

IV - Low pressure methods

The elaboration techniques that we call "low pressure methods", involve mass transport by gaseous species. Crystals and crystalline or amorphous thin films are deposited, eventually on a substrate, vitreous or crystalline.

1. Chemical transport

The nutrient is transformed in the mobile gaseous phase at temperature T_1 , either by :

- sublimation, $I_2(\text{solid}) \rightleftharpoons I_2(\text{gas})$
- decomposition $NH_4Cl(\text{solid}) \rightleftharpoons NH_3(\text{gas}) + HCl(\text{gas})$
- chemical reaction with a transport agent $Fe_2O_3 + HCl(g) \rightleftharpoons 2FeCl_3(g) + 3H_2O(g)$

Mass transport implies that the preceding reactions are, in fact, equilibria which can be displaced to the left side at a different temperature T_2 . The basic principle of transport is $K_p(T_2) < K_p(T_1)$ or $\text{Log } K_p(T_2) < \text{Log } K_p(T_1)$. This condition shows that the temperature gradient $\Delta T = T_2 - T_1$ must be chosen as a function of the sign of the enthalpy variation of the reaction :

$$\text{Log } K_p = -\frac{\Delta G^0}{RT} \Rightarrow \frac{\partial \text{Log } K_p}{\partial T} = \frac{\Delta H^0}{RT^2} \approx \frac{\text{Log } K_p(T_2) - \text{Log } K_p(T_1)}{T_2 - T_1}$$

and : $\Delta H^0 > 0 \Rightarrow T_2 > T_1$ or $\Delta H^0 < 0 \Rightarrow T_2 < T_1$

The equilibrium is realised at T_1 but not necessarily at T_2 ; deposition can occur at $T_1 < T < T_2$ or at $T > T_2$ when the free energy of particle formation is large. Good quality crystals are obtained when the kinetics of transport reactions is mainly governed by diffusion. The total pressure must lie in the range 10^4 - 10^5 Pa.

The matter flux of the i species along the y coordinate of the tube is :

$$J_i = -D_i \frac{\partial C_i}{\partial y} = -\frac{D_i}{RT} \frac{\partial P_i}{\partial y} \quad (C_i = \frac{n_i}{V} = \frac{P_i}{RT})$$

In a steady state hypothesis $\frac{\partial C_i}{\partial t} = \frac{\partial J_i}{\partial y} = 0$, the flux of matter is : $J_i = -\frac{D_i}{RT} \frac{\Delta P_i}{L}$ {18}

ΔP_i and L represent the pressure variation and the distance between the reaction zone and the growth zone ; D_i is supposed constant.

The reaction rate is easily expressed for the reaction : $A(s) + B(g) \rightleftharpoons C(g)$

The growth rate is : $\frac{dn_A}{dt} = -\frac{dn_B}{dt} = \frac{D_B}{RT} \frac{\Delta P_B}{RT} S$. ΔP_B is a function of ΔT and must be maximum.

$K_p = P_C / P_B$ and $(P_B + P_C) / P_0 \approx 10^5 / P_0 = 1$, consequently :

$$\frac{dP_B}{dT} = -\frac{1}{(1 + K_p)^2} \frac{dK_p}{dT} = -\frac{K_p}{(1 + K_p)^2} \frac{\Delta H^0}{RT^2} \quad \{19\}$$

this expression is maximum for $K_p = 1$.

Good transport reactions are obtained when the following experimental conditions are fulfilled : $\Delta G_T^0 \approx 0$, $P_{\text{Total}} \approx 0.1 - 1 \text{ Atm}$ and $\Delta T \approx 20 - 200^\circ \text{C}$. Thermodynamic data, when all the reaction products are known, allow the best experimental parameters to be foreseen.

Reactions are realised either in sealed tubes (glass, silica, Au, Pt) (figure 21) or in open tubes with a flow of inert gas. They can be used for metal purification: pure titanium is prepared industrially by this process. Self repairing of the tungsten filament is due to transport by WI_6 in quartz-iodine light bulbs. Oxides, sulphides, III-V semiconductors or mixed anionic compounds have been also studied (table 4.a).

Large single crystals can be grown by vacuum evaporation, effusion or crystallisation in a profile temperature gradient dT/dy (table 4.b)

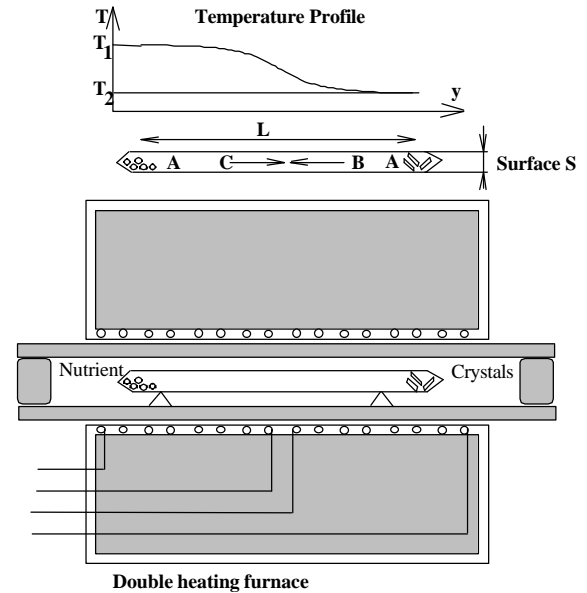


Figure 21. - Principle of crystal growth by transport reaction.

Table 4: Examples of materials grown by vapour phase transport.

a - Closed sealed tube technique

	Transported material	Transport agent(s)	Gaseous species	Temperature T_1 (°C)	Temperature T_2 (°C)
Metals	Ti	I_2	TiI_4	200	1000
	W	I_2	WI_6	400	1400
	Zr	I_2	ZrI_4	280	1430
	Au	Cl_2	Au_2Cl_2	1000	700
	Si	$SiCl_4$	$SiCl_2$	280	1430
III-V	GaAs	GaI_3	As_4-GaI	1070	1030
Oxides	Ta_2O_5	Cl_2-CrCl_3	$TaOCl_3-CrO_2Cl_2$	900	700
Sulfides	FeS	I_2	FeI_2-S_2	900	700
Mixed anions	CrOCl	$CrCl_3$	$CrO_2Cl_2-CrCl_2$	1000	840
	NbO_2F	$NbCl_5$	$NbO_2FCl_2-NbOCl_3$	400	300

b - Vacuum evaporation technique

	T (°C)	Pressure (10^5 Pa)	dT/dy (°C/cm)	Supercooling (°C)	
LiF	1000	10^{-6}	35		
NH_4Cl	150	10^{-4}		25	
CaF_2	1560	10^{-6}	65		
CuBr	410	$2 \cdot 10^{-6}$		15	
CdS	1000	3 (H_2S)	10		whiskers
CdS	1050	1 (H_2S)	10		platelets
Zn	421	$1.3 \cdot 10^{-2}$ (H_2)	20		whiskers
Zn	439	$5 \cdot 10^{-3}$ (H_2)	10		platelets
SiC	2390	$1.6 \cdot 10^{-2}$ (Ar)	34		(polycrystal)

It must be noted that fullerene synthesis is achieved by a low pressure method. An electric spark is produced between two carbon graphite electrodes at low helium pressure. Carbon graphite sheets reorganise at high temperature to give buckyballs C_{60} , C_{70} ..., metallofullerenes $Ln@C_{82}$ ($Ln=La, Y$, rare-earth) or carbon nanotubes.