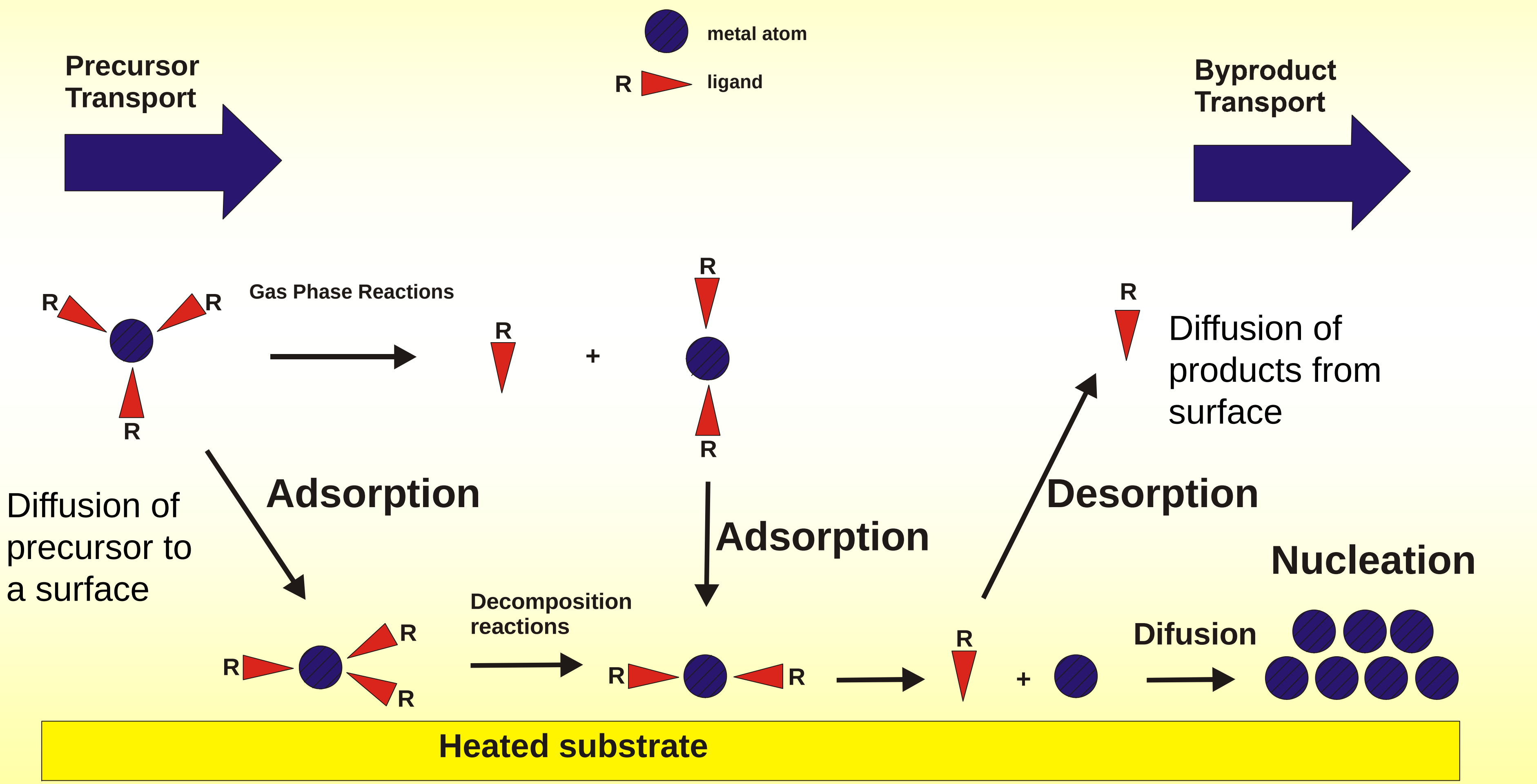
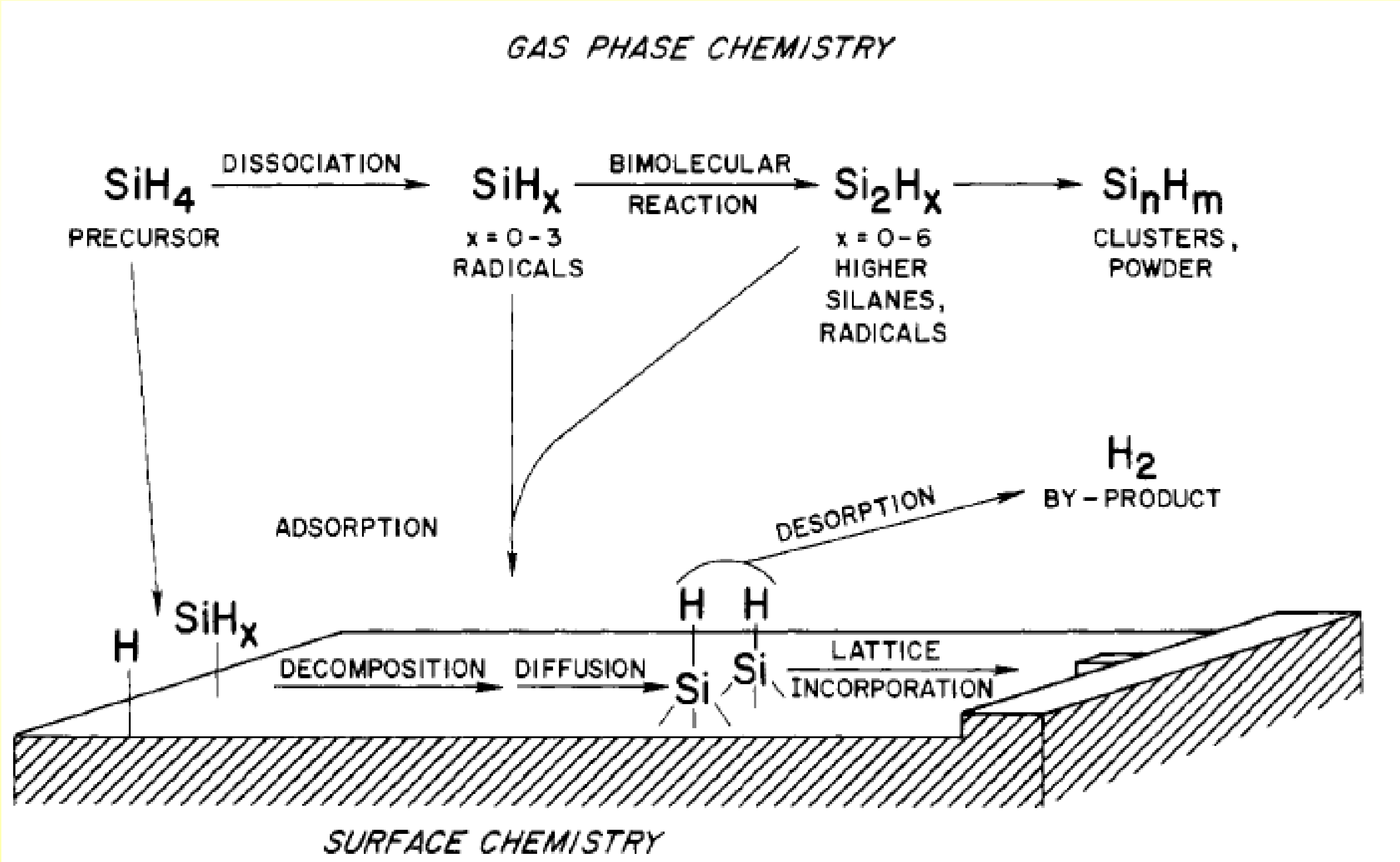
Basic steps in the CVD process

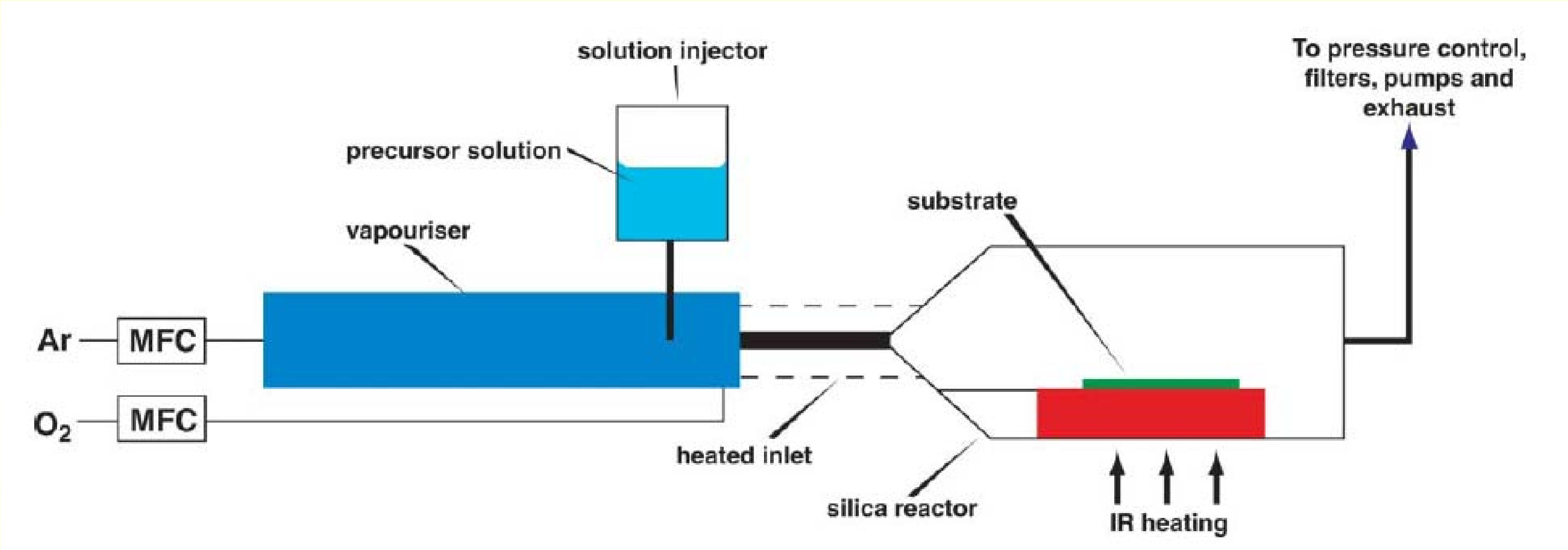


Silicon CVD



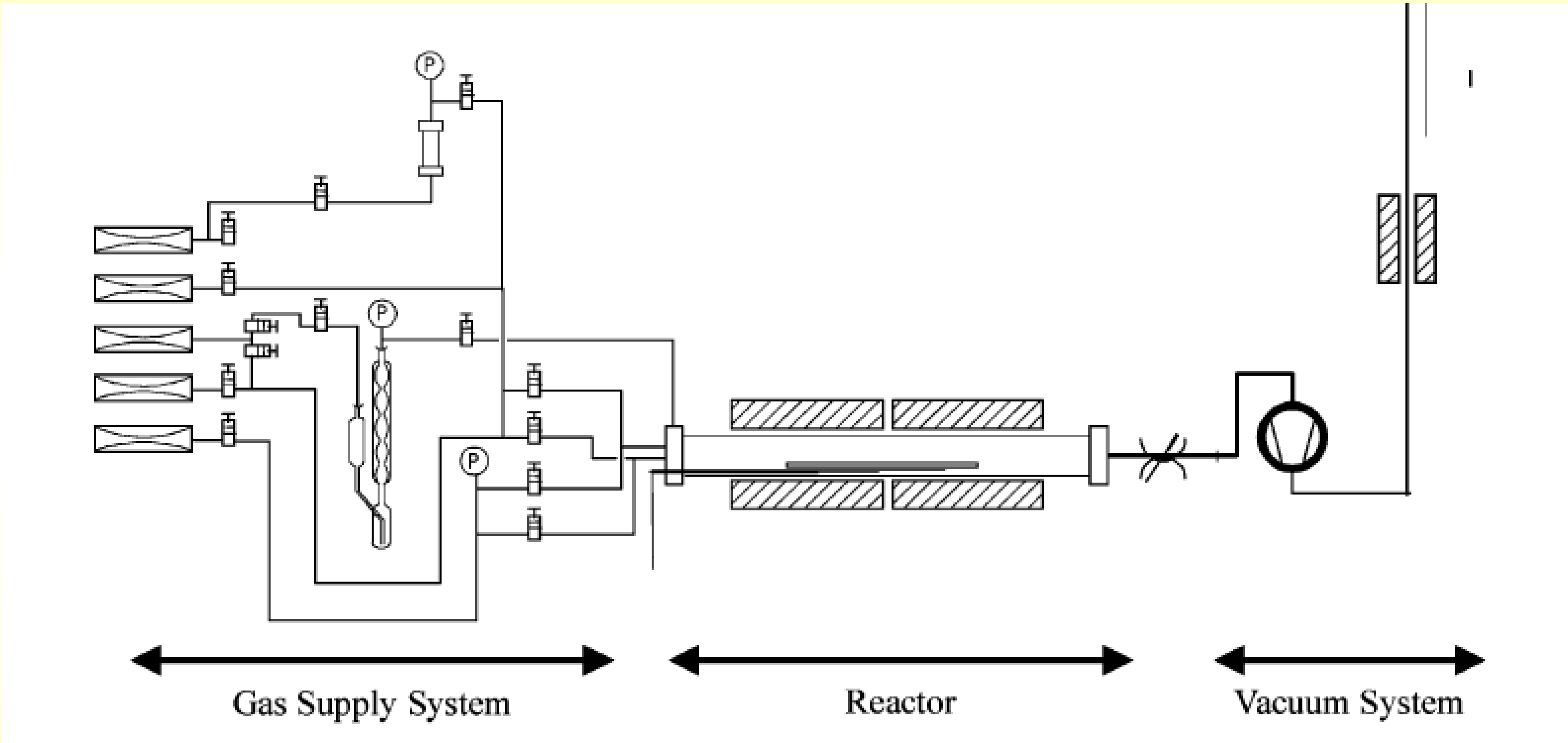
GAS PHASE CHEMISTRY
SiH4
PRECURSOR
DISSOCIATION
SiHx
x = 0 - 3
RADICALS
BIMOLECULAR
REACTION
Si2Hx
x = 0 - 6
HIGHER
SILANES,
RADICALS
SinHm
CLUSTERS,
POWDER
H2
BY - PRODUCT
DESORPTION
ADSORPTION
H
SiHx
H
H
DECOMPOSITION
DIFFUSION
Si
Si
LATTICE
INCORPORATION
SURFACE CHEMISTRY

CVD Reactor



Cold-wall reactor

CVD Reactor



Hot-wall reactor

CVD Kinetics

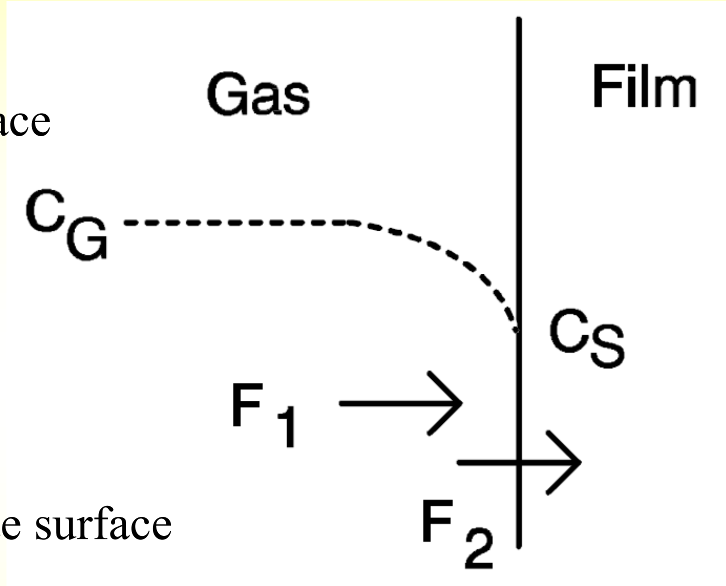
Deposition depends on the sequence of events:

(1) Diffusion of precursor to surface
(2) Adsorption of precursor at surface
(3) Chemical reaction at surface
(4) Desorption of products from surface
(5) Diffusion of products from surface

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

CVD Kinetics

Growth Rate Model



F1 = precursor flux from bulk of gas to substrate surface

$F1 = h_G \cdot (C_G - C_S)$

h_G = mass-transfer coefficient $h_G = D / \delta$

D = gas diffusion constant $D = D_o T^{3/2} / P$

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)

F2 = flux consumed in film-growth reaction (rate of chemical reaction)

$F2 = k_S \cdot C_S$

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

Steady state

F1 = F2 = F

CVD Kinetics

Steady state
F1 = F2 = F

Growth Rate Model

F1 = F2 (rate of transport = rate of reaction)

$\mathbf{h_G \cdot (C_G - C_S) = k_S \cdot C_S}$

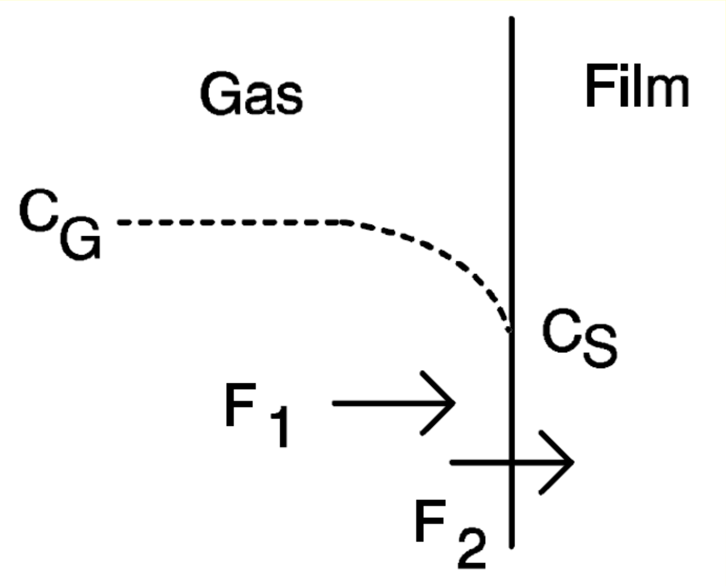
$C_S = C_G / (1 + k_S/h_G)$

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

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

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

Growth rate is determined by:

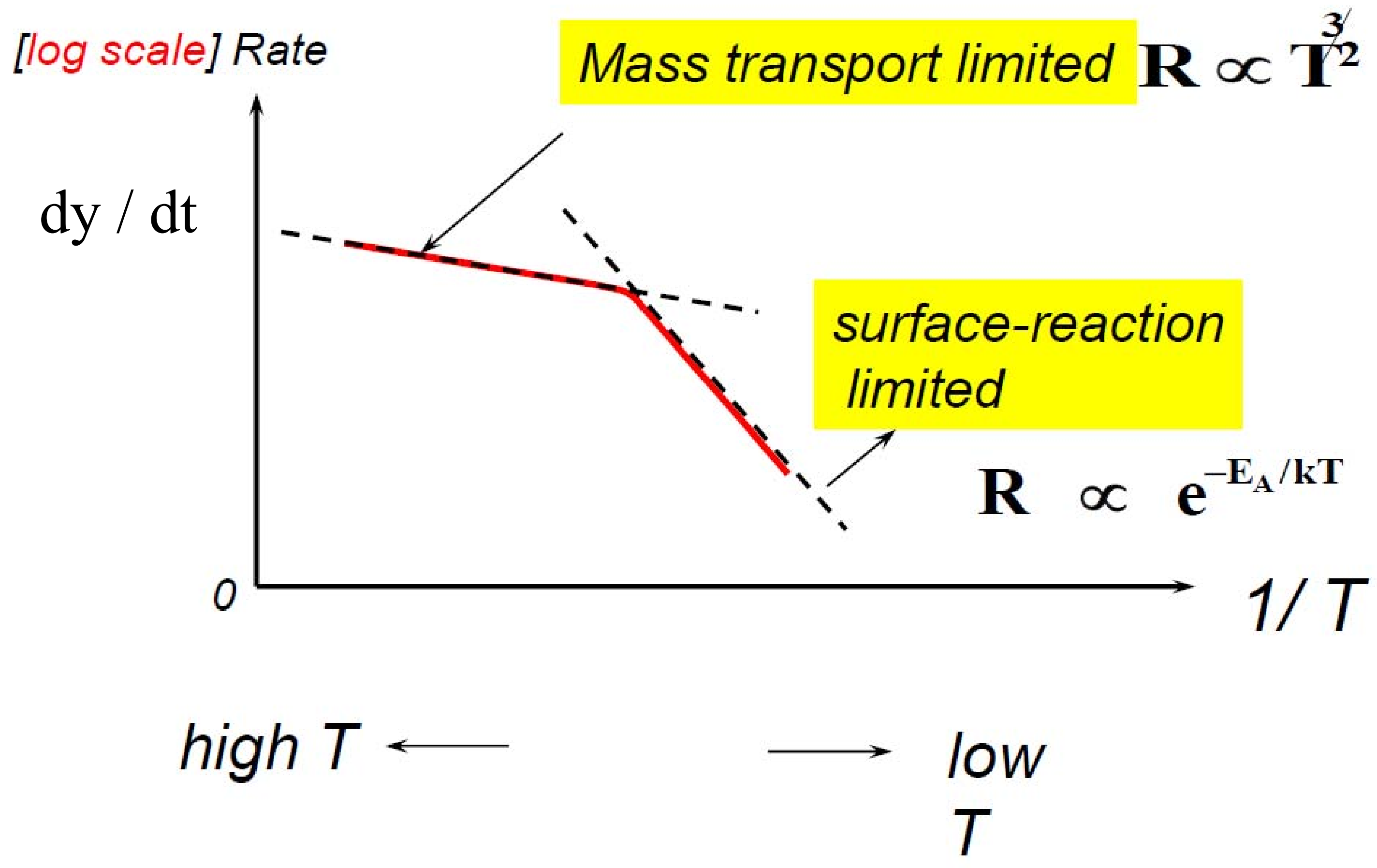
a) Concentration of a precursor in bulk of gas mixture

b) By the smaller of h_G and k_S

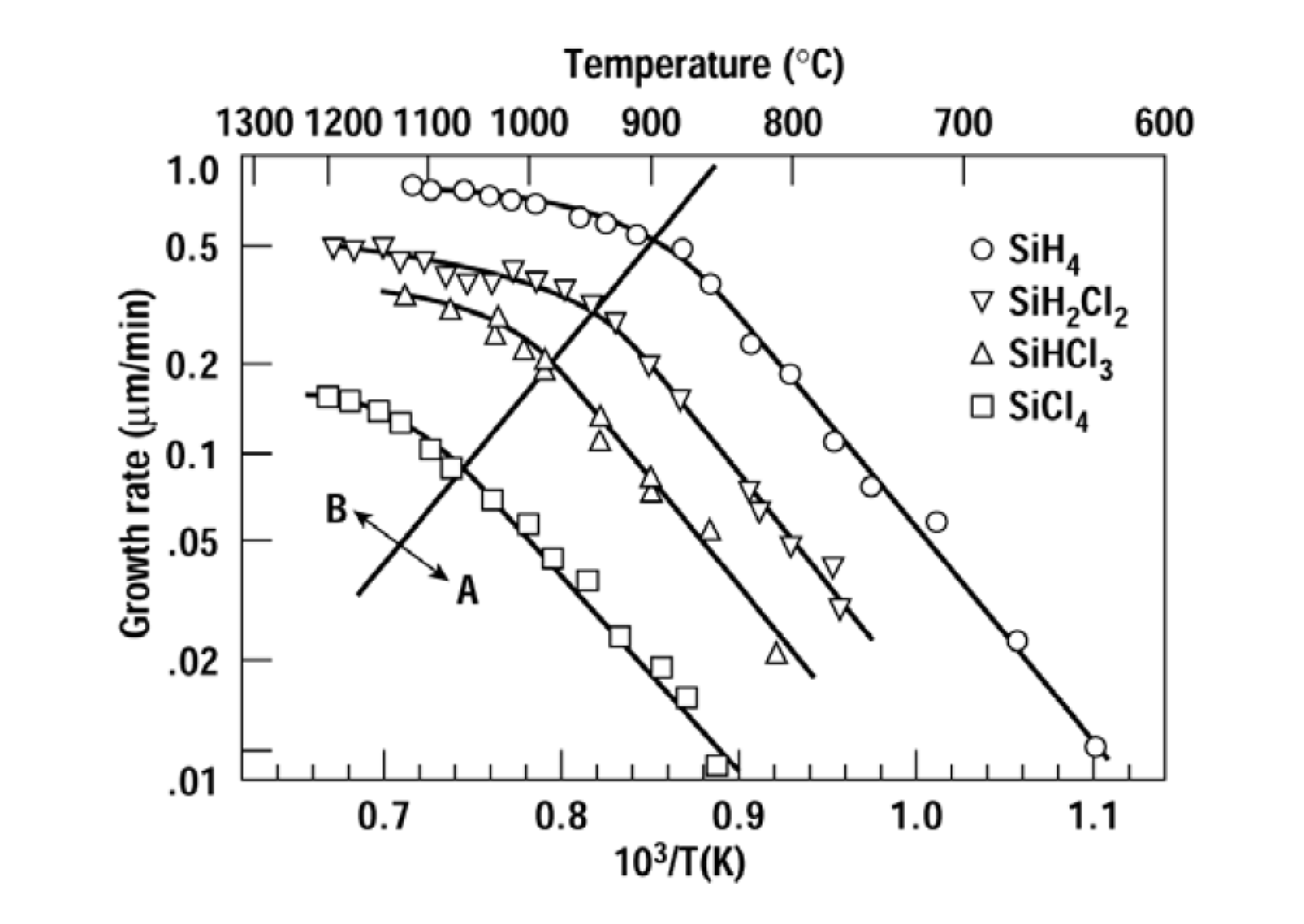
$k_S << h_G$ = Surface reaction limited $dy/dt \sim \exp(-E_a/kT)$

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

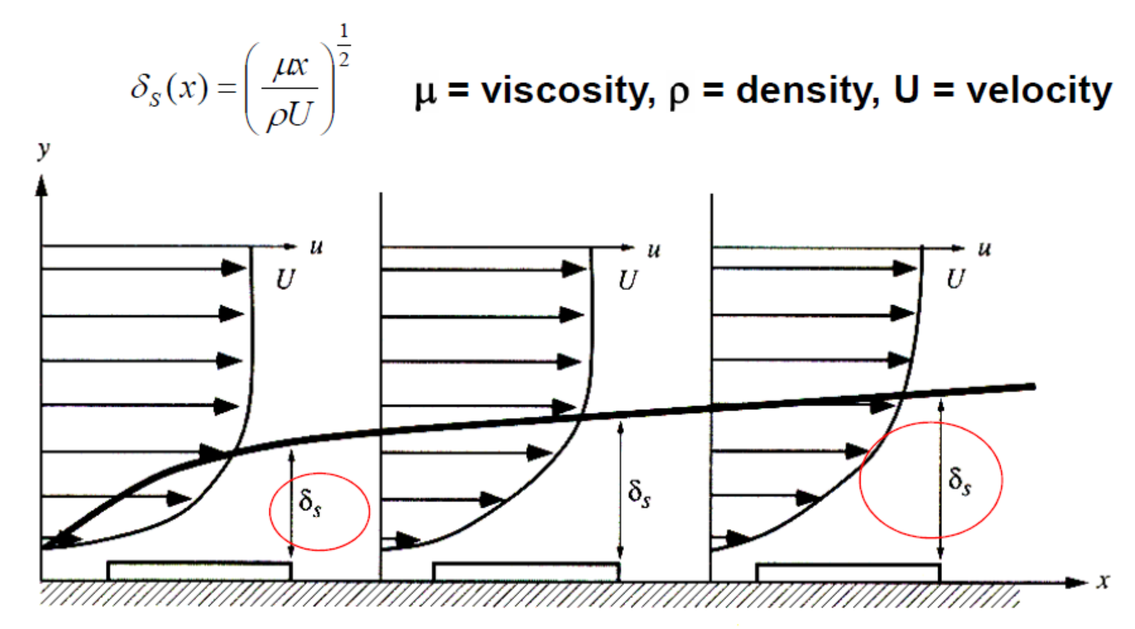
Deposition rate vs. Temperature



Deposition rate vs. Temperature



Growth Rate Dependence on Flow Velocity



$F1 = h_G \cdot (C_G - C_S)$

h_G = mass-transfer coefficient

$h_G = D / \delta$

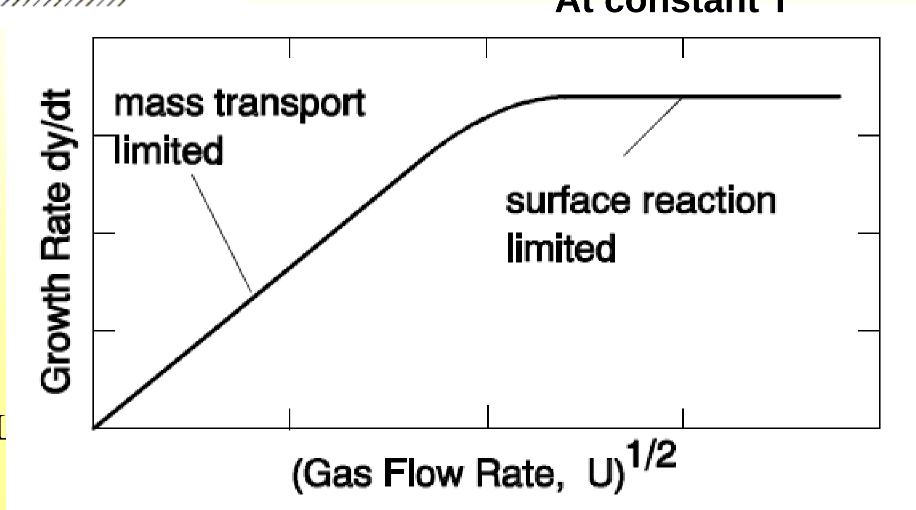
δ = boundary layer thickness

Low flow rate U

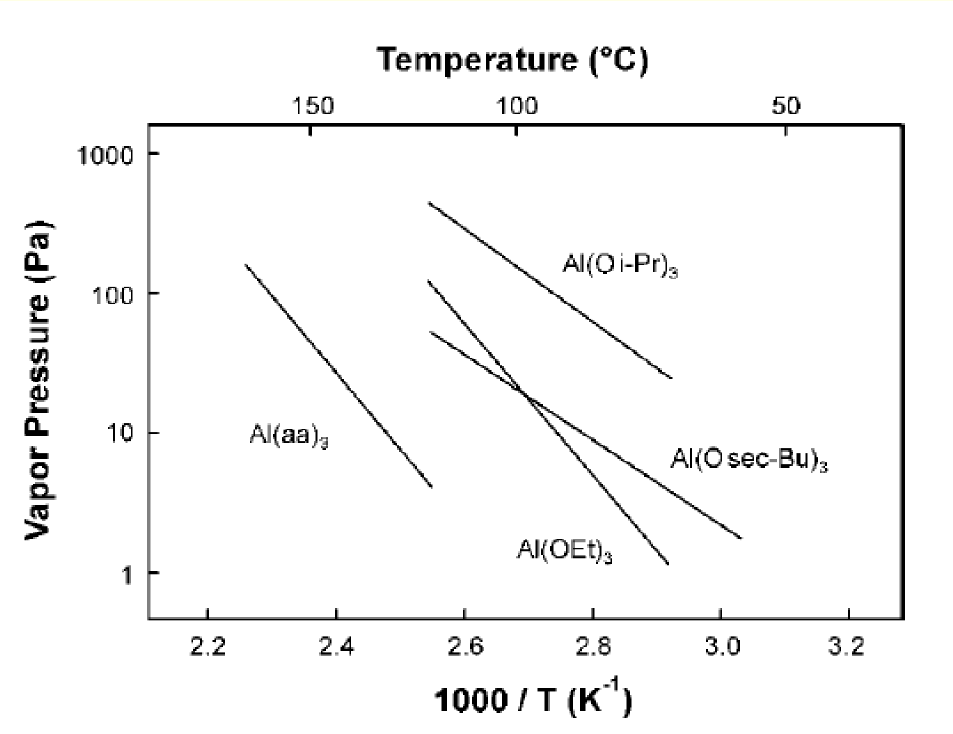
~ large boundary layer thickness δ

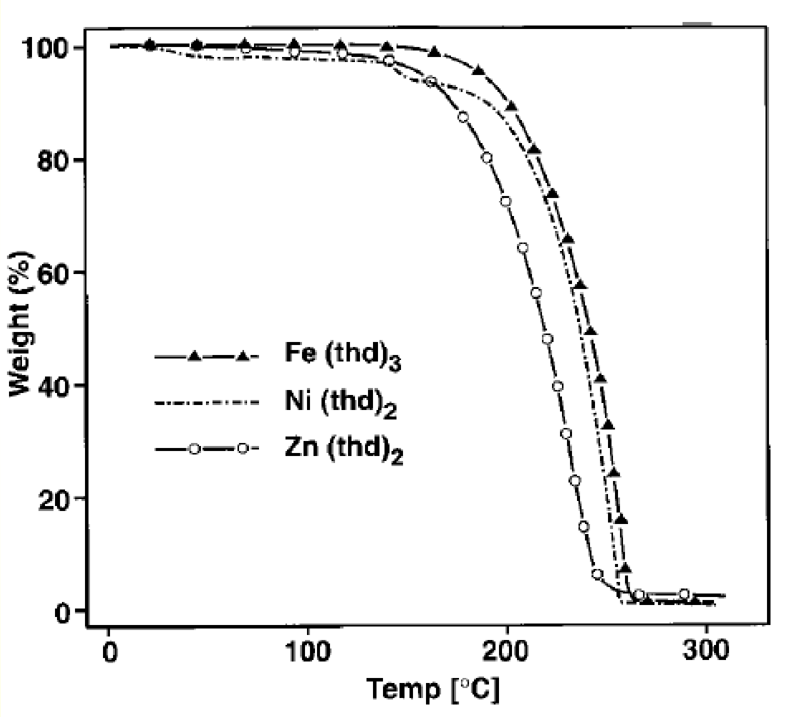
~ slow mass-transfer

At constant T



Precursor Volatility





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

Chemical Vapor Deposition

Aluminum

2.27 μΩcm, easily etched, Al dissolves in Si,

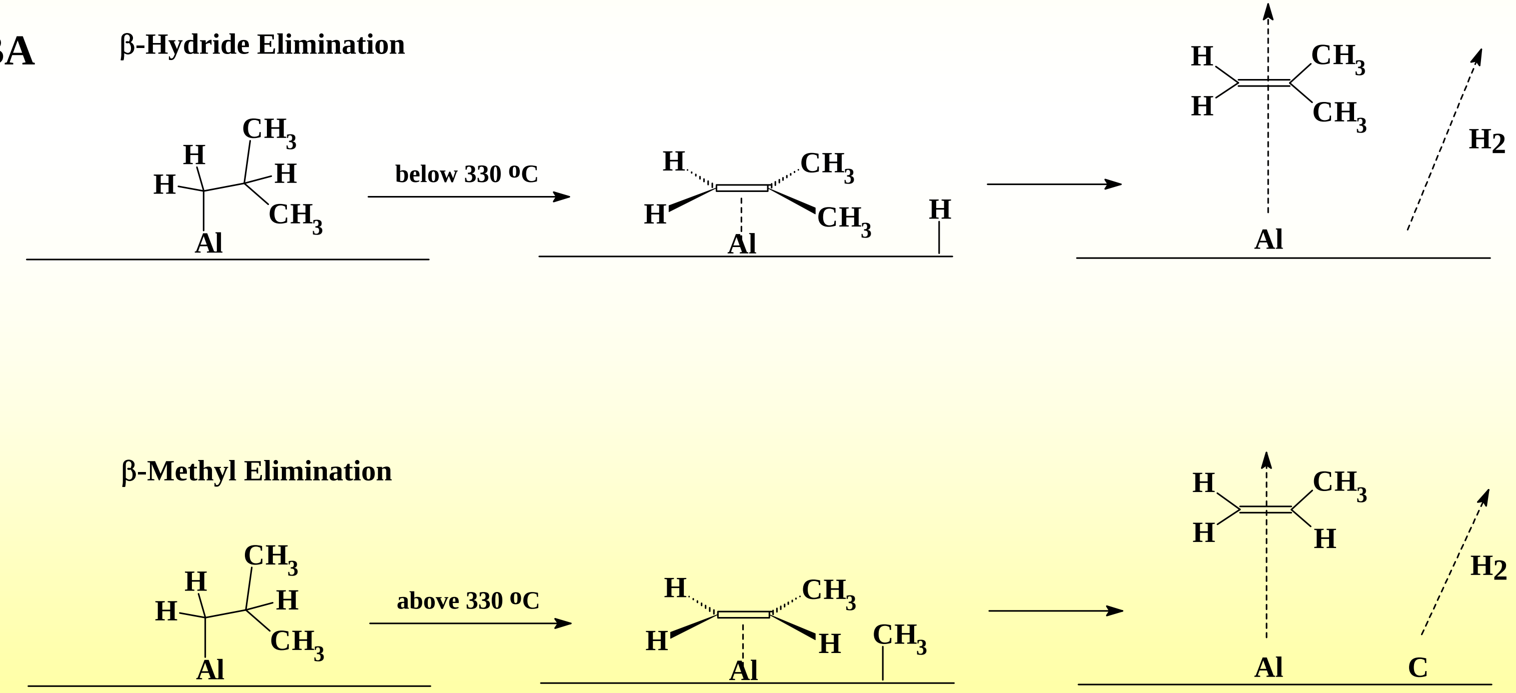
GaAs + Al ⟶ AlAs + Ga

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

TIBA

β-Hydride Elimination

β-Methyl Elimination



Chemical Vapor Deposition

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

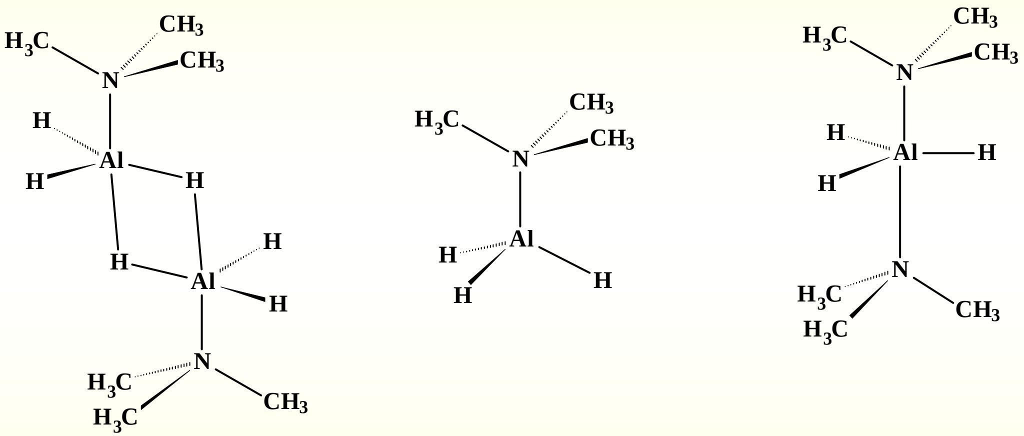
TMA
large carbon incorporation, Al_4C_3, RF plasma, laser

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

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

Chemical Vapor Deposition

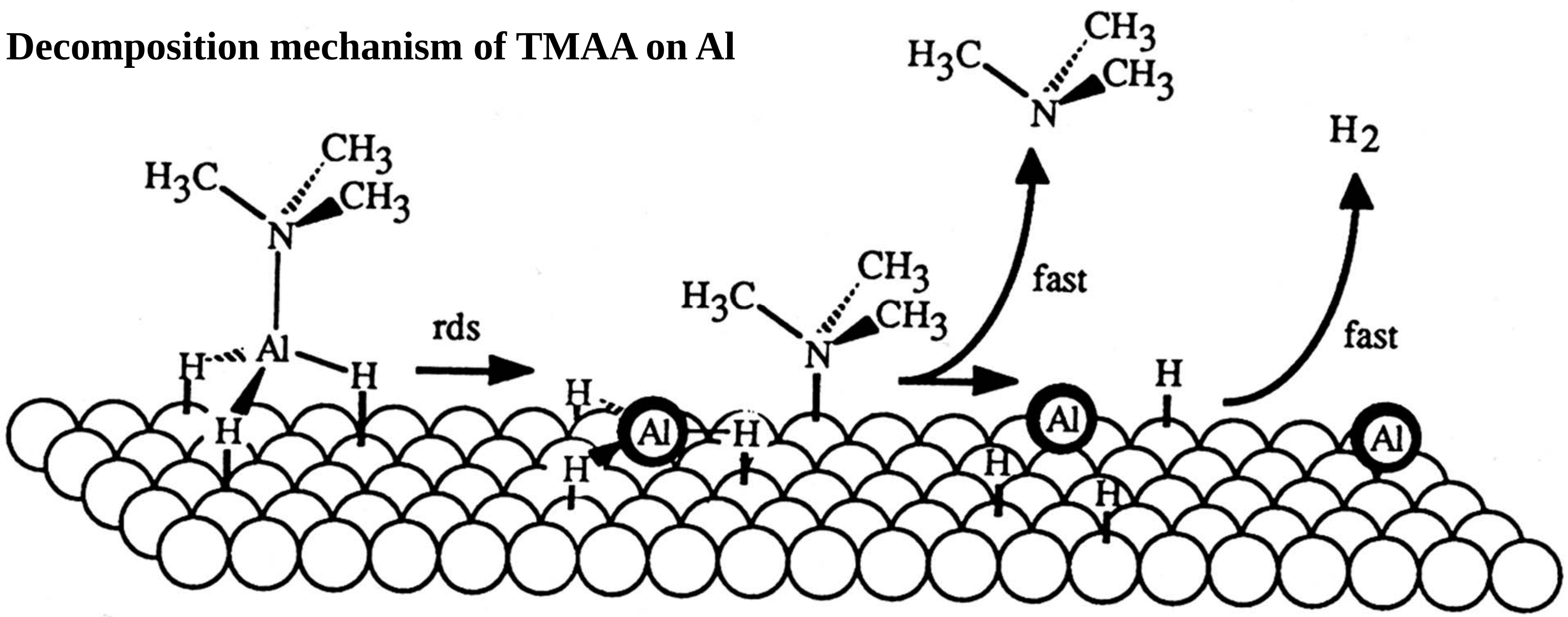
TMAA



$(CH_3)_3N\text{-}AlH_3 \longrightarrow Al + (CH_3)_3N + 3/2\ H_2$ below 100 °C

Chemical Vapor Deposition

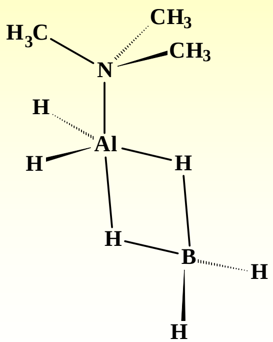
Decomposition mechanism of TMAA on Al



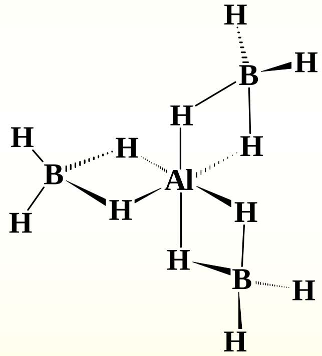
$(CH_3)_3N\text{-}AlH_3 \longrightarrow Al + (CH_3)_3N + 3/2\ H_2$ below 100 °C

Chemical Vapor Deposition

Aluminoboranes



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



DMAH
ligand redistribution

$[(CH_3)_2AlH]_3 \longrightarrow (CH_3)_3Al \Uparrow + AlH_3 \longrightarrow Al + H_2$

at 280 °C, low carbon incorporation

Chemical Vapor Deposition

Tungsten
5.6 μΩcm, a high resistance to electromigration, the highest mp of all metals 3410 °C.

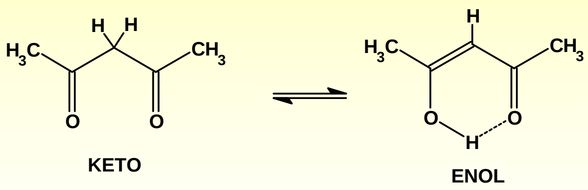
$$2\,WF_6 + 3\,Si \rightarrow 2\,W + 3\,SiF_4$$

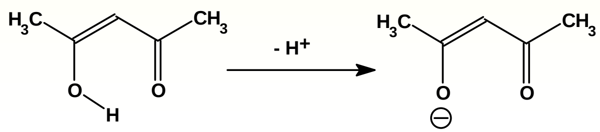
$$WF_6 + 3\,H_2 \rightarrow W + 6\,HF$$

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

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

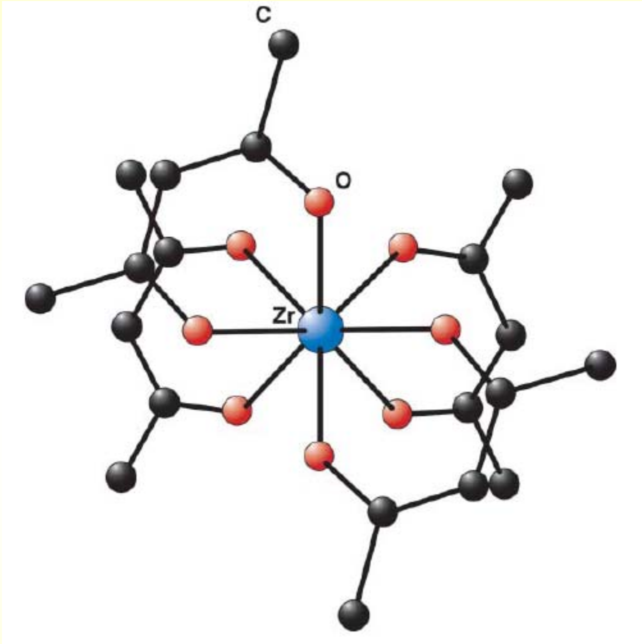
Diketonate Ligands



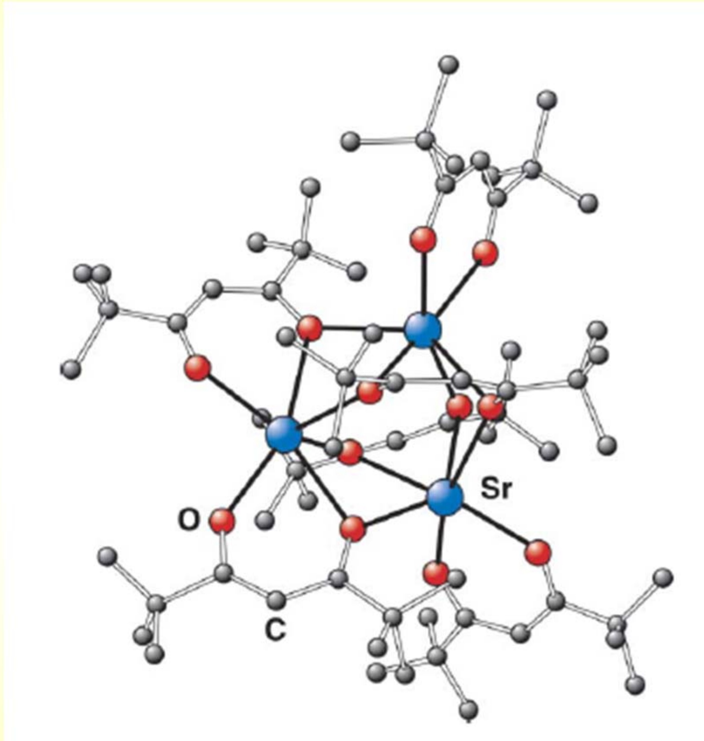


R_1	R_2	Name	Abbreviation
CH_3	CH_3	Pentane-2,4-dionate (acetylacetonate)	acac
CH_3	CF_3	1,1,1-trifluoropentane-2,4-dionate (trifluoroacetylacetonate)	tfac
CF_3	CF_3	1,1,1,5,5,5-hexafluoropentane-2,4-dionate (hexafluoroacetylacetonate)	hfac
CH_3	$C(CH_3)_3$	1,1-dimethylhexane-3,5-dionate	dhd
$C(CH_3)_3$	$C(CH_3)_3$	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

Diketonate Precursors

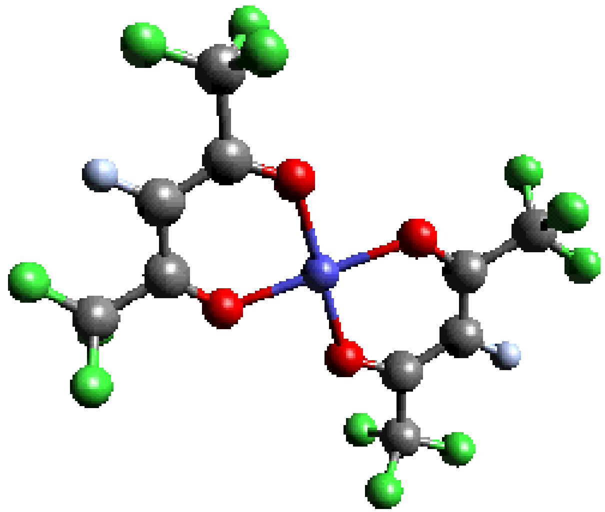


Mononuclear



Polynuclear

Chemical Vapor Deposition



Copper(II) hexafluoroacetylacetonate

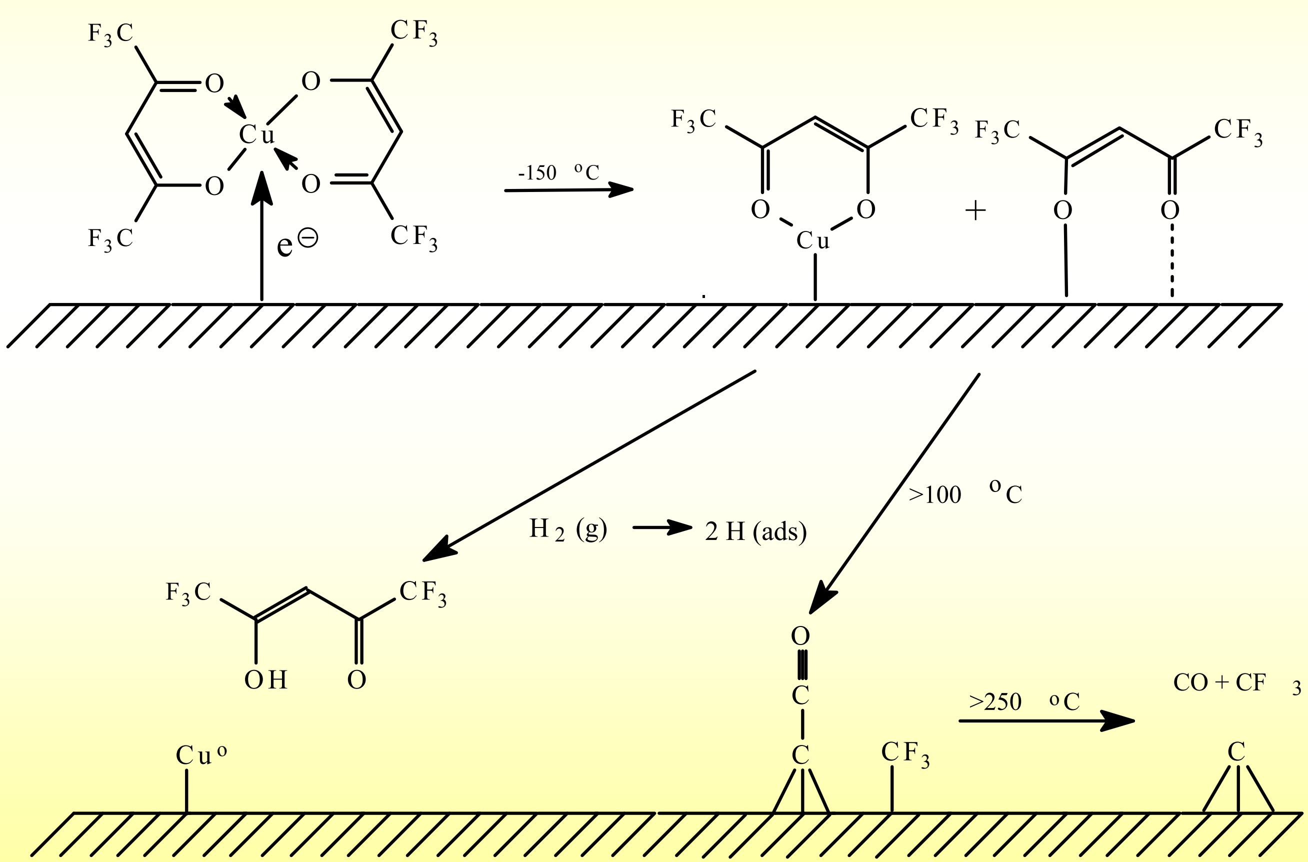
excellent volatility (a vapor pressure of 0.06 Torr at r. t.),
low decomposition temperature,
stability in air, low toxicity,
commercial availability

deposition on metal surfaces (Cu, Ag, Ta)
the first step, which can already occur at -150 °C,
a dissociation of the precursor molecules on the surface (Scheme I).

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.

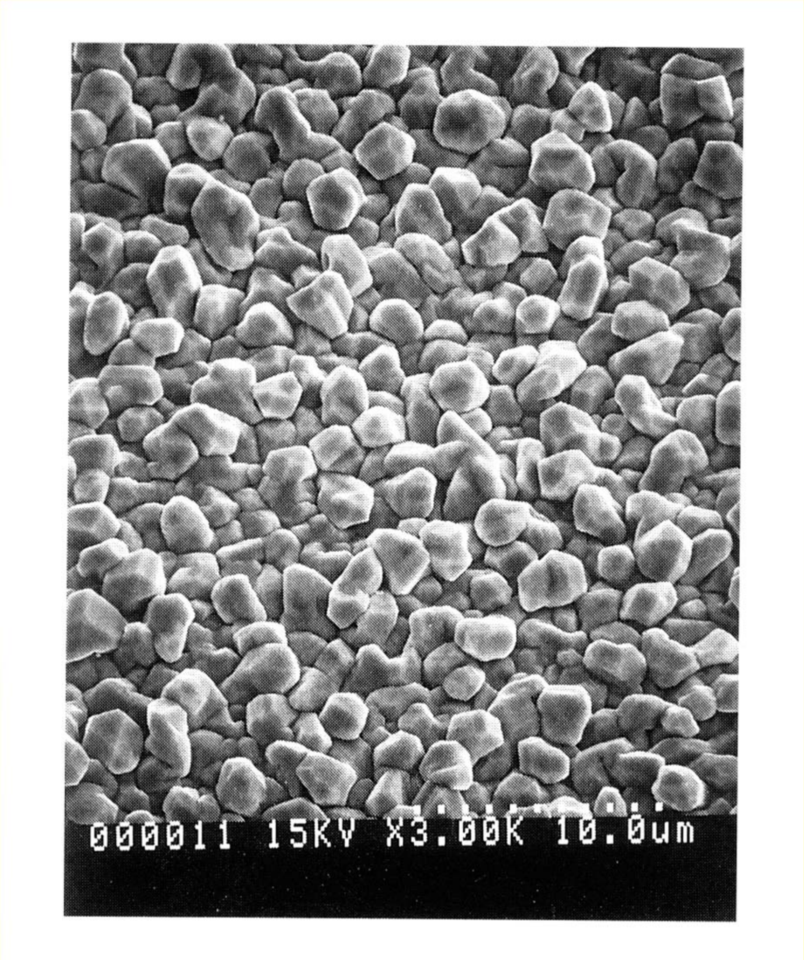
Chemical Vapor Deposition

Scheme I



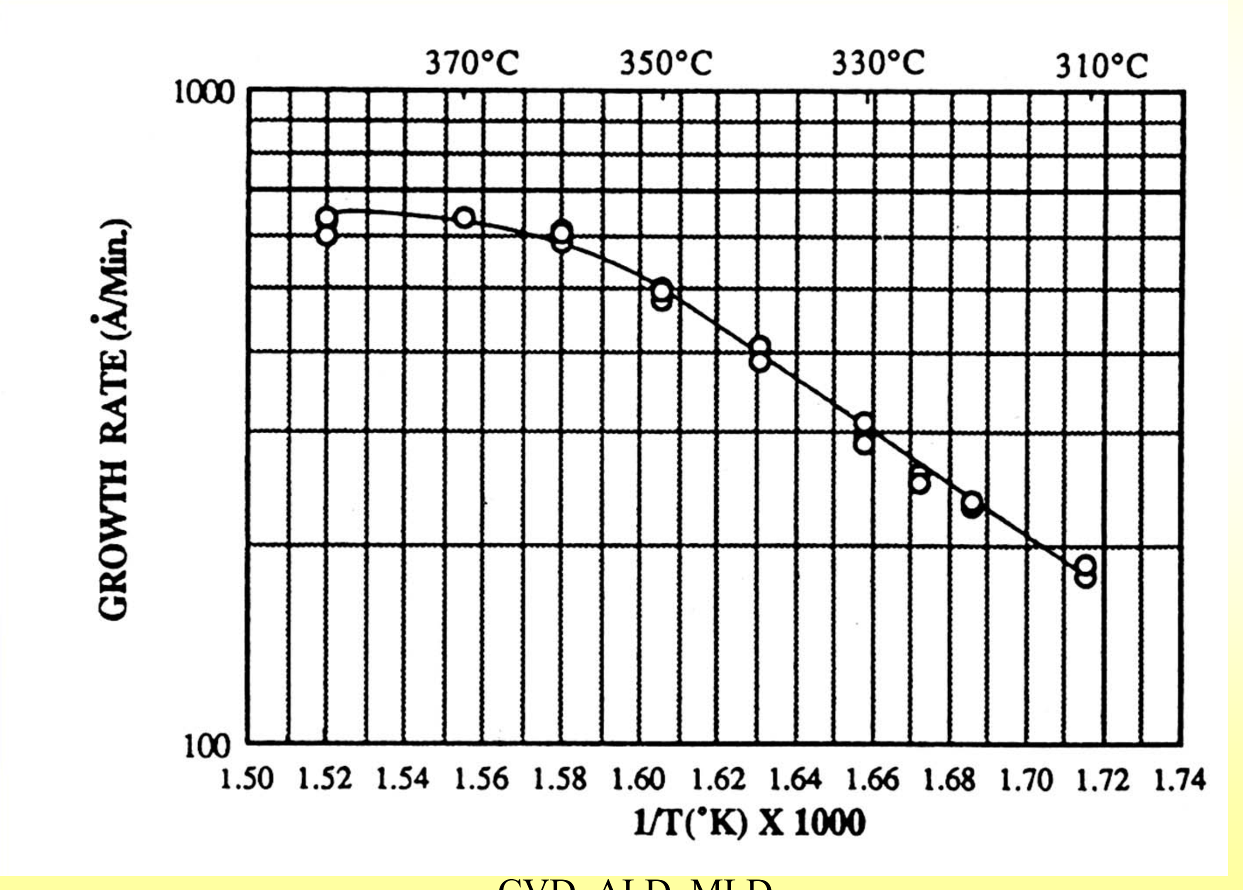
Chemical Vapor Deposition

SEM of Cu film, coarse grain, high resistivity



Chemical Vapor Deposition

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

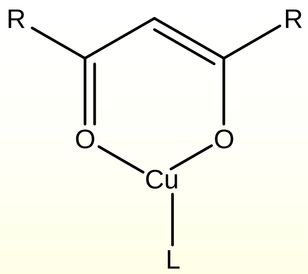


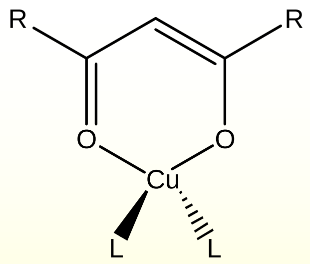
Chemical Vapor Deposition

Cu(I) precursors

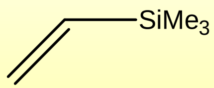
Disproportionation to Cu(0) and Cu(II)

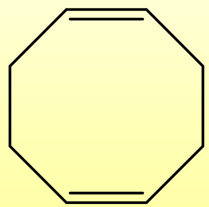
2 Cu(diketonate)L_n $\rightarrow$ Cu + Cu(diketonate)$_2$ + n L





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





Chemical Vapor Deposition

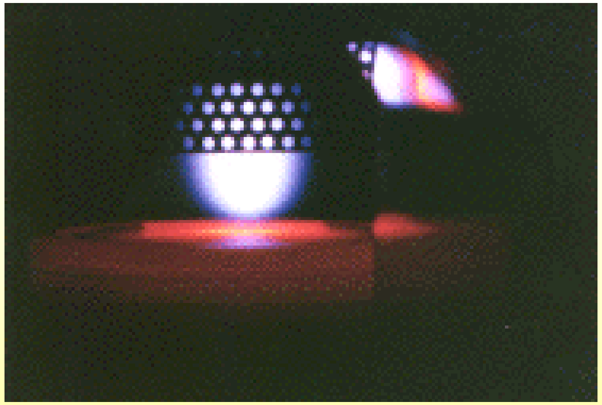
Diamond films

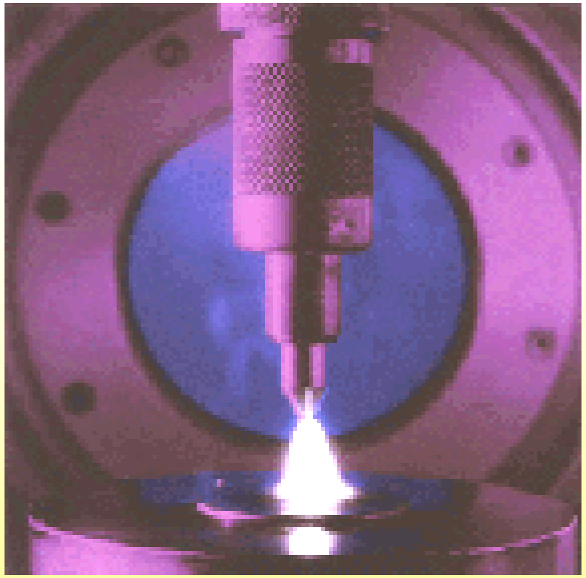
activating gas-phase carbon-containing precursor molecules:

•thermal (*e.g*. hot filament)

•plasma (D.C., R.F., or microwave)

•combustion flame (oxyacetylene or plasma torches)





Chemical Vapor Deposition

Experimental conditions:

temperature 1000-1400 K

the precursor gas diluted in an excess of hydrogen (typical CH_4 mixing ratio ~1-2vol%)

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.

Chemical Vapor Deposition

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 but, under typical CVD conditions,

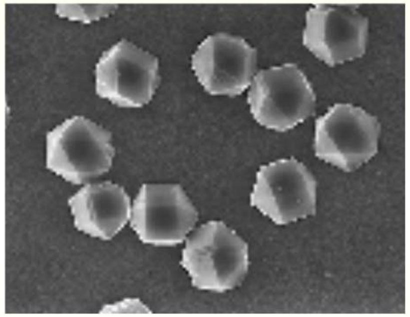
the rate of diamond growth exceeds its etch rate whilst for graphite the converse is true.

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

Chemical Vapor Deposition

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

Chemical Vapor Deposition

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

Chemical Vapor Deposition

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

Chemical Vapor Deposition

Optics - protective coatings for infrared optics in harsh environments,

ZnS, ZnSe, Ge: excellent IR transmission but brittle

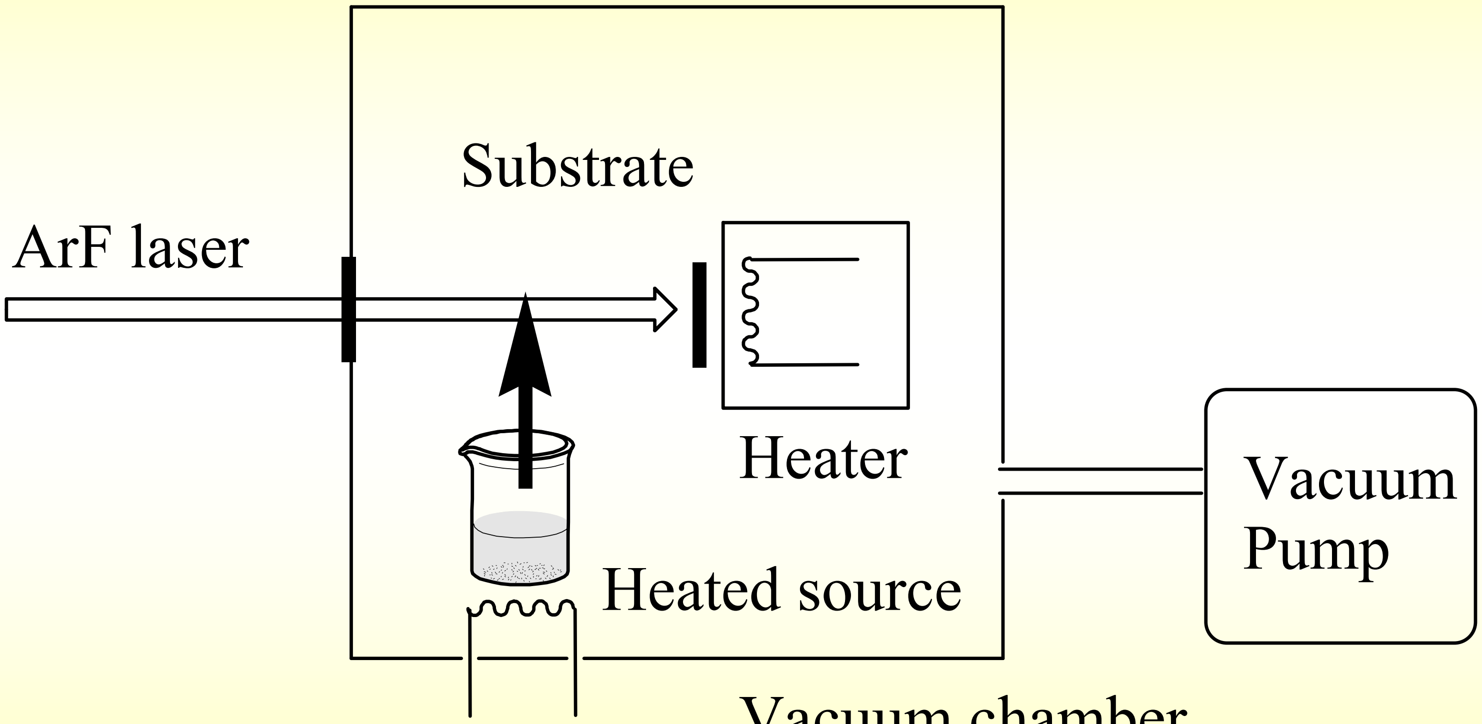
the flatness of the surface, roughness causes attenuation and scattering of the IR signal

Electronic devices - doping, an insulator into a semiconductor

***p*-doping: B_2H_6 incorporates B into the lattice**

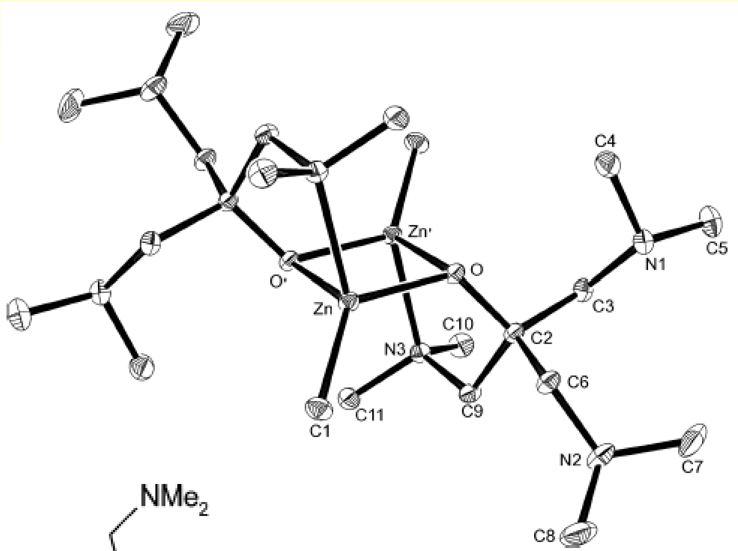
doping with atoms larger than C very difficult, *n*-dopants such as P or As, cannot be used for diamond, alternative dopants, such as Li

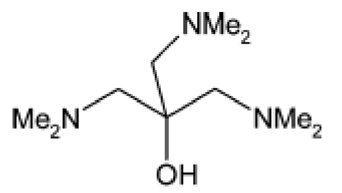
Laser-Enhaced CVD

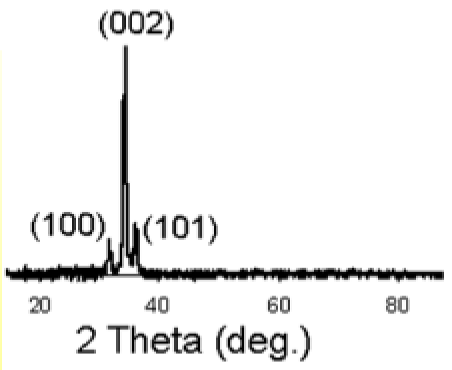


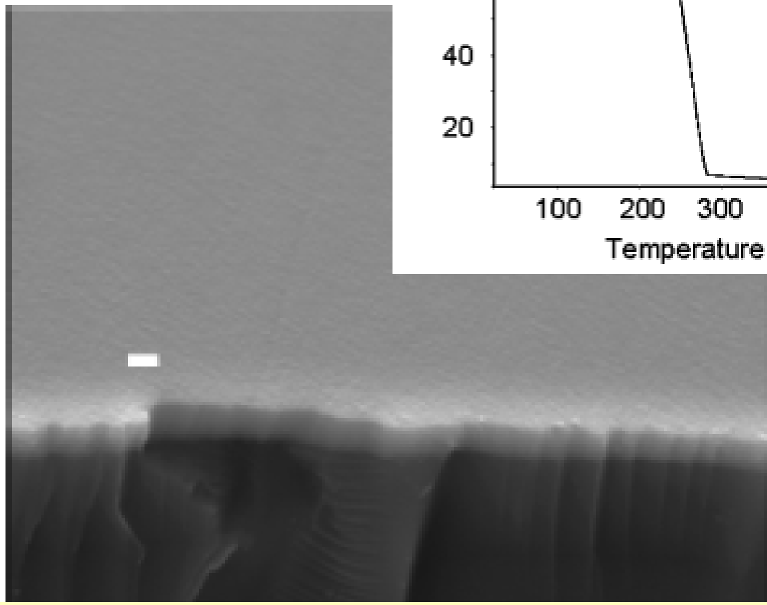
$$Si(O_2CCH_3)_4 \rightarrow SiO_2 + 2\ O(OCCH_3)_2$$

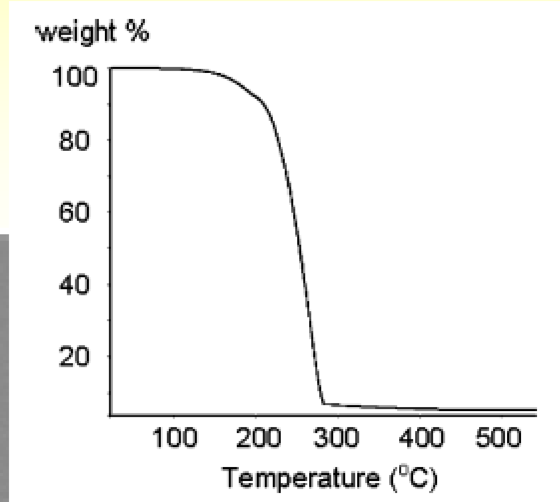
LPCVD of ZnO from Aminoalcoholates







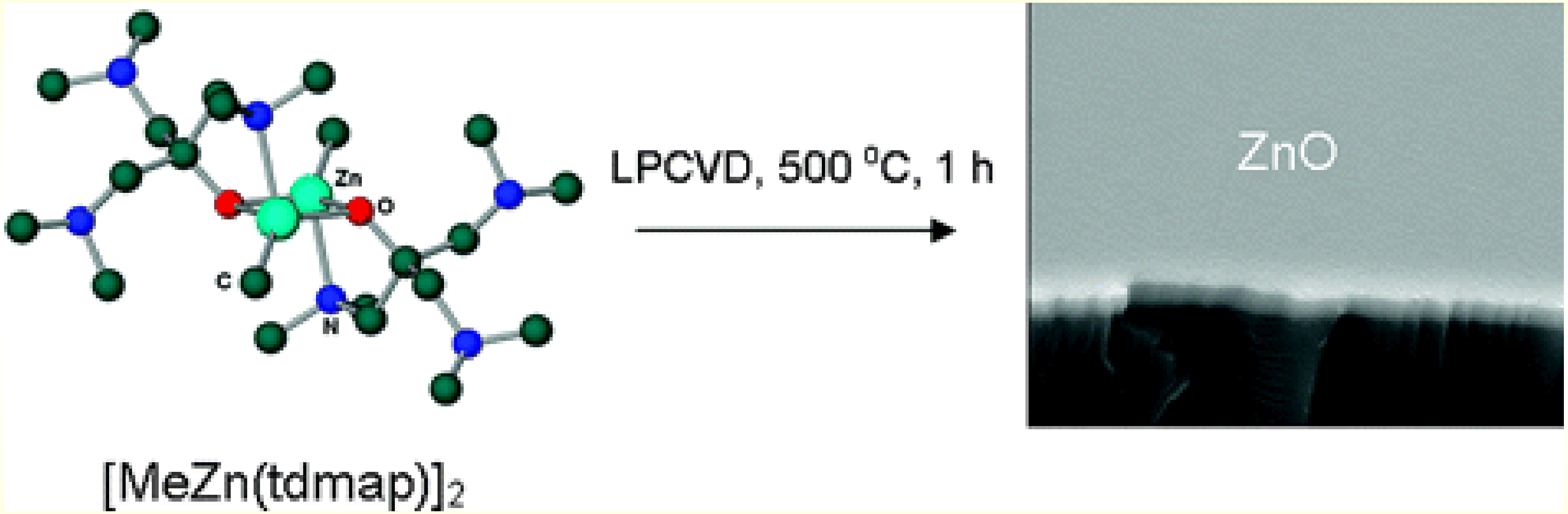




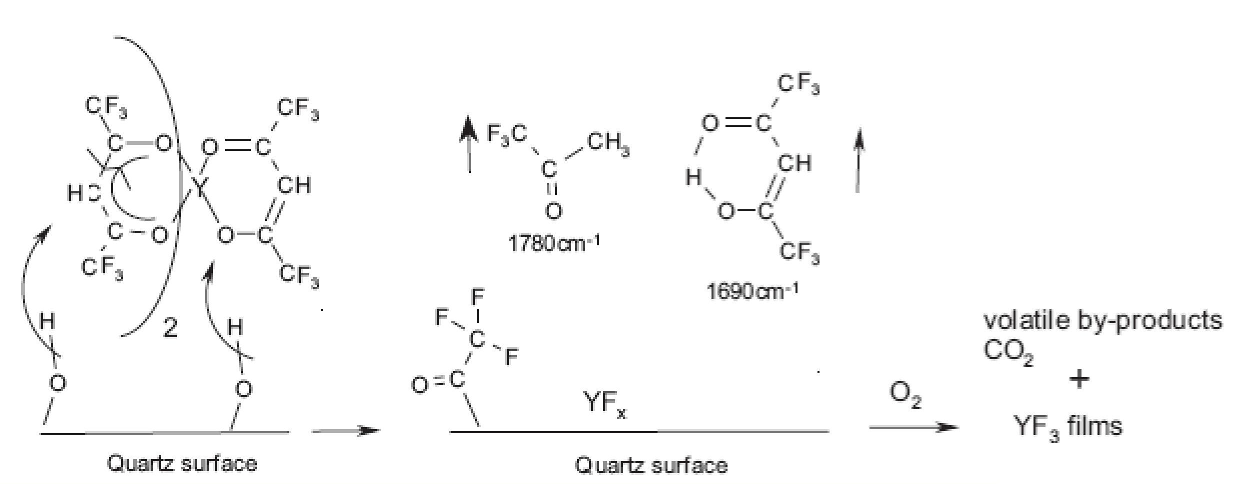
SEM of the film deposited by LPCVD at 500 °C. Bar = 1 μm.

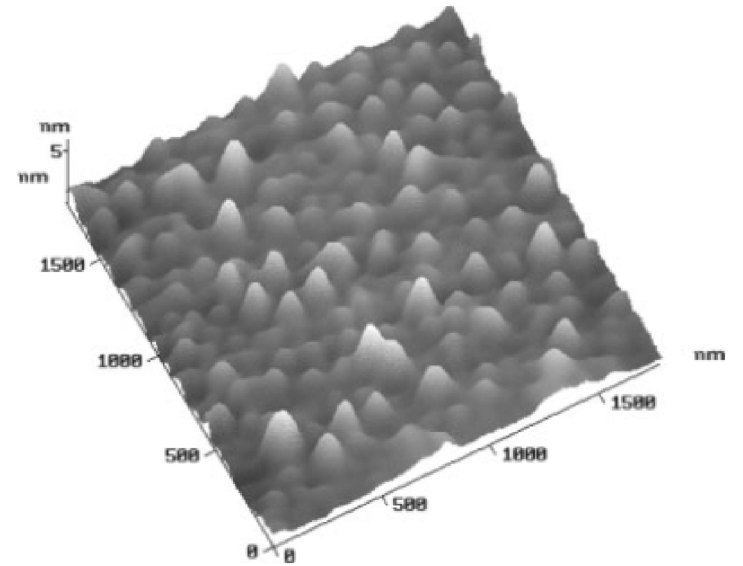
Hexagonal ZnO PDF 79-0208 CVD_ALD_MLD

LPCVD of ZnO from Aminoalcoholates



CVD of YF_3 from hfacac Complex



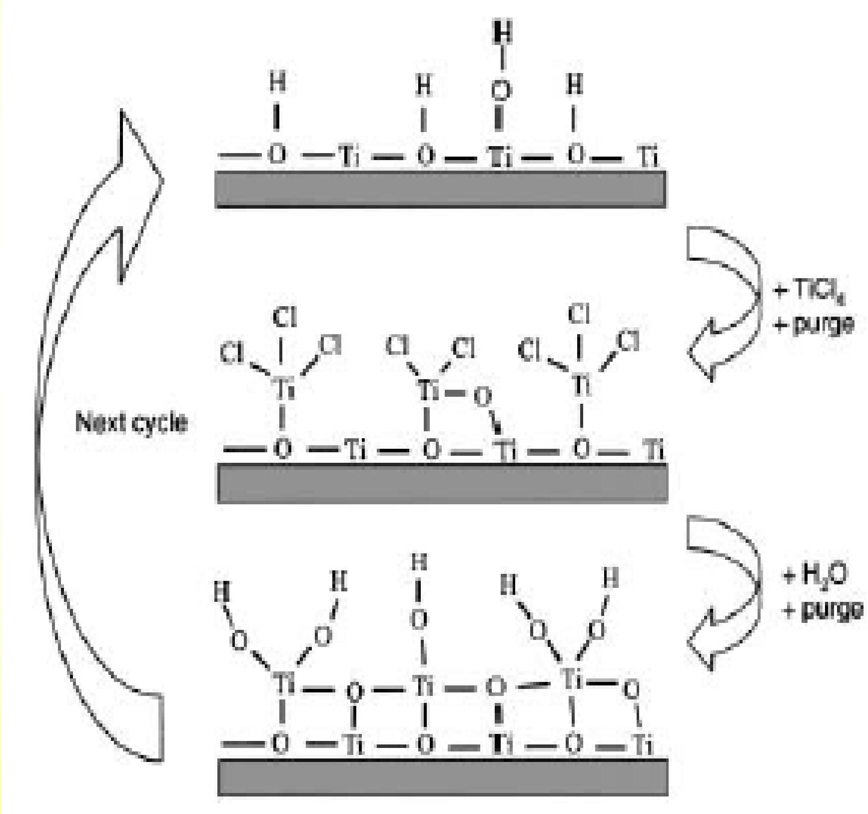


ALD Atomic Layer Deposition

Special modification of CVD
Method for the deposition of thin films
Film growth by cyclic process

4 steps:

1/ exposition by1st precursor
2/ cleaning of the reaction chamber
3/ exposition by 2nd precursor
4/ cleaning of the reaction chamber



ALD Atomic Layer Deposition

Cycle repetitions until desired film thickness is reached

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

Self-Limiting Growth Mechanism
High reactivity
Formation of a monolayer

Control of film thickness and composition

Deposition on large surface area

ALD vs. CVD Comparison

ALD Carried out at room temperature

Control over number of deposited layers = film thickness

Reactor walls inactive – no reactive layer

Separate loading of reactive precursors

Self-limiting growth

Precursor transport to the reaction zone does not have to be highly uniform (as in CVD)

Solid precursors

ALD vs. CVD Comparison

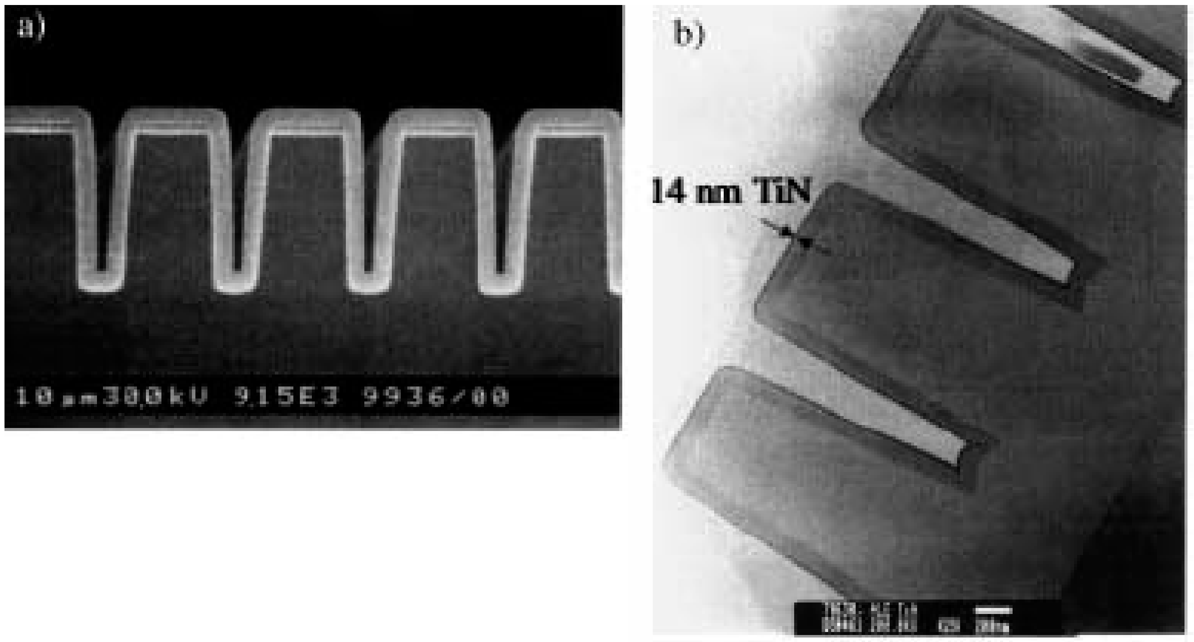


Figure 2. Cross-sectional SEM images for a 300-nm Al_2O_3 film (a) and a 14-nm TiN film (b) deposited on a patterned silicon substrate.

Precursor Properties

Selection of suitable combination of precursors

Molecular size influences film thickness

Gases, volatile liquids, solids with high vapor pressure

Typical precursors:

<u>Metallic</u> - halogenides (chlorides), alkyls, alkoxides, organometallics (cyclopentadienyl complexes), alkyl amides

<u>Nonmetallic</u> - water, hydrogen peroxide, ozone, hydrides, ammonia, hydrazine, amines

Precursor Properties

Thermally stable

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

Thermodynamics

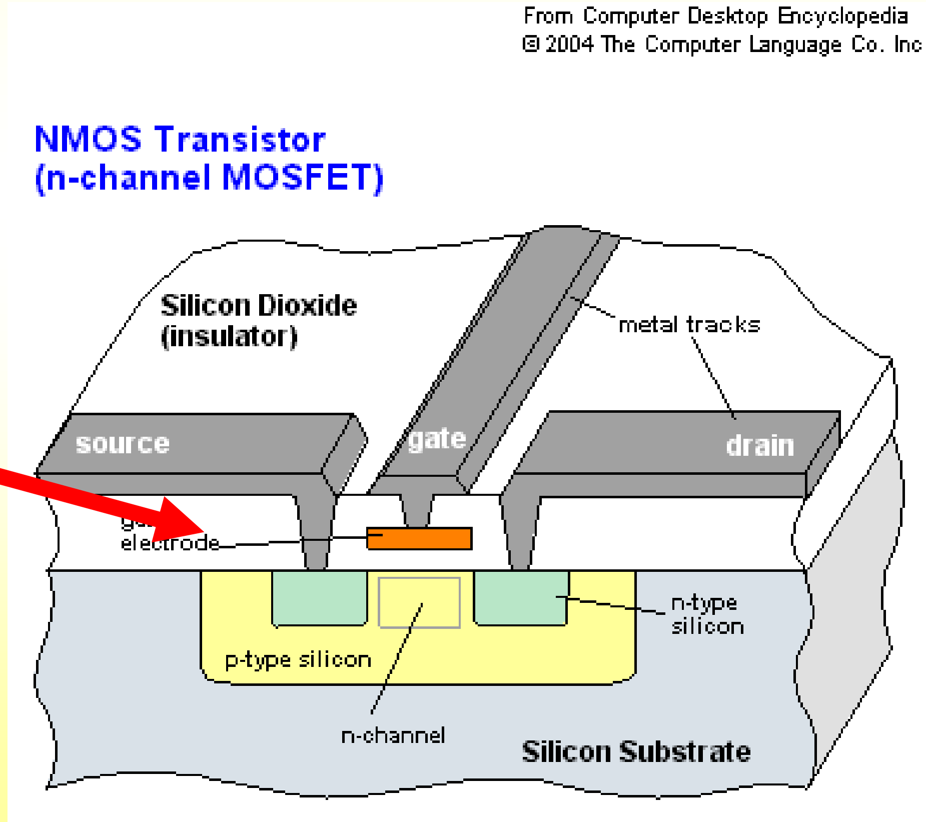
Kinetics

Mechanisms

Examples of ALD

High-permitivity Oxides

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



Examples of ALD

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:

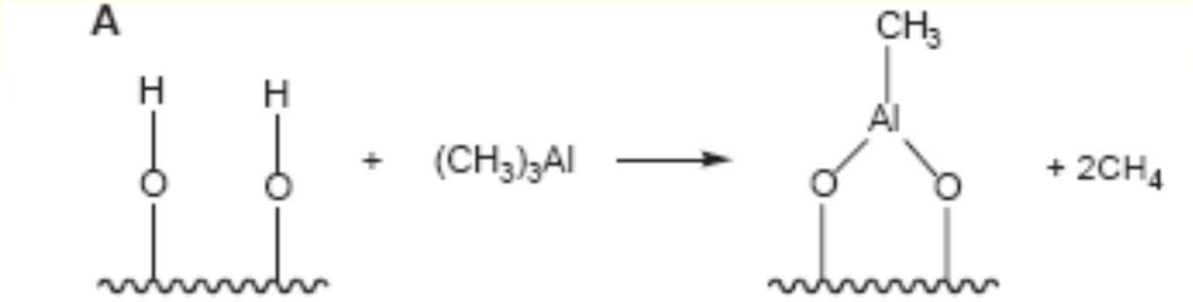
microelectronics

optical filters

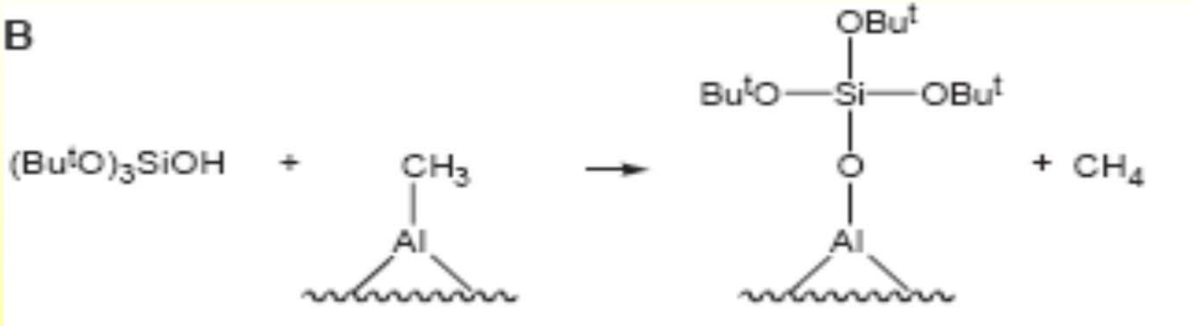
protective layers (against diffusion, oxidation, corrosion)

ALD of SiO_2 and Al_2O_3 Films

Step A

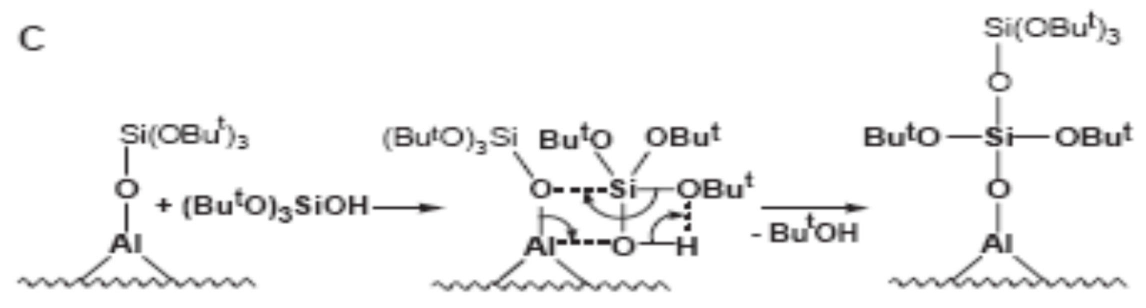


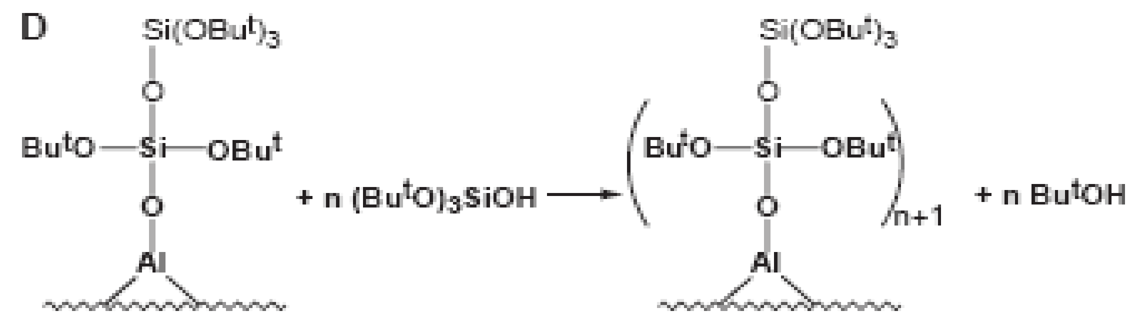
Step B



ALD of SiO_2 and Al_2O_3 Films

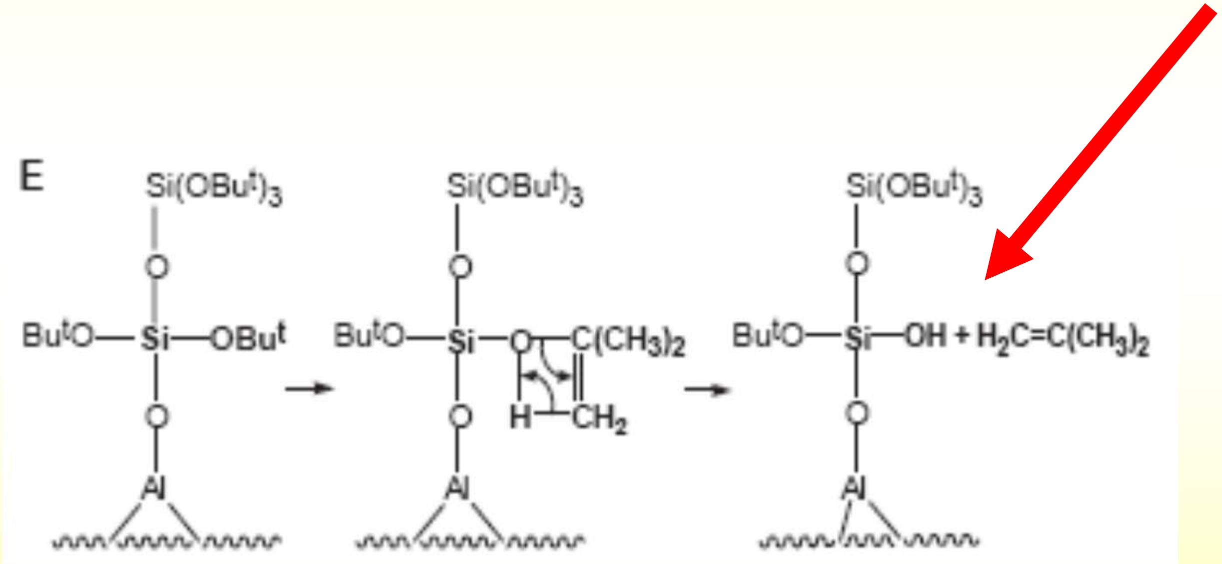
C, D: alkoxide - siloxide exchange





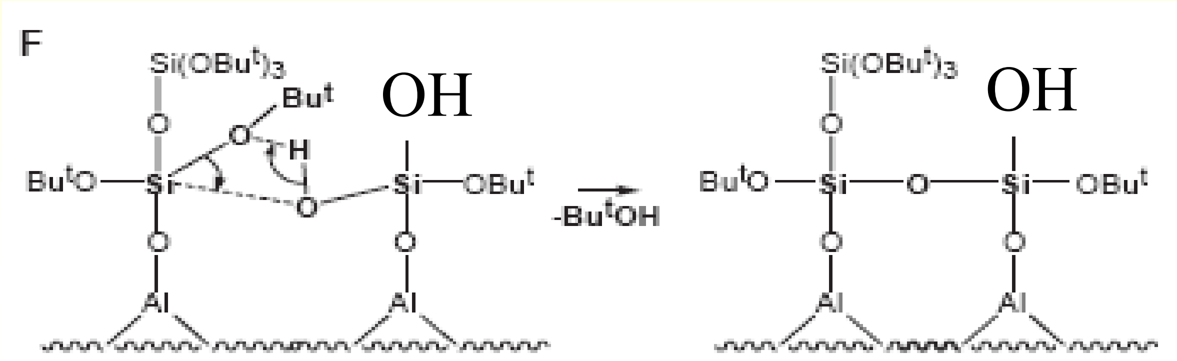
ALD of SiO_2 and Al_2O_3 Films

E: elimination of isobutene = formation of -OH

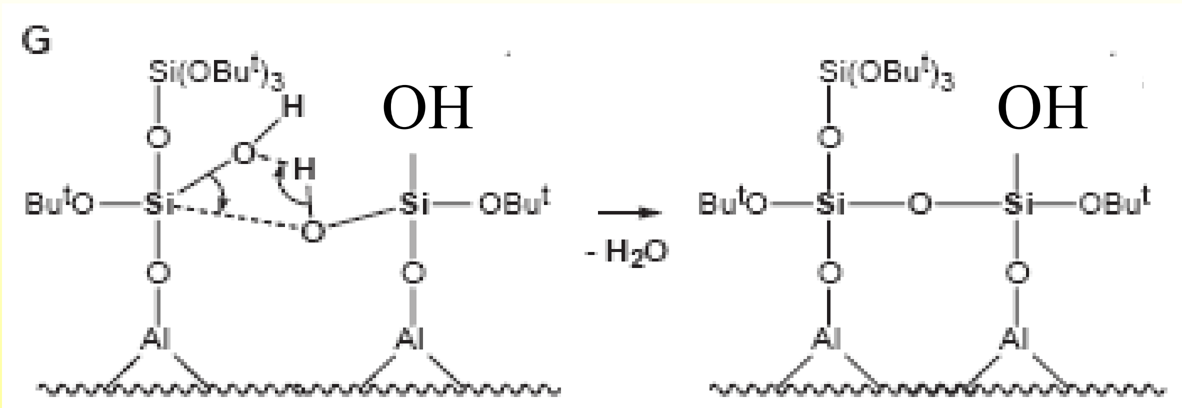


ALD of SiO_2 and Al_2O_3 Films

F: elimination of butanol = condensation

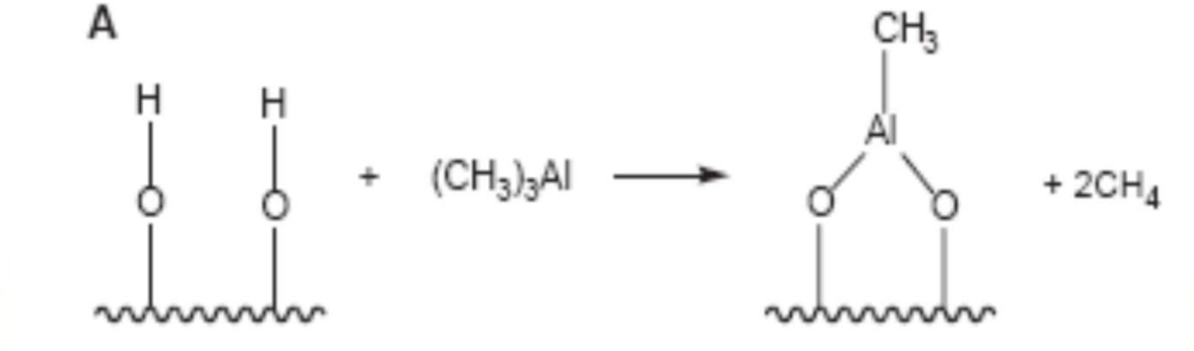


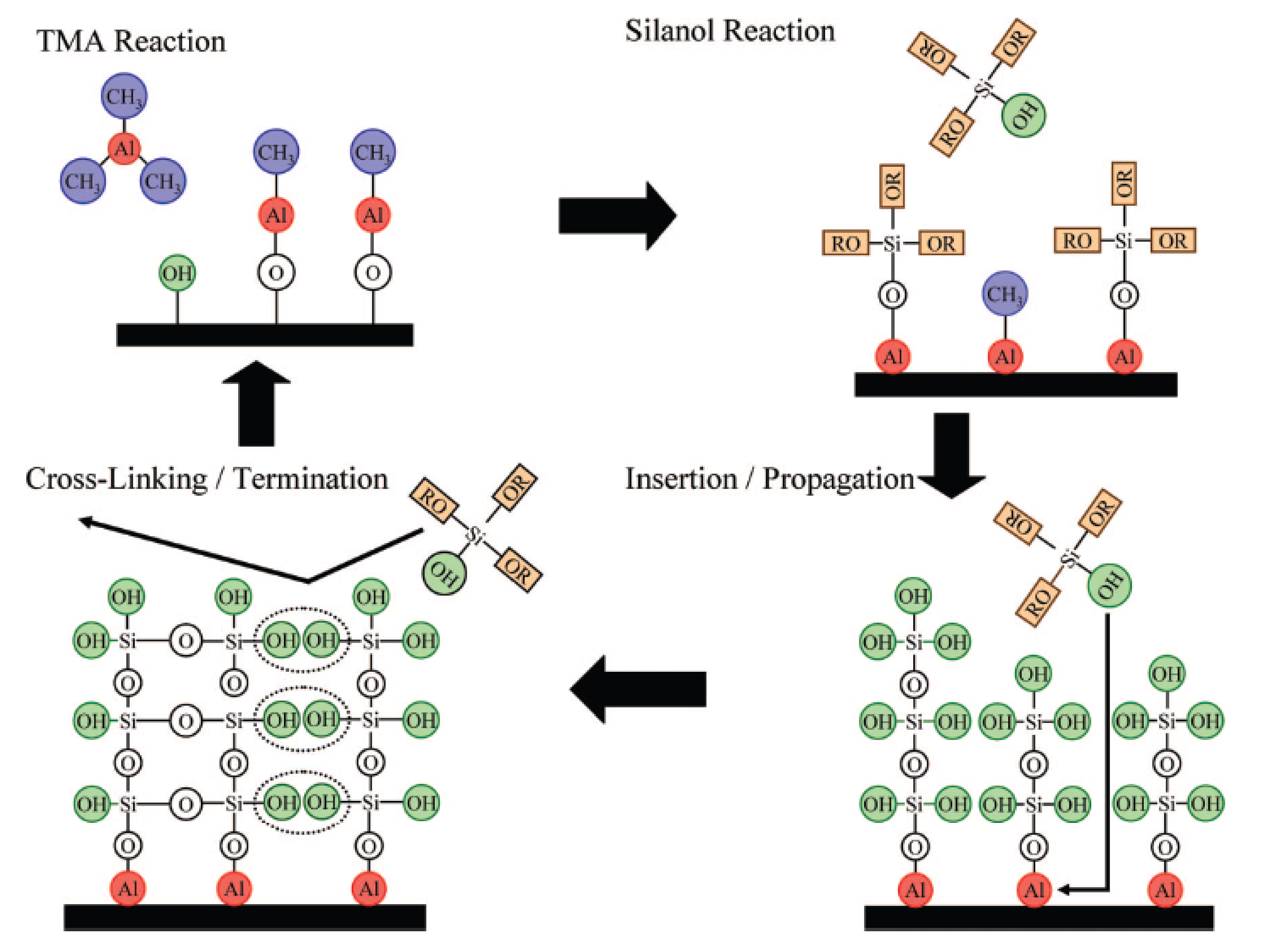
G: elimination of water = condensation



ALD of SiO_2 and Al_2O_3 Films

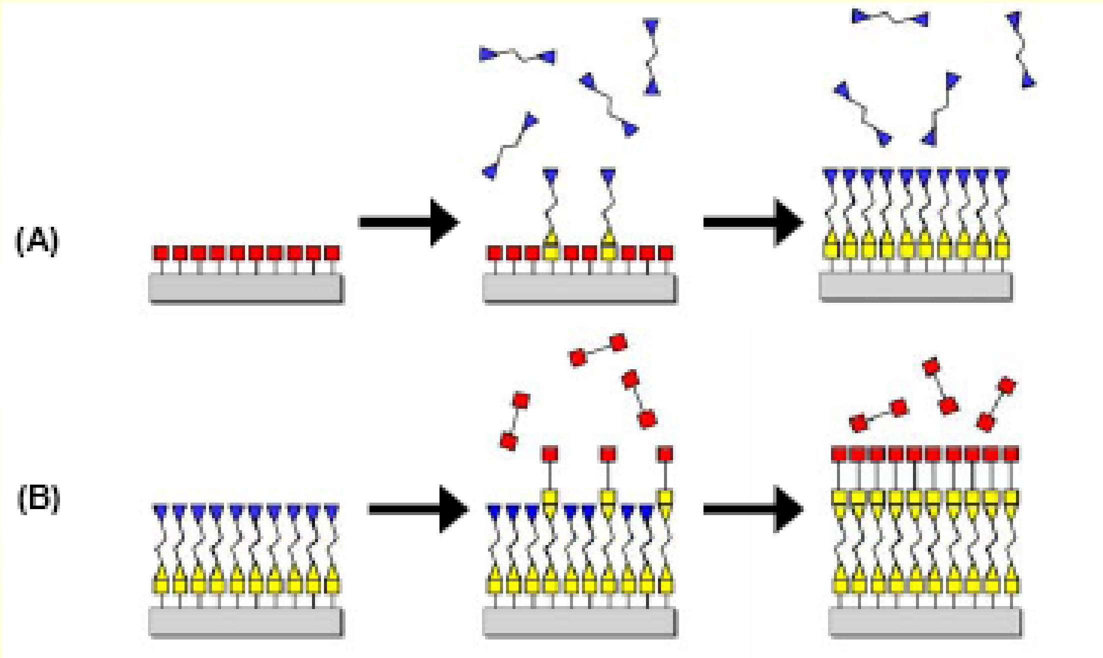
Repeat Step A





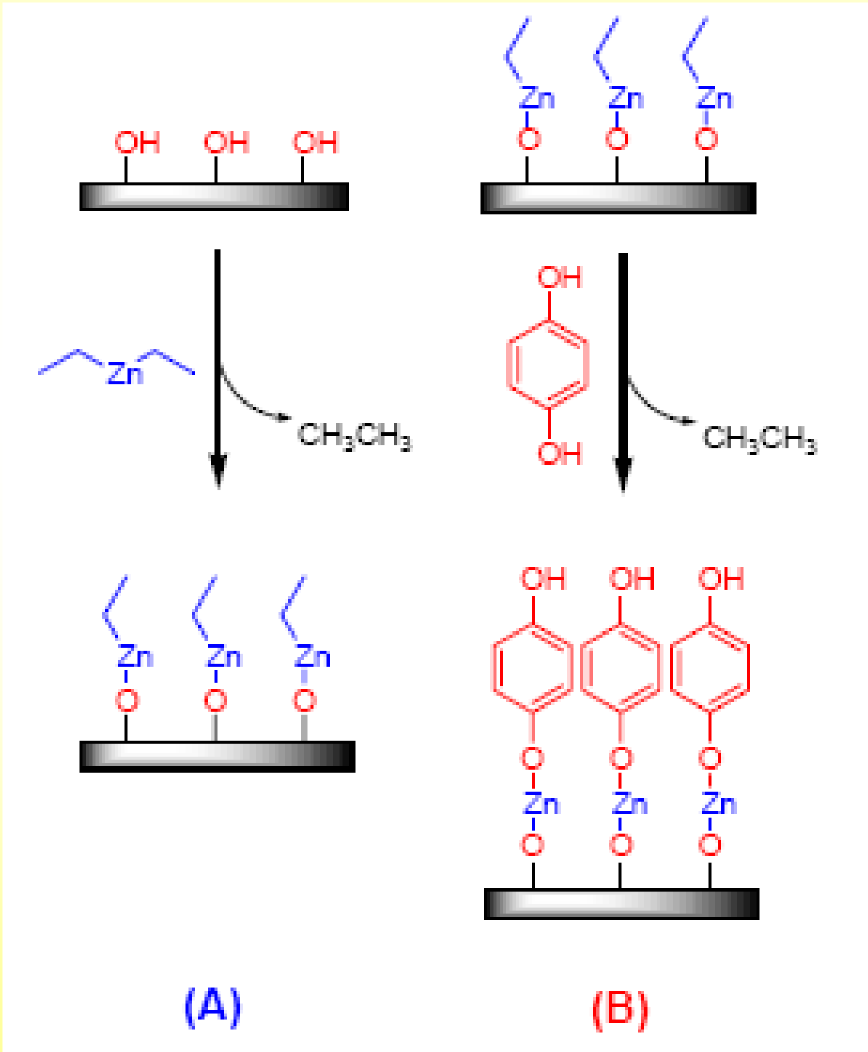
TMA Reaction
Silanol Reaction
Cross-Linking / Termination
Insertion / Propagation

MLD - Molecular Layer Deposition

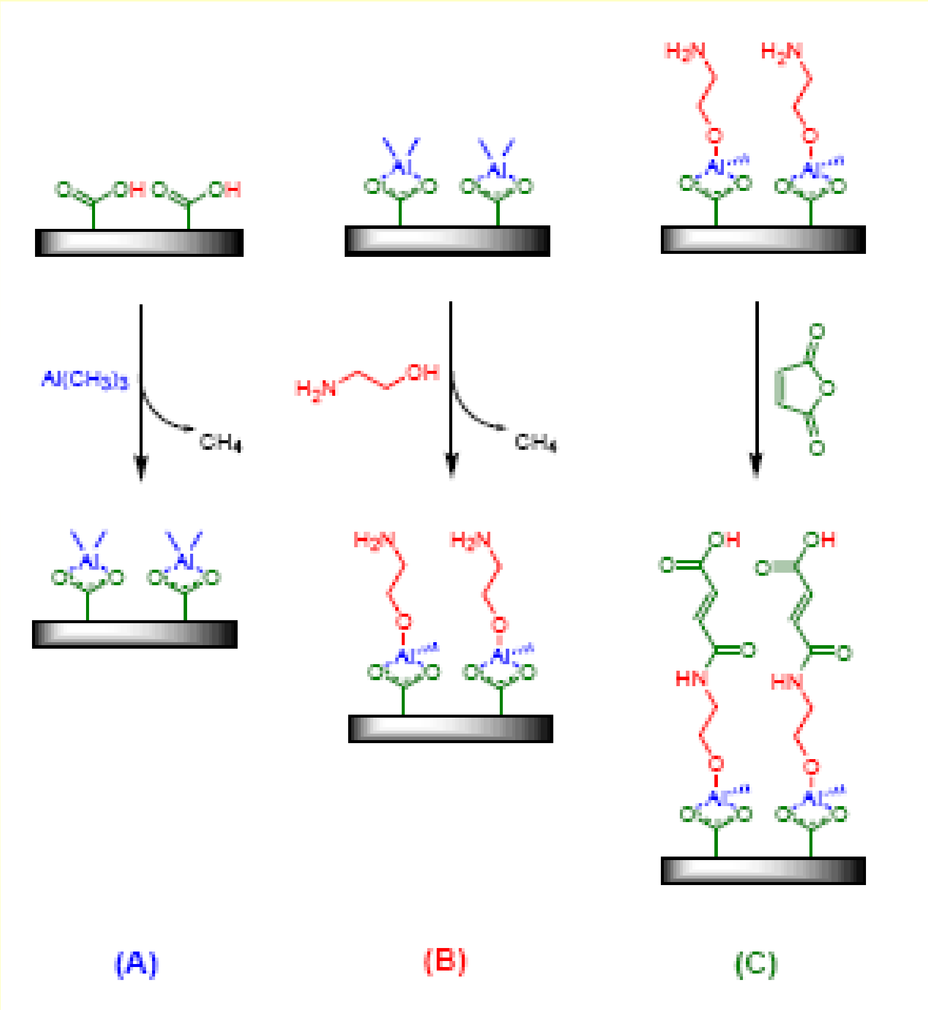


Sequential, self-limiting reactions A and B for MLD growth using two homobifunctional reactants

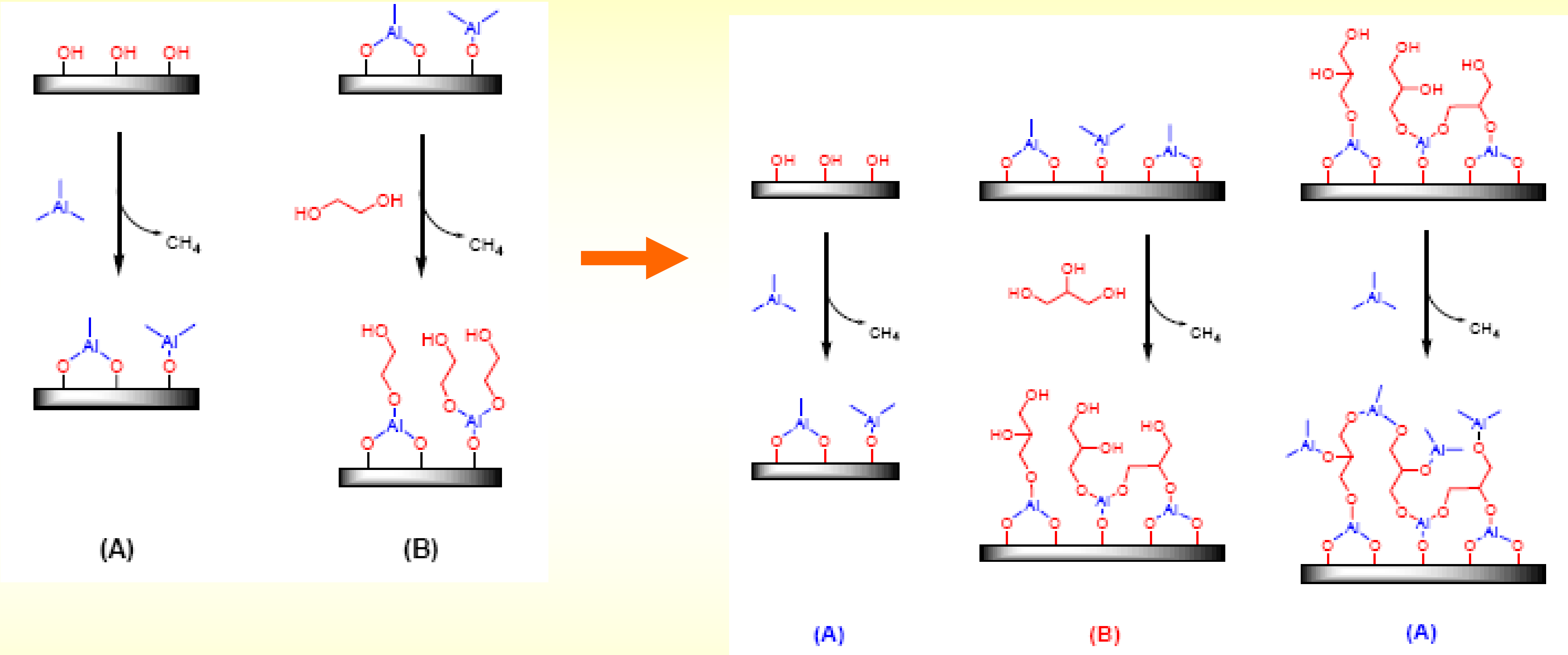
AB MLD


OH OH OH
Zn Zn Zn
O O O
Zn
CH3CH3
OH
OH
CH3CH3
Zn Zn Zn
O O O
OH OH OH
O O O
Zn Zn Zn
O O O
(A)
(B)

ABC MLD

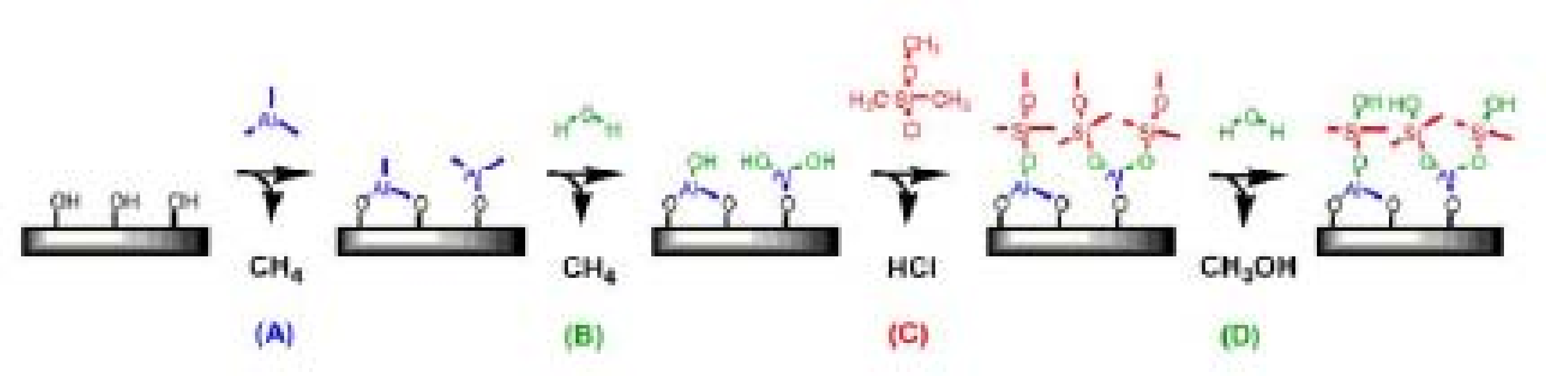


Diols vs. Polyols

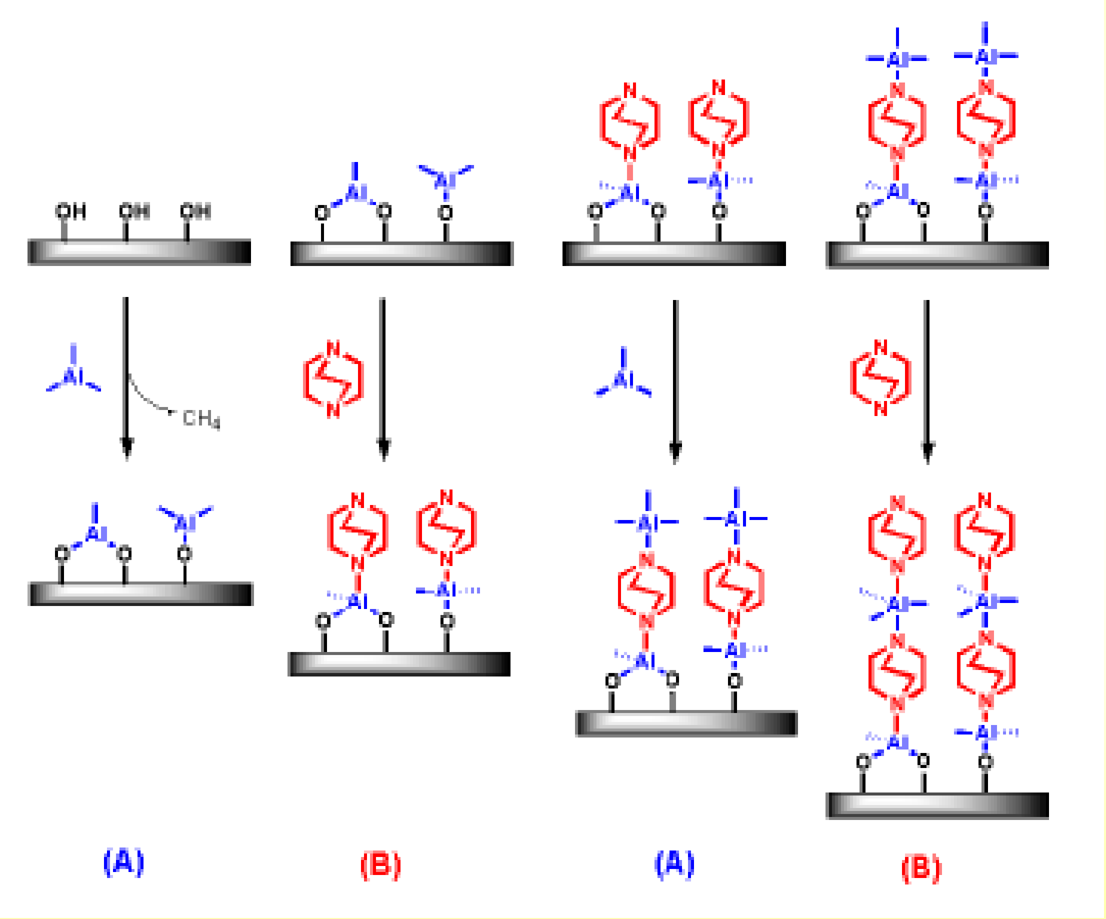


homobifunctional precursors can react twice with the $AlCH_3$* surface species, double reactions lead to a loss of reactive surface sites and decreasing growth rate

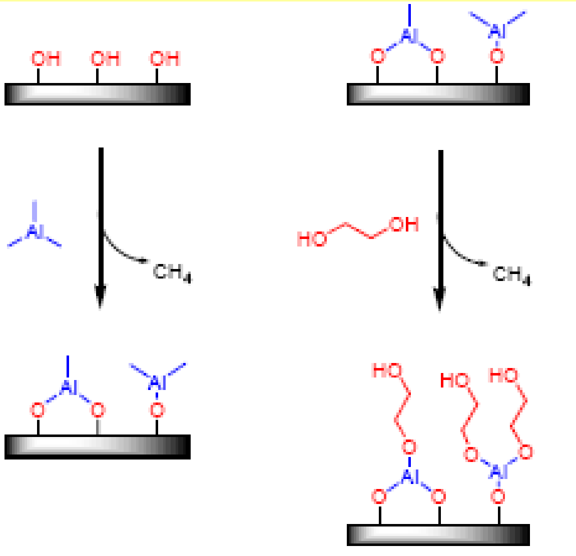
ABCD MLD
growth of an alumina-siloxane



AB Lewis Acid-Lewis Base Reactions

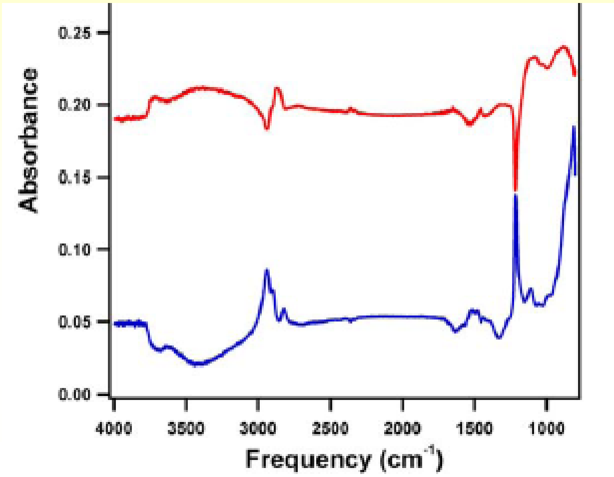


Alucone

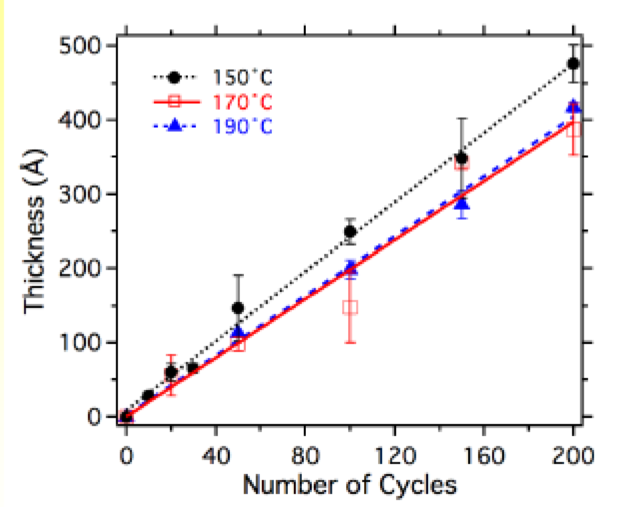


OH OH OH
Al
CH4
HO OH
CH4
HO HO HO
O Al O

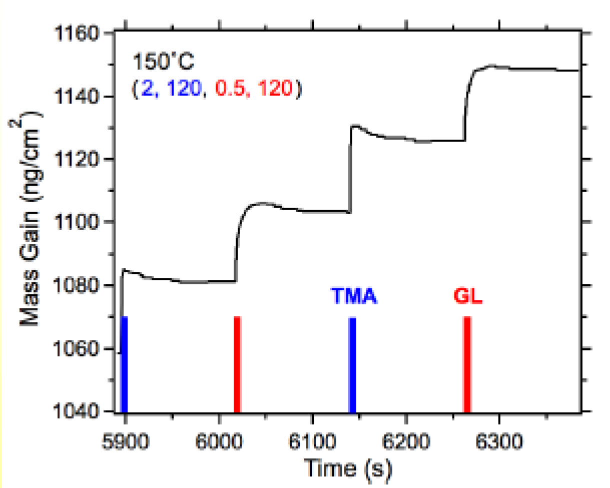
(A) (B)



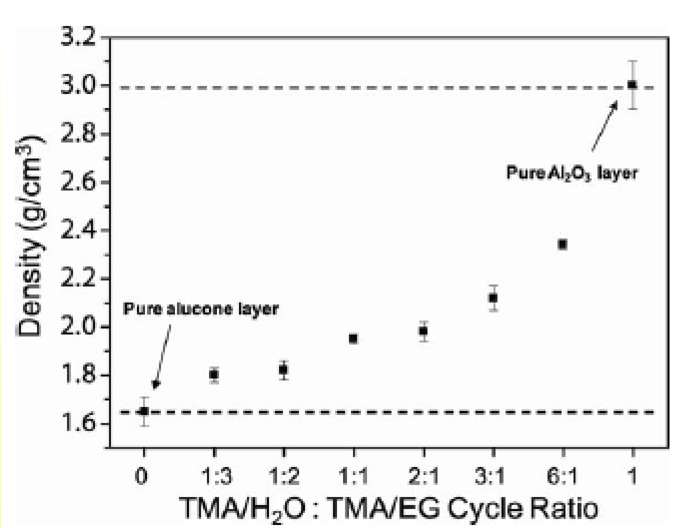
Absorbance
0.25
0.20
0.15
0.10
0.05
0.00
4000 3500 3000 2500 2000 1500 1000
Frequency (cm-1)



150˚C
170˚C
190˚C
Thickness (Å)
500 400 300 200 100 0
0 40 80 120 160 200
Number of Cycles



150˚C
(2, 120, 0.5, 120)
Mass Gain (ng/cm2)
1160 1140 1120 1100 1080 1060 1040
TMA
GL
5900 6000 6100 6200 6300
Time (s)



Density (g/cm3)
3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
Pure Al2O3 layer
Pure alucone layer
0 1:3 1:2 1:1 2:1 3:1 6:1 1
TMA/H2O : TMA/EG Cycle Ratio