Synthesis Techniques in 2D: Films & Coatings

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Outline

1. Introduction
2. Common techniques
3. Fundamental concepts & research
1. Introduction: Basic processes

**Generation:** Species selection

**Transport**

**Deposition (Flux, F)**

**Reflection** (Probability ratio of Adsorption: Reflection = Condensation Coefficient)

**Desorption**

**Adsorption & Diffusion**

**Nucleation & Growth**

**Chemical Reaction**
A few common terms & ideas (exceptions exist)

• Terminology:
  – Substrate = solid support (often inert)
  – Films vs. coatings:
    • Thickness (ca. 100 nm)
    • Purpose: Function vs. protection
  – Freestanding vs. supported
  – Comment: Gravity

• Major variables:
  – Flux = Impingement rate
    • particles/(area x time)
  – Substrate nature & temperature
  – Nature, directionality, and k.e. of the impinging species

• Growth rate (speed) vs. quality
  – Smooth
  – Conformal or shadow-mask
  – (Poly)crystalline, amorphous, epitaxial
  – Uniform

Gas (or liquid) phase
Substrate
2. Classes of common deposition techniques

• Chemical vapor deposition
  – Atomic layer deposition
  – Technology can be relatively simple
  – High growth rates possible

• Physical vapor deposition (direct deposition)
  – Many variants
  – Require high or ultrahigh vacuum
  – Low to high growth rates

• Liquid-based techniques
  – Electrodeposition
  – Spin coating
Chemical Vapor Deposition (CVD)

• Precursor (gas or carried by a gas) reacts on/with substrate. Volatile by-products are usually produced.
• Transport to and from substrate.
• Many variations, e.g.
  – Gas pressure (atmosphere to UHV)
  – Plasma-enhanced CVD
  – Hot wall vs. cold wall CVD
• Precursors (unstable) and products are often highly toxic → safety.
• Substrate at elevated T.
• Drawback: Often, by-products are not cleanly removed → contamination.
• Strength: Highly-conformal films/coatings.
CVD examples

- Polycrystalline silicon from trichlorosilane
  - $\text{SiHCl}_3 \rightarrow \text{Si} + \text{Cl}_2 + \text{HCl}$
- Polycrystalline silicon from silane
  - $\text{SiH}_4 \rightarrow \text{Si} + 2\text{H}_2$
- Silicon oxide from silane and oxygen
  - $\text{SiH}_4 + \text{O}_2 \rightarrow \text{SiO}_2 + 2\text{H}_2$
- Tungsten from tungsten hexafluoride
  - $\text{WF}_6 \rightarrow \text{W} + 3\text{F}_2$
- h-BN from borazane
  - $\text{H}_3\text{BNH}_3 \rightarrow \text{h-BN}$
- Graphene from hydrocarbon
- Multicomponent systems, e.g. $\text{W}_3\text{Si}_5$:
  - May be accessible by using multiple precursors simultaneously.
Case study: CVD of graphene / Cu

- Hydrocarbon such as methane, ethylene = precursor in H₂
- Cu: No stable carbide, very low C solubility → surface confinement
- T ~ 1200 °C for homogeneous C-H cleavage; metal serves as catalyst and allows lower T.
- T ~ 1000 °C promotes dissociation, diffusion and ordering; also low H coverage.
Physisorbed vs. chemisorbed states

- Physisorption:
  - Van der Waals forces
  - No chemical reaction
  - $E_{ad} < 0.5$ eV
Temperature ‘sweet spot’ in CVD

- Low T:
  - Good: Long lifetime—long diffusion length—precursor can sample many sites and find a catalytically-active one before desorbing.
  - Bad: Inefficient conversion from physisorbed to chemisorbed state.
  - Worst: Precursors condense, killing the reaction.

- High T:
  - Bad: Short lifetime—short diffusion length—precursor samples few sites before desorbing.
  - Good: Conversion is more likely.

- Ex: Si is deposited from silane at 500-600ºC

M. Toth et al., Beilstein J. Nanotechnol. 6, 1518 (2015)
A special subset of CVD: The L(ayer) techniques
ALD, MLD, ALE, MLE, …

- Sequential, self-limiting surface reactions $\rightarrow$ single layer accuracy.
  - Gas-phase reaction between blue and red is impossible.

- Extremely smooth, conformal, and thin.
  - Pioneer: Tuomo Suntola, Finland, 1970s.


ALD example with half reactions

• Aluminum oxide from trimethyl aluminum and water (* = surface species)

\[- \text{AIOH}^* + \text{Al(CH}_3\text{)}_3 \rightarrow \text{AlOAl(CH}_3\text{)}_2^* + \text{CH}_4 \]

\[- \text{AlCH}_3^* + \text{H}_2\text{O} \rightarrow \text{AIOH}^* + \text{CH}_4 \]
Two ALD success stories

M. Ritala et al., *CVD* 5 p. 7 (1999)

ALD examples: Net reactions

II/VI Compounds
- ZnS: \[ \text{ZnCl}_2 + \text{H}_2\text{S} \rightarrow \text{ZnS} + 2\text{HCl} \] [6-8]
- CdTe: \[ \text{Cd(CH}_3\text{)}_2 + \text{Te(C}_3\text{H}_7\text{)}_2 \rightarrow \text{CdTe} + 2\text{C}_4\text{H}_10 \]

III/V Compounds
- GaAs: \[ \text{Ga(CH}_3\text{)}_3 + \text{AsH}_3 \rightarrow \text{GaAs} + 3\text{CH}_4 \] [9, 10]
- GaN: \[ \text{Ga(CH}_3\text{)}_3 + \text{NH}_3 \rightarrow \text{GaN} + 3\text{CH}_4 \] [21, 22]

Oxide Compounds
- \( \text{SiO}_2 \): \[ \text{SiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{HCl} \] [15, 17]
- \( \text{Al}_2\text{O}_3 \): \[ 2\text{Al(CH}_3\text{)}_3 + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{CH}_4 \] [11, 15, 16]
- \( \text{SnO}_2 \): \[ \text{SnCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{SnO}_2 + 4\text{HCl} \] [25]
- \( \text{TiO}_2 \): \[ \text{TiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{HCl} \] [12, 19, 26]
- \( \text{ZrO}_2 \): \[ \text{ZrCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 4\text{HCl} \] [13]
- \( \text{In}_2\text{O}_3 \): \[ 2\text{InCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{In}_2\text{O}_3 + 6\text{HCl} \] [28]
- \( \text{HfO}_2 \): \[ \text{HfCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{HfO}_2 + 4\text{HCl} \] [29]

Nitride and Sulfide Compounds
- \( \text{Si}_3\text{N}_4 \): \[ 3\text{SiCl}_4 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 12\text{HCl} \] [30]
- \( \text{AlN} \): \[ \text{Al(CH}_3\text{)}_3 + \text{NH}_3 \rightarrow \text{AlN} + 3\text{CH}_4 \] [31]
- \( \text{In}_2\text{S}_3 \): \[ 2\text{InCl}_3 + 3\text{H}_2\text{S} \rightarrow \text{In}_2\text{S}_3 + 6\text{HCl} \] [32-34]

Elemental Deposition
- Si: \[ \text{H}_2\text{Si(CH}_2\text{CH}_3\text{)}_2 + \Delta T \rightarrow \text{Si} + \text{CH}_2=\text{CH}_2 + 2\text{H}_2 \] [33, 35]
- \( \text{Si}_2\text{Cl}_6 + \text{Si}_2\text{H}_6 \rightarrow \text{Si} + 6\text{HCl} \)
- Ge: \[ \text{H}_2\text{Ge(CH}_2\text{CH}_3\text{)}_2 + \Delta T \rightarrow \text{Ge} + \text{CH}_2=\text{CH}_2 + 2\text{H}_2 \]

But versatility is still a challenge, at least, from a chemist’s perspective.
Classes of deposition techniques

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  – Atomic layer deposition
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Physical vapor deposition

- Gaseous atoms (or molecules) are **generated** from a source and strike the surface without chemical modification.

- **Generation methods:**
  - Heat
    - Molecular Beam Epitaxy
  - Laser
  - Sputtering (ion bombardment)
A type of PVD: Molecular beam epitaxy

**Fig. 14.27.** Schematic sketch of the main facilities used in MBE growth, including deposition sources, shutters, sample at the heating block, RHEED system for monitoring sample surface structure in the course of deposition, all being installed in a UHV chamber.

More about: Molecular beam epitaxy

“MBE growth is evidently not a method used in mass production, but it is indispensable in basic research [104] as demonstrated by a number of Nobel prizes, closely linked to MBE-grown samples:

2007 for Albert Fert and Peter Grünberg
for ‘The Discovery of Giant Magnetoresistance’;
2000 for Zhores Alferov and Herbert Kroemer for ‘developing semiconductor heterostructures used in high-speed- and optoelectronics’ and
1998 for Robert B Laughlin, Horst L Störmer and Daniel C Tsui for ‘their discovery of a new form of quantum fluid with fractionally charged excitations’.”

M. Brehm and M. Grydlik,
Nanotechnology 28, 392001 (2017)
A variation of PVD: Reactive evaporation
Another variant of PVD: Magnetron sputtering

• Basic sputtering processes
Another variant of PVD: Magnetron sputtering

- Magnetic confinement of electrons near target generates a plasma.


Ryan Ott, Ames Lab
3. Fundamental concepts and research
Equilibrated film growth modes

- **Growth Mode** describes vertical structure of the film vs. coverage on an idealized substrate, at or near equilibrium.
  - *perfectly flat* substrate (no steps)
  - *perfectly rigid* substrate.

**Vollmer-Weber** (3D, rough)

**Stranski-Krastanov** (strain-driven or phase-driven)

**Frank van der Merwe** (layer-by-layer, 2D)

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Bauer, Z. Kristallographie, 1958 (2 papers) and Bauer and Van der Merwe, 1986, vol. 33, p. 3657


Pb on HOPG

\[ 3 \mu m \]
Stranski-Krastanov Example: Quantum Dots of Ge/Si(100)

Chip-based optical interconnects

Nature has other options

- **Strain relief**: Dislocations.

- **Step flow**: Small terrace width and long diffusion length (high T) impede nucleation on terraces, favor attachment at steps.

- **Substrate is not rigid, not inert**: Encapsulation. Alloying.

- **Kinetically-limited morphologies**
Closing remarks

• Parameter space for growth of films (2D materials) is very large.
• Realistically, options may be limited by access to instrumentation and expertise.
• Basic processes provide a robust conceptual framework: