Thin layer preparation by physical and chemical vapor deposition

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Literature:

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
\[ T_{\text{substrate}} > T_{\text{source}} \]

b) PVD
Very clean compounds
High-vacuum
\[ T_{\text{substrate}} < T_{\text{source}} \]
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 NiCO₄)
Typical processes during CVD

1. **Input**
   - Alkyls
   - Hydrides
   - Hydrogen

2. **Reactant Wall**
   - Heterogeneous Nucleation
   - Parasitic Deposit
   - Gas Phase Reactions
   - Homogeneous Nucleation

3. **Reactor Wall**
   - Diffusion
   - Desorption of Reaction Products
   - Thermal Decomposition
   - Growth or Incorporation

4. **Substrate**
   - Surface Diffusion

**Diagram by Dirk Rosenthal, Surface Analysis, Dept. AC, Fritz Haber Institute of the MPG, Berlin, Germany**
Complexity of a CVD-experiment

Diagram showing the complexity of a CVD-experiment with factors such as growth rate, composition, doping level, microstructure, electronic properties, chemistry, and geometric complexity.

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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

Process parameter
(T, p, reactor geometry)

Set of partial differential Equations

Thermodynamic properties

CVD Reactor Model:
Conservation equations for Momentum, Total Mass and Energy

Transport Properties

Kinetics

Results
Thermodynamics

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

\[ \text{Rate} = \frac{\gamma_i P_i}{\sqrt{2\pi M_i RT}} \]

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

Gibbs Free Energy: from textbooks

Layer growth: Ratio of surface energies

\[ \sigma_S \sim \sigma_A + \sigma_I \]
**Film growth modes and adhesion**

Thermodynamically derived film growth modes:

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

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<th>Surface Coverage</th>
<th>( \theta &lt; 1 \text{ ml} )</th>
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Adhesion (FM-mode) Interface effects

- Monolayer
- Compound
- Diffusion
Growth rate = $f(T)$

A) Arrhenius for chemical reactions

B) Transport limited

C) Real system
Two types of reactions are possible:

Homogeneous:  gas phase reactions
Heterogeneous: at the surface

That makes modeling sometimes difficult.
Schema for $\text{SiH}_4(\text{g}) \rightarrow \text{Si(s)} + 2\text{H}_2$

Output of sensitivity analysis: 27 contributing reactions of 120

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Surface Chemistry of SiH₄(g)/Si(s)

\[
\begin{align*}
\text{SiH}_4(g) + \text{o} & \rightarrow \text{H} + \text{SiH}_3 \quad (1) \\
\text{SiH}_3 + \text{o} & \rightarrow \text{H} + \text{SiH}_2 \quad (2) \\
2\text{SiH}_2 & \rightarrow \text{H}_2(g) + 2\text{SiH} \quad (3) \\
2\text{SiH} & \rightarrow \text{H}_2(g) + 2\text{o} + \text{Si film} \quad (4) \\
2\text{H} & \rightarrow \text{H}_2(g) + 2\text{o} \quad (5)
\end{align*}
\]

\text{T}<500°C: (4) is rate limiting

\text{T}>700°C: (1) is rate limiting

(sticking coefficient: 2\times10^{-4} – 5\times10^{-5})
Si:Ge heterojunction bipolar transistor

Literally “built” on patterned substrates

Result? Computer!

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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$_2$O$_3$)
2. Growth of Carbon Nanotubes (C$_2$H$_4$ / H$_2$)

Problems

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

\[
\begin{align*}
\text{NH}_3(g) + \text{BCl}_3(g) & \rightarrow \text{BN(s)} + 3\text{HCl(g)} \\
\text{H}_3\text{B}_3\text{N}_3\text{Cl}_3(g) & \rightarrow 3\text{BN(s)} + 3\text{HCl(g)} \\
(\beta\text{-Trichloroborazole})
\end{align*}
\]

- insulating
- high T stable
- stable against oxidation

Every surface scientist who ever opened a device knows this stuff!
PVD – mostly used in surface science

From Thermodynamics we get:

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PVD – Monitoring growth modes with XPS and AES

The “break-argument”

Layer by layer growth (Frank-van der Merwe)

Stranski-Krastanov
p: Pre-monomolecular break
q: Monolayer break

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