2. Chemical vapour deposition (CVD)

In the chemical vapour deposition process (CVD), gaseous species are produced independently and react, after mixing, in a deposition chamber.

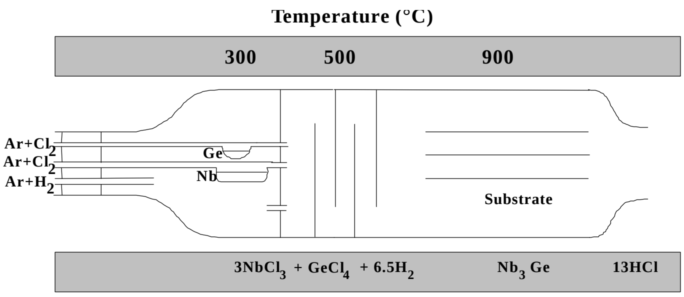


Figure.22
Chemical vapour deposition (CVD) of Nb_3Ge films.

This process is illustrated by the synthesis of Nb_3Ge films (figure 22). Hydrogen reduction of the chlorides is performed at T=900 °C, according to the reaction :

$$3NbCl_3 + GeCl_4 + 6.5H_2 \leftrightarrows Nb_3Ge + 13HCl$$

An argon flow dilutes the $NbCl_3$, $GeCl_4$ and H_2 gases. Chlorides are prepared in a first step by the reactions :

$$3Nb + 4.5Cl_2 \xrightarrow{\approx 300°C} 3NbCl_3$$

$$Ge + 2Cl_2 \xrightarrow{\approx 300°C} GeCl_4$$

They are mixed with hydrogen at a temperature (T<500°C) which prevents from the reduction of chlorides to give Nb_3Ge.

The CVD process allows for the formation of large area films. It is mainly used for semiconductors.

Amorphous hydrogenated silicon was studied for solar applications :

$$SiCl_4 + 2H_2 + \varepsilon(PH_3 \text{ or } 0.5B_2H_6) \xrightarrow{1100°C} Si:(H + P \text{ or } B) + (4 + 3\varepsilon)HCl$$

Silicides exhibit very promising properties for electronic, optical and magnetic component integration : $CoSi_2$, WSi_2, $FeSi_2$. They are grown by vapour phase epitaxy ; the crystalline films are preferentially oriented with respect to the substrate of silicon (111) wafers.

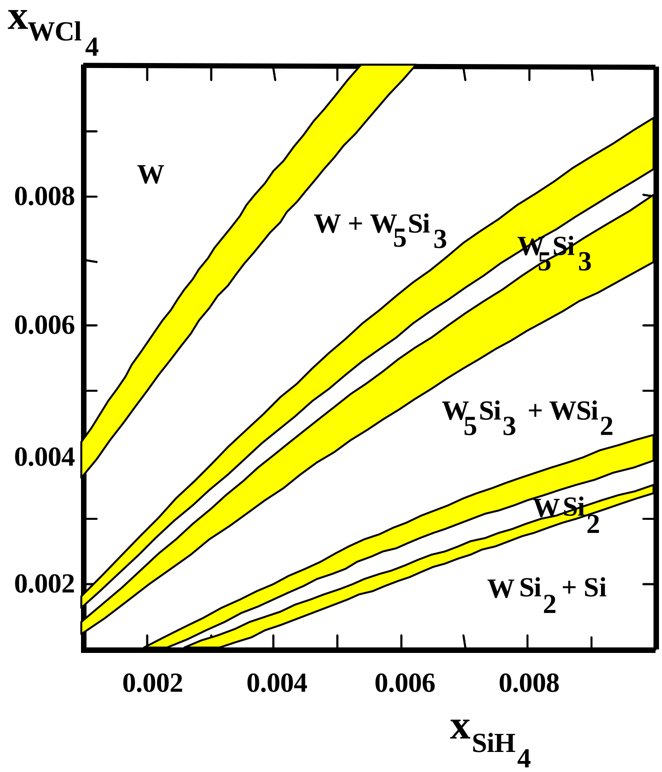
The formation of WSi_2 results from the reaction of SiH_4 silane with WCl_4 :

$$WCl_4 + 2SiH_4 \rightarrow WSi_2 + 2H_2 + 4HCl$$

The partial pressure of WCl_4 is controlled by the chlorine flow and by the temperature in the chlorination chamber : $W + 2Cl_2 \rightarrow WCl_4(g)$.

The CVD phase diagram WCl_4-$SiCl_4$ (figure 23) shows that pure WSi_2 forms, at T=500 °C, in a narrow composition range.

Figure 23. - Phase stability in the CVD diagram W-Si-Cl-H.



A lot of work has been devoted recently to the growth of diamond films. Such films have attracted attention for their expected high hardness, electrical resistivity, thermal conduction and optical transparency. They are formed by decomposition of methane or acetylene in the presence of H_2 and small amounts of O_2, H_2O or CO_2 in a microwave plasma (2.456 GHz, 1 kW) :

$$CH_4 \xrightarrow{H_2+\varepsilon(CO_2+H_2O+O_2)} C_d + 2H_2$$

The substrate is heated at 500 °C<T<700 °C; the total pressure is P≈2000 Pa and the volume ratio V_{CH_4}/V_{H_2} lies in the range 3-10 %. Stepped growth with (111) and (100) faces indicates surface diffusion. However, the growth mechanism, very slow, is not yet well understood. Heterogeneous nucleation on the surface defects (scratches ...) occurs in a first step and the growth rate is very slow : 1 µm per hour or 0.1 g h^{-1} on a silicon wafer of ϕ=20 cm diameter (a layer of 4H-SiC forms at the interface). Diamond coating of high specific area fibres or grids was recently achieved and a mass increase of 5-10 $g.h^{-1}$ was observed on a grid of 200000 wires (ϕ=10 µm, l=50 mm).

It is interesting to note that nanometer size diamond crystals (cubic diamond or hexagonal londsaleite), associated with SiC, are thought to have formed by a CVD process from the ejecta plumes of large meteorite impacts (Ries crater in Germany).

Numerous variants of the CVD method have been devised. They differ from the heating mode : hot filament, DC or microwave plasma PECVD (plasma-enhanced), from the source of gaseous species : OMCVD (organometallic) or from the synthesis conditions : LPCVD (low pressure).

3. Molecular beam epitaxy and related techniques.

Thin films are deposited on substrates in ultrahigh vacuum (10^{-6} Pa). Several methods of material evaporation are used :

- effusion in ovens (Knudsen cells) operating at high temperature (1200-1400 °C for CaF_2 coating on (111)Si) ;
- pulsed Laser heating of targets (high T_c superconductor Hg-1212, $HgBa_2CaCu_2O_{6+\delta}$, deposited from HgO and $Ba_2CaCu_2O_x$ sources on (100) oriented $SrTiO_3$ substrate) ;
- electron beam heating (Si and III-V compounds deposition).

Pressures of approximately 10^{-5} Pa are usually maintained during deposition. Very thin layers, down to the atomic scale, can be obtained. Alternation of layer composition allows to build unknown structures in the bulk.