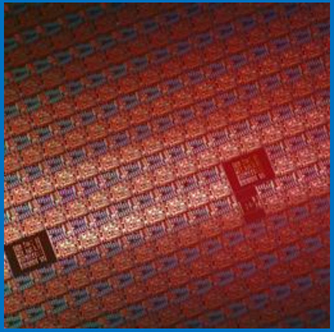
Plasma Processing for Integrated Circuits

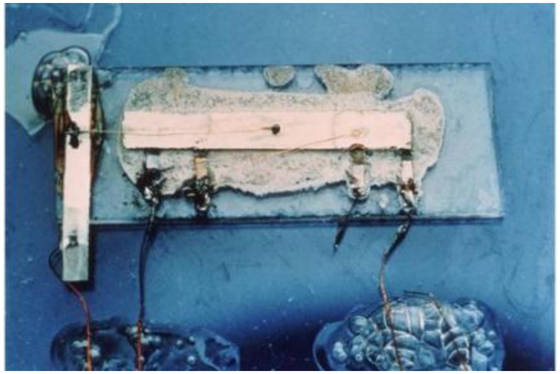


Plasma processing for integrated circuits
Outline

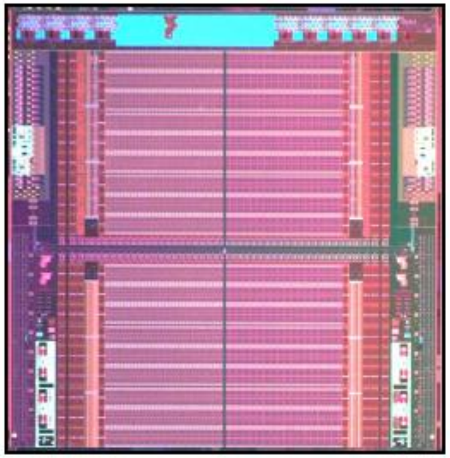
- Introduction to semiconductor processing –chips-
- Definition of a glow discharge –plasma-
- Plasma Etch Chemistry -the magic in the process-
- Atomic Layer Etch -(neutral beam plasma etching)-

Moore’s Law

First IC, 1958 at TI



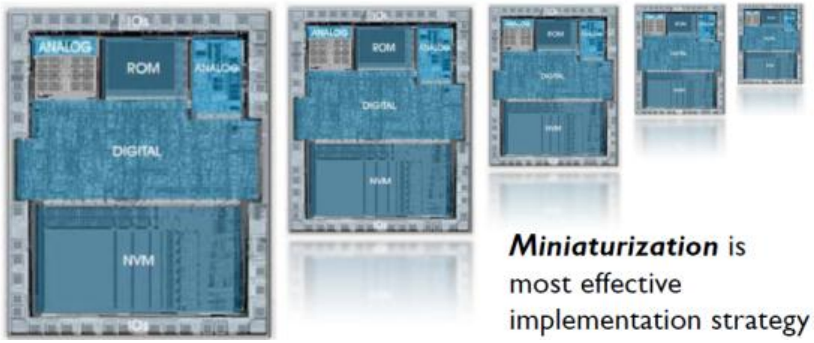
Intel’s 22nm chip



22 nm SRAM, Sept. ‘09

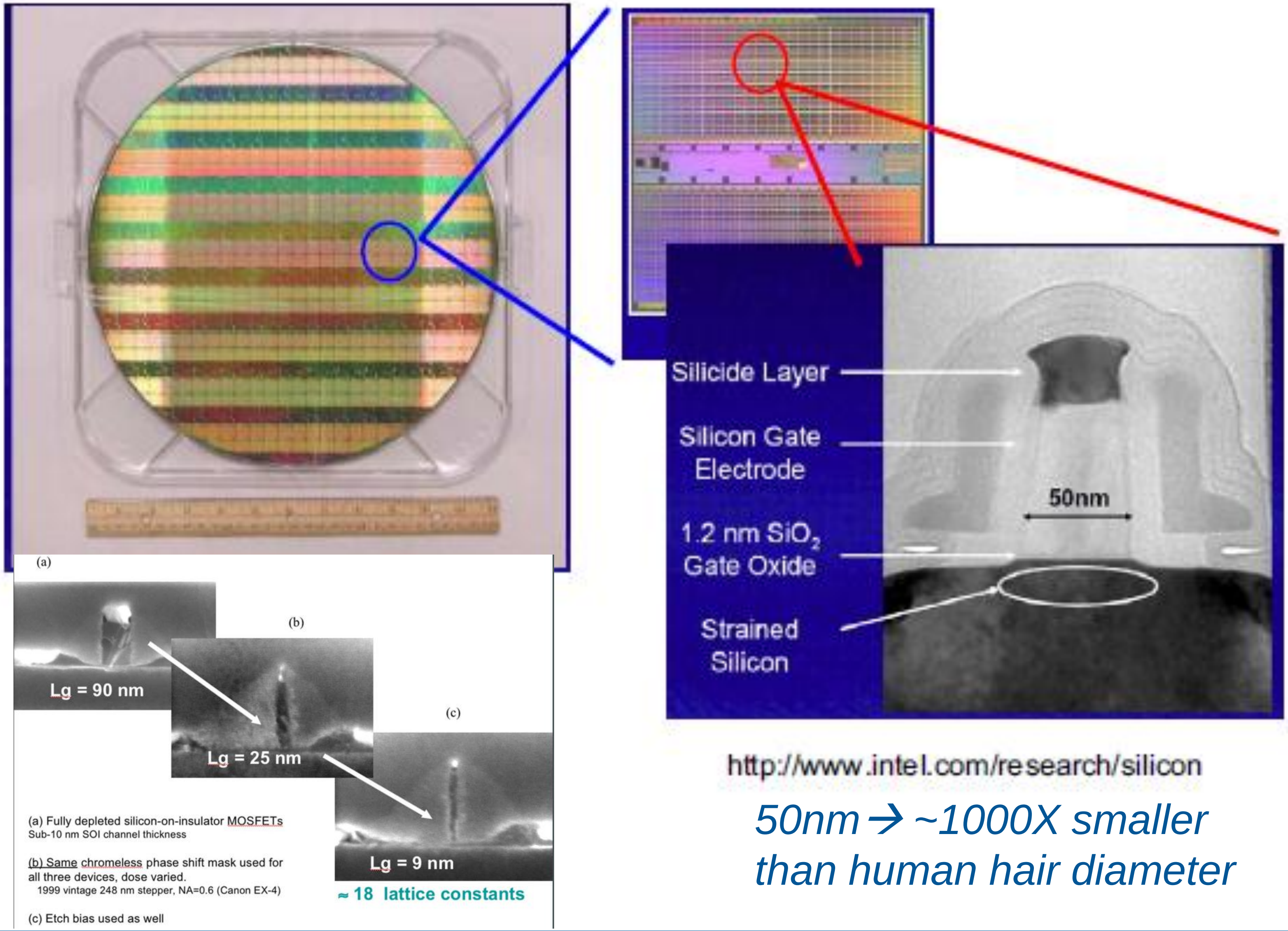
•>2.9 billion transistors/die

Moore’s law (1)= Double the number of devices every 2 years



Miniaturization is most effective implementation strategy

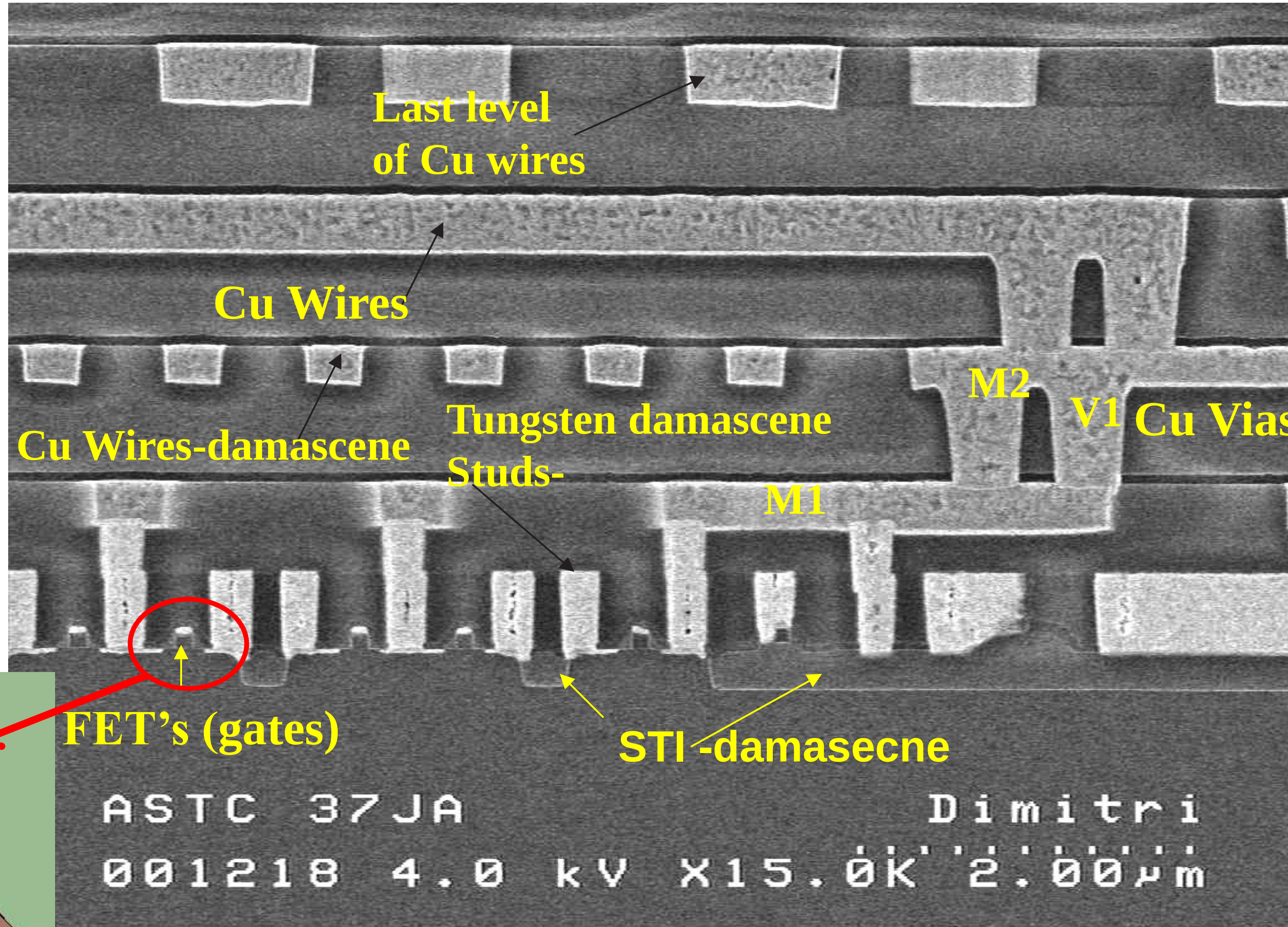
How small is small



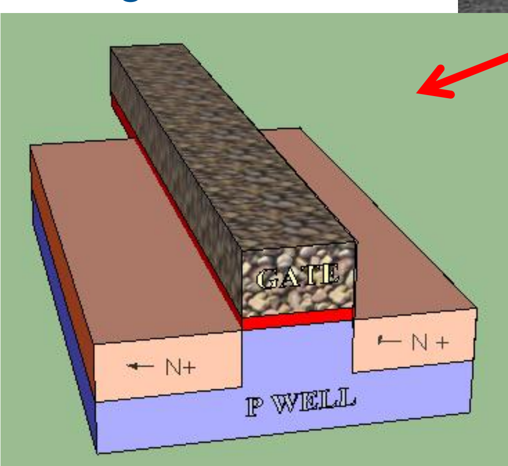
http://www.intel.com/research/silicon

50nm → ~1000X smaller than human hair diameter

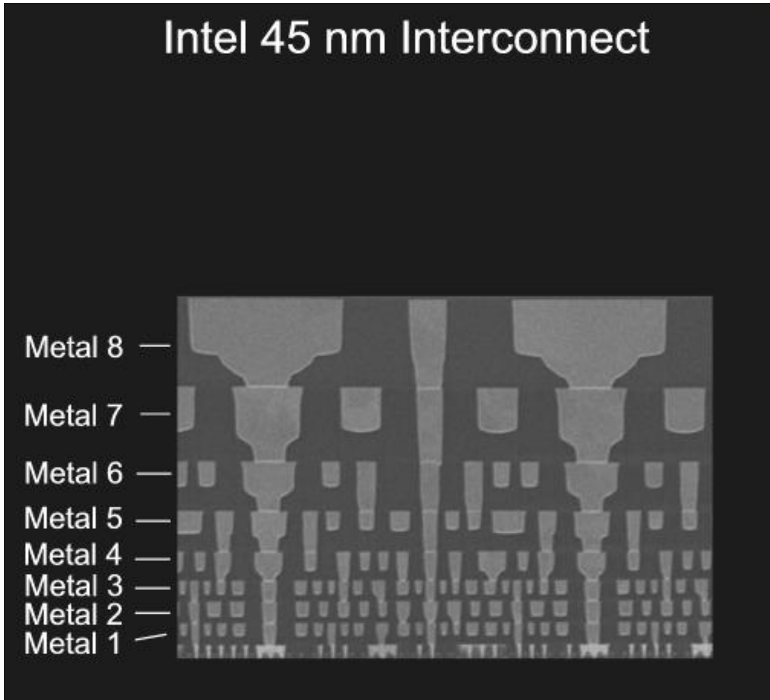
Older Generation chip

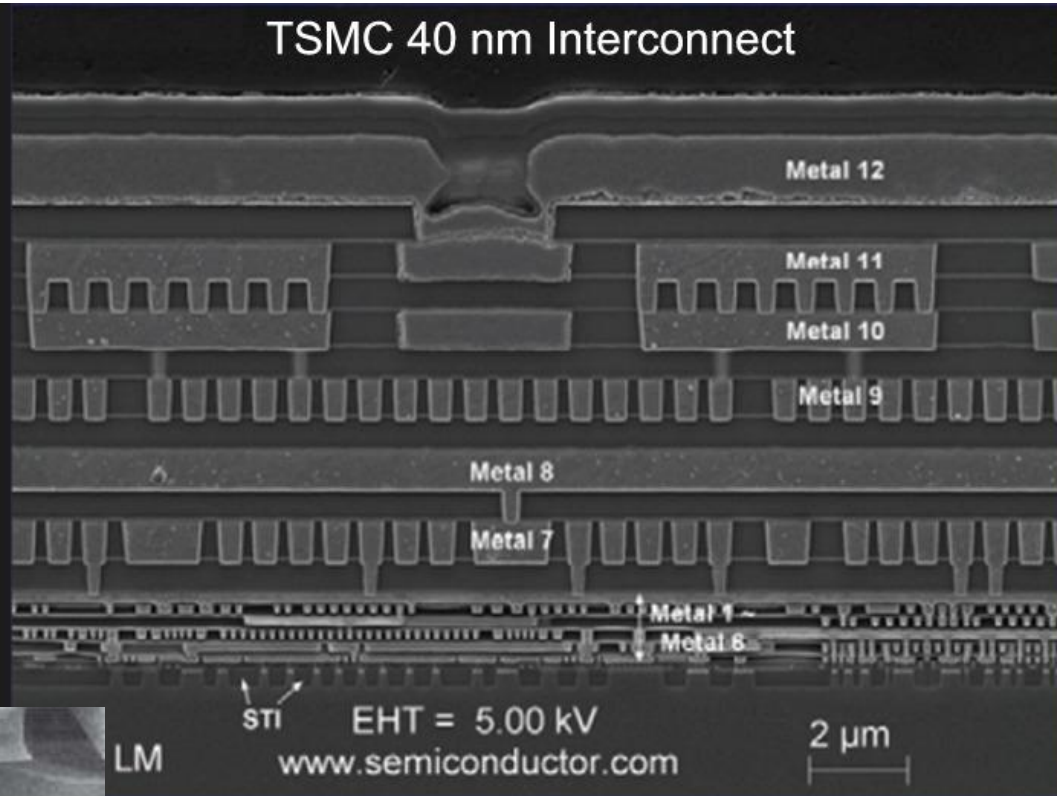


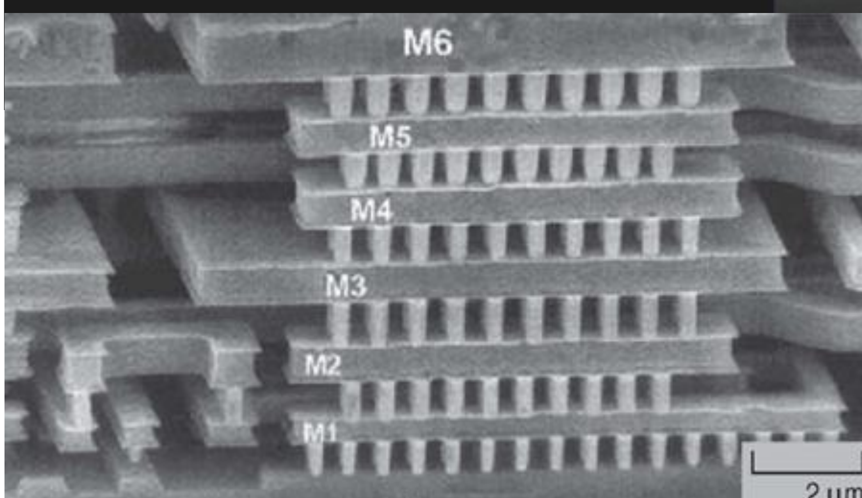
'Logic Transistor'



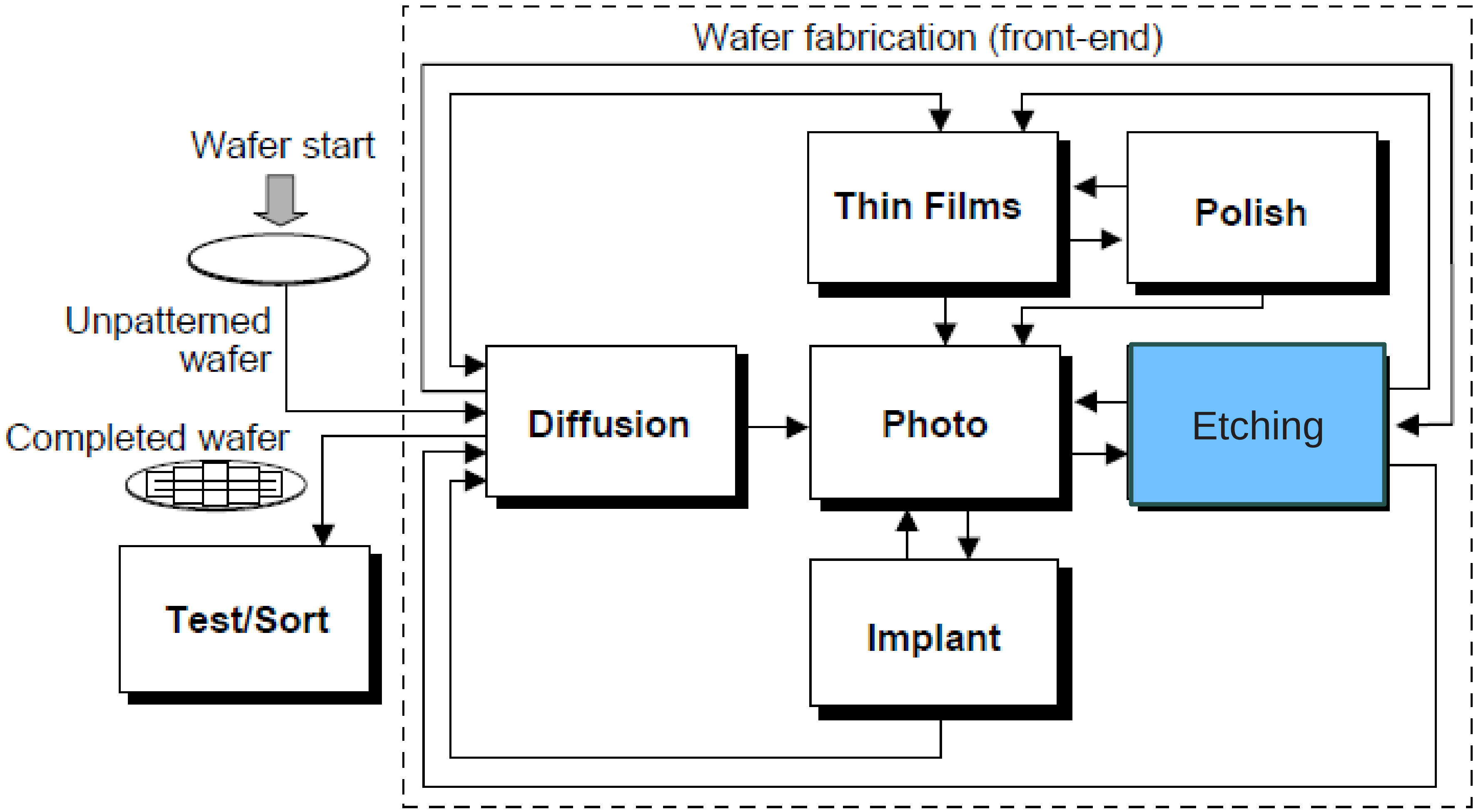
Newer Generation chips







The loop of Wafer fabrication

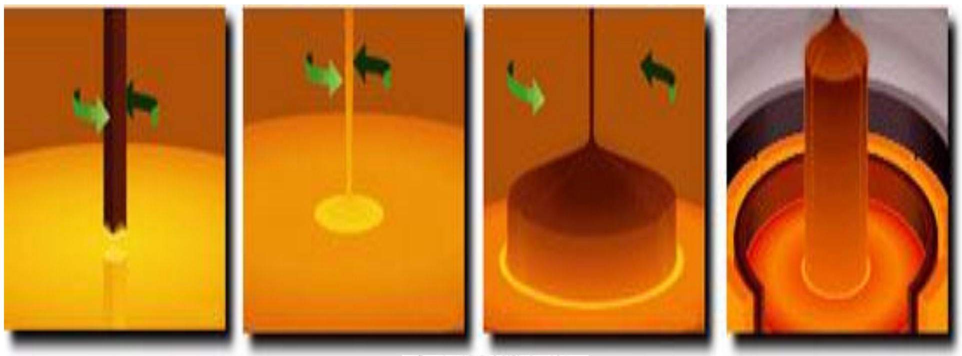


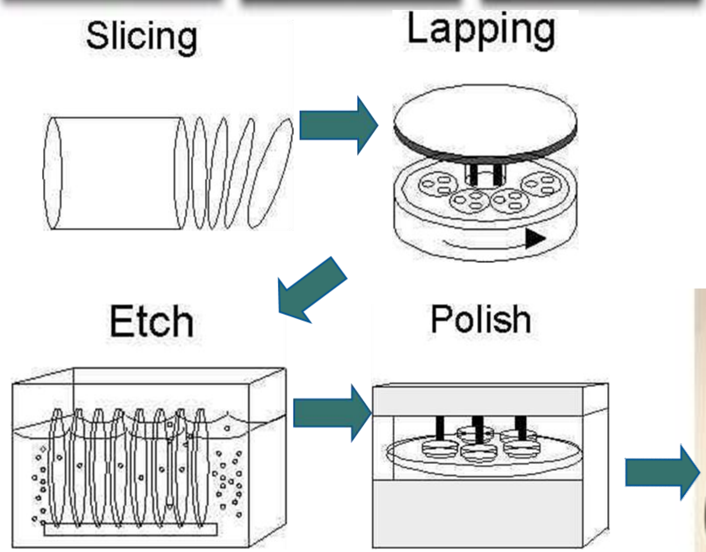
Inside a 300mm wafer fab

http://www.youtube.com/watch?v=yaASEMAMCNM

STARTING from the Beginning…….

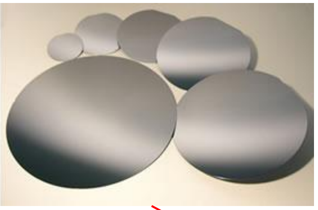
- **The Silicon Cylinder is Known as an Ingot**
- **Typical Ingot is About 1 or 2 Meters in Length**
- **Can be Sliced into Hundreds of Smaller Circular Pieces Called Wafers**

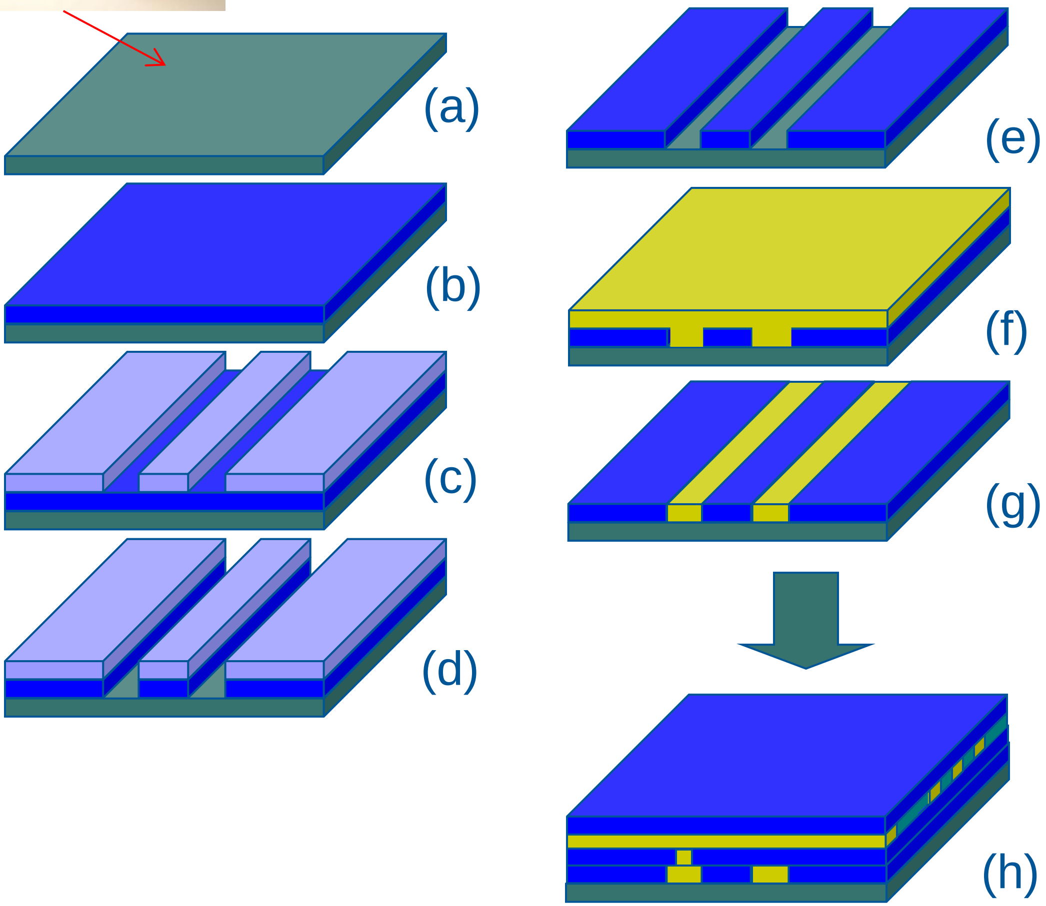


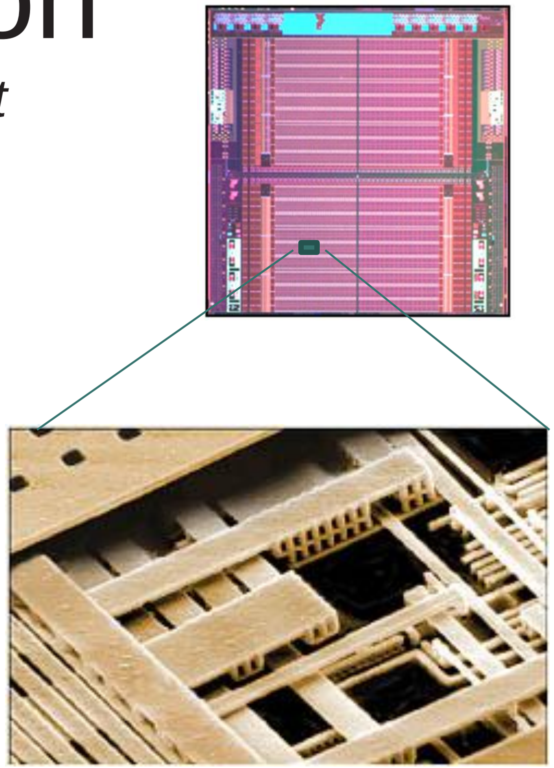


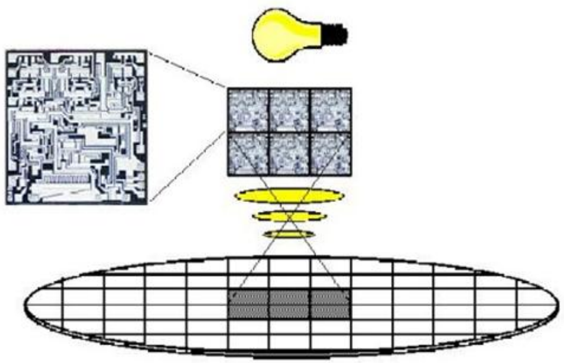
Microfabrication

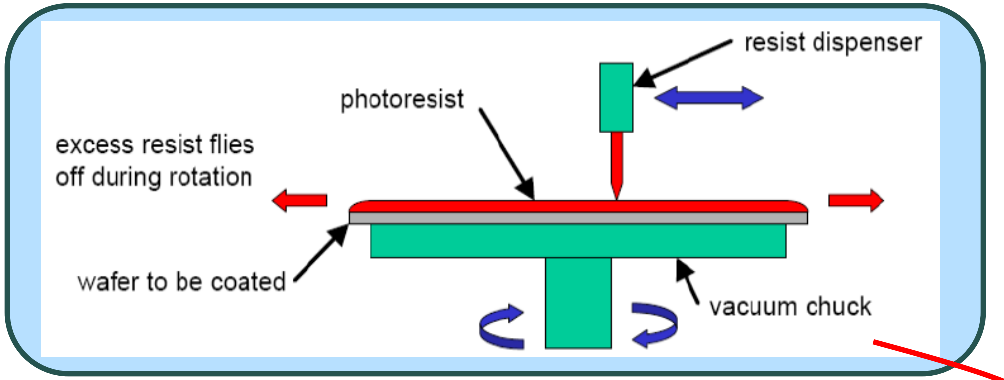
deposit-pattern-etch-repeat

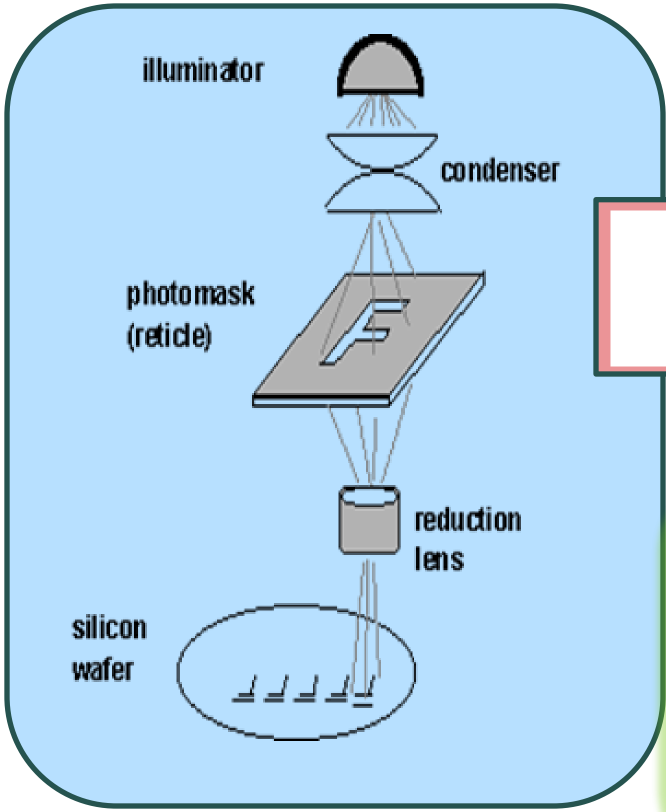


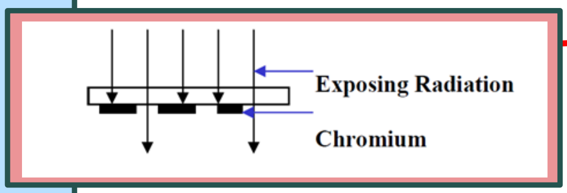


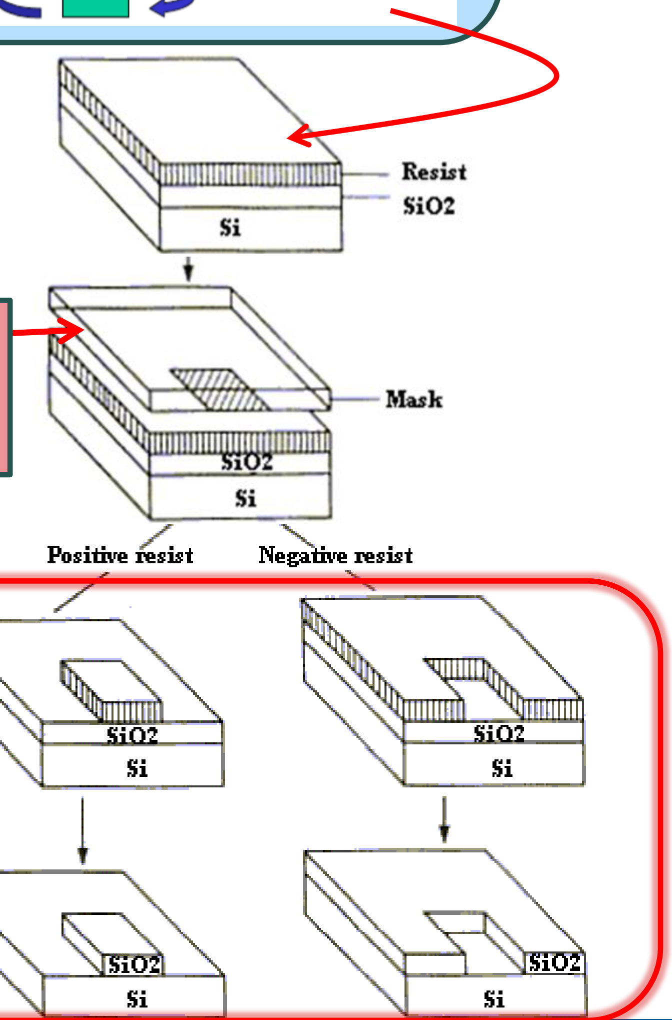






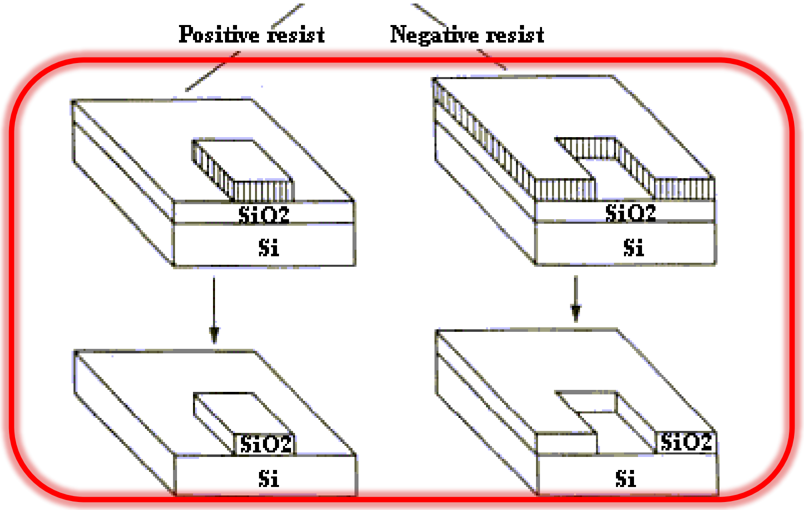






Building a ‘chip’ by depositing, pattern and **etching** layers

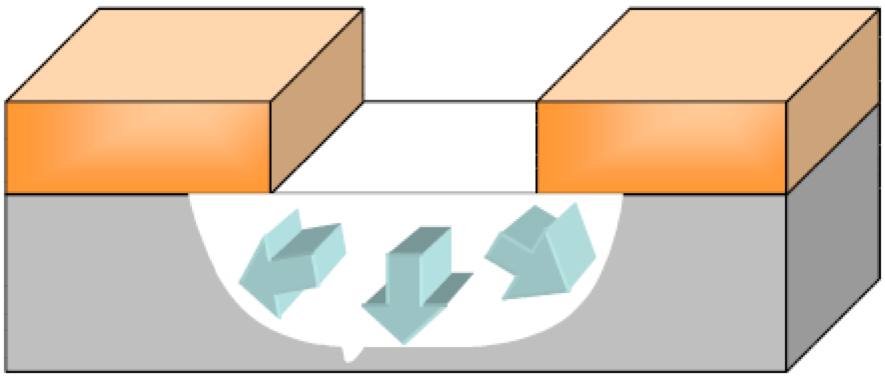
Selective layer removal and anisotropy are keys to microfabrication



Two Kinds of Etching or Removal methods

Wet Etching

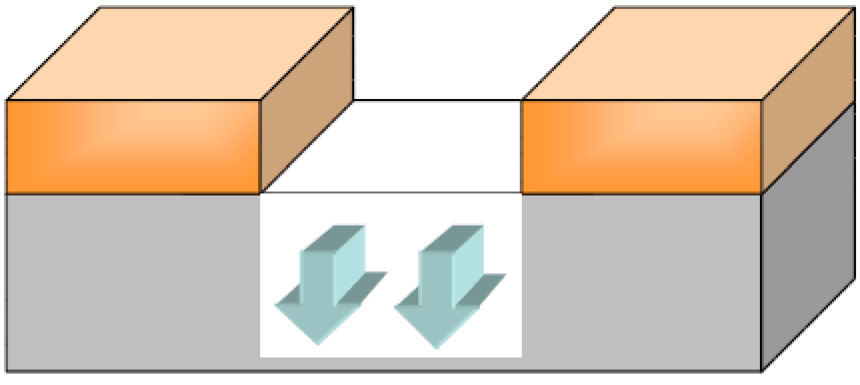
- by Wet chemical solution
- Isotropic etching



Vertical E/R ≒ Horizontal E/R
Pure Chemical Reaction
High Selectivity
CD Loss or Gain

Dry Etching

- by Plasma
- Anisotropic etching



Vertical E/R >> Horizontal E/R
Ion assisted
Relatively low Selectivity
No CD bias

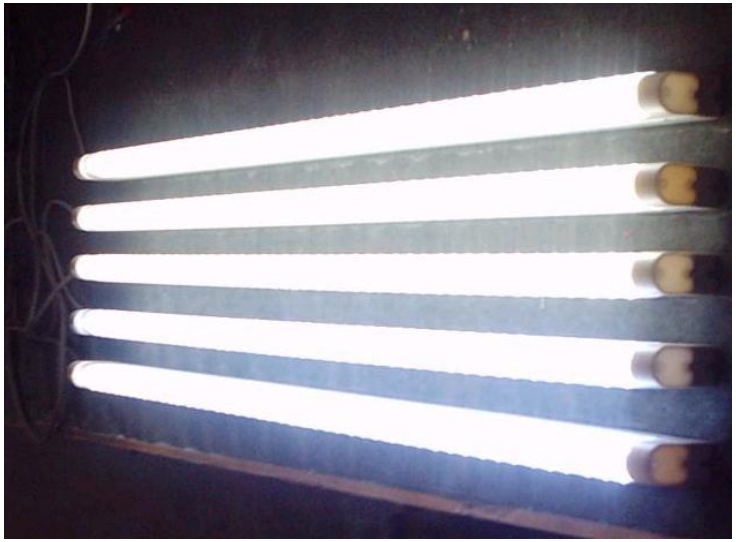
Plasma processing for DRY etching of integrated circuits Outline

- Introduction to semiconductor processing –chips-
- Definition of a glow discharge –plasma-
- Plasma Etch Chemistry -the magic in the process-
- Atomic Layer Etch (neutral beam plasma etching)

Plasma processing?

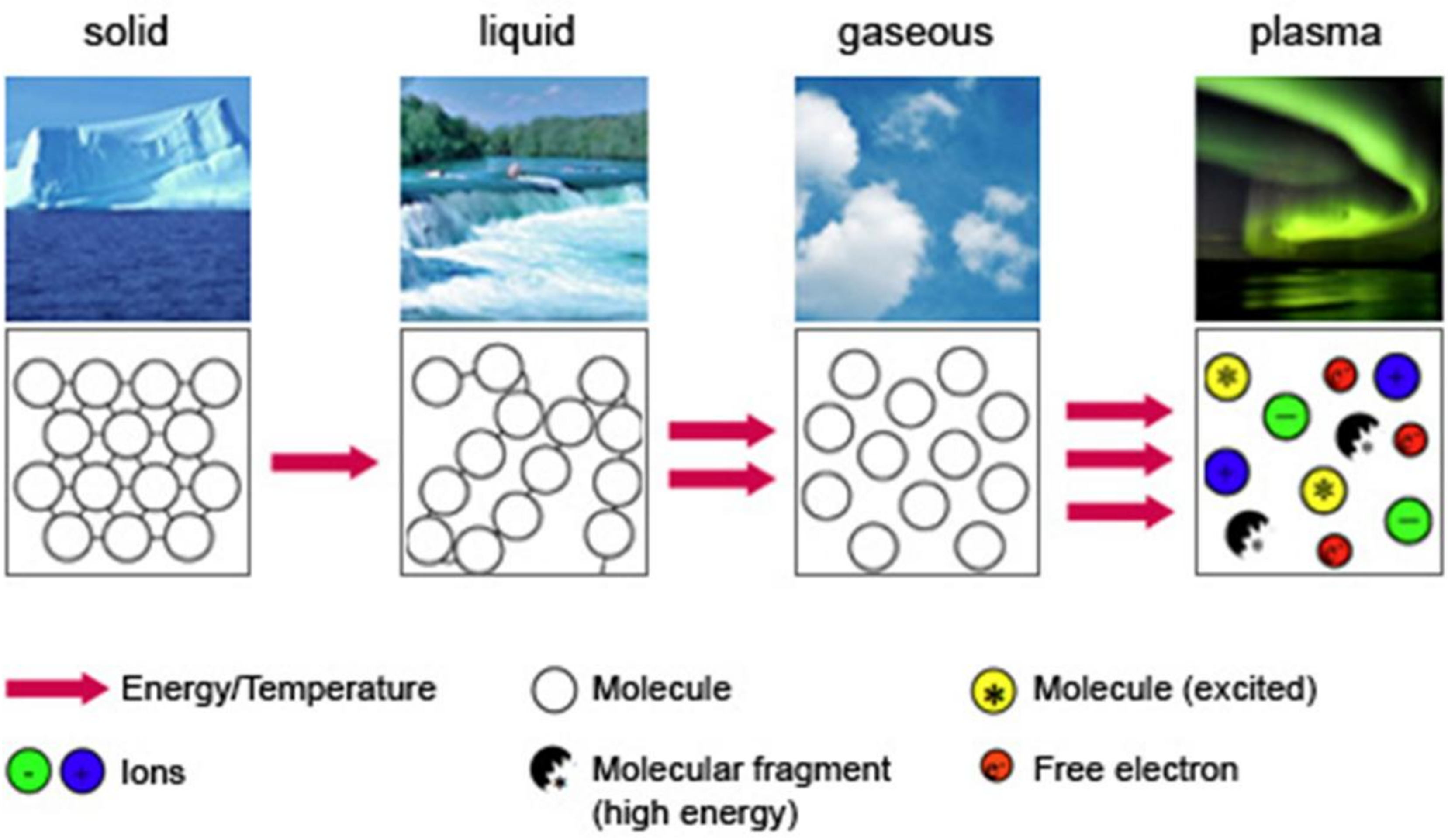
→Plasmas can deliver a high, diverse but selective, reactivity to a surface without heat, and can therefore access a parameter space in materials processing, which is not easily accessible with strictly chemical methods

What is a Plasma?

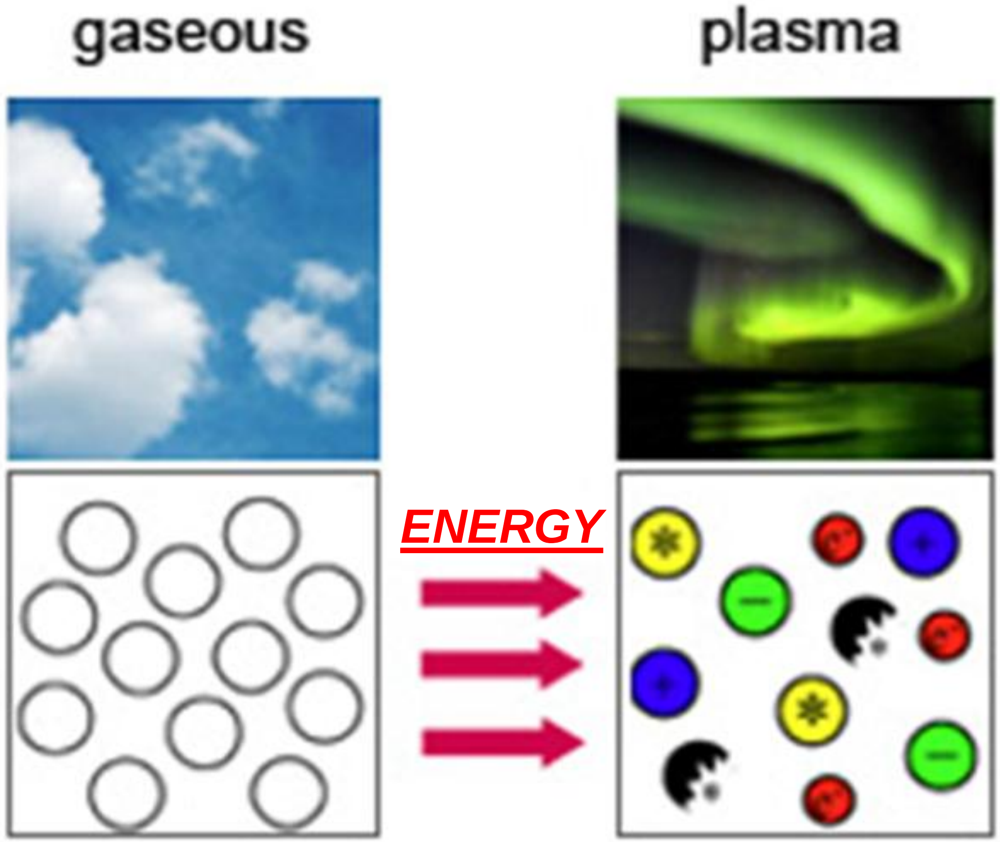


→ ionized gas consisting of atoms, electrons, ions, molecules, molecular fragments, and electronically excited species (*informal definition*)

Plasma – The fourth state of matter



http://www.plasmatreat.com/plasma-technology/what-is-plasma.html



- The reactive species are created in the plasma independently of substrate
- The reactivity of the plasma can be tuned by carefully choosing the plasma operating conditions (gases, flows, power, pressure, etc.)
- Plasma contains 'Electrical' Particles (ions, electrons,..) and highly reactive gas species… Through ion bombardment, additional energy can be provided to a surface
- It emits light → glow (O_2-pale yellow, N_2-pink, CF_4-blue, SF6-white blue, Ar-red, …)

Properties of Cold ("Our") Plasmas

- Pressure: 10^{-4} – 10 Torr (1Torr ≈ $3X10^{16}$ molecules/cm^3)
- Electron (ion) density: 10^9 – 10^{12} cm^{-3}
- Electron energy (temperature): 1 – 10eV (≈10^4 – 10^5 K)
- Ion (and neutral) temperature: ≈ 400K

$$Degree\ of\ ionization = \frac{Charged\ Particles}{Neutral\ Particles} \approx 10^{-6} - 10^{-1}$$

Densities of plasma species in an O_2 plasma

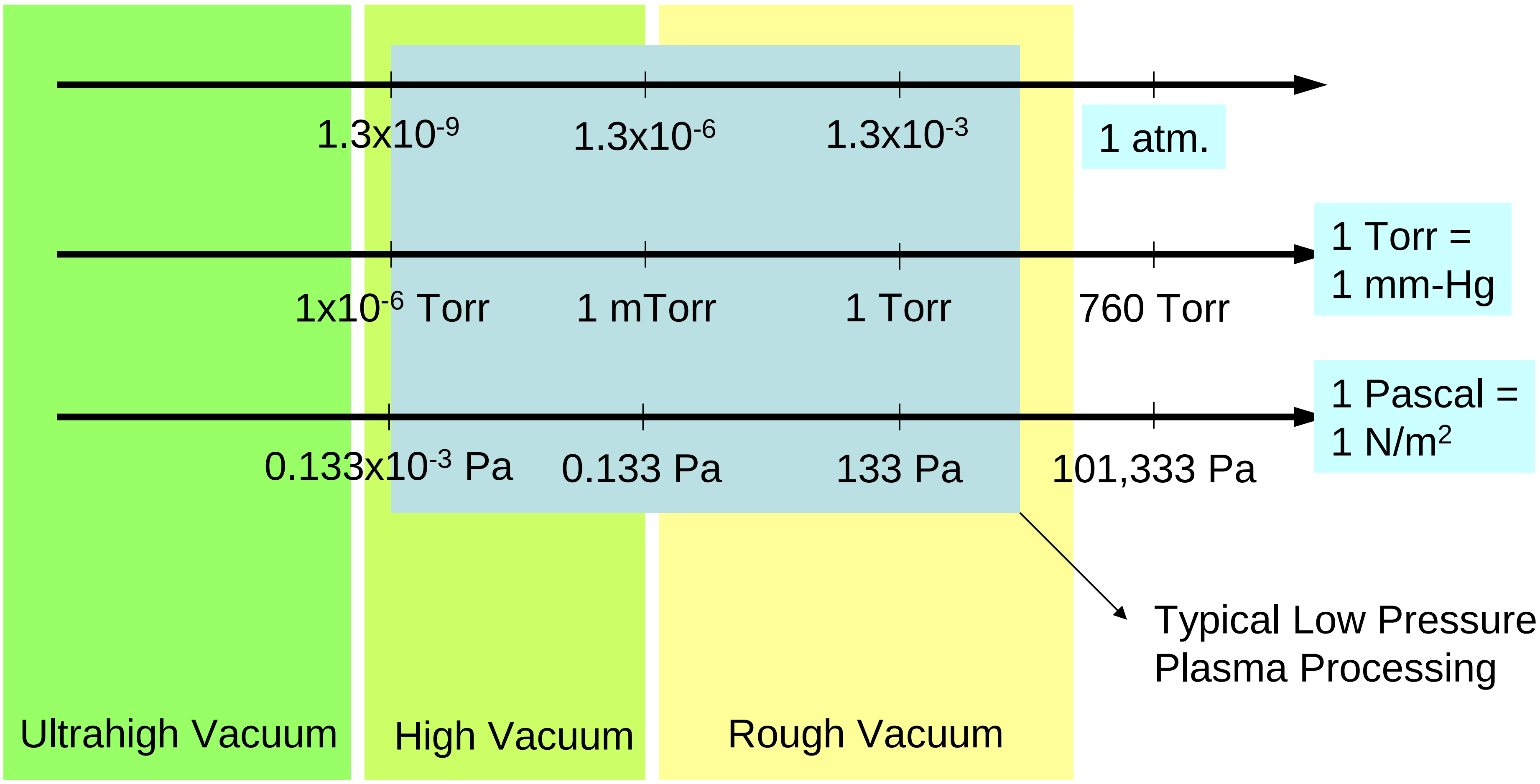
Pressure (mTorr)	O_2 (cm^{-3})	O (cm^{-3})	O_2^* (cm^{-3})	O* (cm^{-3})	O_2^+ (cm^{-3})	O^+ (cm^{-3})	O^- (cm^{-3})	n_e (cm^{-3})
10	3×10^{14}	7×10^{13}	4×10^{13}	4×10^{12}	5×10^{10}	4×10^{10}	2×10^{10}	7×10^{10}
100	3×10^{15}	1×10^{14}	3×10^{14}	5×10^{10}	4×10^{10}	1×10^{9}	3×10^{10}	2×10^{10}

Q & A

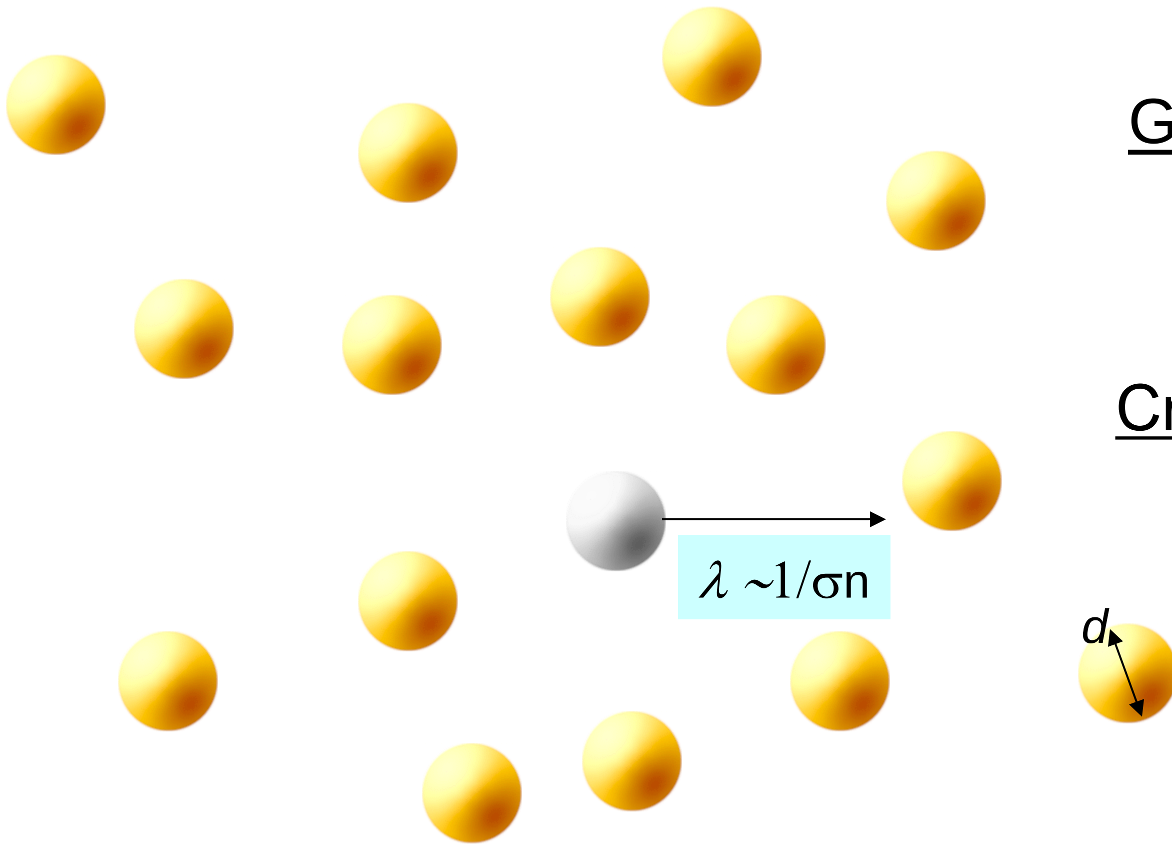
- Why does one need a vacuum chamber to generate a stable plasma?

- At atmospheric pressure (760 Torr), MFP of an electron is very short. Electrons are hard to get enough energy to ionize gases molecules.
- Extremely strong electric field can create plasma in the form of arcing (lightening) instead of steady state glow discharge.

Vacuum (units)



Collisions and Mean Free Path



Gas Density

$n = P/ kT$

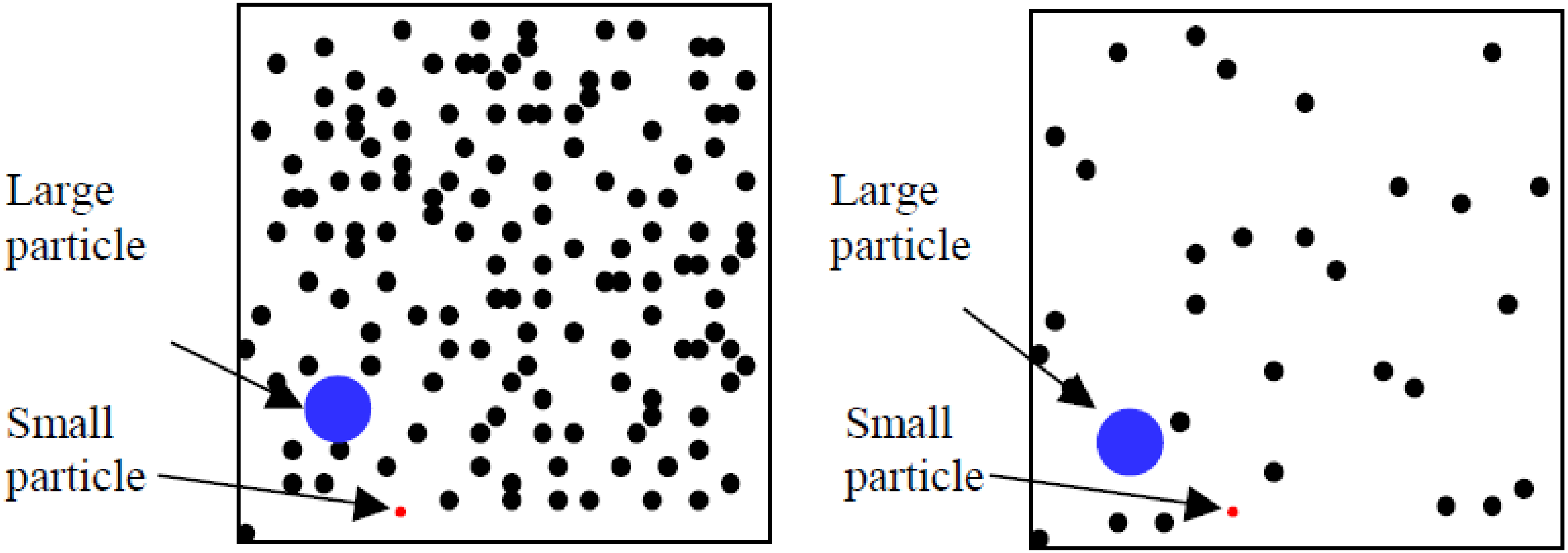
Cross-section

$\sigma \sim \pi d^2$

Rigorous Hard Sphere Collisions: $\lambda = kT / \sqrt{2}\, \pi d^2 P$

$\sigma_{Ar} = 2.6\times10^{-15}\,cm^2 \quad \rightarrow \quad \lambda_{Ar}(cm) \sim 8 / P\ (mTorr)$

MFP Illustration



- Effect of pressure $\lambda \propto \frac{1}{p}$
- Lower pressure, longer MFP

Movement of Charged Particle

- Electron is much lighter than ion

$$m_e << m_i$$

$$m_e : m_{Hydrogen} = 1:1836$$

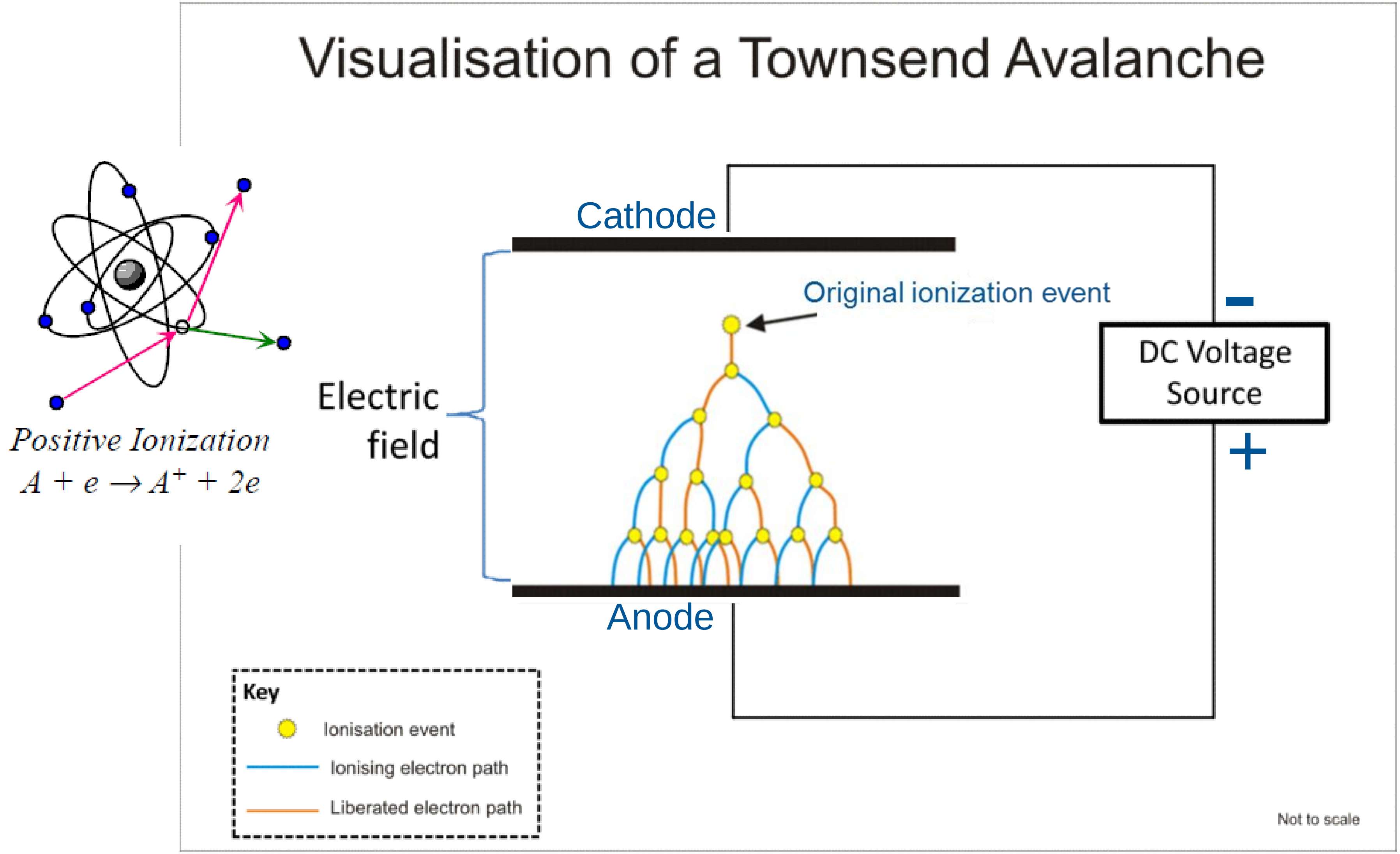
- Electric forces on electrons and ions are the same

$$F = qE$$

- Electron has much higher acceleration

$$a = F/m$$

How is a Plasma produced?

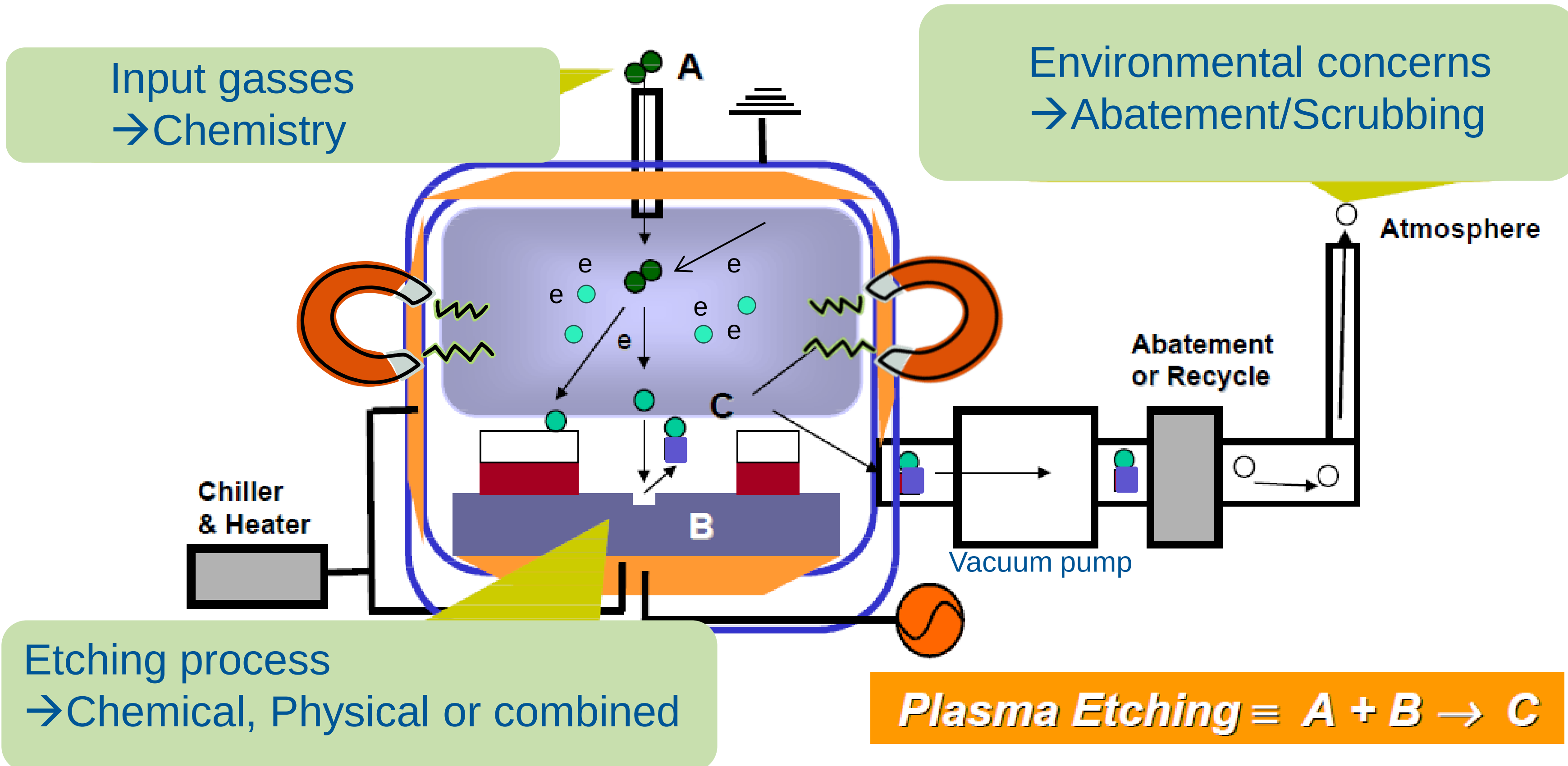


- Gas breakdown by Avalanche Ionization

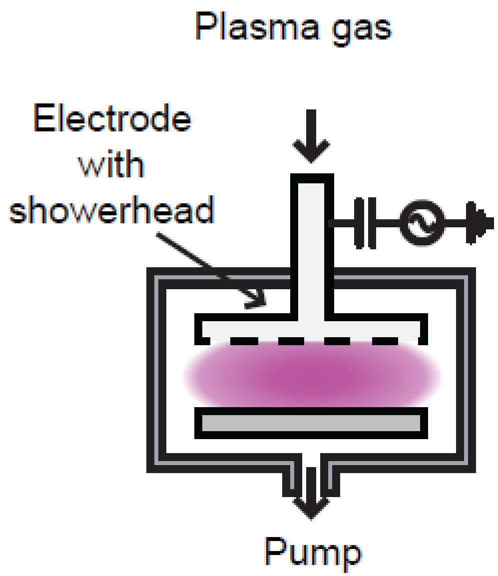
Plasma Etch Chambers

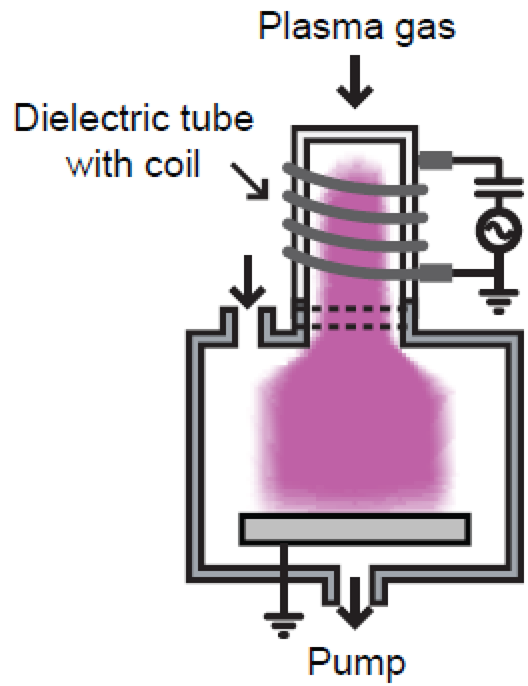
- Etch prefer lower pressure
  - longer MFP, more ion energy and less scattering
- Low pressure, long MFP, less ionization collision
  - hard to generate and sustain plasma
- Magnets are used to force electron spin and travel longer distance to increase collisions

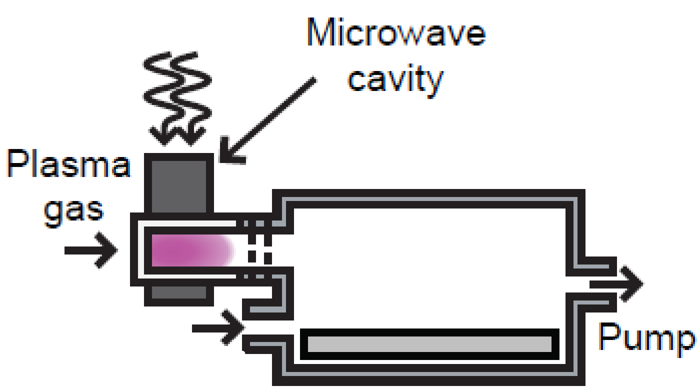
Basic Plasma Etch Tool

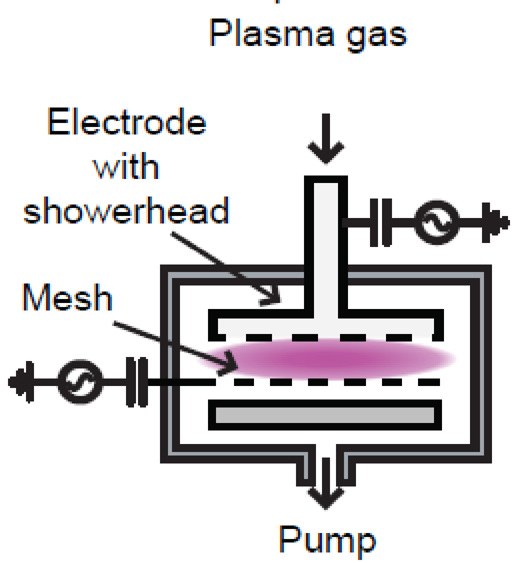


Various Plasma chamber configuration types

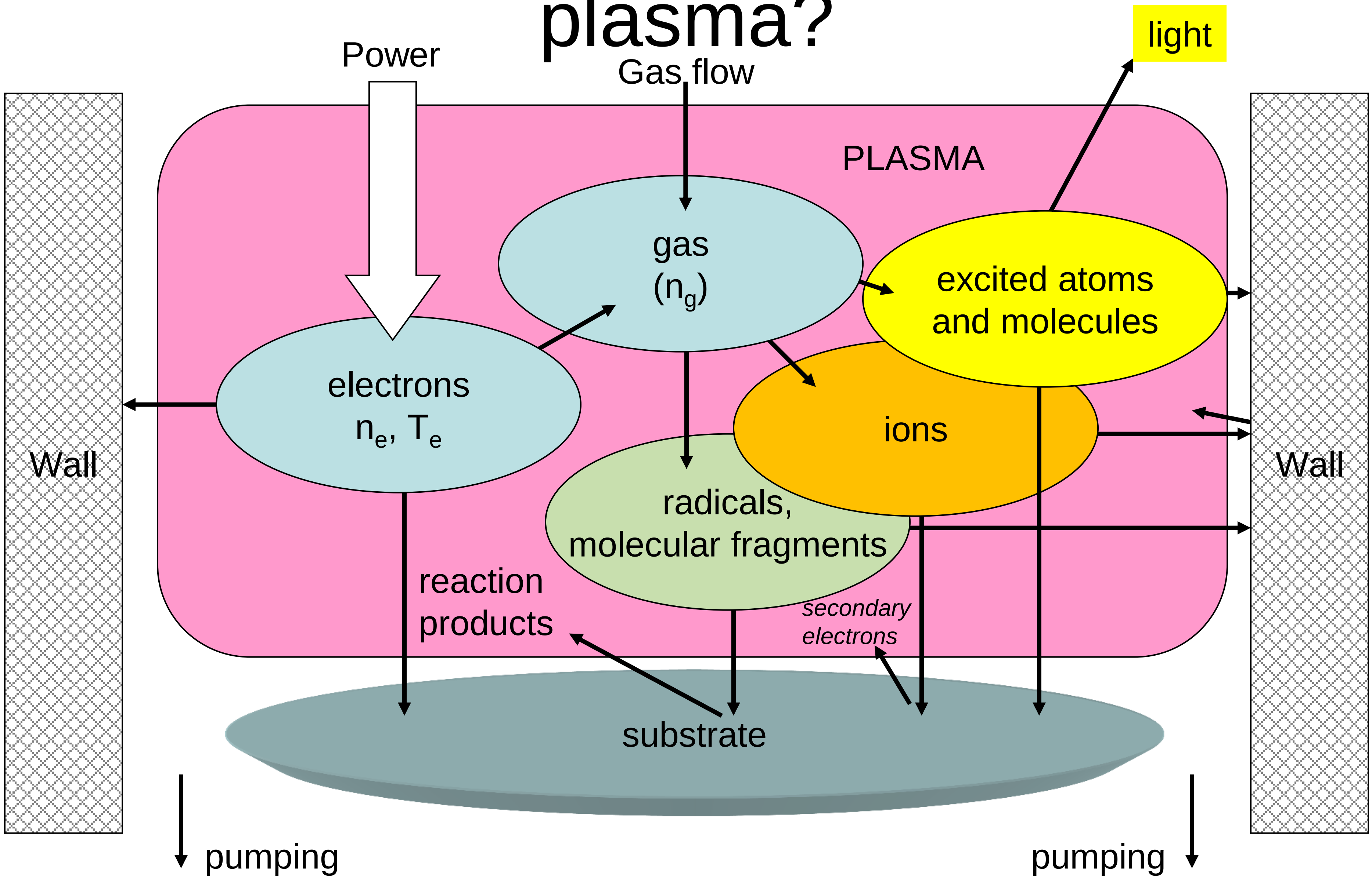




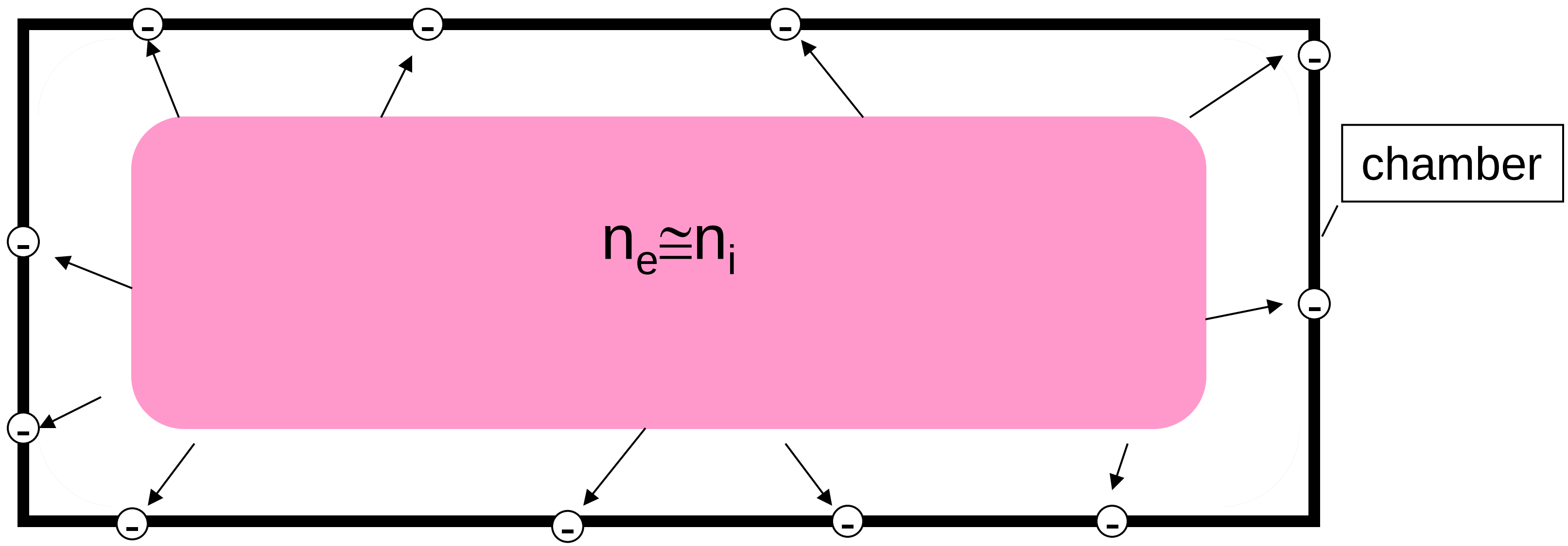




What do we need to know about plasma?



Electron and Ion Loss to the Substrate and Walls
- *the plasma sheath* -

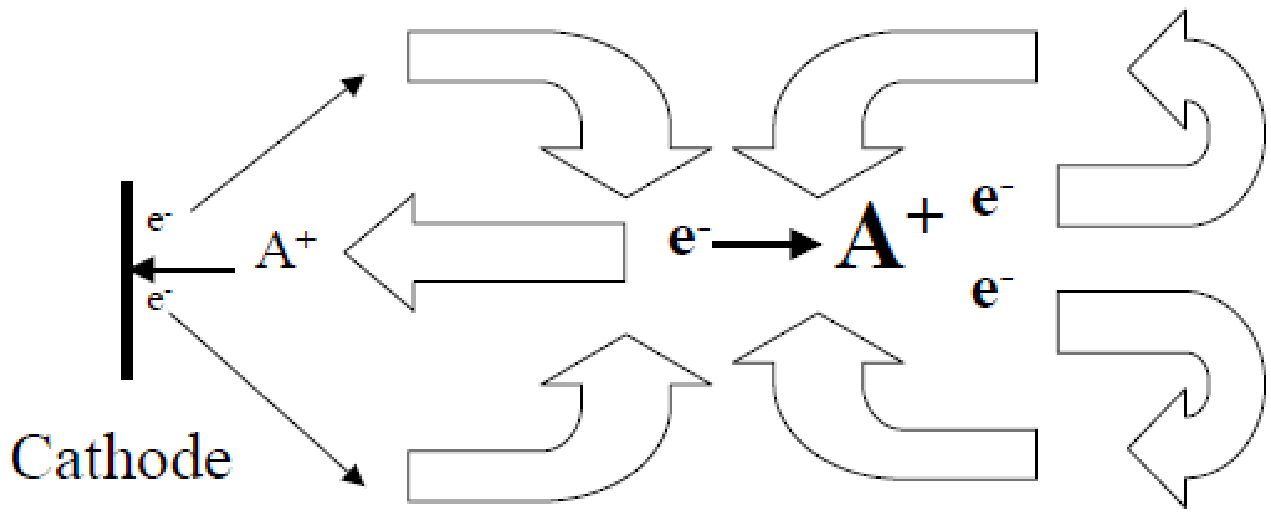


electrons are much more mobile than ions

$$\mu_e = q\langle t\rangle/m_e >> q\langle t_i\rangle/m_i = \mu_i$$

DC Glow Discharge

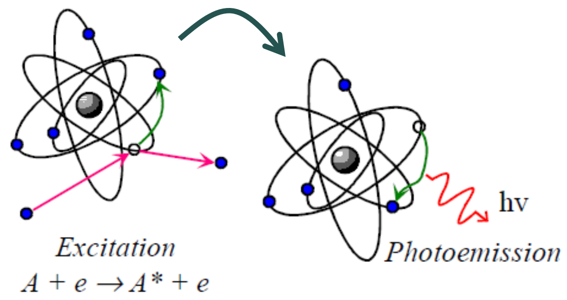
- **Free electrons from secondary emission and from ionization are accelerated in the field to continue the above processes, and a steady state self-sustaining discharge is obtained.**



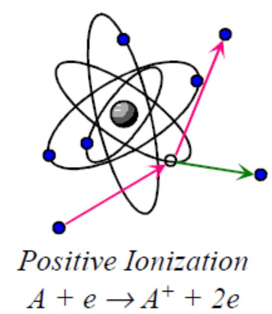
Electron Collisions

- Elastic Collisions:
  - $Ar + e \rightarrow Ar + e$
  - Gas heating: energy is coupled from *e* to the gas

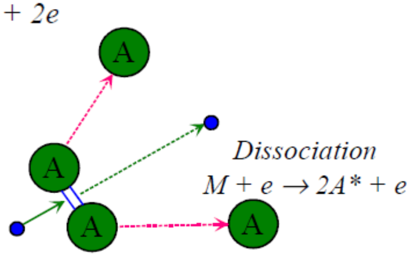
- Excitation Collisions
  - $Ar + e_{hot} \rightarrow Ar^{*} + e_{cold}$, $Ar^{*} \rightarrow Ar + h\nu$
  - Responsible for the characteristic plasma "glow"
  - $E_{electron} > E_{exc}$ (~11.55 eV for argon)



- Ionization Collisions:
  - $Ar + e_{hot} \rightarrow Ar^{+} + 2e_{cold}$
  - electrical energy into producing more e^{-}
  - $E_{electron} > E_{iz}$ *(15.76 eV for argon)*

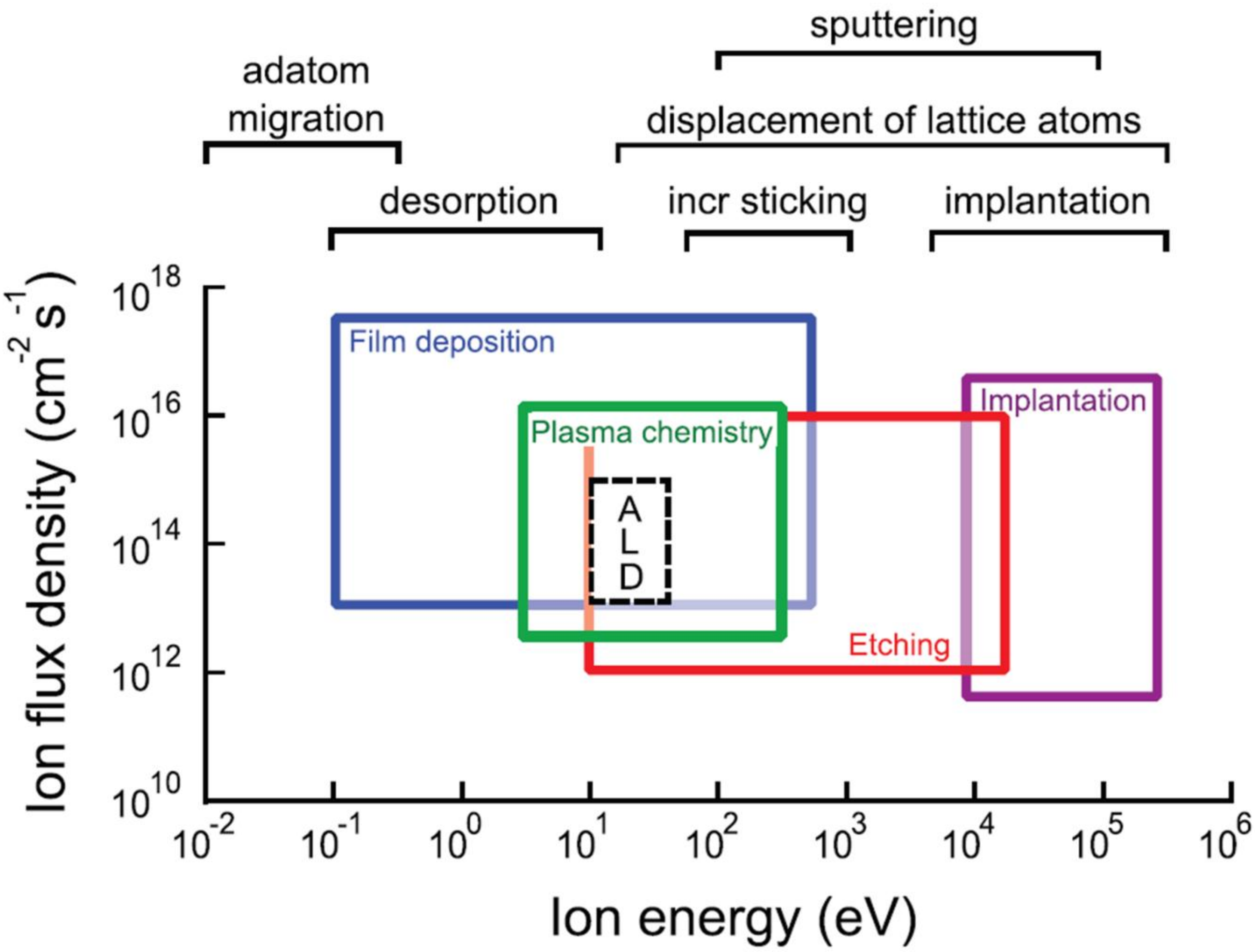


- Dissociation:
  - $O_2 + e_{hot} \rightarrow 2O + e_{cold}$ or $O_2 + e_{hot} \rightarrow O + O^{+} + 2e_{cold}$
  - Creates reactive chemical species within the plasma
  - $E_{electron} > E_{diss}$ (5.12 eV for oxygen)



Dry Etching Spectrum

Pressure		Energy
Low <100 mTorr	**Physical (Sputtering)** Momentum Transfer Directional Etch Possible Poor Selectivity Radiation Damage Possible	High Energy
100 mTorr	**Reactive Ion Etching** Physical and Chemical Variable Anisotropy Variable Selectivity	
400 mTorr	**Chemical Plasma Etching** Fast Isotropic High Selectivity Low radiation Damage Surface modification (oxidation, nitridation, etc…)	Low Energy



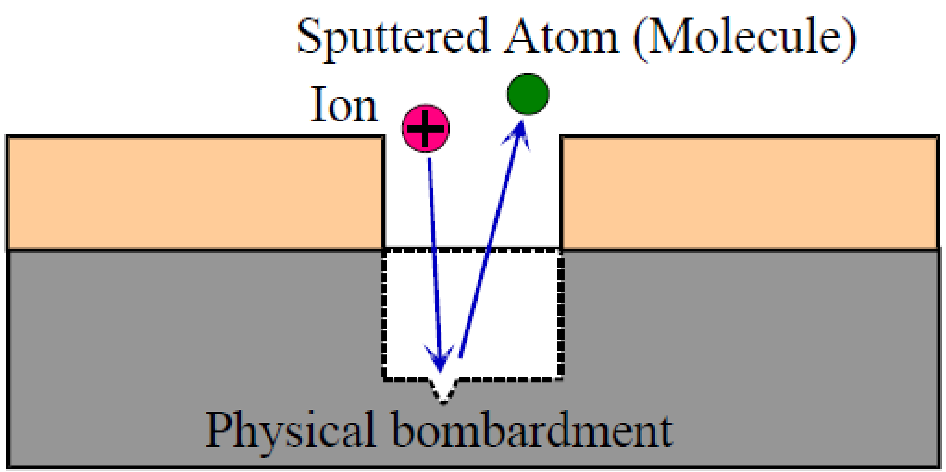
Flux of 10^{15} ~1 monolayer per second

Basic Methods of Plasma Etching

1. ‘Sputtering’ Etching
2. ‘Chemical’ Etching
3. Energetic Ion Enhanced Etching
4. Protective Ion Enhanced Etching

1. Physical (Sputtering)

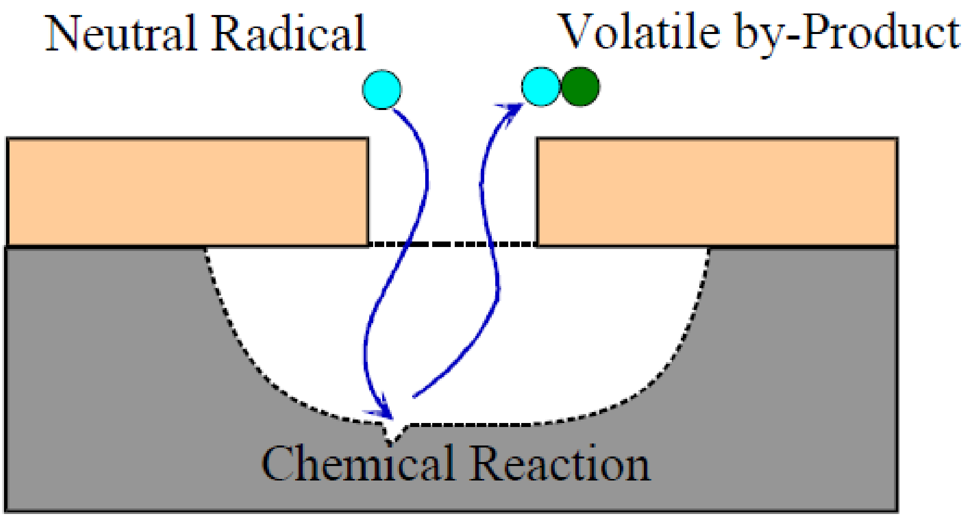
The ion energy mechanically ejects substrate material



- Anisotropic
- by Purely Physical Process
- High Directionality
- Low Pressure
  : long mean free path
- Single Wafer Type
- Low Etch rate

2.Chemical

Thermalized neutral radicals chemically combine with substrate material forming volatile products

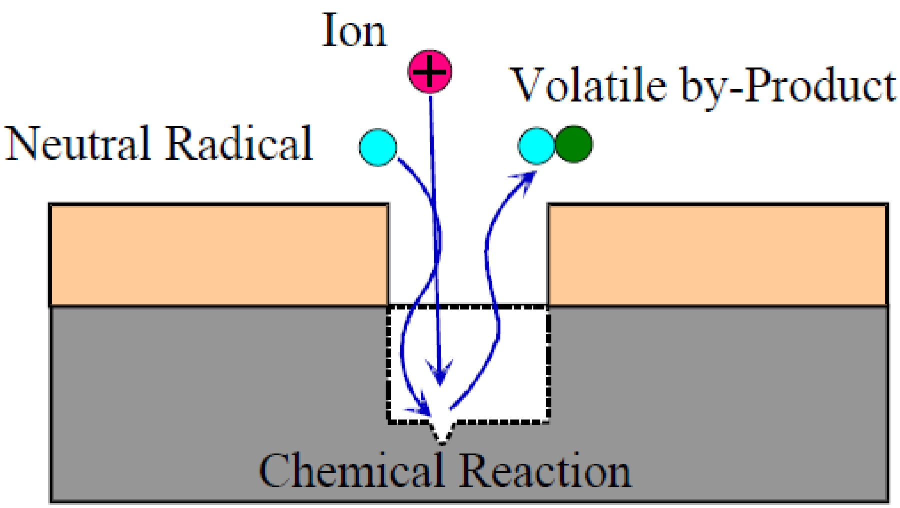


- Isotropic
- Purely Chemical Reaction
- High Pressure
- Batch Wafer Type
- Less Electrical Damage

Physical + Chemical:

3.Energetic Ion Enhanced

Ion bombardment enhances or promotes the reaction between an active species and the substrate material

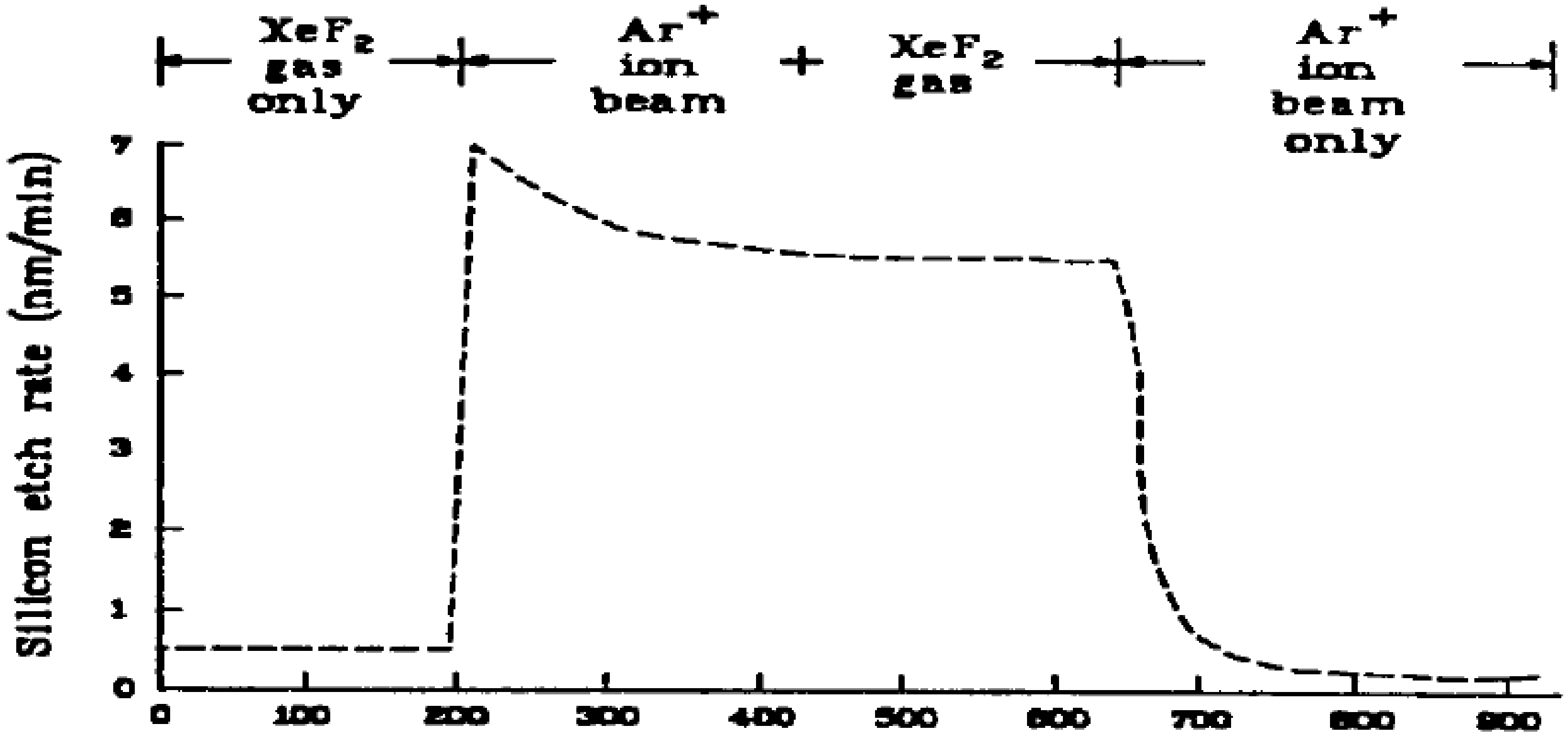


- Damage Enhanced Chemical Reactivity
- Chemical Sputtering
- Chemically Enhanced Physical Sputtering
- Removal of Polymer as a By-product
- Ion Reaction

The ions enhance the chemical etching mechanisms and allow **anisotropic** etching

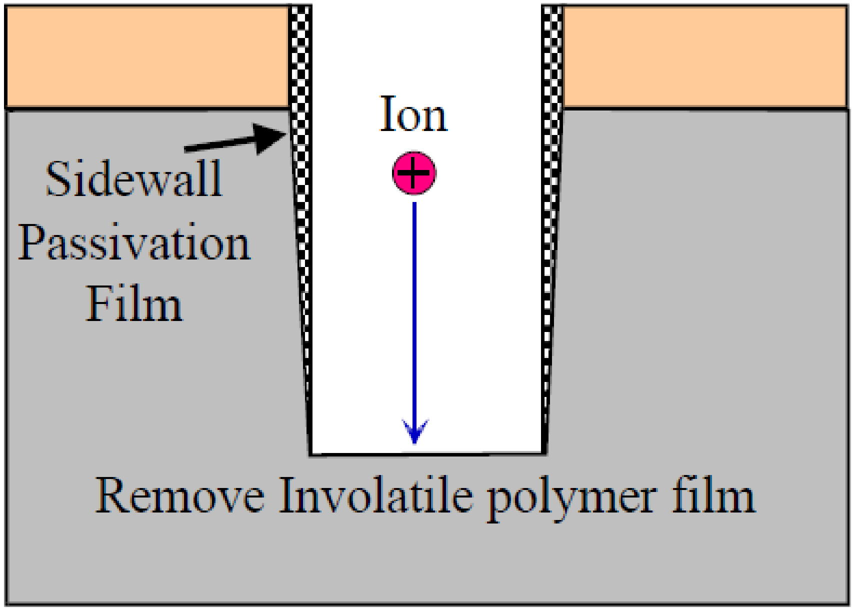
Example of Ion Enhanced Etching

Ar/ XeF_2 Chemistry *for etching Silicon*



4.Protective Ion Enhanced

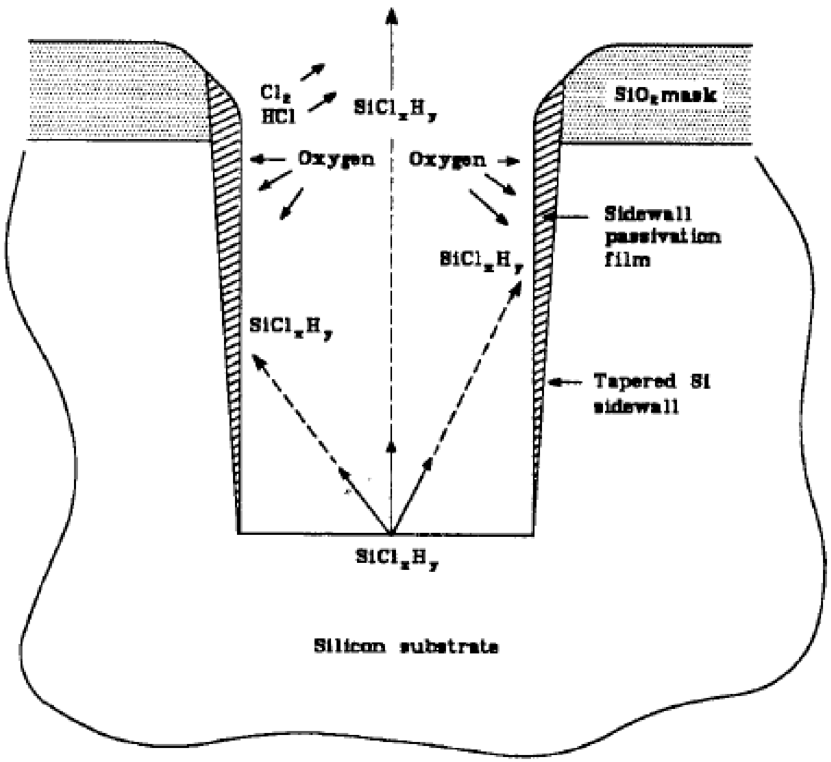
An inhibitor film coats the surface forming a protective barrier which excludes the neutral etchant



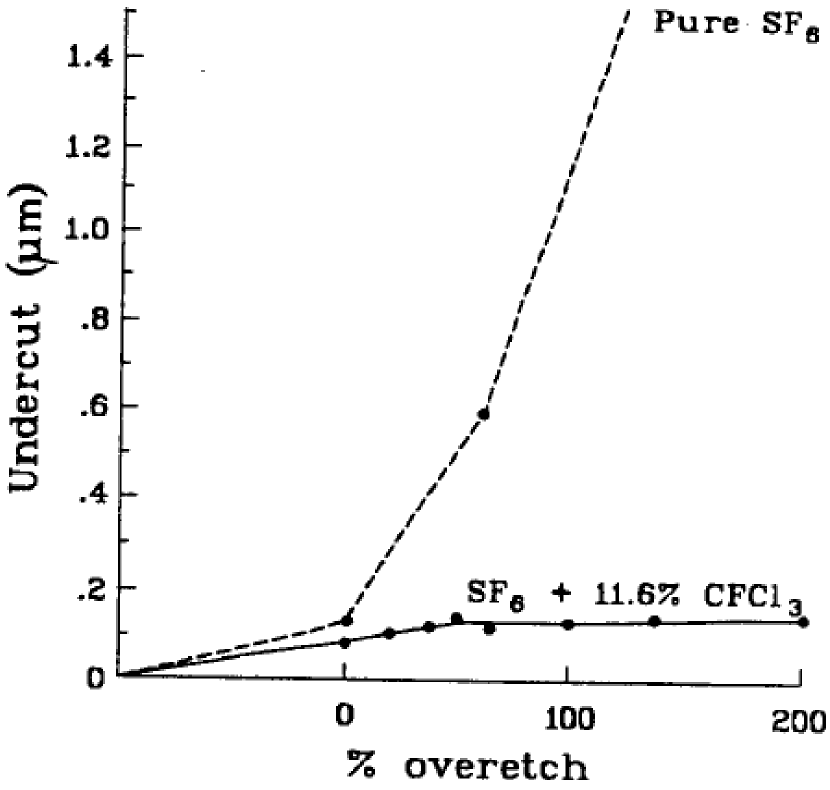
- Sidewall Passivation
- Stopping lateral attack by neutral radical
- Ion directionality
- Involatile polymer film
- Additive film former
  (N_2 , HBr, BCl_3, CH_3F…..)

Examples of Protective Etching

$HCl/O_2/BCl_3$ Chemistry

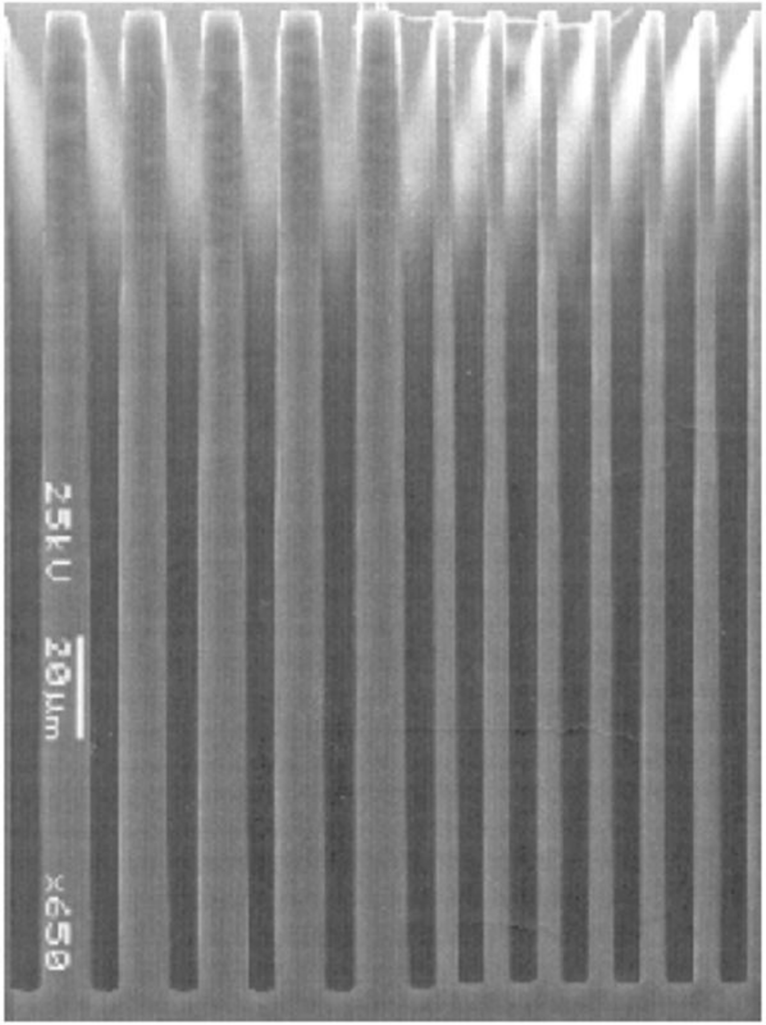


SF_6/ $CFCl_3$ Chemistry



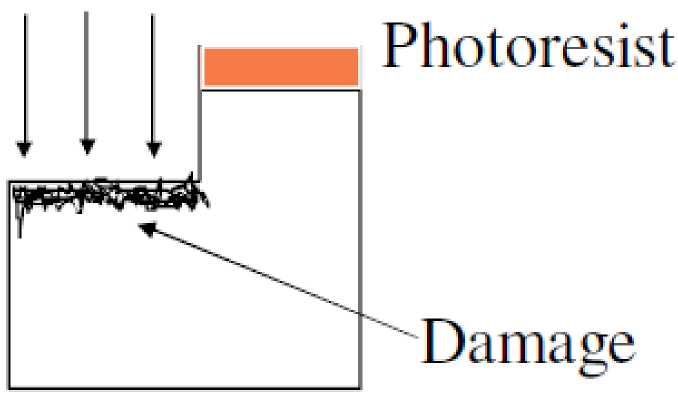
Example of protective etching

- 5µm spaces
- 200µm etch depth
- 40:1 aspect ratio
- 2µm/min Si etch rate
- >75:1 selectivity to photoresist



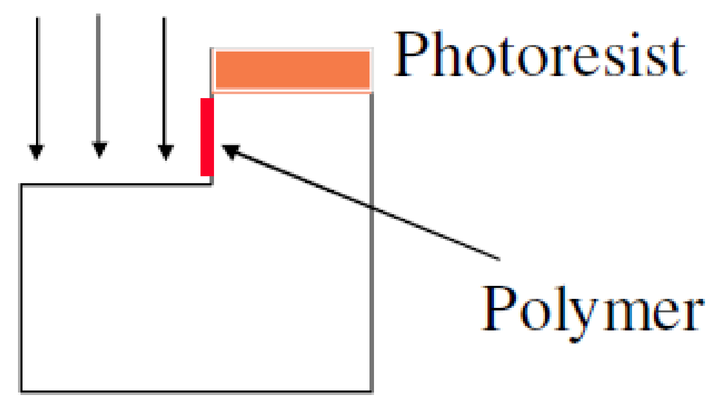
Anisotropic etch mechanisms

SURFACE DAMAGE



Speeds chemical reaction
on horizontal surfaces

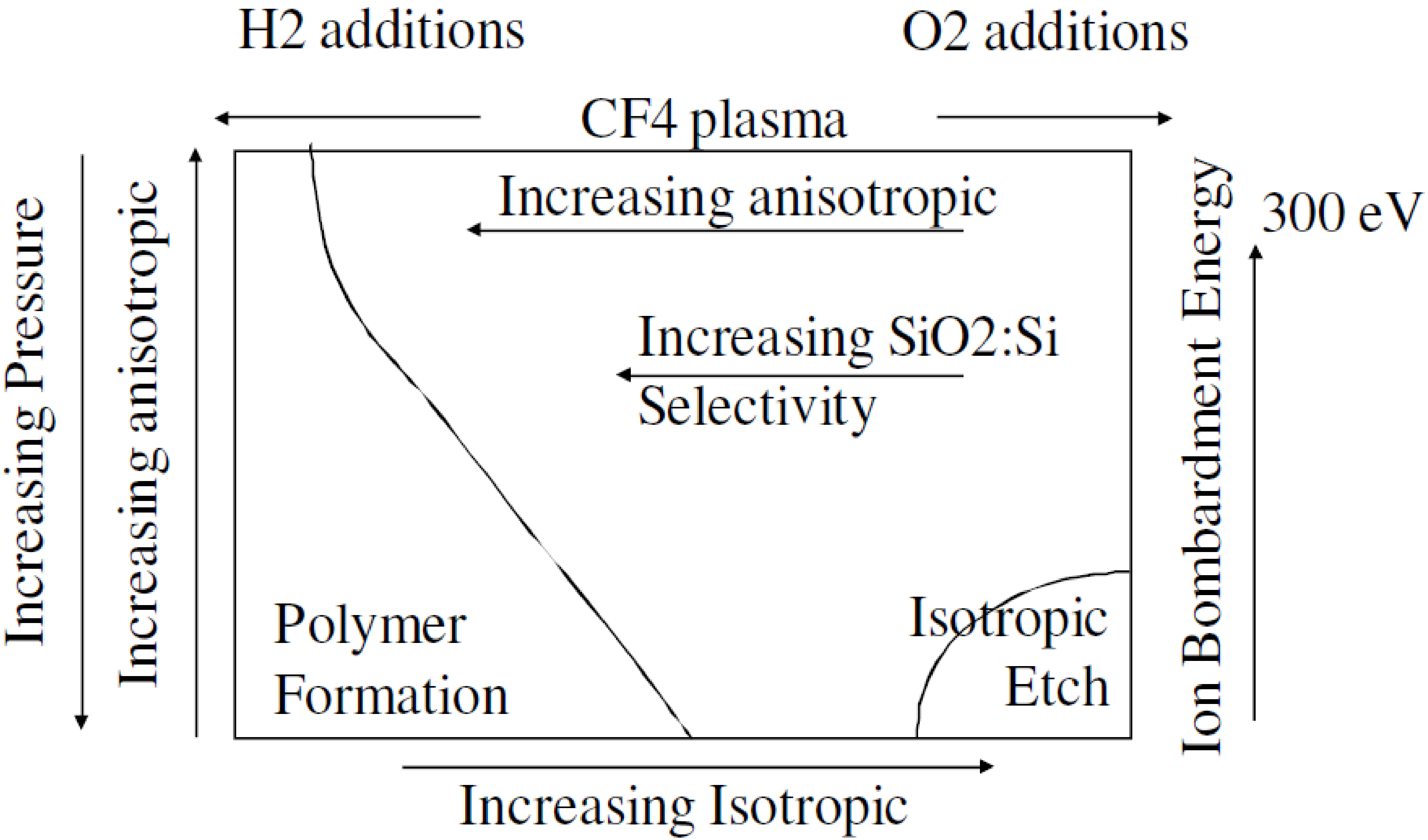
SURFACE INHIBITOR



Slows chemical reaction
on vertical surfaces

Chemistry used to optimize etch

Si SiO$_2$ + CF$_4$ + [H$_2$ or O$_2$] → many different etch results→ Chemistry!!

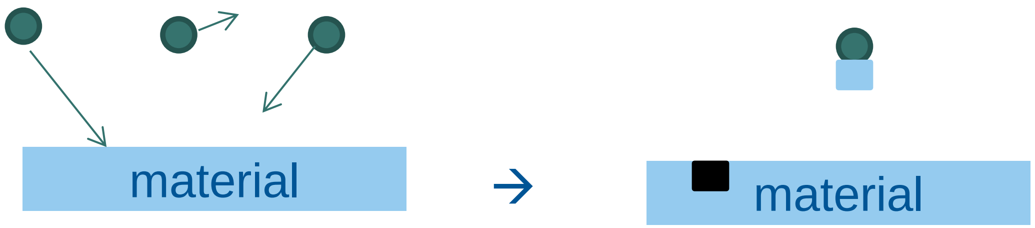


Plasma processing for integrated circuits
Outline

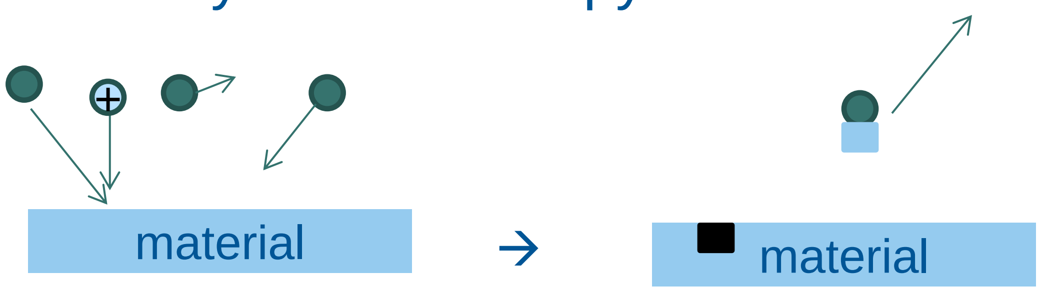
- Introduction to semiconductor processing –chips-
- Definition of a glow discharge –plasma-
- Plasma Etch Chemistry -the magic in the process-
- Atomic Layer Etch (neutral beam plasma etching)

The Desired Dry Etching Process

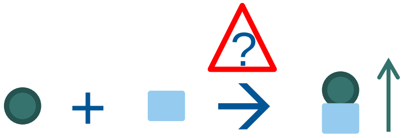
- Reactant + Material → <u>volatile products</u>

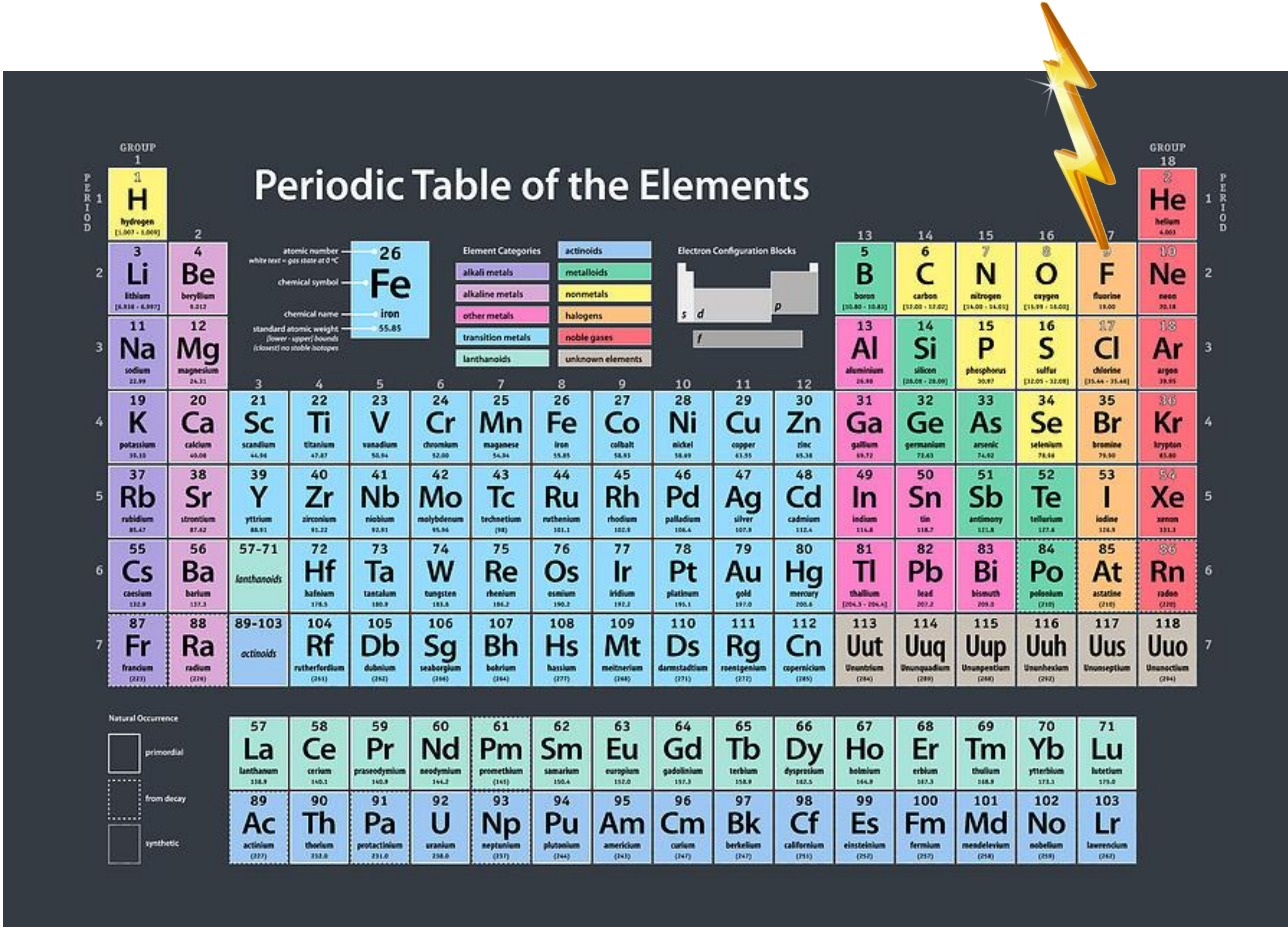


*Can add reactivity and/or isotropy→ still need volatile products!

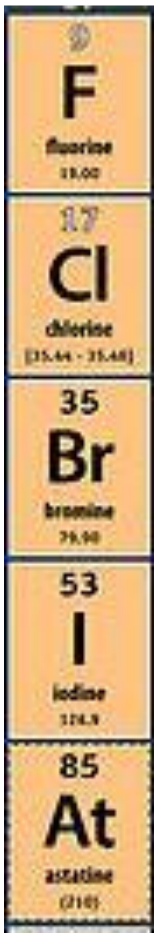


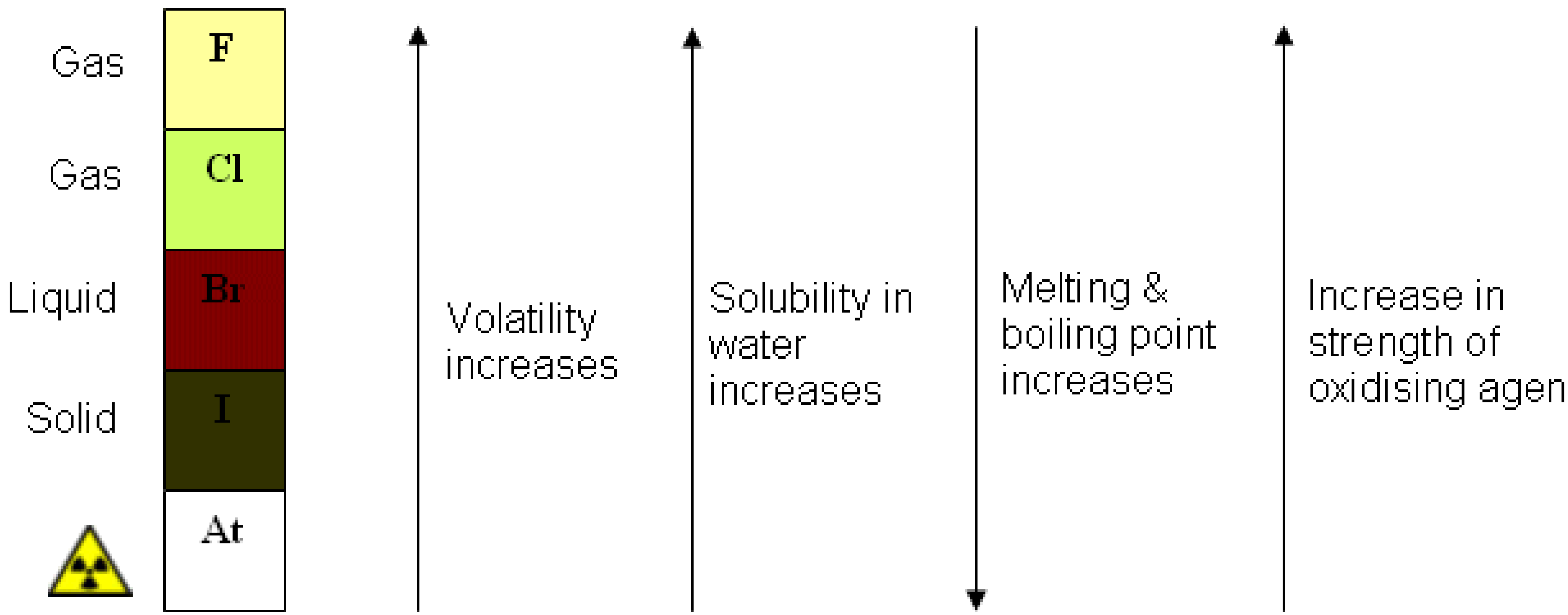
→ Requires Chemistry Understanding!!




Periodic Table of the Elements
GROUP 1
GROUP 18
PERIOD
atomic number
chemical symbol
chemical name
standard atomic weight
26 Fe iron 55.85
Element Categories
alkali metals
alkaline metals
other metals
transition metals
lanthanoids
actinoids
metalloids
nonmetals
halogens
noble gases
unknown elements
Electron Configuration Blocks
s d p f
Natural Occurrence
primordial
from decay
synthetic
1 H hydrogen
2 He helium
3 Li lithium
4 Be beryllium
5 B boron
6 C carbon
7 N nitrogen
8 O oxygen
9 F fluorine
10 Ne neon
11 Na sodium
12 Mg magnesium
13 Al aluminium
14 Si silicon
15 P phosphorus
16 S sulfur
17 Cl chlorine
18 Ar argon
19 K potassium
20 Ca calcium
21 Sc scandium
22 Ti titanium
23 V vanadium
24 Cr chromium
25 Mn maganese
26 Fe iron
27 Co colbalt
28 Ni nickel
29 Cu copper
30 Zn zinc
31 Ga gallium
32 Ge germanium
33 As arsenic
34 Se selenium
35 Br bromine
36 Kr krypton
37 Rb rubidium
38 Sr strontium
39 Y yttrium
40 Zr zirconium
41 Nb niobium
42 Mo molybdenum
43 Tc technetium
44 Ru ruthenium
45 Rh rhodium
46 Pd palladium
47 Ag silver
48 Cd cadmium
49 In indium
50 Sn tin
51 Sb antimony
52 Te tellurium
53 I iodine
54 Xe xenon
55 Cs caesium
56 Ba barium
57-71 lanthanoids
72 Hf hafnium
73 Ta tantalum
74 W tungsten
75 Re rhenium
76 Os osmium
77 Ir iridium
78 Pt platinum
79 Au gold
80 Hg mercury
81 Tl thallium
82 Pb lead
83 Bi bismuth
84 Po polonium
85 At astatine
86 Rn radon
87 Fr francium
88 Ra radium
89-103 actinoids
104 Rf rutherfordium
105 Db dubnium
106 Sg seaborgium
107 Bh bohrium
108 Hs hassium
109 Mt meitnerium
110 Ds darmstadtium
111 Rg roentgenium
112 Cn copernicium
113 Uut Ununtrium
114 Uuq Ununquadium
115 Uup Ununpentium
116 Uuh Ununhexium
117 Uus Ununseptium
118 Uuo Ununoctium
57 La lanthanum
58 Ce cerium
59 Pr praseodymium
60 Nd neodymium
61 Pm promethium
62 Sm samarium
63 Eu europium
64 Gd gadolinium
65 Tb terbium
66 Dy dysprosium
67 Ho holmium
68 Er erbium
69 Tm thulium
70 Yb ytterbium
71 Lu lutetium
89 Ac actinium
90 Th thorium
91 Pa protactinium
92 U uranium
93 Np neptunium
94 Pu plutonium
95 Am americium
96 Cm curium
97 Bk berkelium
98 Cf californium
99 Es einsteinium
100 Fm fermium
101 Md mendelevium
102 No nobelium
103 Lr lawrencium

The Halogens

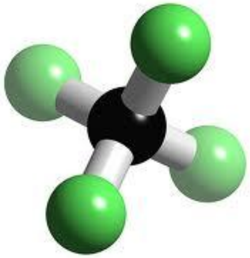


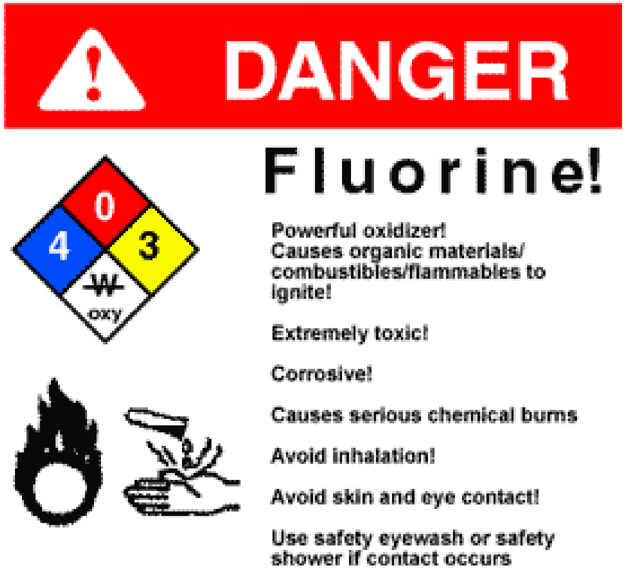


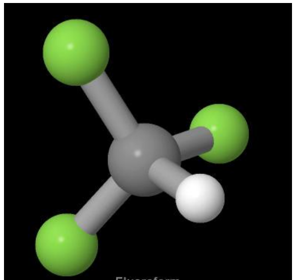
- *Halogens form strong bonds with ‘electropositive’ elements*
- *Halides are relatively volatile*

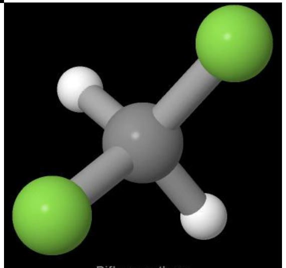
Fluorine

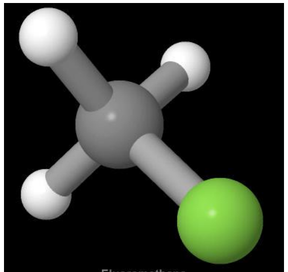
- Widely used in plasma etch of semiconductors (*due to its high reactivity*)
- One of the most reactive elements
    - $Si + CF_4 \rightarrow SiF_4$
    - $W + CF_4 \rightarrow WF_6$
- Wide variety of source gases
    - CF_4
    - CHF_3
    - CH_2F_2
    - CH_3F
    - SF6



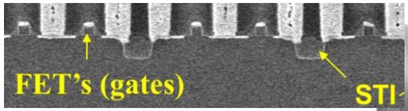


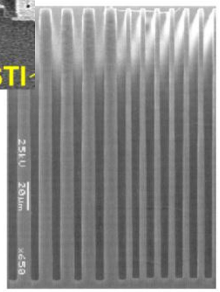

Fluoroform


Difluoromethane

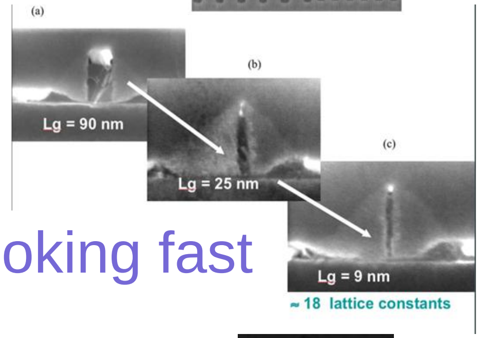

Fluoromethane

Fluorine Plasma application





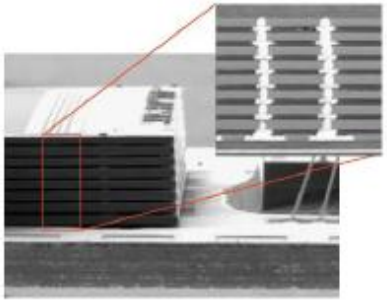
- Shallow (and deep) trench isolation (Si etch)
  - SF_6 plasma
  - Allows PMOS and NMOS on same chip



- Gate sidewall (Poly-Si)
  - CH_3F, CF_4
  - Sidewall is the difference between fast and smoking fast
- Interconnects (SiO_2, SiN)

  - CF_4, CHF_3, C_4F_8
  - Allows path to forms the ‘insulation’ around the wires…

- TSV and Protective over coat
  - Access to the outside world



Source: Samsung

SILICON ETCHING MECHANISM

CF_4 is Freon 14 F/C ratio is 4

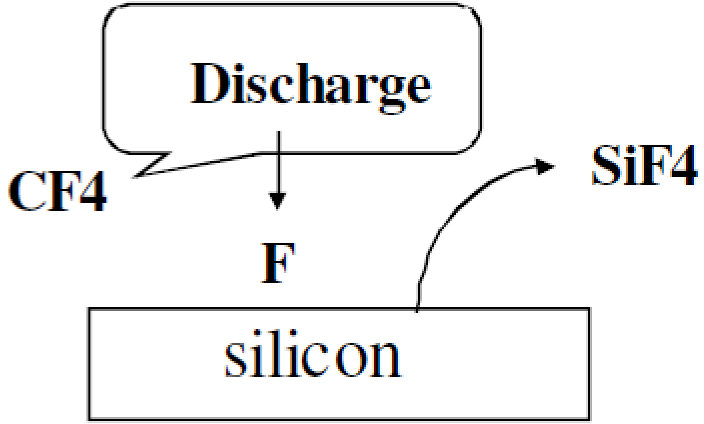
add electron impact to produce fluorine radicals:

$$CF_4 + e \Rightarrow CF_3^+ + F + 2e \quad \text{(Dissociative Ionization)}$$

$$CF_4 + e \Rightarrow CF_3 + F + e \quad \text{(impact dissociation)}$$

1. F radicals adsorb on silicon surface → SiF_4 desorbs
2. CF_3 also adsorbs on surface + F → CF_4 desorbs

- Carbon on surface reduces available reactive F
  - ➢ React with F → volatiles; CF4, etc..⇑
  - ➢ React with F → C-F polymers (inhibits etching)
- High F/C ratio favors etching

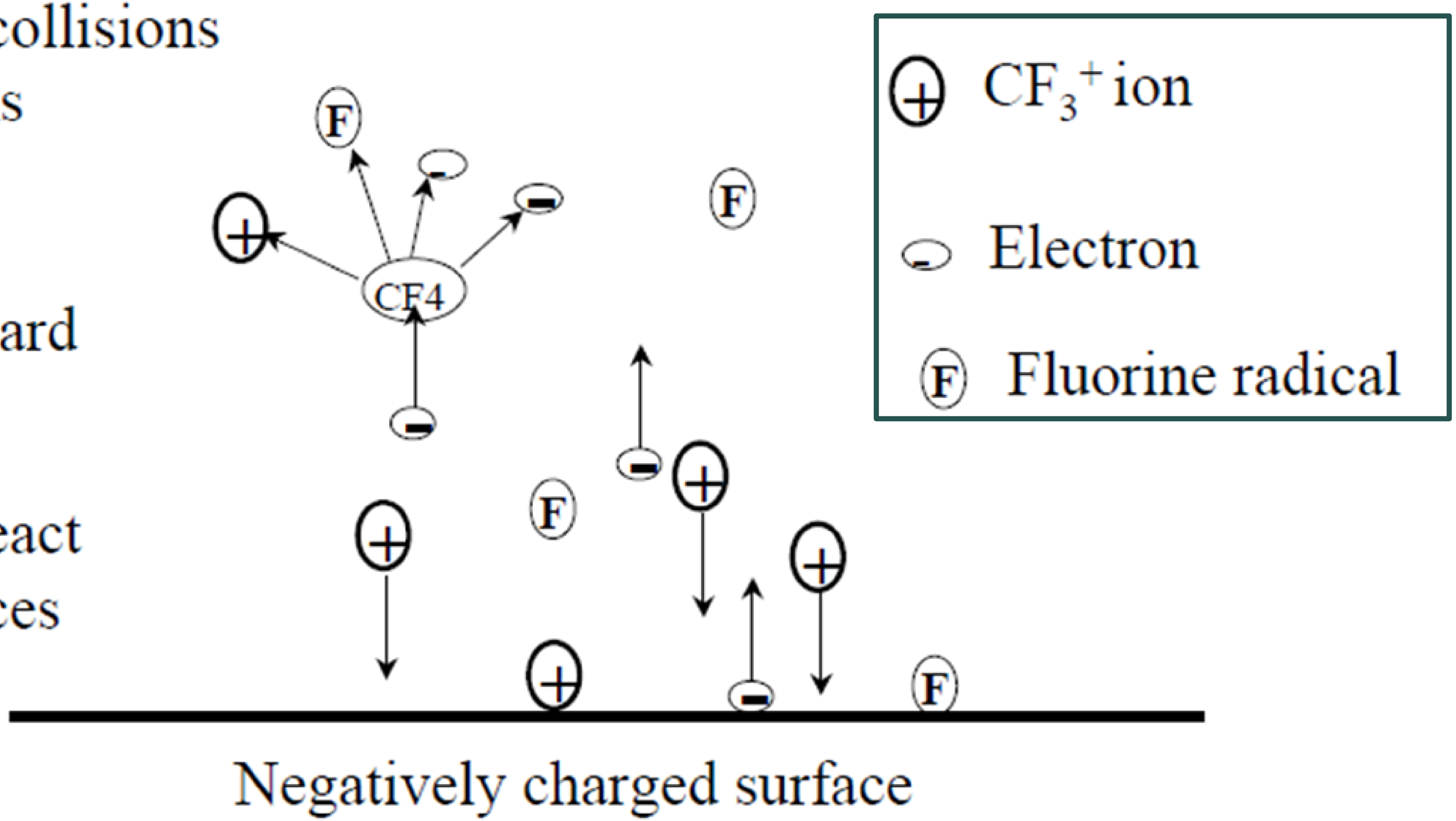


Ion Bombardment at Surfaces

Electron collisions create ions

Ions bombard surfaces

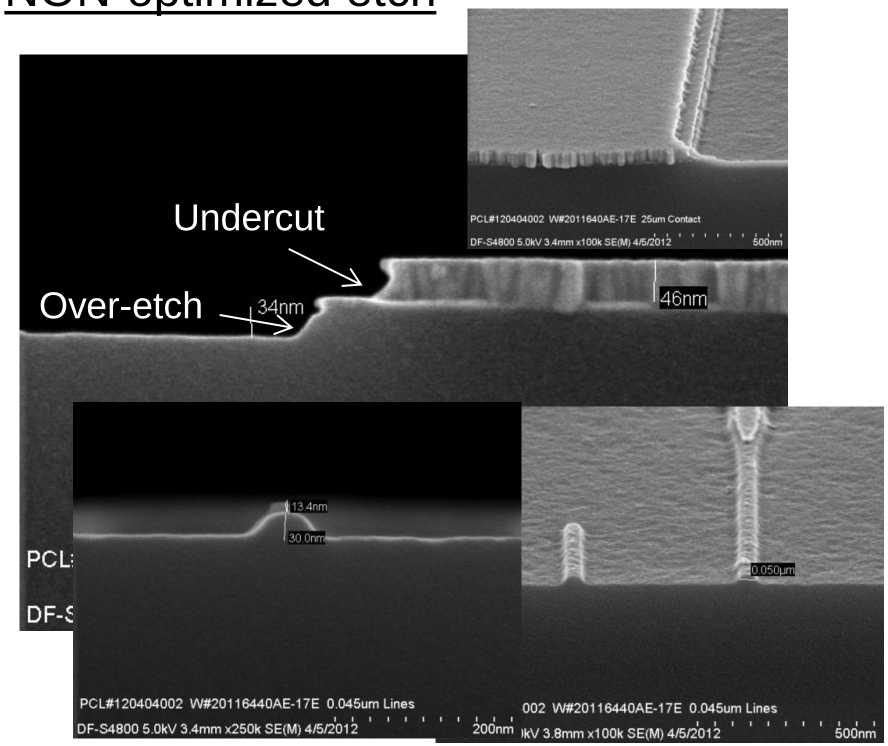
Radicals react with surfaces



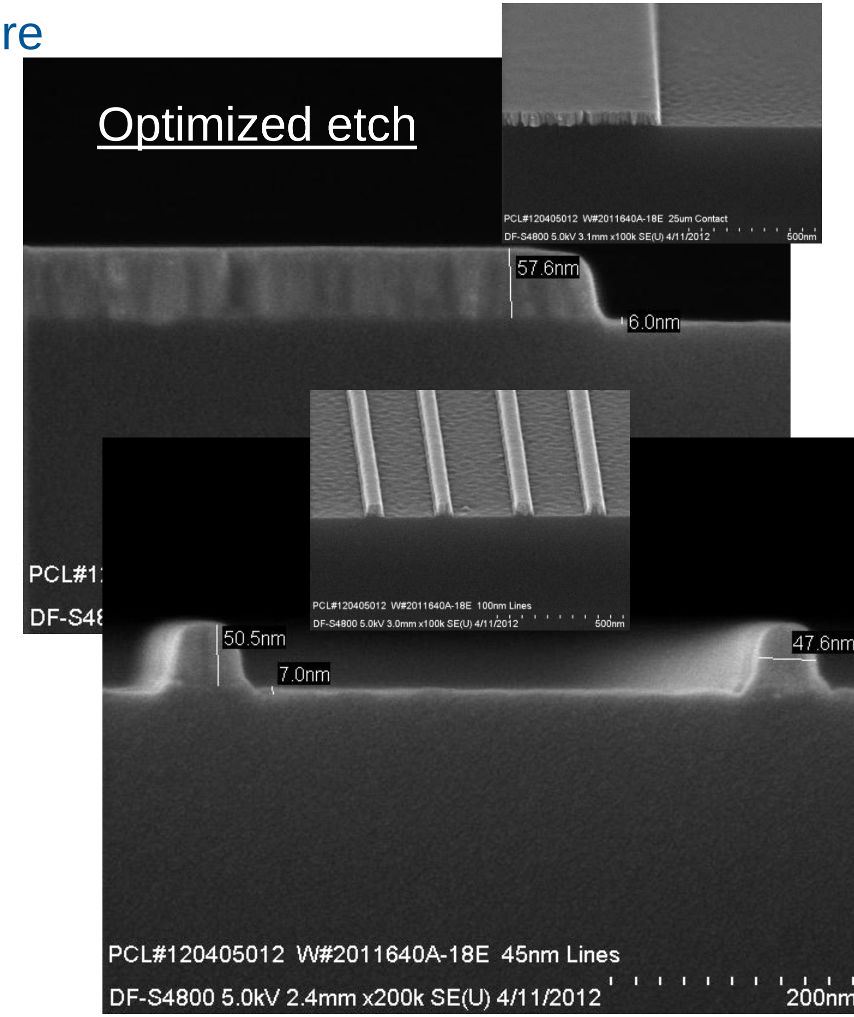
Typical etch optimization experiment

1. Choose gasses
2. Etch test at different power/bias/pressure
3. SEM cross section

NON-optimized etch



Optimized etch



Influencing reactions through Chemistry

- Addition of various gasses can influence the reactions and rates

Hydrogen - reduces fluorine concentration by combination to form HF

- CF4 + e → CF3 + F + e +Si → SiF(4) Lowers etch Si etch rate

  + H → HF ; C/F ratio ↑

Oxygen - Increases fluorine concentration by combining with carbon which would otherwise require fluorine or reacting with CF3 to liberate F

- C + O → CO ↑ or CF3 + O → COF2 + F → C/F ratio ↓

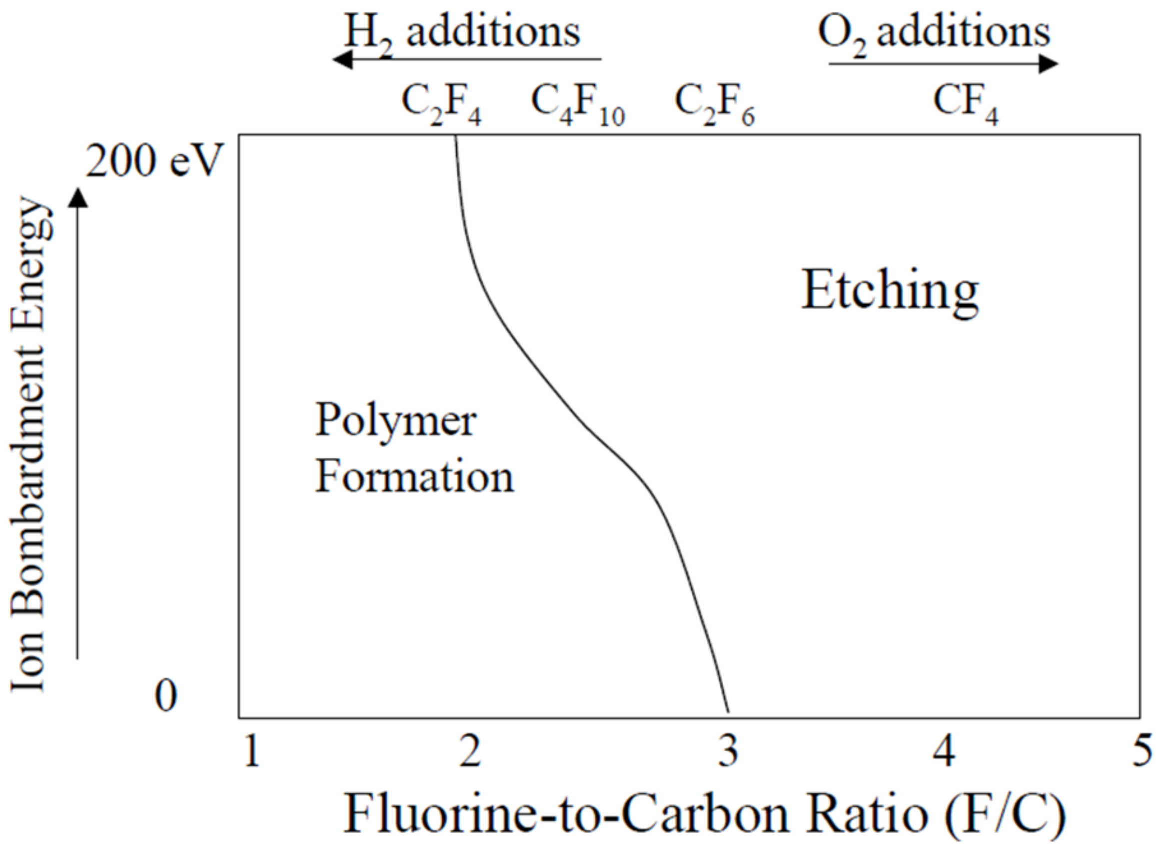
  + F → CF(4)

Argon – Increases plasma density increasing fluorine radical conc.

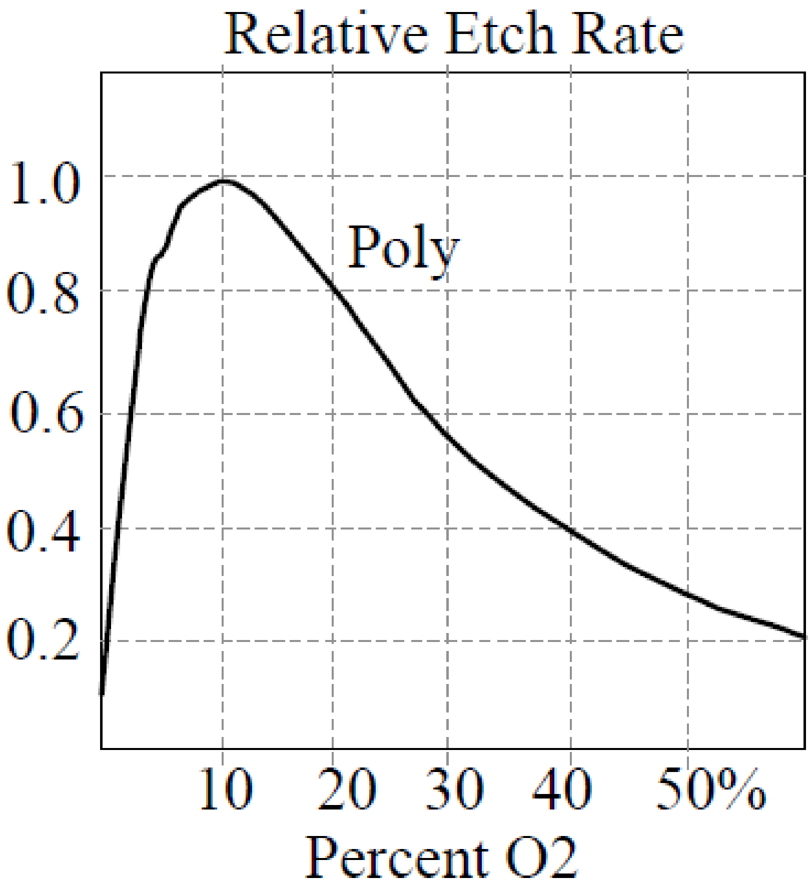
Helium – Carries heat away and helps photoresist survival

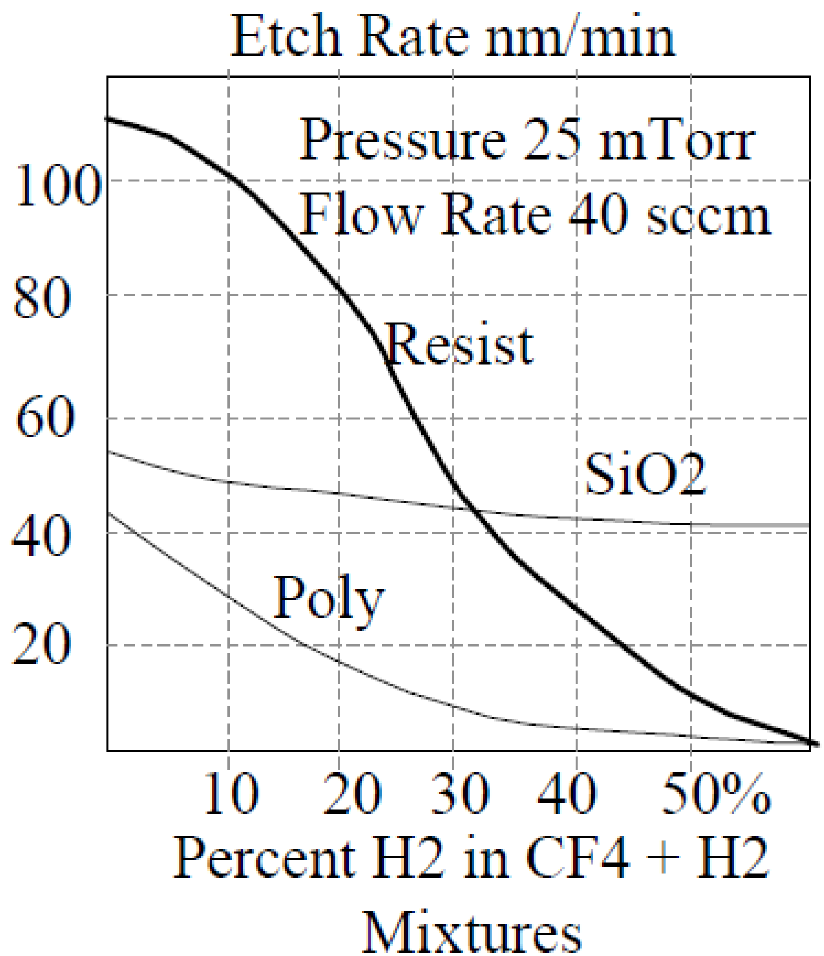
Adjust C:F ratio through F-carrier molecule

Gas	C:F Ratio	SiO2:Si Selectivity
CF4	1:4	1:1
C2F6	1:3	3:1
C3F8	1:2.7	5:1
CHF3	1:3	10:1



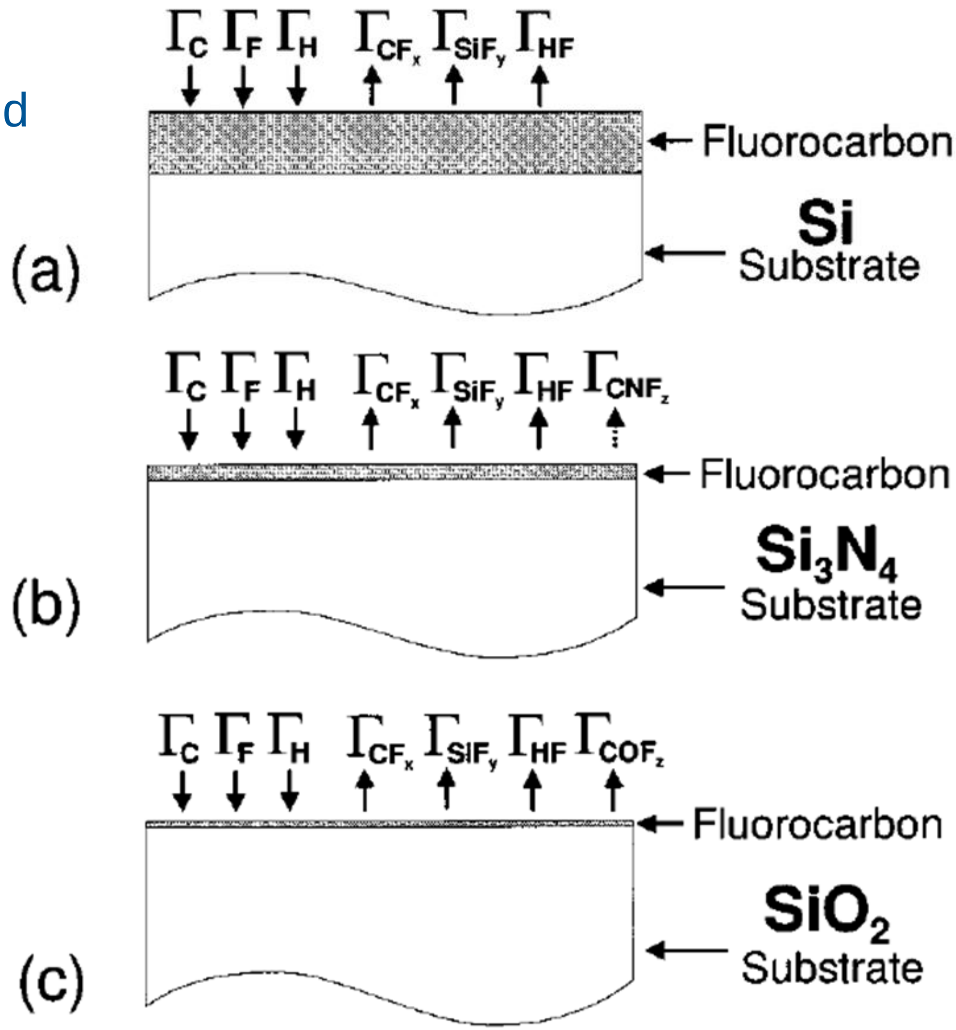
Etch Rates vs Added Gas Concentration





Selectivity mechanism for Si vs SiO_2 (and SiN)

Schematic view of fluxes incident on and outgoing from the surface of (a) Si (b) Si_3N_4 and (c) SiO_2 substrates.



Si film, no volatile product between Si and carbon exists → **thick** steady-state fluorocarbon film can develop.

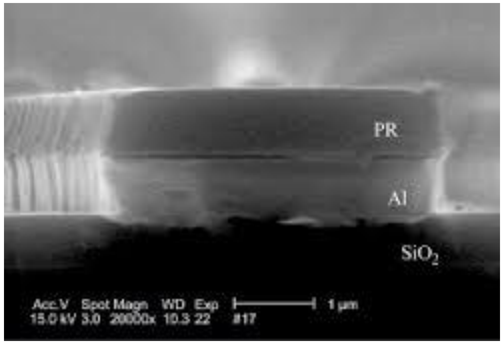
(The Si_3N_4 film has a moderate ability to react with carbon, →steady-state fluorocarbon film of intermediate thickness results)

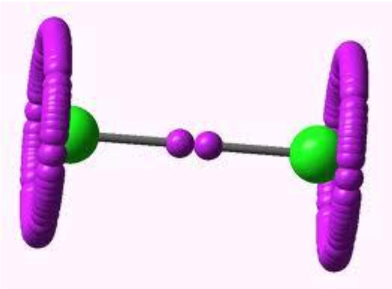
SiO_2 film, most carbon is consumed in reactions with oxygen from SiO_2film → **thin** steady-state fluorocarbon film forms allowing more efficient Si-removal by F

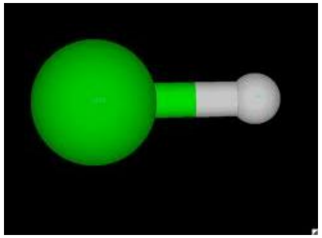
M. Schaepkens, et al., JVST A, 1999

Chlorine

- Very reactive element
  - $Si + Cl_2 \rightarrow SiCl_4$
  - $Al + Cl_2 \rightarrow 2AlCl_3$
- Highly selective gas
  - Cl does not react with SiO_2
- Sources for gas
  - Cl_2
  - HCl
- Application
  - Si and Metals







ALUMINUM ETCHING

BREAKTHROUGH - This is to remove native aluminum oxide (Al_2O_3) from the surface of the wafer by reduction in Hydrogen or by Sputtering by bombardment with Argon at high energies or both. Water vapor will scavenge Hydrogen and grow more Al_2O_3 causing non reproducible initiation times.

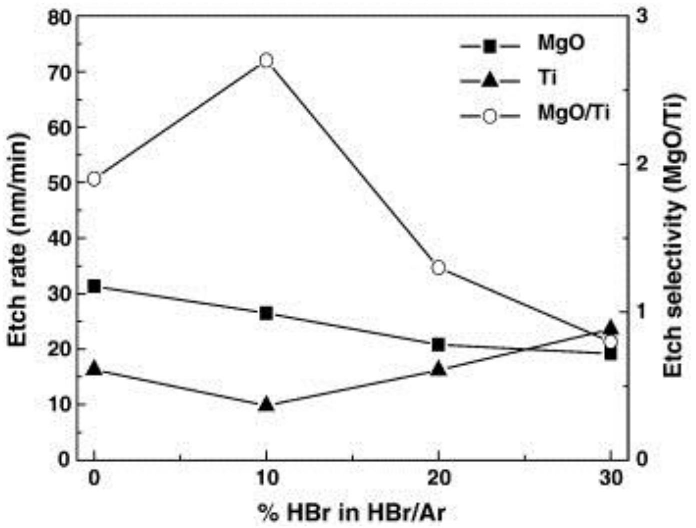
ALUMINUM ETCHING – because AlF3 is not volatile, a Chlorine based etch is needed to etch aluminum. BCl_3, CCl_4, $SiCl_4$ and Cl_2 are all either carcinogenic or highly toxic. As a result the pump oils, machine surfaces and any vapors must be treated carefully. $AlCl_3$ will deposit on chamber walls. $AlCl_3$ is hygroscopic and absorbs moisture that desorbed once a plasma is created causing Al_2O_3 breakthrough problems.

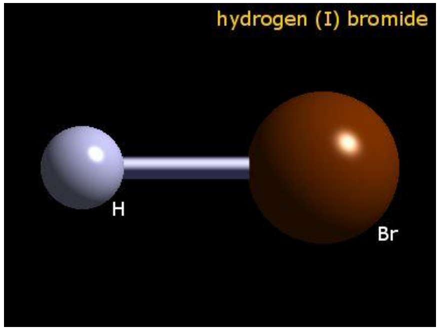
Typical Al etch plasma chemistry:

Cl_2 → Reduces pure Aluminum
BCL_3 → etches native Al_2O_3 (or HfO_2)
N_2 → Dilutant and carrier gas
$CHCl_3$ (Chloroform) → Helps Anisotropy, reduce photo-resist damage

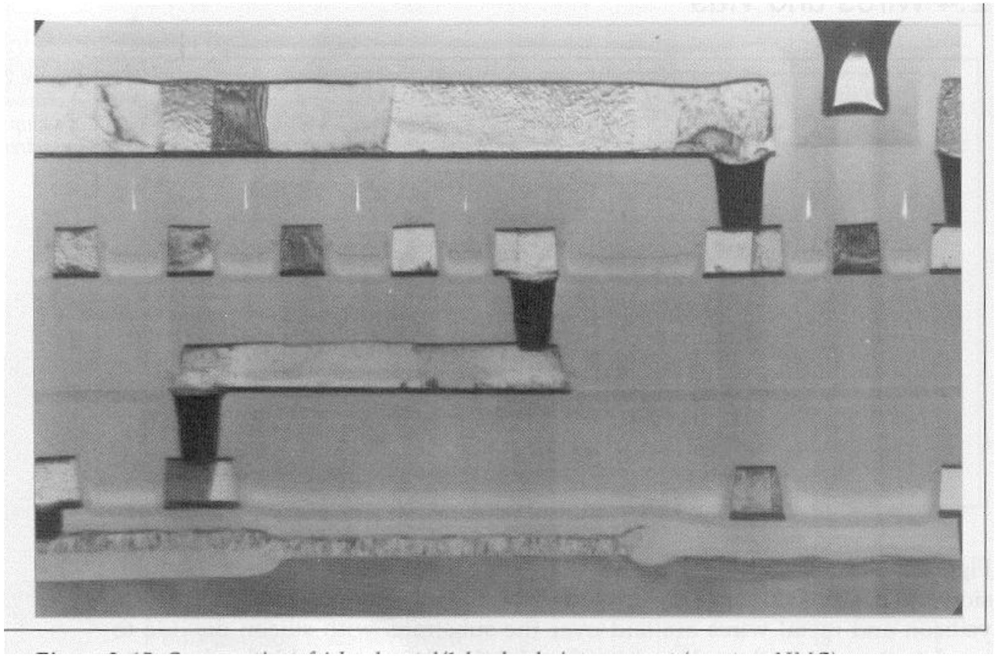
Bromine

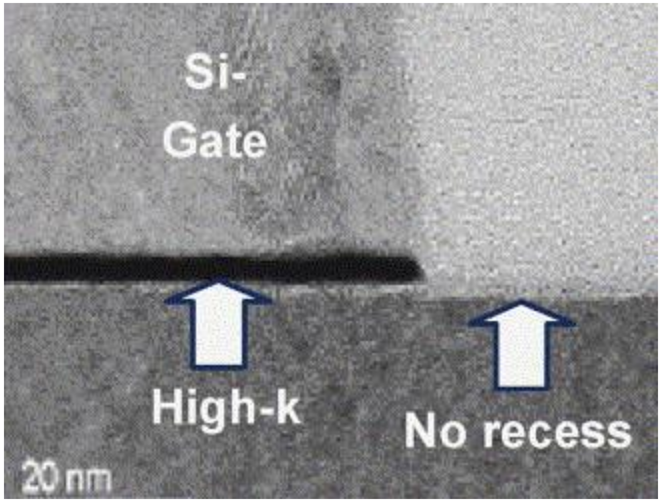
- Br advantage → precision (less reactive / not as spontaneous = slower more selective etch..)
  - $HBr + Si \rightarrow SiBr_4 + H$
  - $HBr + Ti \rightarrow TiBr_4 + H$
  - Good selectivity to oxides (SiO_2, HfO_2, etc..)
  - Br is ‘filet-knife’ (vs. ‘F-based Axe’)
- Major source is HBr
  - Reddish brown liquid
- Handling of HBr
  - Special delivery due to low vapor pressure
  - HBr particles
- Application
  - Metal gate, Si levels

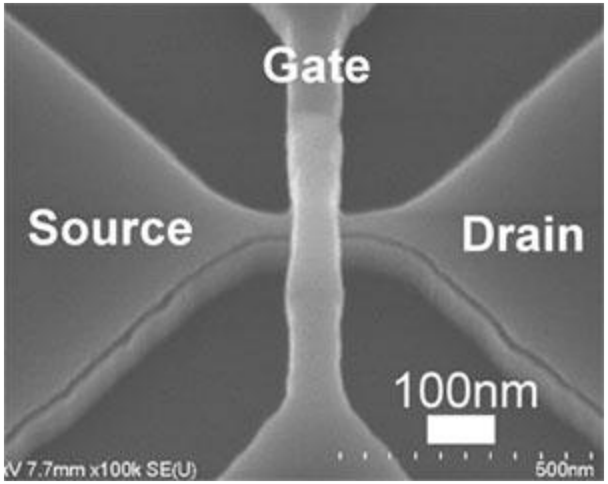




Put it all together







- **We would not have Todays ‘smart’ devices without plasma based etch**

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