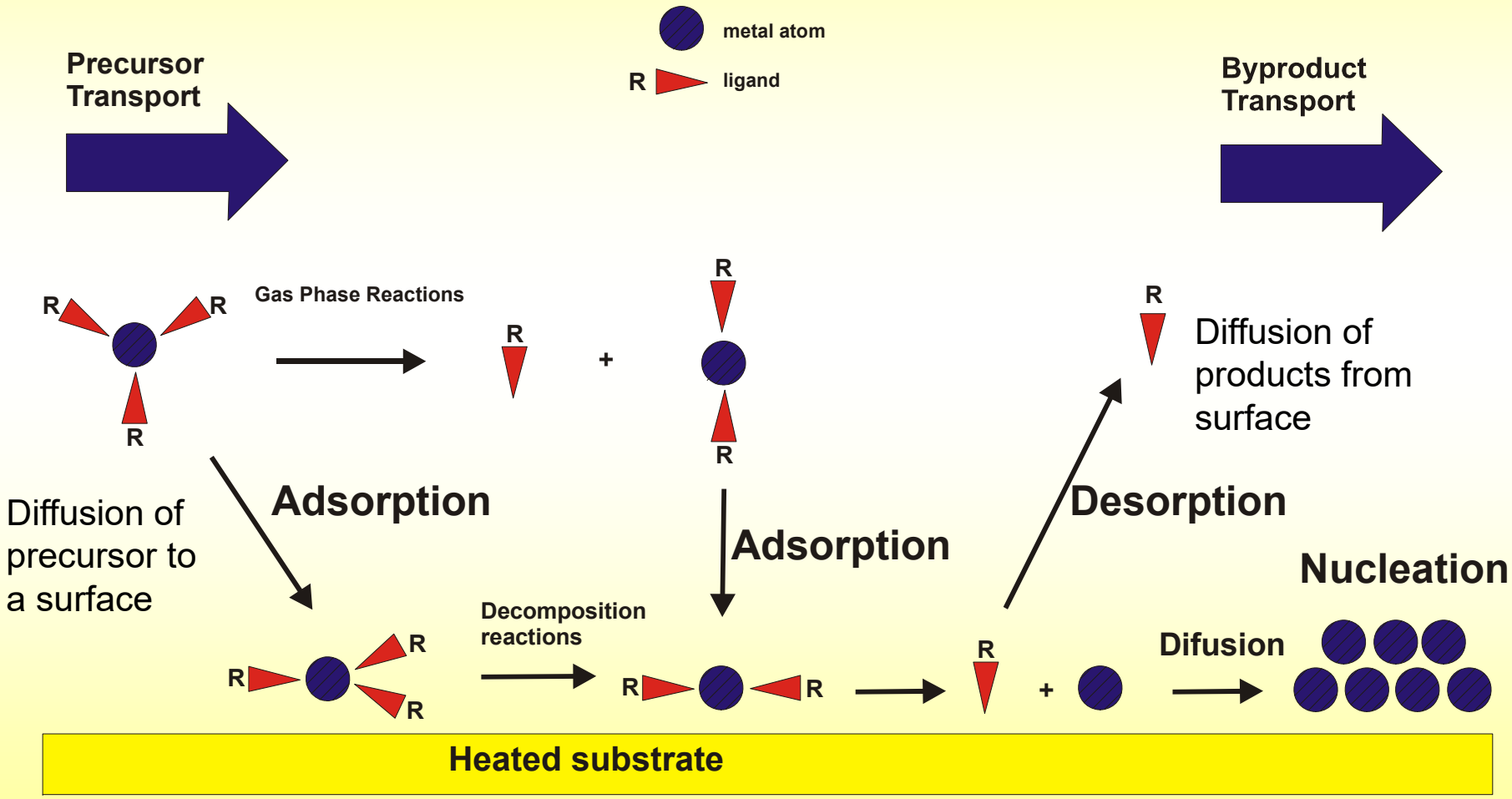
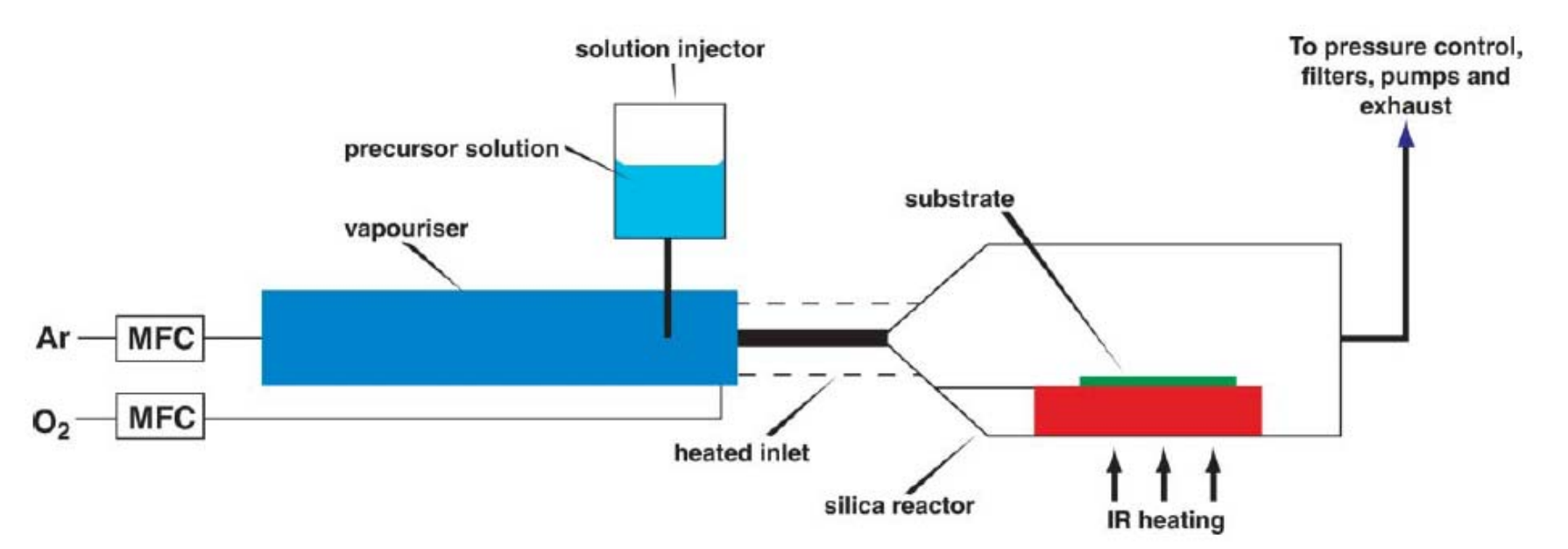
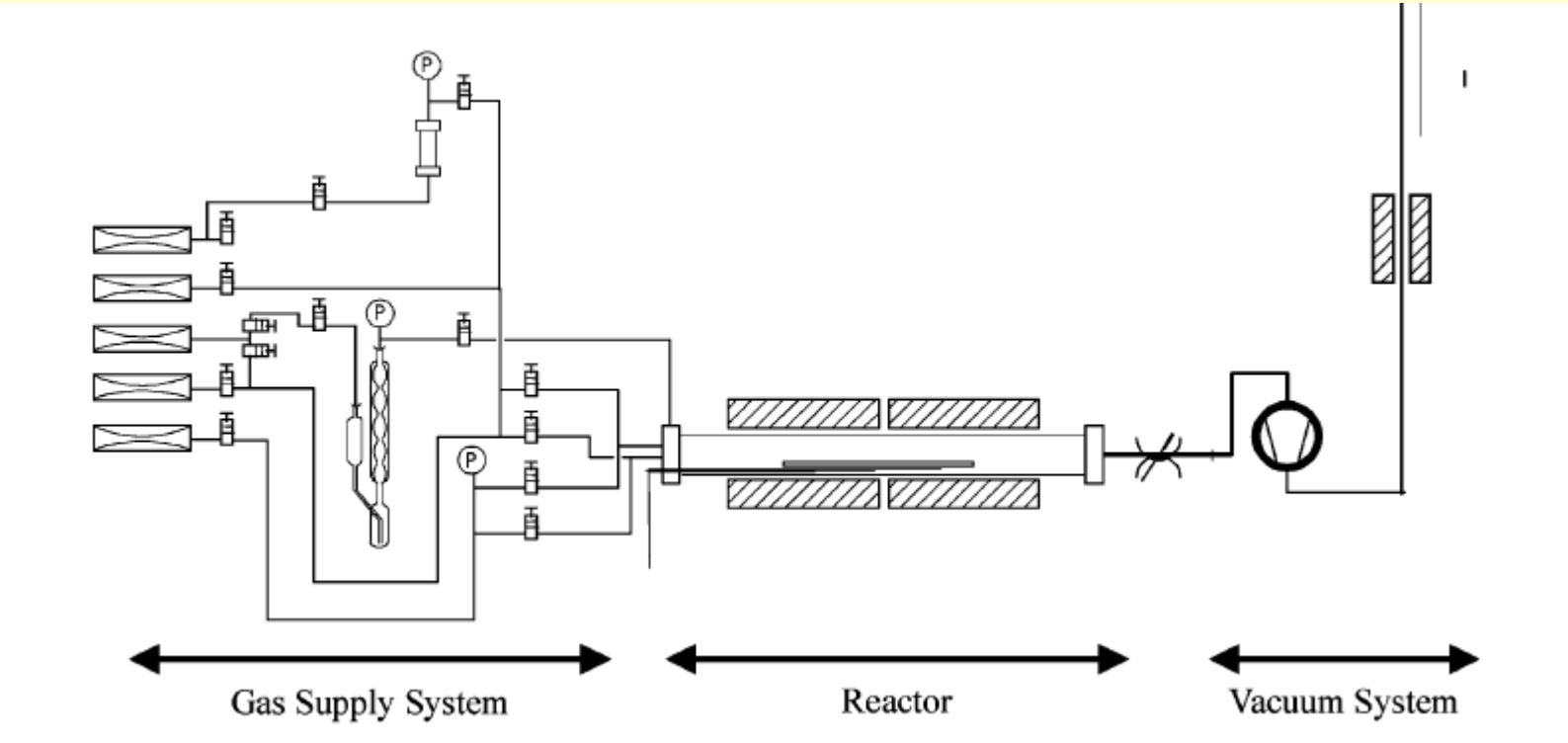
Basic steps in the CVD process



Cold-Wall CVD Reactor



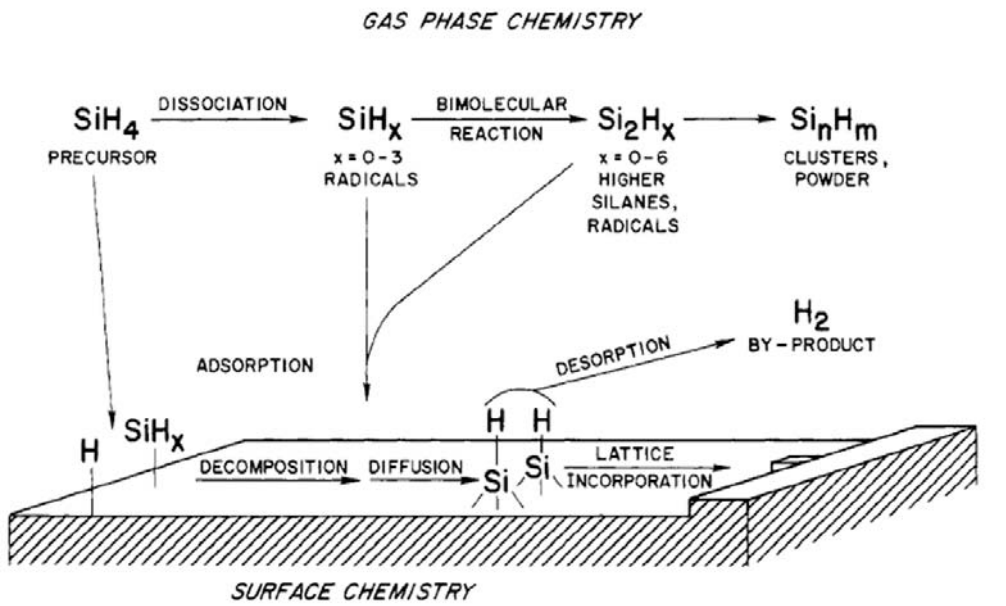
Hot-Wall CVD Reactor



CVD Kinetics

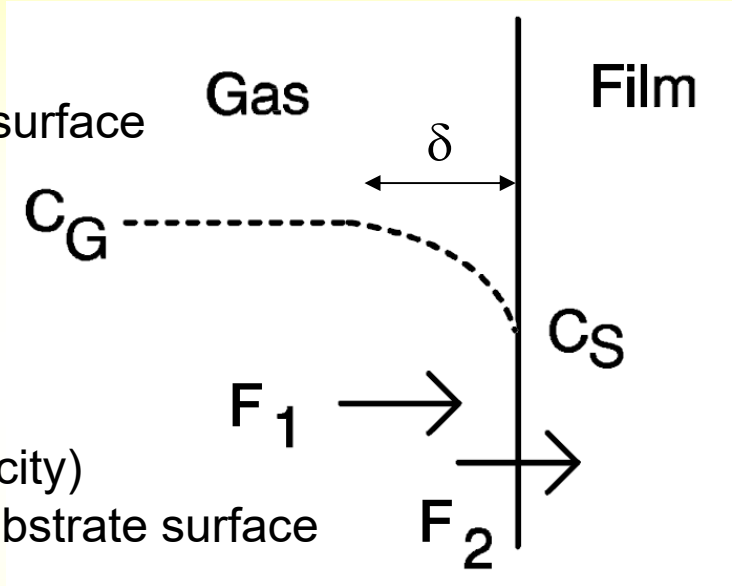
Deposition depends on the sequence of events:
(1) Diffusion of precursor to surface
(2) Adsorption of precursor at surface
(3) Chemical reaction at surface
(4) Desorption of byproducts from surface
(5) Diffusion of byproducts from surface

The *slowest* event will be the rate-determining step



CVD Kinetics

Growth Rate Model



F_1 = precursor flux from bulk of gas to substrate surface

$$F_1 = h_G \cdot (C_G - C_S)$$

h_G = mass-transfer coefficient $\quad h_G = D / \delta$
D = gas diffusion constant $\quad D = D_o T^{3/2} / P$
δ = boundary layer thickness (related to gas velocity)
C_G, C_S = precursor conc. at bulk of gas and at substrate surface
(conc. gradient – driving force for diffusion)

F_2 = flux consumed in film-growth reaction (rate of chemical reaction)

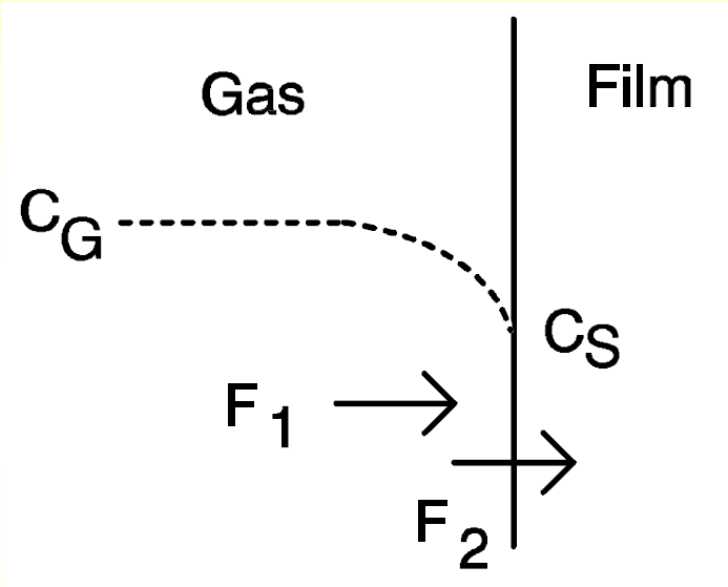
$$F_2 = k_S \cdot C_S$$

k_S = surface-reaction rate constant: $k_S = A \exp(-E_a/kT)$

Steady state
$$F_1 = F_2 = F$$

CVD Kinetics

Steady state
$F_1 = F_2 = F$



Growth Rate Model

$F_1 = F_2$ (rate of transport = rate of reaction)

$$h_G \cdot (C_G - C_S) = k_S \cdot C_S$$

$$C_S = C_G / (1 + k_S/h_G)$$

$$F = k_S h_G C_G / (k_S + h_G)$$

Growth rate (thickness growth rate)

$$dy / dt = F / \rho$$

y = film thickness
ρ = atomic density of film

$$\frac{dy}{dt} = C_G \frac{1}{\rho} \frac{1}{\frac{1}{k_S} + \frac{1}{h_G}}$$

Growth Rate

Growth rate is determined by:

$$\frac{dy}{dt} = C_G \frac{1}{\rho} \frac{1}{\frac{1}{k_S} + \frac{1}{h_G}}$$

a) Concentration C_G of a precursor in bulk of gas mixture

b) By the smaller of h_G and k_S

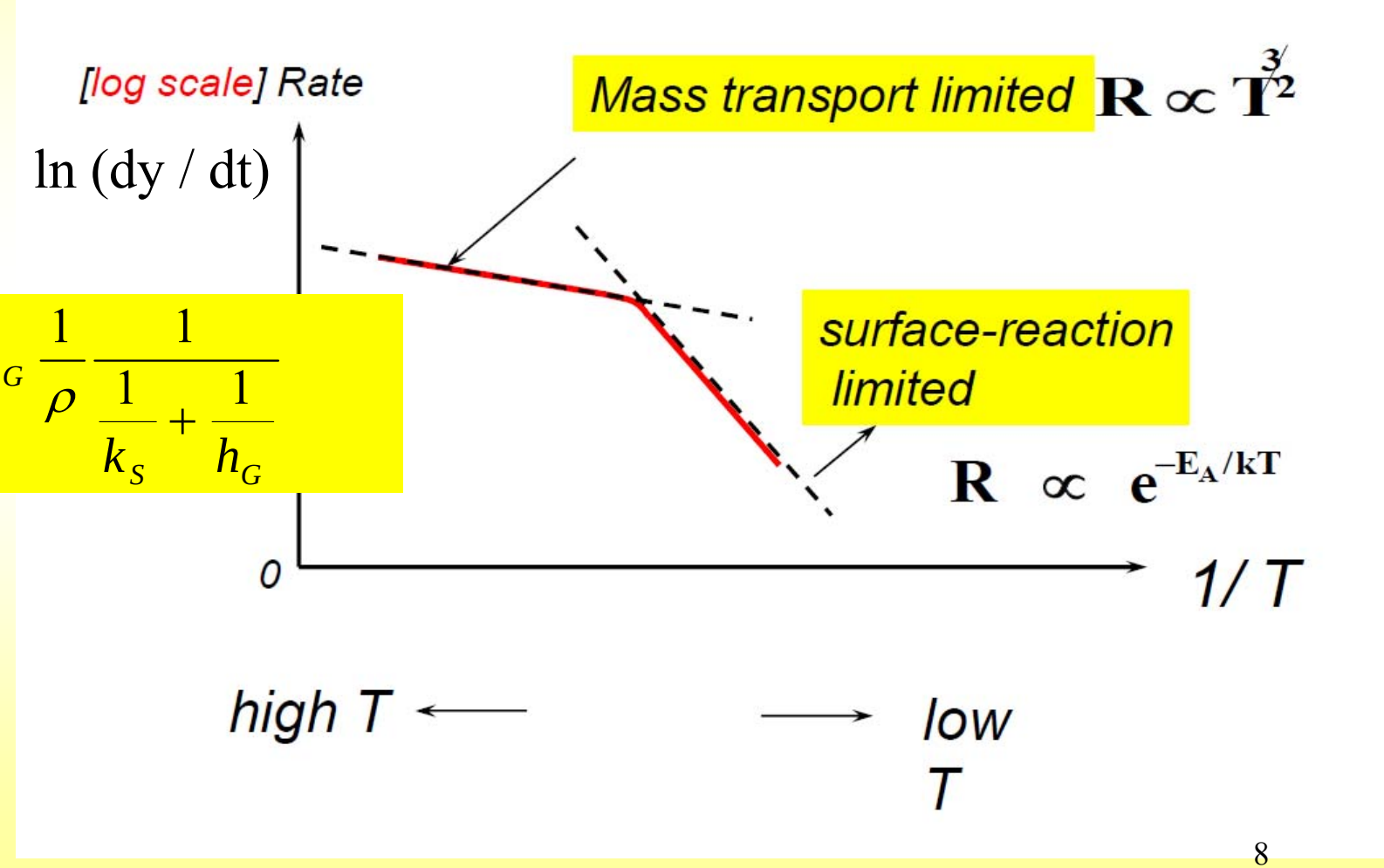
$k_S << h_G$ = Surface reaction limited $dy/dt \sim \exp(-E_a/kT)$

$h_G << k_S$ = Mass transport limited $dy/dt \sim T^{3/2}$

When temperature is low, surface reaction rate is slow, and excess of reactants is available = the reaction is surface reaction limited

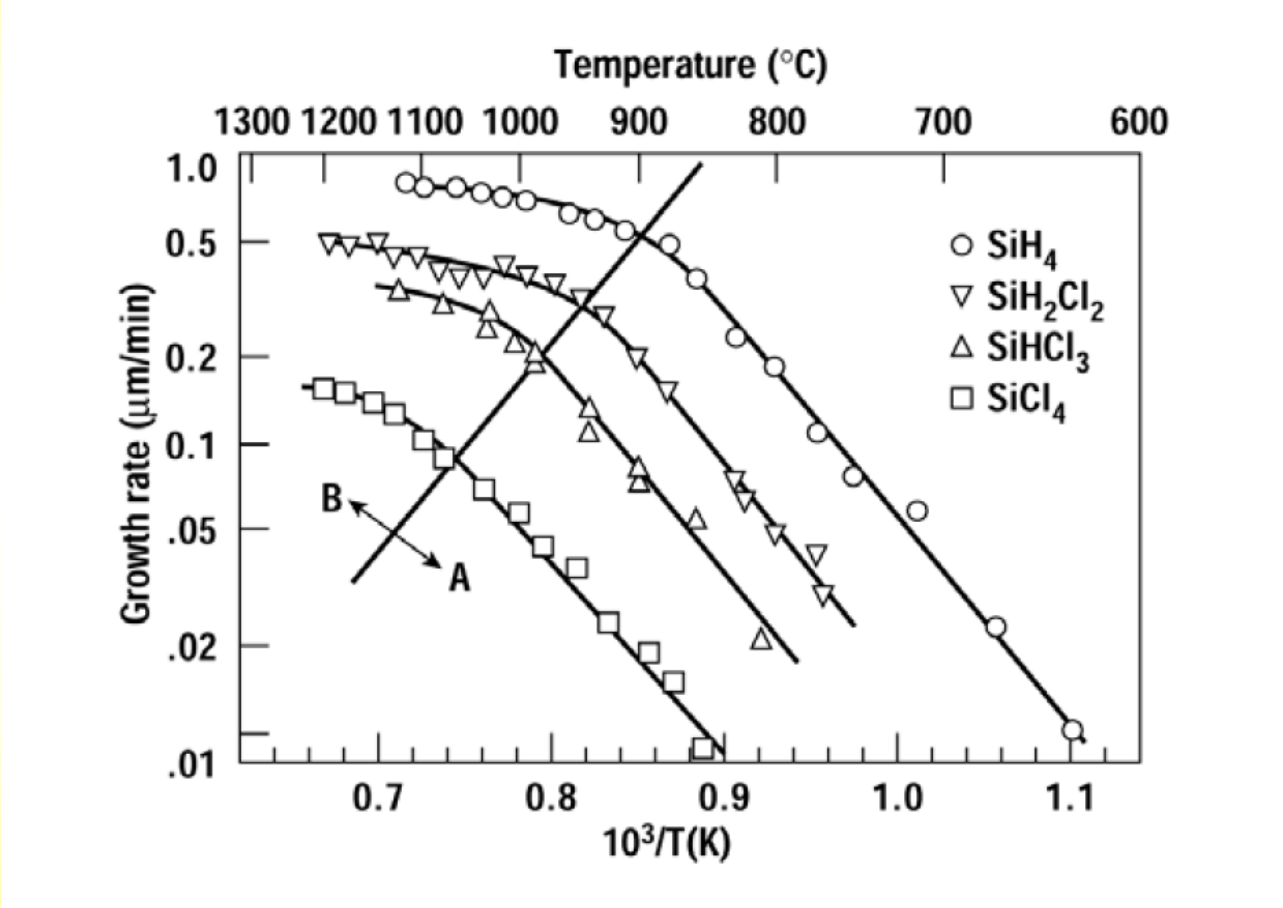
Above a certain temperature all source gas molecules react immediately = the reaction is then in mass-transport limited regime (also diffusion limited and supply limited regime)

Deposition rate vs. Temperature



$$\frac{dy}{dt} = C_G \frac{1}{\rho} \frac{1}{\frac{1}{k_S} + \frac{1}{h_G}}$$

Deposition rate vs. Temperature

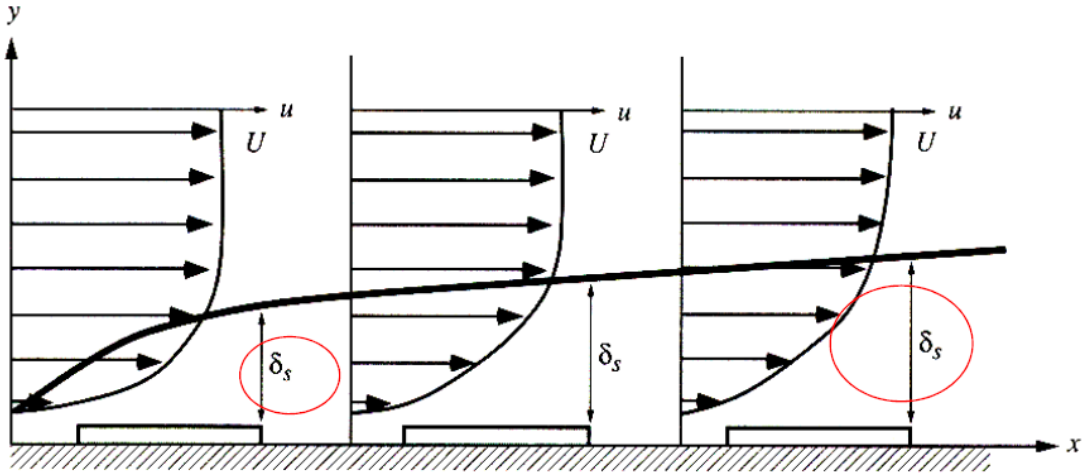


A = Surface reaction limited
B = Mass transport limited

Growth Rate Dependence on Flow Velocity

$$\delta_s(x) = \left(\frac{\mu x}{\rho U}\right)^{\frac{1}{2}}$$

μ = viscosity, ρ = density, U = velocity



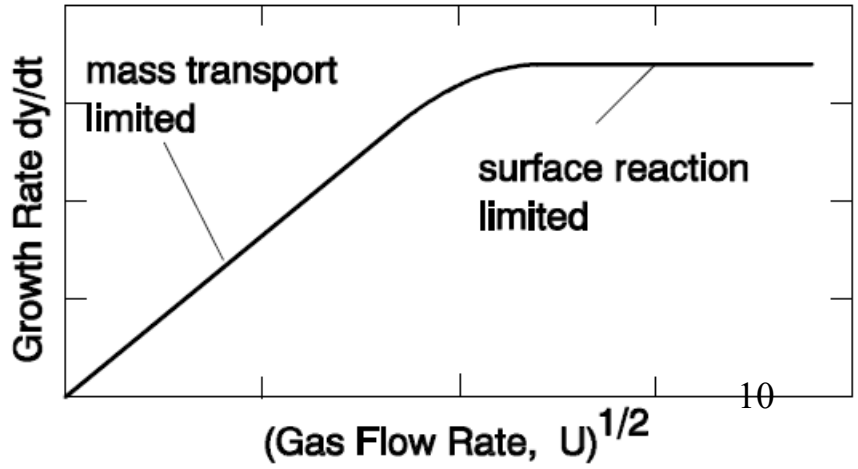
$F_1 = h_G \cdot (C_G - C_S)$

h_G = mass-transfer coefficient

$h_G = D / \delta$

δ = boundary layer thickness

At constant T

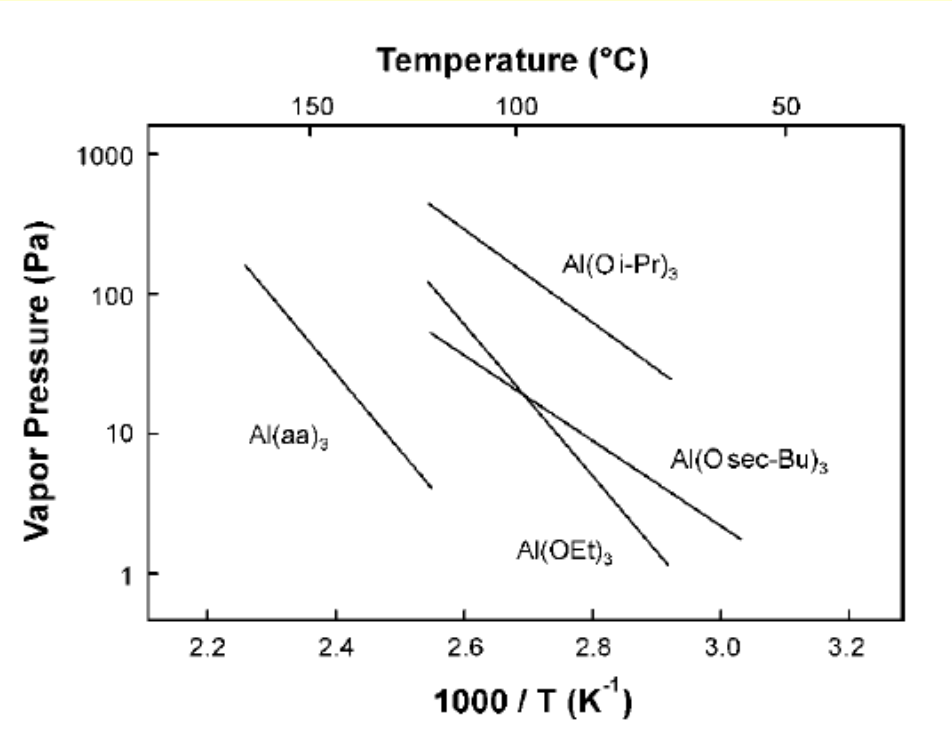


Low flow rate U

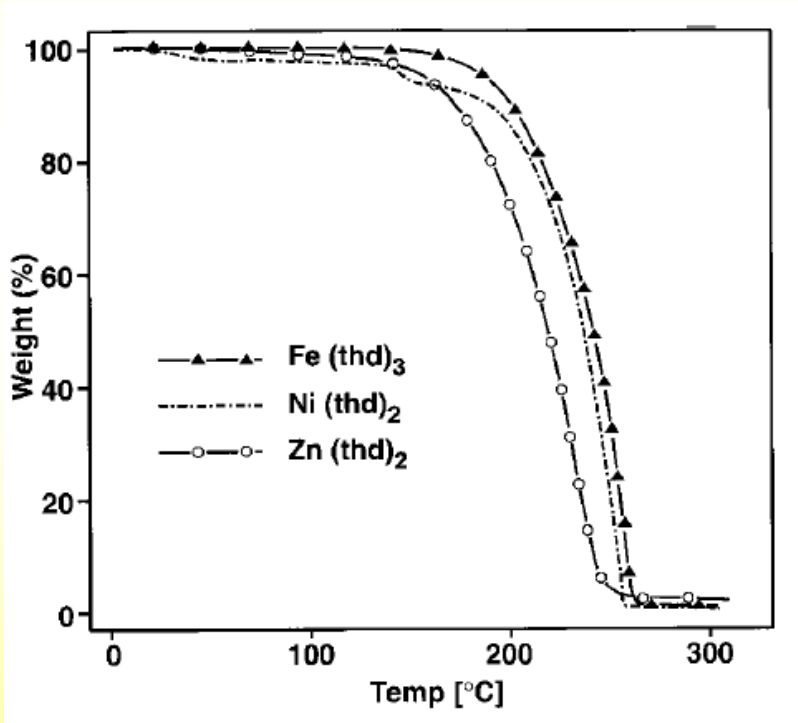
~ large boundary layer thickness δ

~ slow mass-transfer

Precursor Volatility



Thermogravimetric Analysis



Clausius-Clapeyron Equation

$$\ln \frac{p_2}{p_1} = \frac{-\Delta H^0_{subl}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

CVD of Al

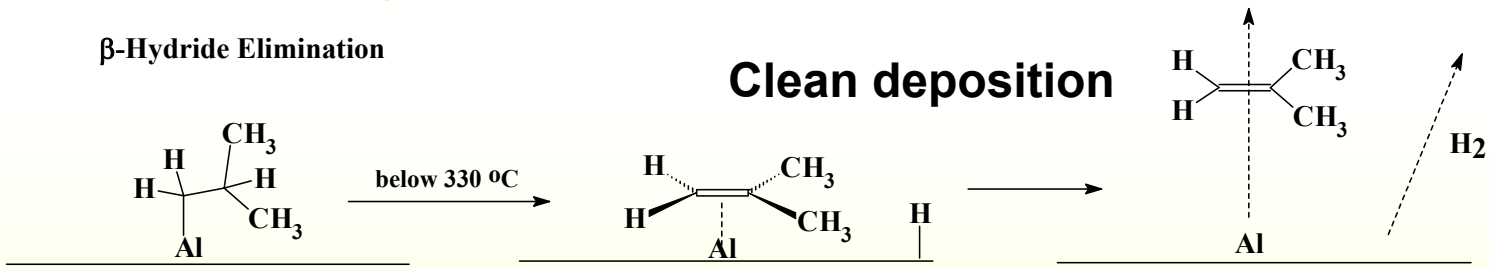
Aluminum

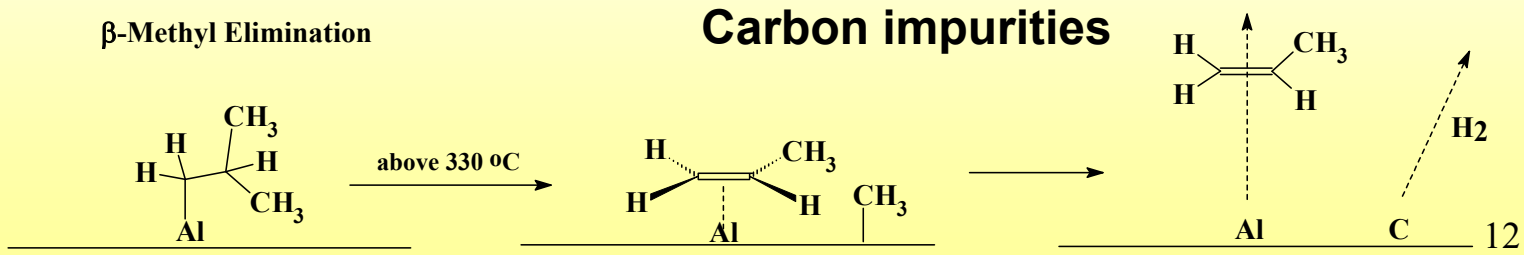
2.27 μΩ cm, easily etched, Al dissolves in Si

GaAs + Al → AlAs + Ga

Gas diffusion barriers, Al on polypropylene, food packaging = chip bags, party balloons, high optical reflectivity = mirrors

TIBA = Triisobutylaluminum





CVD of Al

Al deposits selectively on Al surfaces, not on SiO_2

Laser-induced nucleation
248 nm only surface adsorbates pyrolysed
193 nm gas phase reactions, loss of spatial selectivity control

TMA = Trimethylaluminum
Large carbon incorporation, Al_4C_3, RF plasma, laser

$$Al_2(CH_3)_6 \rightarrow 1/2\ Al_4C_3 + 9/2\ CH_4 \quad \text{under } N_2$$

$$Al_2(CH_3)_6 + 3\ H_2 \rightarrow 2\ Al + 6\ CH_4 \quad \text{under } H_2$$

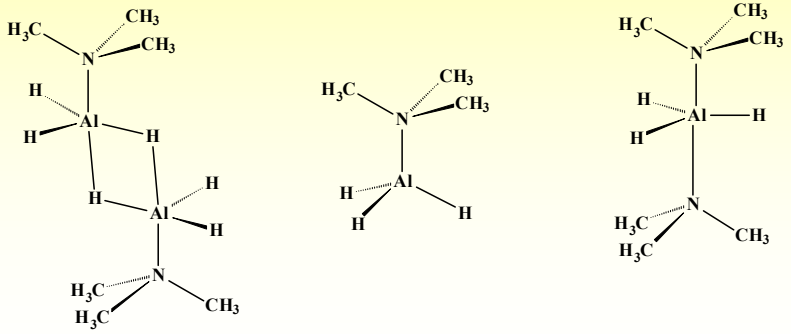
DMAH = Dimethylaluminum hydride
Ligand redistribution

$$[(CH_3)_2AlH]_3 \rightarrow (CH_3)_3Al + AlH_3$$

$$AlH_3 \rightarrow Al + H_2$$ **at 280 °C, low carbon incorporation**

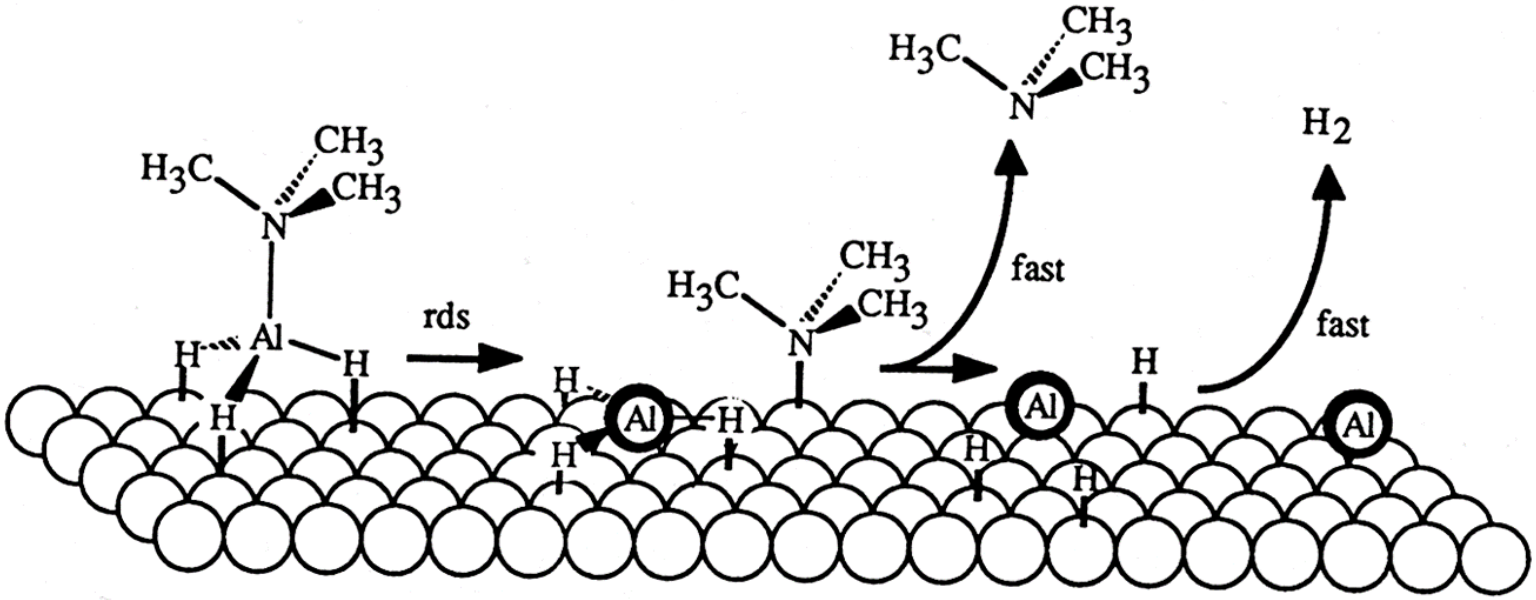
CVD of Al

TMAA = Trimethylammine-alane



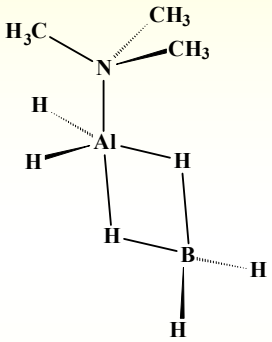
Decomposition mechanism of TMAA on Al – below 100 °C

$$(CH_3)_3N\text{-}AlH_3 \rightarrow Al + (CH_3)_3N + 3/2\ H_2$$

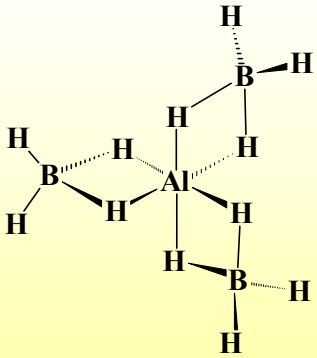


CVD of Al

Aluminoboranes



$$(CH_3)_3N\text{-}BH_3 + Al + 3/2\ H_2$$



$$3/2\ B_2H_6 + Al + 3/2\ H_2$$

CVD of W

Tungsten

5.6 $\mu\Omega$ cm, a high resistance to electromigration, the highest mp of all metals 3410 °C

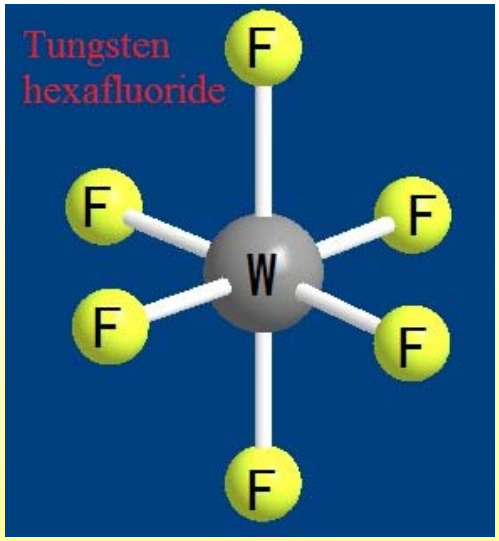
Tungsten hexafluoride (WF_6) is the heaviest known gas at room temperature and pressure, density = 13 g/L
Purity 99.999%, extremely corrosive and toxic

$$2\ WF_6 + 3\ Si \rightarrow 2\ W + 3\ SiF_4$$

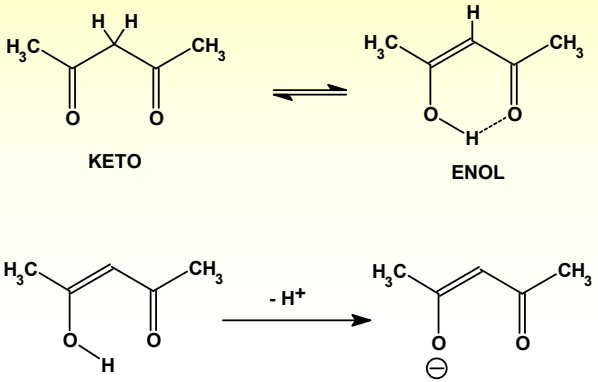
$$WF_6 + 3\ H_2 \rightarrow W + 6\ HF$$

$$WF_6 + 3/2\ SiH_4 \rightarrow W + 3\ H_2 + 3/2\ SiF_4$$

$$W(CO)_6 \rightarrow W + 6\ CO$$

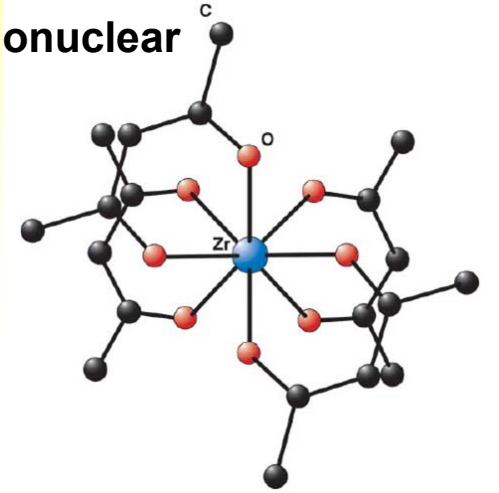


Diketonate Precursors

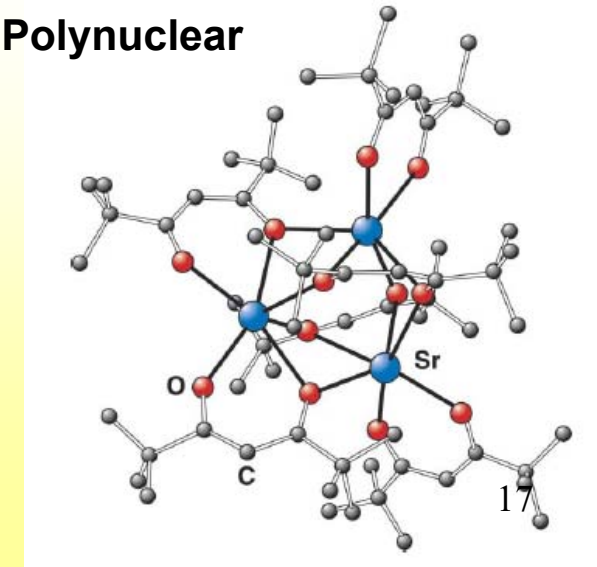


R_1	R_2	Name	Abbreviation
CH_3	CH_3	Pentane-2,4-dionate (acetylacetonate)	acac
CH_3	CF_3	1,1,1-trifluoropentane-2,4-dionate (trifluoroacetylacetonate)	tfac
CF_3	CF_3	1,1,1,5,5,5-hexafluoropentane-2,4-dionate (hexafluoroacetylacetonate)	hfac
CH_3	$C(CH_3)_3$	1,1-dimethylhexane-3,5-dionate	dhd
$C(CH_3)_3$	$C(CH_3)_3$	2,2,6,6-tetramethylheptane-3,5-dionate	thd
CH_3	$CH_2CH(CH_3)_2$	6-methylheptane-2,4-dionate	mhd
$C(CH_3)_3$	$CH_2CH(CH_3)_2$	2,2,7-trimethyloctane-3,5-dionate	tmod
C_6H_5	C_6H_5	1,3-diphenylpropane-1,3-dionate (dibenyzoylmethanate)	dbm

Mononuclear

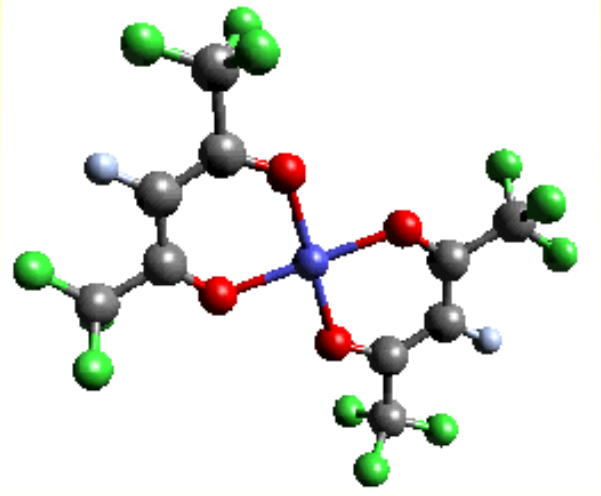


Polynuclear



CVD of Cu

Copper(II) hexafluoroacetylacetonate



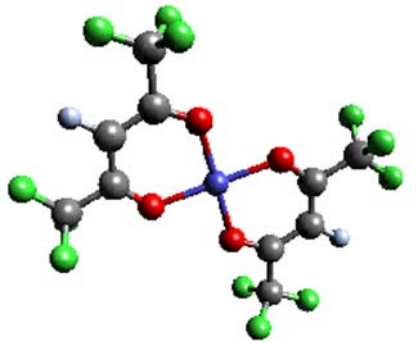
Excellent volatility
CF_3 groups (low polarizibility)
Vapor pressure of 0.06 Torr at r. t.
Low decomposition temperature
Stability in air, low toxicity
Commercial availability

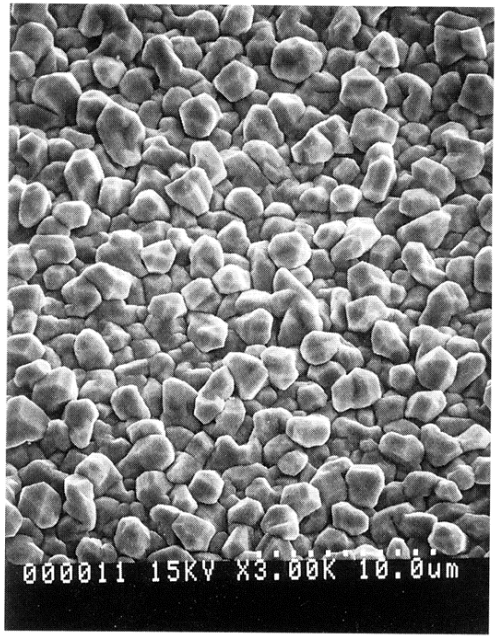
Deposition on metal surfaces (Cu, Ag, Ta)
The first step can already occur at -150 °C
= a dissociation of the precursor molecules on the surface

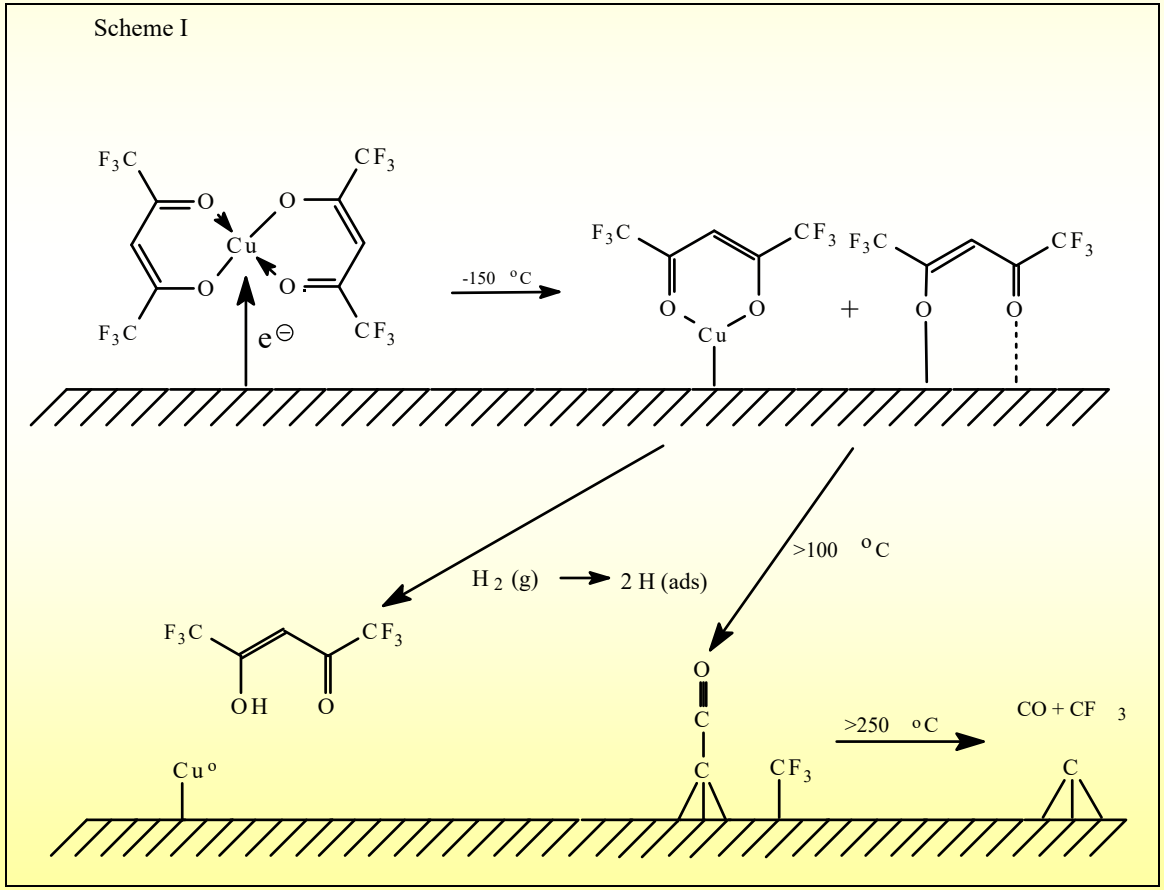
An electron transfer from a metal substrate to the single occupied HOMO, which has an anti-bonding character with respect to copper d_{xy} and oxygen p orbitals, weakens the Cu-O bonds and facilitates their fission

CVD of Cu

Copper(II) hexafluoroacetylacetonate

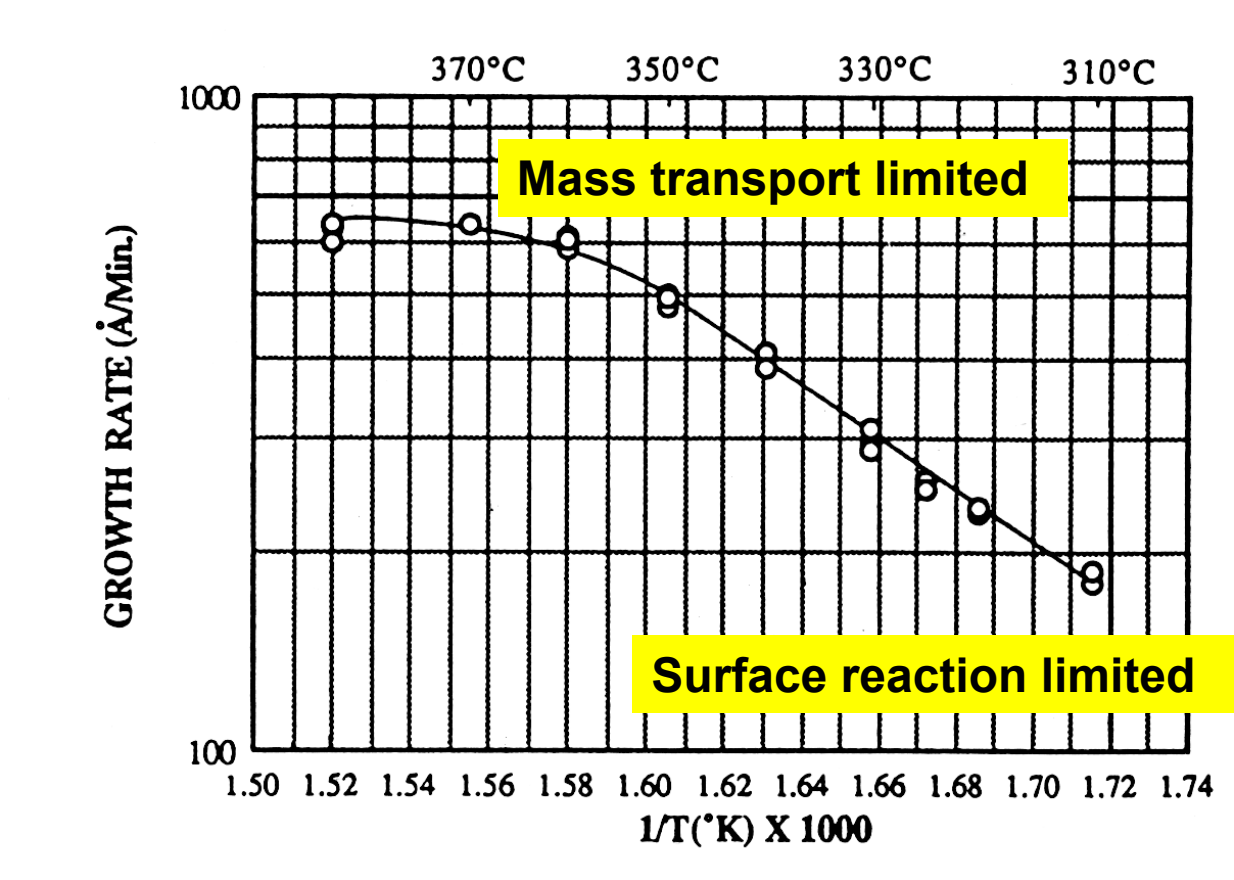






CVD of Cu

Growth rate of Cu films deposited from $Cu(hfacac)_2$ with 10 torr of H_2

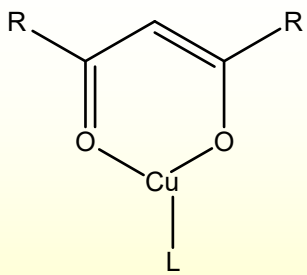


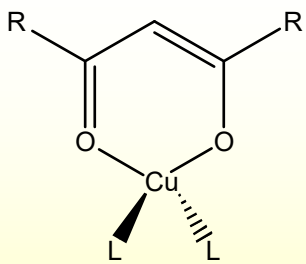
CVD of Cu

Cu(I) Precursors

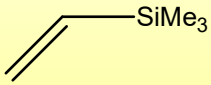
Disproportionation to Cu(0) and Cu(II)

$$2\ Cu(diketonate)L_n \rightarrow Cu + Cu(diketonate)_2 + n\ L$$

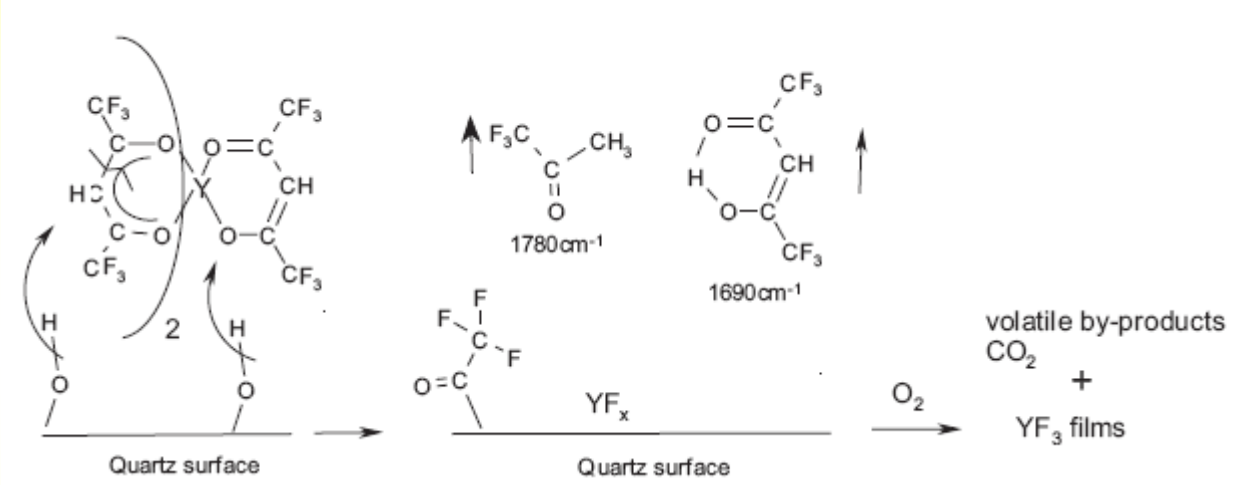


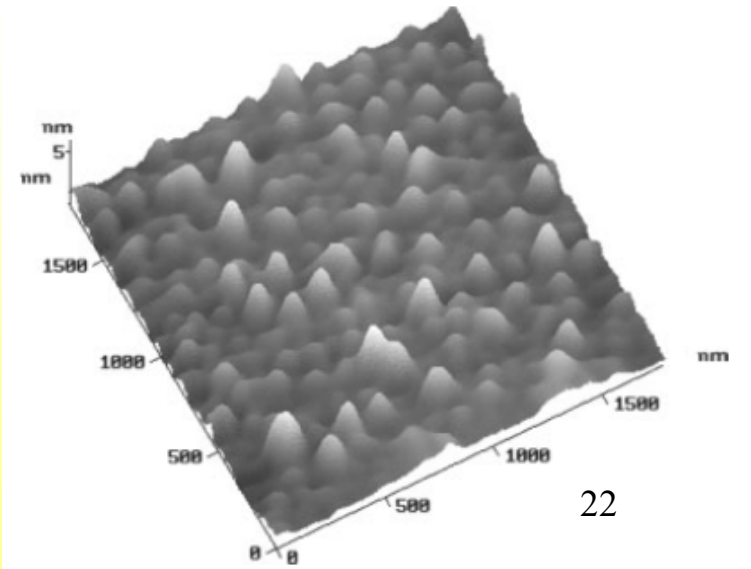


L: PMe_3, PEt_3, CO, CN^tBu,



CVD of YF_3 from $Y(hfacac)_3$ Complex



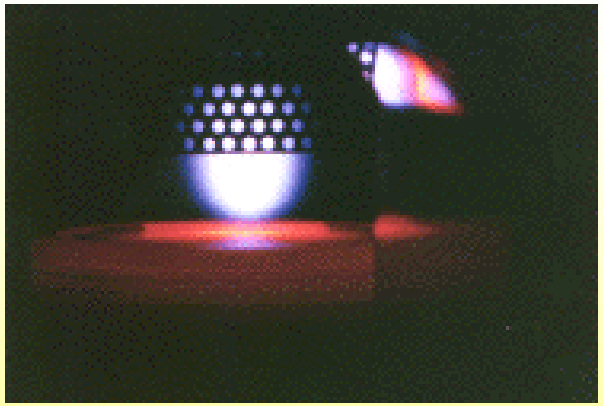


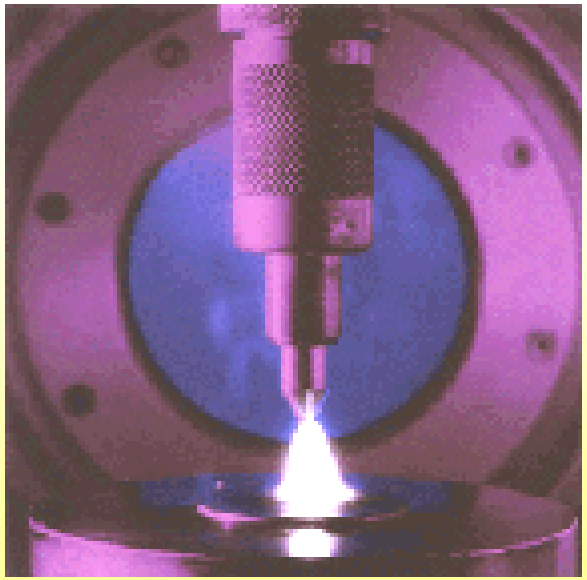
CVD of Diamond

Diamond films

Activating gas-phase carbon-containing precursor molecules:

- **Thermal (*e.g.*, hot filament)**
- **Plasma (D.C., R.F., or microwave)**
- **Combustion flame (oxyacetylene or plasma torches)**





CVD of Diamond

Experimental conditions:

Temperature 1000 - 1400 K

The precursor gas diluted in an excess of H_2

Typical CH_4 mixing ratio ~1-2 vol%

Deposited films are polycrystalline

Film quality:

- **the ratio of sp^3 (diamond) to sp^2-bonded (graphite) carbon**
- **the composition (*e.g.*, C-C versus C-H bond content)**
- **the crystallinity**

Combustion methods: high rates (100-1000 μm/hr), small, localised areas, poor quality films

Hot filament and plasma methods: slower growth rates (0.1-10 μm/hr), high quality films

CVD of Diamond

Hydrogen atoms generated by activation (thermally or via electron bombardment)
H-atoms play a number of crucial roles in the CVD process:

H abstraction reactions with hydrocarbons, highly reactive radicals: CH_3 (stable hydrocarbon molecules do not react to cause diamond growth) Radicals diffuse to the substrate surface and form C-C bonds to propagate the diamond lattice

H-atoms terminate the 'dangling' carbon bonds on the growing diamond surface - prevent cross-linking and reconstructing to a graphite-like surface

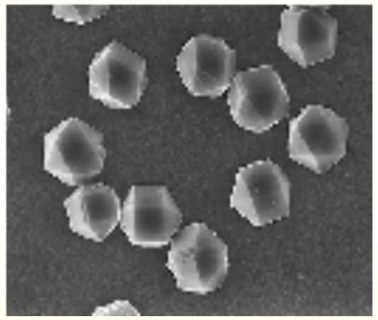
Atomic hydrogen etches both diamond and graphite - under CVD conditions, the rate of diamond growth exceeds its etch rate whilst for graphite the converse is true

This is the basis for the preferential deposition of diamond rather than graphite

CVD of Diamond

Diamond initially nucleates as individual microcrystals,

which then grow larger until they coalesce into a continuous film



Enhanced nucleation by ion bombardment:

- **Damage the surface - more nucleation sites**
- **Implant ions into the lattice**
- **Form a carbide interlayer - glue, promotes diamond growth, aids adhesion**

CVD of Diamond

Substrates: metals, alloys, and pure elements:

Little or no C Solubility or Reaction: Cu, Sn, Pb, Ag, and Au, Ge, sapphire, diamond, graphite

C Diffusion: Pt, Pd, Rh, Fe, Ni, and Ti
The substrate acts as a carbon sink, deposited carbon dissolves into the metal surface, large amounts of C transported into the bulk,
a temporary decrease in the surface C concentration, delaying the onset of nucleation

Carbide Formation: Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, Co, Ni, Y, Al
B, Si, SiO_2, quartz, Si_3N_4 also form carbide layers
SiC, WC, and TiC

Applications of Diamond Films

Thermal management - a heat sink for laser diodes, microwave integrated circuits, active devices mounted on diamond can be packed more tightly without overheating

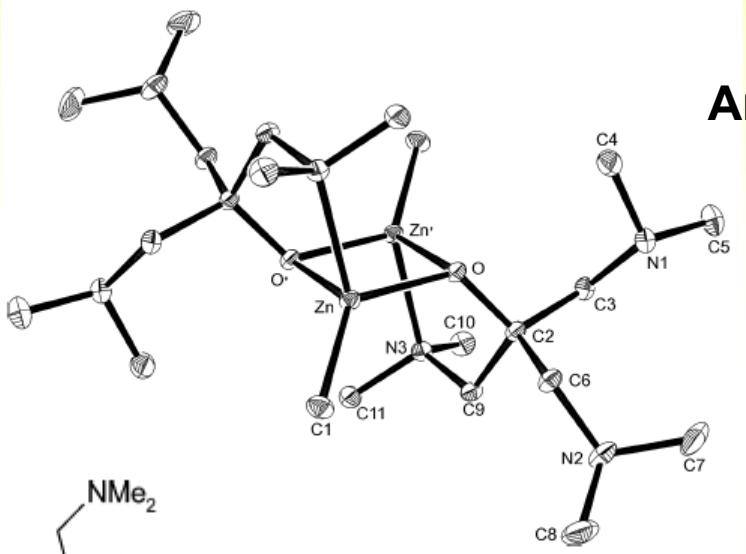
Cutting tools - an abrasive, a coating on cutting tool inserts
CVD diamond-coated tools have a longer life, cut faster and provide a better finish than conventional WC tool bits

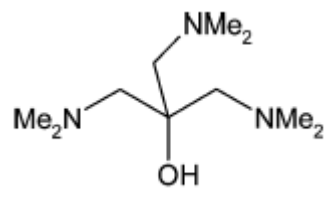
Wear Resistant Coatings - protect mechanical parts, reduce lubrication
gearboxes, engines, and transmissions

Optics - protective coatings for infrared optics in harsh environments
ZnS, ZnSe, Ge: excellent IR transmission but brittle
the flatness of the surface, roughness causes attenuation and scattering of the IR signal

Electronic devices - doping, an insulator converted into a semiconductor
***p*-doping: B_2H_6 incorporates B into the lattice**
doping with atoms larger than C very difficult, *n*-dopants such as P or As, cannot be used for diamond, alternative dopants, such as Li

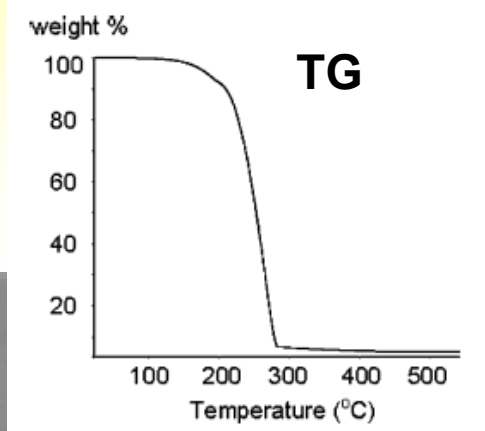
CVD of ZnO

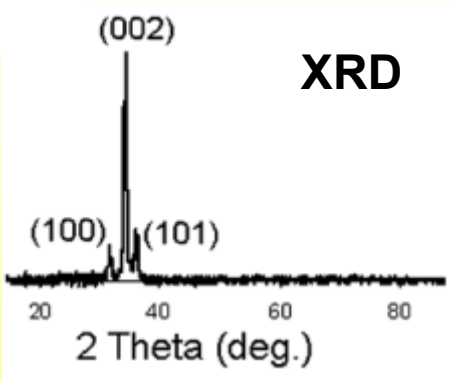




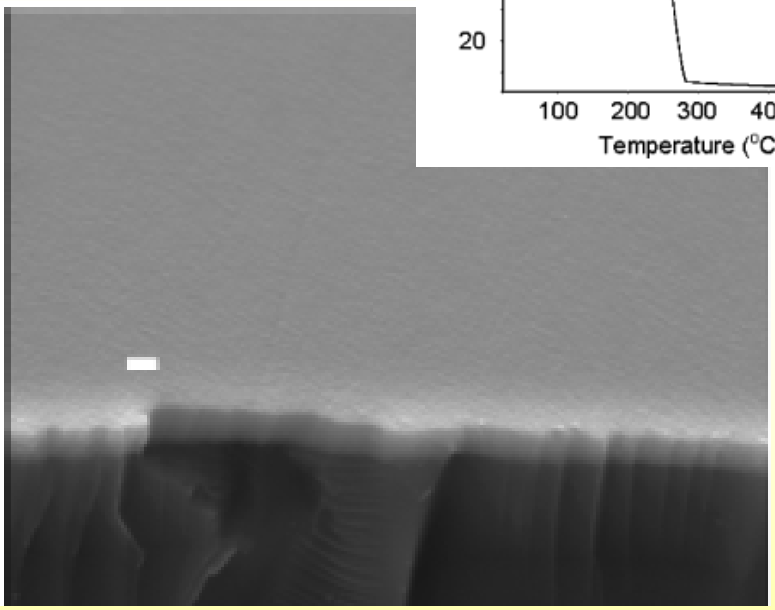
Aminoalcoholates

500 °C, 1 h



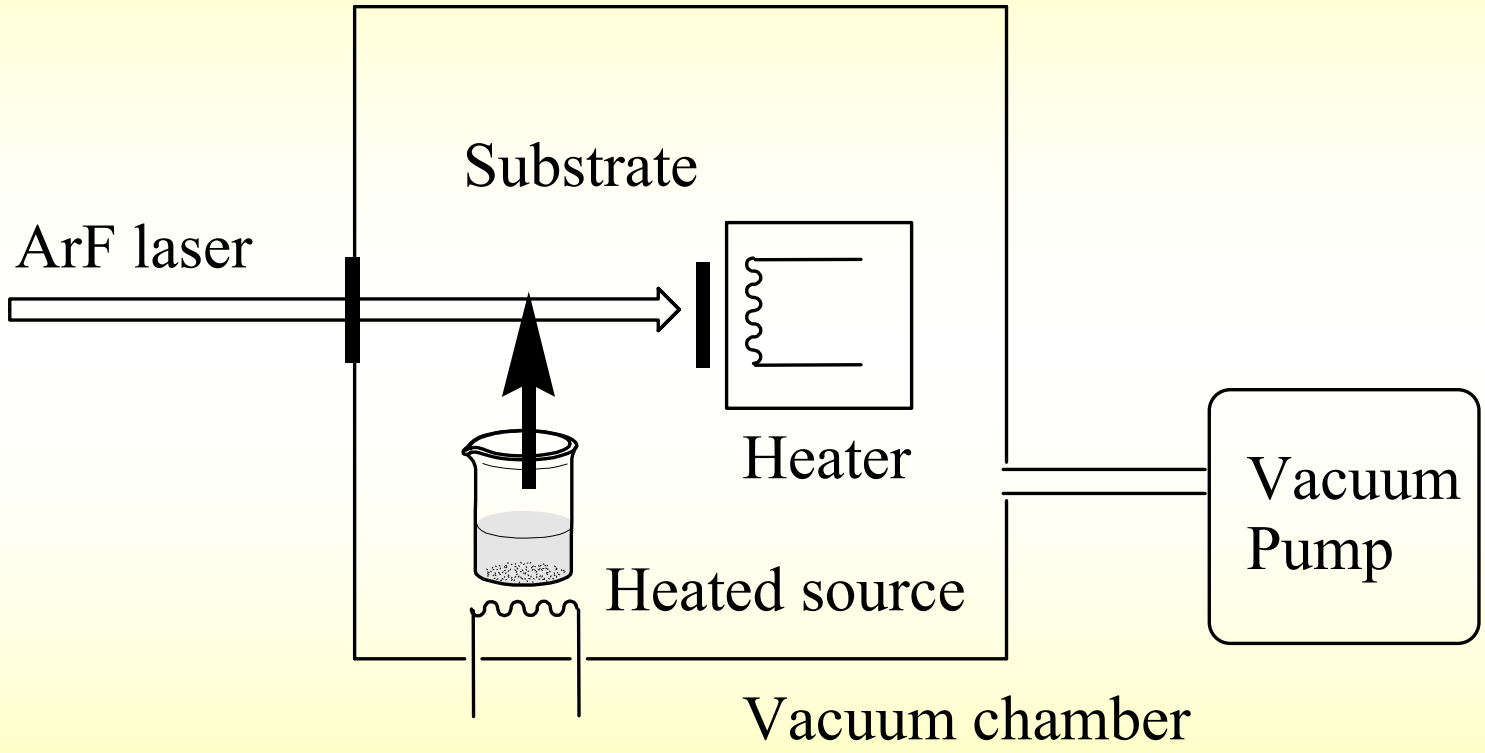


Hexagonal ZnO PDF 79-0208



SEM of the ZnO film
Bar = 1 µm

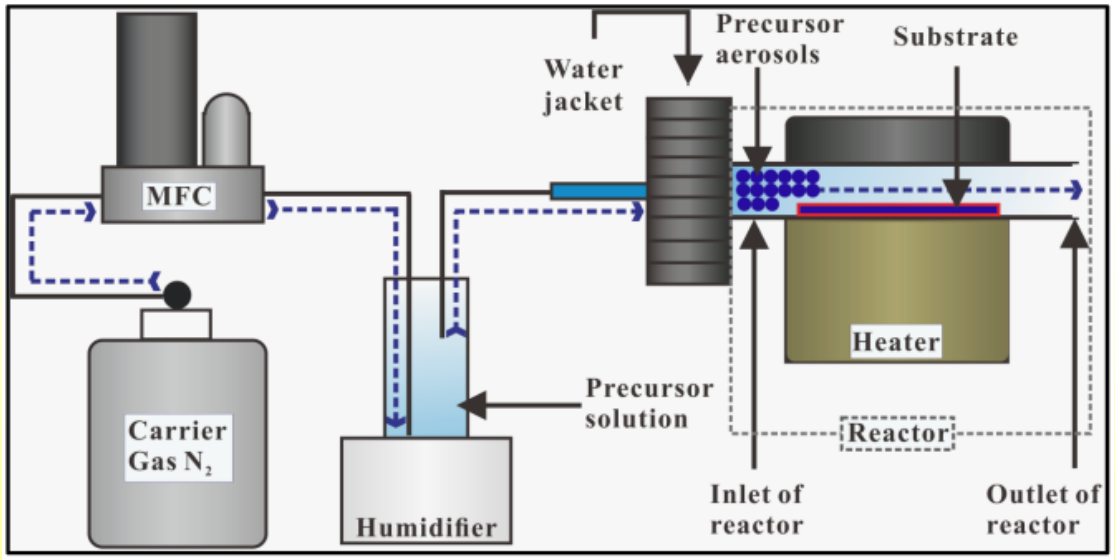
Laser-Enhaced CVD



$$Si(O_2CCH_3)_4 \rightarrow SiO_2 + 2\ O(OCCH_3)_2$$

Aerosol-Assited CVD

Carried out at atmospheric pressure
Non-volatile precursors
Formation of droplets in ultrasonic nebulizer / atomizer
Precursor aerosol delivered by the stream of carrier gas to reactor
Solvent evaporation



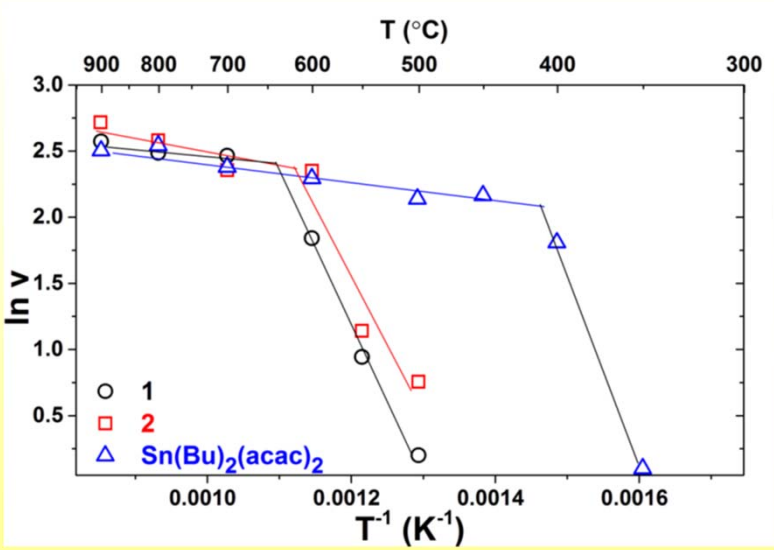
Pulsed Injection MOCVD

Low-pressure hot-wall reactor - vacuum 10 Torr
A pulsed liquid injection system - electromagnetic injector
A metal-organic precursor dissolved in a solvent (DME)
Precise micro-doses (several μL, frequency 2 Hz)
A hot (200 °C) evaporation zone - flash evaporation of micro-doses
A mixture of precursor and solvent vapors carried into the deposition zone with a Ar:O_2 (4:1) gas mixture
Depositions on sapphire-C substrates at 350 - 900 °C

$Sn(OtBu)_2(PyTFP)_2$ (1)

$Sn(OtBu)_2(DMOTFP)_2$ (2)

$Sn(Bu)_2(acac)_2$

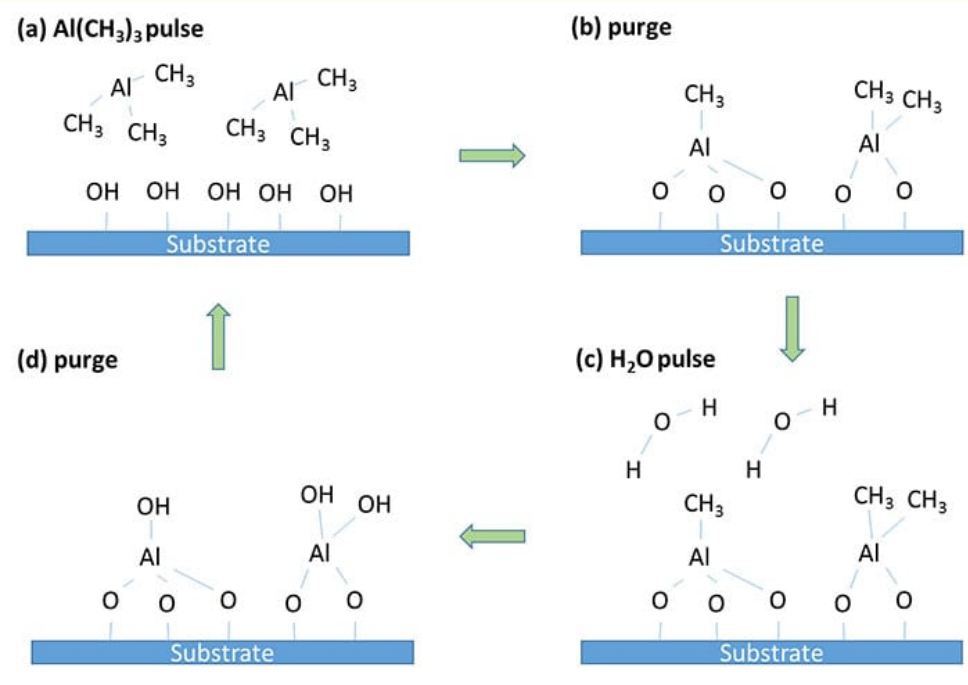


Atomic Layer Deposition ALD

A method for the deposition of thin films

Film growth by cyclic process
4 steps:

1) Exposition by 1st precursor
2) Cleaning of the reaction chamber
3) Exposition by 2nd precursor
4) Cleaning of the reaction chamber

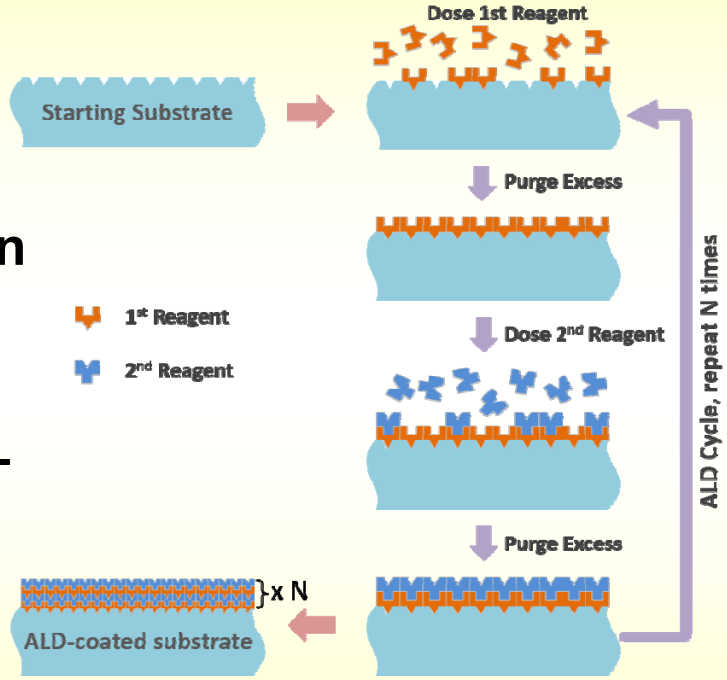


Cycle repetitions until desired film thickness is reached

1 cycle: 0.5 s – several sec. thickness 0.1- 3 Å

Atomic Layer Deposition ALD

- Requires high reactivity
- Self-Limiting growth mechanism
- Formation of a monolayer
- Control of film thickness and composition
- Carried out at room temperature
- Reactor walls inactive – no reactive layer
- Separate loading of reactive precursors – no gas-phase reactions
- Deposition on large surface area
- Highly conformal coverage of surface
- Precursor transport to the reaction zone does not have to be highly uniform



Comparison of ALD and CVD

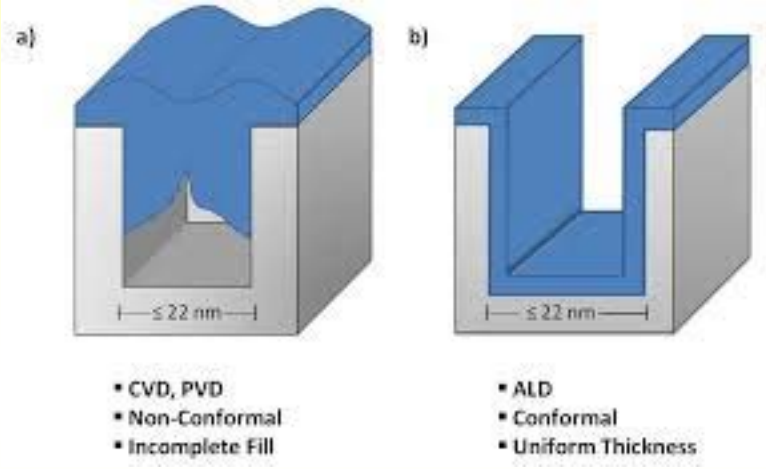
ALD

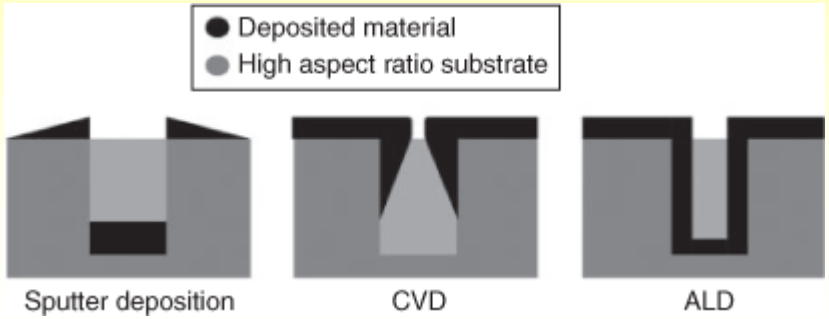
- Highly reactive precursors
- Precursors react separately on the substrate
- Precursors must not decompose at process temperature
- Uniformity ensured by the saturation mechanism
- Thickness control by the number of reaction cycles
- Surplus precursor dosing acceptable

CVD

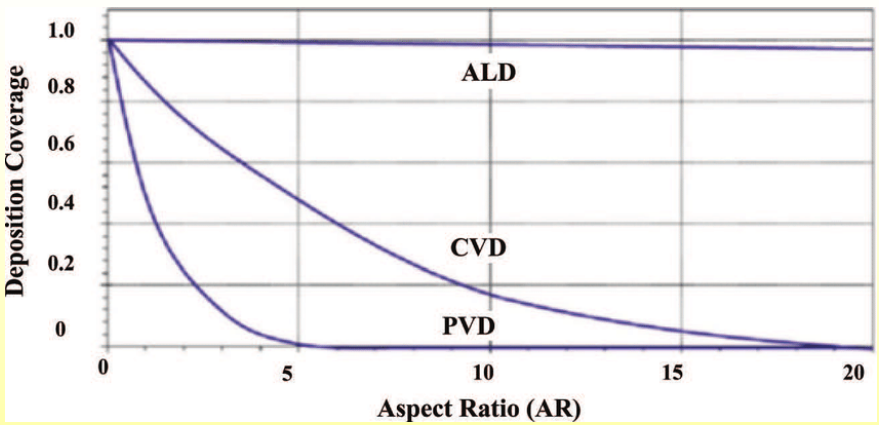
- Less reactive precursors
- Precursors react at the same time on the substrate
- Precursors can decompose at process temperature
- Uniformity requires uniform flux of reactant and T
- Thickness control by precise process control and monitoring of T, flow, time
- Precursor dosing important

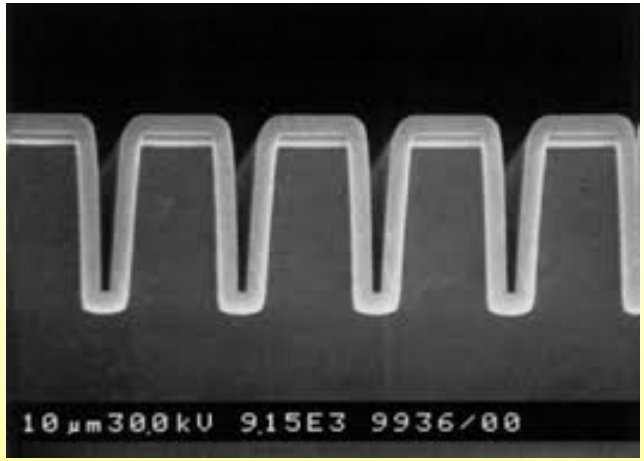
ALD vs. CVD vs. PVD Comparison





Conformal coverage improves





AR = the ratio of width to depth

ALD Precursor Properties

Selection of suitable combination of precursors
Molecular size influences film thickness
Gases, volatile liquids, solids with high vapor pressure

Typical precursors:

Metallic - halogenides (chlorides), alkyls, alkoxides, organometallics (cyclopentadienyl complexes), alkyl amides

Nonmetallic - water, hydrogen peroxide, ozone, hydrides, ammonia, hydrazine, amines

Thermally stable

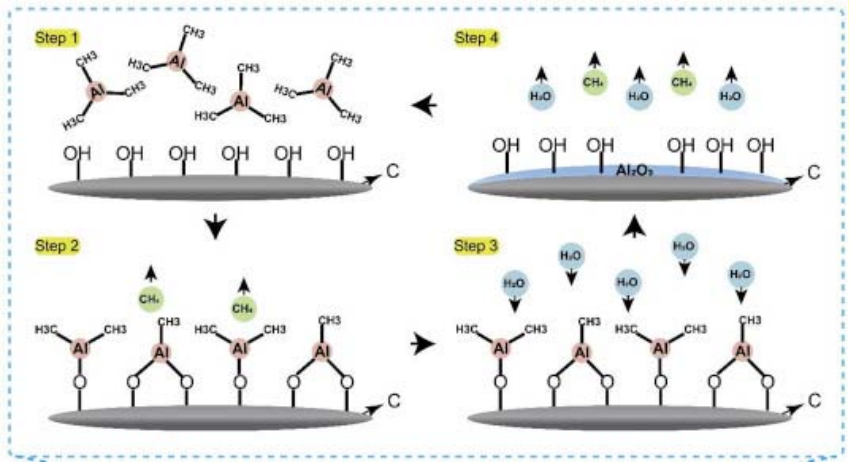
Must react with surface centers (hydroxyl groups on oxide surface)

Thermodynamics – Kinetics – Mechanisms

Examples of ALD

High-permitivity Oxides

- $Al(CH_3)_3$ / H_2O
- $ZrCl_4$ / H_2O
- $HfCl_4$ / H_2O



DRAM capacitors

- $(Ba,Sr)TiO_3$ – Sr and Ba cyclopentadienyl compounds and water as precursors

Nitrides of transition metals

- TiN - $TiCl_4$ and NH_3
- TaN - $TaCl_5$ / Zn / NH_3
- WN - WF_6 and NH_3
- WC_xN_y

Examples of ALD

Metallic films

Difficult by ALD: metal surface has no reaction sites,
low reactivity with reducing agents

W - WF_6 and Si_2H_6

Ru, Pt - organometallic precursors and oxygen
applies to all precious metals capable of catalytic dissociation of O_2

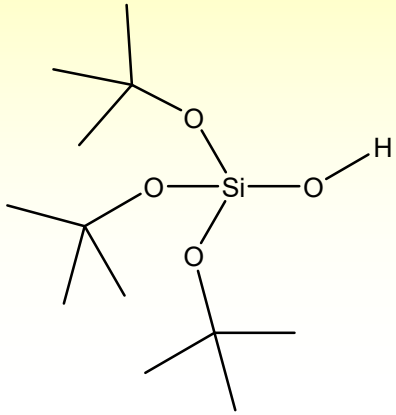
Ni, Cu – metal oxide reduction by hydrogen radicals formed in plasma

Al – direct reduction of $AlMe_3$ by H radicals from plasma

ALD of SiO_2 and Al_2O_3 Films

Precursors:

- **Trimethylalane**
- **Tris(tert-butoxy)silanol**



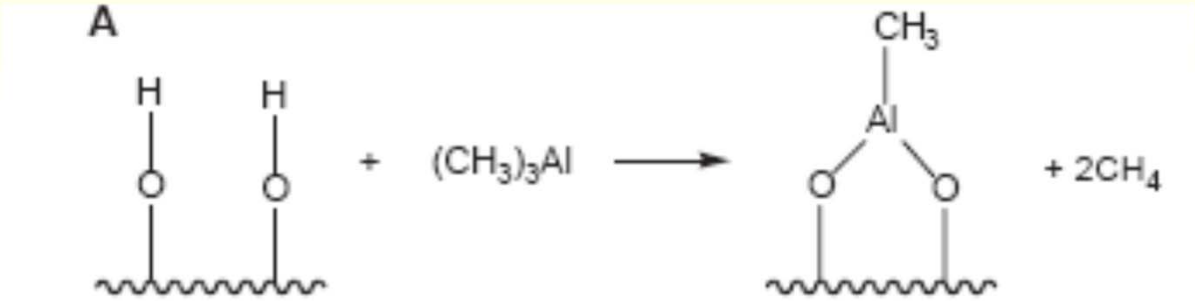
Deposition of amorphous SiO_2 and nanolaminates of Al_2O_3
32 monolayers in 1 cycle

Applications:

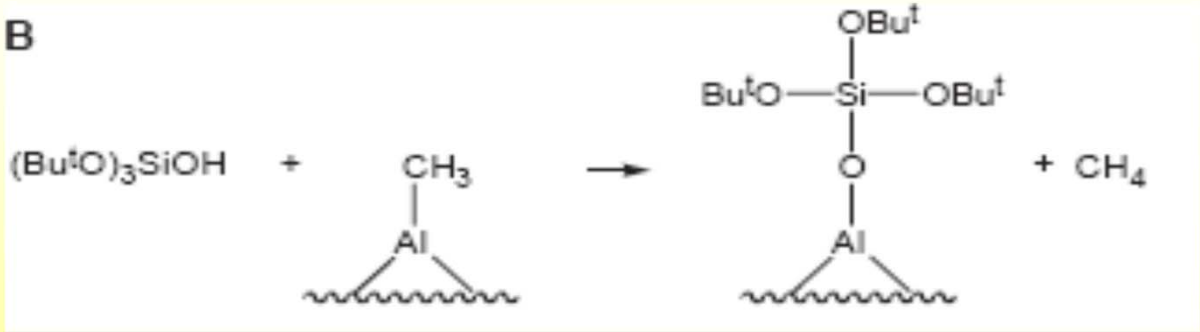
- **microelectronics**
- **optical filters**
- **protective layers (against diffusion, oxidation, corrosion)**

ALD of SiO_2 and Al_2O_3 Films

Step A

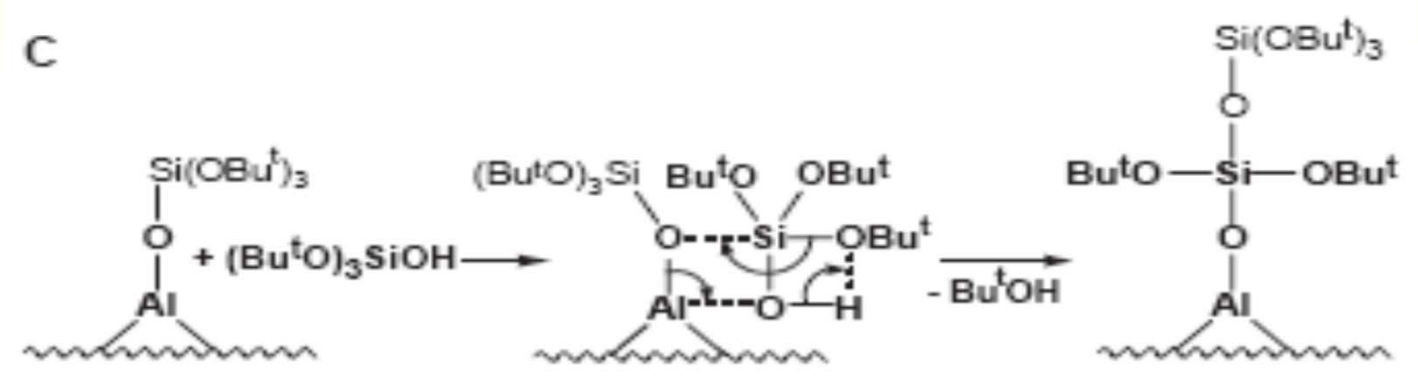


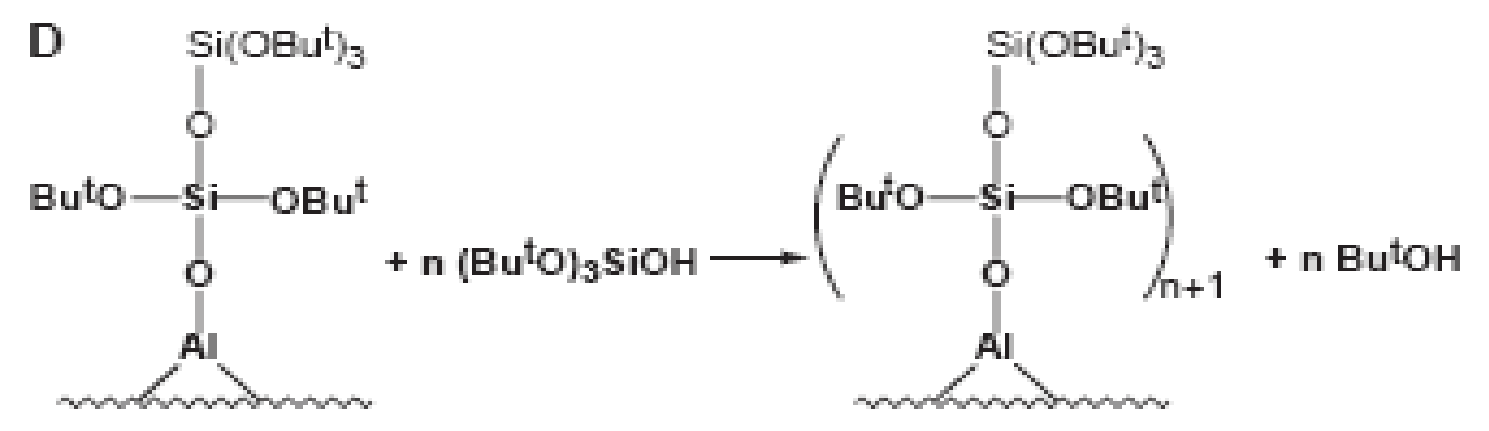
Step B



ALD of SiO_2 and Al_2O_3 Films

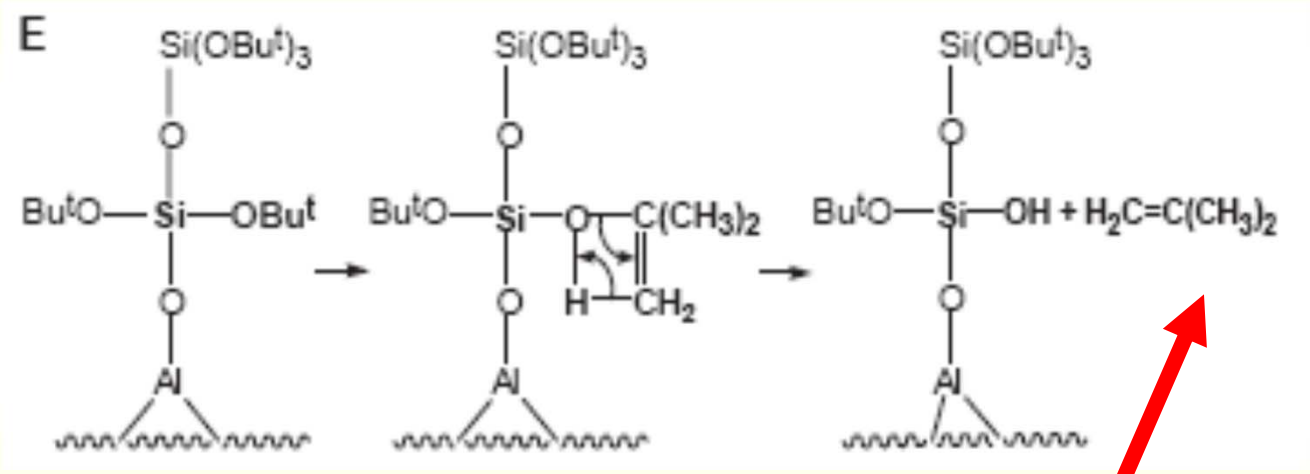
C, D: alkoxide - siloxide exchange

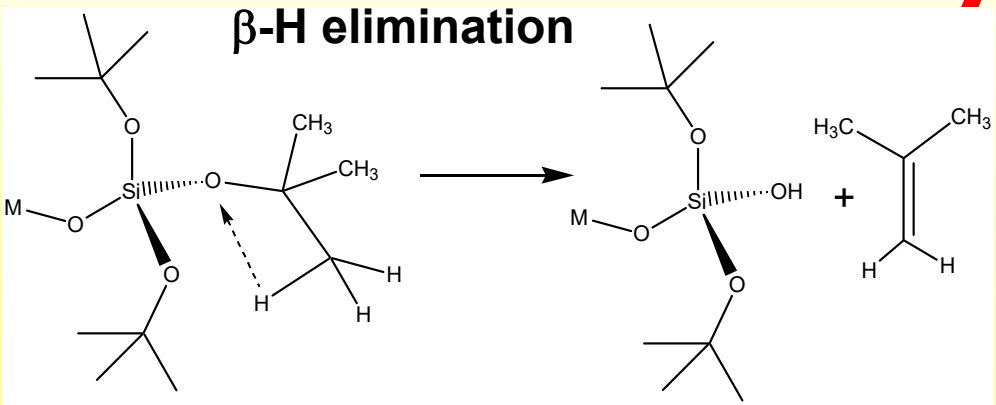




ALD of SiO_2 and Al_2O_3 Films

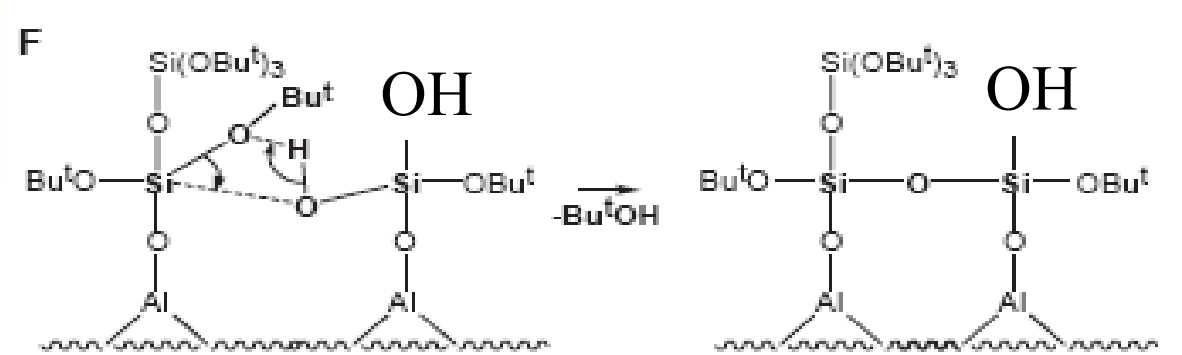
E: elimination of isobutene = formation of -OH



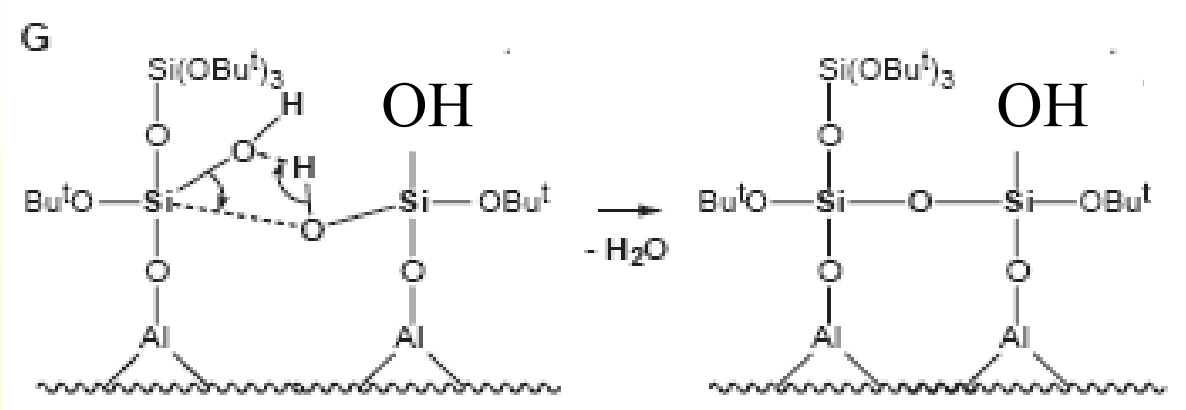


ALD of SiO_2 and Al_2O_3 Films

F: elimination of butanol = condensation

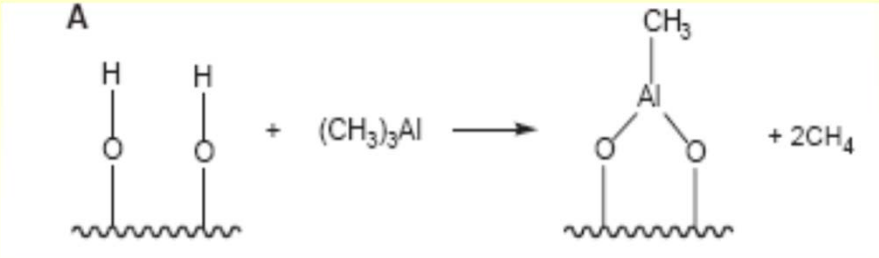


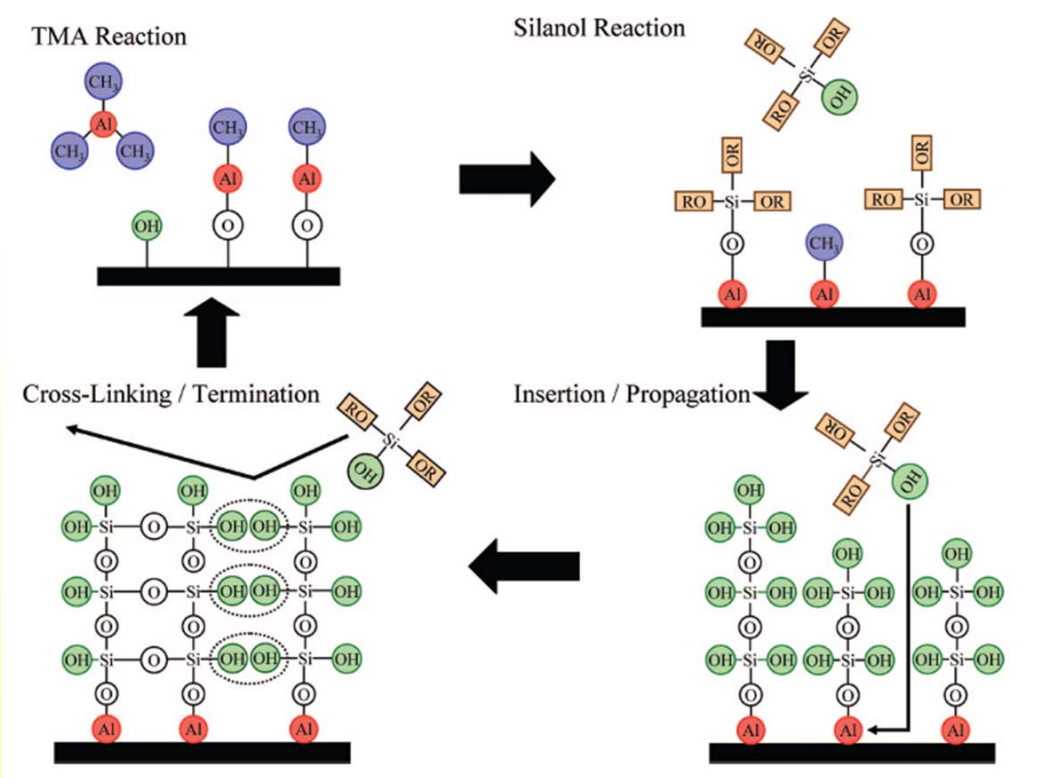
G: elimination of water = condensation



ALD of SiO_2 and Al_2O_3 Films

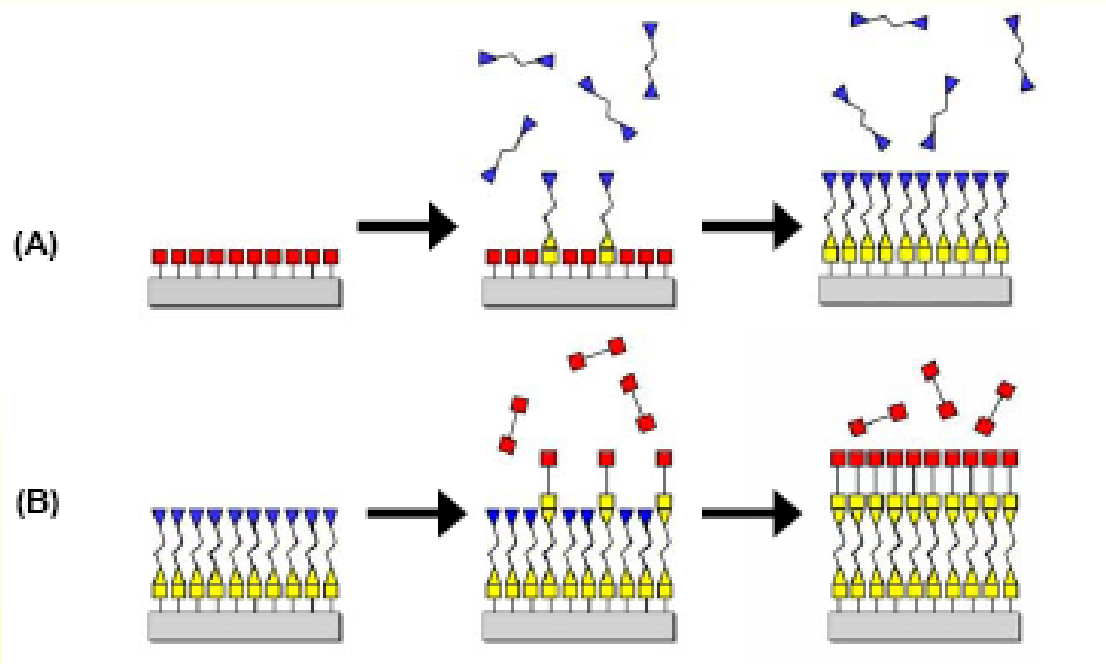
Repeat Step A





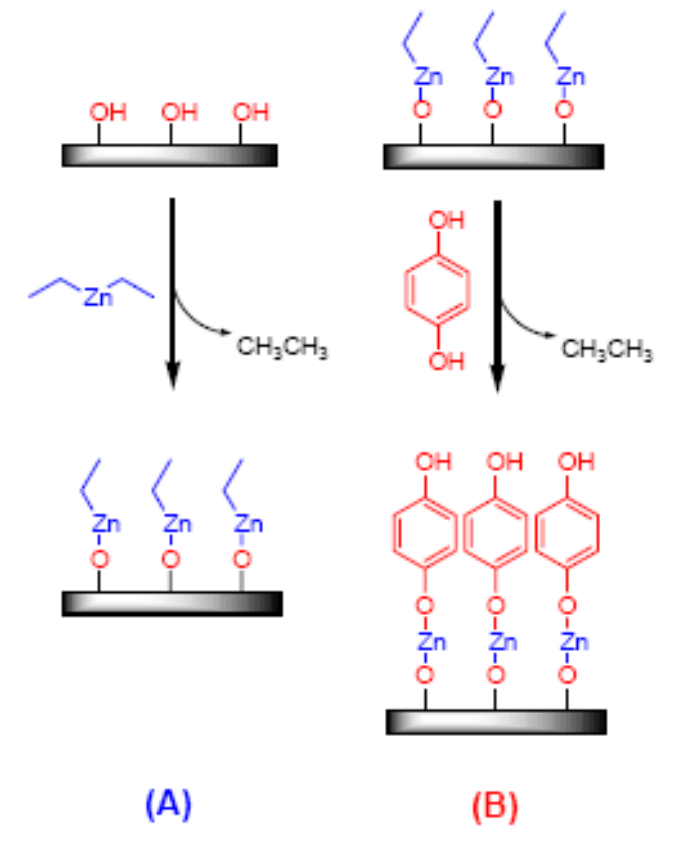
Molecular Layer Deposition MLD

Sequential, self-limiting reactions A and B for MLD growth using two homobifunctional reactants

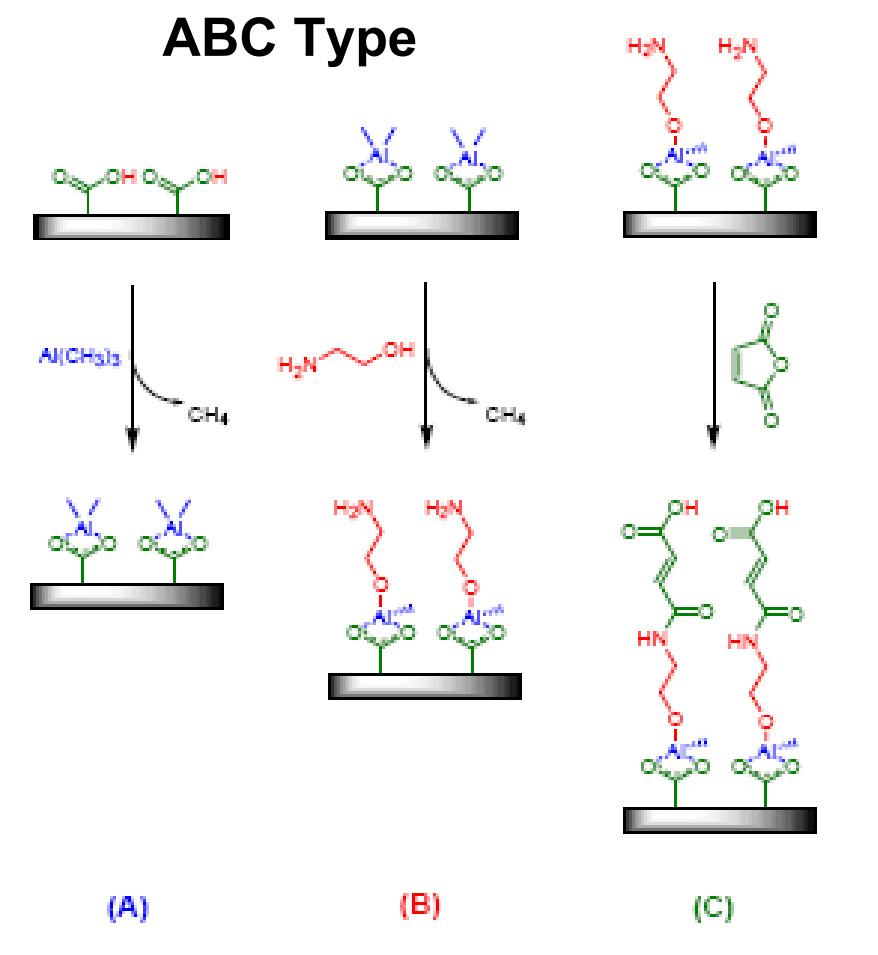


Molecular Layer Deposition MLD

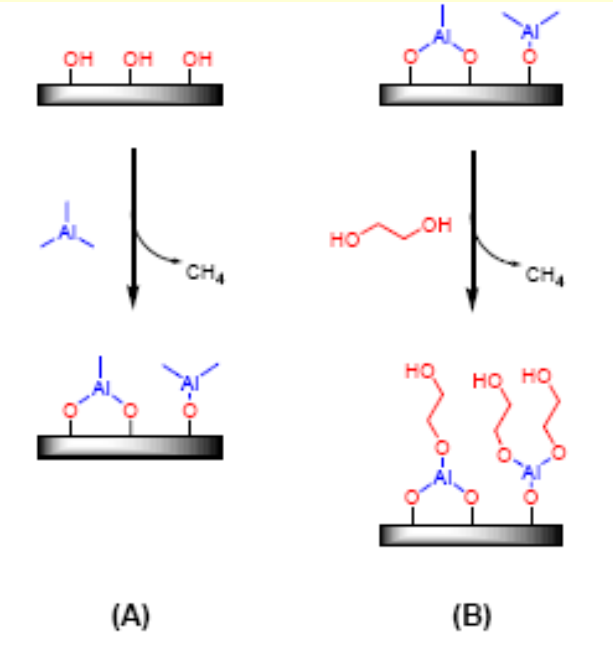
AB Type

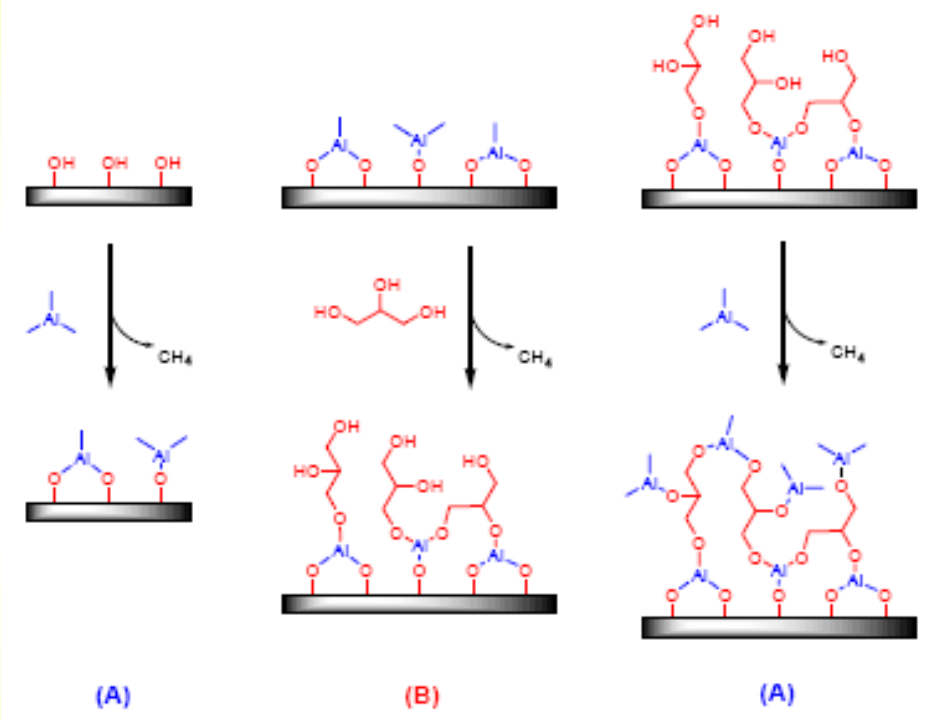


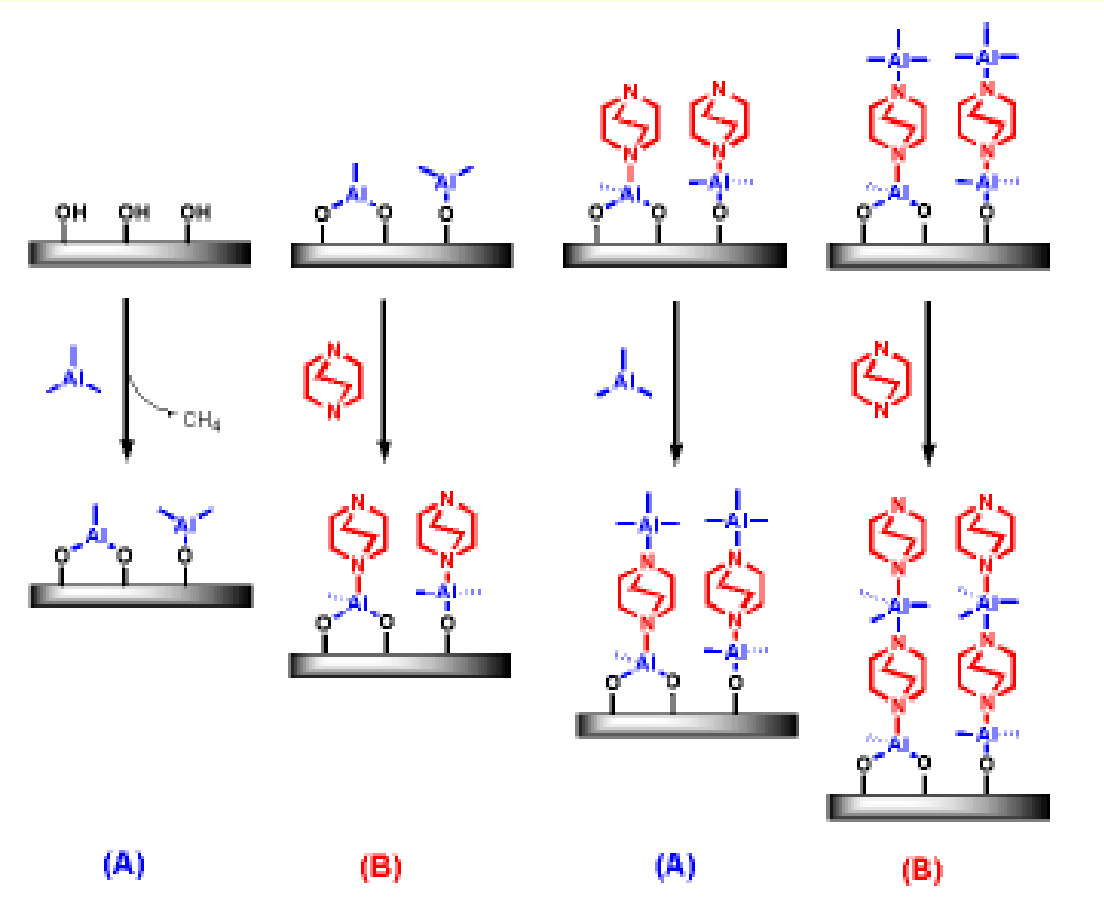
ABC Type



Diols vs. Polyols





Homobifunctional precursors can react twice with the $AlCH_3$* surface species, double reactions lead to a loss of reactive surface sites and decreasing growth rate

AB Lewis Acid-Lewis Base Reactions