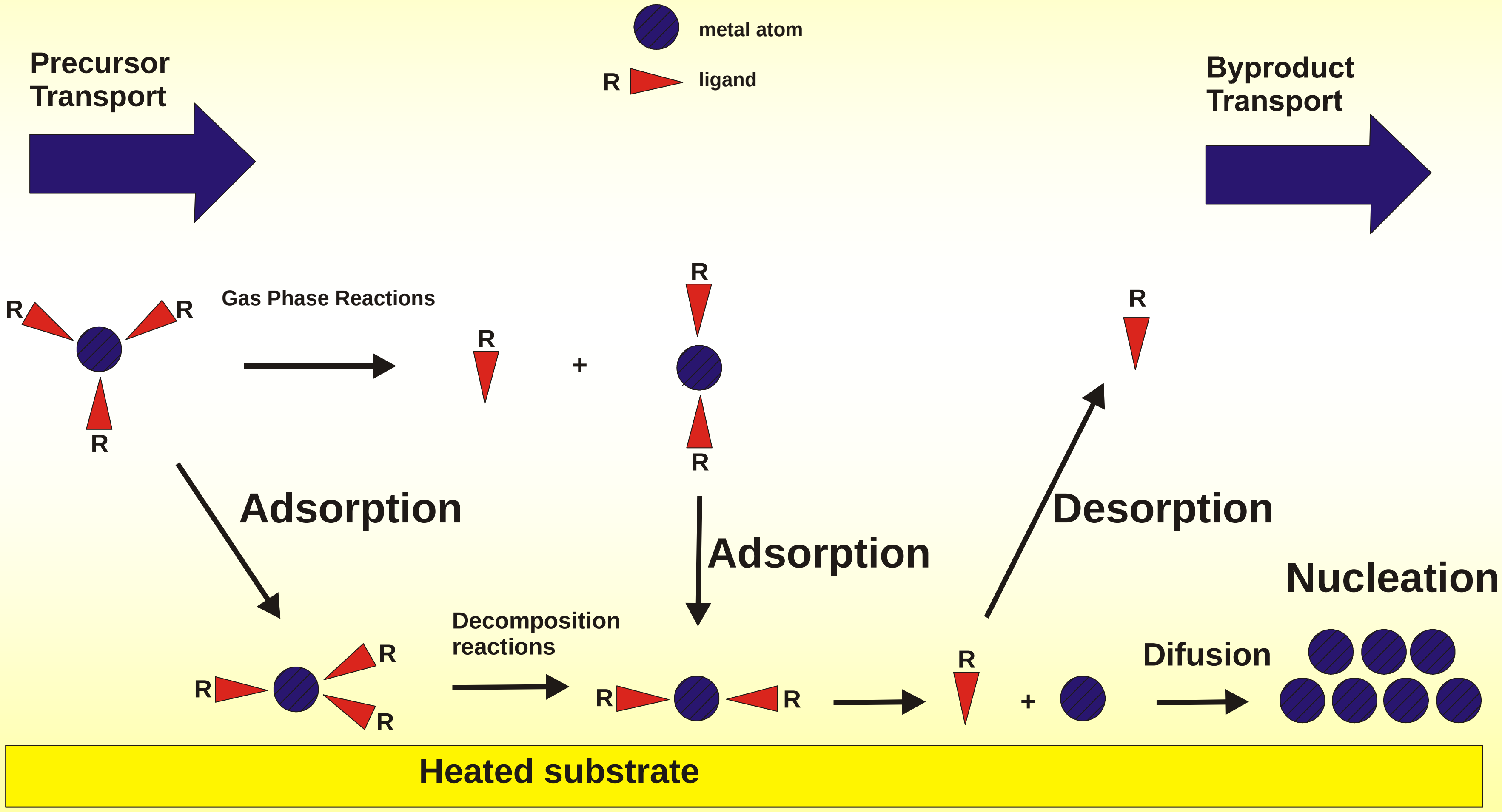
Basic steps in the CVD process



Precursor Transport

Byproduct Transport

Gas Phase Reactions

Adsorption

Adsorption

Desorption

Nucleation

Decomposition reactions

Difusion

Heated substrate

Chemical Vapor Deposition

Aluminum

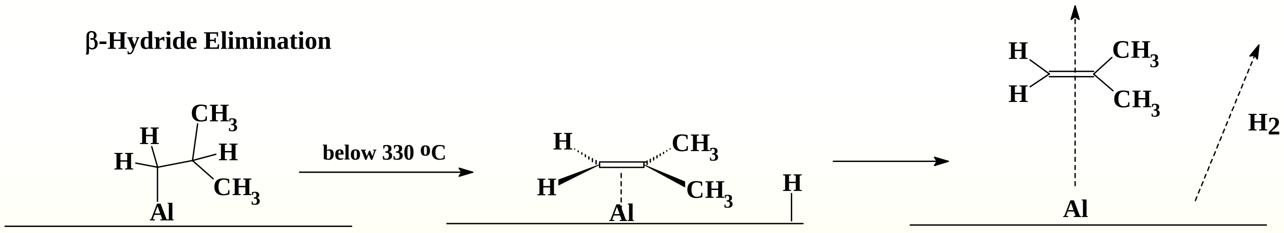
2.27 μΩcm, easily etched, Al dissolves in Si,

GaAs + Al ⟶ AlAs + Ga

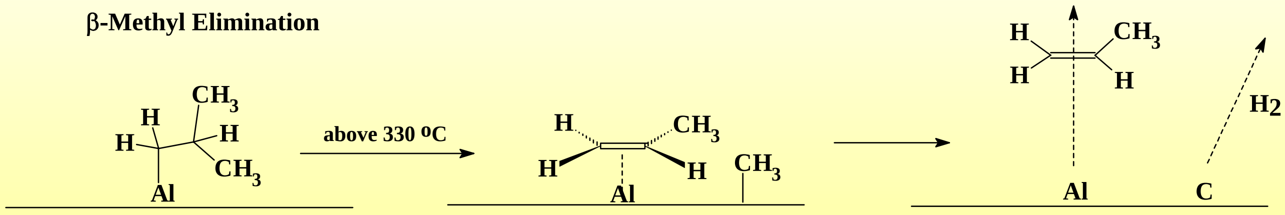
Gas diffusion barriers, Al on polypropylene, food packaging = chip bags, party balloons, high optical reflectivity

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

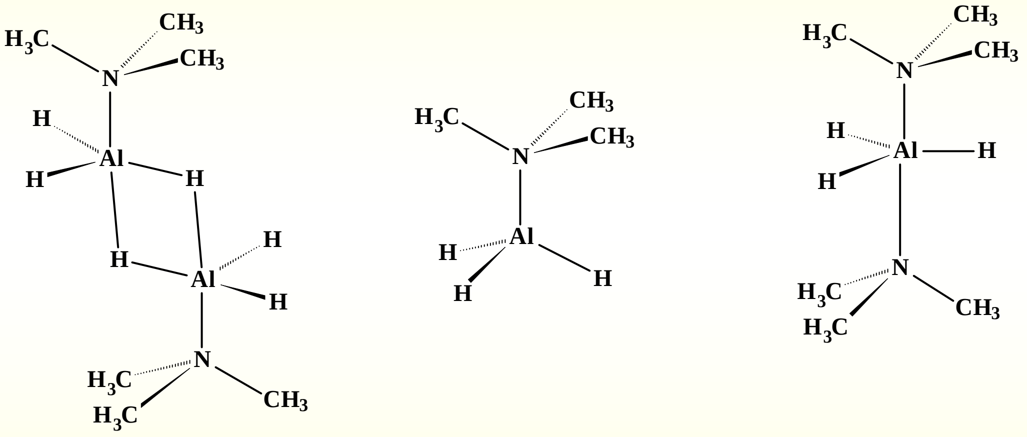
TMA
large carbon incorporation, Al_4C_3, RF plasma, laser

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

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

Chemical Vapor Deposition

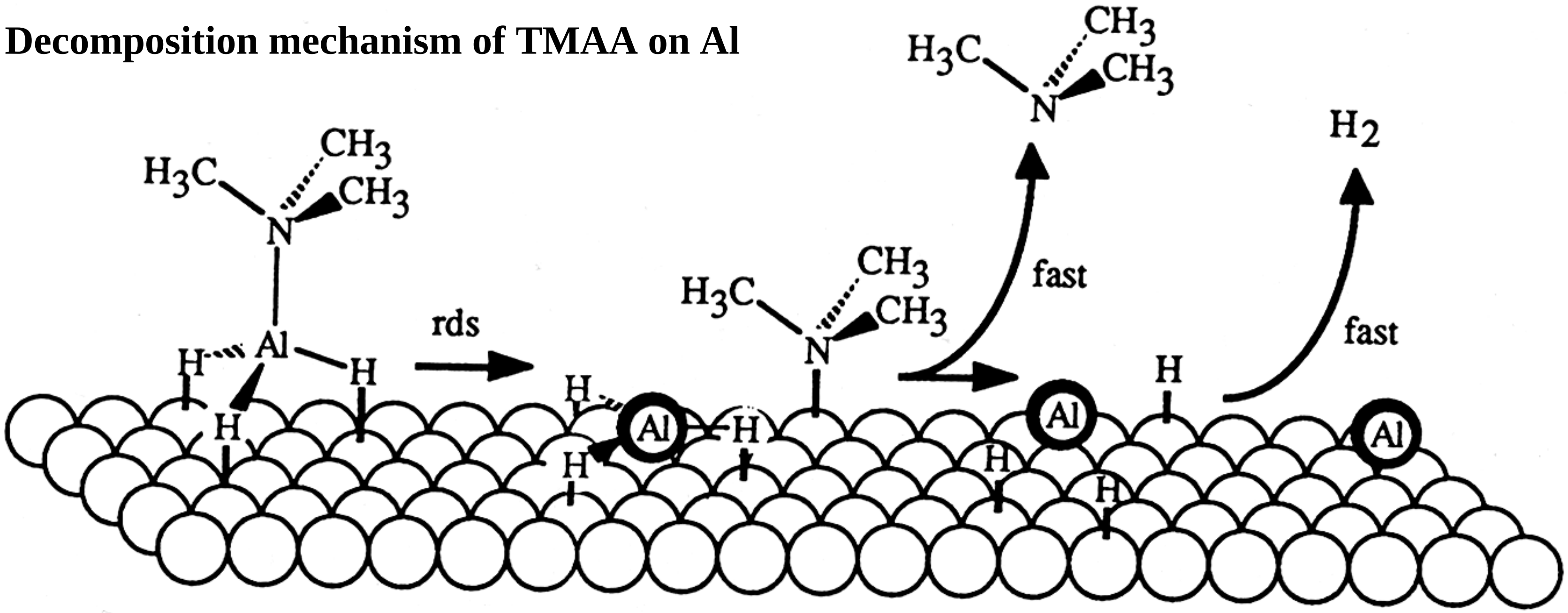
TMAA



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

Chemical Vapor Deposition

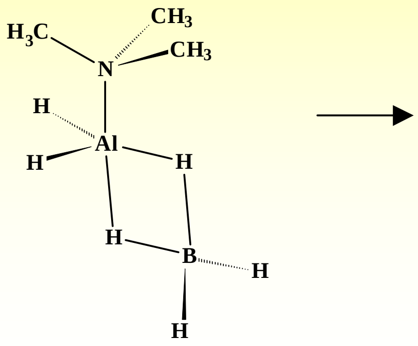
Decomposition mechanism of TMAA on Al



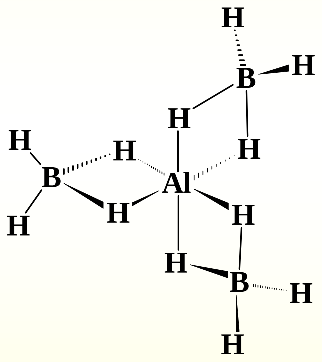
$(CH_3)_3N\text{-}AlH_3 \longrightarrow Al + (CH_3)_3N + 3/2\ H_2$ **below 100 °C**

Chemical Vapor Deposition

Aluminoboranes



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



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.

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

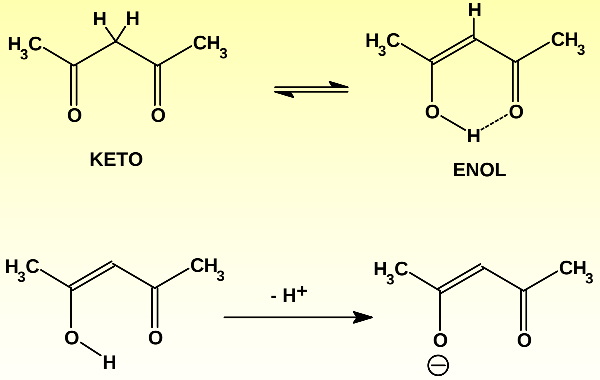
$$WF_6 + 3\ H_2 \rightarrow W + 6\ HF$$

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

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

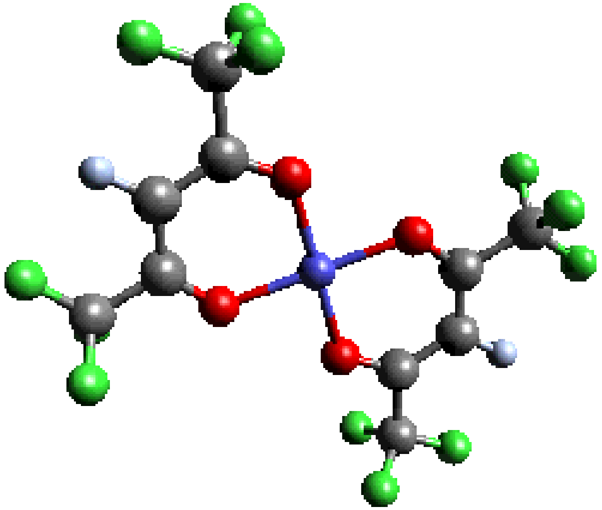
Chemical Vapor Deposition

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

Chemical Vapor Deposition



Copper(II) hexafluoroacetylacetonate

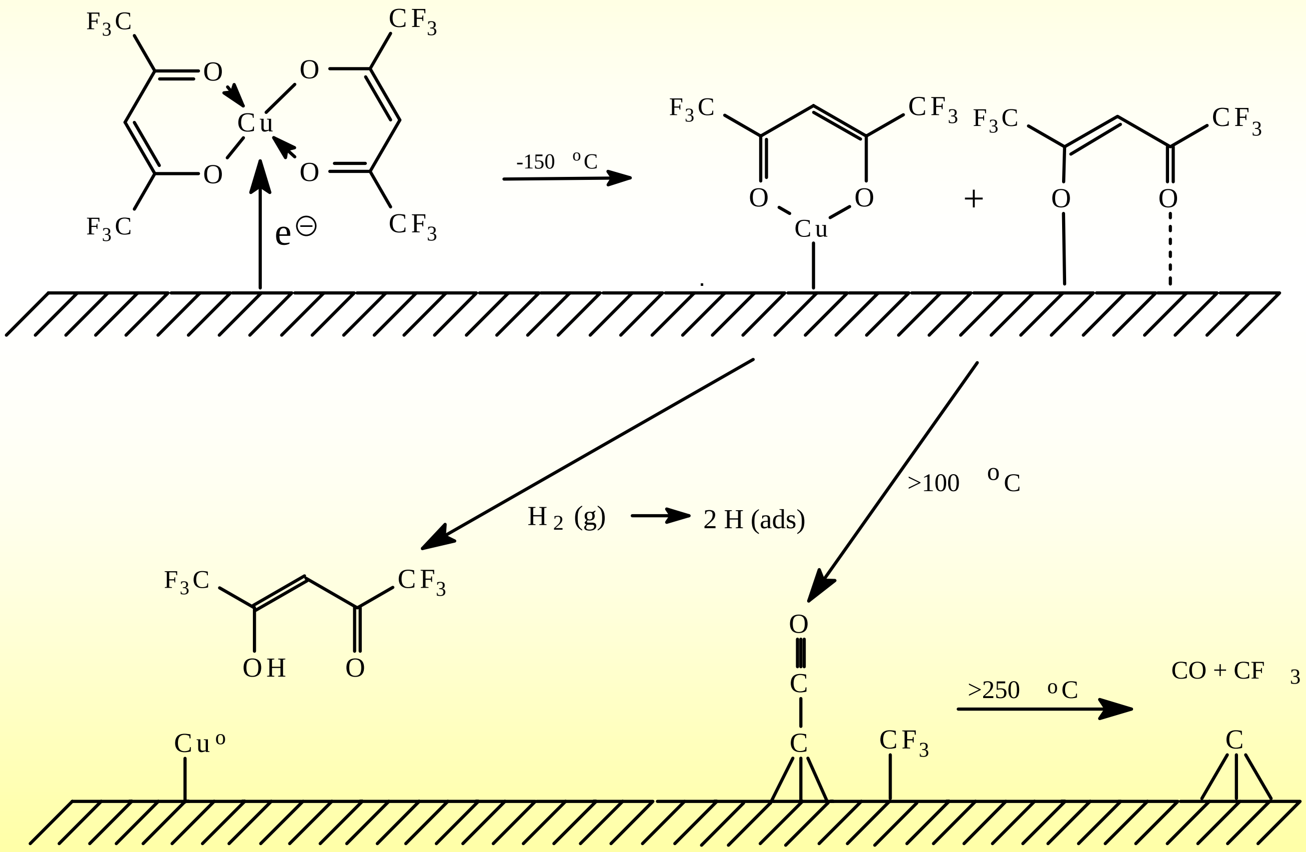
excellent volatility (a vapor pressure of 0.06 Torr at r. t.),
low decomposition temperature,
stability in air, low toxicity,
commercial availability

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.

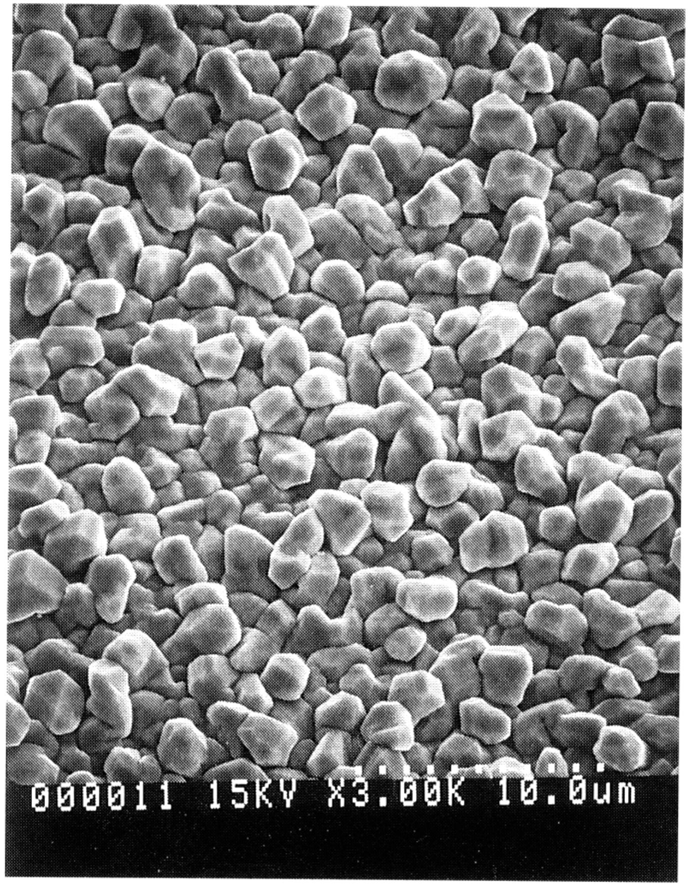
Chemical Vapor Deposition

Scheme I



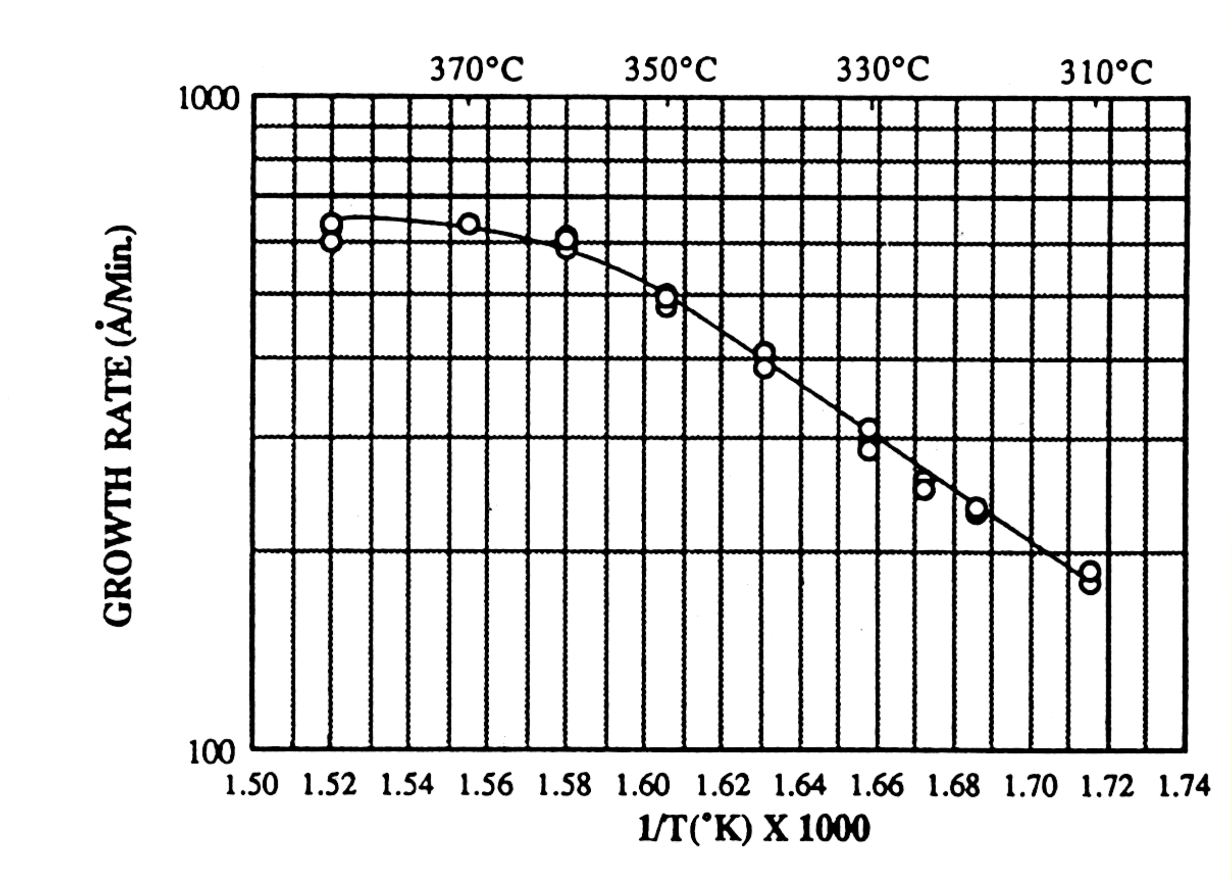
Chemical Vapor Deposition

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

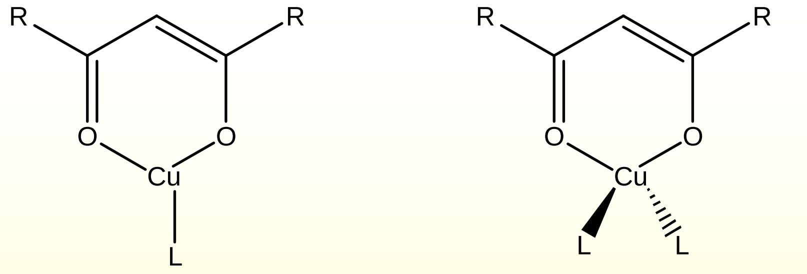


Chemical Vapor Deposition

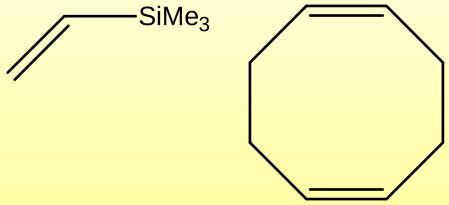
Cu(I) precursors

Disproportionation to Cu(0) and Cu(II)

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



L: PMe$_3$, PEt$_3$, CO, CN^{t}Bu,

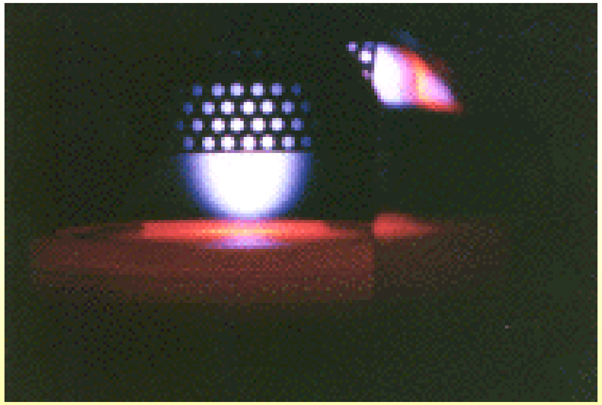


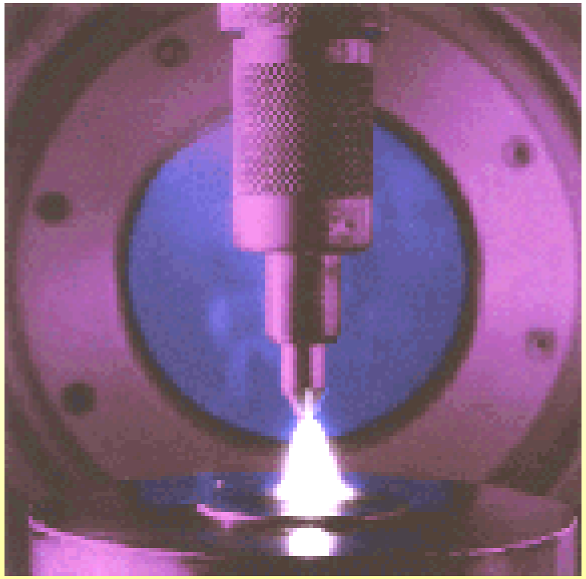
Chemical Vapor Deposition

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,

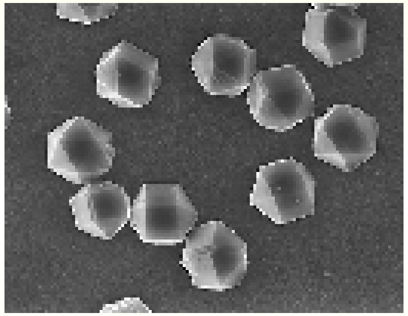
the rate of diamond growth exceeds its etch rate whilst for graphite the converse is true.

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,

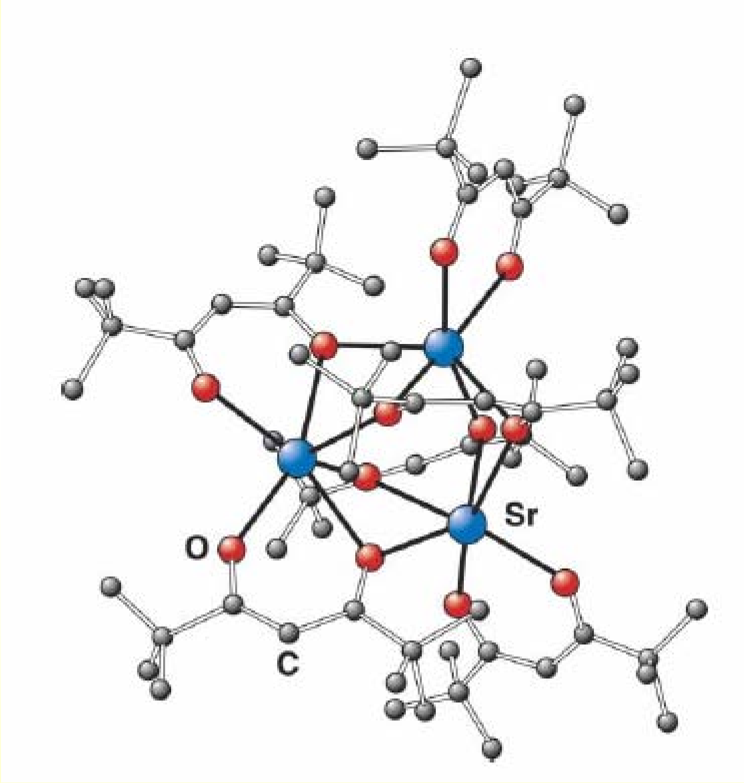
ZnS, ZnSe, Ge: excellent IR transmission but brittle

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

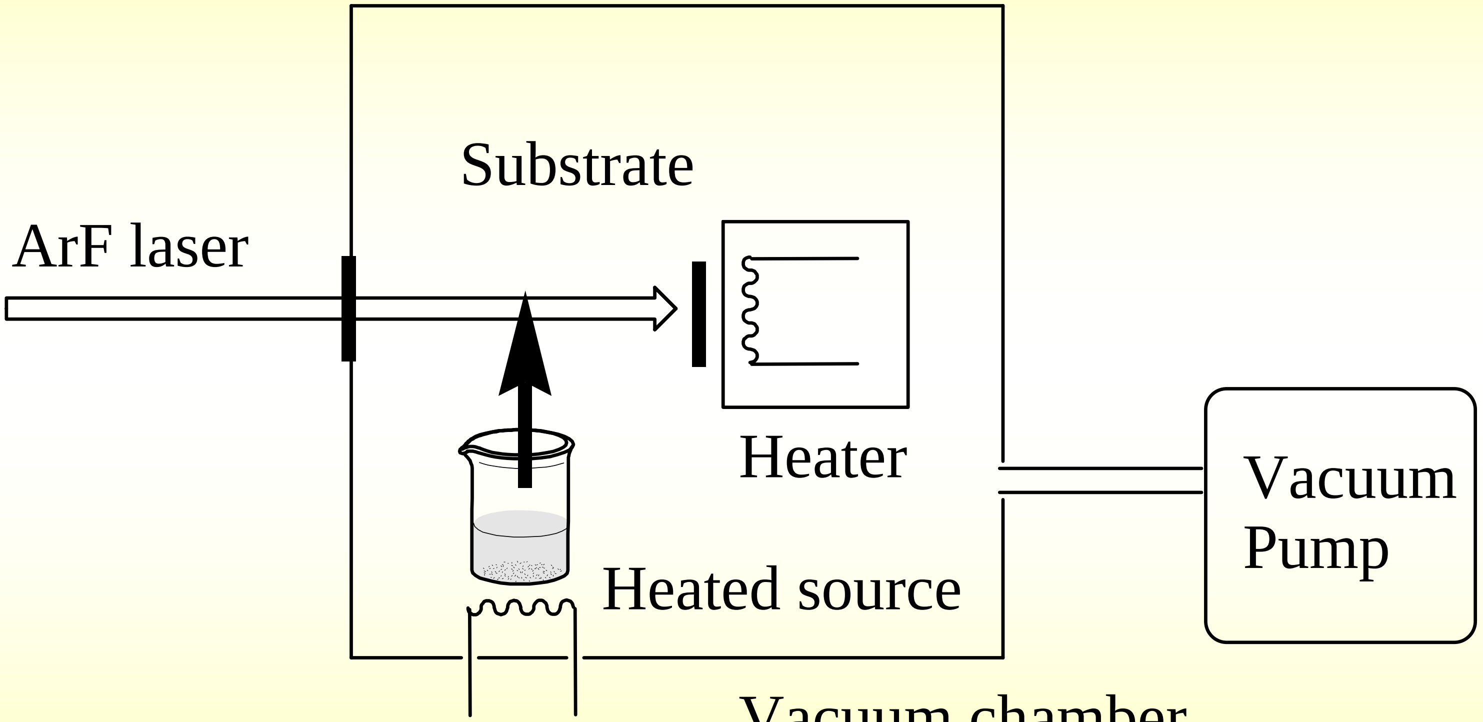
Electronic devices - doping, an insulator into a semiconductor

***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


Sr
O
C

Laser-enhaced CVD



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