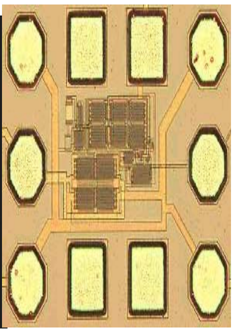
Chemical vapour deposition, CVD

Mainly thin film application

One of the most important methods for preparing thin films and coatings

- **Protection (corrosion, wear…)**
- **Optical properties**
- **Electronic properties**
- **Magnetic properties**
- **Decoration**
- **New properties**



CVD

“Chemical vapour deposition (CVD) is a process where one or more volatile precursors are transported via the vapour phase to the reaction chamber, where they decompose on a heated substrate”

Many materials may be deposited using CVD and related techniques. Metals, oxides, sulfides, nitrides, phosphides, arsenides, carbides, borides, silicides…

Example: Preparation of TiB_2, melting point 3325˚C. May be deposited by CVD at 1000˚C:

$$TiCl_4 + 2BCl_3 + 5H_2 \rightarrow TiB_2 + 10\ HCl$$

CVD was first used for hard coatings (cutting tools etc.)

Microelectronics, 3D-structures

Glass (SnO_2, TiN, SiO_2, TiO_2)

Solar cells, catalysis, membranes, waveguides, mirrors, ”synthetic gold” (TiN_x)

Steps in the CVD process

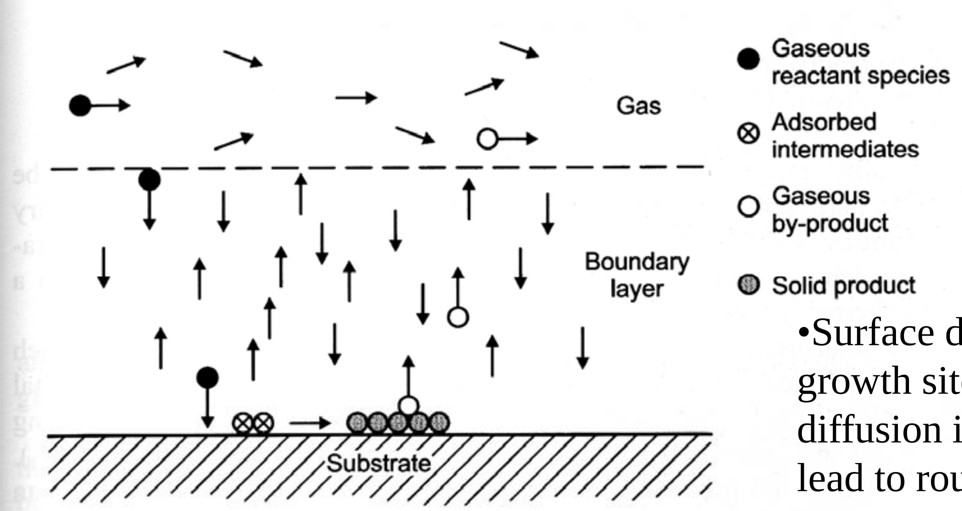


Figure 3-5. Schematic representation of the steps in CVD processes.

- Transport of the reagents (e.g. $TiCl_4$, BCl_3, H_2) in the gas phase (often with carrier gas) to the reaction zone
- Diffusion (or convection) through the boundary layer
- Adsorption of precursors on the substrate
- Surface diffusion of the precursors to growth sites. Reaction without diffusion is not wanted, as this may lead to rough growth surface.
- Surface chemical reaction, formation of a solid film and formation of by-products.
- Desorption of by-products
- Diffusion of by-products through the boundary layer
- Transport of gaseous by-products out of the reactor.

Reactions in the gas-phase is most often unwanted

The ideal precursor

- Liquid rather than solid or gaseous
- Good volatility
- Good thermal stability in the delivery system, during evaporation and transport
- Decompose cleanly and controllably on the substrate without incorporation
- Give stable by-products which are readily removed from the reaction zone
- Readily available in consistent quality and quantity at low cost
- Non-toxic and non-pyrophoric

Impossible to meet all criteria.

Industrially important precursors:

Hydrides: SiH_4, AsH_3 ...
Metal alkyls: Al^iBu_3, $GaEt_3$
Metall halides: WF_6, $TiCl_4$

Precursors

Volatility and gas phase reactivity
Metal-organic and organometallic precursors are often used.
Volatility is enhanced by minimizing intermolecular interactions (e.g. hydrogen bonds, dipole-dipole interaction and van der Waals interactions)
Small molecules generally have higher vapour pressure.
Oligomerization and aggregation should be minimized.
May use e.g. F-substitution

β-diketonate ligands are often used in metal-containing precursors. Bidentate with good chelating properties. Metal diketonates are often monomeric and volatile.

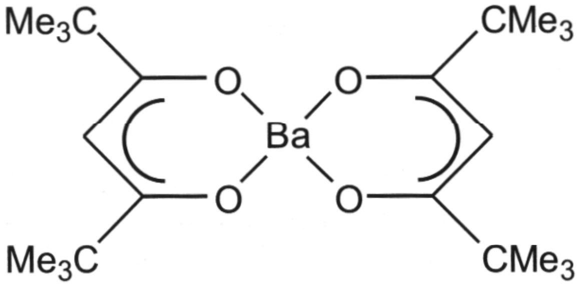


Figure 3-22. Barium dipivaloylmethanate, Ba(dpm)$_2$.

Oligomerization

Metal precursors are often under-coordinated. Oligomerization may occur in order to satisfy the metal coordination.
This may be suppressed by:
•Sterically demanding ligands limits the accessibility of the metal center. These compound are often very reactive towards small molecules (O_2, H_2O) and the bulky ligands may reduce volatility
•Using multidentate, chelating, ligands. May satisfy the metal coordination requirements and prevent oligomerization. However, multidentate ligands may form bridges between molecules and dissociation and oligomerization may occur prior to reaction.

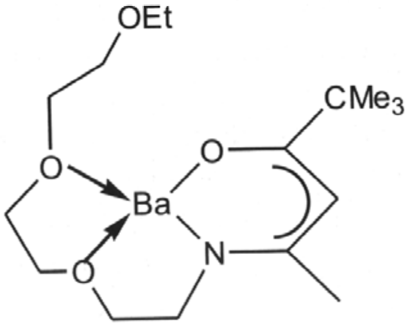


Figure 3-23. A polyether modified bis(β-ketoiminate) barium derivative (only one of the two multidentate [▶ glossary] ligands is drawn for clarity).

Problems also associated with carbon incorporation if the decomposition is not “clean” enough.

Multi element CVD

Two approaches:

Use two (or more) individual precursors. Must decompose individually on the substrate and react to give the desired product.

$$GaMe_3 + AsH_3 \rightarrow GaAs + 3CH_4$$

Problems: Must have similar adsorption and decomposition properties and compatible volatilities. Stoichiometry difficulties.

Single source precursors contain all the elements in the desired stoichiometry. Bonds between the film-forming elements must be stronger than to the ligands in order to obtain clean decomposition. Single source precursor for GaAs:

(3-10)

Problems with single-source precursors are often related to increased molecular weight (low volatility) and to decomposition behaviour.

Equipment

Substrate temperature 200-800˚C, pressure 0.1 mbar – 1 bar

Vapour pressure of precursor should be > 0.01 bar at 25˚C

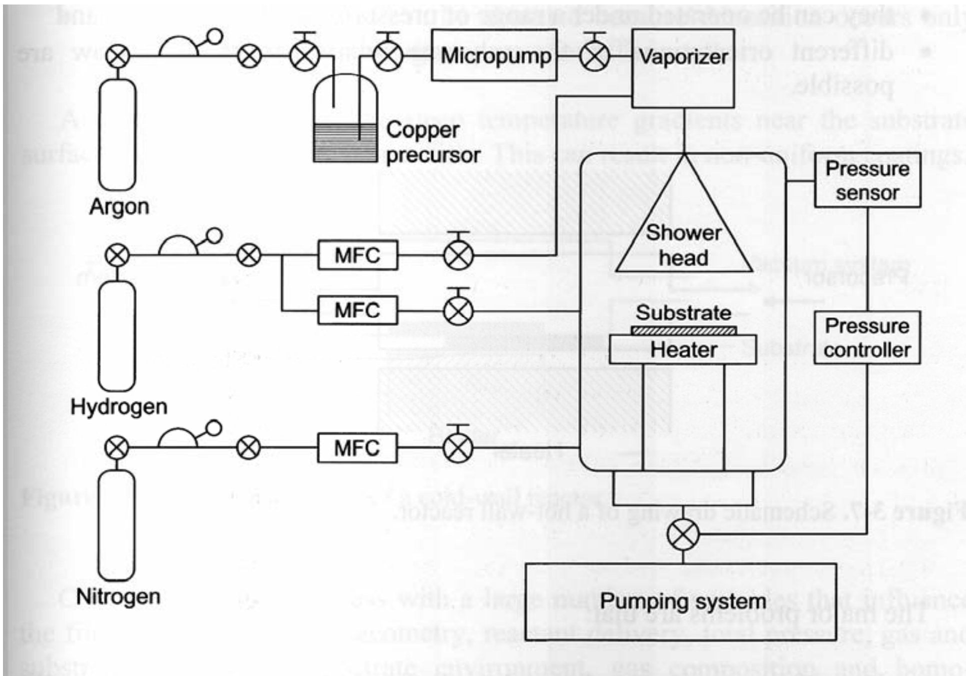


Figure 3-6. Schematic of a thermal CVD reactor for copper CVD from a Cu(II) precursor (see Eq. 3-19) (MFC = mass flow controller).

Hot wall reactor

Advantages:
- Simple to operate
- May accommodate several substrates
- Uniform substrate temperature
- May be operated at a range of temperatures and pressures
- Different orientations of substrate

Disadvantages:
- Deposition occur not only at the substrate, but also on e.g. reactor walls
- The consumption of precursor is large and difficult to control. May result in feed-rate-limited deposition
- Gas-phase reactions may occur

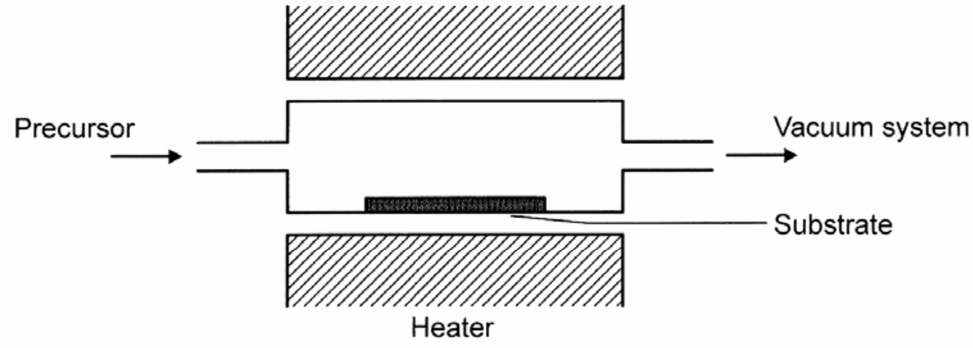


Figure 3-7. Schematic drawing of a hot-wall reactor.

Cold wall reactor

Substrate is at a higher temperature than the reactor walls. Often used in industry

Advantages:
- Pressure and temperature can be controlled
- Plasmas can be used
- No deposition on reactor walls
- Gas-phase reactions are suppressed
- Higher deposition rates may be reached (higher precursor efficiency

Disadvantages:
- Steep temperature gradients near the substrate surface may lead to convection
- Less flexibility on substrate orientation and usually only one substrate at a time.

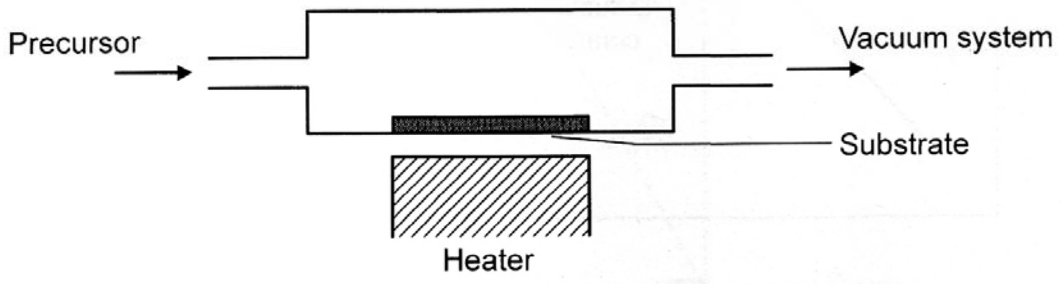


Figure 3-8. Schematic drawing of a cold-wall reactor.

Growth rates

Many parameters influences the growth and coating properties
For industrial use, a growth rate of 0.1μm/min is necessary (for electronics) or higher (e.g. for glass coating)

Three regimes:
- Surface reaction (kinetically) limited.
- Diffusion (or mass transport) limited.
- Increased desorption rate of precursors.

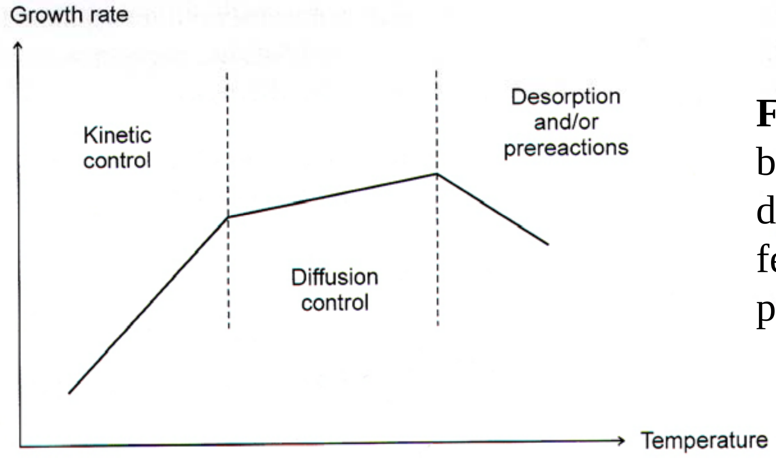


Figure 3-9. Dependence of the film growth rate on the substrate temperature.

Feed-rate limited growth if both mass transport and diffusion is fast compared to feed. Often with low vapour pressure precursors.

Bi-molecular systems

Reaction between A and B
- Elay-Rideal mechanism: Only A is adsorbed, and reacts directly with B in gas-phase. The growth rate shows a saturation with high coverage of the surface with A-molecules.
- Langmuir-Hinshelwood mechanism: Both A- and B-molecules are adsorbed and react on the surface. There is a maximum in growth rate when the surface is equally covered by the two types of molecules.

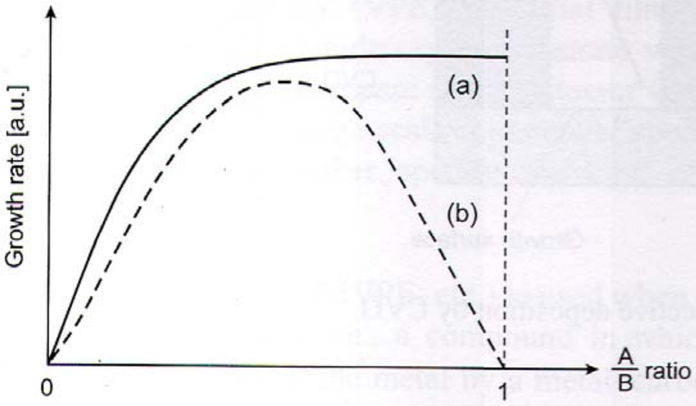


Figure 3-10. Growth rates in bimolecular systems: (a) Elay–Rideal mechanism, (b) Langmuir–Hinshelwood mechanism.

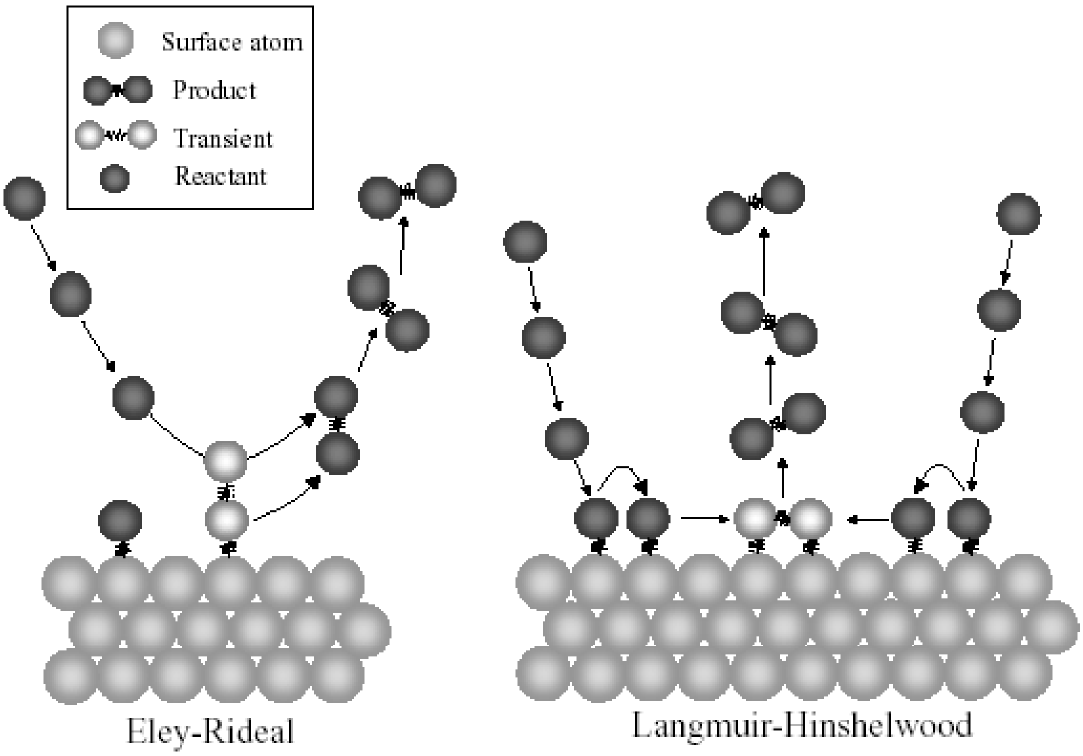


Figure 1.1: *Graphic illustration of the Eley–Rideal (ER see left panel) and the Langmuir–Hinselwood (LH see right panel) mechanism. While in an ER–reaction an adsorbed species reacts by a direct collision with a gas–phase species, reactions proceeding via a LH mechanism reactants are equilibrated to the surface prior to reaction.*

Selective deposition

Especially important in microelectronics; patterning of the surface and 3D-growth

- Reaction rate of precursor is limited on a non-growth surface. E.g. deposition of Cu from (hfac)Cu(PMe_3) occur on Cu, Pt… but not on SiO_2.
- Growth surface acts as co-reactant, and is selectively consumed. E.g. Si reacts with WF_6 or MoF_6, while reaction at SiO_2 or Si_3N_4 is slower.
- A chemical reaction of a gaseous co-reactant occur on the growth surface. E.g. H_2 dissociation on a metal surface, but not on SiO_2 or metal oxide surfaces.
- The rate is increased on part of the surface by irradiation.
- Selective passivation by removal of reactive surface species. (E.g. -OH exch. -$OSiMe_3$)
- Hindering nucleation (e.g. due to high surface energy)

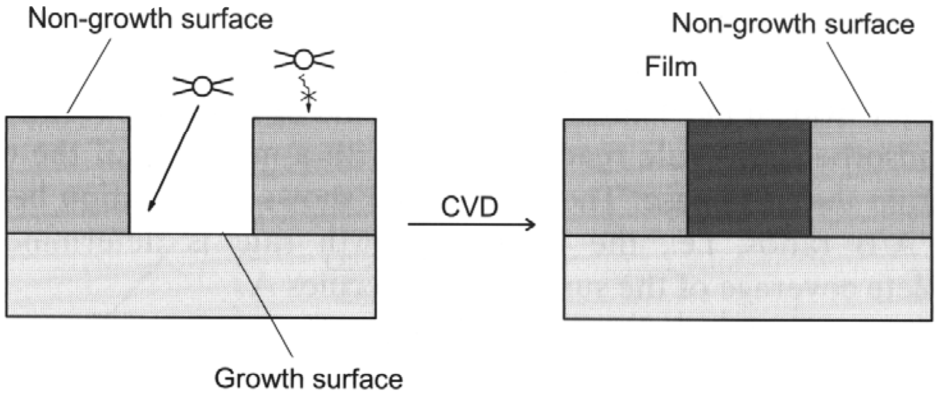


Figure 3-11. Selective deposition by CVD.

CVD-related techniques

Table 3-2. Survey of frequently used acronyms in CVD and related methods.

CVD	chemical vapor deposition
PVD	physical vapor deposition
VPE	vapor phase epitaxy
OMCVD	organometallic CVD
OMVPE	organometallic VPE
MOCVD	metal–organic CVD
MOVPE	metal–organic VPE
LPCVD	low-pressure CVD
PECVD	plasma-enhanced CVD
PACVD	plasma-assisted CVD
LCVD	laser-induced CVD
RPCVD	remote-plasma CVD
CVI	chemical vapor infiltration
ALD	atomic-layer deposition
CBE	chemical-beam epitaxy
MOMBE	metal–organic molecular-beam epitaxy

ALE, ALD

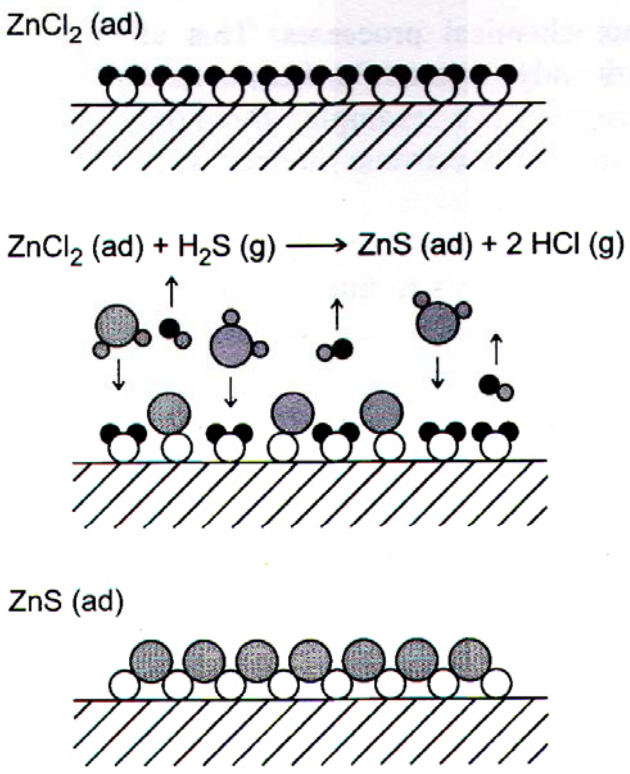
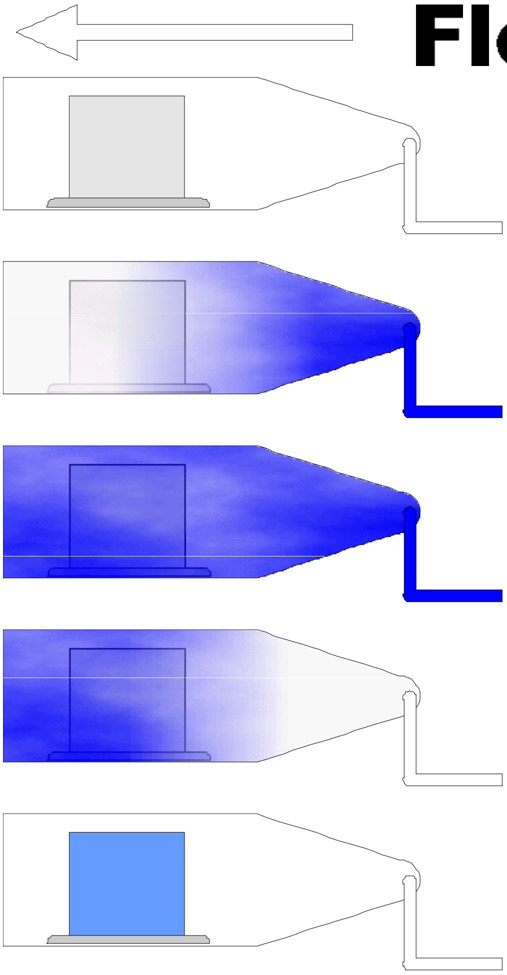
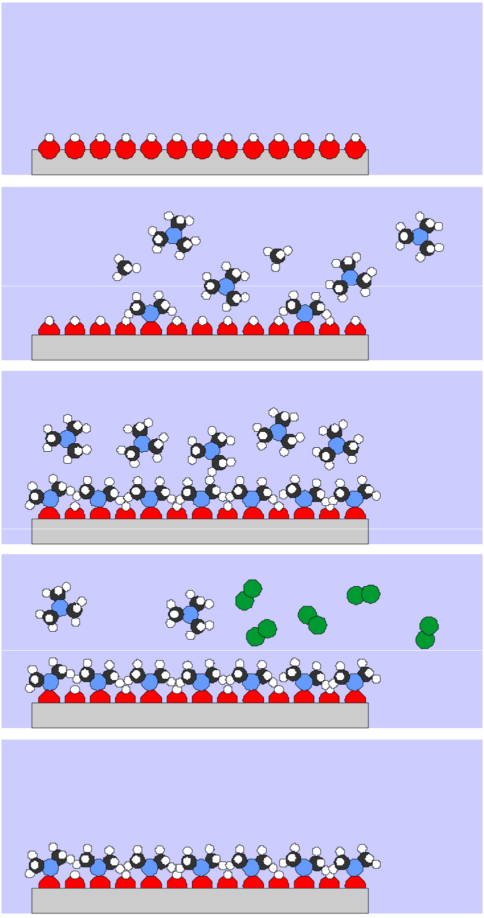


Figure 3-12. ALD reaction cycle leading to the formation of a ZnS thin film.

Flow





Conformal coating by CVD

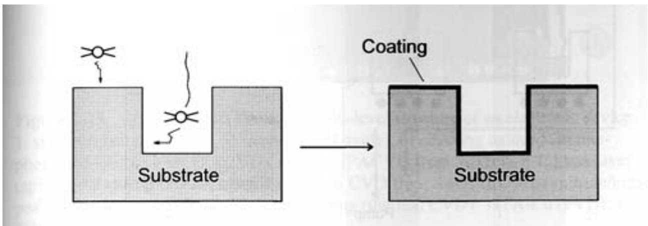
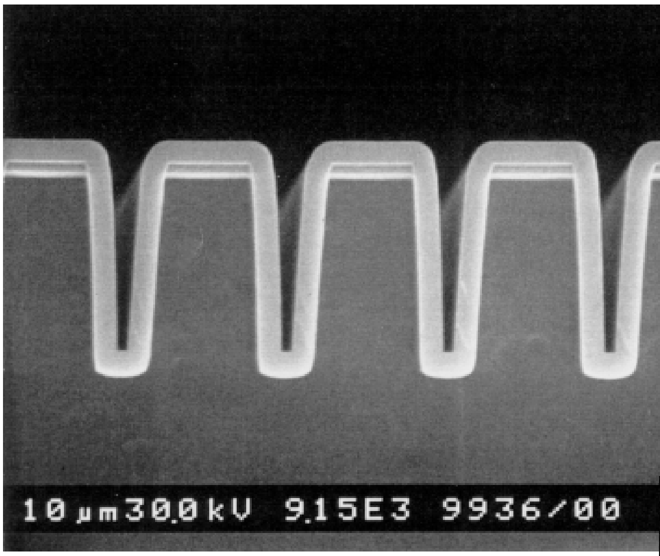
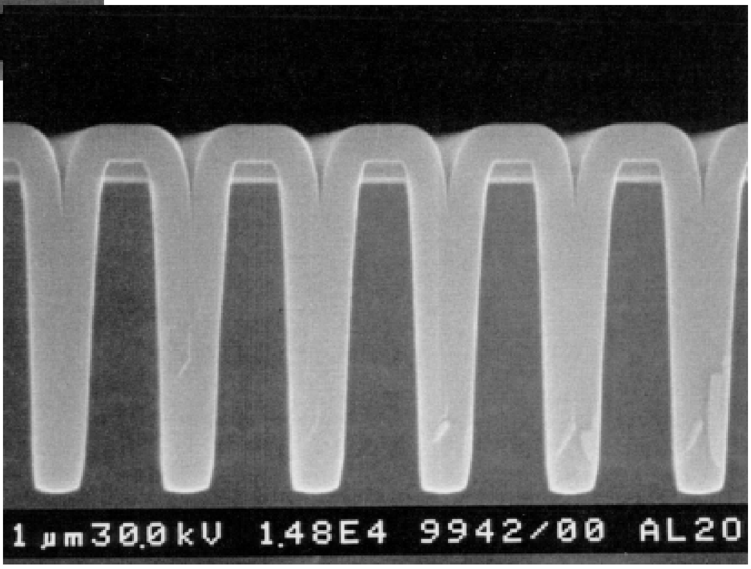


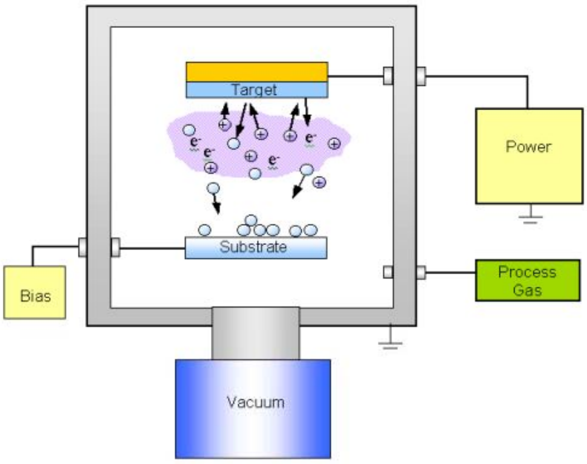
Figure 3-13. Step coverage by CVD methods.





Non-CVD processes for gas phase deposition

PVD, Physical vapour deposition



Evaporation/sputtering of a target material onto a substrate.

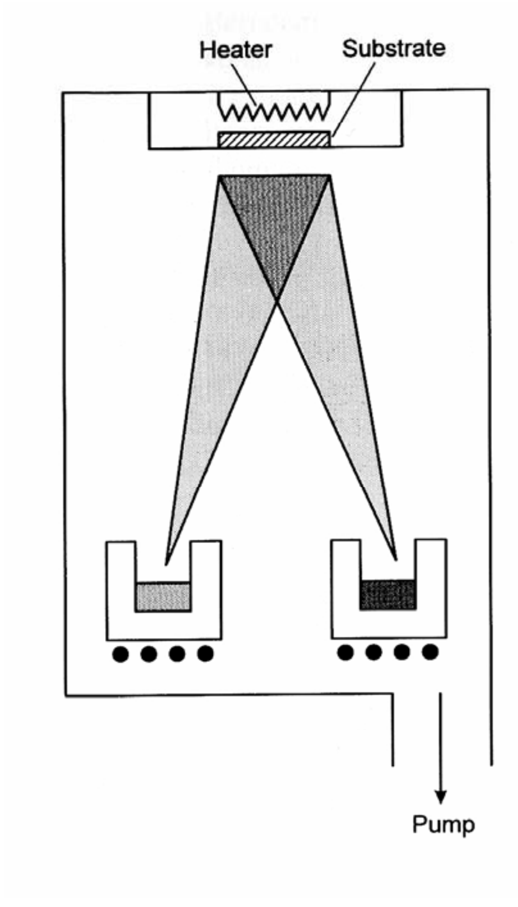
- Evaporation of a solid
- Transport of the gaseous species to the substrate
- Condensing gaseous species on the substrate, followed by nucleation and growth

Thermal evaporation
Electron or laser beam heats the surface
Heating a crucible by induction or resistive heating

Sputtering: Atoms are removed from the target by ion-bombardment (glow discharge or plasma). Ballistic transport pf atoms from the target to the substrate.

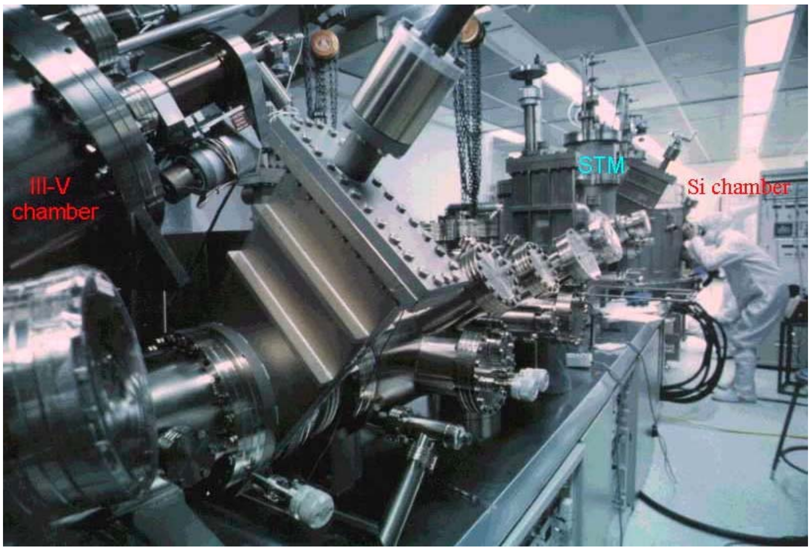
Advantages: E.g. low substrate temperature (allows deposition e.g. on polymers)
Disadvantages: E.g. shadowing effect.

MBE, Molecular beam epitaxy



Evaporation of elemental sources. Independently at a controlled rate.
Molecular beams intercept at the substrate surface.

UHV conditions (10^{-10} bar), low growth rates.
Line-of-sight.
High purity, complex layer structures, good control of doping.



Microelectronics

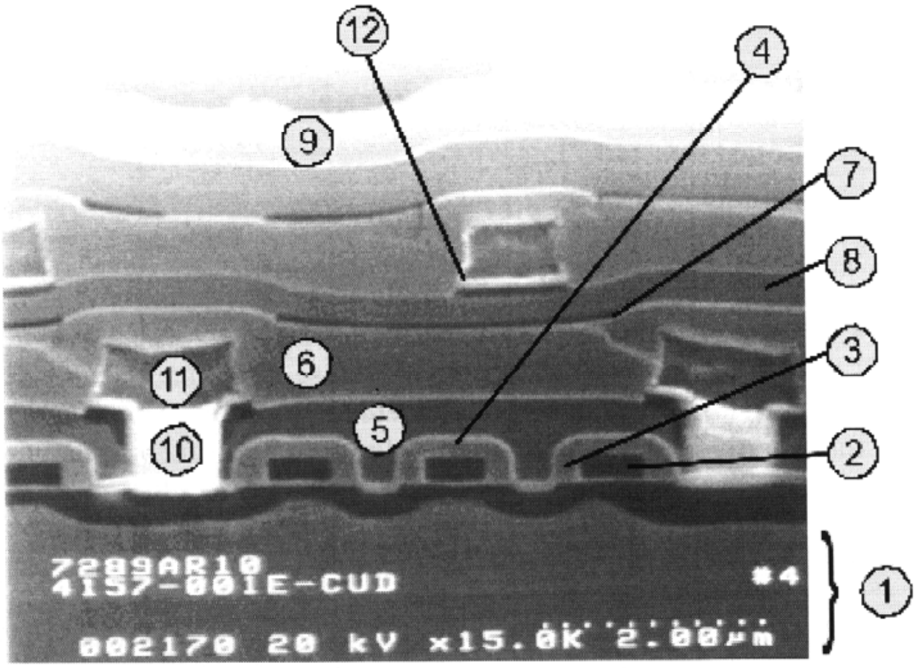


Figure 3-15. A cross-section through a multi-level structure of an electronic device. 1: silicon substrate; 2: gate, 3: spacer (CVD oxide); 4: covering oxide; 5: borate-phosphate-silicate glass (PACVD). 6: silica (PACVD from $Si(OEt)_4$); 7: glass layer (spin-on). 8: phosphate-doped silica (plasma CVD from $Si(OEt)_4$); 9: oxynitride/nitride passivation layer (PACVD); 10: tungsten plug (thermal CVD); 11: AlCu (PVD); 12: TiN barrier (reactive PVD).

Metal CVD

Protective films, reflective or conducting coating, electrodes, microelectronics

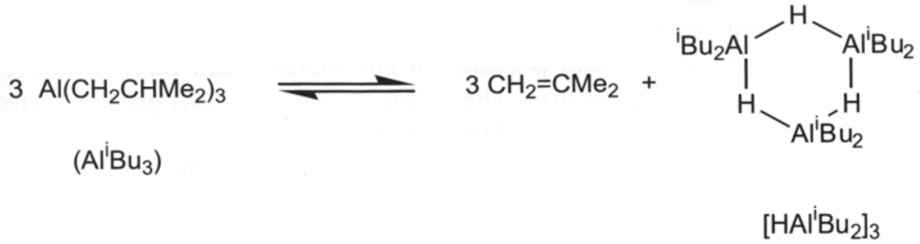
Commercially PVD methods are often used for metallic films. However Al, Cu and W are often deposited by CVD methods.

Aluminium:
- Metallized polymer films in food packaging (gas diffusion barrier), Reflective layers (mirrors, CDs…)
- Interconnects in microelectronics.

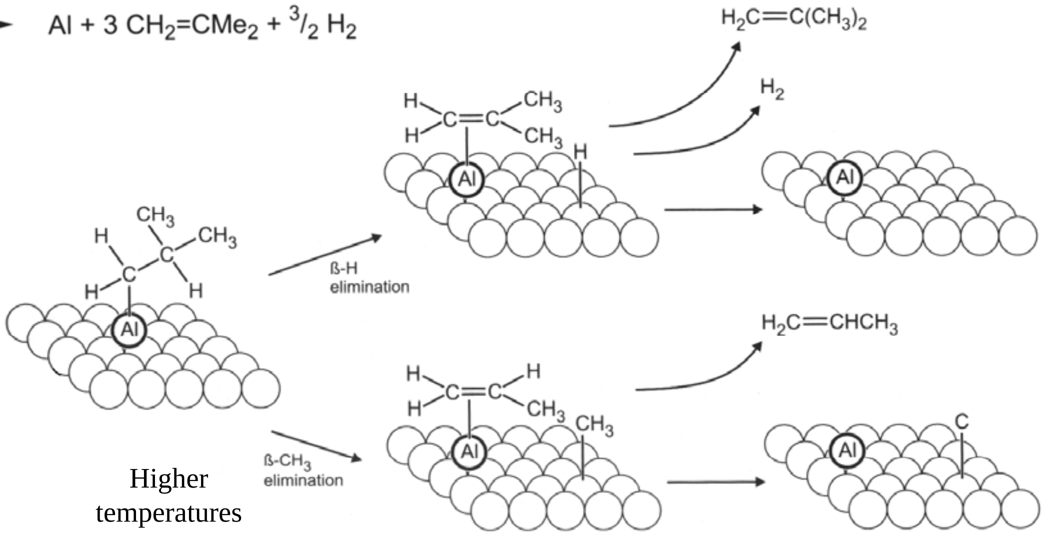
Common precursor for CVD: tributylaluminium: Al^iBu_3,

β-hydride elimination >50˚C, suppressed in the gas phase by adding isobutene

Deposition at 2-300˚C (hot wall reactor) (β-hydrogen elimination)
At temperatures > 330C: b-methyl elimination → carbon incorporation



$Al^iBu_3 \longrightarrow Al + 3\,CH_2{=}CMe_2 + {}^3/_2\,H_2$



Higher temperatures

Figure 3-16. Schematic representation of the thermal decomposition of Al^iBu_3. The upper pathway (at low temperatures) results in the clean deposition. At higher temperatures (lower pathway) carbon impurities may be incorporated into the film.

Al^iBu_3, selective deposition

Growth on Si and Al, but not on silica, SiO_2
On silica, two butyl groups are easily lost,
but elimination of the third is inhibited

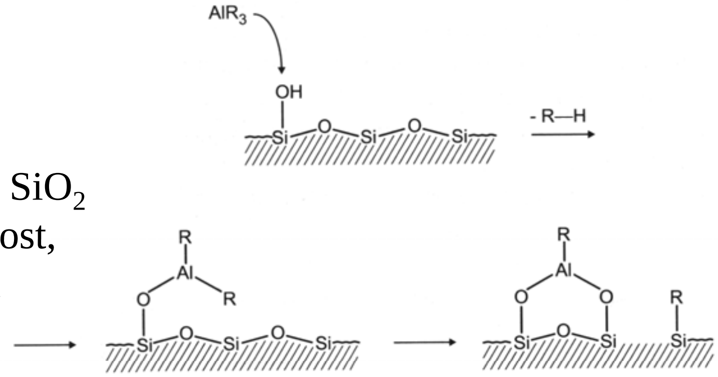


Figure 3-17. Inhibition of Al deposition from AlR_3 on a silica surface.

Tertiary amine adducts of AlH_3 may be used as precursors.

Easy cleaving of Al-N bond, and desorption of trimethylamine

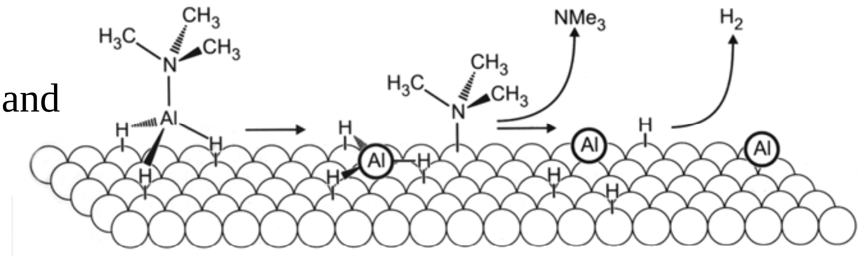


Figure 3-18. Thermal decomposition mechanism of $Me_3N{-}AlH_3$ on Al surfaces.

W-deposition

Important areas of use:

- Wear protection (cutting and grinding) and corrosion protection
- Metallization in integrated circuits. High resistance to electromigration, low thermal expansion and does not react with most semiconductor materials. Low adhesion to SiO_2…

Tungsten hexafluoride (WF_6) Thermal decomposition >750C, reducing agents are used in CVD. (H_2, Si, SiH_4)

$$2WF_6 + 3Si \rightarrow (<400\ °C) \rightarrow 2W + 3SiF_4$$

$$WF_6 + 3Si \rightarrow (>400\ °C) \rightarrow W + 3SiF_2$$

Reacts fast, but reaction stops because Si must diffuse through W
Si is added in the gas stream:

$$2WF_6 + 3SiH_4 \rightarrow (250\ °C) \rightarrow 2W + 6H_2 + 3SiF_4$$

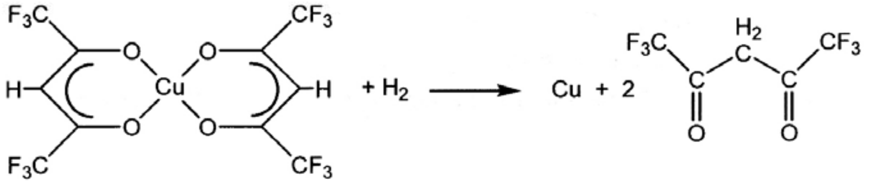
$$4WF_6 + 3SiH_4 \rightarrow (>600\ °C) \rightarrow 4W + 12HF + 3SiF_4$$

Cu CVD

Cu would be a good substitute for Al in integrated circuits. Good conductance, less electroimigration, but higher diffusion rates in Si and SiO_2.

Halides are not volatile enough. Metalorganic Cu compounds are used.

Cu(II) precursors are reduced:



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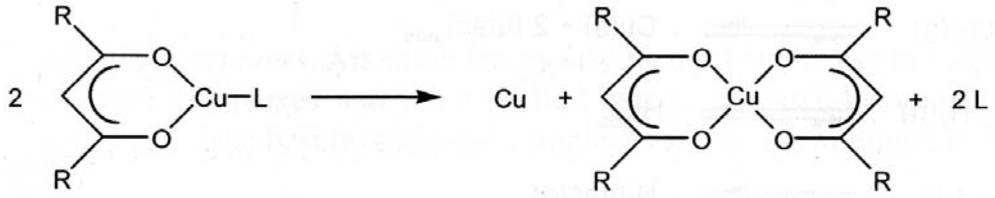
Cu(I) precursors disproportionate:



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Diamond CVD

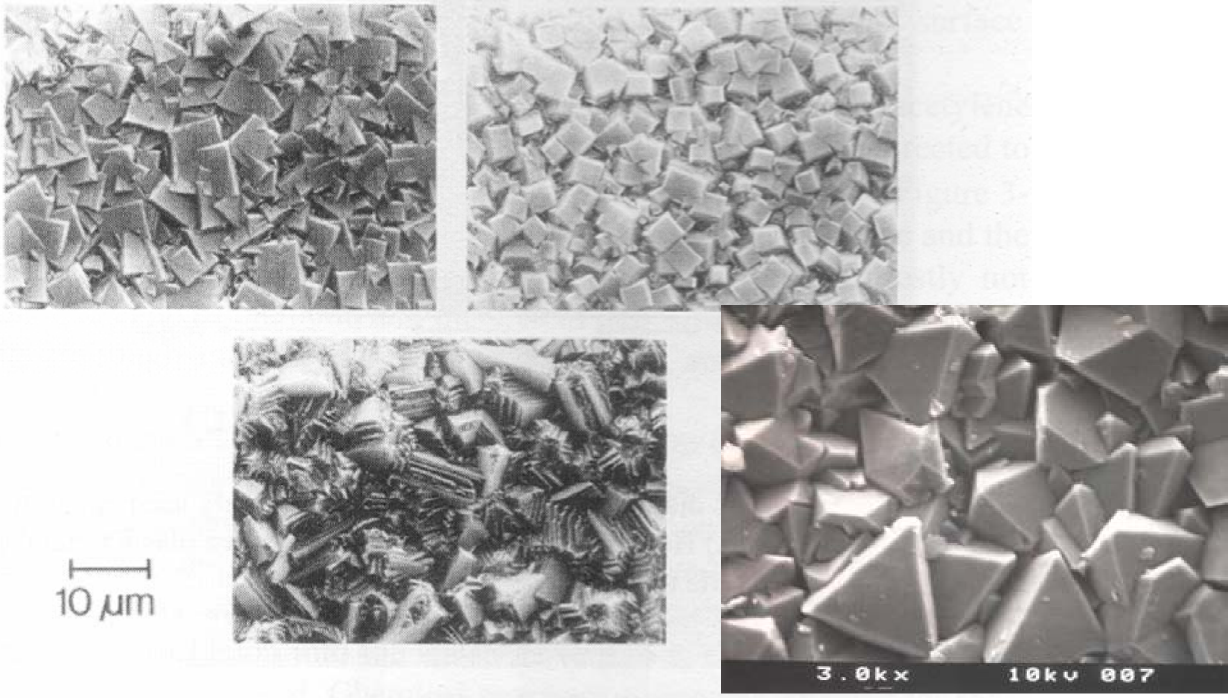
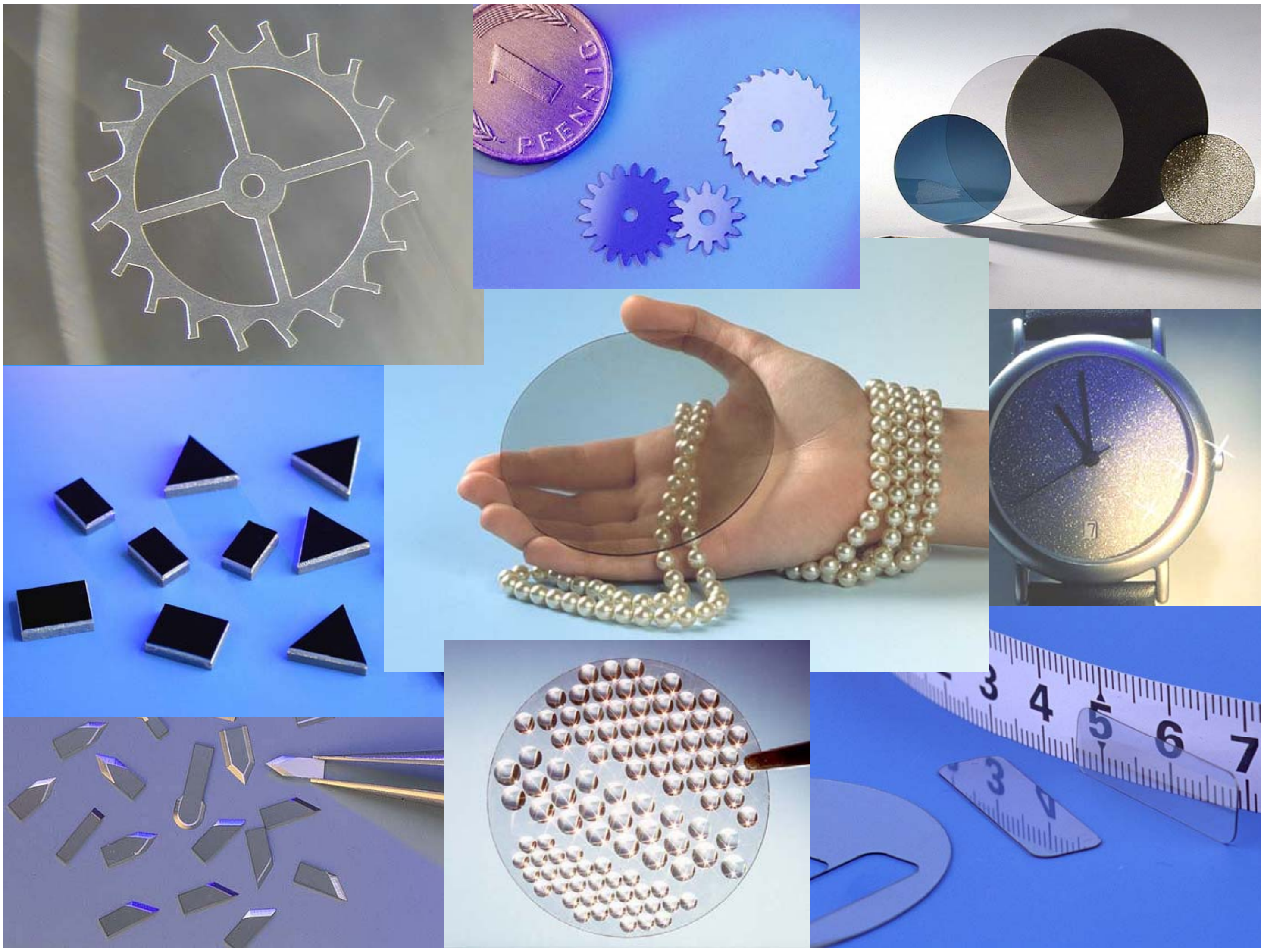


Figure 3-20. Diamond films (on a SIALON surface) deposited by microwave activation of 1.7 % methane in hydrogen. The different morphologies originate from different gas pressures and different microwave powers.



Diamond CVD

Diamond is metastable at low pressure

Growth is possible due to H• present
- Suppression of nucleation of graphite through selective etching
- Diamond surface is stabilized by H

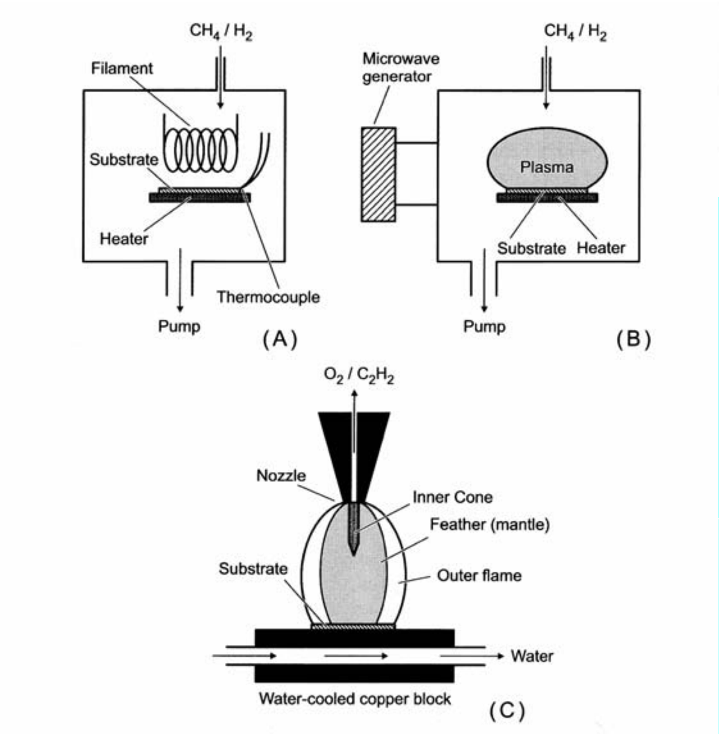
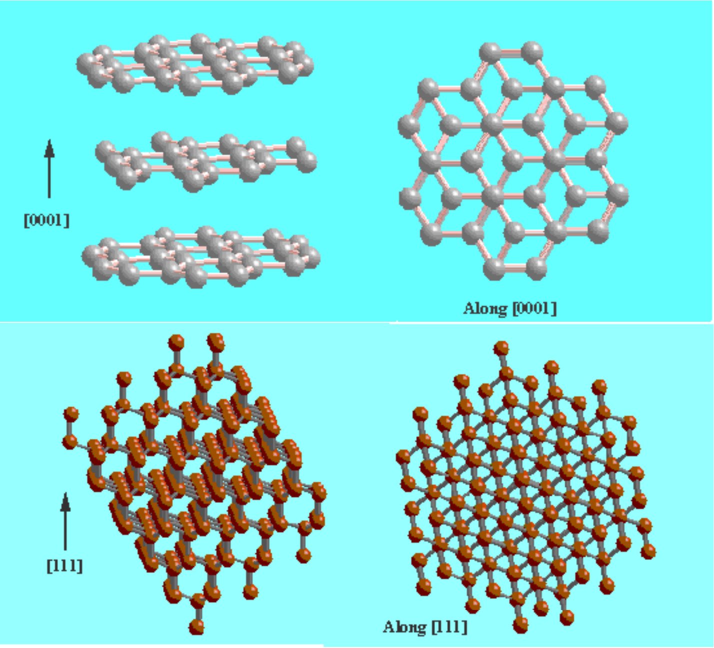


Figure 3-21. Schematic diagrams of the three most commonly used apparatus for diamond deposition. (A) Hot filament reactor. (B) Microwave plasma-enhanced CVD reactor. (C) Oxyacetylene torch.



CVD of metal oxides

Oxides may be formed by using oxidizing gasses as O_2, N_2O, H_2O, H_2O_2.
SiO_2 in microelectronics:
Gate insulating layers, surface passivation, planarization, packaging

Silane precursor

$$SiH_4 + O_2 \longrightarrow SiO_2 + 2\,H_2$$

$$SiH_4 + 2\,O_2 \longrightarrow SiO_2 + 2\,H_2O$$

$$SiH_4 + 2\,N_2O \longrightarrow SiO_2 + 2\,H_2 + 2\,N_2$$

Silicon halides

$$H_2SiCl_2 + 2\,N_2O \longrightarrow SiO_2 + 2\,HCl + 2\,N_2$$

Tetraalkoxysilane
(e.g. TEOS, $Si(OEt)_4$)

$$Si(OEt)_4 \longrightarrow SiO_2 + 2\,C_2H_4 + 2\,EtOH$$

Reaction more complicated…

$$\equiv Si{-}OEt \longrightarrow \equiv Si{-}OH + C_2H_4$$

$$\equiv Si{-}OH + Si(OEt)_4 \longrightarrow \equiv Si{-}O{-}Si(OEt)_3 + EtOH$$

YBCO, yttrium barium copper oxide

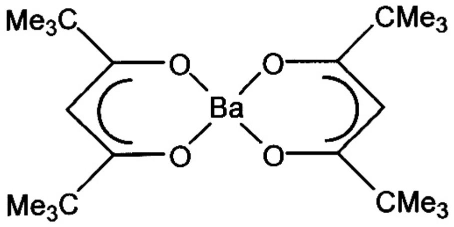


Figure 3-22. Barium dipivaloylmethanate, Ba(dpm)$_2$.

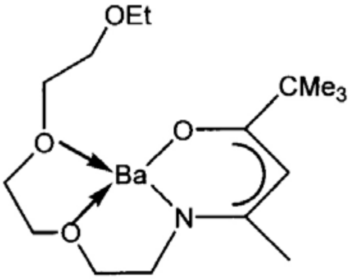


Figure 3-23. A polyether modified bis(ß-ketoiminate) barium derivative (only one of the two multidentate [▸ glossary] ligands is drawn for clarity).

Metal nitrides

Nitrides are often hard compounds, and are used for protection and hard coatings
Nitrogen sources are N_2, NH_3, N_2H_4 (hydrazine)

$$3\,H_2SiCl_2 + 4\,NH_3 \longrightarrow Si_3N_4 + 6\,HCl + 6\,H_2$$

$$2\,TiCl_4 + 4\,H_2 + N_2 \longrightarrow 2\,TiN + 8\,HCl$$

$$6\,TiCl_4 + 8\,NH_3 \longrightarrow 6\,TiN + 24\,HCl + N_2$$

$$NH_3 + HX \rightleftharpoons NH_4X$$

Suppressed at high temperatures

Transamination reactions between metal dialkylamides and ammonia

$$\equiv M{-}NR_2 + NH_3 \longrightarrow \equiv M{-}NH_2 + HNR_2$$

$$3\,\equiv M{-}NH_2 \longrightarrow \underset{\displaystyle M}{M{-}\underset{|}{N}{-}M} + 2\,NH_3$$

$$3\,Si(NMe_2)_4 + 4\,NH_3 \longrightarrow Si_3N_4 + 12\,HNMe_2$$

$$6\,Ti(NR_2)_4 + 8\,NH_3 \longrightarrow 6\,TiN + 24\,HNR_2 + N_2$$

Semiconductors

III-V (GaN, GaAs, InP…) and II-VI (CdS, ZnSe…) semiconductors

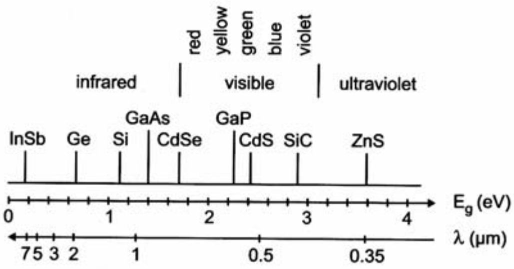


Figure 3-24. The band gaps of common semiconductors.

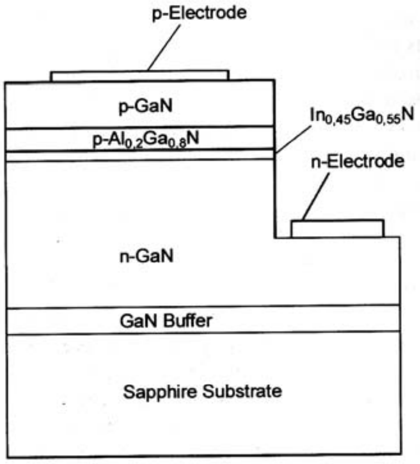
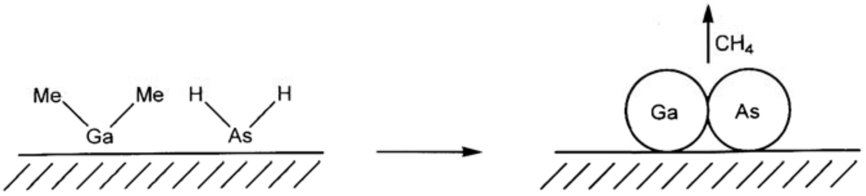


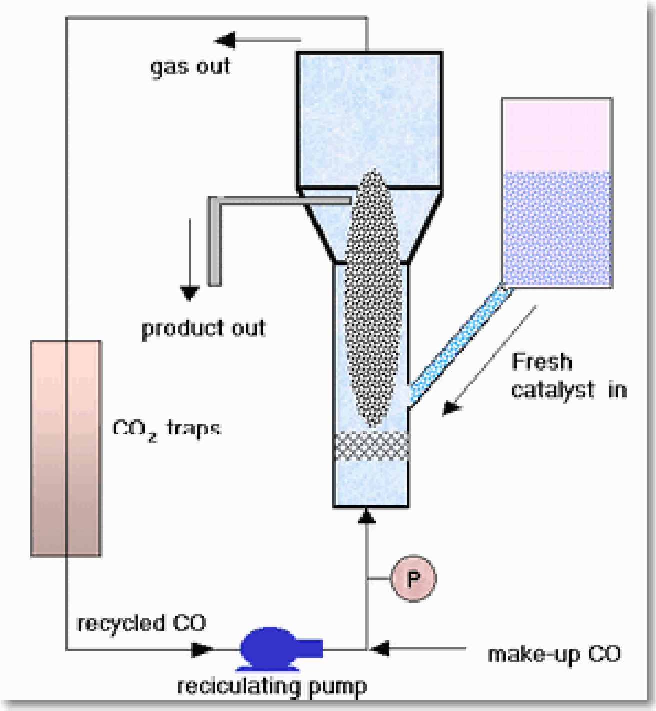
Figure 3-25. Structure of a blue-green LED device. See text for explanations.

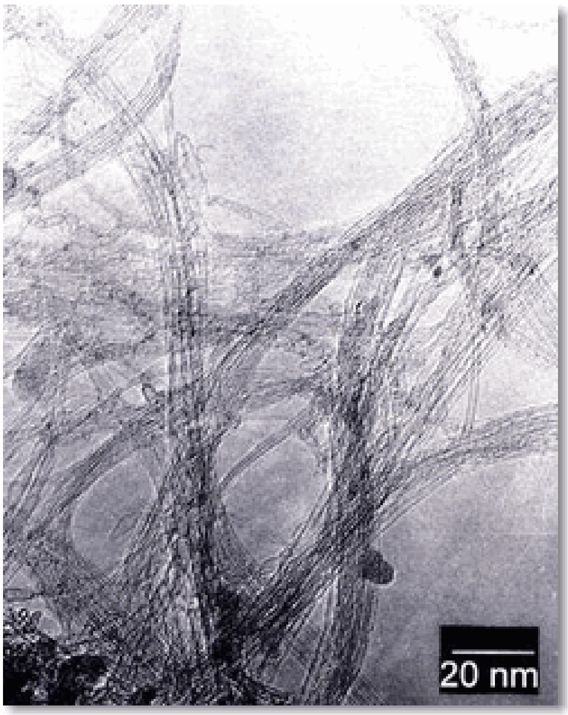
$GaMe_3$ used as a precursor.
Gas-phase reactions occur
$GaMe_x$ (x<3, e.g. x=1)
Reacts with AsH_3 to from e.g. AsH_2

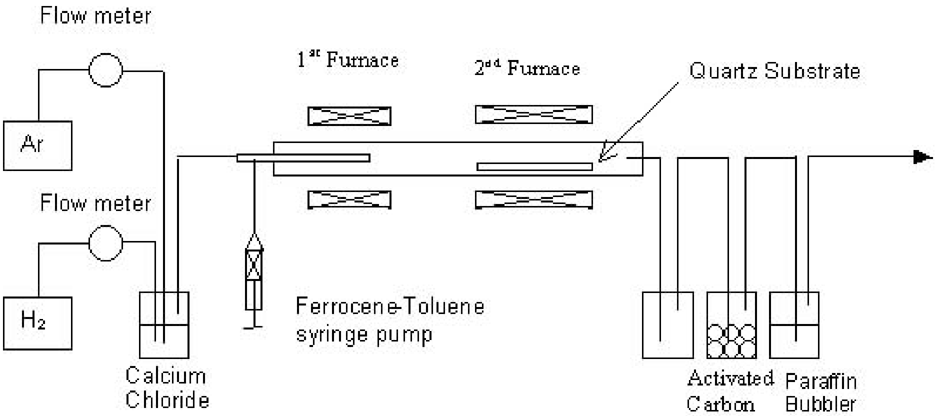


$$GaMe_x + AsH_y \longrightarrow GaMe_{x-1} + AsH_{y-1} + CH_4 \qquad (3\text{-}39)$$

Carbon nanotubes by CVD







CVD production of aligned single walled carbon nanotubes (SWCNT)