Thin layer preparation by physical and chemical vapor deposition

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Literature:

- *Chemical Vapor Deposition*, (Academic Press, London, 1993)
- *Vapor Deposition*, (John Wiley & Sons, Inc., New York, 1966)
- Y. Iwasawa, in *Preparation of Solid Catalysts*, Edited by G. Ertl, H. Knözinger, and J. Weitkamp (Wiley-VCH, Weinheim, 1999), Chap. 4.5
- P. Serp, P. Kalck, and R. Feurer, Chemical Reviews **102,** 3085 (2002)

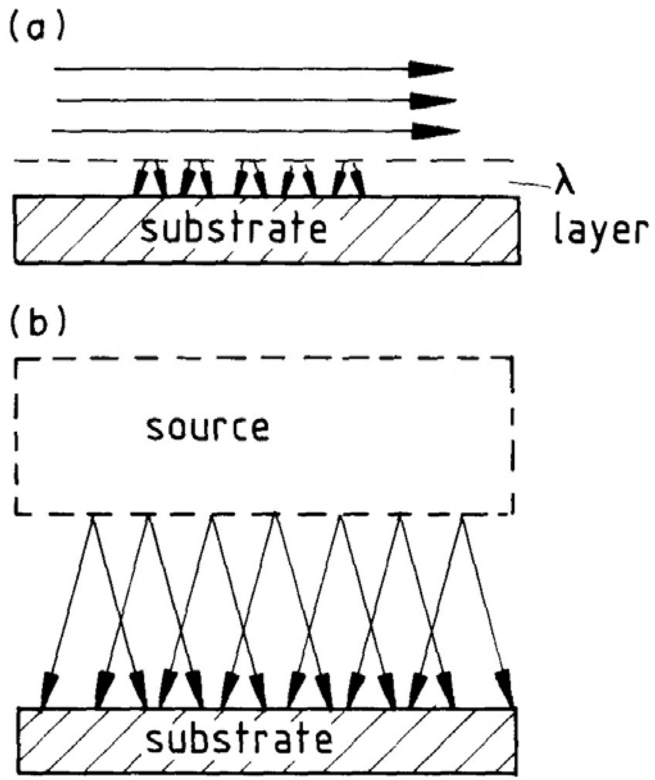
Definition

Vapor deposition:

Condensation of elements or compounds from the gas phase to form solid deposits.

Physical Vapor Deposition (PVD):	vapor phase of the same composition as the deposit – no chemical reaction
Chemical Vapor Deposition (CVD):	deposits are formed by chemical reactions at or near the deposition surface

Differences CVD/PVD



a) CVD

Chemical Reactions

Transport

Diffusion

$T_{substrate} > T_{source}$

b) PVD

Very clean compounds

High-vacuum

$T_{substrate} < T_{source}$

Outline

History

Chemical Vapor Deposition

- Precursors
- Reactors
- Energy “input” for decomposition
- Methods for investigation
- Modeling
- Chemistry
- Applications

PVD

- Thermodynamics
- Monitoring growth by XPS and AES

Summary

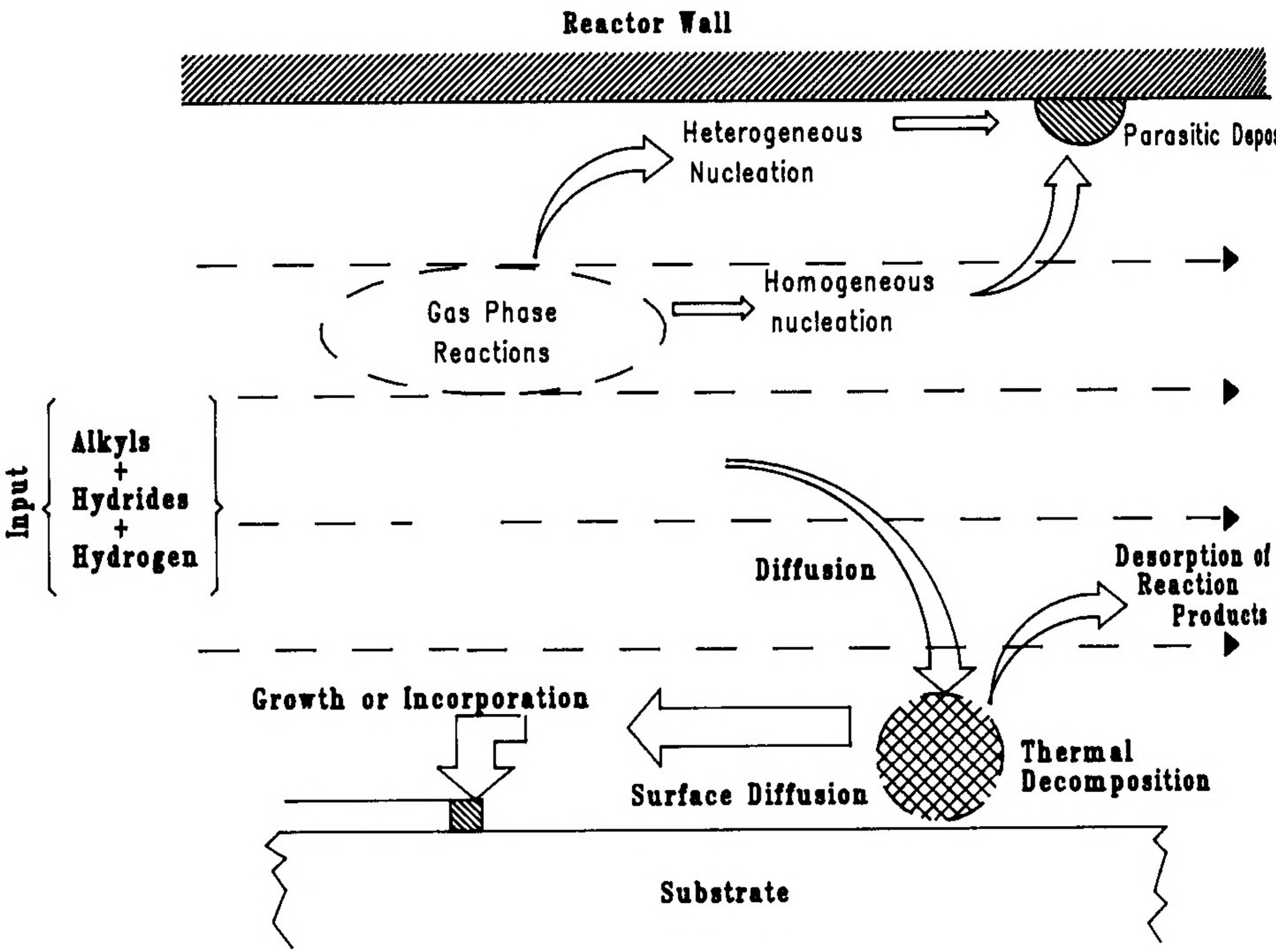
History

One of the oldest PVD processes occurs again yesterday: snowing

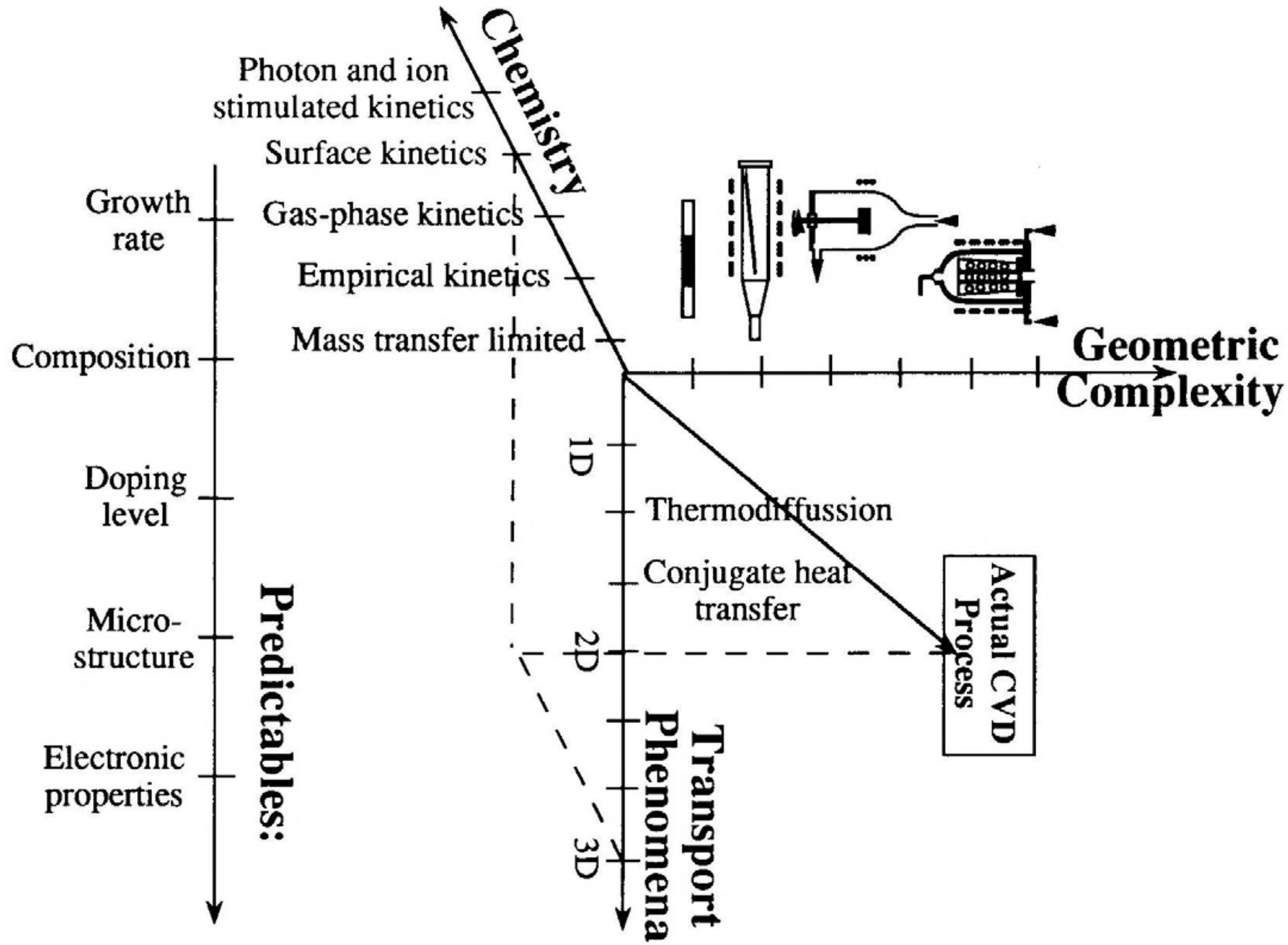
For CVD: Pyrolytic Carbon

Technical: Mond process (purification of Nickel via $NiCO_4$)

Typical processes during CVD



Complexity of a CVD-experiment



CVD fundamentals - Precursors

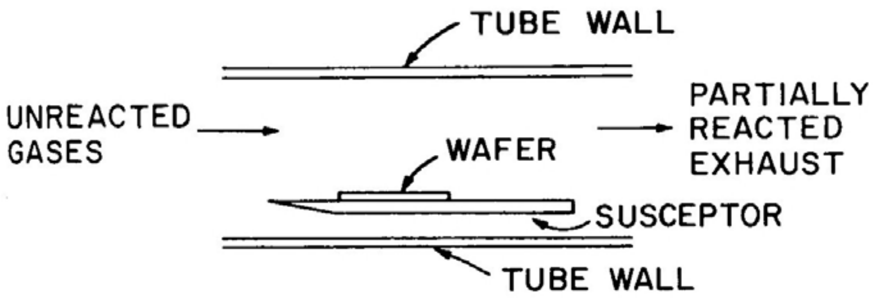
Choice of the precursor:

- Stability at RT
- Sufficient volatility at low T
- High purity compounds
- Clean reaction

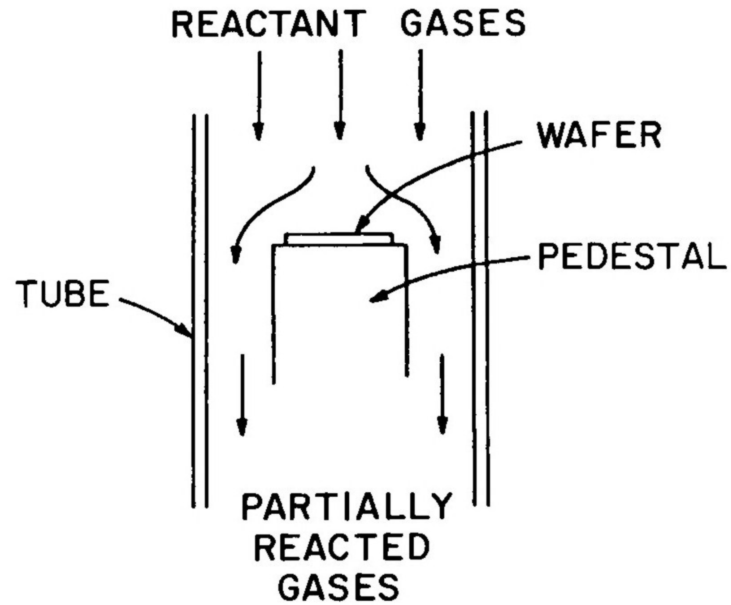
Types of precursors:

- Hydrides
- Carbonyls
- Halides
- Metallo-organic or Organometallic (MOCVD or OMCVD)

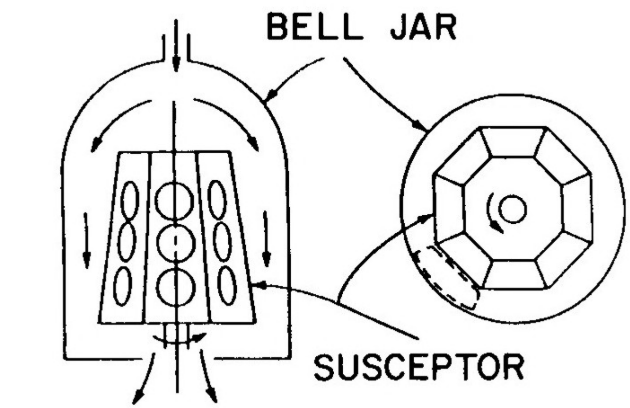
CVD fundamentals - Reactors



(a) HORIZONTAL



(b) VERTICAL



(c) MULTI-WAFER BARREL

Evaluation of
- gas phase
- fluid mechanics

CVD fundamentals – Energy input and methods for investigation

Supply of Energy for decomposition:

- Thermal
- Plasma (PACVD, PECVD) Assisted, Enhanced
- Light (Photo-) (PACVD, PECVD)
- Acoustic

Methods for investigation:

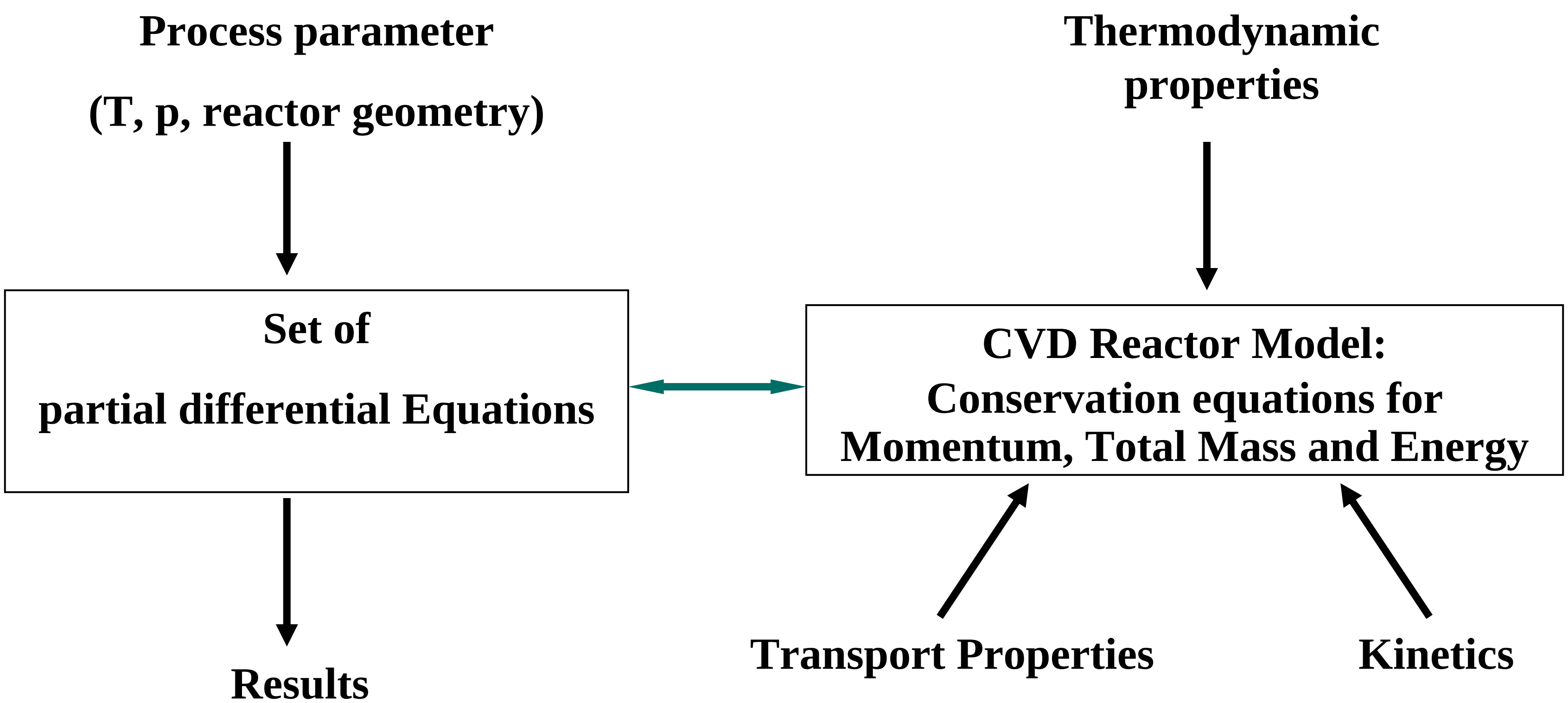
In situ

- EXAFS
- UV/VIS
- Raman
- FTIR
- High-p XPS

Ex situ (UHV)

- ISS
- XPS, AES, UPS
- TDS
- TEM
- SIMS

CVD fundamentals - Modeling



Thermodynamics

From Kinetic Gas Theory:
(Collision rate with the wall)

$$Rate = \frac{\gamma_i p_i}{\sqrt{2\pi M_i RT}}$$

sticking coefficient $\gamma_i = f(T, \Theta)$

Gibbs Free Energy: from textbooks

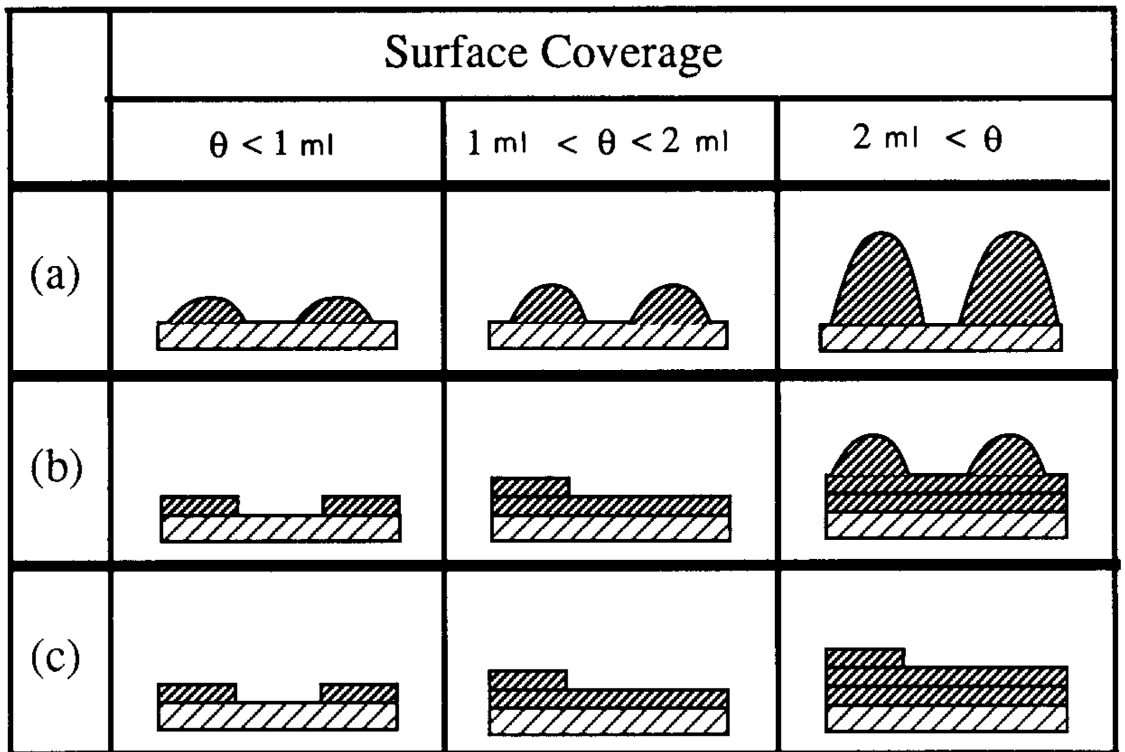
Layer growth: Ratio of surface energies

$$\sigma_S \, ? \, \sigma_A + \sigma_I$$

Film growth modes and adhesion

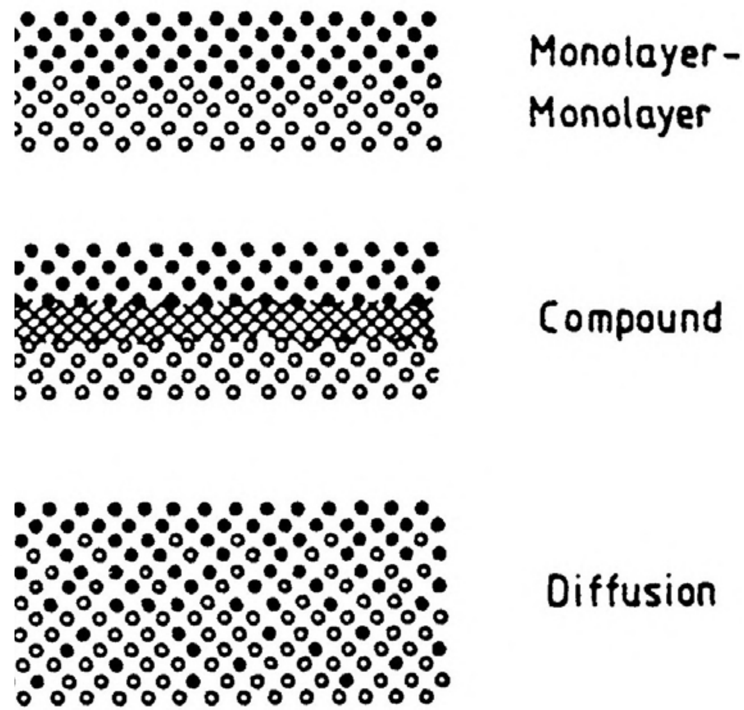
Thermodynamically derived film growth modes:

a) Volmer-Weber
b) Stranski-Krastanov
c) Frank-van der Merwe

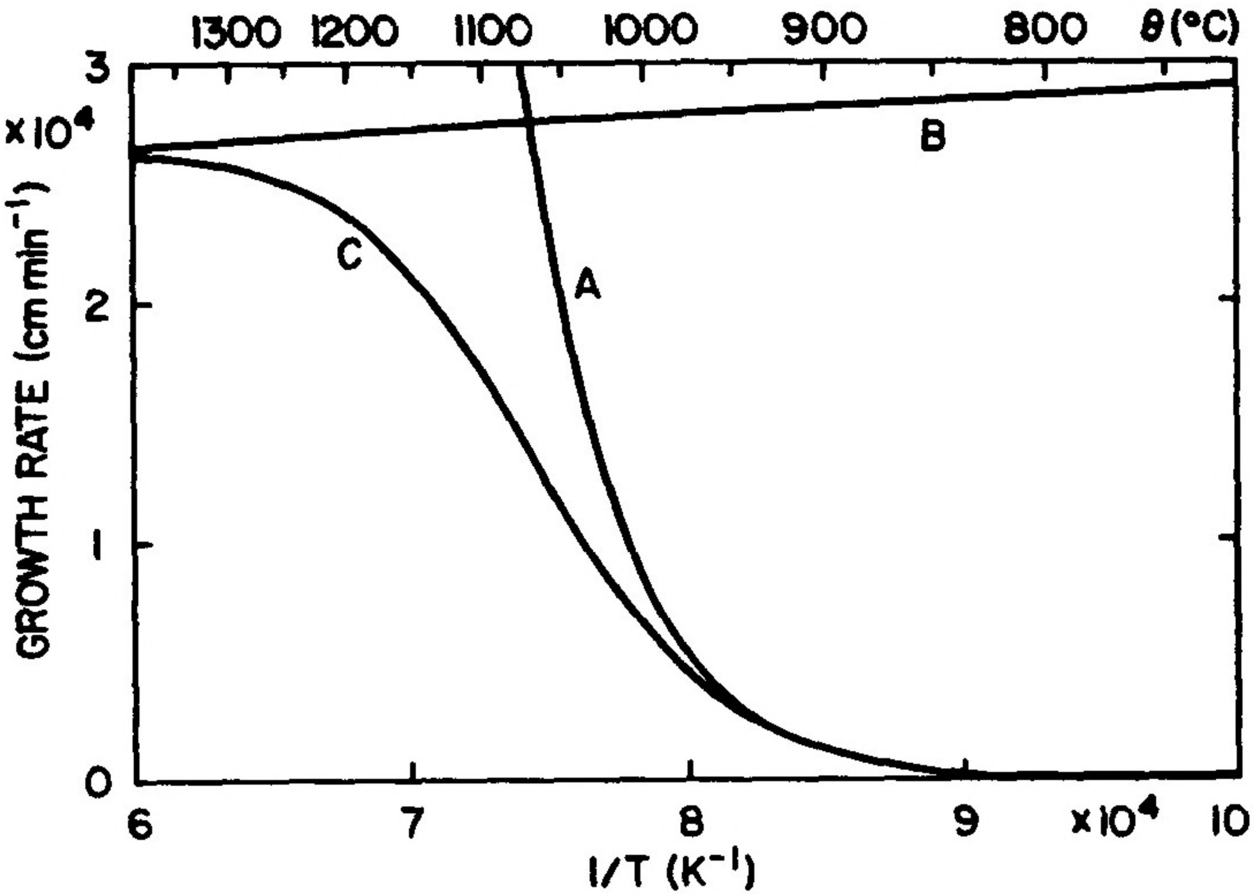


Adhesion (FM-mode)

Interface effects



Growth rate = f(T)



A) Arrhenius for chemical reactions

B) Transport limited

C) Real system

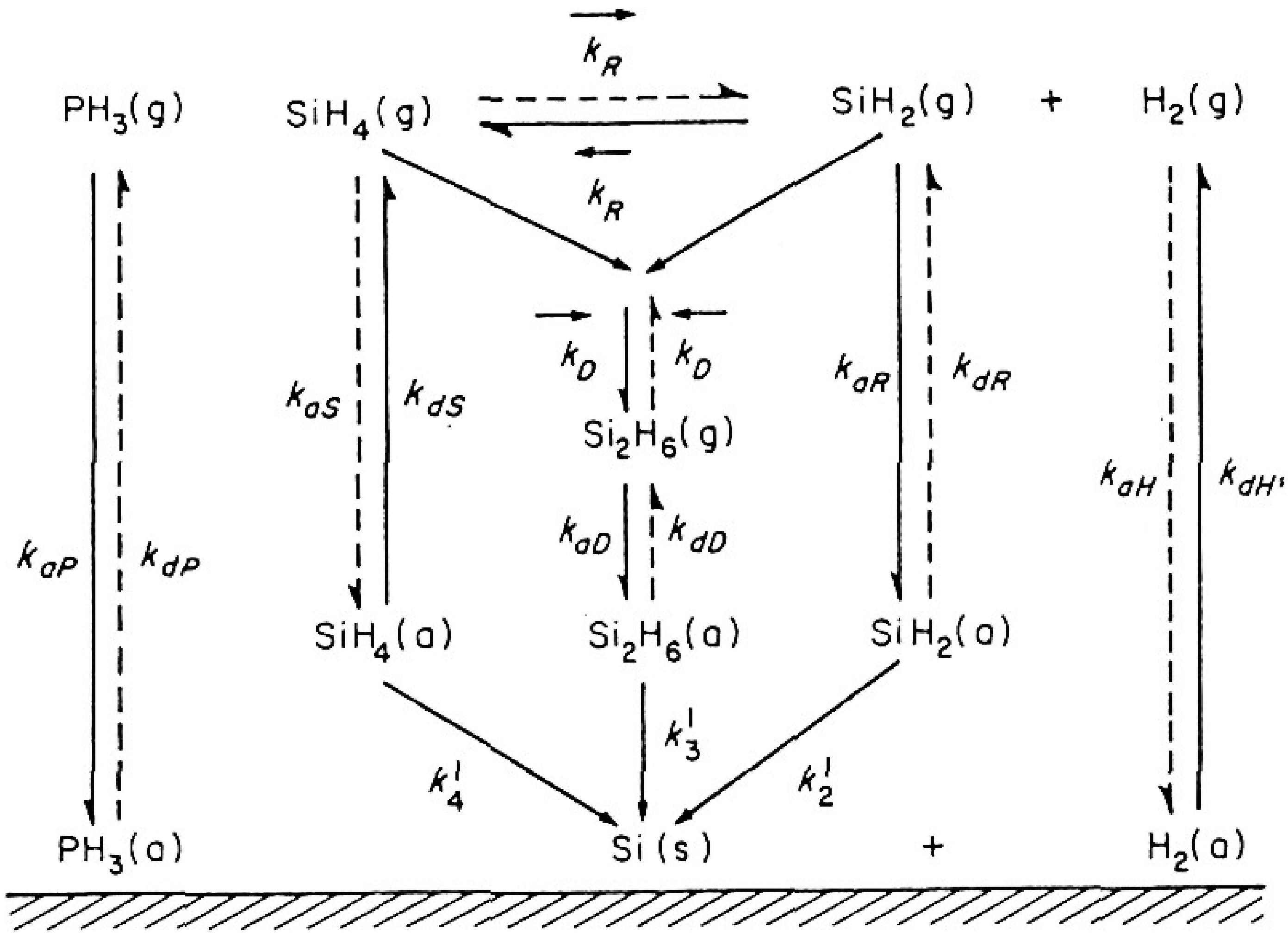
CVD fundamentals - Chemistry

Two types of reactions are possible:

Homogeneous: gas phase reactions
Heterogeneous: at the surface

That makes modeling sometimes difficult.

Schema for $SiH_4(g) \longrightarrow Si(s) + 2H_2$



Output of sensitivity analysis: 27 contributing reactions of 120

Surface Chemistry of $SiH_4(g)/Si(s)$

$$SiH_4(g) + \underline{o} \longrightarrow \underline{H} + \underline{Si}H_3 \quad (1)$$

$$\underline{Si}H_3 + \underline{o} \longrightarrow \underline{H} + \underline{Si}H_2 \quad (2)$$

$$2\underline{Si}H_2 \longrightarrow H_2(g) + 2\underline{Si}H \quad (3)$$

$$2\underline{Si}H \longrightarrow H_2(g) + 2\underline{o} + \underline{\text{Si film}} \quad (4)$$

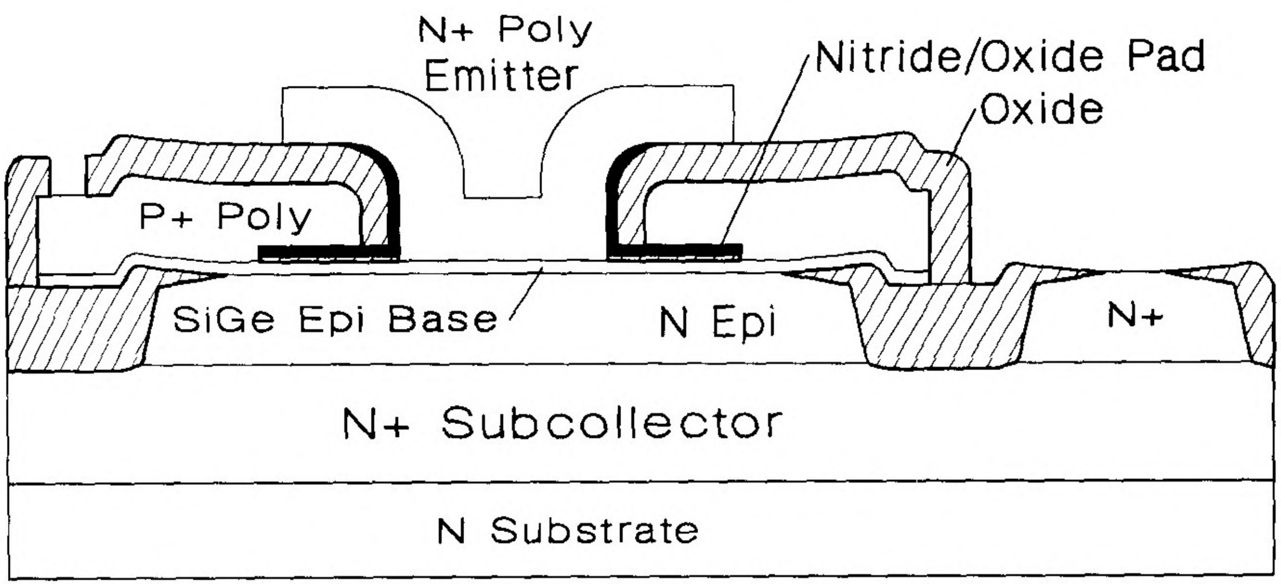
$$2\underline{H} \longrightarrow H_2(g) + 2\underline{o} \quad (5)$$

T<500°C: (4) is rate limiting

T>700°C: (1) is rate limiting

(sticking coefficient: $2 \times 10^{-4} – 5 \times 10^{-5}$)

Si:Ge heterojunction bipolar transistor



Literally “built” on patterned substrates

Result? Computer!

CVD fundamentals - Applications

- Microelectronics
- Optoelectronics
- Protective and decorative coatings
- Optical coatings

Where is catalysis?

Preparation of supported catalysts by CVD is up to now only of academic interest ☹

One exception?

Example 2: CVD of Carbon Nanotubes

CVD at the AC department

Two step process

1. Deposition of the catalyst (Fe or Ni on SiO_2 or Al_2O_3)
2. Growth of Carbon Nanotubes (C_2H_4 / H_2)

<u>Problems</u>

reproducibility

Scale up?

security

Example 2: CVD of Carbon Nanotubes

- old horizontal wobble oven
- for the new one – ask Bernd Kubias or Siegfried Engelschalt

Example 3: Boron Nitride ceramics

$NH_3(g) + BCl_3(g) \longrightarrow BN(s) + 3HCl(g)$

$H_3B_3N_3Cl_3(g) \longrightarrow 3BN(s) + 3HCl(g)$

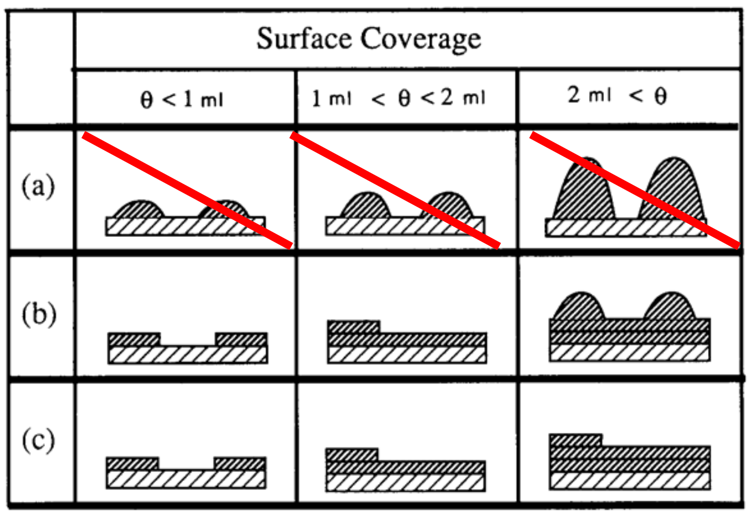
(β-Trichloroborazole)

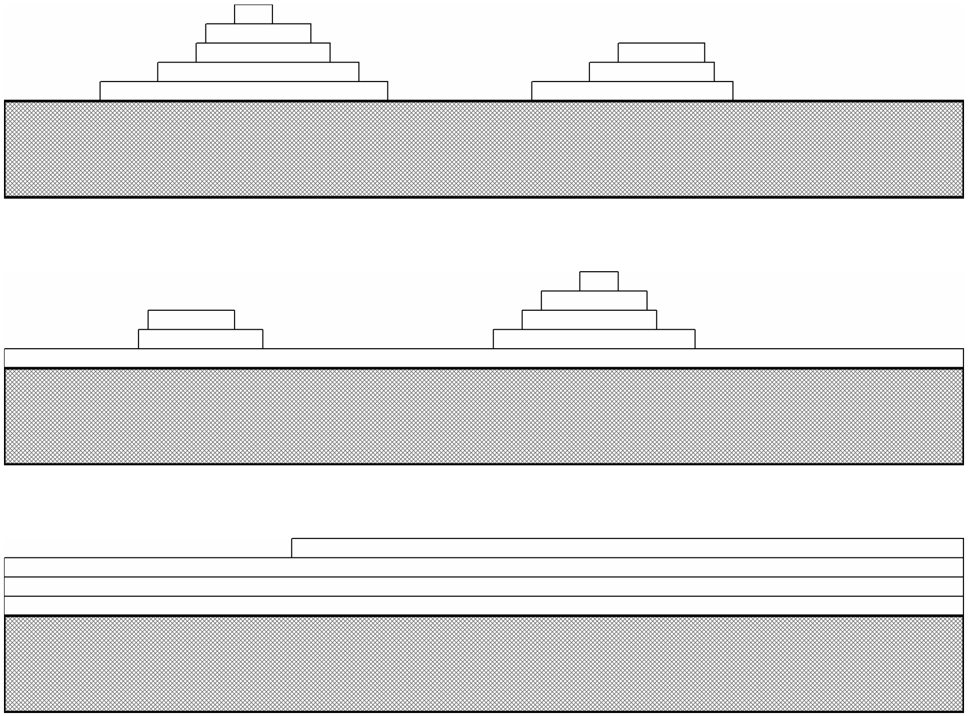
- insulating
- high T stabile
- stabile against oxidation

Every surface scientist who ever opened a device knows this stuff!

PVD – mostly used in surface science

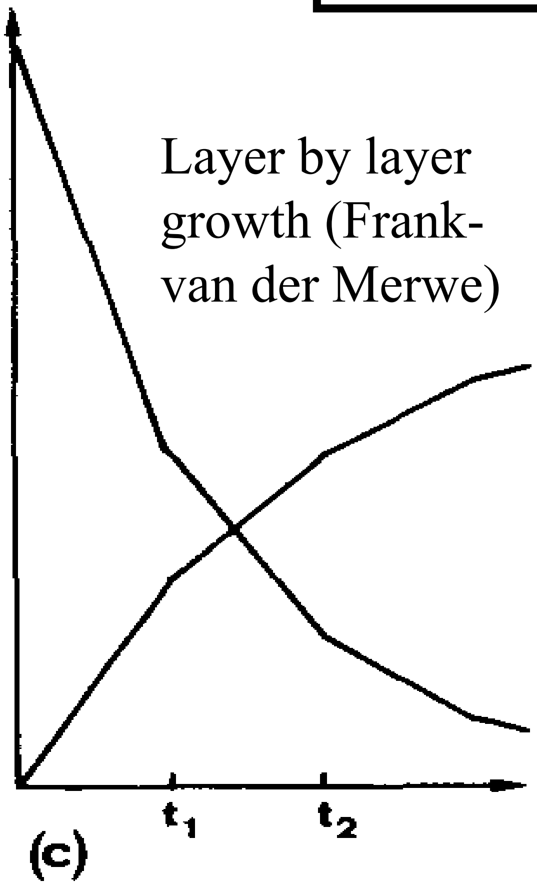
From Thermodynamics we get:

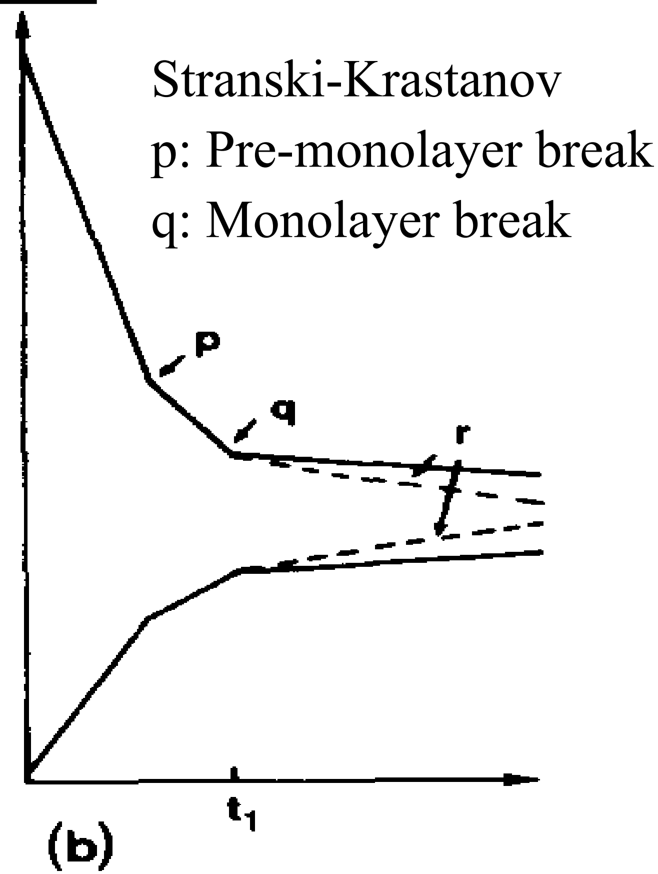




PVD – Monitoring growth modes with XPS and AES

The "break-argument"





C. Argile and G. E. Rhead, Surface Science Reports **10,** 277 (1989), p.281

Summary

- PVD and CVD are complex methods with interdisciplinary background
- CVD is mostly used in opto- and microelectronics as well as for coatings
- Up to now application in design of supported catalysts only of academic interest
- PVD is typical tool in surface science for film deposition

Surface scientists, please never forget:

At least two breaks are necessary for Frank-van der Merwe growth mode