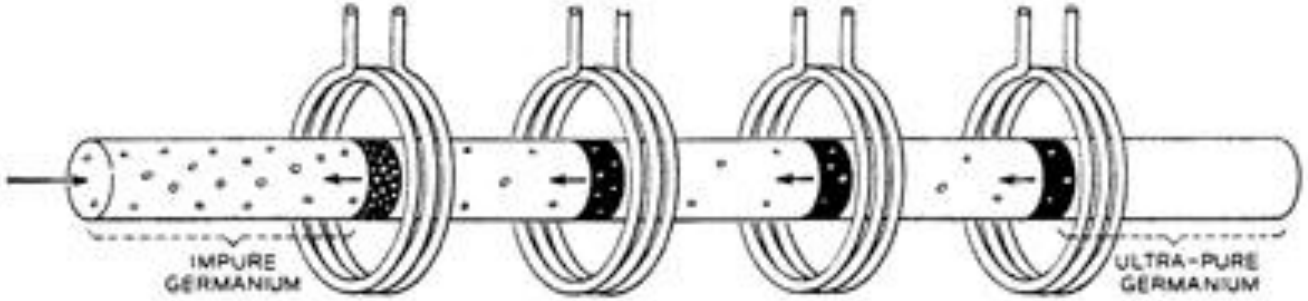
melting zone refining technique



(a) IMPURE GERMANIUM INGOT

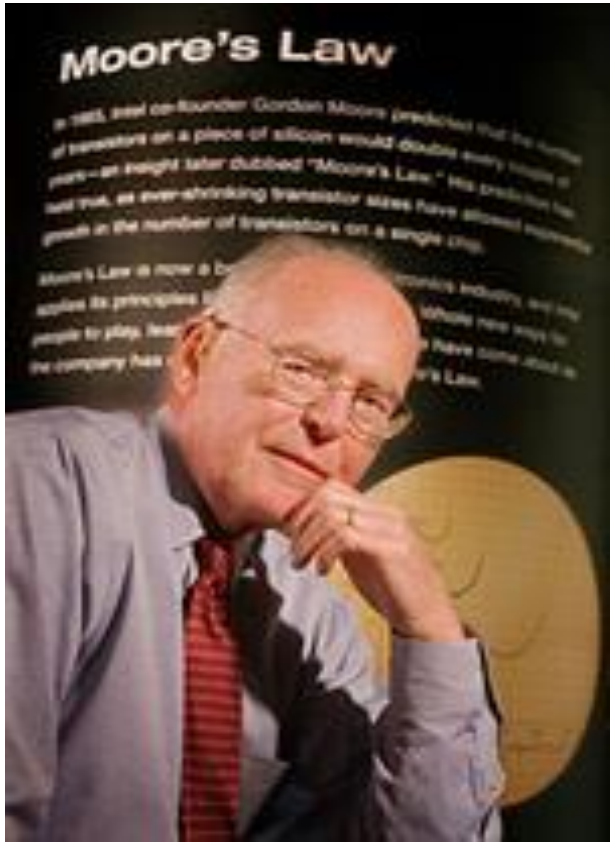


(b) START OF ZONE REFINING



At the solid/liquid boundary, the impurity atoms will diffuse to the liquid zone. Thus, by passing a crystal rod through a thin section of furnace very slowly, only a small region is molten at any time, and impurities segregate at the end of the rod. The rod can grow as a perfect single crystal if a seed crystal is placed at the base to initiate a chosen direction of crystal growth. When high purity is required, the impure end of the rod is cut, and the refining is repeated.

V. M. Donnelly, A. Kornblit
Plasma etching: yesterday, today, and tomorrow
J. Vac. Sci. Technol. A, Vol. 31(5), 2013



Plasmas have been used to etch fine features in Si Integrated circuits for 50 years. Without this technology, we would be stuck in the 1970s, listening through tinny headphones to disco music on our “small” portable cassette tape player. Carrying laptops around would be more for fitness than for convenience, and mobile “smart” phones would require wheels.
Today we take these marvels for granted.

The first commercially available microprocessor, the **Intel 4004**, a 4 bit processor, was launched in 1971 with 2300 transistors, operated at 1.08 MHz clock frequency, with minimum feature size of **10 μm**. Intel 3rd generation multicore processors, launched in 2012, are 64 bit processors, contain 1.4×10^9 transistors, operate at about 3 GHz clock-frequency, and use **22 nm** minimum feature size.

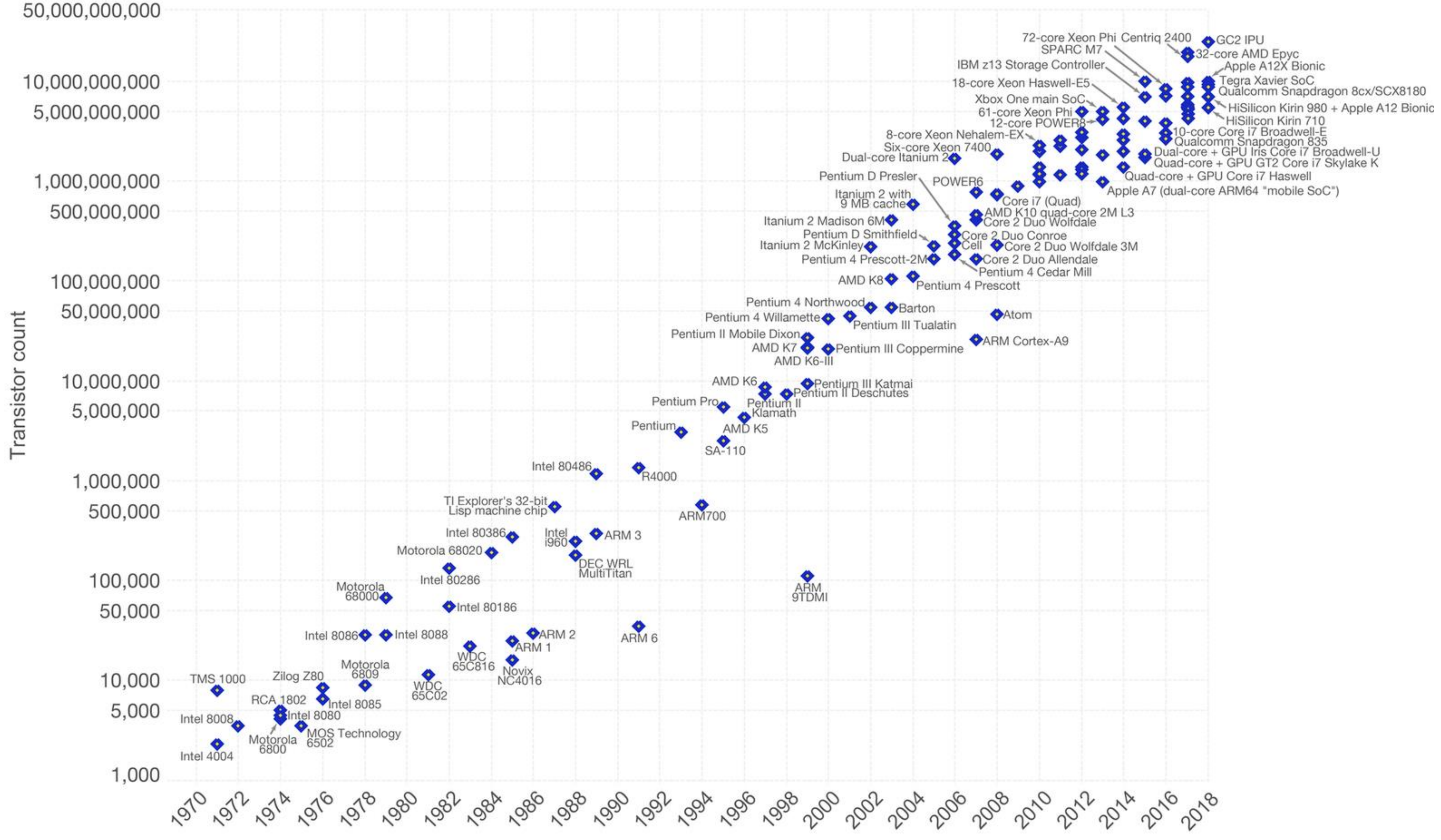
A key element contributing to advances in microprocessors was the ability to fabricate smaller transistors, **due to advancements in lithography and pattern-transfer methods**.

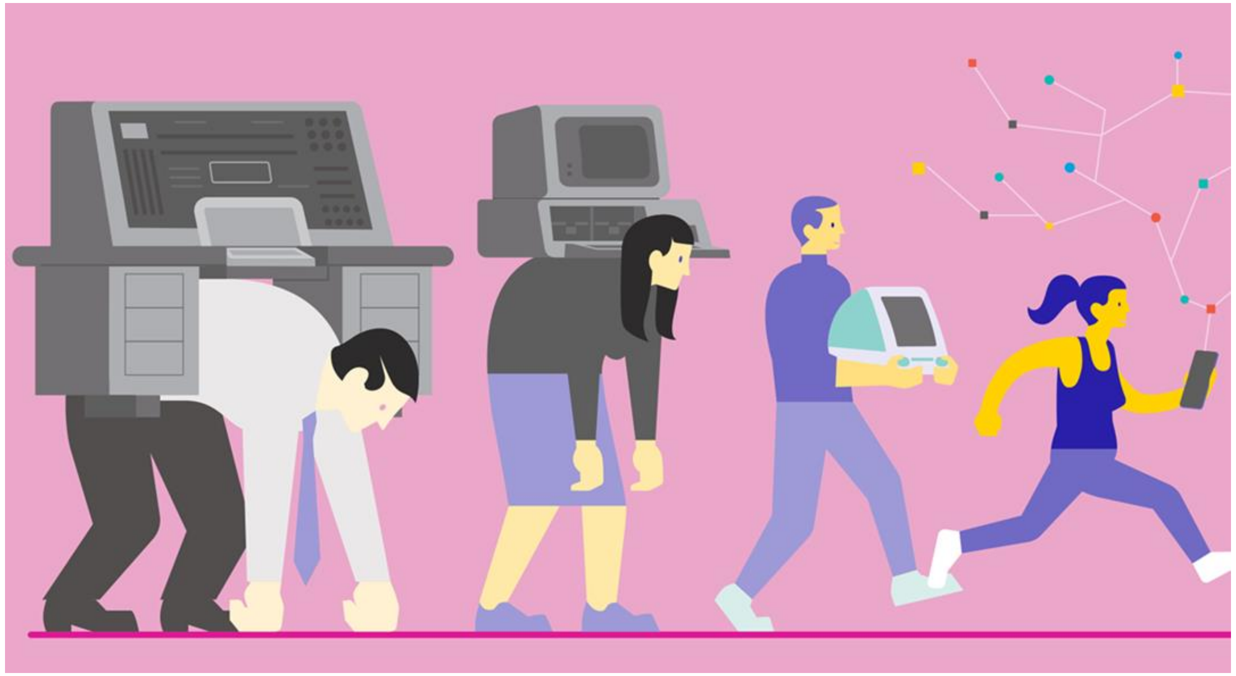
In the early days of IC fabrication, pattern-transfer was accomplished by wet etching. However, with time, **plasma etching became the preferred pattern-transfer method**.

Moore’s Law – The number of transistors on integrated circuit chips (1971-2018)

Moore's law describes the empirical regularity that the number of transistors on integrated circuits doubles approximately every two years. This advancement is important as other aspects of technological progress – such as processing speed or the price of electronic products – are linked to Moore's law.

Our World in Data






1993 vs 2013

Nobel prize for Physics year 2000

Nobel Prize recognizes pioneers of the modern semiconductor industry

In the beginning – the first integrated circuit that Jack Kilby built

Fundamental building blocks of the modern semiconductor industry have been recognized in this year's Nobel Prize for Physics. The annual prize was awarded jointly to Jack Kilby of Texas Instruments for his invention of the integrated circuit, and to Zhores Alferov and Herbert Kroemer for developing semiconductor heterostructures used in high-speed electronic devices and optoelectronics. Alferov is director of the AF Ioffe Physico-Technical Institute in St Petersburg, Russia, while Kroemer is professor of physics at the University of California in Santa Barbara.

The Royal Swedish Academy of Sciences – which awards the prize to scientists who have "made the most important discovery or invention within the field of physics" has recognized the basic work by these scientists in information and communications technologies. The prize is worth SEK 9 million: Kilby will receive half, while Alferov and Kroemer will share the rest.

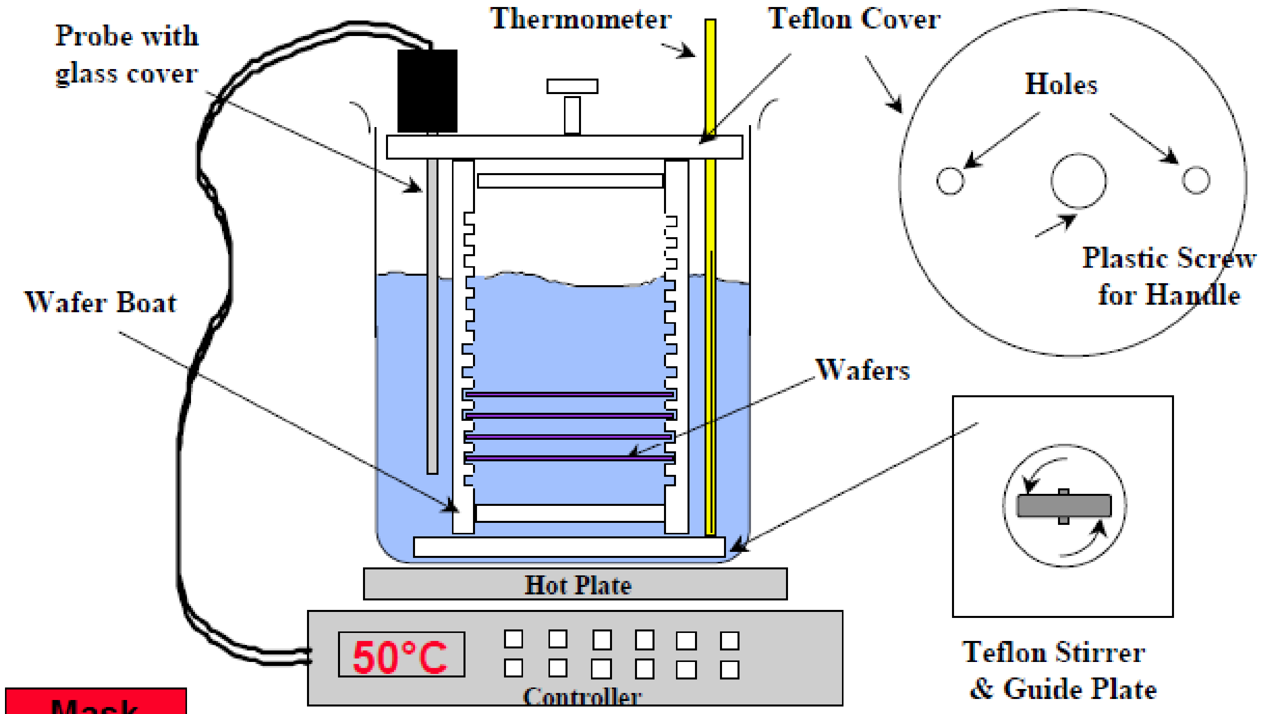
Kilby is recognized for his part in inventing the integrated circuit. He showed in 1958 that a complete circuit could be fabricated in a single piece of germanium. Meanwhile, Robert Noyce at Fairchild Electronics – later to became Intel – developed a method to create an integrated circuit in silicon using aluminium as conducting strips.

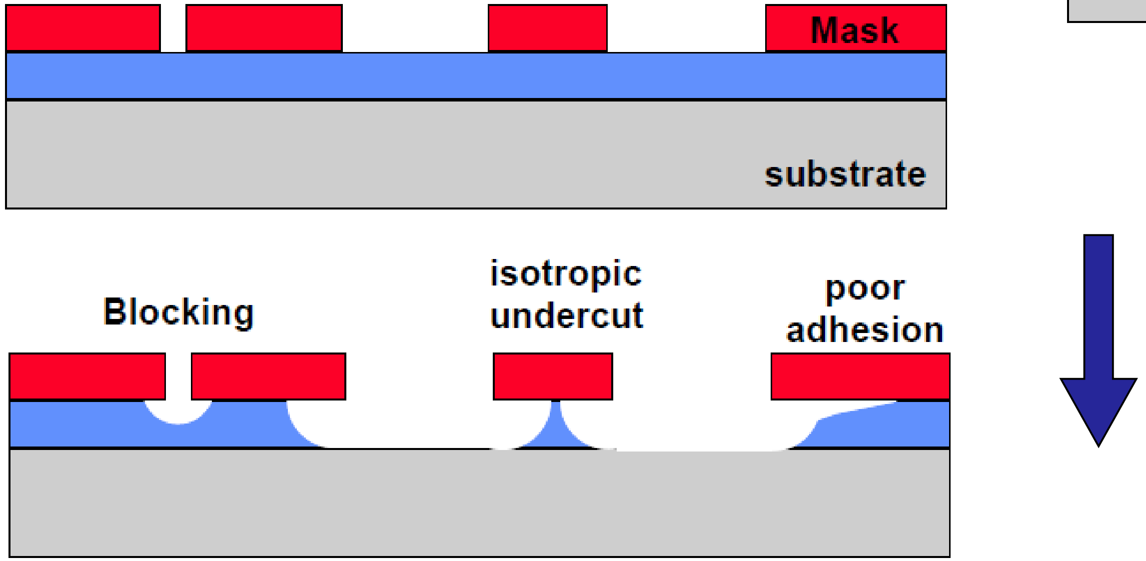
Alferov and Kroemer are honoured for inventing high-speed transistors and optoelectronic components based on multi-layered structures of compound semiconductors. These devices have allowed the development of semiconductor lasers and light-emitting diodes, and also underpin the explosive growth in the communications sector.

● The Nobel Prize for Chemistry recognizes more recent developments in the semiconductor industry. It was awarded to Alan Heeger of the University of California in Santa Barbara, Alan MacDiarmid of the University of Pennsylvania and Hideki Shirakawa of the University of Tsukuba in Japan for discovering that plastic materials can be made to conduct electricity efficiently. Their discovery is fuelling the current drive to produce plastic versions of electronic devices such as light-emitting diodes and displays.

https://www.power-and-beyond.com/what-are-integrated-circuits-definition-types-and-more-a-66046a289105d037a11ba94461ef9c5e/

WET ETCHING

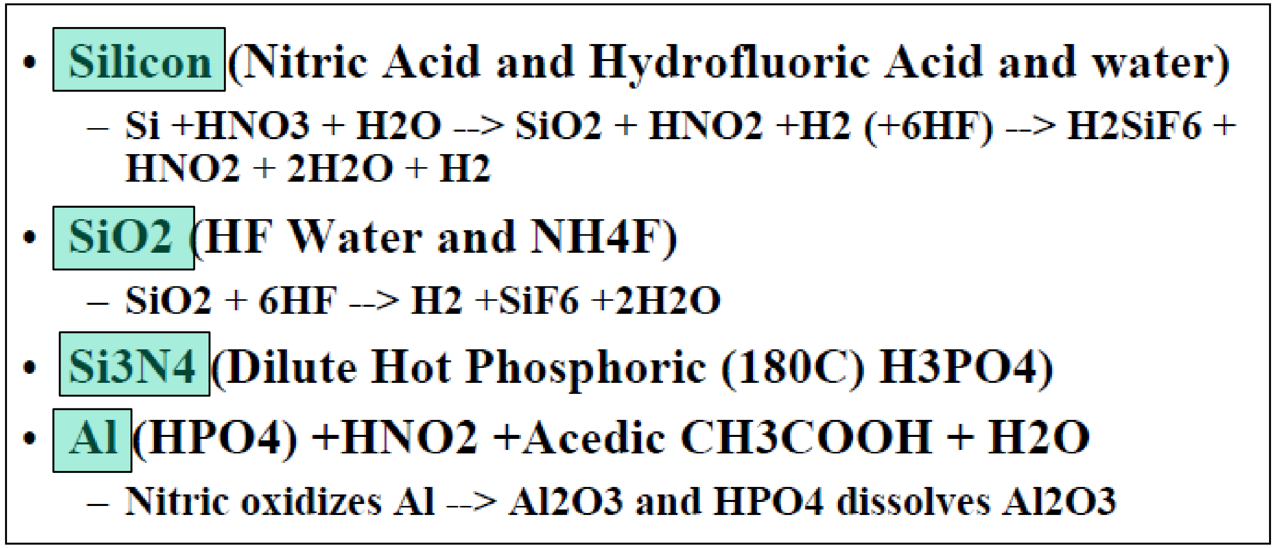




After Isotropic Etch

Generally Wet Etching is Isotropic

WET ETCHING



- **Silicon** (Nitric Acid and Hydrofluoric Acid and water)
  - $Si + HNO_3 + H_2O \rightarrow SiO_2 + HNO_2 + H_2$ (+6HF) $\rightarrow H_2SiF_6 + HNO_2 + 2H_2O + H_2$
- **SiO2** (HF Water and NH_4F)
  - $SiO_2 + 6HF \rightarrow H_2 + SiF_6 + 2H_2O$
- **Si3N4** (Dilute Hot Phosphoric (180C) H_3PO_4)
- **Al** (HPO_4) $+HNO_2$ +Acedic $CH_3COOH + H_2O$
  - Nitric oxidizes Al $\rightarrow Al_2O_3$ and HPO_4 dissolves Al_2O_3

Advantages:

- Simple equipment
- High throughput (batch process)
- High selectivity

Disadvantages:

- Isotropic etching leads to undercutting
- Uses relatively large quantities of etch chemicals, must immerse wafer boats, must discard partially used etch to maintain etch rate
- Hot chemicals create photoresist adhesion problems
- Small geometries difficult, line with > thickness, etch block caused by surface tension
- Critical Etch time, dimensions change with etch time, bias develops
- Chemical costs are high
- Disposal costs are high

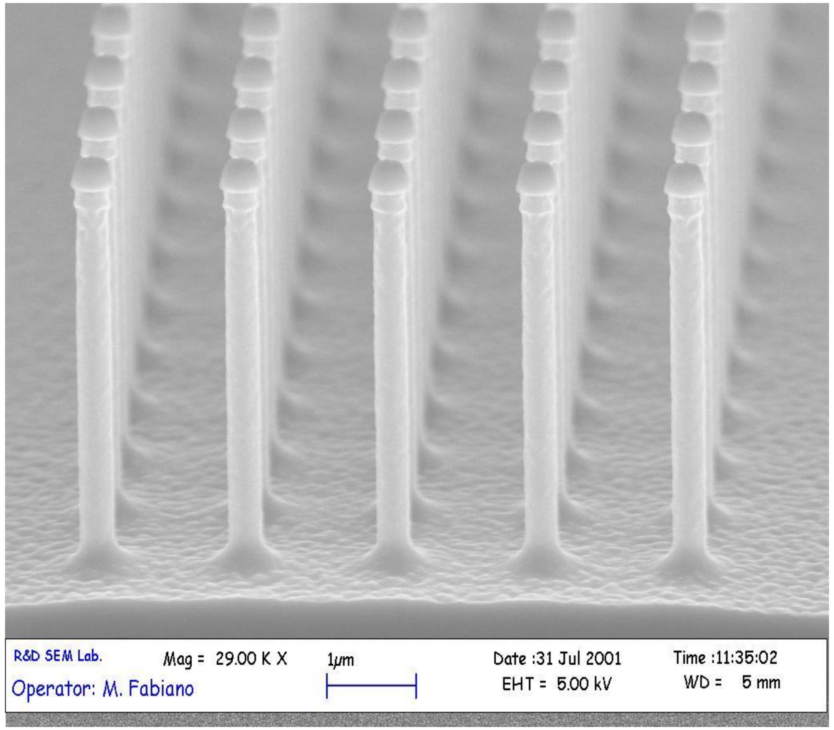
PLASMA
“DRY” ETCHING

reaction between a solid
and a gas reactant (the “etchant”)
with formation of volatile products

a) Directional Etching
anisotropic

b) Isotropic Etching

FIG. 2. Schematic of (a) directional etching, showing a greater rate of material removal in the vertical direction than lateral, and (b) isotropic etching, showing material removed at the same rate in all directions.



dry etching has completely
taken the place of wet etching

a layer can not be etched
if it does not form
volatile products

PLASMA – SURFACE INTERACTIONS

synergistic action of
active species
&
ion bombardment

PLASMALESS ETCHING of SILICON

XeF_2 (F) + Ar^+
Cl_2 (Cl) + Ar^+

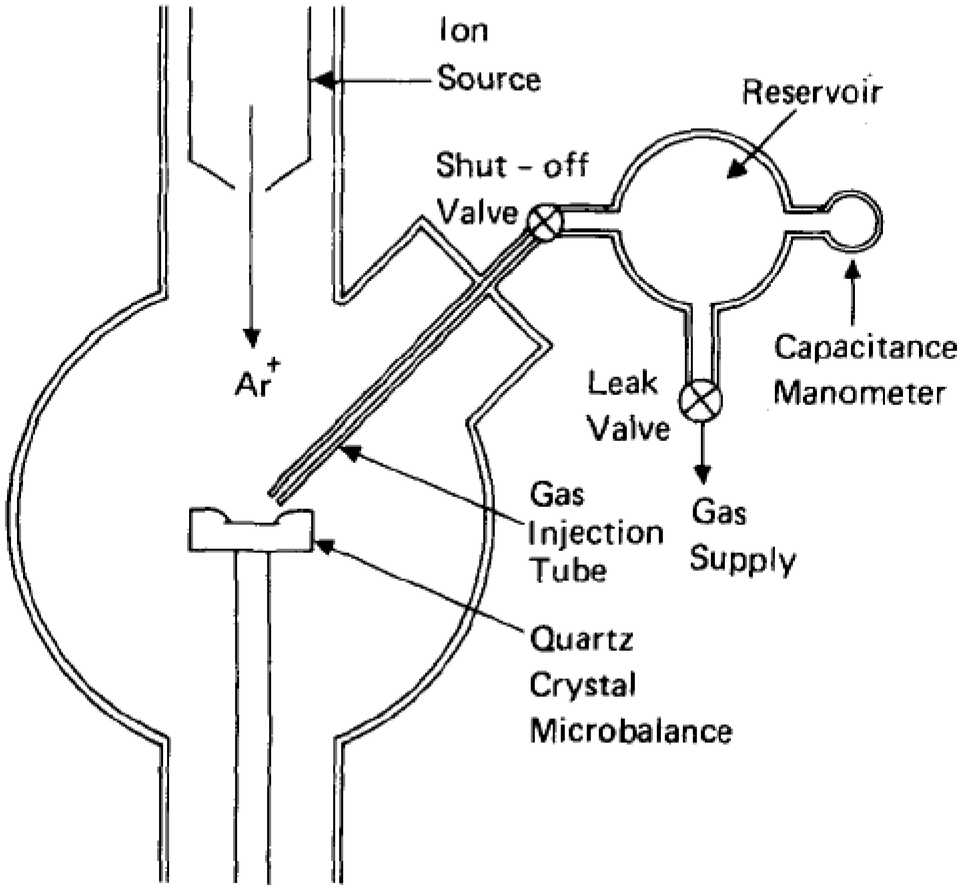
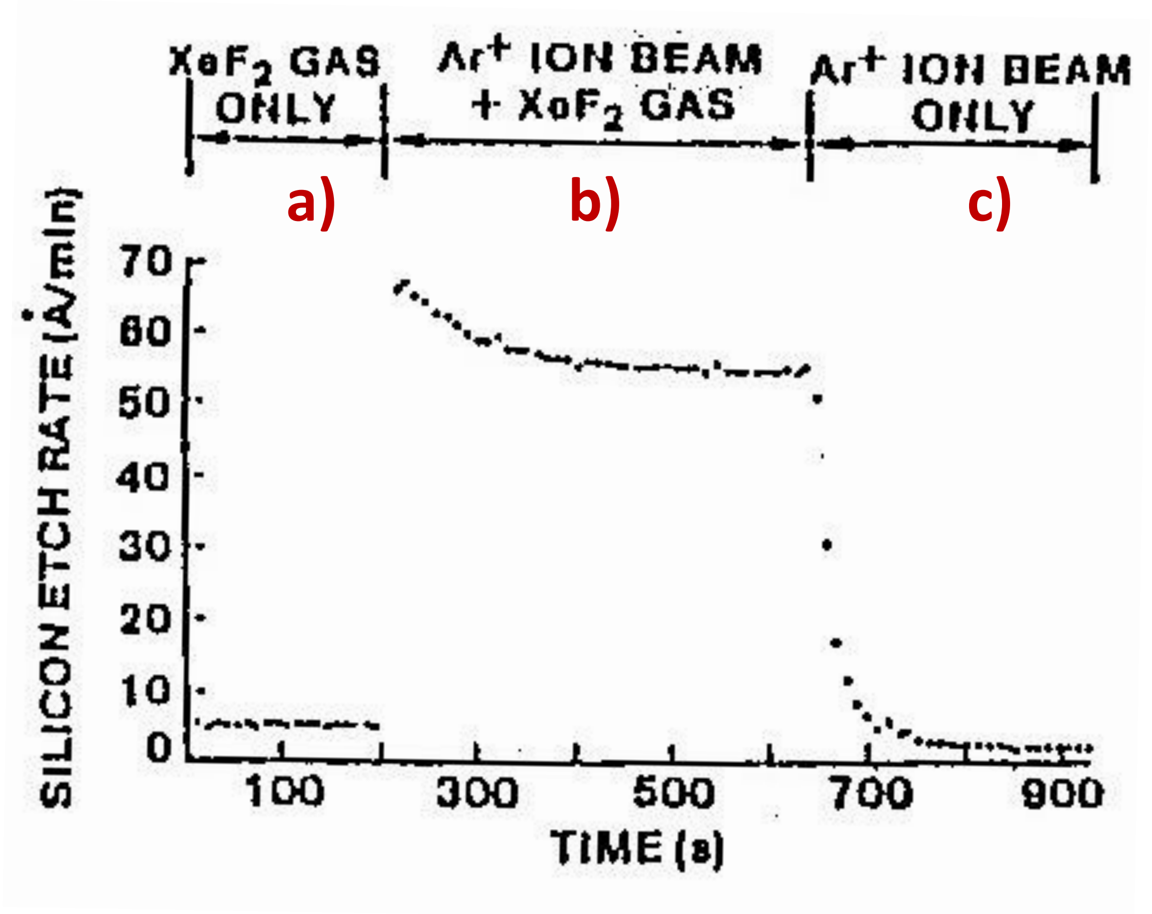


FIG. 1. Schematic diagram of the apparatus used to study ion-assisted gas-surface chemistry. The gas injection tube is 1.6 mm inside diameter and is about 3 mm from the quartz crystal microbalance. The gas flow is determined from the rate of pressure increase in the reservoir when the shut-off valve is closed.

J.W. Coburn, H.F. Winters, *J. Vac. Sci. Tech.* **16**, 391, 1979

Silicon etching with F atoms

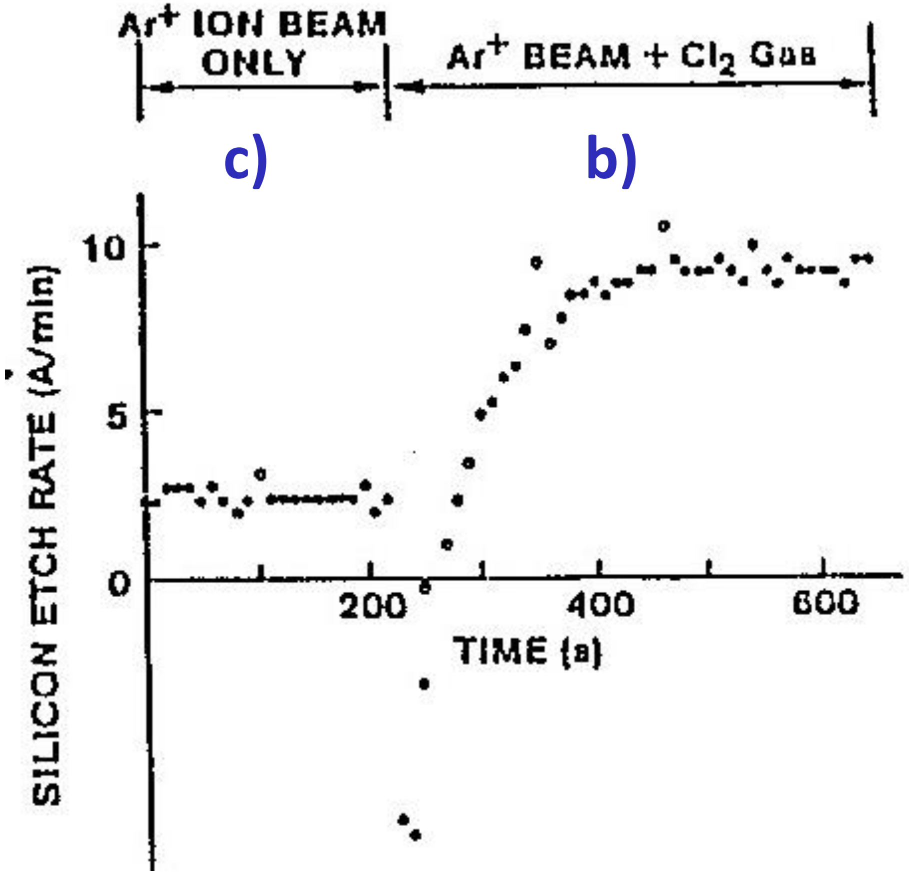


a) $2\ XeF_2\ (F) + Si \rightarrow SiF_4\uparrow + 2\ Xe\uparrow$ slow (chemical etching)

b) $2\ XeF_2\ (F) + Si \xrightarrow{Ar^+\ bomb} SiF_4\uparrow + 2\ Xe\uparrow$ very fast (ion assisted etching)

c) $Si \xrightarrow{Ar^+\ bomb} Si\ (fragments)\uparrow$ slow (sputtering)

Silicon etching with Cl atoms



$2\,Cl_2 + Si \not\rightarrow SiCl_4$ no reaction

b) $Si \xrightarrow{Ar^+ \text{ bomb}} Si$ (fragments) ↑ slow (sputtering)

c) $2\,Cl_2\,(Cl) + Si \xrightarrow{Ar^+ \text{ bomb}} SiCl_4$ ↑ fast (ion assisted etching)

PHOTO LITOGRAPHY

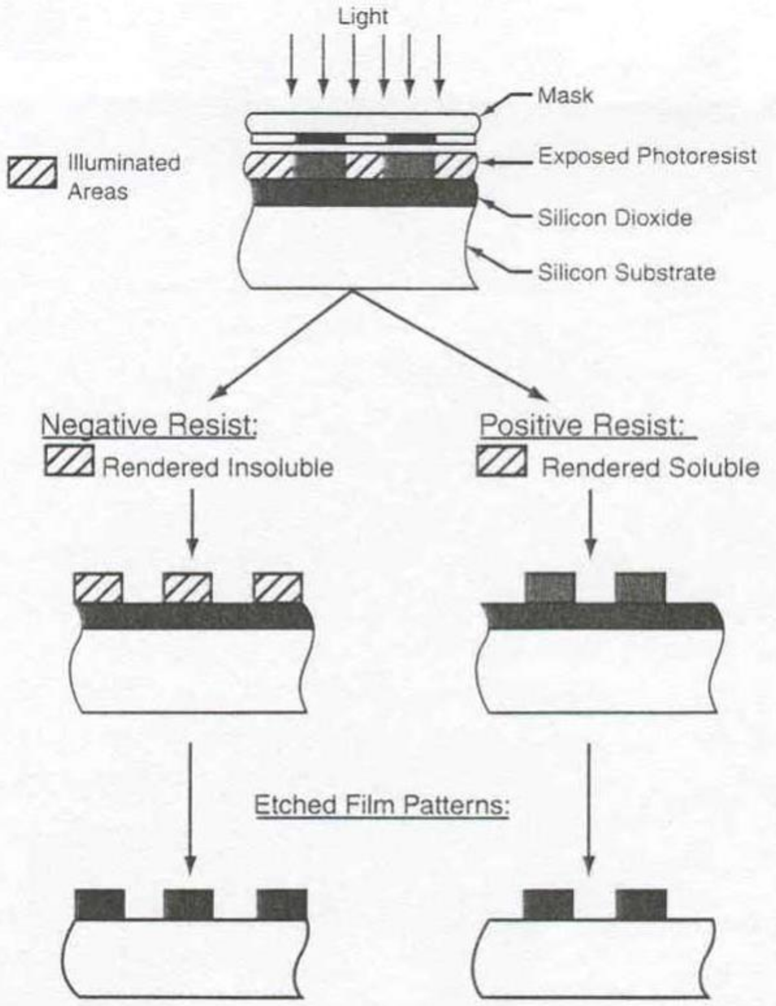
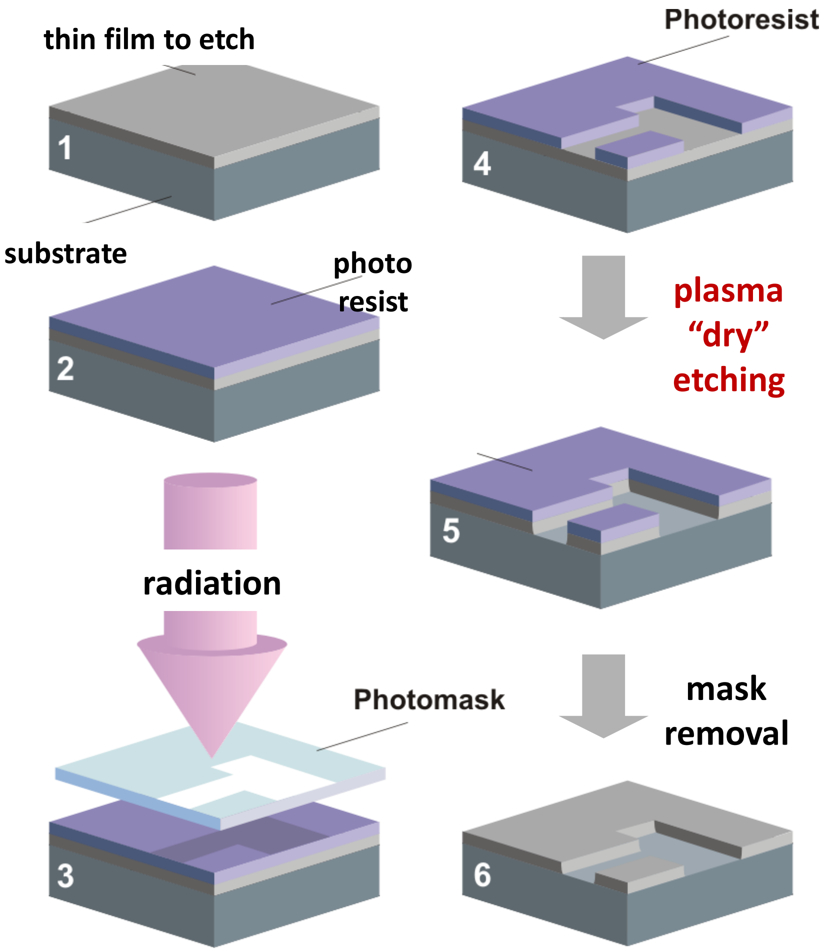
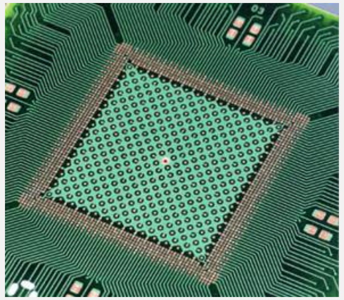


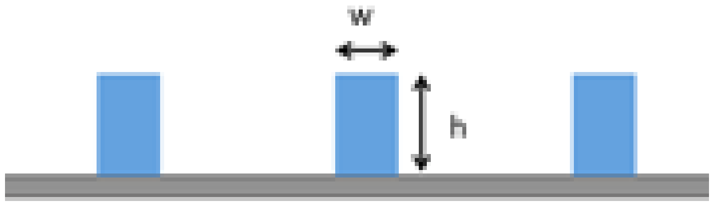
Figure 1.2 Positive and negative resist: exposure, development, and pattern transfer. Positive resists develop in the exposed region. Negative resists remain in the exposed region.



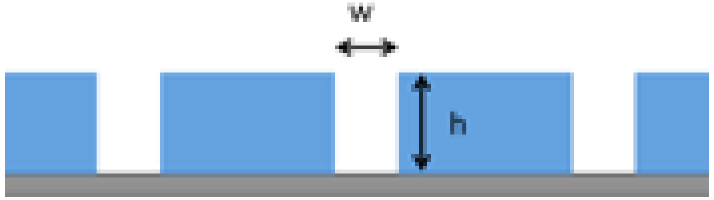
Integrated Circuits



Microelectronics: from sand to chips



Aspect ratio = w/h



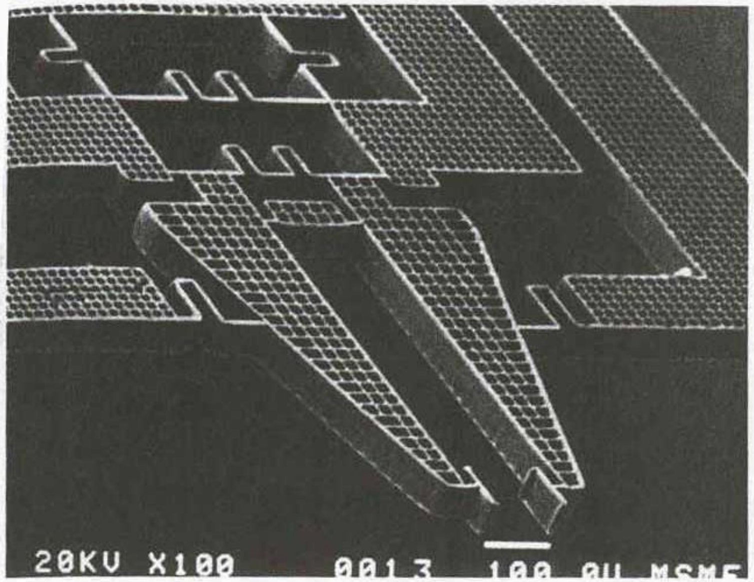
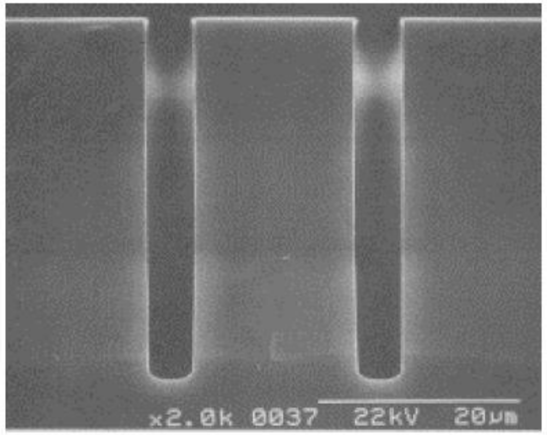
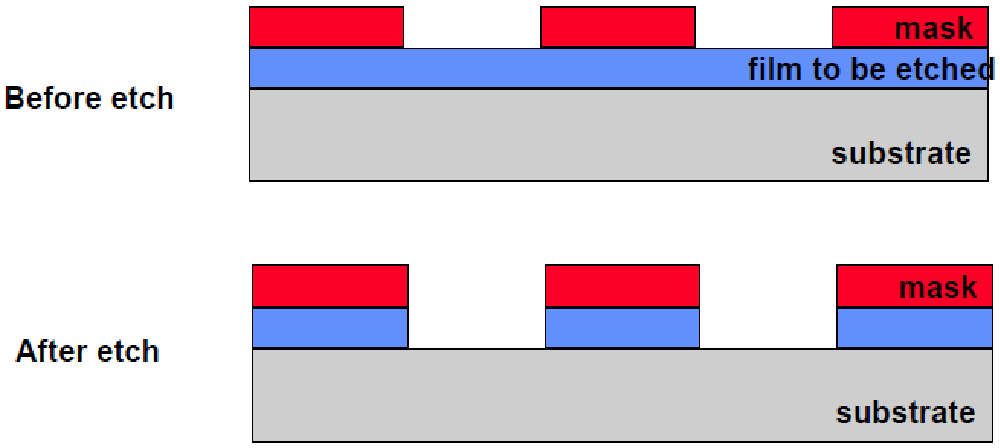


Figure 5.26 SEM micrograph of HEXSIL tweezers: 4 mm long, 2 mm wide, and 80 µm tall. Lead wires for current supply are made from Ni-filled poly-Si beams; *in situ* phosphorus-doped polysilicon provides the resistor part for actuation. The width of the beam is 8 µm: 2 µm poly-Si, 4 µm Ni, and 2 µm poly-Si. (Courtesy of Dr. C. Keller, MEMS Precision Instruments.)

Anisotropic Etch, High Aspect Ratio



Ideal Etching Process



Before etch

mask

film to be etched

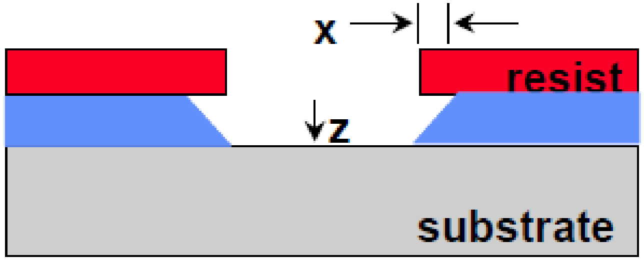
substrate

After etch

mask

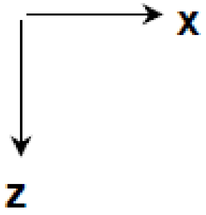
substrate

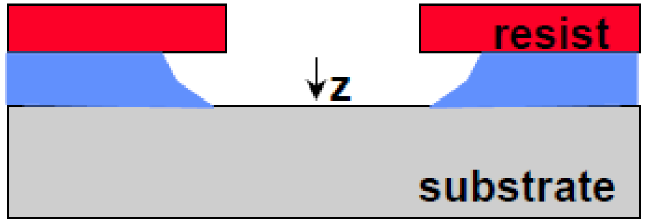
Directionality of Etching



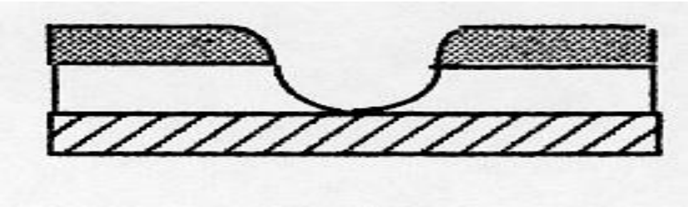
Anisotropic Etch (x < z) 0 < A < 1

Degree of Anisotropy
$A = (z-x)/z$

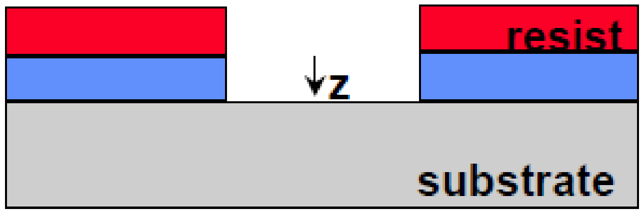




Isotropic Etch (x = z) A = 0



isotropic with mask erosion



Vertical Etch (x = 0) A = 1
(Perfectly anisotropic)

Why Plasma Etching?

Advanced IC Fabrication with small geometries requires precise pattern transfer

Geometry in the < 1.0 micrometer range is common

Line widths comparable to film thickness

Some applications require high aspect ratio

Some materials wet etch with difficulty

Disposal of wastes is less costly

Dry Etching Characteristics

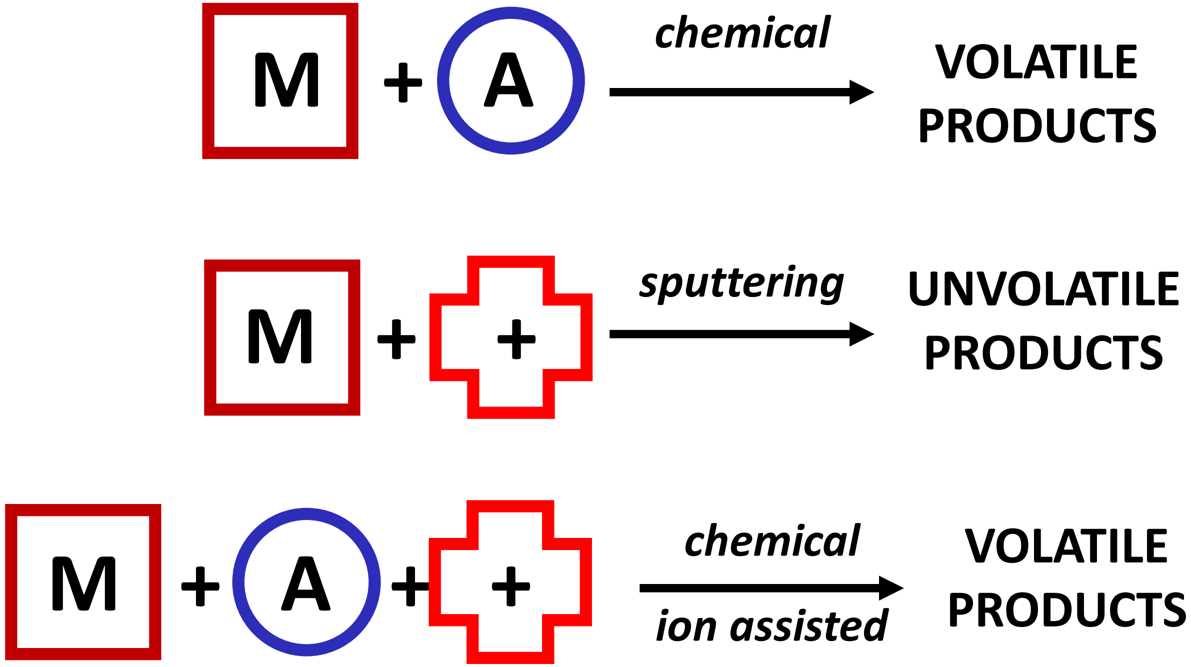
Advantages:
- **No photoresist adhesion problems**
- **Anisotropic etch profile is possible**
- **Chemical consumption is small**
- **Disposal of reaction products less costly**
- **Suitable for automation, single wafer, cassette to cassette**

Disadvantages:
- **Complex equipment, RF, gas metering, vacuum, instrumentation**
- **Selectivity can be poor**
- **Residues left on wafer, polymers, heavy metals**
- **Particulate formation**
- **CFC's**

DRY ETCHING GENERAL MECHANISM

- Generation of etchants in the plasma
- Diffusion of etchants to the substrate surface
- Adsorption (and migration) of etchants
- Reaction between substrate and etchant
- Desorption of by-products
- Diffusion of by-products to the gas phase

M = material A = atom + = ion



$M + A \xrightarrow{\text{chemical}}$ **VOLATILE PRODUCTS**

$M + (+) \xrightarrow{\text{sputtering}}$ **UNVOLATILE PRODUCTS**

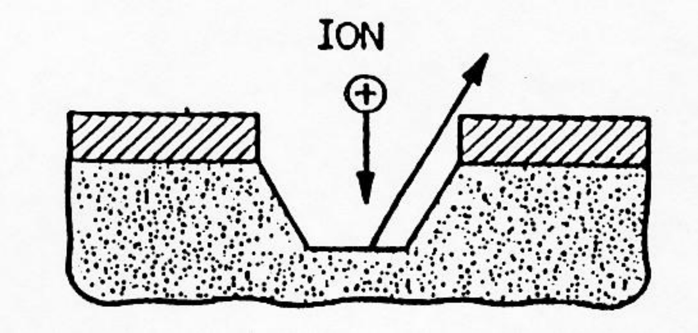
$M + A + (+) \xrightarrow[\text{ion assisted}]{\text{chemical}}$ **VOLATILE PRODUCTS**

each step is characterized by a ΔH and can be influenced by the ion bombardment

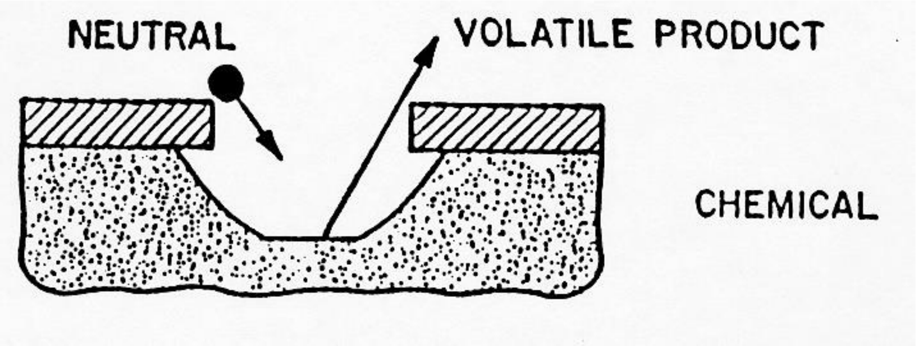
Etching Gas & By-Products

Solid	Etch Gas	Etch Products
Si, SiO_2, Si_3N_4	CF_4, SF_6, NF_3	SiF_4, Si_2F_6,..
Si	Cl_2, CCl_2F_2	$SiCl_4$, $SiCl_2$,..
Al	BCl_3, CCl_4,..	Al_2Cl_6, $AlCl_3$
Refractory Metals (W, Ta, Nb, Mo)	CF_4, Cl_2	WF_6, WCl_6
Organic Solids	O_2, O_2+CF_4	CO, CO_2, HF, H_2O,..
III-V (GaAs, InP)	Cl_2, CCl_2F_2	Ga_2Cl_6, $GaCl_3$, $AsCl_3$
II-VI (HgCdTe, ZnS,..)	$CH_4 + H_2$	$Zn(CH_3)_2$, H_2S

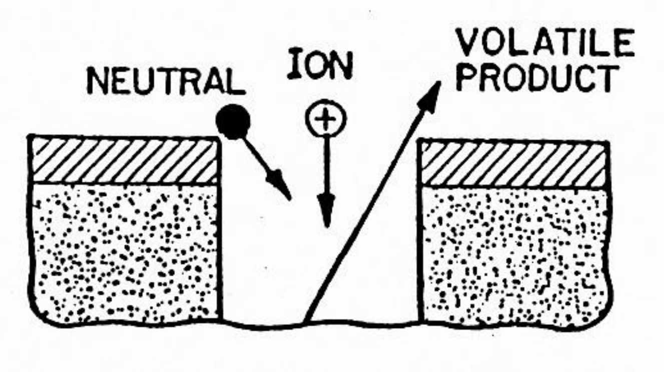
sputtering



chemical

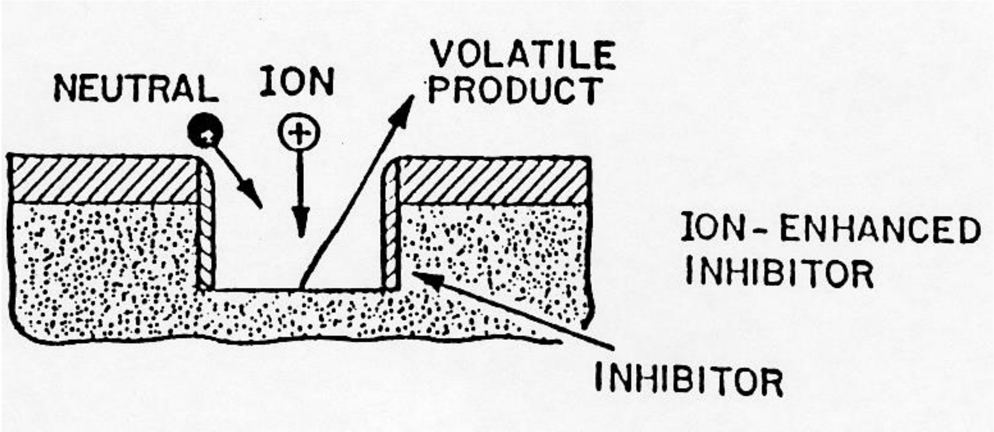


ion assisted



Pi.a. < Ps.i.

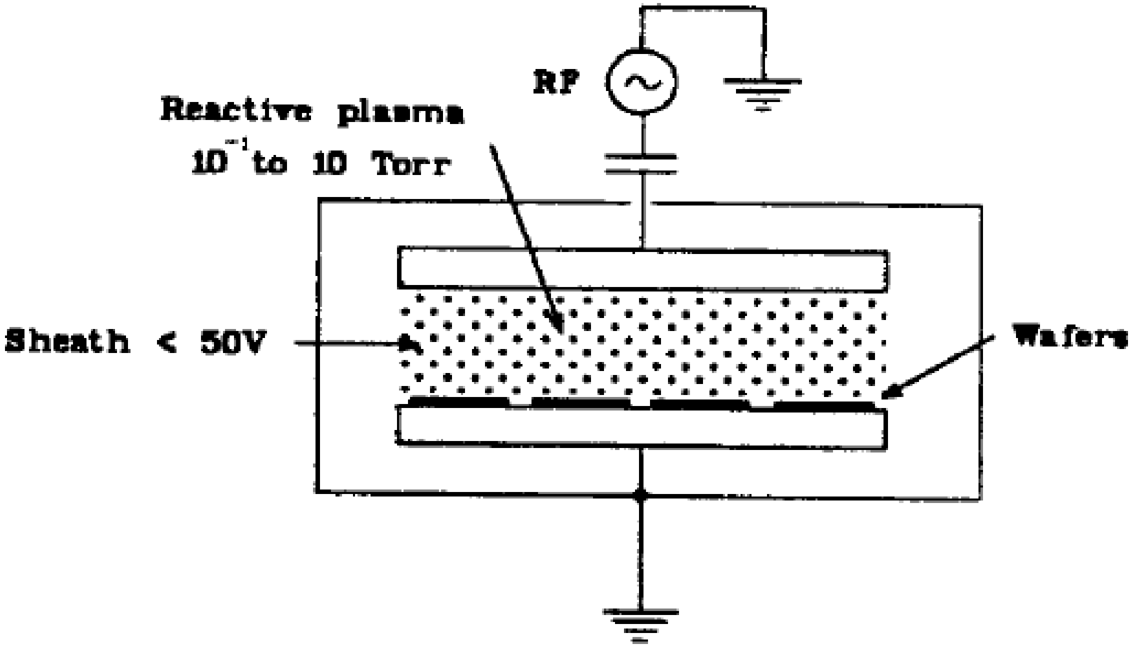
sidewall inhibitor



Low Density Plasma Reactors

Plasma Etcher

- *Plasma Etching Mode in Parallel Plate or Planar Reactor*
- *Wafer placed on the Grounded Electrode*
- *Capacitively Coupled Plasma*

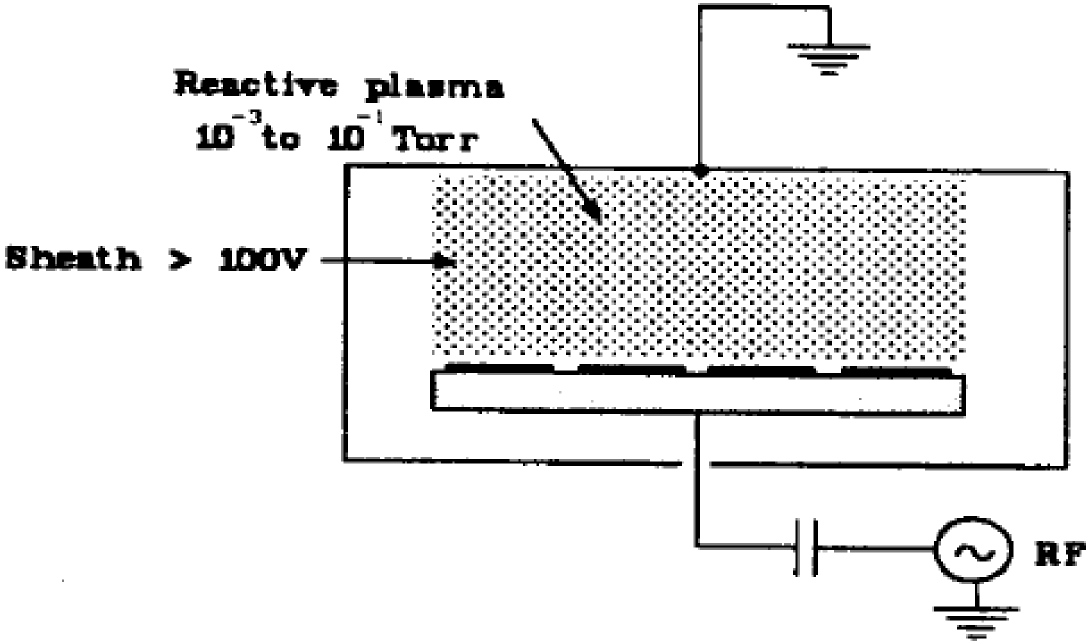


- *Isotropic by Radical*
- *Plasma Potential (Low Ion Energy)*
- *High Pressure*
- *Single Wafer Type*
- *Less Electrical Damage*
- *Reinberg Reactor*

Medium Density Plasma Reactors

RIE Etcher

- *Reactive Ion Etching (RIE) = Plasma Etching + Energetic Ion Bombardment*
- *Reactive Ion Etching (RIE) ≡ Reactive Sputter Etching (RSE)*
- *Wafer placed on the RF-driven Electrode*
- *Capacitively Coupled Plasma*

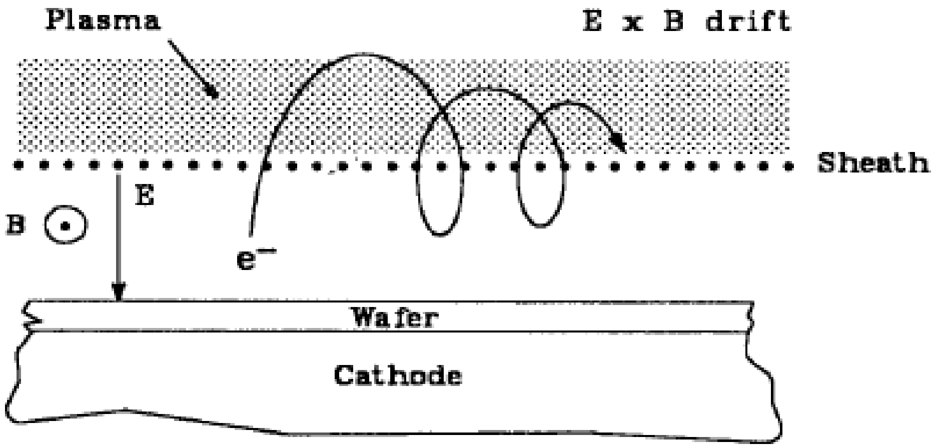


- *Anisotropic by Ion*
- *DC Self-bias*
  (High Ion Energy)
- *Middle Pressure*
- *Single Wafer Type*
- *Electrical Damage*

Medium Density Plasma Reactors

MERIE Etcher

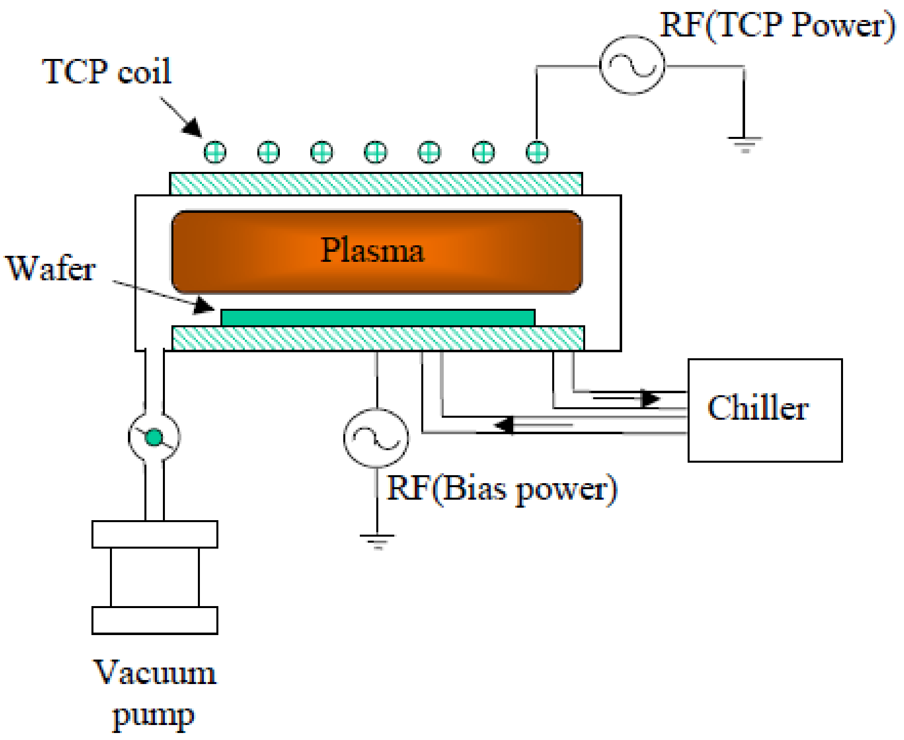
- *Magnetic field is above and Parallel to the cathode surface*
- *Keep the Secondary Electron by Cycloidal Motion in* ***ExB*** *Field*
- *Probability for electron-neutral collisions can be increased*
- *Ionization efficiency in Dark Sheath Region is increased*



- *B field is rotated electrically*
- *Anisotropic by Ion*
- *Low Pressure*
- *Single Wafer Type*
- *Lower Electrical Damage*

High Density Plasma Reactors

Ex)TCP : Lam Research



<Characteristics>

- **Low Pressure Control ≤ 5mT**
- **Independent Power Control**
  - **Plasma Source = TCP power**
  - **High Density Plasma ~ 10^{12}**
  - **Ion DC Bias = Bias Power**
- **Low Temperature Etching**
  : -50°C ~ +50°C
- **Improved Plasma Uniformity**

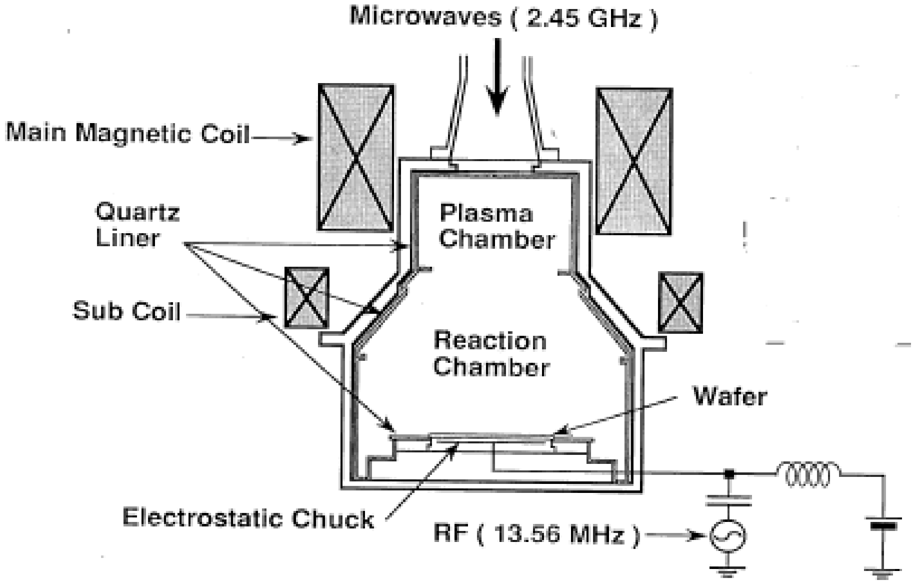
High Density Plasma Reactors

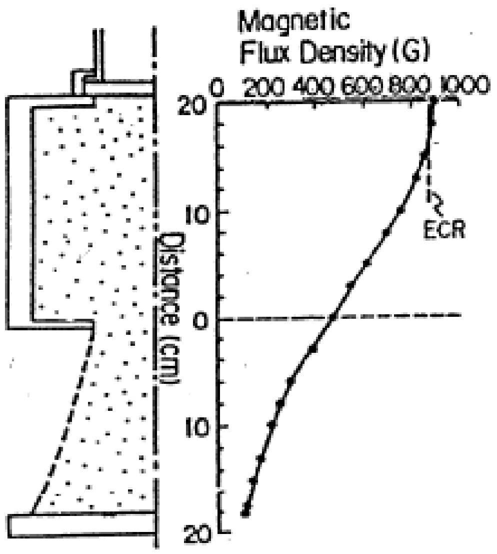
ECR (Electron Cyclotron Resonance)

Cyclotron Resonance = Maximum Electron Energy

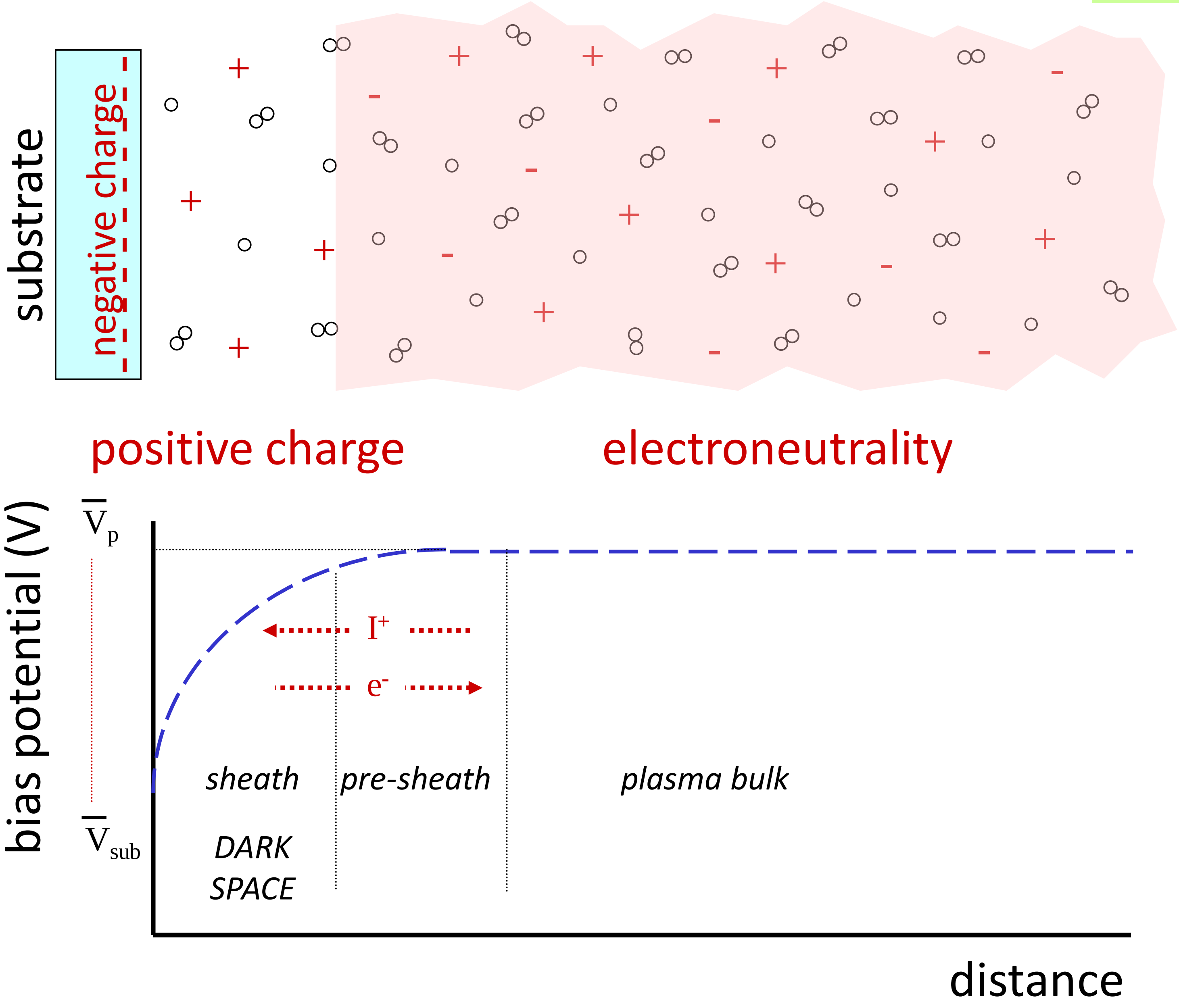
Angular Frequency in B field (875G) =

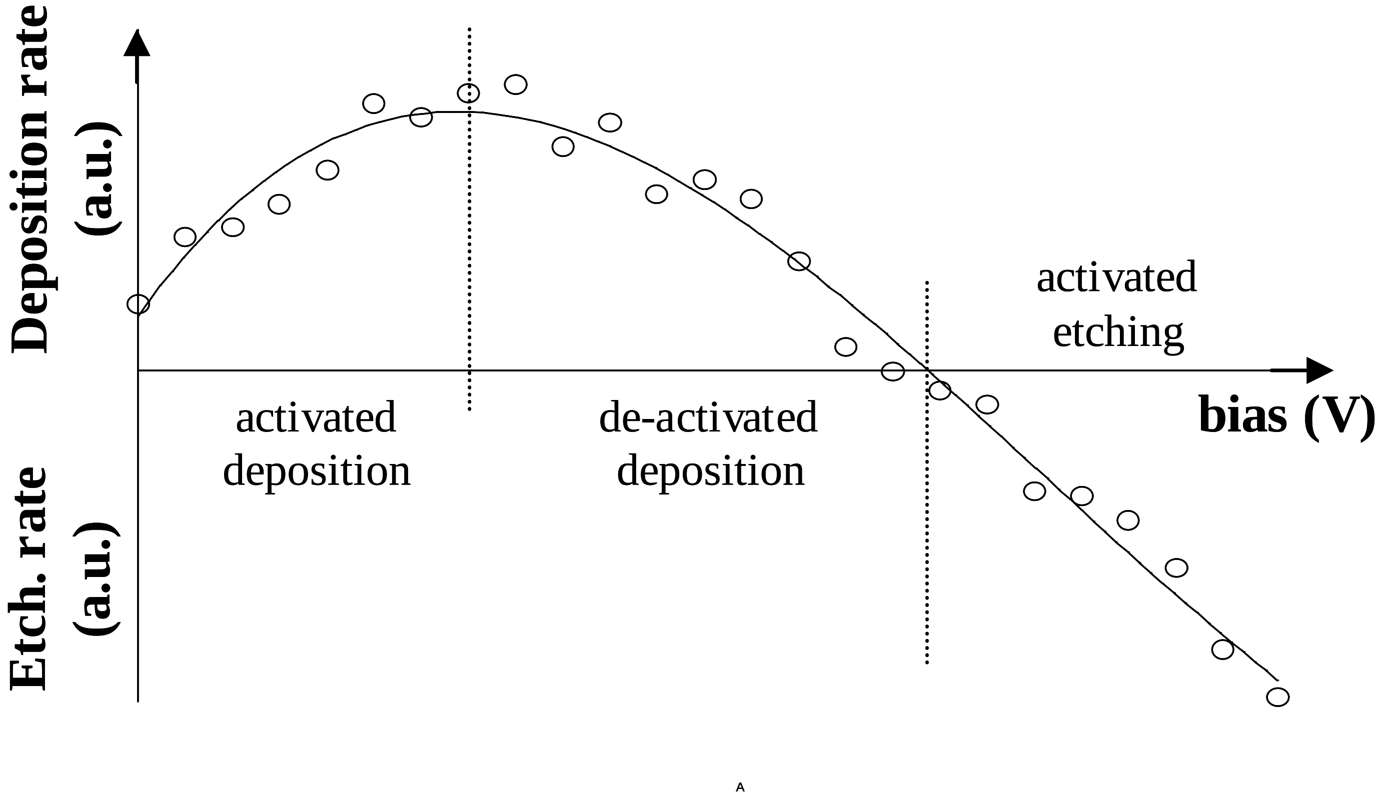
Microwave Frequency (2.45GHz)





bias potential





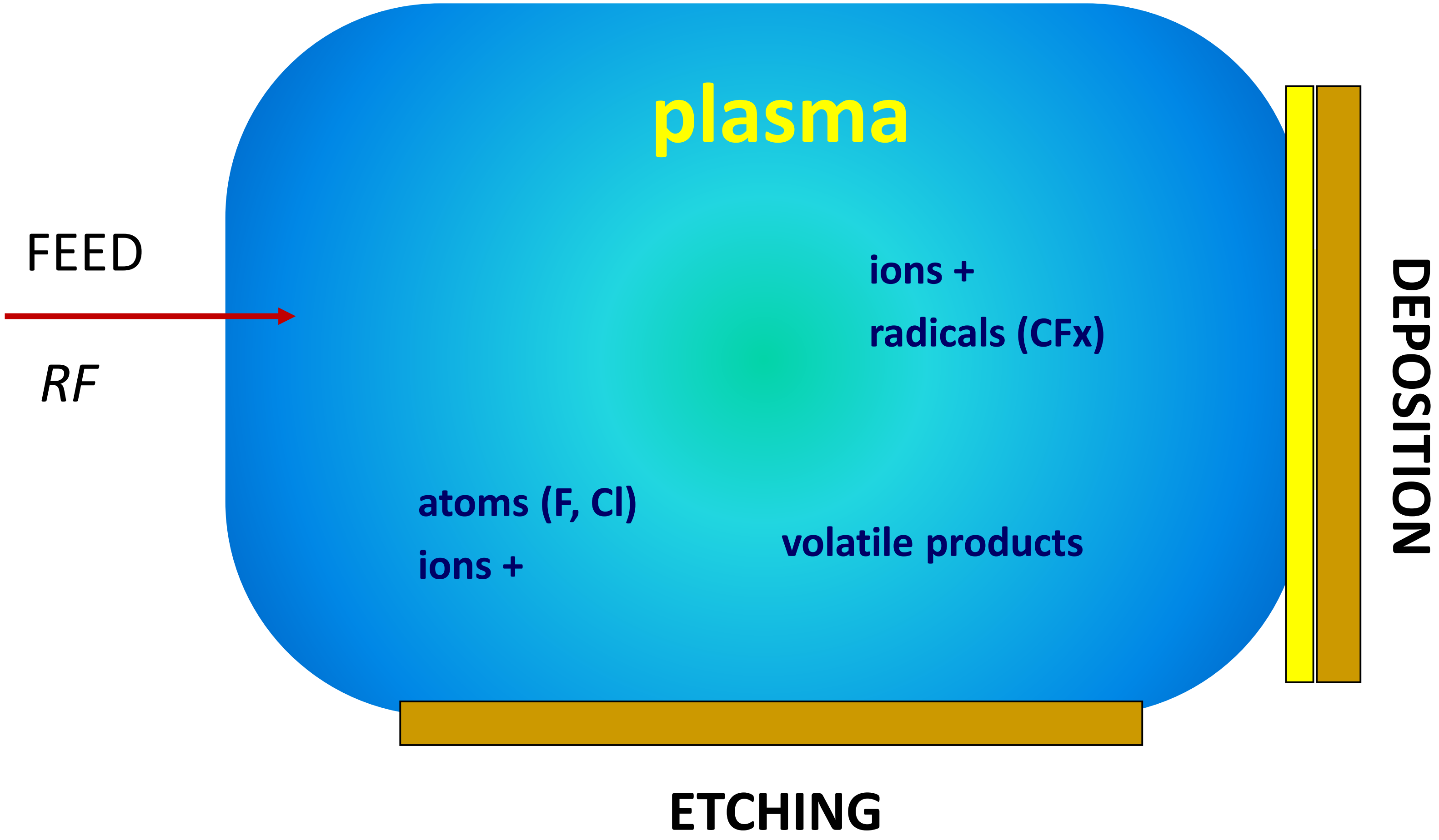
Effect of the bias-induced positive-ion bombardment on the deposition / etching rate of CFx films plasma-deposited in RF glow discharges (CF_4 0.8 / C_2F_4 0.2 feed).

Adapted from F. Fracassi, J.W. Coburn, *J. Appl. Phys.* 63, 1758, 1988.

FACTORS AFFECTING DRY ETCHING

1. Neutrals (active species)
    - gas feed, flow rate
    - power (fragmentation)
    - pressure
2. Substrate temperature
3. Substrate position
4. Ions (positive)
    - substrate bias
    - reactor geometry
    - power
    - pressure
5. Surface contamination
    - polymer, resist residues
    - inorganics
    - non volatile etch products

SUBSTRATE POSITION IN THE REACTOR IS IMPORTANT



EFFECT OF T and CONCENTRATION

E_R depends on the rate limiting step

$$E_R = A\,N_X e^{-Ea/RT}$$

N_X = etchant concentration
E_a = activation energy

E_R increases with

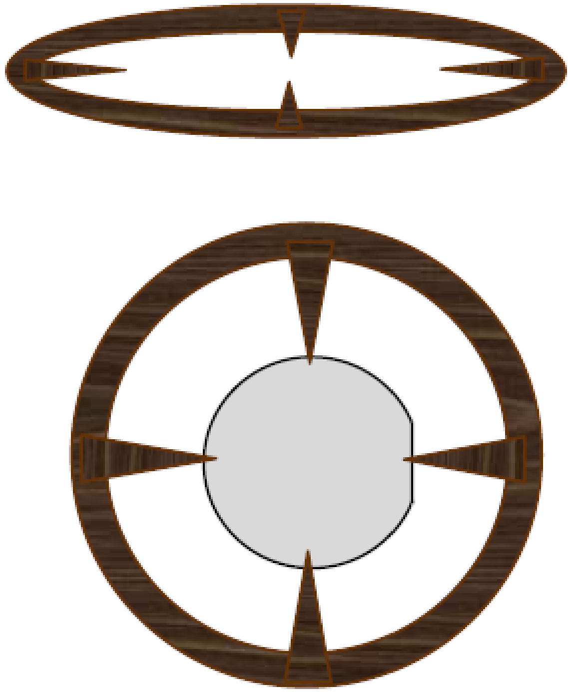
- N_x
- T (as a function of E_a)

	E_a (Kcal/mol)
Si	2.48
SiO_2	3.76

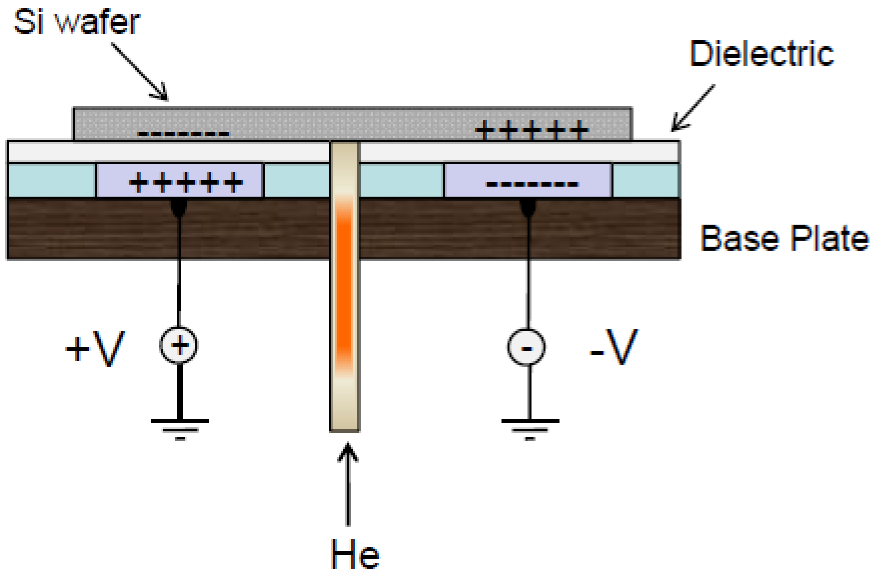
Temperature control of the wafer

Clamp or Electrostatic Chuck

Clamp



Electrostatic Chuck (ESC)



ETCH PROFILES

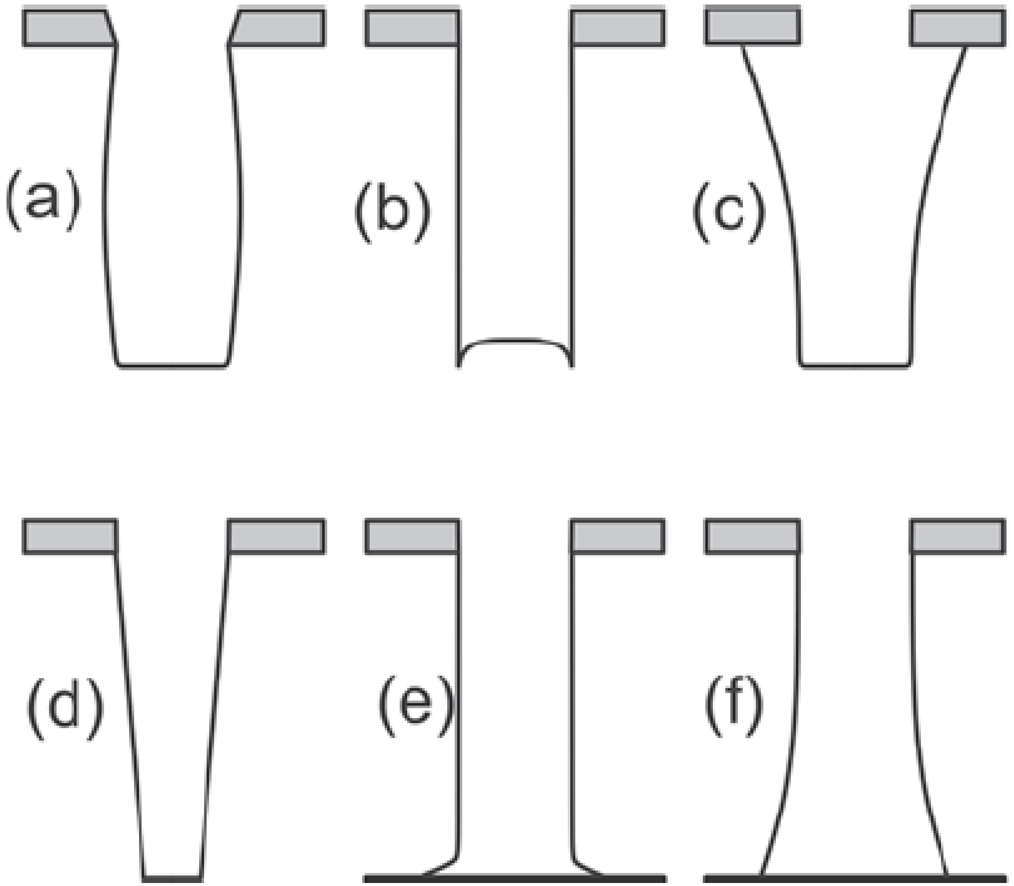
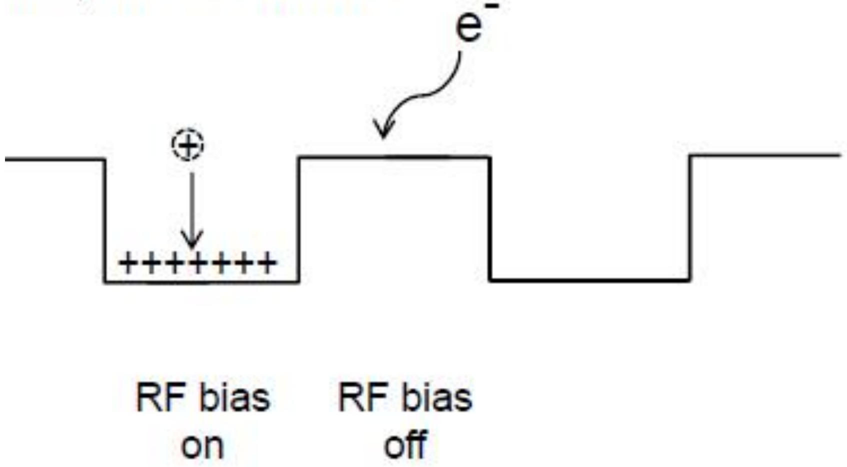


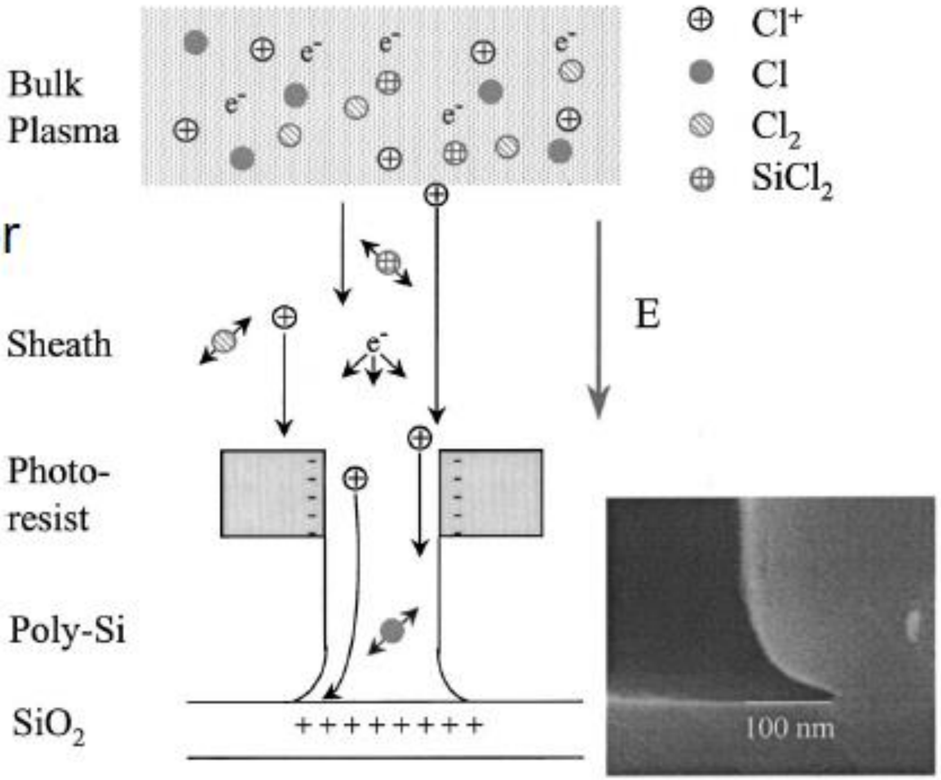
FIG. 31. Various profiles obtained during plasma etching: (a) bowing due to faceting of the mask; (b) microtrenching due to enhanced ion flux along the sidewall; (c) Undercutting due to an isotropic component in the etch process; (d) tapered profile due to deposition on the sidewall; (e) notching at the interface due to inadequate sidewall passivation or charging effects; (f) Re-entrant profile (overcutting) due to inadequate sidewall passivation and/ or ion scattering.

V. M. Donnelly, A. Kornblit
J. Vac. Sci. Technol. A, Vol. 31(5), 2013

Notch Effect

- Notching effect due to charging oxide by ions
- Can be reduced by using low frequency (LF) 380kHz bias generator in pulsed mode

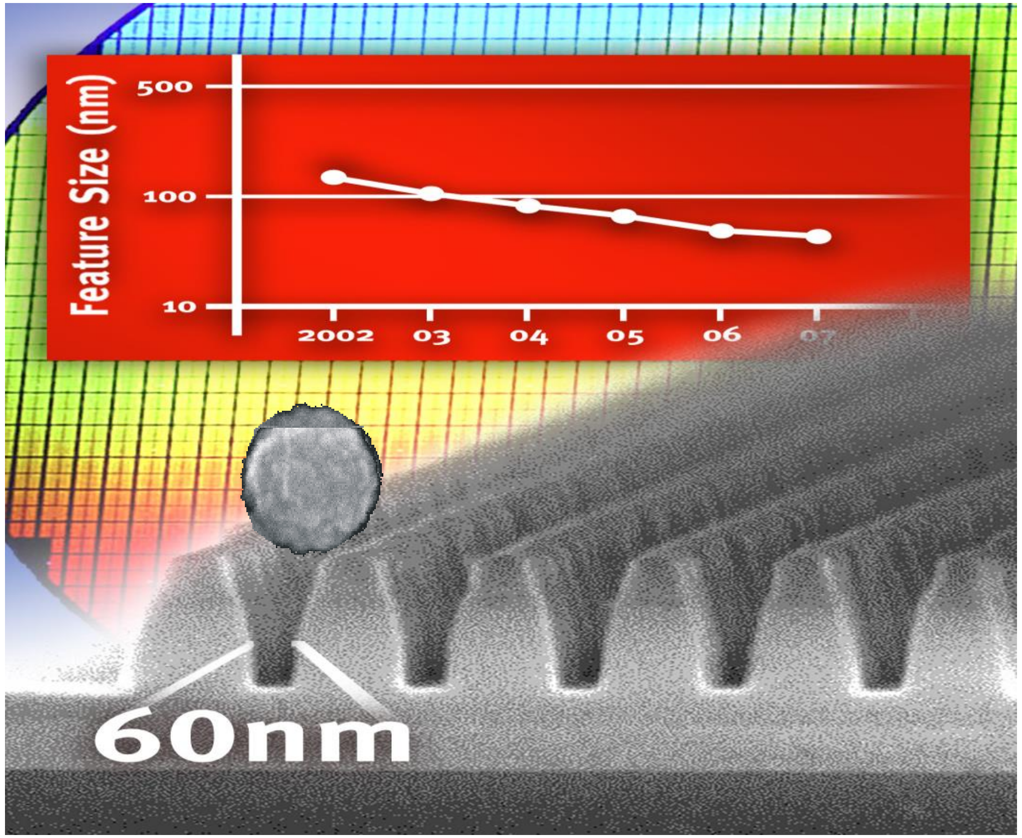




[J. Vac. Sci. Technol. B 19.5., Sep/Oct 2001]

STS ASE has LF pulsed generator!!

killer particles in microelectronics



avoid dust in plasma processing

DRY ETCHING IN FLUORINATED FEEDS

Production of volatile fluorides:

Si, SiO_2, Si_3N_4, W, Mo, Ti, TiN,

feeds utilized: $\xcancel{F_2,}$ CF_4, CF_4/O_2, CF_4/H_2, SF_6,
SF_6/O_2, NF_3, XeF_2

- **CF_4 is the most popular fluorine atom source**
- **similar approach with other fluorocarbons**

F_2 is difficult to handle

CF_4 fragmentation :

$$CF_4 + e^- \Longrightarrow CF_3 + F + e^-$$

$$CF_3 + e^- \Longrightarrow CF_2 + F + e^-$$

$$CF_2 + e^- \Longrightarrow CF + F + e^-$$

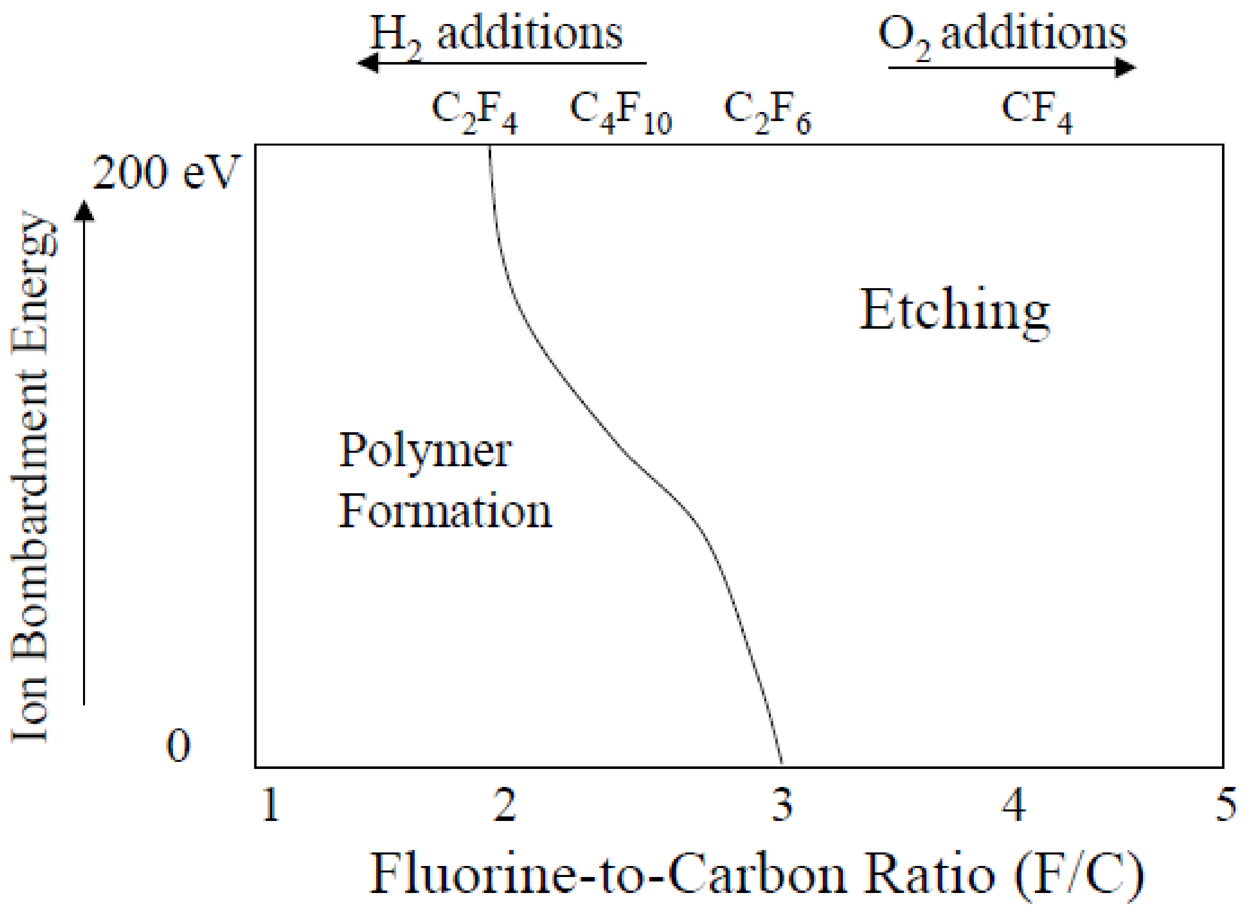
F (etchant)

CF_3, CF_2, CF = CFx (radicals, insaturates)

CFx radicals can deposit fluoropolymer “teflon-like” coatings

The choice of the feed

- **Si materials (Si, SiO_2, Si_3N_4) etch in Fluorine Chemistries (SiF_2 and SiF_4 volatile species)**
- **<u>Fluorine-to-Carbon Ratio Model</u>**
  - **Silicon etch rate**



[F] / [CFx]

relevant internal parameter

the chemistry of fluorocarbon plasmas can be changed with oxidizing and reducing additives

oxidizing additivies → [F] ↑ [CFx] ↓

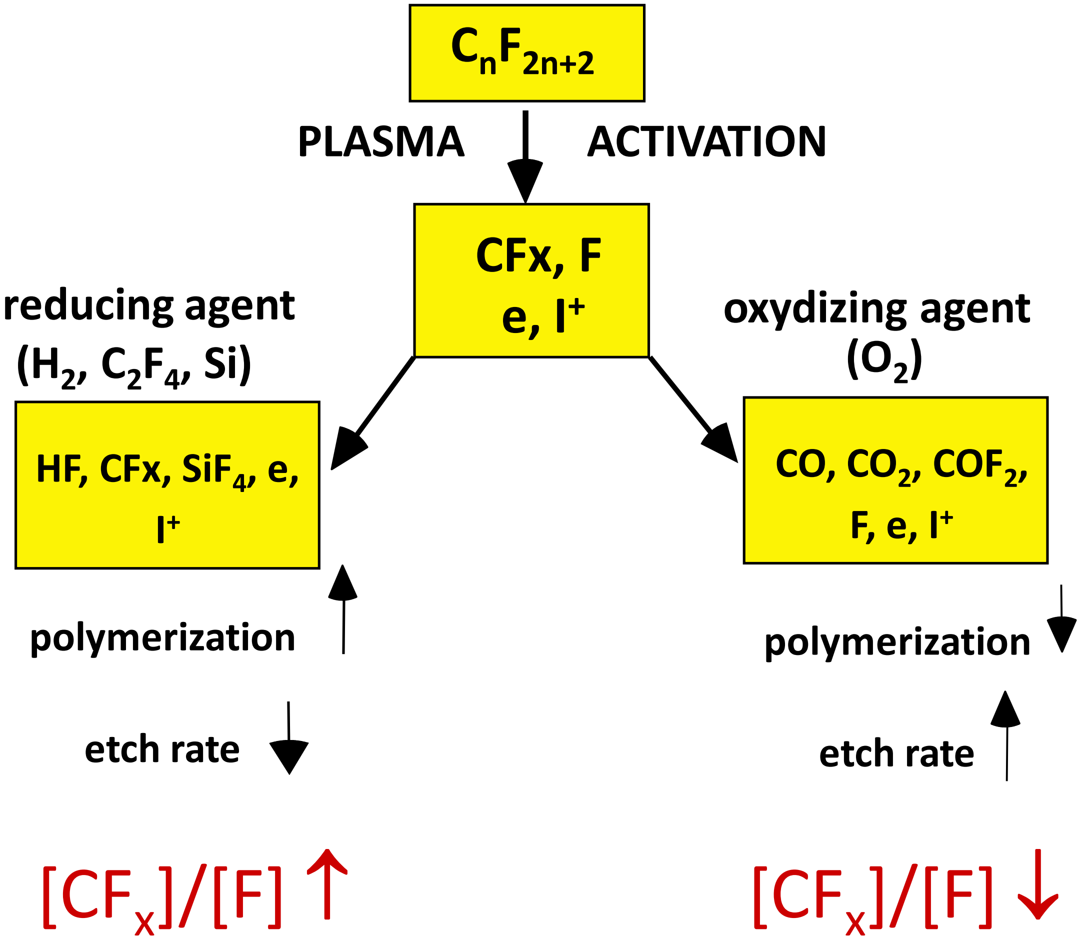
$$CF_x + O\ (O_2) \rightarrow CO,\ CO_2,\ COF_2 + x\ F$$

reducing additivies → [F] ↓ [CFx]

$$CF_x + H\ (H_2) \rightarrow CF_{x-1} + HF\ (+\ H)$$

$$F + H\ (H_2) \rightarrow HF\ (+\ H)$$

PE-CVD OF FLUOROPOLYMERS
ETCHING OF Si and SiO_2



C_nF_{2n+2}

PLASMA ACTIVATION

CFx, F
e, I^+

reducing agent
(H_2, C_2F_4, Si)

HF, CFx, SiF_4, e, I^+

polymerization ↑

etch rate ↓

$[CF_x]/[F] \uparrow$

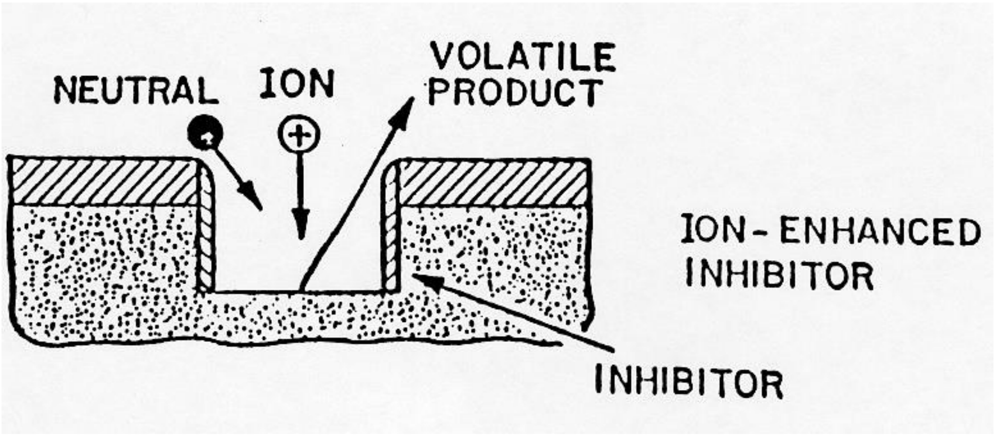
oxydizing agent
(O_2)

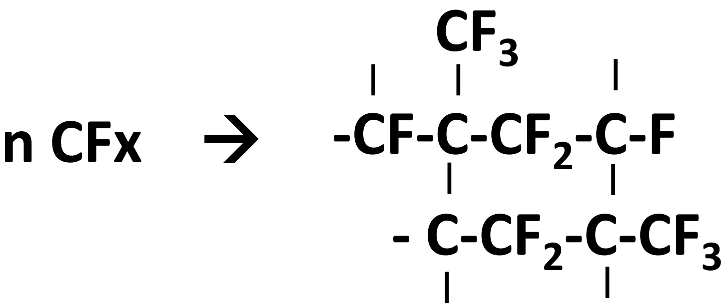
CO, CO_2, COF_2, F, e, I^+

polymerization ↓

etch rate ↑

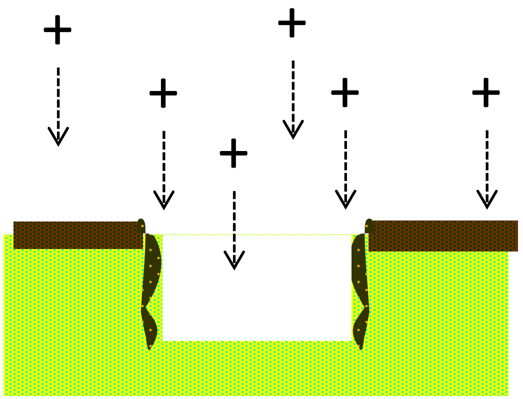
$[CF_x]/[F] \downarrow$





$$n\,CF_x \rightarrow \begin{array}{l} \quad\;\; | \quad\;\; \overset{CF_3}{|} \qquad\quad\;\; | \\ -CF-C-CF_2-C-F \\ \qquad\;\; | \qquad\quad\;\; | \\ \quad - C-CF_2-C-CF_3 \\ \qquad\;\; | \qquad\quad\;\; | \end{array}$$

fluoropolymer “teflon-like” coatings passivate sidewalls and improve etching anisotropy



when the radical density is high the deposition rate becomes too high and etching stops

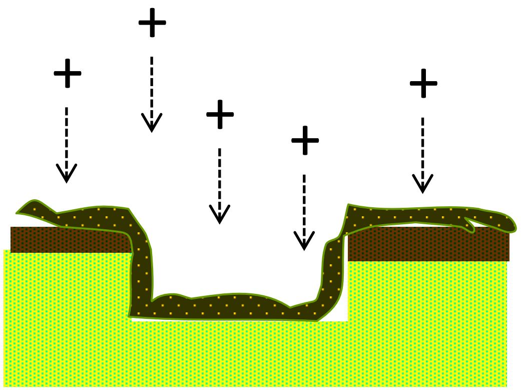


Table 8 Gas additives for plasma etching.

Additive	Purpose	Example (Additive-Etchant Gas : Material)
Oxide Etchant	Etch through material oxide to initiate etching.	$C_2F_6-Cl_2$: SiO_2; BCl_3-Cl_2 : Al_2O_3; CCl_4-Cl_2 : Al_2O_3
Oxidant	Increase etchant concentration or suppress polymer.	O_2-CF_4 : Si; N_2O-CHF_3 : SiO_2; O_2-CCl_4 : GaAs, InP
"Inert" Gas, N_2	Stabilize plasma, dilute etchant, improve heat transfer.	$Ar-O_2$: organic material; $He-CF_3Br$: Ti
Inhibitor-Former	Induce anisotropy, improve selectivity.	$C_2F_6-Cl_2$: Si; BCl_3-Cl_2 : GaAs, Al H_2-CF_4 : SiO_2
Radical-Scavenger	Increase Film-Former, improve selectivity.	H_2-CF_4 $CHF_3-C_2F_6$: SiO_2; H_2-CF_4 : SiO_2
Water/Oxygen-Scavenger	Prevent Inhibition improve selectivity.	BCl_3-Cl_2 : Al; H_2-CF_4 : SiO_2
Volatilizer	Form a more volatile product, increase etch rate	O_2-Cl_2 : Cr, $MoSi_2$

c-C_4F_8 (octa fluorocyclobutane, F/C 2), **c-C_5F_8** (octafluoro cyclopentene, F/C 1.6), and **C_4F_6** (hexa fluoro-1,3-butadiene, F/C 1.5) were chosen in newer generation etchers. Although changing to these gases was driven primarily by performances, there were environmental considerations as well. c-C_5F_8, for instance, has **short atmospheric lifetime** (0.3 vs 3200 years for C_4F_8 and 270 for **CHF_3**) and reduced **Global Warming Potential (GWP)**

Comparisons were made of etching of high aspect-ratio contacts with c-C_4F_8 to c-C_5F_8 and C_4F_6 in a modified **GEC Reference Cell (a parallel plate reference reactor).** The performance of these gases may be different, though, depending on the etcher used.

Common additives include O_2, Ar, CO_2, and CO. The latter is used to control selectivity, since it minimizes the amount of F-rich species.

Special care is needed with CO since it reacts spontaneously with Nickel. All gas delivery hardware, thus, must avoid exposed Ni surfaces (e.g., Ni gaskets). 316 SS is acceptable gasket and tubing material for CO.

feeds with reduced
Global Warming Potential (GWP)

FLUORINE PLASMAS
DRY ETCHING OF Si
(c-Si, 100, 111, polySi, nc-Si, p-Si, n-Si)

- **ETCHANT SPECIES: F**
- **REACTION PRODUCTS: SiF_4 and SiF_2**
- **F atoms do not need ion bombardment to react with Si**
- **ion bombardment increases the etching rate and anysotropy**
- **ion energy threshold at about 10-15 eV**
- **high Si / SiO_2 selectivity (up to 40)**

F is a strong etchant for silicon
the reaction is rapid and spontaneous

↓

Si etching in F-containing plasma is isotropic

anisotropy can be achieved:

at low P, with high substrate bias
to enhance the ion bombardment
(poor Si/SiO_2 selectivity)

at higher P (and, in general)
increasing the concentration of film precursors (CF_x)
by adding reducing agent (sidewall inhibitor)

GENERAL Si ETCHING MECHANISM

1) formation of active species

e.g. $CF_4 \rightarrow CF_x + 4\text{-}x\ F$

2) adsorption of active species

formation of a fluorinated layer
3-5 monolayers thick

3) formation of volatile products

SiF_3 emits at 500 nm

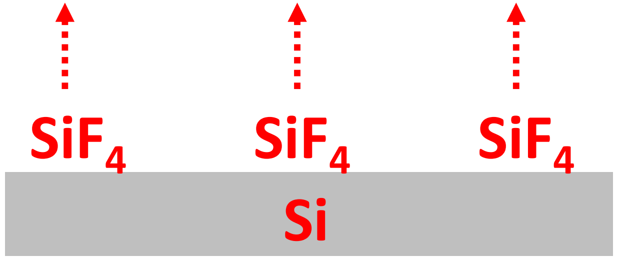
$$Si + F \longrightarrow SiF$$

$$SiF + F \longrightarrow \underline{SiF_2}$$

$$SiF_2 + F \longrightarrow SiF_3{}^{*}$$

$$SiF_3 + F \longrightarrow \underline{SiF_4}$$

4) desorption of products



MANY FEEDS CAN BE UTILIZED:

(~~F_2~~), CF_4, CF_4 / O_2, SF_6 / O_2, NF_3, etc.

F_2 is too reactive (F-F bond is weak),
hazardous, very difficult to handle

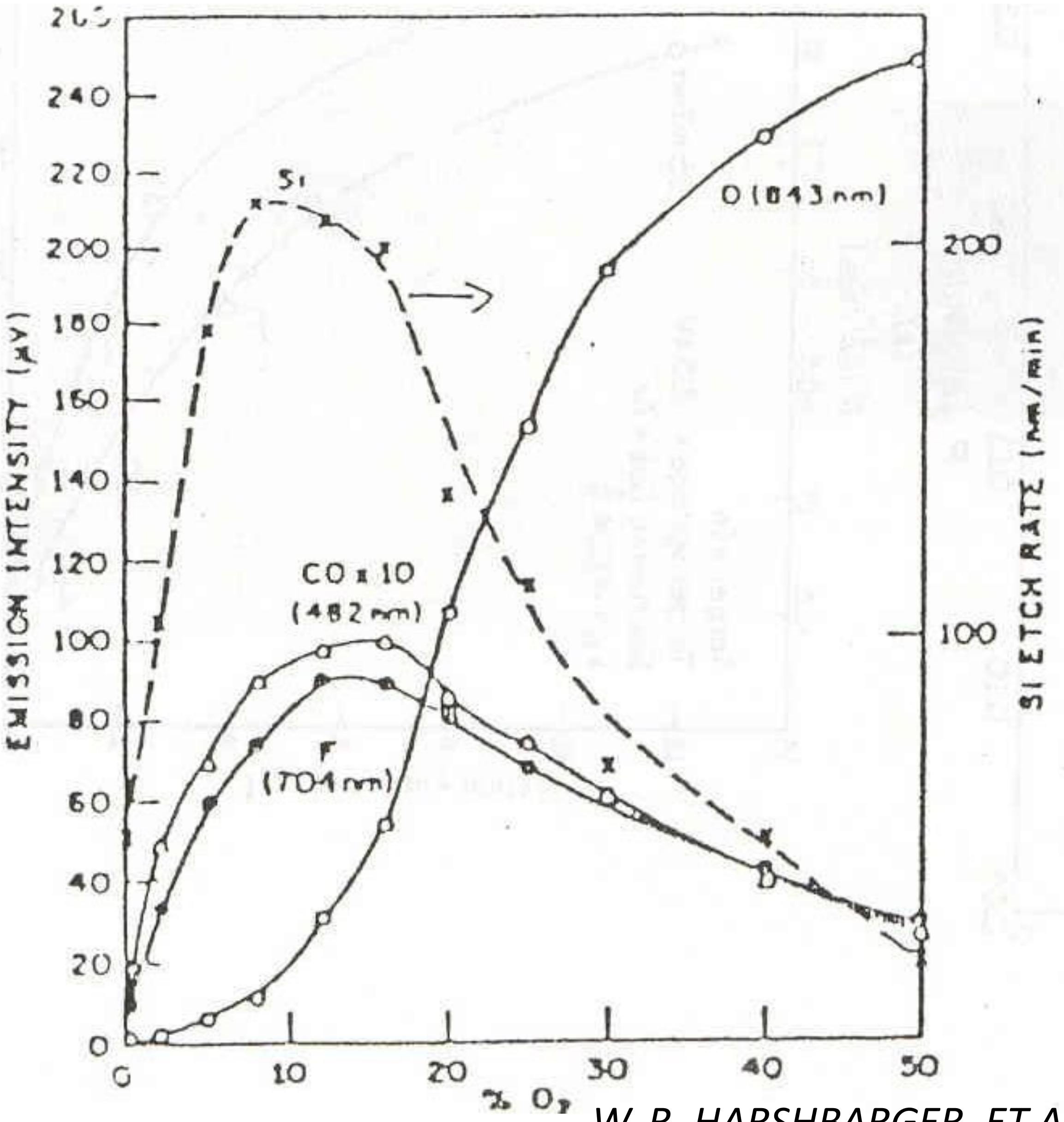
CF_4 and SF_6 are easy to handle and generate high [F]

$$CF_4 \longrightarrow CF_3 + F \longrightarrow CF_2 + F \longrightarrow CF + F$$

CF_x radical deposit fluoropolymer “teflon-like” coatings

SI ETCHING IN CF_4/O_2 RF GLOW DISCHARGES

$CF_x + O\ (O_2) \rightarrow CO,\ CO_2,\ COF_2 + x\ F$



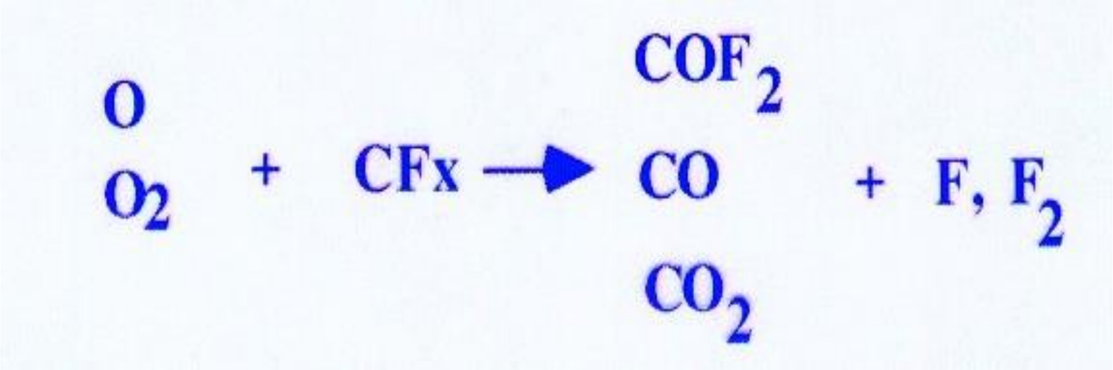
W. R. HARSHBARGER, ET AL. APPL. SPECTROS. 31, 201 (1977)

O_2 ASSISTS THE FORMATION OF CO, CO_2, COF_2 SPECIES

without O_2 addition:

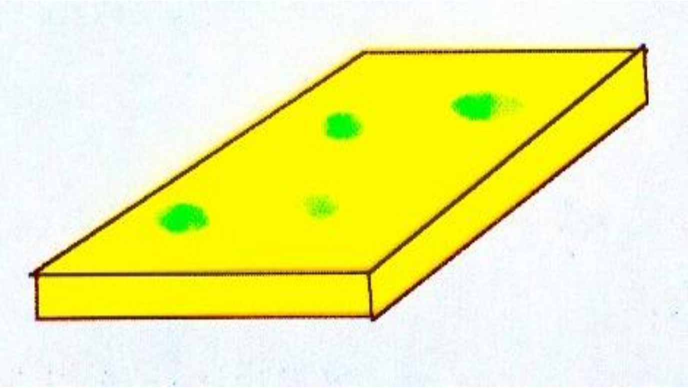
$$E_{Si} = K_E[F]$$

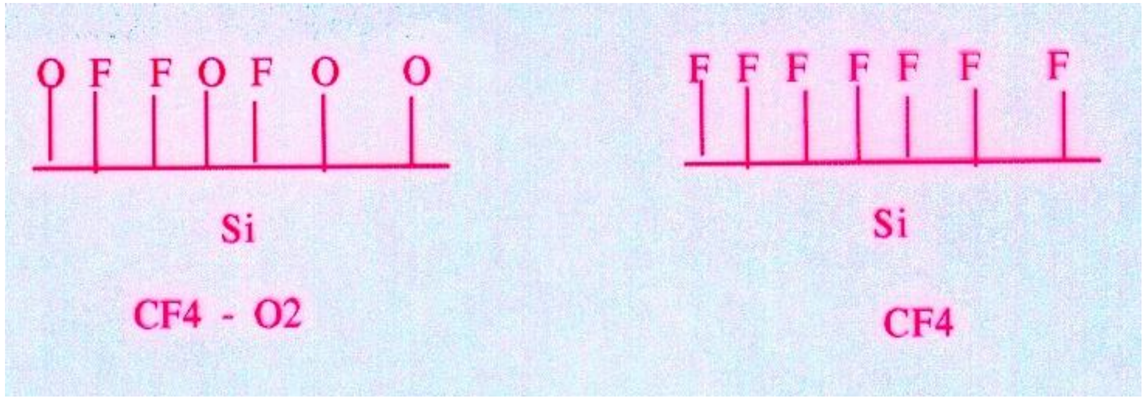
WITH OXYGEN ADDITION



$$\begin{matrix} O \\ O_2 \end{matrix} + CFx \rightarrow \begin{matrix} COF_2 \\ CO \\ CO_2 \end{matrix} + F, F_2$$

oxygen competes with F
in the chemisorption on the Si surface
and in the passivation of Si to SiO_2
and reduces the etch rate



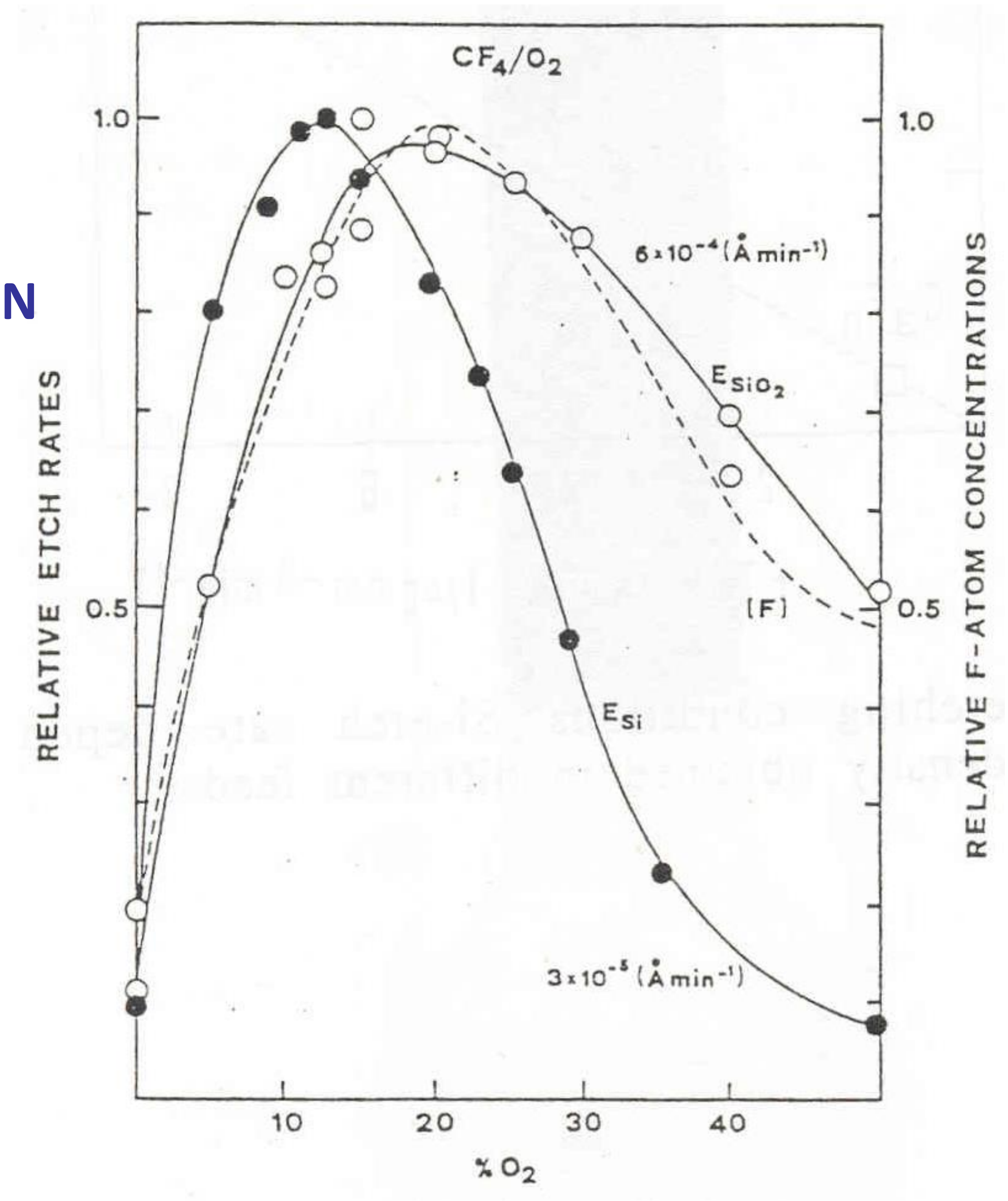


Si AND SiO$_2$ ETCHING IN CF$_4$ / O$_2$ FEEDS

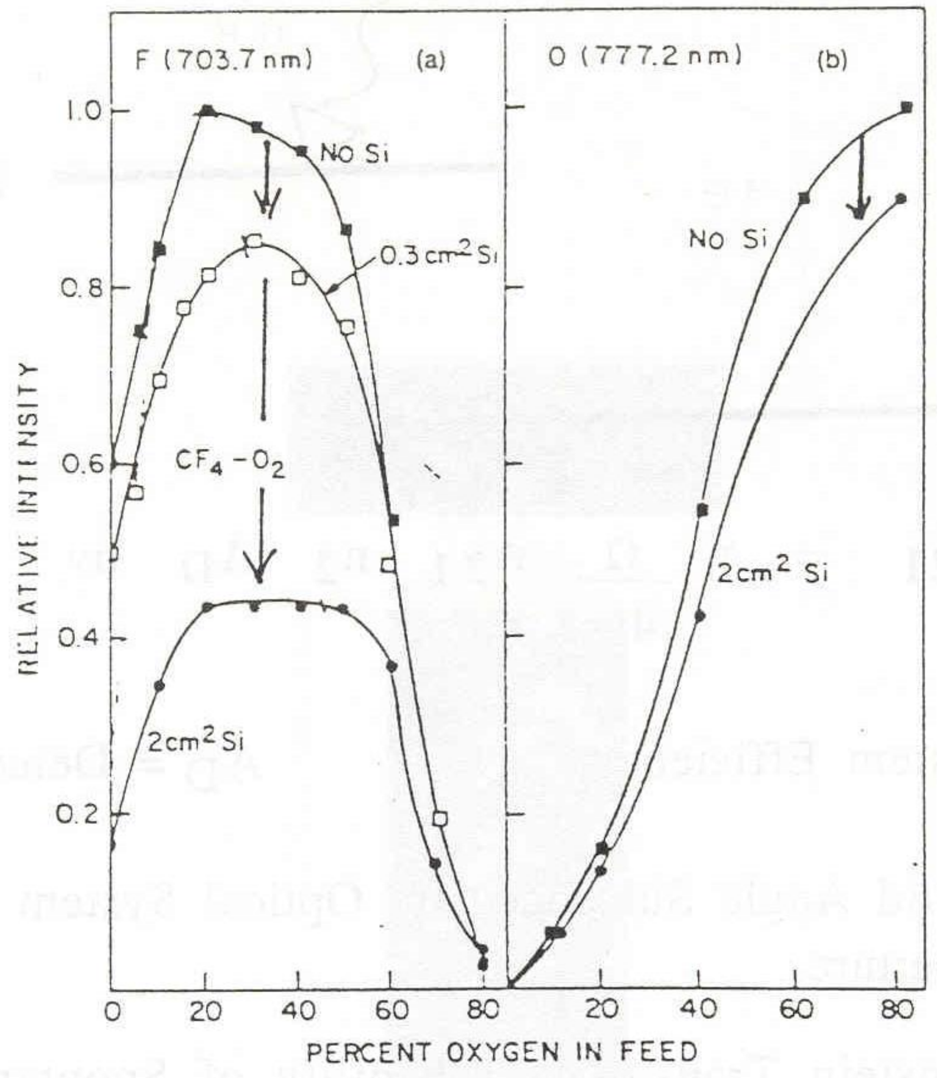
$E_{Si} \neq K$ [F]
DUE TO Si/O INTERACTION

Er Si ≠ k[F]

Er SiO$_2$ = k[F]



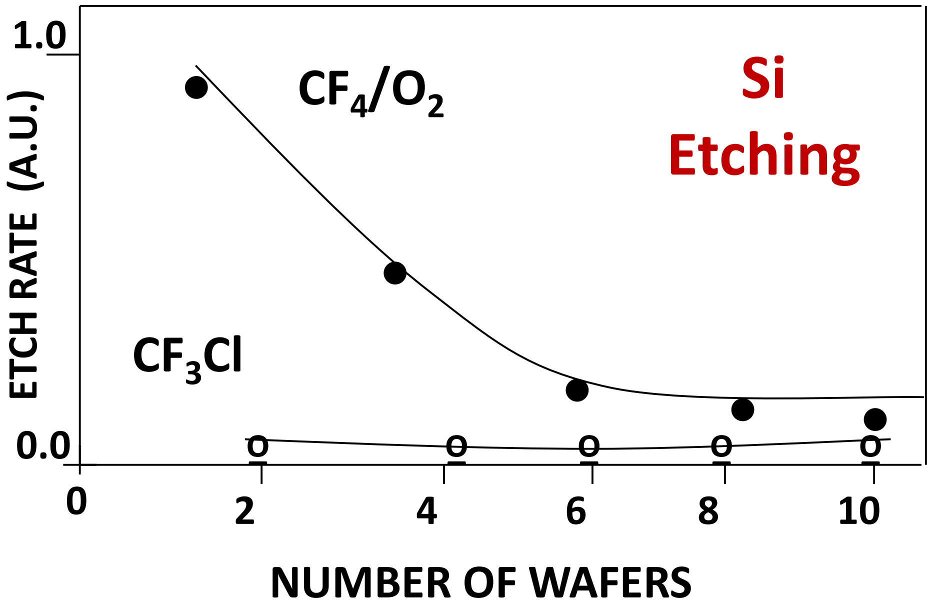
[F] and [O] both decrease when the area of exposed Si increases



R. D'AGOSTINO, D. L. FLAMM,
J. APPL. PHYS., (1981), 52, 162

LOADING

depletion of the etchant in the gas phase due to reaction with the substrate. Reduces the etch rate when the substrate surface exposed to the plasma increases.



SF_6, SF_6 / O_2

SF_6 generates high [F] → high E_R

loading and carbon contaminations are reduced

low anisotropy, high selectivity Si/SiO_2

to avoid S contaminations (whitish powder)
O_2 is added:

$S_x + 2O \rightarrow SO_2$ (volatile)

$SF_6 + O \rightarrow SO_2 + F$

CHLORINE CONTAINING PLASMAS

SILICON ETCHING

$$Si + 4\,Cl \longrightarrow SiCl_4$$

Cl_2 and other feeds are used

spontaneous (no plasma) etching only for n-doped Si

Cl adsorbed on Si does not allow the reaction of other species

the reaction needs ion bombardment

the anisotropy is high for Si and p-Si

for highly n-doped Si inhibitor chemistry (side wall passivation) is needed to obtain anisotropy

The etch rate of n-doped Si with Cl is 15-25 times higher than that of undoped or P-doped (n-doped) Si

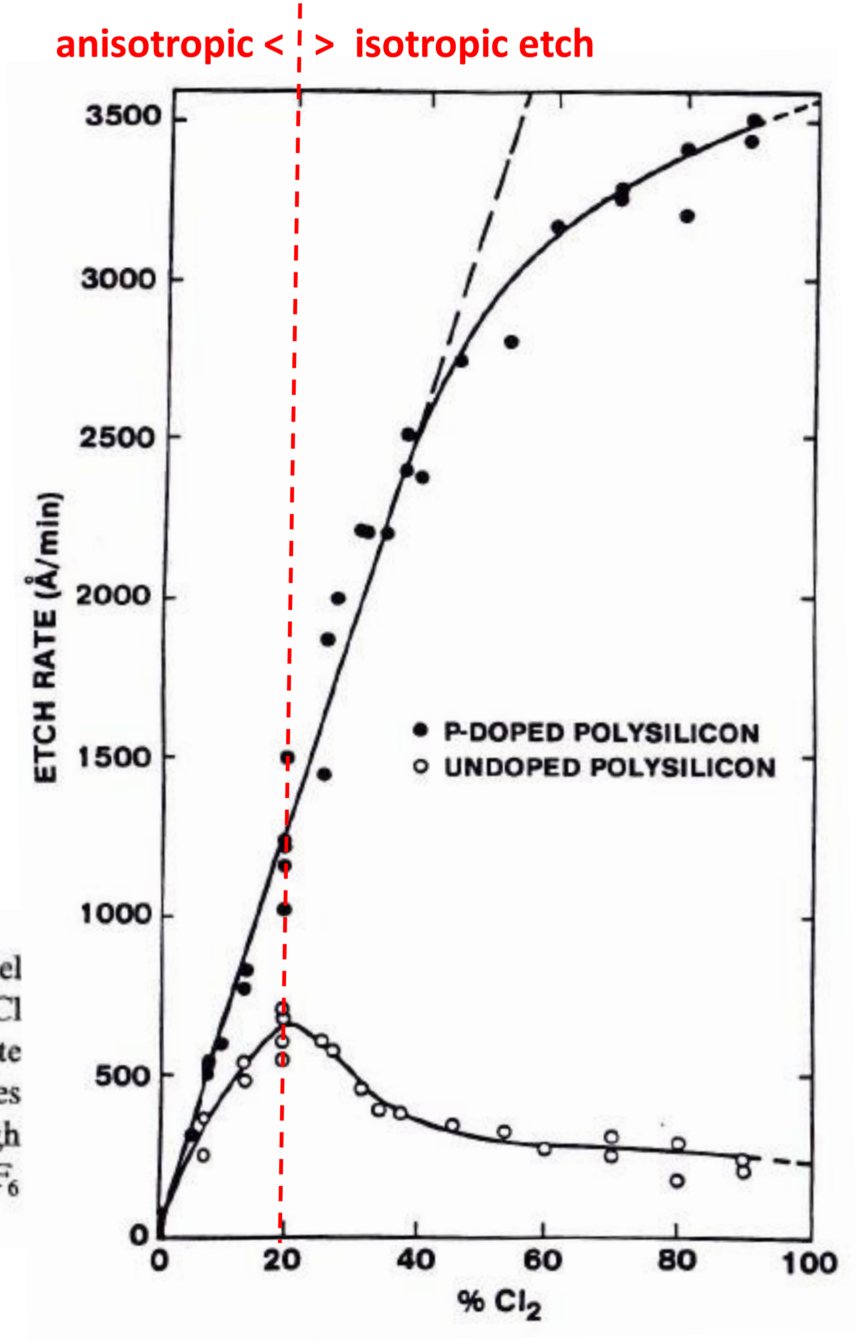


FIGURE 29. Etching of doped and undoped polysilicon using a Cl_2/C_2F_6 feed in a parallel plate reactor at 0.35 Torr, 200 sccm feed, 0.32 W/cm^2 and a 25°C electrode temperature. Cl atoms in chlorine-rich plasmas chemically etch *n*-type *P*-doped polysilicon, while the etch rate of undoped silicon is low. Species from C_2F_6 form a sidewall inhibitor layer which provides anisotropy. Beyond about 20% Cl_2 etching becomes isotropic because there is not enough inhibitor to prevent Cl-atoms from attacking doped polysilicon sidewalls. Species from C_2F_6 also remove native etch native oxide from the Si surface so etching can start (after [157]).

The chemical etching of silicon in halogen-based discharges is affected by the type and concentration of electrically active dopants. In F atom systems, *p*-type doping (boron) suppresses silicon etch rates slightly (by as much as a factor of two) [76, 77, 78, 79, 80], while high concentrations of *n*-type dopants (As or $P \gtrsim 10^{19}\ \mathrm{cm}^{-3}$) enhance etching [76, 77, 78, 79, 81] by a factor of 1.5–2. By contrast heavily *n*-doped (100) and (111) silicon [82, 83, 84] and polysilicon [67, 85, 86, 87, 88, 89] ($\sim 10^{20}\ \mathrm{cm}^{-3}$) in Cl atom plasmas ($Cl_2$, Cl_2/Ar, CCl_4/Ar, CF_3Cl, $SiCl_4/O_2$, CF_3Br/Cl_2, C_2F_6/Cl_2) etch as much as 15–25 times faster than undoped substrates. This enhancement is related to the concentration of *active* *n*-type carriers (e.g., the Fermi level), rather than the chemical identity of the dopant [67, 79, 90, 91, 92]. Unannealed or electrically inactive dopant implants have a minimal influence on etching [67, 90].

The detailed mechanisms through which chlorine-silicon etch rates depend on doping levels are still being studied. However, it is generally agreed that *n*-type doping raises the Fermi level and thereby reduces the energy barrier for charge transfer to chemisorbed chlorine [67, 93, 156]. As depicted in Fig. 28, chlorine and/or bromine atoms are covalently bound to specific sites on an undoped silicon surface. Steric hindrance impedes impinging etchant from penetrating the surface to reach subsurface Si-Si bonds. The formation of a more ionic silicon–halogen surface bond, due to the *n*-type doping and enhanced electron transfer, opens additional chemisorption sites and facilitates etchant penetration into the substrate lattice.

Table 9 Feed gases and mechanisms for plasma etching various materials with chlorine atoms.

Source Gas	Additive	Materials Etched	Mechanism	Selective Over
Cl_2	None C_2F_6 $SiCl_4$	heavily *n*-doped Si	Chemical Ion-inhibitor Ion-inhibitor	SiO_2
Cl_2 CCl_4 $SiCl_4$	None O_2 O_2	Si	Ion-energetic	SiO_2
Cl_2	$SiCl_4$ CCl_4 $CHCl_3$ BCl_3	Al	Ion-inhibitor	SiO_2, Some resists, Si_3N_4
Cl_2	O_2	$MoSi_2$	Ion-energetic	SiO_2
Cl_2 CCl_4 $SiCl_4$	None BCl_3 CCl_4 O_2 O_2	III-V Semiconductors	Chemical-Crystallographic Ion-inhibitor	SiO_2, Resists
Cl_2	O_2, H_2O	III-V Alloys without Al	Chemical-Crystallographic	$AlGa_xAs_y$, $AlIn_xP_y$, SiO_2, Si_3N_4, Resists
CF_2Cl_2	None			Ion-inhibitor

Bulk micromachining of Silicon

Silicon bulk micromachining requires to etch “holes” deeper than 10 μm. It is defined as deep RIE or DRIE. Modified high plasma-density etchers are used, with additional features to facilitate high etch rates with profile control. **SF_6 is used** to achieve high etch rates, sometimes **with O_2** to reduce sulfur build-up. To obtain anisotropy, the sidewalls of the features to be etched must be passivated.

One approach is to cool the substrate to < 220 K and slow the rate of isotropic etching by F-atoms. Ion-assisted etching have little or no T dependence. **The low T also leads to a buildup of SiOxFy byproducts on the sidewalls**, that suppress isotropic etching and produces smoother sidewalls than the **Bosch process**, but time is needed for wafer cooling and warming before & after etch. Once the wafer is warmed, the protection is volatilized, and if additional etch time is needed fter post-etch inspection, under-cutting occurs due to the lack of a protection layer on the sidewall.

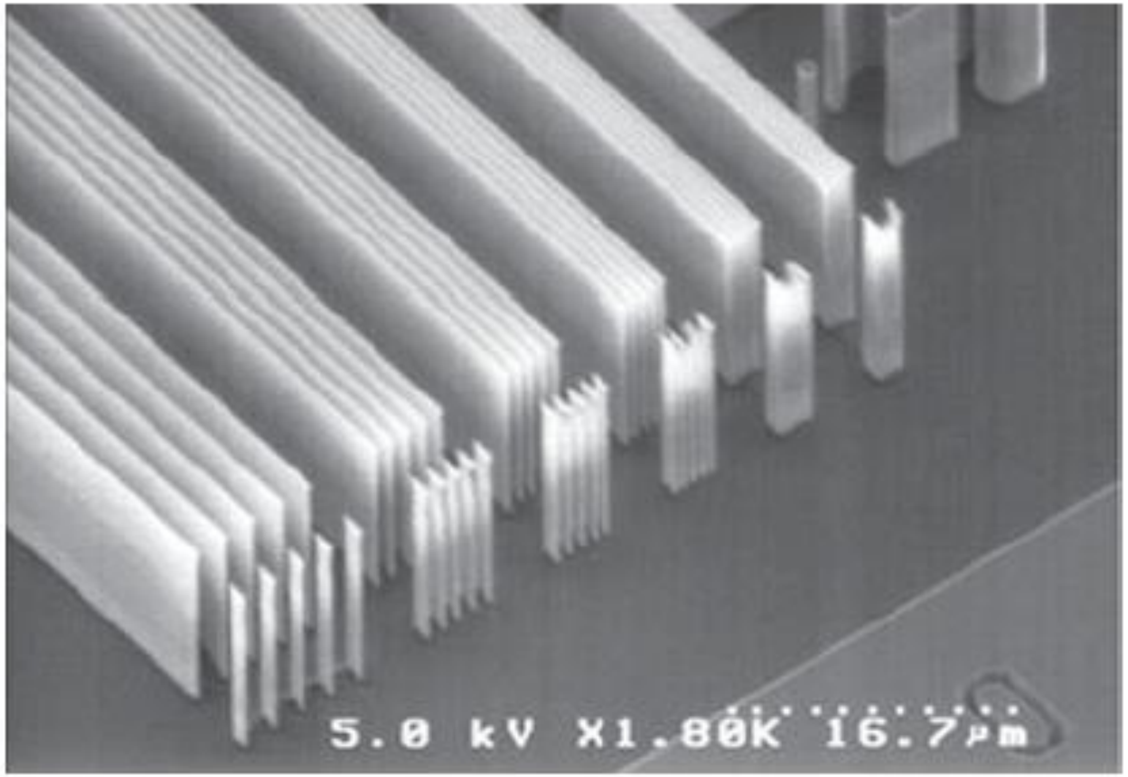


FIG. 41. Surface micromachining. The height of these features is 12 μm, and the minimum dimension is 0.25 μm.

The **Bosch Process** alternates **etching with SF_6 /O_2** and **PE-CVD with c-C_4F_8 /Ar**. The process requires fast mass-flow controllers to switch between etch and deposition, every few seconds. **ICP etchers** are used, and pulsed bias power at few watts only during the etch step. Source power during etching depends on the total gas flow. During PE-CVD a film is formed on horizontal surfaces and on sidewalls. The etch then removes the film from horizontal surfaces and etch Si, while the film on the sidewalls, even though eroded, protects against lateral etch. The resulting sidewalls show striations, and may be an issue when smooth sidewalls are needed. It is good to use etch mask and etch stop materials (if needed) resistant to F atoms. SiO_2, Al_2O_3, and PR masks etch very slowly with 250:1, >10,000:1, and 50:1 selectivity vs Si, respectively.

SiO_2 and Al_2O_3 can be used as etch stop material. Care must be used in choosing such materials, in a way that they do not sputter nonvolatile products that would form “grass” in etched areas due to micromasking.

Etch depths are often hundreds of µm, **sometimes the full thickness of the wafer** (700-750 µm for 200 mm dia). High etching rate can be increased by increasing gas flow and source power. However, selectivity is reduced, since the etching rate of Si increases at a slower rate than the erosion of the mask, due to increased ion flux.

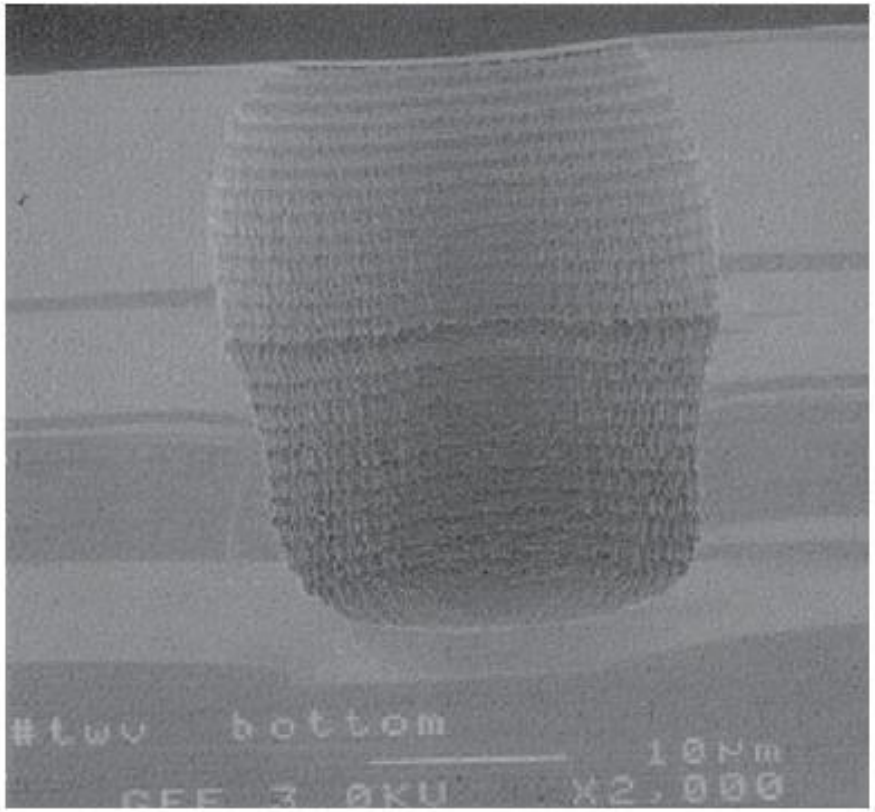
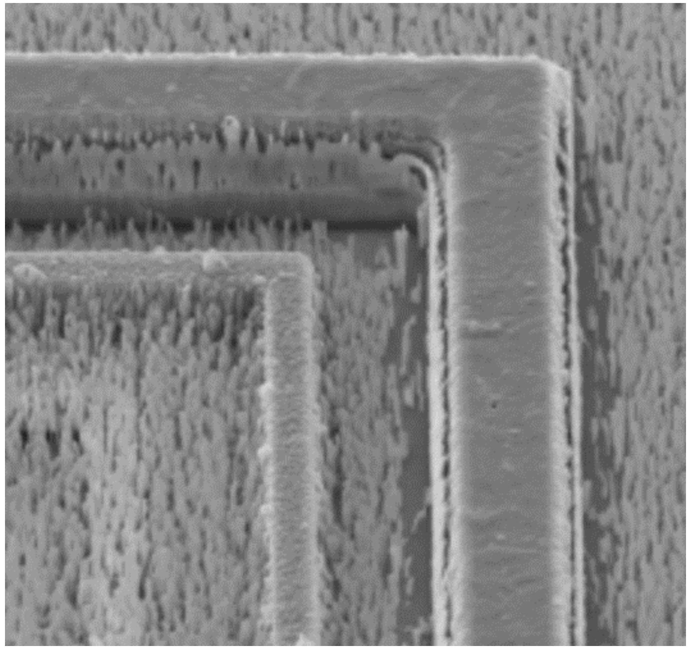


FIG. 42. Scalloping associated with a switched (Bosch) process. The scallops are the result of alternate etch and deposition steps.



formation of ”grass” due to metal sputtered from the mask

STS ASE DRIE
a 6’’ ICP Bosch process
dedicated to Si etching

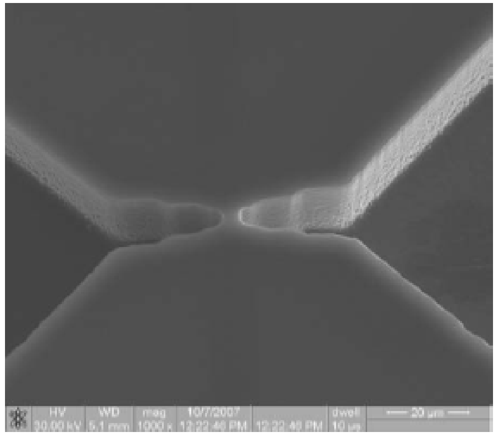
SF_6/O_2 and C_4F_8/Ar alternated feeds

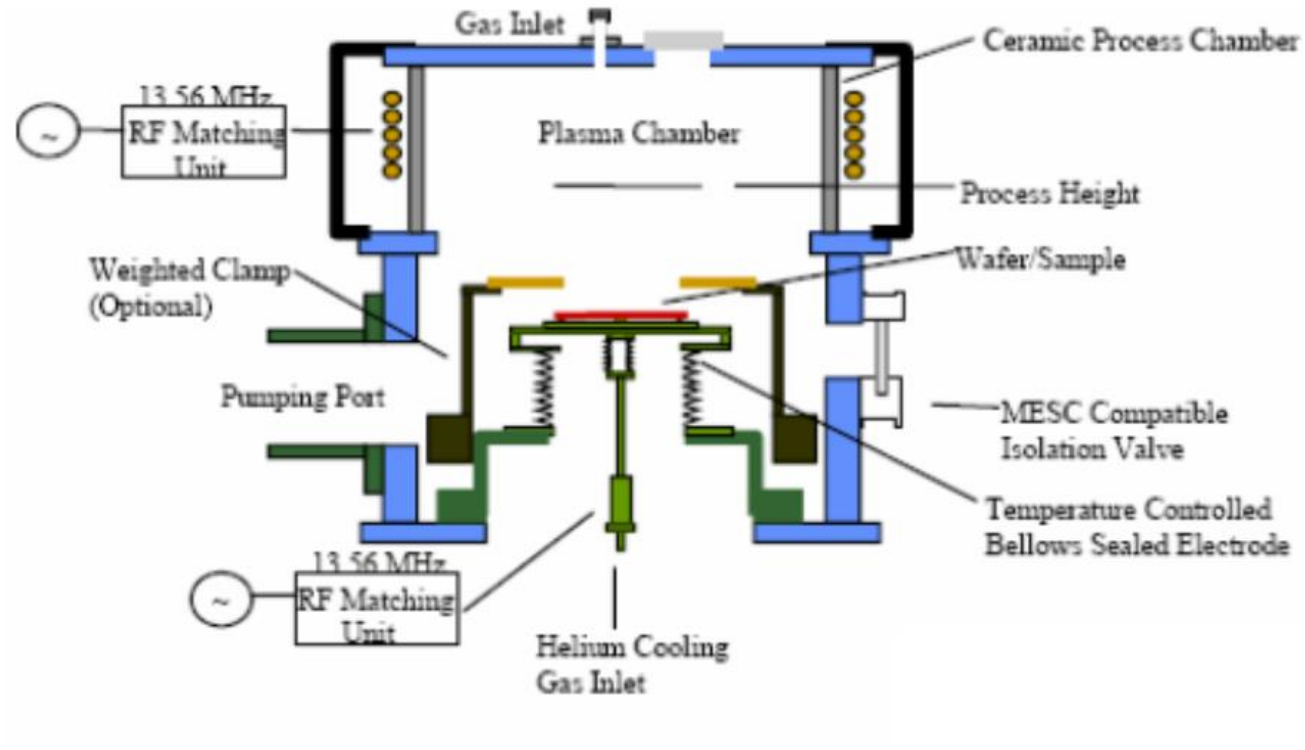
High etch-rate recipe:

	Switching time	Pressure	RF coil power	RF bias power	Gas flow [sccm]
Etch	8.5 sec	40mTorr	2200W	40W	450 SF_6
Passivation	3 sec	14mTorr	1500W	20W	200 C_4F_8

Etch rate ≈ 8µm/min for 500 µm feature size with ~ 20% exposed area

High selectivity to PR ≈ 75-100

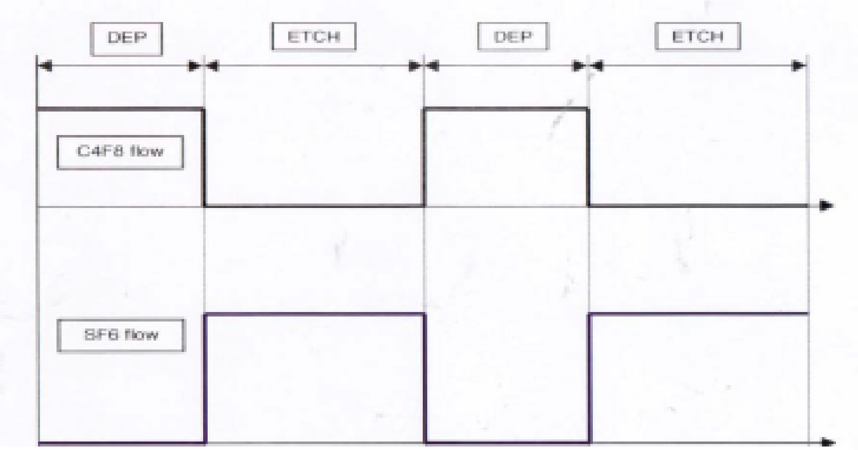


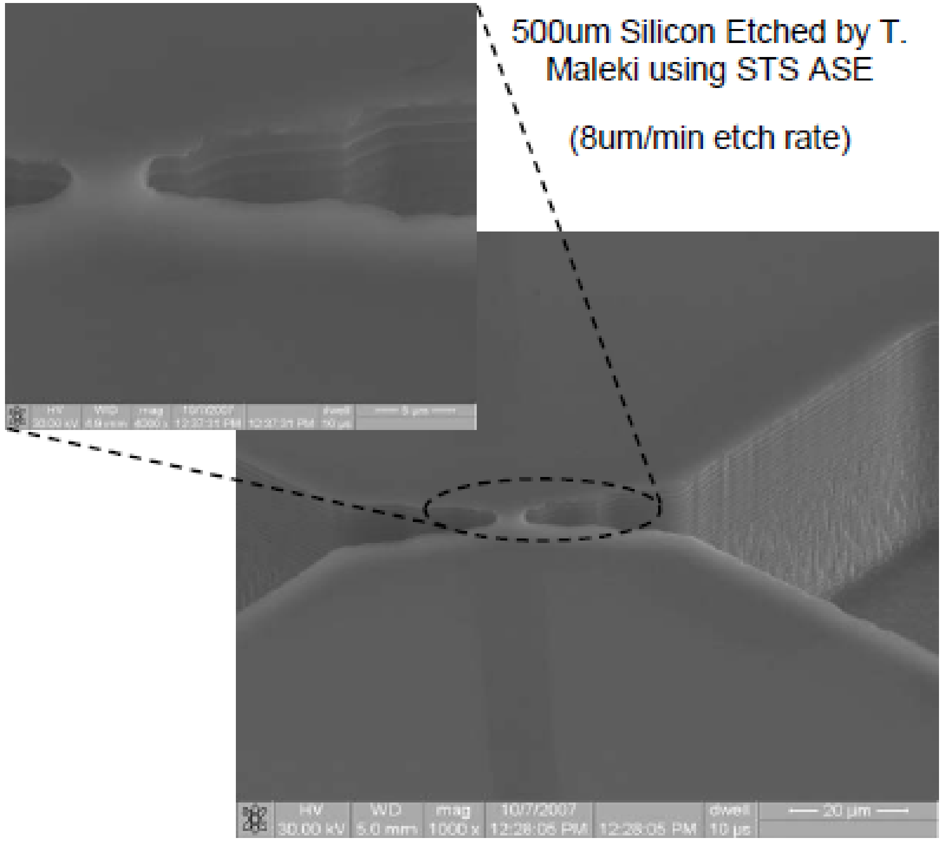


high density plasma reactor

Bosch Process

Switching SF_6 and C_4F_8





500um Silicon Etched by T. Maleki using STS ASE

(8um/min etch rate)

The sidewall film thickness depends to the deposition or passivation time.

SUMMARY 1

In the 70s plasma etching became essential for pattern transfer in silicon ICs. As circuitry become more complex, with smaller and smaller features, the importance of plasma etching still increases.

Plasma etching began roughly 60 years ago when the undercutting of masks in wet etching was no longer tolerable. **Si etching began in F-plasmas** such as CF_4/O_2, but it was quickly realized that the undercut by F atoms was not desirable **and Cl-plasmas gave much better profiles**. Parallel plate CCP reactors were used first for Si etching, then they were replaced by higher density ICP or MW plasmas.

Further improvements were realized by adding HBr to Cl_2. The etching of poly-Si and c-Si occurs by a mechanism where positive ions are accelerated by the voltage drop across the sheath, controlled by a separate bias applied to the substrate. This energetic ion bombardment disrupts the halogenated chemisorbed layer and gives volatile products.

Anisotropic Al etching of interconnects, developed with Cl-based CCP plasmas, later also migrated to higher density ICPs, with a quite different mechanism. Cl and Cl_2 react readily with Al without ion bombardment, which leads to severe mask undercut. To prevent this, BCl_3 or CClx photoresist erosion species are introduced, and bare Al is coated with a passivating layer that prevents chemical etching by Cl and Cl_2. Positive ions keep horizontal surfaces quite clean, allowing chemical etch, with enhancement by ion bombardment. On vertical surfaces, the passivation layer prevents etching and leads to anisotropic profiles.

V. M. Donnelly, A. Kornblit, J. Vac. Sci. Technol. A, Vol. 31(5), 2013

SUMMARY-2

SiO_2 etch for patterned insulating layers between interconnecting Al wires and Si transistors began at the same time. **CFx- plasmas** emerged and remained the only way to achieve anisotropic SiO_2 etching selective vs Si. SiO_2 etching evolved from CCP to ICP and back to CCP etchers. The reemergence of CCP for SiO_2 etch was accompanied by using RF power at 2 (or 3) frequencies. The mechanism of SiO_2 etching was well studied, due to its importance and complexity. **SiO_2 etching is due to a thin CFx film that also inhibits unwanted etching of Si**. Ion bombardment of the CFx layer generates SiF_4, CO, CO_2, and perhaps other products that must then diffuse through the layer.

Insulating materials with dielectric constants lower than SiO_2 (low-k materials) have emerged. These films usually contain Si, C, and O and often have voids to further reduce the dielectric constant. CFx-plasmas etch these materials with a mechanism similar to SiO_2, in the same equipment used to etch SiO_2.

Following the development for **Si, Al, and SiO_2 patterning**, plasma was soon used **for etching other materials**. For the first 25 years or so, plasma etching was used strictly for transferring patterns from PRs to these materials, some of which (e.g., SiO_2 and a-Si) were used as hard masks for underlying layers. In the last 25 years, however, many applications emerged where plasma etching is taking on more of the task traditionally carried out by photolithography. These involve a starting structure with a relatively wide linewidth and then creating 1, 2, or even 3 narrower lines by trimming processes or by depositing thin layers on the sides of lines to be then removed.

The number of such processes will certainly increase in the future.

SUMMARY-3

Future needs will go for tighter control of process variability, higher selectivity and less damage. This may require: **pulsed plasmas, lower ion energies, tighter control of ion energy distributions, reduced photon fluxes**.

Evolution to **Atomic Layer Etching** or **neutral beam etching** could become necessary if sensitive devices can no longer tolerate monolayer-scale damage produced by immersing substrates in the plasma.

Overview of atomic layer etching in the semiconductor industry

Keren J. Kanarik, Thorsten Lill, Eric A. Hudson, Saravanapriyan Sriraman, Samantha Tan, Jeffrey Marks, Vahid Vahedi, and Richard A. Gottscho

Citation: Journal of Vacuum Science & Technology A **33**, 020802 (2015); doi: 10.1116/1.4913379

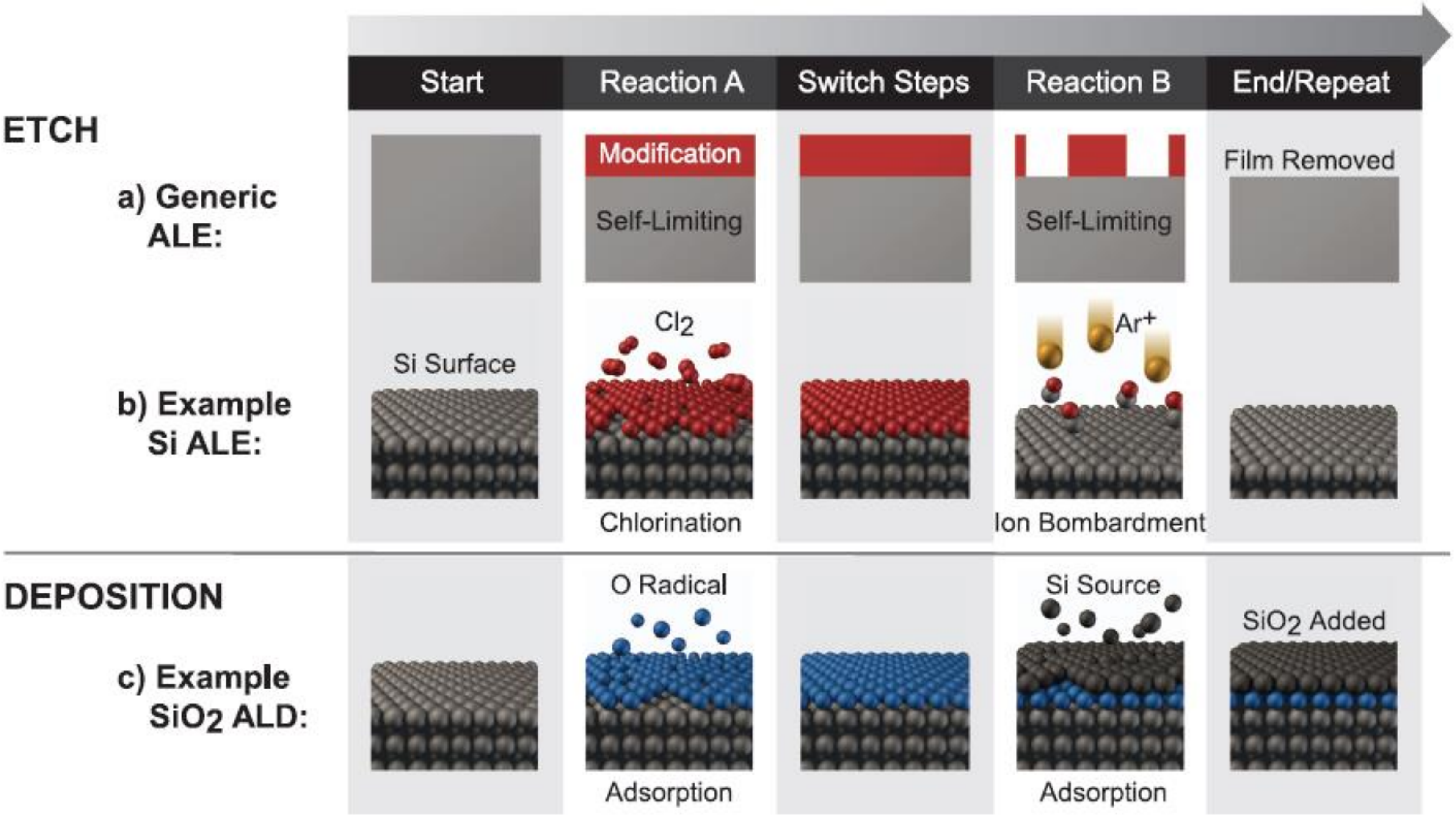


FIG. 1. (Color) Schematic of ALE (a) generic concept, (b) for the silicon case study, and (c) in comparison to ALD. ALE is similar to ALD except that removal takes place instead of adsorption in reaction B.

SUMMARY-4

Future devices will certainly have smaller critical dimensions, will incorporate new materials and structures, and will be fabricated on larger wafers. Although self-assembly is considered for some structures and materials, dry etching will still be used for most of the pattern transfer of the ever-shrinking lithographic features. In some cases, new materials will be incorporated in cavities of traditional SC materials, and in other cases, these materials will require dry etching, and new etching processes will have to be developed.

The choice of structures and materials will be influenced greatly by the capabilities of etching processes and equipment on hand. Control of selectivity (to the substrate and to the mask), profile, lattice damage, plasma damage (which may be enhanced by photon flux), particle formation, process reproducibility, and equipment reliability will dominate future etching technologies and equipment.

Plasma etching technology has evolved from a manually loaded quartz tube with a coil wound around it to sophisticated automatic multimillion dollar machines, with advanced equipment and process control. This evolution continues.

SiOx *quartz-like* plasma-deposited coatings

- **dielectric layers in microelectronics**
- **gas/vapor barrier coatings for food and pharmaceutical packaging**
- **anti corrosion protective layers for car lights and other substrates**

LOW GAS TRANSMISSION RATE
(food, pharmaceutical packaging)

MW compatible

HARDNESS

TRANSPARENCY

INERTNESS

CORROSION PROTECTION

SEAL COATING

(car lights)

DIELECTRIC

PE-CVD from ORGANOSILICON / O_2 feeds

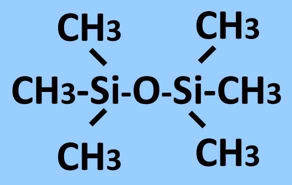
Si(C,H)Ox ---------- SiOx

Key Parameters

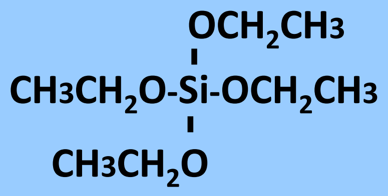
monomer/O_2 ratio

input power (fragmentation)

MONOMERS

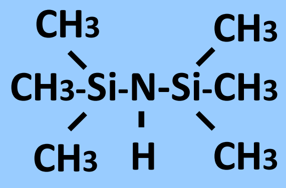


HMDSO

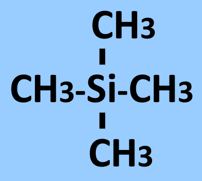


$CH_3CH_2O\text{-}\underset{CH_3CH_2O}{\overset{OCH_2CH_3}{Si}}\text{-}OCH_2CH_3$

TEOS



HMDSN

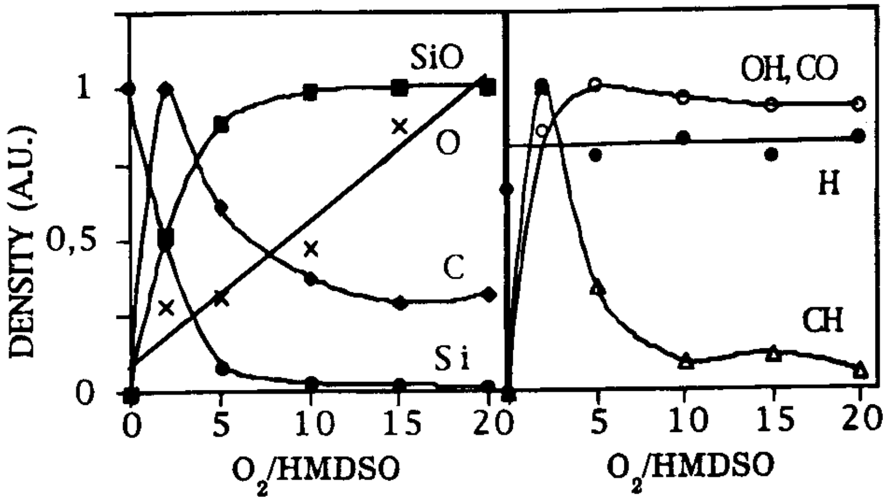


$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$

TMS

HMDSO/O_2

RF GLOW DISCHARGES



Relative concentration trends of (a) Si, SiO, C, O; (b) H, OH, CH and CO species in plasma phase as a function of feed composition.

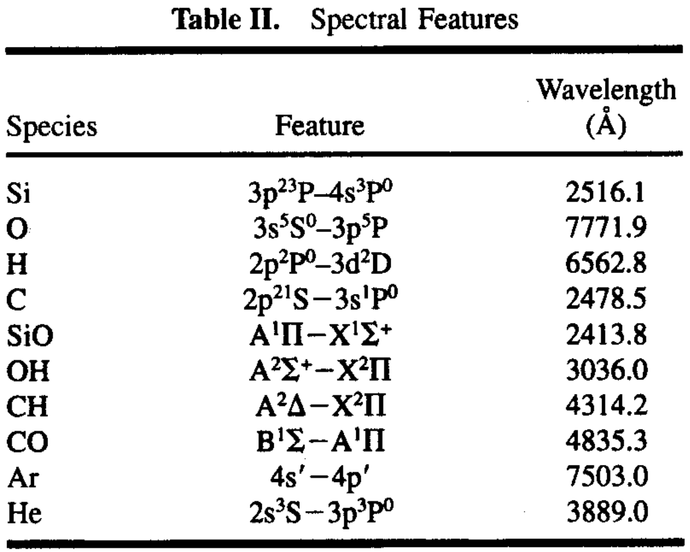
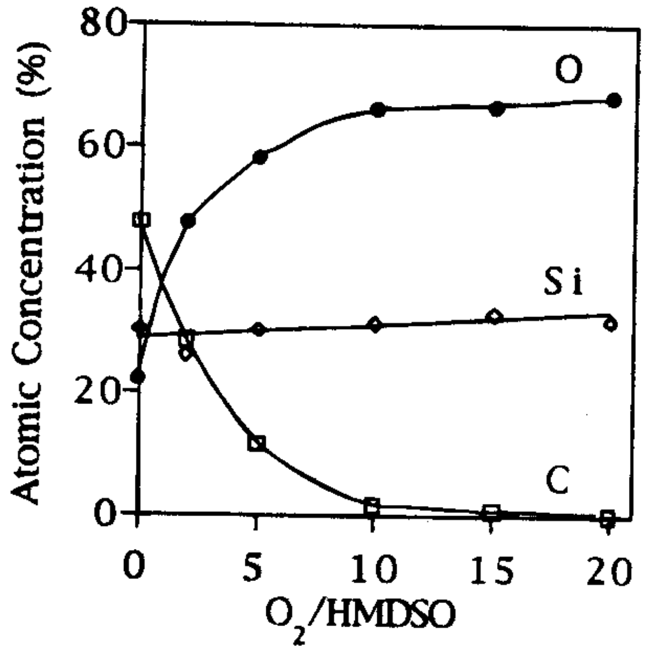


Table II. Spectral Features

Species	Feature	Wavelength (Å)
Si	$3p^{2\,3}P-4s^3P^0$	2516.1
O	$3s^5S^0-3p^5P$	7771.9
H	$2p^2P^0-3d^2D$	6562.8
C	$2p^{2\,1}S-3s^1P^0$	2478.5
SiO	$A^1\Pi-X^1\Sigma^+$	2413.8
OH	$A^2\Sigma^+-X^2\Pi$	3036.0
CH	$A^2\Delta-X^2\Pi$	4314.2
CO	$B^1\Sigma-A^1\Pi$	4835.3
Ar	$4s'-4p'$	7503.0
He	$2s^3S-3p^3P^0$	3889.0



Silicone-like, SiO_2-like

Gas Transmission Rate

500 Å gas barrier coatings on 13 μm PET

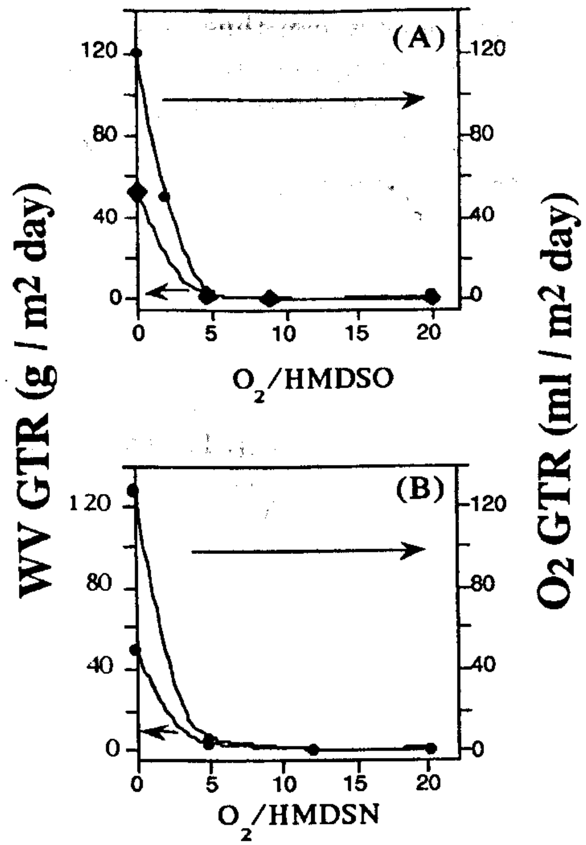


Fig. 2. O_2 and WV GTR of films deposited from (A) O_2/HMDSO and (B) O_2/HMDSN fed RF Glow Discharges.

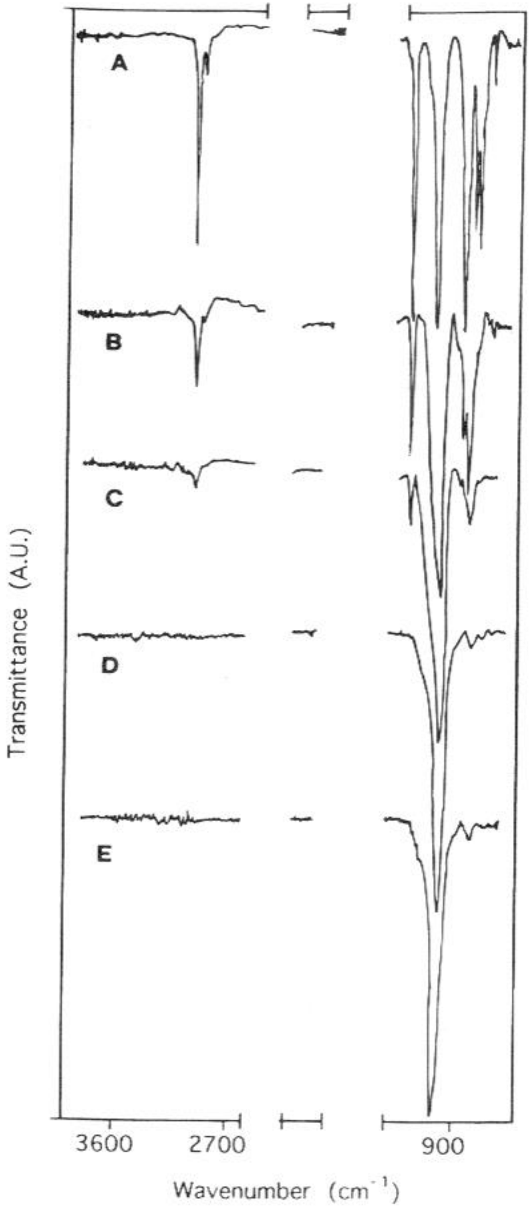


Fig. 6. FT-IR spectra obtained from (a) HMDSO liquid monomer and from films deposited at: (b) 100% HMDSO; (c) O_2/HMDSO=2; (d) O_2/HMDSO=10; (e) O_2/HMDSO=20 feed composition.

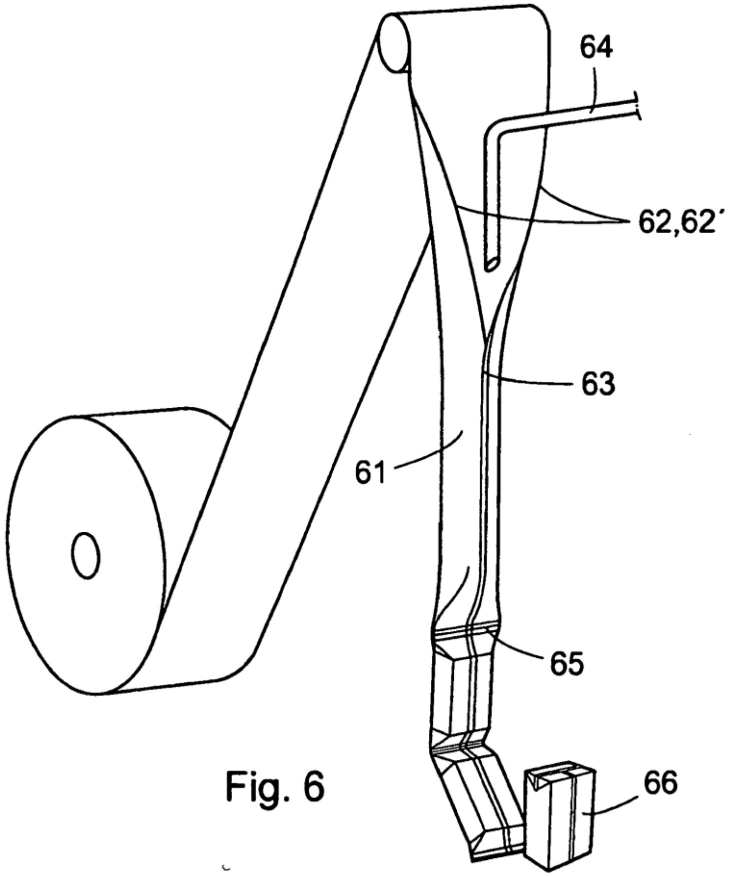
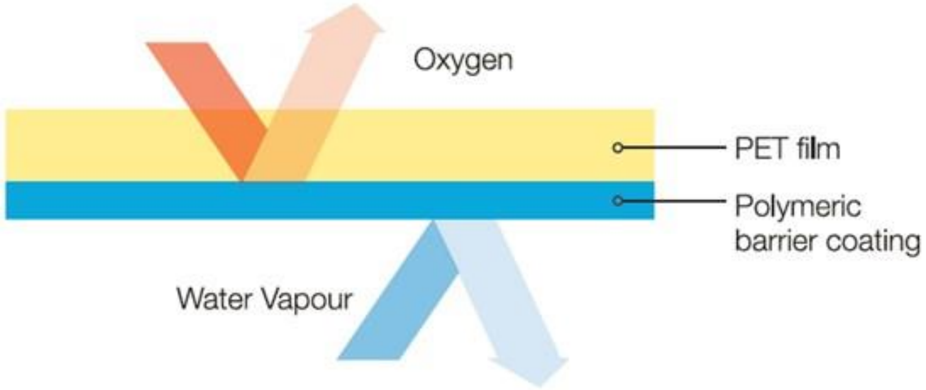
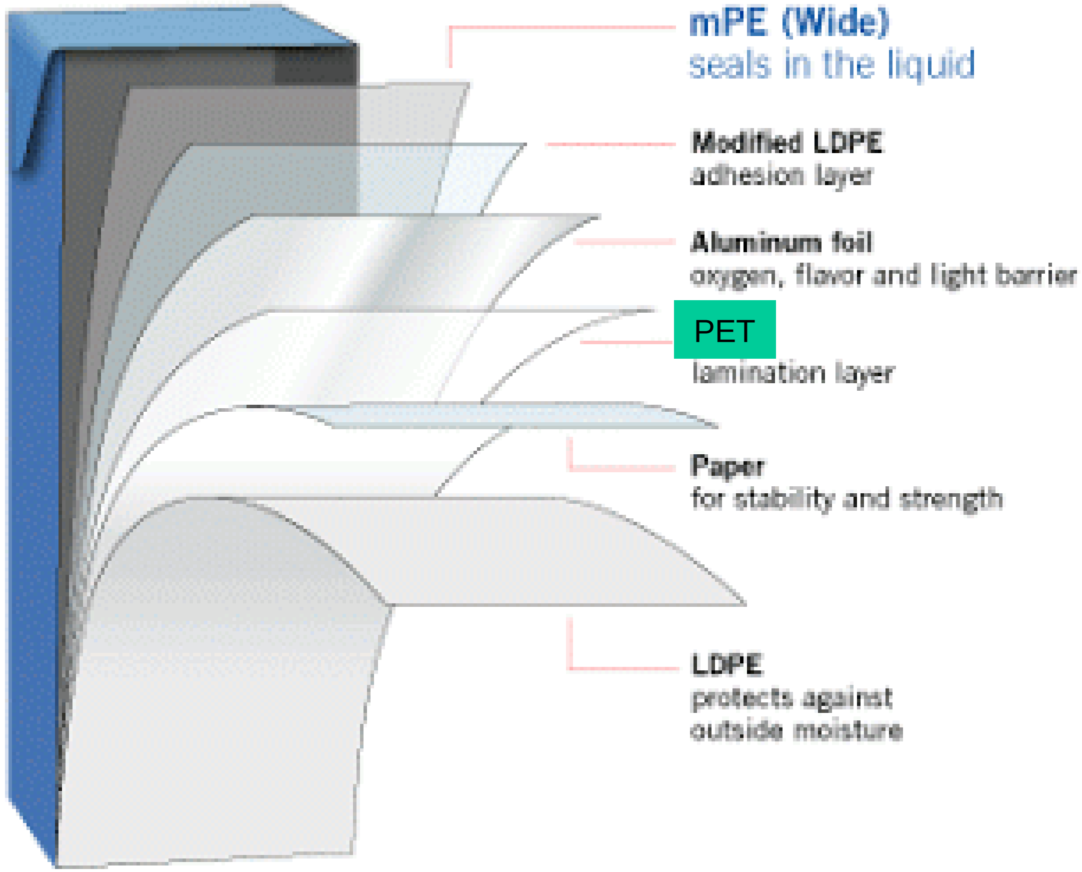


Fig. 6





mPE (Wide)
seals in the liquid

Modified LDPE
adhesion layer

Aluminum foil
oxygen, flavor and light barrier

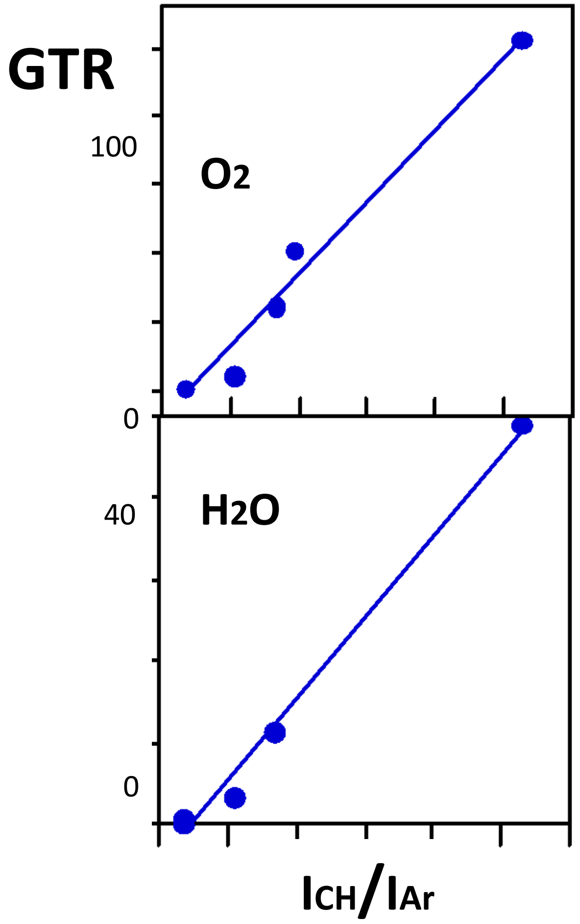
PET
lamination layer

Paper
for stability and strength

LDPE
protects against
outside moisture

PROCESS CONTROL

Silicone-like, SiO_2-like gas barrier coatings on PET



The gas transmission rate (O_2, H_2O) through the SiOx coating depends on its carbon content, which is a function of the density of CH (and C) radicals in the plasma phase.

AT HIGH O_2/MONOMER RATIO (very high barrier, highly inorganic coating) GTR DEPENDS ON Si-OH GROUPS IN THE COATINGS

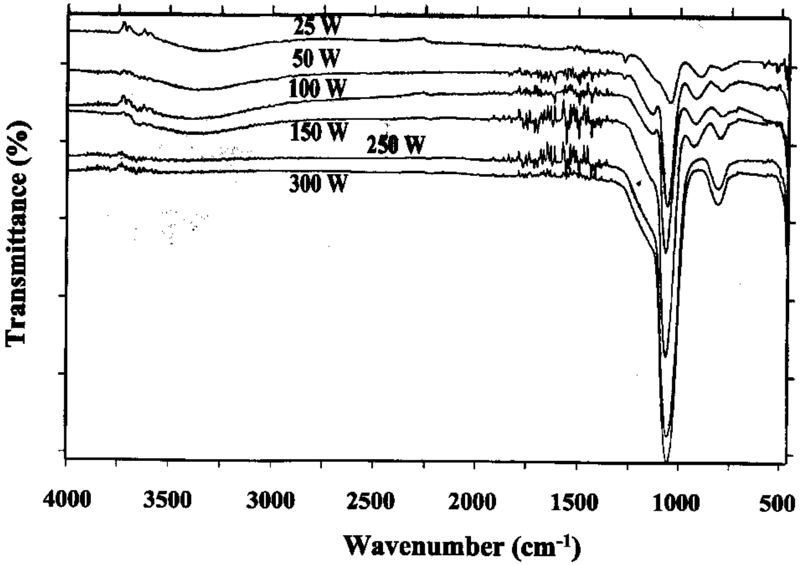
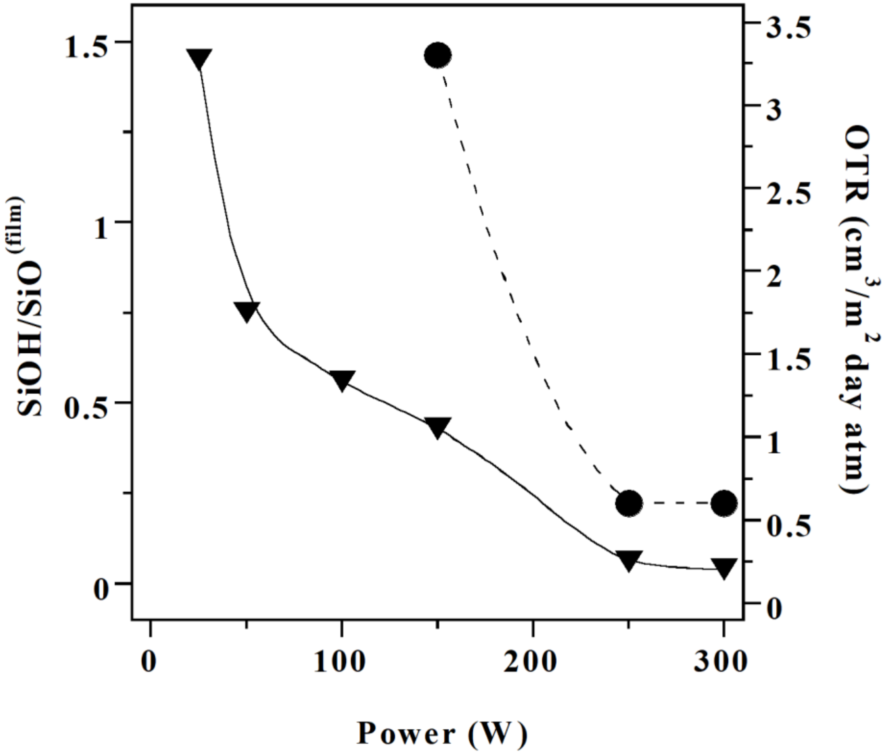


Fig. 2. FT-IR spectra of plasma deposited SiO_x films as a function of the delivered power.



IR-AS PROCESS CONTROL

SiO_2-like gas barrier coatings on PET films for packaging

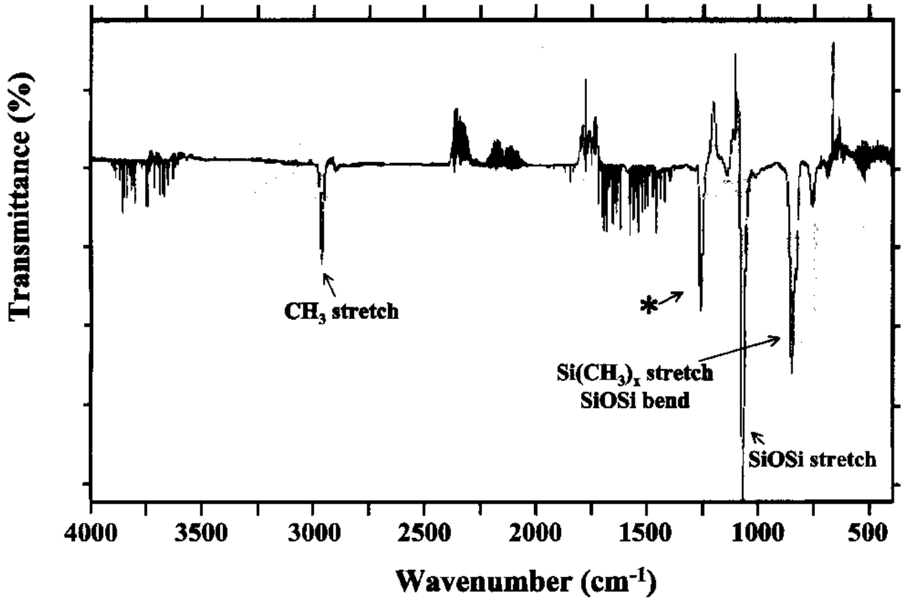
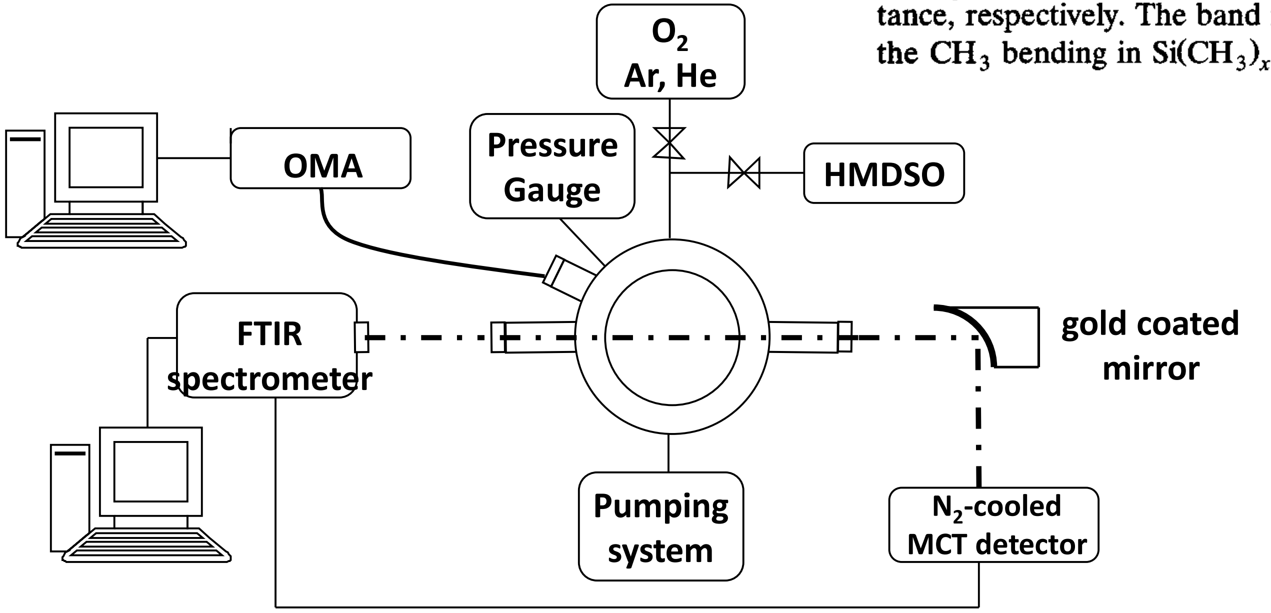


Fig. 4. A characteristic absorbance spectrum of an HMDSO/O_2 (3:17 gas flow rate ratio) plasma reported as $-\ln(T_p/T_g)$, where T_g and T_p are the gas phase (plasma off) and the plasma phase transmittance, respectively. The band marked with (*) has been attributed to the CH_3 bending in $Si(CH_3)_x$.


O_2
Ar, He

OMA

Pressure Gauge

HMDSO

FTIR spectrometer

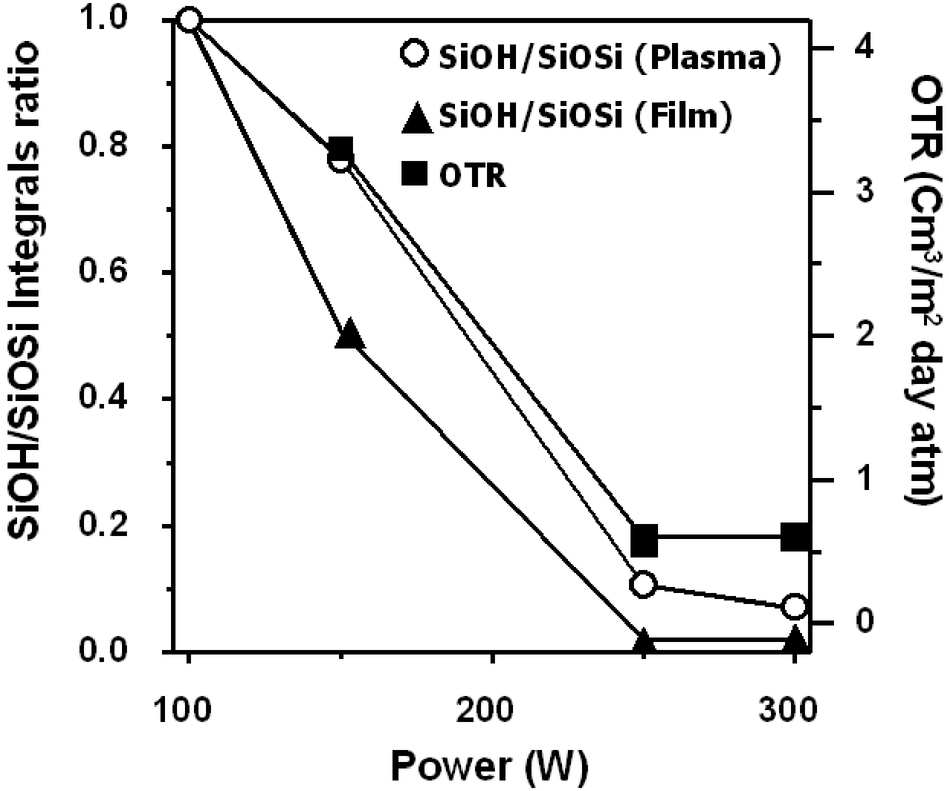
gold coated mirror

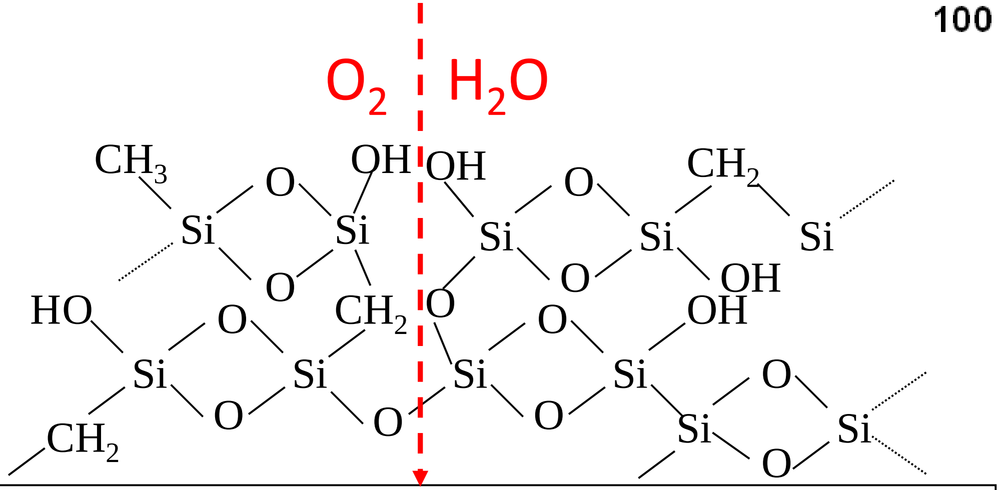
Pumping system

N_2-cooled MCT detector

silanols (Si-OH) moieties open "holes" in SiOx coatings, and allow transport of O_2 and H_2O vapor

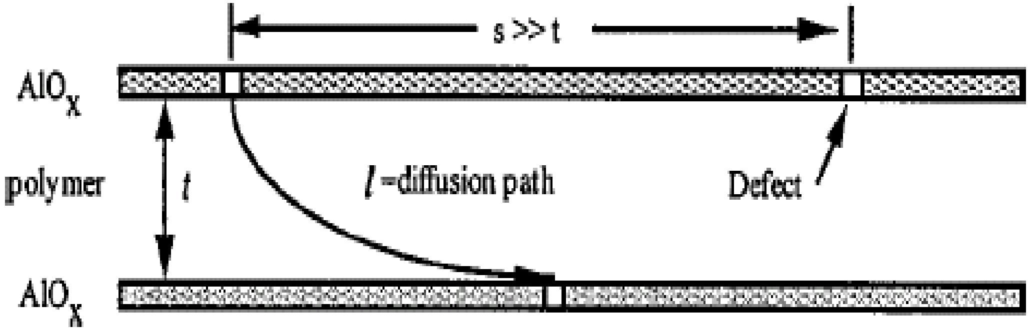
to improve the barrier (and protection) properties the density of Si-OH groups in the coating needs to be minimized



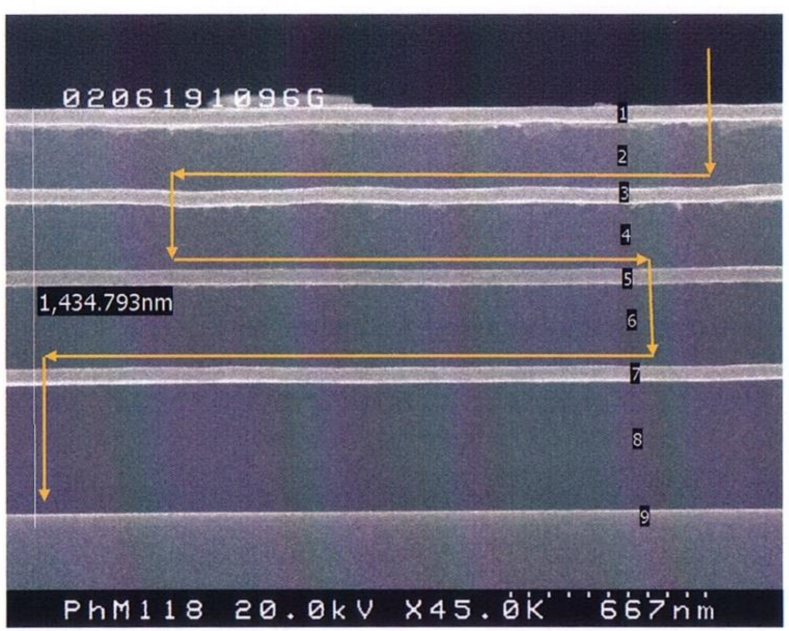


PET 13 μm pellicula for food packaging applications

multilayer stacks improve barrier performances



Graff el al., Journal of Applied Physics, Vol. 96, pp. 1840, 2004

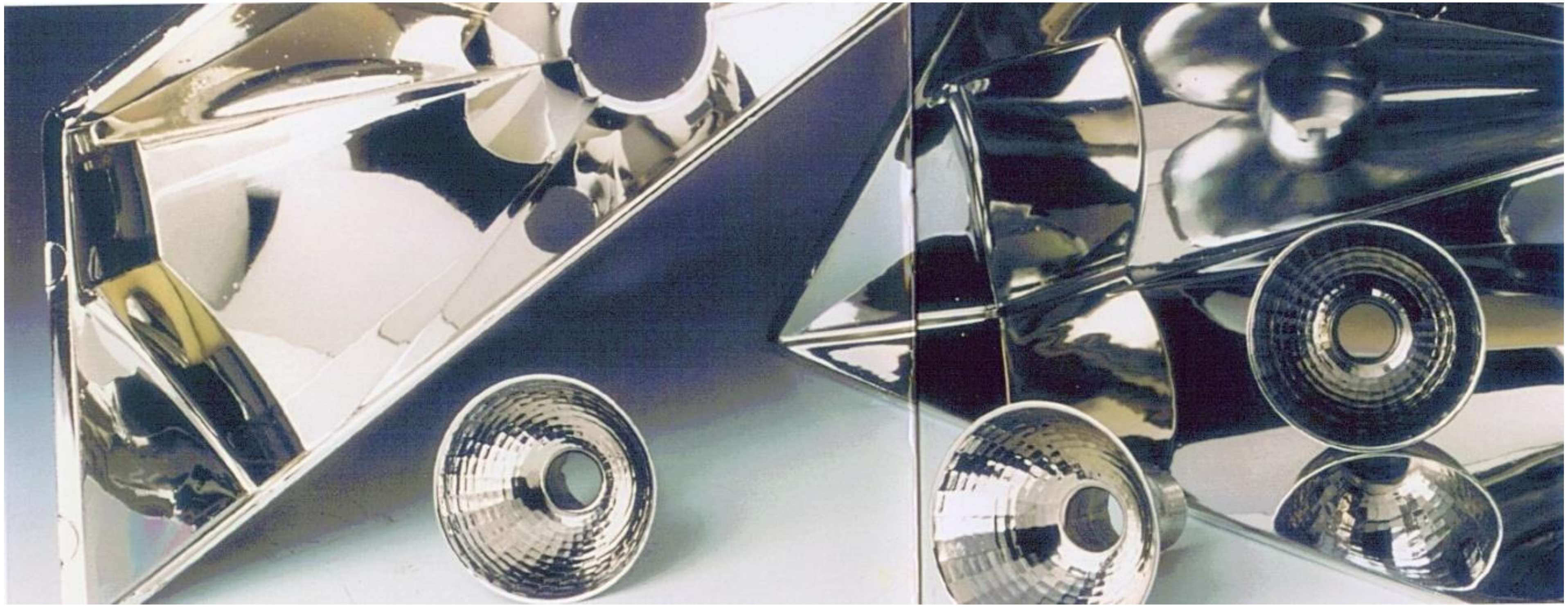


organic layers decouple the defects of two inorganic layers and heals some defects of the next inorganic coating.

SiO_x FOR CORROSION PROTECTION ON METALS/ALLOYS

- Anti-tarnishing silver, copper and brass.
- Jewellery, Mint, ….
- anti-scratch for gold and polymers
- antiscratch for plastic windshields and windows (subway of Nagoya)
- Anti-stain for marble and granites
- barrier films for packaging
- superbarrier for flexible electronics

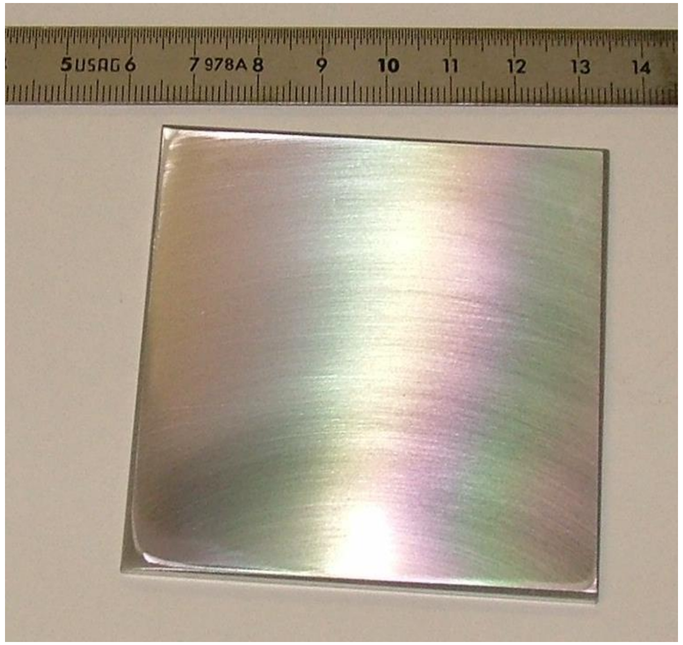
PE-CVD SiOx “protecting seal” coatings on Al-evaporated plastic car lights



rivestimento protettivo SiOx su metalli (Al)

dopo 48 h in camera a nebbia salina

non trattato



trattato

PROTECTION FROM CORROSION: AVOIDING TARNISHING ON SILVER

Silver (and other metal) surfaces darken easily with time for air exposure, due mainly to reactions with S-containing molecules that form sulphides/oxides layers. Technological, artistic and archaeological artefacts undergo a gradual darkenig known as *tarnishing*.

$2\ Ag + S^{2-} \rightarrow Ag_2S + 2e^-$ E_0=0,93 V (SCE)

$2\ Cu + S^{2-} \rightarrow Cu_2S + 2e^-$ E_0=1,17 V (SCE)

$Cu + S^{2-} \rightarrow CuS + 2e^-$ E_0=0,97 V (SCE)

H_2 plasma cleaning

PE-CVD SiOx

trattamento anti-tarnishing e anti ossidazione
monete e medaglie argento, rame

H_2 plasma cleaning

PE-CVD SiOx

bracciali in argento e rame

zona protetta via plasma
dopo 10 cicli di *tarnish* test
(*tarnish* accelerato in NaS 0.1 M)

zona non trattata
dopo 10 cicli di *tarnish* test

http://www.ion-med.com/how.asp

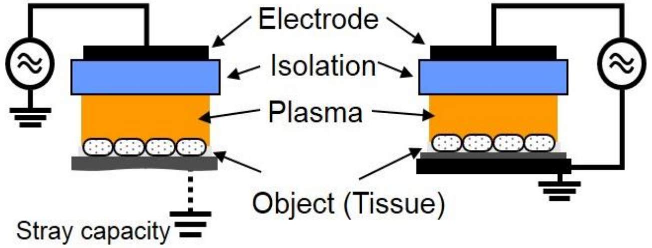
AP plasmas for biomedicine

Two basic principles

Dielectric Barrier Discharge (DBD)

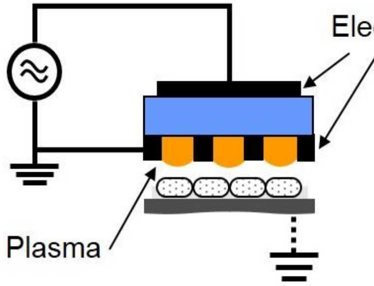
Working gas: mostly ambient air

Volume dielectric barrier discharge (DBD)



CINOGY
plasma technology for health

Surface dielectric barrier discharge (DBD)

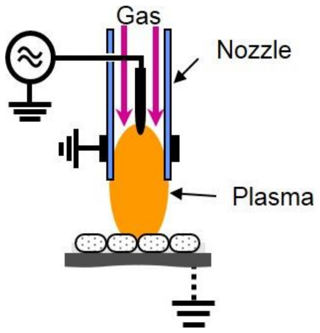


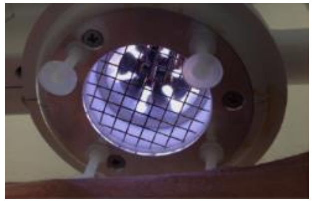
terraplasma
MEDICAL

Plasma Jet

Working gas: noble gases (Ar, He), gas mixtures

Plasma jet

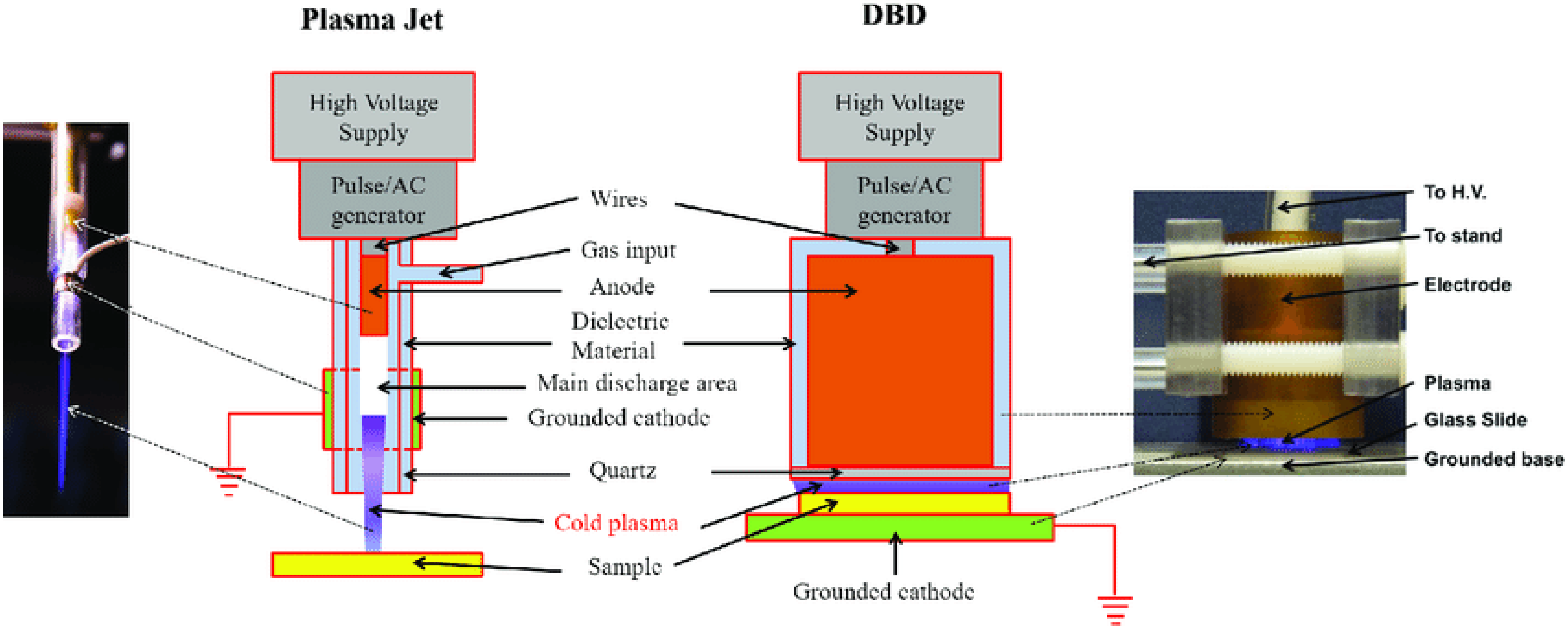




ADTEC Plasma Technology Co.Ltd.

neoplas tools
medical plasma

K.-D. Weltmann, H.-R. Metelmann, Th. von Woedtke, Europhysics News (EPN) 47 No 5-6 (2016) 39-42



Plasma Jet

DBD

High Voltage Supply

Pulse/AC generator

Wires

Gas input

Anode

Dielectric Material

Main discharge area

Grounded cathode

Quartz

Cold plasma

Sample

Grounded cathode

To H.V.

To stand

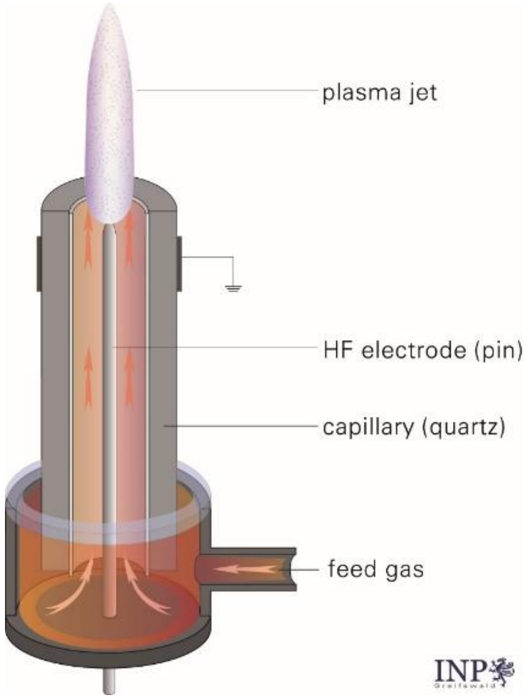
Electrode

Plasma

Glass Slide

Grounded base

Atmopheric pressure plasma jet kINPen MED

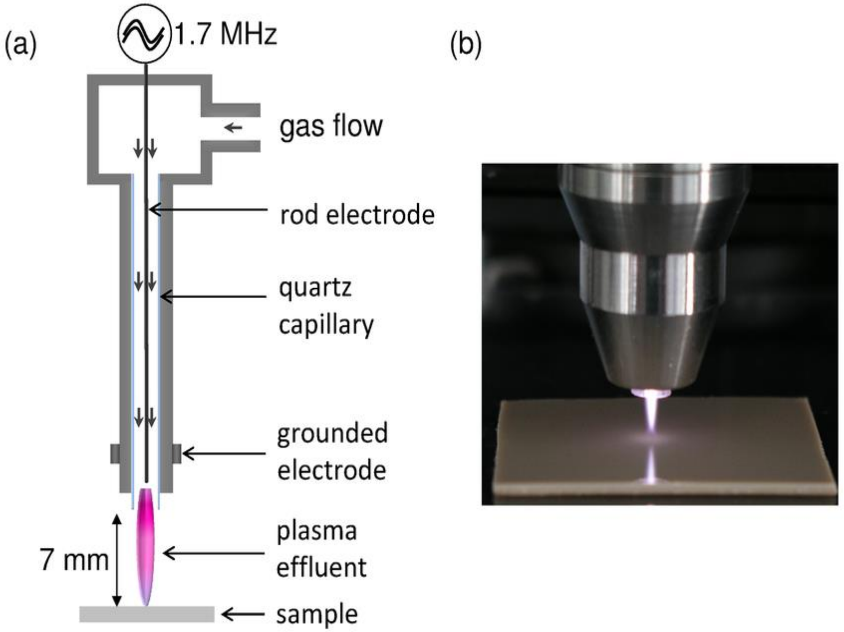


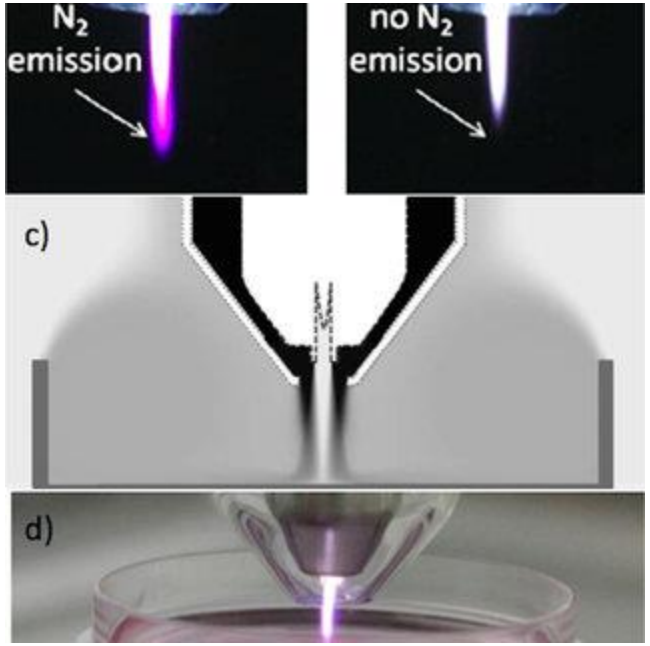
Dimensions:	L = 155 mm, Ø = 20 mm
Weight:	170 g
HF-Voltage:	1.1 MHz; 2…6 kV_{pp}
Gas temp.:	30-50°C
Feed gas:	Argon
Gas flow:	3-5 slm

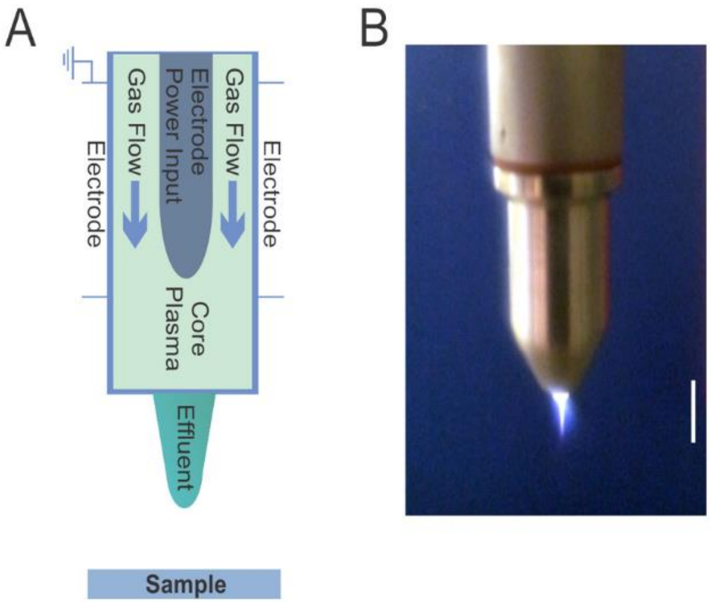
Certified as **medical device class IIa** (June 2013) according to European Council Directive 93/42/EEC

<u>Purpose:</u> Treatment of chronic wounds as well as pathogen-based diseases of skin, skin appandages, extremities and body

K.-D. Weltmann, E. Kindel, R. Brandenburg, C. Meyer, R. Bussiahn, C. Wilke, Th. von Woedtke. Contrib. Plasma Phys. 49 (2009) 631-640;
S. Bekeschus, A. Schmidt, K.-D. Weltmann, Th. von Woedtke. Clin. Plasma Med. 4 (2016) 19–28;
S. Reuter, Th. von Woedtke, K.-D. Weltmann. J. Phys. D: Appl. Phys. 51 (2018) 233001;
www.neoplas-tools.eu


(a)
1.7 MHz
gas flow
rod electrode
quartz capillary
grounded electrode
plasma effluent
7 mm
sample
(b)


N₂ emission
no N₂ emission
c)
d)


A
B
Electrode
Gas Flow
Electrode Power Input
Gas Flow
Electrode
Core Plasma
Effluent
Sample

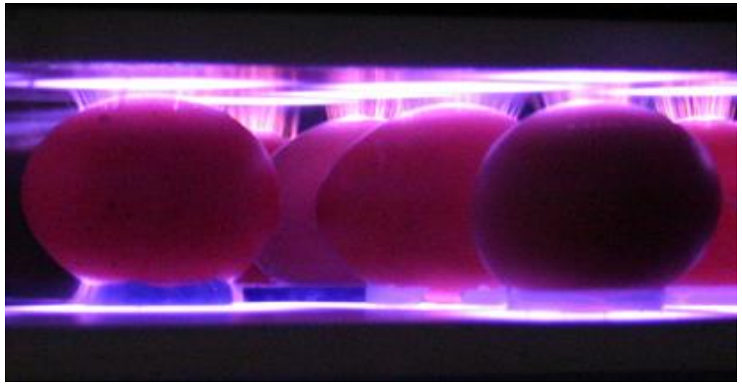
plasma sterilization in hospitals

[(136) STERRAD Plasma Sterilization Technology - YouTube]

Sterrad J&J

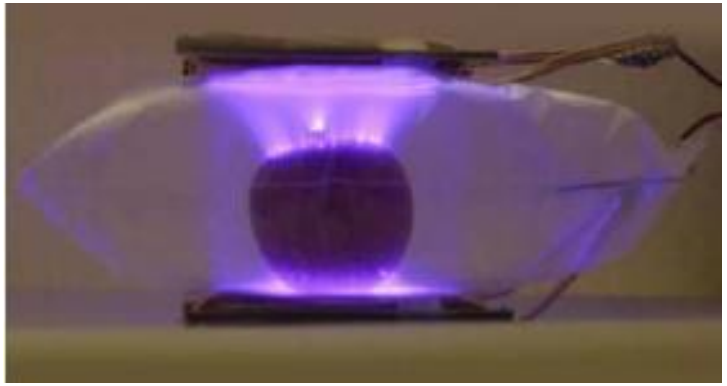
Decontamination / Sterilization

decontaminazione gusci d'uovo



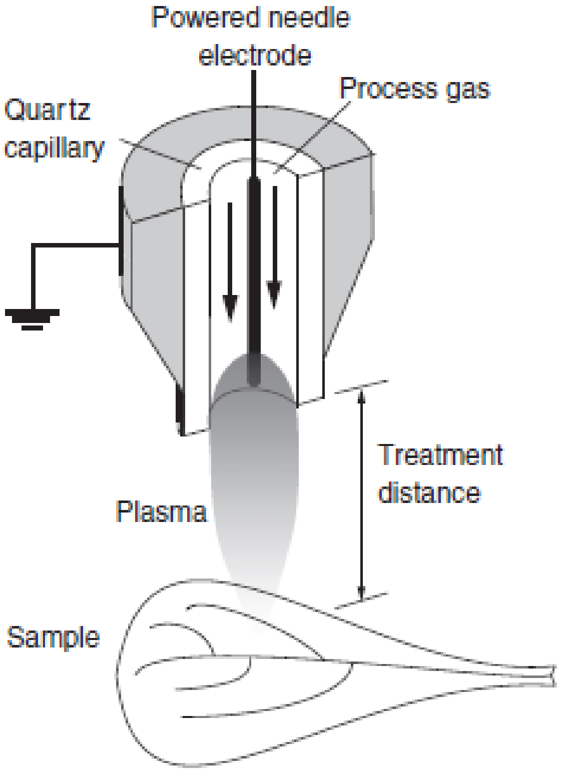
L. Ragni et al. / Journal of Food Engineering 100 (2010) 125–132

decontaminazione in-pack di mele



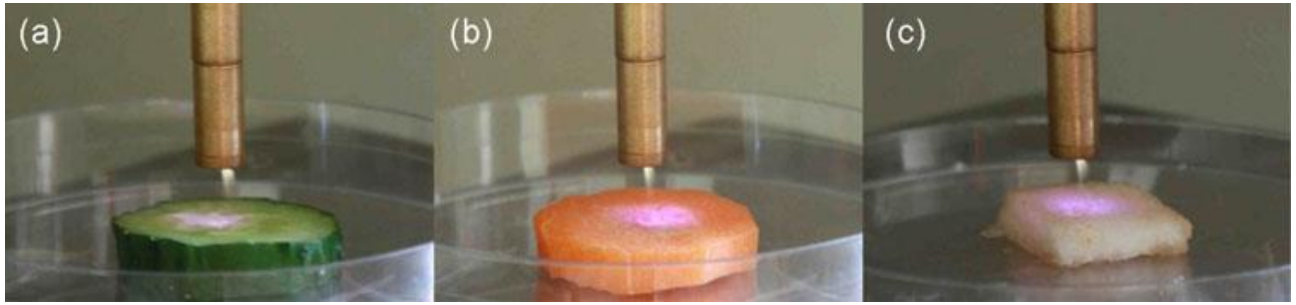
Safe-bag project

decontaminazione di foglie di valeriana



M. Baier et al., Innovative Food Science & Emerging Tech 22 (2014) 147–157

decontaminazione di fette di cetriolo, carota, pera



R.X. Wang et al./ Eur. Phys. J. D (2012) 66: 276