Silicon Epitaxial CVD

- Want to create very sharp PN boundary
  - grow one type layer on other in single crystal form
- High dopant layers on low dopant substrate
  - Creates latch up protection for CMOS
- Buried Epi layer in bipolar transistors
  - do diffusion, grow Epi, out diffuse layer

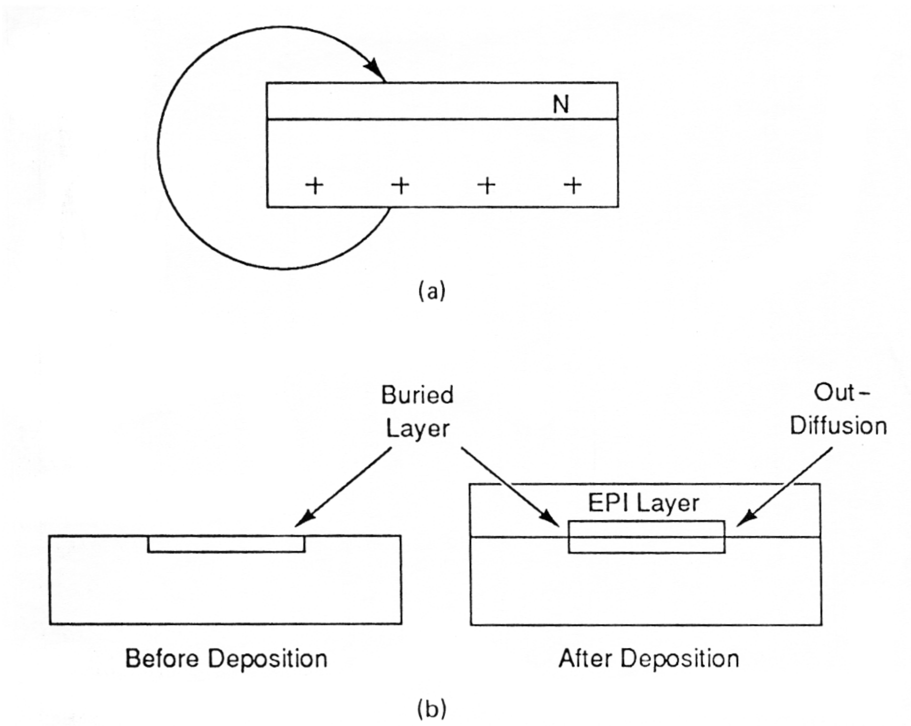
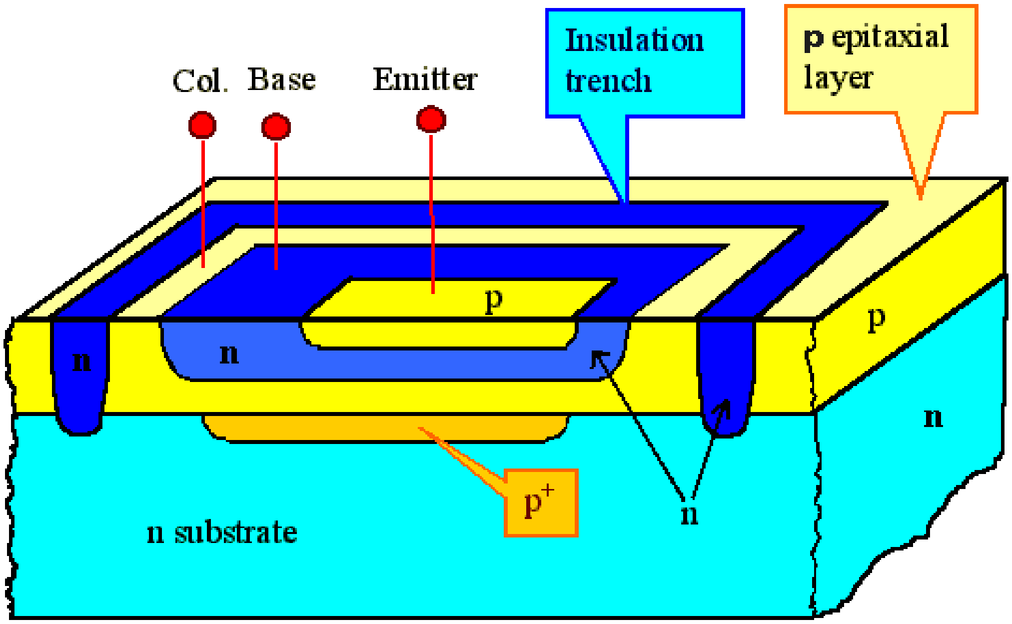


Figure 12.29 (*a*) Epitaxial autodoping and (*b*) out-diffusion.



Epitaxy

- When CVD silicon done on single Si crystal
- At correct temperature get Epi film
  Why: always crystallize in line with Si atoms already deposited
- If other substrates get poly Si
- Due to nucleation effect – not same structure as Si
- Nuclei randomly distributed

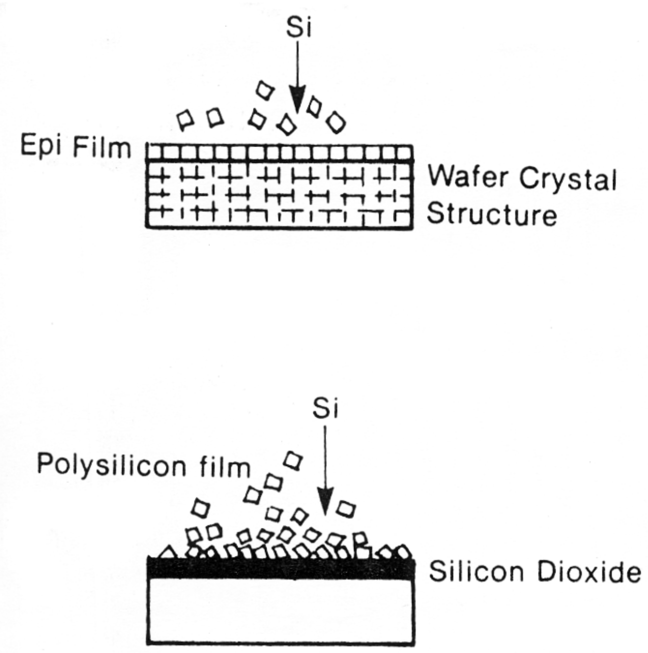
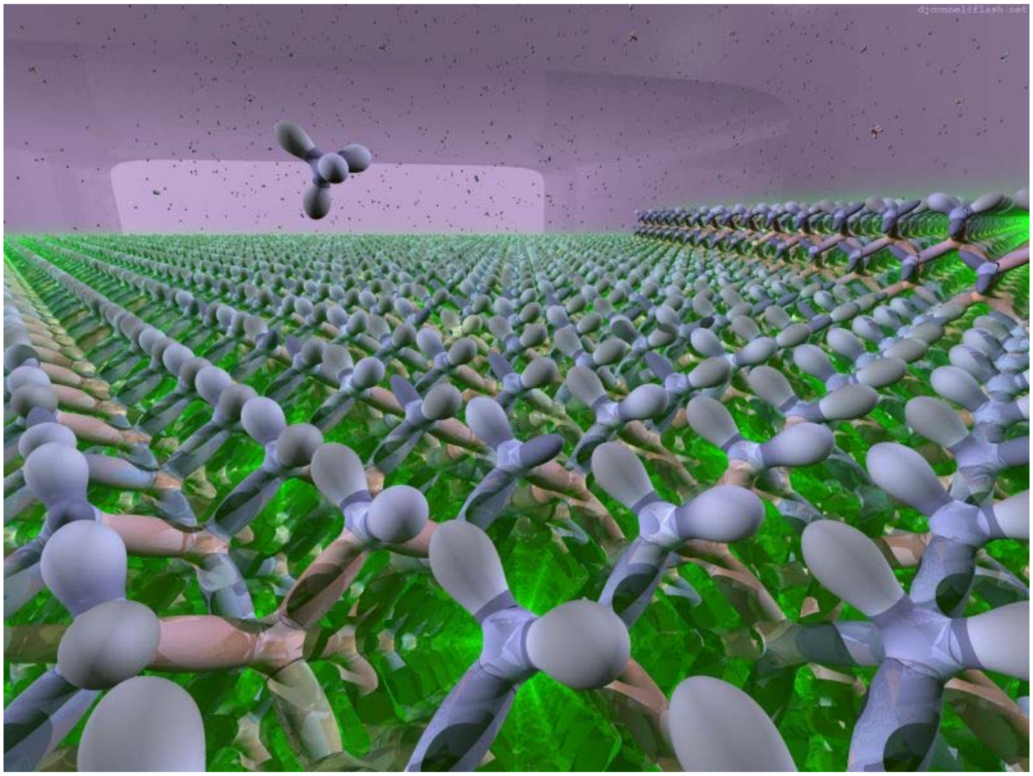
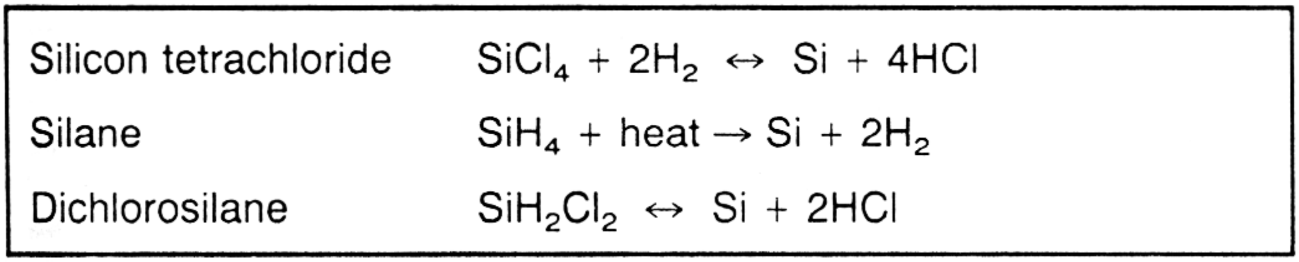


Figure 12.22 Epitaxial and poly-silicon film growth.



Silicon CVD

- Three main chemical processes with source gas
- Silcon tetrachloride reacts with hydrogen by reduction
- Silane decomposes by pyrolysis
- Dichorlosilane also decomposes
- All very toxic
- Dichorlosilane is much less toxic than silane – hence tend to use



Silicon tetrachloride	$SiCl_4 + 2H_2 \leftrightarrow Si + 4HCl$
Silane	$SiH_4 + \text{heat} \rightarrow Si + 2H_2$
Dichlorosilane	$SiH_2Cl_2 \leftrightarrow Si + 2HCl$

Figure 12.23 Epitaxial silicon chemical sources.

Alternative Gases for Si CVD

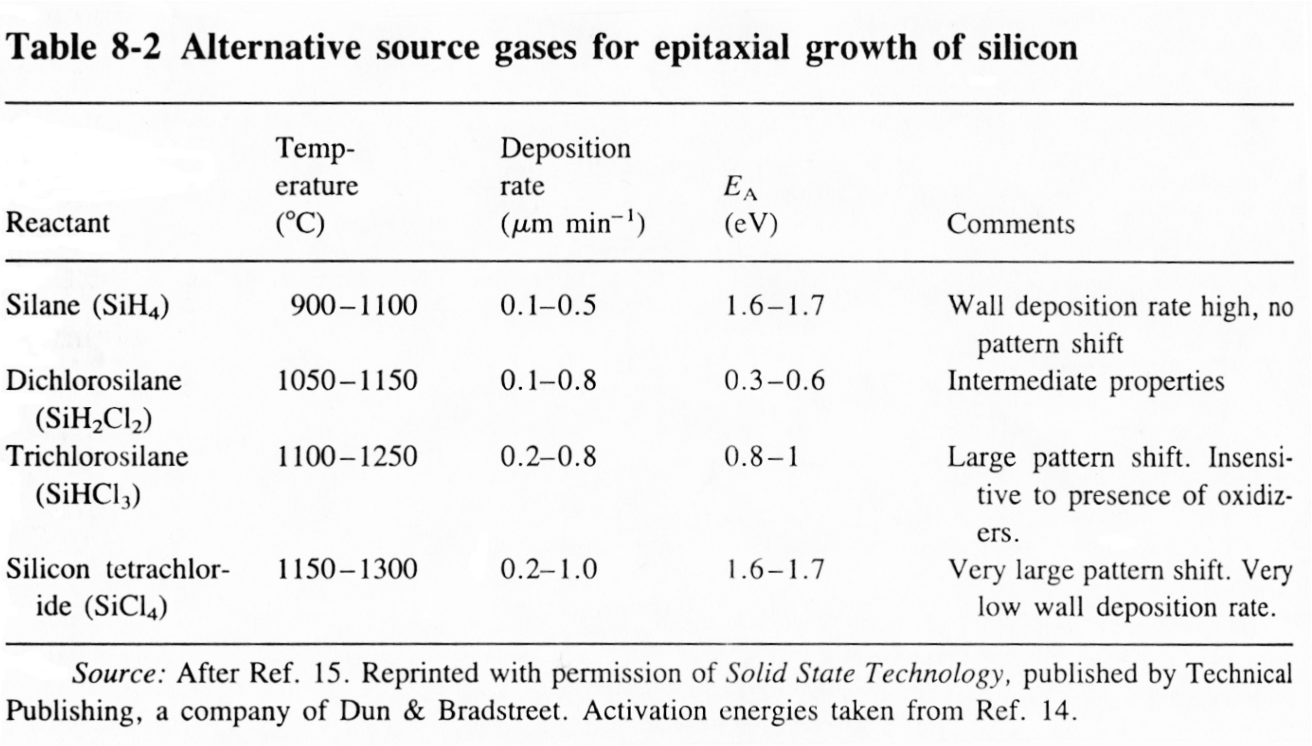


Table 8-2 Alternative source gases for epitaxial growth of silicon

Reactant	Temperature (°C)	Deposition rate (μm min^{-1})	E_A (eV)	Comments
Silane (SiH_4)	900–1100	0.1–0.5	1.6–1.7	Wall deposition rate high, no pattern shift
Dichlorosilane (SiH_2Cl_2)	1050–1150	0.1–0.8	0.3–0.6	Intermediate properties
Trichlorosilane ($SiHCl_3$)	1100–1250	0.2–0.8	0.8–1	Large pattern shift. Insensitive to presence of oxidizers.
Silicon tetrachloride ($SiCl_4$)	1150–1300	0.2–1.0	1.6–1.7	Very large pattern shift. Very low wall deposition rate.

Source: After Ref. 15. Reprinted with permission of *Solid State Technology,* published by Technical Publishing, a company of Dun & Bradstreet. Activation energies taken from Ref. 14.

Effect of Temperature on Poly Si

- Conductivity of the Si dependent on the crystal size
- Crystal size set by Poly deposition temperature
- < 605°C Amorphous, Small grain 630°C
- Large grain Poly 700°C
- Larger grain – closer to single crystal behaviour

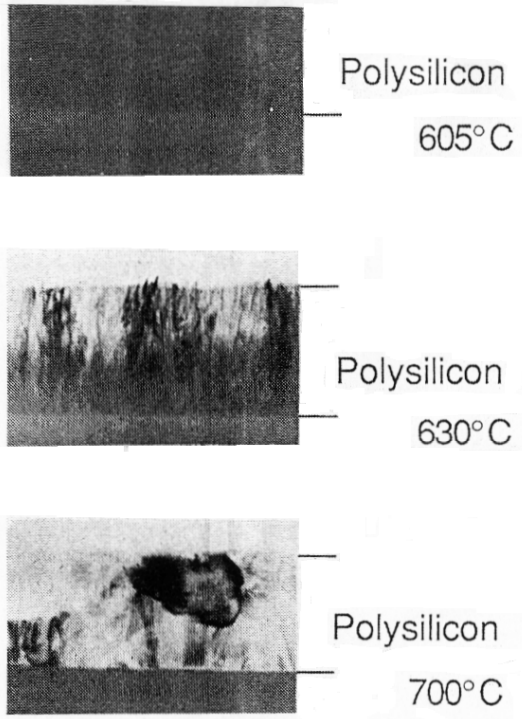


FIGURE 7

TEM cross sections (60,000X) of polysilicon. (a) Amorphous structure deposited at 605°C. (b) Columnar structure deposited at 630°C. (c) Crystalline grains formed by annealing an amorphous sample at 700°C.

Dielectric CVD Processes

- Most dielectrics (insulators) deposited by CVD
- Deposition temperature important
- But this affects rest of wafer (eg Changes diffusions)
- Cannot use CVD with Al if > 600°C deposition

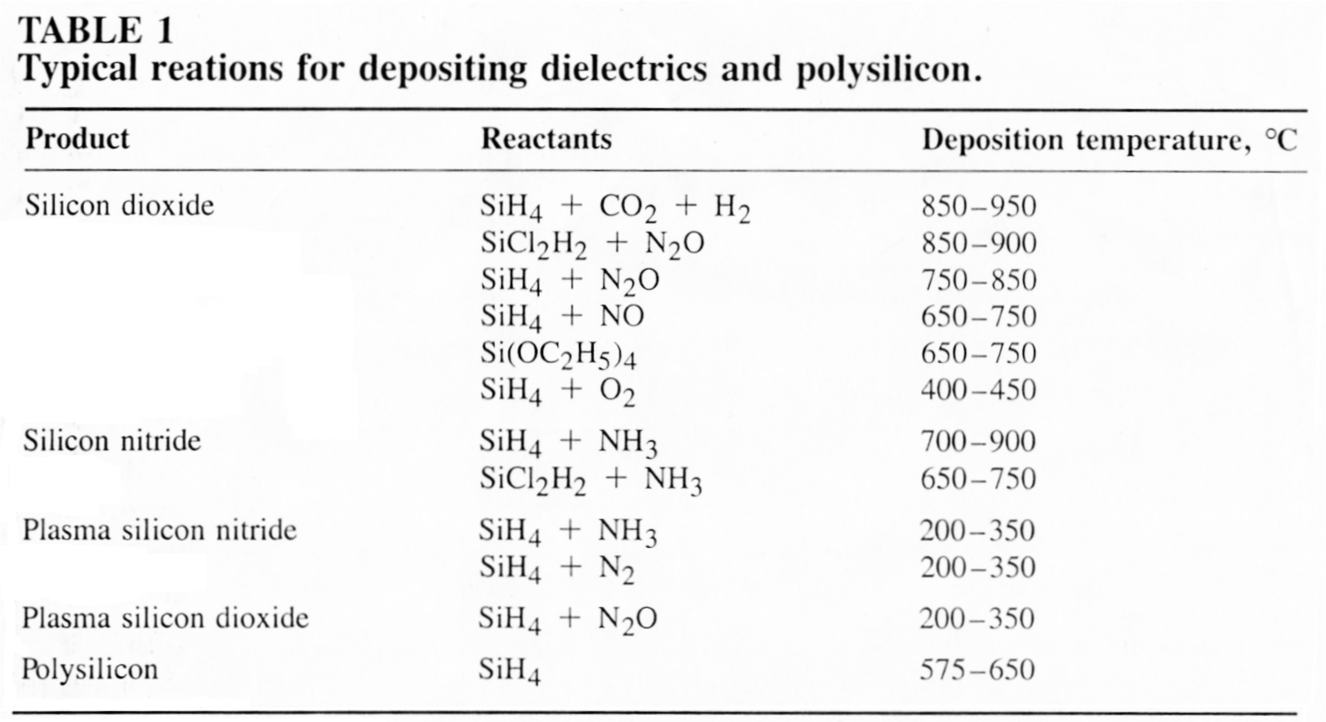


TABLE 1
Typical reations for depositing dielectrics and polysilicon.

Product	Reactants	Deposition temperature, °C
Silicon dioxide	$SiH_4 + CO_2 + H_2$	850–950
	$SiCl_2H_2 + N_2O$	850–900
	$SiH_4 + N_2O$	750–850
	$SiH_4 + NO$	650–750
	$Si(OC_2H_5)_4$	650–750
	$SiH_4 + O_2$	400–450
Silicon nitride	$SiH_4 + NH_3$	700–900
	$SiCl_2H_2 + NH_3$	650–750
Plasma silicon nitride	$SiH_4 + NH_3$	200–350
	$SiH_4 + N_2$	200–350
Plasma silicon dioxide	$SiH_4 + N_2O$	200–350
Polysilicon	SiH_4	575–650

Step Coverage with Dielectrics

- Step coverage very important for dielectrics
- Thin step coverage causes shorts and electrical breakdowns
- Problem: hard for gases to enter deep holes
- Get non conformal coverage

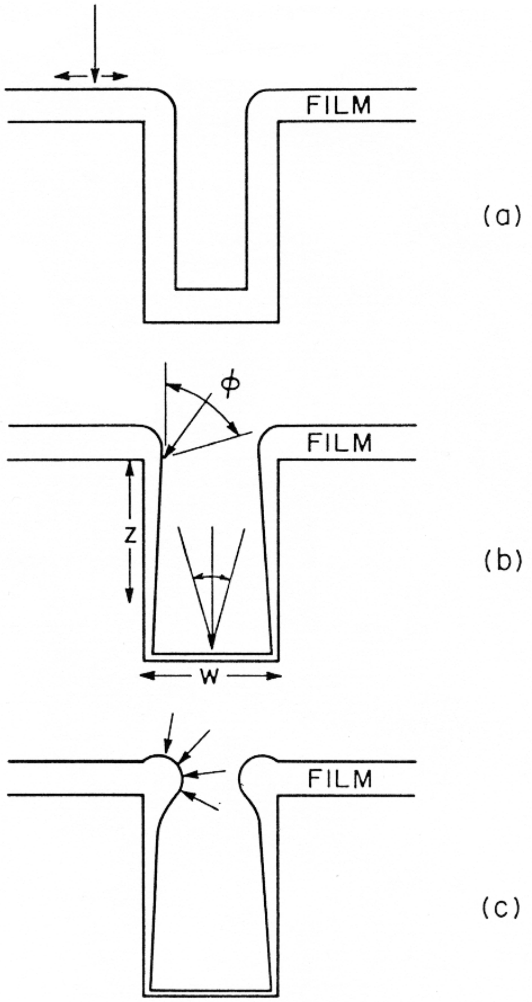


FIGURE 14
Step coverage of deposited films. (a) Uniform coverage resulting from rapid surface migration. (b) Nonconformal step coverage for long mean free path and no surface migration. (c) Nonconformal step coverage for short mean free path and no surface migration.

SEM of PECVD oxide over Poly Lines

- Typically PECVD oxide used as insulator after poly Si
- Oxide is few microns thick

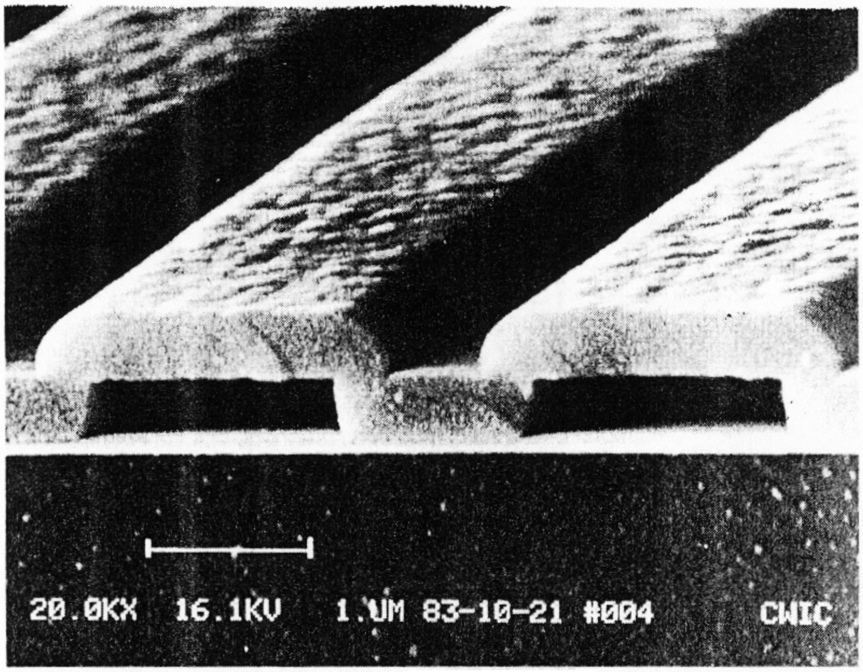
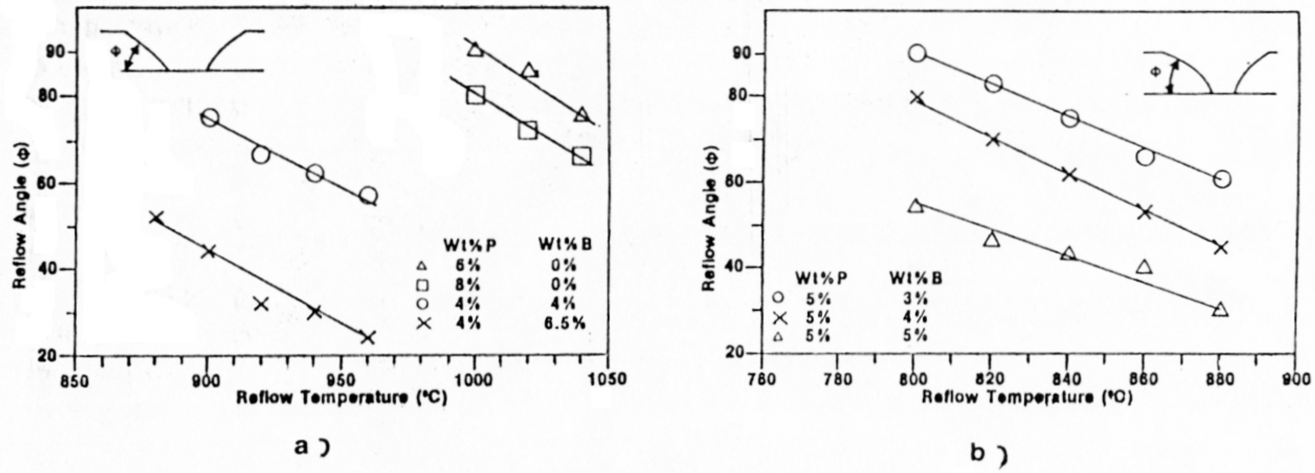


Fig. 21 SEM of PECVD oxide over polysilicon lines. Poly has been removed by wet etch to show detail[12]. Reprinted with permission of Solid State Technology, published by Technical Publishing, a company of Dun & Bradstreet.

Improved Step Coverage: Thermal Reflow of Glass

- Put down PSG (Phospho Silicate Glass)
- Softens and reflows in furnace: sloped sidewalls on steps
- Makes for better step coverage of upper layers



a)

b)

Fig. 23 (a) Reflow angle vs. reflow temperatures in a nitrogen ambient (30 min). (b) Reflow angle vs. reflow temperatures in a steam ambient (30 min). Reprinted by permission of Solid State Technology, published by Technical Publishing, a company of Dun & Bradstreet[37].

Reflow of PSG at 1100 ºC

- Reflow depends on P fraction, temperature & time

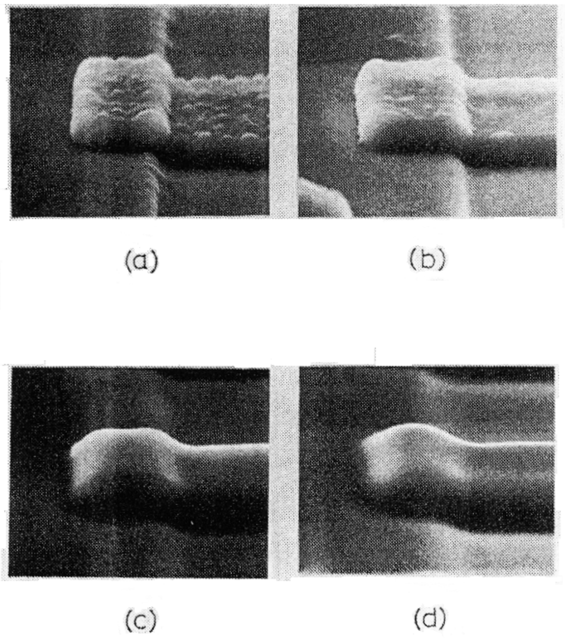


FIGURE 16
SEM photographs (3200X) showing surfaces of 4.6 wt. % P-glass annealed in steam at 1100 °C for the following times: (a) 0 min; (b) 20 min; (c) 40 min; (d) 60 min. (*After Adams and Capio, Ref. 34*.)

Removal of Reentrant Cavity with PSG Reflow

- Note removal of bread loaf type structure

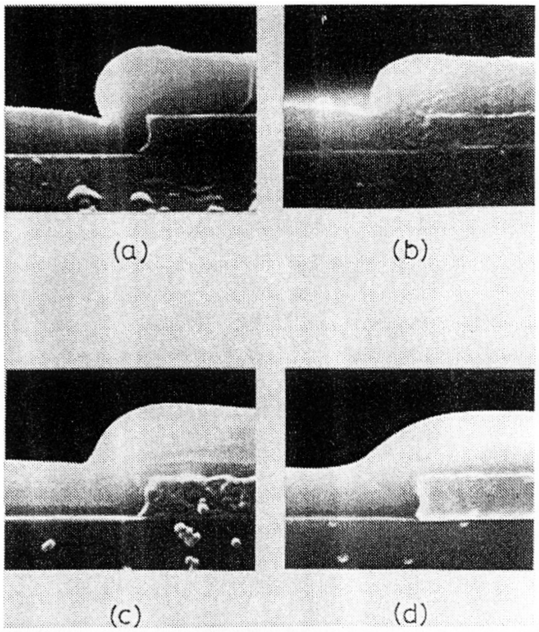


FIGURE 17
SEM cross sections (10,000X) of samples annealed in steam at 1100 °C for 20 min for the following weight percent of phosphorus: (a) 0.0 wt. % P; (b) 2.2 wt. % P; (c) 4.6 wt. % P; (d) 7.2 wt. % P. (*After Adams and Capio, Ref. 34.*)

Boro Phospho Silicate Glass Reflow of Vias

- Hard for gases to enter deep holes
- Get non conformal coverage
- Called BPSG

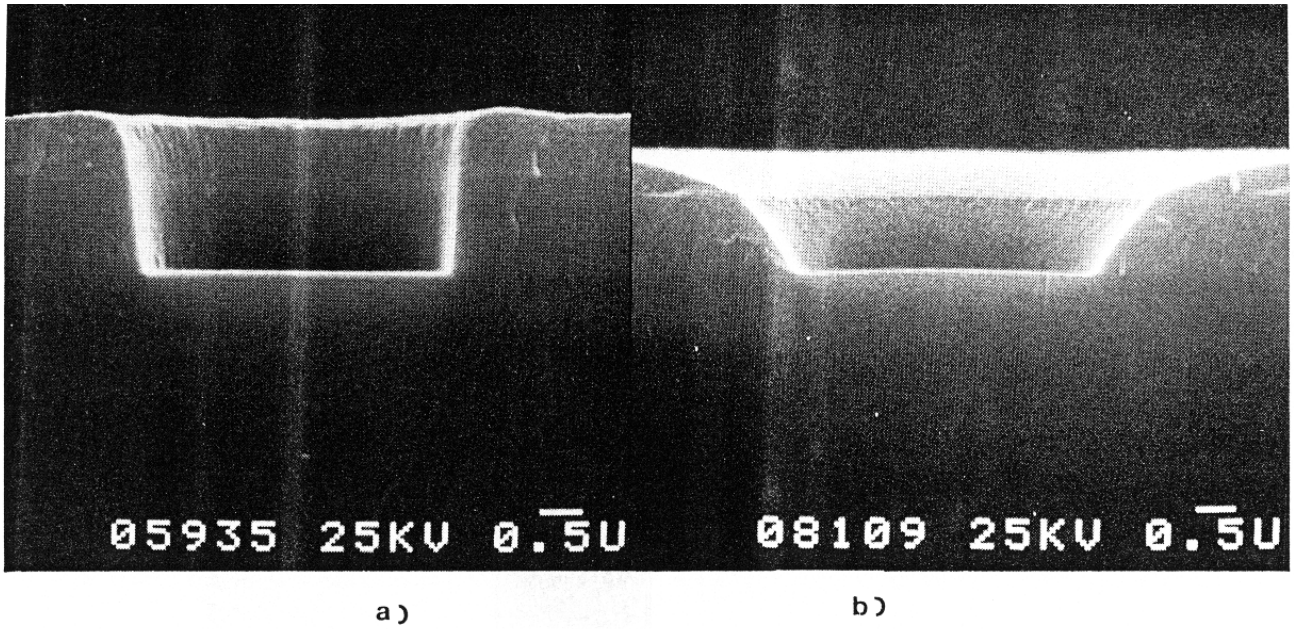


Fig. 24 (a) SEM of dry-etched contact window before reflow. (b) Reflowed BPSG film with 4 wt% P and 4 wt% B. Reflow was 930°C in N_2 for 25 min[37]. Courtesy of Applied Materials, Inc.

Densification of Glass

- CVD films have low density
- Often "Densify" them
- Anneal in furnace at high temperature (400 - 800 ^{o}C)
- Done in Forming Gas: N + about 5% H
  H removes oxygen
- Removes voids from glass
- Reduces etching rate, better dielectric constant

Comparison of Thermal and CVD oxide

- Must watch film stress
- Problems thermal expansion of Si and oxide is very different
- Linear coefficient of Thermal expansion:
- Silicon $2.6\times10^{-6}\ ^{o}C^{-1}$
- Silicon dioxide $5.0\times10^{-7}\ ^{o}C^{-1}$
- Result differential shrinkage when wafer is returned to room temp
- Creates stress in film:
- T = tensile (wafer shrinks slower than film)
- C = compressive (wafer shrinks faster than film)
- The larger the wafer the more stress in general

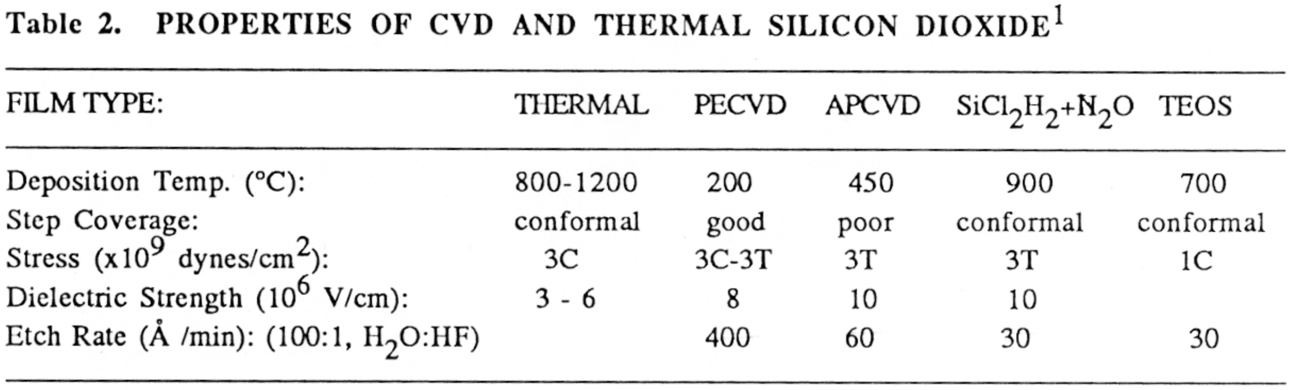


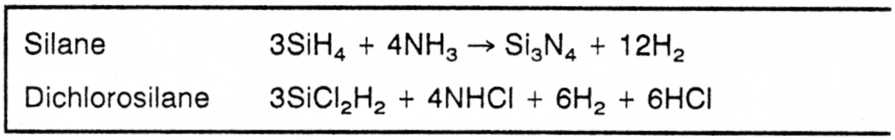
Table 2. PROPERTIES OF CVD AND THERMAL SILICON DIOXIDE[1]

FILM TYPE:	THERMAL	PECVD	APCVD	$SiCl_2H_2+N_2O$	TEOS
Deposition Temp. (°C):	800-1200	200	450	900	700
Step Coverage:	conformal	good	poor	conformal	conformal
Stress ($\times10^{9}$ dynes/cm^2):	3C	3C-3T	3T	3T	1C
Dielectric Strength (10^{6} V/cm):	3 - 6	8	10	10	
Etch Rate (Å /min): (100:1, H_2O:HF)		400	60	30	30

v

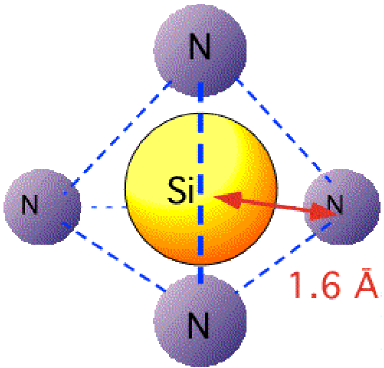
Silicon Nitride

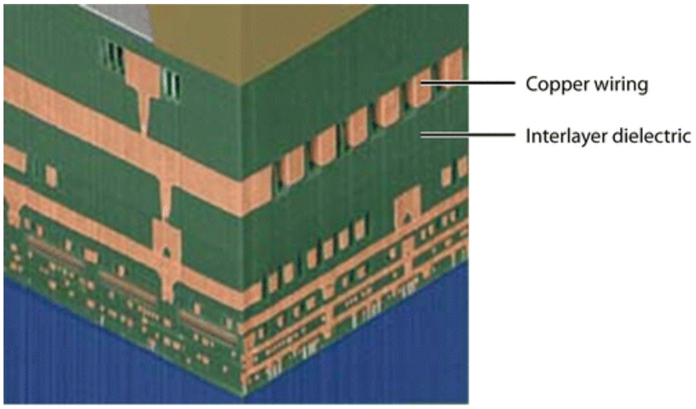
- Nitride of Silicon ideally Si_3N_4
- Higher dielectric constant than oxide (ε_r =6-9 nitride, 3-4 oxide)
- Much stronger than oxide: hence good scratch protect top layer
- Also harder to diffuse into (oxygen, water)
- Hence used as a top encapsulation layer
- Used as intermetal insulator for upper layers
- Very important for Cu conductor diffusion barriers
- Cu diffuses rapidly through oxide but not through SiN
- Higher breakdown voltage than CVD oxides
- Gate Dielectric under poly gates
  (better than oxide for thin insulators)
- Nitride cannot be grown in furnace – only by CVD

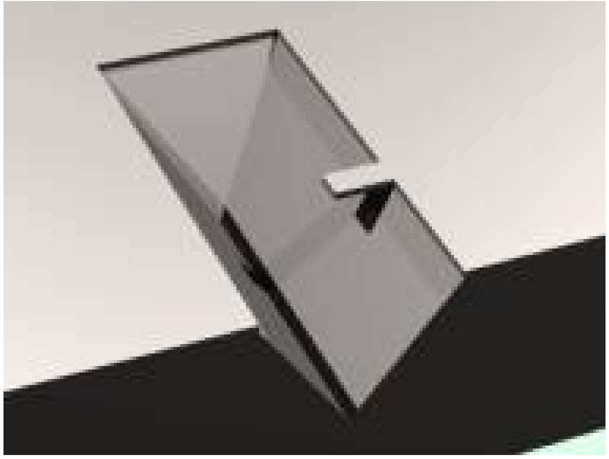


Silane	$3SiH_4 + 4NH_3 \rightarrow Si_3N_4 + 12H_2$
Dichlorosilane	$3SiCl_2H_2 + 4NHCl + 6H_2 + 6HCl$

Figure 12.38 Silicon nitride deposition reactions.





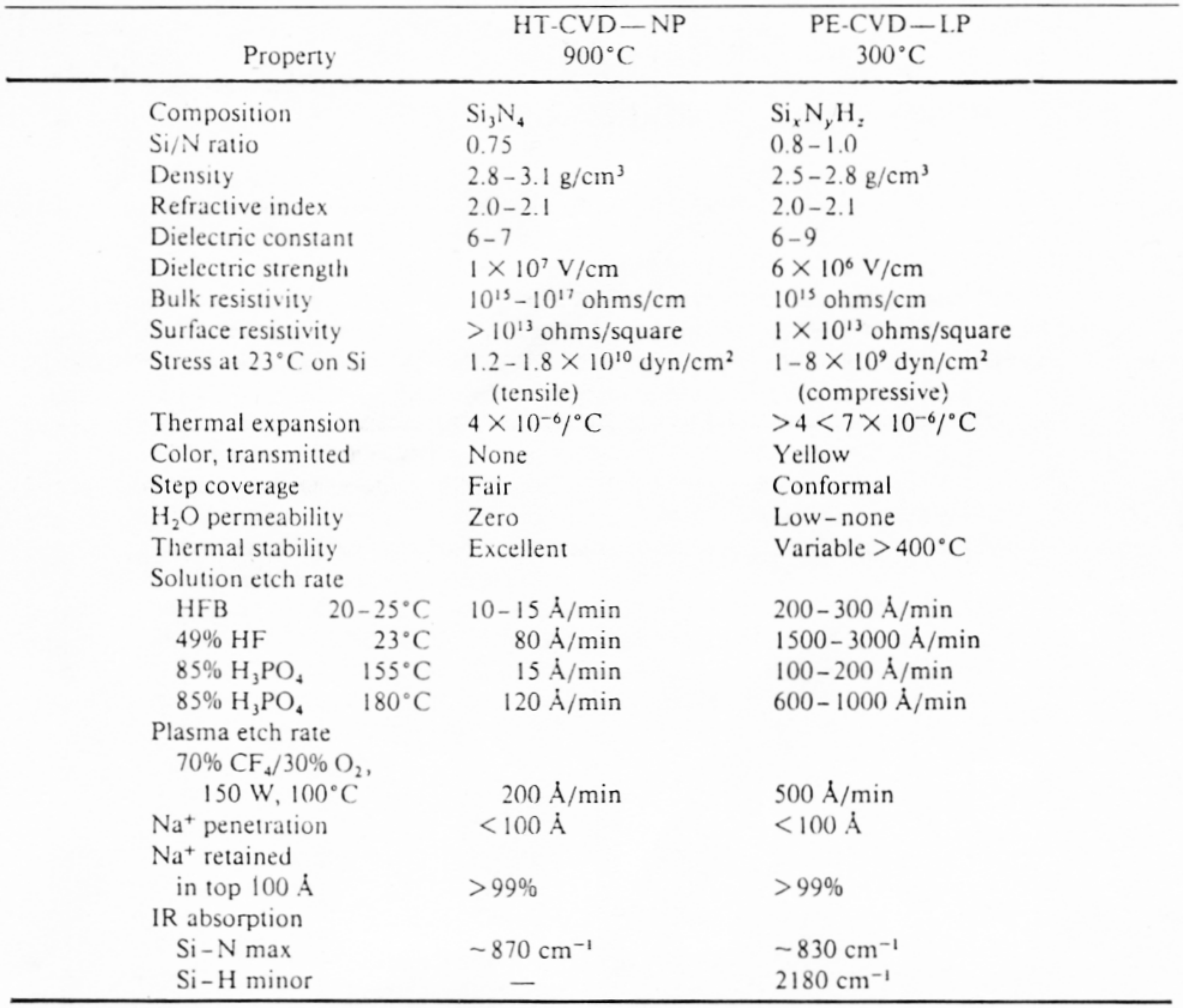


Kohl PA. 2011.
Annu. Rev. Chem. Biomol. Eng. 2:379–401

Silicon Nitride Properties

- Properties very dependent on deposition technique
- Usually non-stoichiometric (not proper composition ratio)
  Si_xN or $Si_xN_yH_z$
- PECVD nitride often Silicon rich – head yellow colour
- High Temperature Nitride better: colourless
- Can grow in furnace oxy-nitride $Si_xN_yO_z$
- Used in High Radiation Resistance devices
  Does not form trapped charges as easily as oxide

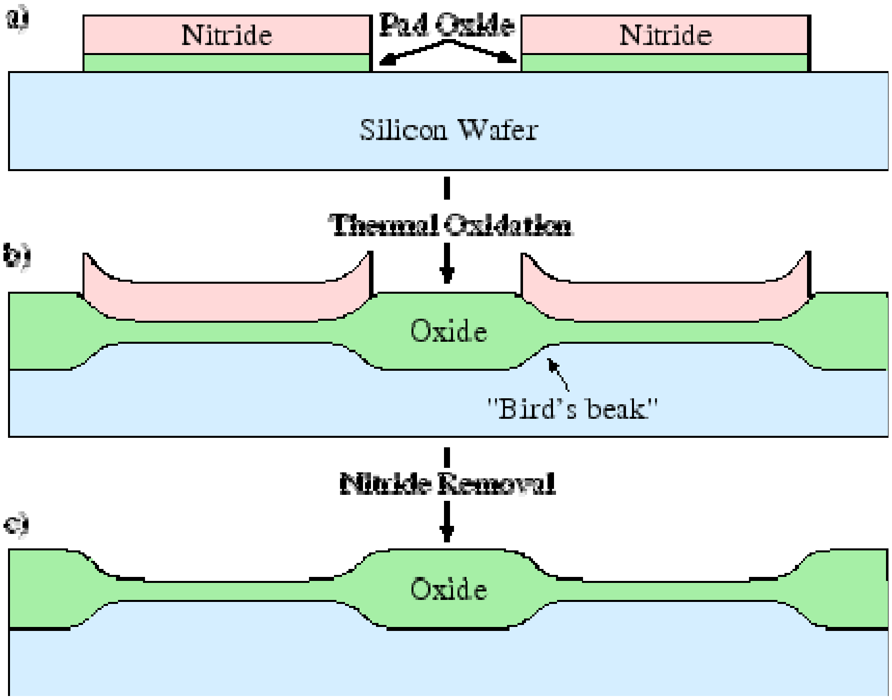
Table 3. Properties of PECVD Silicon Nitride and High Temperature CVD Nitride



Property	HT-CVD—NP 900°C	PE-CVD—LP 300°C
Composition	Si_3N_4	$Si_xN_yH_z$
Si/N ratio	0.75	0.8–1.0
Density	2.8–3.1 g/cm^3	2.5–2.8 g/cm^3
Refractive index	2.0–2.1	2.0–2.1
Dielectric constant	6–7	6–9
Dielectric strength	1×10^7 V/cm	6×10^6 V/cm
Bulk resistivity	10^{15}–10^{17} ohms/cm	10^{15} ohms/cm
Surface resistivity	$> 10^{13}$ ohms/square	1×10^{13} ohms/square
Stress at 23°C on Si	1.2–1.8×10^{10} dyn/cm^2 (tensile)	1–8×10^9 dyn/cm^2 (compressive)
Thermal expansion	4×10^{-6}/°C	$>4 < 7 \times 10^{-6}$/°C
Color, transmitted	None	Yellow
Step coverage	Fair	Conformal
H_2O permeability	Zero	Low–none
Thermal stability	Excellent	Variable >400°C
Solution etch rate		
HFB 20–25°C	10–15 Å/min	200–300 Å/min
49% HF 23°C	80 Å/min	1500–3000 Å/min
85% H_3PO_4 155°C	15 Å/min	100–200 Å/min
85% H_3PO_4 180°C	120 Å/min	600–1000 Å/min
Plasma etch rate		
70% CF_4/30% O_2, 150 W, 100°C	200 Å/min	500 Å/min
Na^+ penetration	<100 Å	<100 Å
Na^+ retained in top 100 Å	>99%	>99%
IR absorption		
Si–N max	~870 cm^{-1}	~830 cm^{-1}
Si–H minor	—	2180 cm^{-1}

Silicon Nitride LOCOS Process

- Oxygen diffuses very slowly through Nitride
- Hence can determine oxide are by SiN done by CVD
- SiN deposited & patterned to create oxide growth areas
- Oxide only grows where no Nitride: LOCOS
  LOCal Oxidation of Silicon
- SiN lifts up at edges where oxide grows
- Oxide grows in substrate
- Strip SiN
- Leaves deep oxide barrier below surface
- Electrically isolates devices



Deposit SiNx

Thermal oxidation
SiN forms barrier

Strip SiN
Leave oxide barrier

Major CVD Reactions & Types

- Major CVD processes are Poly Si, Oxide, Doped Oxide & Nitride
- Doped Oxides are
- Phospho-Silicate Glass PSG,
- Boro-Silicate Glass BSG
- Boro-Phospho-Silicate Glass BPSG

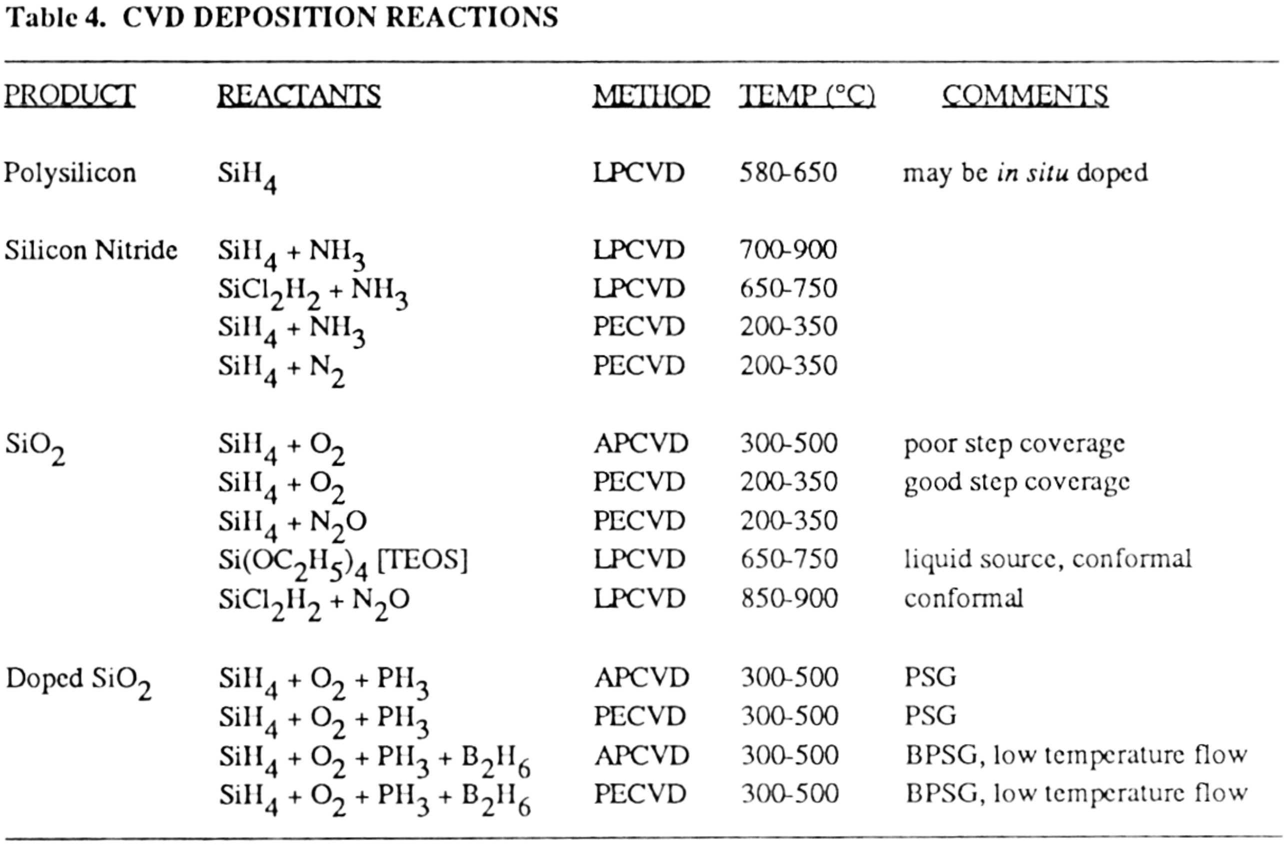


Table 4. CVD DEPOSITION REACTIONS

PRODUCT	REACTANTS	METHOD	TEMP (°C)	COMMENTS
Polysilicon	SiH_4	LPCVD	580-650	may be *in situ* doped
Silicon Nitride	$SiH_4 + NH_3$	LPCVD	700-900	
	$SiCl_2H_2 + NH_3$	LPCVD	650-750	
	$SiH_4 + NH_3$	PECVD	200-350	
	$SiH_4 + N_2$	PECVD	200-350	
SiO_2	$SiH_4 + O_2$	APCVD	300-500	poor step coverage
	$SiH_4 + O_2$	PECVD	200-350	good step coverage
	$SiH_4 + N_2O$	PECVD	200-350	
	$Si(OC_2H_5)_4$ [TEOS]	LPCVD	650-750	liquid source, conformal
	$SiCl_2H_2 + N_2O$	LPCVD	850-900	conformal
Doped SiO_2	$SiH_4 + O_2 + PH_3$	APCVD	300-500	PSG
	$SiH_4 + O_2 + PH_3$	PECVD	300-500	PSG
	$SiH_4 + O_2 + PH_3 + B_2H_6$	APCVD	300-500	BPSG, low temperature flow
	$SiH_4 + O_2 + PH_3 + B_2H_6$	PECVD	300-500	BPSG, low temperature flow

Summary of CVD Reactors and Types

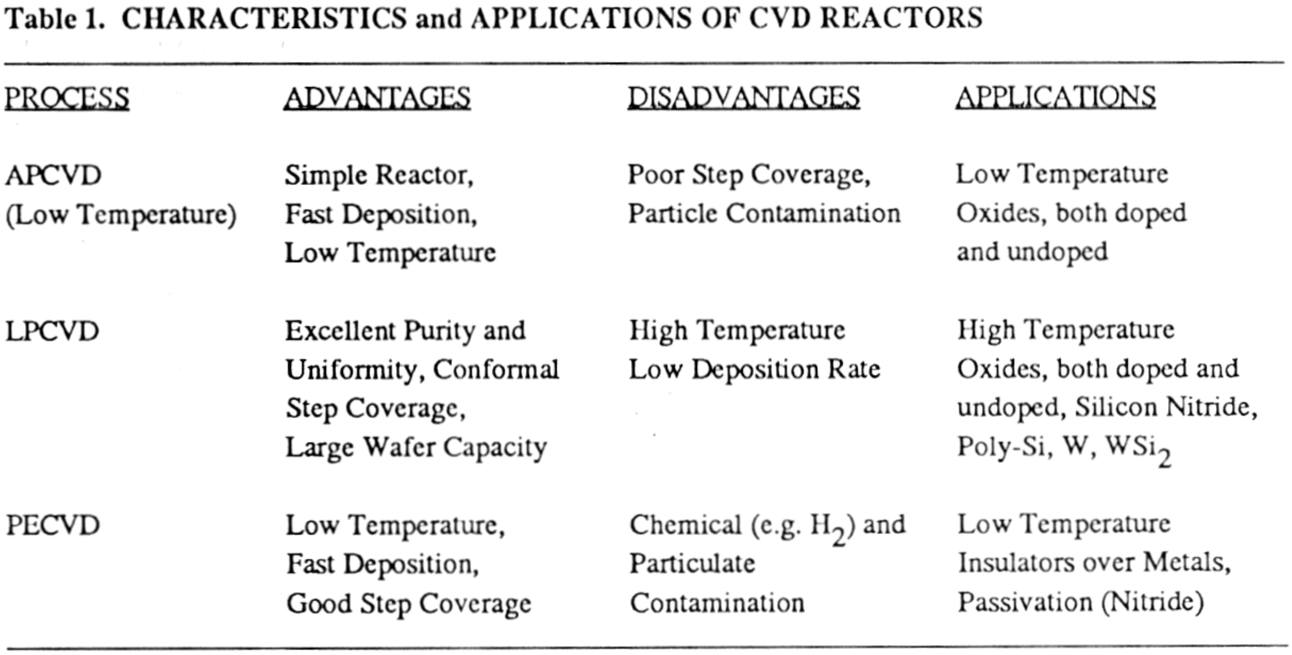
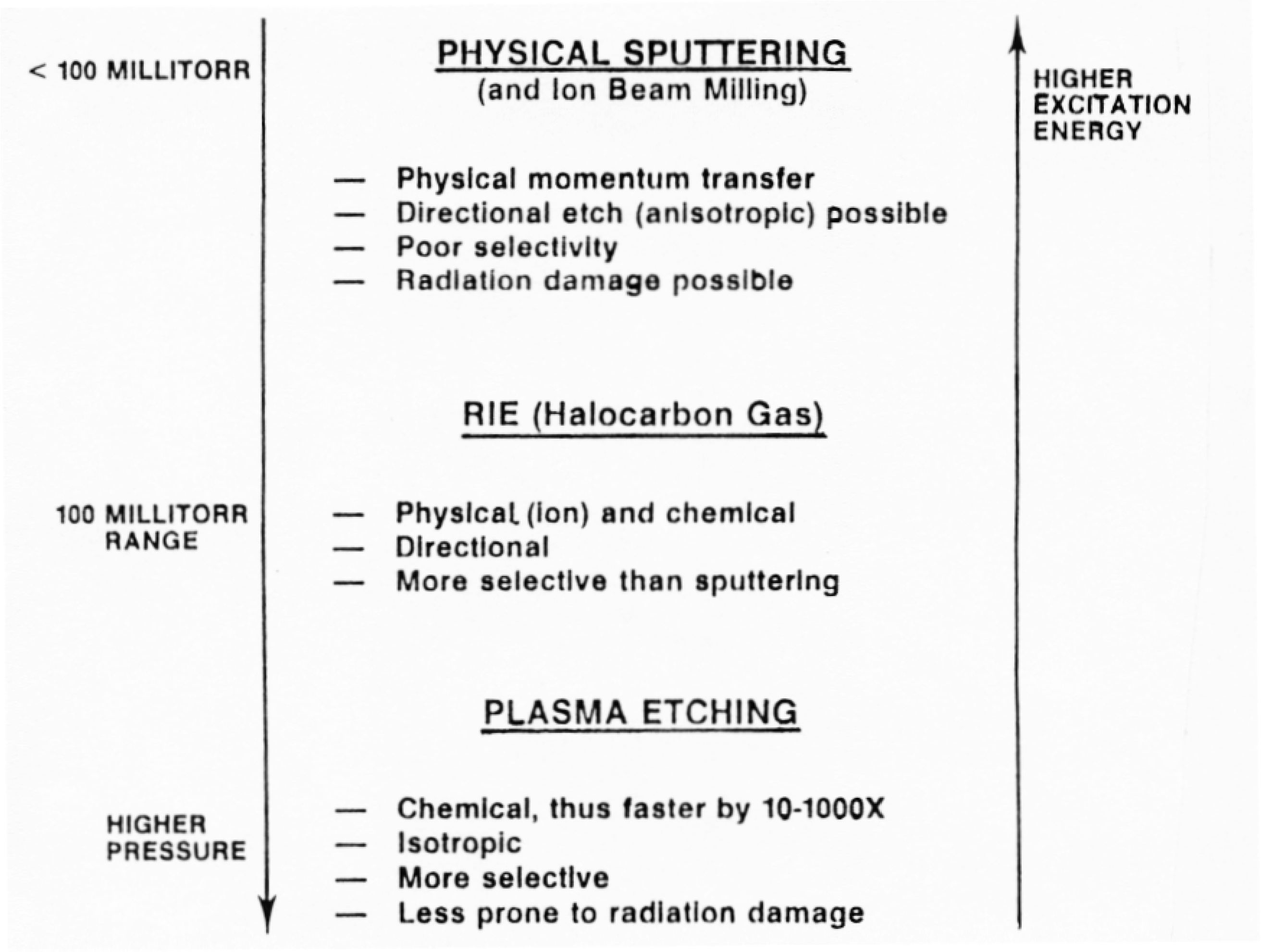


Table 1. CHARACTERISTICS and APPLICATIONS OF CVD REACTORS

PROCESS	ADVANTAGES	DISADVANTAGES	APPLICATIONS
APCVD (Low Temperature)	Simple Reactor, Fast Deposition, Low Temperature	Poor Step Coverage, Particle Contamination	Low Temperature Oxides, both doped and undoped
LPCVD	Excellent Purity and Uniformity, Conformal Step Coverage, Large Wafer Capacity	High Temperature Low Deposition Rate	High Temperature Oxides, both doped and undoped, Silicon Nitride, Poly-Si, W, WSi_2
PECVD	Low Temperature, Fast Deposition, Good Step Coverage	Chemical (e.g. H_2) and Particulate Contamination	Low Temperature Insulators over Metals, Passivation (Nitride)

Dry Etching (Jaeger 2.2.2, Campbell 11, Ruska 6.3)

- Use gas chemicals
- Inject RF field to create plasma
- Plasma creates very reactive process
- Done at modest vacuum about 0.1 torr
- Two main types
- Plasma etching (PE): create simple plasma
- Reactive Ion Etching (RIE)
- Most processes tending to Dry etching
- Very anisotropic
- Excellent etch selection ratios and etch stops



Dry or Plasma Etching System

- Plasma process similar deposition
- RF energy breaks down gas – creates very active species
- Wafers between electrodes of RF signal
- Wafers on planetary for uniformity

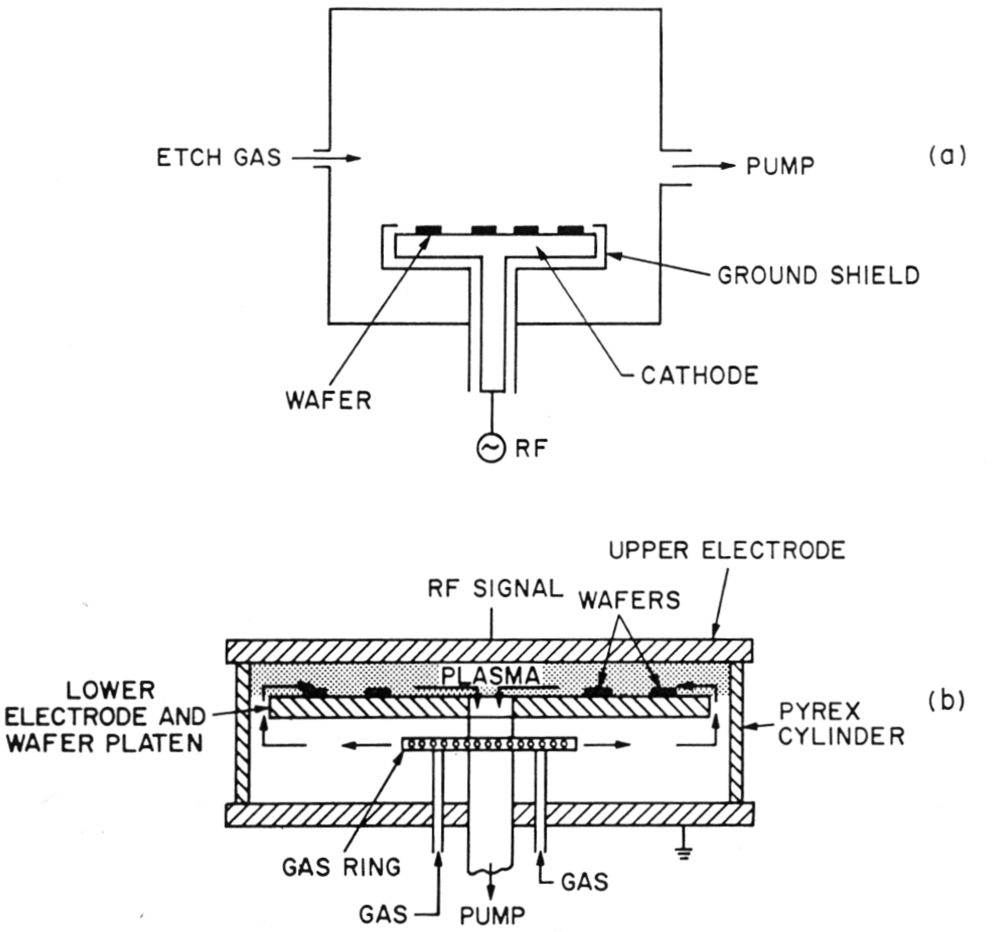
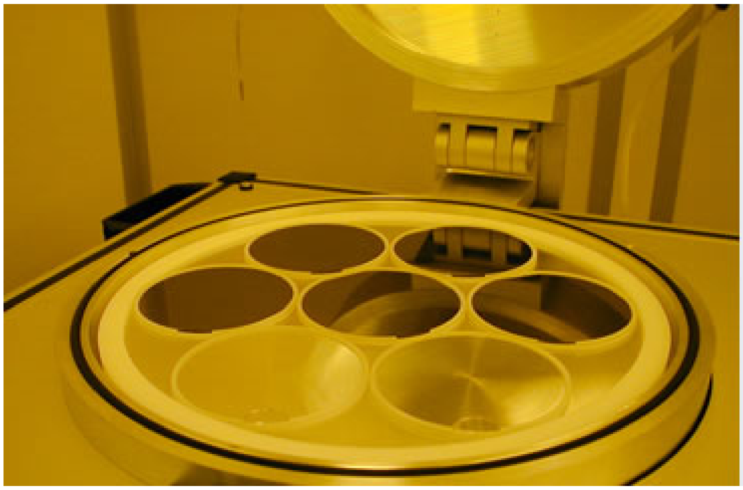


Fig. 27 (*a*) A sputtering-etching system. (*b*) A parallel-plate, plasma-etching system.[3]



Etching Chemistry

- Three main reactants: O, F and Cl plasma creates free atoms
- Extremely reactive in that state
- Oxygen for organics –
- Fluorine for Silicon, glass and nitride
- Chlorine for Aluminum

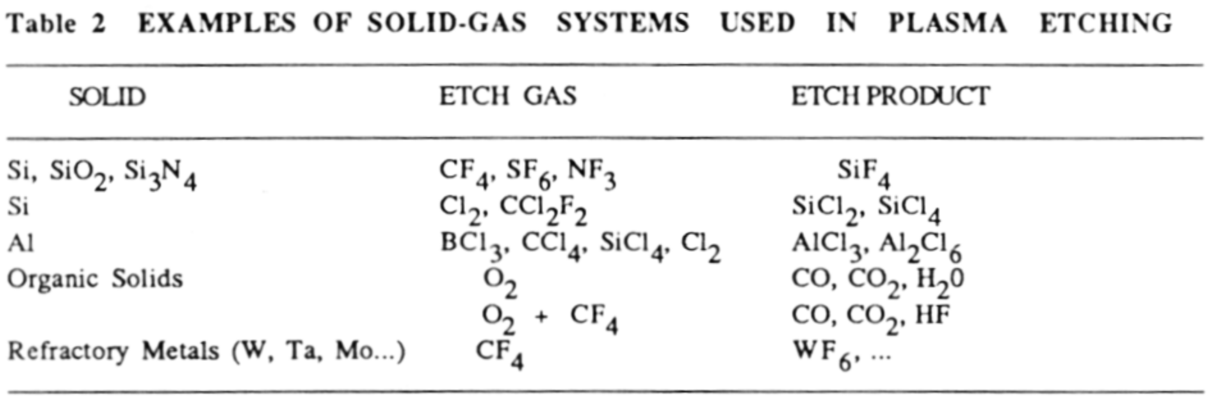


Table 2 EXAMPLES OF SOLID-GAS SYSTEMS USED IN PLASMA ETCHING

SOLID	ETCH GAS	ETCH PRODUCT
Si, SiO_2, Si_3N_4	CF_4, SF_6, NF_3	SiF_4
Si	Cl_2, CCl_2F_2	$SiCl_2$, $SiCl_4$
Al	BCl_3, CCl_4, $SiCl_4$, Cl_2	$AlCl_3$, Al_2Cl_6
Organic Solids	O_2	CO, CO_2, H_2O
	O_2 + CF_4	CO, CO_2, HF
Refractory Metals (W, Ta, Mo...)	CF_4	WF_6, ...

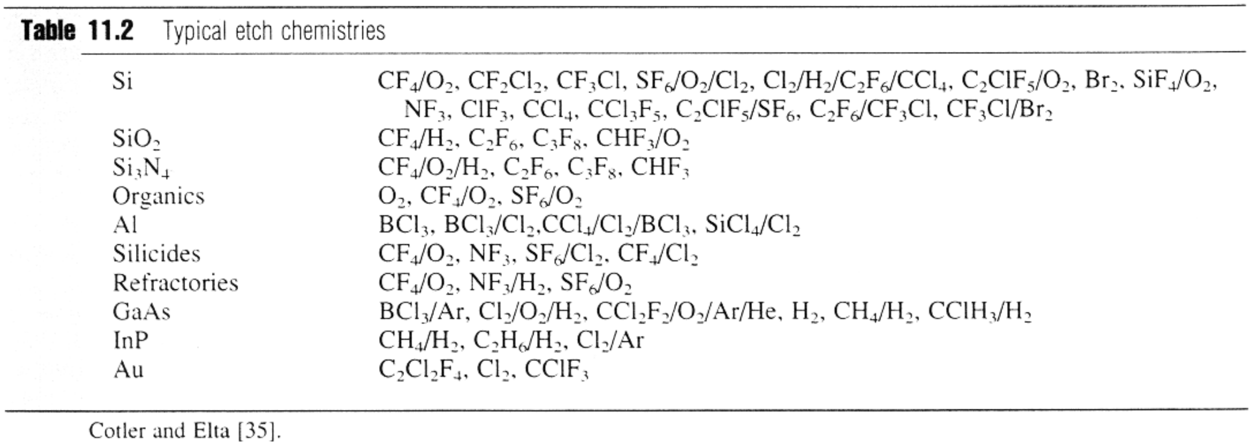


Table 11.2 Typical etch chemistries

Si	CF_4/O_2, CF_2Cl_2, CF_3Cl, $SF_6/O_2/Cl_2$, $Cl_2/H_2/C_2F_6/CCl_4$, C_2ClF_5/O_2, Br_2, SiF_4/O_2, NF_3, ClF_3, CCl_4, CCl_3F_5, C_2ClF_5/SF_6, C_2F_6/CF_3Cl, CF_3Cl/Br_2
SiO_2	CF_4/H_2, C_2F_6, C_3F_8, CHF_3/O_2
Si_3N_4	$CF_4/O_2/H_2$, C_2F_6, C_3F_8, CHF_3
Organics	O_2, CF_4/O_2, SF_6/O_2
Al	BCl_3, BCl_3/Cl_2,$CCl_4/Cl_2/BCl_3$, $SiCl_4/Cl_2$
Silicides	CF_4/O_2, NF_3, SF_6/Cl_2, CF_4/Cl_2
Refractories	CF_4/O_2, NF_3/H_2, SF_6/O_2
GaAs	BCl_3/Ar, $Cl_2/O_2/H_2$, $CCl_2F_2/O_2/Ar/He$, H_2, CH_4/H_2, $CClH_3/H_2$
InP	CH_4/H_2, C_2H_6/H_2, Cl_2/Ar
Au	$C_2Cl_2F_4$, Cl_2, $CClF_3$

Cotler and Elta [35].

Plasma Etching Process

- Neutral atoms excited
- Ionization of plasma
- Plasma causes dissociation of gas get a reactive product

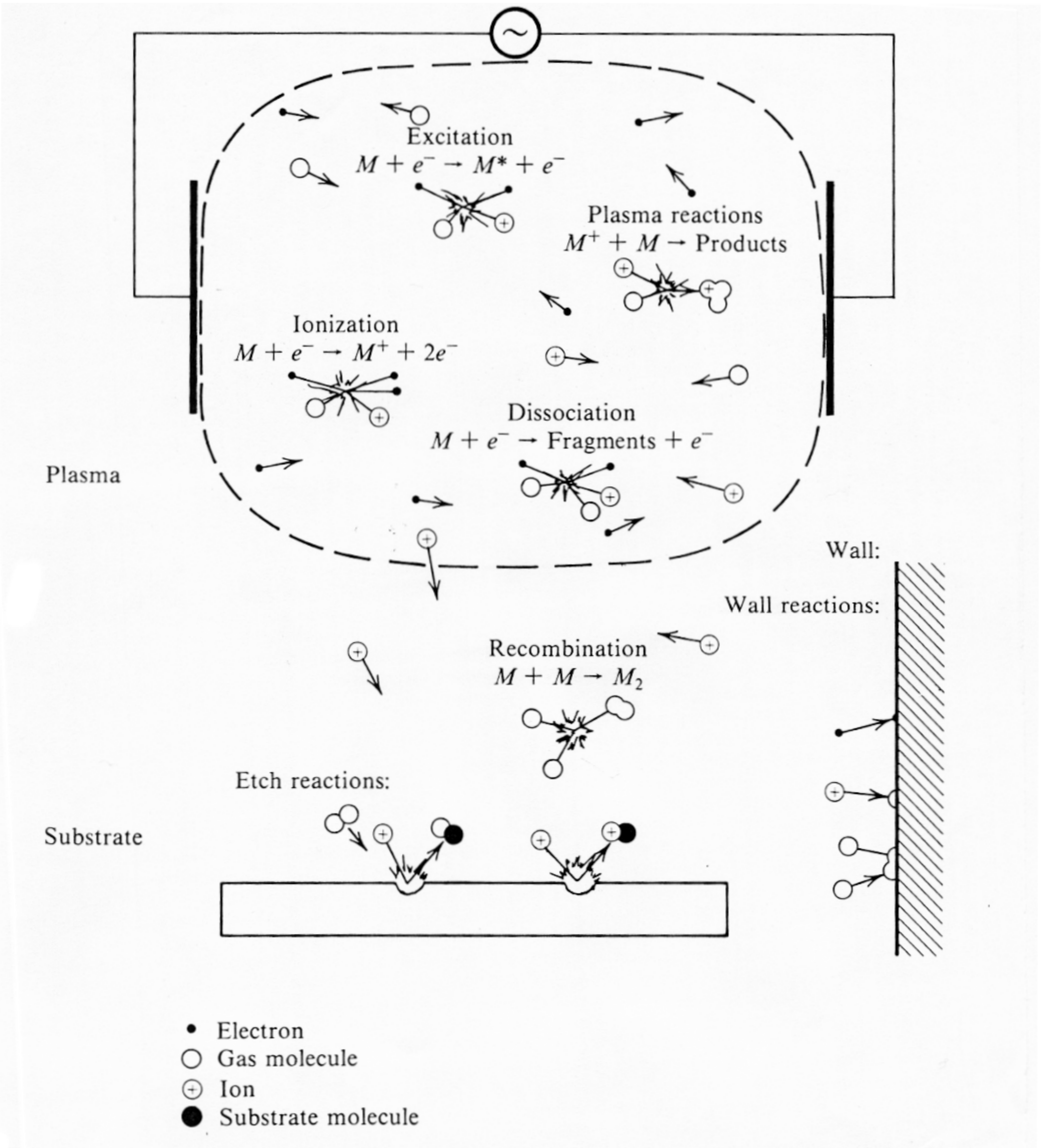


Figure 6-9 The nature of plasma etching, showing reactions in the plasma, reaction at walls and at the substrate surface, and the desorption of reaction products.

Plasma Etching Processes

- Ionization: electron removed leaving +ion
- Dissociation: Molecule broken down
- Excitation: Molecule stays together, but excited state

Homogeneous Reactions

- Occur within plasma

Hetrogeneous Reactions

- Occur at the Surface

Table 1. HOMOGENEOUS REACTIONS (ELECTRON-IMPACT) and HETEROGENEOUS REACTIONS THAT OCCUR IN PLASMAS

Homogeneous Reactions - Electron Impact Reactions

Excitation (rotational, vibrational, electronic):

$e + A_2 \Rightarrow A_2 + e$ $(e + F \Rightarrow F^* + e)$

$(F^* \Rightarrow F + h\nu_F)$

Dissociation:

$e + A_2 \Rightarrow A + A + e$ $(e + O_2 \Rightarrow O + O + e)$

Ionization:

$e + A_2 \Rightarrow A_2^+ + 2e$ $(e + O_2 \Rightarrow O_2^+ + 2e)$

Dissociative Ionization:

$e + A_2 \Rightarrow A^+ + A + 2e$ $(e + O_2 \Rightarrow O^+ + O + 2e)$

Dissociative Attachment:

$e + A_2 \Rightarrow A^+ + A^- + e$

Heterogeneous Reactions

Atom Recombination:

$S - A + A \Rightarrow S + A_2$

Metastable deexcitation:

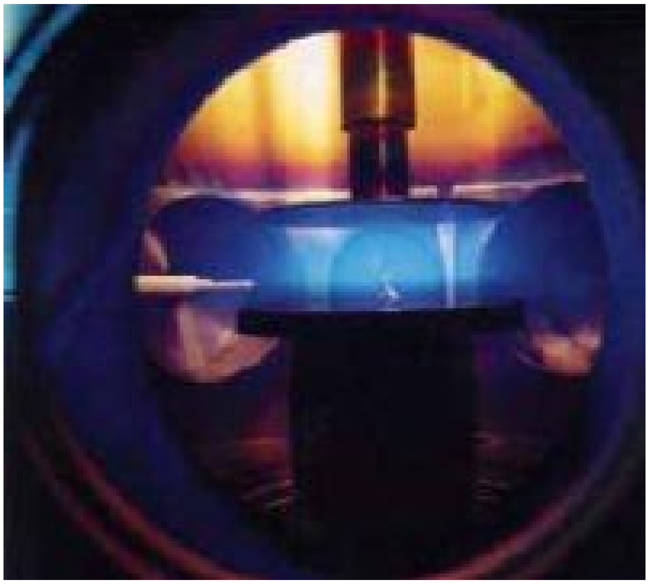
$S + M^* \Rightarrow S + M$

Atom abstraction (etching):

$S - B + A \Rightarrow S^+ + AB$

Sputtering (etching):

$S - B + M^+ \Rightarrow S^+ + B + M$



Effect of Voltage on Etching

- Plasmas start with equal numbers of electrons & ions (a)
- But e more mobile & thus more escape Plasma becomes + charged
- Creates a Sheath separating plasma from objects
- As + charge increases loss of e decreases
- Becomes balanced creating plasma potential
- Potential gradient higher at higher objects:
  hence anisotropic attraction (c)

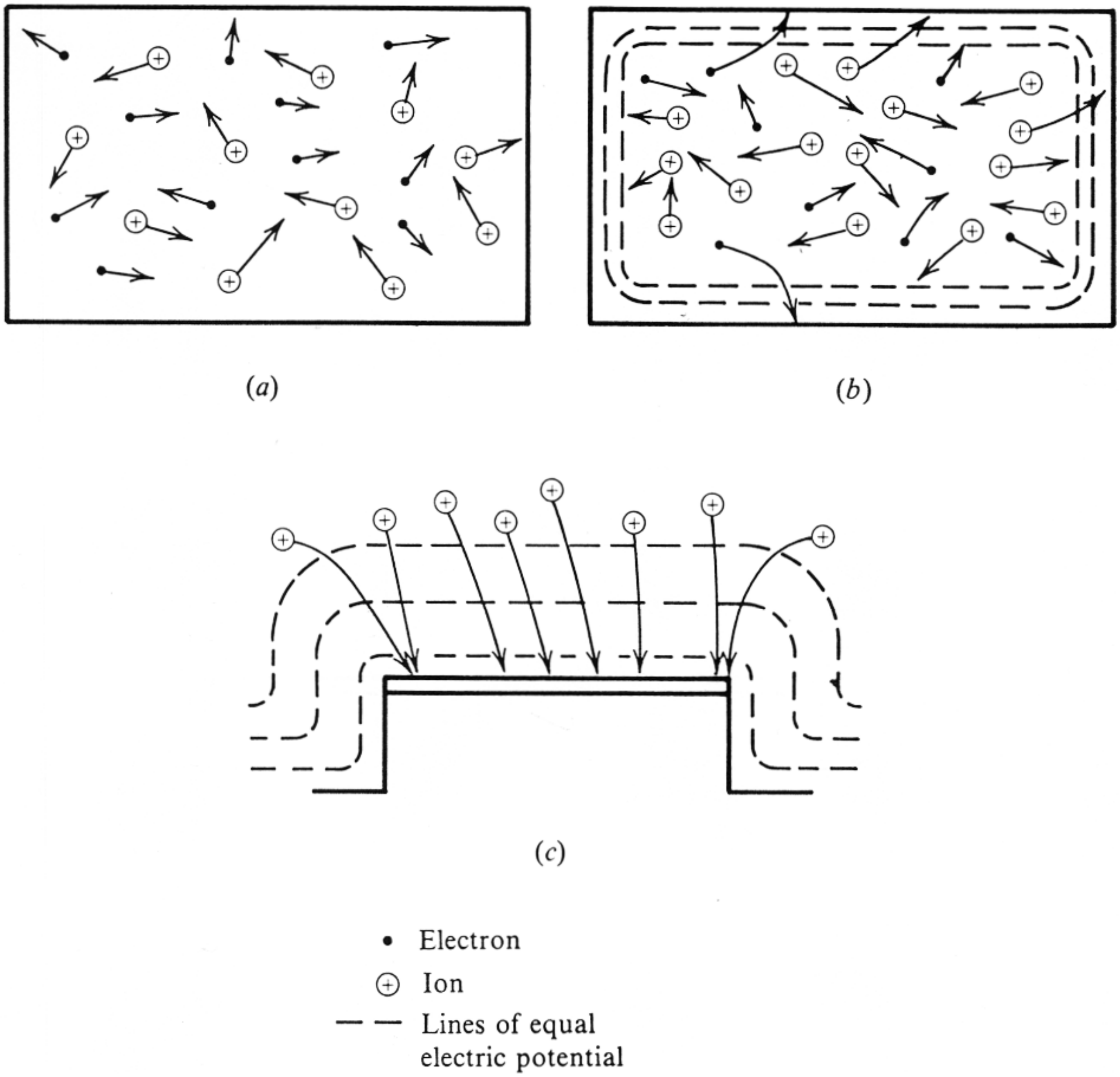


Figure 6-10 Formation of the plasma sheath and resulting ion bombardment. (*a*) Initial condition: equal number of electrons and ions, no plasma potential, loss of electrons exceeds loss of ions. (*b*) Steady-state condition: excess of ions in plasma, positive plasma potential, equal loss of electrons and ions. (*c*) Detail: perpendicular ion bombardment resulting from potential gradient.

Oxygen Etching of Organics

- Oxygen plasma destroys organics
- Simple plasma etcher used to strip resist
- Uses oxygen plasma (sometimes air)
- Non-directional
- Problem – hard to strip anything that is left
- Called strippers or plasmods
- Also use oxygen plasma to etch organics in regular plasma etchers

Etching Sensitivity to Gases

- Change in relative etch rates with Gas Composition
- Thus many variables to get profiles

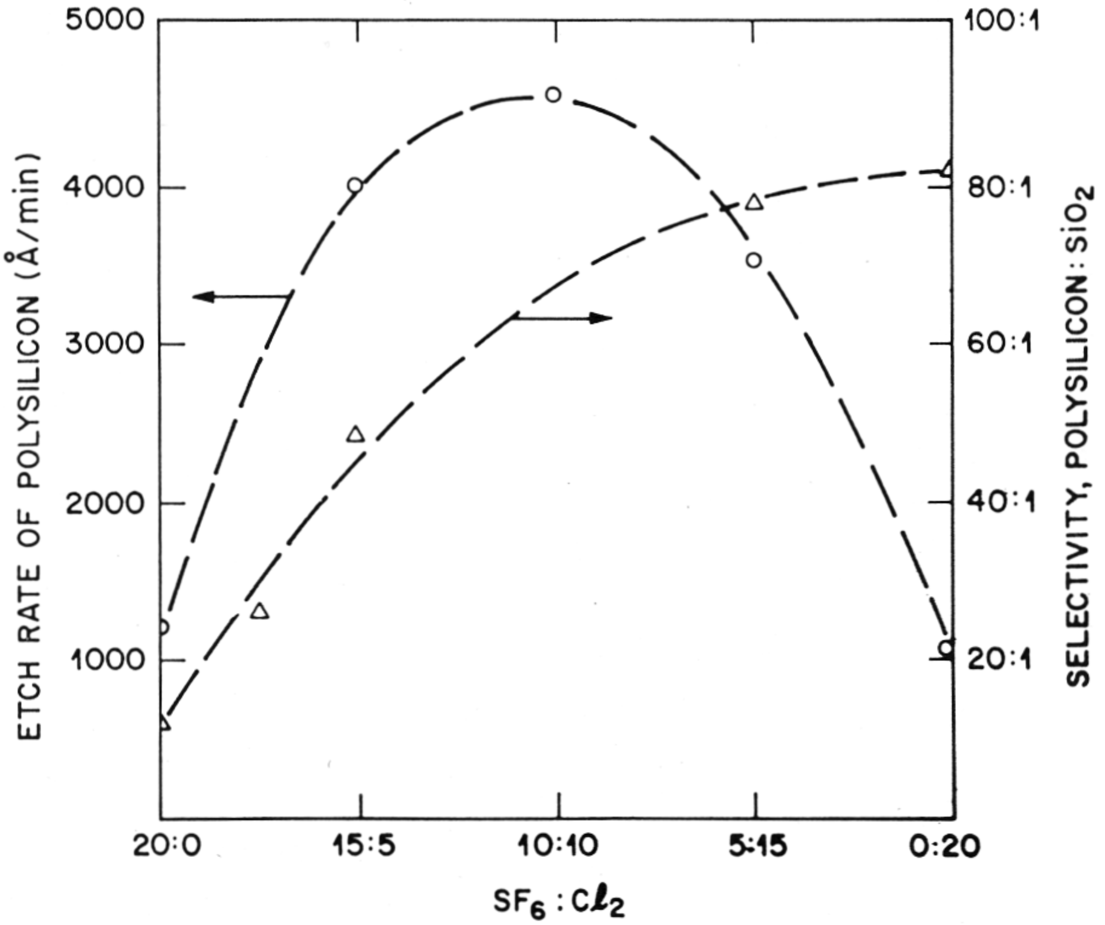


Fig. 31 Dependence of etch rates of polysilicon and selectivity to SiO_2 as gas composition in SF_6–Cl_2 (at 5.5 Pa).[26]

Etching Gas Variations

- Two main reactants: F and Cl buffered with H
- Fluorine used for Si, and glass etching
- Chlorine for metals (especially aluminum) etch
- Recipe determines what is etched & ratio to other materials
- etch gas by what forms a volatile compound with etched layer

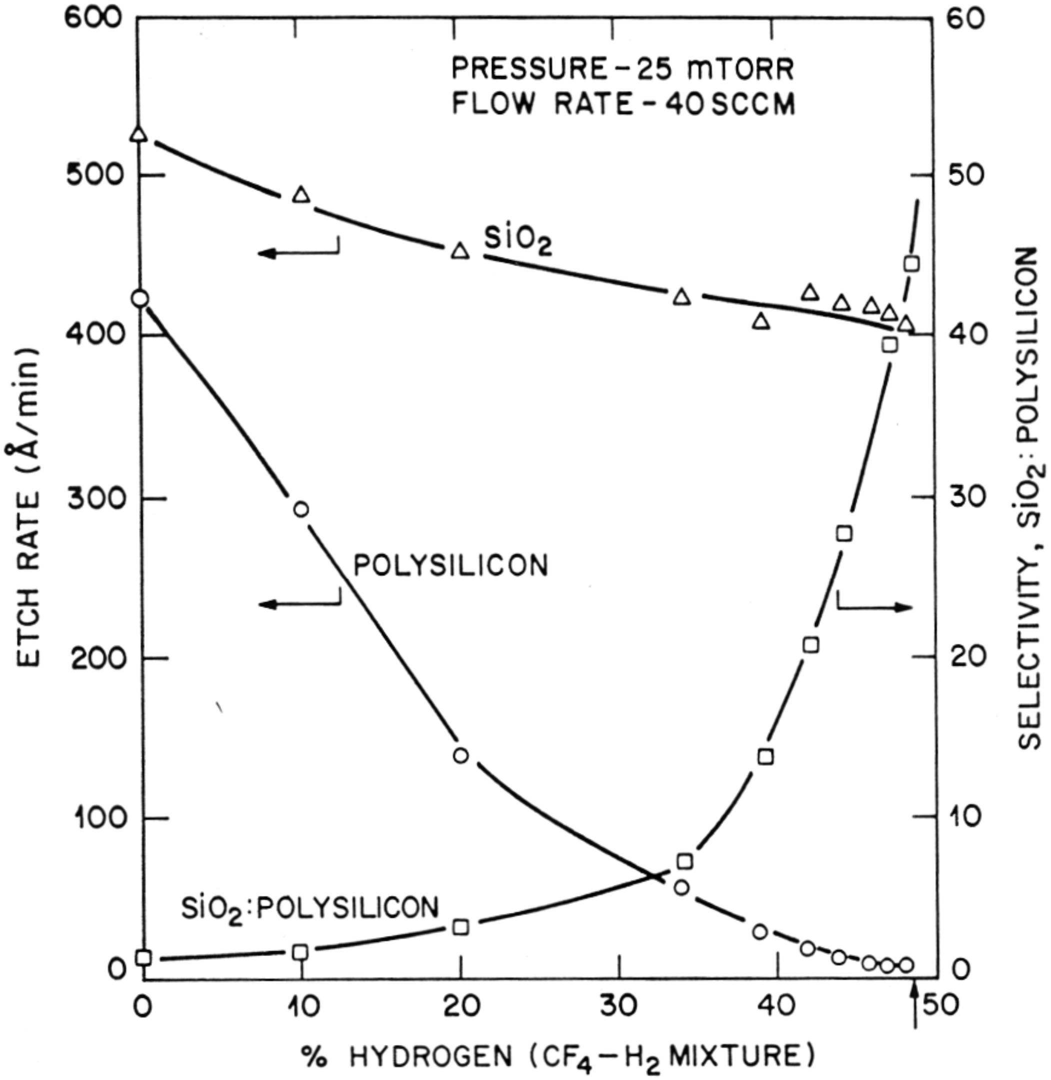


Fig. 30 Etch rates of Si and SiO_2 and the corresponding selectivity as a function o percent H_2 in CF_4.[25]

Profile Changes with Composition

- Change in etch gas changes sidewall profiles

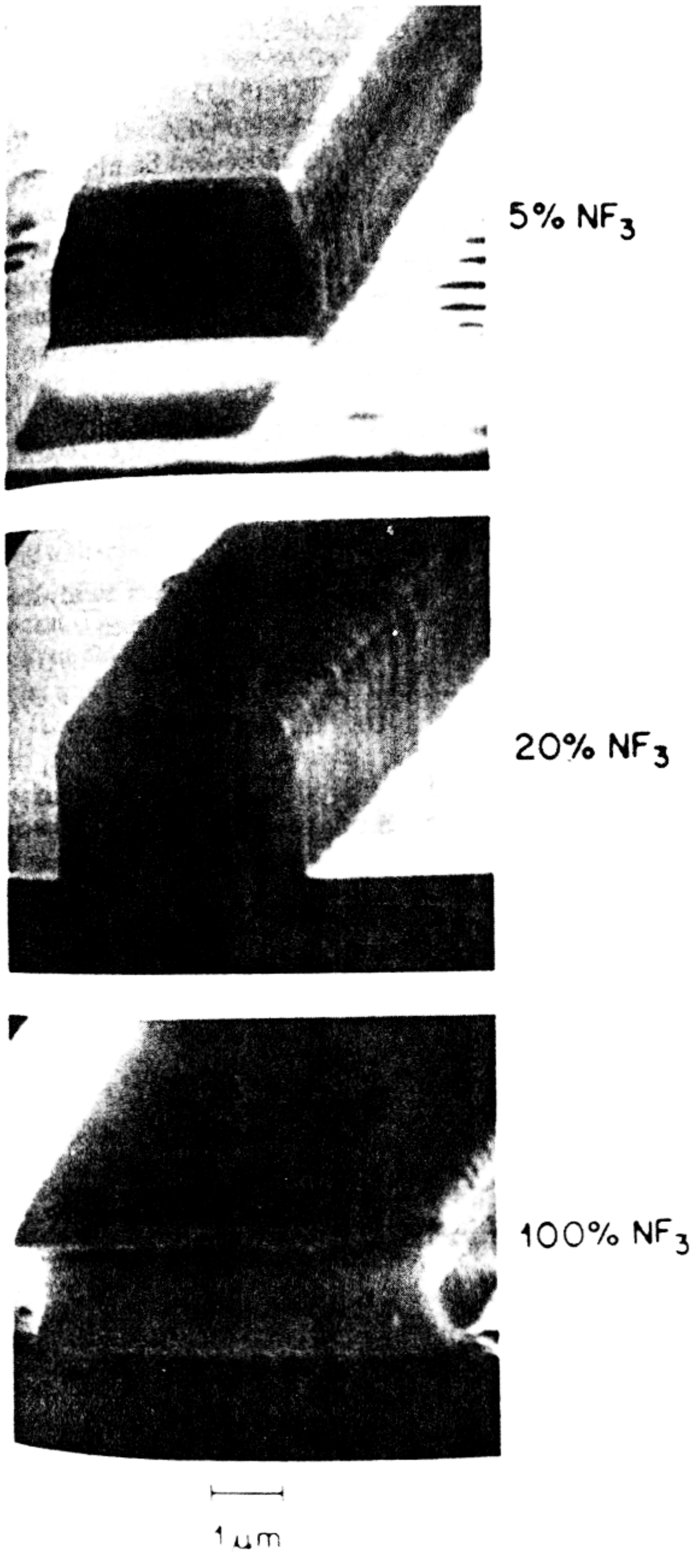


Figure 11-12 Etch profiles of SiO_2 with increasing concentrations of NF_3 *(after Donnelly et al., reprinted by permission AIP*

Basic Etching Steps

- Plasma Generate etchant species
- Diffuse etchant to surface
- Absorption and reaction on surface
- Desorption and Diffusion of reaction products

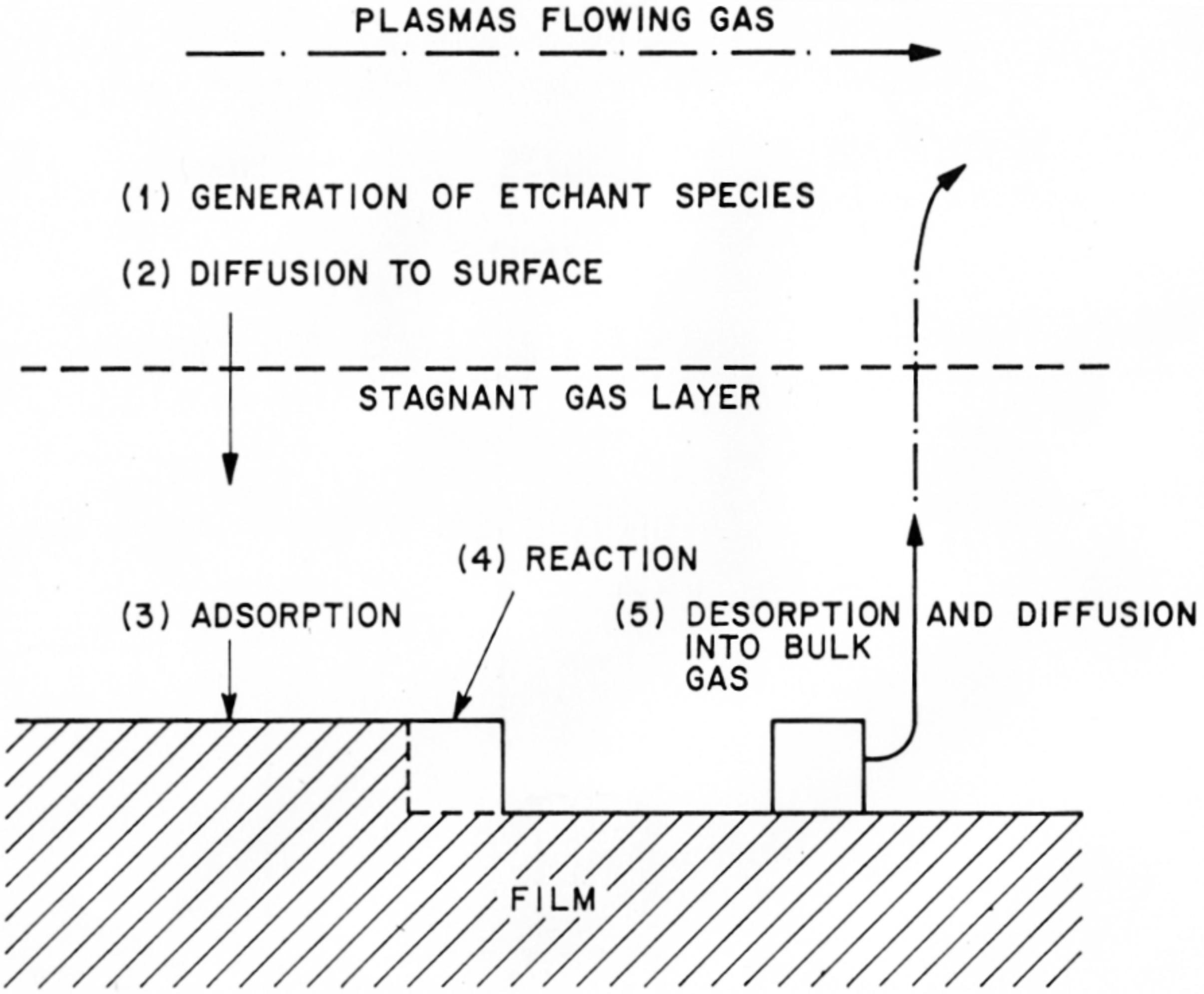


Fig. 28 Basic steps in a dry-etching processing.[23]

Mechanism of Plasma Etching

- Example etching Si with CF_4
- Fluorine breaks off of CF_4 due to plasma
- Build up SiF_x layer on surface
- Additional diffuses F creates SiF_4
- More likely bonds with Si and is volatile
- Eventually SiF_4 form and desorbs

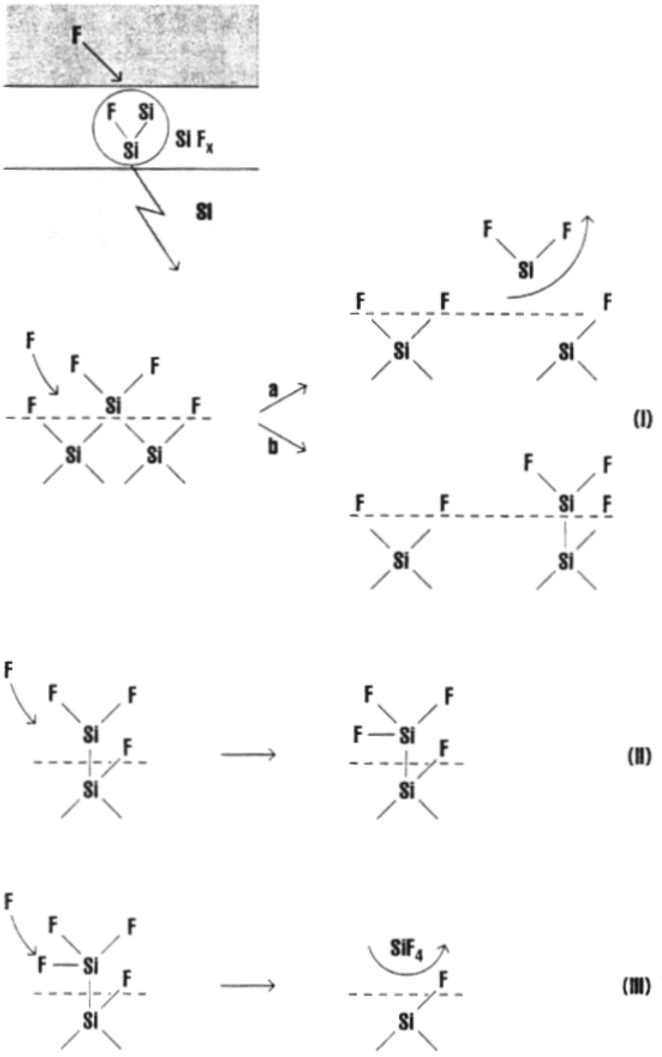


Figure 11-8 Proposed mechanism of plasma etching of silicon in CF_4. A 1–5 atom thick SiF_x layer forms on the surface. A silicon atom on the upper level is bonded to two fluorine atoms. An additional fluorine atom may remove the silicon as SiF_2. Much more likely, however, is that additional fluorine atoms bond to the silicon atom until SiF_4 forms and desorbs *(after Manos and Flamm, reprinted by permission, Academic Press).*