Basic steps in the CVD process

1. Transport of the precursor
2. Gas phase reactions
   - Adsorption
   - Decomposition reactions
3. Adsorption on the substrate
4. Desorption of byproducts
5. Nucleation and growth
6. Diffusion of deposited material

CVD_ALD_MLD
CVD Reactor

CVD_ALD_MLD
CVD Reactor

Gas Supply System  Reactor  Vacuum System

CVD_ALD_MLD
Precursor Volatility

![Graphs showing vapor pressure and weight percentage as functions of temperature for different precursors.](image-url)
Chemical Vapor Deposition

Aluminum
2.27 $\mu\Omega$cm, easily etched, Al dissolves in Si,
GaAs + Al $\rightarrow$ AlAs + Ga
Gas diffusion barriers, Al on polypropylene, food packaging = chip bags, party balloons, high optical reflectivity

TIBA

$\beta$-Hydride Elimination

$\beta$-Methyl Elimination
Chemical Vapor Deposition

Al deposits selectively on Al surfaces, not on SiO₂
Laser-induced nucleation
248 nm only surface adsorbates pyrolysed
193 nm gas phase reactions, loss of spatial selectivity control

TMA
large carbon incorporation, Al₄C₃, RF plasma, laser

\[ \text{Al}_2(\text{CH}_3)_6 \rightarrow \frac{1}{2} \text{Al}_4\text{C}_3 + \frac{9}{2} \text{CH}_4 \text{ under N}_2 \]

\[ \text{Al}_2(\text{CH}_3)_6 + 3 \text{H}_2 \rightarrow 2 \text{Al} + 6 \text{CH}_4 \text{ under H}_2 \]
Chemical Vapor Deposition

TMAA

\[
(CH_3)_3N-AlH_3 \rightarrow Al + (CH_3)_3N + \frac{3}{2} H_2 \quad \text{below 100 °C}
\]
Chemical Vapor Deposition

Decomposition mechanism of TMAA on Al

$\text{(CH}_3\text{)}_3\text{N-AlH}_3 \rightarrow \text{Al} + \text{(CH}_3\text{)}_3\text{N} + 3/2 \text{H}_2 \quad \text{below 100 °C}$
Chemical Vapor Deposition

Aluminoboranes

\[
\text{DMAH ligand redistribution}
\]

\[
[(\text{CH}_3)_2\text{AlH}]_3 \rightarrow (\text{CH}_3)_3\text{Al} \uparrow + \text{AlH}_3 \rightarrow \text{Al} + \text{H}_2
\]

at 280 °C, low carbon incorporation
Chemical Vapor Deposition

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

$$2 \text{WF}_6 + 3 \text{Si} \rightarrow 2 \text{W} + 3 \text{SiF}_4$$

$$\text{WF}_6 + 3 \text{H}_2 \rightarrow \text{W} + 6 \text{HF}$$

$$\text{WF}_6 + 3/2 \text{SiH}_4 \rightarrow \text{W} + 3 \text{H}_2 + 3/2 \text{SiF}_4$$

$$\text{W(CO)}_6 \rightarrow \text{W} + 6 \text{CO}$$
Diketonate Ligands

<table>
<thead>
<tr>
<th>R₁</th>
<th>R₂</th>
<th>Name</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>CH₃</td>
<td>Pentane-2,4-dionate (acetylacetonate)</td>
<td>acac</td>
</tr>
<tr>
<td>CH₃</td>
<td>CF₃</td>
<td>1,1,1-trifluoropentane-2,4-dionate (trifluoroacetylacetonate)</td>
<td>tfac</td>
</tr>
<tr>
<td>CF₃</td>
<td>CF₃</td>
<td>1,1,1,5,5,5-hexafluoropentane-2,4-dionate (hexafluoroacetylacetonate)</td>
<td>hfac</td>
</tr>
<tr>
<td>CH₃</td>
<td>C(CH₃)₃</td>
<td>1,1-dimethylhexane-3,5-dionate</td>
<td>dhd</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>C(CH₃)₃</td>
<td>2,2,6,6-tetramethylheptane-3,5-dionate</td>
<td>thd</td>
</tr>
<tr>
<td>CH₃</td>
<td>CH₂CH(CH₃)₂</td>
<td>6-methylheptane-2,4-dionate</td>
<td>mhd</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>CH₂CH(CH₃)₂</td>
<td>2,2,7-trimethyloctane-3,5-dionate</td>
<td>tmod</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>C₆H₅</td>
<td>1,3-diphenylpropane-1,3-dionate (dibenzoylmethane)</td>
<td>dbm</td>
</tr>
</tbody>
</table>
Diketonate Precursors

Mononuclear

Polynuclear

CVD_ALD_MLD
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

\[
\begin{align*}
&\text{CF}_3\text{CF}_3\text{C} \quad \text{e}^{-} \quad \text{Cu} \quad \text{O} \quad \text{CF}_3\text{F}_3\text{C} \\
&\text{O} \quad \text{Cu} \quad \text{O} \\
&\text{F}_3\text{C} \quad \text{CF}_3\text{C} \quad \text{CF}_3\text{C} \quad \text{OH} \\
&\text{OH} \quad \text{C} \quad \text{O} \quad \text{C} \\
&\text{Cu}^{\circ} \quad \text{C} \quad \text{CF}_3 \quad \text{C} \\
&\text{CO} + \text{CF}_3
\end{align*}
\]

-150 °C

2 H (ads)

>100 °C

>250 °C

H_2 (g) → 2 H (ads)

>250 °C

CO + CF_3

CVD_ALD_MLD
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)

\[ 2 \text{Cu(diketonate)}_n \rightarrow \text{Cu} + \text{Cu(diketonate)}_2 + n \text{L} \]

L: PMe$_3$, PE$_3$, CO, CN$_{tBu}$, SiMe$_3$
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.

CVD_ALD_MLD
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: CH₃
(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.

CVD_ALD_MLD
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

CVD_ALD_MLD
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$_3$N$_4$ 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

\[ p \text{-doping: } B_2H_6 \text{ incorporates } B \text{ into the lattice} \]
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-Enhanced CVD

\[ \text{Si(O}_2\text{CCH}_3)_4 \rightarrow \text{SiO}_2 + 2 \text{O(OCCH}_3)_2 \]
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 by 1st 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 Al₂O₃ 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:

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

**Nonmetallic** - 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

\[ \text{Al(CH}_3\text{)}_3/\text{H}_2\text{O} \]
\[ \text{ZrCl}_4/\text{H}_2\text{O} \]
\[ \text{HfCl}_4/\text{H}_2\text{O} \]
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$_x$N$_y$
Examples of ALD

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

W - WF$_6$ and Si$_2$H$_6$
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$_2$O$_3$ Films

Precursors: trimethylalane, tris(tert-butoxy)silanol
Deposition of amorphous SiO$_2$ and nanolaminates of Al$_2$O$_3$
32 monolayers in 1 cycle

Applications:
microelectronics
optical filters
protective layers (against diffusion, oxidation, corrosion)
ALD of SiO$_2$ and Al$_2$O$_3$ Films

Step A

Step B

CVD_ALD_MLD
ALD of SiO$_2$ and Al$_2$O$_3$ Films

C, D: alkoxide - siloxide exchange
ALD of SiO$_2$ and Al$_2$O$_3$ Films

E: elimination of isobutene = formation of -OH
ALD of SiO$_2$ and Al$_2$O$_3$ Films

F: elimination of butanol = condensation

G: elimination of water = condensation
ALD of SiO₂ and Al₂O₃ Films

Repeat Step A
MLD- Molecular Layer Deposition

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

CVD_ALD_MLD
AB MLD
ABC MLD

CVD_ALD_MLD
Diols vs. Polyols

Homobifunctional precursors can react twice with the AlCH₃* 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