

Lecture 6: Solid state synthesis

- The products are typically **single crystals**, **polycrystalline powders** or **thin films**
 - Recipes? Journal papers!
- Solid state reaction
- Low-temperature methods
- High-pressure synthesis
- Thin films
 - Chemical vapor deposition
 - Atomic layer deposition



Figure: <http://lulelaboratory.blogspot.fi/>



Figure: Aalto University



Figure: Aalto University

Solid state reaction

See [Solid State Chemistry Wiki](#)

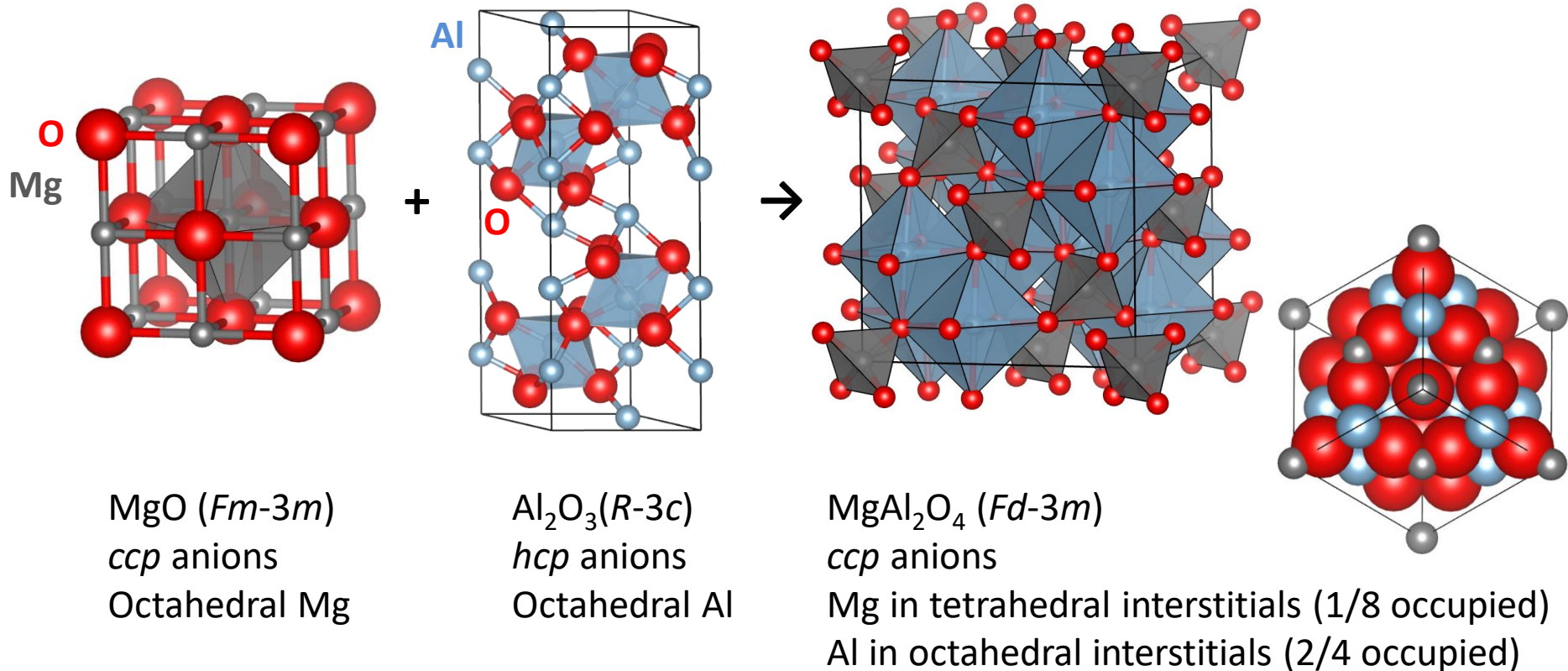
- The oldest, simplest and still most widely used method to make inorganic solids
 - Mix together powdered reactants (and possibly press them into pellets)
 - Heat in a furnace for prolonged periods
- **Diffusion in solids is very slow**, thus high temperatures are needed
 - Although the reactants may be well mixed at the level of individual particles (e.g. μm scale), they are very inhomogeneous on the atomic level
- Solid state reactions are under **thermodynamical control**
 - The most stable phase or mixture at the reaction conditions will form
 - Reaction mechanisms and kinetics are usually not known well
 - Separating impurity phases from the product is usually impossible



Figure: Aalto University

Example: MgAl_2O_4 spinel

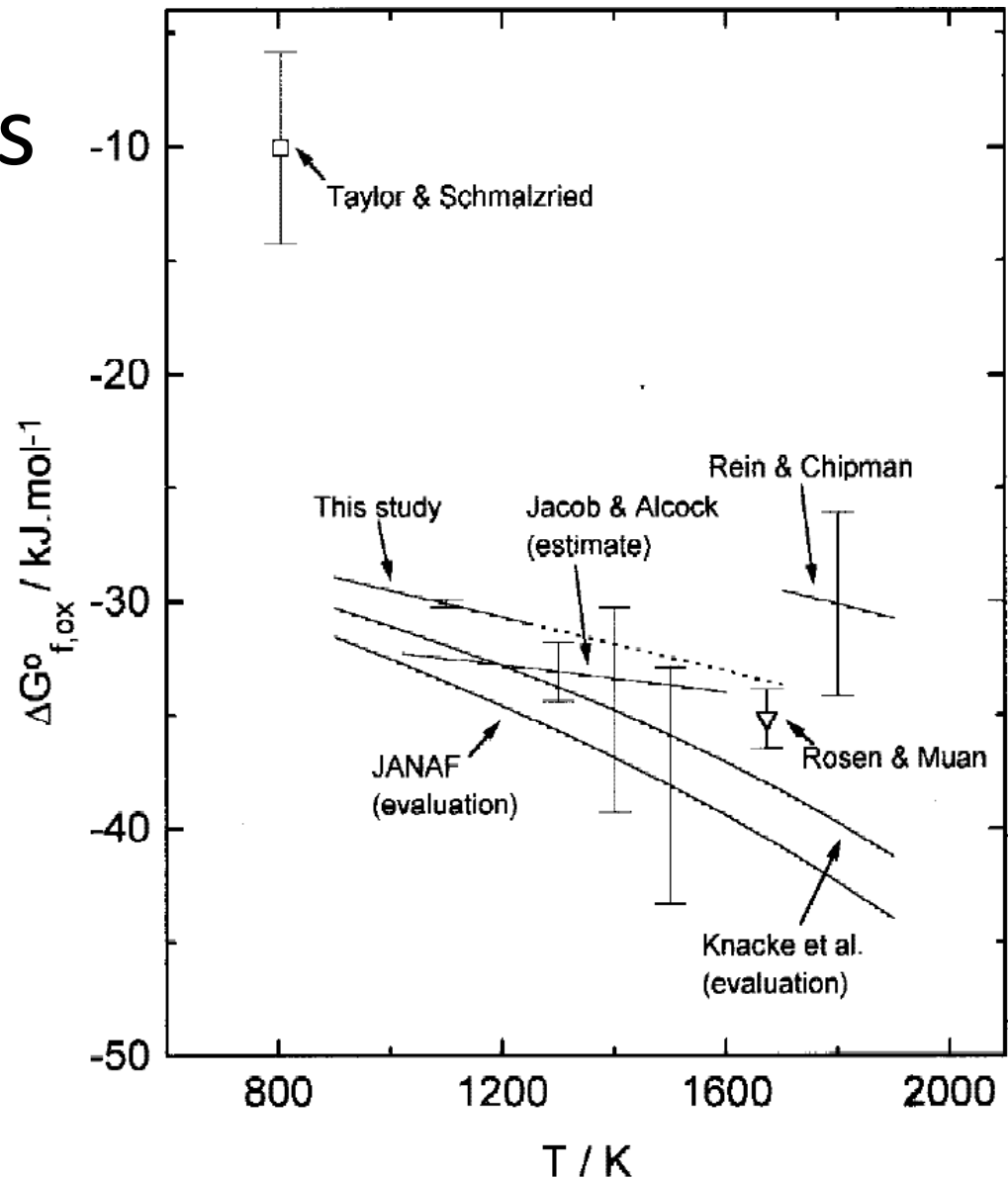
- Let's consider a solid state reaction of MgO and Al_2O_3 powders to MgAl_2O_4 spinel
- Close-packed anions in all three compounds



MgAl₂O₄ thermodynamics

Literature data for Gibbs free energy of formation of MgAl₂O₄ from simple oxides MgO and Al₂O₃ ($\Delta G^0_{f,ox}$)

J. Am. Ceram. Soc., **1998**, 81, 209–212.



MgAl₂O₄ spinel from MgO and Al₂O₃

Ref: West p. 190

- The first few atomic layers of product nuclei may form easily, but subsequent growth or thickening of the product is more difficult
 - The two reactants, MgO and Al₂O₃, are separated by a spinel layer.
- A complex counter-diffusion process of Mg²⁺ and Al³⁺ ions is required
- As the reaction proceeds, the spinel layer thickens, the diffusion path length increases, and the reaction slows down (Mg²⁺ and Al³⁺ diffuse very slowly)
- Heating for **1 week at 1500°C** would be required to form a fairly pure spinel product

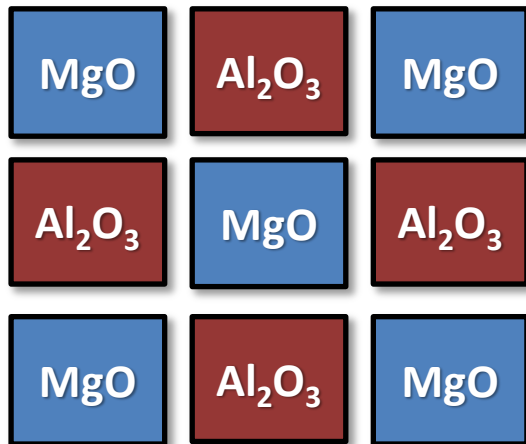
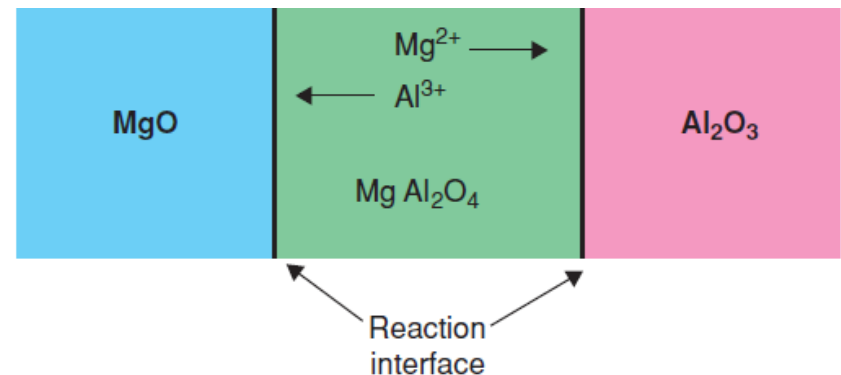


Figure: AJK

Idealized reaction mixture composed of grains of MgO and Al₂O₃. In practice, the grains will be irregular and not so arranged. Spinel formation occurs at the interfaces



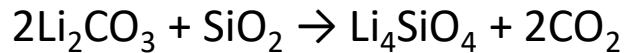
Spinel product layer separating MgO and Al₂O₃ reactant grains

Some practical considerations for solid state reactions

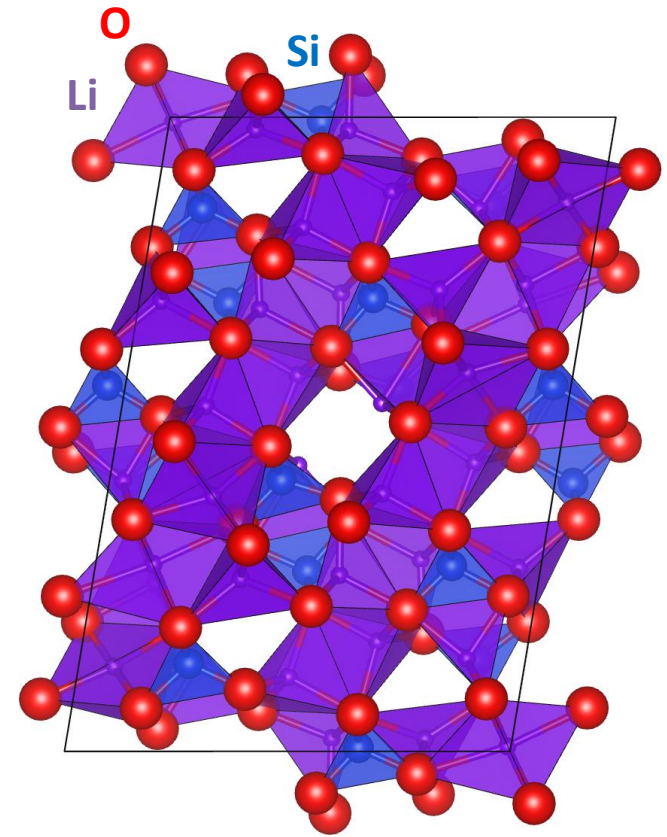
- The MgAl_2O_4 spinel synthesis is difficult since both reagents, MgO and Al_2O_3 , are very stable, inert, non-reactive solids
 - Solid state reactions may be easier if one or more of the starting materials is chemically reactive and/or contains ions that can diffuse easily
- Other possible problems:
 - Loss of reactants by evaporation (e.g. alkali metal oxides, PbO , Bi_2O_3 , HgO)
 - Reactivity towards the container (e.g. transition metal -containing materials).
- Issues to consider when planning a solid state reaction:
 - Choice of starting materials (purity, reactivity, how finely they are ground)
 - Container (Pt / Ta / Au / Al_2O_3 / SiO_2 / graphite)
 - Heat treatment conditions (temperature program)
 - Atmosphere, especially oxygen partial pressure ($p\text{O}_2$) for oxides
 - Oxidizing (Air, O_2)
 - Inert or slightly reducing (vacuum, N_2 , Ar)
 - Strongly reducing (H_2/Ar mix, H_2)

Solid state reaction of Li_4SiO_4

- Lithium orthosilicate Li_4SiO_4 is the parent phase for a family of Li^+ ion conductors that can be prepared by the following reaction (24 h at $\sim 800\text{ }^\circ\text{C}$):



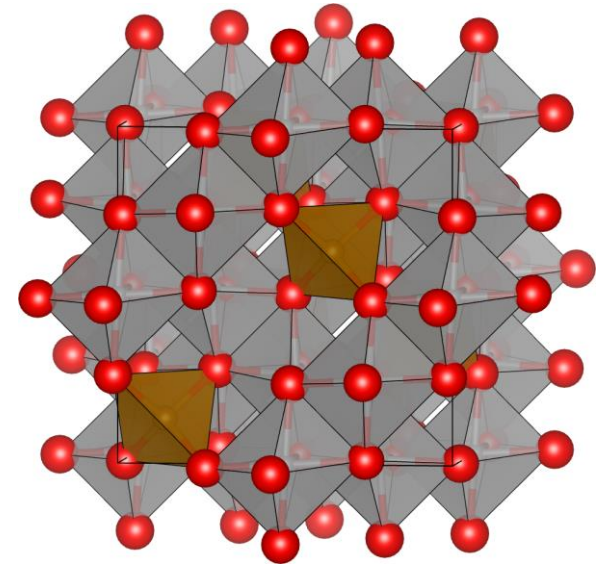
- Problems:
 - Li_2CO_3 melts and decomposes above $\sim 720\text{ }^\circ\text{C}$.
 - It also is reactive towards most container materials, including Pt and silica glass.
- Solution:
 - Use gold containers
 - Carry out decomposition and pre-reaction of Li_2CO_3 at $\sim 650\text{ }^\circ\text{C}$ for a few hours before final firing at $800\text{--}900\text{ }^\circ\text{C}$ overnight.



Li_4SiO_4 ($P 1 21/m 1$)

Use of homogeneous, single-source precursors

- Prepare a crystalline, homogeneous, single-phase precursor material that contains all the required cations in the correct ratio.
- Precursor should decompose to the desired product on heating.
- As an example, let's see how $\text{NH}_4\text{Fe}(\text{CrO}_4)_2$ can be used as a precursor to FeCr_2O_4 .
- The precursor is synthesized by precipitation from aqueous solution:
$$\text{Fe}^{3+}(\text{aq}) + 2\text{CrO}_4^{2-}(\text{aq}) + \text{NH}_4^+(\text{aq}) \rightarrow \text{NH}_4\text{Fe}(\text{CrO}_4)_2$$
- The precursor decomposes on heating (at 1150 °C):
$$\text{NH}_4\text{Fe}(\text{CrO}_4)_2 \rightarrow 2\text{FeCr}_2\text{O}_4 + 2\text{NH}_3 + \text{H}_2\text{O} + 7/2 \text{O}_2$$



FeCr_2O_4 (*Fd-3m*)
ccp anions
(spinel, like MgAl_2O_4)

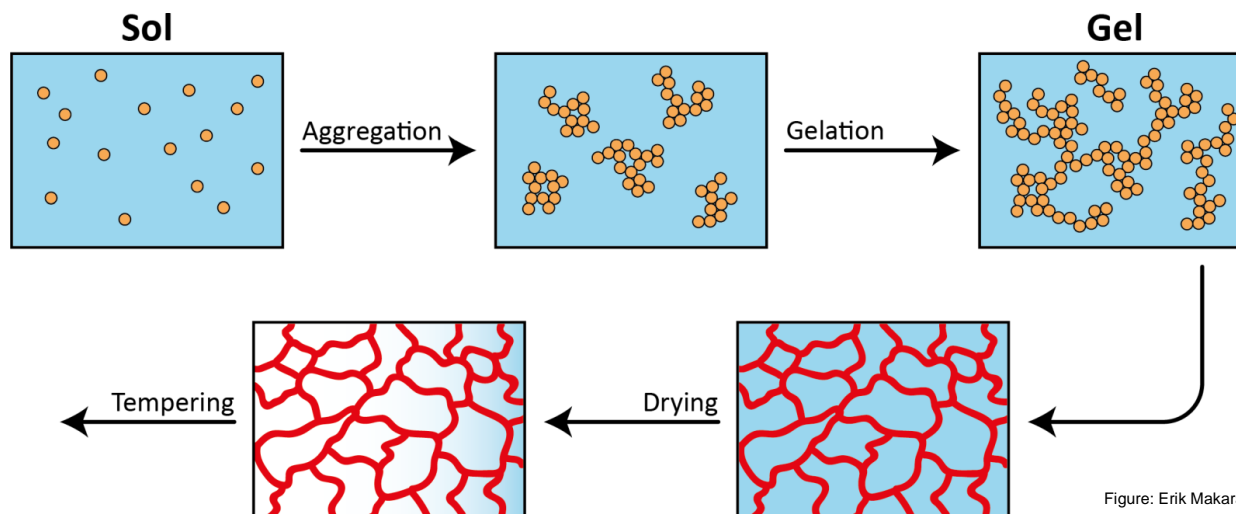
Low temperature methods

- Low temperature methods can be used to achieve atomic scale mixing of reactants, in gas, liquid, or even solid phases
 - Final heating at high T may be needed, especially for ceramic products
- May enable higher purity products than high temperature solid-state reaction, especially if prolonged heating at high temperature can be avoided
 - No contamination from container materials and furnace atmosphere
- Products with high chemical homogeneity are usually obtained
- Disadvantages:
 - Reagents are often costly and difficult to handle on a large scale
 - Considerable research may be required to optimize the synthesis of a particular material
 - Once suitable conditions have been found, they may not be readily applicable to the synthesis of related materials

Sol-gel method

See [Solid State Chemistry Wiki](#)

- The first stage is to prepare a homogeneous solution containing all the cationic ingredients in the desired ratio
- The solution is gradually dried and should transform
 - First to a viscous **sol** (particles of colloidal dimensions, ~1-1000 nm)
 - Finally to a transparent, homogeneous, amorphous solid known as a **gel**
 - Without precipitation of any crystalline phases
- The gel is then heated at high temperatures to remove volatile components trapped in the pores of the gel or chemically bonded hydroxyl and organic side-groups and to crystallize the final product.



Alkoxide sol–gel method

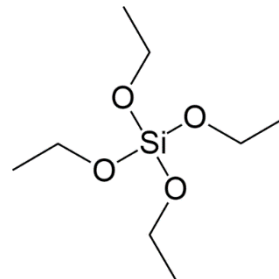
- Organometallic precursors, particularly alkoxides, are widely used for the small-scale synthesis of known or new materials
 - Alkoxide: $[R-O^-]M^+$ (for example, $[CH_3-O^-]Na^+$)
- The alkoxide-based sol–gel method is extremely versatile and can incorporate most elements of the periodic table

4.3.1.1 *Synthesis of $MgAl_2O_4$*

Appropriate reagents are $Mg(OCH_3)_2$ and $Al(O^tBu)_3$. On mixing, hydrolysis, condensation and drying, an amorphous gel is obtained that decomposes to form very fine particles of spinel after final heating at $250\text{ }^\circ\text{C}$. This compares very favourably, in energy terms, with solid state reaction, which typically requires heating for several days at $1500\text{ }^\circ\text{C}$, but the alkoxide reagents are expensive, hygroscopic and difficult to use.

4.3.1.2 *Synthesis of silica glass*

Pure silica glass is difficult, and expensive, to prepare by traditional melting since molten SiO_2 is extremely viscous, even at $2000\text{ }^\circ\text{C}$ (the melting point of SiO_2 is $\sim 1700\text{ }^\circ\text{C}$). Starting from TEOS, it is possible by the sol–gel route to prepare an amorphous product which, to all intents and purposes, resembles silica glass but has never been heated above $1200\text{ }^\circ\text{C}$. Both silica glass and this amorphous silica look-alike are metastable and care is required to avoid some crystallisation at the final processing temperature of $1200\text{ }^\circ\text{C}$.



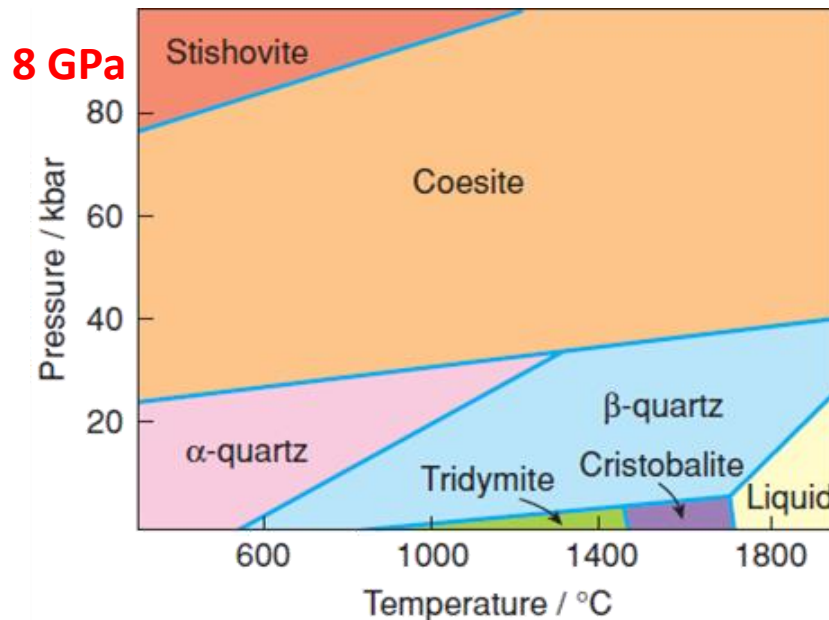
TEOS = Tetraethyl orthosilicate

High-pressure chemistry

High-pressure chemistry (1)

See [Solid State Chemistry Wiki](#)

- High pressures ($> 1 \text{ GPa} = 10\,000 \text{ atm}$) enable the synthesis of huge number of new materials that are unattainable in the atmospheric pressure
- In ultra-high pressures (Mbar range, $> 100 \text{ GPa}$), the compression energy rivals or even exceeds the energy of the chemical bond!
 - New materials that are completely unintuitive from the "normal" point of view



Phase diagram of SiO₂

High-pressure chemistry (2)

Paul F. McMillan, *Chem. Soc. Rev.*, **2006**, *35*, 855 ([DOI](#))

- By the time a typical solid or liquid is compressed to above a few hundred thousand atmospheres, its molar volume is reduced by approximately 50%
- Once the megabar range ($p > 100$ GPa) is reached, average interatomic distances can be decreased by up to a factor of two.
- Major changes will occur in the outer electron shells, leading to substantial modifications of the chemical and physical properties.
- Even the arrangement of the periodic table has to be reconsidered for high pressure conditions.

- As a simple example, let's consider the typical alkaline earth metals such as Ca and Sr that possess a fully close-packed ***fcc*** structure at ambient conditions.
- Pressurising Ca to $p > 200$ kbar (20 GPa) causes it to transform to a ***less efficiently*** packed ***bcc*** structure with a lower coordination of the metal atoms
 - Pressure-induced mixing occurs between 3d and 4s electronic shells, giving Ca the character of a *d*-metal rather than an alkaline earth element

High-pressure chemistry (3)

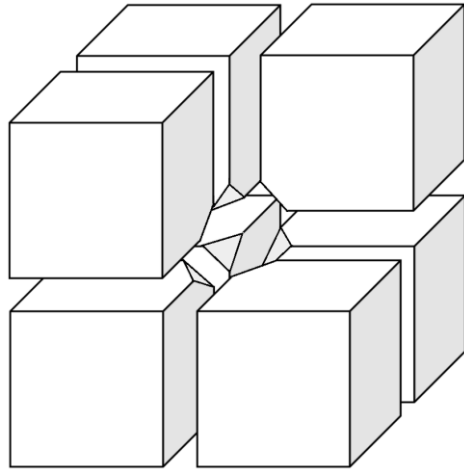
- Ultimately, most substances should become metallic at the most extreme pressures, as the close approach of atoms results in electronic overlap
- In moderate pressures ($p < 10$ GPa), the pressure effects are not as extreme as in ultra-high pressures and typical phenomena are for example the increase of coordination number and the change of the structure type
 - In moderate pressures, a huge number of new materials that are only metastable in atmospheric pressure can be realized
 - Often the new materials remain intact in atmospheric pressure (e.g. diamond!)

Table 4.5 *High-pressure polymorphism of some simple solids*

Solid	Structure and coordination number	Typical transformation conditions		High-pressure structure and coordination number
		P/kbar	$T/^\circ\text{C}$	
C	Graphite, 3	130	3000	Diamond, 4
CdS	Wurtzite, 4:4	30	20	Rock salt, 6:6
KCl	Rock salt, 6:6	20	20	CsCl, 8:8
SiO ₂	Quartz, 4:2	120	1200	Rutile, 6:3
Li ₂ MoO ₄	Phenacite, 4:4:3	10	400	Spinel, 6:4:4
NaAlO ₂	Ordered Wurtzite, 4:4:4	40	400	Ordered Rock salt, 6:6:6

Multi-anvil press

- Sample is compressed between anvils, either cubic or octahedral
- Heating by running a current through graphite
- Pressures of up to 20 GPa (200 000 atm)
- Used mainly for materials synthesis
- Characterization done mainly *ex-situ* (outside the press)



Octahedral 8-anvil with eight corner-cut cubes enclosing an octahedral sample space (Kawai cell)

<https://wiki.aalto.fi/display/SSC/High-pressure+synthesis>



Figures: Linda Sederholm / Aalto

Diamond anvil cell

In-situ X-ray or Raman spectroscopy possible

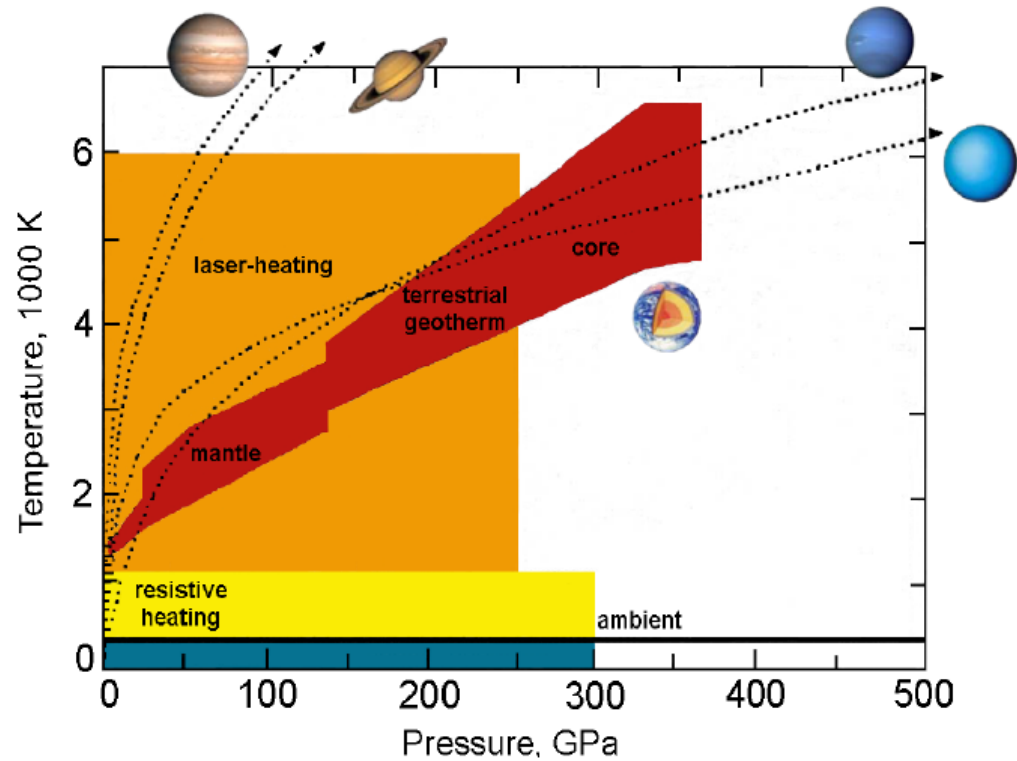
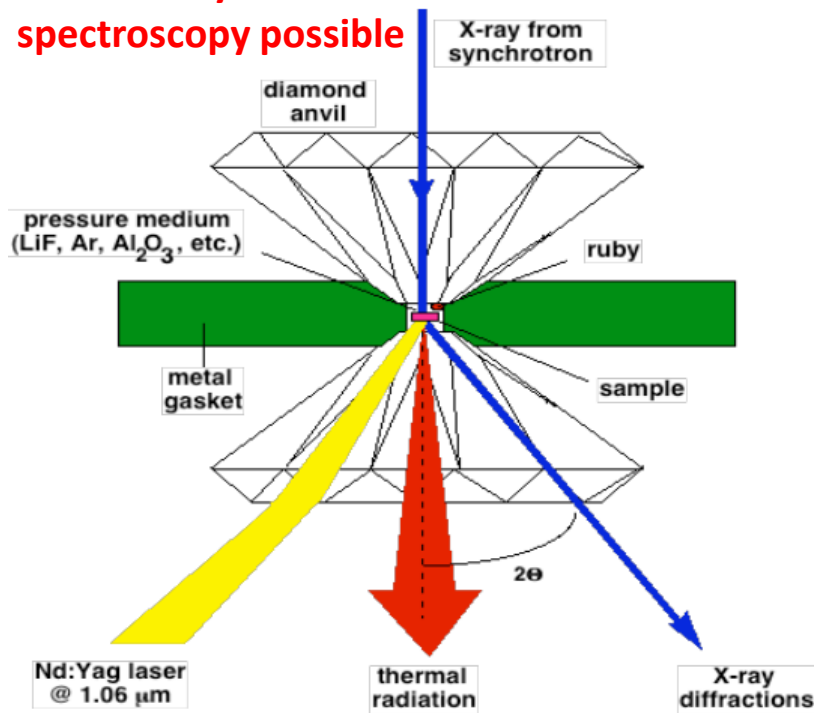


Figure: Choong-Shik Yoo, Washington State University

The most incompressible metal osmium at static pressures above 750 gigapascals <https://doi.org/10.1038/nature14681>

10 SEPTEMBER 2015 | VOL 525 | NATURE | 227

Great demonstrations from Dr. Timothy Strobel:

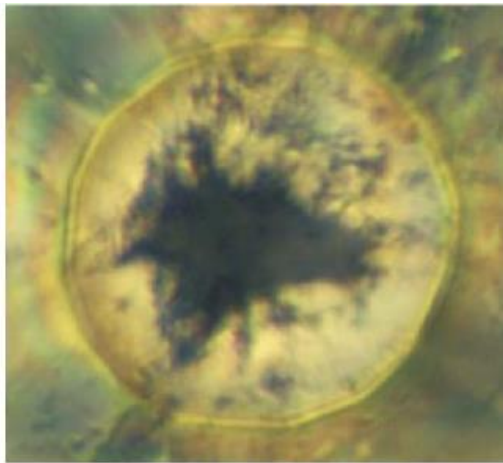
<https://www.youtube.com/watch?v=pxrQxgC01zE&t=19s>

Transparent dense sodium

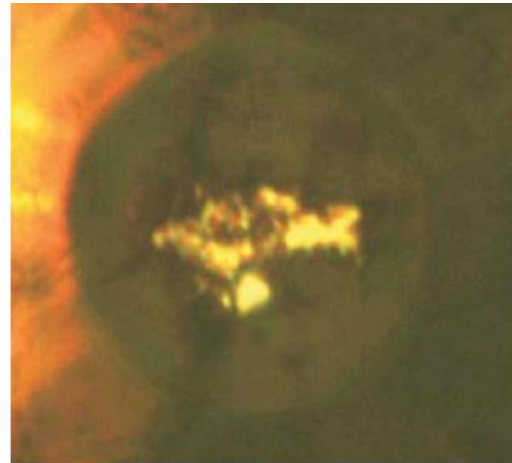
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LETTERS

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156 GPa

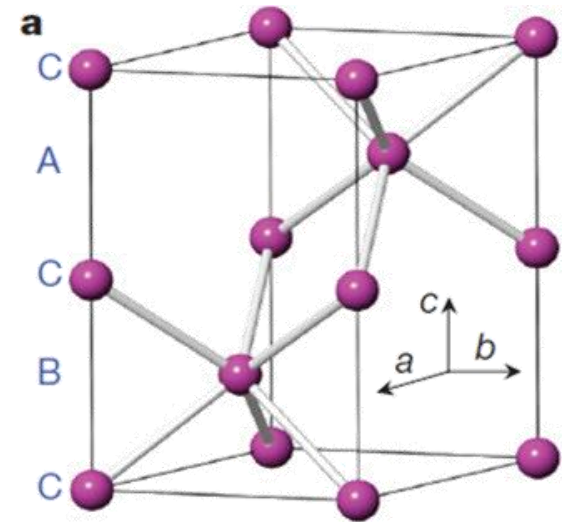


199 GPa

Na-Na distance decreases from **3.72 Å** to **1.89 Å**

Na 3s valence electrons are pushed to the interstitial space

Na metal transforms to optically transparent "self-salt" (Na⁺ / interstitial e⁻)



Structure of Na-*hP4* (*P6₃/mmc*) predicted by USPEX

Thin-film techniques



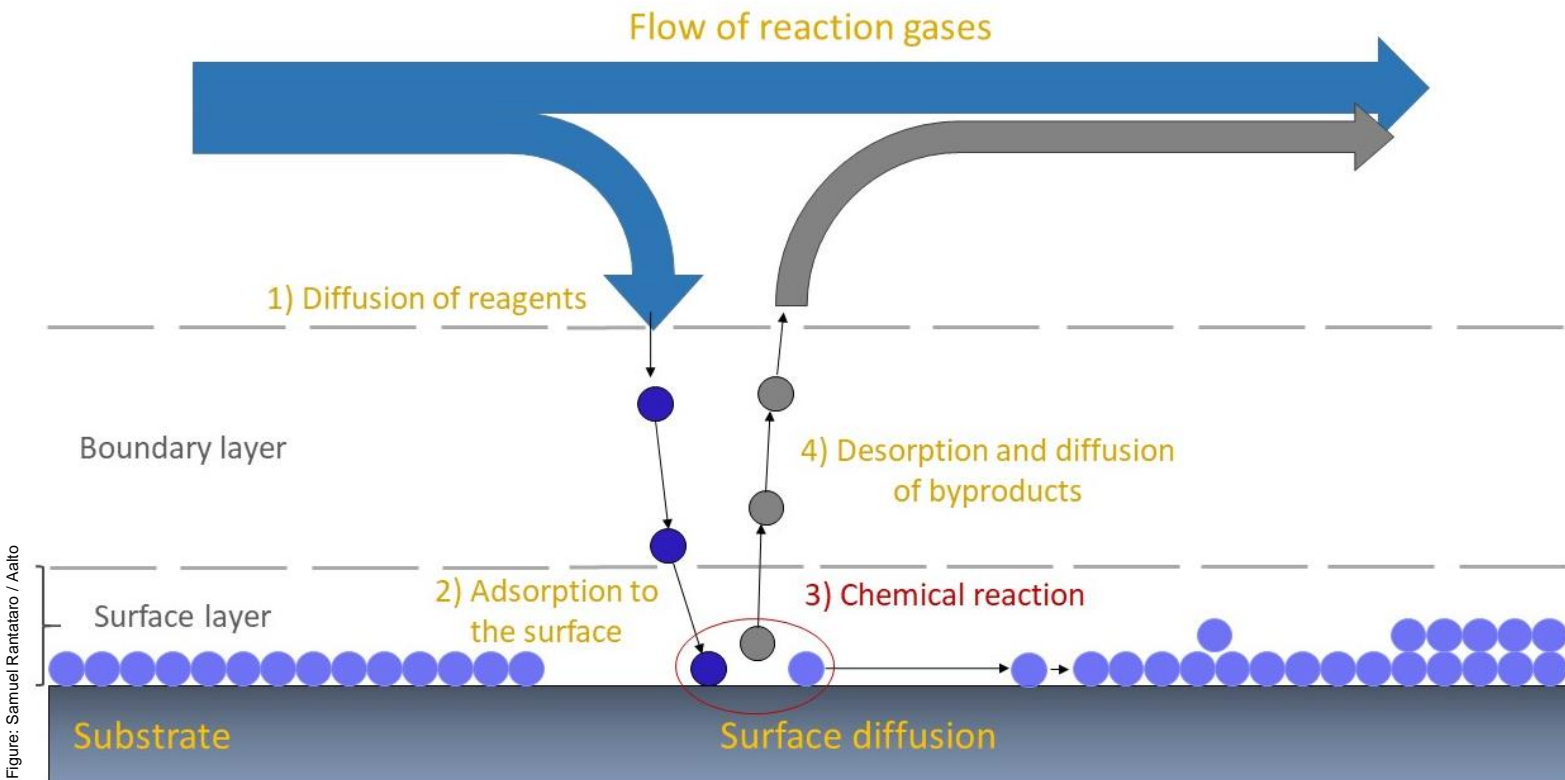
Figure: [MPA industrie](#)

Chemical Vapor Deposition reactor for TiC, TiCN, Al₂O₃, and TiN deposition on hard metals and steels

Chemical Vapor Deposition (1)

See [Solid State Chemistry Wiki](#)

- Important technique of making high-purity thin films and coatings for
 - Industrial applications, especially in electronics,
 - Fundamental scientific research
- Precursor molecules containing the elements of interest are **decomposed in the gas phase** and the products deposit as thin films.



Chemical Vapor Deposition (2)

- Example of a simple, volatile precursor molecule:

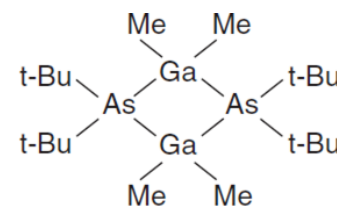
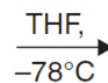
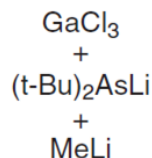
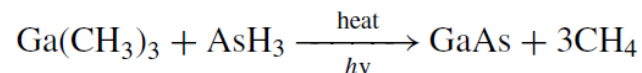
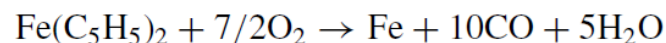
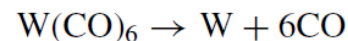
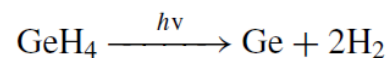
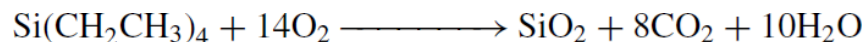


- Other examples of CVD processes

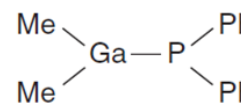
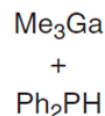
- To deposit compounds such as GaAs, a mixture of precursors is needed

- An alternative for GaAs is to use (organometallic) **single-source precursors** which contain all the elements of interest and in the correct ratio

- Examples of **metal-organic CVD (MOCVD)**:



(a)

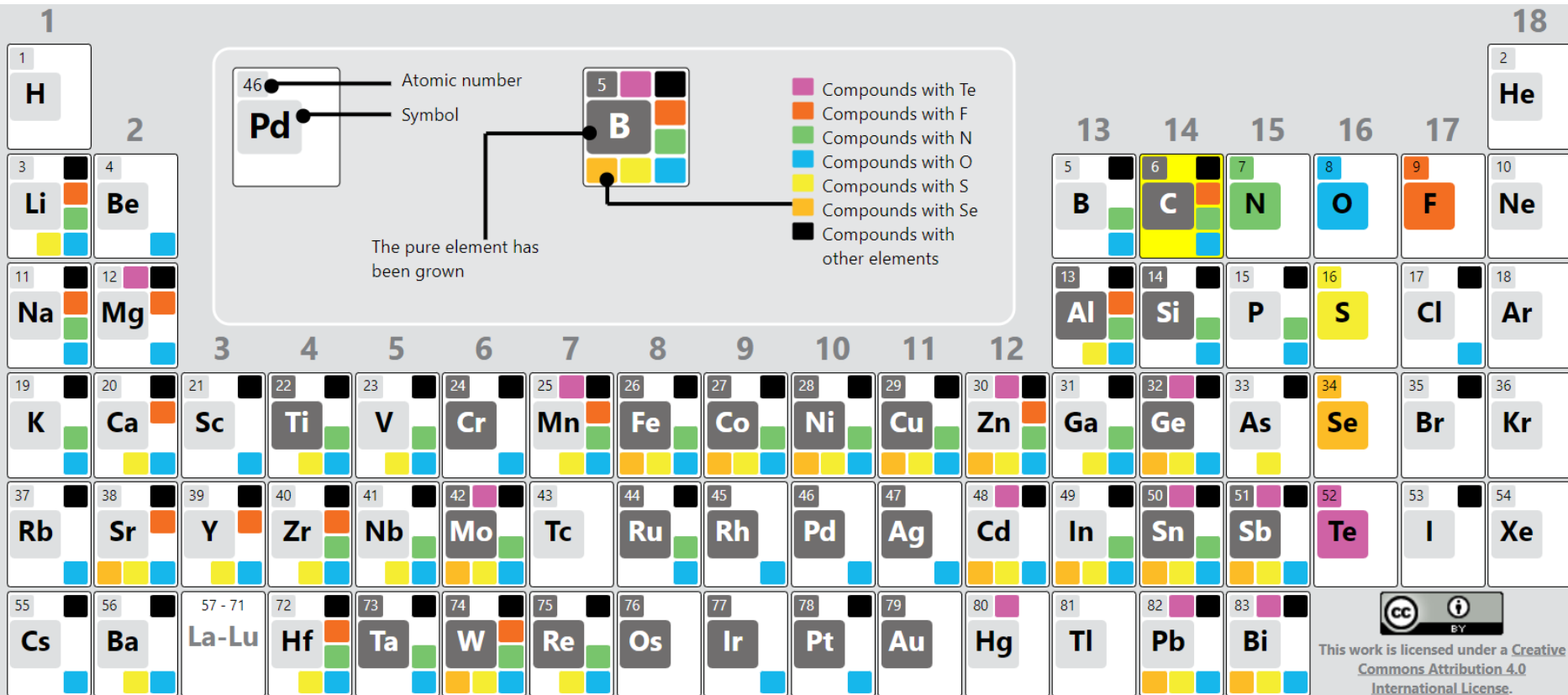


(b)



Atomic Layer Deposition (1)

- See [Solid State Chemistry Wiki](#)
- Database of ALD review papers: <https://www.atomiclimits.com/reviewbase-aldale/>
- Database of ALD processes: <https://doi.org/10.6100/alddatabase>



Atomic Layer Deposition (2)

For example: ZnO

<https://doi.org/10.1016/j.mattod.2014.04.026>

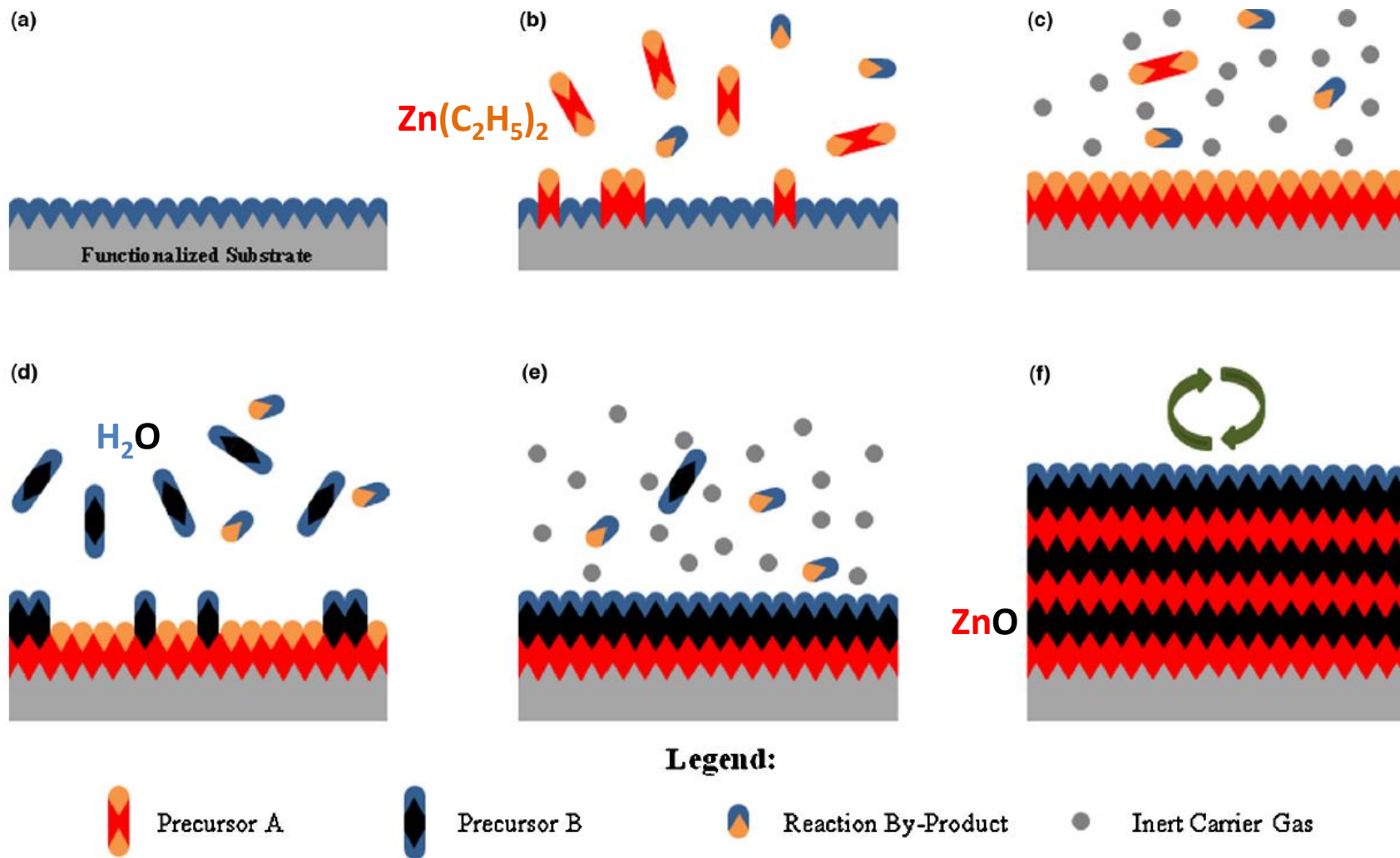


FIGURE 1

Schematic of ALD process. (a) Substrate surface has natural functionalization or is treated to functionalize the surface. (b) Precursor A is pulsed and reacts with surface. (c) Excess precursor and reaction by-products are purged with inert carrier gas. (d) Precursor B is pulsed and reacts with surface. (e) Excess precursor and reaction by-products are purged with inert carrier gas. (f) Steps 2–5 are repeated until the desired material thickness is achieved.

Atomic Layer Deposition (3)

- ALD is based on sequential, self-limiting reactions
 - Offers exceptional conformality on high aspect ratio structures
 - Thickness control at the Ångstrom level (usually ~10-100 nm thickness; max ~1 μm)
 - Tunable film composition
- Powerful tool for many industrial applications (for example, microelectronics)

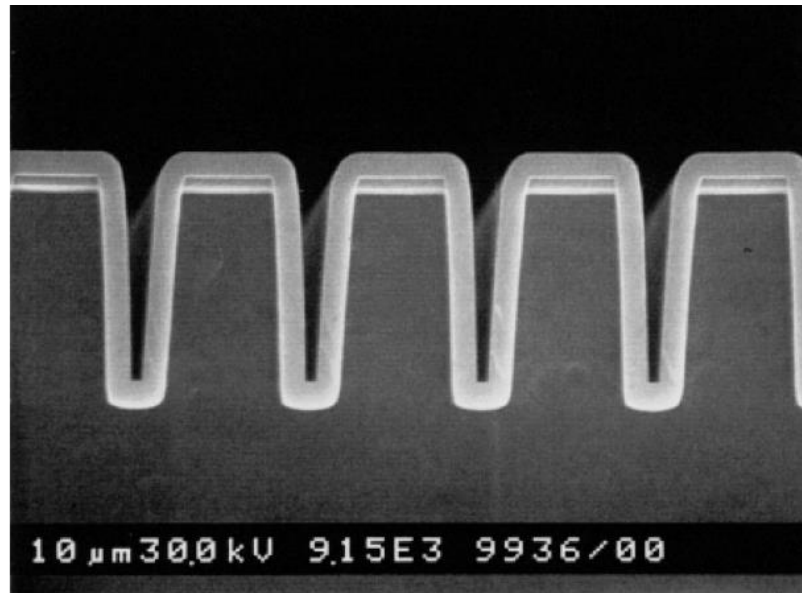


Figure 3. Cross-sectional SEM image of an Al₂O₃ ALD film with a thickness of 300 nm on a Si wafer with a trench structure.

Additional solid-state synthesis methods in SSC Wiki

- <https://wiki.aalto.fi/display/SSC/Solid-state+synthesis+methods>
- [Hydrothermal and solvothermal synthesis](#)
- [Spin coating](#)
- [Microwave synthesis](#)
- [Chemical vapor transport \(CVT\)](#)
- [Electrochemical deposition](#)
- [Spark plasma sintering for synthesis](#)
- [Ball milling as a synthesis method](#)
- <https://wiki.aalto.fi/display/SSC/Sputtering>
- [Plasma-Enhanced Atomic Layer Deposition \(PEALD\)](#)
- [Molecular layer deposition \(MLD\)](#)
- [Atomic Layer Etching \(ALE\)](#)
- [Solid state synthesis from the perspective of green chemistry](#)