SYNTHESIS OF INORGANIC MATERIALS AND NANOMATERIALS

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Outline

III - FORMATION OF SOLIDS FROM THE GAS PHASE

- **1) Chemical vapor transport**
  - **a) General aspects of chemical transport**
  - **b) Halogen lamp**
  - **c) Transport reactions**

- **2) Chemical vapor deposition (CVD)**

- **3) Aerosol processes**

$$A(s) + B(g) = AB(g)$$

Closed system

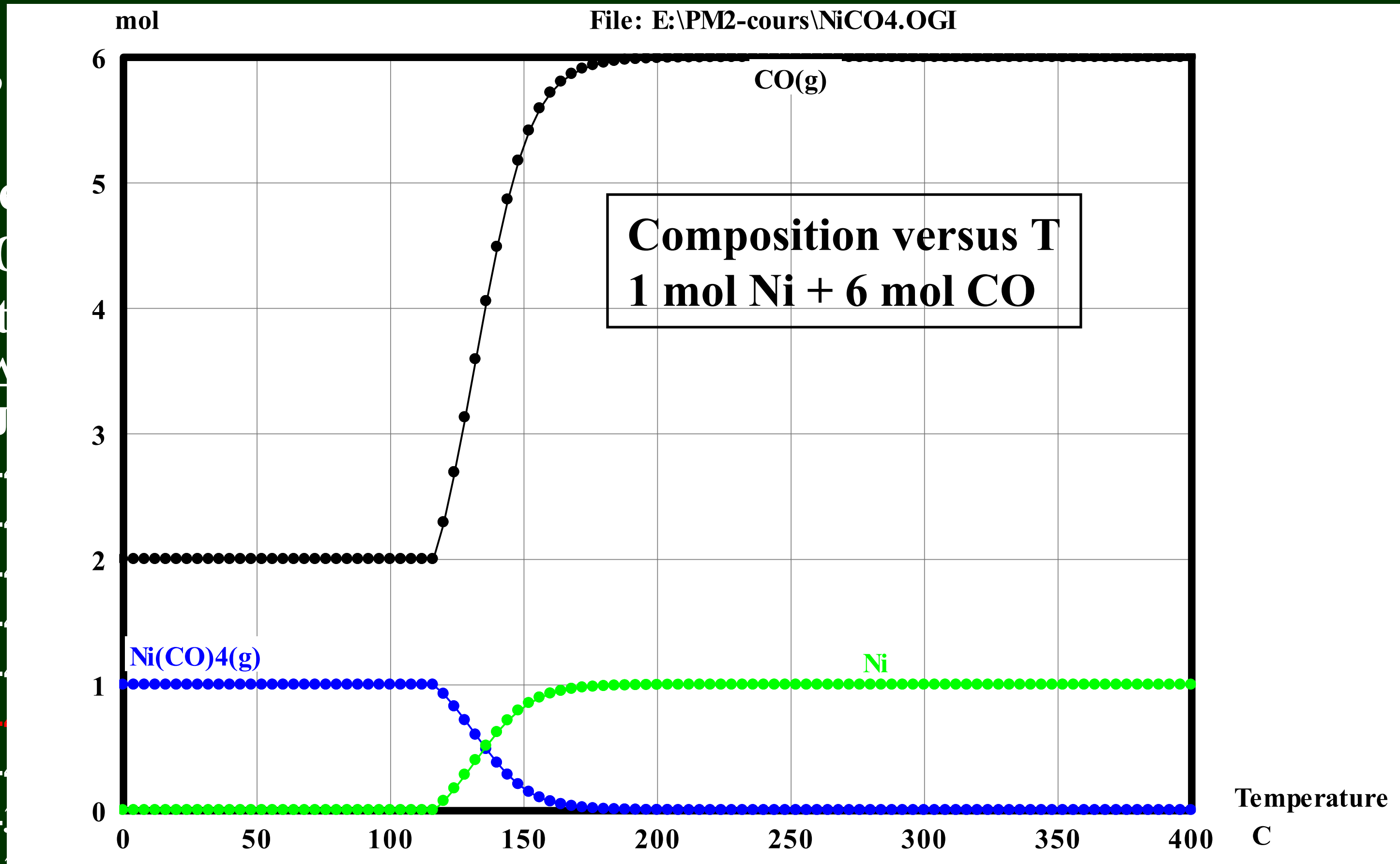
Parameters: pressure,

Ex. 1: Mond proc

$Ni(s) + 4$ C

Results from HSC soft

T	$\Delta_r H°$	Δ	
°C	kJ mol^{-1}	J	
0.000	-159.538	-4	
25.000	-159.435	-4	
50.000	-159.231	-4	
75.000	-158.967	-4	
100.000	-158.657	-4	
125.000	-158.309	-	
150.000	-157.932	-4	
175.000	-157.532	-	
200.000	-157.122	-399.008	31.669
225.000	-156.706	-398.153	41.634



$Ni(s) + 4\,CO(g) \rightarrow Ni(CO)_4(g)$ 80 °C

$Ni(s) + 4\,CO(g) \leftarrow Ni(CO)_4(g)$ 230 °C

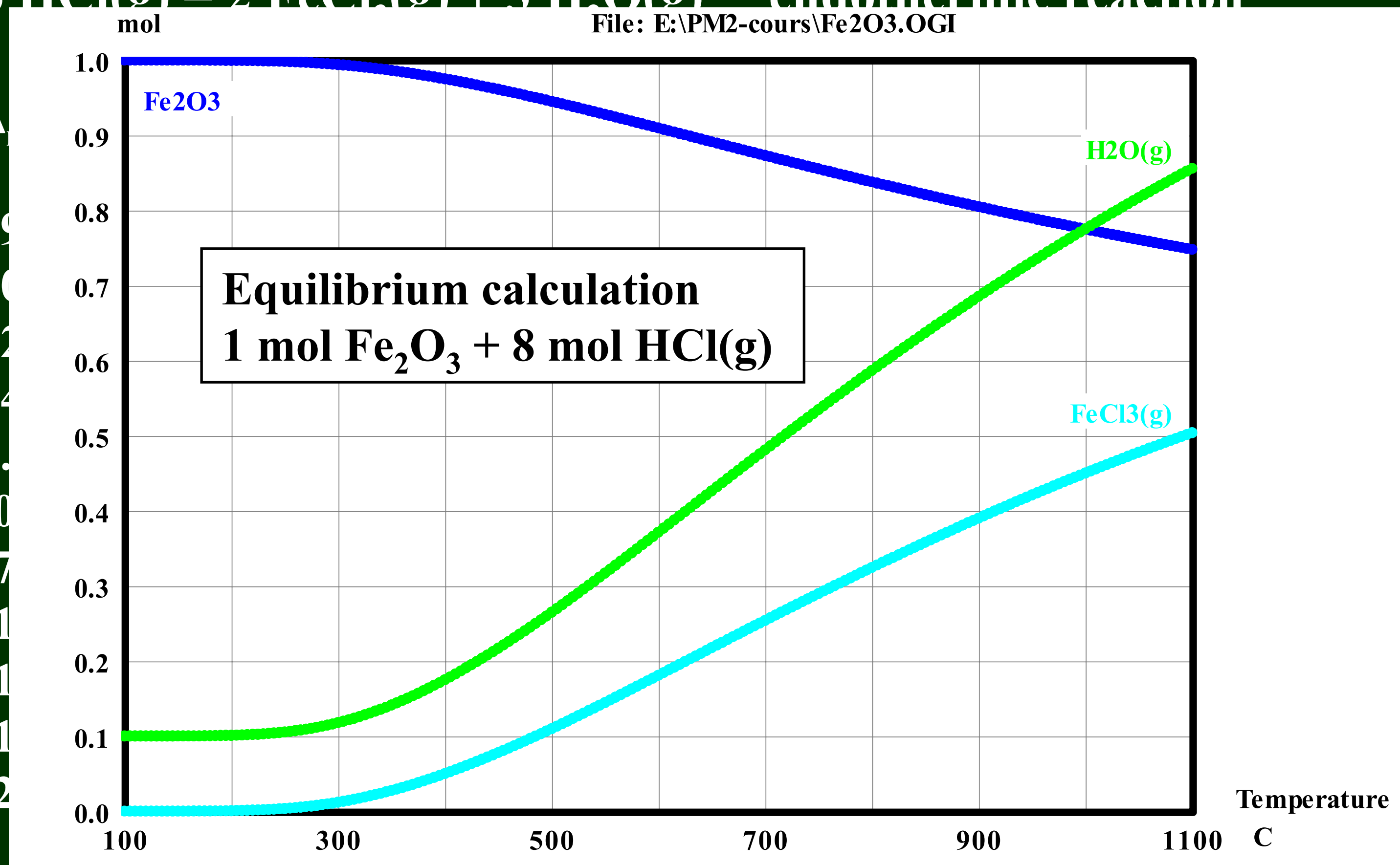
$$A(s) + B(g) = AB(g)$$

Closed system

Parameters: pressure, temperature (see figure)

Ex. 2: $Fe_2O_3(s) + 6\ HCl(g) = 2\ FeCl_3(g) + 3\ H_2O(g)$ endothermic reaction

T	$\Delta_r H°$	Δ
°C	kJ mol^{-1}	J
100.000	142.845	39
200.000	139.123	30
300.000	134.923	22
400.000	130.231	14
500.000	124.933	7.
600.000	118.751	-0
700.000	111.486	-7
800.000	106.949	-1
900.000	102.855	-1
1000.000	98.814	-1
1100.000	94.788	-2



➔ Geological interest for transportation of Fe_2O_3 in volcanos

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1) Chemical vapor transport b) Halogen lamp

1879: first incandescent lamp with carbon filament;
carbon filament replaced by tungsten filament

- low vapor pressure
- high melting point (3400 °C)
- inert gas filling ($Ar + N_2$)
- but condensation at the colder region of the lamp bulb
- wire becomes thinner ➔ wire rupture

How to avoid this rupture?
➔ introduction of traces of I_2 (0.1 mg per cm^3) and O_2

$W(s) + I_2(g) + O_2(g) = WO_2I_2(g)$ exothermic
600 °C ➔
3000 °C ⇦

➔ self-healing process (see figure)

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1) Chemical vapor transport c) Examples of vapor reactions

Ex. 1: $Cr_2O_3(s) + 1/2\ O_2(g) + 2\ Cl_2(g) = 2\ CrO_2Cl_2(g)$

Ex. 2: $Cr(s) + I_2(\ +g) = CrI_2(g)$

Applications: van Arkel – de Boer process ➔ purification of Ti, Zr, V, Cr

Ex. 3: $TiCl_4(g) + 2\ Mg(g) = Ti(s)\ (foam) + 2\ MgCl_2(g)$

Ex. 4: $ZrI_4(g) = Zr(s) + 2\ I_2(g)$

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2) Chemical vapor deposition (CVD)

➡ a) General aspects

b) Metal CVD

c) Diamond CVD

d) CVD of metal oxides

e) CVD of metal nitrides

f) CVD of semi-conductors

3) Aerosol processes

2) Chemical Vapor Deposition (CVD) a) General aspects

Ex.: $SiH_4(g)$ → Si(layer) +2 $H_2(g)$

$AsH_3(g)$ → As(layer) + 3/2 $H_2(g)$

→ formation of thin layer: metals, oxides, sulfides, nitrides, phosphides, borides…

→ applications: electronic, cutting tools, optics, solar cells

Reaction mechanism: (see figure, dynamic flow reactor)

1) diffusion of AB through the boundary layer
2) adsorption of AB
3) surface diffusion to growth site
4) surface reaction
5) diffusion of B through the boundary layer

→ avoid decomposition reaction in the gas phase

→ monoelement layer: W (WF_6); Ti ($TiCl_4$); Ga ($Ga(C_2H_5)_3$)

→ multielement layer:

Ex. 1: TiB_2 $TiCl_4(g)$ + 2 $BCl_3(g)$ + 5 $H_2(g)$ → TiB_2(layer) + 10 HCl(g)

Ex. 2: GaAs $Ga(CH_3)_3(g)$ + $AsH_3(g)$ → GaAs(layer) + 3 $CH_4(g)$

→ this requires the exact stoichiometry

2) Chemical Vapor Deposition (CVD) a) General aspects

Ex. 3: GaAs from one precursor

$[(C_2H_5)_2Ga\text{-}As(^tBu)_2]_2 \rightarrow GaAs(layer) + 4\ C_2H_4(g) + 4\ CH_2{=}C(CH_3)_2(g) + 4\ H_2(g)$

(β-elimination)

Growth rate > 0.1 µm min^{-1} kinetic control versus diffusion control (see figure)

Two classical mechanisms for the reaction A(g) + B(g)

ER or Eley-Rideal: → reaction between A (ads) and B(g)

LH or Langmuir-Hinshelwood → reaction between A(ads) and B(ads)

How to differentiate both mechanisms?

→ rate versus A/B ratio (see figure)

2) Chemical Vapor Deposition (CVD) a) General aspects

CVD related techniques:

- VPE (Vapor Phase Epitaxy) ➔ semi-conducting layers on single crystal
  - same orientation
  - similar lattice constants

- PECVD (Plasma Enhanced CVD); low pressure (0.1 to 1 mbar)
cold plasma (only electrons at thermodynamic equilibrium)
Collision between electron and molecules
➔ excited molecules ➔ lower reaction temperatures

$3\ SiH_4(g) + 4\ NH_3(g) \rightarrow Si_3N_4(s) + 12\ H_2(g)$

$SiH_4(g) + 2\ H_2O(g) \rightarrow SiO_2(layer) + 4\ H_2(g)$

- LCVD (Laser-assisted CVD

- ALE (Atomic Laser Epitaxy)

$ZnCl_2(g) + H_2S(g) \rightarrow ZnS(layer) + 2\ HCl(g)$

➔ control of growth layer by layer

2) Chemical Vapor Deposition (CVD) a) General aspects

Non-CVD process for gas phase deposition of thin films

➔ **PVD or Physical Vapor Deposition**

➔ **thermal evaporation of metal ➔ metallic films**
- **metal vaporized by electron beam or laser beam**
- **high vacuum needed to increase the mean path length (10-5 to 10-8 mbar)**

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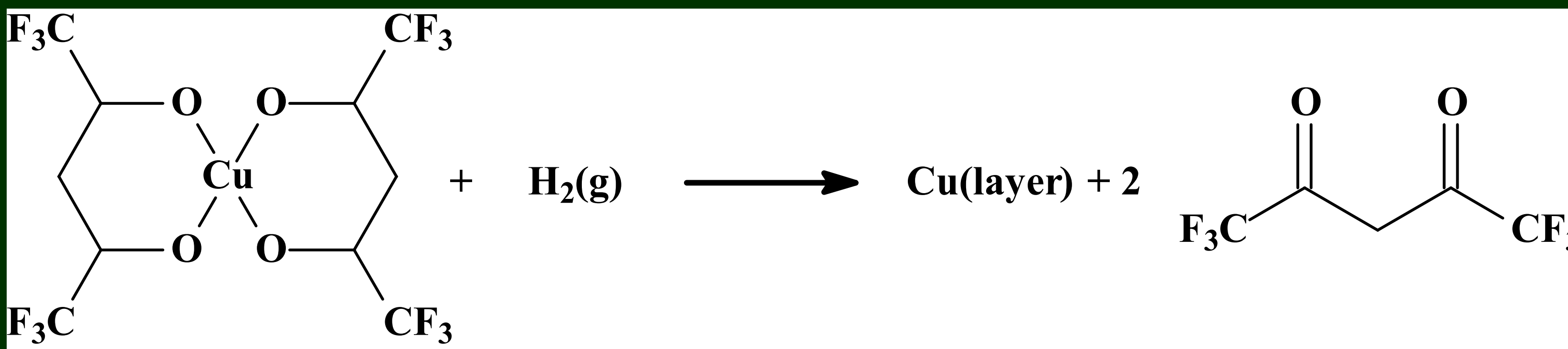
3) Aerosol processes

2) Chemical Vapor Deposition (CVD) b) Metal CVD

➔ **Al** $Al(^iBu)_3(g)$ as precursor ^iBu = $-CH_2-CH(CH_3)_2$
0.1 mbar, 200 to 300 °C growth rate: 20 to 80 nm min^{-1}

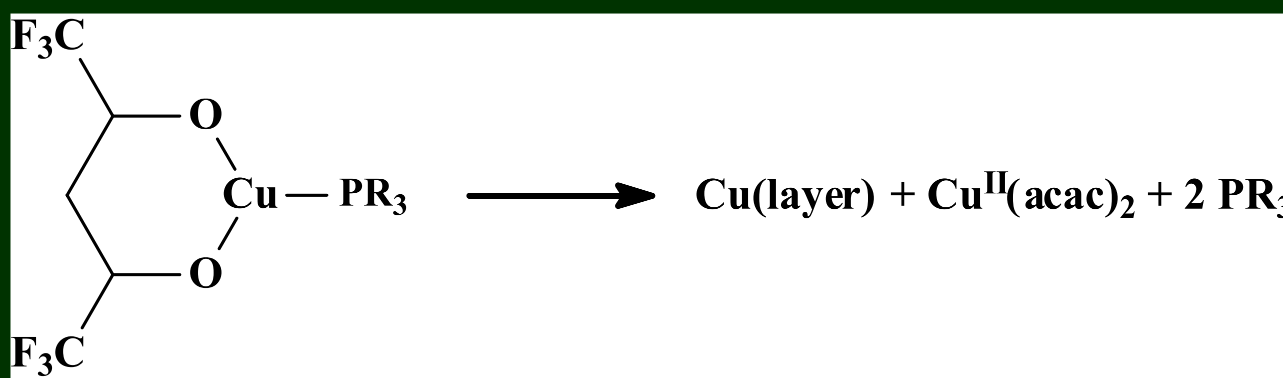
➔ **W** $2\ WF_6(g) + 3\ SiH_4(g) \rightarrow 2\ W(layer) + 6\ H_2(g) + 3\ SiF_4(g)$
room temperature increase hardness of cutting tools

➔ **Cu** Cu^{II} precursors ➔ rate 0.1 to 0.5 nm min^{-1}, 400 °C



Cu^{I} precursors

disproportionation reaction



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2) Chemical Vapor Deposition (CVD) c) Diamond CVD

- 1 % CH_4(g) in excess H_2(g)
- hot filament, plasma or O_2-C_2H_2 torch
- temperature > 2000 °C

  - increase hardness
  - increase thermal conductivity
  - heat sink for electronic devices

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3) Aerosol processes

2) Chemical Vapor Deposition (CVD)   d) CVD of metal oxides

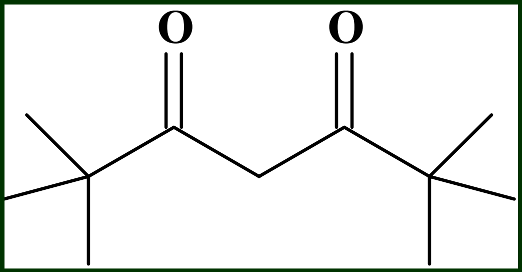
➔ SiO_2 thin film ➔ isolating layer in microelectronic

$$SiH_4(g) + O_2(g) \rightarrow SiO_2(layer) + 2\ H_2O(g)$$

➔ superconductors $YBa_2Cu_3O_{7-x}$ (YBaCuO)

precursors

- $Ba^{II}(acac)_2$
- $Cu^{II}(acac)_2$
- $Y^{III}(acac)_3$



800 – 900 °C, in $O_2(g)$ or $N_2O(g)$

(See video)

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3) Aerosol processes

2) Chemical Vapor Deposition (CVD)   e) CVD of metal nitrides

➔ Si_3N_4 insulating properties ➔ microelectronics, encapsulation

➔ TiN conducting properties

hardness, melting point 3300 °C

chemical inertness

$6\ TiCl_4(g) + 8\ NH_3(g) \rightarrow 6\ TiN(layer) + 24\ HCl(g) + N_2(g)$

replacement of NH_3 by more reactive nitrogen source: N_2H_4 (hydrazine)

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3) Aerosol processes

2) Chemical Vapor Deposition (CVD) f) CVD of semi-conductors

The semi-conductors can be sorted by band gap energy:

	InSb	Ge	Si	GaAs	CdSe	GaP	CdS	SiC	ZnS
gap /eV	0.2			1.2	←	visible range		→	3.6

Ex.: $Ga(CH_3)_3(g) + AsH_3(g) \rightarrow GaAs(layer) + 3\ CH_4(g)$ (600 to 750 °C)

Application: LED devices

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3) Aerosol processes

➔ preparation of powder in gas phase ➔ formation of nanosized particles

TiO_2: white paint pigment, support for photochemical reactions

SiO_2: aerosil (Degussa)

C, Al_2O_3

Very low apparent density (about 50 g L^{-1})

Reaction in a torch flame: $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$ (see figure)

$SiCl_4(g) + 2\ H_2O(g) \rightarrow SiO_2(s) + 4\ HCl(g)$

Particle size: 7 to 50 nm

Specific surface area: 400 to 50 $m^2\ g^{-1}$

Model of non-porous spherical particles:

particle diameter d volume $v = \pi\ d^3/6$ surface $s = \pi\ d^2$

surface/volume ratio $s/v = 6/d$

➔ specific surface area $S = 6/d\ \rho$

For SiO2 ➔ $\rho = 2.3$ g cm^{-3}

d = 7 nm ➔ S = ? d = 50 nm ➔ S = ?

d = 7 nm ➔ S = 373 $m^2\ g^{-1}$ d = 50 nm ➔ S = 52 $m^2\ g^{-1}$