Lecture 12:

PVD and CVD

(Physical Vapor Deposition and Chemical Vapor Deposition)

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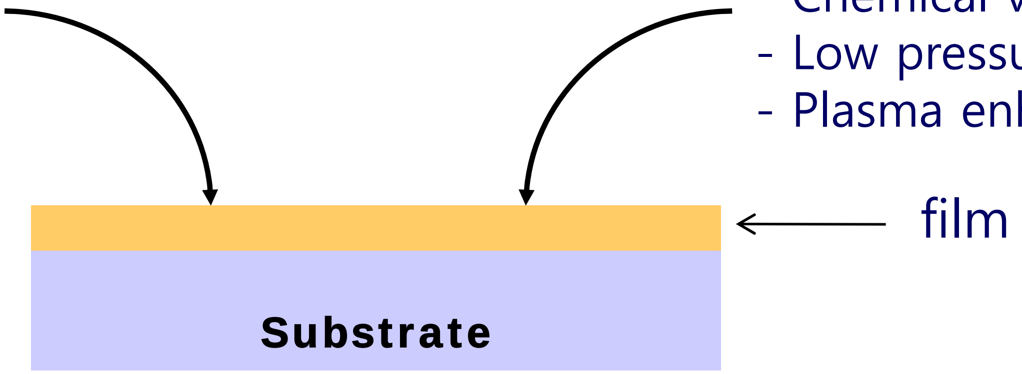
Thin Film Deposition (1)

- Deposition
  - The transformation of vapors into solids, frequently used to grow solid thin film and powder materials

Physical methods
- Evaporation
- Sputtering

Chemical methods
- Chemical vapor deposition
- Low pressure CVD
- Plasma enhanced CVD



Applications:

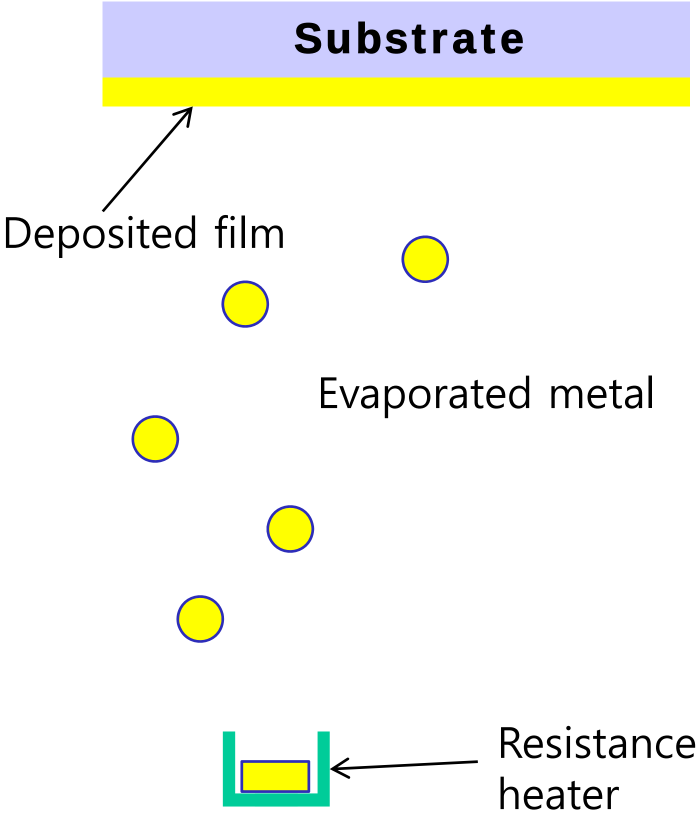
Metalization (Al, W, silicide)
Poly-Si
Dielectric layers: surface passivation

Thin Film Deposition (2)

- Physical Vapor Deposition (PVD)
  - Direct impingement of particles on the hot substrate surface
  - Thermal evaporation, electron-beam evaporation, sputtering

- Chemical Vapor Deposition (CVD)
  - Convective heat and mass transfer as well as diffusion with chemical reactions at the substrate surfaces
  - More complex process than PVD
  - More effective in terms of the rate of growth and the quality of deposition
  - LP/AP CVD, Thermal/PE/Ph/LC CVD

PVD : Evaporation (1)

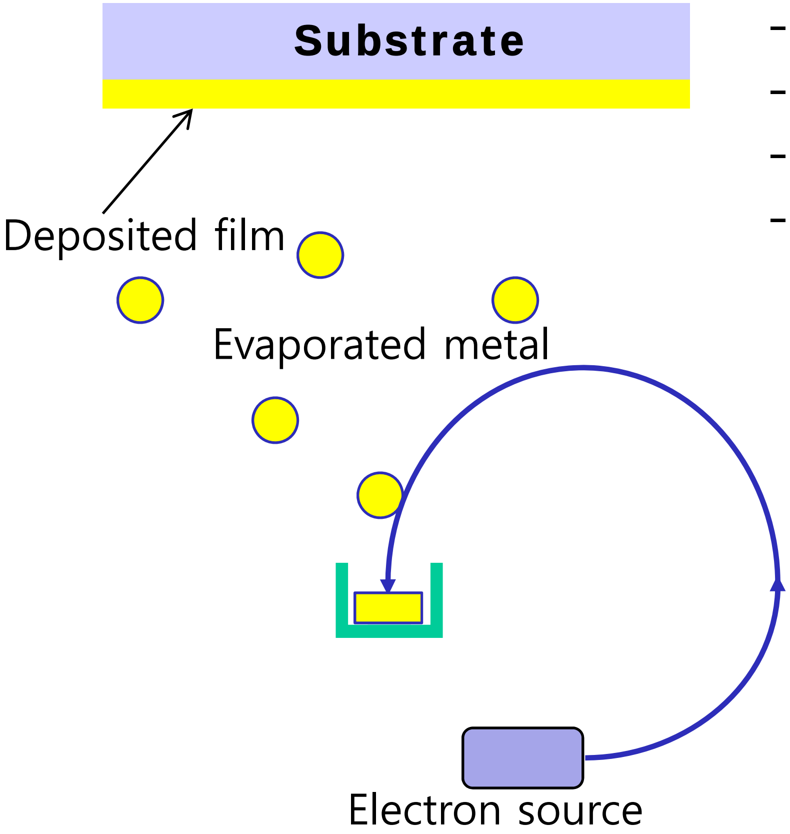


Thermal Evaporation

Gas Pressure : 10^{-5} Torr

- Thermal evaporator
- Materials: Au, Al, Ti, Cu, Ni, Cr, Ag, Co, Sn, Pd

PVD : Evaporation (2)

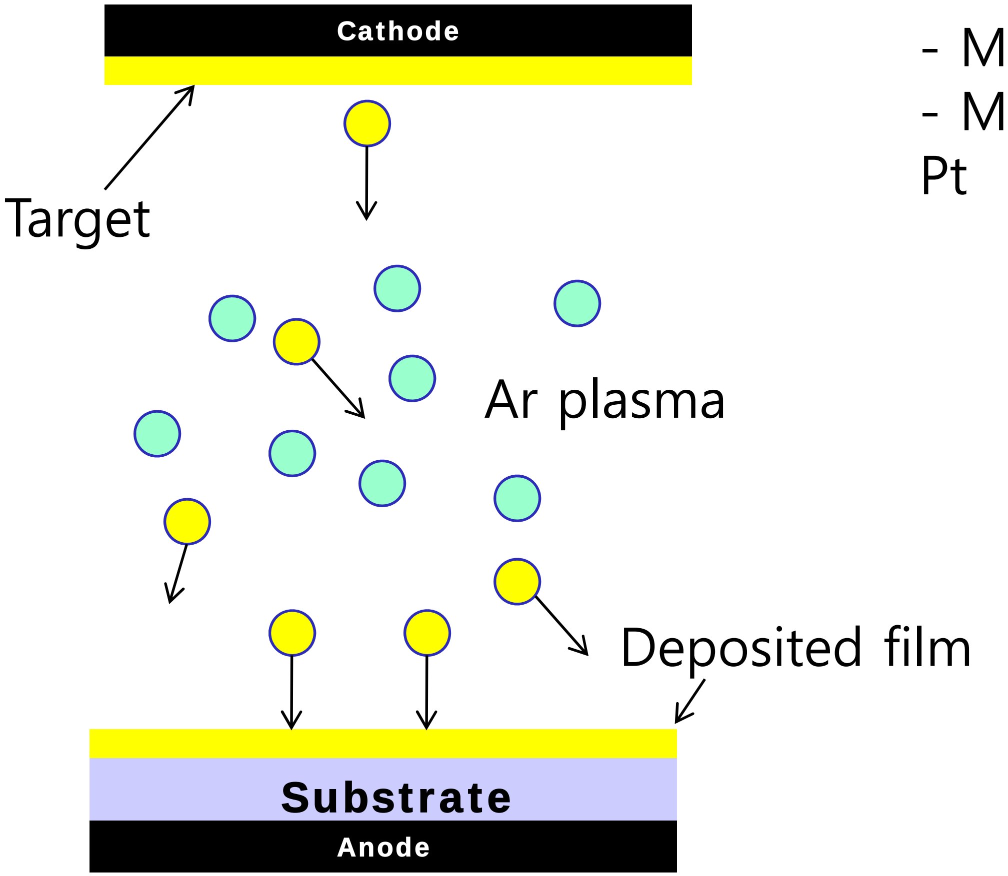


- E-gun evaporator
- Materials: Ti, Cr, Au, Al, Ni, Ag
- Within wafer uniformity: < 5%
- Crucible liner 6pocket crucible

Electron Beam Evaporation

Gas Pressure : 10^{-5} Torr

PVD : Sputtering (1)



- Metal sputter
- Materials: Cr, Mo, Ti, Cu , Al , W, Ni, Pt

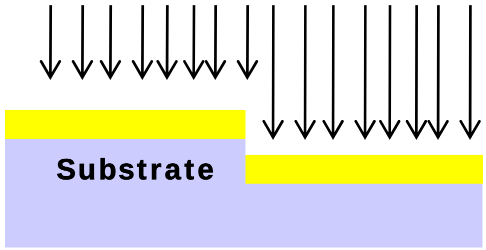
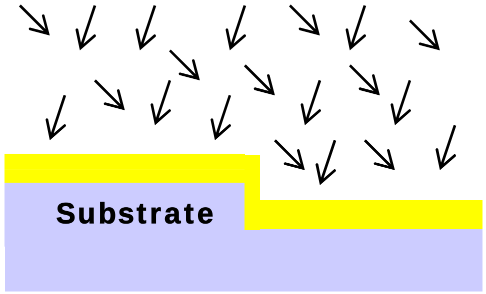
Gas Pressure : 1~ 10 mTorr

PVD : Sputtering (2)

- Wavics sputter
- Materials: Ti, Al , Mo, Cu

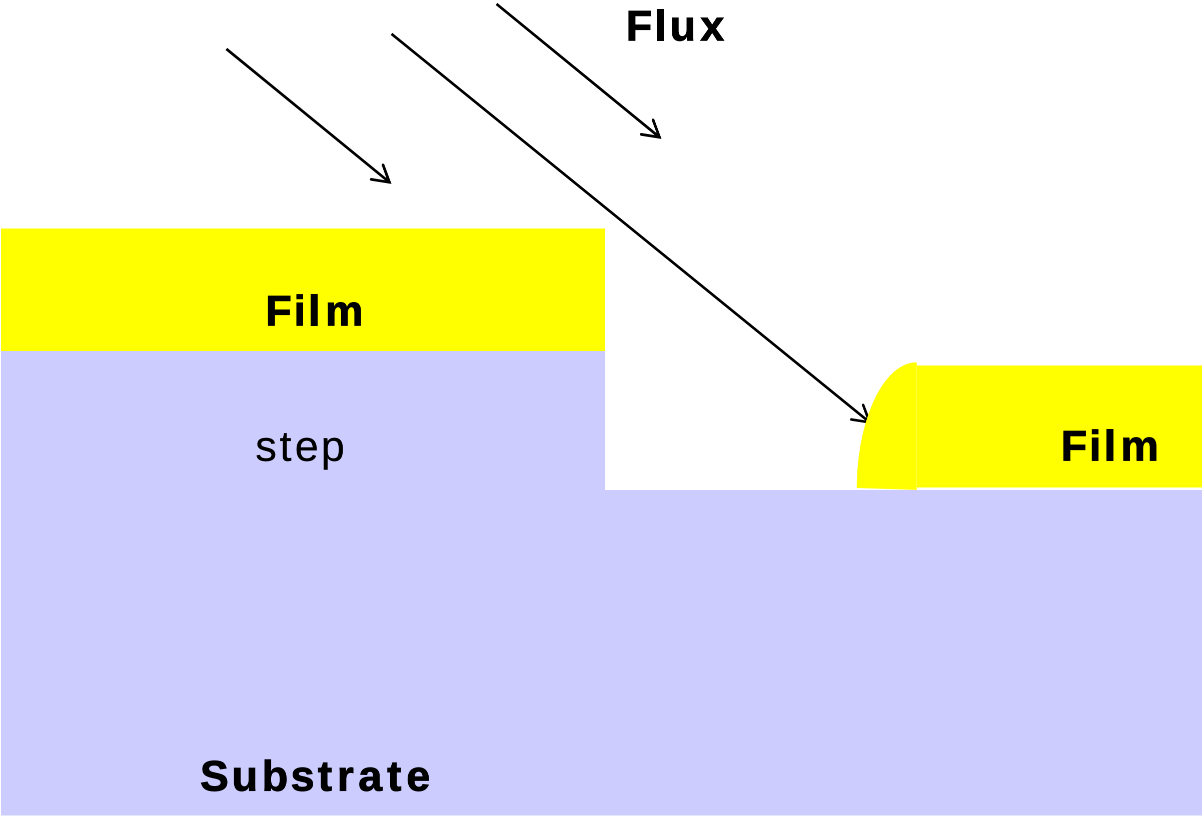
- Au sputter
- Materials: Au, Ti (adhesion, Cr (adhesion)
- Within wafer uniformity: < 5%
- Wafer heating : 20℃ ~ 250℃

Thermal evaporation VS Sputtering

	Thermal Evaporation	Sputtering
Rate	Thousand atomic layers at a time	On atomic layer at a time
Choice of materials	Limited	Almost unlimited
Surface damage	Very low	Ionic bombardment damage
Adhesion	Poor	Good (on most materials)
Uniformity	Difficult to control	Easy to control
Film properties	Difficult to control	Can be controlled by pressure and temperature
Step coverage	 	

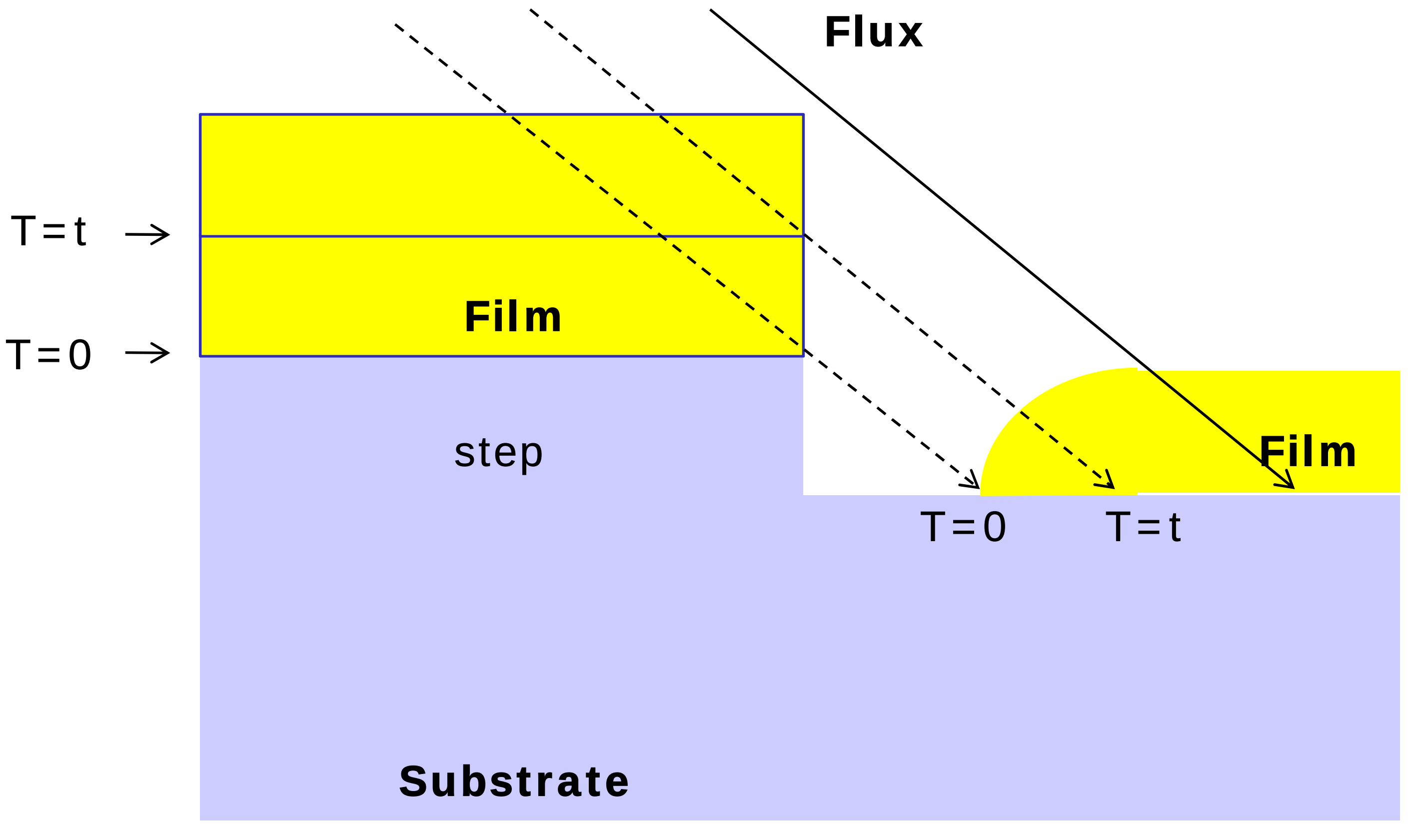
Step coverage problem with PVD (1)

- Geometrical shadowing



Step coverage problem with PVD (2)

- Self-shadowing



Methods for minimizing step coverage problems

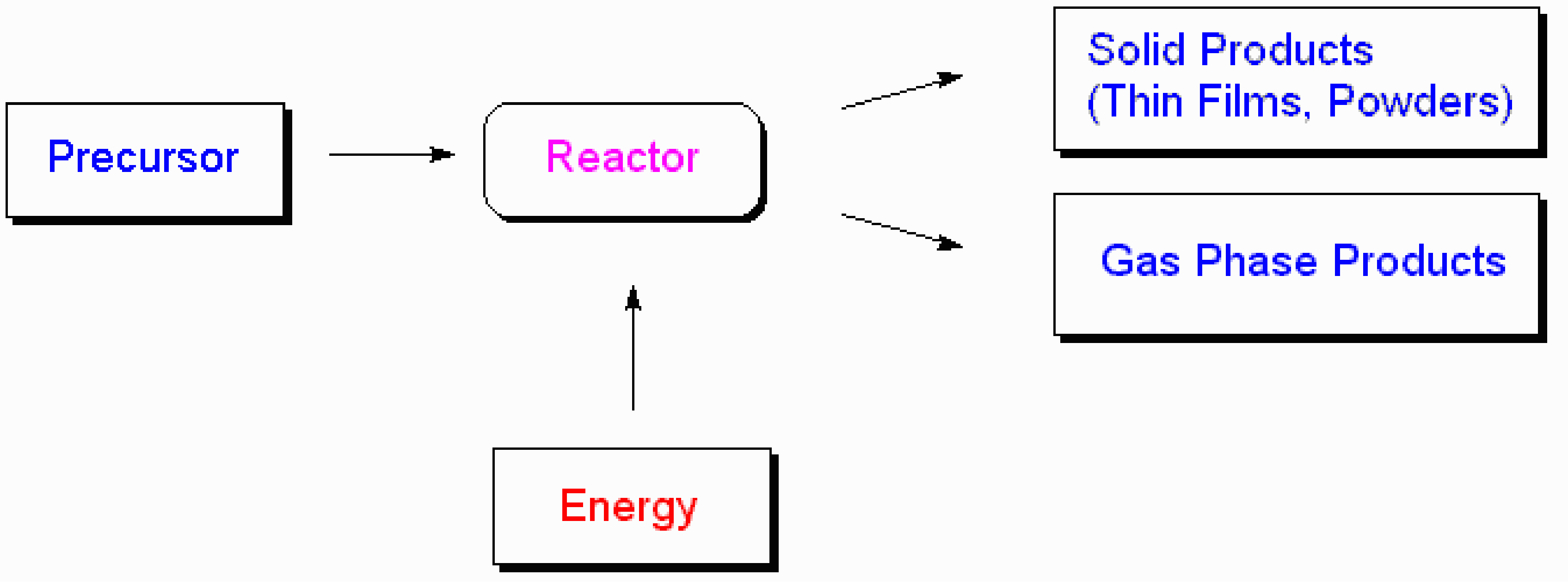
1. Rotate +Tilt substrate during deposition

2. Elevate substrate temperature (enhance surface diffusion)

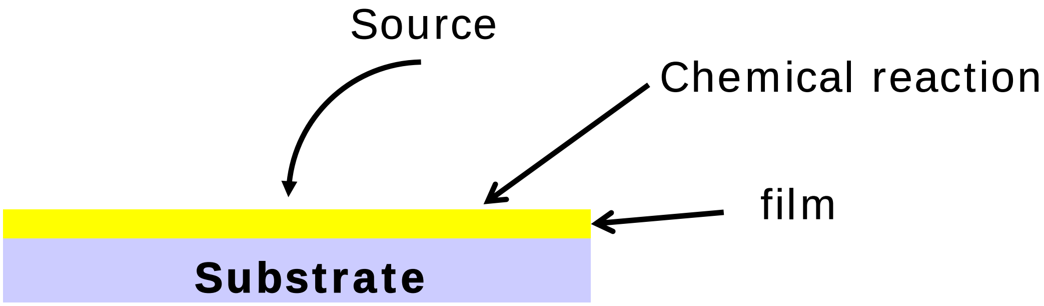
3. Use large-area deposition source

Chemical Vapor Deposition (1)

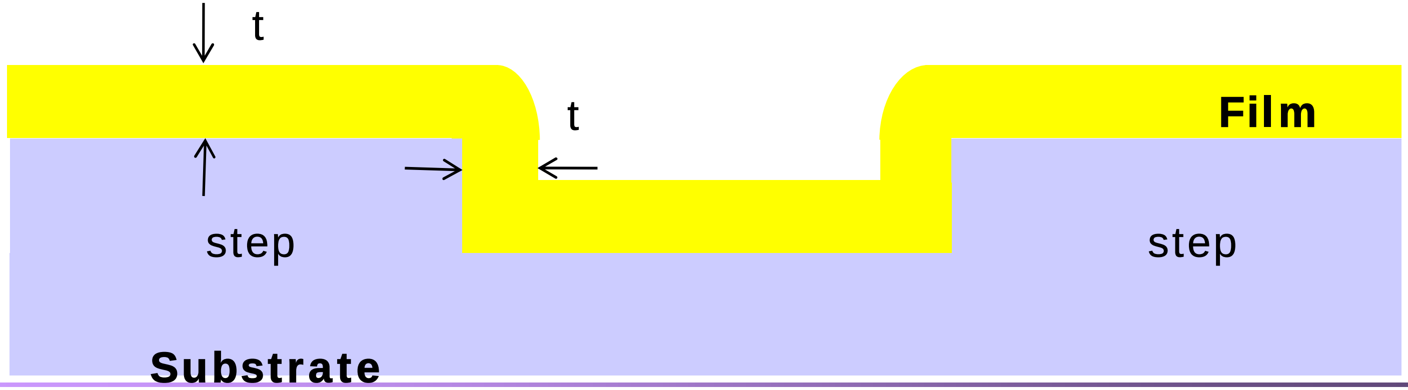
- What is Chemical Vapor Deposition?
  - **Chemical reactions which transform gaseous molecules, called precursor, into a solid material, in the form of thin film or powder, on the surface of a substrate**



Chemical Vapor Deposition (2)



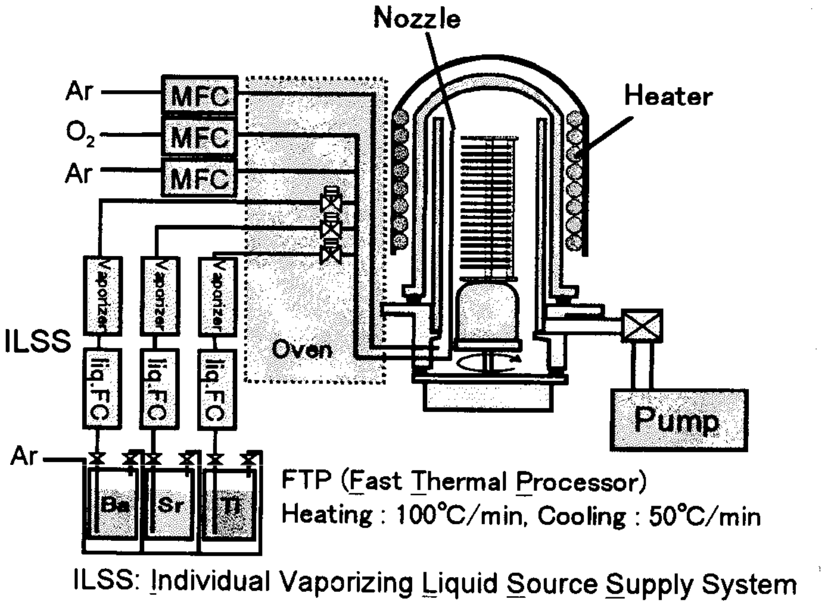
More conformal deposition vs. PVD



CVD Reactor Parameters

Parameters	Variations
Temperature range	Low, Medium, High
Deposition pressure	ATM, Low
Reactor geometry / Wall temp.	Hot wall, Cold wall
Energy source	Temp., R.F, UV-light
Deposition film	Dielectric, Metal
Reactant / Carrier gases	Metal Organic, Inorganic

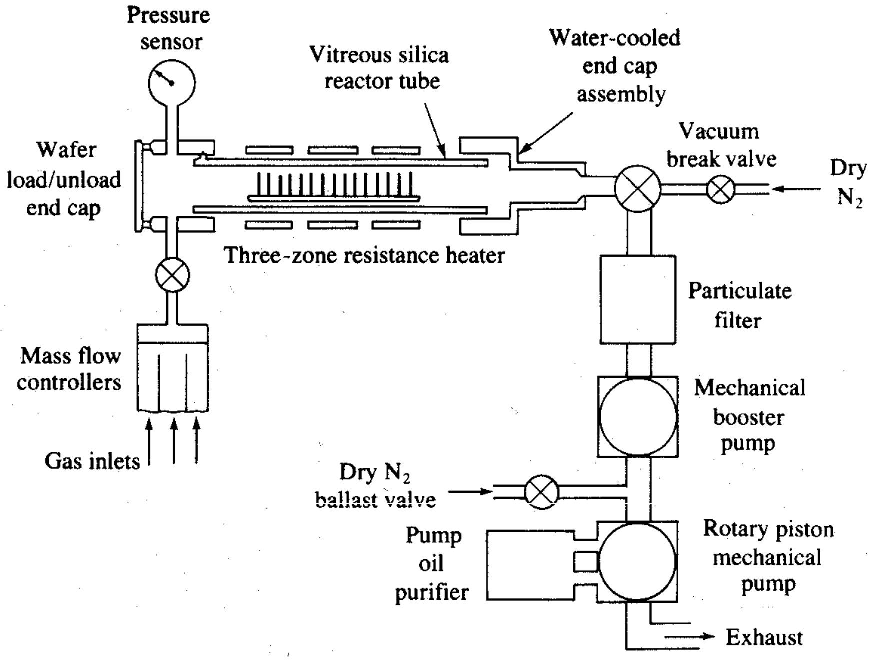
Examples : CVD reactors (1)



FTP (Fast Thermal Processor)
Heating : 100°C/min, Cooling : 50°C/min

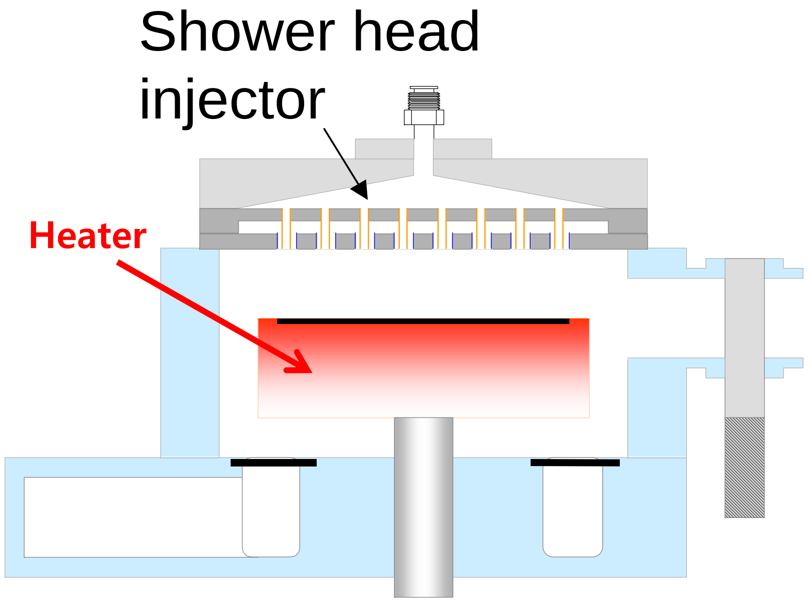
ILSS: Individual Vaporizing Liquid Source Supply System

Vertical CVD Reactor

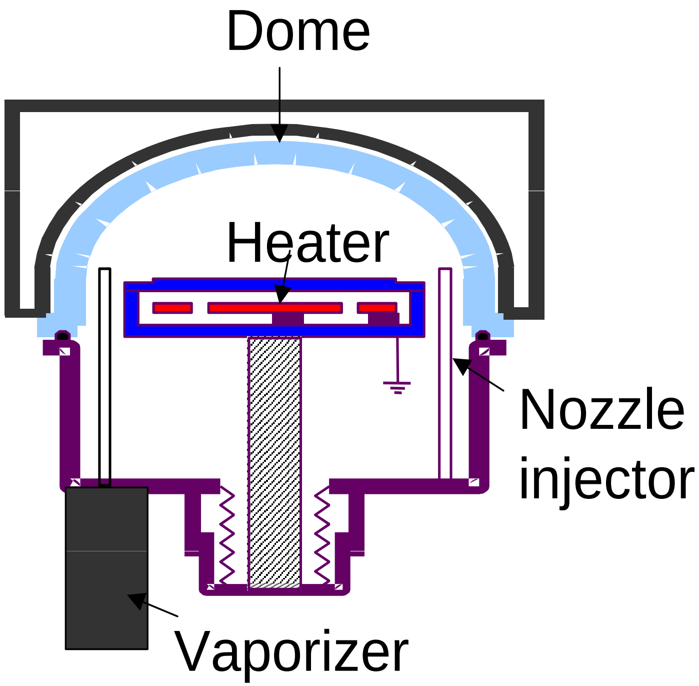


Horizontal CVD Reactor

Examples : CVD reactors (2)



Shower Head



Injector

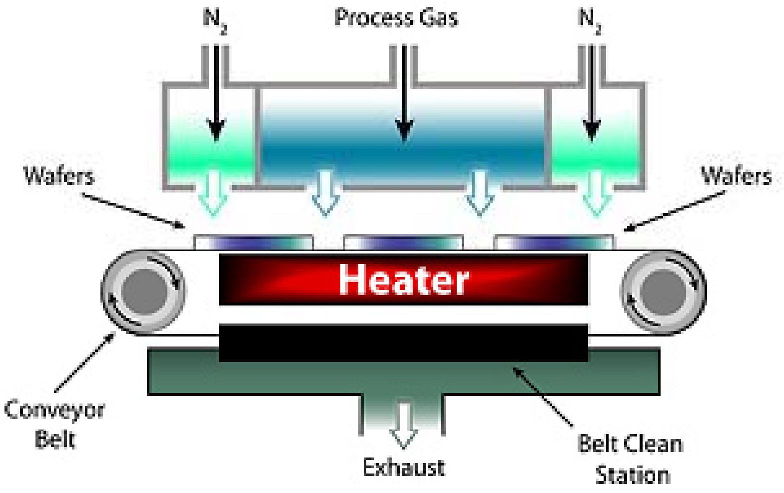
CVD systems

Type	Advantage	Disadvantage	Usage	Pressure/temp
APCVD Atmospheric pressure CVD	Simple, fast	Poor step coverage	Low temp oxides	10 ~ 100 kPa 350 ~ 1200 ˚C
LPCVD Low pressure CVD	Excellent cleanness, conformity and uniformity	High temp, low deposition rate	Polysilicon, nitride, oxide	100 Pa 550 ~ 600 ˚C
PECVD Plasma enhanced CVD	Low temp	Risc for particle and chemical contamination	Low temp oxides, passivation nitrides	200 ~ 600 Pa 300 ~ 400 ˚C

APCVD is mass transport controlled, LPCVD is surface reaction controlled

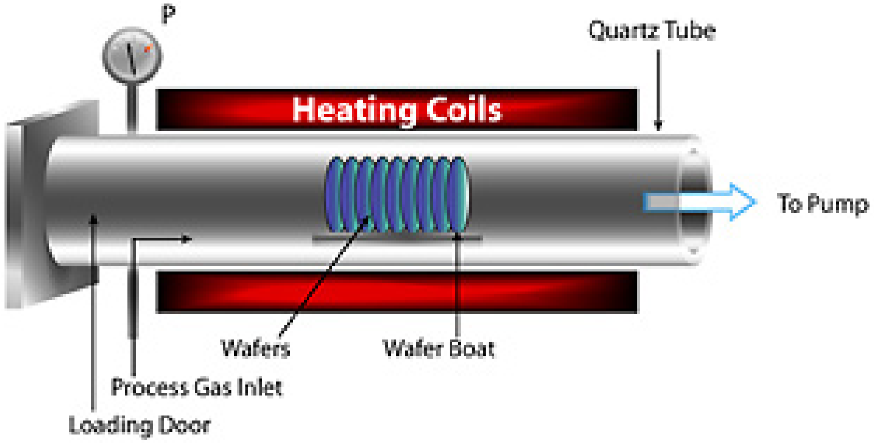
Atmospheric Pressure CVD

- APCVD (Atmospheric Pressure Chemical Vapor Deposition)
  - High deposition rate, poor uniformity, high contamination level, 250-450 ℃
  - Cold wall process
  - Material: epitaxial Si, poly-Si, Si_3N_4, SiO_2, etc.



Low Pressure CVD

- LPCVD (Low Pressure Chemical Vapor Deposition)
  - Low deposition rate, high uniformity, 575-650 ℃
  - Good uniformity, property
  - Material: Si_3N_4, SiO_2, poly-Si, etc.



LPCVD at ISRC (2)

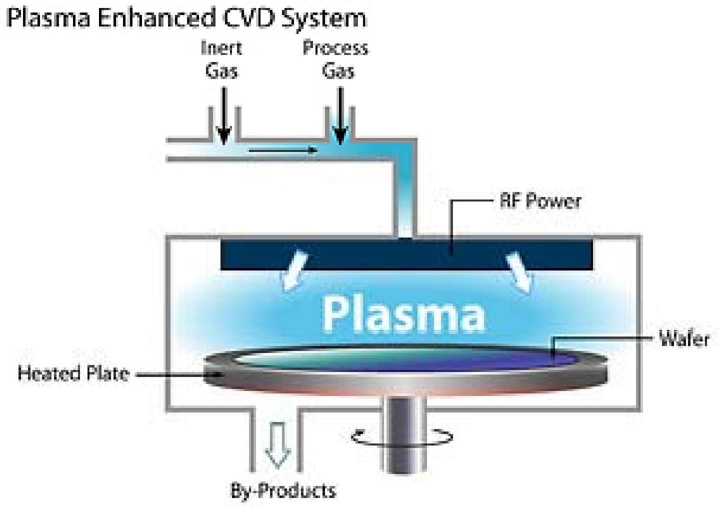
Process name	POLY Si		
Dep. Temp.	622℃ / 624℃ / 625℃	Dep. rate	100Å/min
Gas	SiH4 : 60sccm		
Process pressure	270mTorr		

Process name	α -Si		
Dep. Temp.	549.5℃ / 555℃ / 555℃	Dep. rate	24Å/min
Gas	SiH4 : 60 sccm		
Process pressure	250 mTorr		

Process name	Low stress Nitride		
Dep. Temp.	825℃ / 828℃ / 825℃	Dep. rate	27Å/min
Gas	DCS-L: 21sccm, DCS-R: 30sccm,NH3-L:3.5sccm,NH3-L:5sccm		
Process pressure	150mTorr		

Plasma Enhanced CVD (1)

- PECVD (Plasma Enhanced Chemical Vapor Deposition)
  - Ionized chemical species allows a lower process temperature.
  - Film properties can be tailored by controllable ion bombardment with substrate bias voltage.
  - Material: Si_3N_4, SiO_2, amorphous-Si, etc.
  - Faster rate and lower deposition temperature than thermal CVD
  - Cracks, pin holes, and poor stoichiometry



Plasma Enhanced CVD at ISRC (2)

- P-5000 II

RF power (W)	Pressure (Torr)	Gas flow		Dep. R ate (Å/min)
		TEOS	O_2	
350	9	220	220	About 100

Plasma Enhanced CVD at ISRC (3)

- STS PECVD

Nitride					
Gas flow (sccm)			Pressure (mTorr)	RF power (W)	Dep. rate (Å/min)
$5\%SiH_4/N_2$	NH_3	N_2			
800	10	1200	580	Low Frequency (187kHz), 60W	160

Oxide					
Gas flow (sccm)			Pressure (mTorr)	RF power (W)	Dep. rate (Å/min)
$5\%SiH_4/N_2$	NH_3	N_2			
160	1500	240	550	Low Frequency (187kHz), 60W	340

Oxinitride					
Gas flow (sccm)			Pressure (mTorr)	RF power (W)	Dep. rate (Å/min)
$5\%SiH_4/N_2$	NH_3	N_2			
800	250	60	580	Low Frequency (187kHz), 60W	300

Low stress nitride					
Gas flow (sccm)			Pressure (mTorr)	RF power (W)	Dep. rate (Å/min)
$5\%SiH_4/N_2$	NH_3	N_2			
800	10	1200	580	High Frequency (13.56MHz) : 20W(6sec), Low Frequency (187kHz) : 20W(1.5sec)	100

Common CVD films

Thin film	Typical Reactions	Equipment	Comments
SiO_2	$SiH_4 + O_2 \rightarrow SiO_2 + H_2$ $Si(OC_2H_5)_4(+O_3) \rightarrow SiO_2$ + byproducts	LPCVD, PECVD, HDPCVD	200 ~ 800 ˚C 200 ~ 500 ˚C (LTO) – may require high T anneal. 25 ~ 400 ˚C (TEOS-ozone, PECVD, HDPCVD)
Si_3N_4	$3SiH_4 + 4NH_3 \rightarrow Si_3N_4 + 12H_2$ $3SiH_2Cl_2 + 4NH_3 \rightarrow Si_3N_4 + 6N_2 + 6HCl$	LPCVD, PECVD	650 ~ 800 ˚C for oxidation mask 200 ~ 400 ˚C (PECVD) for passivation
Poly-silicon	Same as epitaxial Si	LPCVD	575 to 800 ˚C Grain structure depends on deposition conditions and doping
Epitaxial silicon	$SiH_4 \rightarrow Si + 2H_2$ $SiCl_4 + 2H_2 \rightarrow Si + 4HCl$ Also $SiHCl_3$, SiH_2Cl_2	APCVD, LPCVD	1000 ~ 1250 ˚C If using reduced pressure, 700 to 900 ˚C

CVD Chemistries (1)

- Silicon Oxide
  - Dry oxidation : $Si + O_2 \rightarrow SiO_2$
  - Wet Oxidation : $Si + 2H_2O \rightarrow SiO_2 + 2H_2$
  - $SiH_4 + O_2 \rightarrow SiO_2 + 2H_2$
  - $SiH_4 + N_2O \rightarrow SiO_2 +$ byproducts
  - $SiCl_2H_2 + N_2O \rightarrow SiO_2 +$ byproducts
  - $Si(OC_2H_5)_4 \rightarrow SiO_2 +$ byproducts

Example : Silicon dioxide

- Thermally driven reaction
  - Mid-temperature : ~ 500 ˚C
    - "LTO" (low-temp. oxide) T < ~ 500 ˚C
  - $SiH_4 + O_2 \rightarrow SiO_2 + H_2$
  - Cold-wall, atmospheric, ~ 0.1 μm/min
  - Hot-wall, LPCVD, ~ 0.01 μm/min
- Plasma-enhanced reaction (PECVD)
  - Low temperature : ~ 250 ˚C
- High temperature: ~ 700 ˚C
  - Tetraethyl orthosilicate (TEOS)
    - $Si(OC_2H_5)_4 \rightarrow SiO_2$ + byproducts

CVD Chemistries (2)

- Silicon Nitride
  - $3SiH_4 + 4NH_3 \rightarrow Si_3N_4 + 12H_2$
  - $3SiH_2Cl_2 + 4NH_3 \rightarrow Si_3N_4 + \text{byproducts}$
  - $3SiH_4 + 4N_2O \rightarrow Si_3N_4 + \text{byproducts}$
  - $3SiH_4 + N_2 \rightarrow Si_3N_4 + \text{byproducts}$

Example : Silicon nitride

- Uses
  - Diffusivity of O_2, H_2 is very low in nitride
    - Mask against oxidation, protect against water/corrosion
  - Diffusivity of Na also very low
    - Protect against mobile ion contamination
- Deposition
  - Stoichiometric formulation is Si_3N_4
    - In practice Si/N ratio varies from 0.7 (N rich) to 1.1 (Si rrich)
  - LPCVD : ~ 700 ˚C ~ 900 ˚C
    - $3SiH_4 + 4NH_3 \rightarrow Si_3N_4 + 12H_2$; $3SiH_2Cl_2 + 4NH_3 \rightarrow Si_3N_4 + 6N_2 + 6HCl$
    - ρ : ~ 3 g/cm^3
    - Stress : ~ 10 Gdyne/cm^2, tensile
  - PECVD
    - $aSiH_4 + bNH_3 \rightarrow Si_xN_yH_z + cH_2$; $aSiH_4 + bN_2 \rightarrow Si_xN_yH_z + cH_2$
    - ρ : 2.4 ~ 2.8 g/cm^3
    - Stress : ~2C ~5T Gdyne/cm^2

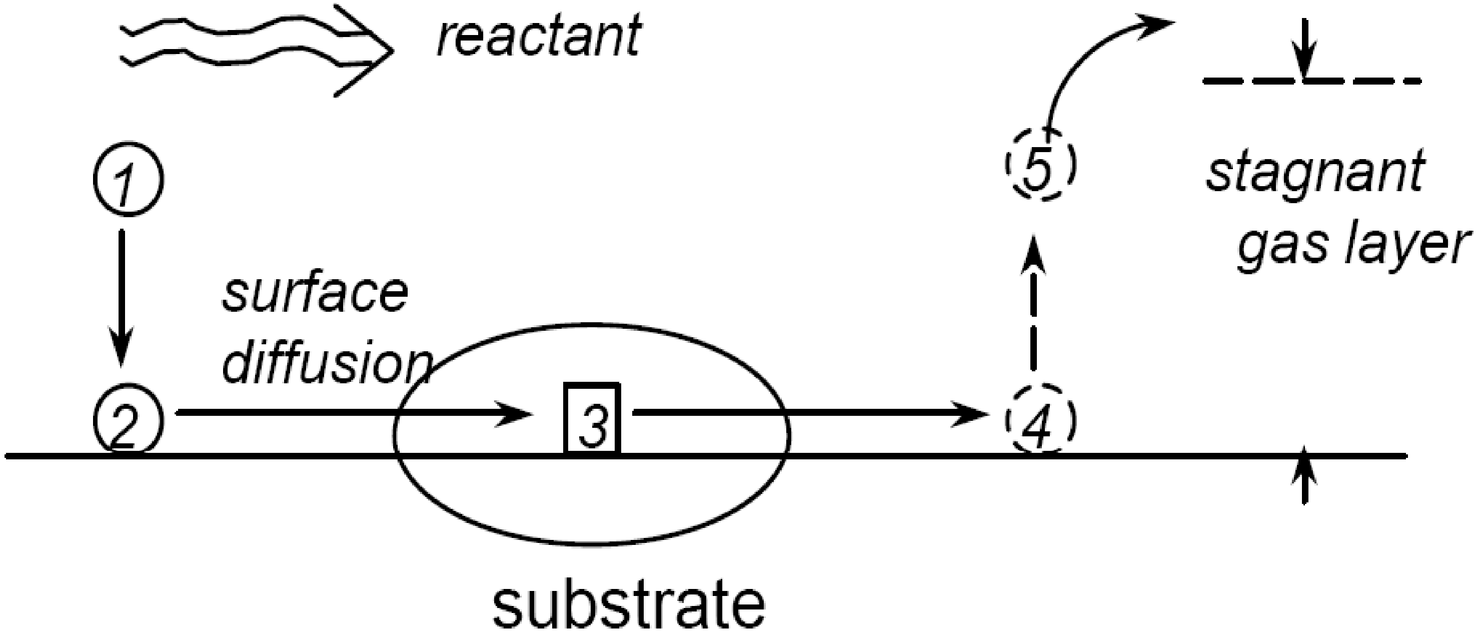
CVD Chemistries (3)

- Poly-silicon : $SiH_4 \rightarrow Si + 2H_2$
- Silicon Carbide
- Polycrystalline Diamond
- Parylene (polymerized p-xylylene)
- Refractory Metals : $2WF_6 + 3SiH_4 \rightarrow 2W + 3SiF_4 + 6H_2$
- II-VI compounds

Exaple : polysilicon

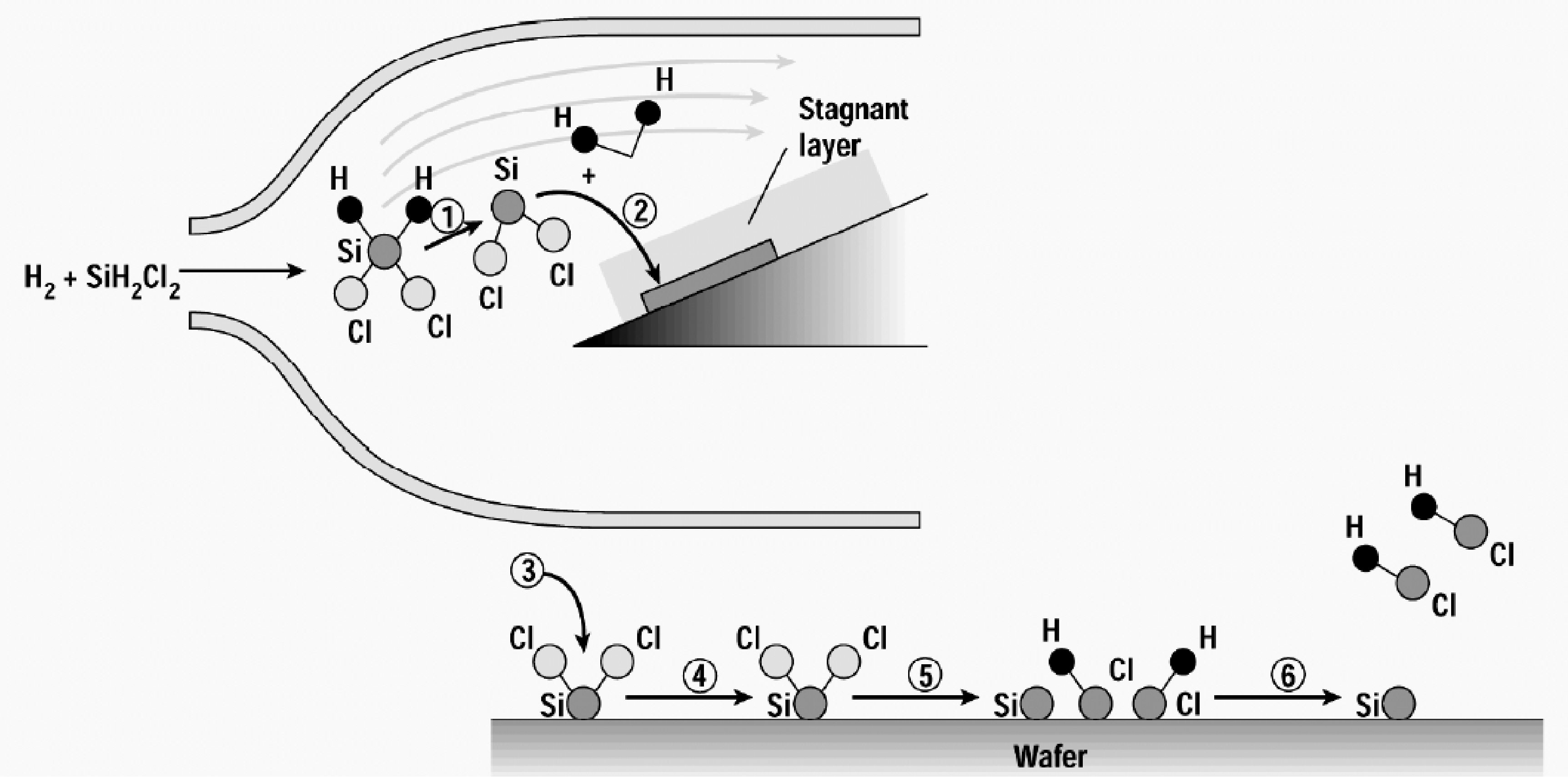
- Uses
  - Gates, high value resistors, “local” interconnects
- Deposition
  - Silane pyrolysis : 600 ~ 700 ˚C , $SiH_4 \rightarrow Si + 2H_2$
    - Atmospheric, cold wall, 5% silane in hydrogen, ~1/2 μm/min
    - LPCVD (~ 1 Torr), hot wall, 20 ~ 100% silane, ~ hundreds nm/min
  - Grain size dependent on growth temperature, subsequent processing
    - 950 ˚C phosphorus diffusion, 20 min; ~ 1 μm grain size
    - 1050 ˚C oxidation; 1~3 μm grain size
- In-situ doping
  - P-type: diborane B_2H_6
    - Can cause substantial increase in deposition rate
  - N-type: arsine AsH_3, phosphine PH_3
    - Can cause substantial decrease in deposition rate
- Dope after deposition (implant, diffusion)

CVD mechanisms



1 = Diffusion of reactant to surface
2 = Absorption of reactant to surface
3 = Chemical reaction
4 = Desorption of gas by-products
5 = Outdiffusion of by-product gas

Example Poly-Si deposition



(1) gas-phase decomposition and (2) transport to the surface of the wafer. At the surface the growth species must (3) adsorb, (4) diffuse, and (5) decompose, and (6) the reaction byproducts are desorbed.

Kinetics of CVD thin film deposition (1)

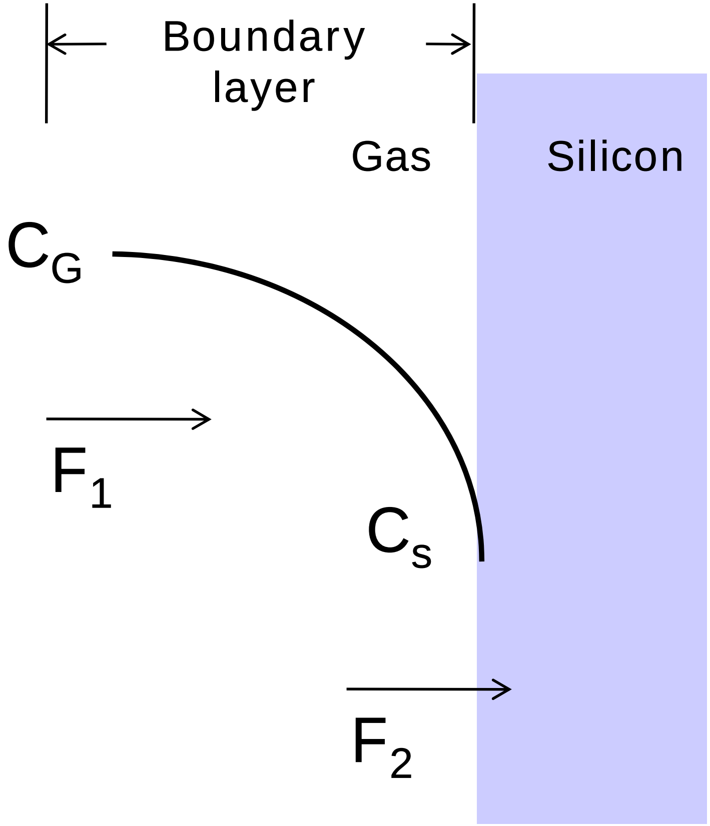
- We consider the fluxes for the two important process such as **mass transfer** and **surface reaction**.
- F_1 = diffusion flux of reactant species to the wafer = mass transfer flux.

$$\mathbf{F_1 = h_G(C_G\text{-}C_S)}$$

- Where (C_G-C_S) term is the difference in concentration of the reactants species between the main gas flow and the wafer surface, and h_G is the mass transfer coefficient.
- Similarly, F2 = flux of reactant consumed by the surface reaction = surface reaction flux.

$$\mathbf{F_2 = K_S C_S}$$

- Where K_S is the chemical surface reaction rate and C_S is the concentration of the reacting species at the surface.



Kinetics of CVD thin film deposition (2)

- In steady state

$F_1 = F_2$ → $C_S = \frac{h_G}{(h_G + k_S)} C_G$

Growth Rate

$R_G = F_2/N_{Si}$ (N_{Si} : # of Si atoms in a unit volume)

$$R_G = \frac{1}{N_{Si}} \frac{h_G k_S}{h_G + k_S} C_G$$

Surface reaction rate

$$k_S = k_0 \exp(-\frac{E_A}{kT})$$

E_A : activation energy

k : Boltzmann constant

Kinetics of CVD thin film deposition (3)

- Limiting cases of growth rate

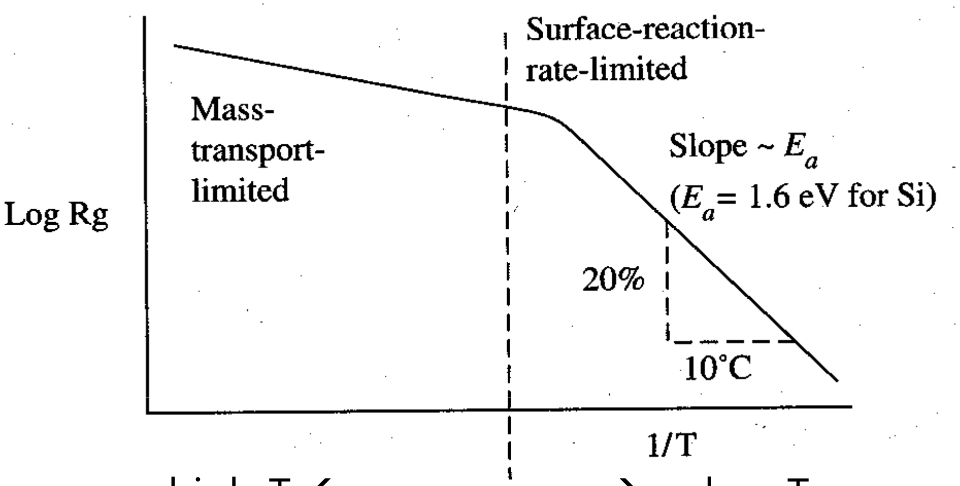
1. If $K_S << h_G$, then we have the surface reaction controlled case:

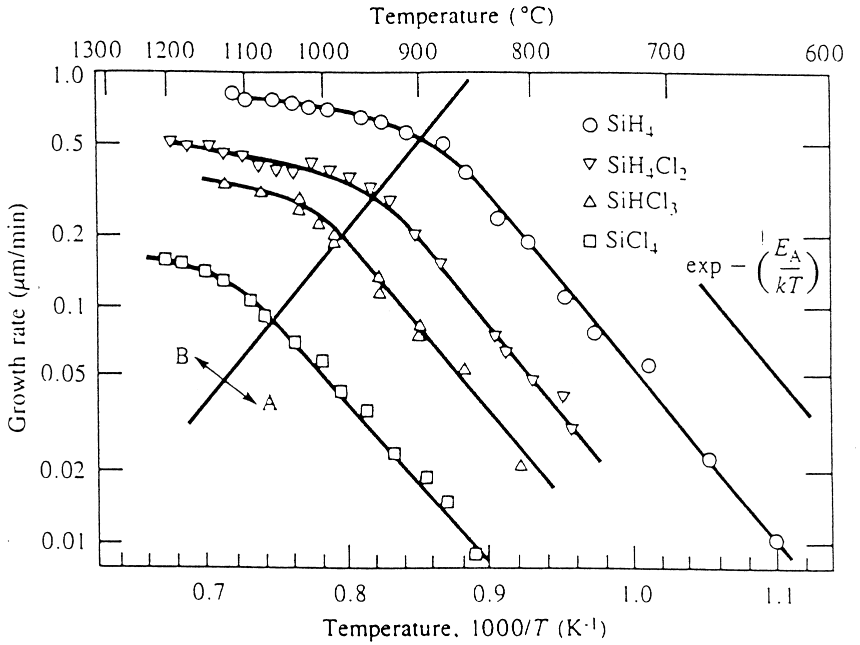
$$R_G = \frac{1}{N_{Si}} k_S C_G$$

2. If $h_G << K_S$, then we have the mass transfer, or gas phase diffusion controlled case:

$$R_G = \frac{1}{N_{Si}} h_G C_G$$

Deposition rate versus Temp





high T ← → low T

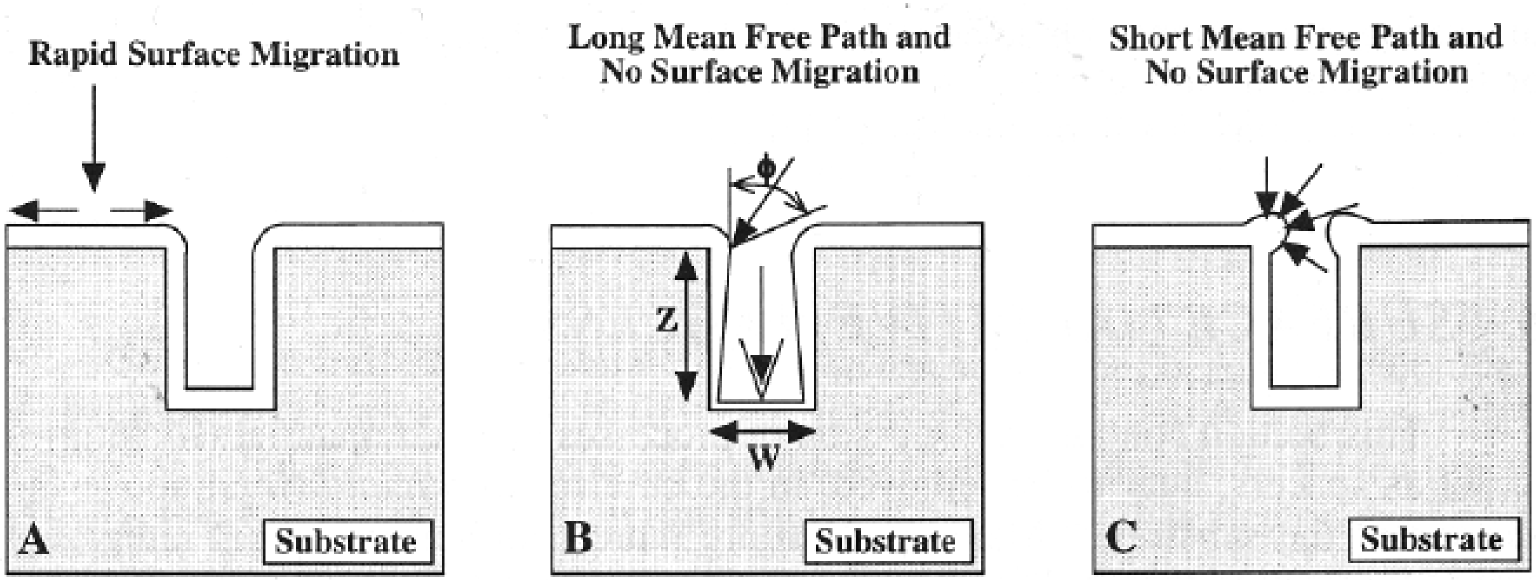
- K_S limited deposition is **VERY temp sensitive.**
- h_G limited deposition is **VERY geometry sensitive**.

- Si epi deposition often done at high T to get high quality single crystal growth.

  ∴ h_G controlled.
- Polysilicon is usually deposited at lower temperature surface reaction regime.

Step Coverage Profile (1)

- Step coverage profile



A: Rapid surface migration process (before reaction), yielding uniform coverage since reactants adsorb and move, then react

B: Long mean free path process and no surface migration, with reactant molecule arrival angle determined location on features (local "field of view" effects are important)

C: Short mean free path process with no surface migration, yielding nonconformal coating

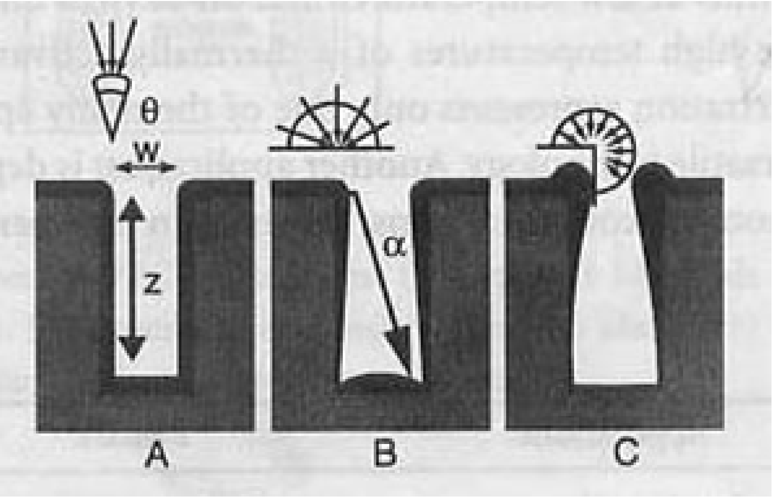
Step Coverage Profile (2)

- Key Parameters
  - Mean Free Path
  - Surface Migration Energy (E $\propto$ Temperature)
  - Arrival angle

- For conformal step coverage
  - α < l (mean free path)
  - α = arctan (w/z)
  - High Surface Mobility

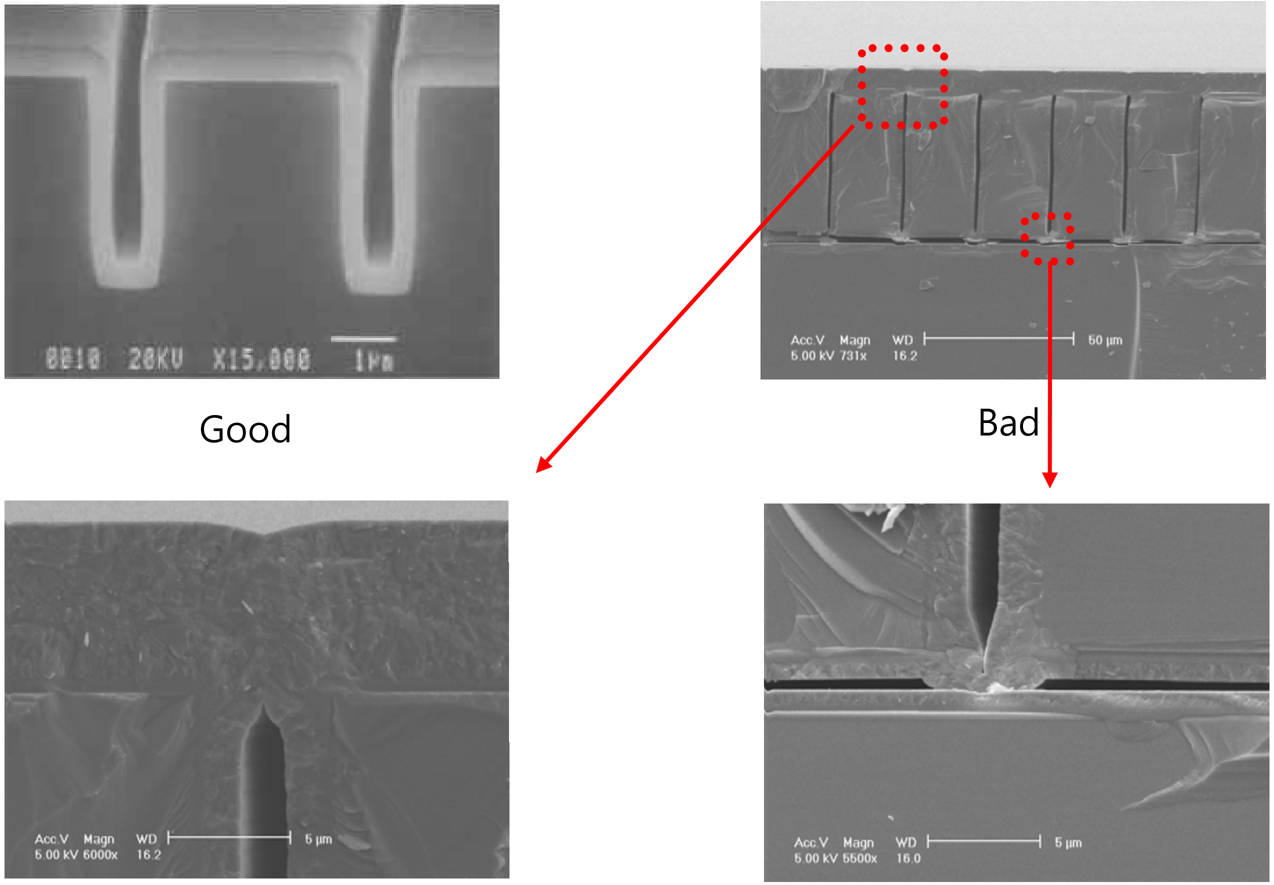
- Process tendency
  - A: LPCVD
  - B: PECVD

    Evaporated & Sputtered Metal



Step Coverage Profile (3)

- Step coverage profile example

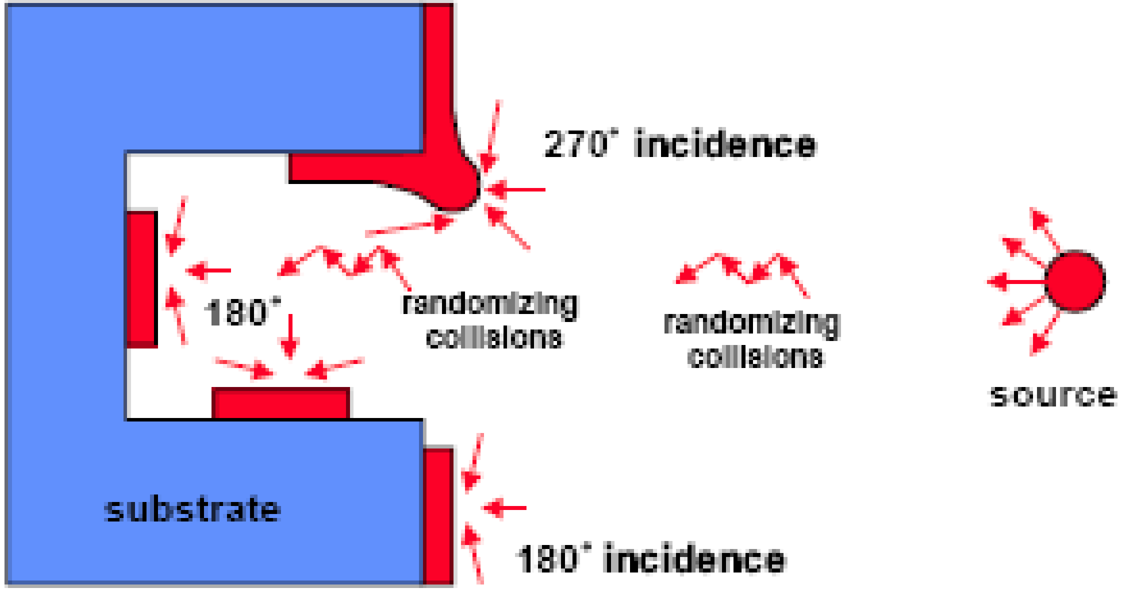


Good

Bad

Impact of pressure on deposition conditions (1)

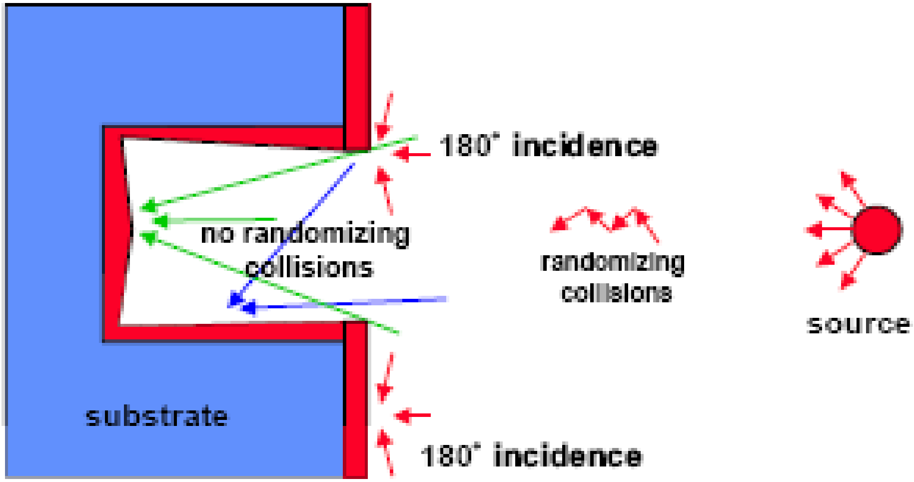
- Material arrival angular distribution
  - Depends on mean free path compared to both size of system and size of wafer "steps"
- Case I: "atmospheric pressure": 760 Torr → $\lambda = 0.07\ \mu m$
  - Isotropic arrival on ALL surfaces



Assume material does not migrate after arrival.

Impact of pressure on deposition conditions (2)

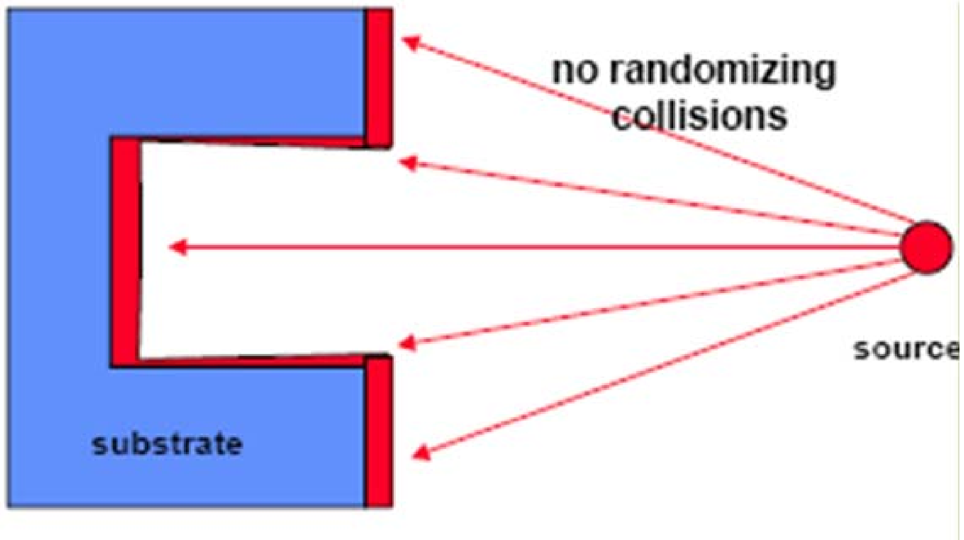
- Case II: 10^{-1} Torr → λ = 0.5 mm
  - Small compared to system, large compared to wafer features
  - Isotropic arrival at “flat” surface
- But no scattering inside “hole”
  - Shadowing by corners of features
  - “anisotropic” deposition



Assume material does not migrate after arrival.

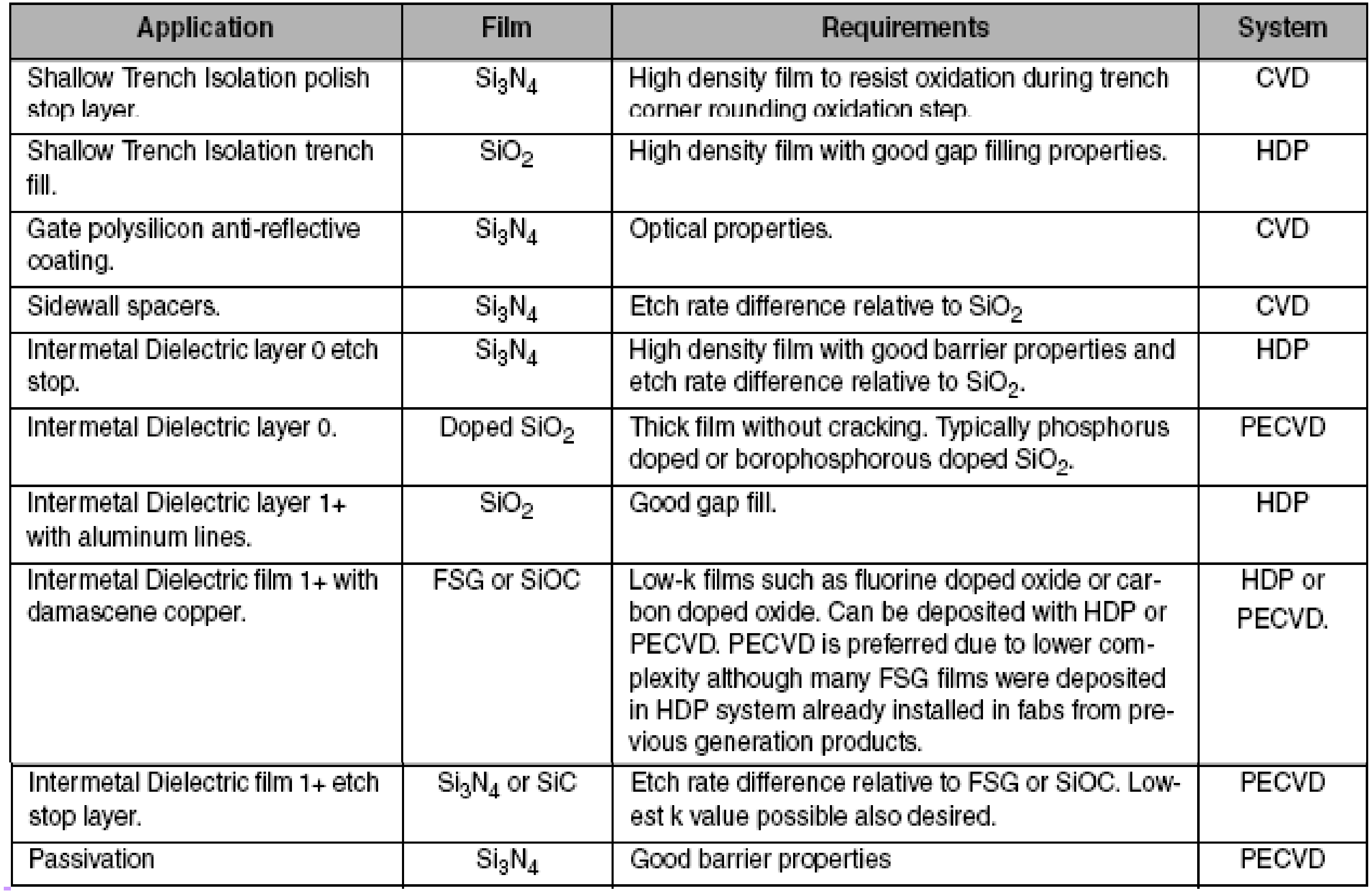
Impact of pressure on deposition conditions (3)

- Case II: 10^{-5} Torr → λ = 5 m
  - Long compared to almost everything
- Anisotropic arrival at all surfaces
  - Very thin on "side walls"
  - Very dependent on source configuration relative to sample surface



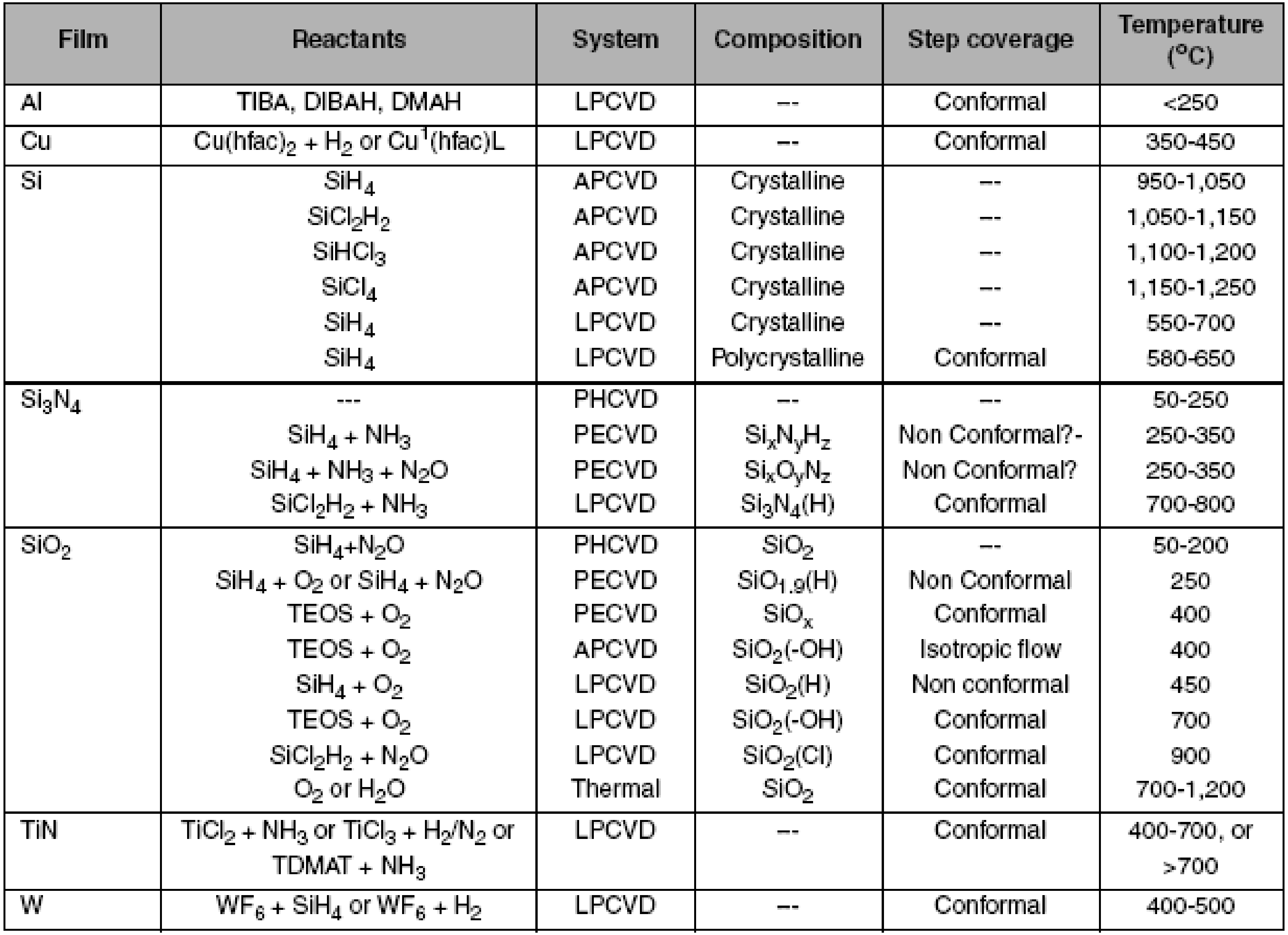
Assume material does not migrate after arrival.

Dielectric deposition applications summary



Application	Film	Requirements	System
Shallow Trench Isolation polish stop layer.	Si_3N_4	High density film to resist oxidation during trench corner rounding oxidation step.	CVD
Shallow Trench Isolation trench fill.	SiO_2	High density film with good gap filling properties.	HDP
Gate polysilicon anti-reflective coating.	Si_3N_4	Optical properties.	CVD
Sidewall spacers.	Si_3N_4	Etch rate difference relative to SiO_2	CVD
Intermetal Dielectric layer 0 etch stop.	Si_3N_4	High density film with good barrier properties and etch rate difference relative to SiO_2.	HDP
Intermetal Dielectric layer 0.	Doped SiO_2	Thick film without cracking. Typically phosphorus doped or borophosphorous doped SiO_2.	PECVD
Intermetal Dielectric layer 1+ with aluminum lines.	SiO_2	Good gap fill.	HDP
Intermetal Dielectric film 1+ with damascene copper.	FSG or SiOC	Low-k films such as fluorine doped oxide or carbon doped oxide. Can be deposited with HDP or PECVD. PECVD is preferred due to lower complexity although many FSG films were deposited in HDP system already installed in fabs from previous generation products.	HDP or PECVD.
Intermetal Dielectric film 1+ etch stop layer.	Si_3N_4 or SiC	Etch rate difference relative to FSG or SiOC. Lowest k value possible also desired.	PECVD
Passivation	Si_3N_4	Good barrier properties	PECVD

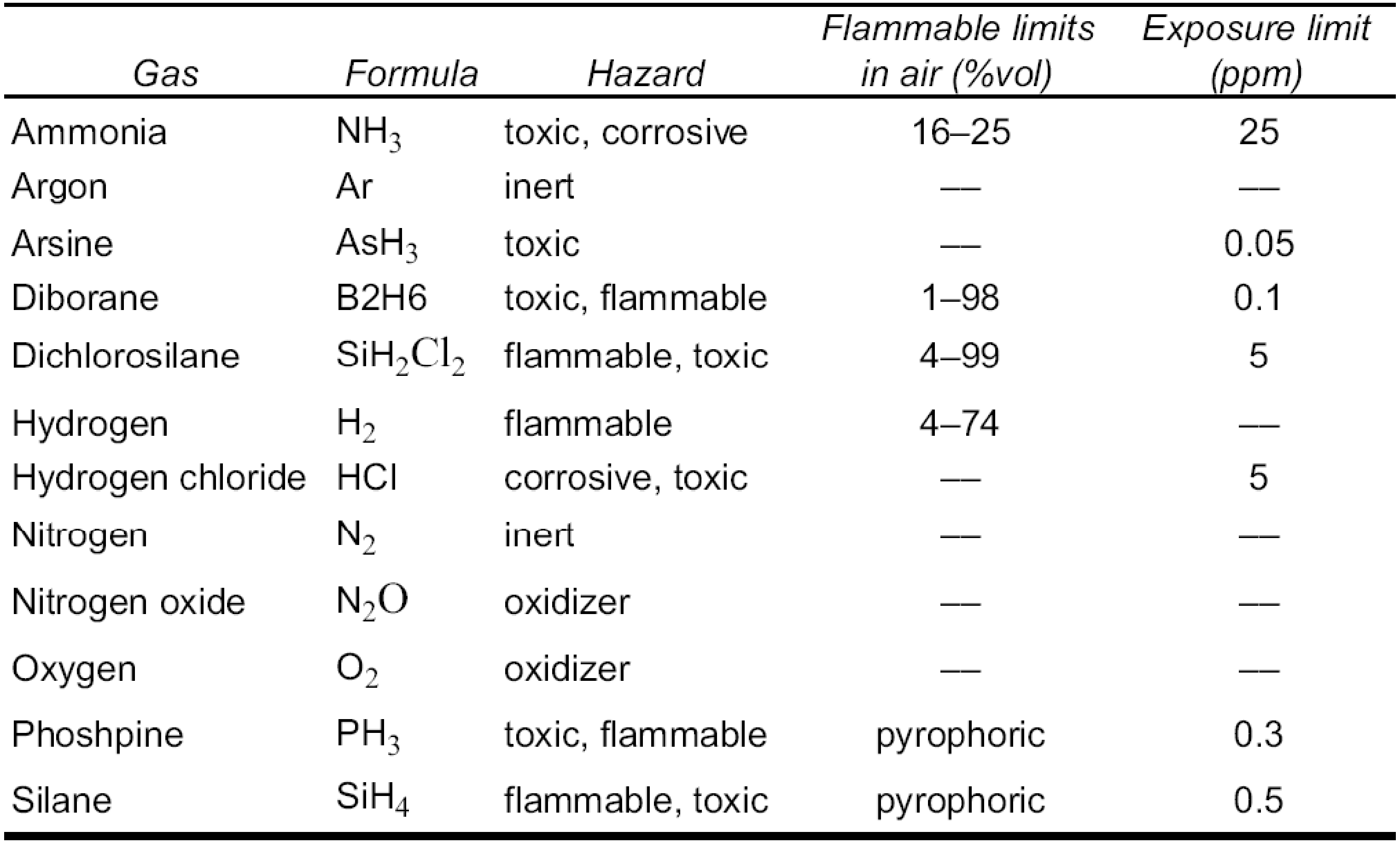
Common CVD deposition reactants



Film	Reactants	System	Composition	Step coverage	Temperature (°C)
Al	TIBA, DIBAH, DMAH	LPCVD	--	Conformal	<250
Cu	Cu(hfac)$_2$ + H_2 or Cu^1(hfac)L	LPCVD	--	Conformal	350-450
Si	SiH_4	APCVD	Crystalline	--	950-1,050
	$SiCl_2H_2$	APCVD	Crystalline	--	1,050-1,150
	$SiHCl_3$	APCVD	Crystalline	--	1,100-1,200
	$SiCl_4$	APCVD	Crystalline	--	1,150-1,250
	SiH_4	LPCVD	Crystalline	--	550-700
	SiH_4	LPCVD	Polycrystalline	Conformal	580-650
Si_3N_4	---	PHCVD	--	--	50-250
	SiH_4 + NH_3	PECVD	$Si_xN_yH_z$	Non Conformal?-	250-350
	SiH_4 + NH_3 + N_2O	PECVD	$Si_xO_yN_z$	Non Conformal?	250-350
	$SiCl_2H_2$ + NH_3	LPCVD	Si_3N_4(H)	Conformal	700-800
SiO_2	SiH_4+N_2O	PHCVD	SiO_2	--	50-200
	SiH_4 + O_2 or SiH_4 + N_2O	PECVD	$SiO_{1.9}$(H)	Non Conformal	250
	TEOS + O_2	PECVD	SiO_x	Conformal	400
	TEOS + O_2	APCVD	SiO_2(-OH)	Isotropic flow	400
	SiH_4 + O_2	LPCVD	SiO_2(H)	Non conformal	450
	TEOS + O_2	LPCVD	SiO_2(-OH)	Conformal	700
	$SiCl_2H_2$ + N_2O	LPCVD	SiO_2(Cl)	Conformal	900
	O_2 or H_2O	Thermal	SiO_2	Conformal	700-1,200
TiN	$TiCl_2$ + NH_3 or $TiCl_3$ + H_2/N_2 or TDMAT + NH_3	LPCVD	--	Conformal	400-700, or >700
W	WF_6 + SiH_4 or WF_6 + H_2	LPCVD	--	Conformal	400-500

CVD Hazards

- Many gases used in CVD systems are toxic (hazardous to humans), corrosive (causes corrosion to stainless steel and other metals), flammable (burns when exposed to an ignition source and an oxygen source), explosive and/or pyrophoric (spontaneously burn or explode in air, moisture or when exposed to oxygen)



Gas	*Formula*	*Hazard*	*Flammable limits in air (%vol)*	*Exposure limit (ppm)*
Ammonia	NH_3	toxic, corrosive	16–25	25
Argon	Ar	inert	—	—
Arsine	AsH_3	toxic	—	0.05
Diborane	B2H6	toxic, flammable	1–98	0.1
Dichlorosilane	SiH_2Cl_2	flammable, toxic	4–99	5
Hydrogen	H_2	flammable	4–74	—
Hydrogen chloride	HCl	corrosive, toxic	—	5
Nitrogen	N_2	inert	—	—
Nitrogen oxide	N_2O	oxidizer	—	—
Oxygen	O_2	oxidizer	—	—
Phoshpine	PH_3	toxic, flammable	pyrophoric	0.3
Silane	SiH_4	flammable, toxic	pyrophoric	0.5

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