Lecture: Solid State Chemistry - WP I/II

Chapter 3: Chemical preparation and crystal groth

3.1 Possible reaction paths of solid state reactions
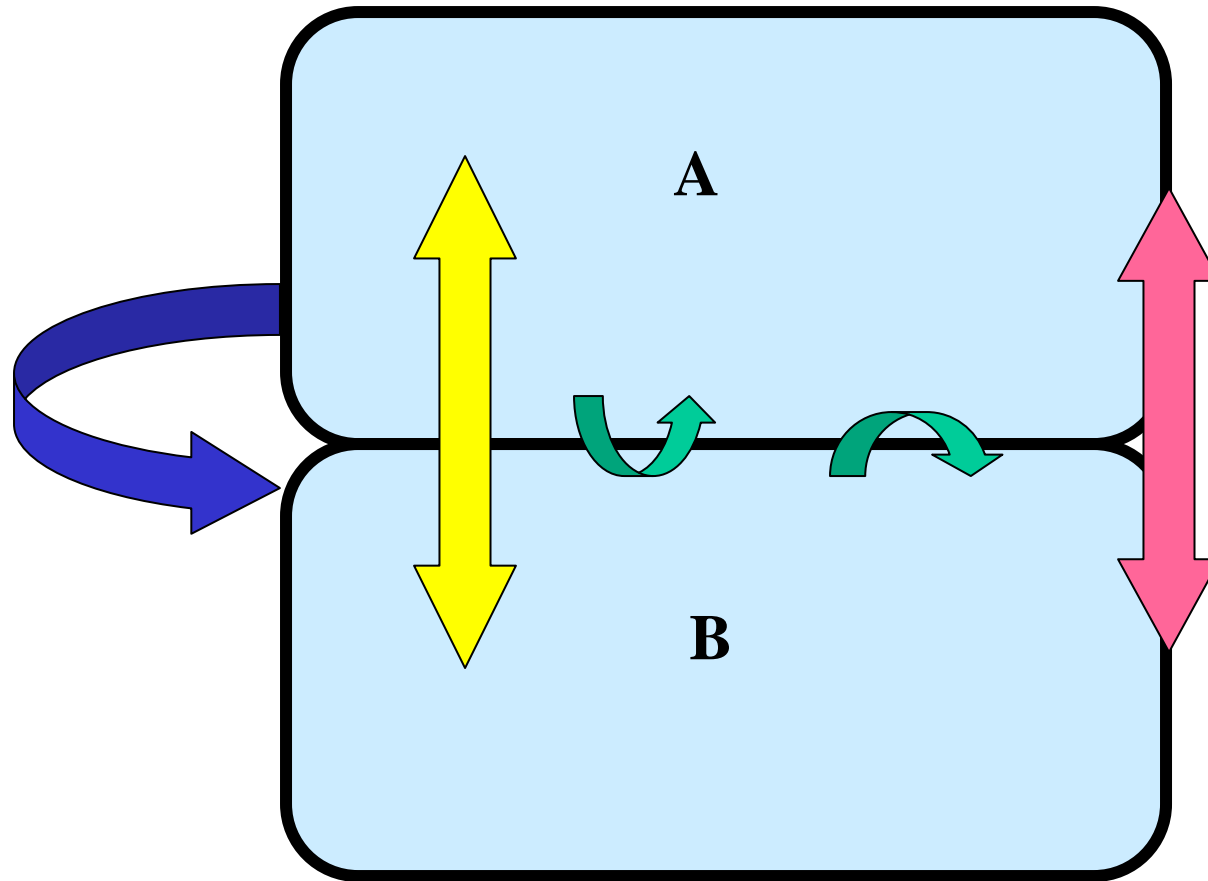
3.2 Chemical transport reactions

3.3 Crystal refinement by floating zone melting

3.4 Growth of single crystals

3.5 Chemical Vapor Deposition (CVD)

3.6 High pressure syntheses

3.1 Possible reaction paths between two solid grains A and B
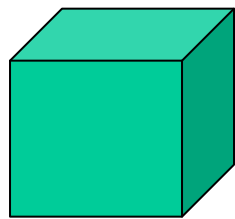

A

B

	gas phase diffusion		interface diffusion
	volume diffusion		surface diffusion

3.1 Importance of the surface aerea for solid state reactions

The *common surface* of reacting grains influences strongly the reaction rate
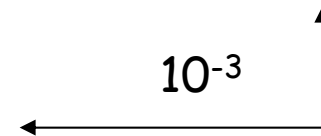
grinding

Typical 10 μm edge length

$10 \ \mu m = 10^{-5} \ m \rightarrow S = 6 \times 10^{-10} \ m^2$

10^9 particles $\rightarrow S_{total} = 6 \times 10^{-1} \ m^2$

Cube: 1cm edge length

Surface aerea $S = 6 \ cm^2 = 6 \times 10^{-4} \ m^2$

10^{-3}

Enlargement of the surface aerea by a factor of 10^3

3.1 Velocity of diffusion of particles (ions, atoms ...) in a solid

- mass transport and concentration gradient for a given point in a solid!

$$J_i = -D_i \bullet \delta c_i / \delta x \quad [\text{mol cm}^{-2}\text{ s}^{-1}]$$

(1st law of Fick)

- **J_i: flow of diffusion (mol s^{-1} cm^{-2});**
- **D_i: diffusion coefficient (cm^2 s^{-1})**
- **$\delta c_i / \delta x$: concentration gradient (mol cm^{-3} cm^{-1}) (i.e.**
  change of concentration along a line in the solid!)

- Typical diffusion coefficients D_i for ions (atoms) in a solid at room temperature are about 10^{-13} cm^2 s^{-1}.
- In solid state ionic conductors (e.g. Ag-ions in α-AgI) the values are greater by orders of magnitude ($\approx 10^{-6}$ cm^2 s^{-1})

3.1 Diffusion coefficients show an exponential temperature dependence (Arrhenius type)

$$D = D_\infty \exp(-Q/kT) \quad (D_\infty: D \text{ für } T \to \infty, Q: \text{activation energy of diffusion}, k: \text{Boltzmann-faktor})$$
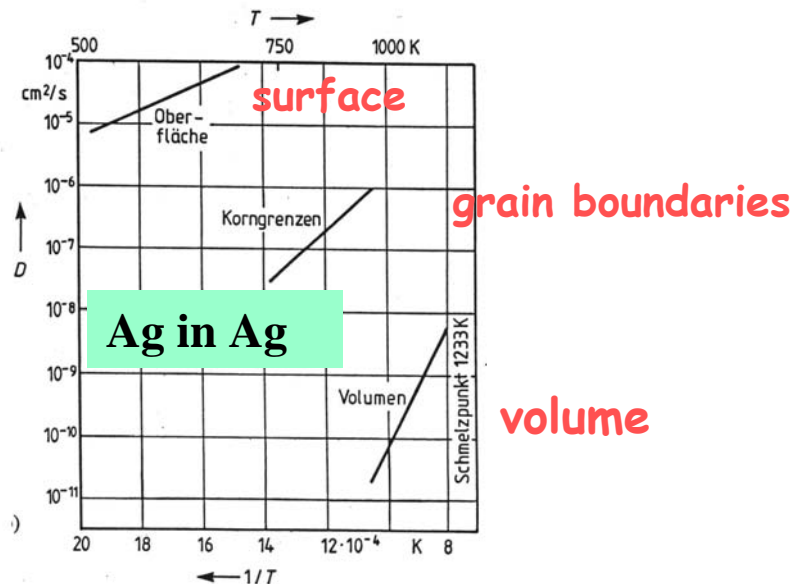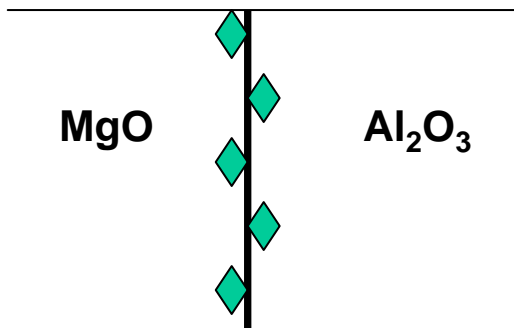

The logarithmic representation of D verus 1/T is linear, the slope corresponds to the activation energy and the intercept to D_∞.

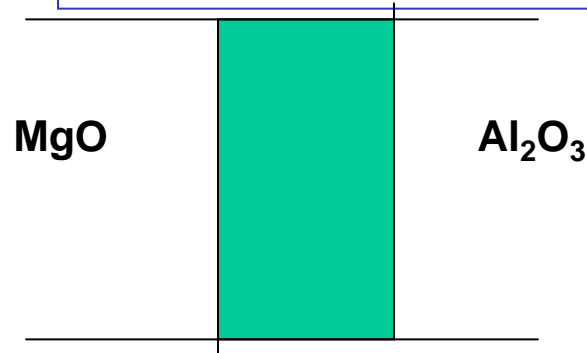# 3.1 Model for a classical solid-solid reaction (below melting point !): Planar interface between two crystals

Assumed: single crystals and volume diffusion only (see transparency 1)
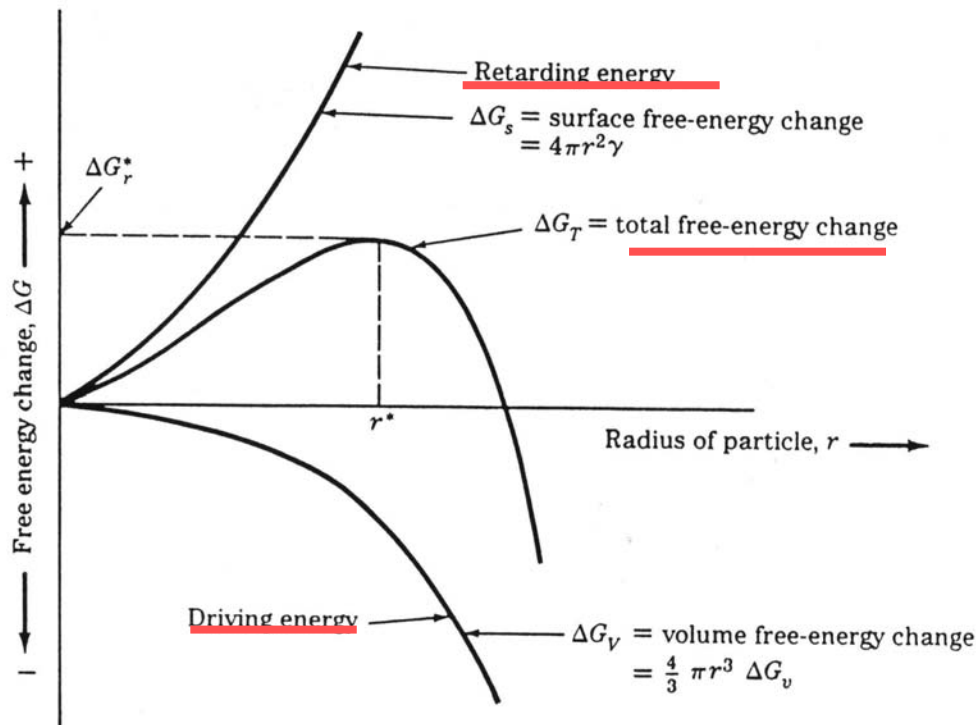
$$MgO + Al_2O_3 \rightarrow MgAl_2O_4 \text{ (spinell)}$$

Phase 1:
formation of seeds

MgO   Al₂O₃

Phase 2:
growth of seeds

MgO   Al₂O₃

Free energy change, ΔG

ΔG_r^*

Retarding energy

ΔG_s = surface free-energy change
= $4\pi r^2 \gamma$

ΔG_T = total free-energy change

Radius of particle, r

r^*

Driving energy

ΔG_v = volume free-energy change
= $\frac{4}{3}\pi r^3 \Delta G_v$

r: radius of spheric seed
r*: critical radius
(**r>r* seed grows by itself**)

ΔG: <u>total</u> free energy change
ΔG_s: <u>surface</u> free energy change
ΔG_v: <u>volume</u> free energy change

($\Delta G = \Delta G_s 4\pi r^2 + \Delta G_v 4/3\pi r^3$)

3.1 Container materials for solid state reactions

a) glasses   b) ceramics   c) metals

- depends on the maximum reaction temperature and/or the type of reacting material (e.g. quartz is an „acidic" solid unsuitable for „basic" reactands)

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a) types of glasses:

PYREX (DURAN): borosilicate glass (76% SiO_2, 16% B_2O_3, BaO ...) $T_{max.}$ ~ 400 °C,
QUARTZ: Pure amorphous SiO_2, $T_{max.}$ ~ 1100 °C

b) ceramics

Al-silicates: $T_{max.}$ ~ 1700 °C   Corundum (α-Al_2O_3): T_{max} ~ 1900 °C
MgO: T_{max} ~ 2200 °C   BN: ~ 2900 °C

c) metals

Steel: ~ 1400 °C (under inert gas) Pt: ~ 1600 °C (PtO↑), Mo: ~ 2000 °C
   Ta: ~ 2500 °C

3.2 Chemical transport reaction

A <u>solid</u> ist <u>dissolved</u> in the <u>gas phase</u> at one place (T=T1) by reaction with a <u>transporting agent</u> (e.g. I_2).

At another place (T=T2) the solid is <u>condensed</u> again.

Whether T1 < T2 or T1 > T2 depends on the <u>thermochemical balance</u> of the reaction !
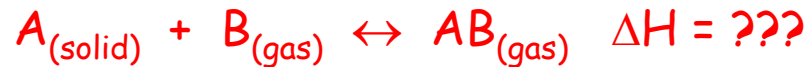Transport can proceed from <u>higher to lower</u> or from <u>lower to higher</u> temperature

trace of a transporting agent (e.g. I_2)

T1

T2
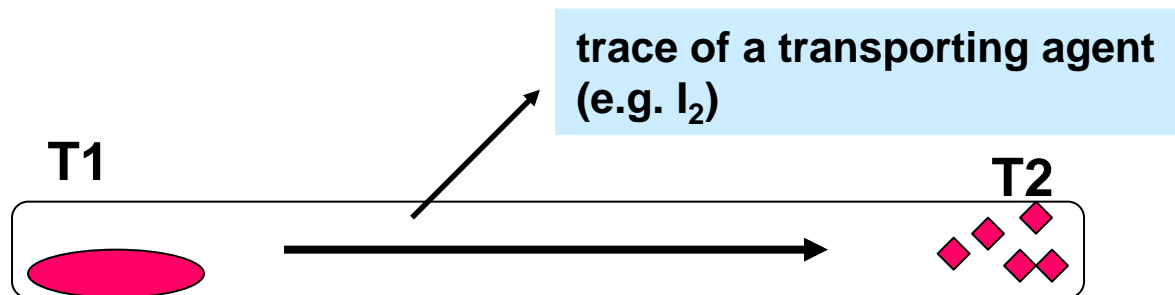
3.2 Transport direction and examples for chemical transport reactions

Transport direction
    hot $\rightarrow$ cold   or   cold $\rightarrow$ hot
depends on the enthalpy of the transport reaction

$$A_{(solid)} + B_{(gas)} \leftrightarrow AB_{(gas)} \quad \Delta H = ???$$

$\Delta H > 0$ (endothermic): hot $\rightarrow$ cold $\Delta H < 0$ (exothermic): cold $\rightarrow$ hot

Some examples for transport reactions:

$$\begin{array}{lll} & & T1/T2\ ^oC \\ W + 3Cl_2 \leftrightarrow WCl_6 & 400/1400 & (exo) \\ Ni + 4CO \leftrightarrow Ni(CO)_4 & 50/190 & (exo) \\ & & \\ 2Al + AlCl_3 \leftrightarrow 3\ AlCl & 1000/600 & (endo) \\ 4Al + Al_2S_3 \leftrightarrow 3Al_2S & 1000/900 & (endo) \end{array}$$
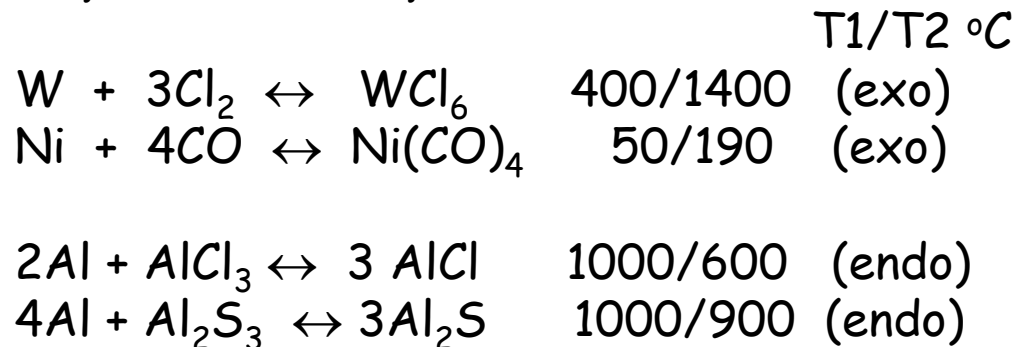
Main application: *crystallisation and purification* of solids

3.2 Estimation of ΔH for a transport reaction e.g.:

$ZnS_{(s)} + I_{2(gas)} \leftrightarrow ZnI_{2(gas)} + S_{gas}$ $\Delta H = ??$

$Zn_{(s)} + I_{2(g)} \leftrightarrow ZnI_{2(gas)}$ $\Delta H = -88$ kJ mol^{-1}

$ZnS_{(s)} \leftrightarrow Zn_{(s)} + S_{(g)}$ $\Delta H = +201$ kJ mol^{-1}

Σ $ZnS_{(s)} + I_{2(gas)} \leftrightarrow ZnI_{2(gas)} + S_{gas}$ $\Delta H = +113$ kJ mol^{-1}
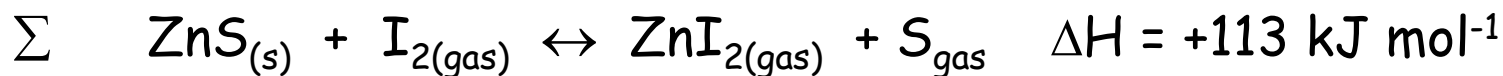
transport from hot to cold (normal conditions provided)!

Question: Which informations/corrections are nesessary to calculate the enthalpy values for „realistic" conditions ?
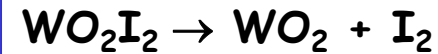
W-filament

quartz wall

- I_2 as CH_3I and traces of O_2

W O_2 O_1

WO O_2 O_1

WO_2

WO_2I_2

3000

600

Temperatur [°C]
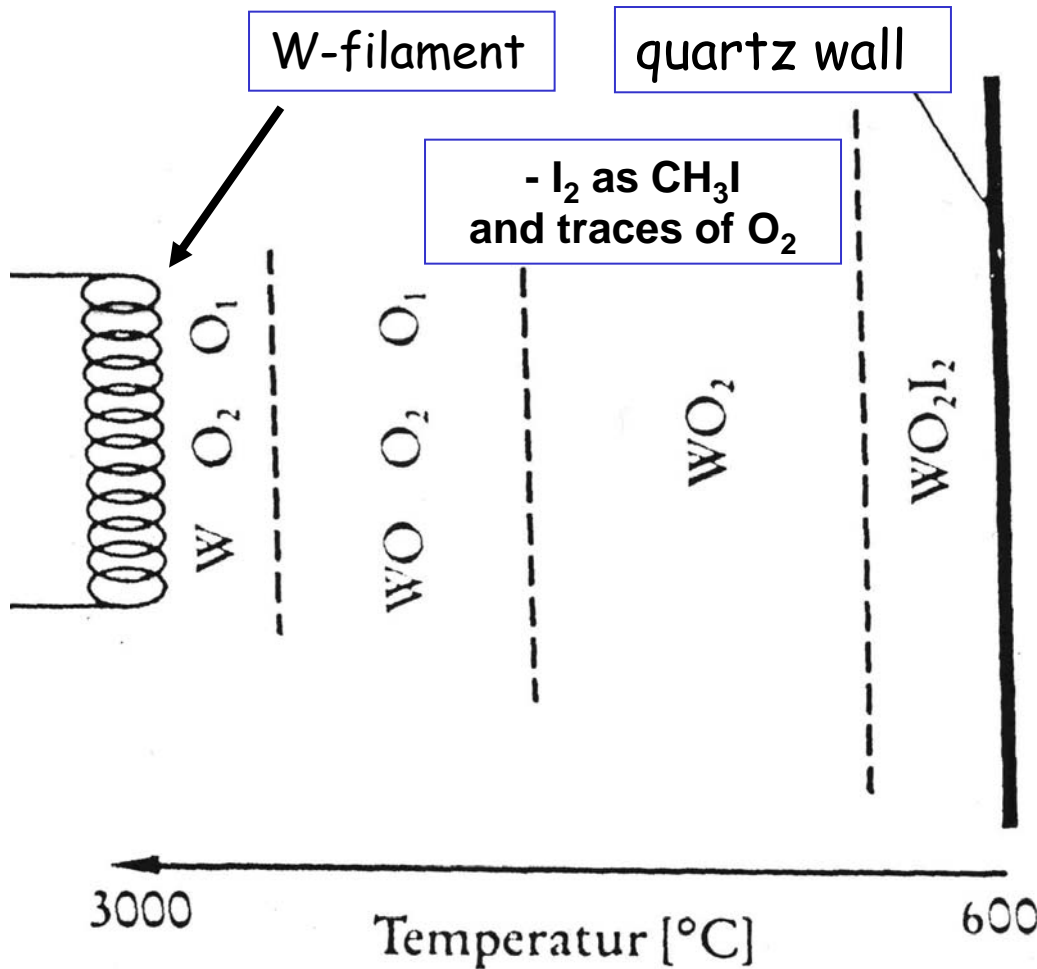
initial asumption: „self repair mechanism": W condenses at the hot/thin parts of the filament:

$W + \frac{1}{2}O_2 + I_2 \rightarrow WO_2I_2$ $\underline{\Delta H \text{ exo (!)}}$

however:

$WO_2I_2 \rightarrow WO_2 + I_2$
$WO_2 \rightarrow WO + \frac{1}{2} O_2$

final reaction near the filament:
$W_s + \frac{1}{2} O_2 \rightarrow WO_g$ $\underline{\Delta H \text{ endo (!)}}$

(W condenses at the cold /thick parts of the W filament) sorry!

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transport reaction: Ti + $2I_2$ → TiI_4 $\Delta H = -376$ kJ mol^{-1}
(exothermic: transport from <u>cold to hot</u>)

W-filament (ca. 1500 K)
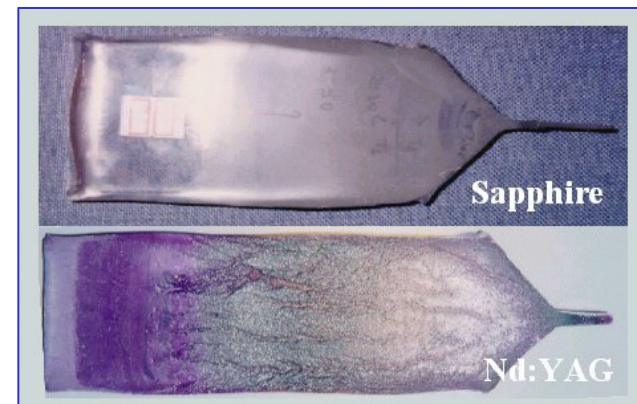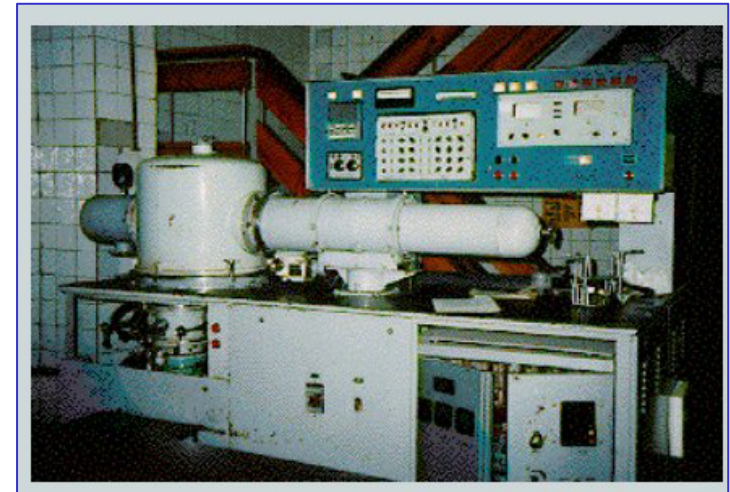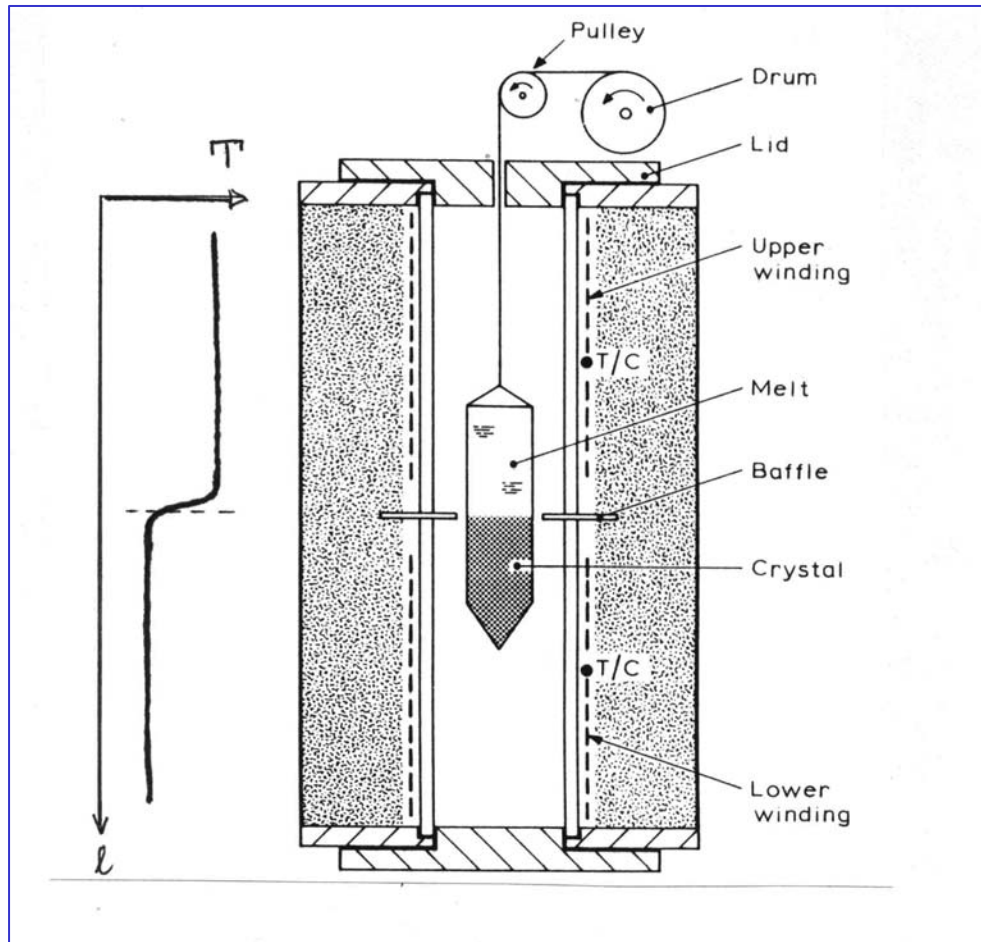
Ti-crystals

I_2

Ti-powder (ca. 800 K)

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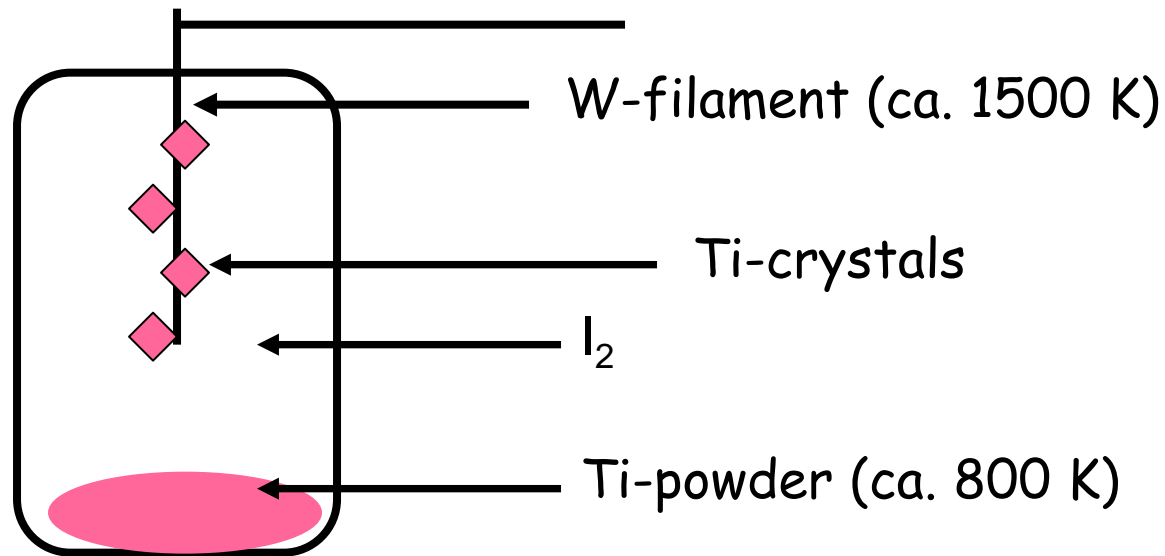
3.3 Crystal refinement by floating zone melting

- A small slice of the sample is molten and moved continuously along the sample
- **impurities** normally dissolve **preferably** in the **melt** (!! icebergs in salt water don't contain any salt !!)

- Segregation coefficient k:

$$k = c_{solid}/c_{liquid}$$

  (c: concentration of an impurity)

Only impurities with k < 1 can be removed by zone melting !!

SrTiO₃

Bild 6.13. Prinzip der Einkristallherstellung nach dem tiegelfreien Zonenschmelzen (floating zone technique)

1 Ziehstange
2 Stabhalterung
3 polykristalliner Ausgangsstab
4 Schmelzzone
5 wassergekühlter Induktor
6 Einkristallkeim
7 Keimhalter
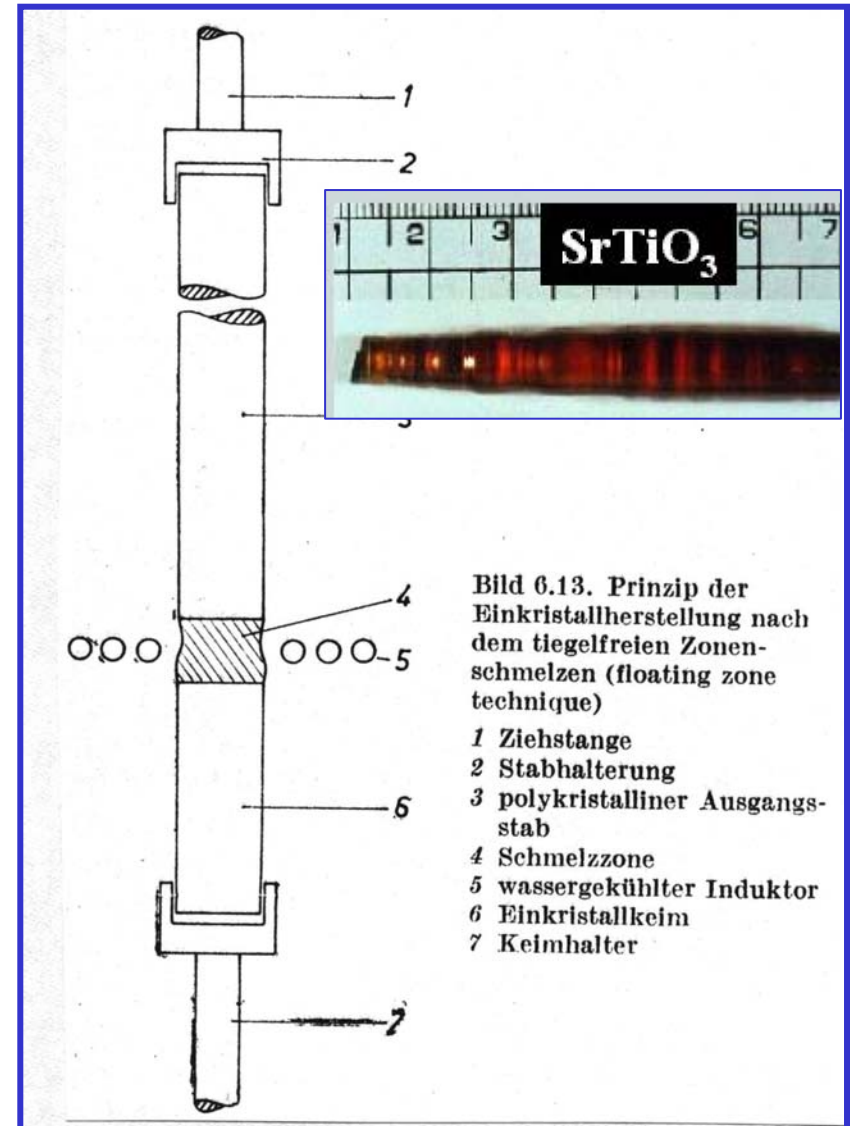
3.4 Growth of single crystals: Bridgman-Stockbarger-process (moving temperature gradient, vertical or horizontal)

Pulley

Drum

Lid

Upper winding

T/C

Melt

Baffle

Crystal

T/C

Lower winding

T

ℓ

Sapphire

Nd:YAG

3.4 Groth of single crystals: Bridgman-Stockbarger-process

→ preferably: crystal growth of <u>congruently</u>
<u>melting</u> compounds

crystal	mp (^{o}C)	velocity of grad.	container material
Al_2O_3	2037	2-8 mm h^{-1}	Mo
$FeAl_2O_4$	1790	5-10	Ir
Cu	1083	6-60	graphite
AgBr	434	1-5	Pyrex
Ar (!)	-189	0,5-1,5	Mylar

- A rotating seed crystal is raised slowly from a melt with equal composition

Single crystal being withdrawn from molten silicon

Seed crystal

Solid-liquid interface

Heating coils

Molten silicon
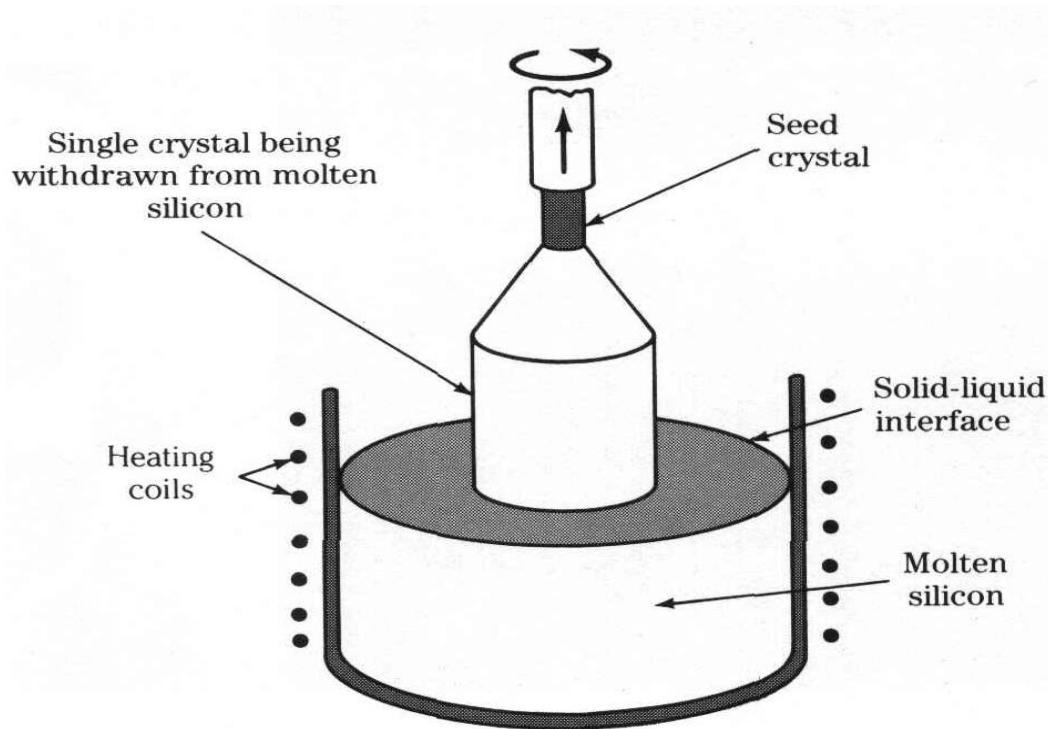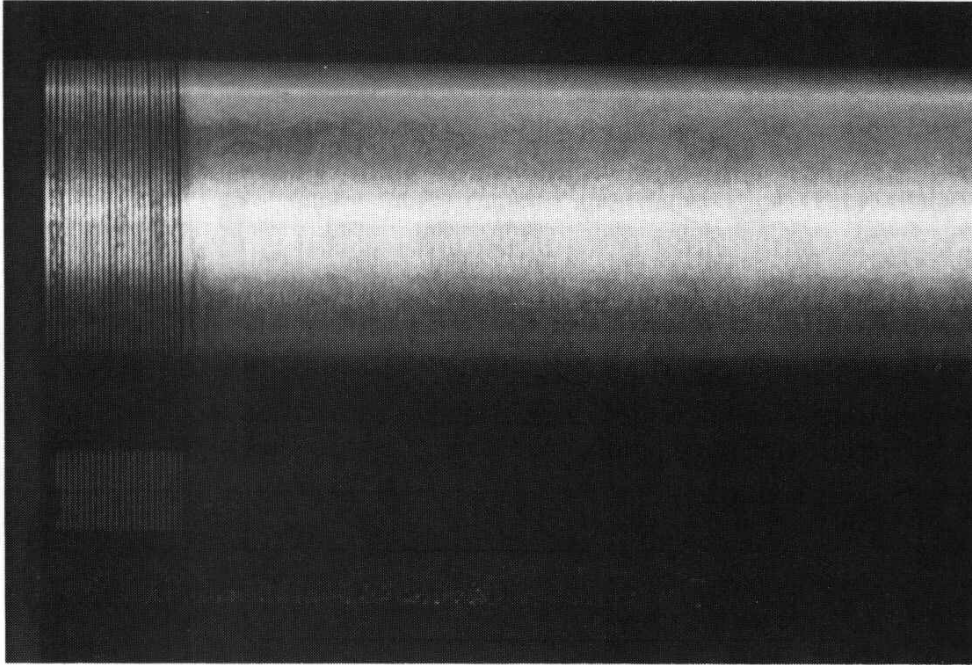
(a)

(b)

The single crystal is ground to a precision diameter and then sliced into wafers 1 mm thick. The wafers are then chemically etched and polished with successively finer polishing abrasives until a defect free mirror finish is achieved.
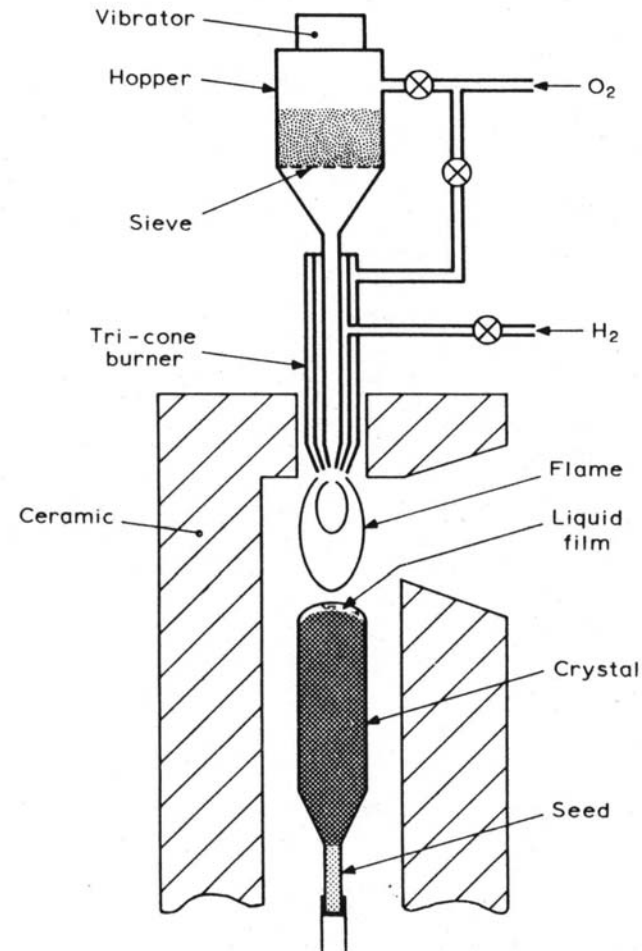
3.4 Groth of single crystals: Verneuil process

- Preferably for high melting oxides (T > 2000 K)

- Powdered sample is blown into a oxyhydrogengas burner

Synthetic corundum crystals obtained by the Verneuile process

Figure 5.1 A system for the Verneuil growth of oxidic materials. Note that the burner is composed of three coaxial tubes. Some workers use more tubes, and there are also designs using many small parallel tubes. With these it is possible to produce wider flames, and by having independent controls on various sets of tubes it is possible to optimize the heat input to give a nearly flat growth face on a large crystal.

Chemical transport in supercritical aquous solution (H_2O: T_k= 374 °C, p_k= 217,7 atm)

Autoclave for the growth of SiO_2 single crystals (1 m NaOH, 1500 bar,

T- gradient 400 →380 °C

1: nutrient (powder), 2: seed crystal,
3: mechanical fixing of crystal
4: product crystal

Lit.: Die Rolle der Hydrothermalsynthese in der präparativen Chemie, A. Rabenau,
Angew. Chem. *97* (1985) 1017

380 °C

400 °C

Calcite

Quartz
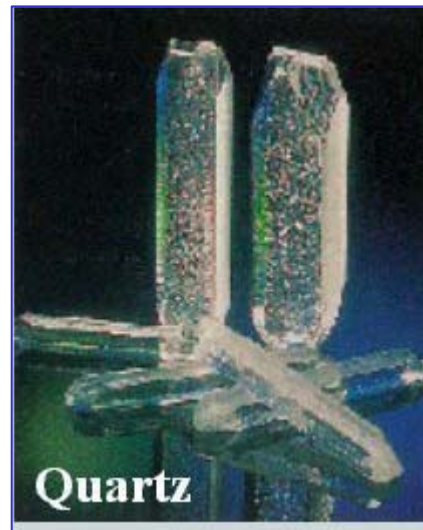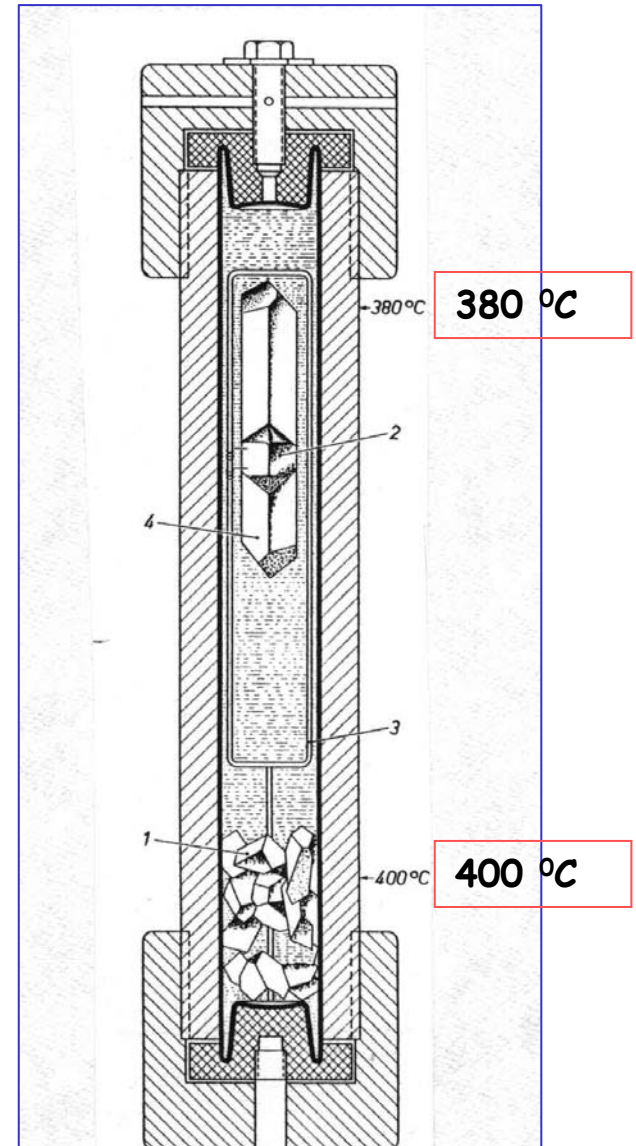
3.5 Chemical Vapor Deposition (CVD)

General term for a variety of methods (including epitaxy and sputtering) to deposit a range of inorganic materials for use in semiconducting devices, ceramic coatings, electrooptic devices etc.

CVD setup for the production of high purity silicon

CVD assembly for the epitaxial growth of GaAs$_{1-x}$P$_x$

PH$_3$, AsH$_3$, H$_2$
H$_2$, HCl
H$_2$
Flowmeter
Ga source
Substrate
Exhaust gases
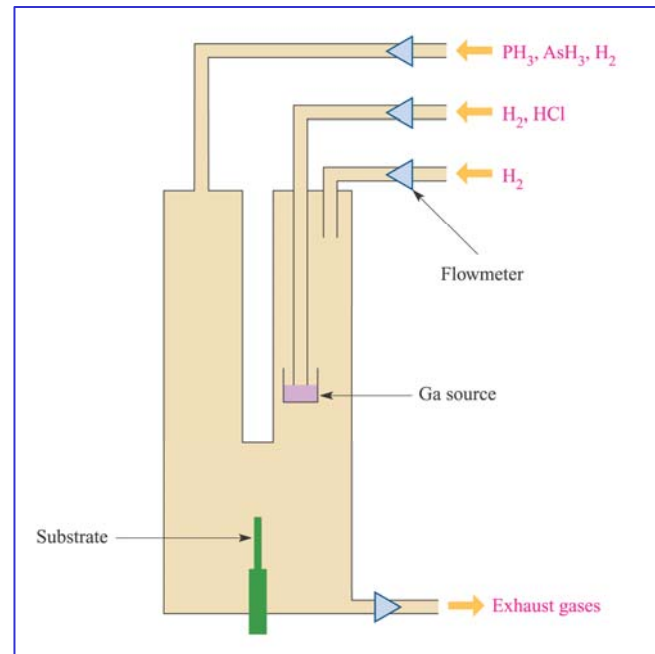
# 3.5 Physical and chemical methods to produce thin layers of chemical compounds or to clean surfaces

1. **„Sputtering"**: (to sputter: zischen, brutzeln, spritzen ...)
    - originally: method to **clean surfaces**, Ar⁺-ions ar accelerated in an electrical field and „hit" the target that has to be cleaned; as a consequence surface atoms or molecules are removed from the surface

2. **Epitaxy**: „Thin" **oriented** layers (thickness of some μ**m or nm**) are deposited on a „**substrate** with the same or a similar crystal structure. The deposition starts from gaseous precursors, which condensate or decompose on the surface of the substrate.
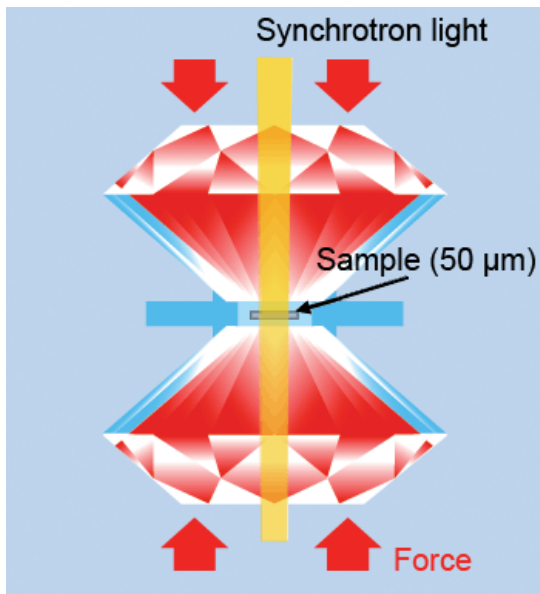
reactor

precursor support
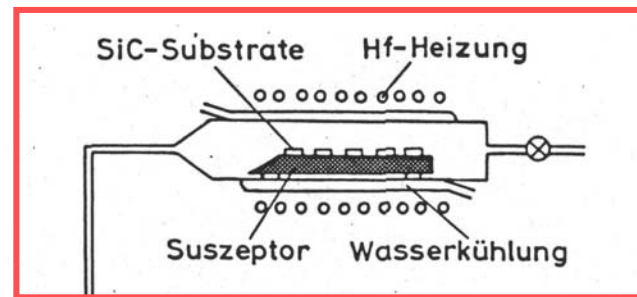
Assembly for the epitactical deposition of SiC on a substrate
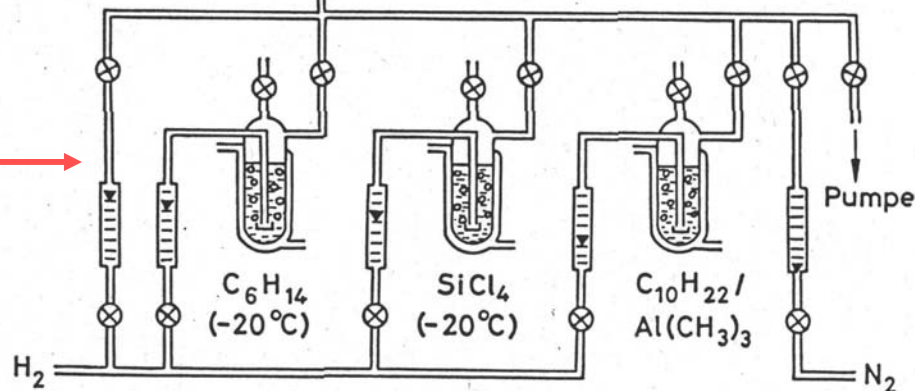
3.6 High pressure syntheses

Diamond anvil cell

about 1000 kbar (100 GPa)
(1 bar = 10^5 Pascal)

Starting mixture is encapsulated and heated under pressure!

By rapid pressure release and quenching metastable products are eventually stabilized

In general the high pressure phase has a higher density and the coordination numbers (and interatomic distances!) of corresponding atoms are higher than in the low pressure phase, e.g.

SiO_2 (Si: CN=4) $\rightarrow$ SiO_2 (Si: CN=6)
(quartz)   (Stishovit, rutile structure)
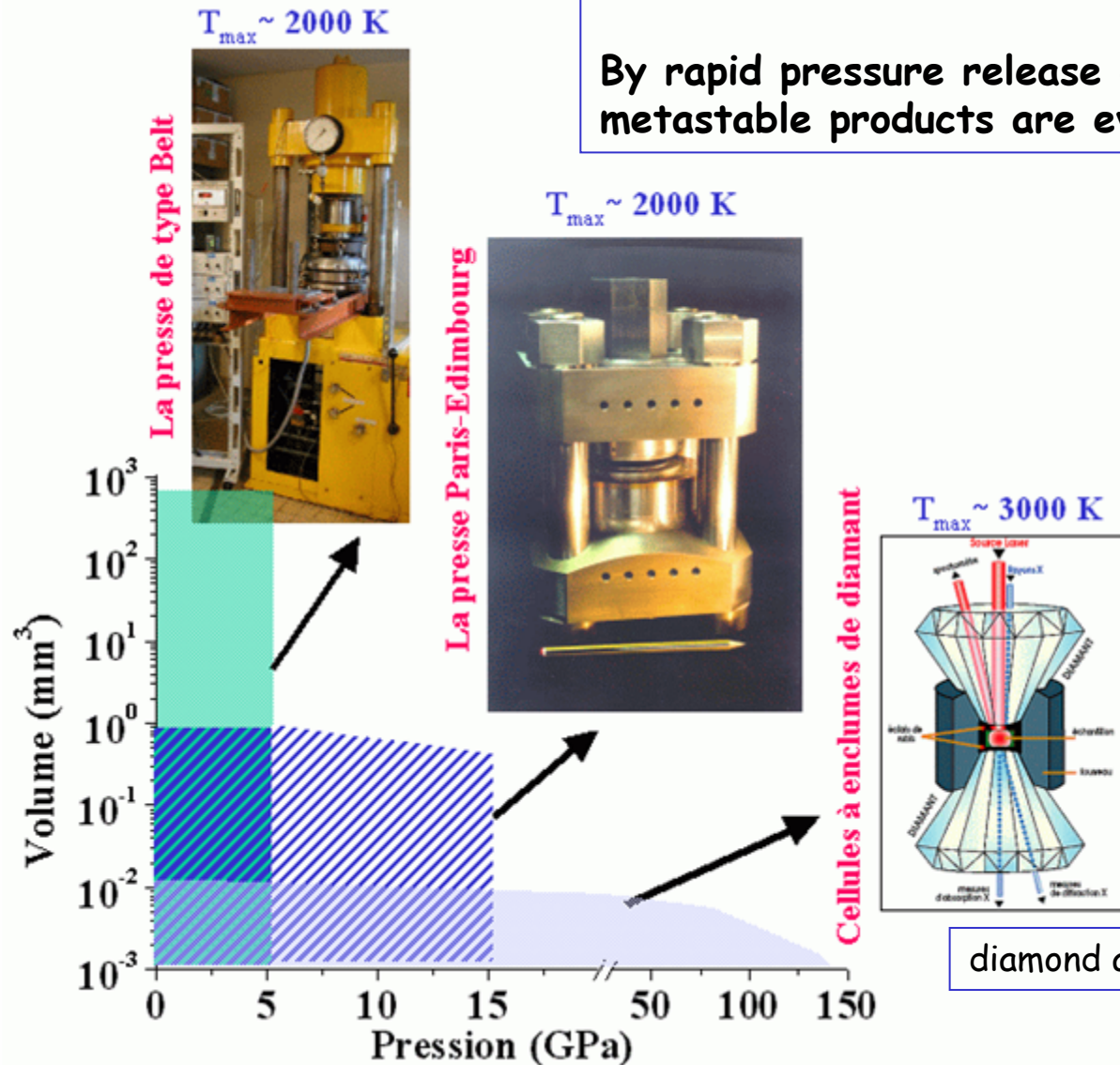
$\rightarrow$ „pressure-distance-paradoxon"

Starting mixture is encapsulated and heated under pressure!

By rapid pressure release and quenching metastable products are eventually stabilized

diamond anvil cell

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