Process Engineering Applications of Plasma Technologies
IISc Bangalore
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Plasma Reaction Engineering – Silicon Etch Applications

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Outline:

1. Plasma Reaction Engineering

(i) Plasma physics and Plasma chemistry
(ii) Plasma reactor designs

2. Silicon Etch Applications

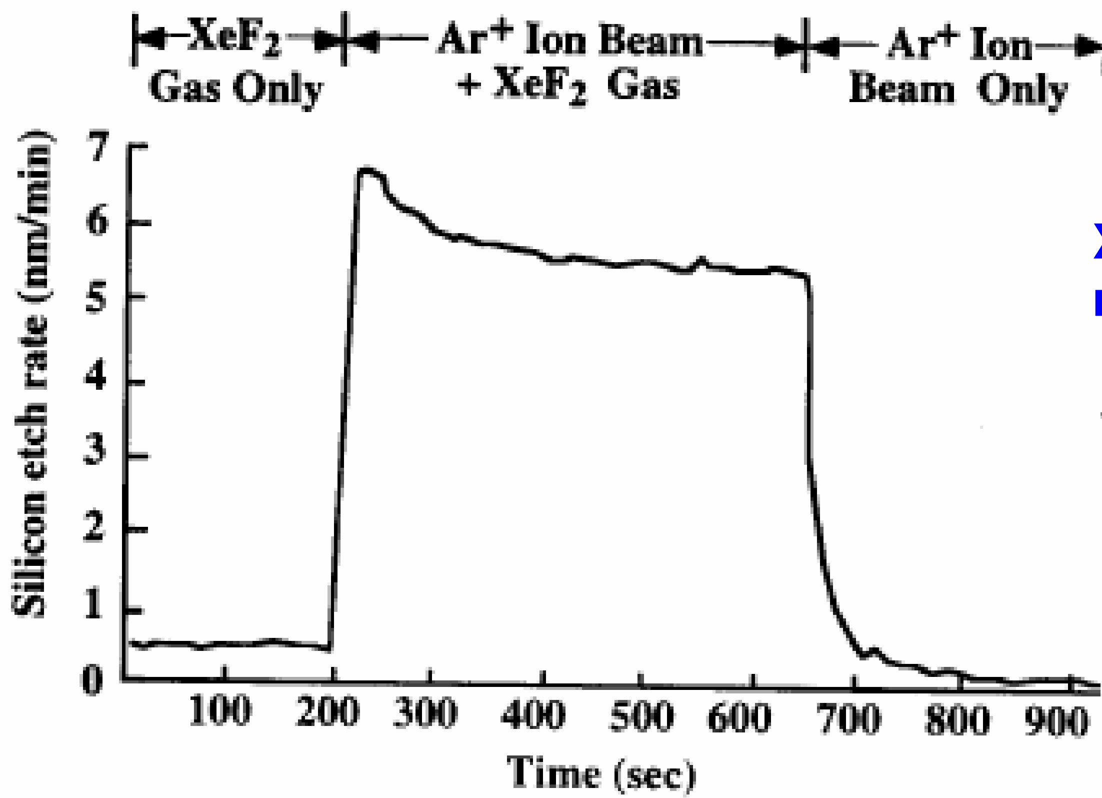
(i) Selected applications
(ii) Plasma silicon etch – mechanisms
(iii) Silicon deep trench – formation dynamics
(iv) Silicon deep trench – etch issues
(a) RIE lag (b) Loading (c) Charging effects

3. Summary and Outlook

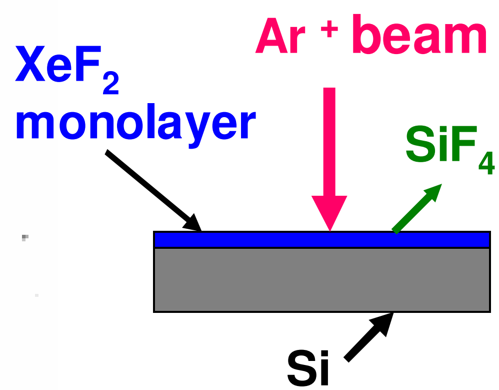
1. Plasma Reaction Engineering*

(*Acknowledgement – Dr. G.S. Mathad)

(i) Plasma Physics and Plasma Chemistry



Coburn and Winters



$XeF_2 \rightarrow Xe + 2F$

$Si + 2F \rightarrow SiF_2$

$SiF_2 + 2F \rightarrow SiF_4$

Basic plasma chemical reactions:

- electron initiated (elastic collisions with gas) reactions in bulk

  - dissociation

    $$A_2 + e \rightarrow A + A + e$$

  - ionization

    $$A_2 + e \rightarrow A_2^+ + 2e$$

  - dissociative ionization

    $$AB + e \rightarrow A + B^+ + 2e$$

- ion activated heterogeneous reactions at surfaces

  - ion energy dependent on plasma <u>sheath</u> thickness

- **Physics -- fundamental structure & behavior of matter**
- **Chemistry -- interaction of matter**

electron:A collision cross-section

Maxwell electron energy distribution function

- $$R_{eA} = n_A \int \sigma_{eA}(\varepsilon)\, \nu_e(\varepsilon)\, f(\varepsilon)\, d\varepsilon$$

reaction rate of electrons with A

electron speed

$$= n_A\, \nu_{Ae}(\varepsilon)$$

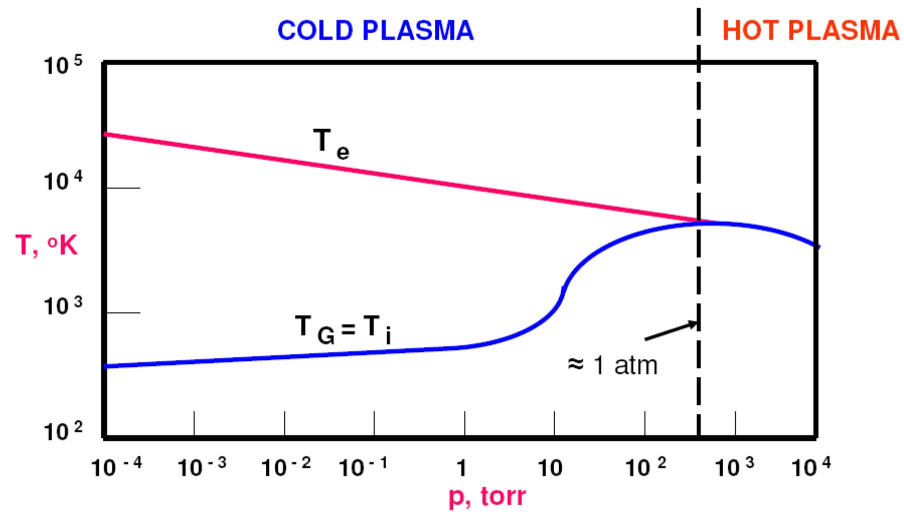
number density of species A

reaction frequency of A with electrons

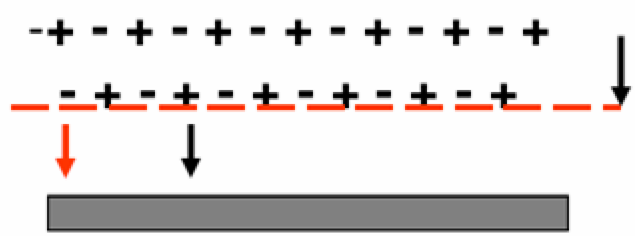
Plasma properties

1. Electric and magnetic fields

2. Plasma species temperatures



3. Plasma sheath



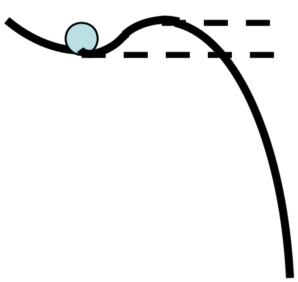
Two aspects of chemical reactions

1. Reactions -- thermodynamically feasible

A + B → C + D $\Delta F_o^R = -X$ **kcal**

reactants products

2. Reaction rates -- high (throughput) – activation energies



C (s) + O_2 (g) → CO_2 (g) $\Delta F^o = -94$ kcal @ 298 K

Features of plasma chemical reactions

1. Reaction enabler

   → Shifts reactions towards thermodynamic feasibility

2. Reaction enhancer

   → Increases reaction rates

Reaction enabler

Example 1

SiO_2 etch

Conventional chemistry

$$SiO_2 (s) + CF_4 (g) \rightarrow SiF_4 (g) + CO_2 (g) \qquad \Delta F^0_R = 113 \text{ kcal}$$

Plasma chemistry

ion bombardment (> 100 eV)

$$Si - - O_2 + CF_4 (g) \rightarrow SiF_4 (g) + CO_2 (g) \qquad \Delta F^0_R = - 79 \text{ kcal}$$

Example 2:

Manufacture of acetylene in plasma arc

$$2\,CH_4\,(g) \xrightarrow{\text{1 atm}} C_2H_2\,(g) + 3\,H_2\,(g) \qquad \Delta F^o_R = 74 \text{ kcal @ } 298\text{ K}$$

$$\Delta F^o_R = -24 \text{ kcal @ } 4000\text{ K}$$

For C_2H_2 (g),

$$\Delta F^o = 50 \text{ kcal/mole @ } 298\text{ K}$$

$$\Delta F^o = 0 \text{ kcal/mole @ } \sim 4000\text{ K}$$

Reaction enhancer

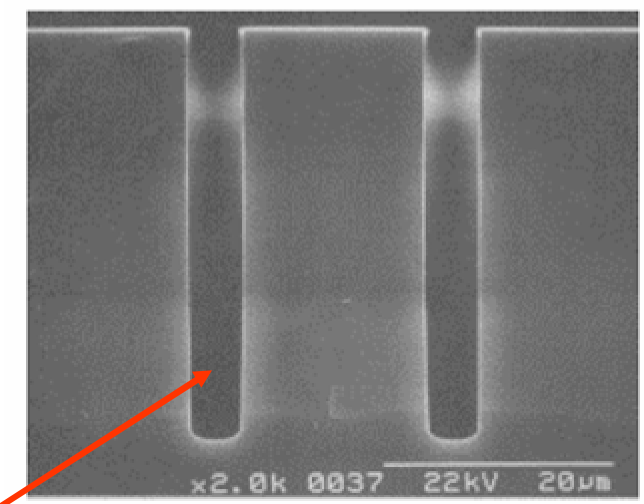
Example 1

Deep silicon etch

$Si\ (s) + 2\ F_2\ (g) \rightarrow SiF_4\ (g) \quad \Delta F^o_R = -137$ kcal @ 298 K

(reaction rate is slow @ near-room temperature)

Reaction rate enhanced (~ 50X) by using ion bombardment induced, non-thermal (T_s ~ 100 C) activation

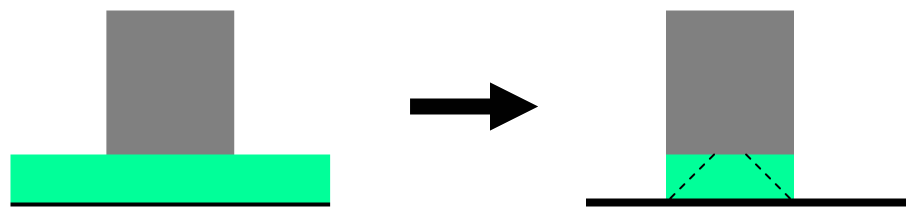


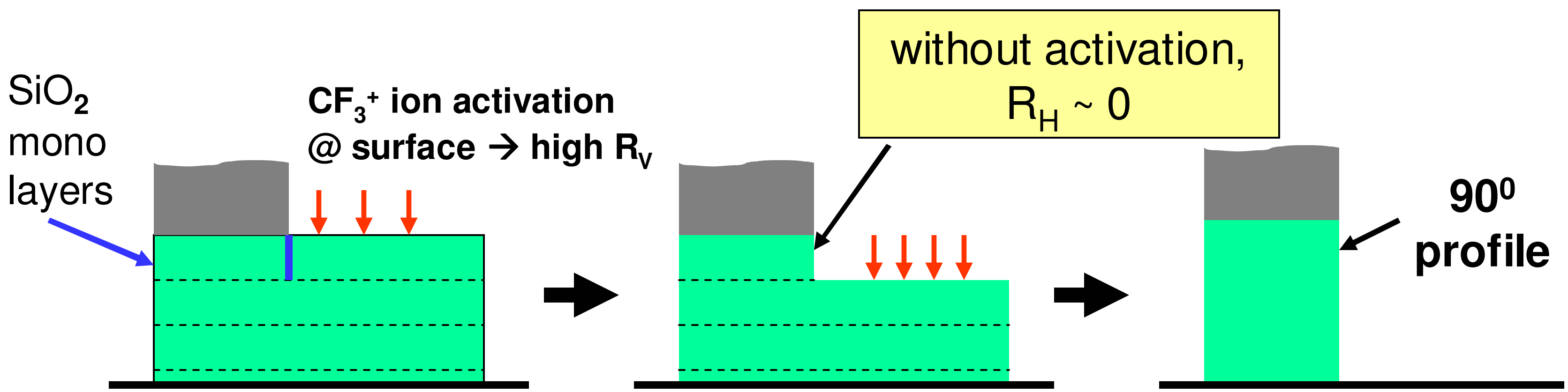
Deep Si - Holes

Example 2

Plasma can directionally increase reaction rates.

$$SiO_2\,(s) + CF_4\,(g) \rightarrow SiF_4\,(g) + CO_2\,(g) \quad R_V >>> R_H$$





Activation energy

Source:

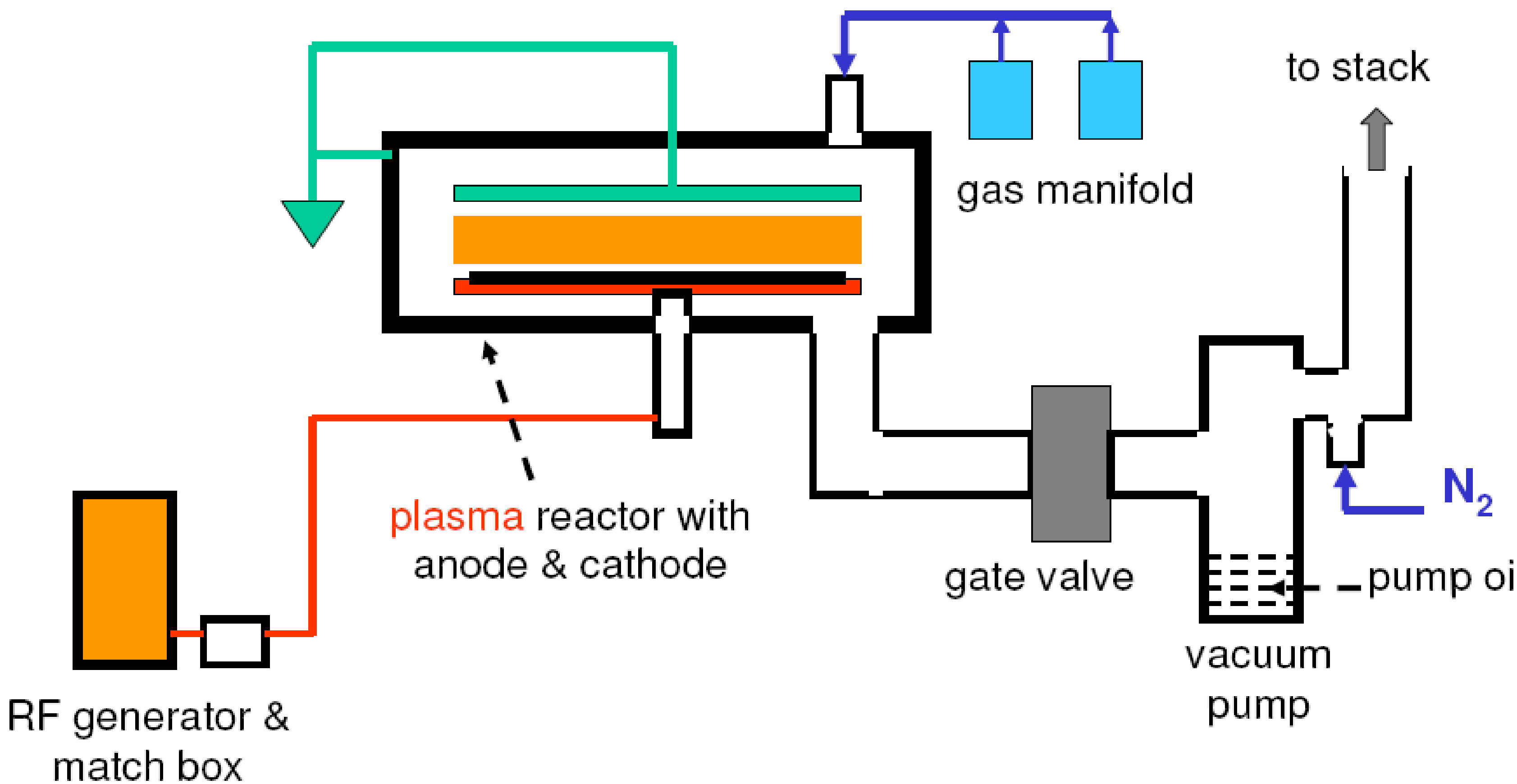
• **Heat**	→	**Thermo-chemistry**
• **Photons**	→	**Photo Chemistry**
• **Electrons/ Ions/Radicals**	→	**Plasma Chemistry**

Plasma species and bond energies

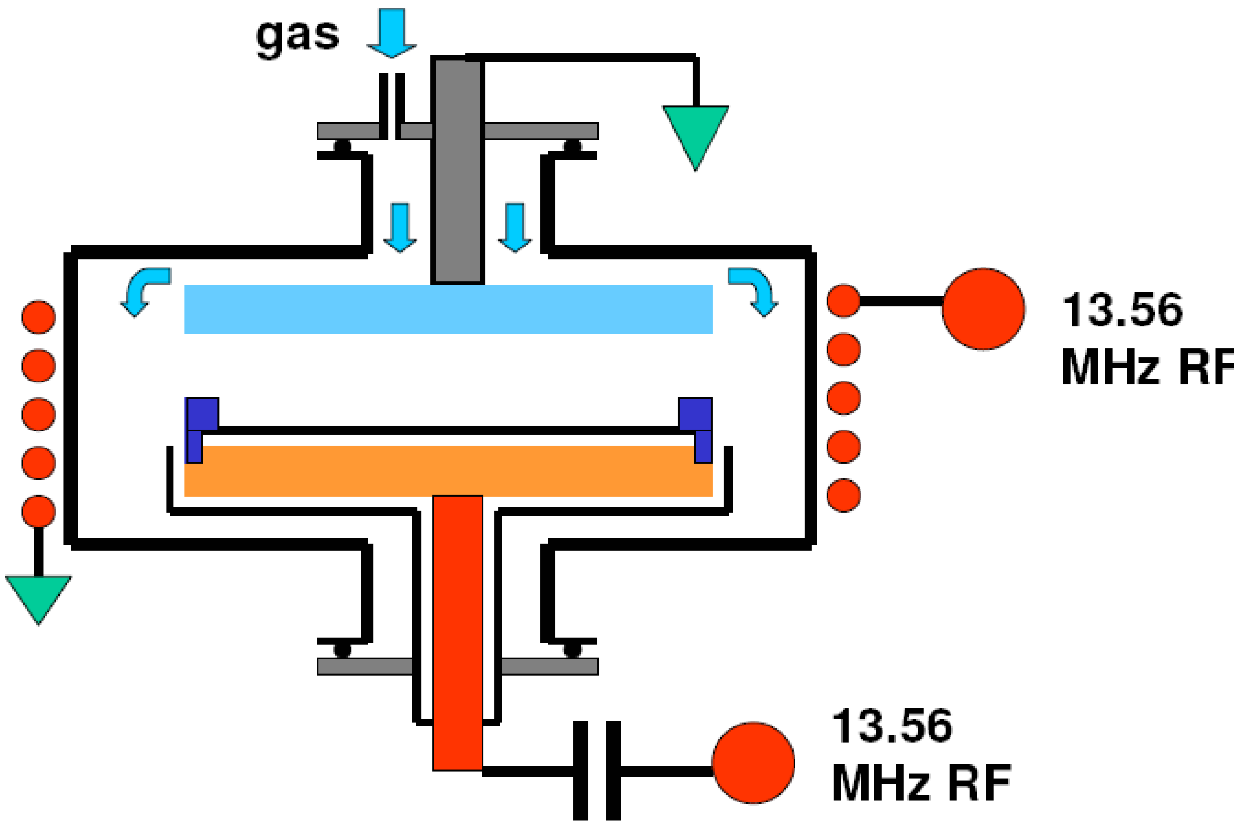
Plasma Species:	eV
• Electrons	0 – 20
• Ion (within bulk plasma)	0 – 2
• Metastables	0 – 20
• UV/Visible	3 – 40
Chemical Bonds:	
• C – H	4.3
• C – F	4.4
• C – C	3.4
• C = C	6.1
• C = O	8.0

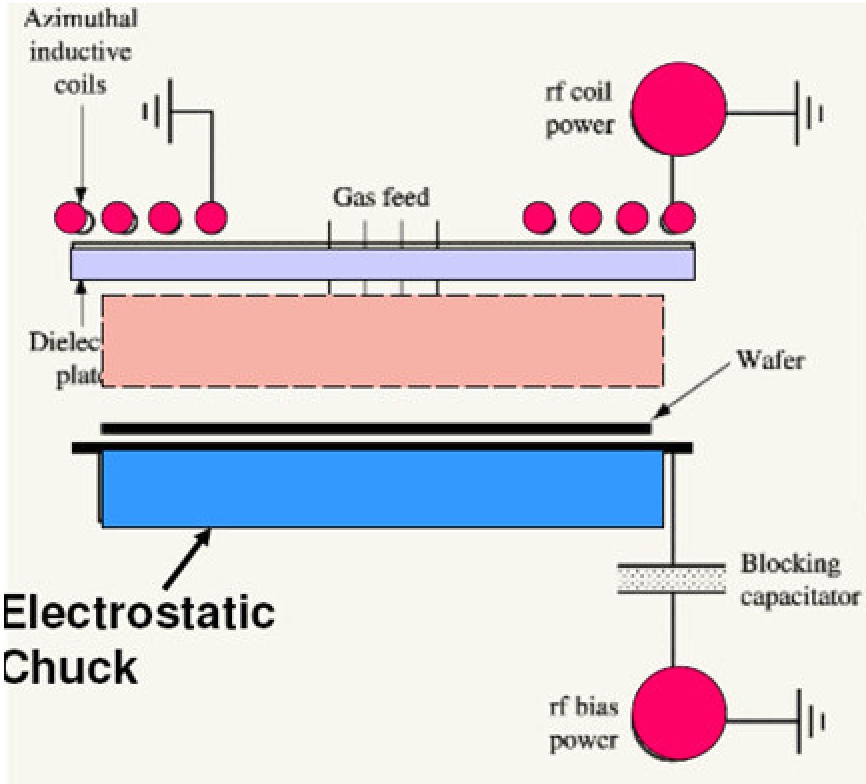
(ii) Plasma Reactors

Capacitively Coupled Plasma



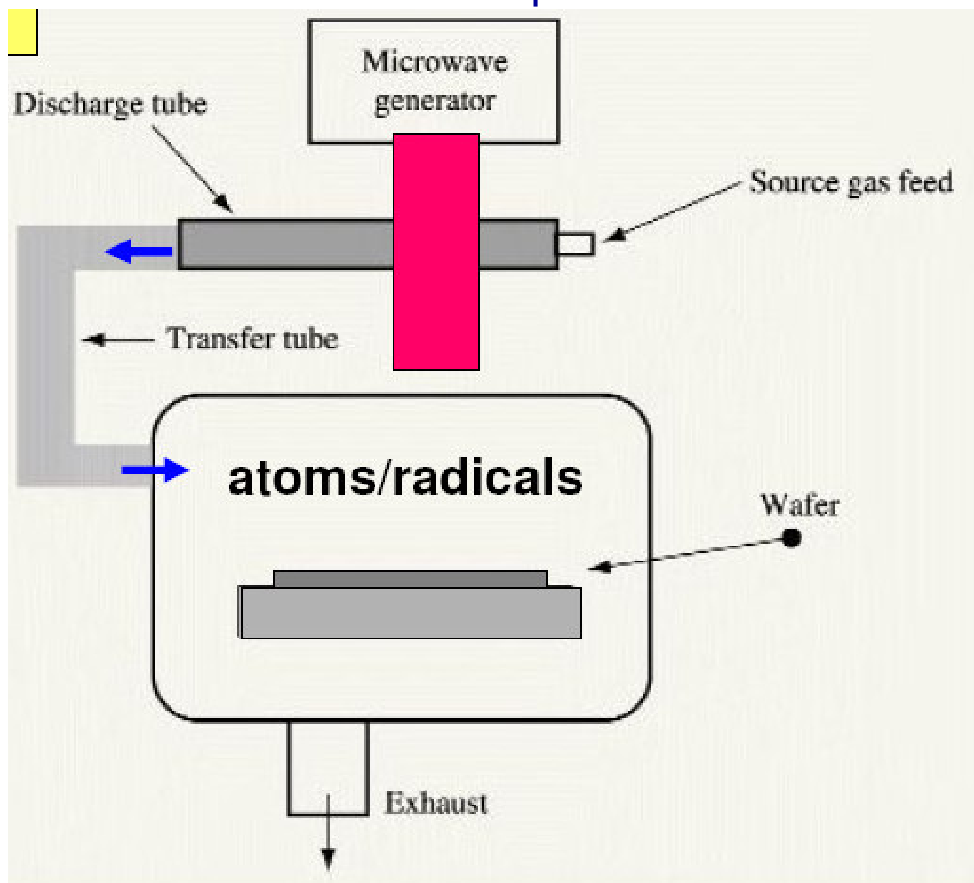
Inductively Coupled Plasma





HD (Magnetron)

Remote plasma



Operating variables

* Pressure
* Gas flow rate, composition
* Geometry
* Power
* Frequency
* Reactor materials

Key Plasma Properties

* Electron, ion densities
* Reaction rate constants
  (a) electron impact
  (b) thermal
* Electron energy distribution
* Electric field
* Ion energy and flux

Performance

* Etch rate
* Uniformity
* Anisotropy
* Selectivity
* Radiation damage

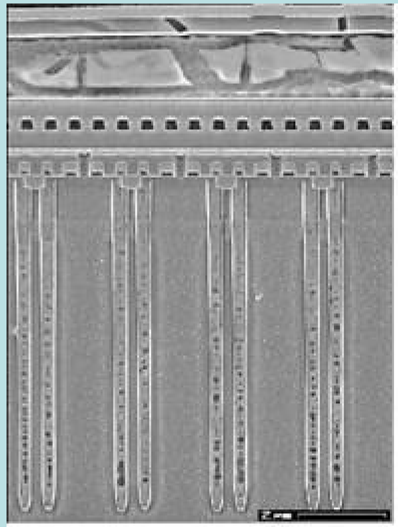
(Economou, in Electronic Materials Chemistry, 1996)

2. Silicon etch applications

(i) Selected applications

Microelectronics

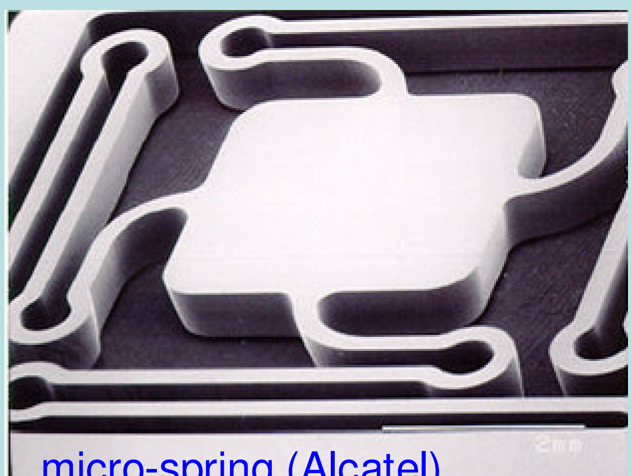
trench capacitors
trench isolation
through-silicon vias
channels



DRAMs (Siemens)

MEMS

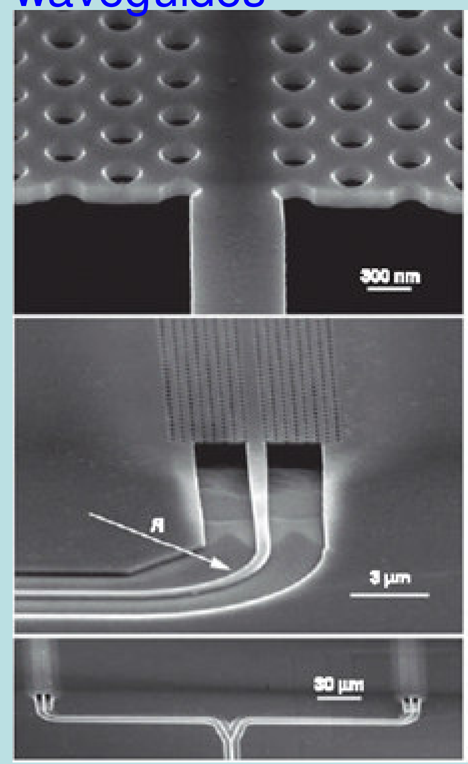
channels
gears
springs
cantilevers
AFM tips



micro-spring (Alcatel)

Optoelectronic/ Photonics

solar cells
lasers
waveguides

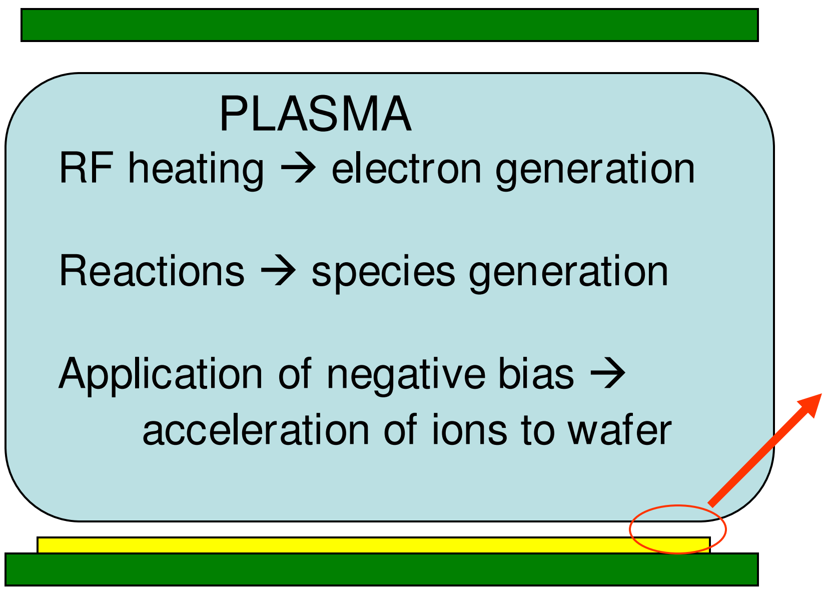


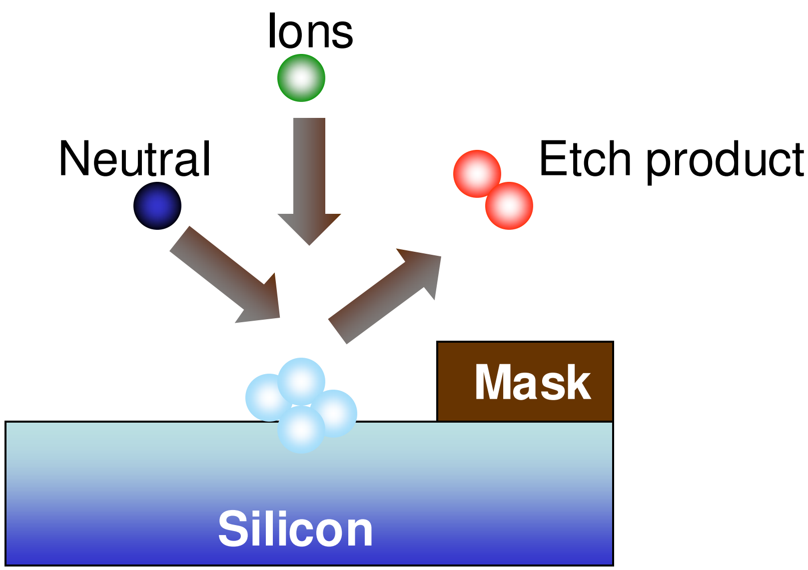
Waveguides in silicon
Vlasov et al. (Nature, 2005)

(ii) Plasma silicon etch - mechanisms

Typical etchants – halogens

F – CF_4, NF_3, SF_6
Cl – Cl_2, HCl
Br -- HBr





Possible reactions (sample NF_3) – gas phase and surface chemistry

Plasma

Thermal reactions

$$NF_i \rightarrow \begin{cases} NF_{i-1} + F \\ NF_{i-2} + F_2 \end{cases}$$

$$NF_i + \begin{Bmatrix} F \\ F_2 \\ NF_j \end{Bmatrix} \rightarrow \begin{cases} NF_{i-1} + F_2 \\ NF_{i+1} + F \\ NF_{i-1} + NF_{j+1} \end{cases}$$

Electron impact reactions

$NF_i + e \rightarrow NF_i^* + e$ (energetic radicals)

$NF_i + e \rightarrow NF_i^+ + 2e$ (ions)

$NF_3 + e \rightarrow NF_3^+ + 2e$ (ionization)

$NF_3 + e \rightarrow NF_2^+ + F + 2e$ (dissociative ionization)

$F_2 + e \rightarrow F_2^+ + 2e$

radicals

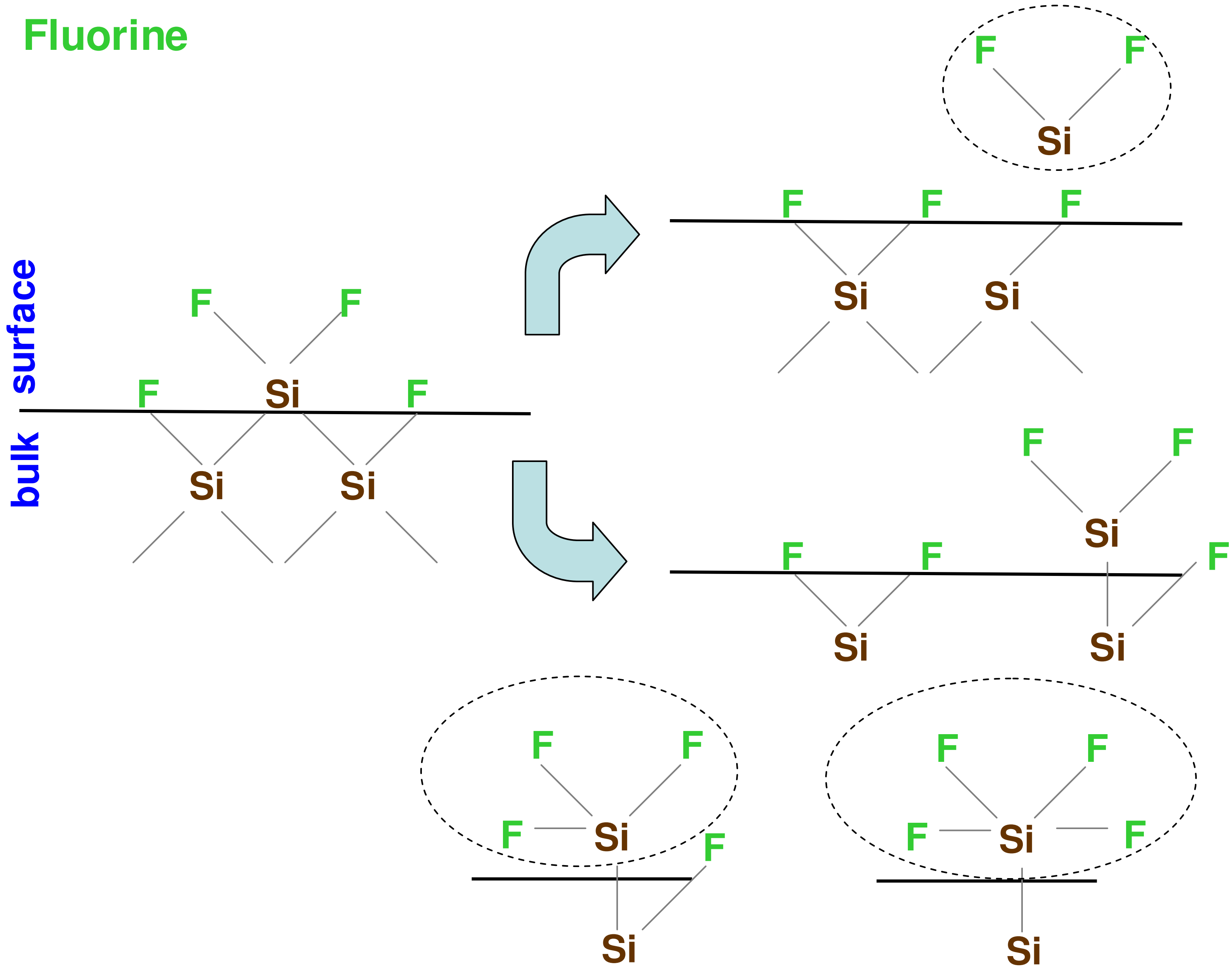
NF_3^*, NF_2^*, NF^*, F^*, N^*

ions

NF^+, NF_2^+, NF_3^+

Wafer

Fluorine



surface
bulk
F
F
F
Si
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F
Si

Fluorosilyl (SiF_x) layer on surface

SiF, SiF_2, SiF_3, SiF_4

→ volatility

} Ion bombardment

Re-arrangement to the more volatile component

Fluorine with Oxygen

Source of O → feedgas
exposed quartz parts

Competition of F and O for Si sites

SiF_xO_y layer on surface

Bromine

Silicon etch with Br different from that with F

(i) penetration of halides in silicon surface

(ii) volatility of silicon halides

size Br $>$ F

$SiBr_x$ less volatile

Bromine and Oxygen

Oxidation of surface

$SiBr_xO_y$ layer on surface

(iii) Silicon deep trench – formation dynamics

Etch rate of Silicon

F > Cl > Br

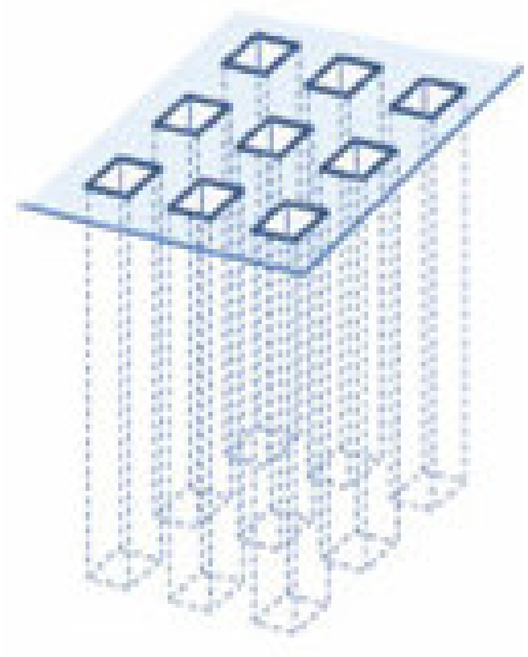
* reactivity (energy of reaction)
* smaller atomic size

F – too high reactivity
isotropic attack

Cl – better control
subsequent problems

Br – slow etch rate but better control

O – purpose?



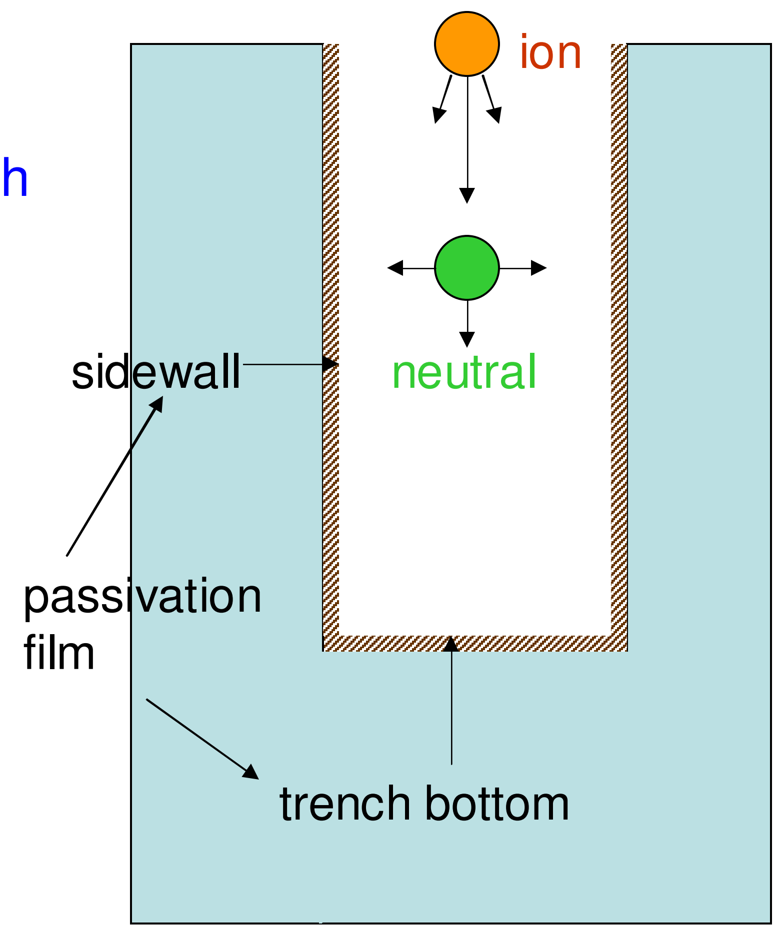
(Gostein, Future Fab Int., 2007)

Passivation film

Etch front (trench bottom)

- ➔ surface layer inhibits further etch
- ➔ ion flux clears film
- ➔ etch progresses

(if insufficient clearing of film
==> etch rate slows)



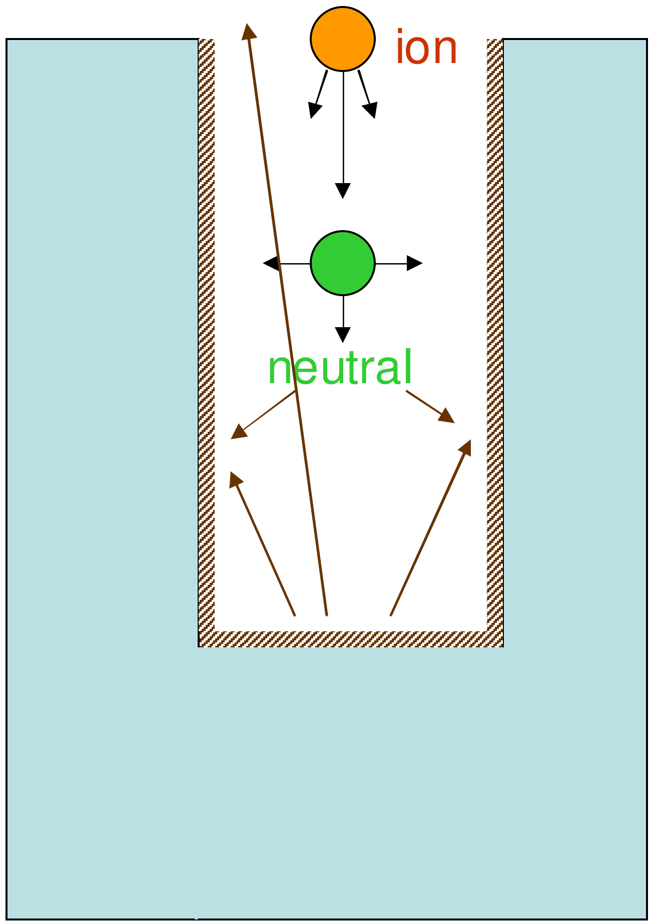
Sidewall

Layer on surface when cleared

some escapes out of trench

some re-deposits on sidewall
➔ forms passivation film

Passivation film protects silicon sidewall against attack by neutrals



Pressure in chamber ~ 100 mT
Knudsen flow regime

(iv) Silicon deep trench – etch issues

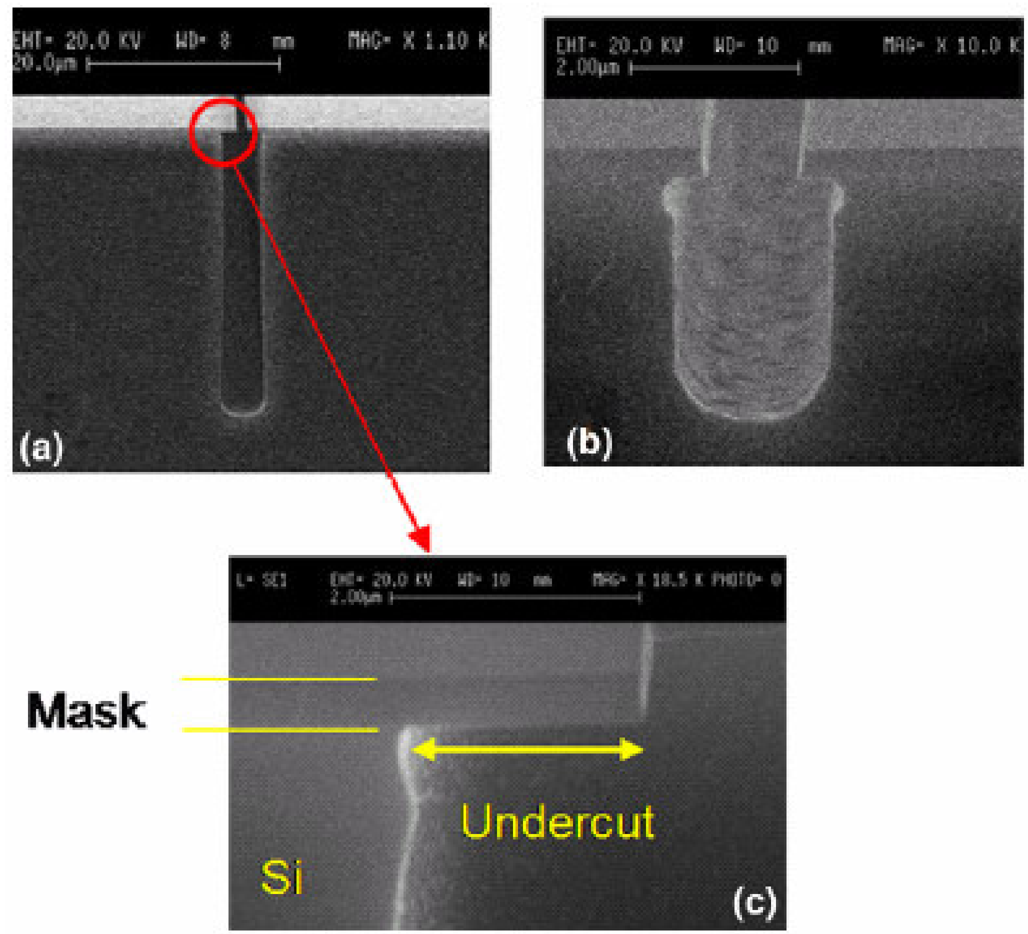
Requirements

* Desired depth

* Sidewall slope

* Structural integrity

Several problems!

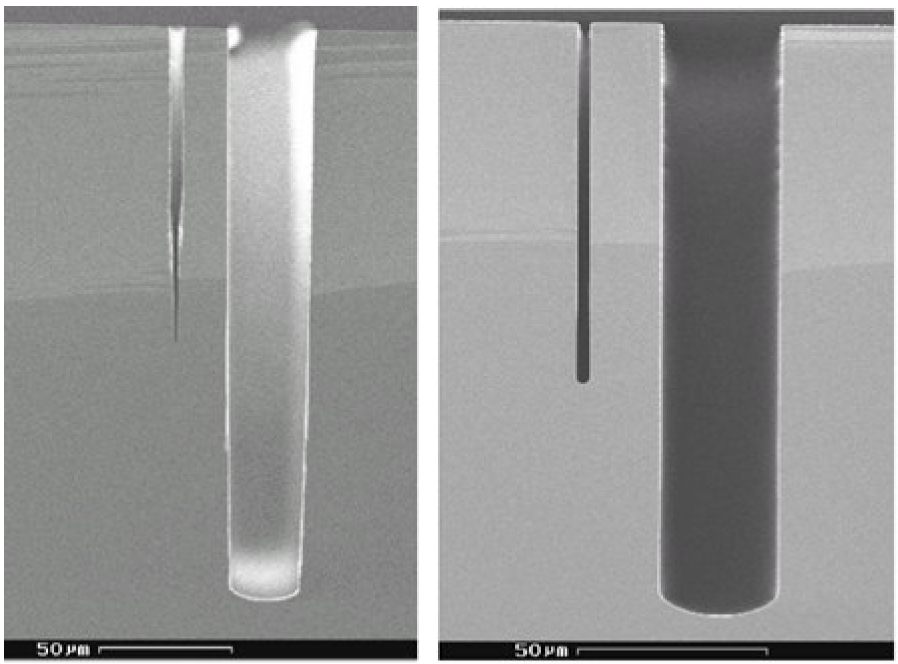


(Boufnichel et al.,
Microelectronic Engineering, 2005)

(a) RIE lag

smaller features etch slower (smaller depth)

(Ayon et al., Sens. Act., 2001)



(Wise et al., Future Fab Int., 2001)

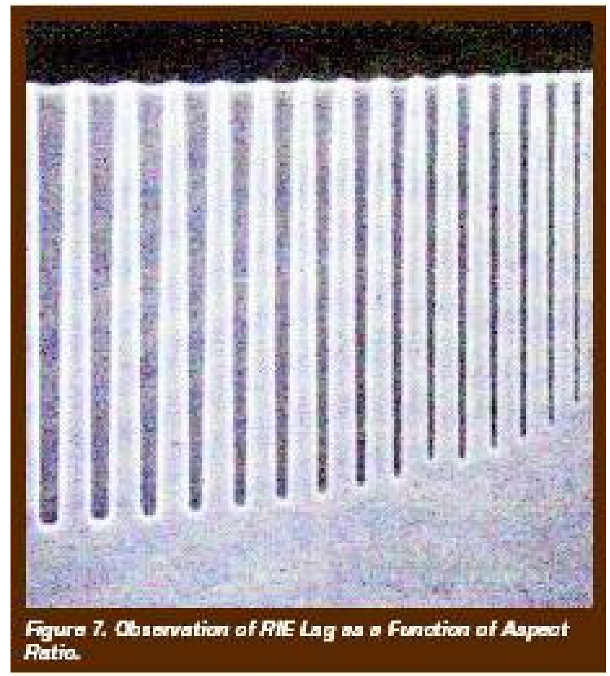
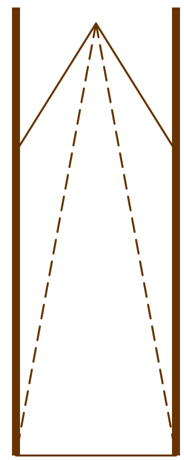


Figure 7. Observation of RIE Lag as a Function of Aspect Ratio.

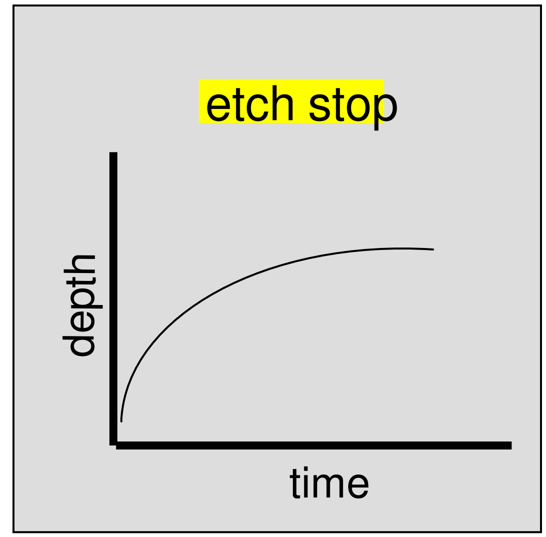
Contribution to RIE lag

* geometric effect

decreasing flux
at higher depths

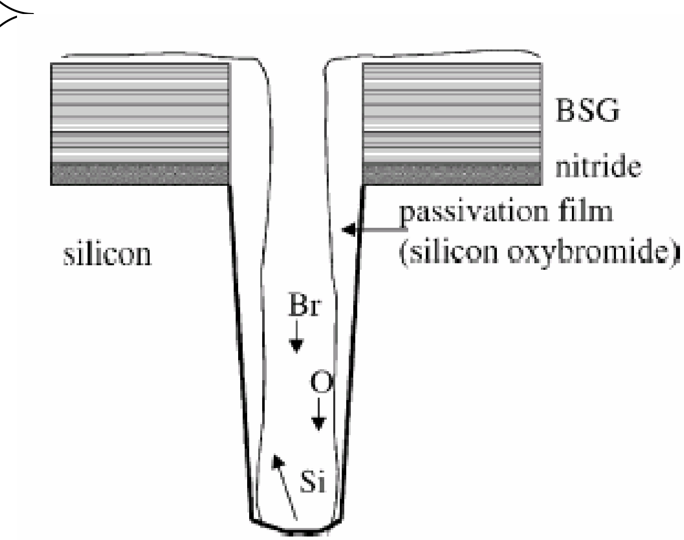


etch front



* passivation film -

trench mouth/sidewall
trench bottom



(Panda et al., Microelectronic Engineering, 2004)

(b) Charging

Plasma – electrically neutral

Ions and electrons → surface

Ions – energy distribution more anisotropic

Electrons – energy distribution more isotropic
higher mobility

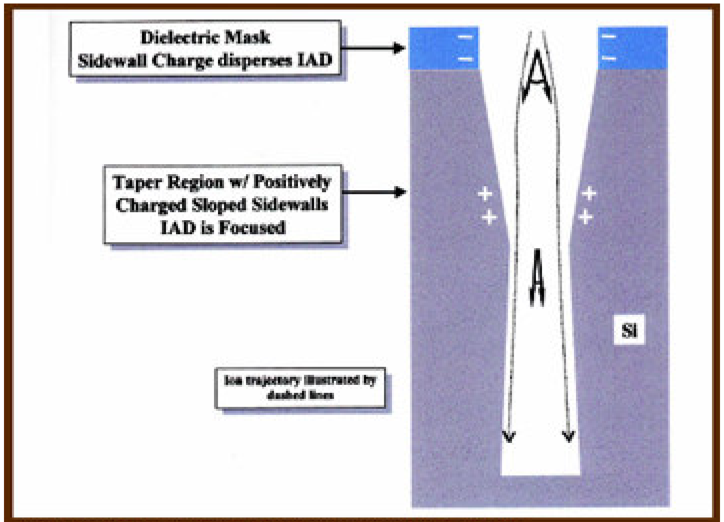


Figure 5. Deep Trench Profile showing top taper region, dispersion and re-focusing of IAD.

Non-conducting surfaces in trench –

charged

➔ affect incoming charged species

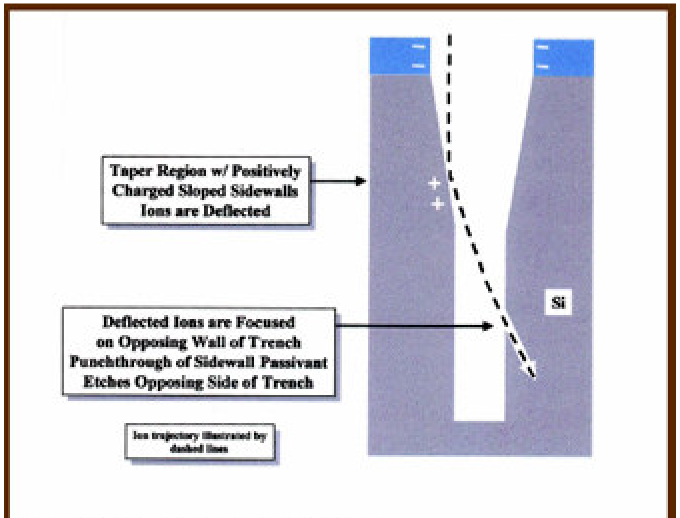


Figure 8(a). Ion Deflection on Sloped Features Resulting in Angled Etch.

(c) Loading effect

Dependence of etch rate of the quantity of material being etched

1/ER   proportional to exposed area to be etched

(Mogab, J. Electrochem Soc., 1977)

Inverse loading effect

opposite – i.e. higher ER with higher exposed area

Reasons –

differences in mechanism of etch

Summary and Outlook

1. Plasma reaction engineering

* Plasma physics, plasma chemistry, plasma reactor engineering closely interlinked

* Reaction enabler, reaction rate enhancer, directionality

2. Silicon etch applications

* Specific reaction mechanisms

* Etch features affect performance → need for plasma reaction engineering

3. Newer applications and challenges

Thank you