

# PVD & Plasma Etching

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2018. 12. 7.

진공기술현장교육: 삼성SDI

# 강의 순서

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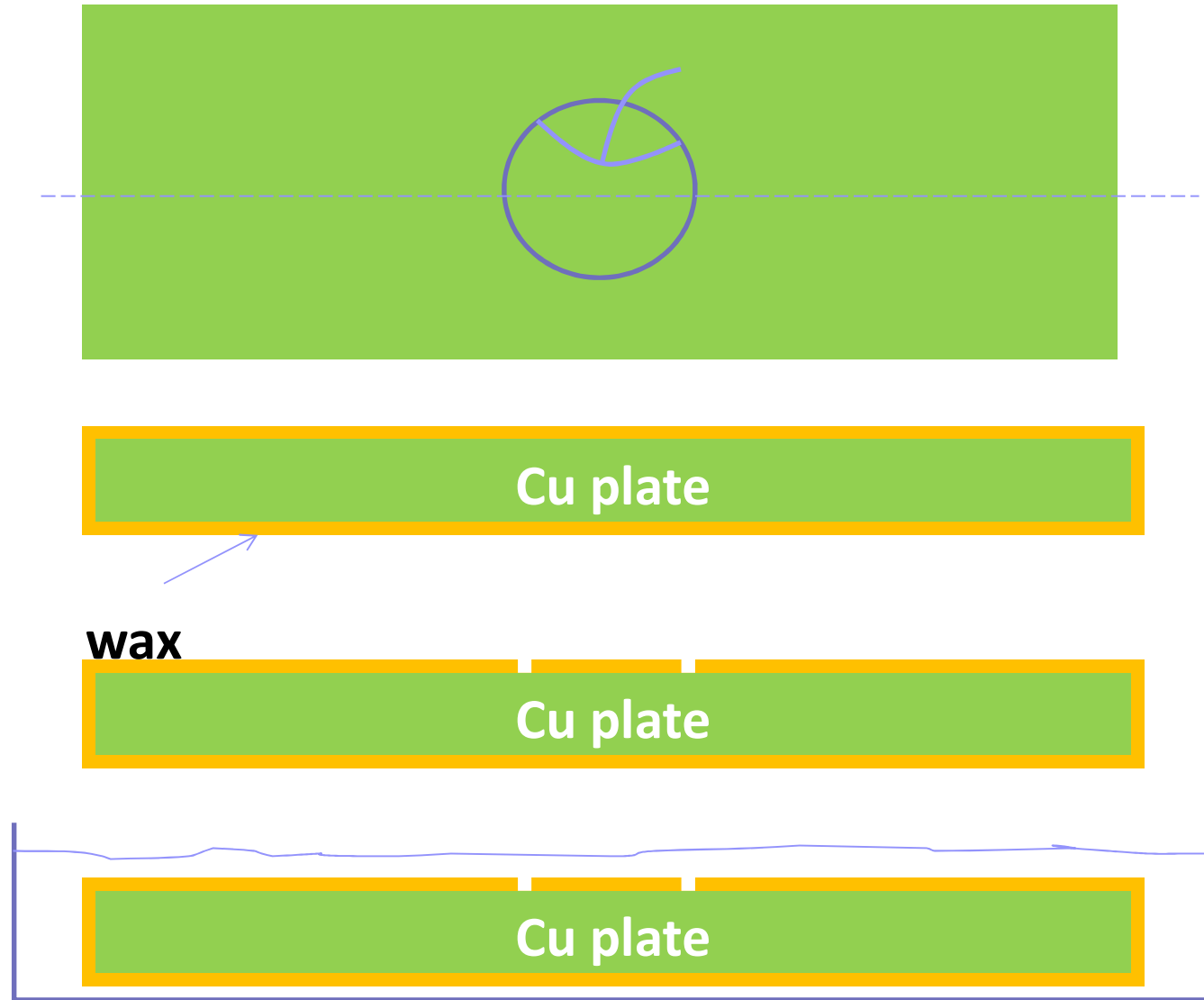
- Semiconductor Processing & Etching
- Plasma Fundamentals
- PVD: Plasma Sputtering
- PVD: Evaporation
- Plasma Etching: Chemistry and Surface Reactions
- Plasma Etcher
- Plasma Diagnostics
- Summary
- 참고자료: Issues of Plasma Etching

# **Semiconductor Processing & Etching**

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# Etching (동판화)

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# Etching

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- 에칭:

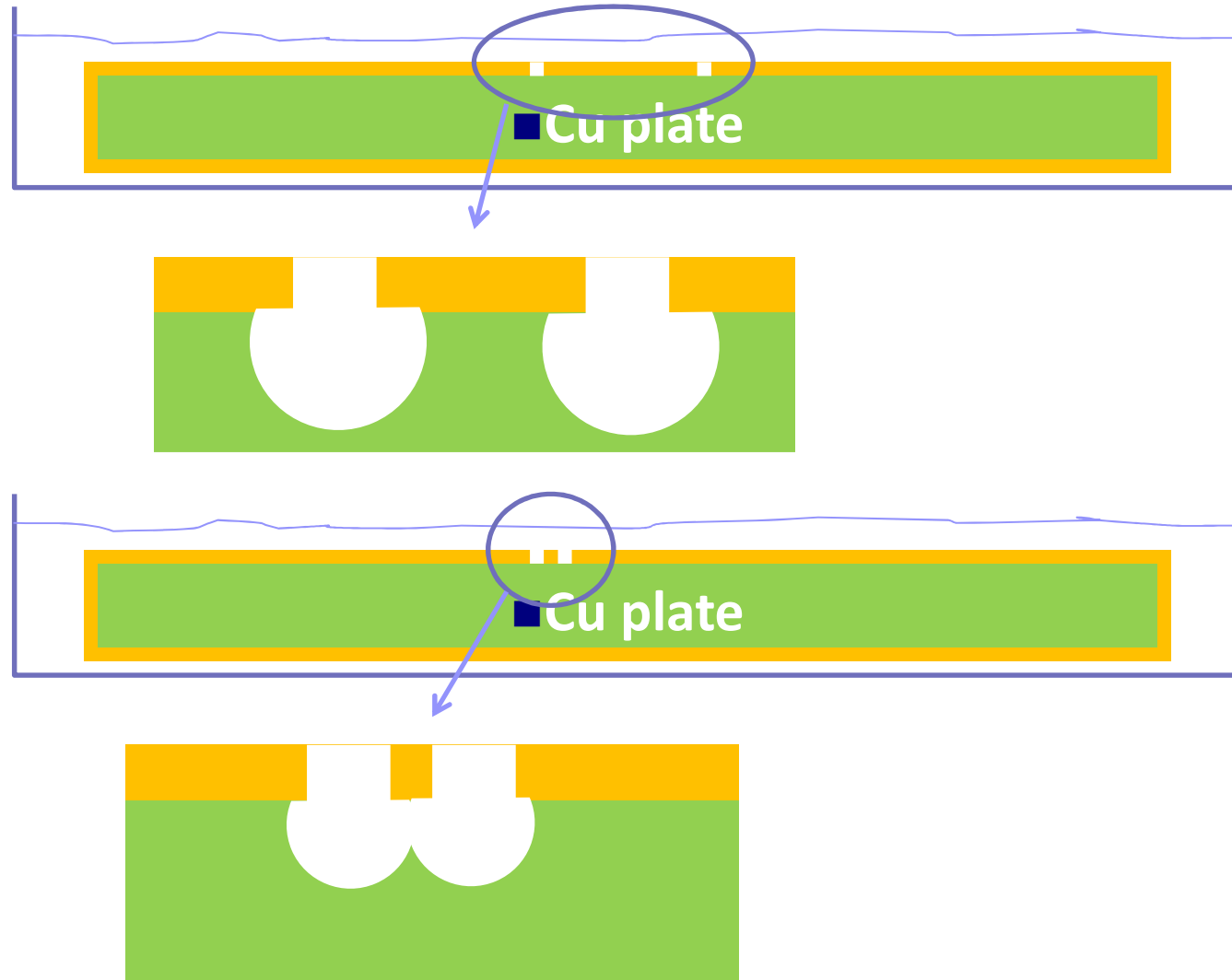
- 먼저 동판화에서 쓰이는 금속판 위에 밀랍을 주성분으로 한 그라운드를 바른 후 에칭니들이나 그 밖의 날카로운 도구로 그라운드 위를 긁으면 긁힌 부분은 그라운드가 벗겨져 판이 노출된다. 이 판을 산 속에 일정 시간 부식시키면 긁힌 부분, 즉 선을 그린 부분만 부식 정도에 따라 움푹 들어가게 되고 이곳에 잉크가 괴며 찍힌다.

- 산과 금속 부식제

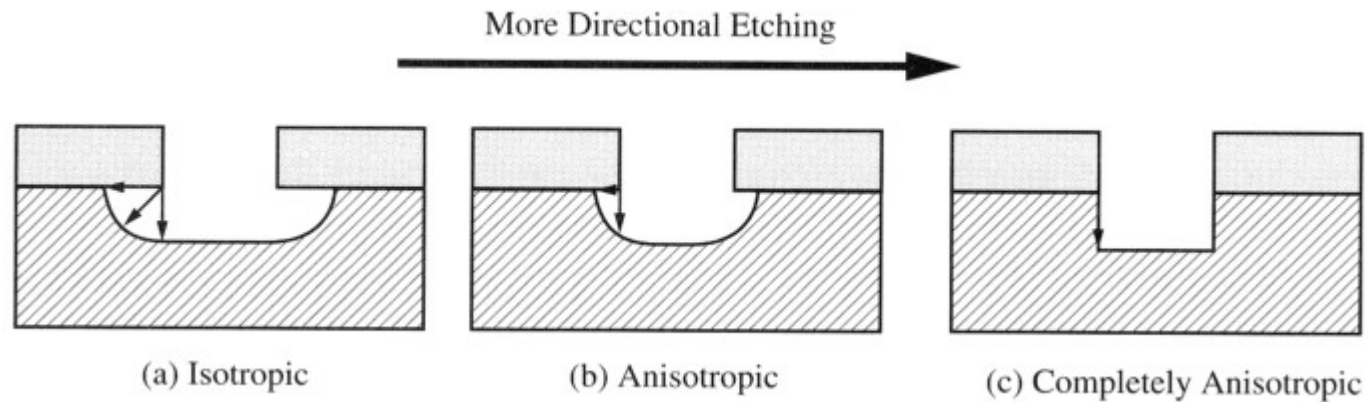
- 질산과 철, 과염화물이 가장 많이 사용된다. 동, 아연, 철에 질산 사용한 금속을 사용한 것에 다른 금속을 사용하면 좋지 않다. 사용전에 물과 희석하여 원하는대로 섞는다.(산:물=1:3) 질산은 매우 빨리 작용하고 에칭라인의 가장자리는 매우 가볍게 침식된다. 철, 과염화물은 특히 동에 적합하다. 천천히 작용하지만 에칭 라인에 해 없이 깊이 작용한다.
- 이것은 희석하지 않고 46°C B나 물과 희석해서 사용한다. 30°C B를 올리면 작용이 빨라지고 희석하지 않은 산은 위험하다. 마스크, 장갑 착용등이 꼭 요구되며 적당히 환기도 해야한다. 처음 만든 질산과 철, 과염화물은 이미 사용된 것 5%를 첨가해서 사용하기 전에 오래 나뉘야한다.

출처:네이버 백과사전

# Etching (동판화)



# Isotropic vs. Anisotropic Etching

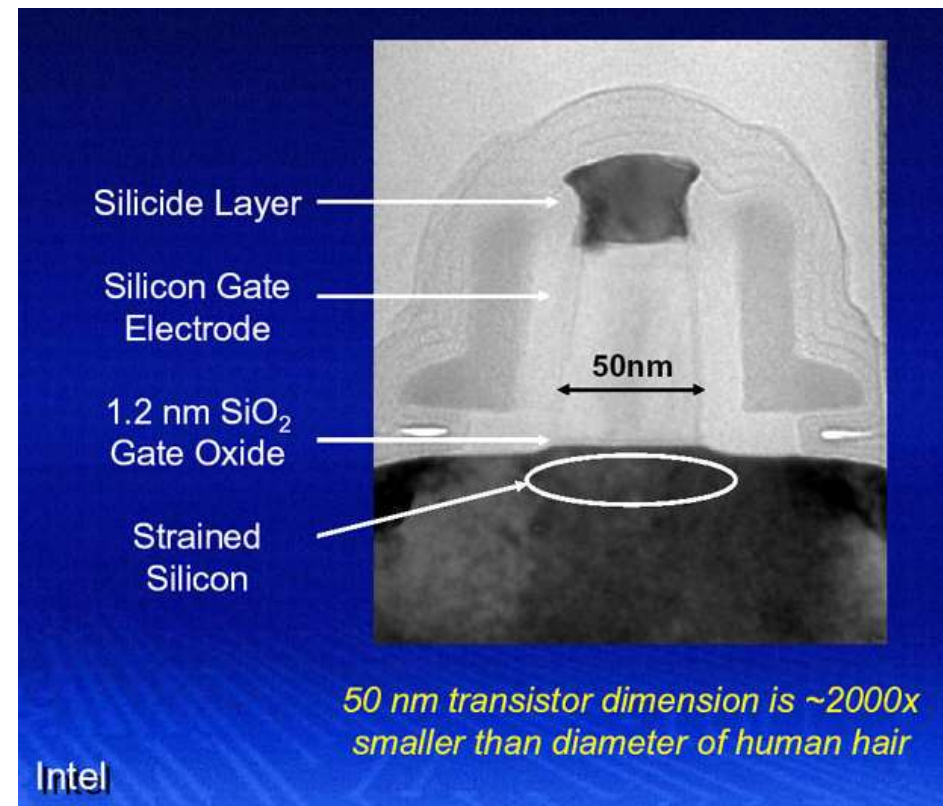
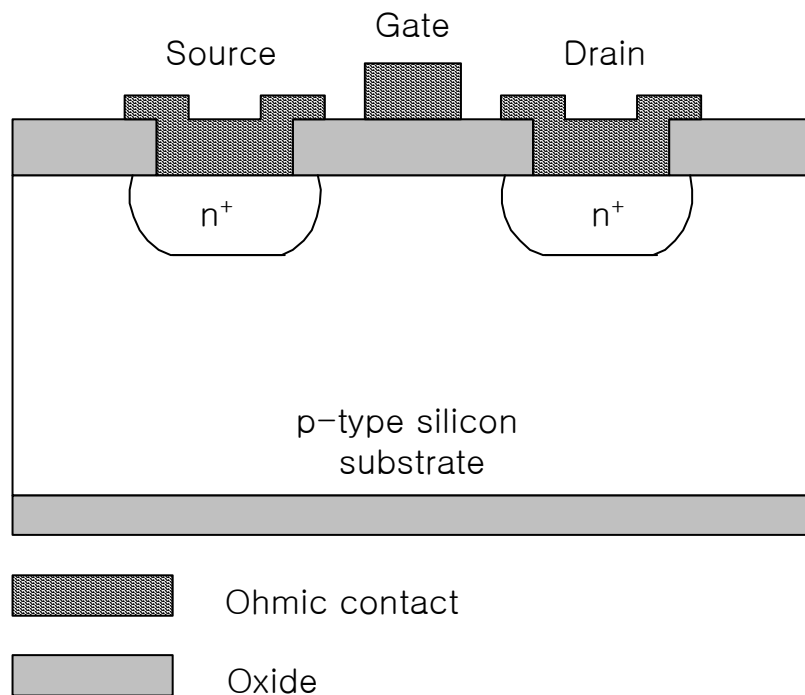


- - Wet Etching
- - Chemical Etching

- Dry Etching
- Plasma Etching
- Physical Etching
- Physical/Chemical Etching

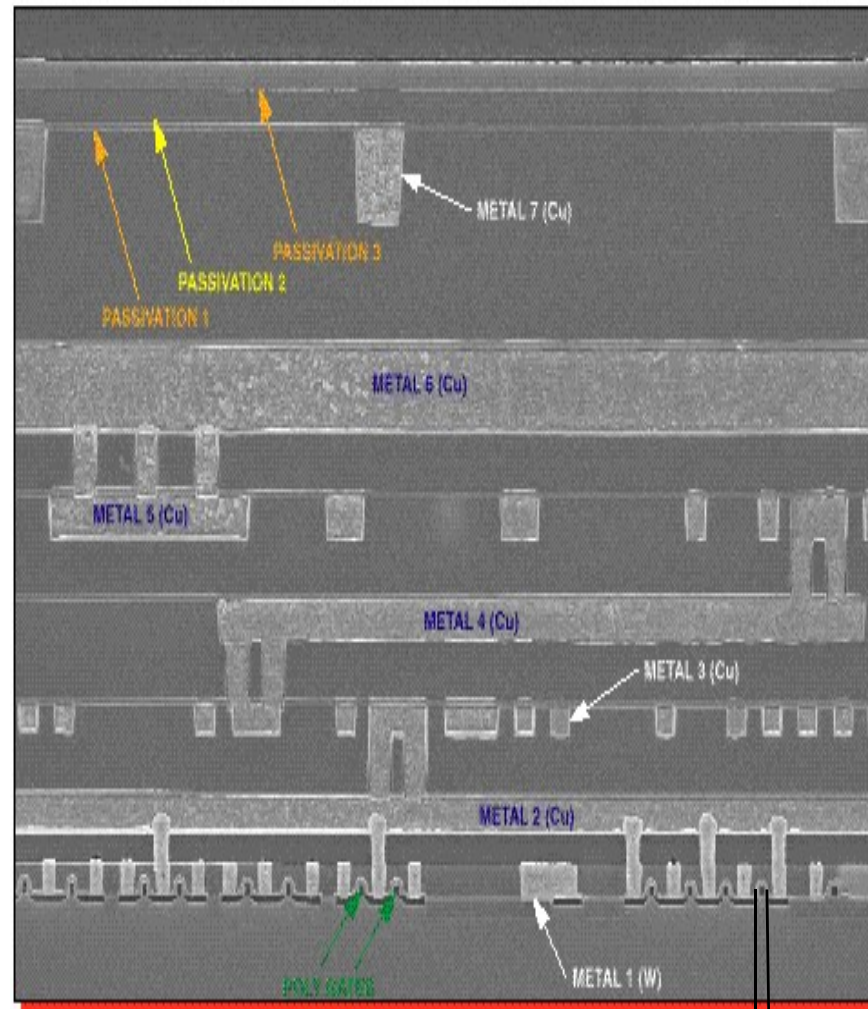
# Transistor

- MOSFET (metal-oxide-semiconductor field effect transistor)



# Plasma Applications to Nano-Chip Processing

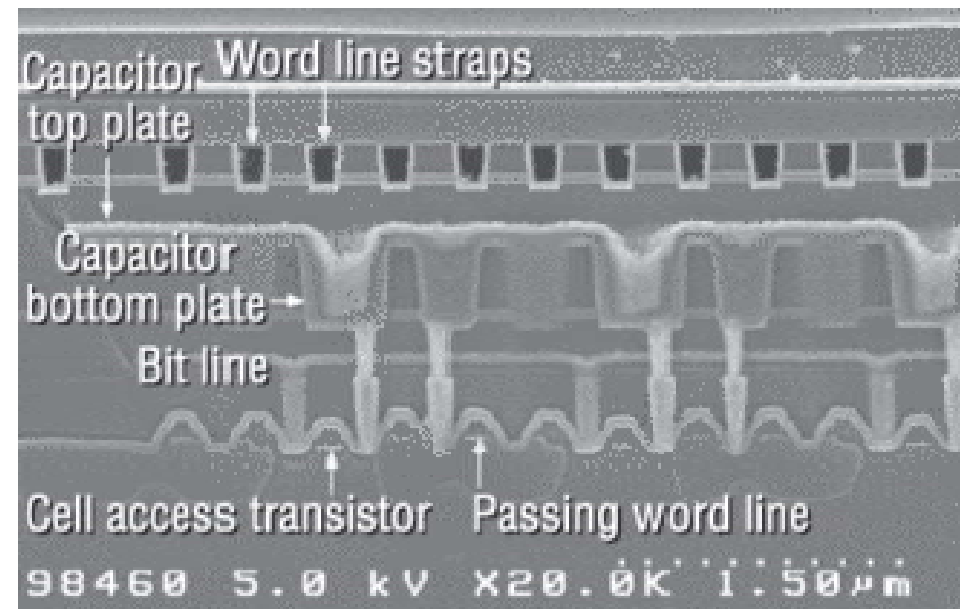
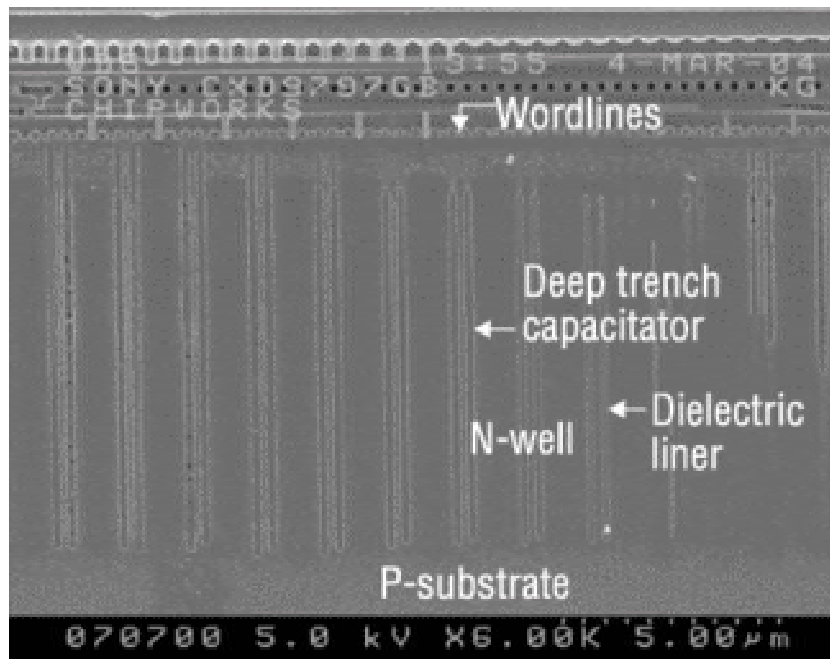
- About 40% of semiconductor process steps are plasma related



System IC

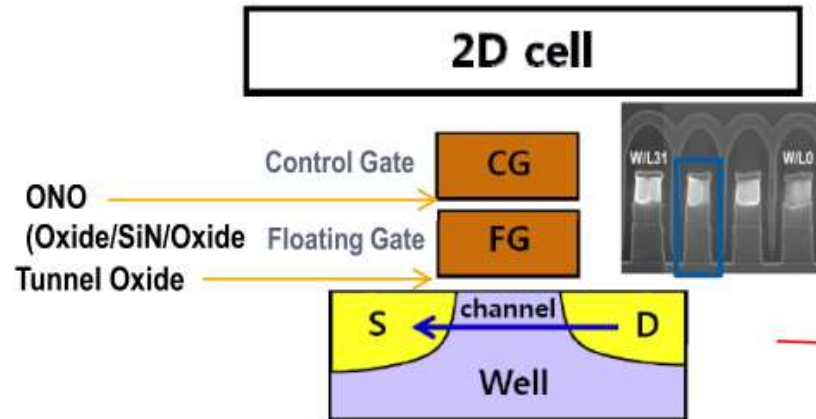
< 100nm @ 2008

# DRAM Cross-section

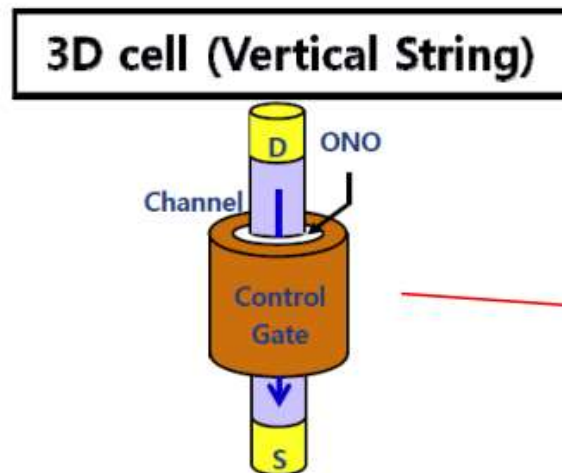
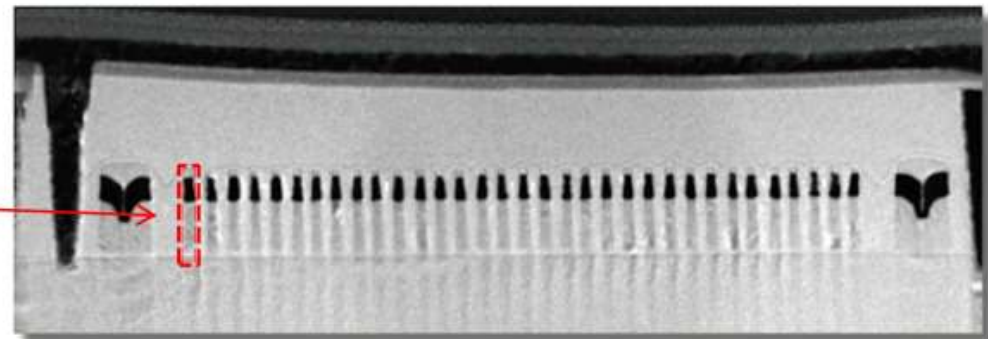




# 3D NAND cells require high aspect ratio plasma etching



- Single crystal Si channel
- Floating gate (or TANOS)
- 1-side gate



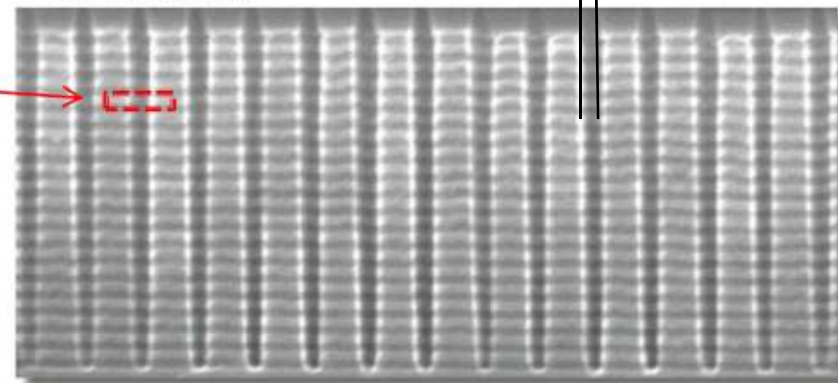
- Poly-Si channel
- SONOS (Si / Oxide / SiN / Oxide / SiN)
- All-around gate
- Channel-last process
- 1 step litho (hole)

<http://gigglehd.com/zbxe/613729/>

Micron

Wednesday, August 10, 2011

< 50nm @ 2014



Charges stored in FG  
Charges in/out through the tunnel oxide.

# Materials in Semiconductor Processing

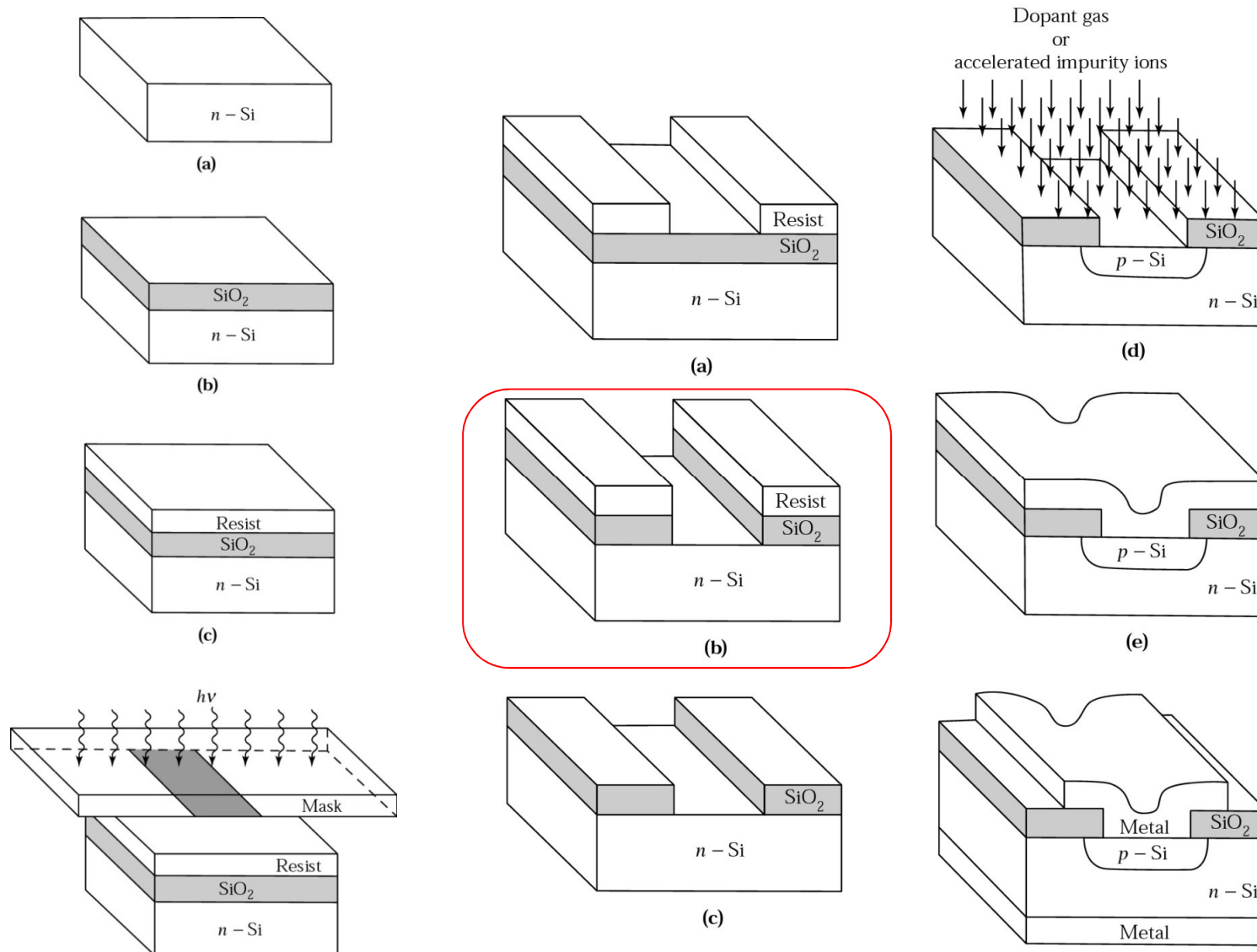
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	Traditional Materials	New Materials
Semiconductor	Si, Ga-As, In-P	Si-Ge
Dielectric	Thermal SiO <sub>2</sub> for gate PECVD SiO <sub>2</sub> , Si <sub>3</sub> N <sub>4</sub>	High-k for gate oxide Carbon doped oxide Organic low-k
Metal	Al, W	Cu, TiN, TaN
Organic	G-line photoresist I-line photoresist 248nm photoresist	193nm photoresist Si-containing photoresist



Element	IV-IV	III-V	II-VI	IV-VI
<b>Si</b>	SiC	GaAs, GaP	GdS, CdSe	PdS
Ge	SiGe	InAs, InP	CdTe, ZnS	PbTe
		InSb	ZnSe, ZnTe	

# Process Overview

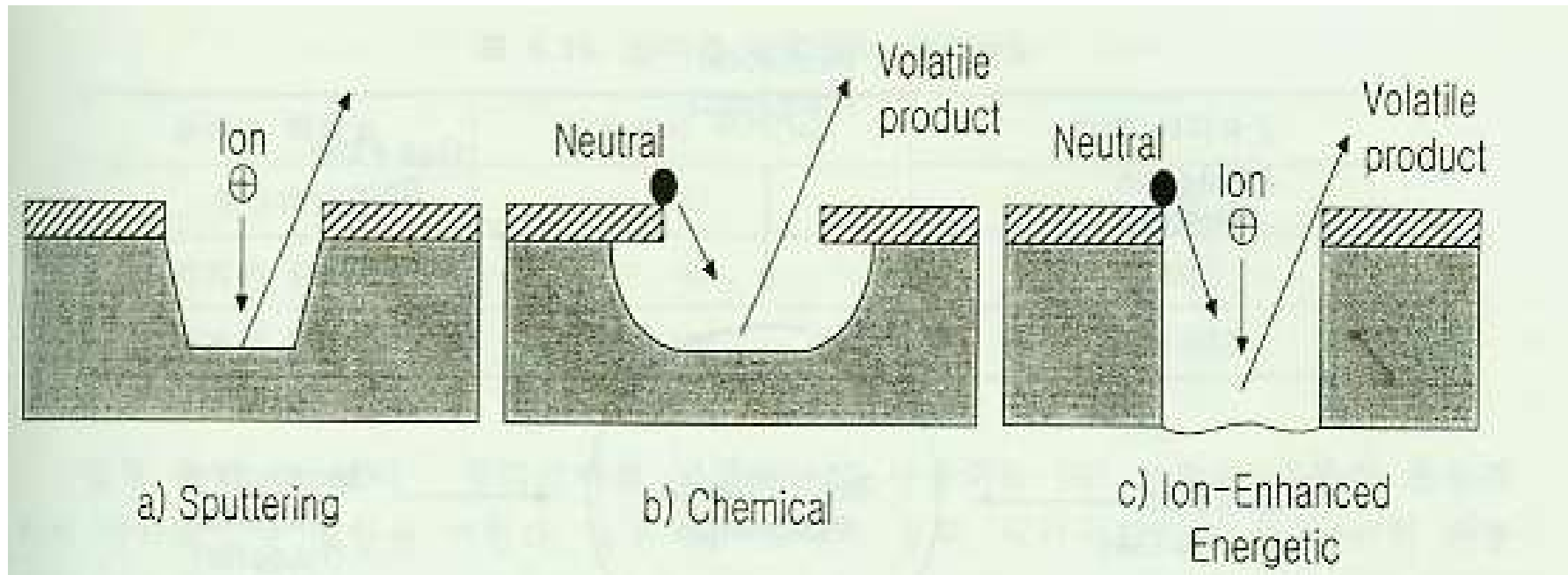


# Dry (Plasma) Etching Types

Physical Process

Chemical Process

Physical + Chemical Process



- anisotropic
- low selectivity
- low etch rate

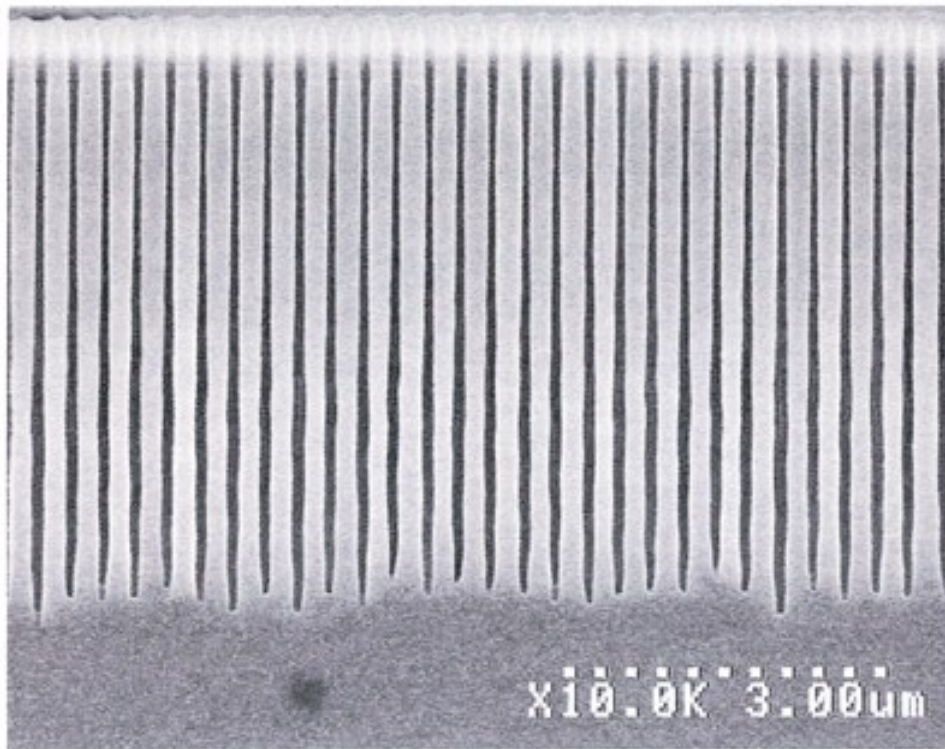
- isotropic
- high selectivity
- low etch rate

- anisotropic
- high selectivity
- high etch rate

# Plasma Etching

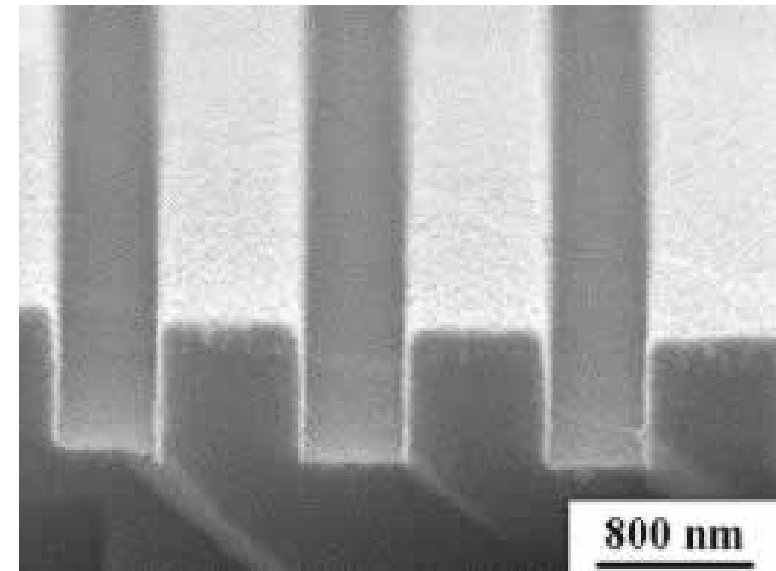
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## High Aspect Ratio Si Etching



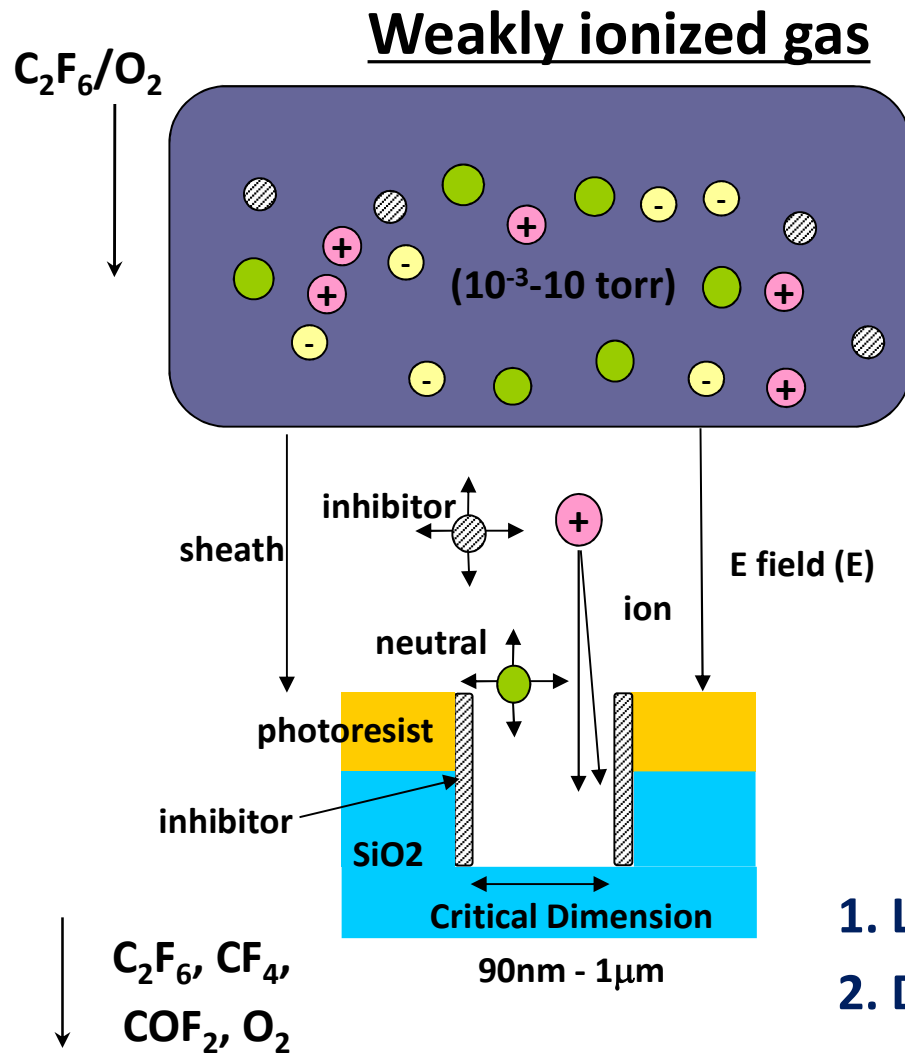
■ <http://www.future-fab.com/assets/images/FFI11E1123F8b.htm>

## Squared Etch Profile



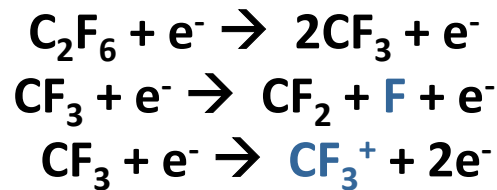
■ [http://www.iom-leipzig.de/pic\\_schw/caibe1.jpg](http://www.iom-leipzig.de/pic_schw/caibe1.jpg)

# Plasma – Reaction Example

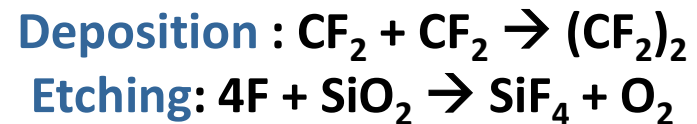


## Example

### Dominant Reactions in Plasma (example)



### Dominant Surface Reactions (example)



1. Low T processing by reactive radicals & ions
2. Directionality due to ion and electric field

# Wet Etching vs. Dry Etching

	Wet Etching	Dry (Plasma) Etching
Process/ Reaction	Solid + Liquid $\rightarrow$ Soluble Prod. $\text{Si(s)} + 2\text{OH}^- + 2\text{H}_2\text{O} \rightarrow$ $\text{Si(OH)}_2(\text{O}^-)_2 (\text{aq}) + 2\text{H}_2 (\text{g})$	Solid + Gas $\rightarrow$ Volatile Prod. $\text{SiO}_2(\text{s}) + \text{CF}_4 \rightarrow \text{SiF}_4(\text{g}) + \text{CO}_2(\text{g})$
Advantage	<ul style="list-style-type: none"> <li>- Relatively simple</li> <li>- Easy to get high selectivity</li> </ul>	<ul style="list-style-type: none"> <li>- Anisotropic etching (suitable for the feature smaller than <math>1\mu\text{m}</math>)</li> <li>- Ease to automate the process</li> <li>- Less toxic</li> </ul>
Disadvantage	<ul style="list-style-type: none"> <li>- Isotropic process (not suitable for the feature smaller than <math>3\mu\text{m}</math>)</li> <li>- High cost in etchant</li> <li>- Toxic/Explosive</li> <li>- Bubble -Non-uniform</li> </ul>	<ul style="list-style-type: none"> <li>- Complex system</li> <li>- Difficulty to control</li> <li>- Device damage by energetic ions</li> <li>- Less selective than wet process</li> </ul>

# Merits and Demerits of Plasma Processing

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## ■ Merits

- ☐ Low temperature processing
- ☐ Micro- and nano-scale patterning
- ☐ Dry processes and less waste generation than wet processes
- ☐ Chemistry control is possible

## ■ Demerits

- ☐ Requires RF or DC power generators.
- ☐ Requires vacuum in typical cold plasma processing
- ☐ Chemistry is complex and difficult to control.

# Plasma

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	Electron	Ion	Radical	Molecules
Mass				
Fraction				
Density				
Energy				
Function				

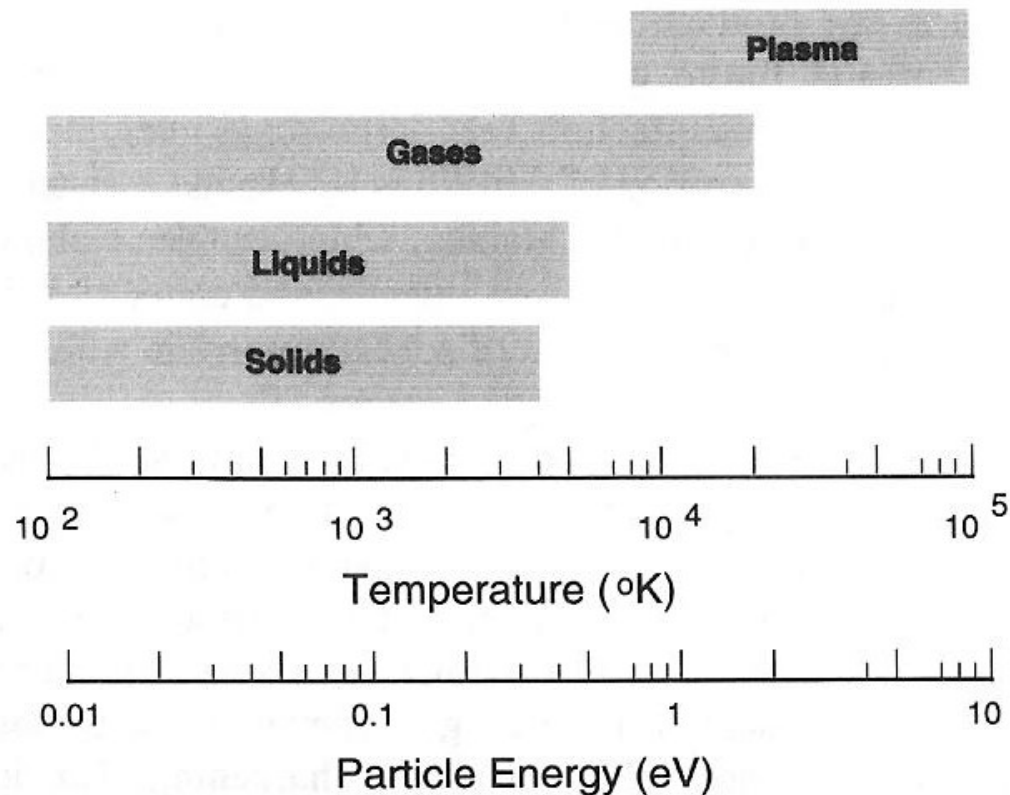




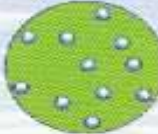
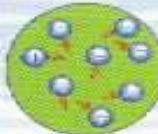
# Plasma Fundamentals

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# Plasma

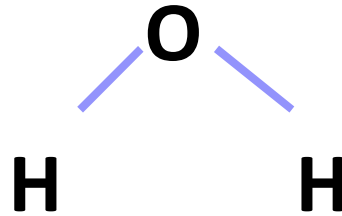
- Plasma (soup of ions, electrons & neutrals)
  - 4<sup>th</sup> state of matter
  - Ionized Gas



Solid	Liquid	Gas	Plasma
Example <b>Ice</b> $H_2O$	Example <b>Water</b> $H_2O$	Example <b>Steam</b> $H_2O$	Example <b>Ionized Gas</b> $H_2 \rightarrow H^+ + H^+ + 2e^-$
<b>Cold</b> $T < 0^\circ C$	<b>Warm</b> $0 < T < 100^\circ C$	<b>Hot</b> $T > 100^\circ C$	<b>Hotter</b> $T > 100,000^\circ C$ $I > 10$ electron Volts
			
<b>Molecules Fixed in Lattice</b>	<b>Molecules Free to Move</b>	<b>Molecules Free to Move, Large Spacing</b>	<b>Ions and Electrons Move Independently, Large Spacing</b>

# Breakdown of H<sub>2</sub>O molecules

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Radicals

Ions

Electrons

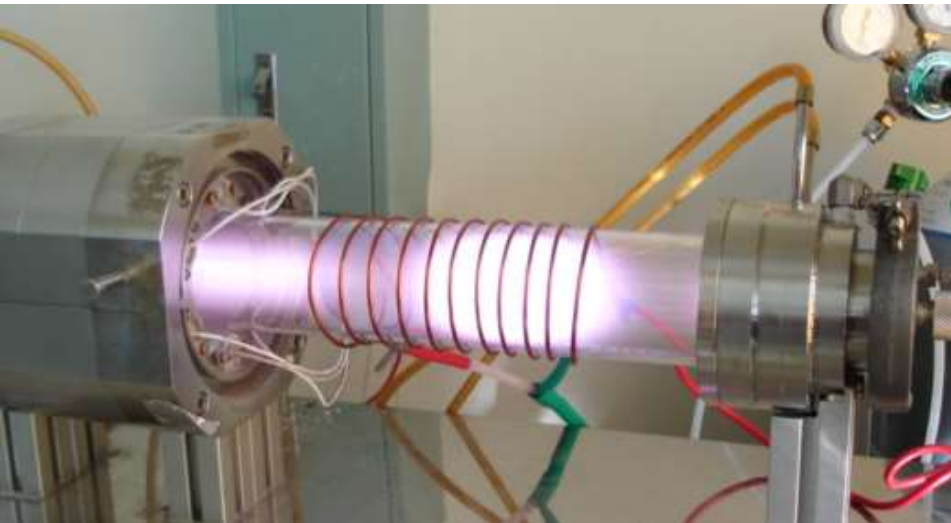
# Plasmas in Material Processing

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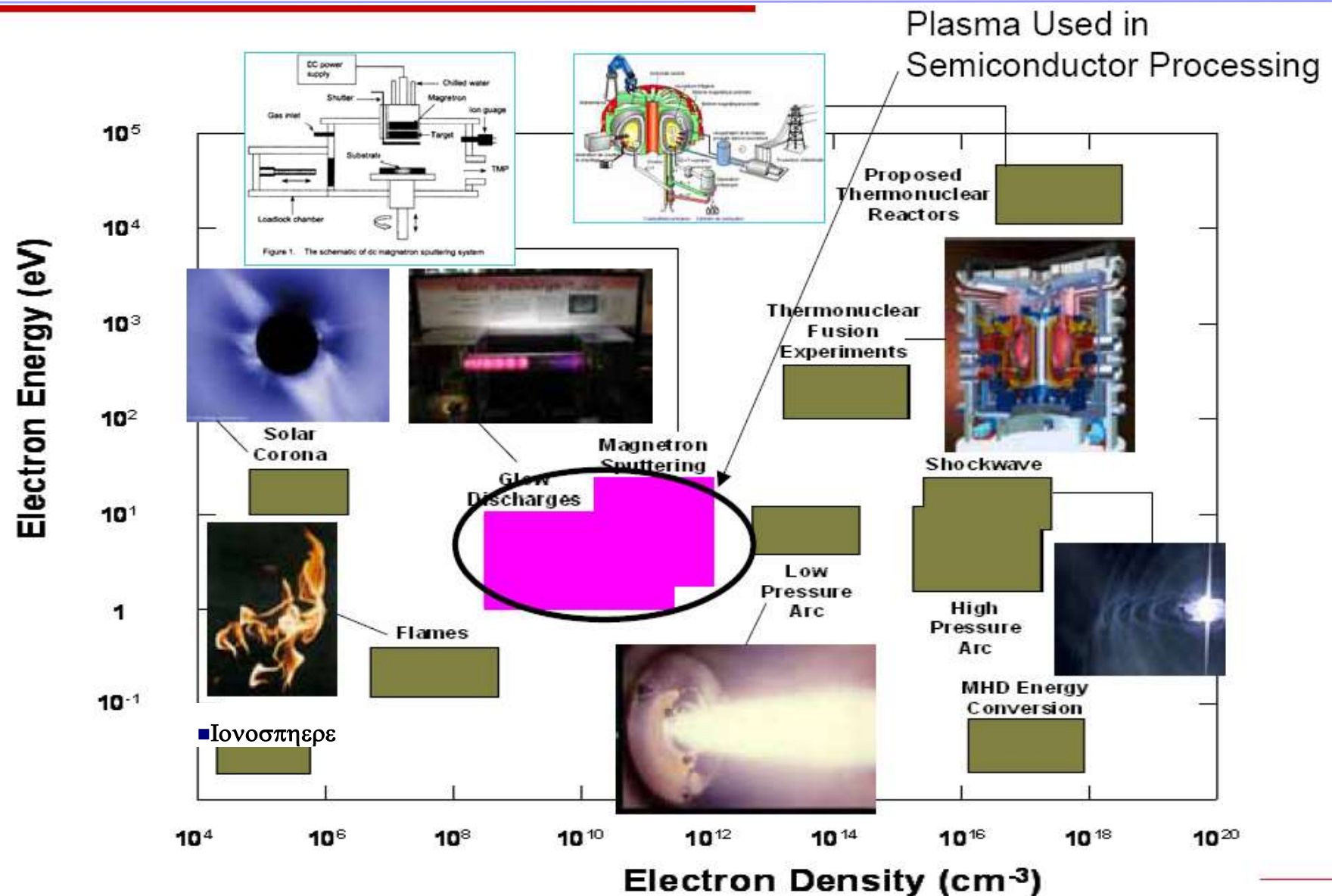


Graphics provided by UCLA

The low effluent temperature of atmospheric-pressure plasma makes the device ideal for several decontamination applications.

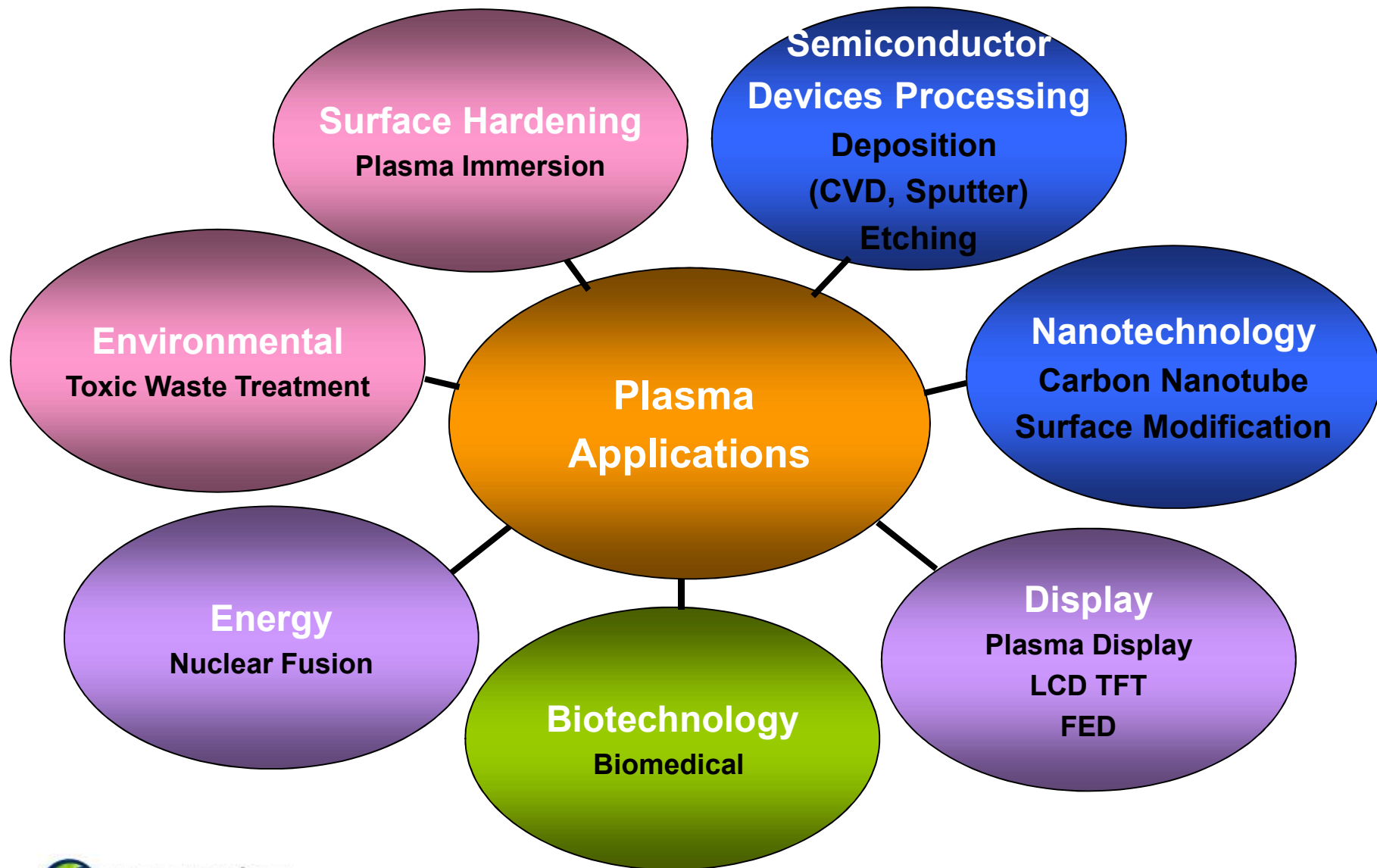


# Plasmas as Function of Electron Energy & Density



# Plasma Application Areas

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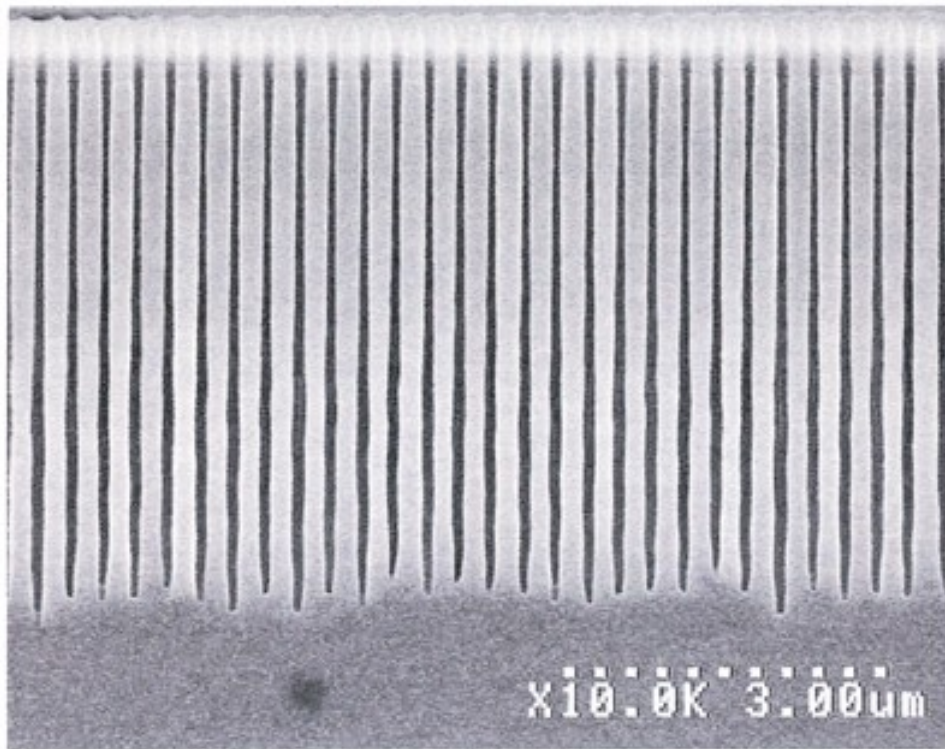




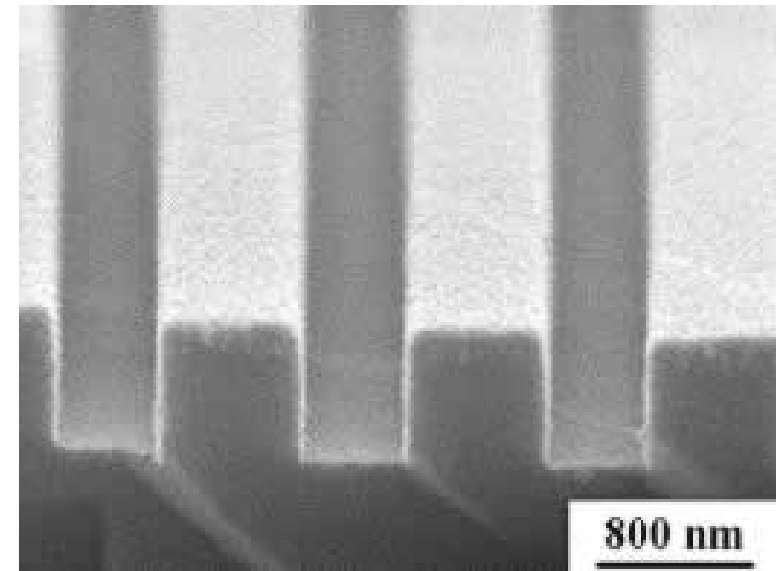
# Plasma Etching

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## High Aspect Ratio Si Etching



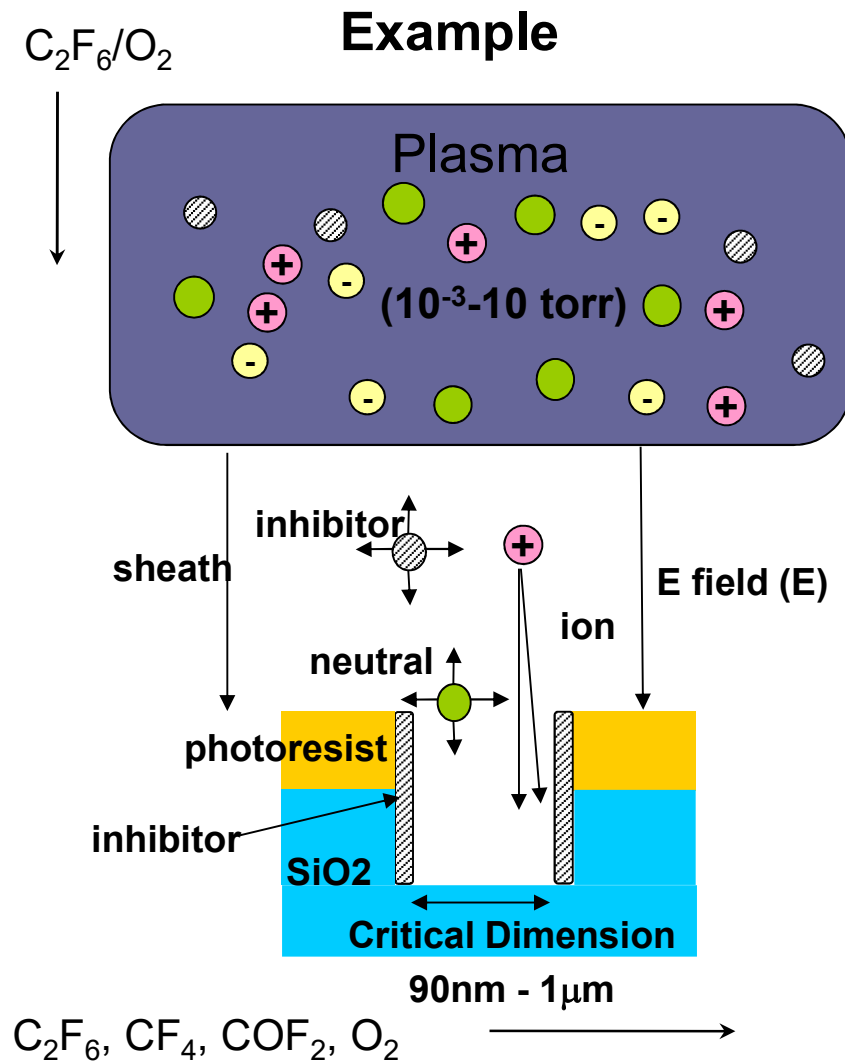
## Squared Etch Profile



[http://www.iom-leipzig.de/pic\\_schw/caibe1.jpg](http://www.iom-leipzig.de/pic_schw/caibe1.jpg)

■ <http://www.future-fab.com/assets/images/FFI11E1123F8b.htm>

# Plasma – Generation Process



## Plasma = Ionized Gas

Plasma (Soup of electrons, ions, radicals and molecules)

- Electric energy transferred to electron (1-5eV)
- Electron collides with molecules to generate ions and neutrals
- Ions and electrons are in balance (quasi-neutral)
- Ions are accelerated in sheath (high energy ions)
- Surface reacts with ions and neutrals



# Why Plasma ?

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## ■ Radicals:

- ☐ atomic or molecular species with unpaired electrons on an otherwise open shell configuration. These unpaired electrons are usually highly reactive, so radicals are likely to take part in chemical reactions. (Ex: CH, CF, CF<sub>2</sub>, OH, ...)
- ☐ For PECVD, cleaning, ashing, etc.

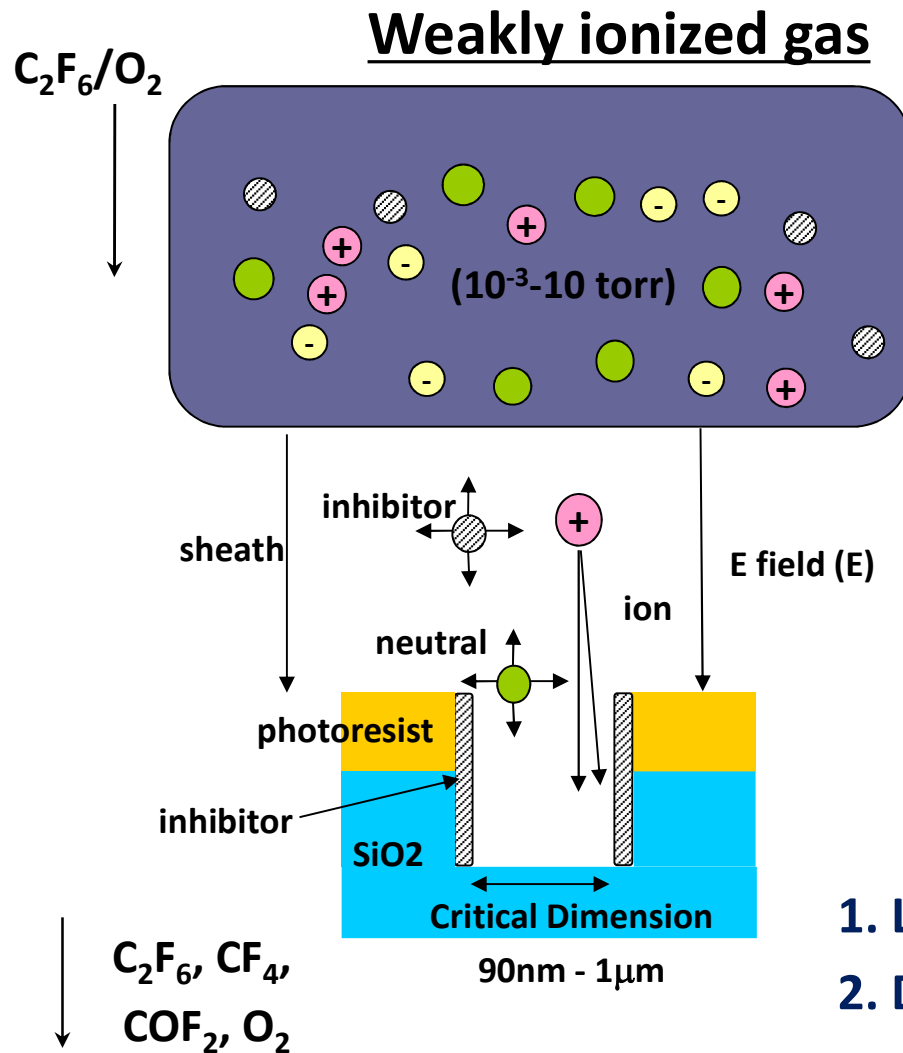
## ■ Ions

- ☐ Ions deliver energy to surface with electric field in sheath.
- ☐ For sputtering and anisotropic etching

## ■ UV light

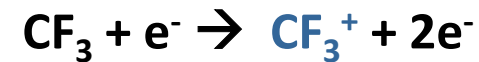
- ☐ Plasma emits UV and visible light.
- ☐ Applied to plasma display panel

# Plasma – Reaction Example



## Example

### Dominant Reactions in Plasma (example)



### Dominant Surface Reactions (example)



1. Low T processing by reactive radicals & ions
2. Directionality due to ion and electric field

# Plasma

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	Electron	Ion	Radical	Molecules
Mass				
Fraction				
Density				
Energy				
Function				

# Plasma in IC Processing

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Property	Range
Pressure	0.001 – 10 torr
Electron density - Low density - High density	$10^9 - 10^{11} \text{ cm}^{-3}$ $10^{11} - 10^{13} \text{ cm}^{-3}$
Average electron energy	1 – 10 eV
Average neutral and ion energy, $k_B T$	0.025 – 0.05 eV
Free radical density	5 – 90 %
Ionized fraction of gas - Low density - High density	$10^{-5} - 10^{-7}$ $10^{-3} - 10^{-1}$
Neutral diffusivity	20 – 20,000 $\text{cm}^2/\text{s}$
Power dissipation	0.1 – 10 $\text{W}/\text{cm}^2$ (or $\text{W}/\text{cm}^3$ )

# Plasma Potential in DC Glow Discharge

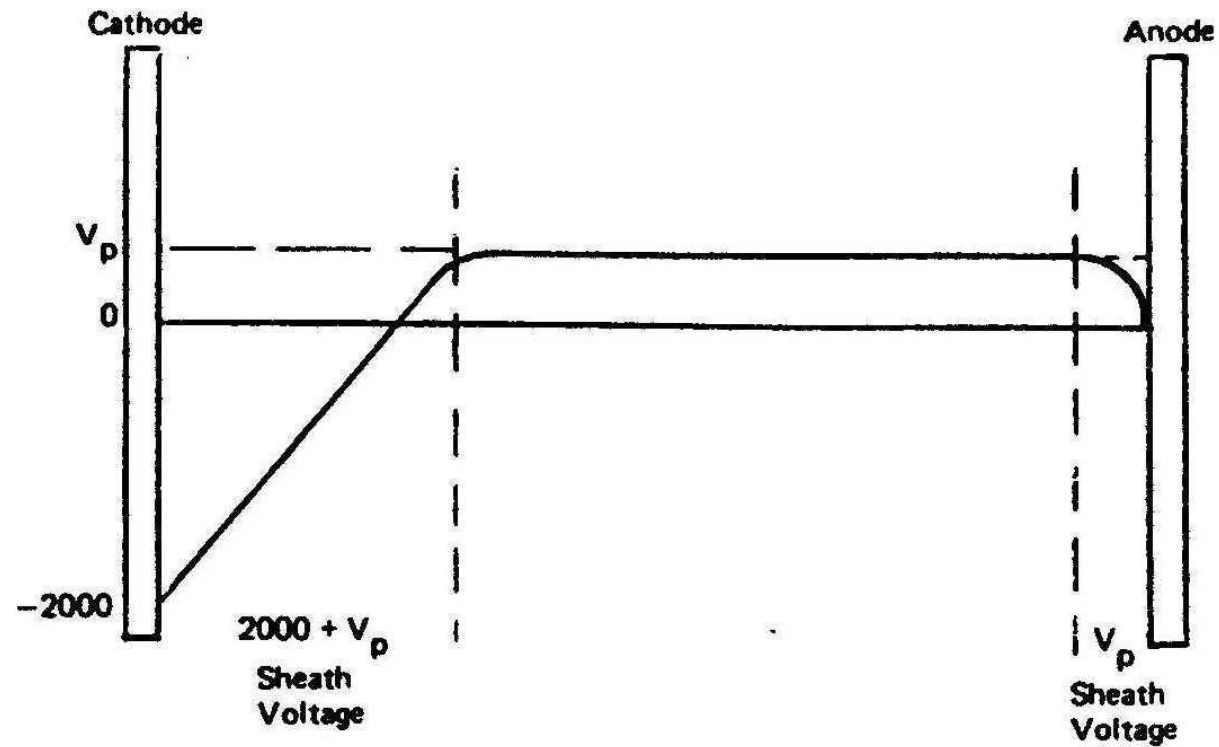
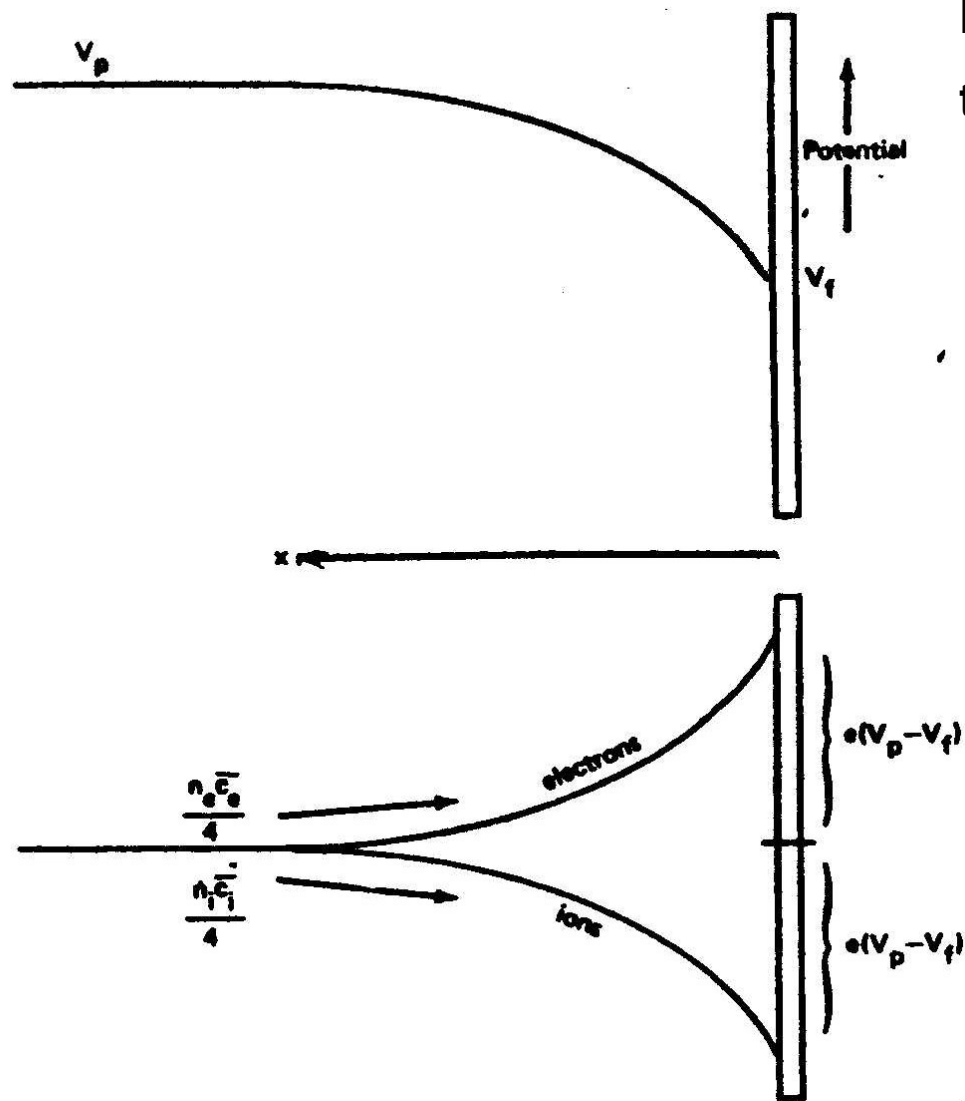
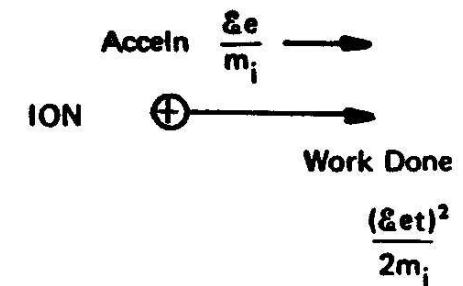
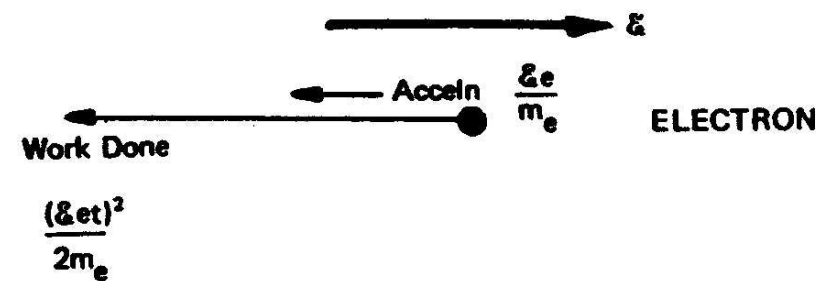


Figure 4-4. Voltage distribution in a dc glow discharge process

# Energy Transfer from the Electric Field in Sheath



Energy Transfer from the Electric Field  
to electrons and ions

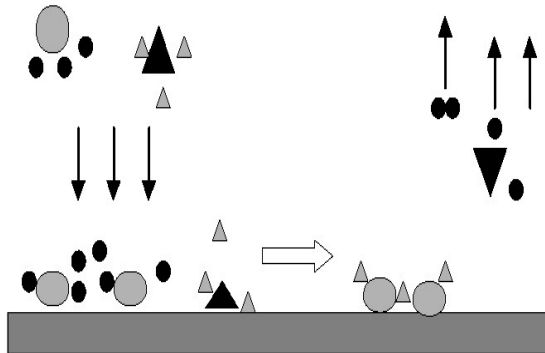


# **Physical Vapor Deposition: Plasmas Sputtering & Evaporation**

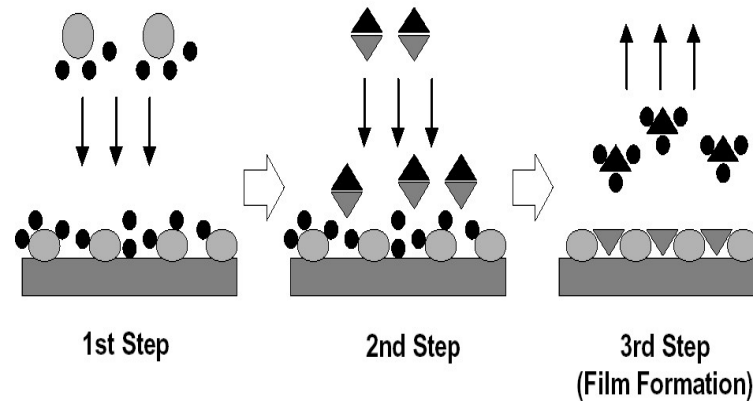
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# Models of Thin Film Deposition

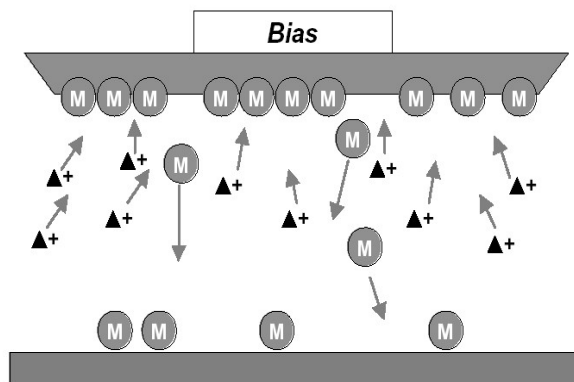
CVD Model



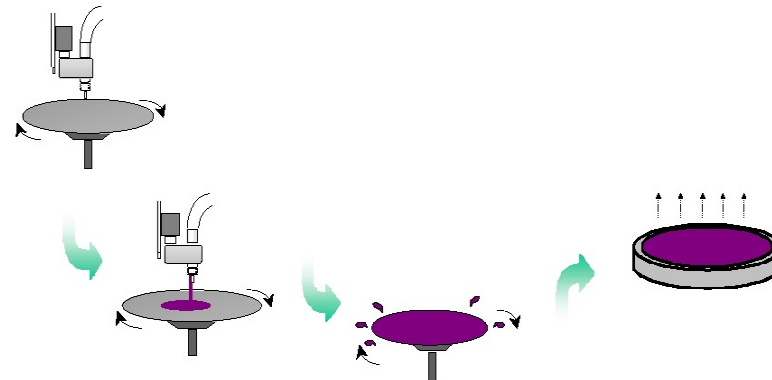
ALD Model



PVD Model



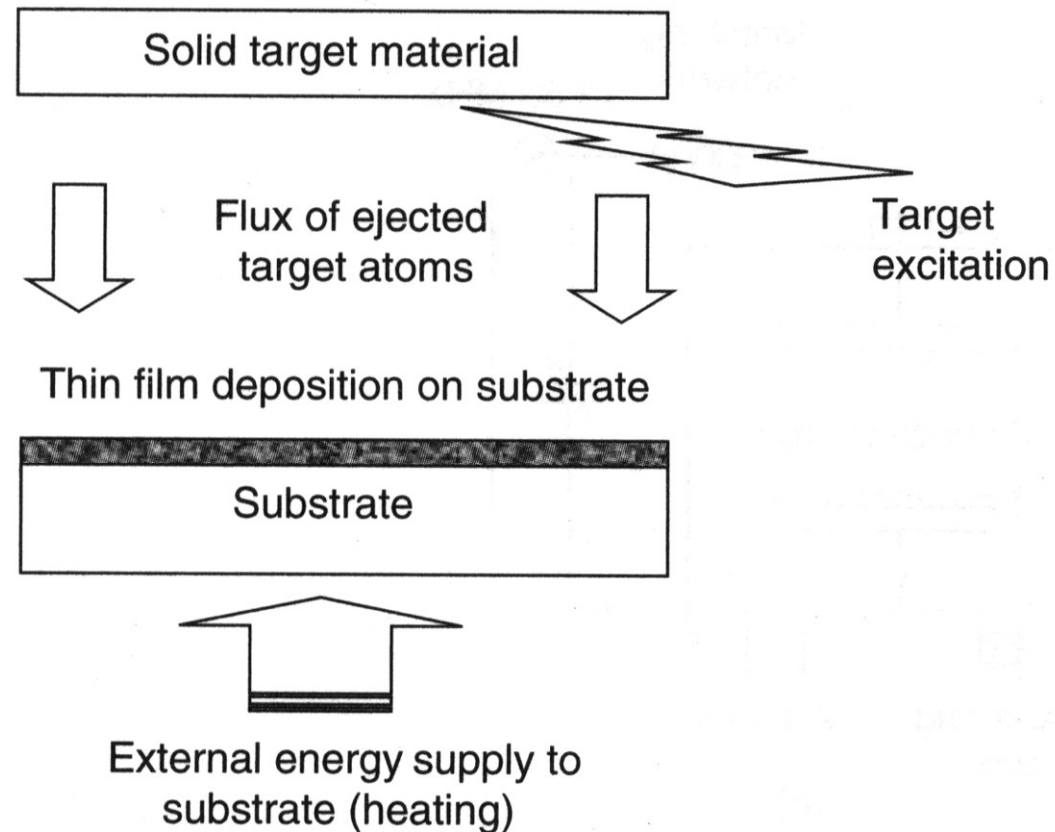
SOD Model





# Physical Vapor Deposition (PVD)

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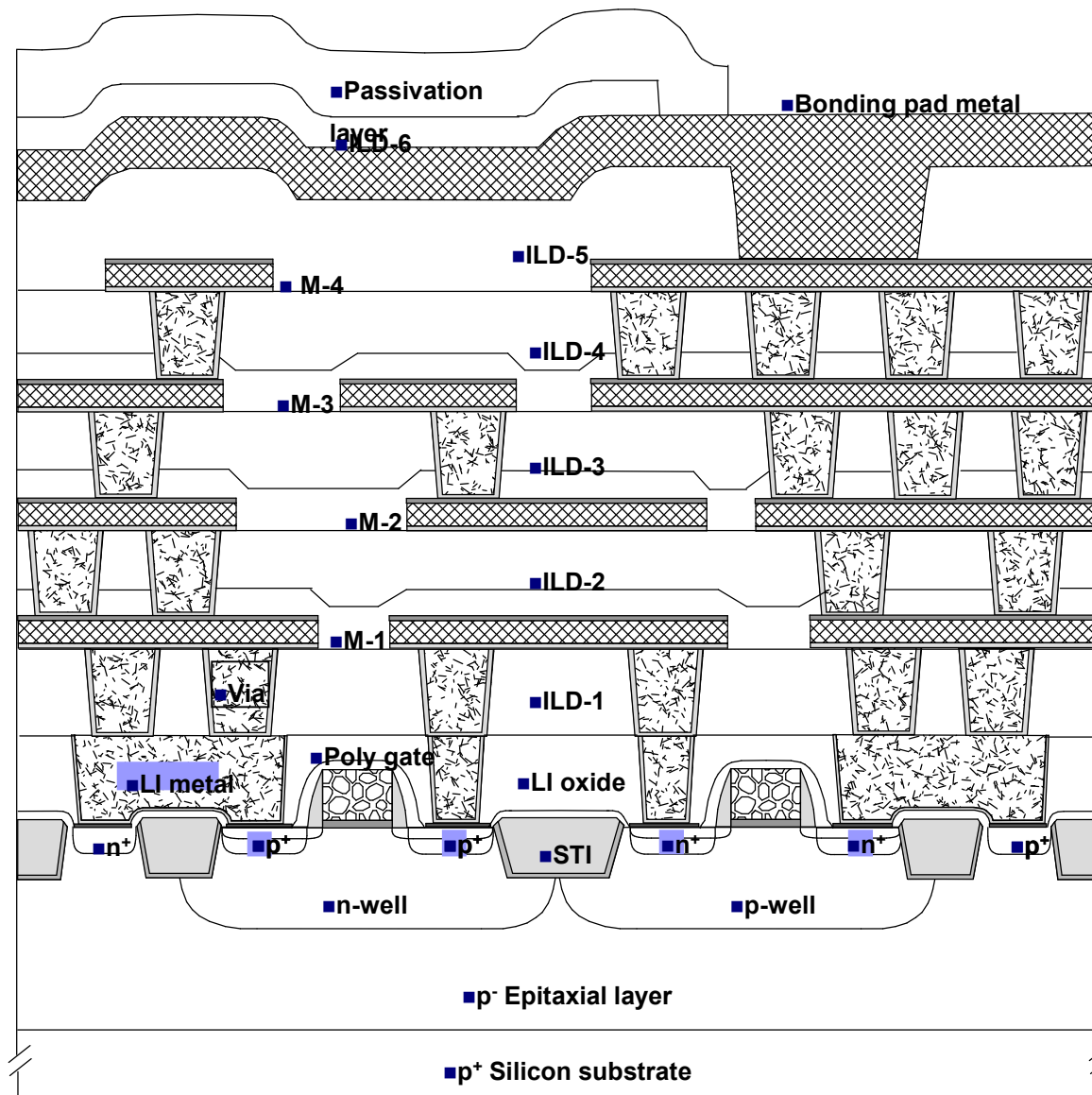
**Figure 5.2** The principle of physical vapour deposition in a vacuum system

# Characteristics of Deposition Processes

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	PE-CVD	LP-CVD AP-CVD	PVD	ALD	SOD
<b>Fine THK Control</b>	bad	good	bad	Excellent	Good
<b>Step Coverage</b>	bad	Very good	bad	Excellent	Excellent
<b>Throughput</b>	high	low	high	Very low	high
<b>Pin Hole Density</b>	Not bad	Not bad	high	low	high
<b>Film</b>	SiO <sub>2</sub> , SiN, SiC, SiOC, a-C	Si, SiO <sub>2</sub> , SiN, W, WSi <sub>x</sub>	Ti, TiN, Al, Cu, TaN, W	SiN, TiN, Al <sub>2</sub> O <sub>3</sub> , TaO, HfO	SiO <sub>2</sub> , SiOC, a-C:H

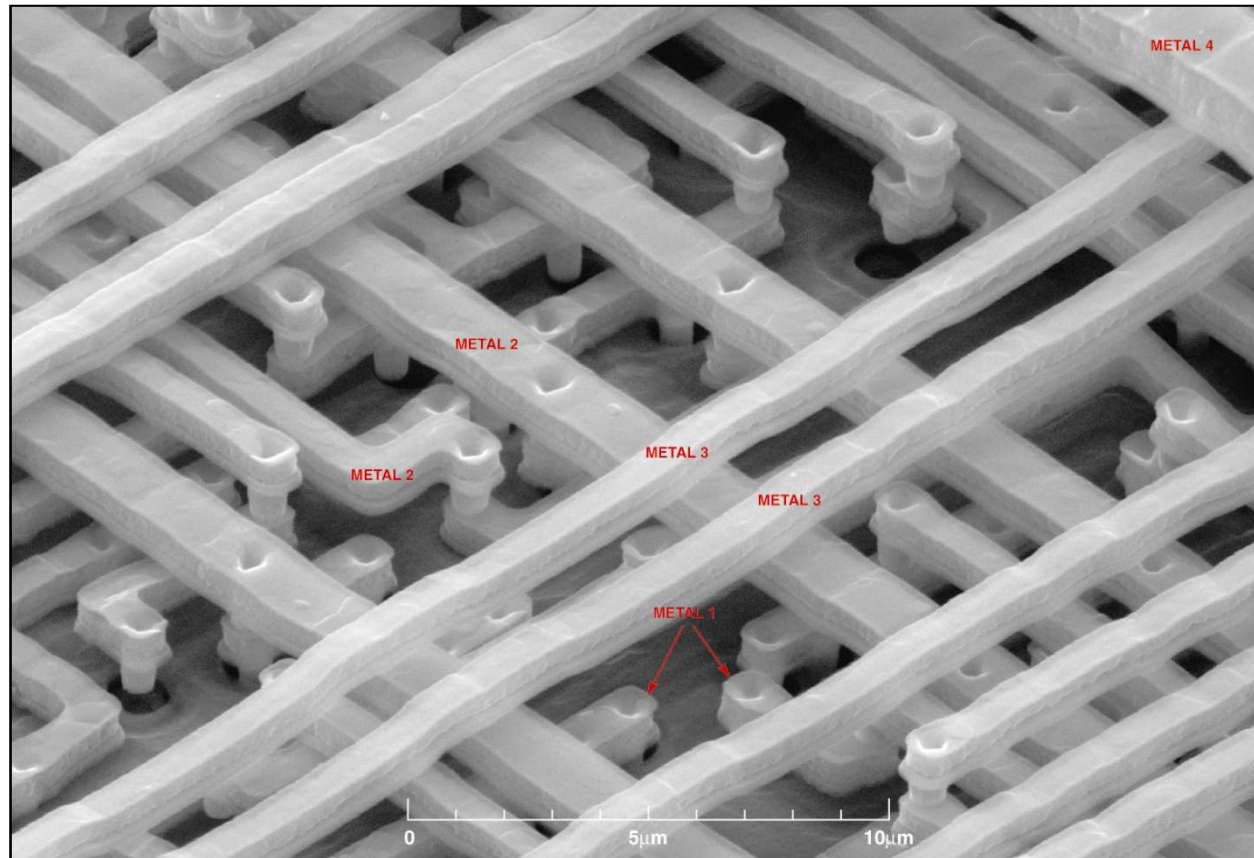
# Multilevel Metallization on a ULSI Wafer



■ M. Quirk, J.  
Serda

# Metal Layers in a Chip

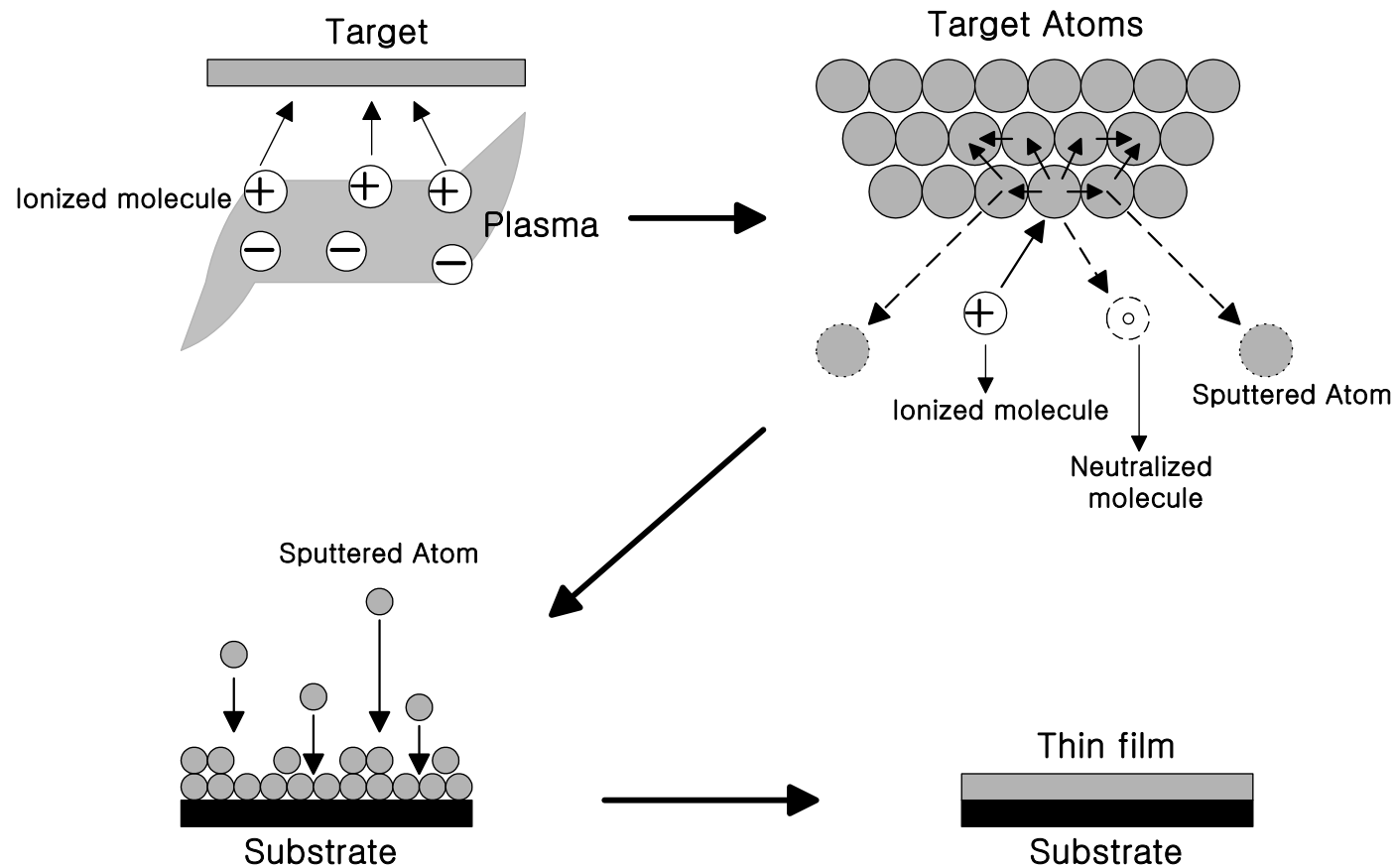
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■ Micrograph courtesy of Integrated Circuit Engineering

■ M. Quirk, J. Serda, Semiconductor Manufacturing Technology

# PVD: Sputtering



- High energy ions generated by plasma strike target materials and target material is deposited on substrate

# Why Plasma ?

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- Radicals:

- ☐ atomic or molecular species with unpaired electrons on an otherwise open shell configuration. These unpaired electrons are usually highly reactive, so radicals are likely to take part in chemical reactions. (Ex: CH, CF, CF<sub>2</sub>, OH, ...)
- ☐ For PECVD, cleaning, ashing, etc

- Ion

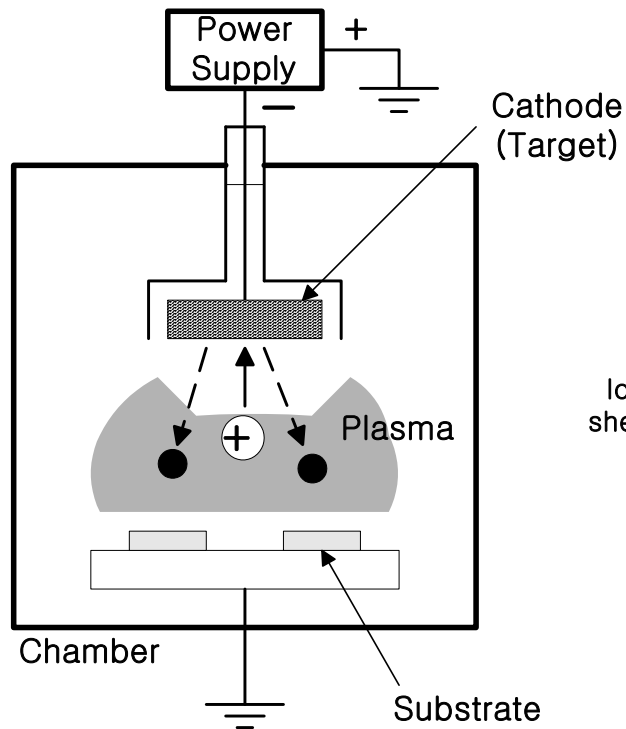
- ☐ Ions deliver energy to surface with electric field in sheath.
- ☐ For sputtering and anisotropic etching

- UV light

- ☐ Plasma emits UV and visible light.
- ☐ Applied to plasma display panel

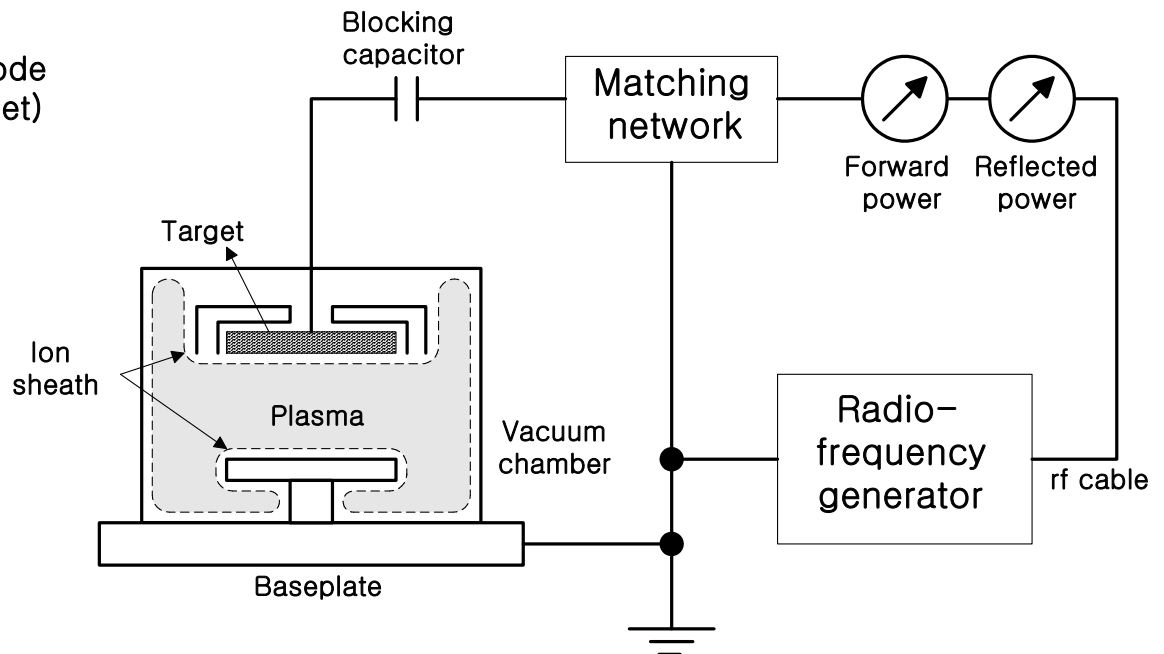
# PVD: Sputtering Types

## ■ DC powered plasma



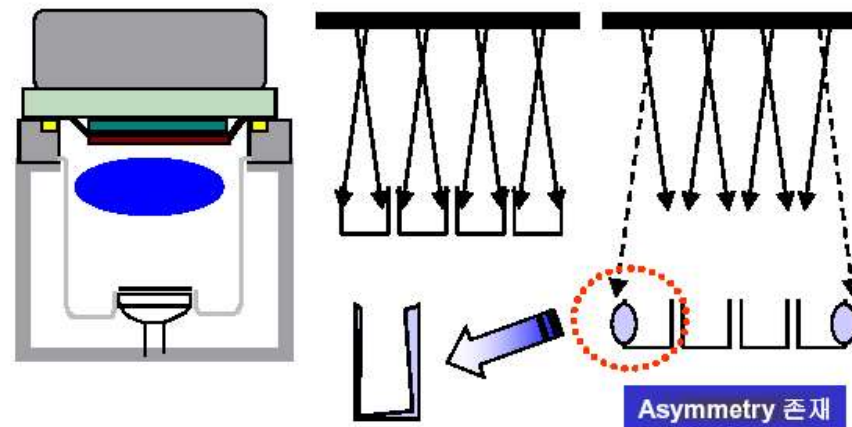
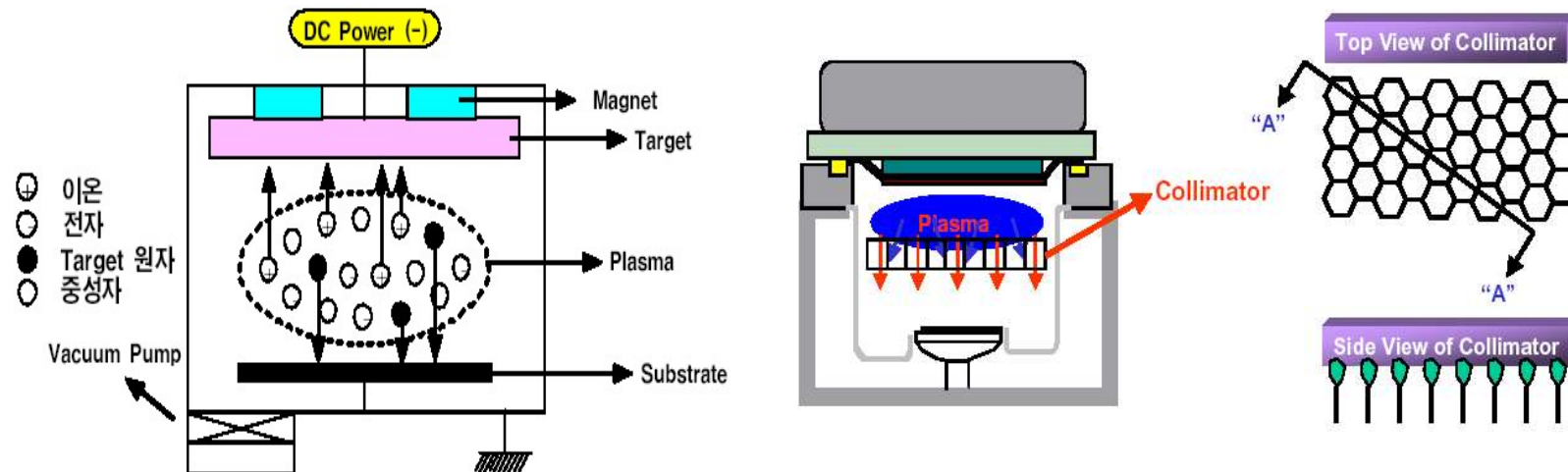
- Relatively simple
- Dielectric materials cannot be sputtered due to charge build-up

## □ RF powered plasma



- Radio-frequency power used
- Dielectric material can be sputtered

# PVD 장비



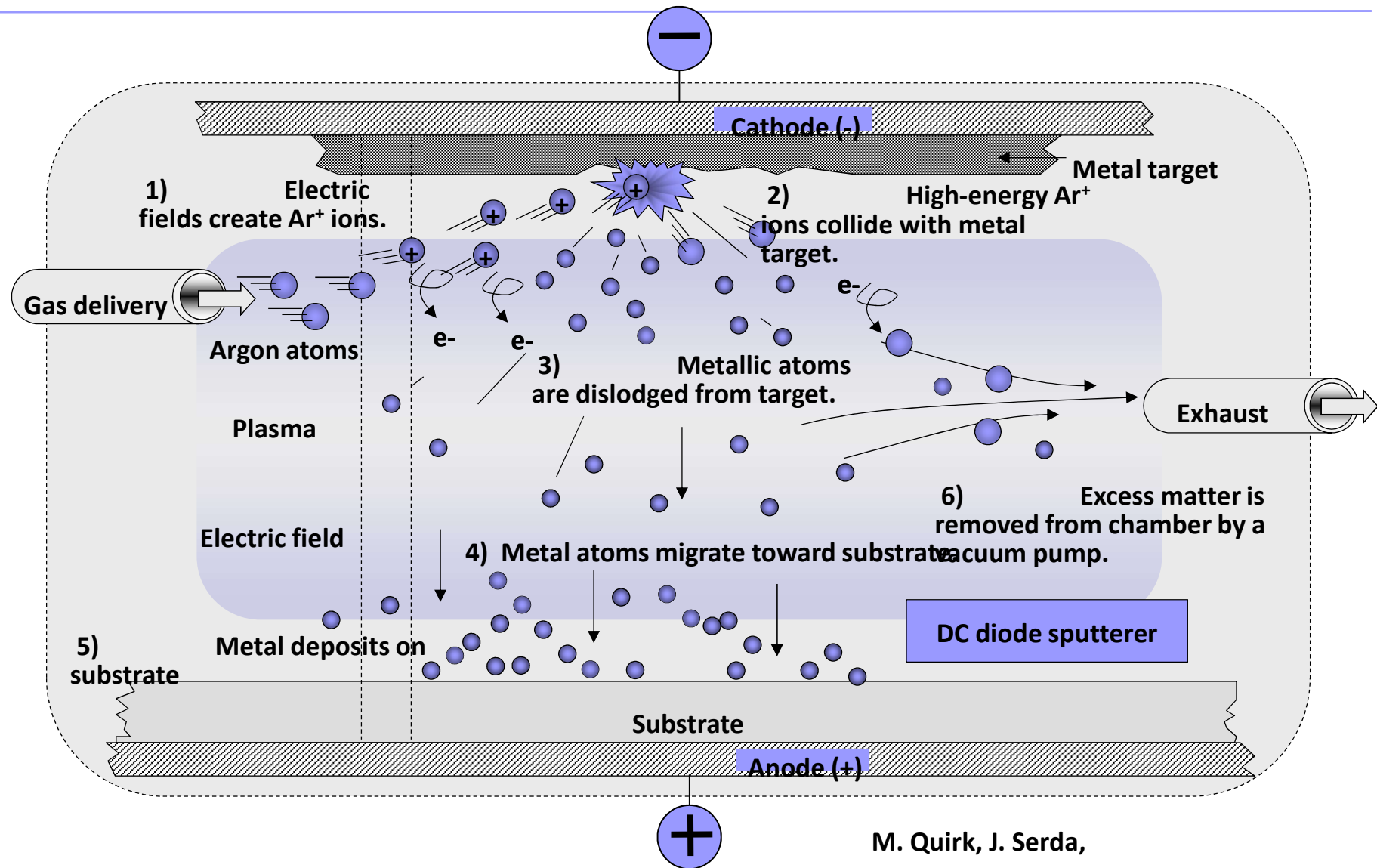


# Some Advantages of Sputtering

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1. Ability to deposit and maintain complex alloys.
2. Ability to deposit high-temperature and refractory metals.
3. Ability to deposit controlled, uniform films on large wafers (200 mm and larger).
4. Ability of multichamber cluster tools to clean the wafer surface for contamination and native oxides before depositing metal (referred to as in situ sputter etch).

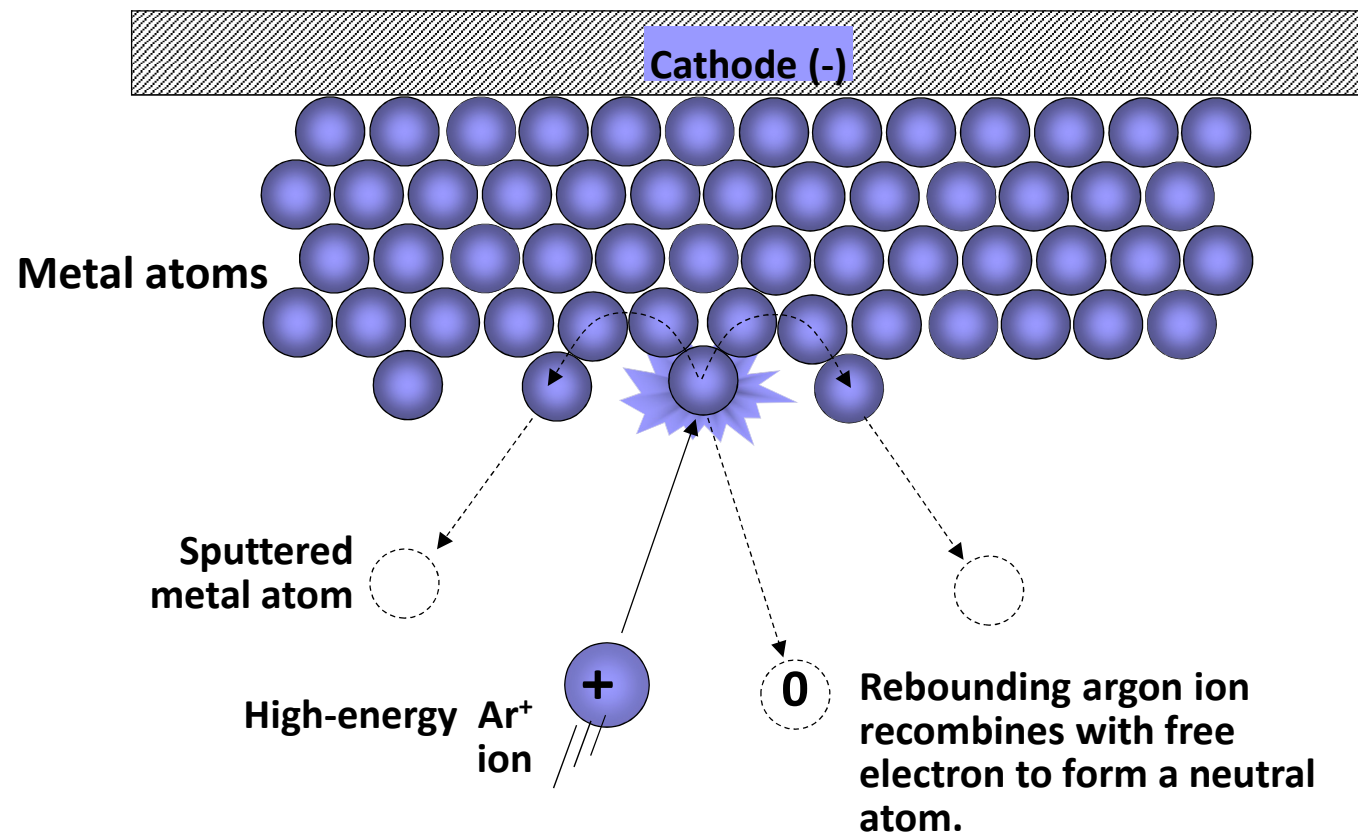
# Simple Parallel Plate DC Diode Sputtering System



M. Quirk, J. Serda,

Semiconductor Manufacturing Technology

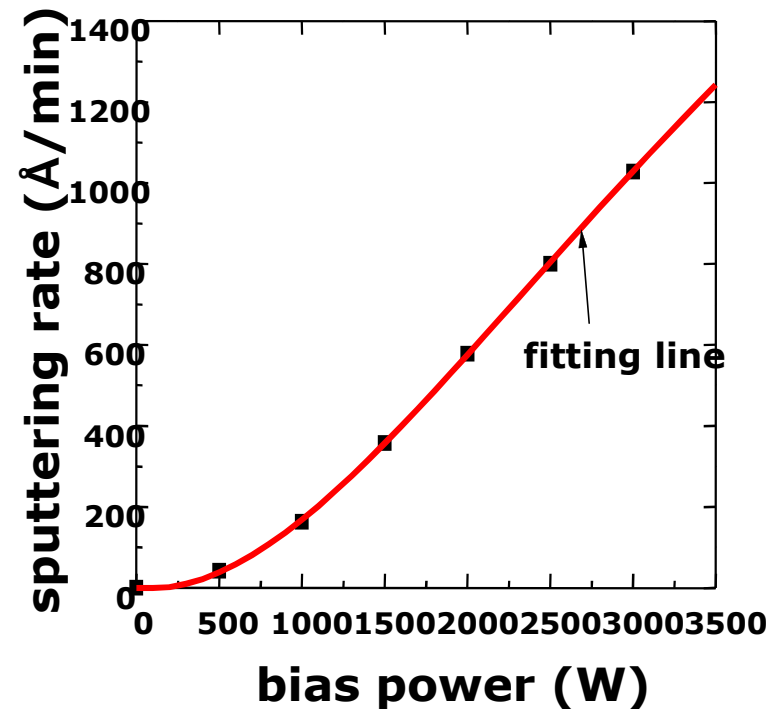
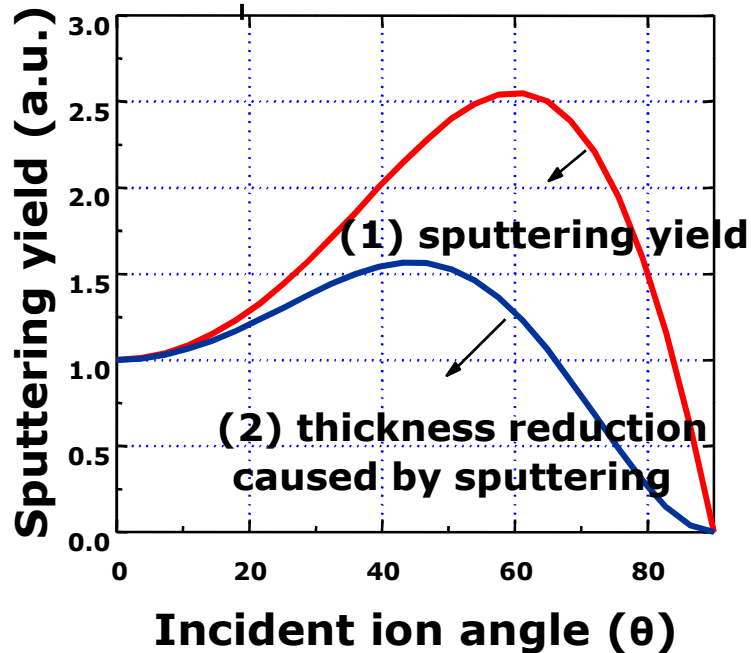
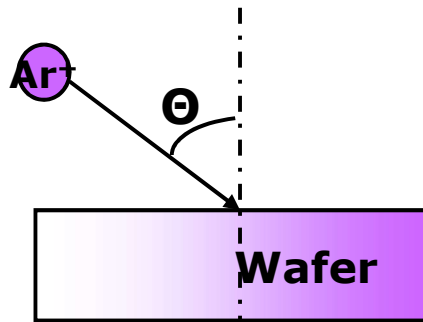
# Dislodging Metal Atoms from Sputtering Target



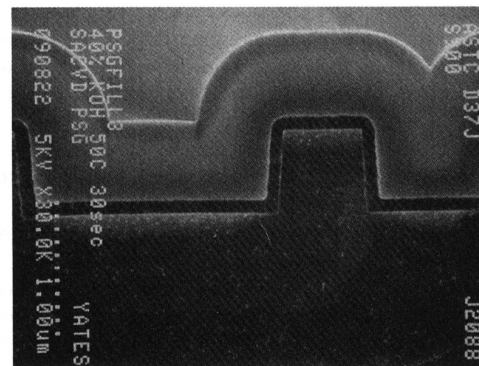
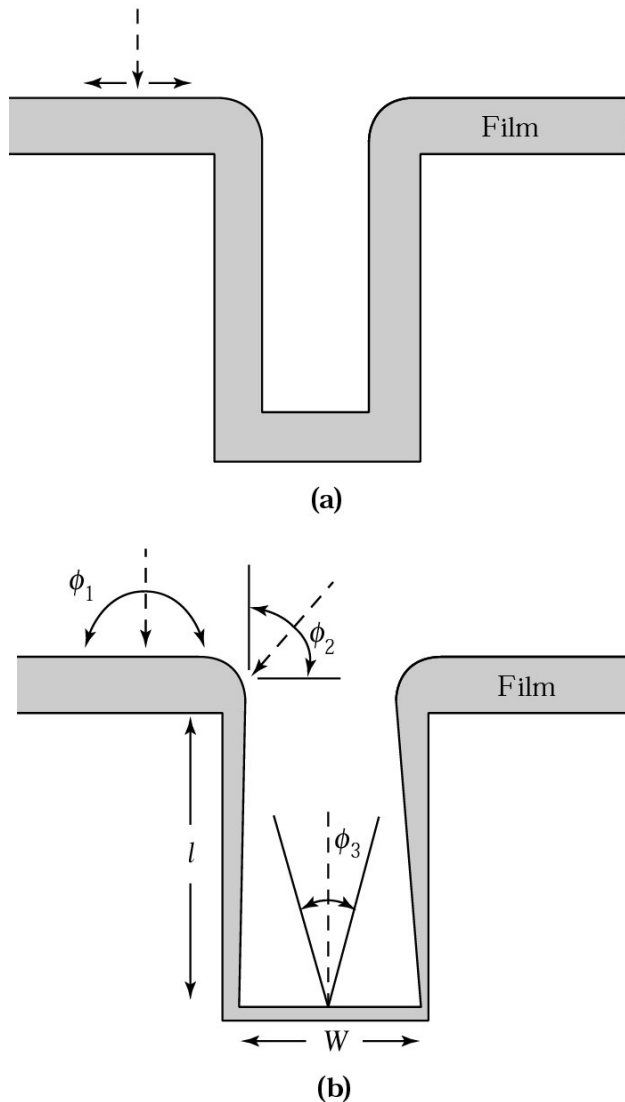
M. Quirk, J. Serda, Semiconductor Manufacturing Technology

# Factors affecting sputtering yield

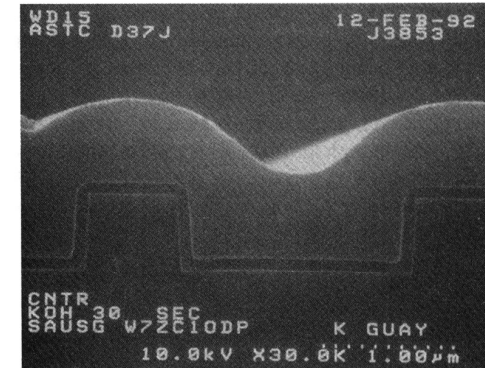
1. Incident angle of the bombarding ions.
2. Composition and geometry of the target material.
3. Mass of bombarding ions.
4. Energy of the bombarding ions.



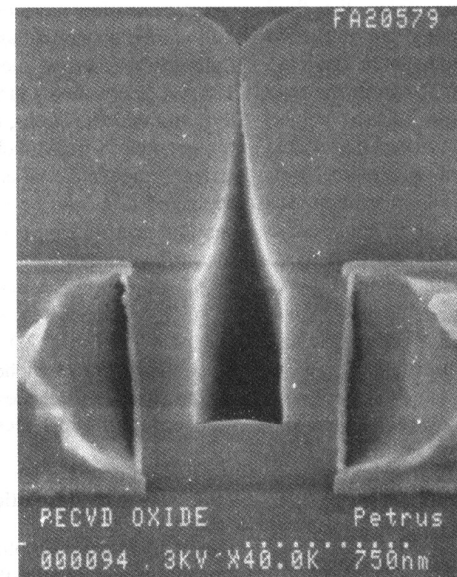
# Step Coverage



(a)



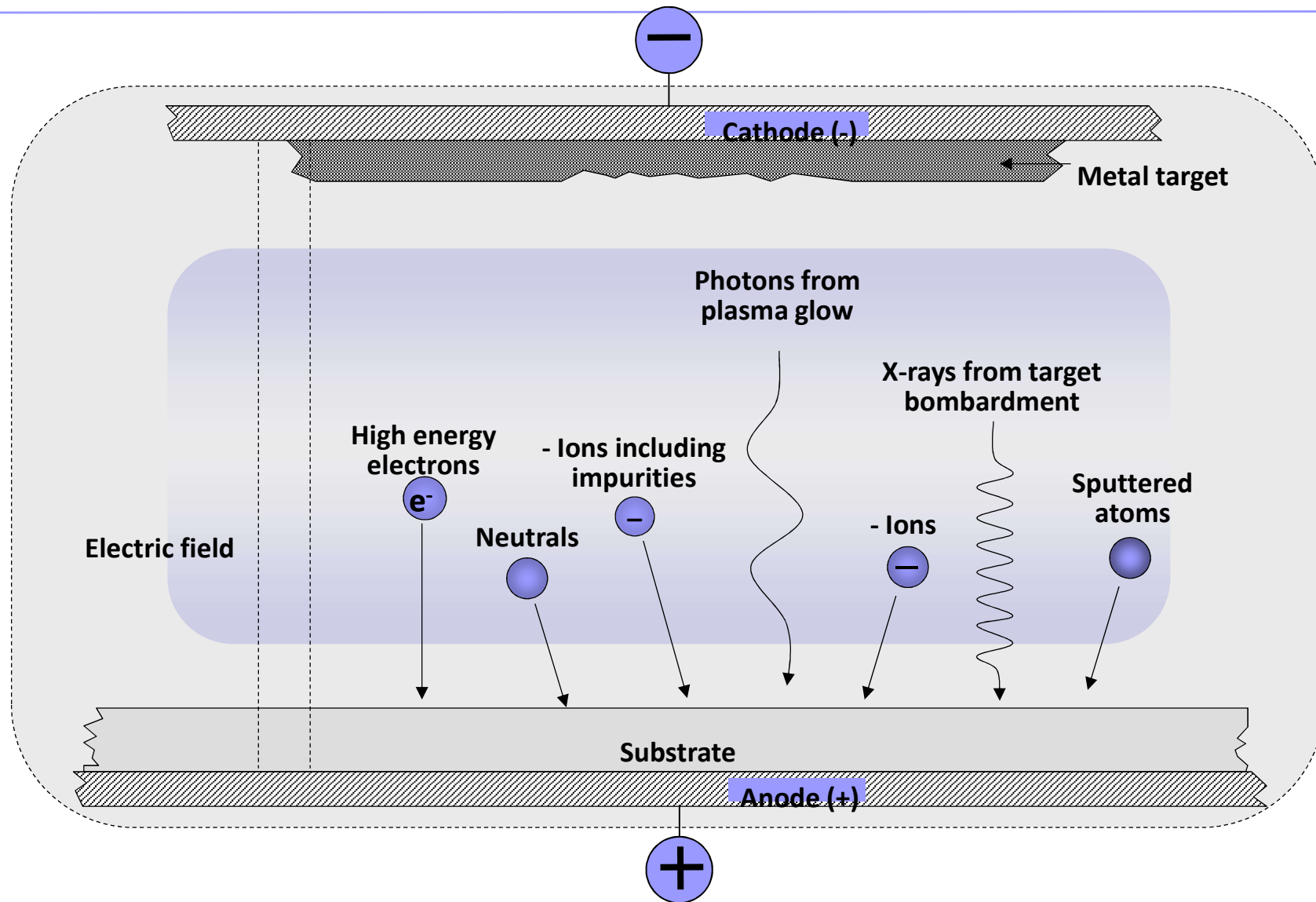
(b)



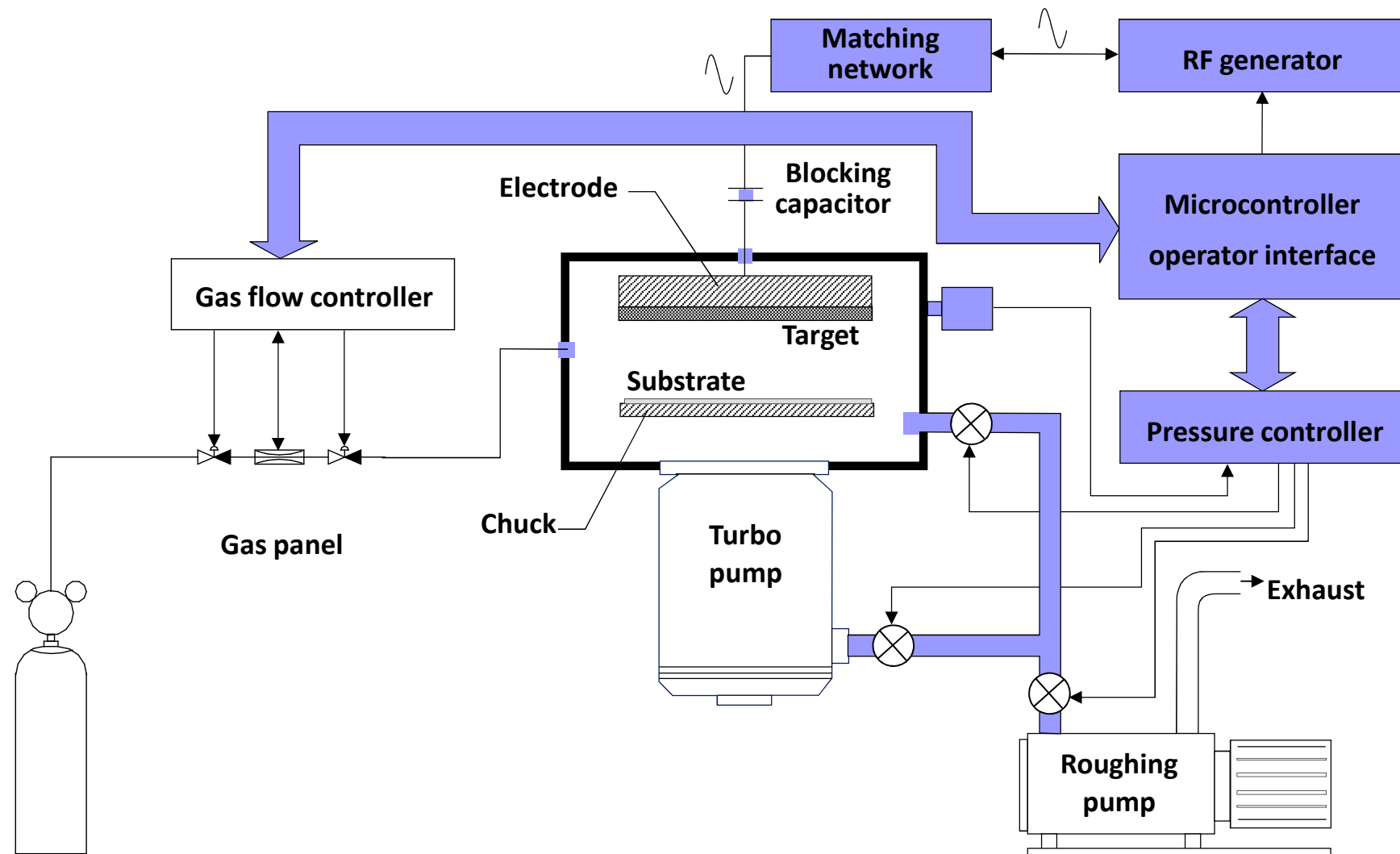
(c)

**Figure 7.16** Step coverage in different CVD processes: (a) phosphorus doped CVD oxide with conformal (100%) step coverage, (b) undoped CVD oxide with flow-like profiles and (c) PECVD oxide from silane/nitrous oxide reaction leads to a void formation. Reproduced from Cote, D.R. *et al.* (1995), by permission of IBM

# Different Species Landing on Substrate



# RF Sputtering System

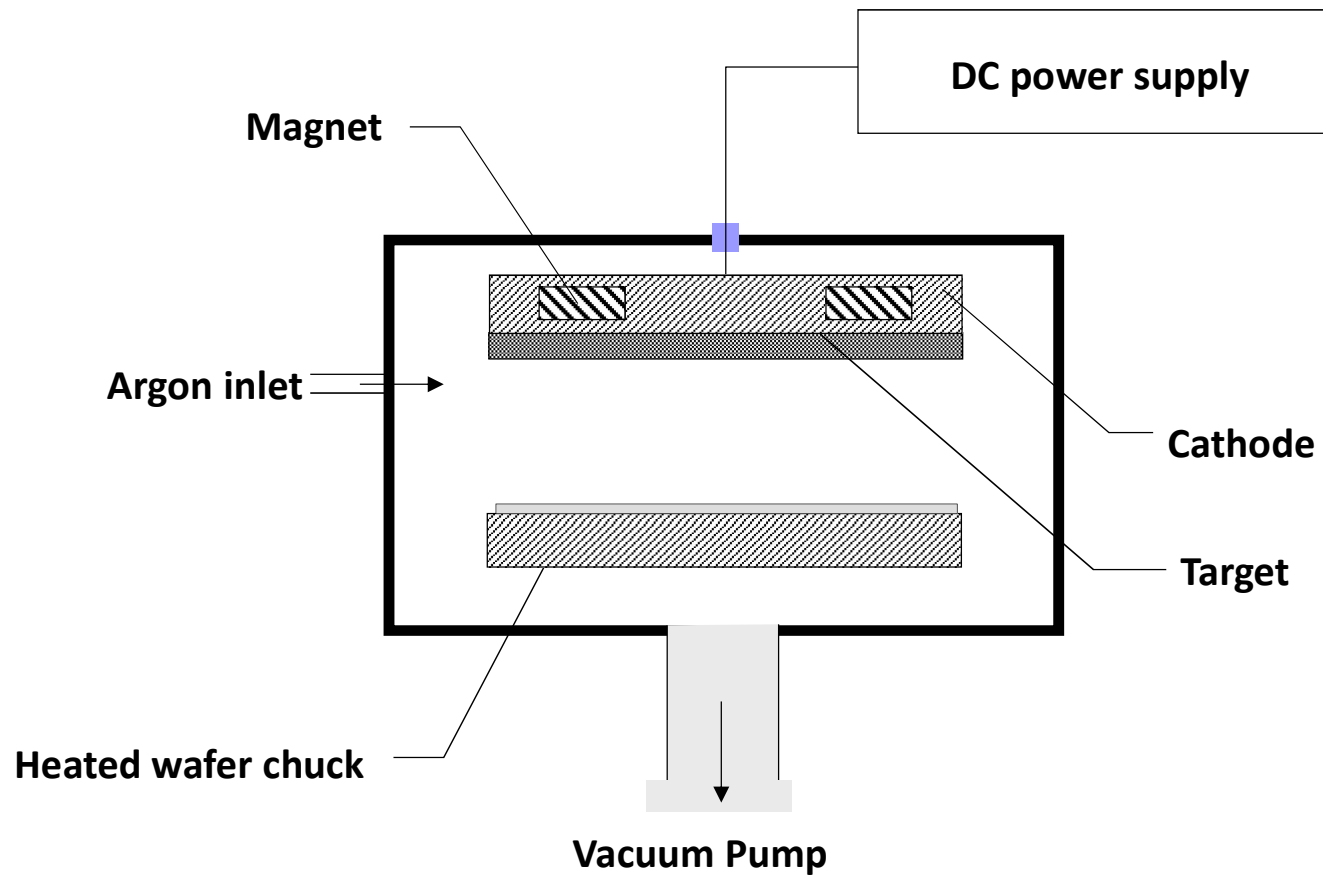


Argon



# Magnetron Sputtering

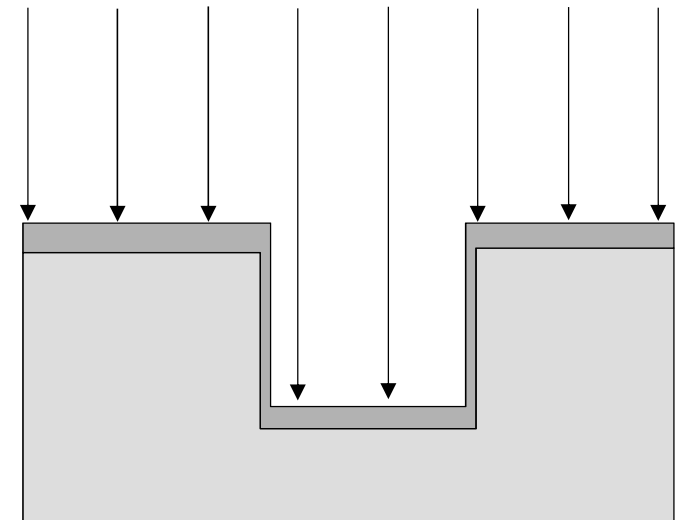
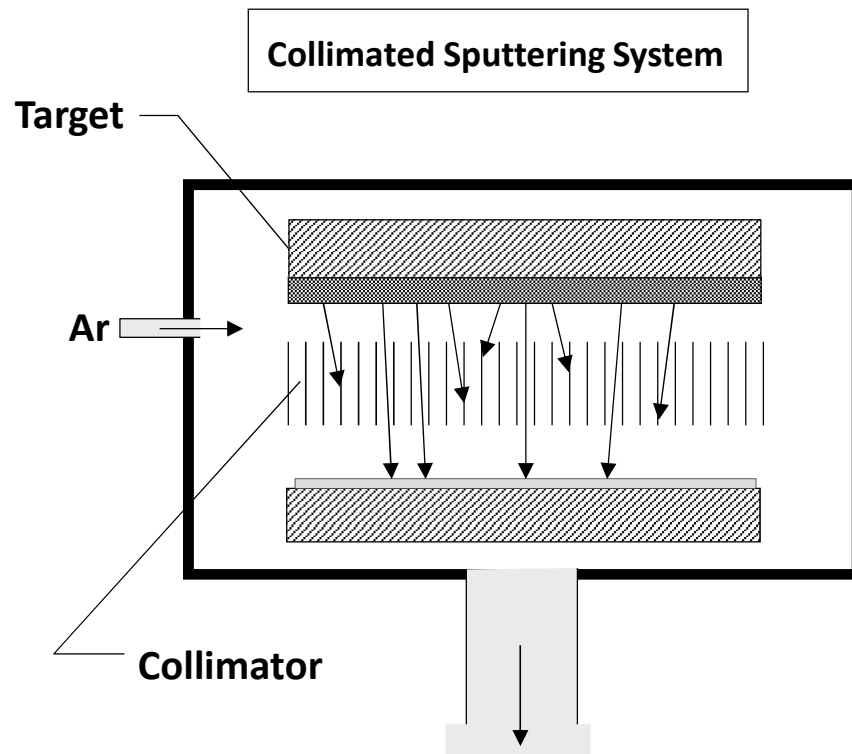
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Technology

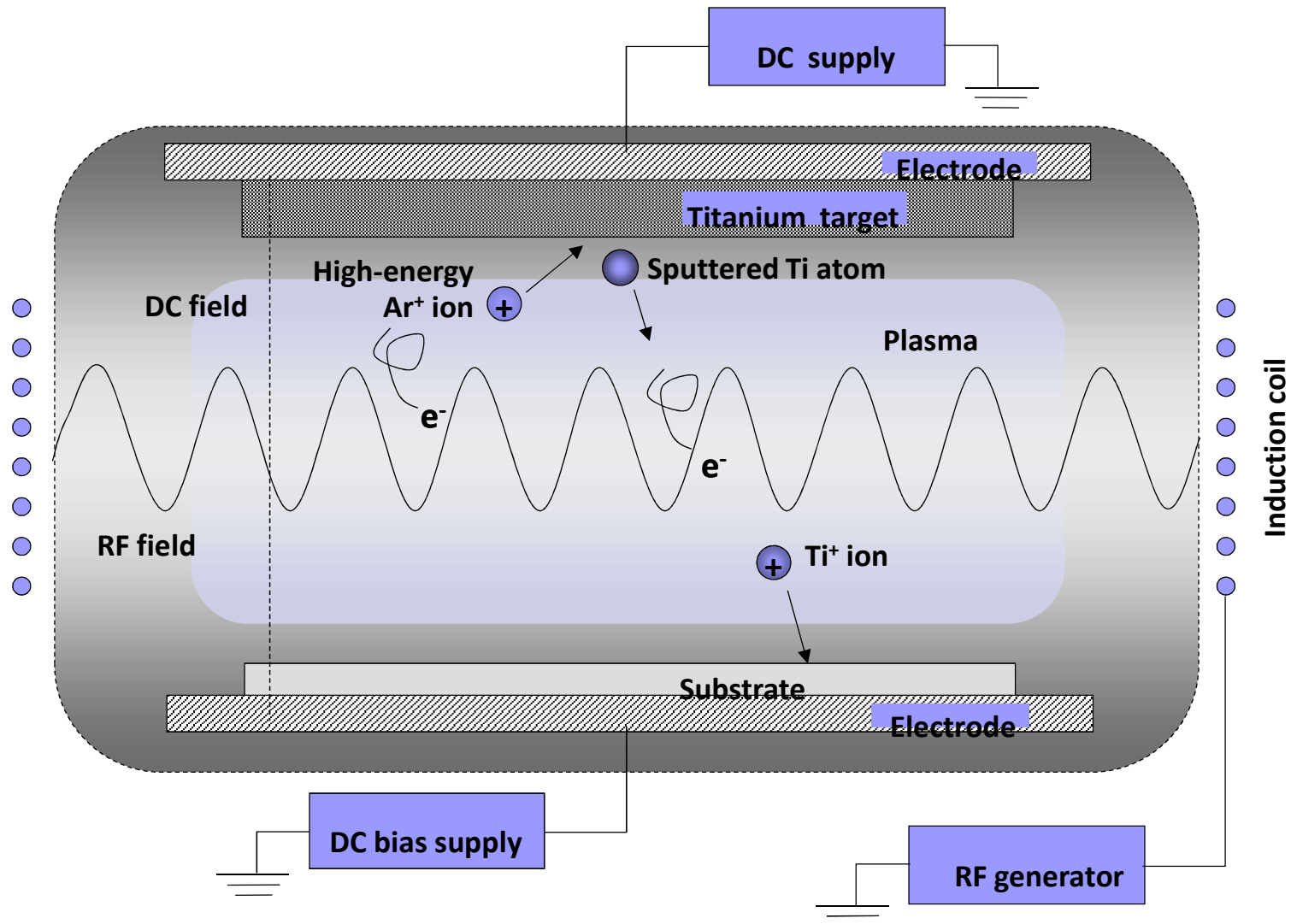


# Collimated Sputtering



Cross section of via showing coverage of resulting sputtered film.

# Concept of Ionized Metal Plasma PVD



M. Quirk, J. Serda, Semiconductor Manufacturing Technology

# PVD Cluster Tool

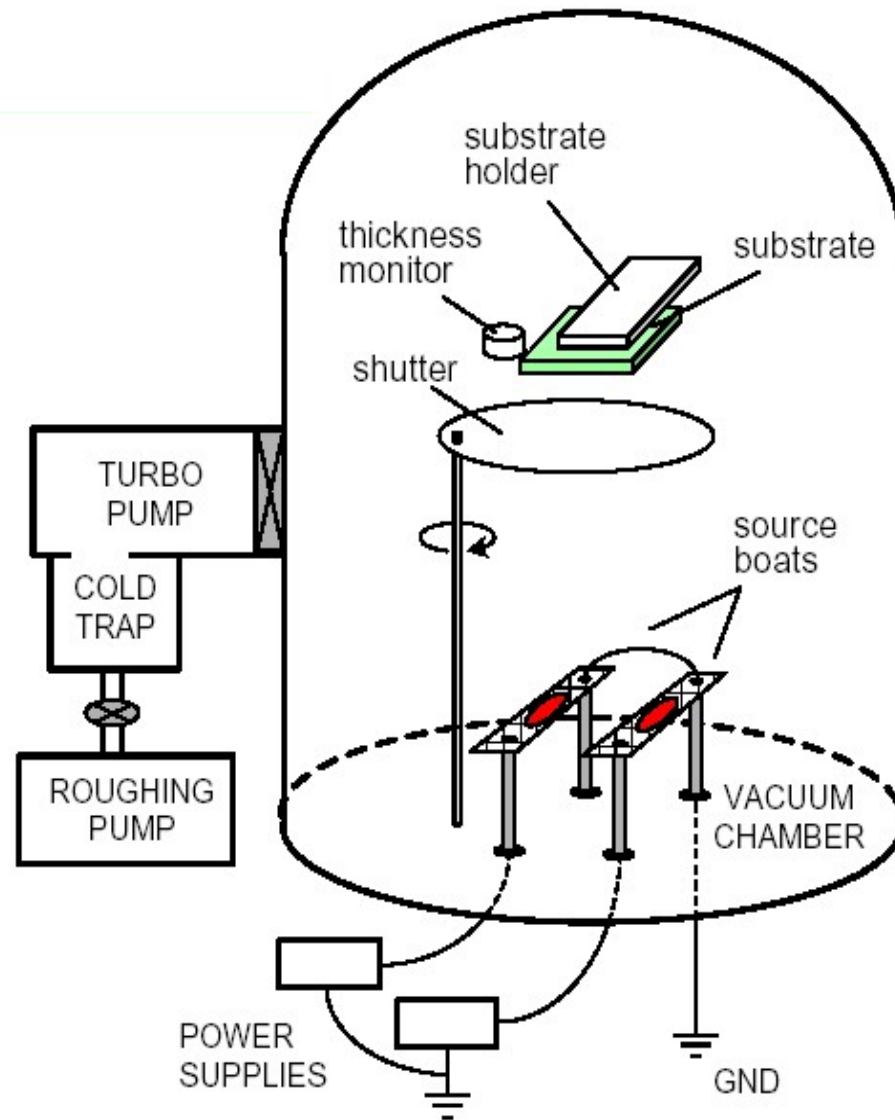
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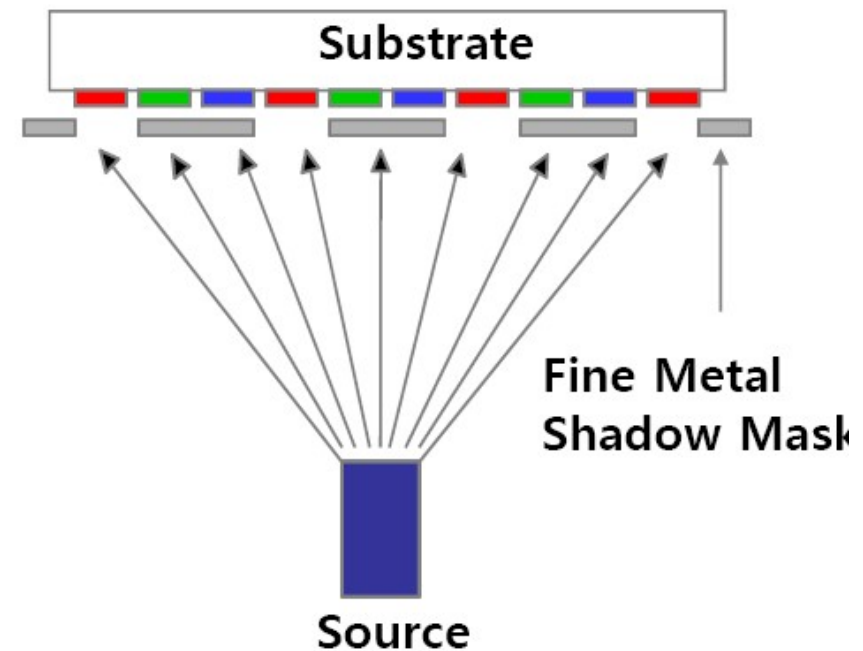
Applied Materials

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Semiconductor Manufacturing  
Technology

# Evaporation Process

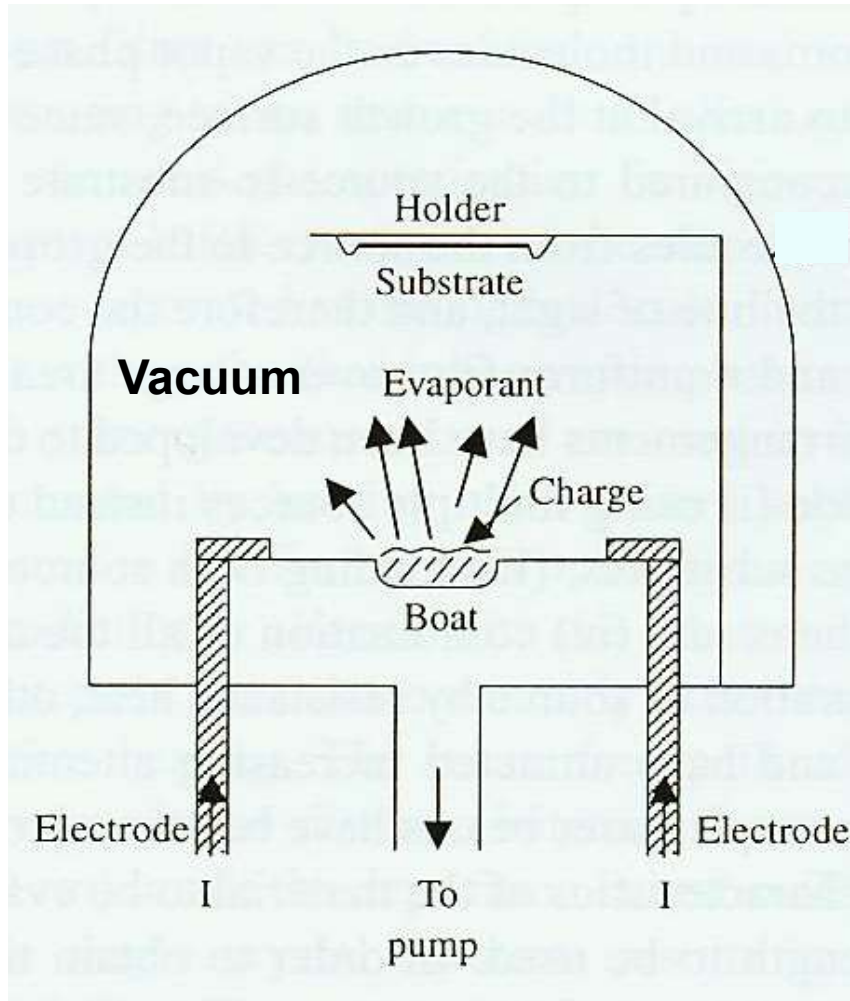


Thin film deposition for small molecules



- + Established technology
- Non-uniformity
- Waste of materials

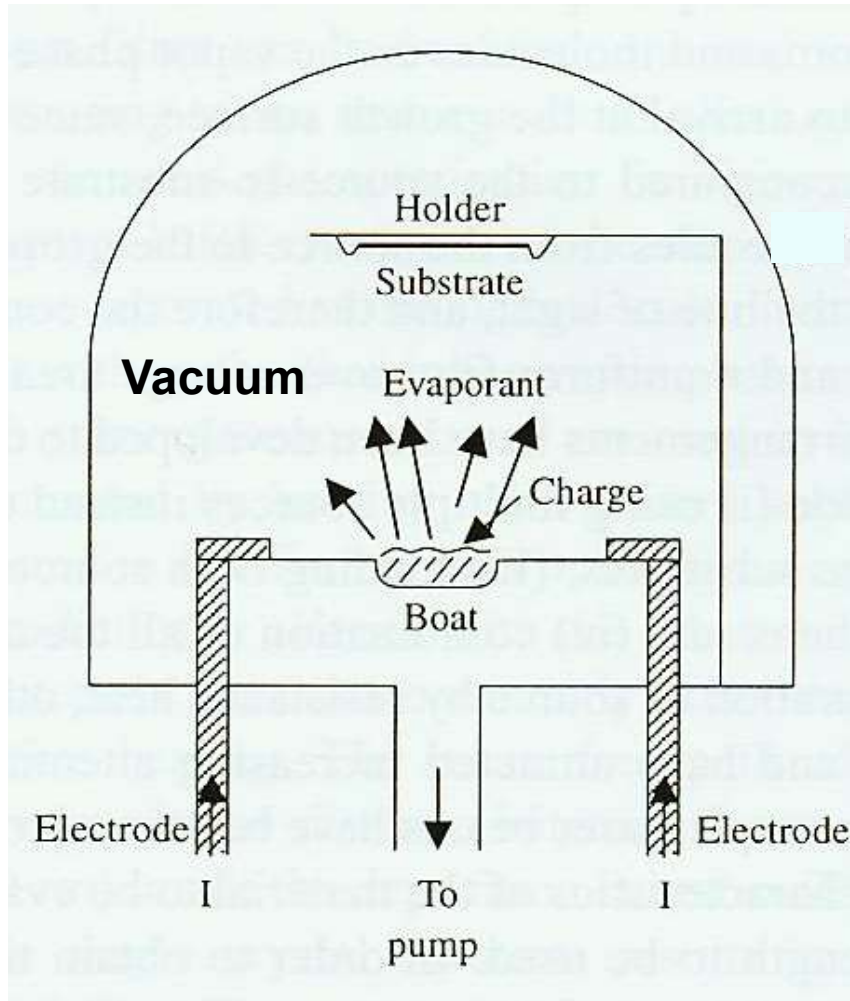
# PVD: Evaporation



- Simple deposition technique
- Operated in  $10^{-3} \sim 10^{-10}$  torr
- Vapor phase do not collide with each other since m.f.p. is large
- Line of sight deposition
- Relatively poor uniformity over a wafer
- For better uniformity
  - ☐ Multiple sources
  - ☐ Rotating the substrates
  - ☐ Loading both source & substrate on the surface of a sphere
- Source heating techniques
  - ☐ Resistive heating
  - ☐ Laser beams
  - ☐ Electron beams
  - ☐ Arc evaporation

# PVD: Evaporation

- Evaporation is operated at vacuum to increase mean free path



$$\Gamma = \frac{nc}{4}$$

$$n = \frac{N}{V} = \frac{p}{k_B T}$$

$$c = \sqrt{\frac{8k_B T}{\pi m}}$$

**a** : evaporation coefficient

**p''**: vapor pressure

at evaporation surface

**p**: hydrostatic pressure

$$\Gamma = \frac{nc}{4} = \frac{1}{4} \frac{p}{k_B T} \cdot \sqrt{\frac{8k_B T}{\pi m}} = \frac{p}{\sqrt{2\pi m k_B T}}$$

*Deposition Rate by Hertz – Knudsen eq.*

$$R_{\text{evaporation}} = \frac{a(p'' - p)}{\sqrt{2\pi m k_B T}}$$



# Vapor Pressure as a function of temperature

## Cosine law of deposition

mass deposited per unit area

$$R_D = \frac{M_e}{\pi r^2} \cos \phi \cos \theta$$

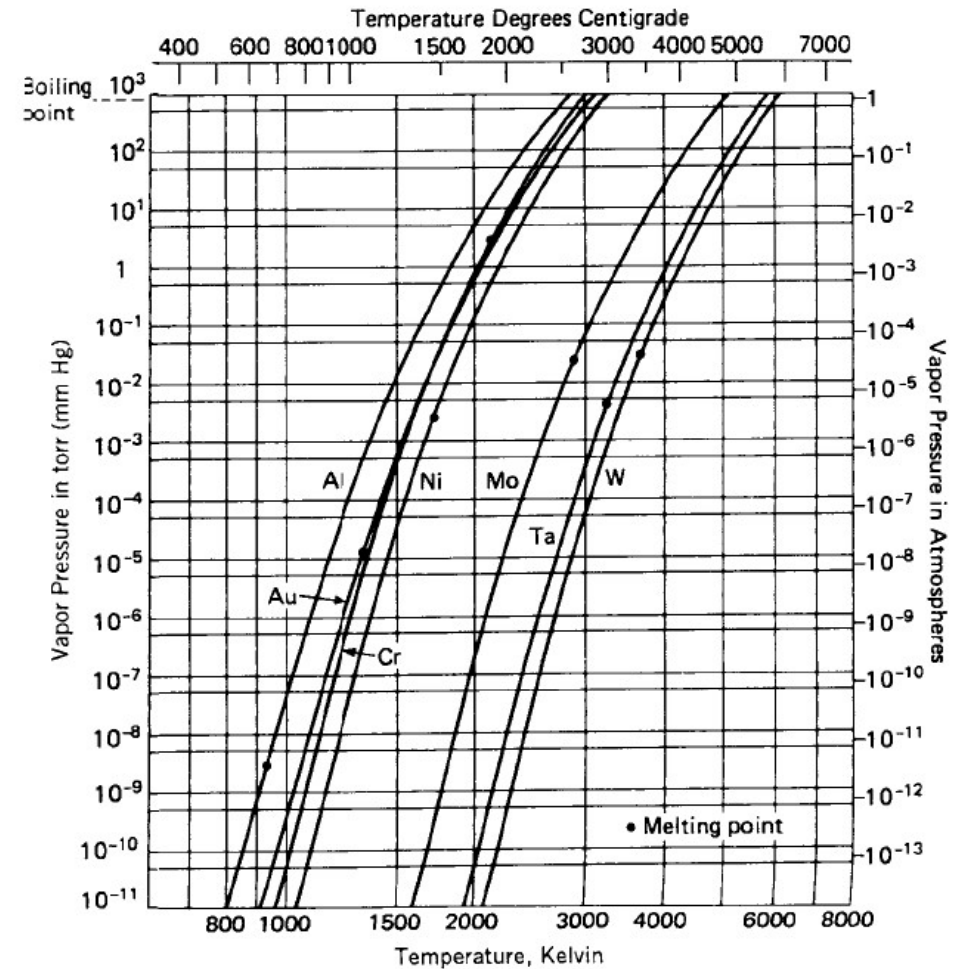
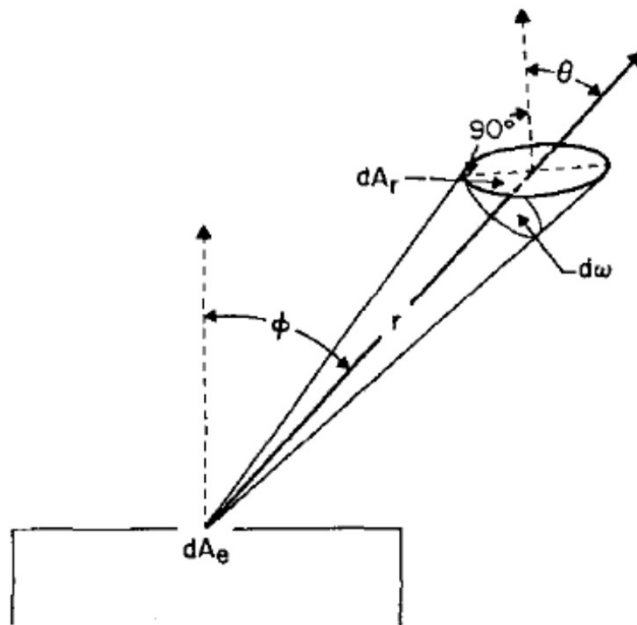


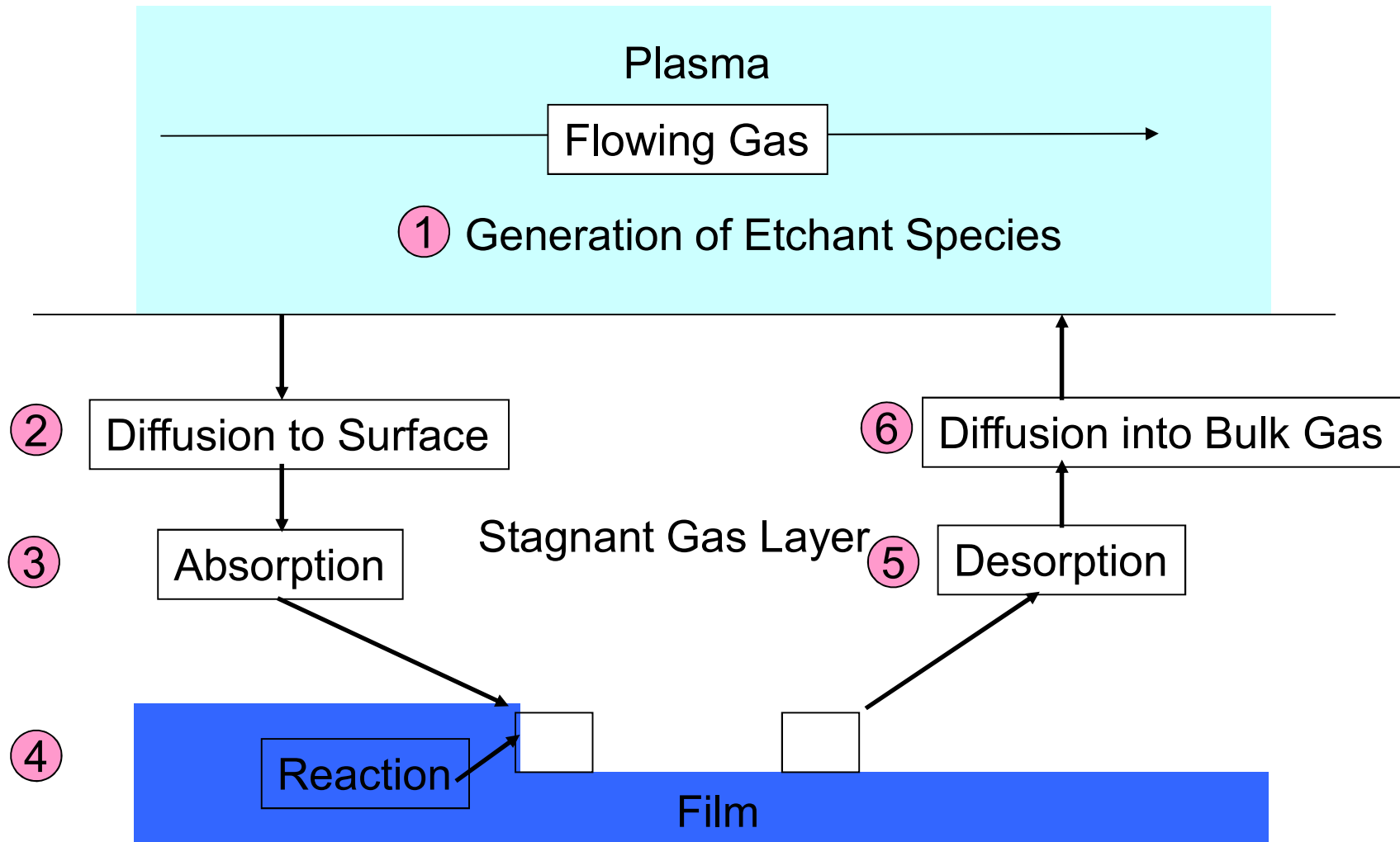
Fig. 8.1 Vapor pressure curves for selected materials. Adapted from [2].

# **Plasma Etching Chemistry & Surface Reactions**

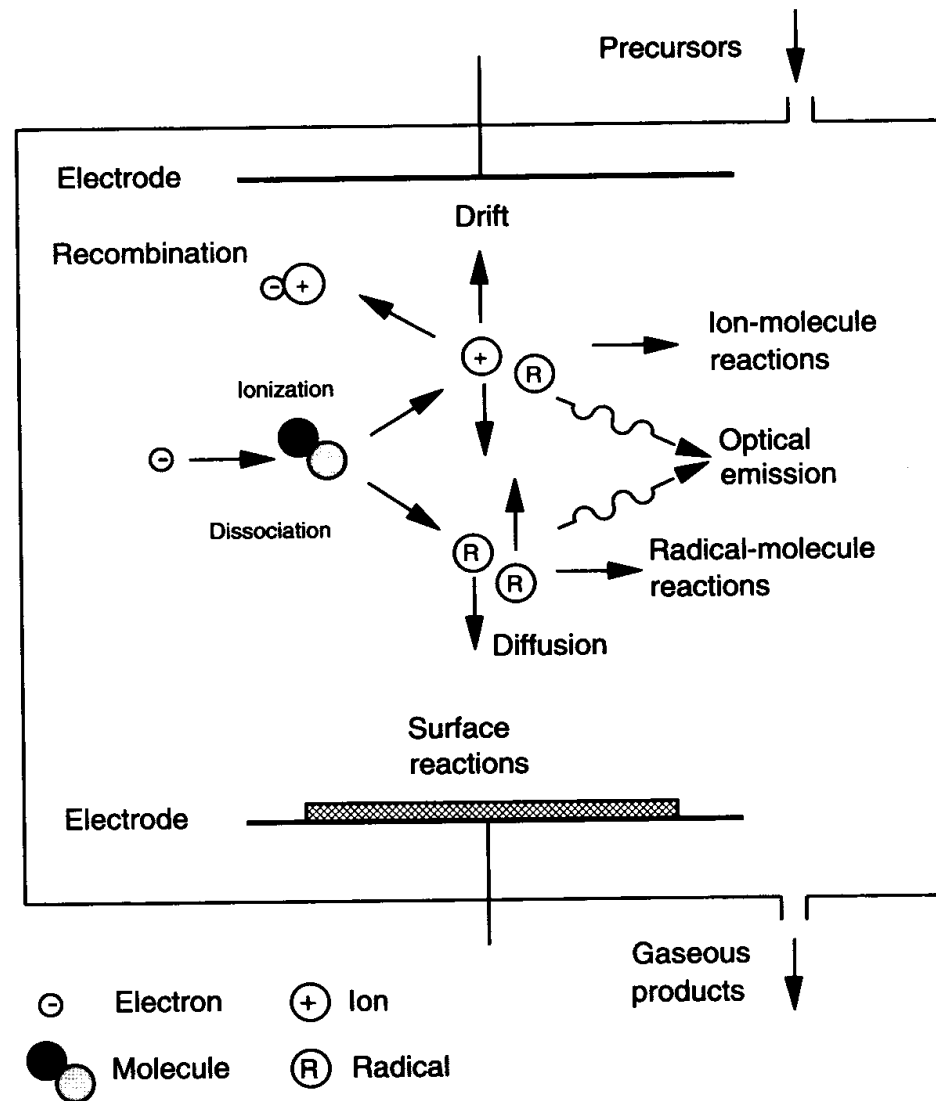
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# The 6 Steps of Plasma Chemical Etching



# Reactions in Plasma



# Reactions with Electrons in Plasma Discharge

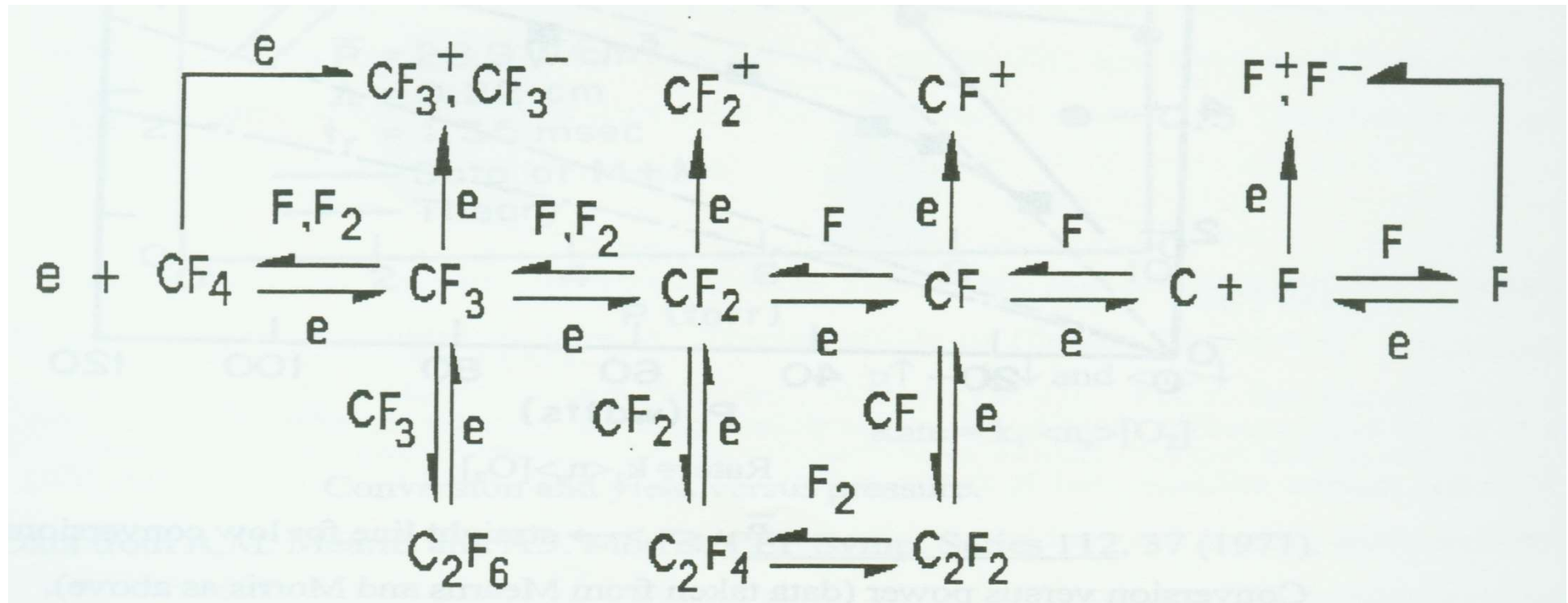
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- Excitation:  $\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^* + \text{e}^-$
- Dissociation:  $\text{SF}_6 + \text{e}^- \rightarrow \text{SF}_5^* + \text{F}^* + \text{e}^-$
- Ionization:  $\text{Ar} + \text{e}^- \rightarrow \text{Ar}^+ + 2\text{e}^-$
- Recombination:  $\text{e} + \text{Ar}^+ \rightarrow \text{Ar} + h\nu$
- Dissociative attachment:  $\text{O}_2 + \text{e} \rightarrow 2\text{O} + \text{e} \rightarrow \text{O} + \text{O}^-$

**Table 11.5** Bond energies (kJ/mol)

C–O	1080	Si–F	550
Si–O	470	Si–Cl	403
Si–Si	227	Si–Br	370

# Reactions in CF<sub>4</sub> Discharge



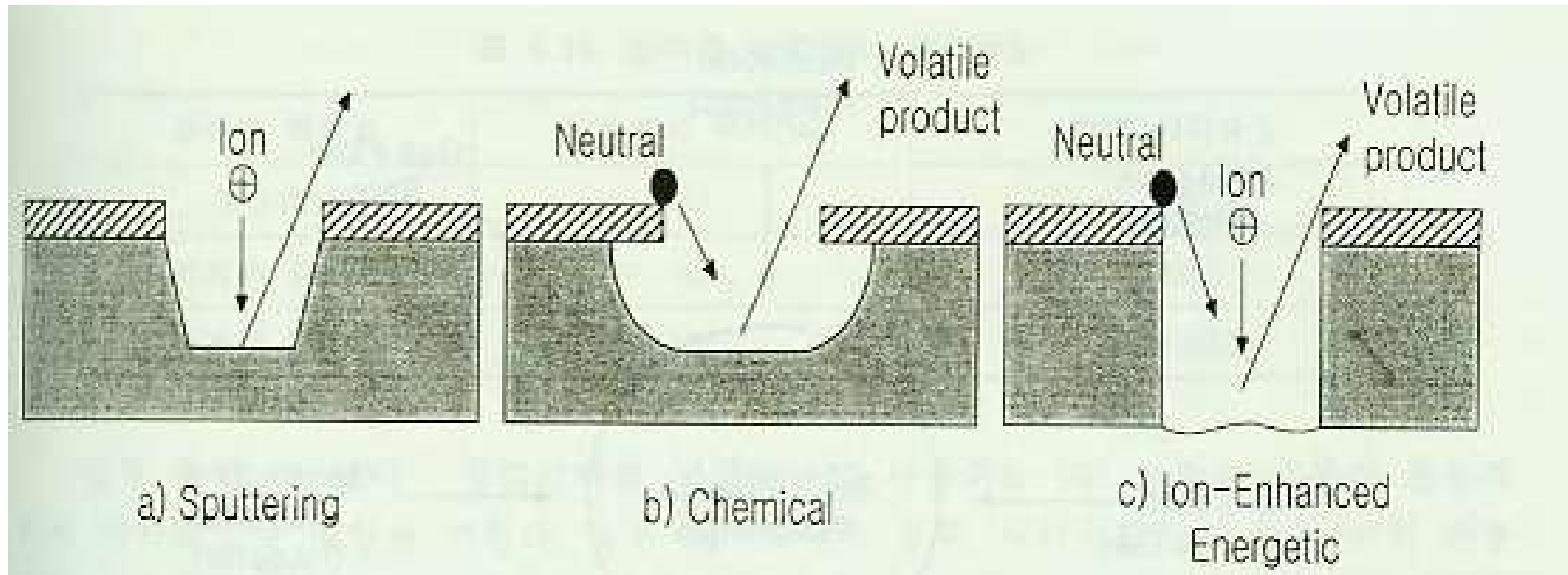
■ M.J.Kusher, J.Appl.Phys.53, 2923 (1982)

# Dry (Plasma) Etching Types

Physical Process

Chemical Process

Physical + Chemical Process

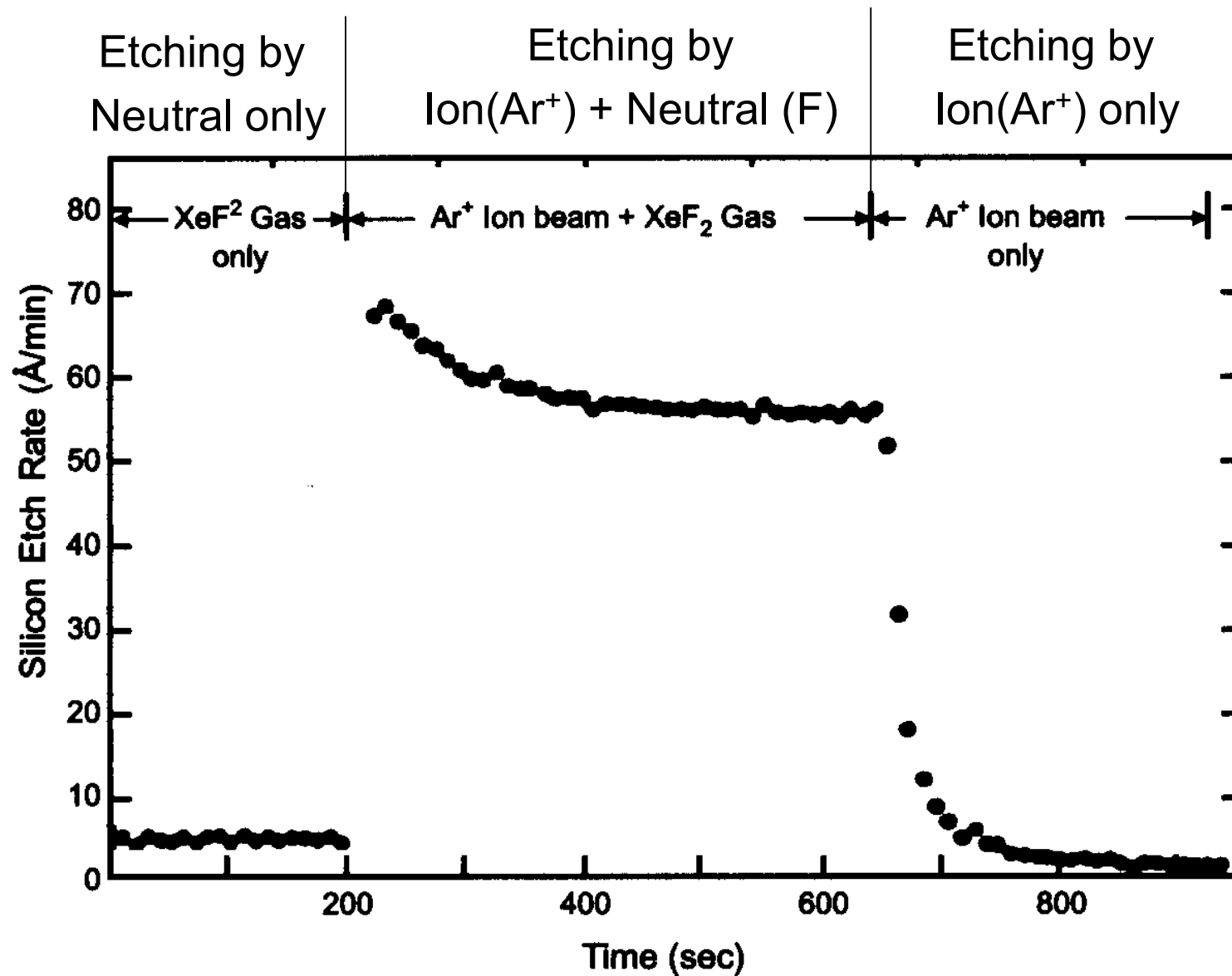


- anisotropic
- low selectivity
- low etch rate

- isotropic
- high selectivity
- low etch rate

- anisotropic
- high selectivity
- high etch rate

# Reactive Ion Etching



# Typical Etch Gases

---

**Table 11.4** Typical etch gases

Fluorine	Chlorine	Bromine	Stabilizers	Scavengers/ others
CF <sub>4</sub>	Cl <sub>2</sub>	HBr	He	O <sub>2</sub>
SF <sub>6</sub>	BCl <sub>3</sub>		Ar	
CHF <sub>3</sub>	SiCl <sub>4</sub>		N <sub>2</sub>	
NF <sub>3</sub>	CHCl <sub>3</sub>			
C <sub>2</sub> F <sub>6</sub>				
C <sub>4</sub> F <sub>8</sub>				
XeF <sub>2</sub>				

# Etch Products

**Table 11.6** Etch product boiling points ( $T_{bp}$ , °C)

SiF <sub>4</sub>	−90	SiCl <sub>4</sub>	−70	CO <sub>2</sub>	−56
NF <sub>3</sub>	−206	AlCl <sub>3</sub>	190	PH <sub>3</sub>	−133
WF <sub>6</sub>	2.5	GaCl <sub>3</sub>	78	AsH <sub>3</sub>	−116
WOF <sub>4</sub>	110	TiCl <sub>4</sub>	−25		
TaF <sub>5</sub>	96.8	WOCl <sub>4</sub>	211	SiBr <sub>2</sub>	5.4
MoF <sub>6</sub>	17.5	WCl <sub>6</sub>	275		
MoOF <sub>4</sub>	98	InCl <sub>2</sub>	235		
NbF <sub>5</sub>	72	MoCl <sub>5</sub>	194		
	PtCl <sub>4</sub>	370d			
	PbCl <sub>4</sub>	−15			
	Cr(CO) <sub>6</sub>	110d			

Note: d – decomposition

**Table 11.7** Non-etchable reaction products ( $T_{bp}$ , °C)

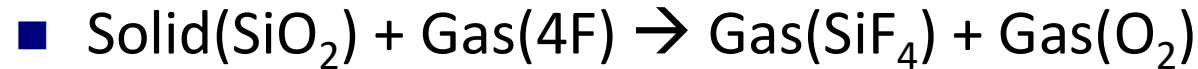
CuCl <sub>2</sub>	620	TiF <sub>4</sub>	>400
CuF <sub>2</sub>	950d	PbF <sub>2</sub>	855
CrCl <sub>2</sub>	824	CrF <sub>2</sub>	1100
AlF <sub>3</sub>	1290s	TiF <sub>3</sub>	1200

Note: d – decomposition; s – sublimation



# Gases used in Dry Etching Processes

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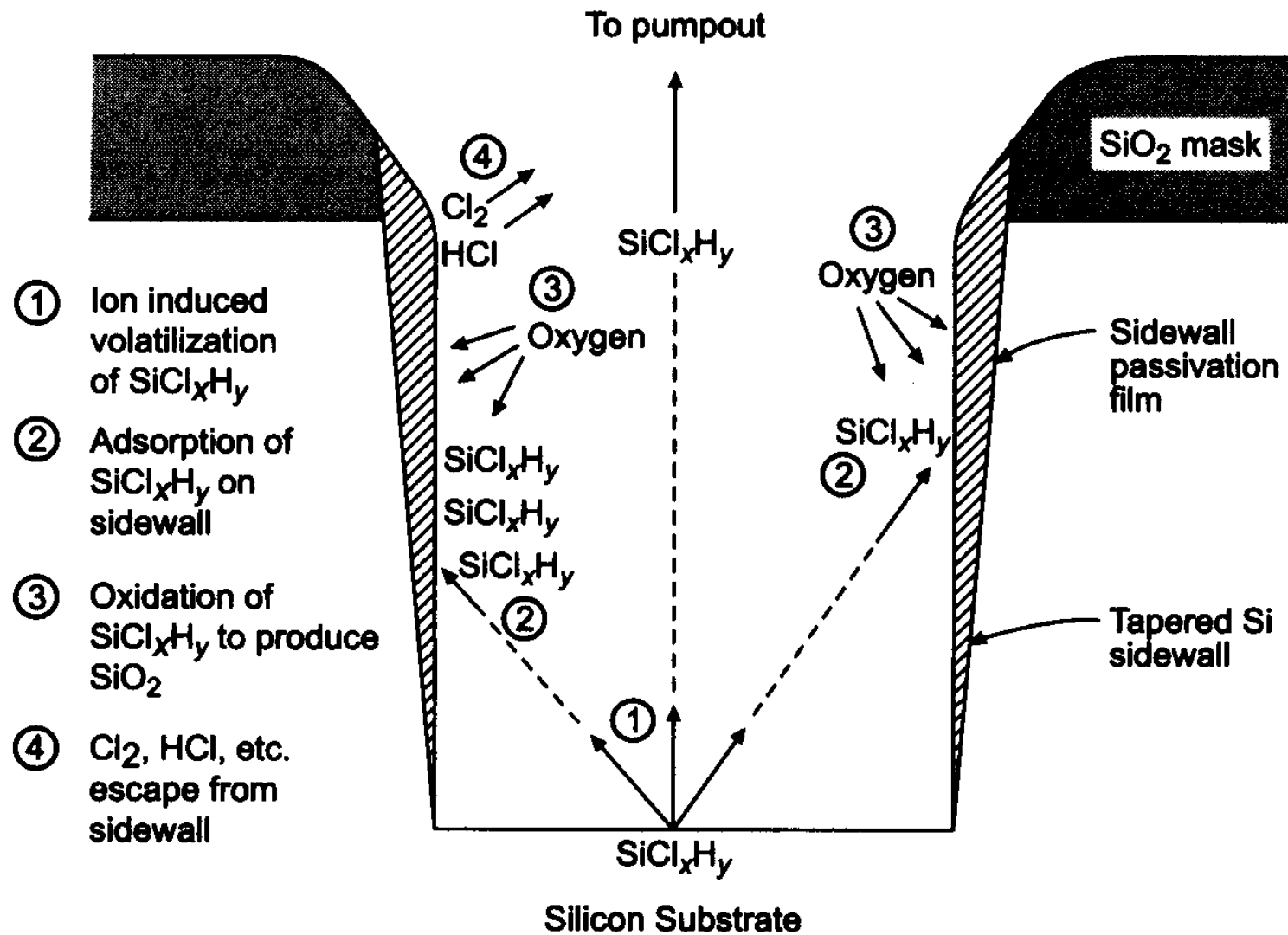


Etch target		Gases for etching
Si	F containing Cl-F containing Cl containing Br containing	$\text{CF}_4$ , $\text{SF}_4$ , $\text{NF}_3$ , $\text{SiF}_4$ , $\text{BF}_3$ , $\text{CBrF}_3$ , $\text{XeF}_2$ $\text{CClF}$ , $\text{CCl}_2\text{F}_2$ , $\text{CCl}_3\text{F}$ , $\text{C}_2\text{ClF}$ , $\text{C}_2\text{Cl}_2\text{F}_4$ $\text{CCl}_4$ , $\text{SiCl}_4$ , $\text{PCl}_3$ , $\text{BCl}_3$ , $\text{Cl}_2$ , $\text{HCl}$ $\text{HBr}$ , $\text{Br}_2$
$\text{SiO}_2$	F-H containing $\text{F/C} < 4$	$\text{CHF}_3$ , $\text{CF}_4 + \text{H}_2$ $\text{C}_2\text{F}_6$ , $\text{C}_3\text{F}_8$ , $\text{C}_4\text{F}_8$
Al	Cl containing Br containing	$\text{CCl}_4$ , $\text{BCl}_3$ , $\text{SiCl}_4$ , $\text{Cl}_2$ , $\text{CCl}_2\text{F}_2$ , $\text{CCl}_3\text{F}$ $\text{Br}_2\text{BBr}_3$

# Gases for Plasma Etching

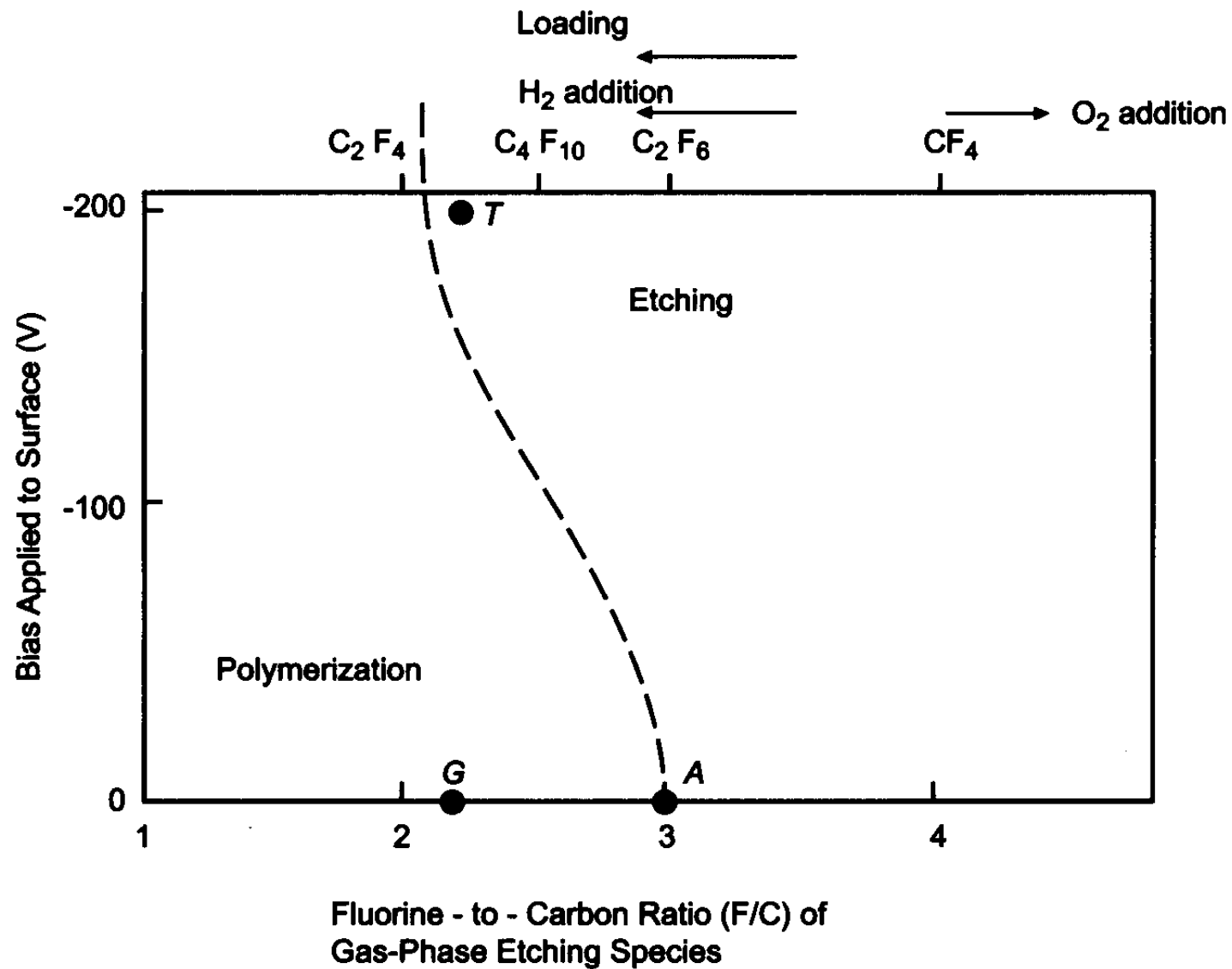
**TABLE 8-2 Plasma Gases Used for Etching of Different Materials (from [ 26 ])**

Material	Gases
Silicon	$\text{CF}_4/\text{O}_2$ , $\text{CF}_2\text{Cl}_2$ , $\text{CF}_3\text{Cl}$ , $\text{SF}_6/\text{O}_2/\text{Cl}_2$ , $\text{Cl}_2/\text{H}_2/\text{C}_2\text{F}_6/\text{CCl}_4$ , $\text{C}_2\text{ClF}_5/\text{O}_2$ , $\text{SiF}_4/\text{O}_2$ , $\text{NF}_3$ , $\text{ClF}_3$ , $\text{CCl}_4$ , $\text{CCl}_3\text{F}_5$ , $\text{C}_2\text{ClF}_5/\text{SF}_6$ , $\text{C}_2\text{F}_6/\text{CF}_3\text{Cl}$ , $\text{Br}_2$ , $\text{CF}_3\text{Cl}/\text{Br}_2$
$\text{SiO}_2$	$\text{CF}_4/\text{H}_2$ , $\text{C}_2\text{F}_6$ , $\text{C}_3\text{F}_8$ , $\text{CHF}_3/\text{O}_2$
$\text{Si}_3\text{N}_4$	$\text{CF}_4/\text{O}_2/\text{H}_2$ , $\text{C}_2\text{F}_6$ , $\text{C}_3\text{F}_8$ , $\text{CHF}_3$
Organics	$\text{O}_2$ , $\text{CF}_4/\text{O}_2$ , $\text{SF}_6/\text{O}_2$
Silicides	$\text{CF}_4/\text{O}_2$ , $\text{NF}_3$ , $\text{SF}_6/\text{Cl}_2$ , $\text{CF}_4/\text{Cl}_2$
Al	$\text{BCl}_3$ , $\text{BCl}_3/\text{Cl}_2$ , $\text{CCl}_4/\text{Cl}_2/\text{BCl}_3$ , $\text{SiCl}_4/\text{Cl}_2$
Cr	$\text{Cl}_2$ , $\text{CCl}_4/\text{Cl}_2$
Mo, Nb, Ta, Ti, W	$\text{CF}_4/\text{O}_2$ , $\text{SF}_6/\text{O}_2$ , $\text{NF}_3/\text{H}_2$
Au	$\text{C}_2\text{Cl}_2\text{F}_4$ , $\text{Cl}_2$ , $\text{CClF}_3$
GaAs	$\text{BCl}_3/\text{Ar}$ , $\text{Cl}_2/\text{O}_2/\text{H}_2$ , $\text{CCl}_2\text{F}_2/\text{O}_2/\text{Ar}/\text{He}$ , $\text{CCl}_4$
InP	$\text{CH}_4/\text{H}_2$ , $\text{C}_2\text{H}_6/\text{H}_2$ , $\text{Cl}_2/\text{Ar}$



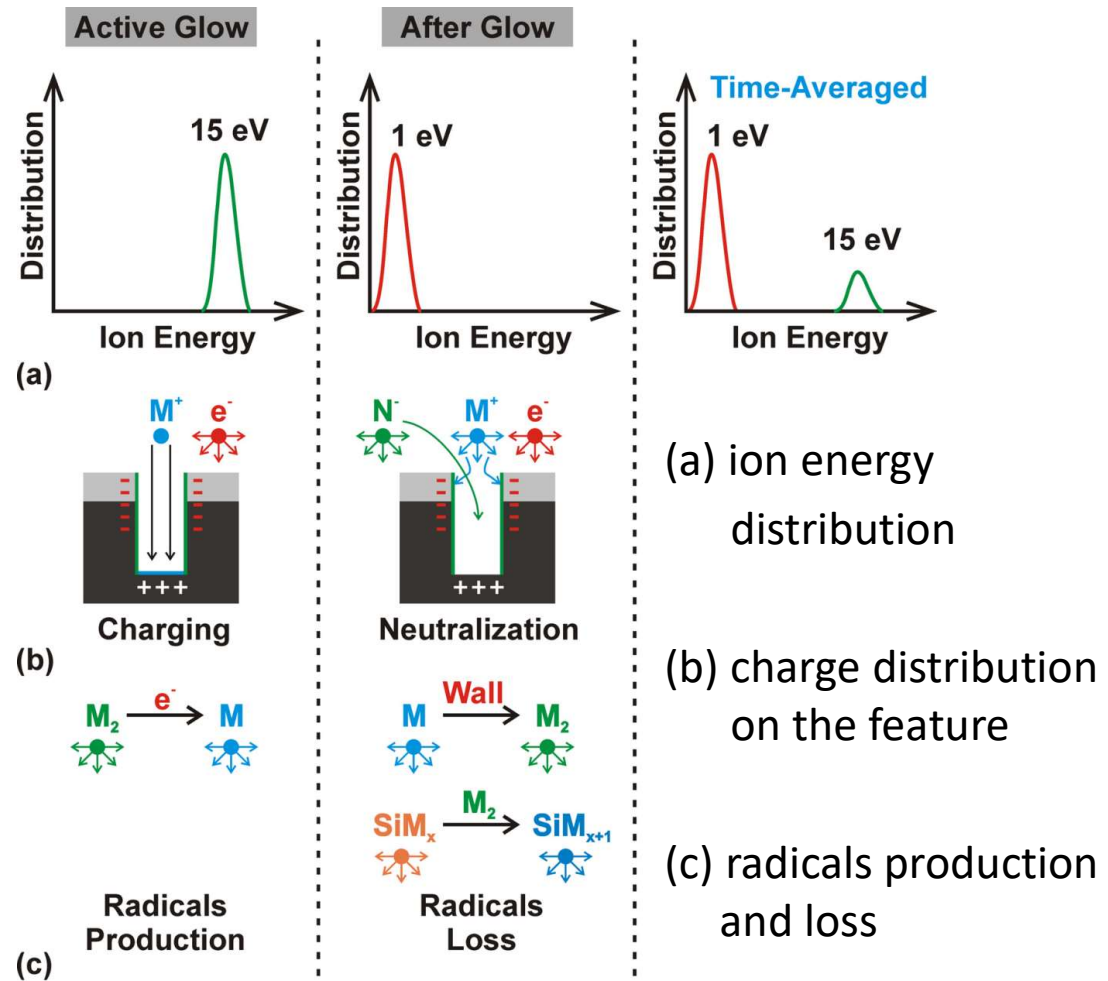
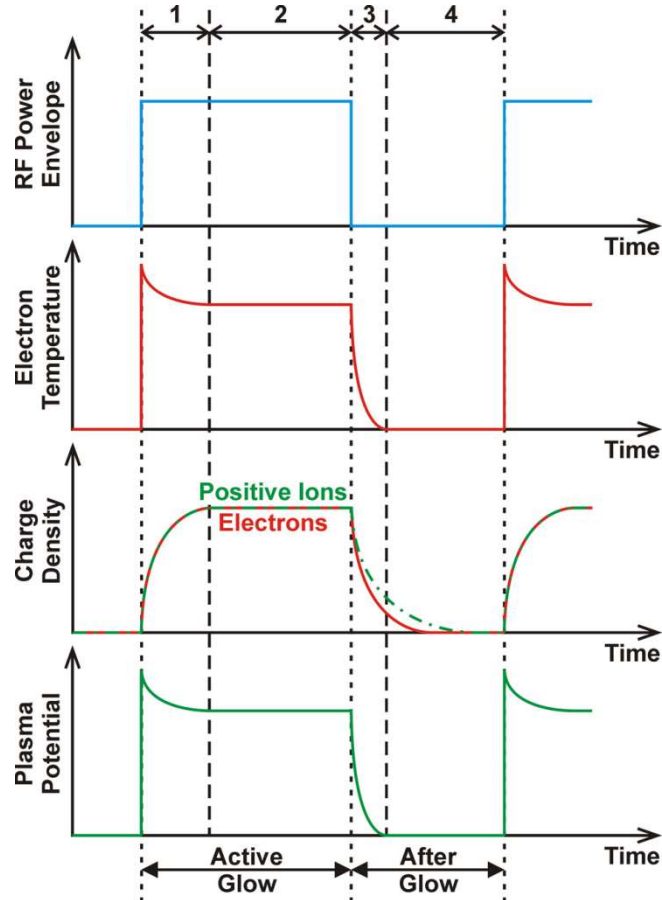
**Fig. 8-7** A model for sidewall film formation in a  $\text{HCl}/\text{O}_2/\text{BCl}_3$  RIE (from [20]),

# Fluorocarbon Plasma Chemistry



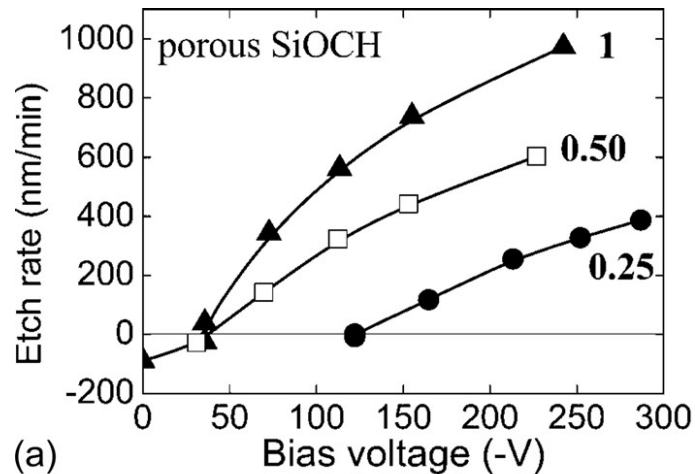
# Pulsed Plasma Source

## Mechanisms

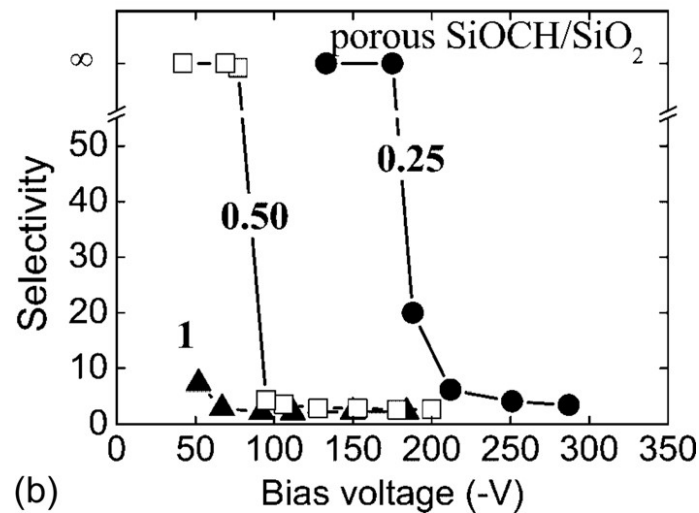


■ S. Banna et al., J. Vac. Sci. Technol. A 30, 040801 (2012)

# Pulsed Plasma Source



(a)



(b)

(a)

- Impact of the pulsed bias voltage duty cycle (1, 0.50, 0.25) on the porous SiOCH etch rate in CHF<sub>3</sub> plasma.

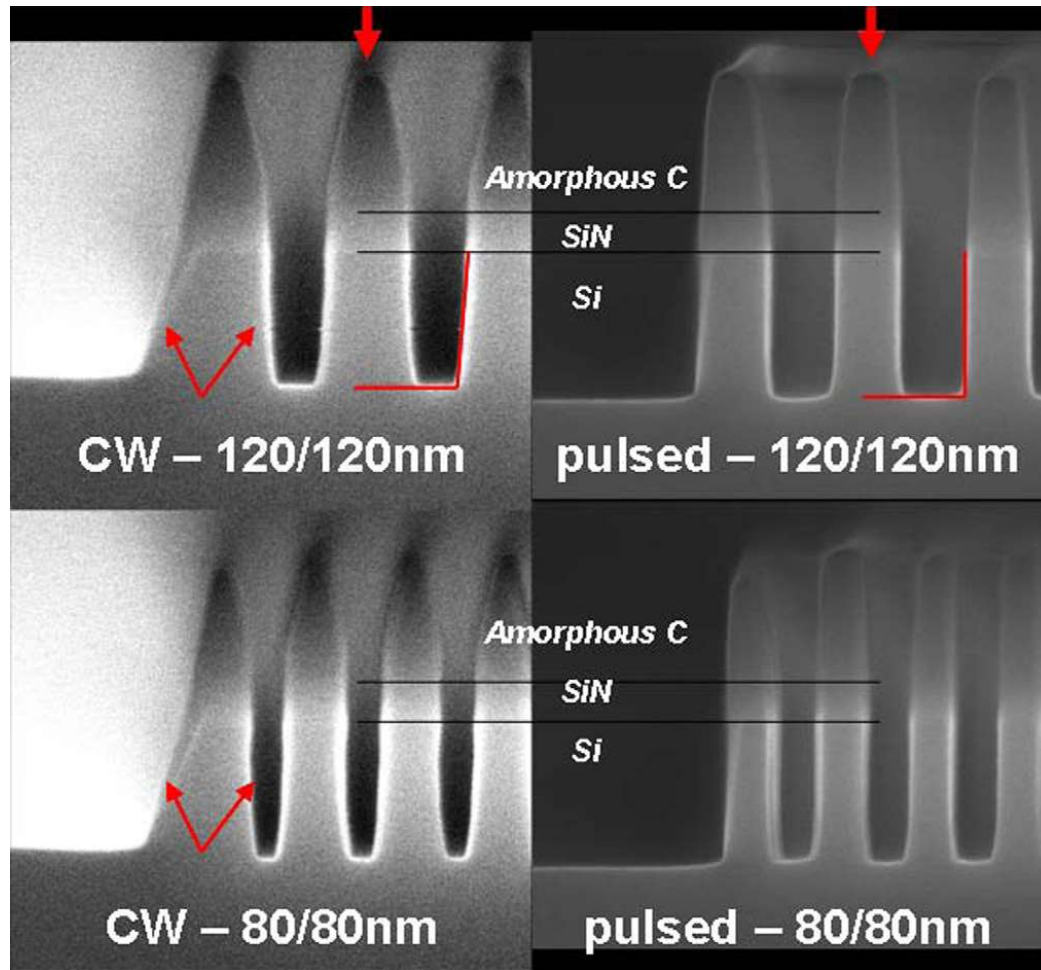
- The modulation frequency was fixed at 1 kHz.

- Decreasing the duty cycle led to a decrease of etch rates and to a shift of the etching/deposition threshold to higher bias voltage.

(b) - Impact of the pulsed bias voltage duty cycle (1, 0.5, 0.25) on the selectivity between porous SiOCH and SiO<sub>2</sub> in CHF<sub>3</sub> plasma

# Pulsed Plasma Source

## ■ Etch Profiles



HBr/O<sub>2</sub> plasma etching in Si  
Continuous wave (CW)  
and Synchronous pulsing

1. 120 nm-wide with space of 120 nm trenches
2. 80 nm-wide with space of 80 nm trenches.

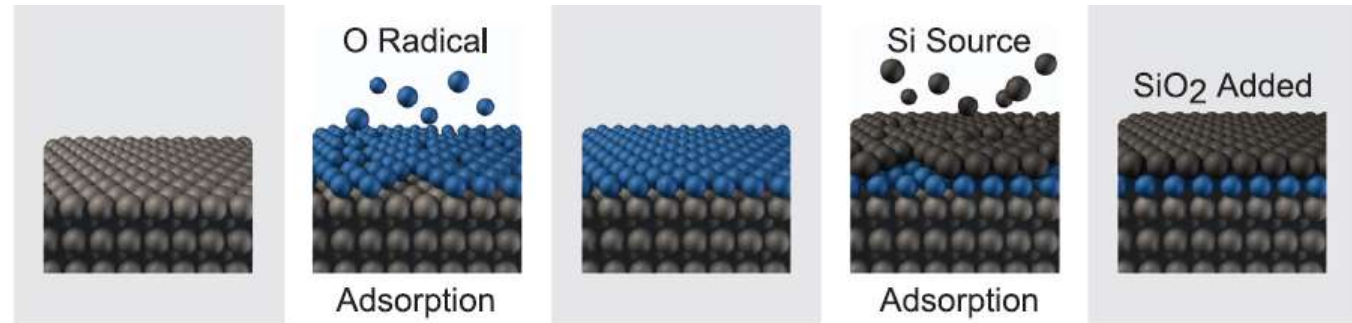
S. Banna et al., J. Vac. Sci. Technol. A 30, 040801 (2012)



# ALD and ALE

## DEPOSITION

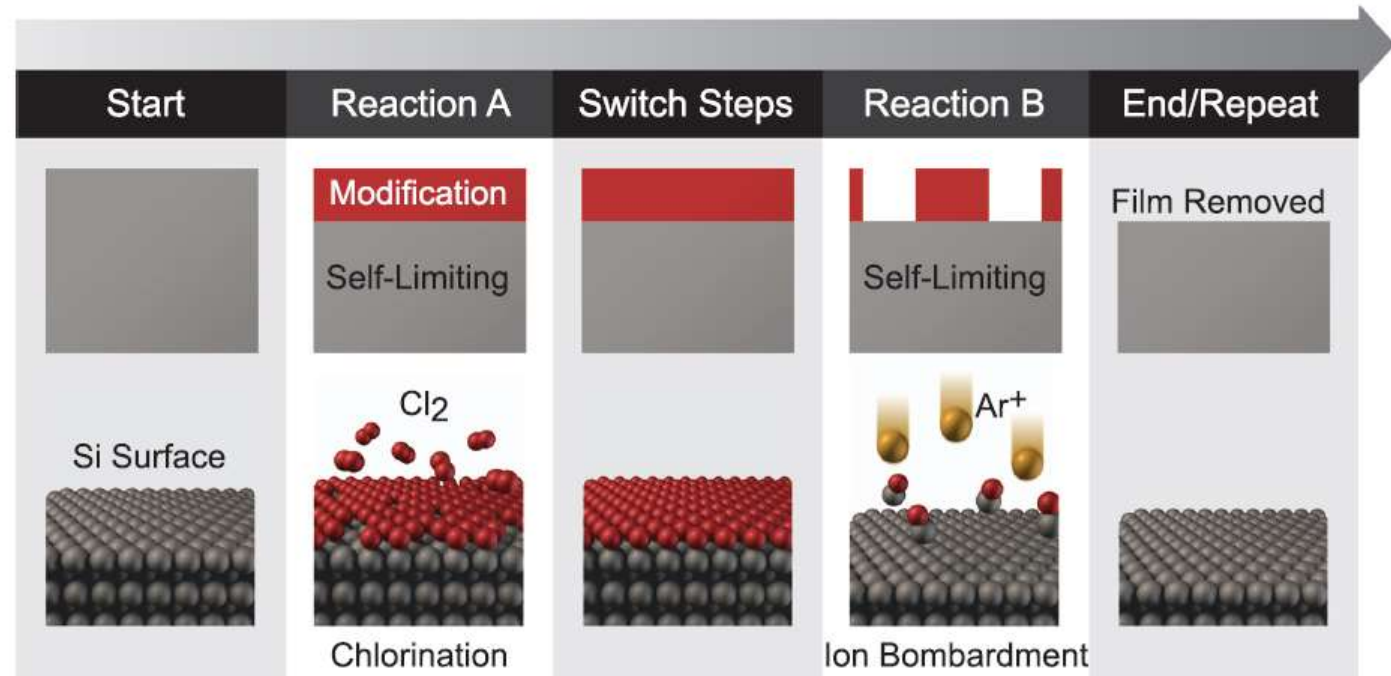
c) Example  
SiO<sub>2</sub> ALD:



## ETCH

a) Generic  
ALE:

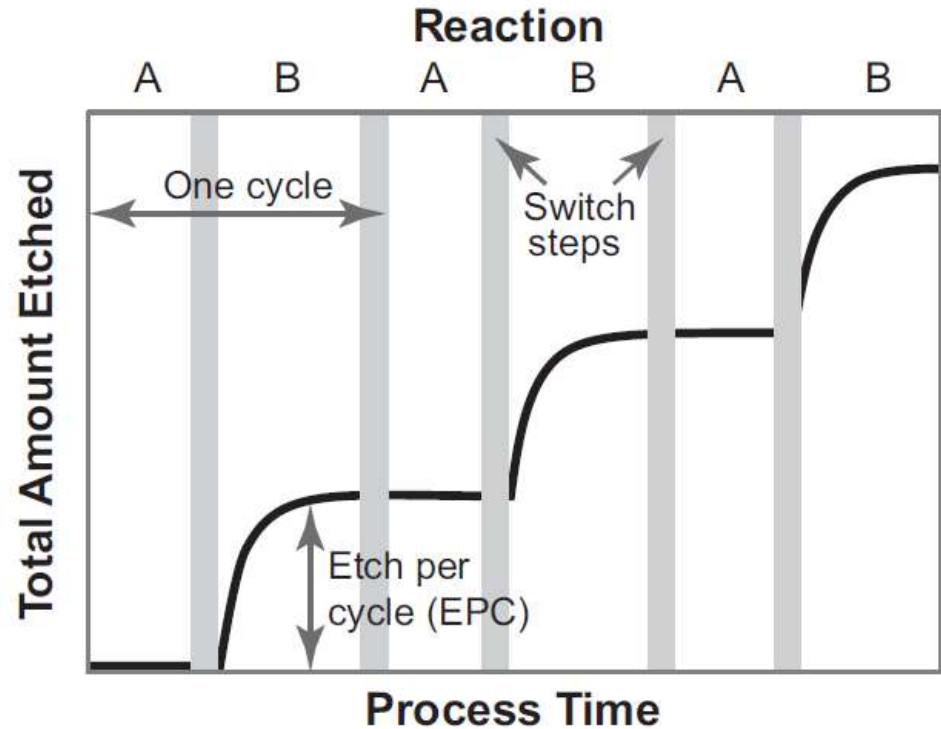
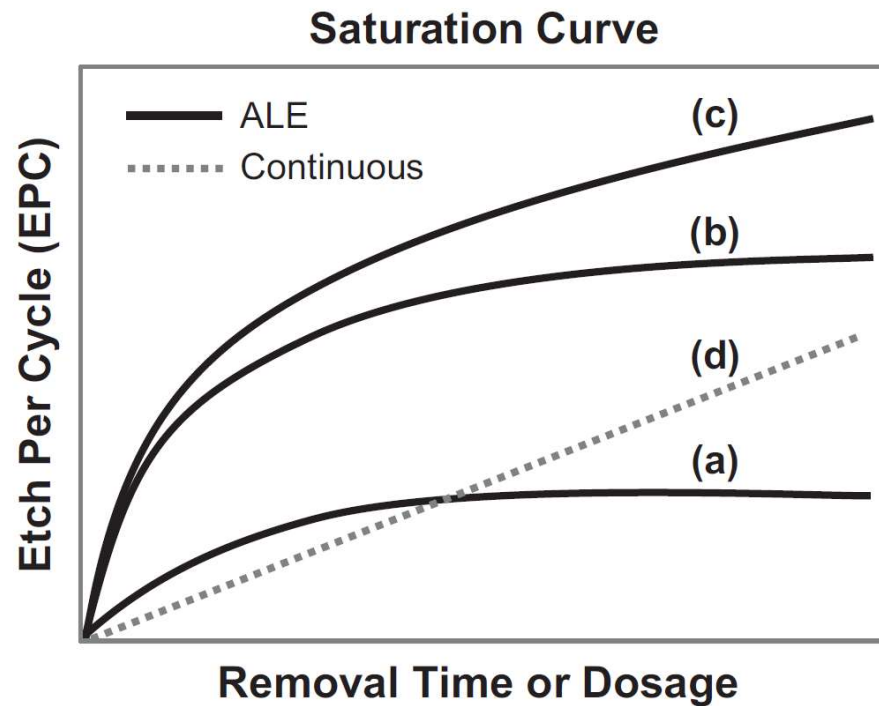
b) Example  
Si ALE:





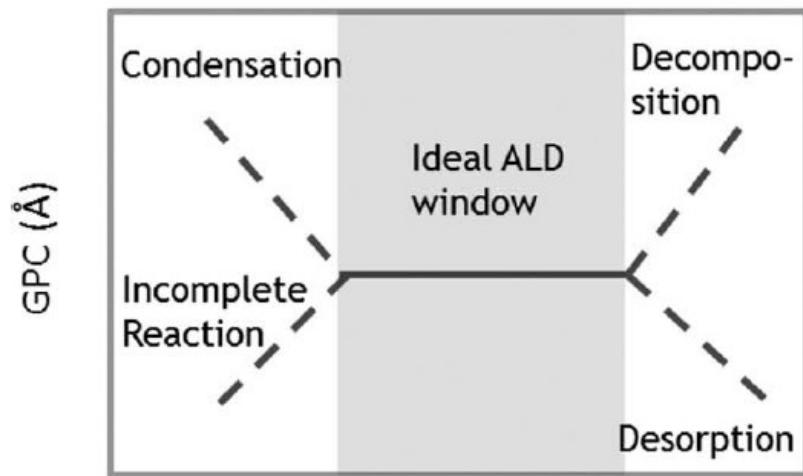
# Atomic Layer Etching

## ◆ Self-limited Reaction

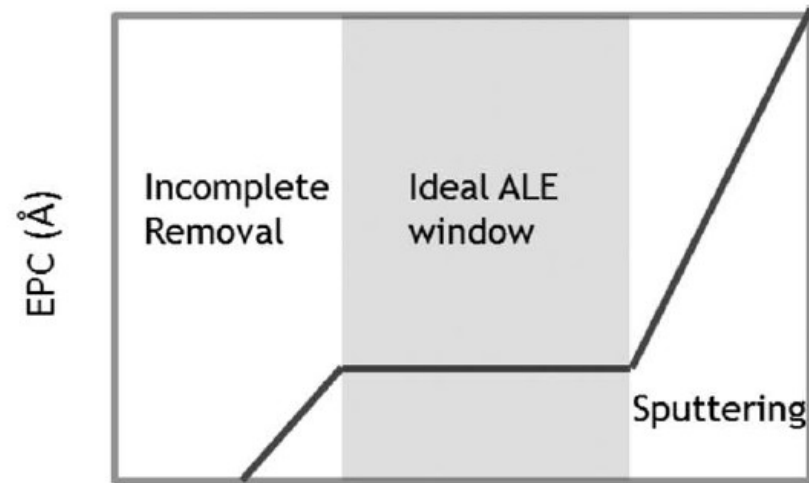


■ K. Θ. Καναρικ et al, Θ. ζαχ. Σχι. Τεχνηολ. Α 33(2), (2015)

# ALD and ALE

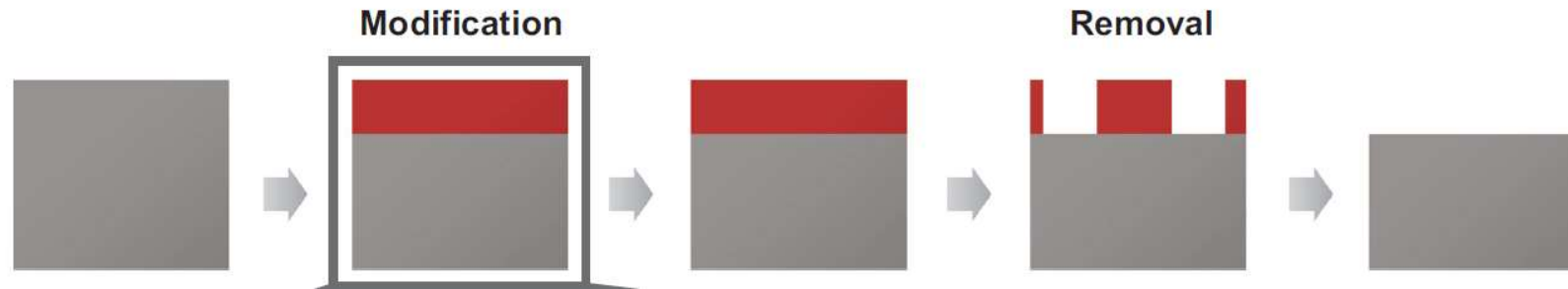


a. Surface Temperature

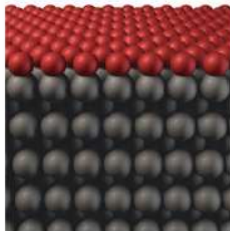


b. Ion energy

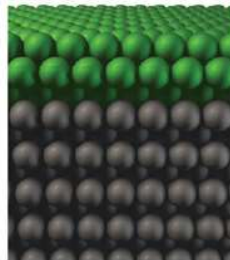
# Atomic Layer Etching



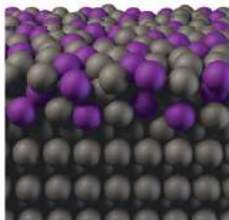
a) Chemisorption



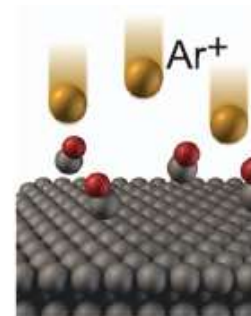
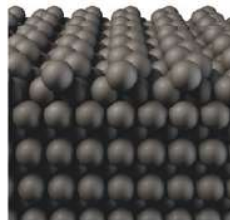
b) Deposition



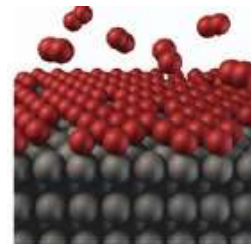
c) Conversion



d) Extraction



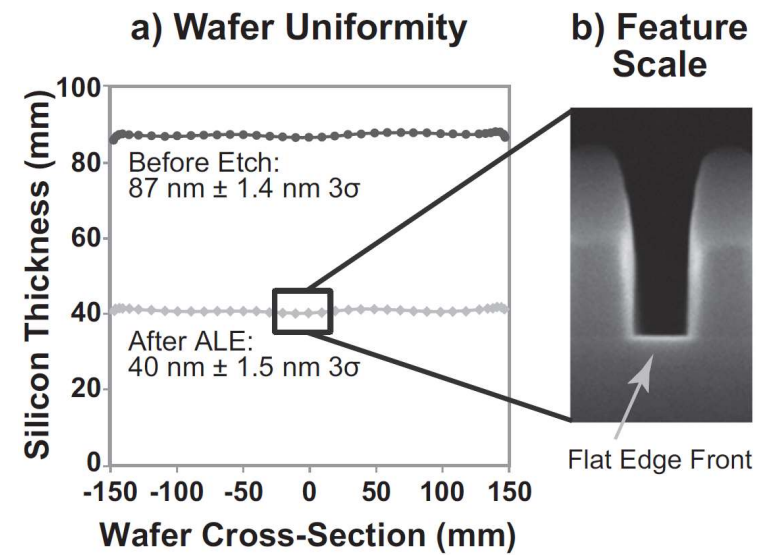
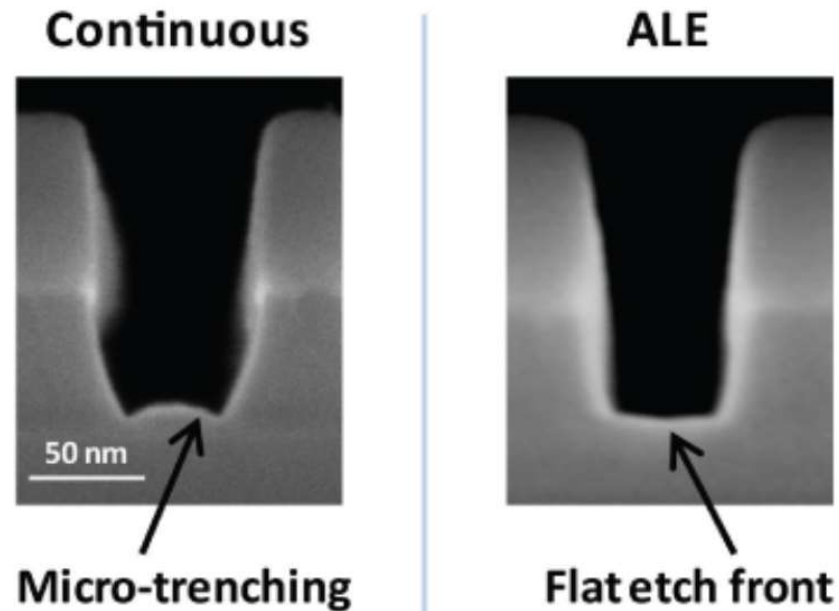
■ Ion bombardment



■ Thermal desorption

Αδσορπτιον  $\theta(t) = 1 - \exp(-K \cdot P \cdot t)$

# Advantages of Atomic Layer Etching



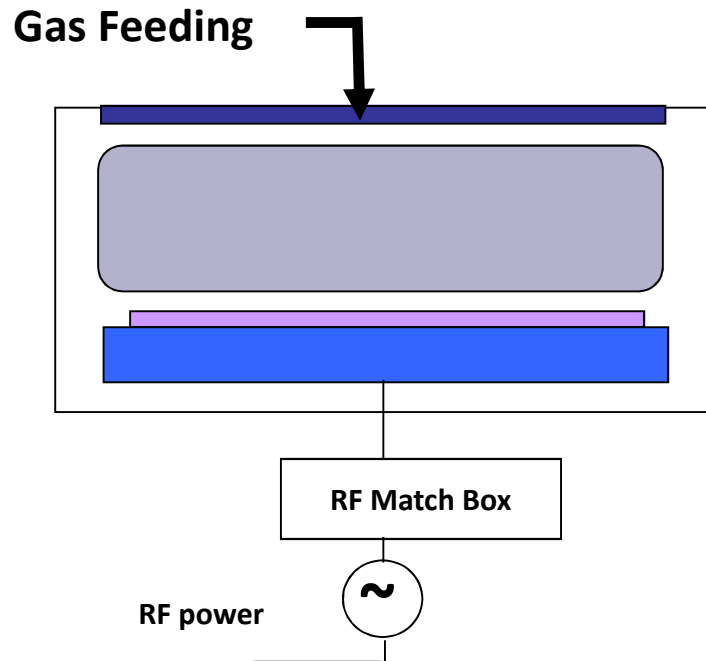
J. Phys. D: Appl. Phys. 47 (2014) 273001

# Plasma Etchers

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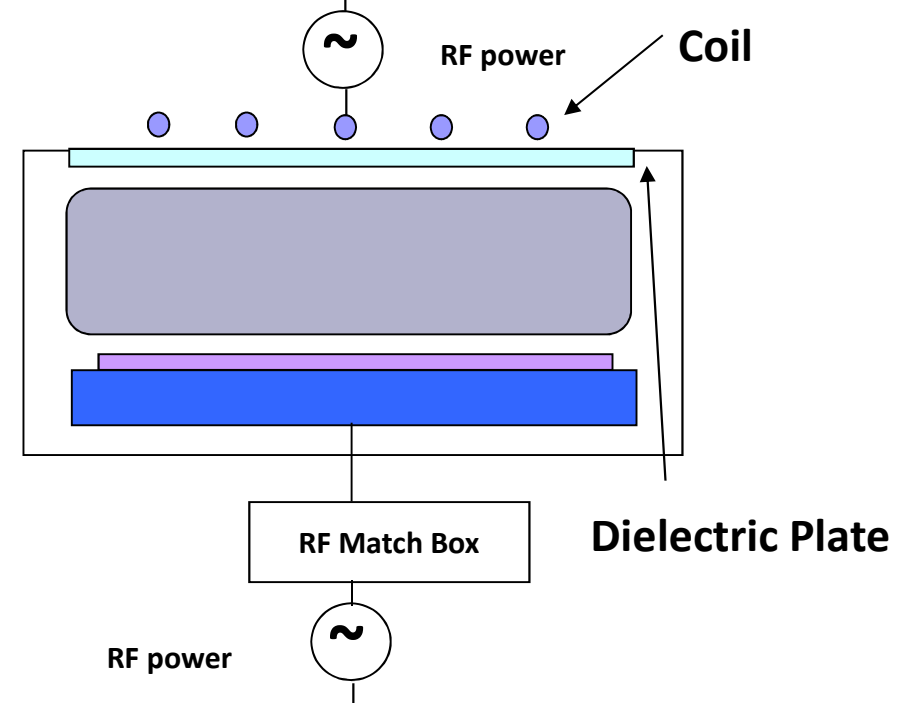
# CCP and ICP

## Capacitively Coupled Plasma (CCP)



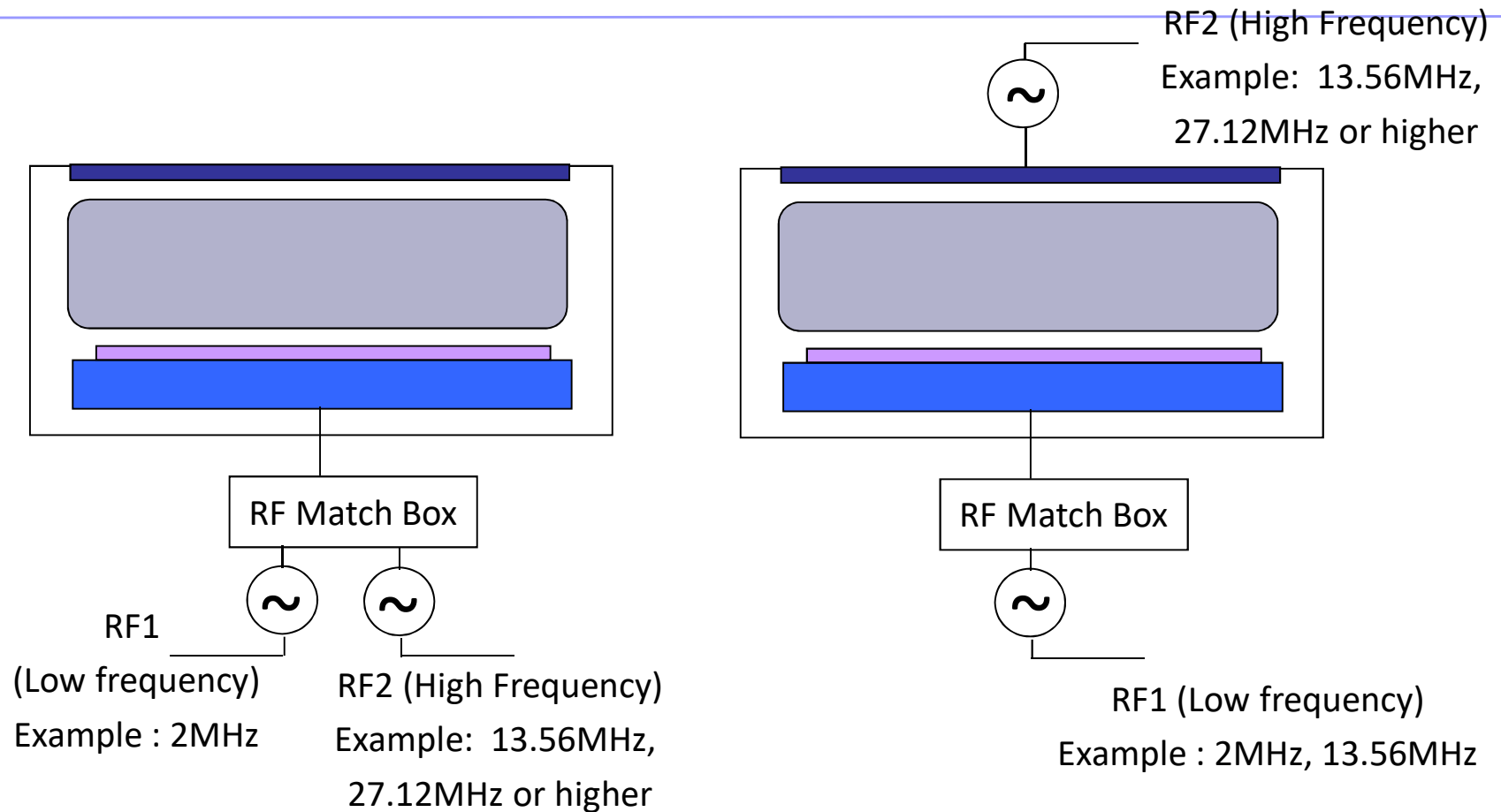
Power delivered through parallel plates  
Relatively uniform plasma  
Low-to-medium density plasma :  
 $10^8 \sim 10^{11} \text{ cm}^{-3}$   
High energy ion acceleration

## Inductively Coupled Plasma (ICP)



Power delivered through coils  
Relatively non-uniform plasma  
Medium-to-High density plasma ( $10^{10} \sim 10^{12} \text{ cm}^{-3}$ )  
Independent ion energy control is possible  
with separate power

# Dual Frequency CCP

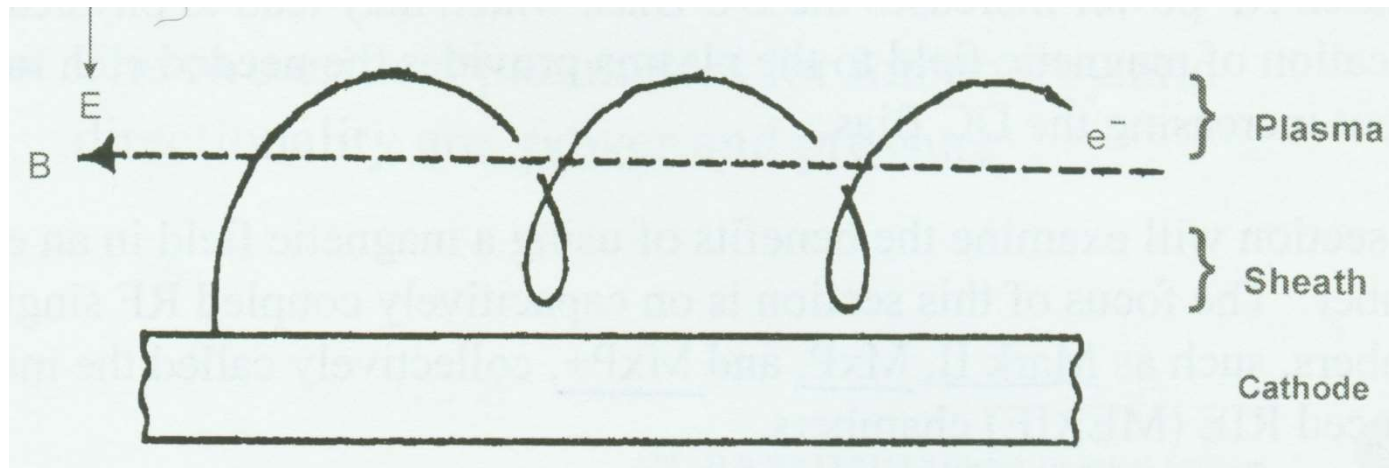


## Decoupled plasma control

- Low frequency RF : ion energy control
- High frequency RF: plasma density control

# Effect of Magnetic Field

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- Magnetic field makes the electron moving path longer
- Magnetic field increases plasma density
- Magnetically Enhanced Reactive Ion Etcher (MERIE)



# Plasma Reactors

Parameters	ICP	ECR	Helium	SPRP	MERIE	RIE	PE
Frequency	13.56 MHz	2.45 GHz	13.56 MHz	400 kHz	13.56 MHz	13.56 MHz	13.56 MHz
Gas pressure (torr) *	$\sim 1^{-3}$	$\sim 4^{-4}$	$\sim 1^{-3}$	$\sim 1^{-1}$	$\sim 1^{-2}$	$\sim 7^{-2}$	$\sim 1^{-1}$
Electron temperature (eV)	$\sim 4$	$\sim 4$	$\sim 4$	$\sim 10$	$\sim 5$	$\sim 8$	$\sim 8$
Plasma density (cm <sup>3</sup> ) *	$\sim 5^{11}$	$\sim 3^{11}$	$\sim 5^{11}$	$\sim 8^{10}$	$\sim 5^{10}$	$\sim 1^{10}$	$\sim 3^8$
Ion current density (mA/cm <sup>2</sup> )	$\sim 10$	$\sim 10$	$\sim 10$	$\sim 2$	$\sim 1$	$\sim 0.1$	$\sim 0.1$
Ion energy (eV)	Controllable	Controllable	Controllable	30–150	$\sim 200$	200–1000	$\sim 20$

ICP – inductively coupled plasma

ECR – electron cyclotron resonance

SPRP – split power reverse phase/rainbow 4500

\* indicates  $\sim \times 10^x$

MERIE – magnetically enhanced RIE

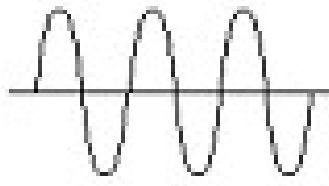
RIE – reactive ion etching

PE – plasma etching

# RF Power Supply and Matching Network

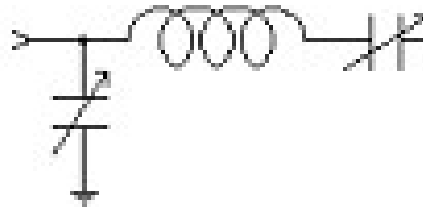


RF GENERATOR  
13.560MHz MAX 300W



MODEL - R300A

MATCHING NETWORK

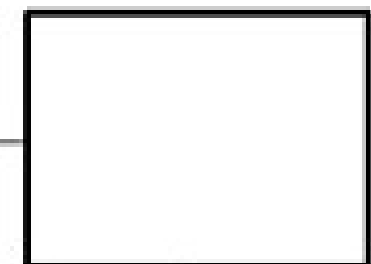
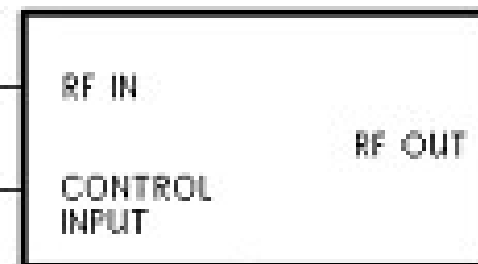


MODEL - ALC300



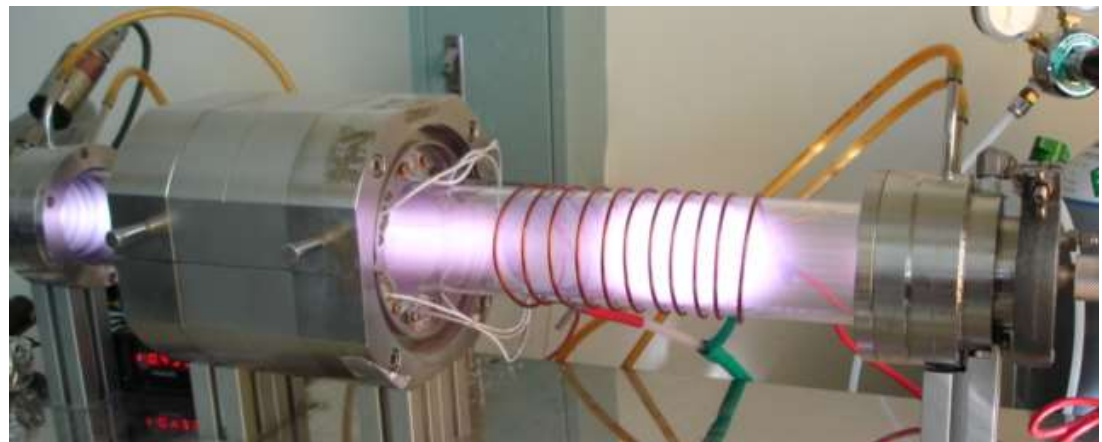
VACUUM CHAMBER

AC 220V  
60Hz



# Plasma Reactors

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# Commercial Plasma Etchers

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MERIE



ICP



VHF Dual Frequency CCP



[http://www.appliedmaterials.com/products/assets/brochures/etch\\_english\\_1204.pdf](http://www.appliedmaterials.com/products/assets/brochures/etch_english_1204.pdf)

# Plasma Diagnostics

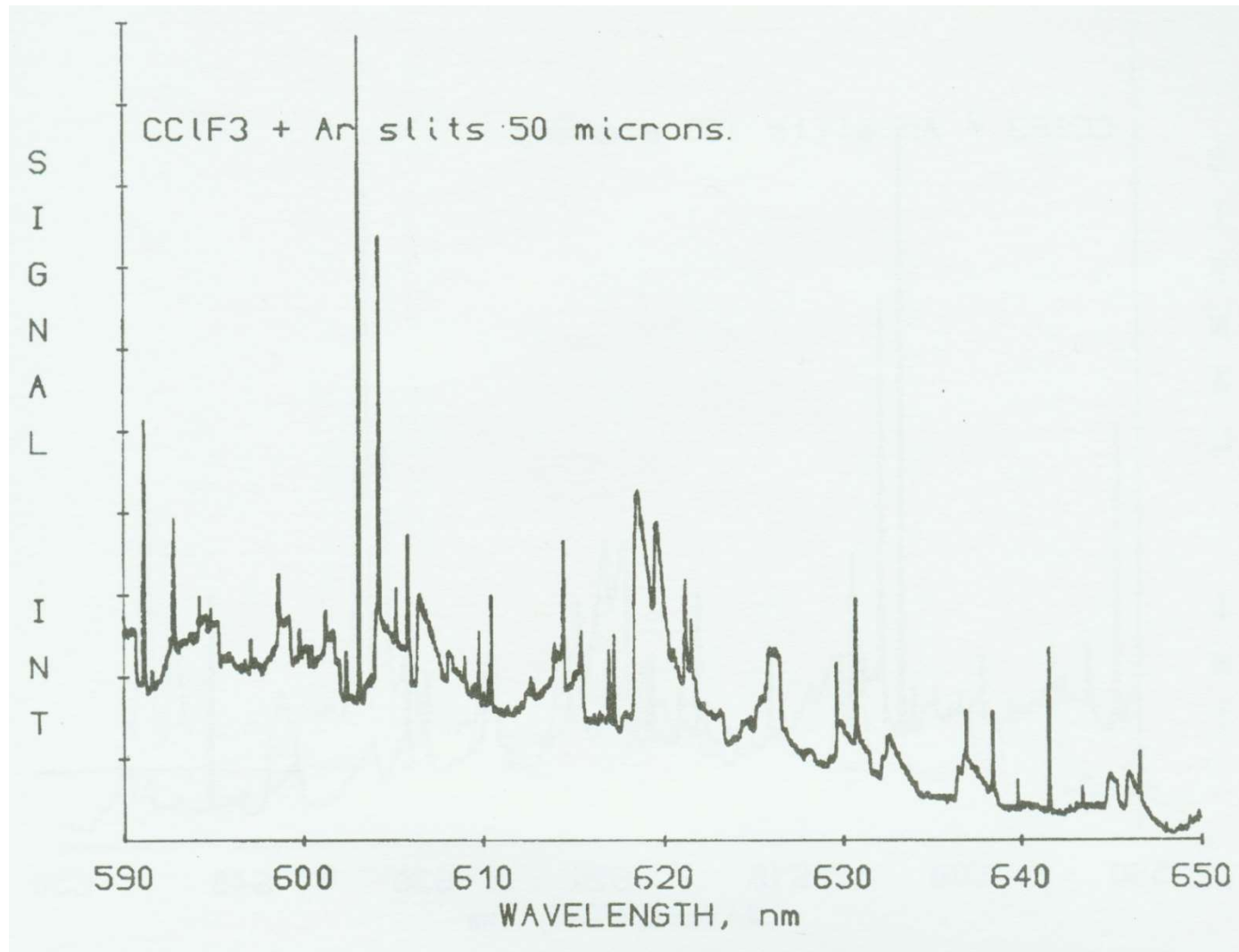
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# Plasma Diagnostics

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- Optical Emission Spectroscopy (OES)
- Mass Spectroscopy (MS)
- Langmuir Probe
- Endpoint Detection for Plasma Etching

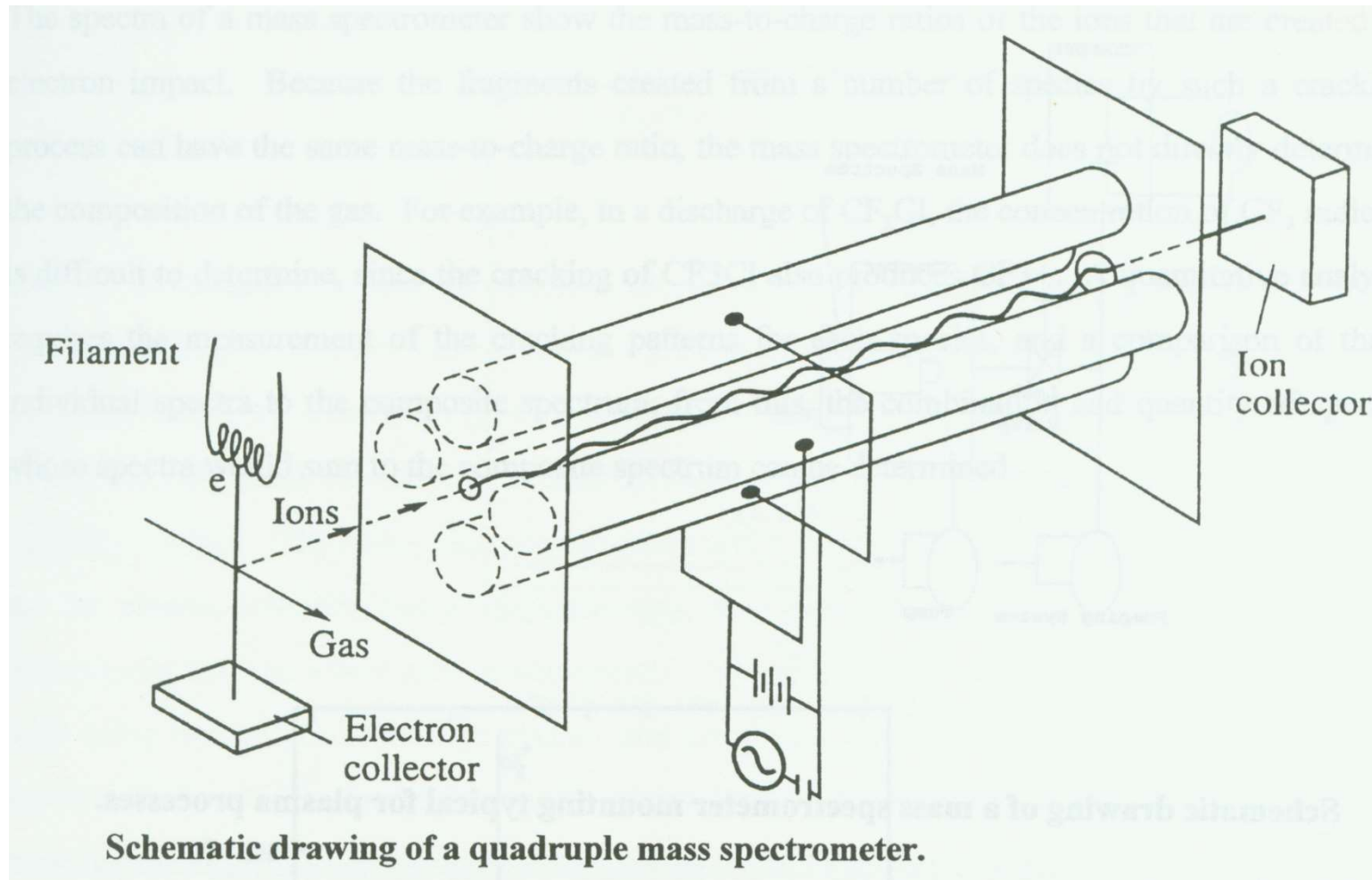
# Optical Emission Spectroscopy (OES)





# Mass Spectrometer

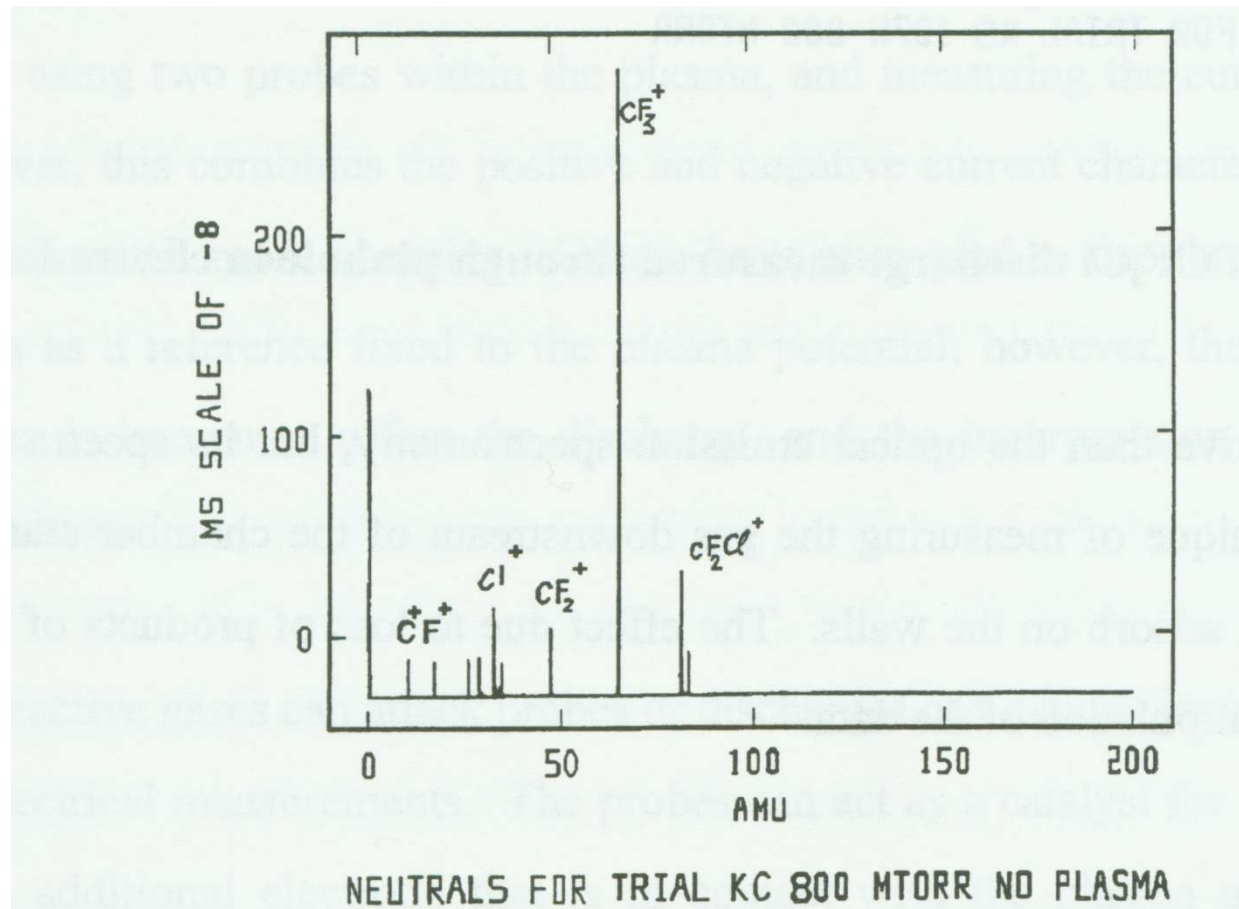
- For ion and neutral identification



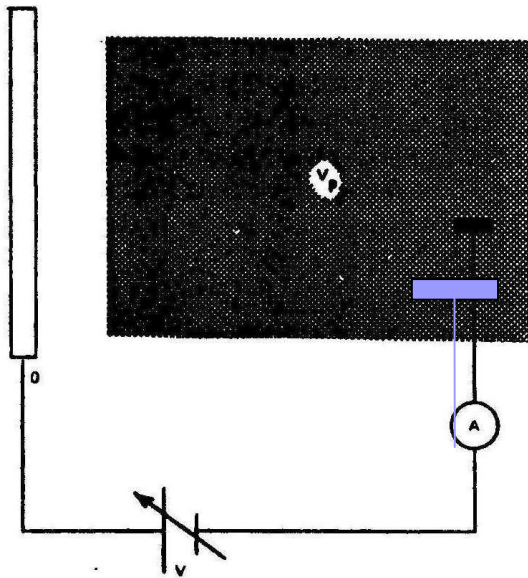


# Mass Spectroscopy

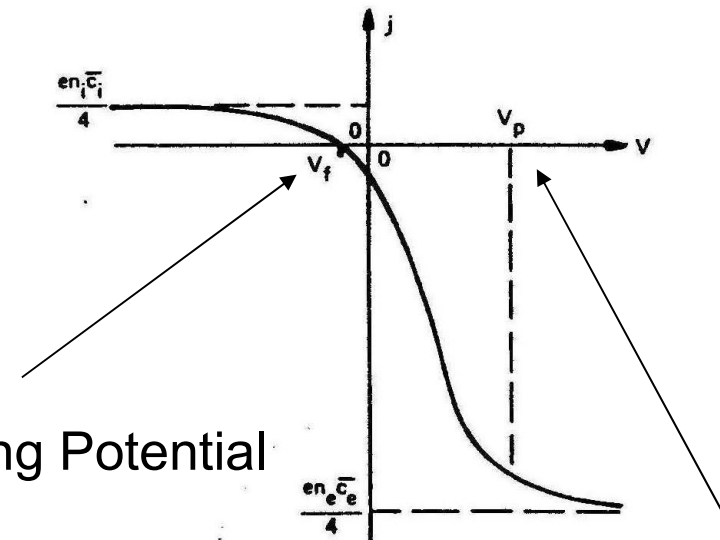
## ■ Spectrum of $\text{CF}_3\text{Cl}$



# Langmuir Probe and IV Curve

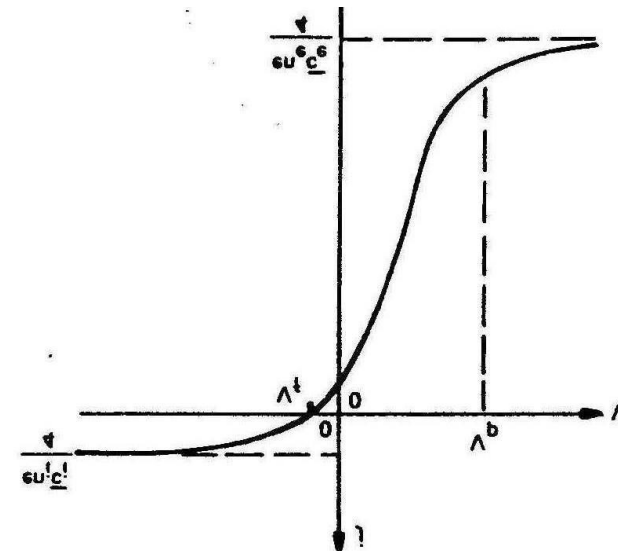


$$V_f = -\frac{kT_e}{2e} \ln\left(\frac{m_i}{2.3m_e}\right)$$



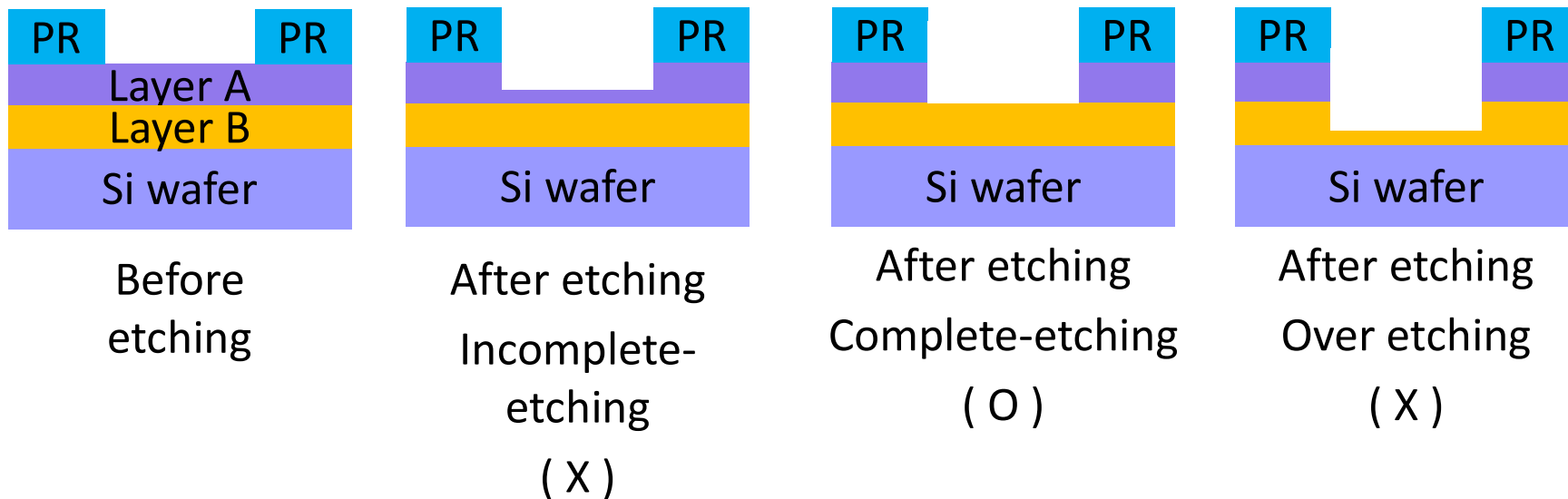
■ Floating Potential

■ 상하대칭 (Symmetry)      ■ Plasma Potenti



# Plasma Monitoring: Endpoint Detection

- To control etching rate is important for IC manufacturing.
- It is necessary to avoid incomplete-etching & over-etching.
- Decreasing feature size, it becomes more and more challenging to detect endpoint.



- It is critical to end the plasma etching process at target depth.
- Sensitive plasma monitoring required.

# Plasma Monitoring Tools

## Physical

### Non-Invasive Ion Monitor



$\Gamma_i, n_i, T_e$

Dielectric Window

Gas Inlet

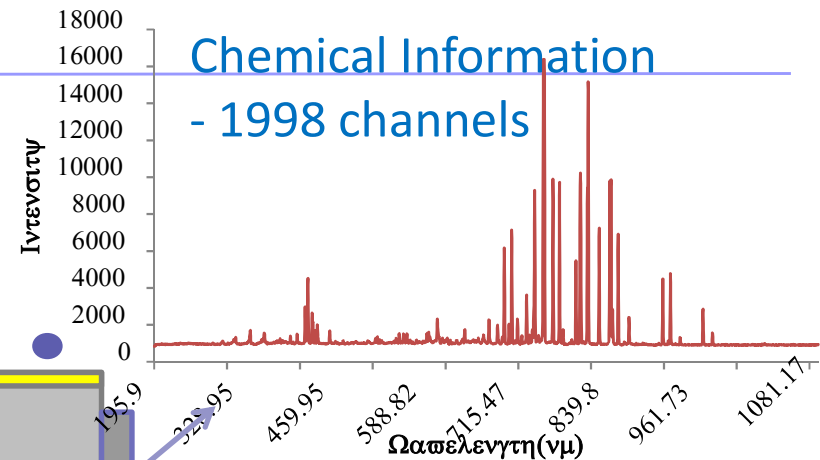
Plasma

Wafer

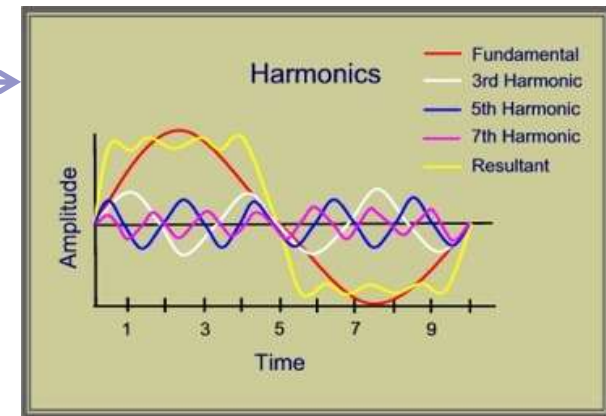
Vacuum Exhaust Foreline

VI Probe

RF Bias Power  
(12.56MHz)

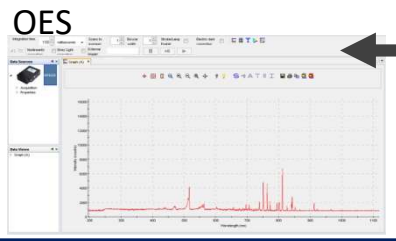


## Physical information $V, I, \theta, 1^{st}-5^{th}$ harmonics

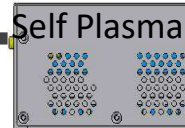


## Chemical

### SPOES



1998 χηαννελς



- Chemical and physical sensors are required for plasma analysis
- Big data mining techniques applied to increase sensitivity of sensors

# End Point Detection

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Method	Measuring	Monitoring
Optical Emission Spectroscopy	Intensity of light emitted from discharge	Emission from reactive species and/or etch products
Optical reflection (Interferometry)	Interference phenomena or reflectivity differences	Changes in film thickness
Mass spectrometry	Gas composition	Etch products
Impedance Monitoring	Impedance/ Mismatch	Voltage/Phase change
Langmuir Probe	Changes in electron density or average energy	Current from probe energy
Pressure	Total pressure	Changes in total pressure

# Plasma Monitoring: Principal Component Analysis (PCA)

Measured variable 'x, y, z'			
measuring	x	y	z
1	$x_1$	$y_1$	$z_1$
2	$x_2$	$y_2$	$z_2$
.			
.			
n	$x_n$	$y_n$	$z_n$

■ Data

$t_i$  : new independent variables

$$t_1 = p_{11}x + p_{12}y + p_{13}z$$

$$t_2 = p_{21}x + p_{22}y + p_{23}z$$

$$t_3 = p_{31}x + p_{32}y + p_{33}z$$

(Matrix)

$$t_i = Xp_i$$

Contribution ratio

measuring	$t_1$	$t_2$	$t_3$
1			
2			
.			
.			
n			

■ Principal Component Score

Increasing information intensity of  $t_i$

Maximizing  $s_{t_i}$  (variance of  $t_i$ )

$$\text{Constraint : } p_{i1}^2 + p_{i2}^2 + p_{i3}^2 = 1$$

$$Sp_i = \lambda p_i \quad S = \left( \frac{1}{n-1} \right) X^T X$$

Finding  $\lambda$  &  $p$  from  $S$  (variance-covariance matrix)

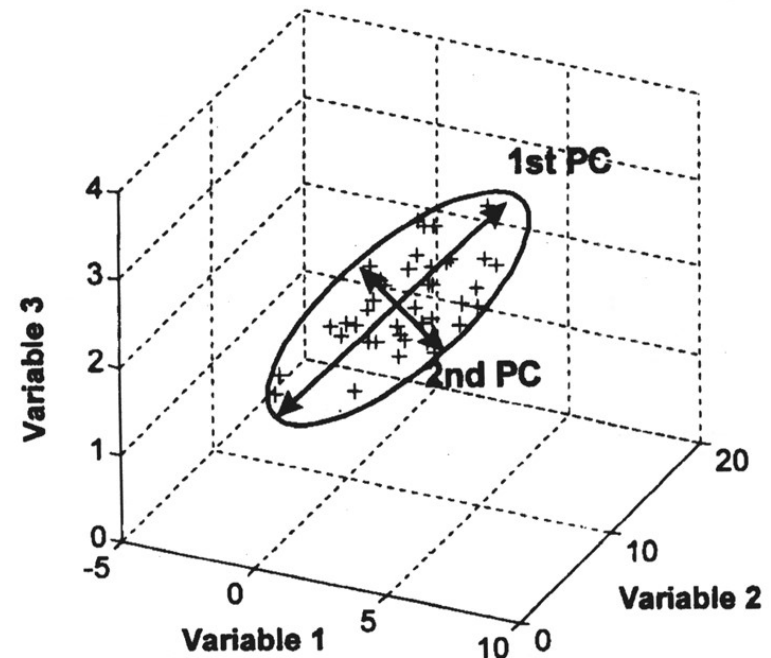
$$|S - \lambda I| = 0$$

$\lambda$  (eigenvalue) = Relative information intensity

$p_i$  (eigenvector) = loading vector

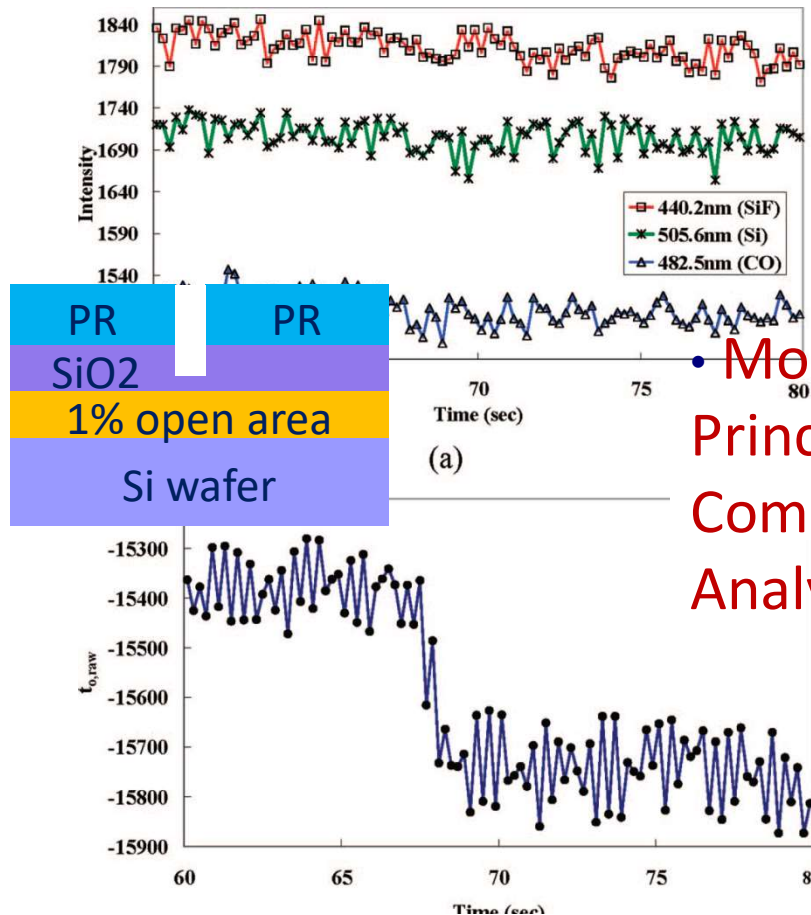
= coefficient of principal components

$t_i$  = score vector

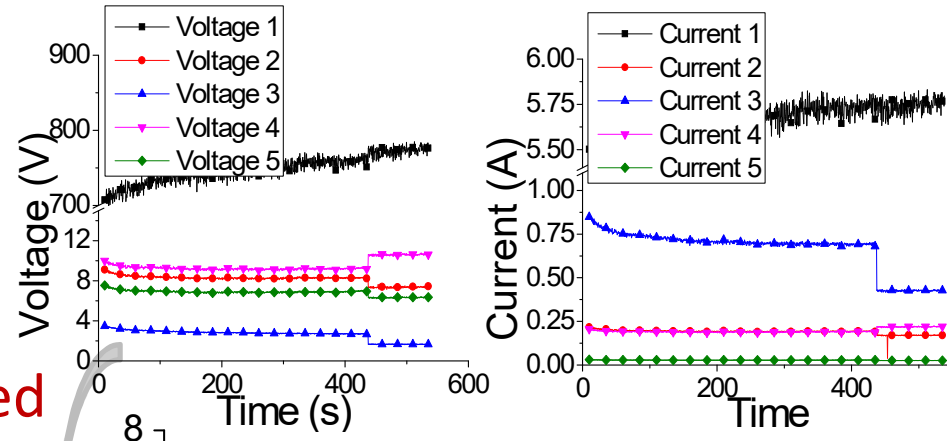


# Plasma Monitoring @ SKKU

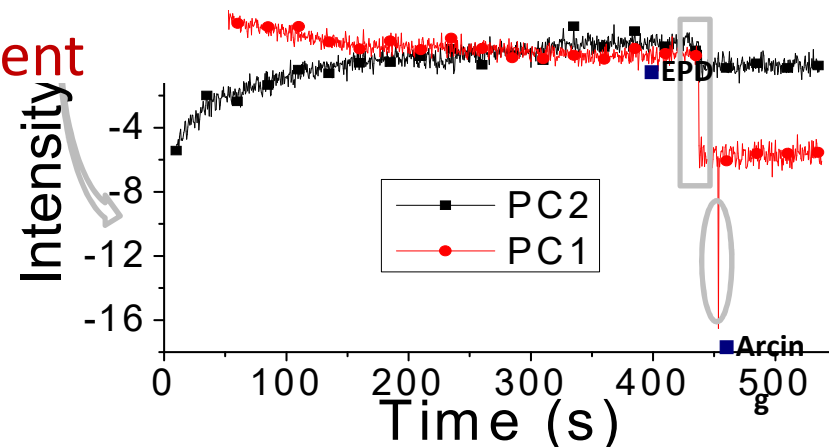
EPD (OES) : chemical information



EPD (VI probe): physical information



Modified  
Principle  
Component  
Analysis



Ind. Eng. Chem. Res, 47, 11, (2008)

Plasma process polym. 10, 850 (2013)

- Endpoint detection sensitivity improved by PCA algorithm

# Summary

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- Plasma Etching by Radicals and Ions
- Plasma Etching Chemistry
  - F, Cl, and Br containing compounds for Si etching
  - F containing compounds for SiO<sub>2</sub> etching
  - Cl, and Br containing compounds for Al etching
- Plasma Diagnostics
  - Physical: Langmuir Probe, Impedance
  - Chemical: OES, Mass Spectroscopy
- Issues of plasma etching
  - Process: Profile, Uniformity, Selectivity, Striations
  - Productivity: Etch rate, Cleaning



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- B. Chapman, “Glow Discharge”, Academic Press, 1980
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