TENTATIVE LECTURE SCHEDULE

		Date	Topic
1.	Wed	07.09.	Course Introduction & Short Review of the Elements
2.	Fri	09.09.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Mon	12.09.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Fri	16.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
5.	Mon	19.09.	Transition Metals: General Aspects & Pigments
6.	Wed	21.09.	Redox Chemistry
7.	Fri	23.09.	Crystal Field Theory (Linda Sederholm)
8.	Mon	26.09.	V, Nb, Ta & Metal Complexes & MOFs
9.	Wed	28.09.	Cr, Mo, W & 2D materials
10.	Fri	30.09.	Mn, Fe, Co, Ni, Cu & Magnetism & Superconductivity
10.	Mon	03.10.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
11.	Fri	07.10.	Lanthanoids + Actinoids & Luminescence
12.	Mon	10.10.	EXTRA
14.	Wed	12.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
15.	Fri	14.10.	Inorganic Materials Chemistry Research

EXAM: Oct. 18, 9:00-12:00

QUESTIONS: Lecture 4

1. Among the following four elements, Zn, Ti, Zr, and Hf, only one forms compounds at +III oxidation state. Just by looking at the Periodic Table, predict which element this is. Most importantly, explain why you predicted so.

2. Hf is mostly found in nature in trace amounts in Zr minerals. Why it is so easy for Hf to replace some of the Zr in these minerals?

3. Which element is commonly used as a substituent to create oxygen vacancies in ZrO_2? Explain why ?

4. Why in ALD technique:

   (a) Film thickness control is straightforward?

   (b) Conformal coating is readily achieved?

INSTRUCTIONS for SEMINAR PRESENTATIONS

- Presentation (~20 min) is given in a group of (two or) three persons
- It is evaluated in the scale: 15 ~ 25 points
- Presentation is given in English, and the slides are put up in MyCourses afterwards
- Content of the presentation:

- ELEMENT: discovery, origin of name, abundancy, world production, special features if any, etc.

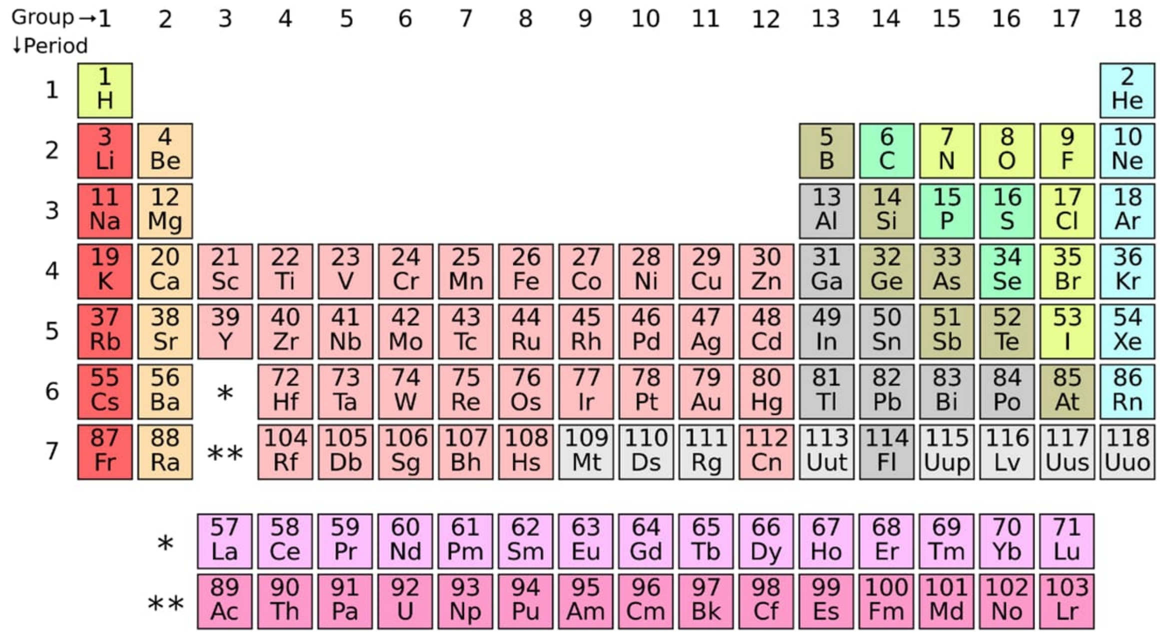
- CHEMISTRY:, electronic configuration, oxidation states, metal and ionic sizes, reactivity, etc., **regarding the position in Periodic Table**

- COMPOUNDS: examples of important compounds, their properties and applications, etc.

- SPECIFIC FUNCTIONALITIES/APPLICATIONS: Two or three examples of exciting functionalities/applications of the element or its compounds. <u>Here the meaning is to discuss why this specific element is needed in each selected application.</u> **You will be given one or two scientific articles for a reference, and you should search for couple of more (recent) articles to be discussed in the presentation**.

PRESENTATION TOPICS/SCHEDULE

Fri	16.09.	Zn:	Rautakorpi, Stenbrink & Hyvärinen
Mon	26.09.	Nb:	Sousa, Rahikka & Tong
Wed	28.09.	Mo:	Alimbekova & Tran (Nhi)
		(Ti:	Mäki & Israr)
Fri	30.09.	Mn:	Tao & Song (Zonghang)
		Cu:	Marechal, Weppe & Ishtiaq
		Ru:	Järvinen & Verkama
Fri	07.10.	Eu:	Bardiau, Wolfsberger & Klingerhöfer
		Nd:	Helminen
		U:	Airas & Holopainen
Wed	12.10.	Co:	Song (Yutong) & Wang
		In:	Antila & Wallius
		Te:	Peussa & Heylen



Zn	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$
Ti	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2$
Zr	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^2$
Hf	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^2$

Zn^{2+}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$
Ti^{4+}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
Zr^{4+}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6$
Hf^{4+}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 4f^{14}$

No partly-filled d or f orbitals

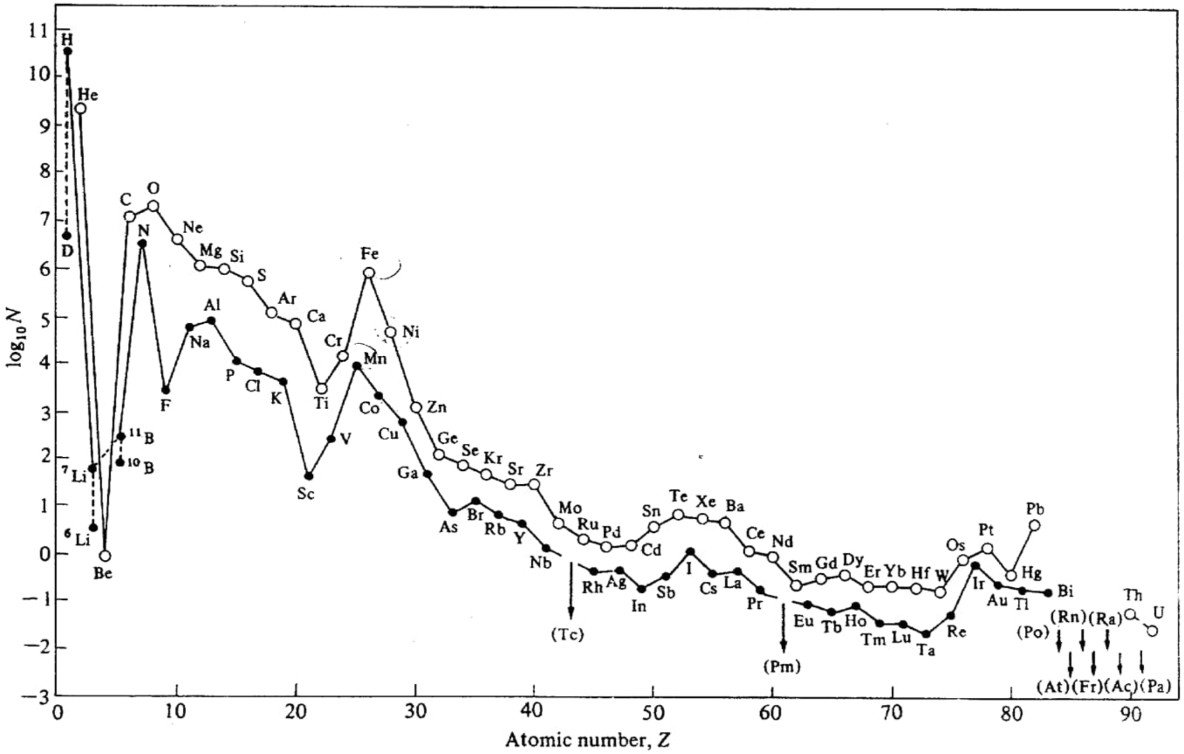
IONIC RADII (in Å)

		Ti	Zr	Hf	Zn
+2	CN-4	-	-	-	0.60
	CN-5	-	-	-	0.68
	CN-6	0.86	-	-	0.74
	CN-8	-	-	-	0.90
+3	CN-4	-	-	-	-
	CN-5	-	-	-	-
	CN-6	0.67	-	-	-
+4	CN-4	0.42	0.73	0.72	-
	CN-5	0.51	-	-	-
	CN-6	0.61	0.86	0.85	-
	CN-8	0.74	0.98	0.97	-

http://abulafia.mt.ic.ac.uk/shannon/ptable.php

OCCURRENCE of the METALS: Zn, Ti, Zr, Hf

- **Zn** (d[10], not transition metal) is the fourth most common metal <u>in use</u> (after Fe, Al and Cu) with an annual production of ca. 13 million tonns
- Among the transition metals, most common are: Fe, **Ti**, Mn, Cr, …
- **Ti**: widely distributed, many minerals, most common rutile and ilmenite
- **Zr** is found in more than 40 minerals
- **Hf** much more rare, no own minerals, in Zr minerals: Hf/Zr ≈ 2 %



TITANIUM: Use as a metal / in metal alloys

- **Corrosion resistance: pulp and marine industry, chemical processing, and energy production and storage application**
- **High specific strength (strength/weight ratio): automotive industry, aerospace applications, sports equipment, jewelry, eyeglass frames**
- **Inertness in human body: surgery/artificial implants**
- **DISADVANTAGE: cost (Ti 6 times more expensive than Al)**

PRODUCTION OF TITANIUM

- **Oxide minerals: rutile (TiO_2) or ilmenite ($FeO\text{-}TiO_2$; 97-98 % TiO_2)**
- **Oxides are transformed to $TiCl_4$ which is a liquid and can be distilled for purification, e.g. by chloride process:**
  - $TiO_2 + 2\,Cl_2 + 2\,C\ (800\,°C) \rightarrow TiCl_4 + 2\,CO$
  - $2\,TiFeO_3 + 7\,Cl_2 + 6\,C\ (900\,°C) \rightarrow 2\,TiCl_4 + 2\,FeCl_3 + 6\,CO$
- **$TiCl_4$ is reduced in argon with molten Mg (Kroll process)**
  - $TiCl_4 + 2\,Mg\ (1100\,°C) \rightarrow Ti + 2\,MgCl_2$
- **$MgCl_2$ is reduced back to Mg such that it can be recycled**
- **Product: Titanium sponge (porous)**

Zr & Hf

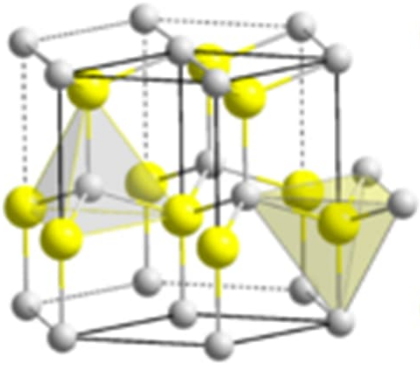
- **Exactly the same size (due to shielding effect/lanthanide contraction)**
- **Of all the 4d-5d transition metal pairs, Zr and Hf are the most similar**
- **Separation of Hf from Zr very difficult**
- **Hf was discovered as late as 1922 (Zr more than 100 years earlier)**
- **Hf was the first element which was searched for and found based on the quantum theory (lat. *Hafnia* = Copenhagen)**
- **Differencies:** - **density (atomic weight ratio Zr:Hf = 1.0:2.0)**
  - **neutron absorbtion (Hf 600-times stronger): different (opposite) uses in nuclear power plants**

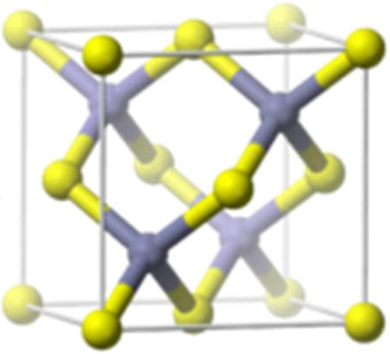
SEPARATION of Zr and Hf

- **Zr:** very low neutron absorption → used to make containers for nuclear fuel
- **Hf:** very high neutron absorption → used in control rods
- For the use of Zr in nuclear fuel containers it is crucial to ensure that the Zr metal used has extremely low Hf content

ZnO

- 4-coordination in hexagonal wurtzite or cubic zinc blende (diamond like) structure
- Additive in various applications: rubbers, plastics, ceramics, glass, cement, lubricants, paints, ointments, adhesives, sealants, pigments, foods, batteries, ferrites, fire retardants, first-aid tapes, etc.
- Wide-bandgap II-VI semiconductor
- Native doping due to excess zinc/oxygen vacancies/hydrogen → n-type doping
- Al^{3+}-for-Zn^{2+} doping for enhanced n-type doping
- Problem: p-type doping has not been achieved
- Attractive properties for optoelectronics: wide bandgap, tunable electrical properties, high transparency, high electron mobility → transparent electrodes, liquid crystal displays, energy-saving windows, electronics as thin-film transistors and light-emitting diodes



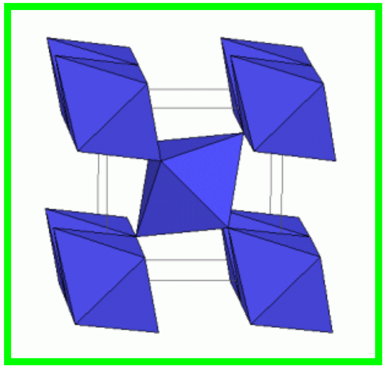


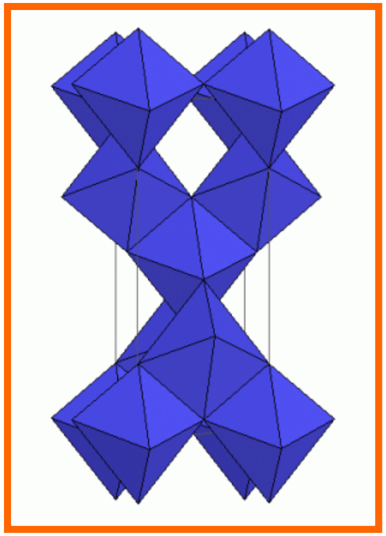
Zinc in Biology (protein functions)

- Essential for humans, animals and plants
- Crucial for the catalytic functions in enzymes
- Stabilizes the folding of protein subdomains
- Why Zinc ?

  - **widely available** in environment
  - **fixed oxidation state** (+II): completely resistant to redox changes and thus not affected by redox potentials in the organisms
  - prefers **tetrahedral coordination** (unlike many other metals): tetrahedral coordination of the metal site seems to be a key feature in most zinc enzymes
  - d^{10} configuration and **no crystal field effect**: flexible for adjustment of nearest-neighbour surroundings

TiO_2 (important chemical produced worldwide)

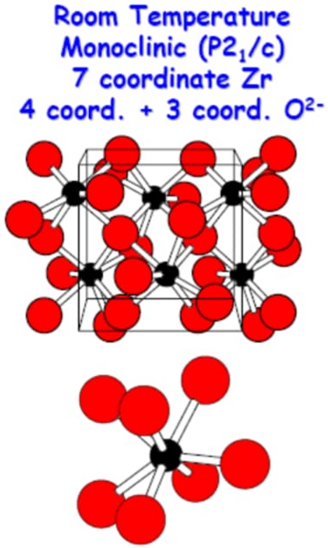


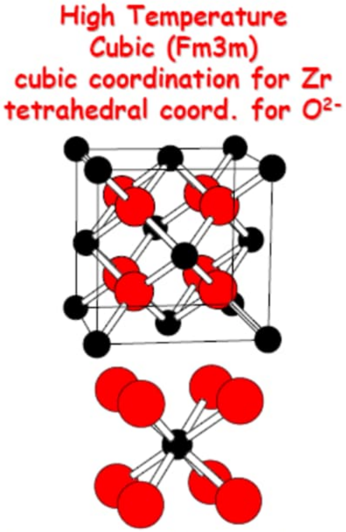


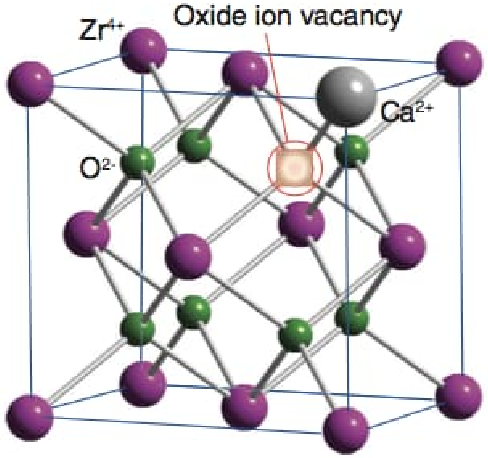
- **Crystal structures:** - rutile, anatase, brokite
- **White pigment:**
  - large refractive index
  - used in paints, paper, plastics, cosmetics, foods, tooth pastes, …
- **UV protection:** - sunscreens, plastics
- **Inert:** - filler material in pharmaceuticals
- **Photocatalytic:**
  - Akira Fujishima 1970s
  - water splitting
- **Antibacterial:**
  - decomposition of organics with UV light
  - 3-times stronger compared to chlorine, 1.5-times stronger compared to ozone
- **Superhydrophilic:**
  - Akira Fujishima 1996
  - after UV radiation
  - water spreads (no droplets) on TiO_2
  - e.g. sauna mirrors

ZrO_2

- Used as industrial ceramics, protective coating (e.g. on TiO_2 pigment particles) and refractory material in e.g. insulation
- Monoclinic (7-coordination) structure at RT &
cubic (8-coordination) structure at high temperatures
- Y^{III}-for-Zr^{IV} substitution stabilizes the cubic ZrO_2 structure
- Yttrium-stabilized zirconia (YSZ) for oxygen sensors and fuel cells owing to its low electronic conductivity but high oxide ion conductivity ($Y^{3+} \rightarrow Zr^{4+} \rightarrow$ oxygen vacancies)
- Synthesized in various colours (gemstone & diamond simulant)

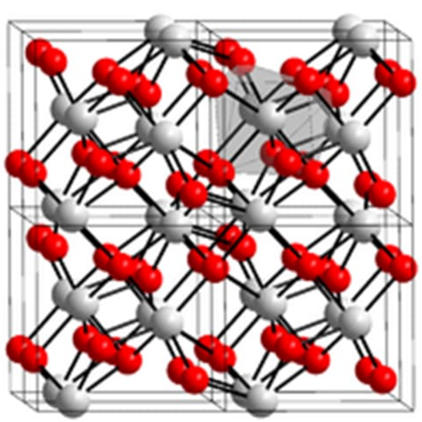






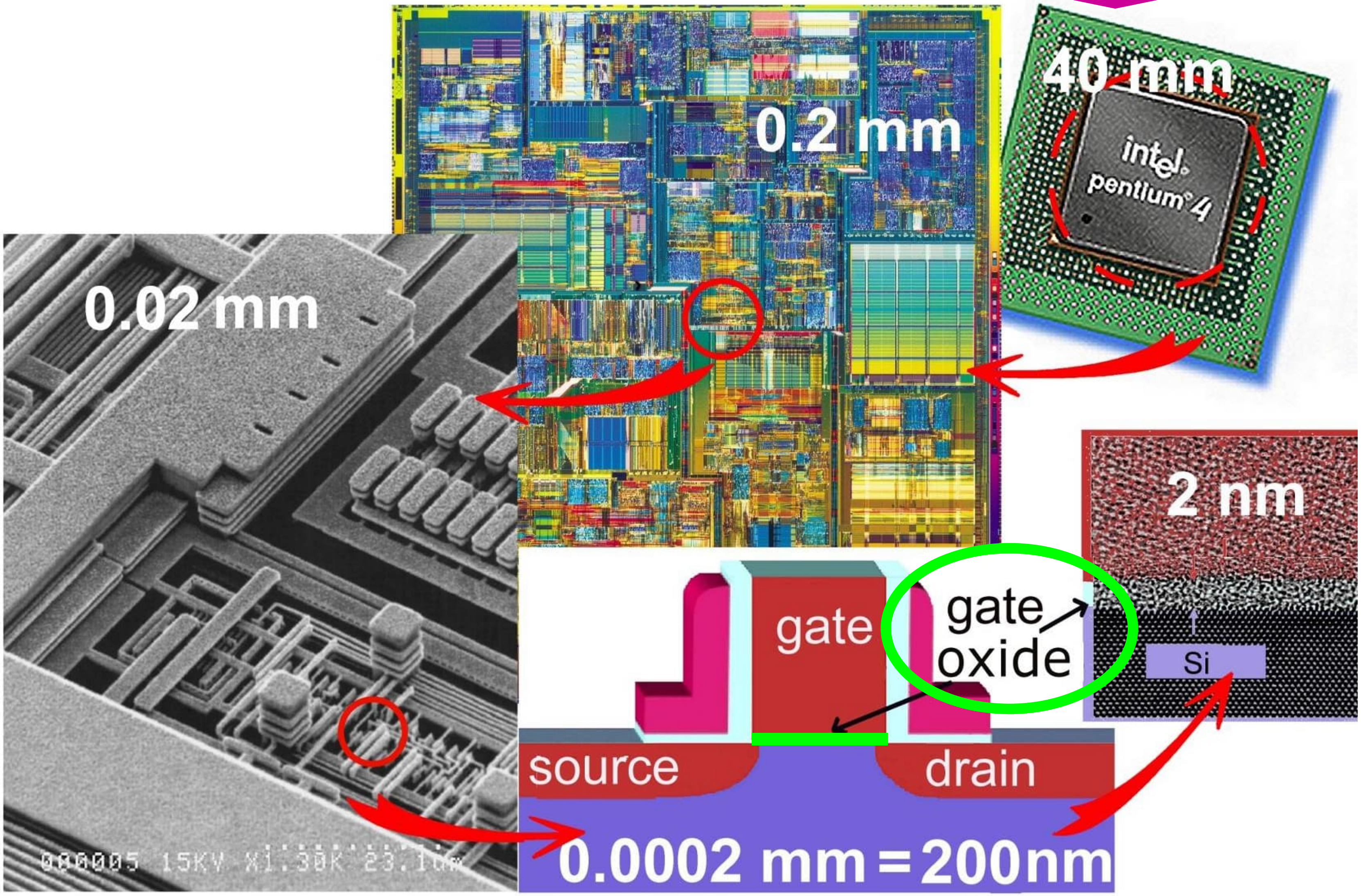
HfO_2

- Similar monoclinic (7-coordination) crystal structure to that of ZrO_2
- Very high melting point → refractory material for insulation (e.g. in thermocouples) → operates up to 2500 °C
- Multilayered HfO_2 coatings reflect sunlight & block heat conduction → passive cooling of buildings → several degrees cooler than surrounding materials
- **HfO_2 high-κ dielectrics** → dielectric constant 5 times higher compared to SiO_2 → high-κ material in DRAM (dynamic random access memory) and CMOS (complementary metal-oxide semiconductor) microelectronics devices
- Intel 2007 → replacement of SiO_2 as gate insulator in FETs (field-effect transistor) → deposition of high-quality amorphous films using ALD
- Partial substitution of Hf by Si (or Al) increases the crystallization temperature



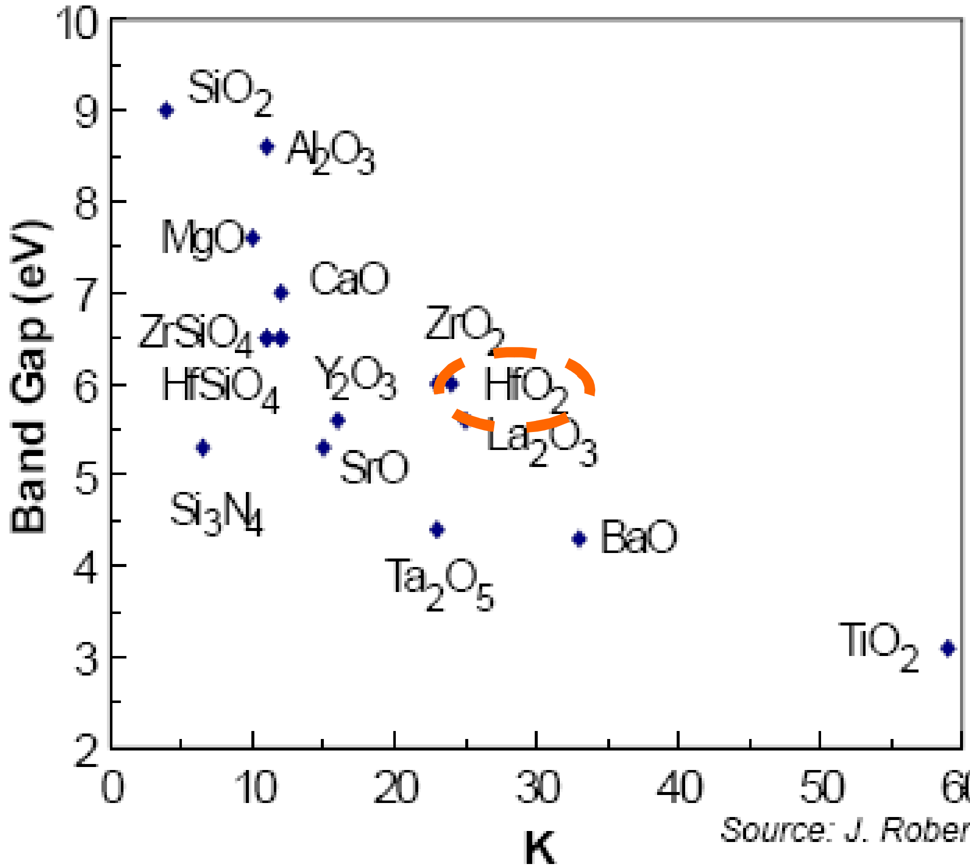
CMOS transistor

smaller transistors → lower gate voltage
same electric fields → thinner dielectric
SiO_2 → HIGH-*k* DIELECTRICS



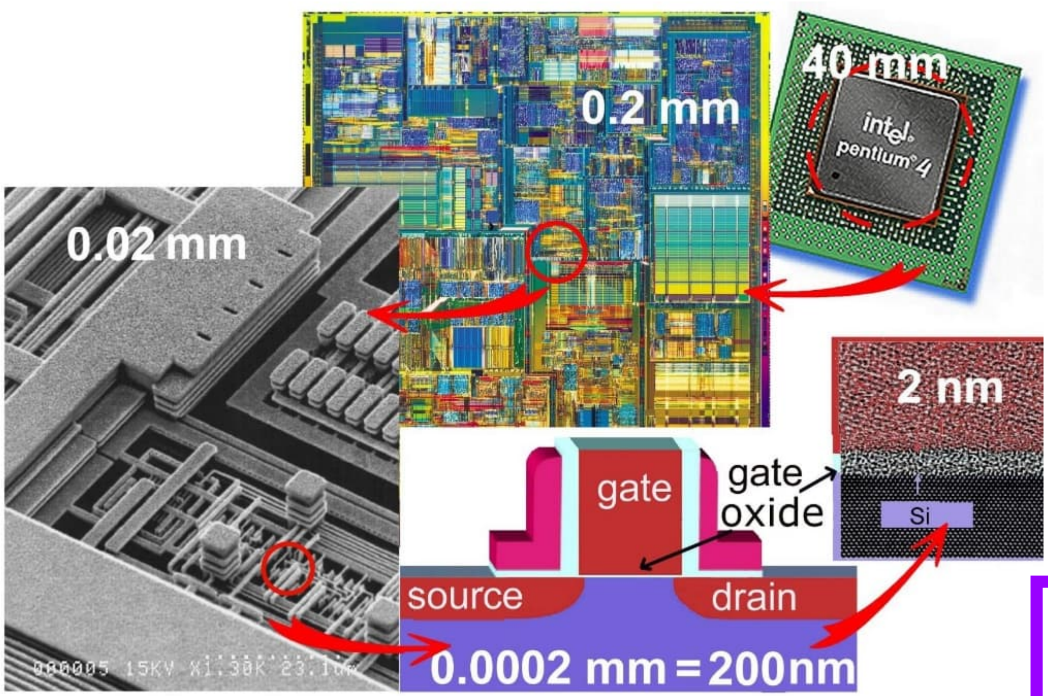
Conditions for high-*k* dielectrics

- **High enough dielectric constant *k***
- **Wide band gap for low leakage**
- **Stable – no reaction with Si**
- **Good interface, low impurities**



Source: J. Robertson

Atomic Layer Deposition (ALD) Technology

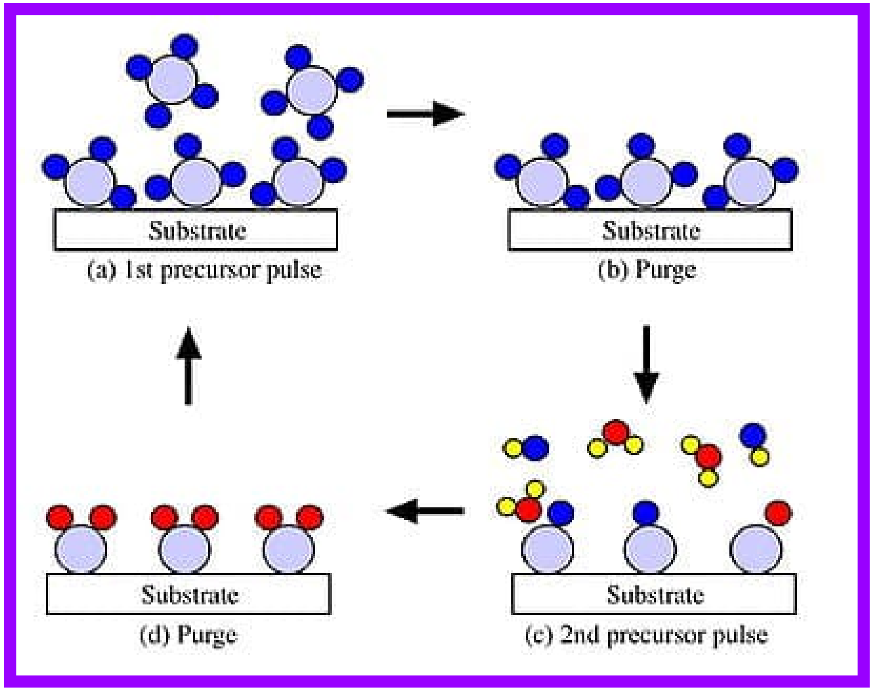


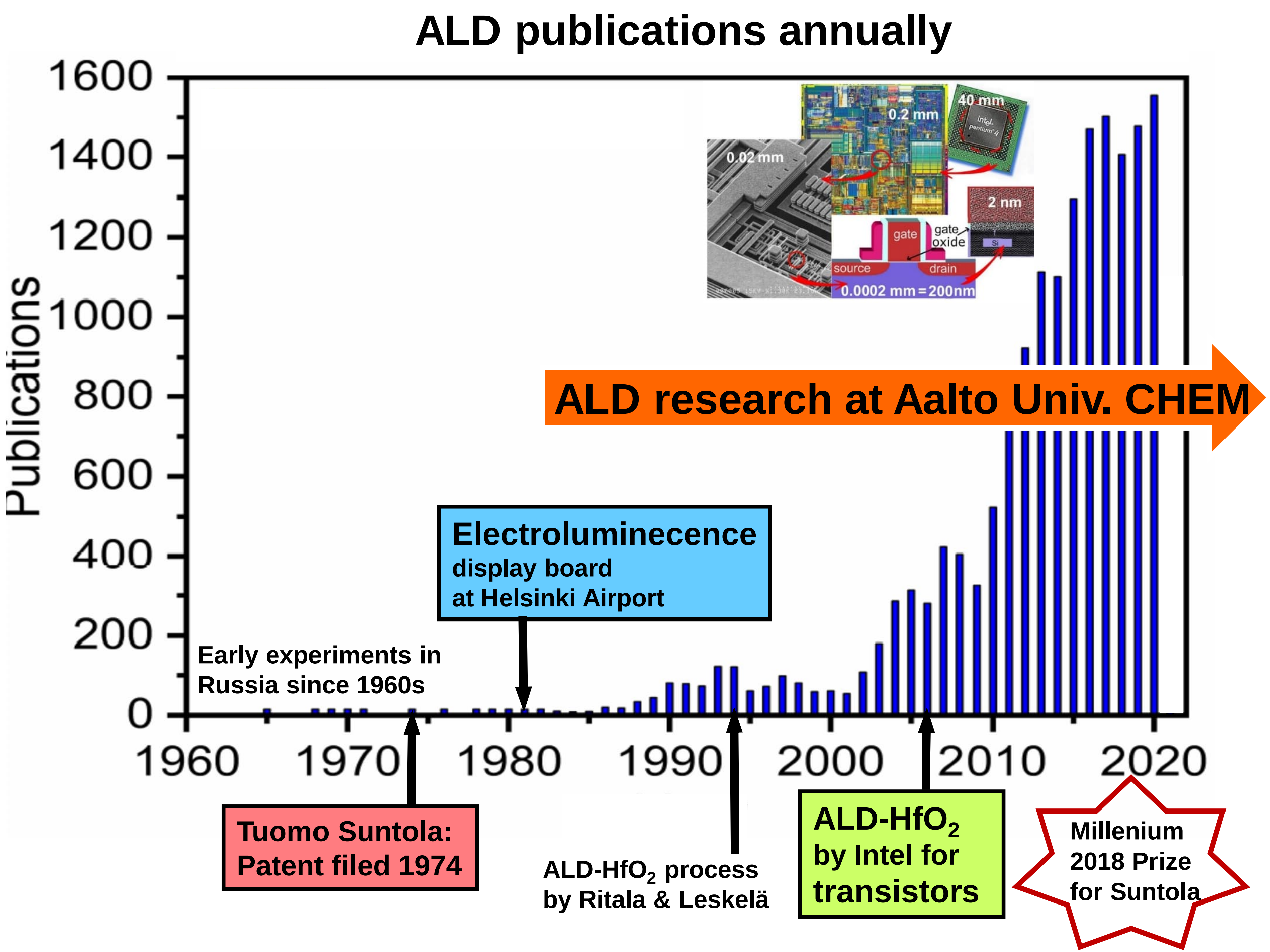
- High-quality (pinhole-free)
- Thickness control (atomic level)
- Large-area homogeneity
- Conformity → Nanostructuring

CMOS transistor

- 2-nm amorphous HfO_2 gate-oxide layer deposited by ALD

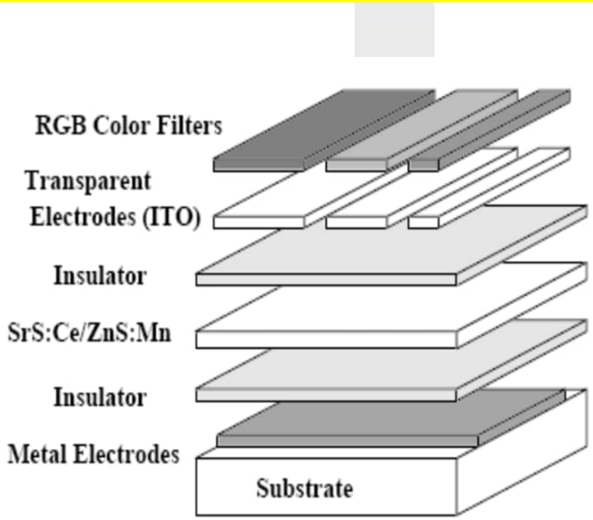
ALD: $HfCl_4$+H_2O




ALD publications annually
Publications
1600
1400
1200
1000
800
600
400
200
0
1960
1970
1980
1990
2000
2010
2020
0.2 mm
40 mm
0.02 mm
2 nm
gate
gate oxide
source
drain
0.0002 mm = 200nm
ALD research at Aalto Univ. CHEM
Electroluminecence
display board
at Helsinki Airport
Early experiments in
Russia since 1960s
Tuomo Suntola:
Patent filed 1974
ALD-HfO_2 process
by Ritala & Leskelä
ALD-HfO_2
by Intel for
transistors
Millenium
2018 Prize
for Suntola

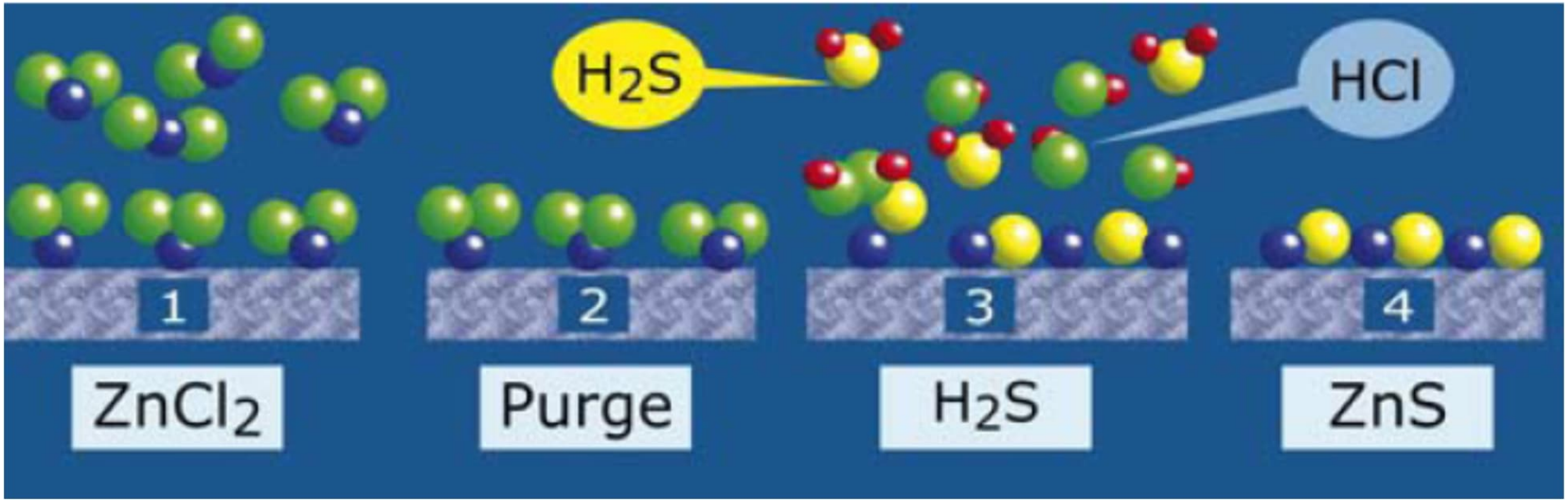
Atomic Layer Deposition (ALD) Thin-Film Technique

- **Gaseous precursors & Self-limiting surface reactions**
- **Precisely thickness-controlled, Large-area homogeneous & Conformal thin films**



Electroluminescent display

Instrumentarium / Finlux / Planar

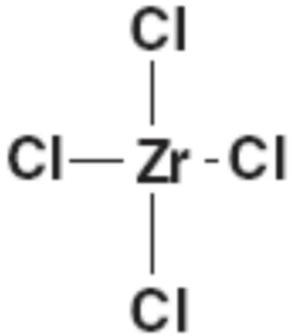


OXIDES (Al_2O_3, ZnO, TiO_2, ZrO_2 & HfO_2) & ALD (atomic layer deposition) thin-film technology

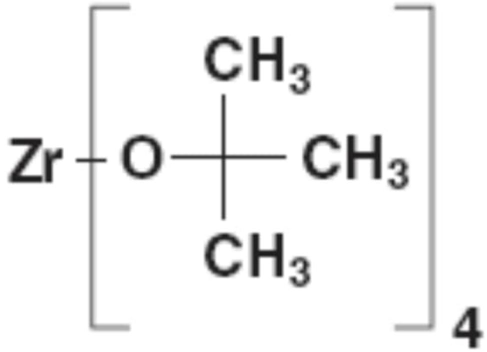
EXAMPLES of APPLICATIONS

- ALD-HfO_2 (amorphous): high-k dielectrics
- ALD-ZrO_2 (amorphous): barrier coating
- ALD-TiO_2 (crystalline): photovoltaics
- ALD-ZnO (crystalline): thermoelectric material

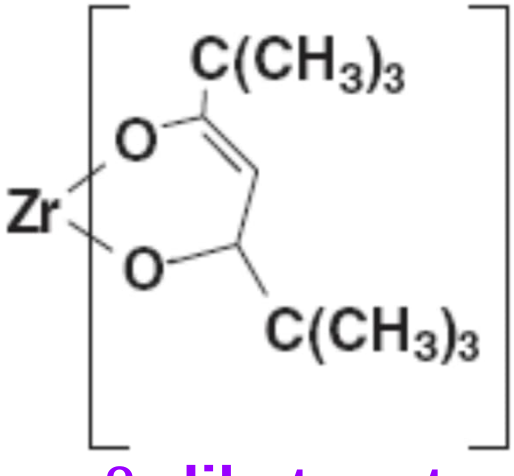
COMMON PRECURSORS in ALD



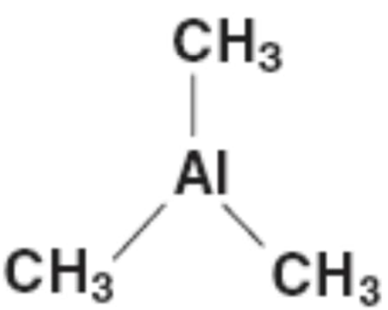
halides

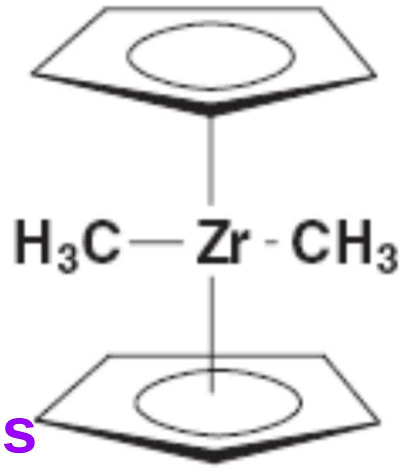


alkoxides

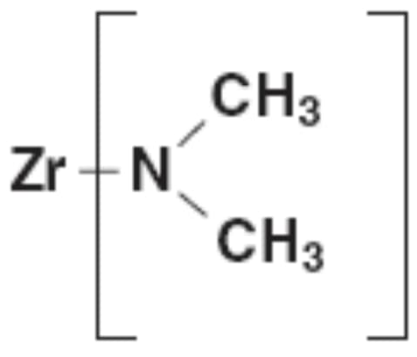


β-diketonates





organometallics



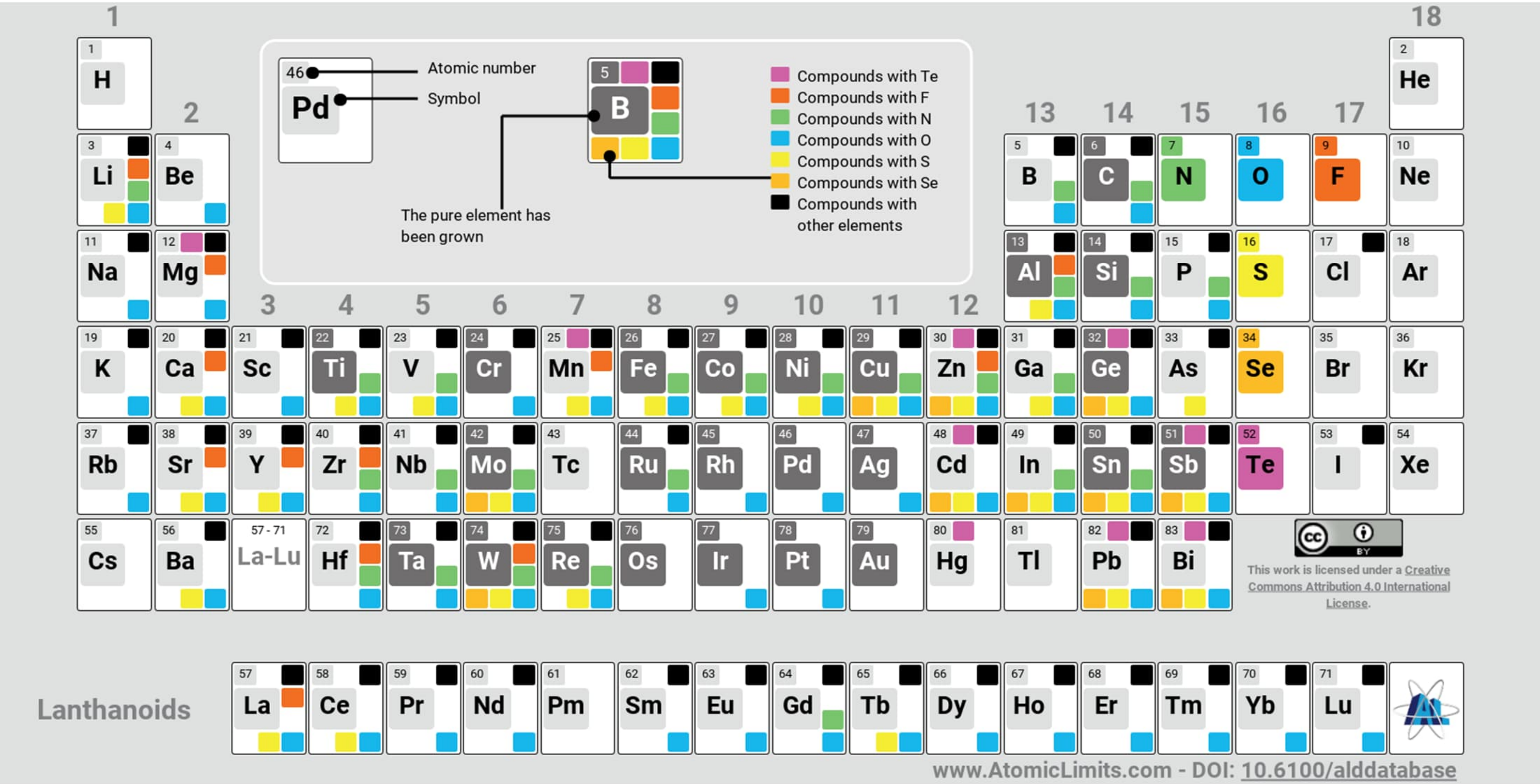
amido complexes

e.g. cyclopentadienyls

Common CO-REACTANTS (second precursor):

- **Water H_2O (e.g. with $TiCl_4$, $Al(CH_3)_3$ or $Zn(CH_2CH_3)_2$) → Oxides**
- **Ozone O_3 (e.g. with metal β-diketonates) → Oxides**
- **Dihydrogensulfide H_2S (e.g. with $ZnCl_2$) → Sulfides**
- **Ammonia NH_3 → Nitrides**

Periodic Table of ALD Processes



mons.wikimedia.org/w/index.php?curid=78838925

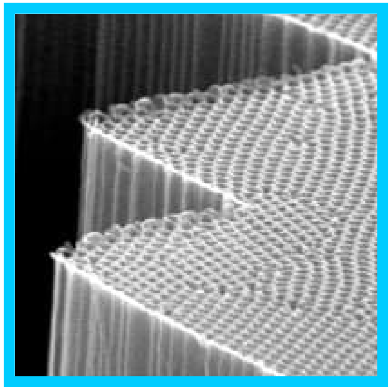
Advantages of ALD

ELECTRONICS

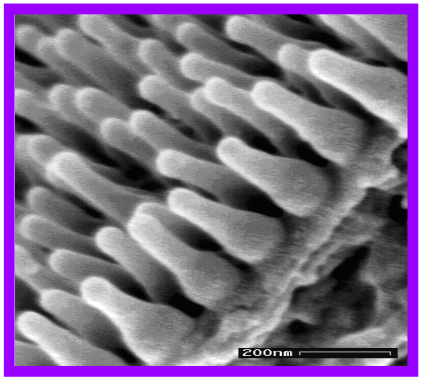
- Relatively inexpensive method
- Excellent repeatability
- Dense and pinhole-free films
- Accurate and simple thickness control
- Large area uniformity

NANO

- Excellent conformality



BIO



- Low deposition temperature
- Gentle deposition process

NEW

- Organic/polymer films
- Inorganic/organic hybrid materials

Kalevala Koru (Finland):

- **traditional silver jewelry**

Beneq (Finland):

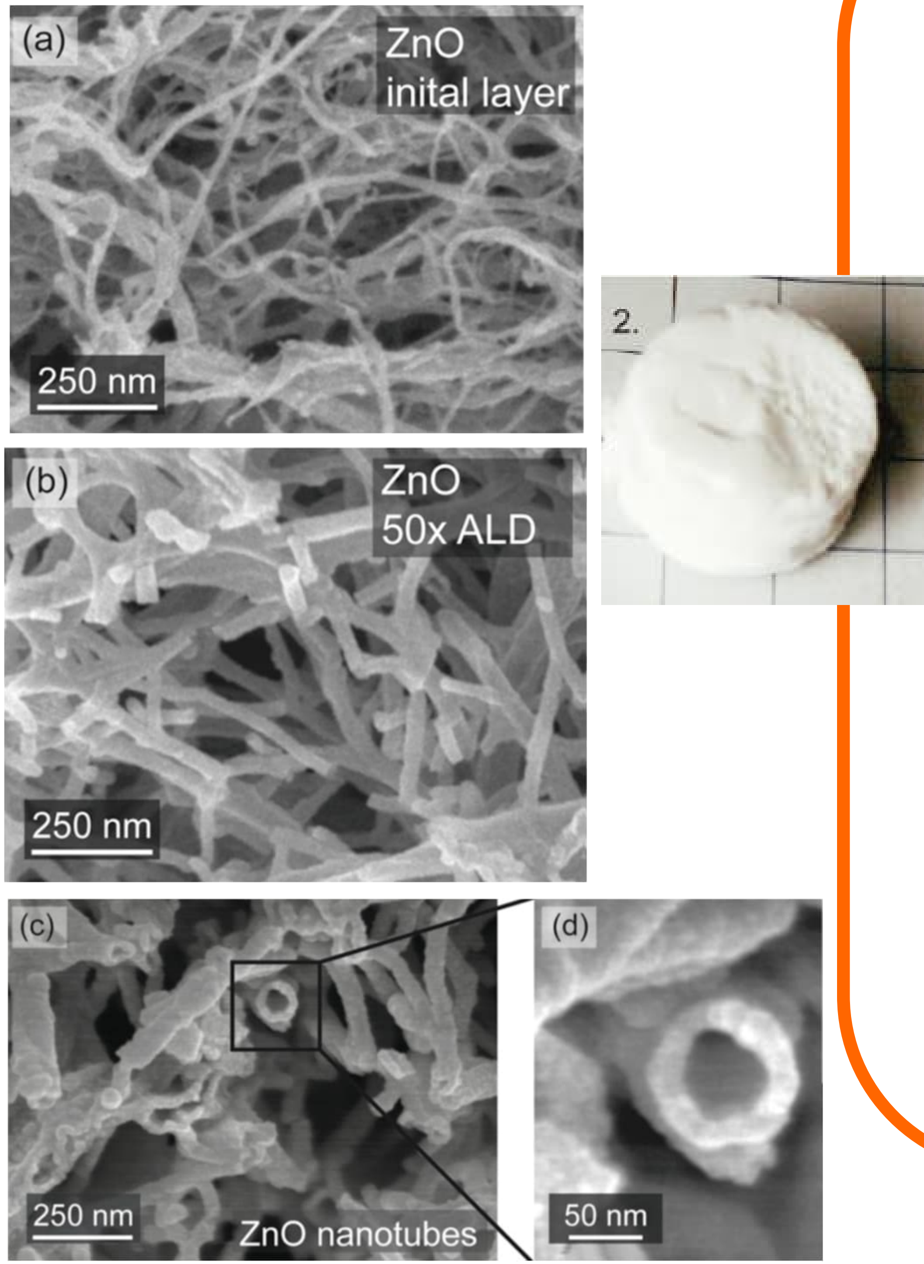
- **Al_2O_3 coating by ALD**

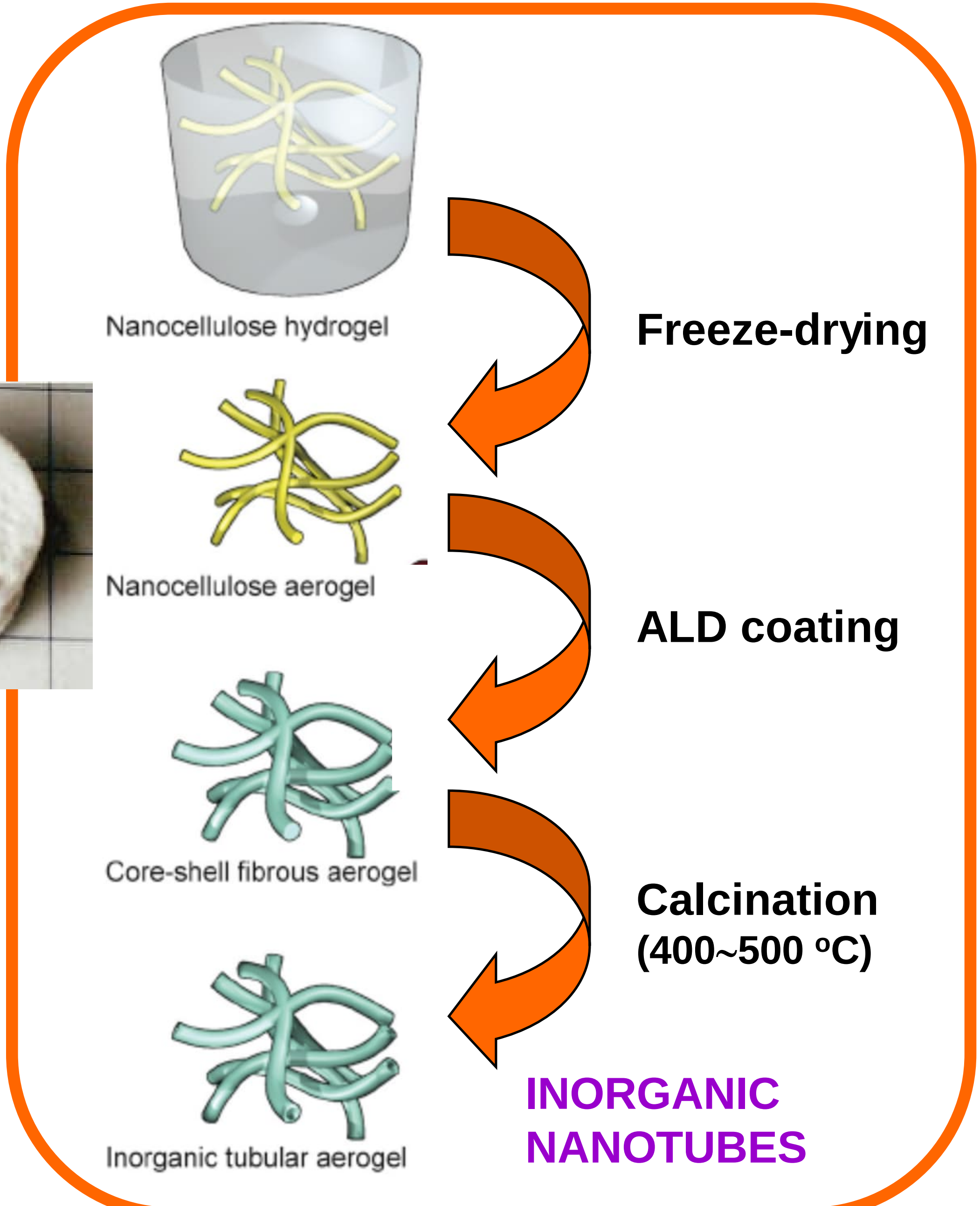
uncoated **Al_2O_3-coated**

BEFORE **AFTER TARNISHING TEST**

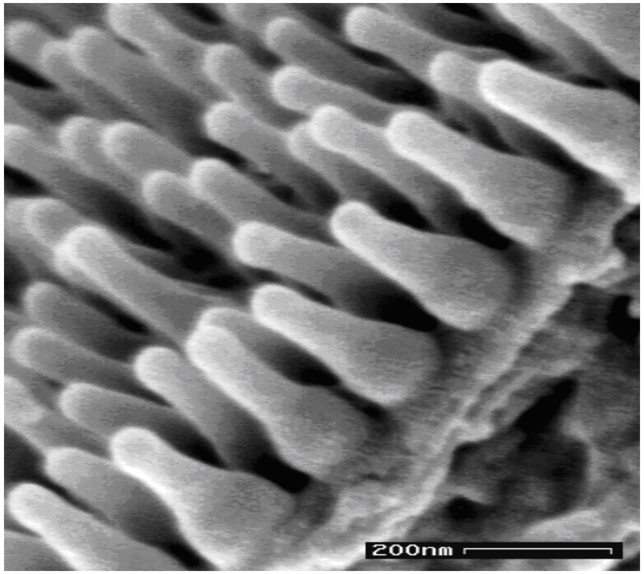
Dense, pinhole-free & highly conformal ALD-Al_2O_3-nanocoating efficiently protects silver jewelries from tarnishing

NANOSTRUCTURING by ALD
- nanocellulose aerogel template





J.T. Korhonen, J. Malm, M. Karppinen,
O. Ikkala & R.H.A. Ras, *ACS Nano* 5, 1967 (2011).



CICADA WING

- **Peculiar surface-nanostructure**

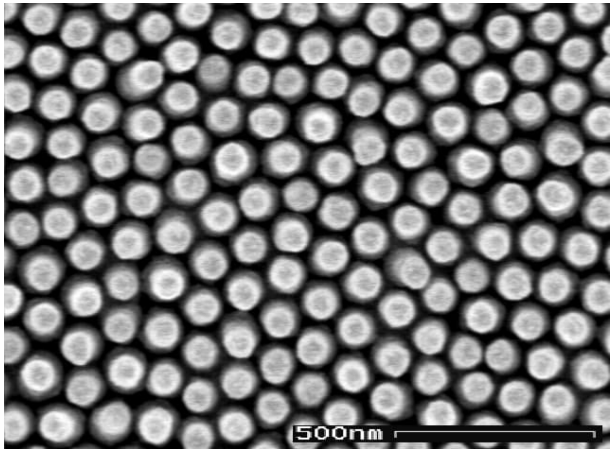
  200-nm high nanopillars coated with a waxy layer
- **superhydrofobic**

ZnO

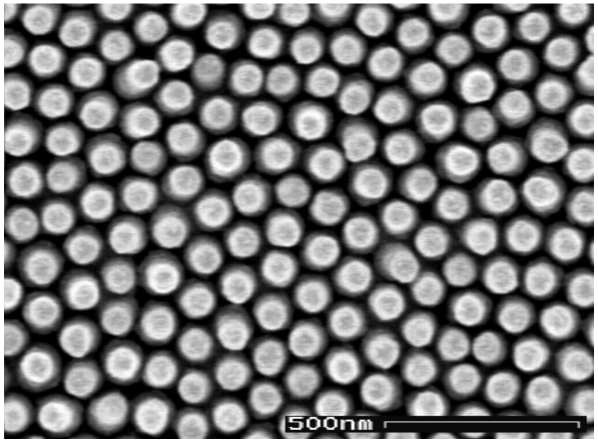
- **Reversible change from hydrofobic to hydrophilic upon UV-radiation**

CICADA WING + ZnO

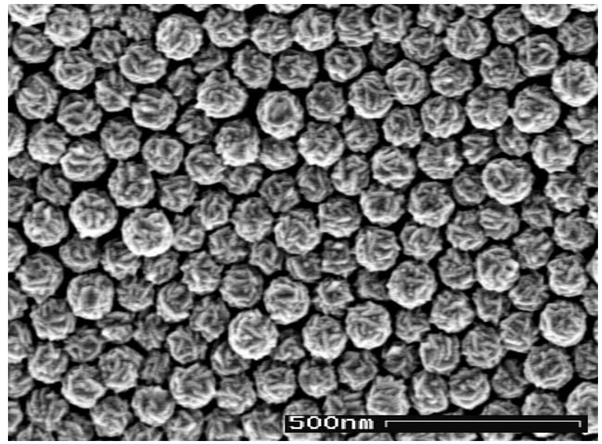
- **Conformal coating of the wing by a thin layer of ZnO (~20 nm) by means of ALD**
- **Reversible change from superhydrofobic to superhydrophilic upon UV-radiation**



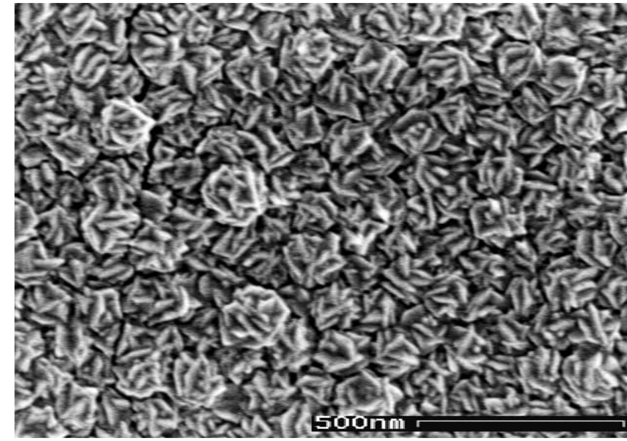
J. Malm, E. Sahramo, M. Karppinen & R. Ras, *Chem. Mater.* **22**, 3349 (2010).



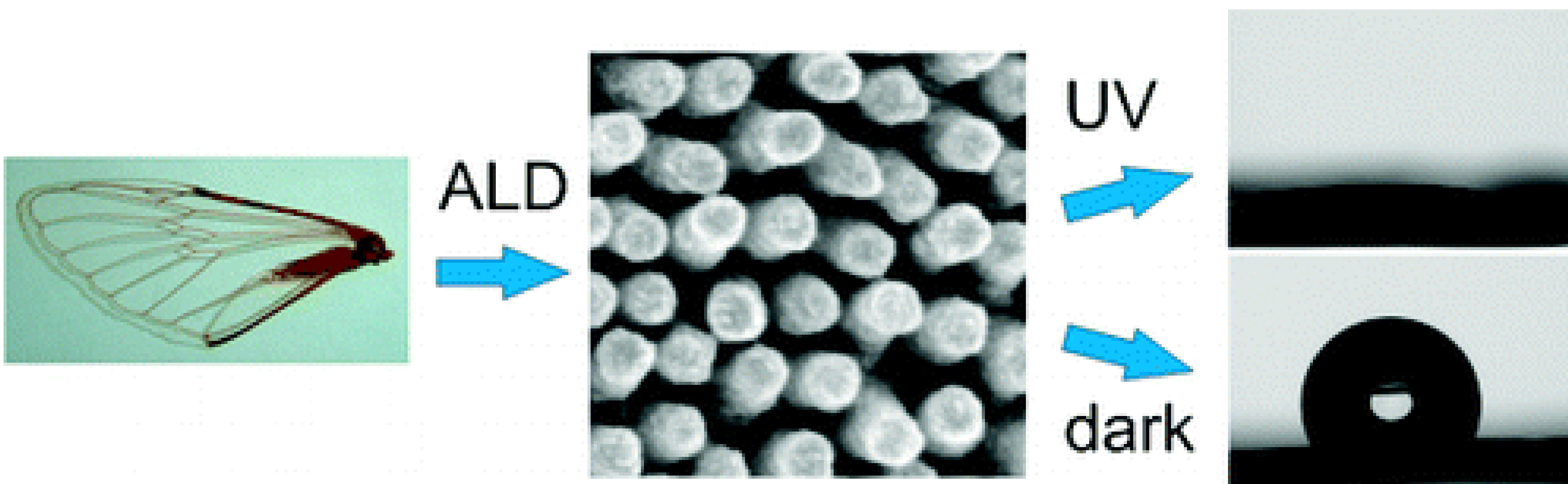
100 cycles (20 nm)

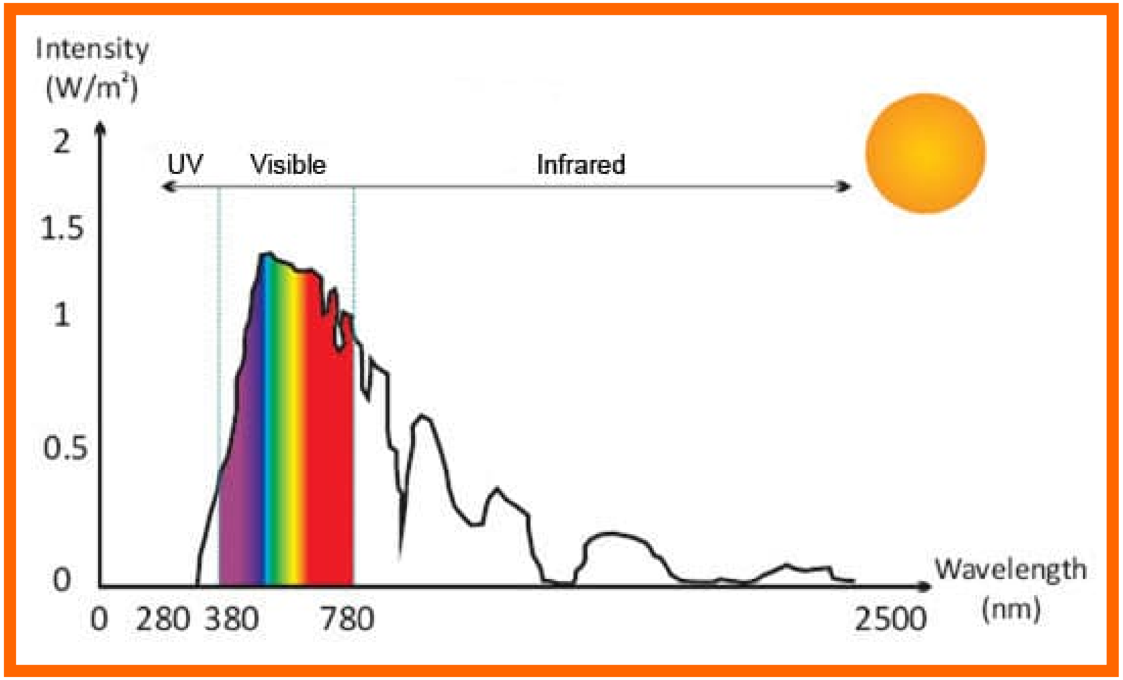


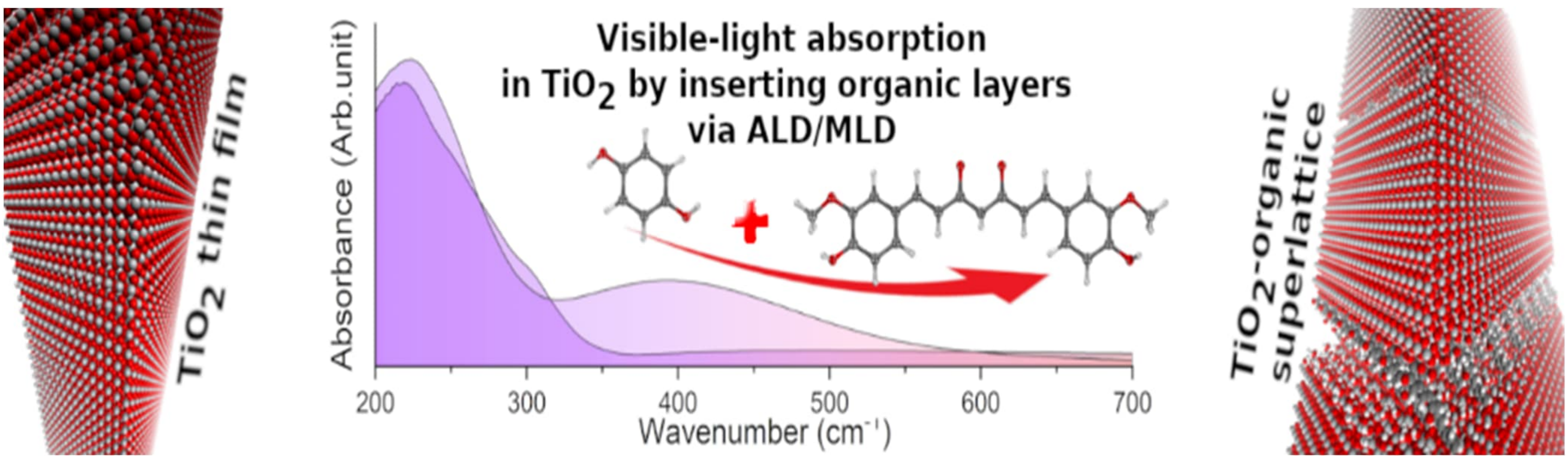
300 cycles (60 nm)



500 cycles (100 nm)







Visible-light absorbing TiO_2:curcumin thin films with ALD/MLD,
A. Philip, R. Ghiyasi & M. Karppinen, *ChemNanoMat* **7**, 253 (2021).